

Alternative Feedstocks Program Technical and Economic Assessment

Thermal/Chemical and Bioprocessing Components

Prepared for

**The U. S. Department of Energy
Office of Industrial Technologies**

by

Argonne National Laboratory

Idaho National Engineering Laboratory

National Renewable Energy Laboratory

Oak Ridge National Laboratory

Pacific Northwest Laboratory

**Joseph J. Bozell
Ron Landucci
Editors**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.

Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report ascribes research to the United States Department of Agriculture (USDA) but does not attempt to provide a comprehensive review of all USDA work. In addition, land use data may not reflect updated information available from the USDA. The reader is referred to USDA offices for more complete information.

Acknowledgements

We hope that this document will be a valuable resource to help interested individuals in academia, industry, and government identify promising opportunities for producing chemicals from alternative feedstocks. This document is the result of the hard work of many individuals at the Departments of Agriculture and Energy, and the National Laboratories that make up the National Laboratory Team for Alternative Feedstocks. However, to paraphrase one of the reviewers, "national labs do not write documents, people write documents." We would like to thank the following individuals at the National Laboratories and the Departments of Agriculture and Energy for a true team effort in assembling this report.

Argonne National Laboratory: Jim Frank, Rathin Datta, Shih-Perng Tsai, Mark Donnelly, Seung-Hyeon Moon, Jo Ann Parnell, Marianne Schiffer, Satya Kakar, Fred Stevens, Deborah Hanson, Norm Sather, Christopher Reilly, Patrick Bonsignore, and Cynthia Sanville-Millard.

Idaho National Engineering Laboratory: Kevin Polman, Debonny Shoaf, Lynn Apel, Robert Bumbar, Gene A. Giesbrecht, Graham F. Andrews, Elmer H. Fleischman, Gregory A. Bala, Jack Prendergast and Joseph G. Keller.

National Renewable Energy Laboratory: Barb Goodman, Arthur J. Power (NREL subcontractor and president of Arthur J. Power and Associates), Mark Finkelstein, Steve Kelley and Foster Agblevor.

Oak Ridge National Laboratory: Brian H. Davison, Timothy C. Scott, J. W. Ranney, and Lynn Wright.

Pacific Northwest Laboratory: Douglas C. Elliott and David E. Eakin.

United States Department of Agriculture: Hosein Shapouri, Douglas Beach, W. Lamar Harris, and Rich Greene.

United States Department of Energy: Linda Beth Schilling, Daniel E. Wiley, David J. Boron, Clement Yonker, Gregory Dilworth, Gesina C. Carter, Oscar Manley, Leonard Keay, and Patricia St. Clair.

We would also like to thank the laboratory team coordinator, Gene Petersen (NREL), and the resource management team, Helena Chum (NREL), LaMar Johnson (INEL), Bill Schertz (ANL), Chuck Scott (ORNL), John Sealock (PNL), and Charlie Wyman (NREL), for their continuing support, input, and advice.

Joseph J. Bozell
Ron Landucci
National Renewable Energy Laboratory
Editors

July, 1993

TABLE OF CONTENTS

Acknowledgements	1
TABLE OF CONTENTS	3
LIST OF FIGURES	7
LIST OF TABLES	8
1.0 EXECUTIVE SUMMARY	11
1.1 Report Overview	11
1.1.1 Introduction	11
1.1.2 Overview of the Technoeconomic Evaluation of Proposed Process Routes from Renewables	14
1.1.2.1 Overview of Technoeconomic Evaluation of Thermal and Chemical Processes	14
1.1.2.2 Overview of Technoeconomic Evaluation of Biological Processes	15
1.1.2.3 Improving the Evaluation Process	15
1.2 Recommendation Overview	15
1.2.1 Thermal and Chemical Recommendations	15
1.2.2 Bioprocessing Recommendations	16
1.2.3 Developmental Process for Recommended Products and Processes	16
1.2.4 Near Term RD&D Opportunities	17
1.2.5 Mid Term RD&D Opportunities	18
1.2.6 Long Term RD&D Opportunities	18
1.2.7 Related RD&D Opportunities	19
2.0 OVERVIEW OF FACTORS CONTRIBUTING TO ANALYSIS	21
2.1 Energy Considerations	21
2.2 Environmental Considerations	24
2.3 Legislative Considerations	25
2.3.1 Chemical Industries	25
2.3.2 Pulp, Paper and Paperboard Industries	27
2.4 Windows of Opportunity	28
2.4.1 Example - Biodegradable Polymers	28
2.4.2 Example - Fast Pyrolysis of Biomass	28
2.4.3 Example - Bioprocessing of Renewables	29
2.4.4 Examples - Technical Advances and New Applications	29
2.5 Overview of Key Industrial Sectors	31
2.5.1 The Chemical Industry	31
2.5.1.1 The Petrochemical Industry	33
2.5.2 The Renewables Industry	36
2.5.2.1 Chemicals and Materials Currently Produced from Alternative Feedstocks	37
2.5.2.2 Integrated Processing	37
2.5.2.3 Use of a Specific Crop for Producing Industrial Chemicals and Materials	37
3.0 AVAILABILITY, USE, AND COMPOSITION OF BIOMASS	41
3.1 General Overview	41
3.2 Characterization of Representative Feedstocks	45
3.3 Representative Alternative Feedstocks	49
3.3.1 "Waste" Materials	49
3.3.1.1 Materials from Food Processing	49
3.3.1.2 Materials from Cellulosic Biomass	51
3.3.1.3 Dedicated Crops	51
3.3.1.4 Conventional Food Crops	52
3.4 Advantages and Disadvantages of Selected Renewable Feedstocks	55

3.4.1	Feedstocks for Bioprocesses	55
3.4.2	Lignocellulosic Feedstocks	58
4.0	THERMAL/CHEMICAL ROUTES TO PRODUCTS	61
4.1	General	61
4.2	Description of Screening Methodology for Thermal and Chemical Processes	63
4.2.1	Screening Based on Comparative Raw Materials Cost Contribution	64
4.2.2	Preliminary Detailed Process Evaluation	66
4.3	Summary of Technoeconomic Evaluation	67
4.4	Current and Projected Markets for Selected Chemicals from Biomass	67
4.4.1	Butadiene	67
4.4.2	Pentanes, Pentenes	71
4.4.3	Benzene	71
4.4.4	Toluene	72
4.4.5	Xylenes	73
4.4.6	Acetic Acid	73
4.4.7	Formic Acid	74
4.4.8	Propionic Acid	74
4.4.9	Phenol	74
4.4.10	Resorcinol	75
4.4.11	Furfural	75
4.4.12	Glucose	76
4.4.13	Gluconic Acid	76
4.4.14	Sorbitol	77
4.4.15	Mannitol	77
4.4.16	Xylitol	78
4.4.17	Acrylic Acid	78
4.4.18	Cellulose Derivatives	78
4.4.18.1	Rayon Fibers	78
4.4.18.2	Cellulose Acetate Fibers	79
4.4.18.3	Cellulose Acetate Flake and Related Cellulose Esters	79
4.4.18.4	Cellulosic Surface Coatings	80
4.4.18.5	Cellulose Ethers	81
4.4.18.6	Cellophane	81
5.0	INDIVIDUAL RAW MATERIALS COST COMPARATIVE EVALUATIONS	83
5.1	Direct Substitution	83
5.1.1	Butadiene	83
5.1.2	Pentanes/Pentenes	87
5.1.3	Benzene/Toluene/Xylene (BTX)	88
5.1.4	Acetic/Formic/Propionic Acids	89
5.1.5	Hydroxyacetaldehyde	90
5.1.6	Phenolics (by pyrolysis routes)	91
5.1.7	Resorcinol	92
5.1.8	Vinyl Phenol, an Example of a High Value Phenolic Produced by Biomass Pyrolysis	93
5.1.9	Phenolics from Wood Phenolation	94
5.1.10	Phenolics (by hydrotreating of lignin)	95
5.1.11	Syn Gas	96
5.1.12	Acetic Acid from Syn Gas	97
5.1.13	Peracetic Acid	98
5.1.14	Anthraquinone	99
5.1.15	Acrylic Acid/Esters	100
5.2	Improved Production	102
5.2.1	The NREL Clean Fractionation Process	102
5.2.1.1	Glucose	104

5.2.1.2	Xylose	106
5.2.2	5-Hydroxymethylfurfural	107
5.2.3	Levulinic/Formic Acids	107
5.2.4	Succinic Acid	108
5.2.5	Gluconic Acid	109
5.2.6	Sorbitol	110
5.2.7	Mannitol	111
5.2.8	Xylitol	111
5.2.9	Furfural	112
5.2.10	Furfuryl Alcohol	113
5.2.11	Furan/Tetrahydrofuran (THF)	114
5.2.12	Polyhydroxybutyrate/Polyhydroxyvalerate (PHB/PHV)	115
5.3	New Building Blocks/Products	116
5.3.1	Levoglucosan	116
5.3.2	Cellulose (Kraft)/Anthraquinone	117
5.3.3	Cellulose (Organosolv)/Anthraquinone	117
5.3.4	Starch Plastics	118
5.3.5	Acetylated Wood	118
5.4	Selected Detailed Production Cost Estimates	119
5.4.1	General Information	119
5.4.2	Detailed Process Analysis - Anthraquinone (AQ) from Low Molecular Weight Lignin	121
5.4.2.1	Definition of Process Chemistry	121
5.4.2.2	Definition of Base Cases	122
5.4.2.3	Results of Evaluation	122
5.4.2.4	Evaluation of Competing Routes to AQ	122
5.4.3	Detailed Process Analysis - Phenolics from Biomass by Pyrolysis and Wood Phenolation	126
5.4.4	Detailed Process Analysis - Clean Fractionation of Lignocellulosics	126
5.4.5	Detailed Process Analysis - Acetylated Wood	128
5.4.6	Detailed Process Analysis - Starch Plastics	129
6.0	BIOPROCESSING ROUTES TO CHEMICALS AND MATERIALS	131
6.1	Introduction and Rationale	131
6.2	Target Products and Markets for Chemicals	132
6.2.1	Direct Substitution for Existing Chemicals	132
6.2.2	Development of New Chemicals, Materials, and Feedstocks	132
6.3	Opportunities for Technology Improvement	133
6.3.1	New Technologies in Genetic and Metabolic Engineering	134
6.3.1.1	Future Technological Advances	135
6.3.2	Advanced Bioprocessing Concepts	136
6.4	Product/Process Selection	137
6.4.1	Initial Product Screening Methodology	138
6.4.1.1	Fraction of Revenue for Feedstock	140
6.4.1.2	Feedstocks Evaluated	140
6.4.1.3	Byproducts	141
6.4.1.4	Experimental Yields	142
6.4.1.5	Theoretical Yields	142
6.4.1.6	Product Values	144
6.4.1.7	Summary	144
6.4.2	Comparative Evaluations	144
6.4.3	Integrated Product/Process Screening Methodology	147
6.4.3.1	Process Design	147
6.4.3.2	Profitability Analysis	148
6.4.3.3	Economic Assumptions	149

6.4.3.4	Sensitivity Analyses	149
6.4.3.5	Summary	149
7.0	RESULTS OF INITIAL ANALYSIS	153
7.1	Initial Targets	153
7.2	Applying Prioritization Methodology	153
7.3	Comparative Evaluations	158
7.3.1	Acetic Acid	159
7.3.2	Acetone	161
7.3.3	2,3-Butanediol	163
7.3.4	Butanol	165
7.3.5	Butyric Acid	167
7.3.6	Glycerol	169
7.3.7	Isopropanol	171
7.3.8	Malic Acid	173
7.3.9	Polyhydroxybutyric Acid	175
7.3.10	Propionic Acid	177
7.3.11	Propylene Glycol	179
7.3.12	Succinic Acid	181
7.4	Qualitative Influences	183
7.5	Initial Candidates for Process Evaluation	186
7.5.1	Organic Acids (Succinic/Malic/Fumaric)	186
7.5.1.1	Market Definition	186
7.5.1.2	Process Evaluation	188
7.5.1.2.1	Process Concept	188
7.5.1.2.2	Profitability Analysis	190
7.5.1.3	Application of New Technologies in Genetic and Metabolic Engineering to Succinic Acid	196
7.5.1.4	Advanced Bioprocessing Concepts	196
7.5.2	Neutral Solvents (Butanol)	201
7.5.2.1	Market Definition	201
7.5.2.2	Process Evaluation	203
7.5.2.3	Application of Genetic and Metabolic Engineering to Butanol Production	207
7.5.2.4	Advanced Bioprocessing Concepts	207
8.0	RECOMMENDATIONS	211
8.1	Criteria for Recommendations	211
8.2	Crosscutting Technical Barriers	215
8.3	Near Term Opportunities	216
8.4	Mid Term Opportunities	219
8.5	Long Term Opportunities	220
8.6	Recommendations in Other DOE Program Areas and in Other Federal Agencies ...	221
8.7	Timeframe for Completion	225
9.0	REFERENCES AND SELECTED BIBLIOGRAPHY	227

LIST OF FIGURES

Figure 2.1	Different Ways of Measuring Energy Consumed in Manufacturing	23
Figure 2.2	Scheme of the Chemical and Allied Products and Petroleum Refining Industries ...	34
Figure 2.3	Interrelationships and Materials Flow for the Pulp and Paper Industry, 1986	38
Figure 2.4	Corn Products Industry	39
Figure 2.5	Cotton Products Industry	40
Figure 3.1	Production of a Generic Feedstock Intermediate from Representative Biomass-Based Raw Materials	43
Figure 3.2	Comparison of Selling Prices of Chemical Products with Representative Raw Feedstock Materials	48
Figure 3.3	Projected and Current Domestic Production of Organic Acids and Neutral Solvents	50
Figure 4.1	Schematic Outline of Technoeconomic Analysis	63
Figure 5.1	Flowchart for Production of Product Families from Clean Fractionation	103
Figure 5.2	Comparison of Costs; Base Cases for Anthraquinone Production	124
Figure 5.3	Amortized Production Costs of AQ from Different Starting Materials.	125
Figure 5.4	Alternative Routes to Anthraquinone	125
Figure 6.1	Metabolic Engineering	134
Figure 6.2	Screening and Ranking Methodology	139
Figure 6.3	Initial Product Screening Methodology	145
Figure 6.4	Generic Example of Sensitivity Analysis	150
Figure 6.5	Integrated Product/Process Screening Methodology	151
Figure 7.1	Estimated Raw Material Cost Ratio versus Glucose Cost, Acetic Acid Production	160
Figure 7.2	Estimated Raw Material Cost Ratio versus Glucose Cost, Acetone Production	162
Figure 7.3	Estimated Raw Material Cost Ratio versus Glucose Cost, 2,3-Butanediol Production	164
Figure 7.4	Estimated Raw Material Cost Ratio versus Glucose Cost, Butanol Production	166
Figure 7.5	Estimated Raw Material Cost Ratio versus Glucose Cost, Butyric Acid Production	168
Figure 7.6	Estimated Raw Material Cost Ratio versus Glucose Cost, Glycerol Production	170
Figure 7.7	Estimated Raw Material Cost Ratio versus Glucose Cost, Isopropanol Production	172
Figure 7.8	Estimated Raw Material Cost Ratio versus Glucose Cost, Malic Acid Production ...	174
Figure 7.9	Estimated Raw Material Cost Ratio versus Glucose Cost, Polyhydroxybutyric Acid Production	176
Figure 7.10	Estimated Raw Material Cost Ratio versus Glucose Cost, Propionic Acid Production	178
Figure 7.11	Estimated Raw Material Cost Ratio versus Glucose Cost, Propylene Glycol Production	180
Figure 7.12	Estimated Raw Material Cost Ratio versus Glucose Cost, Succinic Acid Production	182
Figure 7.13	Process Concept for Bioproduction of Succinic Acid	189
Figure 7.14	Metabolic Pathway for Production of Succinic Acid	197
Figure 7.15	Process Concept for Bioproduction of Butanol	204
Figure 7.16	Metabolic Pathway for Butanol Production	208
Figure 8.1	Flowchart for Production of Chemicals Available from Renewable Materials	212
Figure 8.2	Production of Consumer Products from Renewable Feedstocks	214
Figure 8.3	Coordination of Research and Development Opportunities Across Federal Agencies	222
Figure 8.4	Typical Demonstration and Commercialization Time Frame	225

LIST OF TABLES

Table 2.1	Energy Intensity in Manufacturing Industry Groups: 1980, 1985, and 1988	22
Table 2.2	Environmental Legislation Affecting the Pulp and Paper Industry Since 1970	27
Table 2.3	Shipments from the United States Chemical Industry by Relevant Sectors	32
Table 2.4	Selected Prices in Constant 1990 Dollars for Primary Petrochemicals	32
Table 2.5	Source of Primary Petrochemicals in the United States (1990)	35
Table 2.6	Selected End Uses of Plastic Products	35
Table 2.7	Plant Matter Derived Industrial Materials and Important Intermediate Chemicals in the United States	38
Table 3.1	Representative Alternative Feedstocks: Primary Feedstock Constituents and Current Uses	46
Table 3.2	Recoverable Biomass Wastes	46
Table 3.3	Prices, Production, Potential Fermentable Sugar Yields, and Productivities of Representative Feedstocks (United States)	47
Table 3.4	Corn Kernel: Composition of Parts (% Dry Basis)	52
Table 3.5	Protein in Corn Grain Fractions (% of Total Nitrogen)	52
Table 3.6	Corn Germ Meal Composition (Solvent Extracted)	53
Table 3.7	Corn Oil Components	53
Table 3.8	Refined Corn Oil; Average Fatty Acid Composition	53
Table 3.9	Corn Bran (Hull) Composition	53
Table 3.10	Major Components of Corn Wet Milling Steepwater	55
Table 3.11	Corn Cobs: Proximate Composition (% As Is)	55
Table 3.12	Positive and Negative Characteristics of Representative Feedstocks	57
Table 3.13	Cell Wall Constituents of Biomass (%)	59
Table 3.14	Chemical Composition of Some Common Fibers	59
Table 4.1	Summary of Compounds Selected for Screening	65
Table 4.2	Detailed Process Evaluations Performed	66
Table 4.3	Market Information for Selected Chemicals	68
Table 5.1	Summary of Phase I Screening Results (Raw Materials Cost Contribution)	84
Table 5.2	Summary of Key Economic Contributors to Amortized Production Costs from More Detailed Analysis	120
Table 5.3	Additional Assumptions for Process and Capital Cost Evaluations	123
Table 5.4	Comparative Summary of Base Case Capital Investments (Millions of \$)	124
Table 5.5	Comparative Summary of Base Case Costs of Production (\$/lb of Product)	124
Table 5.6	Summary of Base Case Capital Investments (Millions of \$)	127
Table 5.7	Summary of Base Case Costs of Production (\$/lb of Product)	127
Table 5.8	Summary of Base Case Capital Investments (Millions of \$)	127
Table 5.9	Summary of Base Case Costs of Production (\$/lb of Product)	127
Table 5.10	Comparative Summary of Base Case Capital Investments (Millions of \$)	128
Table 5.11	Comparative Summary of Base Case Costs of Production (\$/lb of Product)	129
Table 5.12	Comparative Summary of Base Case Capital Investments (Millions of \$)	129
Table 5.13	Comparative Summary of Base Case Costs of Production (\$/lb of Product)	129
Table 6.1	Feedstocks Evaluated and Current Prices	140
Table 6.2	Feedstock Compositions	141
Table 6.3	Feedstock Coproduct Values	142
Table 6.4	Technical and Economic Assumptions	149
Table 7.1	Bioprocessing Element Product Portfolio Candidates and Market Values	154
Table 7.2	Portfolio Candidate Yields: Demonstrated and Theoretical	154
Table 7.3	FRF Results using Wet-Milled Corn as the Feedstock	156
Table 7.4	FRF Results using Hybrid Poplar as the Feedstock	156
Table 7.5	Initial Candidate Classification	157
Table 7.6	Qualitative Influences on Selection Process	184

Table 7.7	Market Information for Succinic Acid/Succinic Anhydride and Potential Derivatives	187
Table 7.8	Unit Raw Material Costs	190
Table 7.9	Unit Utility Costs	190
Table 7.10	Manufacturing Cost Summary, Succinic Acid from Glucose Syrup	192
Table 7.11	Performance Criteria Comparisons for Advanced Technologies, Succinic Acid Production	200
Table 7.12	Market Information for Butanol and Potential Derivatives	202
Table 7.13	Manufacturing Cost Summary for Butanol Production from Glucose Syrup	205
Table 7.14	Performance Criteria Comparisons for Advanced Technologies Butanol Production	210

1.0 EXECUTIVE SUMMARY

1.1 Report Overview

1.1.1 Introduction

Chemicals from renewable resources!

Since the oil crises of the mid 1970s, the idea of deriving our vital chemical feedstocks from renewable resources in a sustainable manner has been frequently suggested as an alternative to producing chemicals from petroleum-based feedstocks imported from unstable political regions. This resource document on biomass to chemicals opportunities is a joint effort between industry and a national laboratory team consisting of the National Renewable Energy Laboratory (NREL), Argonne National Laboratory (ANL), Idaho National Engineering Laboratory (INEL), Oak Ridge National Laboratory (ORNL), the Pacific Northwest Laboratory (PNL), and funded by the Office of Industrial Technologies of the U. S. Department of Energy (DOE). The report describes the development of a technical and market rationale for the incorporating renewable feedstocks into the chemical industry in both a qualitative and quantitative sense. The term "renewable feedstocks" can be defined to include a huge number of materials (as this report will reveal) such as agricultural crops rich in starch, lignocellulosic materials (biomass), or biomass material recovered from a variety of processing wastes. It is hoped that this report can be used as a starting point for industry, academia, and government RD&D programs to further develop strategies to match their core capability with opportunities in specific biomass to chemicals product families.

The goal of the DOE Alternative Feedstocks Program is to develop cost-effective and environmentally acceptable technologies for producing chemicals and materials from the large, underused renewable feedstock capacity in the United States. **An opportunity exists to displace an estimated 3 quads¹ of the energy consumed as raw materials by the chemical and petroleum refining industries if RD&D are carried out with industry, and commercialization is successful (1988 EIA/DOE MECS). The target for the Alternative Feedstocks program is to displace 1 quad by 2030.**

No less than a national team effort is needed to realize these goals. Although technologies exist to significantly reduce energy consumption using renewables, converting these technologies into cost effective applications is difficult. Through the Alternative Feedstocks Program, a team approach involving government, national laboratories, universities, and industries will be pursued to meet this challenge and sharpen America's economic growth and competitive edge in world markets. New technologies being developed for this program include integrating advanced biological processes for renewables into the mainstream of chemical processing; employing thermal and chemical processes for rapidly and selectively converting renewable resources into new chemicals; developing renewables-based processes that will reduce waste emissions and increase both energy and economic efficiencies; and establishing the concept of biomass refineries and chemical coproduct opportunities for other industries (agriprocessing, pulp and paper) that will provide domestic sources of chemical raw materials and simultaneously create new American job opportunities.

Today, the civilian market is the driving force behind advanced technology, such as that described in this report. The Alternative Feedstock Program will stimulate the manufacturing base in the United States as well as expand existing and future efforts in the chemical, biotechnology, petrochemical, and agriprocessing industries. The industries with the most to gain by this program have a great impact on the domestic economy. In terms of employment, the renewables sector employs more than 3 million people (agriculture/forestry, lumber/wood products, furniture, textile mill products, and paper/allied products). The petroleum exploration and related chemical industries employ nearly 1.4 million people

¹One quad = 1 quadrillion (10¹⁵) British thermal units (Btu) = 2.52 x 10¹⁴ kcal = 1.0559 x 10¹⁸ J

(oil/gas extraction, chemicals and allied products, petroleum and coal products, and rubber and miscellaneous plastic products). Adding new crops and products destined for chemical processing facilities could stimulate regional economic development in currently depressed sectors and be an integral part of a more secure job infrastructure for the 21st century.

This report will demonstrate the benefits of a wider incorporation of renewable alternative feedstocks into the chemical industry as raw materials. The chemicals and allied products and petroleum and refining industries used 11.7 quads of energy in 1988 (DOE/EIA-0552, adjusted for electric power generation efficiencies) giving them a significant role in the nation's energy consumption. In addition, the chemicals industry has the distinction of being one of the few industrial sectors in the United States that has maintained a positive balance of trade in recent years. However, the continued growth of this sector of the economy is at risk. Many of these raw materials used by this sector are now imported from sources that are politically unstable and in the long term whose supply will continue to be depleted until prices become prohibitive.

Several authors have correctly stated that petroleum is and will continue to be a major motivating force of the industrial society (Yergin, 1991). Natural gas and its liquids are important and their role will continue in the near future in the industrial economy. Some estimates suggest that relatively cheap hydrocarbon-based feedstocks will be available well into the next century (Spitz 1988). Specifically, as crude oil prices continue to increase, C-1 chemistry, based on coal gasification and converting coal-derived synthesis gas to chemicals and other alternatives (such as natural gas) will become important.

However, other pressures are coming to bear on "business as usual." In spite of a seeming complacency about oil and natural gas as primary resources for energy and chemicals, there is a climate change in industry. One driver for the changes is growing public concern about the environment and the resulting legislative response. Recognition that increased levels of atmospheric carbon dioxide produced in burning organic materials (primarily fossil products) could result in global climate change has made developing renewable sources of fuels and chemical feedstocks important to the nation's security. The cost of compliance with environmental laws is increasing (for example, difficulties in obtaining drilling rights on Alaska's North Slope, or in offshore areas). Other drivers include a simultaneous globalization of the industry that allows other countries to offer lower cost feedstocks and a variety of business and other incentives. To avoid such a shift and maintain jobs, it is essential to provide domestic industrial sectors with opportunities to increase their profitability in the United States by improving the efficiency of their processes and competitiveness of their products. Alternative feedstocks strategies have the potential to be cost-effective because they expand value-added product opportunities unique to renewables or advanced processing technologies that protect the environment, and will allow the United States to avoid importing a substantial fraction of its refined petroleum-based chemical building blocks in the future.

Many different components impinge on the concept of integrating renewable feedstocks into the nation's chemical production stream, and a single report can only offer a guide to many of the issues involved. However, this report is intended to begin describing in a qualitative and quantitative manner the advantages that would result from a large scale implementation of this program. For example:

- Substituting renewable feedstocks for petroleum-based chemical intermediates could potentially lower crude oil demand, thus limiting economic downturns in the chemical industry due to oil price volatility.
- Using biomass feedstocks can expand the options of the chemicals industry by increasing feedstock flexibility and by broadening the spectrum of potential chemical products (Biomarkets: 43 Market Forecasts for Key Product Areas 1991).
- Because imports are reduced as biomass is substituted for fossil resources, the balance of payments deficit also decreases.

- Producing biobased chemicals may provide an acceptable answer to the current problems that the petroleum-based chemicals industry faces in terms of generating hazardous waste and responding to public and political pressure to protect the environment (Russell et al. 1992; Stavins and Whitehead 1992).
- Carbon dioxide is recycled when new biomass is grown to replace that harvested for producing chemicals, and there is not a significant contribution to carbon dioxide accumulation in the atmosphere. In fact, if durable goods are made from biomass, carbon is sequestered for long periods of time, actually countering a build up of carbon dioxide in the atmosphere from fossil fuel use.
- Advances in metabolic engineering, bioprocessing, and separations technologies currently provide an unprecedented opportunity to overcome the key technical and economic hurdles limiting industrial applications.
- Environmentally sound biological processes for new products from renewable resource feedstocks could enhance industrial productivity. Indeed, it is estimated that the bioprocessing industry could grow to become a \$50 billion/yr industry by the year 2000 if sufficient investments are made in research and education (National Academy of Sciences 1992). Producing chemicals based on renewable resources represents an opportunity to realize this potential, and enable U.S. industry to dominate in this area in the future with economically and environmentally sound products and technologies.
- The window of opportunity for global commercialization of several products and technologies is in the near to mid-term timeframe (0-5 years, 5-10 years, respectively); however, they must be developed and demonstrated at sufficient scale to lower the investment risk to United States industry for commercialization.

What will the reader find in this report? First, for convenience, two broad areas of investigation are covered throughout the report: converting renewable materials into useful feedstocks by thermal or chemical means, and converting materials through bioprocessing. Although a number of the sections are divided according to these disciplines, the reader must recognize that different approaches offer different advantages. Some materials may be best prepared by thermal or chemical technology, and others are most efficiently obtained through bioprocessing. In many cases, a hybrid chemical/biological approach could offer the most cost-effective route to a product.

Section 2.0 attempts to review the many factors potentially influencing the feasibility of an Alternative Feedstocks program. Summarizing this vast amount of information in a readable form is an extremely difficult task, and a single report cannot give exhaustive coverage of all areas. Readers are directed to consult the other references listed in section 9.0 for more detail.

Section 3.0 moves more deeply into a key issue confronting an alternative feedstocks program, specifically, the availability of the renewable material necessary for producing chemicals. Questions of feedstock quality, long-term availability, production infrastructure, and feedstock flexibility will all impact the success of an industrial effort.

More importantly, sections 4.0 - 7.0 of the report describe a methodology developed to identify different promising RD&D opportunities on a more quantitative basis, and categorize them as near (0-5 years), mid- (6-10 years), and long-term (greater than 10 years) possibilities. Since each reader will bring his or her own perspective to this report, no attempt has been made to "sell" certain opportunities at the expense of others. Rather, readers in government, industrial, and academic environments are encouraged to use the results of this report within the unique context they can provide. As an example, DOE has used the information provided in this report to prepare a program document that provides a

general overview of the alternative feedstocks effort, a description of the specific RD&D areas recommended for funding that fit current DOE goals.

1.1.2 Overview of the Technoeconomic Evaluation of Proposed Process Routes from Renewables

A key component and the major portion of this report describes a quantitative, comparative technoeconomic evaluation of the potential costs and benefits of incorporating renewables into the nation's chemical feedstock stream. A screening methodology was needed so that technologies for chemicals and materials from biomass could be organized for near-, mid-, and long-term development objectives. The methodology needed to identify necessary RD&D that could be carried out with industry to develop the most promising examples of these technologies to commercial success.

An evaluation was carried out on both the proposed thermal, chemical and biological processes, and where possible, directly compared to existing hydrocarbon-based technologies. Some differences exist in the details of the evaluation methodology employed for the chemical and biological evaluations (described in depth in sections 4.0 - 7.0 of the report), but both attempt to answer a central question: *Given a wide range of possibilities, how can an informed decision be made as to which materials to investigate more thoroughly?*

Caution must be used when reading the results of these technoeconomic evaluations. They are approximations, and intended to serve as "pointers" to those biomass-based processes that appear to have a reasonable chance of competing with their hydrocarbon-based counterparts. However, a wide range of subjective judgement is possible among many of the processes evaluated. The evaluations are only as good as the process information currently available, and when exact information cannot be obtained, then reasonable estimates must be made regarding potential process performance. As a result, a process that shows high potential may not immediately be identified for further research because the actual process needs more definition. Conversely, a process showing less favorable potential after evaluation may be ideal for further study because a well defined process exists. Other criteria can also be important, including energy impact, environmental quality, economic competitiveness, and probability of success. It is expected that readers of this report will impose their own expertise and additional judgement criteria on chemicals and processes of interest. Feedback from readers on how to make the screening methodology more valuable will be greatly appreciated and encouraged by DOE.

Evaluating the processes and materials provided an additional benefit. This investigation helped define related RD&D areas that, if pursued, would improve the outlook of certain processes, and of the overall industrial concept. These related areas are also listed as part of the recommendations.

1.1.2.1 Overview of Technoeconomic Evaluation of Thermal and Chemical Processes

The evaluation of thermal or chemical processes uses a simple but well established method: the raw material cost contribution for producing a chemical from biomass is compared to that for producing the same chemical from hydrocarbons. In those cases where a direct comparison was not possible (for example, in situations where a petrochemical-based process is not known), a comparison was made between the existing process and processes that could improve production of that material.

Because new ventures always involve some uncertainty, the evaluation of the biomass-based process was then adjusted upward by a risk factor of 30%, i. e., any new process should show a 30% improvement over existing technology to justify investment (a well established rule of thumb in industry for a pioneering new venture). These two simple steps provide a set of numbers for comparison as the ratio:

$$\frac{\text{Raw Materials Cost Contribution for Petrochemical (or other) Process}}{\text{Raw Materials Cost Contribution for Biomass Process} \times 1.3 \text{ (risk factor)}}$$

Those ratios significantly less than one indicate that the existing routes to a chemical have a considerable advantage over a new biomass-based process, and ratios significantly greater than one indicate that the biomass-based process could be an attractive candidate for further investigation. However, these numbers are approximations and are intended to augment an informed judgement by the reader. A ratio of 0.9 or even 0.8 is certainly not a reason for a "no go" decision; a ratio of 1.2 or 1.3 is not a reason to devote all efforts to a single material.

Where existing research results and process information warrants, a more detailed analysis has been made. These evaluations (detailed in section 5.0) include an analysis of expected capital and operating costs of a large scale biomass-based facility for producing certain chemicals, and projects an amortized production cost for the chemical.

1.1.2.2 Overview of Technoeconomic Evaluation of Biological Processes

The screening methodology used to select and classify biological processes is similar to that used for the thermal and chemical processes. The first step evaluates products using very approximate economic analysis based only on the prices of the products and starting materials, and compares the cost of the feedstock to the value of the material derived from that feedstock. Very simply, if the cost of the feedstock is more than the value of the products, then the process will probably not be economically viable.

The second step is a comparative analysis of the proposed bioprocessing route with the conventional petrochemical processing route. These results are also approximate because the method considers only the major raw material cost contribution of each route, similar to the method used in the evaluation of the thermal and chemical routes. This step of the evaluation also includes the 30% adjustment to cover uncertainties in projecting the costs associated with a new process.

The results of this analysis are used with various qualitative judgements to decide the order in which products are evaluated under the final screening stage. This qualitative opinion falls under the four broad categories of Energy Impacts, Environmental Quality, Economic Competitiveness, and Probability of Success. The final screening is a preliminary grade estimate of the total capital investment for the project, and using various economic assumptions, a prediction of a required product selling price. This predicted selling price is compared to the current market value and the products are ranked according to this difference.

1.1.2.3 Improving the Evaluation Process

One of the significant products from this study has been the development of a methodology for assessing and screening the economic potential of a variety of processes to produce biobased products. The screening and analysis methodology provides a rational and systematic approach to discriminate between potential processes. The methodology has largely been market based, but environmental costs are an important dimension that was not included in the initial analysis. It is the intention of the Alternative Feedstocks program to investigate, evaluate, and quantify the environmental aspects of a potential product or process for incorporation in the overall evaluation methodology. This will provide another dimension to the screening and permit an estimate of the environmental costs associated with the use of any specific process.

1.2 Recommendation Overview

1.2.1 Thermal and Chemical Recommendations

As a result of the evaluation process, several processes or materials have emerged as potential RD&D opportunities. A number of different criteria were used in assigning these areas, including current level of knowledge, current scale of operation, estimated time required for potential commercialization, etc.

Some of these processes proceed well, but only on a laboratory scale. Others have been operating for several years at multipound scales, or have been commercialized in the past. Details for each of these processes are given in later sections of the report. However, they fall nicely into the near-, mid-, and long-term scenarios. Of course, readers will bring their own criteria to this report and may find it more logical to reclassify some of the processes and materials assessed.

It is important to note that placing a given chemical or process into one of these three categories does not immediately mean that RD&D will realize a result within the broad definitions of each of these timeframes. Certain materials may better be classified as near-mid or mid-long. RD&D could reveal that an opportunity originally classified as near-term requires more investigation; conversely, an originally long-term proposition may be brought to commercialization rapidly by unexpected breakthroughs. However, for simplicity, subdividing the categories was not considered.

The analysis of potential products from thermal or chemical processes suggests that four products could be suitable for further development within either near- or midterm timeframes: cellulose, lignin, and hemicellulose from clean fractionation of lignocellulosics and the production of acrylic acid, anthraquinone or peracetic acid. It should again be emphasized that this analysis and selection was made from a limited range of options and hence is limited in scope. As a wider range of options is analyzed, equivalent or even better choices may become obvious.

1.2.2 Bioprocessing Recommendations

Over the past decade a series of technological advances has occurred that promise, in concert, to significantly improve the economic competitiveness of biobased processes. Evaluation of this window of opportunity focuses on the inherent attributes of biological processes, application of new technology to overcome past limitations, and integration with nonbiological process steps.

The bioprocessing element of the Alternative Feedstocks Program is attempting to define the most economical chemical candidates that could be produced biologically from renewable resources to provide feedstock flexibility to the chemical industry and accrue multiple benefits to the United States economy in energy security, economic growth, and environmental stewardship.

The initial emphasis of the program has been on the evaluation of the potential and economic opportunity of biobased products. The ongoing product/process screening analysis is supplemented by surveys on feedstock availability, market potential, improved biochemical pathways, and advanced bioprocessing concepts. Literature surveys and evaluations have been done in consultation with an industrial panel. The results of the initial product screening analysis and industrial participation gave two classes of potentially important bioproducts: organic acids and neutral solvents. Specific representative targets, succinic acid and butanol, respectively, were selected for further evaluation. Additional product classes are being examined.

A focused research and development effort is needed for portfolio candidates classified as near-term opportunities to improve both the process and the microbial metabolism. Six primary criteria will be used to evaluate possible advanced bioprocessing concepts and the potential of metabolic pathways modifications. Each of the possible innovations will be considered on the basis of (1) volumetric productivity (2) yield as a fraction of theoretical (3) the product quality in purity and concentration (4) the energy use inherent in the process (5) the potential environmental impact and (6) the operability.

1.2.3 Developmental Process for Recommended Products and Processes

The program will take advantage of basic concepts, initiated under other programs, which show potential of marketability for biobased products. These concepts will be economically evaluated to estimate the impact. The best concepts for the target compounds will generally be taken directly to the developmental stages. Industrial involvement is considered critical and will be actively pursued

throughout all phases of the development efforts. Often, it will be apparent that additional research is necessary to utilize the process. Research support will be sought from other DOE offices or other federal agencies to address these research issues.

A laboratory demonstration of the process components will be performed for the target compound. This work may be carried out at various sites. Results from this demonstration will be used to design a complete field pilot unit for testing at an industrial site. The results will also be used to refine the economic model. It is expected that industrial participant(s) will have an increased role at each stage of development. The final stage will be a pilot plant constructed through cost sharing with the industrial participant.

Projects in the program will be market driven. However much of the RD&D may have generic applicability to an entire class of materials, such as improved separation for organic acids or improved pretreatment of lignocellulosics. The projects will tend to focus on the actual developmental demonstration and economic evaluation of real products and processes. Near-term projects (1 to 5 years) were preferred for this first screening, but mid-term (5 to 10 years) projects were also considered. Advanced techniques will be employed when they enhance process economics.

Many technical issues exist, both generically and specifically for certain target products. Although this program will focus on commercialization of specific representatives of chemical product families, there are barriers that are common to many potential products from renewables. Broader infrastructure barriers that must be examined for the larger industry include: the interface between the agribusiness and the chemical processing industry, the presence of a qualified pool of trained personnel for this new industry (National Academy of Sciences 1992), and the consumer acceptance or awareness of "green" products from renewables.

1.2.4 Near Term RD&D Opportunities

The evaluation process identified several possible RD&D opportunities that fall roughly into the near-term timeframe. For bioprocesses, succinic acid was identified as one opportunity. For thermal chemical processes, two potential opportunities were identified which will need further evaluation prior to actual development: producing cellulose, lignin, and hemicellulose by clean fractionation and producing acrylic acid. Additional thermal and chemical opportunities are identified here and additional bioprocessing options are described in sections 6.0 and 7.0, and specifically in Table 7.5.

1. **Succinic acid produced from corn syrups** provides an opportunity that has significant potential to demonstrate the feasibility of producing a commodity type chemical from renewable resources.
2. **Clean fractionation of biomass** is a process being developed at NREL that allows separating lignocellulosic material into its three primary components (cellulose, hemicelluloses, and lignin), more cleanly than current technologies.
3. **Acetylated wood**, a material that can be made from wood and waste fibers that shows significant improvements in dimensional stability and resistance to biological degradation in comparison to other materials, appears to be ready for process development and pilot demonstration if industrial interest and markets can be developed.
4. **Starch plastics** are materials that find uses in producing biodegradable plastic packaging or other applications. Further evaluation of their production will be important, especially where chemical modification is used to impart specific properties.
5. **Fast pyrolysis of wood** offers phenolics to be used in molding compounds and adhesives manufacture and other promising chemicals. A related process, lignin hydrotreatment, also

offers a route to these materials. Another related process, **wood phenolation**, involving the catalyzed reaction of phenol and wood gives a liquid product used in producing phenol-formaldehyde thermosetting resins.

6. **Benzene, toluene, and xylene** can be made from wood, but are currently experiencing a static market in the United States. These materials could be developed on a small scale in countries that need these chemicals and cannot import or produce them, but have a renewable feedstock base available.
7. **Acrylic acid** can be prepared using a process being developed at PNL. The process uses bioprocessing and chemical processing for converting waste starch products. Engineering development of the process will help to validate initial technoeconomic assessments.

1.2.5 Mid Term RD&D Opportunities

The evaluation process identified several possible RD&D opportunities that fall roughly into the mid-term time frame for development. These are generally processes or products that require some additional research and development to improve market acceptability or process economics. They are likely candidates for the next generation of product candidates for the program. For bioprocesses, one opportunity was identified among the neutral solvents, butanol production. For thermal and chemical processes, two potential candidates were identified, anthraquinone and peracetic acid. Additional thermal and chemical examples are identified here and the additional bioprocessing opportunities are discussed in sections 6.0 and 7.0, and specifically in Table 7.5.

1. **Butanol** from bioprocessing could be a major commodity chemical that has application as a feedstock for such products as butyl butyrate, which is being considered as a "green" solvent.
2. **Xylose, xylitol, furfural, furan resins, tetrahydrofuran, glucose, gluconic acid, sorbitol, mannitol, levulinic acid, and succinic acid** are materials that could be prepared from inexpensive cellulose and hemicellulose derived sugars, available from clean biomass fractionation.
3. **Anthraquinone**, a well known pulping catalyst and chemical intermediate, can be prepared from lignin using a process being developed at NREL and the Institute of Paper Science and Technology. Engineering and parallel process development should be pursued to validate initial laboratory test results.
4. **Butadiene and pentane/pentenes** can be prepared using fast pyrolysis followed by catalytic upgrading on zeolite-type catalysts. The process could become important if feedstocks such as refuse-derived fuel from municipal solid waste can be shown to perform adequately.
5. **Acetic acid** can be produced from syn gas, a route that appears to be an interesting match given the unique composition of synthesis gas available from biomass, and makes possible a balanced process (through intermediate methanol) without the costs of syn gas reforming.
6. **Peracetic acid** is an oxidant that is a good non-chlorine containing pulp bleaching agent, but its high cost is the key impediment to a more widespread use. A more detailed analysis of the means of reducing the costs of peracetic acid would guide proposed research and permit market penetration of this chemical into the pulp and paper industry.

1.2.6 Long Term RD&D Opportunities

Several interesting opportunities were noted during the analysis process as long-term opportunities. They are characterized as needing significant RD&D prior to consideration as a potential product line.

Some examples of the thermal or chemical and bioprocessing options are listed here. More complete analysis results are found in sections 4.0-7.0.

1. **Levoglucosan** can be prepared from fast pyrolysis of biomass and is a starting material for the producing high value materials and specialty polymers. A specific levoglucosan derivative is **resorcinol**, a cold setting adhesive that would have additional markets at lower cost. Markets for these products will develop as research in Japan, Canada, and the United States increases.
2. **Vinylphenol**, a high-value specialty monomer used in coatings and microlithography, can be made from biomass pyrolysis. With suitable biomass feedstocks, NREL research has shown that significant yields of this monomer can be produced.
3. **Hydroxyacetaldehyde** is a byproduct of the fast pyrolysis of wood. Methods to separate the product need to be developed so it is valuable to the biomass pyrolysis refinery.
4. **Polyhydroxybutyrate/valerate** can be prepared from biomass derived syngas and could be a cheaper precursor than glucose for these useful and biodegradable biopolymers. Verification of the preliminary technoeconomic assessment would enhance the outlook of this process.

1.2.7 Related RD&D Opportunities

1. A basic understanding of reactions for selectively converting biomass and biomass derived materials into chemicals is needed. A fundamental understanding of new catalytic processes for selectively manipulating and modifying carbohydrates, lignins, and other biomass fractions will greatly improve the ability to bring biomass derived products to market. The behavior of oxygenated molecules on zeolite and other shape selective catalysts could lead to a better design of processes for chemicals from biomass. Developing special catalysts for biomass processing is not a high priority for the chemicals industry, but is essential for this new field if it is to compete with petroleum resources and cost-effectively produce fuels and chemicals.
2. Databases that compile the details of producing candidate chemicals from renewables relative to production from conventional processes would be useful for performing sensitivity analyses. Including environmental databases would allow these analyses to address environmental costs.
3. The number of candidate chemicals and materials undergoing evaluation should be increased using input from industry and the national laboratory team.
4. Several bioprocessing issues need to be addressed by basic and applied research. These include processing dilute product streams, improving bioprocessing catalysts (usually microorganisms), improving and adapting reactor designs, integrating feedstock preparation with bioprocess operations, and developing process controls specifically applicable to renewables processing.
5. A fundamental understanding of clean biomass fractionation into its three subcomponents is needed. The method being developed at NREL can carry this out relatively cleanly, but the process is not yet well enough understood to permit widespread use among all biomass options.
6. Investigating the possible monomers that can be derived from pyrolytic processes would expand the possibilities of using biomass as sources for chemical feedstocks.
7. Developing fast analytical methodologies for analyzing biomass is an enabling area for the production of chemicals from renewables. These methodologies, that include new analytical techniques and sensors, provide the basis for automated process control necessary for operations with complex feedstocks and product mixtures, an important component of optimized industrial production of chemicals and materials.

2.0 OVERVIEW OF FACTORS CONTRIBUTING TO ANALYSIS

Integrating renewables into the feedstock supply of the chemical industry is a complicated matter, and requires consideration and knowledge of many different but interrelated factors. This section offers an overview of several of these key factors that impinge on the potential benefits of the program (section 1.1.1).

2.1 Energy Considerations

A huge amount of energy equivalent is available in the form of renewable biomass. "Renewables" in the context of this report refers to biomass derived from photosynthesis driven by solar energy and residues from processing biomass resources into conventional products such as food, feed, and fiber. The availability (in energy equivalent) of renewable resources is estimated (Szmant 1986) to be:

Worldwide biomass production:	6.9×10^{17} kcal/yr (2740 quads)
Worldwide biomass utilization:	4.7×10^{16} kcal/yr (190 quads)

i. e., humankind uses only 7% of the worldwide biomass production for food, feed and fiber.

Using renewables in the United States reflects the low worldwide trend. Current levels of using renewable resources for all uses (converted into energy equivalent) are:

Forestry/Pulp and Paper (without fuel use)	4.6 quads (energy equivalent)
Agriculture grains only	5.3 quads (energy equivalent)
Biomass industrial/residential	2.7 quads (energy)
Biomass to electric power generation	0.8 quads (energy)
Biomass transportation fuels (corn-to-ethanol)	0.1 quads (energy)

This breakdown gives a total of 13.5 quads currently used for conventional food, feed, and fiber and emerging energy technology applications (Overend and Chum 1991).

Contrast the numbers for renewables with those for energy production and use from conventional sources. In 1990, the United States produced 67.5 quads of energy (32% from coal, 27% from natural gas, 26.5% from crude oil, 9% from nuclear and 4% from hydroelectric), but consumed 81.5 quads, that required importing 14 quads. The major consumers of energy were the industrial sector (30 quads), buildings (29.3 quads), and transportation (22.2 quads).

The activity of the industrial sector is of primary interest to the Alternative Feedstocks program and a deeper investigation of its energy needs is illustrative. The energy intensity of the industrial sector alone, shown in Table 2.1, gives a different way of understanding its energy consumption (the Standard Industrial Classifications are shown for convenience), and is a useful starting point for considering energy used by the various manufacturing sectors. It is clear from Table 2.1 that chemicals and allied products is especially energy intensive, ranking fourth only to the paper and allied products, and the key inorganic and metals industries. Importantly, note that the petroleum refining industry is one of the few examples of industrial sectors in which the energy usage is *increasing* with time. More energy is required because the quality of starting crude oils is decreasing with time. This trend is expected to continue as easily available and higher quality crude oil sources are depleted.

An interesting shift in the order of energy consumption presented in Table 2.1 results when other sources of energy consumption are included (Figure 2.1; EIA Annual Energy Outlook 1992). For example, the pulp and paper industry consumes large amounts of wood bark and associated processing wastes from its chemical recovery processes to supply a little more than half the energy it requires (base plus renewables). Other sectors shown on the graph do not have access to this energy source. Therefore, the chemicals industry consumes large amounts of its petroleum and natural gas as feedstocks for

manufacturing products, but also must use large amounts of conventional fuels for process heat and power, both of which can be viewed as an energy equivalent (Base, Renewable, Feedstocks). In addition, inefficiencies in generating electricity have to be considered. With these additions, the chemicals industry clearly becomes the largest energy consumer of the industrial manufacturing sectors, and an appropriate candidate for RD&D to reduce this consumption.

Table 2.1 - Energy Intensity in Manufacturing Industry Groups: 1980, 1985, and 1988 (Thousands BTU/constant 1982 Dollars)

<u>SIC</u>	<u>1972 Standard Industrial Classification</u>	<u>1980</u>	<u>1985</u>	<u>1988</u>
32	Stone, Clay & Glass Products	21.5	16.7	16.7
33	Primary Metals Industry	16.3	14.6	14.4
26	Paper & Allied Industries	15.9	14.0	12.9
28	Chemicals & Allied Products	14.9	12.4	11.3
22	Textile Mill Products Industry	5.7	4.8	4.8
29	Petroleum & Coal Products	5.3	4.9	5.7
30	Rubber & Misc. Plastic Products	4.3	3.1	3.2
20	Food & Kindred Products	3.5	2.7	3.0
34	Fabricated Metal Products	2.7	2.3	2.4
25	Furniture & Fixtures Industry	1.9	1.6	1.7
35	Fabricated Machinery & Equipment	1.7	0.9	0.8
36	Electronic & Other Electric Equipment Industry	1.7	1.25	1.2
39	Miscellaneous Manufacturing Ind.	1.7	1.4	1.4
37	Transportation Equipment Industry	1.5	1.2	1.1
38	Instruments & Related Products	1.6	1.2	1.2
	All Manufacturing	5.8	4.4	4.2

Source: Changes in Energy Intensity in the Manufacturing Sector 1980-1988. Manufacturing Energy Consumption Survey. DOE/EIA-0552 (80-88), December 1991; for comparability, the data are calculated based on the 1972 Standard Industrial Classification System

Chemical production is also heavily dependent on fossil-based feedstocks. The chemical and allied products and the petroleum refining sectors derive more than 98% of their primary organic petrochemicals (methane, ethylene, mixed aromatics, etc.) from two feedstocks, crude oil and natural gas (including two- to four-carbon natural gas liquids). Roughly 11.7 quads (5.0 in producing nonenergy materials and 6.7 in process energy) are associated with using crude oil for producing chemicals. Over the last 25 years, the nation's supply of crude oil has been increasingly derived from foreign imports, making our supply of vital feedstocks vulnerable to politically unstable governments and the natural volatility of crude oil prices. As supplies from these sources continue to be depleted, their price will rise (and so will most prices of products that rely on oil derived sources for energy), as will the manufacturing cost of refining crude oil or natural gas, again because of the decreasing quality of available feedstocks. Considerable RD&D has focused on developing alternative fossil-based starting materials for chemicals, including coal, oil shale, and tar sands. RD&D of conversion technologies using these alternatives continues worldwide; fossil-based feedstocks, primarily coal and oil shale, are the subject of extensive RD&D in the United States and other countries. Some of these resources, such as electric energy production from coal, are already major players in the energy field in the United States and other countries.

Energy Consumed in Manufacturing

Four Ways of Measuring It

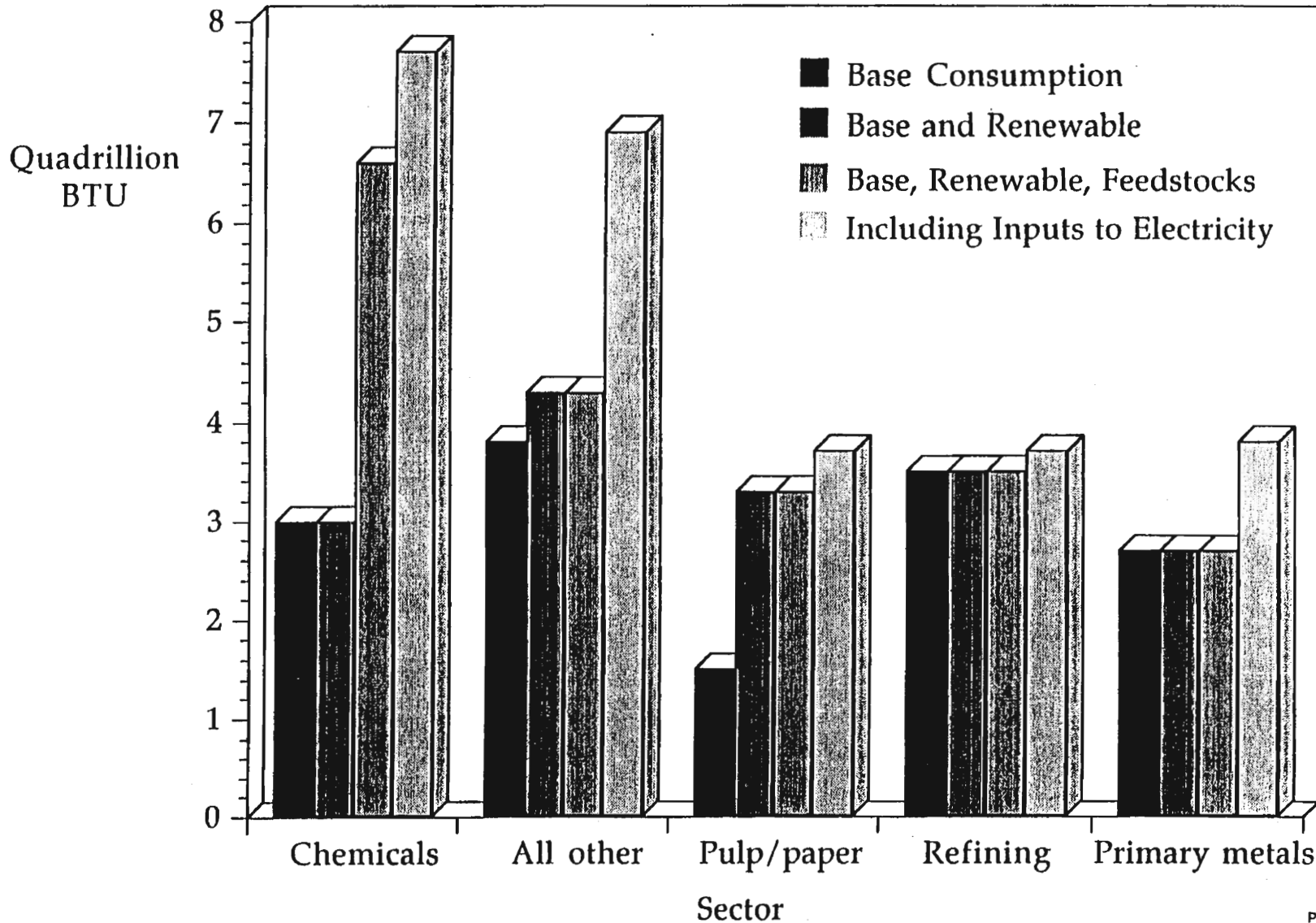


Figure 2.1 - Different Ways of Measuring Energy Consumed in Manufacturing

2.2 Environmental Considerations

Today, industrial criteria for developing new processes and products continue to involve the traditional parameters:

- Economics
- Productivity
- Efficiency and functionality

Industry's view includes globalized market economies, that decrease constraints of operating within the boundaries of one nation. Government tends to impose additional criteria:

- Sustainability, stewardship, and managing national resources
- Economic growth
- Maintaining and improving living standards

However, a newer parameter is rapidly growing in importance as industry considers new processes:

- *Environmental impact both before and after using a product (waste management) and maintaining, preserving, and improving the environment for future generations.*

Selecting appropriate feedstocks for the future will ultimately be based on a balance between several criteria, that include the cost of production and a global assessment of the cost to the environment, however, industry is being asked to reevaluate its priorities and consider additional factors as they assess their operations. These include:

- Minimizing emissions to air, land, and waters in manufacturing products.
- Assessing the toxicity and hazards of final or intermediate products to decrease the risk of the operations on workers and neighborhoods.
- The effect of processes and products on the global environment – the compatibility of products and processes with the environment.
- Waste management and disposal of waste (industrial/post-consumer) in an environmentally and ecologically sound and cost effective manner. Product recycling and biodegradation strategies are needed by industry as they are required by consumers and municipalities.
- Resource conservation - efficient use of resources and minimizing effects of extracting resources from the earth.
- Alternative resource development - are there resources that could lead to better products with less environmental impact with sufficient RD&D and commercialization?

Renewables can potentially address the energy and feedstock needs of industry without many of the environmental costs incurred by continued use of fossil-based materials. The key word is "environmentalism", that will become a major business in the '90s and beyond (Narayan, in Rowell 1992).

The idea that a "greening" of industry is needed resulted in key international companies and industrial organizations meeting in Rotterdam to endorse a set of principles and a charter that will commit them to environmental protection into the 21st century. A business charter for sustainable development was adopted by more than 150 companies and 35 organizations. In support of this document, 16 principles developed by the Paris-based International Chamber of Commerce (ICC) were adopted. These principles are designed to place environmental management high on corporate agendas and to encourage policies and practices for carrying out operations in environmentally sound ways. ICC's U.S. affiliate is the U.S. Council for International Business, that expects that American corporate awareness of sustainable development will emerge. Examples of principles in the ICC charter are:

- Developing and operating facilities that undertake activities with energy efficiency, sustainable use of renewable resources, and waste generation in mind.
- Supporting and performing research on the impact of raw materials, products and processes, emissions and wastes, and ways to minimize this impact.
- Modifying manufacturing, marketing, or using products and services to prevent serious or irreversible environmental damage; developing products and services that do not harm the environment.
- Contributing to the transfer of environmentally sound technologies and management methods.

The Earth Summit in 1992 also emphasized the need for developing partnerships that include many countries, industries, and governments for establishing stewardship over the planet's resources and environment. The Agenda 21 established 150 recommendations and a blueprint for the future, that 114 heads of state signed. Paramount was the concept of global partnership leading to the sustainable development of the world. Recent United States signing of the carbon dioxide Rio accord that limits greenhouse gas emissions in the year 2000 to 1990 levels suggests that alternative feedstocks could play an important role in decreasing emissions. A national team approach of the Alternative Feedstocks Program between laboratories, industries, and agriculture could provide a role model for this global partnership for renewable-based economic sectors.

2.3 Legislative Considerations

Closely related to the growing public concern over the environment is the legislative response to this concern. Industry is facing increasingly more stringent environmental regulations. The Chemical Manufacturer's Association estimated that in 1990, capital expenditures by the chemical industry for pollution abatement amounted to \$1.68 billion and annualized operating expenditures amounted to about \$3.83 billion. The figures for the pulp and paper industry are similar. In 1990, the National Council of the Paper Industry for Air and Stream Improvement (NCASI) estimated that the necessary capital expenditures for regulatory compliance were \$1.27 billion, and consisted primarily of water pollution abatement (50%), air pollution abatement (30%), and solid waste abatement (20%). These capital investments, coupled with administering applicable laws and regulations have increased the product costs by \$22/ton. Adding operating and maintenance costs results in an overall increase of \$35/ton of paper and paperboard produced, a total of \$2.7 billion for the industry. These expenditures represent a 20% increase in costs over 1989.

The chemical and pulp and paper industries are subject to a number of common regulations, but the impact of some is more important to one sector relative to the other. The following sections give details about some of the key environmental legislation.

2.3.1 Chemical Industries (United States Department of Commerce, 1992)

Emergency Planning and Community Right-to-Know Act (3rd Title of the Superfund Amendments and Reauthorization Act - 1986) -- Title III

This act mandates emergency planning and gives communities the right to know about certain hazardous materials used, produced, purchased, stored or shipped by industries. Title III sets specific reporting requirements and deadlines. They include inventories of specific chemicals, material safety data sheets, annual inventory of materials kept, and their releases into the environment. EPA has the list of chemicals in a computerized data base, that the public has access to and the number of chemicals covered is expanded periodically as is the level of the reporting required of the industry.

Clean Air Act (CAA)

This act prohibits hazardous pollutant discharges into the atmosphere in excess of emission standards. The 1990 amendments impose new standards and regulate how many of these chemical pollutants will

need controls in place by certain times. Thus, an added 41 compounds must be in place by 1995 and another 148 by 2003.

Toxic Substances Control Act (TSCA)

This act regulates testing and manufacturing of chemical substances and mixtures. TSCA authorizes Environmental Protection Agency (EPA) to require testing certain substances. The number of substances is being expanded and the specific testing requirements are being streamlined. The goal of the act is to extend the number of chemicals tested through an international program with the Organization for Economic Cooperation and Development. Each company is required to submit a premanufacture notification (PMN) for each new chemical they wish to produce. This has a major impact on the chemicals from biomass that are new or not identical to those produced through conventional methods. The PMN is reviewed and additional testing may be required before production and commercialization. The act can prohibit, limit, or ban the manufacturing, processing, and using chemicals. Substantial risk information has to be reported under the act with substantial penalties for violations (e.g., \$25,000/day in civil penalties).

Resource Conservation and Recovery Act (RCRA)

RCRA regulates managing hazardous waste from generation to disposal. Land disposal of hazardous wastes has been banned unless no migration from the waste facility will occur as long as the waste remains hazardous or the waste is treated to levels established by EPA. A number of regulations exist that control handling and disposal, underground storage, and the number of chemicals that fall under this category.

Implications of the act to the chemical industry according to the CMA is that \$9-60 billion could be required to clean up hazardous and non-hazardous sites during the next decade, depending on the rate of program implementation and levels required.

Clean Water Act (CWA)

CWA guarantees continued progress in insuring high quality water. It prohibits discharges of pollutants into navigable waters without a permit and increases the severity of civil and criminal penalties for violations of the act.

Safe Drinking Water Act (SDWA)

National standards are set for contaminants to drinking waters. There are nine chemicals in the current standard and an additional 62 are being added. Protecting groundwater quality and wellheads are part of this act.

Chemical Diversion and Trafficking Act

The act addresses the problem of diverting chemicals to make illegal drugs. This act requires controlling records of sales of chemicals, reporting suspicious transactions/unusual transactions, and controlling export/import transactions.

Occupational Safety and Health

The Occupational Safety and Health Administration (OSHA) requires extensive documentation of chemicals in trade, in the working place, and mandates warning labels on containers. Estimated annual costs of compliance are about \$400 million annually. OSHA also sets a hazard communications standard, and state and local laws, that give workers the right to know about hazardous chemicals in

the workplace. The chemical industry currently complies with permissible exposure limits for about 600 hazardous substances.

2.3.2 Pulp, Paper and Paperboard Industries

In addition to the above mentioned acts that also pertain to this sector, the Environmental Pesticide Control Act applies to this industry. A summary of the legislation affecting the pulp and paper (much of it in common with the chemicals industry) is shown in Table 2.2.

Particular problems of this industry pertain to the water pollutant discharges and control of dioxins. These issues figure prominently as a major compliance requirement. Preventing dioxins and related compounds from forming has had major impacts on the bleaching sector of the industry, both in the technologies used (chlorine-free: oxygen, ozone, peracids, and other oxidizers) as well as developing strategies to recycle the mill waters. EPA is developing a national industrial effluent limit guidelines and standards based on the best-available, economically achievable technologies to reduce dioxin contaminants and total chlorinated organics from manufacturing bleached paper products.

Table 2.2 - Environmental Legislation Affecting the Pulp and Paper Industry Since 1970

<u>Year</u>	<u>Legislation</u>
1970	Air Quality Standards Act (Clean Air Act; P. L. 91 - 604) Water Quality Improvement Act (P. L. 91 - 224) Resource Recovery Act (P. L. 91 - 512) Occupational Safety and Health Act (P. L. 91 - 596)
1972	Water Pollution Control Act Amendments (P. L. 92 - 500) Environmental Pesticide Control Act (P. L. 92 - 516)
1973	Clean Air Act Amendments (P. L. 93 - 15)
1974	Safe Drinking Water Act (P. L. 93 - 523) Clean Air Act Amendments (P. L. 93 - 319)
1976	Toxic Substances Control Act (P. L. 94 - 469) Resource Conservation and Recovery Act (P. L. 94 - 580)
1977	Clean Air Act Amendments (P. L. 95 - 95) Clean Water Act Amendments (P. L. 95 - 217)
1978	Resource Conservation and Recovery Act Amendments (P. L. 95 - 509)
1980	Solid Waste Disposal Act (P. L. 96 - 482) Comprehensive Response, Compensation and Liability Act (Superfund; P. L. 96 - 510)
1986	Superfund Law Safe Drinking Water Act Amendments
1987	Clean Water Act Amendments
1989-90	Clean Air Act Amendments

Source: Pulp and Paper 1992 North American Factbook, p. 77.

Another industry trend is increased use of internal manufacturing waste streams and post-consumer recycling, that complies with the various requirements at state and local levels (that can be different from place to place) as to the level of recycling imposed by legislation.

All of these regulations will apply to new processes and products from biomass, and the awareness of these evolving regulations is necessary so that programs are designed to help industry develop new technologies that are environmentally sound and cost effective.

2.4 Windows of Opportunity

Because of increases in demand, processing plant obsolescence, increased costs for environmental compliance, and new technology development, windows of opportunity to commercialize new products and processes in the chemical industry emerge every three to five years. In advance of these windows of opportunity, new technologies must move from the laboratory and be demonstrated at sufficient scale to reduce the risks for commercial introduction. The economic gain from exploiting a window of opportunity can only be realized if the research has been supported well in advance of the need for new technology. Several examples are presented to illustrate the diversity of characteristics that can combine to create these windows of opportunity, followed by technical advances that promise to contribute to expanding these windows into new applications.

2.4.1 Example - Biodegradable Polymers

Currently, there exists a window of opportunity for developing and commercializing biodegradable polymers. Technologies to produce and use polylactic acid, a chemical used in biodegradable polymers, are examples of science and technology meeting an environmental and market need.

In the United States, almost half the current lactic acid market is supplied by a U.S. company that manufactures lactic acid through a synthetic process. The remainder of lactic acid used in the United States is imported from countries that produce lactic acid primarily by fermentation (HRA, Inc. 1991). In this case, lactic acid produced synthetically is more expensive than that produced by fermentation. As opportunities for increased use of biodegradable polymers emerge, the demand for lactic acid increases. Rather than import lactic acid or increase production through the more expensive synthetic route, the industry is building domestic plants that can produce lactic acid through fermenting sugars derived from agricultural waste. This positive economic alternative is possible because government sponsored research was conducted in the past five years to enable industry to take advantage of a window of opportunity.

2.4.2 Example - Fast Pyrolysis of Biomass

Pyrolysis of biomass has been practiced for many decades for preparing charcoal, along with gases and an oil. Only 100 years ago, wood pyrolysis was the source of chemicals such as methanol, acetone, acetic acid, among others through wood distillation. The wood methanol along with coal tar phenolics was the source of the first phenolic resins prepared by Baekeland (the bakelites).

Research and development in the field of biomass pyrolysis has, in recent years, developed an understanding both of the science and of the engineering necessary to begin controlling the composition of the fast pyrolysis products. Because biomass pyrolysis vapors are reactive oxygenated low molecular weight chemicals, it was necessary to learn to form them quickly through a suitable fast heat transfer mechanism, and also to remove them from the heated zone to avoid uncontrolled decomposition reactions. The fast pyrolysis process is also called flash pyrolysis.

Controlling reaction conditions — high temperature, fast heating rate, and short residence time— allows pyrolysis products to be produced economically, moving the field to move toward technology transfer and commercialization potential worldwide. Pyrolysis in the range of 500-550°C and within a

few seconds residence time, gives high (60-70%) yields of liquid products, that efficiently converted into desirable products through a variety of post pyrolysis processes such as solvent fractionation, catalytic processes, and post thermal cracking.

The control of the fast heating rate and short vapor residence time can be accomplished most readily in three types of reactors: the entrained flow, the fluidized bed, and the ablative reactor (also called vortex reactor). These reactors operate on scales from pounds/hour to hundreds of pounds/hour. Pyrolysis experience at these scales is around thousands of hours of operation. Several engineering groups in industry and academia are using this technology. Their parallel developments and the start of commercialization in companies in several countries indicate that the field is poised for demonstrating and commercializing the most promising concepts. To this end, NREL has formed the Pyrolysis Materials Research Consortium to exploit pyrolysis oils as components of phenolic-based adhesives.

2.4.3 Example - Bioprocessing of Renewables

New opportunities for large-scale bioprocessing will be driven by the need to competitively resolve issues related to the environment and energy. Some of these opportunities include feedstocks for degradable products (e.g., biodegradable plastics), oxygenated transportation fuel additives, oxygenated chemicals, and "natural" or "green" products. Some large-scale bioprocesses have already demonstrated significant advantages over existing technology where technology advances have been successfully integrated. For example, the bioleaching of ores accounts for about 25% of copper produced in the United States and constitutes a \$650 million/yr business. Producing amino acids is now a \$2 to \$3 billion/yr industry, that developed through improvements in microbial strains and the fermentation process. Corn wet milling also utilizes fermentation and enzymatic conversion for producing ethanol, high fructose corn syrup, and other chemicals in an industry that produces more than \$6 billion/yr in revenue and utilizes 22.7 billion kg (50 billion pounds) or 12%-14% of the U.S. corn crop (Datta 1992). This latter industry represents an appropriate model for integrating commodity chemical or energy production with specialized or intermediate chemical production through bioprocessing.

2.4.4 Examples - Technical Advances and New Applications

Barriers always exist to incorporating new technologies, however, in the case of renewables, most of the technical barriers are incremental rather than "fatal flaws." The fundamental objectives are to reduce feedstock costs, to increase product yields and rates, and to develop ways to separate products efficiently and economically. Setting priorities for appropriate target product families and technologies for the near-, mid-, and long-term is important. Such priorities cannot be determined without industrial participation to provide insight into strategies for overcoming obstacles. Past attempts by industry to produce chemicals from renewable feedstocks have failed due to lack of adequate technology. Fortunately, there have been major advances in metabolic engineering, advanced fermentation, reactor development and separations and fractionation technology that were not available as few as five years ago. *These advances can be used not only to exploit, but also to create windows of opportunity.* These advances can overcome some major technical hurdles and are applicable to both bioprocessing and thermal and chemical methods for chemical production. They include:

- "Energy crops," such as varieties of sorghum, napier grass switch grass, or hybrid poplar developed primarily for transportation fuels or power generation over the past decade could be used as renewable feedstocks for chemicals. Some of these energy crops can produce 2 to 3 times the biomass yields of the same crops that are conventionally used for food, feed, or fiber. Many of them well known genetically and can be genetically designed and grown to produce different amounts of lignin, protein, starch, cellulose, hemicellulose, or sugars. Different types of sugars can also be produced.

- New separation technology for the high yield production of levoglucosan from biomass pyrolysis has been developed. Levoglucosan, a derivative of glucose, has traditionally been considered a high value specialty chemical. New techniques for its isolation from pyrolysis mixtures offers the possibility of this complex sugar being used as a feedstock for a variety of applications.
- New catalysis methodology is being developed for converting biomass derived materials into useful products. This technology is being investigated for producing high value sugars from simple starting materials such as glucose, sorbitol, mannitol, etc., as well as for preparing useful chemicals from lignin.
- Well developed methods for transferring DNA, the genetic material that controls biochemical pathways, can be exploited to create novel metabolic capabilities. Examples include the introducing two foreign genes into *E. coli* to produce a strain capable of converting sugars primarily to ethanol, normally a minor product of *E. coli* metabolism (Ingram 1990), and transferring of five bacterial genes into bakers' yeast to generate a strain that produces high value colorants not produced at all by parent yeast (Ausich et al. 1992).
- Microbes currently used in industrial processes often are not well suited for genetic manipulation using the standard tools of molecular biology. New methods have recently been developed for introducing DNA into microbes, such as using electrical discharges or small projectiles coated with DNA (Klein, et al. 1992). These approaches bypass the specificity that limits the use of standard tools, and promise to transfer DNA into a wider variety of organisms.
- "Clean fractionation" technology for separating lignocellulosic material into its constituent components offers a unique, cost effective source of cellulose, xylose, and lignin as raw materials for chemical production.
- More efficient technologies for the pyrolyzing biomass are being developed to increase the selectivity for converting renewables into useful chemicals.
- New strategies have been developed whereby introducing DNA into cells antagonistic to the host's DNA alters the activity of a metabolic pathway (Cohen 1989). This approach has been used, for example, to alter crops for controlling ripening and pigment production (Bramley, et al. 1992).
- Methods have been developed that greatly facilitate isolating and manipulating the genes encoding individual enzymes (protein biocatalysts) that perform the stepwise conversions of metabolic pathways. In particular, the polymerase chain reaction (PCR), permits the altering of genes to generate specific changes in the structure of the protein they encode (Arnheim et al. 1990). Altering proteins has been exploited to generate enzymes that perform novel reactions of industrial use (Wilks et al. 1992). Alternatively, an enzyme can be engineered to function in a different environment, for example in an organic solvent (Gupta 1992).
- Developments in fermentation and bioreactor technologies have been designed that enable immobilizing microorganisms with a 100- to 1,000-fold intensification of microbial biomass, and result in a concomitant increase in rates. Fluidized-bed reactor technology is being used for the simultaneous fermentation and separation of lactic acid (Davison and Thompson 1992), and producing ethanol (Davison and Scott 1988). A significant improvement in retention time (five minutes rather than several hours) was achieved when fluidized bed reactors replaced conventional activated sludge systems in removing benzene, toluene, and xylene (BTX) from waste streams (Frank 1992; Hickey and Owens 1981).

- Electrodialysis-based separation processes with novel bipolar membranes have produced acid and base from salt using low amounts of power. This enables the recovery and purification of organic acids from dilute, impure broths without creating a salt by-product. This advance is being exploited to commercialize new lactic acid technology for biodegradable plastic production (Datta 1989, 1992; Glassner and Datta 1990). Other advanced separations technologies including adsorption and extraction, and reversible chemical complexation are also available to replace distillation or precipitation.

2.5 Overview of Key Industrial Sectors

The Alternative Feedstocks program is closely related to how several industrial sectors operate, including the chemical industry, the petroleum refining industry, and the renewables industry. Because of this close relationship, it is important to outline the nature of these industries and some of the challenges they face in the future to best direct the program to their needs.

2.5.1 The Chemical Industry

The chemical industry is one of the most critical in the United States from several perspectives, including industrial and military security, quality of life (Szmant 1989), and balance of trade (Chemical and Engineering News 1991).

In 1992, 632 billion pounds of the top (in terms of level of production) 50 chemicals were produced in the United States (Chemical and Engineering News 1992); these were the same levels of production achieved in 1990, and a modest 1.4% growth over the 1989 production. Of those, producing inorganic chemicals accounted for 408 billion pounds. The chemical industry also employed 946,000 people, that accounts for about 5% of all domestic manufacturing jobs (Chemical and Engineering News 1991). Since 1980, the chemical industry has enjoyed a trade surplus of \$138 billion during a period when overall United States trade has accumulated a deficit of more than \$1 trillion. The 1991 trade surplus in the chemical industry of \$18.8 billion is second only to the \$27 billion trade surplus of aircraft manufacturers (Chemical and Engineering News 1991). However, the trade surplus for 1992 declined to \$16.7 billion (Chemical and Engineering News 1993).

The top two organic chemicals produced in 1991 were ethylene and propylene at 39.2 and 22.0 billion pounds, respectively, with ethylene production showing a 7.5% increase from the levels of 1990. Overall, production of the top thirty five organic chemicals in 1991 was 224 billion pounds, up slightly from 219 billion pounds in 1990. Many of these organic chemicals were employed in manufacturing roughly 63 billion pounds of plastics. Oxychemicals, a chemical industry segment also targeted by this program, represent about 20% of this market (Szmant 1989). Paints and coatings represented 1 billion gallons of production whereas the number of units of aerosol products consumed declined to 2.8 billion. Pesticides stalled in growth with 1.1 billion pounds. Fertilizer consumption was down for all but nitrogen-containing compounds, with a total of 40.6 billion pounds. Agrochemicals used by the renewables industry are a major sector of the chemicals industry.

Table 2.3 compares the overall value of shipments of the chemicals and allied products sector to other selected manufacturing sectors of relevance to this report. Interestingly, the value of shipments has so far been able to weather the volatility of petroleum feedstock prices, which have varied by as much as a factor of four from the seventies to the peaks of 1980-1982 (Table 2.4). Over the period 1981 - 1991, the value of the chemical and allied products industry has been steadily increasing, demonstrating the robust nature of this industrial sector. However, a large and unexpected increase in petroleum feedstock prices, such as that experienced in the mid-1970s, could change this trend.

The chemical industry faces several challenges in the future. Despite the strength of the U.S. chemical industry, there are signs that foreign companies are strengthening their competitive position. Contributing factors to this outlook include the declining crude oil production and associated refining

capacity in the United States, the increasing dominance of OPEC nations in petroleum markets, and the increasing environmental regulations in the United States. The resulting massive structural changes in the United States petroleum refining industry will have a definite impact on refined feedstock supply sources for the chemicals industry (Osten and Veno 1991).

Table 2.3 - Shipments from the United States Chemical Industry by Relevant Sectors

<u>Sector</u>	<u>Value of Shipments (Billions of \$)</u>				
	<u>1981</u>	<u>1985</u>	<u>1988</u>	<u>1990</u>	<u>1991</u>
All Manufacturing Industries	2017	2279	2611	2917	2863
Chemicals and Allied Products	180	197	240	285	288
Petroleum and Coal Products	224	179	124	179	167
Rubber and Plastic Products	53	71	91	92	93
Paper and Allied Products	80	93	124	129	122

Source: Chemical and Engineering News, June 29, 1992, p. 48

Table 2.4 - Selected Prices in Constant 1990 Dollars for Primary Petrochemicals (cents/gallon)

<u>Year</u>	<u>Methanol</u>	<u>Ethylene</u>	<u>Propylene</u>	<u>Butadiene</u>	<u>Benzene</u>	<u>Toluene</u>	<u>Xylenes</u>
1972	28.28	9.19	7.92	29.98	59.39	65.04	67.87
1975	79.83	22.18	17.74	44.35	188.49	137.04	121.96
1980	108.94	37.44	27.62	49.10	253.18	191.80	168.79
1985	51.58	18.08	18.08	35.28	175.49	143.48	147.03
1990	38.50	21.50	14.25	28.50	130.00	100.00	95.00
1991	48.52	18.58	14.07	15.53	101.90	82.98	82.01

Source: Chemical Economics Handbook, SRI International, 1992.

Competition by developing countries that have ample petroleum and natural gas resources has been increasing in recent years. These countries now produce not only crude oil for export, but have also moved into producing primary chemical building blocks, and commodity products derived from these building blocks (Szmant 1989; List 1986). For example, Saudi Arabia has become in just a dozen years a large-scale producer of methanol, polyethylene, styrene, ethylene glycol, ethylene dichloride, vinyl chloride monomer, polyvinylchloride (PVC), ethyl alcohol, methyl tert-butyl ether (MTBE), and other chemicals (Szmant 1989). Even though fixed capital costs are about 20% higher in Saudi Arabia than in the United States, low feedstock costs can allow Saudi Arabia to compete in product areas where feedstock cost is an overriding factor in other countries (Lee 1990).

The basis for the current United States competitive edge in chemical manufacturing over countries using inexpensive feedstocks is the low-cost incremental expansion of existing facilities compared to building new plants from scratch. However, as incremental expansions become limited by capacity, or environmental or social constraints, new plant construction will increasingly take place overseas where less expensive feedstocks are available. This pattern has been documented in the case of MTBE, that has experienced strong market growth in the past three to four years. However, the marginal economics of constructing new methanol (GRI 1991) or butane plants in the United States suggests that much of the new capacity will be built in other countries. These trends indicate that U.S. companies are increasingly concentrating on high-tech specialty chemicals at the expense of intermediate and commodity chemicals (Szmant 1989).

A reduction in domestic manufacturing of intermediate and commodity chemicals with increased reliance on imported refined feedstocks or petroleum-based products (e.g. plastics) is indicated as United States petroleum feedstock costs continue to rise, domestic oil production decreases, and oil

imports increase from 40% (1989) to 66% (expected 2010, GRI, 1991). Environmental regulations in the United States are expected to further exacerbate this situation. For example, it is estimated that if two key provisions of the Resource Conservation and Recovery Act (RCRA) were to be strictly applied to the U.S. oil and gas industry, 8 out of 10 wells producing in 1991 would be shut down, 2.5 billion barrels in oil reserves and 10.2 quads of recoverable gas reserves would be permanently unrecoverable, and 148,655 jobs would be lost (API 1991). These trends are expected to continue and will lead to increasing foreign competition in the chemical industry as incremental capacity is consumed, current local feedstock reserves diminish, and regulation continues.

The trend toward increasing petroleum imports also directly affects the chemical industry with respect to energy use and potential energy savings. The total industrial energy demand is projected to grow from 24.2 quads in 1989 to 32.2 quads by 2010 (GRI 1991). The chemical industry alone accounts for about 25% (or 5.6 quads) of industrial energy consumption; the industry grew at an annual average rate of 6.6% per year between 1986 and 1989. Petroleum accounts for 3.9 quads, natural gas, 0.6 quads, and coking coal, 1.1 quads (GRI, 1991). Total industrial petroleum feedstock consumption is projected to grow from 3.9 quads in 1989 to 5.2 quads in 2010 and accounts for more than 80% of the growth in petroleum consumption of feedstocks between 1989 and 2010.

These observations suggest that using renewable feedstocks in the raw material stream of the chemical industry would be in the best interests of the United States. A number of factors support this:

- The chemicals that can be made from renewable feedstocks comprise a significant portion of the chemicals industry, and windows of opportunity for commercialization of some of these chemicals are within a favorable 5 to 10 year timeframe.
- The bioprocessing industry is rapidly developing new technologies (section 2.3.4) that can now be applied. Novel thermal and chemical technologies are also available for more selective feedstock conversion.
- Using renewable feedstocks and local processing can increase jobs, sales, and infrastructure in the agriculture industry.
- The prospect that the United States can lead the way in the "greening" of the chemical industry by producing environmentally acceptable products using domestically grown feedstocks in U.S. based chemical production facilities.

Chemical facilities using renewable resources can provide flexibility because refining capacities and corresponding capital investments are estimated to be roughly an order of magnitude lower than equivalent petrochemical plants. In general, plants based on renewable resources range in capacity from 22.7-136.0 million kg/year (50-300 million pounds per year) or less (Szmant 1986) compared to petrochemical plant capacities of 180-1800 million kg/year (400-4000 million pounds per year, Bond 1990) as a result of differing economies of scale. A notable exception are large pulp and paper plants that can be 3 - 4 times larger than typical renewables-based plants. In addition, biomass conversion technologies could be integrated with existing facilities to provide feedstock flexibility for functionally similar product lines.

2.5.1.1 The Petrochemical Industry

The petroleum refining and chemicals and allied products sectors are closely linked to one another. These close interrelationships between sectors can be described, in a simplified way, by the diagram in Figure 2.2, that shows how producing chemicals relies on the availability of refined feedstocks from the petroleum industry. Of course, the petroleum industry relies on the availability of crude oil feedstocks. In addition, the chemical industry uses a considerable amount of petroleum and natural gas as fuel for their operations.

The basic building blocks of the chemical industry, methane, methanol, ethylene, propylene, butanes, butenes, butadiene, and the aromatics benzene, toluene, and mixed xylenes, are derived from petroleum, natural gas and natural gas liquids (two- to four-carbon hydrocarbons) via refining of petroleum through thermal or catalytic processes. For most of the downstream organic chemicals manufactured, these few primary building blocks are sufficient. Table 2.5 summarizes the specific primary source of these building blocks.

These few primary petrochemicals serve as starting materials for a huge array of end products. As a single example, consider the wide variety of products produced by the plastics industry (Figure 2.2). General classes of products are plastics, fibers, and elastomers. Plastics are a particularly important component of the economy, and are the only commodity to show an increase in its growth index (4%) for the period 1990-1991. In comparison, chemicals and related products showed no growth, while the total manufacturing sector decreased by 3% for the same period. These products (Figure 2.2) penetrate a wide variety of end uses, summarized in Table 2.6.

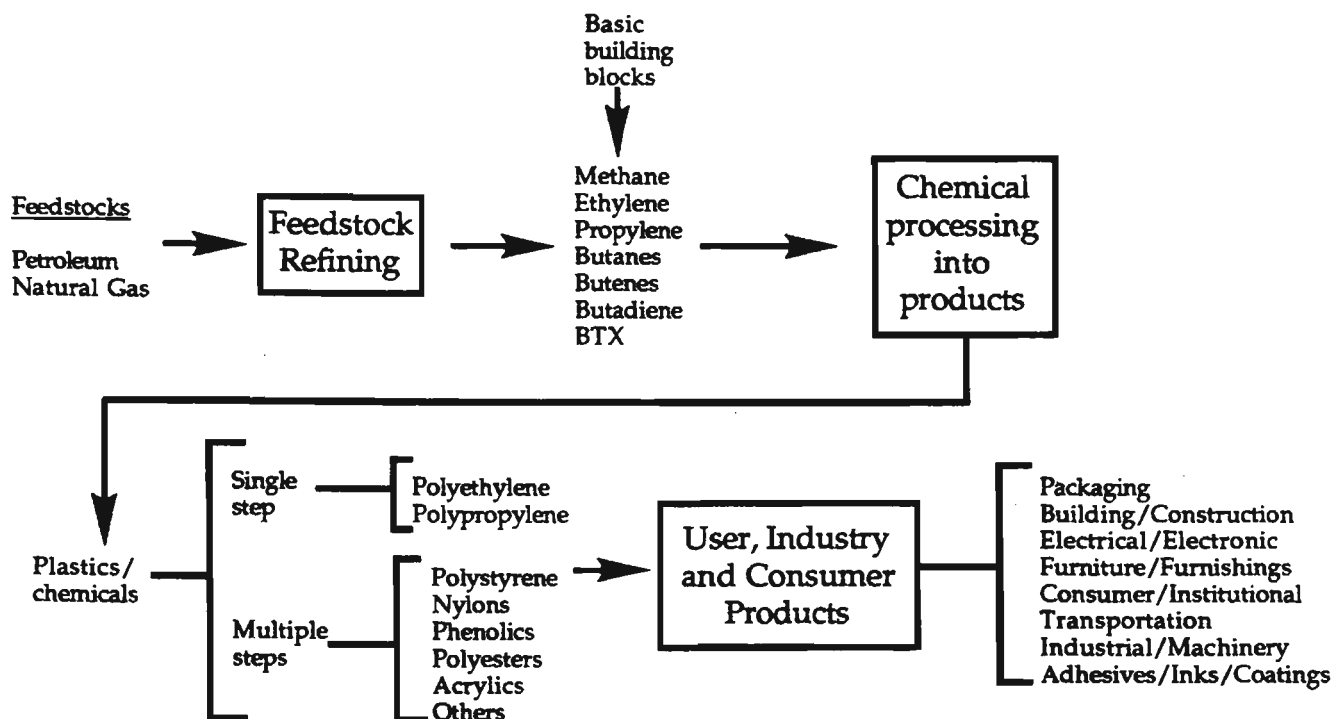


Figure 2.2 - Scheme of the Chemical and Allied Products and Petroleum Refining Industries

Only about 15-20 key types of plastics, along with wood and renewables-derived materials, make up the bulk of the nonmetallic materials used in these applications. The importance of organic chemicals derived from primary feedstocks to the plastic industry is obvious; of the 219 billion pounds of the top thirty five organic chemicals produced in 1990, most were employed in manufacturing roughly 63 billion pounds of plastics, including:

- 8 billion pounds of synthetic fibers (acrylic, nylon, olefins, and polyesters)
- 2.1 billion pounds of synthetic rubbers
- 6.4 billion pounds of thermosetting resins (epoxy, melamine, phenolic, polyester, and urea)
- 47 billion pounds of thermoplastics (polyethylene, polypropylene, styrene polymers, polyamide, vinyl resins, and thermoplastic polyesters).

Table 2.5 - Source of Primary Petrochemicals in the United States (1990)

<u>Source</u>	<u>Percent</u>	<u>Product</u>	<u>Percent Made From Source</u>
Natural Gas	8.2	Methanol	95.3
Natural Gas Liquids and Refinery Off-Gases	38.0	Ethylene	71.0
		Propylene	68.0
		Butadiene	48.0
		Aromatics	very low
Petroleum	53.0	Ethylene	29.0
		Propylene	32.0
		Butadiene	52.0
		Benzene	99.6
		Toluene	99.6
		Xylenes	99.6
Coal	0.8	Methanol	4.7
		Benzene	1.6
		Toluene	0.4
		Xylenes	0.4

Source: Chemical Economics Handbook - SRI International

Table 2.6 - Selected End Uses of Plastic Products

<u>General Use Area</u>	<u>Examples</u>
packaging	containers, coatings, foams, flexible packaging, films
building/construction	pipe/fittings, interior/exterior materials, air-supported structures
electrical/electronic	appliance, communications, business machines, records, tapes, batteries, furniture/furnishings: carpets, wall coverings
consumer/institutional	disposable food serviceware, photographic equipment, luggage, lawn and garden, toys, sporting goods, cleaning products
industrial/machinery	signs, farm and construction equipment, machine tools, engine parts
transportation	land-, water-, and air-based for civilian or military applications
others	adhesives, inks, coatings, textiles

Other significant product classes are also derived from primary petrochemicals and include solvents, surfactants, coatings, aerosols, pesticides and fertilizers.

The plastics industry is but one component of the nation's chemical output that could suffer severe economic impact in the event of a significant increase in the price of the key primary feedstocks, crude oil and natural gas. Incorporating domestically available renewables into this supply stream could provide an important buffer to such a price increase. By developing new technologies for products and processes, indigenous supplies of selected chemicals could be made. In addition, renewables-derived materials could complement current plastics and offer environmentally acceptable strategies to a variety of packaging products.

2.5.2 The Renewables Industry

For this analysis, the renewables industry includes forestry and forest products as well as agriculture and related products. Therefore, renewable industries represent a large segment of the United States economy. Only a small fraction of their output is directed towards producing chemicals (starch chemicals, cellulose esters and ethers, lignin chemicals, lubricants and additives), but the sector is active in housing and furnishings by virtue of the wide array of inexpensive commodities it produces. In 1989, the farm income in the United States was \$159 billion (47.3% crops, 52.6% livestock/products) using more than 2.2 million farms and nearly 990 million acres. Government payments amounted to \$10.9 billion (6.8% of the farm income).

The United States has vast supplies of diverse renewable resources that are available for converting to many different chemicals. The Department of Agriculture has projected that the U.S. feed grain (corn, sorghum, oats, barley) production will increase by 14 percent to 249 million tons in 1992-1993, and the domestic share of the world market will increase by 3% to 56% during 1993 (USDA May 1992). The U.S. sugar industry projects a 1993 production of 7,500,000 tons of raw sugar, that is a 4.2 percent increase over 1992 (USDA June 1992b). Hawaii alone produced approximately 800,000 tons of raw sugar and 220,000 tons of molasses in 1990 from the cane sugar industry, although their share of the market is decreasing (Hawaii Sugar Planters' Association 1991).

Using U.S. agricultural products as feedstock for chemicals and materials would benefit the nation by supplying a new industrial market for agriculture, an industry that often produces more than it can sell. This has resulted in acreages of 30 million hectares (or 74 million acres) or more, that are set aside through payments to farmers in payment in kind programs (PIK, Frank and Smith 1986; Szmant 1986). An opportunity to use some of this surplus, in place of imported petroleum, could have major benefits that address goals in the National Energy Strategy, such as achieving greater energy security through increased fuel and feedstock flexibility and use, waste minimization, and increased process efficiency. This program would help energy security by shifting the feedstock from petroleum to renewable (domestically grown) resources. It would also reduce net CO₂ emissions and enhance environmental quality by making environmentally compatible products such as "green" solvents, biodegradable plastics, or other petrochemical substitutes.

The pulp and paper industry is a vital component of the renewable feedstocks industry. Shipments of the paper and allied products industry in 1989 totalled \$131 billion to provide 157 billion pounds of paper and paperboard products made from 122 billion pounds of wood pulp in 1989. The sector decreased its shipment values from the peak in 1989 (see Table 2.3) as the industry installed increased capacity in the United States at a time when the economy was taking a downturn, however, the volume of products continues to increase. This is not unusual; most sectors of the renewables industries are currently depressed because they are linked with the construction industry and the overall economy of the nation. They could be revitalized by adding new crops and products, that would increase regional economic development through increased employment.

In contrast to petroleum derived materials, the average price of the paper and paperboard products has had a much smaller volatility over time, with the range over the last five years (1985-1990) being \$0.20-\$0.24/pound of composite product. Indeed, using a renewable resource could provide a much more stable indigenous basis for commodities and chemicals. It already contributes a very significant fraction of our commodity materials for the same types of applications that the plastics currently hold, but with heavier emphasis on the housing and furnishings sectors.

Renewable feedstocks add flexibility as starting materials for the huge array of end products currently produced by the nation's chemical industry. It is necessary to identify the most promising from a technical, economic, and market point of view.

2.5.2.1 Chemicals and Materials Currently Produced from Alternative Feedstocks

The use of renewable resources for producing industrial chemicals and materials today can be characterized by two types of activities: first, integrating processes for the maximum use of products, byproducts, and incidental wastes of the primary economic activity, and second, using a specific crop for producing industrial chemicals and materials.

2.5.2.2 Integrated Processing

The renewable industry can integrate food, chemicals, feed, and fuels, to allow a swing of products capability that maximizes the industry's economic activity. For example, the forest products industry supplies lumber and pulp for manufacturing solid wood and composite products, paper and paperboard (Figure 2.3, Szmant 1986). By-product use developed an industry that converts some pulping liquors into specific chemicals such as inexpensive lignosulfonate surfactants and dimethylsulfoxide or using tall oil for products. Incidental wastes such as bark became, in part, a source of chemicals such as tannins. Many wastes became feedstocks for additional products or energy.

The corn industry produces food (corn, oil, cereals, sweeteners, spirits, etc.), feed (gluten, meal, distillers dried grains with solubles), starch-derived chemicals and materials (for paper sizing and adhesive applications, plastics), ethanol fuel, and other products (Figure 2.4). Meat, milk, and cereal grains processing has led to the developing adhesives from casein (milk), foundry resins from furfural and furan (from oat/corn cobs and other residues), fat by-products, and other materials.

Most other food processing industries, including apple juice plants, bean canneries, and potato processors, have not achieved high levels of economic efficiency. Streams high in starch and sugars are discharged into sewers, incurring BOD (biological oxygen demand) charges from the local municipality because these streams may overload sewage treatment plants (Leeper et al. 1991). Waste minimization is now a goal of food processing plants (as it is for most U.S. industries), and some have already converted their "waste" streams to coproduct fermentation feedstocks. The Alternative Feedstocks program can advance technologies that will provide these industries with a choice of fermentation products. The most common alternatives are low value fuels such as ethanol and methane (fuels not included in the scope of this program). A more attractive alternative is producing higher value chemicals, such as organic acids, that can be made in significant amounts (relative to their total market size) from these feedstocks, and produce a higher return on the investment.

2.5.2.3 Use of a Specific Crop for Producing Industrial Chemicals and Materials

The natural fiber industry, based on cotton, cotton byproducts (cotton linters) and seeds produces oil, meal, fatty acids, and soaps (Figure 2.5, after Szmant 1986). Chemically modified wood pulps converted to rayon and acetate, wool, and cotton account for nearly half of the textile fibers produced. These fibers have experienced heavy competition from the inexpensive synthetic fibers. In many areas the plant-derived fibers have remained competitive because of properties desired by the consumer.

Other examples are oil seeds, including rape, mustard, wallflower, nasturtium, and others, that lead to oil-derived products such as fatty acids, fatty alcohols, glycerol, soaps, specialty fatty acids, and a number of derivatives.

Important industrial chemicals derived from renewable resources are listed in Table 2.7.

Table 2.7 - Plant Matter Derived Industrial Materials and Important Intermediate Chemicals in the United States

<u>Product</u>	<u>Current Production (millions of tons)</u>	<u>Plant Matter Derived (%)</u>	<u>Conventional Product Cost (\$/lb)</u>	<u>Plant Matter Product Cost (\$/lb)</u>
Wall Paints	7.8	3.5	0.50	1.20
Special Paints	2.4	2.0	0.80	1.75
Pigments	15.5	6.0	2.00	5.80
Dyes	4.5	6.0	12.00	21.00
Inks	3.5	7.0	2.00	2.50
Detergents	12.6	11.0	1.10	1.75
Surfactants	3.5	35.0	0.45	0.45
Adhesives	5.0	40.0	1.65	1.40
Plastics	30.0	1.8	0.50	2.00
Plasticizers	0.8	15.0	1.50	2.50
Acetic Acid	2.3	17.5	0.33	0.35
Furfural	0.3	17.0	0.75	0.78
Fatty Acids	2.5	40.0	0.46	0.33
Carbon Black	1.5	12.0	0.50	0.45

NOTE: Market share of plant matter represents both wholly and partially plant matter derived products. The cost premium of plant matter based products is calculated based on the average median costs of commercially available products in a given category.

Sources: Chemical Marketing Reporter; Chemical & Engineering News; U.S. Department of Commerce, "U.S. Industrial Outlook," Washington, DC; Chemical Week; The Carbohydrate Economy

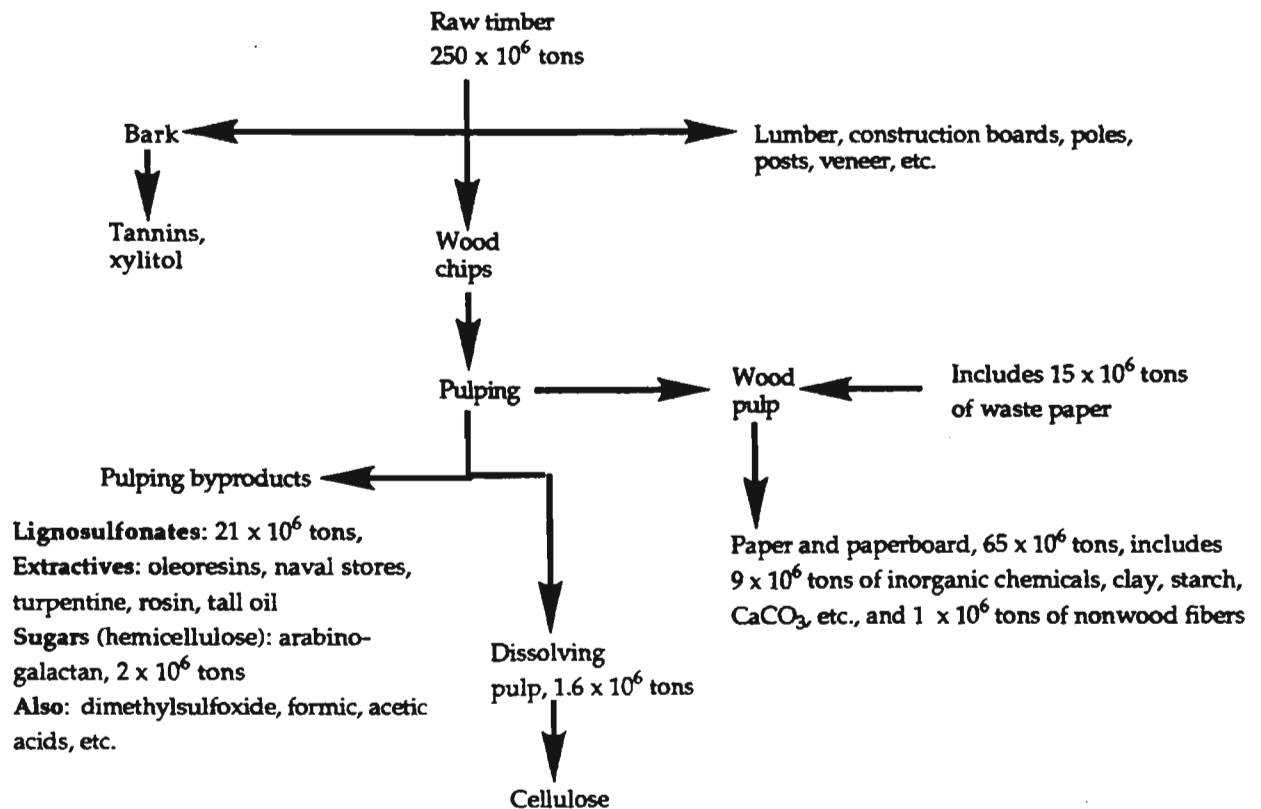


Figure 2.3- Interrelationships and Materials Flow for the Pulp and Paper Industry, 1986

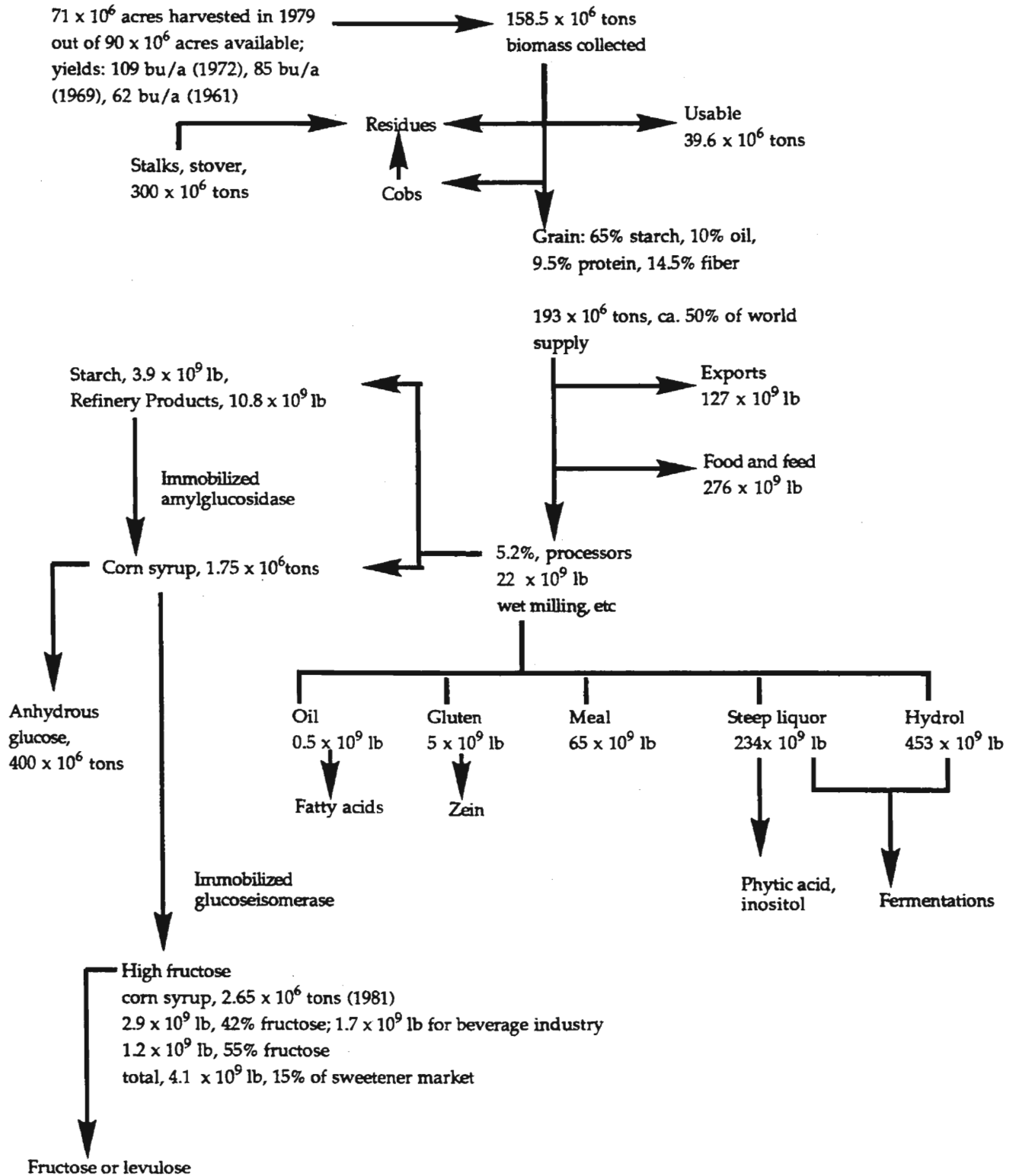


Figure 2.4 - Corn Products Industry (after Szmant; data as of 1980, or as indicated)

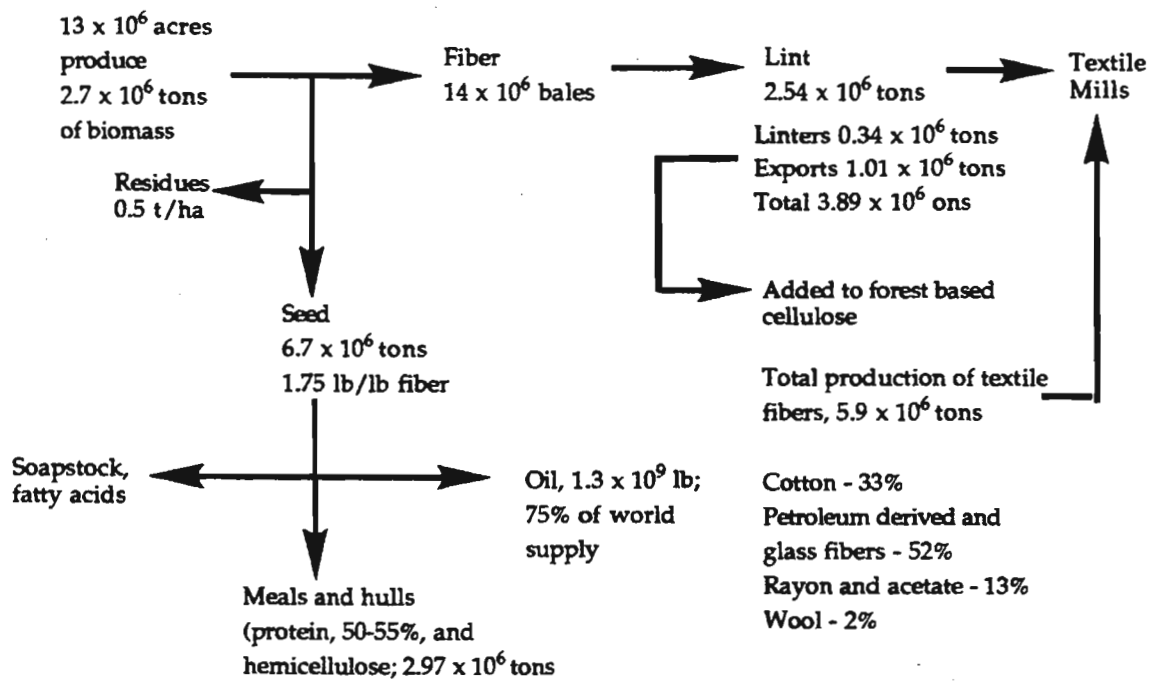


Figure 2.5 - Cotton Products Industry

3.0 AVAILABILITY, USE, AND COMPOSITION OF BIOMASS

3.1 General Overview

Adopting any industrial process that relies on a primary raw material necessitates that the raw material be: available in sufficient (if not excessive) quantities to supply the demand for the end product; and relatively inexpensive, because raw material costs make up a large portion (up to 70%) of total production costs of high volume chemicals in mature processes. The availability of feedstocks does not appear to be an issue; current data indicate that biomass-based feedstock materials are produced in the United States in quantities great enough to supply raw materials for producing several commodity chemicals (Leeper et al. 1991). There is also a potential for new dedicated production of biomass crops based on the vast amount of available cropland in the United States (USDA 1987; USDA 1991). This is a strong advantage for the United States with regard to future competitiveness in a global biomass-based chemicals industry. Much of the feedstock material available is inexpensive and would be ideal for producing chemicals. However, several general issues must be considered.

The first issue is one of *feedstock diversity*. Biomass-based feedstock materials used in producing chemicals can be obtained from a large variety of sources. If considered individually, the number of potential renewable feedstocks can be overwhelming, but they tend to fall into three simple categories (EG&G Idaho, Inc. 1981; Leeper et al. 1991): waste materials (e.g., food processing wastes), dedicated feedstock crops (e.g., silviculture [agroforestry], short rotation woody crops or herbaceous energy crops such as perennials or forage crops), and conventional food crops (e.g., corn, wheat, etc.). In addition, these raw materials are composed of several similar chemical constituents, i.e., carbohydrates, proteins, lipids, lignin, and minerals. Thermal or chemical processing of these materials is typically accomplished by novel separation and conversion methodology (sections 4.0, 5.0), leading to chemicals similar to those from conventional petrochemical starting materials. Bioprocesses focus on microbiological conversion of fermentable sugars that are derived from these materials by thermal, chemical, or enzymatic means to commodity and specialty chemicals (sections 6.0, 7.0).

Different sources of feedstock material are referred to according to their current usage. However, in choosing a feedstock for a given product, it is important not to be diverted by semantic differences that arise due to its current usage. For example, switchgrass grown on currently idle cropland for chemical production would be considered a "dedicated crop". Corn stover derived from existing corn production is considered a "waste product." Despite their categorization based upon current use (or non-use), both are sources of biomass that are similar in cellulosic composition. If corn stover were adopted as a feedstock for chemicals production, then it would no longer be designated as a "waste" but as another product of corn agriculture. The entire corn industry provides a good example of how a single agricultural commodity can be developed into multiple valued products. This is clearly illustrated by corn processing plants, which are so well integrated that it is difficult to distinguish any primary products from byproducts which is why the term "coproducts" is preferred.

Once a "waste product" is identified as having use, supply and demand dictates that its value will increase; no feedstock is "free." The Brazilian ethanol industry provides an example of how dedicated crops become coproducts (Maiorella 1985). The bagasse left after extracting the sugar from the cane was originally treated as a waste. Later, it was burned to provide energy for distillation. Finally, it was sold to other industries as a boiler fuel, making a significant contribution to the process economics. At each step, the value of the bagasse increased.

Feedstock diversity leads to a key component of this program: *feedstock flexibility*. If the supply of one feedstock raw material inadvertently drops below demand level, a given process must be able to adapt and substitute another raw material. Different biological or chemical processing techniques can be used, depending on the feedstock currently available. For example, the main disadvantage of lignocellulosic feedstocks from the standpoint of bioprocessing is that they are more difficult to process into an acceptable fermentation substrate, because the biomass consists of cellulose, hemicellulose, and

lignin, complex polymers that are relatively difficult to break down into sugars readily metabolized by microorganisms (Office of Technology Assessment 1984). This disadvantage is more acute from the perspective of producing lower value biofuels as products; it may be less significant for producing higher value chemical products. In addition, certain microorganisms can ferment cellulose directly to products, that can make cellulosic biomass more attractive. Thermal or chemical technology could be useful in pre-processing these feedstocks to fermentable sugars that could then be converted biologically to commodity chemicals.

Conversely, bioconversion technologies could be used with feedstocks rich in starch, because they are readily converted (by feedstock processing or selective separation technology) to fermentable sugars (e.g., glucose, Figure 3.1). Fermentable sugar is ideal as a generic feedstock for bioconversion processes because it is easily converted by biocatalysts into many different chemicals (Leeper et al. 1991). In addition, many feedstocks can be processed into this single generic material that can be used either in chemical or biochemical processes.

A third issue is one of *feedstock availability*. Large scale use of biomass as a raw material requires that dedicated feedstock supply systems (DFSS) be established, that would guarantee the resource, increase employment for a wide variety of sectors (nurseries/farm, heavy machinery, fertilizer, plant equipment, distribution systems), decrease our heavy dependence on imported oil and increase economic development in rural areas in the United States. These developments would complement a higher technology driven agribusiness in which renewable resources would play progressively more important roles in the economy. Importantly, DFSS could avoid critical supply problems, such as those experienced in California with their use of biomass agricultural wastes for electrical power generation. Prior to the project, low, and even negative costs typified the feedstock. However, as the project began, demand grew, feedstock prices soared, and a shortage of feedstock resulted (DOE 1993)

Earlier penetration of these processes using alternative feedstocks could be achieved by using specific waste biomass resources. Waste materials could establish the proof-of-concept of these technologies and pave the way for their adoption in the future, when the realization of the overall energy savings of these routes could be achieved through the DFSS coupled with producing chemicals, fuels, and electric power.

An ongoing DOE program, field managed by ORNL, is examining both short rotation woody and herbaceous crops for biofuels production. The program is screening different species to identify the best match between individual plant characteristics and the wide variety of soil types and geographic regions where the DFSS could be established. Several important economic and environmental criteria have been associated with this investigation. The crops being developed should be low cost, highly productive, require low fertilizer and water inputs, and be generally easy to manage. The goal of these activities is to reach a production cost for delivered biomass of \$40/dry ton. Future work in the program will scaleup to larger plots so that productivity can be measured more meaningfully. These larger demonstrations will also lead to better cost estimates of this technology. Significant interest by the private sector in DFSS was demonstrated by the over 300 responses received to a Letter of Interest issued by DOE through NREL in April, 1993.

Each type of energy crop exhibits its own advantages and disadvantages. Herbaceous crops require less time to establish compared to woody crops, but this advantage is partially offset by the potentially lower overall costs of the woody crop concept. Short-rotation trees, that represent a new type of crop production system, carry greater risks in harvesting than herbaceous perennial crops, that employ modifications of conventional forage production systems. The woody crops also require the willingness of the landowner to dedicate his or her acreage to that use for six years or more, versus two years in the case of herbaceous crops. The choice will ultimately depend on many factors, including the location, soil diversity, and biodiversity needs of the United States. The biodiversity and ecosystem impacts of large scale use of these crops is currently being evaluated by a joint Electric Power Research Institute, DOE/NREL and Audubon Society "Biomass Roundtable" that includes utilities, land managers,

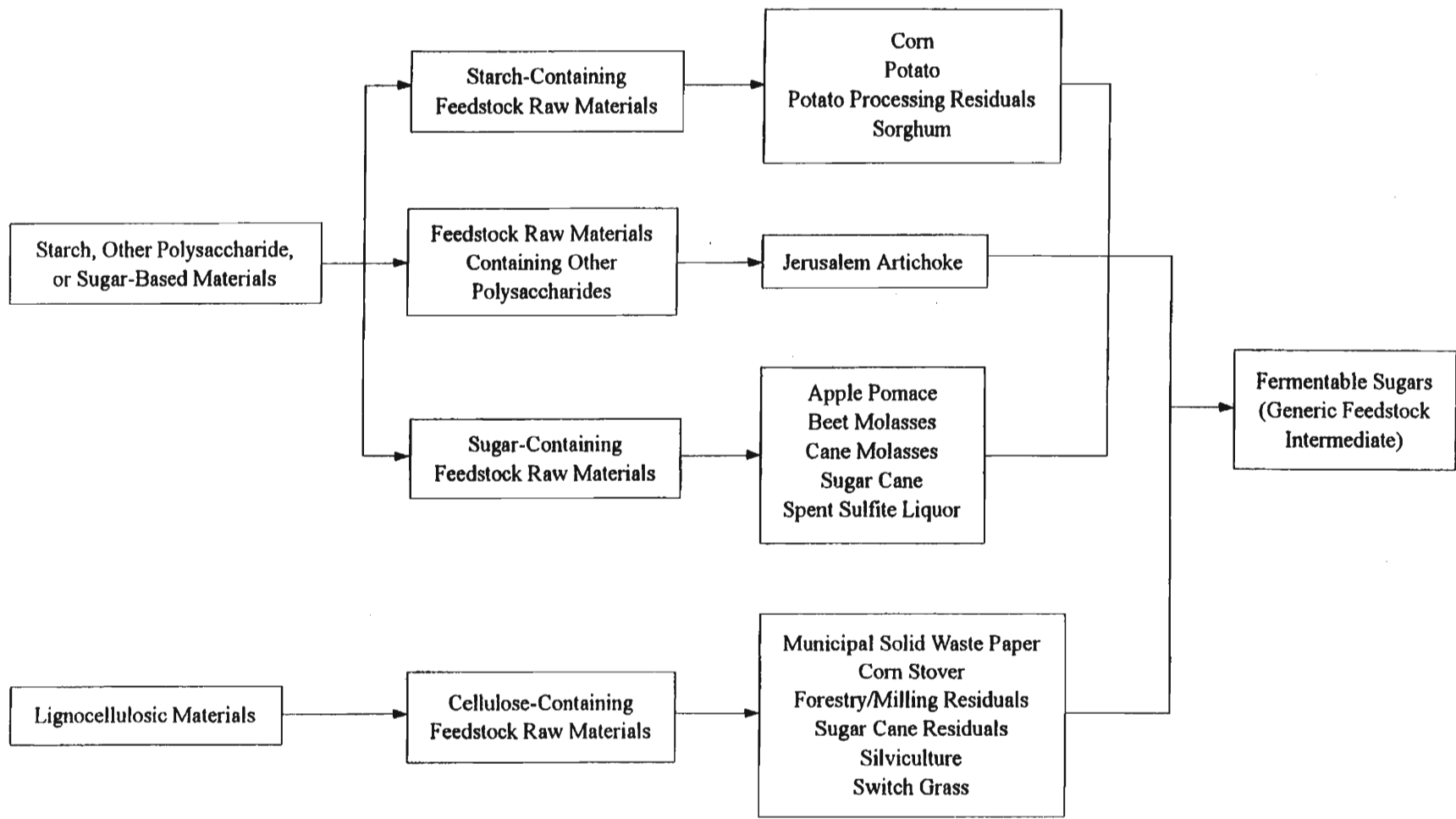


Figure 3.1 - Production of a Generic Feedstock Intermediate from Representative Biomass-Based Raw Materials

ecologists, environmentalists and technology developers. The results and final report of this roundtable will be published shortly.

Because the various conversion processes use biomass components differently, the best feedstocks for a specific product will vary. For instance, high moisture content feedstocks are more suited for bioprocessing than for thermal conversion processes, that require drier feedstocks. Bioprocessing routes will profit from a high carbohydrate content, balanced with a certain amount of lignin as a heat or electricity source so that the overall process will have a good energy balance. Energy balance is defined as the energy content in the fuel plus electricity exported (from burning the lignin fraction, if available) over required inputs of energy in the plantation, transportation, net chemicals used, product distribution, and plant amortization (Lynd 1991). As is well known, in the current grain-to-ethanol case, this ratio can be near or less than one, because of the high level of agricultural inputs required and the lack of a lignin fraction for power or process heat production. In the case of ethanol from lignocellulosics, this ratio approaches five, if the fertilizer inputs to the DFSS are low.

Models such as the Agricultural Resource Interregional Modeling Systems (ARIMS) have been used to project land use for the established biomass applications (food, feed, and fiber) and are now being modified to incorporate fuels and chemicals production along with electric power generation. From the initial use of this model, it appears that sufficient land exists for fuels and chemicals production as well as electric power generation, justifying the investment of RD&D dollars in these various programs. The models need to be refined to take into account the profit maximization that will drive farmers and investors to these areas, as well as the local (county) levels of land use for food, forage, fibers, and the new products, searching for the early market penetration and identifying potential partners for their development in specific geographic areas.

For maximum feedstock use in a sustainable biofuels industry, the feedstock conversion plant should be capable of handling multiple feedstocks, if not at the same time, on a block operation basis (several months on one feed, then several months on another feed). For some woody species, the ability to handle mixed wood species (e.g., poplars and silver maple from the same region) is desirable. The ability to start testing conversion processes on suitable agricultural residues is a good way to demonstrate the conversion technologies, and then evolve into dedicated crops for maximum energy impact.

A final, and very important issue is one of *feedstock cost*. Large scale use of renewables for producing chemicals requires a balance between two factors: producing biomass must be profitable enough for growers to pursue, yet the cost to chemical manufacturers must be low enough to offer incentives for its use.

The diversity of feedstocks available makes choosing a single price to use in process evaluation difficult. Therefore, the feedstock cost used becomes process dependent. For the purposes of the evaluations presented in this report (sections 4.0 - 7.0), a delivered cost of \$40/dry ton has been chosen for those processes that are based on lignocellulosic biomass. For processes based on "waste" material (as defined above), a true cost of feedstock is estimated because a "waste" material's value will rise to its market level once a use is found for it.

The value used for lignocellulosic biomass is based on research carried out on small demonstration plots under the direction of the ORNL Short Rotation Woody Crops Program (Wright 1990), and has tried to address the cost by including an extensive list of variables. These include projections on costs for site preparation, herbicide and fertilizer use, planting, supervision, and maintenance. Current results from existing plots show delivered costs between \$42.57/dry ton for a location in the northwest United States, to \$54.45/dry ton for locations in the northeast. However, their results document that a cost of \$40/dry ton could be realized under attainable conditions.

The issue remains complex, even though a given feedstock cost may be considered reasonable in certain applications. The number of different stimuli that can affect this cost are surprising. Water availability, susceptibility to disease or drought, crop location, etc., are all additional issues that could be considered. However, concern over a long list of "what-ifs" is also symptomatic of a process in its infancy. Because no large scale biomass production and delivery system has been demonstrated, some questions remain to be answered. Recently, ORNL has started preparing for much larger scale demonstrations of dedicated feedstock production. The results of this project will help verify the cost projections of the smaller scale experiments.

3.2 Characterization of Representative Feedstocks

In the last ten years, approximately 50 different sources of renewable biomass have been suggested for use as alternative feedstocks for producing valued chemicals (Leeper et al. 1991). Sixteen of these 50 possibilities were selected as sample representative of families of biomass-based feedstocks (cellulose, starch, free sugar, and inulin, another polysaccharide similar to cellulose and starch) that could support chemical production (Table 3.1). These materials are also diversified according to their current use, including materials that are food crops, sources of animal feed, waste materials, and materials that currently have no significant use.

In addition, a summary of the availability of biomass wastes, that includes the agricultural residues, was compiled by Alan Schroeder of DOE's Office of Industrial Technologies, Waste Material Management Division. The list presents numbers of availability that correspond to 20% of the agricultural residues that are expected to be economically recoverable. The wastes that were considered of high priority because of their size and potential ease of recovery, and the energy savings associated with those wastes are shown in Table 3.2.

Prices of representative raw feedstock materials range from \$0.07/lb for potatoes to almost negligible levels for those feedstocks, such as waste paper and spent sulfite liquor, that make up waste streams and are currently liabilities for the industries that produce them (Table 3.3). All prices shown are low when compared to the market prices of products that are under consideration, i.e., commodity and specialty chemicals; product prices range from \$0.50/lb, for commodity neutral solvents up to \$5.00/lb for a specialty organic acid (Figure 3.2, Chemical Marketing Reporter 1992). Recall, however, that once a "liability" is found to have a marketable use, its value will necessarily rise to the level the market is willing to bear.

Production levels that are shown in Table 3.3 are illustrative of the vast and increasing amount of renewables that are produced in the United States (USDA 1991; EG&G Idaho, Inc. 1981; Leeper et al. 1991). Also shown are levels of biomass supply that could be a part of a dedicated production of feedstocks. For waste materials, dedicated levels usually equal all of the current supply. For crops, dedicated production is that level that could potentially be reached using idle U.S. cropland. Dedicated production levels for crops were calculated based on current yields for those crops, and idle cropland available in regions that are suitable for their growth (USDA 1991; Bergez et al. 1991; Electric Power Research Institute 1991; Leeper et al. 1991). Potential dedicated levels of production range from 0.8 million metric tons/year (1.8 billion lb/year) of potato processing residuals up to 742 million metric tons/year (1633 billion lb/year) of potatoes.

Dedicated production levels of crops shown in Table 3.3 are based on region-specific availability of some or all of the 27 million hectares (68 million acres) of idle cropland in the United States in 1989 (USDA, 1991). The amount of idle cropland in the United States fluctuates on a yearly basis. In 1992, there were approximately 22 million hectares (54 million acres) of idle cropland in the United States; this amount could decrease or increase in 1993 based on the prevailing circumstances (USDA September 1992). At the present time, this land is part of the Conservation Reserve Program (CRP) and the Acreage Reduction Program (ARP), both sponsored by the USDA. These programs control the use of designated cropland, to protect the environment by regulating soil erosion, and reducing crop surpluses.

Table 3.1 - Representative Alternative Feedstocks: Primary Feedstock Constituents and Current Uses

<u>Feedstock</u>	<u>Primary Feedstock Constituent¹</u>	<u>Current Uses</u>
Corn	Starch	Food, animal feed, ethanol
Potato	Starch	Food, animal feed, ethanol (low level)
Potato processing residuals	Starch	Animal feed, waste, ethanol (low level)
Sorghum	Starch	Animal feed
Municipal solid waste paper	Cellulose	Waste
Corn stover	Cellulose	Waste
Forestry/milling residuals	Cellulose	Waste
Sugar cane residuals	Cellulose	Waste, fuel
Silviculture	Cellulose	Proposed for chemicals
Switchgrass	Cellulose	Proposed for chemicals
Apple pomace	Sugars	Waste
Beet molasses	Sugars	Animal feed, fermentation feedstock
Cane molasses	Sugars	Animal feed, fermentation feedstock
Sugar cane	Sugars	Food
Spent sulfite liquor	Sugars	Waste
Jerusalem artichoke	Inulin	Minor use as food

¹Primary feedstock constituent = chemical component of raw material that will be used to derive fermentable sugars for chemicals production.

Table 3.2- Recoverable Biomass Wastes

<u>Recoverable Biomass</u>	<u>Millions of dry tons</u>	<u>Millions of Btu/ton</u>	<u>Trillion Btu total savings</u>
Wheat straw and husks	2.5	14.2	35.9
Corn stover, cobs, husks	14.1	14.2	201.0
Rice stover and hulls	0.37	14.0	5.2
Barley straw	0.69	14.9	10.3
Sorghum straws	1.35	14.0	18.9
Orchard prunings	0.45	16.3	7.3
Feedlot manures	22.5	13.0	292.0
Cheese whey as dry waste	0.5	110.0	55.0
Potatoes processing wastes (dry)	0.35	110.0	38.5
Waste woods and bark from processing	3.0	18.0	53.5
Waste woods from in-forest residue	35.4	17.0	601.0
Paper mill sludge	2.4	12.0	29.2
Corrugated cardboard	8.4	14.1	118.0
Waste newsprint	5.9	16.0	94.0
Waste printing/writing	11.6	10.5	121.0
Waste paper packaging/brown paper	2.2	14.5	31.2
Waste boxboard, other board	3.5	14.1	49.1
Carbon dioxide	1000.0	0.04	40.0

Source: A. Schroeder, Waste Material Management Division, Office of Industrial Technologies, 1991

Table 3.3 - Prices, Production, Potential Fermentable Sugar Yields, and Productivities of Representative Feedstocks (United States)

<u>Feedstock</u>	<u>Price</u> ¹	<u>Production</u> ²	<u>Yield</u> ³	<u>Idle Land</u> ⁴	<u>Dedication</u> ⁵	<u>Sugar Yields</u> ⁶	<u>Productivity</u> ⁷
Corn	9 (4)	191 (421)	7294 (6513)	27 (68)	201 (442)	135 (297)	4.9 (4374)
Potato	16 (7)	17 (37)	32368 (28900)	23 (56)	742 (1633)	121 (267)	5.3 (4724)
Potato processing residuals	LTP	0.8 (1.8)	-	-	0.8 (1.8)	0.14 (0.3)	-
Sorghum	9 (4)	16 (34)	3474 (3102)	16 (41)	58 (127)	45 (99)	2.7 (2409)
Municipal solid waste paper	LTP	95 (209)	-	-	95 (209)	74 (164)	-
Corn stover	None	105 (232)	-	-	52 (116)	19 (42)	-
Forestry/milling residuals	LTP	100 (220)	-	-	50 (110)	29 (58)	-
Sugar cane residuals	4 (3)	3.6 (8)	-	-	3.6 (8)	1.9 (4.1)	-
Silviculture	None	-	9993 (8922)	27 (68)	276 (608)	154 (338)	5.6 (4956)
Switch grass	None	-	7392 (6600)	27 (68)	204 (450)	75 (165)	2.7 (2421)
Apple pomace	LTP	1.3 (2.8)	-	-	1.3 (2.8)	0.09 (0.2)	-
Beet molasses	9 (4)	1 (2.3)	-	-	1 (2.3)	0.54 (1.2)	-
Cane molasses	9 (4)	1 (2.3)	-	-	1 (2.3)	0.54 (1.2)	-
Sugar cane	3 (2)	25 (56)	78176 (69800)	(3.5) 8.6	272 (599)	114 (252)	32.9 (29371)
Spent sulfite liquor	LTP	28 (62)	-	-	28 (62)	0.4 (0.8)	-
Jerusalem artichoke	None	-	29120 (26000)	23 (56)	668 (1470)	111 (245)	4.8 (4328)

¹Price of raw material, cents/kg (cents/lb); "LTP" = liability to the producer, and has negligible or no price;

"None" = the material is not currently a U.S. commodity; (Leeper et al. 1991; Salunkhe et al. 1991; USDA, 1991).

²Total annual U.S. production of raw material, metric tons x 10⁶/year (billion lb/year); (-) = not currently produced as a commodity product; (EPRI, 1991; Leeper et al. 1991; Salunkhe et al. 1991; USDA, 1991)

³For crops, kg/hectare/year (lbs/acre/year); (-) is used for waste products, even those that are agricultural by-products (because their supply is not dependent on land dedicated to chemicals production; sources of information include Bergez et al., 1991; EG&G Idaho, Inc., 1981; Electric Power Research Institute, 1991; USDA, 1991).

⁴Idle cropland available within the U.S., hectares x 10⁶ (acres x 10⁶); acreage for each crop was determined by totalling available cropland in those states where that crop is currently grown or could grow (USDA, 1991).

⁵Projected level of raw material production dedicated to chemicals production; based on availability of U.S. idle cropland for that particular crop, metric tons x 10⁶/year (billion lbs/year); information concerning appropriate land use based on particular crops, crop yields, and regional availability of idle cropland in the U.S.: USDA, 1991 (corn, potato, sorghum, sugar cane); USDA, 1991; Bergez et al., 1991 (silviculture) USDA, 1991; Electric Power Research Institute, 1991 (switchgrass); USDA, 1991; Leeper et al., 1991; EG&G Idaho, Inc., 1981 (Jerusalem artichoke); complete dedication is assumed for waste materials; 50% dedication is assumed for corn stover and forestry/milling residuals because some of this material must be returned to fields as part of sound soil conservation practice (Leeper et al., 1991; Oak Ridge National Laboratory, 1991).

⁶Maximum potential yields of fermentable sugar based on dedicated production values of raw materials, metric tons x 10⁶/year (billion lbs/year); sources of information that gave cellulose, starch, inulin, or sugar compositions of feedstocks were Almosnino and Belin, 1991; Electric Power Research Institute, 1991; Leeper et al., 1991; Salunkhe et al., 1991; USDA, 1991; Watson and Ramstad, 1987; Wayman et al., 1992.

⁷Metric tons of sugar/hectare/year (lbs of sugar/acre/year); these are projected values derived from sugar yields.

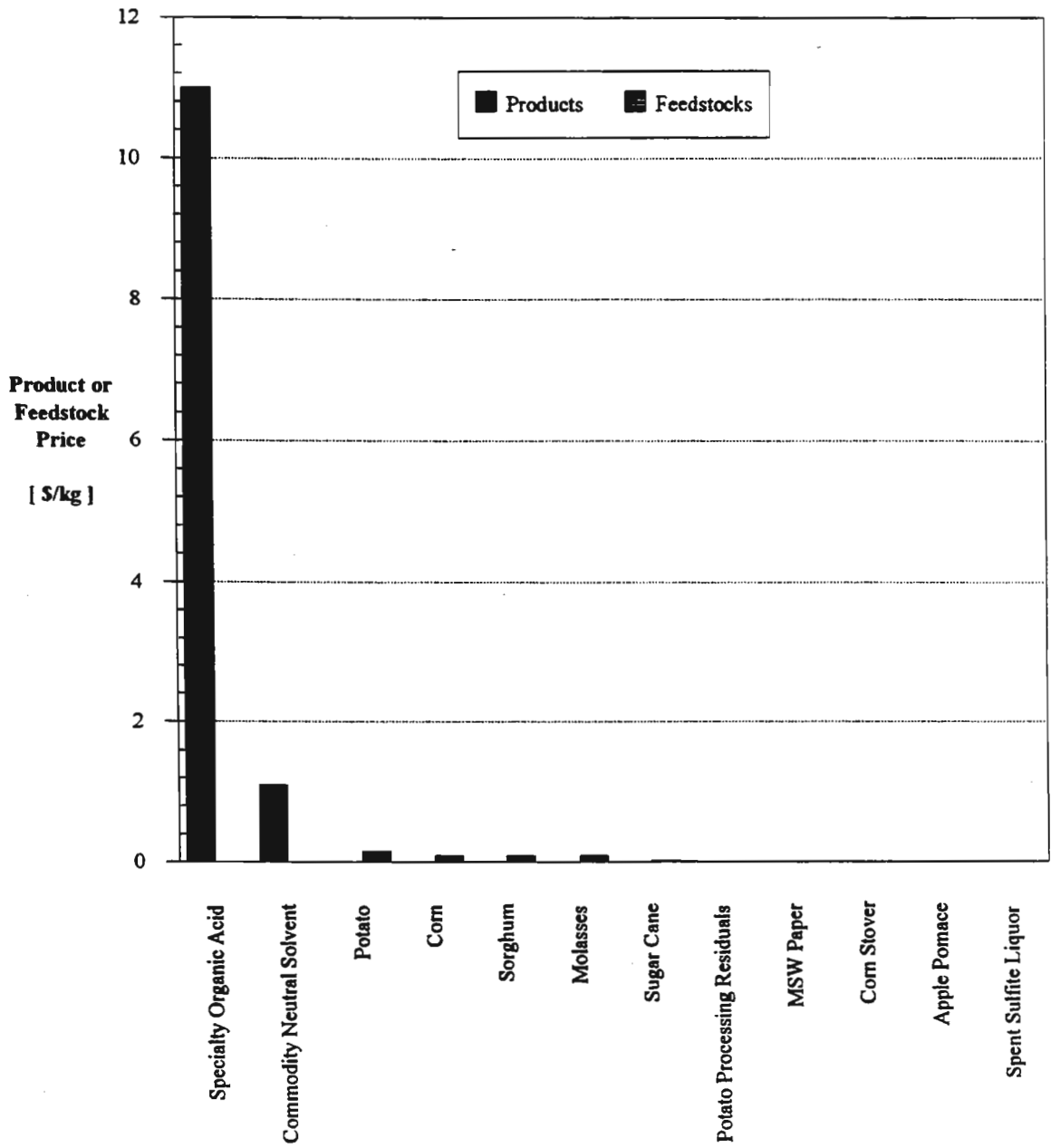


Figure 3.2 - Comparison of Selling Prices of Chemical Products with Representative Raw Feedstock Materials

Land that is designated as CRP- or ARP-committed is not available for extensive cultivating and harvesting food, feed, and forage crops. However, there may be potential for this land for other uses such as producing biomass feedstock with appropriate changes in legislation; this biomass could be used for producing biofuels and chemicals. If CRP- and ARP-committed land were used for biomass crops (or other crops), then appropriate measures would have to be taken to maintain sound soil conservation, environmental policy, and increased biodiversity.

Dedicated production levels for raw materials were used to derive maximum theoretical fermentable sugar yields. Values range from 0.09 million metric tons sugar/year (0.2 billion lb/year) for apple pomace up to 154 million metric tons glucose/year (338 billion lb/year) for silviculture (agroforestry). The amount of fermentable sugar that is derived from a particular feedstock is directly proportional to the potential energy displacement (i.e. displacement of petroleum feedstocks) for that feedstock in terms of chemicals production.

A moderate production level of 13 million metric tons sugar/year (29 billion lb/year), which is approximately a tenth of that potentially generated from dedicated corn crops, could theoretically supply 12 million metric tons (26 billion lb) of a single organic acid (based on a theoretical yield of 0.98 for a representative organic acid, succinic acid) or 5 million metric tons (11 billion lb) of a neutral solvent (based on a theoretical yield of 0.41 for a representative neutral solvent, butanol) from appropriate bioprocessing technology. These quantities are much greater than current and projected demands for these types of chemicals. The total potential sugar produced from switchgrass could yield 73 million metric tons (161 billion lbs) of an organic acid, e.g. succinic acid, or 31 million metric tons (68 billion lbs) of a neutral solvent, e.g. butanol. Based on current production in the United States of 4.5 million metric tons (10 billion lbs) of total organic acids/year and 9 million metric tons (20 billion lbs) of total neutral solvents/year (Leeper et al. 1991), the United States has enough raw feedstock material to completely support producing many commodity chemicals (Figure 3.3).

Note that certain feedstocks may be particularly suitable for specific chemical products based on projected production levels. For example, if 45 million kg (100 million lbs) is the desired single plant output for a chemical, then a feedstock should be selected that will produce enough fermentable sugar to meet this demand. Regional differences in feedstock availability will also affect feedstock selection, e.g., if the proposed chemical production plant is located in the northeastern United States, then a feedstock whose production is concentrated in that area should be selected (Oak Ridge National Laboratory 1992). In any given chemical plant scenario, most of the 16 representative feedstocks could meet the needs of a plant (because of feedstock flexibility described above), but there will be one or more "best choices" based on required production level, regional considerations, and pre-processing costs. Feedstock selection should be analyzed for individual scenarios; the top selections would be the primary (but not necessarily exclusive) feedstocks used.

3.3 Representative Alternative Feedstocks

Biobased feedstocks can be considered coproducts of agriculture and forestry, or their associated processing industries. The United States' strong global position in these industries makes it a logical leader in developing these feedstocks into chemicals (USDA 1987). As noted earlier, three broad categories can be defined: "waste" materials, dedicated crops, and conventional food crops.

3.3.1 "Waste" Materials

3.3.1.1 Materials from Food Processing

The food processing industry produces a variety of coproducts that were formerly considered to be waste streams (Levy et al. 1983; Leeper et al. 1991). Before World War II, a significant part of the United States' chemicals industry depended on producing acetone, butanol, and ethanol by fermentation (Linden et al. 1985; Maiorella 1985). The usual feedstock was molasses, a by-product of the sugar

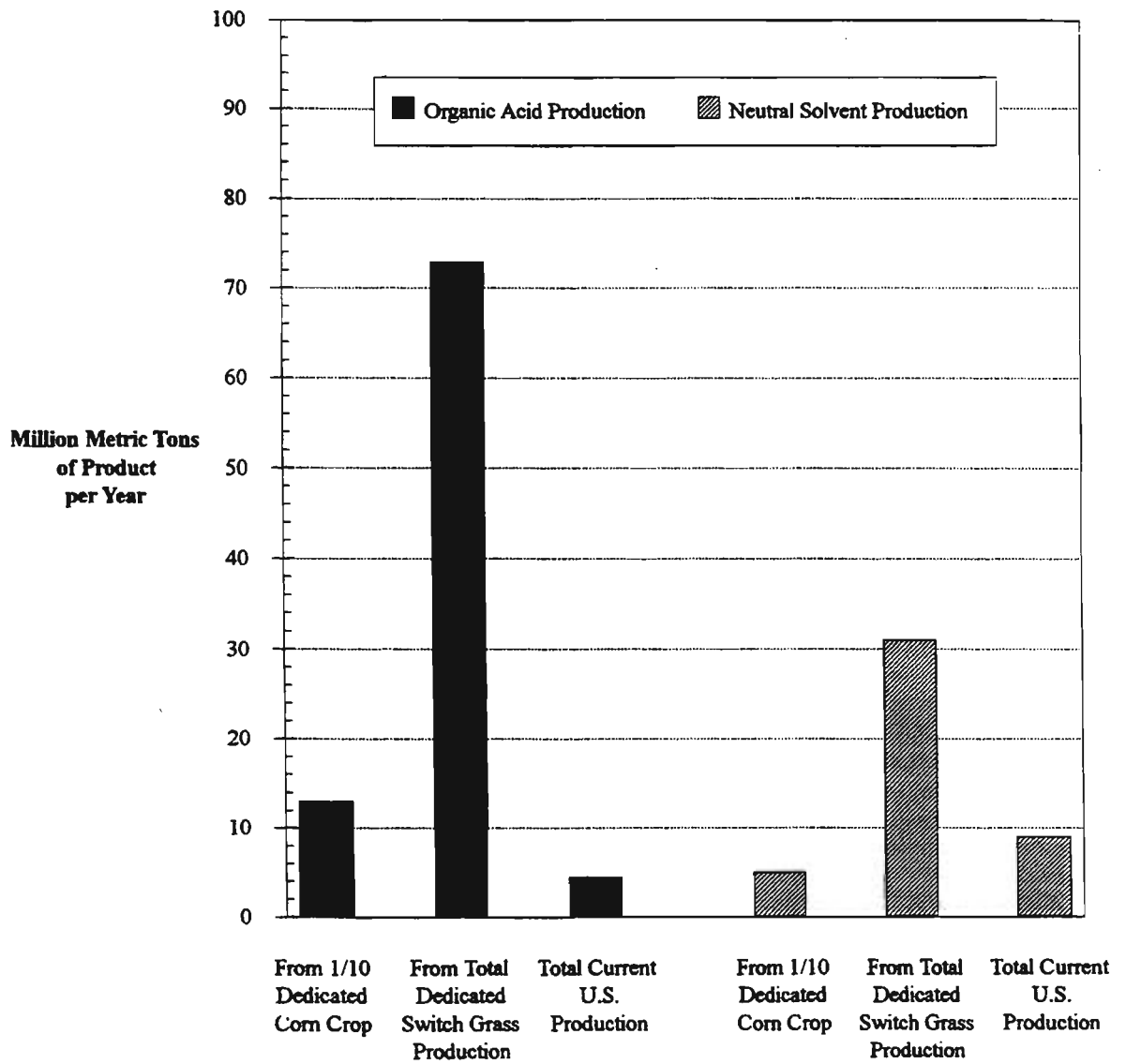


Figure 3.3 - Projected and Current Domestic Production of Organic Acids and Neutral Solvents

industry. Since then, the growth of the chemical industry has not been matched by a corresponding expansion of the sugar industry; consequently, the primary fermentation feedstock in the United States for ethanol is now derived from other sources, e.g., corn (Electric Power Research Institute 1991).

The modern corn processing plant achieves levels of product integration that rivals an oil refinery (Watson and Ramstad 1987). Corn oil, corn starch, high protein animal feeds, corn steep liquor, and corn syrup are produced. Some of the latter is fermented on site to fuel ethanol, and some is sold as a feedstock for the biological production of chemicals such as citric, itaconic, and amino acids. A projected 5% increase in fuel ethanol production from corn is predicted for 1993 (USDA May 1992).

Cheese processing plants can also show economic efficiency. Cheese whey, once considered a waste, can now be processed to make a valuable whey protein concentrate and a sugar solution that can be fermented to make fuel (ethanol or methane) (Leeper et al. 1991; USDA 1980).

3.3.1.2 Materials from Cellulosic Biomass

The United States produces a large quantity of corn stover (Elshafei et al. 1991; Table 3.3). Fifty percent of crop residues need to be left in the fields to protect the soil from water and wind erosion, and to recycle organic material (Leeper et al. 1991; Oak Ridge National Laboratory 1992). Despite using such recommended practices, there is still a large quantity of this feedstock material that is available for producing chemicals. In fact, if a large portion of the stover not needed for soil conservation were fermented to ethanol, it would satisfy a significant fraction of our demand for liquid fuels.

Forestry residues (including branches, wood chips, and sawdust) have a similar composition to agricultural residues, and can be used in the same way. There is a large supply of this material, so diverting a fraction of these feedstocks to the biological production of commodity chemicals would have little impact on their other current uses (Leeper et al. 1991). The biofuels potential from combined agricultural and forestry residues is approximately two quads (Oak Ridge National Laboratory 1992). However, using these residues must be consistent with sound soil conservation practices (Oak Ridge National Laboratory 1992).

3.3.1.3 Dedicated Crops

Dedicated crops are those that are to be grown specifically to produce fuels, chemicals, or electric power. The emphasis in selecting a suitable dedicated crop is on maximizing the rate of return per unit area of land in an environmentally acceptable manner (Oak Ridge National Laboratory 1992). The choice of a dedicated crop will vary according to geographic region, and ecological and other land use considerations (Oak Ridge National Laboratory 1992). Examples include herbaceous oil crops, such as soybeans, short rotation woody crops, such as poplar-based agroforestry (USDA January 1992; USDA October 1992; Office of Technology Assessment May, 1991; Leeper et al. 1991; Bergez 1991) or switch grass, napier grass and other forage-type crops that are native American species. Dedicated crops also may include crops currently grown, as well as new crops, such as the Jerusalem artichoke, that show particular promise as fermentation feedstocks (Leeper et al. 1991; Narayan et al. 1988; Manzoni and Cavazzoni 1992). The most extensive examples of dedicated crops as feedstocks for a chemicals is the Brazilian ethanol production program based on an immense crop of sugar cane (Maiorella 1985) and their use of eucalyptus for charcoal production.

An important criterion in choosing a dedicated crop is the amount of energy in the form of fuel, pesticide, and fertilizer required to grow it (Perlack et al. 1992). If the necessary amount is high, then the overall process may not achieve the goal of conserving energy. Total energy cycle analysis from the crop generation stage through the industrial process, consumption, and emission stages are needed to quantify energy conservation benefits. Production costs of crops, which are directly related to the amount of energy expended, are quite variable, ranging from \$50/acre for barley to as high as \$320/acre for rice (USDA 1990). Additional information concerning energy balance and environmental impact

analyses of dedicated feedstock crops has been detailed as part of the Biofuels Feedstock Development Program at Oak Ridge National Laboratory (Wright et al. 1992).

3.3.1.4 Conventional Food Crops

Another plentiful source of renewable raw materials is corn. The total supply in the United States in 1986-1987 period was about 13 billion bushels, of which the projected domestic use was 5.5 billion bushels. Exports constituted 1.1 billion bushels, leaving a surplus of about 6.4 billion bushels. Such a corn surplus represents the ability to make 227 billion pounds of starch, a remarkable number! The worldwide trend is to increased grain self-sufficiency. The increased United States grain productivity will lead to increasingly larger surplus grain production. Some of the corn byproducts are primarily sold to the European market. Changes in import levels for these products could greatly impact the United States' export ability in this area.

This section overviews the makeup of corn, and describes some of the products available when it is used as a raw material. The first few tables in this section overview the various components in corn and corn byproducts. The composition of corn is given in Table 3.4. Tables 3.5-3.9 present the composition of the main products from corn processing. Table 3.5 describes the protein content of the various parts of the corn grain. The corn germ metal composition is described in Table 3.6. Table 3.7 describes the oil components of corn oil, while Table 3.8 reports the average fatty acid composition of refined corn oil. Corn hull (bran) compositions is assembled in Table 3.9.

Table 3.4 - Corn Kernel: Composition of Parts (% Dry Basis)

	<u>Proportion of Whole Kernel</u>	<u>Starch</u>	<u>Protein</u>	<u>Oil</u>	<u>Ash</u>	<u>Sugar</u>
Kernel	100.0	71.5	10.3	4.8	1.44	1.97
Endosperm	81.9	86.4	9.4	0.8	0.31	0.64
Germ	11.9	8.2	18.8	34.5	10.1	10.81
Hull	5.3	7.3	3.7	1.0	0.84	0.34
Tip Cap	0.8	5.3	9.1	3.8	1.59	1.61

Source: Earle et. al, Cereal Chemistry, 1946, 23, 504.

Table 3.5 - Protein in Corn Grain Fractions (% of Total Nitrogen)

<u>Nitrogen Distribution</u>	<u>Corn</u>	<u>Endosperm</u>	<u>Germ</u>	<u>Hull</u>
Nonprotein	2.0	1.2	3.4	7.7
Albumins	7.0	3.5	28.0	6.5
Globulins	10.0	2.5	24.0	11.8
Zein	39.0	45.8	5.0	4.0
Glutelin	35.0	38.0	30.0	12.0

Source: J.S. Wall and J. W. Paulis, Advances in Cereal Science and Technology, Vol. 2, Y. Pomeranz, Ed., Am. Assoc. Cer. Chem., 1978

Table 3.6 - Corn Germ Meal Composition (Solvent Extracted)

	<u>% Dry Basis</u>
Protein	25-27
Starch	20
Fat	5.1
Cellulose	13
Hemicellulose	32
Lignin	1
Ash	4.1

Source: S.A. Watson, Corn Refiners Association, 1986 Scientific Conference

Table 3.7- Corn Oil Components

	<u>Crude Oil (%)</u>	<u>Refined Oil (%)</u>
Triglycerides	95.6	98.8
Free Fatty Acids	2.5	0.05
Waxes	0.01	0.0
Phospholipids	1.5	0.0
Cholesterol	0.0	0.0
Phytosterols	1.2	1.1
Tocopherols	0.12	0.09

Source: Corn Oil, Corn Refiners Association, 1986

Table 3.8 - Refined Corn Oil; Average Fatty Acid Composition

	<u>Percent</u>
Palmitic (16:0)	11
Stearic (18:0)	2
Oleic (18:1)	24
Linoleic (18:2)	62
Linolenic (18:3)	1

Source: Refiners and Grooding, "Corn: Culture, Processing, Products", G. E. Inglett, Ed., Avi., 1970

Table 3.9 - Corn Bran (Hull) Composition

	<u>% Dry Basis</u>
Cellulose	23.0
Protein	7.5
Xylan	42.1
Lignin	4.9
Starch	7.8
Fat	3.2
Ash	0.8

Source: F. Hooper, Ind. Eng. Chem., 1942, 34, 728.

The key polysaccharide present in the kernel is starch. In starch, glucose units present a stereochemical arrangement different from that of cellulose. Four hundred to one thousand α -D-glucose units (in the pyranose form) are linked together by α -1-(1-4) linkages; this linkage yields the linear polymer, amylose. Alternatively, 10,000-40,000 α (1-4)-linked and α (1-6) linked glucose units yield the branched polymer amylopectin. Starch is a non-structural carbohydrate that acts as energy reserve for the plants. Because of the branched structures, access of the structures by enzymes is facilitated. Thus, starch has been a traditional substrate for fermentation. Most of the common starches contain 17-27% amylose; the remainder is amylopectin. Grains have been developed, however, with widely variable composition. Properties and uses of industrial starches have been reviewed (James 1974).

The key process for producing starches is corn-wet milling. It can yield, on a dry basis, about 65% starch, 5.5% gluten protein, 8% germ (oil, 4% and meal, 4%), 11.5% fiber, and 7.5% steepwater (Table 3.10). The starch portion can be used for manufacturing modified starches, corn syrup with a high fructose content, dextrose, ethanol, and maltodextrins, as main products. The industry has a high capability to swing from product to product with the ability to produce either syrups or alcohol depending on the markets. Such flexibility is not present in the second most common processing method for corn, dry milling, in which ethanol and animal feed are the key products. The corn industry is an example of an industry that explores and uses byproducts to improve their overall profitability, much like the petroleum refining industry.

A variety of starch products have been developed that are valuable in manufacturing paper products (sizing products), textiles, foods, pharmaceuticals, building materials, etc. Starch also serves as the feedstock for manufacturing a number of chemical compounds such as glucose, maltose, sorbitol and ethanol. Starch is also the source of sweeteners such as high fructose corn syrup. Other parts of the plant are also feedstocks for a number of products; furfural from corn cobs is one example. The composition of corn cobs is illustrated in Table 3.11.

Dr. Morton W. Rutenberg (vice president, Research and Development, National Starch & Chemical Corp., Bridgewater, New Jersey) states that key to starch use is its chemical modification. Though some of this modification can be accomplished genetically, it is still necessary to perform chemical modifications. The modification enhances (or represses) inherent properties, or builds new properties. Examples of major modification routes are crosslinking for increasing starch granule toughness; hydrolysis to lower the viscosity of starch solutions (by reducing molecular weight); oxidation to reduce molecular weight and increase the stability of solutions; esterification to stop retrogradation and lower gelatinization temperature; etherification to introduce anionic, cationic, amphoteric, or hydrophobic groups to starch; and polymerization to add functional properties through graft and block polymers.

Cationic starch ethers are used as additives for paper manufacture. Paper pulp is negatively charged and the cationic starches neutralize the paper pulp and increase the paper production. There are, however, competing cationic products that can be used in this application. Hydrophobic esters are added to food products for forming emulsions and encapsulating food products. Using starch in grafting and merging natural and synthetic polymers will still require research and development according to Dr. Rutenberg. Many possibilities exist for extrusion cooking starch.

Other promising uses of starch as a raw material include synthesizing glycosides, that could be used in urethane foams, but their cost may still be too high for competing with existing products. A number of cyclodextrins (cycloamyloses) can be produced from starch, that can be used for enhancing wettability and solubility, and could find uses in slow release applications. Glucose esters may be used as fat substitutes. In addition, a number of plasticizer applications can be envisioned.

Protein fiber zein, present in the corn, is also useful. It can yield fibers and form films. It is solvent soluble and water insoluble. It is thermoplastic and resistant to hydrolysis and microorganisms, to some extent. Many of these properties have been explored in producing textile fibers, in coatings of pharmaceutical tablets, food, paper, varnishes, etc., and finally, in printing inks.

Table 3.10 - Major Components of Corn Wet Milling Steepwater

<u>Steepwater:</u>	<u>Major Components</u>
	<u>(Condensed Fermented Corn Extractives: 40% - 50% Solids)</u>
	<u>% Dry Basis</u>
Nitrogen	7.5
As Protein (N x 6.25)	47
Lactic Acid	18-26
Reducing Sugars	10-20
(As Glucose)	
Phytic Acid	7.8
Lipid	0.4
Phosphorus (Total)	3.3
Phytin P	
Potassium	4.5
Magnesium	1.5
Total Ash	15.7

*Peptides, Free Amino Acids, Ammonia Comprise 80% of Total Nitrogen

Source: S.A. Watson: Corn Refiner Association, 1986 Scientific Conference

Table 3.11 - Corn Cobs: Proximate Composition (% As Is)

	<u>Cob</u>	<u>Woody Portion</u>	<u>Pith/Chaff Portion</u>
Cellulose	41.2	47.1	35.7
Hemicellulose	36.0	37.3	37.0
Lignin	6.1	6.8	5.4
Pectins ^a	3.1	3.2	3.2
Starch ^a	0.014	0.014	0.015
Lipids	0.041	0.028	0.081
Pentosans	34.6	36.5	34.7
Xylan	30.0	31.6	30.1

^a) Dry Basis

Source: Foley & Vander Hooven in "Cereals: A Renewable Resource", Pomeranz & Munck, Ed., A.A.C.C., 1981

3.4 Advantages and Disadvantages of Selected Renewable Feedstocks

Feedstock flexibility allows users of biomass to tailor their production to the feedstock that is available as a function of season, geographical location, weather, etc. This section notes the advantages and disadvantages of several readily available feedstocks of use to both bioprocesses and thermal or chemical processes.

3.4.1 Feedstocks for Bioprocesses

Table 3.12 summarizes advantages and disadvantages for use of representative feedstocks typically used in bioprocessing. All of the criteria listed are important when considering the suitability of a

particular feedstock for industrial level production of chemicals. Using the criteria shown in Table 3.12, an ideal feedstock material might have the following characteristics: minimal dependency on crop hardiness, low price, minimal pre-processing (to a fermentable sugar) requirements, minimal storage requirements, high sugar yield, chemicals production as a high value option compared to current use (e.g. food, feed, fiber, or waste), high degree of technological advancement in producing and processing raw material, and high efficiency in terms of environmentally acceptable land use.

The decision analysis of the "best" feedstocks for producing chemicals might be considered in the context of near-term versus long-term goals. With respect to short term (0 - 5 years) adoption of alternative feedstocks technology, the raw materials that currently have the greatest number of positive aspects in the 16 samples assessed are beet and cane molasses. These feedstocks share the following advantageous properties: processing costs are low, because they are already in a fermentable form; the technology base for using molasses as a fermentation feedstock is large; they are waste materials (which means that they are not directly dependent on degree of crop hardiness and do not directly affect land use); and they have minimal storage requirements. Chemicals production represents a potential high value option for these feedstocks, and the conversion technology will directly transfer to dedicated crops with similar fermentable sugars, such as sugar beets and sugar cane. However, the uses developed will have to compete with various feed applications.

Although corn does not possess as many positive attributes as beet and cane molasses, its well established technical, industrial, and agricultural base could also make it a possible candidate. For short term considerations, the feedstocks that have the greatest number of negative attributes in relation to the other feedstocks are silviculture, switchgrass, and Jerusalem artichoke. These are potentially disadvantaged from a chemical processor's view by lack of a significant technology base for feedstock pre-processing or production.

With respect to long-term (10 - 15 years) adoption of alternative feedstocks technology, the raw materials that have the greatest number of positive aspects are corn stover, forestry/milling residuals, municipal solid waste paper, and sugar cane residuals (Table 3.12).

For long term scenarios, feedstocks were rated without considering pre-processing and technology base factors, because problems in these areas would probably have been worked out in 10 to 15 years time. These feedstocks are good choices for chemicals production for reasons that include:

- chemicals production represents a high value option,
- supply does not have to be from land dedicated to chemical production
- raw material prices are low, and
- storage requirements are minimal.

The technology used for developing these feedstocks would also be directly applicable to the use of dedicated crops, such as silviculture and switch grass. For long-term considerations, the feedstock that has the greatest number of negative attributes (in relation to the other 16 representative feedstocks) is potato. Potatoes are primarily disadvantaged by the high cost of raw feedstock material in relation to other feedstocks listed.

Recent technological advancements in sustainable farming/forestry practices and feedstocks pre-processing (to fermentable sugars) should improve the clarity of an already bright picture. Such advancements include genetic engineering of crops, such as potatoes, to bring about an increase in dry matter production (Salunkhe et al. 1991). Genetic engineering can also bring about increased crop hardiness (Salunkhe et al. 1991). By May 1991, the USDA and EPA had approved 236 field tests for reviewing genetically modified plants and microorganisms (Office of Technology Assessment 1991). The Biofuels Feedstock Development Program at ORNL includes (among other projects) major efforts in genetic improvement research for woody and herbaceous crops (Wright et al. 1992). One of the results of this research program has been developing hybrid poplar trees that have greatly increased yield,

Table 3.12 - Positive and Negative Characteristics of Representative Feedstocks¹

Feedstock	Hardiness ²	Price ³	Processing ⁴	Storage ⁵	Sugar Yield ⁶	Waste Minimization ⁷	Technology Base ⁸	Land Usage ⁹
Corn	-	+/-	+/-	+	+	-	+	-
Potato	-	-	+/-	+/-	+	-	+	-
Potato processing residuals	+	+	+/-	-	-	+	+/-	+
Sorghum	-	+/-	+/-	+	+	-	+	-
Municipal Waste Paper	+	+	-	+	+	+	-	+
Corn stover	+	+	-	+	+	+	-	+
Forestry/milling residuals	+	+	-	+	+	+	-	+
Sugar cane residuals	+	+	-	+	+	+	-	+
Switch Grass	-	+/-	-	+	+	+/-	-	-
Silviculture	-	+/-	-	+	+	+/-	-	-
Apple pomace	+	+	+/-	-	-	+	+/-	+
Beet molasses	+	+/-	+	+	+	+	+	+
Cane molasses	+	+/-	+	+	+	+	+	+
Sugar cane	-	+/-	+/-	+	+	-	+	+/-
Spent sulfite liquor	+	+	+	-	-	+	-	+
Jerusalem artichoke	-	+/-	+/-	+/-	+	+/-	-	-

¹Sources are the same as those for Table 3.3, and *Agriculture 2000: A Look into the Future*, 1983. ²Crop hardiness; (+) indicates that supply of the raw material is not directly influenced by the success of a crop dedicated to chemicals production; (-) indicates the raw material is derived from a crop that is dedicated to chemicals production; for example, the corn crop that is referred to above would be one that was grown expressly for providing feedstock material for the production of chemicals; however, the corn stover supply listed above would be derived from currently existing corn production (not dedicated to chemicals production); thus, corn stover is not directly dependent upon the success of a dedicated crop -- it is a waste material that will always be available in large quantities; even if existing corn production has a bad year, corn stover will be available in large quantities, since current corn production is very high (see Table 3.3). ³Price of raw materials; (+) indicates that the price is less than 1 cent/kg; (+/-) indicates a current price (or probable price) of 1 to 10 cents/kg; (-) indicates a price of greater than 10 cents/kg (see Table 3.3). ⁴Level of pre-processing of feedstock necessary prior to utilization as a fermentation substrate; (+) indicates little or no processing necessary; (+/-) indicates moderate level of processing necessary; (-) indicates extensive processing necessary. ⁵Storage properties. (+) indicates long-term storage possible; (+/-) indicates medium-term storage possible, (-) indicates long-term storage possible only if costly storage quality criteria are met. ⁶Maximum potential fermentable sugar yield from dedicated production values of raw material; (+) indicates greater than or equal to 0.54 million metric tons of sugar/yr; (-) indicates less than 0.54 million metric tons of sugar/yr; cutoff value is based on 0.54 million metric tons of sugar required to produce 0.27 million metric tons of a commodity chemical (at a yield of 0.5) at 6 chemical production plants [based on 6 U.S. agricultural regions, (Battelle Memorial Institute, 1983); 0.045 million metric tons (100 million pounds) of chemical/plant/yr] (see Table 3.3). ⁷(+) indicates usage of feedstock constitutes a potential solution to a waste liability, or is a high value option for the material, (-) indicates that the material is already a commodity product, (+/-) indicates that the material is neither waste nor a commodity product. ⁸Level and success of research and development associated with production and processing of feedstock. (+) indicates high level and success; (+/-) indicates medium level and success; (-) indicates low level, or high level but low success. ⁹Utilization of land for growth of feedstock; emphasis is on reduction of environmental stress by using as little land as possible; (+) indicates that the material is not derived from land dedicated to producing feedstocks for chemicals production; (+/-) indicates a productivity greater than or equal to 1 to 10 metric tons sugar/hectare/year; (-) indicates a productivity of less than 10 metric tons sugar/hectare/year (refer to Table 3.3).

and thus exhibit greater potential as energy crops (Oak Ridge National Laboratory 1992). This was developed by implementing hybridization and clonal selection, innovative physiology studies, and crop management studies.

Recent research concerning pretreating cellulosic materials has positively affected the potential use of those type feedstocks (Lynd et al. 1991; Teunissen et al. 1992; Wayman et al. 1992). In addition, the U.S. Department of Agriculture has historically sponsored much research concerning advancing crop generation. Because these research efforts directly address problems (e.g. fermentable sugar yield and raw material pretreatment) which affect process cost sensitivity, taking advantage of the opportunities that these types of recent technological advances present is a key component in the development of a biobased chemicals industry.

3.4.2 Lignocellulosic Feedstocks

In general, the composition of lignocellulosic feedstocks reveals common constituent polymers. Tables 3.13 and 3.14 summarize the chemical composition of several of the feedstocks described in this section.

Hardwoods could be an excellent raw material for bioconversion because of their availability and desirable properties. Although some hardwoods are valuable and much in demand, many are considered a silvicultural problem because of their poor performance when compared with softwoods in producing cellulose pulp by the pulp and paper industry. Often the trees are of small diameter and without a usable trunk, and are therefore usually weeded from forests to make space available for softwood plantations.

The advantages of using hardwood material for bioconversion include the high density of many species, the relative ease of delignification and accessibility of the wood carbohydrates, and the presence of only one hemicellulose, xylan, that can be more easily removed than softwood hemicelluloses. Other advantages include low ash content, particularly silica, and slightly higher total carbohydrate and cellulose content. The possibility of byproduct use is great, especially when compared to softwoods. Hardwoods have a higher acetyl content than softwoods and most grasses and would yield more acetic acid. Xylan conversion to furfural would produce a product with a potential market (Parker et al. 1983). The small amount of glucomannan hemicellulose could probably be converted together with cellulose, especially if fermentation is considered.

Softwoods have considerable value as construction lumber and pulpwood, thus using this raw material for biomass conversion might not be economically beneficial. However, the pulp and paper industry has large amounts of logging and manufacturing residues that could serve as raw material for converting to other materials, because they are normally unsuitable for use in normal cellulose pulp production. Branches and tops constitute most of the logging residues. Because of the higher density of branch wood, diffusion of pulping liquor into the cell wall is difficult. The probable presence of compression wood in branches also is a problem because the higher and more condensed lignin content of compression wood together with a thicker cell wall makes any adequate delignification difficult. Compression wood also has a lower total carbohydrate content (especially cellulose), making it less desirable as a raw material for pulp production. The tops of trees have many branches and may have considerable juvenile wood in the main stem. Because juvenile wood has a low density and thin cell walls, it would be overreacted before the branch wood could be adequately treated. Therefore, logging residues probably are best used as a fuel source or could serve as feedstocks for thermochemical processes.

The primary manufacturing residues of the pulp and paper industry are debarking residues, sawdust, and sanderdust. Bark, especially from thick barked softwood species, is not readily adaptable to nor desirable for wood carbohydrate use. However, the need for suitable uses of bark is great and developing chemical processes for its conversion to new materials is needed. In certain regions, much more sawdust is produced than can be consumed in the pulping industry; often sanderdust is also available. The primary impediment to their use is the type of lignin present in softwoods. Not only is

Table 3.13- Cell Wall Constituents of Biomass (%)

<u>Normal Wood</u>	<u>Softwoods</u>	<u>Hardwoods</u>	<u>Grasses</u>	<u>Comments</u>
Cellulose	41-43	43-45	35-39 ^a	^a May be higher
Lignin (average)	28	22 ^b	16 ^b	^b Some soluble lignin
Range	24-33	16-24	15-18	
Xylan (Pentosans)	8-14 (5-10)	20-30 (12-24)	27-34 (25-29)	
Glucmannan	16-22 ^c	305	None	^c Contains variable gal-actose amounts

<u>Reaction Wood</u>	<u>Compression (Softwood)</u>	<u>Tension (Hardwood)</u>	<u>Comments</u>
Cellulose	32	56 ^d	^d Excess in G layer
Lignin	40	14	
Xylan	variable	low	
Glucmannan	low	low	
Galactan ^e	8-16	0-8	

Table 3.14- Chemical Composition of Some Common Fibers

<u>Type of Fiber</u>	<u>Chemical Component (percent)</u>				<u>Silica</u>
	<u>Cellulose</u>	<u>Lignin</u>	<u>Pentosan</u>	<u>Ash</u>	
Stalk Fiber					
Straw					
Rice	28-36	12-16	23-28	15-20	9-14
Wheat	29-35	16-21	26-32	4.5-9	3-7
Barley	31-34	14-15	24-29	5-7	3-6
Oat	31-37	16-19	27-38	6-8	4-6.5
Rye	33-35	16-19	27-30	2-5	0.5-4
Cane					
Sugar	32-44	19-24	27-32	1.5-5	0.7-3.5
Bamboo	26-43	21-31	15-26	1.7-5	0.7
Grass					
<i>Esparto</i>	33-38	17-19	27-32	6-8	---
<i>Sabai</i>	---	22.0	23.9	6.0	---
Reed					
Phragmites	44.75	22.8	20.0	2.9	2.0
Bast Fiber					
Seed Flax	47	23	25	5	---
Kenaf	31-39	15-19	22-23	2-5	---
Jute	45-53	21-26	18-21	0.5-2	---
Leaf Fiber					
Abaca (Manila)	60.8	8.8	17.3	1.1	---
Sisal (agave)	43-56	7-9	21-24	0.6-1.1	---
Seed Hull Fiber					
Cotton Liner	80-85	---	---	0.8-1.8	---

Source: Rowell, R.M. in ACS Symposium Series, 476, p. 19, 1992

delignification more difficult than with hardwoods, but opening the cell wall structure and providing access to the cellulose is more difficult. On the average, softwoods have less total carbohydrate and slightly less cellulose than the hardwoods. The hemicellulose fraction is also more complex, with less pentosan available for possible conversion to furfural.

Lignin use still presents the greatest challenge. Most prior lignin research aimed at using lignin involved softwood lignin, but hardwood lignin may have some advantages. Hardwood lignin is less condensed, meaning it has a lower degree of polymerization and less carbon-carbon bonding. Hardwood lignin also has less tendency to condense under acid or alkaline conditions. Hardwood lignin has a greater methoxyl content, that in destructive distillation of wood resulted in more methyl alcohol (wood alcohol), thereby making hardwoods preferred over softwoods. It may be possible to obtain methyl alcohol from hardwood lignin without pyrolysis. Hardwood lignin becomes plastic at a lower temperature than softwood lignin, that is the basis for using hardwoods in wood bending. Perhaps this property could also be exploited.

The immediate use for lignin produced by bioconversion would be as a fuel because it has a much higher energy value than wood. This byproduct lignin should be evaluated for use as a raw material for synthesis gas formation. For higher quality use of lignin, some chemical modification, e.g., removing aromatic ring substitution groups, such as methoxyls, without introducing another functional group would probably be necessary. Potential markets for lignin use have been reviewed by Chum et al. (1985) and by Chem Systems (1987).

Agricultural residues have an advantage resulting from their chemical composition. Because of the amount and nature of the lignin present, grasses are easily delignified and the carbohydrates are made readily accessible. Because the hemicellulosic fraction is closely related to xylans with no glucomannans present, this also simplifies chemical conversion. Xylans are much more susceptible to acid hydrolysis and alkaline extraction than cellulose and can be readily removed if necessary. The technology is available for converting xylans to furfural, an industrial chemical used in adhesives and resins and as a plasticizer. Corn stover (cornstalks) is unique and occupies a similar position among agricultural residues as aspen does among the hardwoods. It has a lignin content of only 14% rich in esterified acid groups, and has a xylan rich in both acetyl and uronic acids. Very mild treatment will make the cellulose accessible. The availability of cornstalks for bioconversion, however, is limited because of their competing use as silage.

A problem with agricultural residues is that the quantity available is only a small fraction of that available from hardwoods. Also harvesting agricultural residues usually takes place within a short time span once a year, necessitating that storage space must be provided for an annual supply. Agricultural residues are quite susceptible to microbiological degradation, particularly when wet, that can destroy their bioconversion potential in a matter of days. Most agricultural residues are best stored under shelter, thereby adding to their cost and complexity of storage. Agricultural residues tend to be bulky because of their low density, thus complicating transportation, handling, and storage, and generally result in higher costs than for the same operation using wood. Digester capacity is greatly reduced and the liquor-to-residue ratio substantially increased due to low bulk density. In the actual processing, the high silica content of most agricultural residues may cause substantial abrasion and may necessitate more frequent changing of cutting edges and operating down time due to equipment problems.

4.0 THERMAL/CHEMICAL ROUTES TO PRODUCTS

4.1 General

Developing renewables-based technologies to produce both simple chemical building blocks and new materials offers many new opportunities, and faces many challenges, as outlined in sections 1.0-3.0 of this report. However, any new technology under consideration by the chemical industry, regardless of the feedstock employed (renewable or nonrenewable) must meet important criteria: *will the new process be economically viable, and will it be advantageous to replace existing technology?* A preliminary overview of the potential of renewables suggests that hundreds, and perhaps thousands of materials could theoretically be prepared from biomass (e.g., Szmant 1986) that makes selecting a few promising opportunities for more detailed RD&D difficult. Additional reports support this conclusion (Rowell 1992, USDA 1992) and yet not every opportunity makes economic sense. An intelligent analysis of RD&D opportunities requires an efficient, quantitative selection methodology, based on economic considerations, because of the wide range of potential processes, catalysts, and products available.

A key component of the Alternative Feedstocks program has been developing such a comparative selection methodology. This approach (described in detail in section 4.2) is being used to prioritize options for a focused research start-up and to outline opportunities in three areas. First, near-term opportunities that already appear cost-effective according to the available data are identified. These chemicals or processes could lead to marketable products fairly quickly, and additional RD&D with industry could expedite their penetration into the marketplace. Second, mid-term opportunities are identified and include concepts that require additional RD&D to provide experimental data to validate the technoeconomic assumptions and demonstrate that yields/cost/properties are appropriate for further engineering, development, and commercialization with industry. Finally, long-term RD&D opportunities are identified and include developing research needs that underpin the science of renewable resources. This effort is a necessary component of the overall program if the potential of these resources is to be achieved for these purposes. Through scientific discoveries and this portfolio of near-, mid-, and long-term opportunities the use of renewables could become a major contributor to production of the country's fuels, chemicals, and electric power in the 21st century.

A unique feature of the Alternative Feedstocks program is a consistent, quantitative methodology to identify new renewable primary building blocks (analogous to methane, ethylene, etc.) that could serve in similar capacities and lead to new technology for preparing known and new end products exploiting the uniqueness of biopolymers.

The DOE Separations Division of the Office of Industrial Technology funded NREL to develop the technoeconomic evaluation process to be used in this quantitative analysis, and systematically screen the wide range of products that could be produced from renewable feedstocks. For convenience, the chemicals assessed have been divided into two categories: those available from thermal and chemical processes (summarized in Table 4.1), and those available from biotechnological routes (summarized in Table 7.1). Both biological and thermal and chemical processing routes are included in these assessments since the catalysts used in thermal and chemical processes and the enzymes employed in bioprocessing can lead to the true potential of chemicals from biomass in the near-, mid-, and long-term.

Interestingly, a systematic, quantitative screening methodology that considers yields of processes, improvements in the technologies, and various feedstocks, had not been developed for using renewables as chemical feedstocks. Most studies claiming to provide this information were carried out by a variety of process analysts and the various assumptions among them were not uniform. This study places existing previous data into a new consistent methodology and begins a systematic evaluation of chemicals and materials from renewable resources. As additional chemicals and materials are identified as the program proceeds, the routes will be investigated using the same consistent methodology, eventually leading to a database for uses of biomass available to researchers,

government managers and policy makers, and industrial researchers and managers, that will help communities decide which routes fit their own unique needs and context.

The methodology developed is simple and thus of wide applicability. The initial screening simply compares the raw material cost contribution of the proposed new process to the existing process (section 4.2). This comparative approach allows researchers and managers to be more aware of the current methodologies and what is necessary for these new routes to penetrate the marketplace. Certainly, improving conventional technology is an ongoing process and an alternative to introducing new processes. Over time, the comparative order and costs of biomass and conventional processes could vary as improvements and breakthroughs are made in existing processes. However, many conventional processes are based on mature technology, for which most of the gains in process improvements have been made. Under these conditions, those processes are dependent exclusively on the feedstock cost and product market considerations. It is possible that renewables could penetrate some areas in which the existing capacity has been reached and increases could be considered at smaller size plants. Thus, the other main difference between this study and previous ones is including market parameters and globalization considerations in selecting targets for future RD&D with industry.

Renewables have not normally been considered as sources of end use chemicals. For this reason, a large number of both short- and long-term research questions are being identified. To effectively address the technology and basic science needs of the program as identified by this quantitative assessment, parallel research tracks will be recommended to leverage synergistic funding resources. The DOE/OIT Separations Division will receive recommendations to support process development and improvement using those materials for which a fairly well defined route exists (near term opportunities). Mid-term opportunities will be recommended to the DOE/OIT Biological and Chemical Technologies Research Program. This includes cases for which the use of a given feedstock as a starting material for products traditionally derived from petrochemicals is unknown, or more extensive RD&D is necessary to bring a material to market. A longer term basic research effort will also be undertaken to understand processes and chemicals that show promise, but require a more fundamental understanding before being moved toward a market application. This basic effort also includes investigating the more generic areas of novel conversion methodology, separation chemistry, and new methods of using these materials.

A wide range of informational sources has been used to help guide this assessment effort. A key feature has been establishing an industrial panel for both the thermal and chemical processing and bioprocessing elements of the program. This panel provides industrial input as to which feedstocks and end-use products hold the greatest interest and potential for commercial application. The first meeting of the industrial panel was held in February 1992 to develop an industrial perspective and suggest an initial direction for the screening procedure. The industrial panel will also participate in reviews of the opportunities identified for chemicals production and will continue to provide feedback on the structure and direction of the Alternative Feedstocks Program.

Additional informational support for this technoeconomic evaluation has been provided by the National Academy of Sciences (NAS) through their recently completed study entitled "Putting Biotechnology to Work: Bioprocess Engineering." The objective of this study was to address key aspects of research and commercialization of bioprocessing applied to the emerging families of food, agricultural products, and industrial chemicals generated by biological routes that will require innovative, world-class bioprocessing techniques for their manufacture. A committee of 12 experts examined future bioprocessing opportunities in view of recent advances in biotechnology and the chemical and material sciences. Workshops dealing with key research and commercialization aspects were held to augment the information base of the committee. This report provides an authoritative perspective on bioprocessing and a critical reference for future actions by government, industry, and academia. The information gained through this NAS study will be incorporated into the analysis planned for the Alternative Feedstocks program to select products and processes for focused attention. The NAS is involved in a second study entitled "Biobased Industrial Products: National Research and Commercialization Priorities." This study will follow a similar format to that outlined above. The

emphasis of this study is on biobased materials and engineering for applications to both specialty, high-value products and commodity, low-value materials.

Additional studies focusing on thermal and chemical processes have been conducted through a group of volunteers during American Chemical Society meetings in Washington (1992) and Denver (1993). In Denver, an international group was convened to discuss producing chemicals, fuels, and electric power from renewables and policy implications worldwide. It is expected that a Biomass and Bioenergy special volume will be published from the Denver meeting. This will be a valuable source of information for planning similar to that resulting from the 1990 Washington meeting (Rowell 1992).

4.2 Description of Screening Methodology for Thermal and Chemical Processes

The study started with the 70 most promising chemicals and materials that can be produced from renewable feedstocks through thermal and chemical or bioprocessing processing routes (35 products each). Sections 4.0 and 5.0 present the results of the quantitative assessment of thermal/chemical routes to chemicals and materials. The results from the bioprocessing element of the study are presented in sections 6.0 and 7.0. In the future, more candidates will be added to the screening process on an annual basis. Upon completion of the screening of this initial portfolio of candidates, the most promising feedstocks/products could be selected to begin further investigation in a multilaboratory research effort with industry participation.

Although the methodology used to identify RD&D opportunities is simple, its description is more complex. Figure 4.1 overviews the approach schematically.

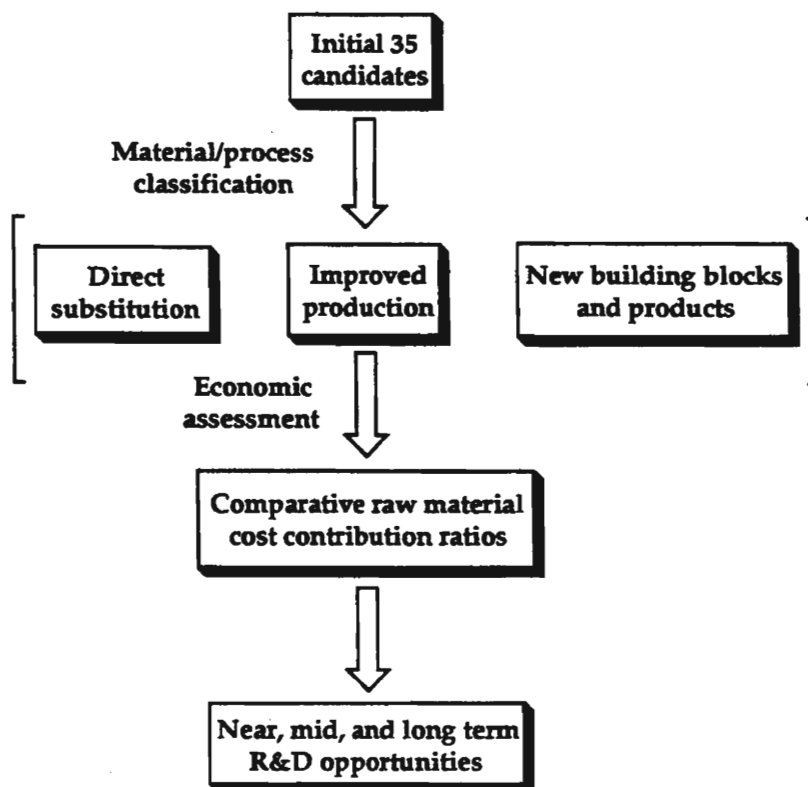


Figure 4.1 - Schematic Outline of Technoeconomic Analysis

The 35 candidates subjected to the economic analysis represent a complicated mix of processes, feedstocks, chemical building blocks, and new applications. Therefore, it was convenient to first separate the candidates into three categories (Table 4.1):

- *Direct Substitution:* This category describes compounds, that if produced from renewables, could directly replace the same compounds currently produced from petrochemicals (for example, butadiene).
- *Improved Production:* This category describes potential building blocks that are currently produced from renewables, but not normally considered as feedstocks since building blocks currently produced from petrochemicals are more economical. These renewable building blocks could substitute for certain petrochemicals if their production methods could be improved (for example, glucose).
- *New Building Blocks/Products:* This category describes new chemicals and efficient processes based on renewables, that could replace a variety of petrochemicals in selected applications, but whose specific end uses have not been defined (for example, levoglucosan).

4.2.1 Screening Based on Comparative Raw Materials Cost Contribution

Throughout this and subsequent sections, a number of comparative evaluations between biomass and petrochemical-based processes are made. The terms "raw materials cost" and "raw materials cost contribution" appearing in these comparative assessments are used to refer to the raw materials cost contribution to the total manufacturing cost, that includes appropriate adjustments to the market price for: 1) the starting material, 2) the process stoichiometry, and 3) the yields of the various process steps. When definitive information is not available, reasonable projections based on using the chemical and patent literature, as well as RD&D experience were made.

After separating the 35 candidate chemicals and processes into three categories, each is subjected to a three step screening procedure, based on the raw materials cost contribution:

- A raw materials cost assessment of the biomass route is performed.
- A raw materials cost assessment of the corresponding route from petrochemicals is performed, if a comparable route exists. If a petrochemical route is unknown, the comparison is made with the known existing route to the material.
- *The cost of the biomass route is adjusted "upward" by 30% and is compared in the form of a ratio to the petrochemical route.*

An important component of this evaluation is the incorporating the "30% rule." A process based on biomass is considered a promising opportunity for further RD&D when the difference in raw material costs for a biomass-based process is around 30% less than costs for a current petrochemical-based process.

Incorporating the "30% rule" is shown in the calculations by including a risk factor of 1.3, to account for possible problems, unknowns, intangibles, etc., in a given biomass-based process. This factor is also an approximation of the minimum cost reduction incentive needed to induce an operator of an existing technology to invest in the new technology and phaseout the old.

The result of these simple steps provides a set of numbers for comparison in the form of the ratio:

$$\frac{\text{Raw Materials Cost Contribution for Petrochemical (or other) Process}}{\text{Raw Materials Cost Contribution for Biomass Process} \times 1.3 \text{ (risk factor)}}$$

Table 4.1- Summary of Compounds Selected for Screening

<u>Compound</u>	<u>Process or Starting Material for Production from Biomass</u>
<i>Direct Substitution</i>	
Butadiene	Fast pyrolysis/catalytic upgrading
Pentanes/Pentene	Fast pyrolysis/catalytic upgrading
Benzene/Toluene/Xylene	Fast pyrolysis/catalytic upgrading
Acetic/Formic/Propionic Acids	Fast pyrolysis
Hydroxyacetaldehyde	Fast pyrolysis
Phenolics	Fast pyrolysis
Resorcinol	Fast pyrolysis to levoglucosan and chemical processing to resorcinol
Vinyl Phenol	Fast pyrolysis
Phenolics	Wood phenolation (liquefaction)
Phenolics	Lignin hydrotreatment
Acetic Acid	Syngas
Peracetic Acid	From black liquor acids or starch derived lactic acid
Anthraquinone	From black liquor or organosolv low molecular weight lignins
Acrylic Acid	Thermal dehydration of starch derived lactic acid or esterification and dehydration of starch derived lactic acid
<i>Improved Production</i>	
Glucose	From bagasse, corn wet milling, or steam explosion of lignocellulosics
Glucose and Xylose	NREL clean fractionation
5-Hydroxymethyl Furfural	Glucose
Levulinic/Formic Acids	Glucose
Succinic Acid	Glucose
Gluconic Acid	Glucose
Sorbitol	Glucose
Mannitol	Glucose
Xylose	Xylose from bagasse or wood
Xylitol	Xylose
Furfural	Xylose
Furfuryl Alcohol	Xylose
Furan/Tetrahydrofuran	Xylose
Polyhydroxybutyrate/Valerate	Syngas and glucose
<i>New Building Blocks/Products</i>	
Levoglucosan	Fast pyrolysis
Cellulose/Hemicellulose/Lignin	Clean fractionation
Cellulose/Anthraquinone	Kraft process
Cellulose/Anthraquinone	Organosolv pulping
Starch Plastics	Reactive extrusion
Acetylated Wood	Esterification

A ratio considerably less than unity indicates that a biomass route could have difficulty competing with the current petrochemical route. Conversely, a ratio greater than unity indicates a process that has potential for replacing a given existing route to the material under consideration.

Implicit in this procedure is the definition or consideration of six key components:

- the starting materials that can be used
- the catalysts that can promote product synthesis
- the process type (chemical/thermal or biotechnological)
- the potential volume of the product
- the market price or value of the products
- the costs of the starting materials

4.2.2 Preliminary Detailed Process Evaluation

One outcome of evaluating the 35 candidates based on a simple raw materials cost comparison is identifying processes that show particular economic promise. Some of these processes have been carried on to a second, more detailed level of screening to incorporate the costs of processing to predict an amortized production cost. However, selecting a candidate chemical or process for this more detailed evaluation depends on more than a promising ratio from the raw materials cost comparison. Also needed are laboratory results that help clearly define the process parameters necessary for an in-depth analysis. The key data gathered for this level of technoeconomic evaluation are rates, yields, and product concentrations, based on existing technologies for selected product or process options that meet or surpass the "30% rule." Overall process-flow diagrams are then devised for each product, and approximate equipment sizes are determined from the performance and physical property data. Capital and operating costs are estimated, and a product amortized production cost is calculated. The equipment sizes, capital costs, and operating expenses are approximate and are derived by a rule-of-thumb approach to accommodate the largest number of possible options.

Six processes and products were chosen, based on a combination of favorable raw materials cost contributions, and reliable process performance data obtained from laboratory research (Table 4.2). These processes have been analyzed in more depth through flowsheets of mass and energy balances, and amortized production costs have been calculated. Details of these assessments are found in section 5.4.

Table 4.2 - Detailed Process Evaluations Performed

<u>Compound</u>	<u>Processes Evaluated</u>
<i>Direct Substitution</i>	
Anthraquinone	NREL/IPST Kraft lignin Organosolv lignin Five conventional processes
Phenolics	NREL Fast Pyrolysis/Fractionation University of Kyoto (wood phenolation)
<i>Improved Production</i>	
Clean fractionation	NREL process
<i>New Building Blocks/Processes</i>	
Acetylated wood	USDA/FPL
Starch plastics	Michigan Biotechnology Institute

4.3 Summary of Technoeconomic Evaluation

Section 5.0 describes the results of the simple comparative evaluation of raw material costs for biomass versus petrochemical processes. For each chemical evaluated in this section, a block diagram for both the biomass and petrochemical routes is included to give a rapid description of the technology employed. The results were prepared using the methodology described in section 4.2, and then subjected to the "30% rule." Those chemicals identified as most promising have been, or will be, carried on into the more detailed process evaluation. Several of these more detailed evaluations are given in section 5.4. Where appropriate, projections of conditions necessary to make a presently unfavorable process economically viable have been made.

Caution must be used when evaluating these results. Evaluation is only as good as the process information currently available, and when exact information cannot be obtained, then reasonable estimates must be made regarding potential process performance. As a result, a process that shows an excellent raw materials cost comparison (for example, hydroxyacetaldehyde, section 5.1.5) may not be immediately identified as a candidate for further process evaluation because the process is only poorly defined. Conversely, some comparisons (for example, phenolics from pyrolysis, section 5.1.6) show a smaller difference between the biomass- and petrochemical-based routes. However, this process has undergone considerable, more detailed evaluation because the process is much more clearly defined and projections can be made based on actual laboratory RD&D results.

4.4 Current and Projected Markets for Selected Chemicals from Biomass

This section will summarize the market target potentially available to chemicals prepared from biomass by thermal or chemical processes, and will identify specific market areas where the chemicals will find a use. Where possible, projections of the market potential in future years are presented. Complete information in every category is difficult to obtain. Market sizes are given for the U. S. and the world where available. Information for this section was collected from several sources, listed in the references. A summary of pertinent market information gathered for these compounds is presented in Table 4.3.

DIRECT SUBSTITUTION

4.4.1 Butadiene

Elastomers

The largest use of butadiene is for producing elastomers used primarily by the automotive industry, and account for 60% of the domestic butadiene consumption. The polymers used in these applications include styrene/butadiene elastomers, polybutadiene, neoprene, and nitrile rubber. Other polymer applications of butadiene include acrylonitrile/butadiene/styrene (ABS) resins, adiponitrile, used as a precursor to hexamethylenediamine for nylon 6,6 production, styrene/butadiene latexes, polybutadiene, and styrene-based block copolymers, each accounting for 5%-15% of the butadiene consumption.

The greatest proportion of styrene/butadiene elastomer consumption (70%) and the largest single market for butadiene is in the tire and tire products industry. This industry also accounts for 78% of polybutadiene consumption. About 20% of polybutadiene is used in combination with polystyrenes for the consumer products industry. Another 2% of polybutadiene consumption is in manufacturing industrial products, such as conveyor belts, hoses, seals, and gaskets.

Neoprene production consumes 5% of butadiene production. Neoprene finds its greatest use in nontire applications where a polymer with good resistance to weathering and oxidation is necessary. Specific uses include in manufacturing hoses, belts, and adhesives.

Table 4.3 - Market Information for Selected Chemicals
(all units in thousand metric tons, unless otherwise indicated)

Direct Substitution

Chemical	Price (\$/lb)	U. S. Capacity	U. S. Production	U. S. Consumption	World Capacity	World Production	World Consumption
Butadiene	0.19	1,737 (1989)	1,400 (1989)	1,713 (1989) 1,894 (1994 estimate)	8,080 (1989)	6,400 (1989)	3,967 (1989)
Pentanes, Pentenes		116(n-pentane; 1988) 131(mixed pentenes 1988)					
BTX (mixture)	0.103	16,958 (1989)	19,743 x 10 ⁶ gallons (1988) 20,692 x 10 ⁶ gallons (1993 forecast)		32,923 (1989); world = N. America, W. Europe, Japan		
<i>a. Benzene</i>	0.15	8,067 (1988)	5,681 (1987)	6,102 (1987)	25.1 x 10 ⁶ tons (1989) 26.4 x 10 ⁶ tons (1993 forecast)		19.9 x 10 ⁶ tons (1987; forecast of 3%-3.5% growth through 1993)
<i>b. Toluene</i>	0.11	5,116 (1992) 5,116 (1997 forecast)	3,082 (1991)	3,600 (1991)	15,796 (1992) 17,092 (1997 forecast)	7,399 (1991; world = N. America, W. Europe, Japan)	7,257(1991; world = N. America, W. Europe, Japan)
<i>c. Xylenes (mixed)</i>	0.11	5,650 (1988)	2,694 (1988)		16,598 (1988)		
Acetic Acid	0.33	1,647 (1990) 1,737 (1995 forecast)	1,618 (1990) 1,687 (1995 forecast)	1,547 (1990) 1,610 (1995 forecast)	5,593 (1990) 6,123 (1995 forecast)	4,668 (1990) 5,487 (1995 forecast)	4,617 (1990) 5,364(1995 forecast)
Formic Acid	0.407	16 - 18 (1992)	11 - 12 (1991)	24-25 (1991)	260 (1987)		
Propionic Acid	0.41 - 44	102 (1989)	55 (1988)	45 (1988)			
Phenol	0.285	1,578 (1988) 1,711 (1993)	1,520 (1987)	1,480 (1990)	4,339 (1988) 5,052(1987)	4,214 (1987)	4,637 (1990)

<i>a. Phenolic Resins</i>		748 (1989)	721 (1989) 783 (1994 forecast)		1,467 (1989)	1,402 (1989) 1,530 (1994 forecast)	
Resorcinol	6.74	20.4 (1990)	14.5 (1990)	10.3(1990)	41 (1990; world = U. S., W. Europe, Japan)	30 (1990; world = U. S., W. Europe, Japan)	24.1 (1990; world = U. S., W. Europe, Japan)
Acrylic Acid and Esters	0.69	731 (1991)	1,110 (1988)	957 (1988)	3,212 (1988)	2,127 (1988; world = U. S., W. Europe, Japan)	1,967(1988; world = U. S., W. Europe, Japan)

Improved Production

Chemical	Price (\$/lb)	U. S. Capacity	U. S. Production	U. S. Consumption	World Capacity	World Production	World Consumption
Glucose	0.26 (hy) 0.51 (anhy)	2,320 (1986)	1,850 (1986)	510 in food applications (1986)	3,510 (1986)		
Gluconic Acid (and Sodium Gluconate)	0.45	16-19 (1989 estimate)	6.8 (1989 estimate)	9.1 (1989 estimate)	60 (1985)		36-42 (1985 estimate)
Sorbitol	0.77	287 (1990)	178-183 (1990)	180-185(1990)	927 (1990; world = U. S., W. Europe, Japan, Mexico)	511(1990; world = U. S., W. Europe, Japan)	495 (1990; world = U. S., W. Europe, Japan)
Mannitol	3.32			10 (1980)			
Furfural	0.79	72 (1989)	35 (1989)	39 (1989) 43 (1994 forecast)	240 (1989)	48 (1988; world = U. S., W. Europe)	93 (1988; world = U. S., W. Europe, Japan)
Furfuryl Alcohol	0.80	25 (1989)	20 (1989)	15 for furan resins (1989)			
<i>a. Furan Resins</i>			19.5				

Tetrahydrofuran	1.28	92 (1990) 133 (1995 forecast)	82 (1990) 95-99 (1995 forecast)	63(1990) 75-79 (1995 forecast)	141 (1990 world = U. S., W. Europe, Japan) 210(1995forecast; world = U. S., W. Europe, Japan)	123 (1990 world = U. S., W. Europe, Japan) 173-184 (1995 forecast; world = U. S., W. Europe, Japan)	122 (1990 world = U. S., W. Europe, Japan) 163-174 (1995 forecast; world = U. S., W. Europe, Japan)
-----------------	------	----------------------------------	---------------------------------------	--------------------------------------	---	---	---

New Building Blocks/Processes

Chemical	Price (\$/lb)	U. S. Capacity	U. S. Production	U. S. Consumption	World Capacity	World Production	World Consumption
Cellulose derivatives							
<i>a. Rayon fibers</i>		240 (1988)	204 (1987)	204 (1988)		2,593 (1987)	
<i>b. Cellulose acetate fibers</i>		307 (1990)	300 (1990)	169 (1990) 177 (1994 estimate)	751 (1989)	682 (1989)	
<i>c. Cellulose acetate flake</i>		476 (1992)		345 (1990) 376 (1995 estimate)	890 (1992)		757(1990)
<i>d. Cellophane</i>		39 (1988)	38 (1987)	40 (1987)			

Notes for Table

Compounds listed in *italics* are subsets of the chemicals immediately preceding them and have not been subjected to the economic analysis methodology but are included because they represent products of industrial utility that could be produced from biomass.

Certain materials are not commercial products and therefore, production information is not available. These materials include: levoglucosan/levoglucosenone, hydroxyacetaldehyde, vinyl phenol, 5-hydroxymethylfurfural, and levulinic acid.

Nonelastomer Uses

About 15% of the domestic butadiene consumption is used in producing adiponitrile. Almost all of this material is used to make hexamethylenediamine, a component in the production of nylon 6,6. In 1989, the United States produced 488×10^3 tons of adiponitrile and 540×10^3 tons of hexamethylenediamine.

Another 11% of butadiene production is used in manufacturing styrene/butadiene latexes for use in the paper coating and carpet backing markets.

Production of ABS resins consumes smaller amounts of butadiene, primarily for the electronic equipment industry. Other major applications include appliance components, pipes and plumbing fixtures, luggage, cases and toys.

Other Uses

Butadiene is a starting material for producing 1,4-butanediol, vinyl cyclohexene (a starting material for styrene production), olefin oligomers such as 1,5,9 cyclododecatriene for nylon production via nickel catalyzed oligomerization, and 1-octene, used as a copolymer in producing high quality LDPE. Butadiene also serves as a starting material for producing pelargonic acid, a precursor for heat resistant lubricants. Pelargonic acid can also be prepared from biomass.

4.4.2 Pentanes, Pentenes

Pentanes and pentenes are obtained from distillation and dehydrogenation processes from petroleum or natural gas liquids. n-Pentane and i-pentane are obtained as a separable mixture and are used in solvent applications, as blending components in high octane gasolines, and in producing isoprene.

Pentenes are used in many of the markets for alpha-olefins in general, including the plasticizer and detergent markets, and as precursors for brominated alkanes that are converted into thiols, amines, N-oxides, and ammonium salts. Pentenes have also been used as monomers in producing petroleum resins, and low molecular weight thermoplastic materials. Copolymers of pentenes with styrene, divinylbenzene, or vinyl toluene have also been produced.

4.4.3 Benzene

Ethylbenzene

The largest single use for benzene in the United States is for producing ethylbenzene, the intermediate for producing styrene. In 1988, ethylbenzene accounted for 54% of the total benzene demand. In 1990, the United States produced $4,076 \times 10^3$ tons of ethylbenzene, a production level that is expected to rise to $5,280 \times 10^3$ tons in 1993. Styrene is widely used in polymer applications for producing polystyrene, acrylonitrile/butadiene/styrene (ABS) and styrene/acrylonitrile resins, and styrene/butadiene latexes.

Cumene

Another 23% of domestic benzene production (1988) is consumed in reaction with propylene to give cumene, the starting material for phenol. The United States produced $1,698 \times 10^3$ tons of cumene in 1986, 98% of which was used in the phenol/acetone process. Phenol is consumed primarily in producing phenolic resins, bisphenol A (a key monomer in the production of polycarbonate resins and other high value engineered products), and caprolactam, the precursor to nylon 6. Further information about phenol markets will be given below.

Cyclohexane

Catalytic hydrogenation of benzene to make cyclohexane accounted for 14% of the domestic benzene demand in 1988, primarily for producing adipic acid or caprolactam (nylon precursors). In 1988, the United States produced $1,273 \times 10^3$ tons of cyclohexane.

Nitrobenzene/Aniline

An additional 5% of the domestic benzene demand is for producing nitrobenzene and aniline. The primary use of aniline is in producing diphenylmethane-4,4'-diisocyanate (MDI), a monomer for producing polyurethane foams. Polyurethane foams are useful as insulators and as a component in the reaction injection molding system used for manufacturing flexible bumpers for the automobile industry. Aniline is also used in preparing accelerators and antioxidants for the rubber processing industry, and as a key starting material for a number of large volume herbicides, notably Monsanto's Lasso[®]. Nitrobenzene is used in producing para-aminophenol, a key component of acetaminophen (i. e., Tylenol[®]). About $9-11 \times 10^3$ tons of nitrobenzene are used for this purpose.

Other Uses

About 110×10^3 tons of benzene, 2% of the total domestic demand, is used for producing linear and branched alkylbenzene sulfonates for use in laundry detergents, and as surfactants. Benzene is also used in producing chlorobenzenes (as solvents, insecticide precursors, polymer manufacture), biphenyl (dye industry), hydroquinone (photographic developer, antioxidant, polymerization inhibitor), and resorcinol (adhesives, pharmaceutical precursor).

4.4.4 Toluene

The large majority of toluene (>90%) is consumed as a component of gasoline. The remainder of the toluene produced is used in chemical products and solvents.

Benzene

The largest nonfuel use of toluene is in producing benzene by hydrodealkylation procedures. This process consumes 60-70% of the toluene produced for nonfuel purposes.

Other Uses

Toluene is an important component of many solvent systems, especially to produce coatings, paints, and lacquers for wood furniture, containers, and automotive finishes. However, new methods of coating are causing a shift away from toluene-based solvent systems, driven by industry's desire to minimize emissions of volatile organic materials.

About 8% of the total toluene demand is for producing toluene diisocyanate (TDI), a monomer for flexible and rigid polyurethane foams.

Toluene is also used for producing benzoic acid, an intermediate in certain processes for phenol production. Obviously, this process contributes only a small amount of phenol to the nation's supply, because more than 96% of domestic phenol is produced from cumene. Benzoic acid also serves as a plasticizer, a starting material for other chemical intermediates, and a food additive. Toluene is also a starting material in preparing benzyl chloride (plasticizer and quaternary ammonium salt precursor), vinyl toluene (occasional replacement for styrene in certain applications), p-cresol (used primarily in preparing BHT, an antioxidant), toluene sulfonic acid (a dye intermediate), benzaldehyde (flavor and fragrance), and other chemicals.

4.4.5 Xylenes

Xylene Isomers

Mixed xylenes find their principal use as a source of the individual ortho-, meta-, and para- isomers. o-Xylene is a starting material for preparing phthalic anhydride, a widely used plasticizer component. m-Xylene is used for producing isophthalic acid, a component of polyester resins. The para-isomer is used for manufacturing dimethyl terephthalate and terephthalic acid, important intermediates for producing polyterephthalates.

Mixed xylenes are also used as solvents, primarily in the paints and coatings industry. Other solvent uses include agricultural sprays, and in adhesives and rubber in the automotive industry.

4.4.6 Acetic Acid

Vinyl Acetate

Vinyl acetate monomer is the largest and fastest growing outlet for acetic acid in the United States, and accounted for 55% of the total acetic acid consumption in 1990. The United States produced $1,161 \times 10^3$ tons of vinyl acetate monomer in 1988, most of which was used in polyvinyl acetate emulsions and resins, and for producing polyvinyl alcohol. Polyvinyl acetates are used mostly in packaging and labelling as white glue and in construction applications for laminating wallboard and as a smoothing compound for taped joints. Polyvinyl acetates are also used in latex paints and for finishing wood composition board. Polyvinyl alcohol is used mostly in textile warp sizing, adhesives and paper sizing. Other vinyl acetate derivatives include polyvinyl butyral (laminated automobile safety glass, architectural uses), ethylene/vinyl acetate copolymers (film production, wire and cable, hot melt adhesives), and ethylene vinyl alcohol (packaging film, microwave food containers).

Acetic Anhydride

An additional 16% of the domestic consumption of acetic acid was used in producing acetic anhydride (1990). The United States produced 928×10^3 tons of acetic anhydride in 1989, and more than 80% of it was used in producing cellulose acetate, the precursor for cigarette filter tow. Other major markets for cellulose acetate include textile fibers, plastics, and photographic films. Domestic cellulose acetate production was 421×10^3 tons in 1990. Acetic anhydride is also used in smaller markets, for producing aspirin and acetaminophen (Tylenol®), semiconductor processing and manufacturing herbicides and food additives.

Acetic Acid Esters

About 11% of the domestic acetic acid demand is used in producing various esters, including butyl acetate, propyl acetate, ethyl acetate, glycol ether acetates, and amyl acetates. These materials are used mostly as solvents for inks, paints, and coatings.

Terephthalic Acid/Dimethyl Terephthalate

Producing these materials accounts for 11% of the domestic acetic acid consumption. They are used mostly in producing polyester fibers, film, resins, coatings and plastics.

Other Uses

Acetic acid is also used for preparing chloroacetic acid, an important chemical intermediate in producing carboxymethylcellulose, herbicides, surfactants, and various esters. Acetic acid is also used in the textile industry in wool dyeing, silk cleaning, printing and finishing.

4.4.7 Formic Acid

A variety of markets exist for formic acid. About 13-15% of the consumption is in the rubber chemicals industry where formic acid is used in producing antiozonants and other rubber chemicals, and for coagulating rubber latex. Manufacturing catalysts based on aluminum and nickel consumes another 10-15% of the formic acid production. The leather and tanning industry consumes an additional 10-15% in operations related to hide preparation, although this market has decreased significantly in recent years. Formic acid is also used in textile dyeing and finishing operations to set and retain colors in fibers, and as an epoxidation agent in producing plasticizers.

4.4.8 Propionic Acid

As with formic acid, a wide range of markets also exists for propionic acid. About 30% of the domestic consumption (1988) of propionic acid was for preserving grain and animal feed. Converting propionic acid to the corresponding sodium and calcium salts accounts for an additional 25% of the domestic consumption. These materials are useful as food and animal feed preservatives. Producing carboxylic acid herbicides consumed about 15% of the domestic propionic acid. Propionic acid is also used in cellulose plastics, pharmaceuticals, and as a solvent.

4.4.9 Phenol

Phenol Resins

Producing phenolic resins takes the greatest share of the phenol market (36% in 1992). The industry contains many producers because the technology is simple, the capital investment relatively low, and the range of end products large. About 85-90% of the phenolic resin production is directed toward bonding and adhesive applications in plywood, insulation, wood, and laminates. The remainder are used in molding compounds for producing heat-resistant components for appliances, and the electrical and automotive industries, in protective coatings, and other miscellaneous applications.

Bisphenol A

An additional 36% of the domestic phenol production is directed to preparing bisphenol A, a key monomer in producing polycarbonate resins, materials of importance in automotive, appliance, and electronic applications. Other applications for polycarbonate resins are found in producing water and milk bottles. A additional major use for bisphenol A is in producing epoxy resins, a component of surface coatings and fiber reinforced laminates for printed circuit boards. Epoxy resins are also expected to show growth in the aerospace and automotive industries, especially for producing advanced composites.

Caprolactam

Producing caprolactam, an intermediate for producing nylon 6, accounts for about 17% of the phenol consumed domestically. Most of the nylon 6 produced is consumed by the carpet industry. The remaining caprolactam production is dominated by resin and film production, used in engineering thermoplastics for the automotive, machinery, film, and wire industries.

Aniline

About 6% of the domestic phenol consumption is directed to producing aniline. Uses and markets for aniline are described in the section on benzene.

Other Uses

Phenol is also a starting material for producing 2,6-xylenol, a precursor to polyphenylene oxides that form high impact and heat resistant polymers when alloyed with polystyrene. 2,6-Xylenol is also converted to polyphenylene ethers to give polymers with similar properties, again by alloying with polystyrene. These copolymers find uses in the automotive market, as well as metal replacements in the cabinetry and electrical industries. The byproduct of this polymer manufacture is o-cresol, that is used in resin production, and as a polymerization inhibitor and antioxidant.

Phenol can be alkylated to give long chain alkylphenols, specifically nonyl- and dodecylphenol, materials that are used in manufacturing nonionic surfactants and detergent grade lubricating oil additives. Other alkylphenols are used in producing phenolic resins and other polymer additives.

Adipic acid, a key component in the production of nylon 6,6, can be produced from phenol. Adipic acid results as a byproduct from the production of caprolactam from phenol.

Phenol is the primary raw material used for production of salicylic acid, the precursor to aspirin. Salicylic acid is also a precursor for wintergreen oil, a flavor and fragrance ingredient, as well as a pharmaceutical intermediate.

4.4.10 Resorcinol

Rubber Products Applications

Most domestic resorcinol production (70%) is consumed in the rubber products industry as a resorcinol/formaldehyde resin in a dip treatment for tire carcasses and tread rubber. Resorcinol/formaldehyde adhesives are also used in other fiber reinforced rubber goods, such as belting, rubberized hose, and rubberized textile sheets.

Wood Adhesive Resins

Resorcinol is used in specialty thermoset resins, either as a straight mix with formaldehyde, or in a phenol modified resorcinol/formaldehyde mixture. The resins cure at much lower temperatures than typical phenol/formaldehyde resins to give a strong waterproof and fungus resistant adhesive. These features give resorcinol/formaldehyde compositions an advantage in structural applications. For example, about 98% of all structural laminated beams are made using a straight resorcinol-based adhesive. Phenol modified resorcinol/formaldehyde resins show intermediate properties. The advantages of a resorcinol-based adhesive must be weighed against the higher cost of resorcinol in any application.

Other Uses

Resorcinol also serves as an intermediate in producing ultraviolet absorbers in various polyolefin and cellulose acetate plastic materials. Resorcinol derivatives are also used in consumer sunscreen formulations, a market certain to grow in the future. Resorcinol is a precursor for a number of dye products and pharmaceuticals, including a series of antiasthmatic agents.

4.4.11 Furfural

Furfuryl Alcohol/Furan Resins

Preparing furfuryl alcohol represents the largest domestic use of furfural. Furfuryl alcohol is used almost completely for producing the so-called "furan resins," a somewhat misleading term since the monomer used in their preparation is furfuryl alcohol and not furan. Furan resins are important as

foundry binders for producing cores and molds used in casting metals. The chemical, thermal, and mechanical properties of these resins contribute to their use for this purpose. Smaller markets also exist for furan resins, including producing corrosion resistant and chemically inert grouts, mortars and molded articles, such as pipe fittings, joints, and valves.

Tetrahydrofuran

A small amount of furfural is used for producing tetrahydrofuran, a material used as a solvent for resins and plastics and as a reaction solvent in producing pharmaceuticals. The United States produced 73×10^3 tons of tetrahydrofuran (1989), with the largest fraction (71%) used for producing polytetramethylene ether glycol, a component of cast and thermoplastic urethane elastomers (for solid tires and industrial rolls), spandex fibers, and copolyester/ether elastomers (automotive components and hoses).

4.4.12 Glucose

Food Additives

Glucose finds its largest use in the food industry in baking, beverages, canning, confectionery and dairy applications. In 1986, these food industries consumed 510×10^3 tons of crystalline glucose, $6,410 \times 10^3$ tons of glucose-fructose syrups, and $2,313 \times 10^3$ tons of other glucose containing syrups. One of the largest areas of growth for glucose consumption is in producing glucose-fructose syrups such as sweeteners. Glucose can be enzymatically isomerized to fructose and the combination of the two carbohydrates gives a syrup that is as sweet as natural sucrose. Glucose is also used as a starting material for producing food grade citric, lactic, and acetic acids, enzymes, amino acids, vitamin C, and certain antibiotics.

Other Uses

The largest nonfood use of glucose is in producing food grade ethanol. The United States reportedly had an ethanol production capacity of 3.9×10^9 liters in 1988. Glucose is also the starting material for the dehydrative production of 5-hydroxymethylfurfural, and the coproducts levulinic and formic acid. 5-Hydroxymethylfurfural is useful as a component of both phenolic and urea/formaldehyde-based plastics. Glucose can be converted in the presence of hydrogen chloride and methanol into an insulating foam, and with hydrogen into sorbitol. Glucose is also used for producing adhesives, wallboard and leather tanning.

4.4.13 Gluconic Acid

Chelating Agents

Most gluconic acid used domestically is handled as the sodium salt, sodium gluconate. An important use of gluconic acid and its sodium salt, (sodium gluconate) is in alkaline systems for chelation and removal of metal ions, particularly calcium, magnesium, iron, and aluminum. About 70% of the total sodium gluconate/gluconic acid consumption in the United States is for metal cleaning and finishing applications. Other uses include bottle washing, equipment cleaning, in the dairy, beer, and food service industries, metal etching, degreasing, and electroplating, rust inhibition, and catalyst cleaning.

Other Uses

Gluconic acid/sodium gluconate is also used in producing sodium aluminate, in textile processing, and in the food industry as a suppressor of the saccharin taste in low calorie foods. Additional markets in the health food and pharmaceutical industries exist for salts other than sodium gluconate.

4.4.14 Sorbitol

Personal Care Products

The largest outlet for sorbitol in the United States is in producing toothpaste, cosmetics, and toiletries, accounting for 32% of the total domestic sorbitol consumption. A large proportion of this use is in the toothpaste industry where sorbitol can be used as a humidity control agent, a plasticizer, and a viscous delivery vehicle. This market is influenced by competition with glycerol, which can be used for many of the same purposes. However, in recent years sorbitol has been used more widely at the expense of glycerol. Sorbitol is also used in producing mouthwashes, imparting a pleasant, cooling, sweet taste to these products. The cosmetic industry also uses sorbitol as a humidity control agent and as a gel base. Because it is hygroscopic, it also serves as an emollient in creams and lotions.

Food Applications

An additional 30% of the total market for sorbitol is in food and confections. Sorbitol has been granted a "generally recognized as safe" designation by the Food and Drug Administration, a confirmation of its well known nontoxic nature. Sorbitol is classified as a seminatural, nutritive sweetener with 60% of the sweetness of sucrose. Since sorbitol is resistant to tooth decay bacteria, it is widely used in many sugarless products, such as sugarless mints and gums, soft candies, chewing gums, and fruit flavored lozenges.

Sorbitol is also used in food as a bulking agent, peeling aid, and flavoring agent. A recent application of sorbitol is as a cryoprotectant (to maintain the structural integrity of frozen food), for example, to produce seafood analogs (e. g., imitation crab).

Vitamin C

About 17% of sorbitol production is directed toward manufacturing vitamin C. Most vitamin C produced is used in nutritional supplements and multivitamin preparations, with lesser amounts being used in food, beverages, and animal feed.

Surfactants

Producing surfactants accounts for about 10% of the domestic consumption of sorbitol. The surfactants are prepared by esterification of sorbitol to provide a wide range of different materials. The major use of these materials is as lubricant additives, softeners in textile manufacture, plasticizers, antifog agents, antistatic agents, and components in dry cleaning detergents. Sorbitol-based surfactants are also used in foodstuff, cosmetic, and pharmaceutical manufacture.

Other Uses

Sorbitol finds additional uses in the pharmaceutical industry as a stabilizer, or sweetening agent for a number of preparations including cough syrups, and multivitamins. Isosorbide, an antianginal drug, is prepared directly from sorbitol. Various polyethers can be made from sorbitol, and are used as polyol components of polyurethane resins and foams.

4.4.15 Mannitol

Mannitol is a coproduct of producing sorbitol from the catalytic hydrogenation of sucrose. About 10×10^3 tons of mannitol were produced in 1980. It has a smaller volume than either glucose or sorbitol, but is used in many of the same areas. Mannitol is the second most important reduction product of sugar and is used to produce dry electrolytic capacitors, synthetic resins, pharmaceuticals, lubricants and

stabilizers. It is also used as a nutritive sweetener and is the starting material for synthesis of the vasodilator mannitol hexanitrate.

4.4.16 Xylitol

Xylitol is produced by the catalytic reduction of xylose. It has a smaller market than mannitol, but is used as a sweetener, and as a humidity control agent.

4.4.17 Acrylic Acid

Acrylate Esters

The largest use (72%) for acrylic acid is in producing acrylic esters, precursors in a wide range of polymeric applications, including latexes, textiles, adhesives, paper, leather, polishes, sealants, and printing inks. A number of new markets are developing for specialty esters, especially as cross linking agents for producing hard, cured surfaces. Specific examples of these materials include hydroxyalkyl acrylates, used for automotive coatings. Multifunctional acrylates are used as part of radiation curable coatings on film and rigid plastics.

Polyacrylic Acid and Salts

Applications of nonester polymers of acrylic acid, available in a wide range of molecular weights, have shown considerable growth recently. Traditionally, these materials are used as flocculants, dispersants, sequesterants and thickeners. More recently, new types of polyacrylic acids have been developed as superabsorbants, that can absorb up to 100 times their weight in water, making them superior fill for disposable diapers. Another potential growth area for polyacrylic acids is in detergent applications where the polymers can be used as builders to replace phosphates.

4.4.18 Cellulose Derivatives

A number of derivatives of cellulose, available from pulping wood, have large domestic markets. This section describes a few of the materials produced from cellulose.

4.4.18.1 Rayon Fibers

Rayon fibers are a diverse group of materials, but all are derived from regenerated cellulose. Several different types of rayon fibers are recognized, depending on their properties. Regular rayon fibers have a relatively low degree of polymerization, and a cellulose purity of 90-95%. Fabrics made with this material are smooth, but show poor dimensional stability when wet and dry very slowly. High wet modulus fibers are made up of higher (95%) purity α -cellulose, and thus have a greater degree of polymerization. This property results in a fabric with more desirable laundering properties and a much shorter drying time. Further increase in the degree of polymerization affords the modified high tenacity rayons, characterized by even greater structural stability as well as high tensile strength. Polynosic rayons are made in Europe and Japan, and exhibit a degree of polymerization similar to the high wet modulus rayons.

Apparel

About 51×10^3 tons of rayon fibers were consumed in the domestic production of apparel in 1987. Almost all rayon used in apparel is in the top-weight category, i. e., fabrics used for production of pants, sportswear, and other items requiring a heavier fabric. The fabrics are cotton-like, but exhibit greater uniformity and smoothness. About 96% of the rayon used in apparel was consumed for woven materials, and the remainder was consumed by knits.

Home Furnishings

Domestic consumption of rayons to produce coverings for home furnishings was comparable to that of apparel. Curtains, draperies, and upholstery account for almost 90% of the rayon use in this category. Although there was once an oversupply of rayon, in recent years it has become a specialty for use in higher priced fabrics.

Nonwovens

Producing nonwovens accounted for 32% of the domestic rayon consumption in 1987. The market for these materials has remained steady since 1983. Rayon nonwovens are used in producing disposable medical and surgical products, towels, fabric softeners, and interlinings.

Rubberized Goods

A small portion of continuous filament yarn fibers is consumed in the production of tire components and hoses for the automotive industry. This market has lost ground to competing polyester fibers.

4.4.18.2 Cellulose Acetate Fibers

Cigarette Filter Tow

The largest single domestic use for cellulose acetate fibers is for cigarette filter tow, representing 63% of the domestic consumption in 1989. However, the call for cellulose acetate fibers has fallen considerably in recent years with the greater recognition of the health hazards associated with smoking, higher cigarette prices and taxes, and more legislative restrictions on smoking in public places. Currently, other markets for this material are opening in Japan and China, as the demand for filtered cigarettes in these countries increases.

Apparel

Apparel is the largest textile market for cellulose acetate fibers. The fibers exhibit a softness, dyeability and breathability that makes them suited for manufacturing lining fabrics such as satins, taffetas, and twills. Interestingly, as consumers mature, they are expected to demand more of this material for lined business apparel.

Other

Cellulose acetate fibers are also used for producing curtain and drapery material. However, use of acetate fibers in home furnishings has generally been declining since 1983. Cellulose acetate fibers also are used in a number of small volume applications such as wire and cable wrappings, and paper and tape reinforcement.

4.4.18.3 Cellulose Acetate Flake and Related Cellulose Esters

Cigarette Filter Tow and Textile Fibers

Cellulose acetate flake serves as the starting point for these materials, as described in section 4.3.18.2.

Cellulose Ester Plastics

Cellulose esters are the nation's oldest thermoplastics and their market share has been declining gradually. A considerable portion of the cellulose ester production (34%) is directed to manufacturing molded and extruded articles, such as tool handles, toys, automotive parts, and other consumer goods.

However, similar petrochemical derived materials have taken away from these markets. Cellulose acetate extruded materials have an advantage in certain niche markets (for example, to produce steering wheels for luxury automobiles) because of their superior toughness and "feel" upon the hand.

Photographic Film

About 38% of the cellulose acetate used in plastics production was used in manufacturing photographic film. The amateur and professional photographic and motion picture industries are still dominated by cellulose acetate film. However, films derived from polyethylene terephthalate are beginning to compete in some fields despite a higher cost because of greater dimensional stability and a lower sensitivity to temperature and humidity variations.

Film and Sheet

The remainder of the cellulose plastic consumption is used for producing films and sheets. Because it can be cast very thin, cellulose acetate sheeting can be used for print lamination, giving a product with high optical clarity. This gives the glossy finishes for postcards, book covers, etc. In addition, the light gauges available make cellulose acetate films ideal for producing pressure sensitive tape, such as 3M's Scotch Brand Magic Transparent Tape. Cellulose acetate is also used for producing ophthalmic sheet used for eyeglass frames.

4.4.18.4 Cellulosic Surface Coatings

An important group of products derived from different cellulose esters (and ethers, described in section 4.3.18.5) is cellulosic surface coatings. The bulk (over 75%) of the ester derived coatings comes from nitrocellulose and the rest is produced from cellulose acetate butyrate (CAB) and other esters. These materials are used in a number of areas.

Wood Furniture

Finishes for household furniture, kitchen cabinets, and other domestic wood materials account for the greatest consumption of cellulosic coatings. Most of the demand was for nitrocellulose-based material. These finishes have had little competition in the furniture market because they exhibit a superior ability to protect wood, have a good gloss, and are easily repaired. An important challenge to this market results from environmental concerns. The finishes are normally applied as solutions in organic solvents, and the finished product results from solvent evaporation. New laws restricting solvent emissions will affect the use of these materials and has spurred the search for low solvent replacements. To date, the quality of the replacements has been inferior to current formulations.

Other

Cellulose-based lacquers are used in a number of other markets. The automotive industry uses nitrocellulose-based lacquers as primer surface coatings. However, this market is also under environmental pressure to reduce solvent emissions. Nitrocellulose lacquers are used in the paper and film industry as coatings to reduce moisture permeability, although this market is decreasing because of competition from wraps based on polyvinylidene chloride (i. e., Saran Wrap). These lacquers can also be used for coating of paper, book covers, wallpaper, etc. Other smaller coating markets exist in the machinery, container and fabricated plastics industries.

4.4.18.5 Cellulose Ethers

Sodium Carboxymethylcellulose

The most widely used cellulose ether is sodium carboxymethylcellulose (CMC), accounting for 39% of the domestic consumption of cellulose ethers in 1990. The greatest proportion of this material (17%) is used in the food industry as a stabilizer, thickener, and moisture retention aid. It is used as an additive in diet foods because it is not metabolized.

An additional 12% of the CMC produced is used by the oil drilling industry where it is used as a viscosity enhancing agent in drilling muds used to cool and lubricate drill bits. CMC is used as a partial replacement for bentonite clays in the mud formulations.

A number of other markets exist for CMC use. CMC is used in the pharmaceutical and cosmetic industries as a thickener and binder. It serves as a soil antiredeposition agent in detergents, and as a water retention aid in paper coatings. When it is coated on yarn filaments, CMC holds fibers together during weaving. A possibly emerging market for CMC is as a binder in taconite pellets produced by the iron ore industry.

Hydroxyethylcellulose

An additional 31% of the cellulose ether consumption is for producing hydroxyethylcellulose (HEC), and the related carboxymethylhydroxyethylcellulose. Most of the HEC production is used in manufacturing surface coatings, for example, in water-based latex paints.

HEC forms protective colloids in the polymerization of vinyl acetate and acrylics. The result is an improvement in polymer particle size, reaction yield and stability.

Other applications of HEC are found again in oil drilling operations, building products, pharmaceuticals, and in manufacturing personal care products.

Other

Other cellulose ethers are used in similar markets. Materials manufactured include methylcellulose, hydroxypropyl cellulose, ethylcellulose, and ethyl hydroxyethyl cellulose.

4.4.18.6 Cellophane

Cellophane's introduction in 1924 caused a revolution in the packaging industry, and it quickly became a key material in the domestic consumer market. However, the market has declined from a high of 200×10^3 tons in 1960 to 40×10^3 tons in 1987, as a result of increasing competition from petrochemical derived packaging materials. The market could be affected by environmental concerns in the future, as cellophane is the only packaging material that is biodegradable.

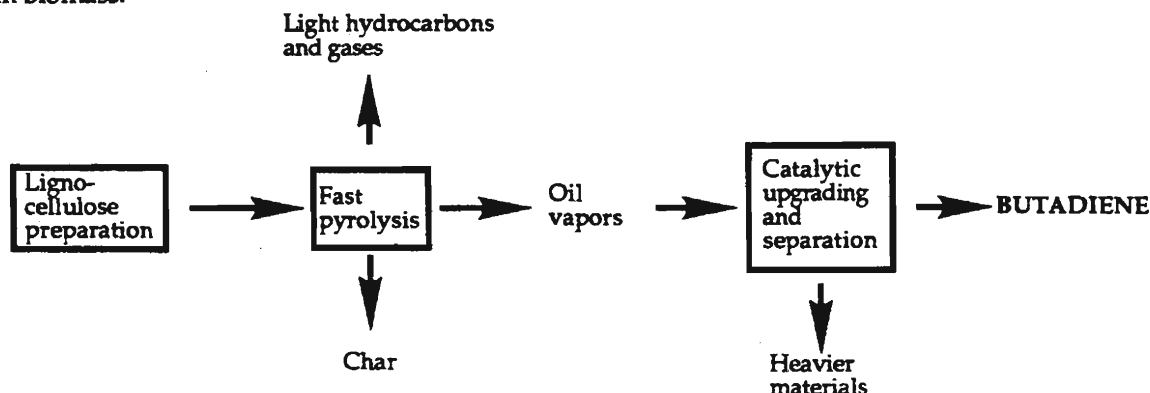
5.0 INDIVIDUAL RAW MATERIALS COST COMPARATIVE EVALUATIONS

A summary of the results of this evaluation is found in Table 5.1.

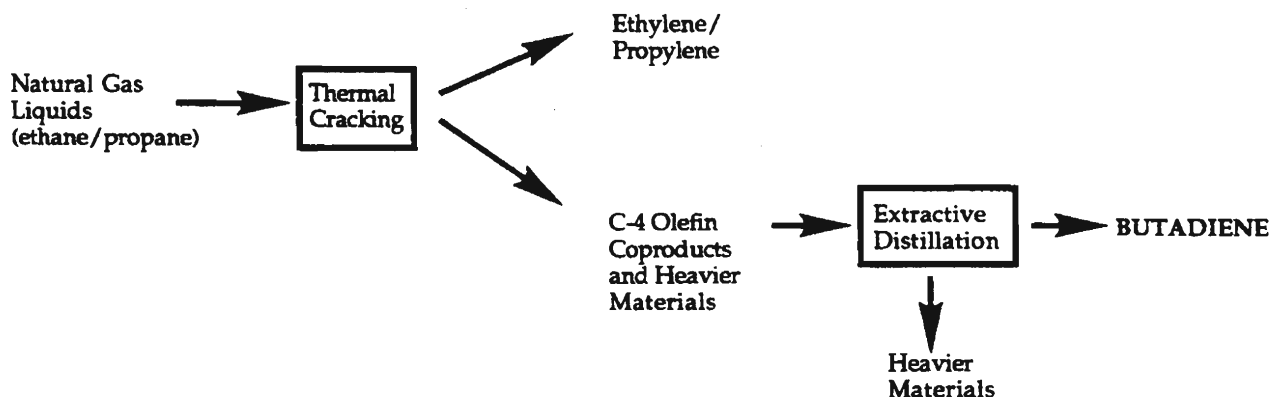
5.1 Direct Substitution

5.1.1 Butadiene

From biomass:



From petrochemicals:



Processes Compared: The biomass-based route to butadiene begins with the fast pyrolysis of wood. Butadiene is prepared by dehydrogenation of mixed three- and four-carbon streams resulting from the interaction of the pyrolysis vapors with a zeolite-type catalyst. Almost all domestic butadiene is produced commercially by the pyrolysis of ethane or propane, isolated from natural gas liquids. This thermal cracking produces about 22 million lb/year of butadiene as a coproduct among a variety of other materials from distillation (for example, pentanes and pentenes, as shown in section 5.1.2).

Raw Materials Cost Comparison: The current production cost of the ethane starting material from natural gas fractionation is about \$0.055/lb, assuming the natural gas feedstock costs \$1.66/thousand cubic feet. Current RD&D results indicate a potential 16% yield of butadiene from wood feedstock, giving a raw material cost contribution of \$0.091/lb, assuming the wood feedstock is available at \$40/dry ton. The ratio of the petrochemical and biomass raw material costs is then

$$0.055/0.091 = 0.60$$

and when a risk factor of 1.3 is included, the ratio becomes

$$0.60/1.3 = 0.47$$

Table 5.1- Summary of Raw Materials Cost Contribution Screening Results

Direct Substitution

<u>Chemical</u>	<u>Existing Commercial Process (\$/lb)</u>	<u>Proposed Biomass Based Process, (\$/lb)/Yield to Achieve (%)</u>	<u>Comparative Ratio, Existing/Biomass x 1.3</u>	<u>Necessary Conditions for Biomass to Compete</u>
1) Butadiene	0.055	0.091/16	0.47	higher efficiency or crude oil at \$35/barrel and wood at \$20/ton; new feedstocks, e. g., RDF
2) Pentanes/Pentenes	0.057	0.102/12.4	0.43	higher efficiency or crude oil at \$35/barrel and wood at \$20/ton; new feedstocks, e. g., RDF
3) BTX	0.103	0.082/24	0.97	already promising, but 30% yield would improve outlook
4) Acetic/Propionic/Formic acids	0.03 (as NaCl for road deicing)	0.043/10	0.69	new product applications; higher yield in acids production
5) Hydroxyacetaldehyde	0.086	0.053/10	1.25	80% recovery of HAA from pyrolysis oils
6) Phenolics by pyrolysis	0.135	0.094/21	1.17	already competitive; recommended.
7) Resorcinol	0.153	0.156/80	0.75	further study needed to define process conditions
8) Vinyl Phenol	4.82	0.5/10	7.40	already competitive; further study needed to define process conditions
9) Phenolics by Wood Phenolation	0.135	0.106	1.09	already competitive; RD&D to improve process will improve outlook
10) Phenolics by Lignin Hydrotreating	0.135	0.12/10	1.22	already competitive; RD&D to improve process will improve outlook
11) Acetic acid from Biomass Syn Gas	0.052	0.041	see text	nearly competitive; RD&D to improve process will improve outlook

Table 5.1 - continued

12) Peracetic Acid from kraft black liquor	0.16	0.15/90 in chemical steps	0.82	possibly competitive; RD&D needed to evaluate process
from starch	0.16	0.20/90 in chemical steps	0.61	
13) Anthraquinone	1.00 - 1.98	0.822 - 1.04	0.92 - 2.57	already competitive
14) Acrylic Acid	0.145	0.076/36	0.30 - 1.47	already competitive

Improved Production

<u>Chemical</u>	<u>Existing Commercial Process (\$/lb)</u>	<u>Cost by Improved Biomass Route (\$/lb)</u>	<u>Comparative Ratio, Existing/Biomass x 1.3</u>
1) Glucose			
from bagasse	0.08	0.032 (3 coproducts)	1.92
from corn starch	0.05	0.032 (3 coproducts)	1.20
from steam explosion	0.056	0.032 (3 coproducts)	1.35
			0.043 (1 coproduct)
2) 5-Hydroxymethylfurfural	0.102	0.088 (1 coproduct) 0.065 (3 coproducts)	1.21
3) Levulinic/Formic Acids	0.164 (levulinic) 0.064(formic)	0.105 (3 coproducts) 0.041 (3 coproducts)	1.20 1.20
4) Succinic Acid	0.11	0.16	0.53
5) Gluconic Acid	0.058	0.040	1.12
6) Sorbitol	0.059	0.056 (2 coproducts)	1.31
7) Mannitol	0.065	0.043 (3 coproducts)	1.16
8) Xylose			
from lignocellulose, 3 coproducts	0.09	0.027	2.56
from lignocellulose, 2 coproducts	0.09	0.034	2.04
9) Xylitol	0.103	0.037	2.14

Table 5.1 - continued

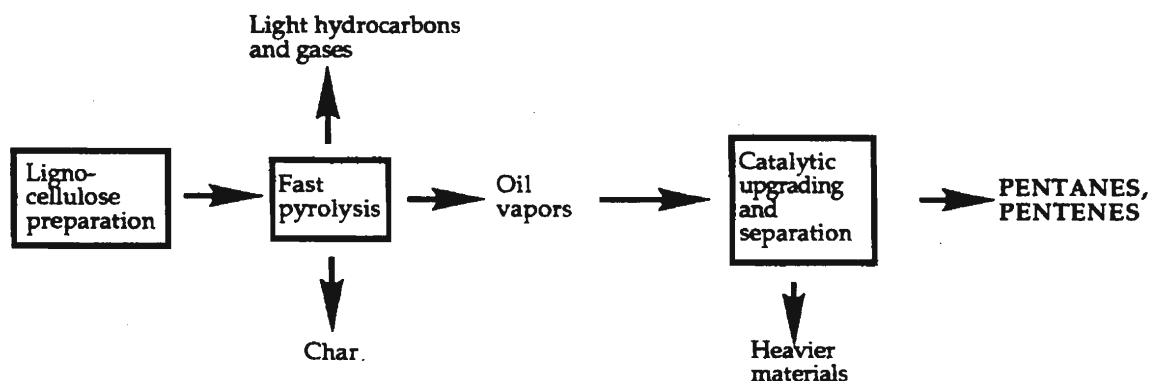
10) Furfural	0.10	0.062	1.24
11) Furfuryl alcohol	0.116	0.075 (3 coproducts)	1.35
12) Furan/Tetrahydrofuran	0.104	0.095 (3 coproducts)	
13) Tetrahydrofuran	0.108	0.117 (3 coproducts)	0.71
14) Polyhydroxybutyrate/ polyhydroxyvalerate	0.58	0.10	4.46

This low ratio indicates that the biomass-based route to butadiene probably cannot compete with the petrochemical route given current feedstock prices and yields of butadiene. However, manipulating feedstocks, or changes in raw material costs could present conditions conducive to using biomass derived butadiene in the future.

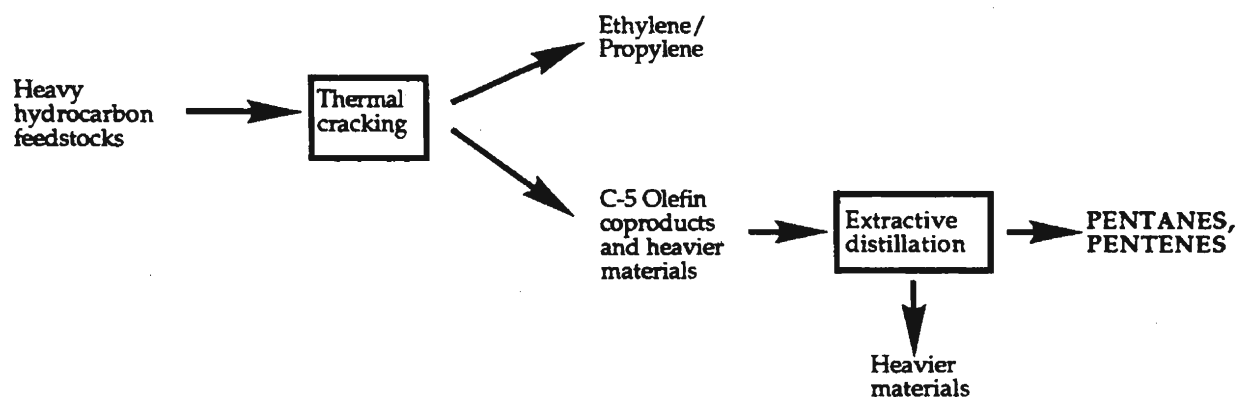
Future Projections: If the price of crude oil rises to \$35/barrel and the price of the wood feedstock drops to \$25/dry ton, a similar calculation shows that the ratio of raw material costs rises to 0.93, suggesting that a biomass-based route to butadiene might have a chance to compete. Alternatively, waste feedstocks rich in polyolefins (such as refuse derived fuel) are attractive for routes to butadiene, since the yield of hydrocarbon from these materials is substantially greater than from lignocellulose (Rejai, et al, 1991). The ratio that results from comparing the biomass and petrochemical routes then is significantly greater than unity, justifying further RD&D to optimize the process.

5.1.2 Pentanes/Pentenes

From biomass:



From petrochemicals:



Processes Compared: The processes compared are similar to those described for producing butadiene. Pentanes and pentenes can be produced from biomass by treating vapors derived from the fast pyrolysis of wood over a zeolite-type catalyst. Heavy hydrocarbons, such as naphtha and gas oil, are partially converted into five-carbon units as part of the wide range of materials produced by cracking to produce primarily ethylene and propylene. The most widely used five-carbon olefin in the United States is isoprene, with a total domestic production of about 300 million lb/year.

Raw Materials Cost Comparison: The current raw material cost for the heavy hydrocarbon feedstock for pentane/pentene production from petrochemicals is \$0.057/lb, assuming a crude oil price of \$20.00/barrel. A biomass-based route gives about a 12% yield of pentanes/pentenes from wood

pyrolysis. The raw material cost for the biomass-based route is \$0.102/lb of pentanes/pentenes, assuming wood feedstock costs \$40/dry ton, and a fuel value credit for the other coproducts produced during pyrolysis. The ratio of the petrochemical and biomass raw materials costs is then

$$0.057/0.102 = 0.56$$

and when a risk factor of 1.3 is included, the ratio becomes

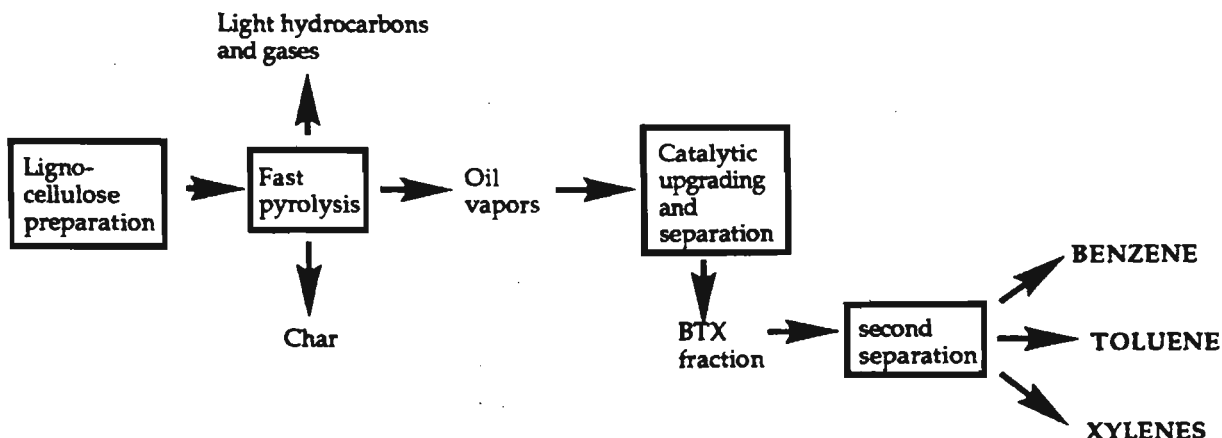
$$0.56/1.3 = 0.43$$

The low value of the ratio shows that a biomass-based route to pentanes/pentenes probably would not be competitive with the current petrochemical routes, given current feedstock prices and yields of the biomass processes. As in the case of butadiene, manipulating feedstocks, or changes in raw material costs could present conditions conducive to using biomass derived pentanes and pentenes in the future.

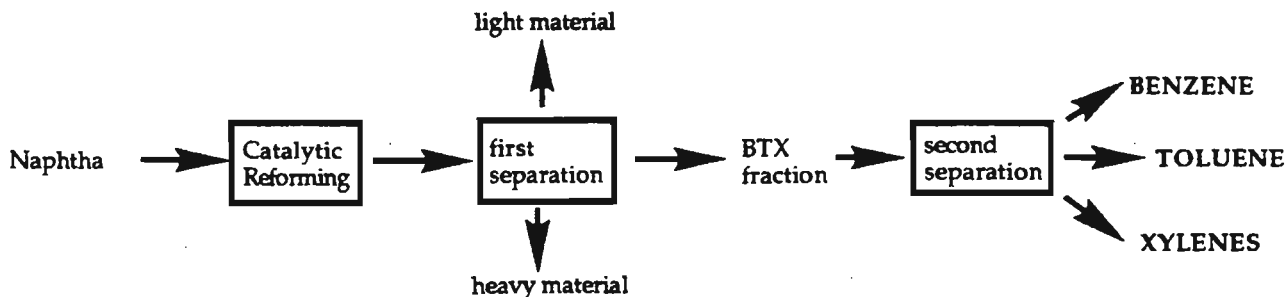
Future Projections: If the price of crude oil rises to \$35/barrel and the price of the wood feedstock drops to \$25/dry ton, the ratio of raw material costs rises to 1.03, suggesting that a biomass-based route to these materials might have a chance to compete. Alternatively, waste feedstocks rich in polyolefins (such as refuse derived fuel) are an attractive feedstock for routes to monomeric olefins, because the yield of hydrocarbon from these materials is substantially greater than from lignocellulose (Rejai, et al, 1991). The ratio that results from comparing the biomass and petrochemical routes then is significantly greater than unity, justifying further RD&D to optimize the process.

5.1.3 Benzene/Toluene/Xylene (BTX)

From biomass:



From petrochemicals:



Processes Compared: BTX can be produced from biomass by the fast pyrolysis of wood, followed by catalytic conversion of the vapors to gasoline and recovering the BTX from the gasoline product. Two routes exist for catalytic conversion and upgrading. A low pressure route can be thermally integrated with the pyrolysis through vapor phase catalytic cracking, or the liquid phase can be hydrotreated at high pressure (Elliott et al, 1991). BTX is produced in a similar manner commercially, by recovering the BTX fraction from gasoline derived from catalytic reforming of naphtha feedstocks that are available from crude oil.

Raw Materials Cost Comparison: The raw material cost contribution to commercially produced BTX is \$0.103/lb, assuming a crude oil costs \$20/barrel. The biomass-based process affords a 24% yield of BTX, giving a raw material cost contribution of \$0.082/lb, assuming wood feedstock costs to be \$40/dry ton. Comparing the two costs gives a ratio

$$0.103/0.082 = 1.26$$

and when a risk factor of 1.3 is included, the ratio becomes

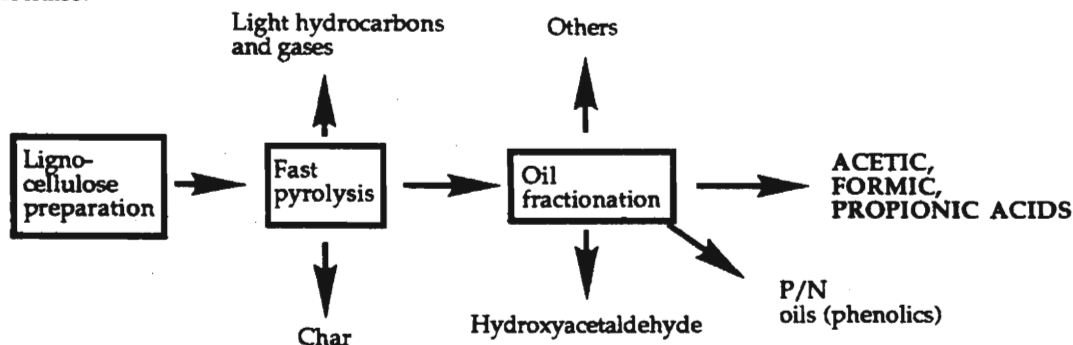
$$1.26/1.3 = 0.97.$$

The relatively high value of this number, based on actual process results, indicates that a process to produce BTX from biomass could be competitive with the current petrochemical process.

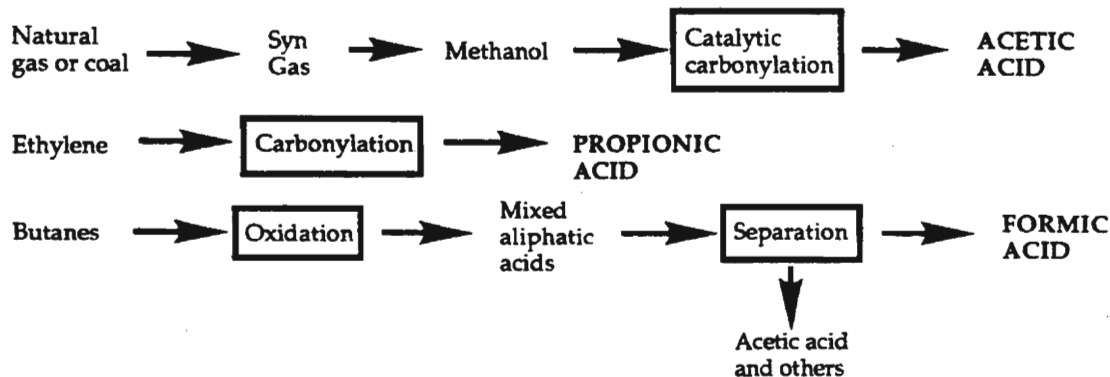
Future Projections: Introducing lower cost feedstocks, such as waste, will further increase the value of the petrochemical/biomass ratio, indicating that BTX from a biomass route could compete with the petrochemical processes. This process has been evaluated at a much higher level of detail (Diebold et al, in press).

5.1.4 Acetic/Formic/Propionic Acids

From biomass:



From petrochemicals:



Processes Compared: A mixture of acetic, formic, and propionic acids is available from the fractionation of crude pyrolysis oil derived from wood. About a 10% yield of mixed acids is currently obtained from the pyrolysis of wood feedstock. For simplicity, the mixture was considered to be pure acetic acid, and was compared to the commercial acetic acid process from methanol described above. Petrochemicals are converted into the acids of interest in routes using several feedstocks. Almost 75% of the domestic acetic acid production starts from natural gas using the Monsanto process, with the remainder being prepared by alternate routes. Ethylene, from the pyrolysis of ethane derived from natural gas, can be carbonylated to give propionic acid. Finally, formic acid can be obtained as one component of a mixture of acids resulting from the partial oxidation of butane.

Raw Materials Cost Comparison: Fast pyrolysis does not produce high yields of the acids, therefore, the acids need to find a cost effective use as a mixture. For example, converting this acid mixture to a mixture of acid salts to use as a road deicer was considered. The raw material cost of preparing the acid salts was compared to the raw material cost of the most widely used road deicer, sodium chloride. The raw material cost for producing mixed acid salts is \$0.043/lb, assuming acetic acid costs \$0.065/lb, lime (required to convert pyrolysis acids into the corresponding salts) costs \$0.02/lb, and a quantitative yield of salts from the simple acid/base reaction. Sodium chloride costs \$0.03/lb giving the ratio

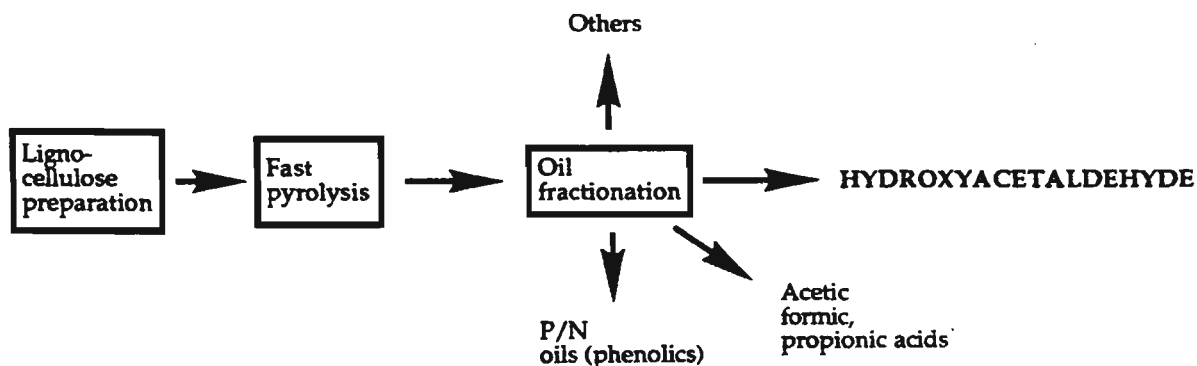
$$0.03/0.043 = 0.69.$$

A risk factor was not included in this analysis since the reaction between acid and lime is operationally simple and proceeds in almost quantitative yield.

Future Projections: If the yields of the acids produced during pyrolysis can be increased, or new, higher value applications for the mixed acid salts in solution are developed or lower cost feedstocks are used, the ratio between biomass and petrochemical derived materials would increase, indicating that mixed acids from a biomass route could eventually compete as a precursor to road deicing material.

5.1.5 Hydroxyacetaldehyde

From biomass:



Processes Compared: Hydroxyacetaldehyde is a potential coproduct from the fast pyrolysis of wood. It is present in the mixed acid fractions (evaluated above) in a yield of about 10%. Since it is not currently a commercial product, there is no petrochemical route for comparison. Instead, the cost of hydroxyacetaldehyde from biomass is compared to glyoxal, a known cross-linking agent for manufacturing resins. Hydroxyacetaldehyde is predicted to be a promising replacement for glyoxal for this use. Glyoxal is produced by the catalytic oxidation of ethylene glycol using oxygen as the oxidant.

Raw Material Cost Comparison: The raw material for producing hydroxyacetaldehyde from biomass in a coproduct recovery scheme is \$0.053/lb, assuming wood feedstock costs of \$40/dry ton. Production of

glyoxal from petrochemicals requires a raw material contribution of \$0.086/lb. Comparing the petrochemical route to the biomass route gives the ratio

$$0.086/0.053 = 1.62$$

and when a risk factor of 1.3 is included, the ratio becomes

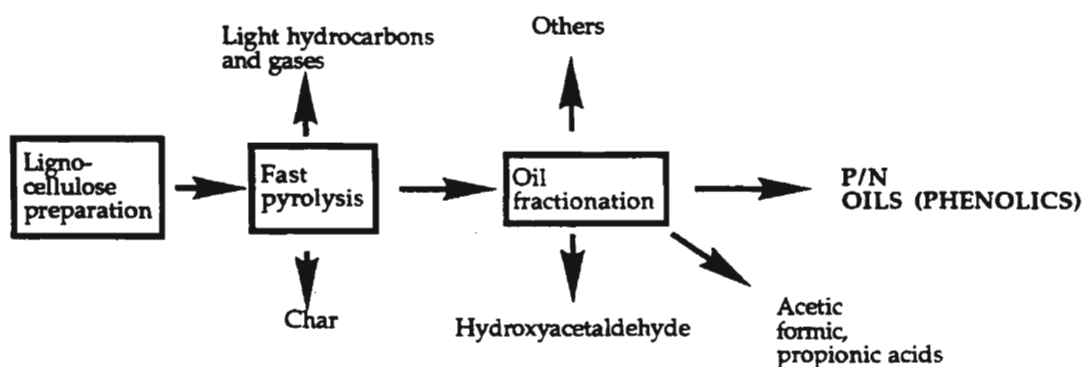
$$1.62/1.3 = 1.25.$$

This relatively large ratio suggests that hydroxyacetaldehyde prepared from biomass could favorably compete with glyoxal from petrochemicals in the crosslinker market, *based on raw material costs only*. However, little is currently known about methodology to separate the hydroxyacetaldehyde from the crude acid mixture derived from pyrolysis. Losses would certainly occur, and could cause the ratio to drop.

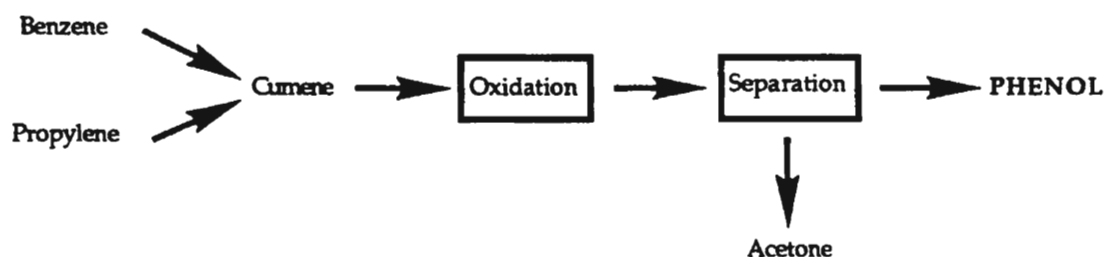
Future Projections: Further information on separation technology is necessary before a complete evaluation can be made.

5.1.6 Phenolics (by pyrolysis routes)

From biomass:



From petrochemicals:



Processes Compared: Mixed phenolics are available as one of the components derived from a post-pyrolysis fractionation of oil. The oil comes from wood in a weight percent yield of 20-25% from a softwood feedstock, or 18-20% from a hardwood feedstock (Chum and Black 1990; Chum et al, 1989). Phenol is produced commercially from petrochemicals by the cumene process, starting from benzene and propylene, which generates acetone as a coproduct.

Raw Materials Cost Comparison: The raw materials cost of phenol produced by the commercial cumene process is \$0.135/lb phenol, assuming benzene costs \$0.157/lb, propylene costs \$0.13/lb, and assigning propylene costs to acetone. These costs assume crude oil costs \$20/barrel. The raw materials cost of

mixed phenolics produced by wood pyrolysis is \$0.094/lb, assuming softwood feedstock costs \$40/dry ton. Comparison of the petrochemical and biomass-based processes give the ratio:

$$0.135/0.094 = 1.44$$

and when a risk factor of 1.3 is included, the ratio becomes

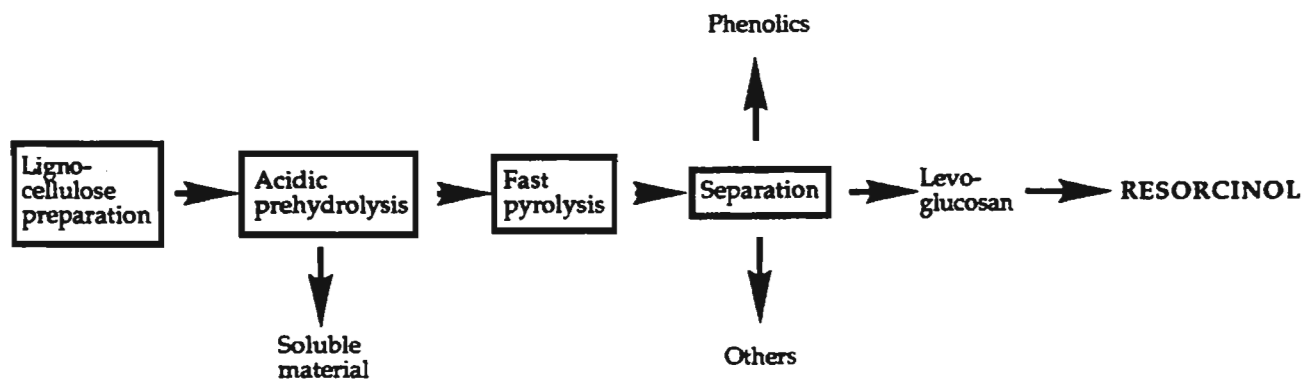
$$1.44/1.3 = 1.17.$$

A comparison of this ratio to that obtained in the hydroxyacetaldehyde case (section 5.1.5) is interesting. The absolute values of the ratios, after applying the "30% rule", suggests that hydroxyacetaldehyde (ratio of petrochemical/biomass routes = 1.25) should be considered more strongly than a biomass route to phenolics, with a ratio of 1.17. However, the results for producing phenolics is based on an established process, verified by repeated trials in an RD&D environment. *No similar information base is available for producing hydroxyacetaldehyde from biomass.* The information used in the hydroxyacetaldehyde evaluation is from smaller scale runs (Scott, et al, 1982) and not from isolating hundreds of pounds of material as practiced in the P/N oil production. This process is an important component of the ongoing NREL program to develop new methods for the converting biomass into useful chemicals. Using this material in the adhesives industry is the basis of the current DOE/OIT/NREL Pyrolysis Materials Research Consortium (Chum et al, 1991). In this case, we envision that waste wood would be the feedstock that would make the already attractive biomass/petrochemical ratio even higher. The intent is to partially replace phenol in phenol/formaldehyde thermosetting resins, an application that does not need pure phenol.

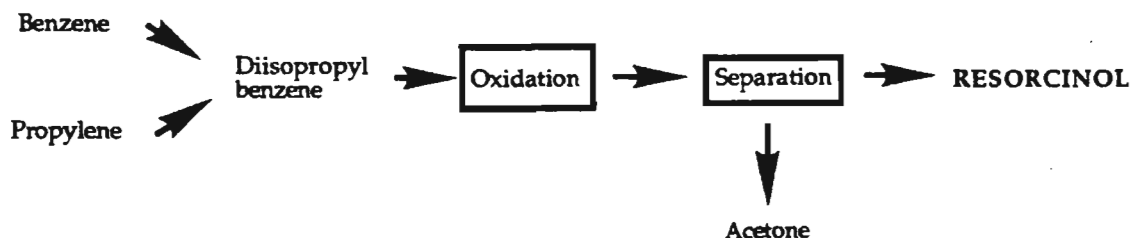
Future Projections: A more detailed process and capital cost evaluation of the biomass-to-phenolics route is certainly warranted, and more RD&D information is necessary on a route to hydroxyacetaldehyde from biomass.

5.1.7 Resorcinol

From biomass:



From petrochemicals:



Processes Compared: Resorcinol is potentially available from biomass by a two-step procedure that first converts cellulose to levoglucosan (section 5.3.1) using fast pyrolysis of acid treated biomass, and then to resorcinol by an electrochemical process. Resorcinol can be produced from petrochemicals by two methods starting from benzene. The first route is similar to the cumene route for converting benzene to phenol. Benzene is treated with excess propylene to give diisopropylbenzene, followed by oxidation to give resorcinol and acetone as coproducts. Alternatively, benzene is sulfonated with sulfuric acid and the resulting material is fused with alkali to give resorcinol. The alkali fusion route was not evaluated because of the high raw material costs.

Raw Material Cost Comparison: The raw material cost contribution to resorcinol for a biomass-based process is \$0.156/lb, assuming levoglucosan costs \$0.068/lb (cost derivation given below in section 5.3.1), electricity costs \$0.05/kwh, and there is a yield of 80% in the conversion. Since the electrochemical step is supplying electrons, electricity can be evaluated from a cost standpoint as another raw material. Resorcinol from petrochemicals is produced at a raw materials cost of \$0.153/lb, assuming benzene costs \$0.157/lb, neglecting the cost of the materials in subsequent steps, which are assumed to be small, and assuming a 90% yield in each of the chemical steps.

Comparing the petrochemical route to the biomass route gives a ratio

$$0.153/0.156 = 0.98$$

and when a risk factor of 1.3 is included, the ratio becomes

$$0.098/1.3 = 0.75.$$

Note that including all the costs of the petrochemical route to resorcinol would only improve the projection.

Future Projections: The biomass/petrochemical ratio indicates that resorcinol from biomass has a chance of competing with the current petrochemical route. However, the current process description is rough and has used reasonable estimates of yields for the converting levoglucosan into resorcinol. Therefore, further laboratory RD&D is necessary to obtain the necessary process performance information for a more detailed evaluation.

5.1.8 Vinyl Phenol, an Example of a High Value Phenolic Produced by Biomass Pyrolysis

From petrochemicals:



From biomass:



Processes Compared: Vinyl phenol, a specialty monomer and additive in the food and fragrance industry, is currently produced on a small scale as a fine chemical. The process begins from phenol, proceeds through nine separate chemical operations, and consumes malonic acid, acetic anhydride, hydrogen chloride, hydrogen cyanide, caustic, and sulfuric acid. Vinyl phenol is also available as one of the products obtained upon fast pyrolysis of lignocellulosics.

Raw Material Cost Comparison: Because of the complexity of the petrochemical route, a number of assumptions were necessary. The raw material cost contribution to vinyl phenol from petrochemicals is about \$4.82/lb, assuming the starting phenol costs \$0.40/lb, and there is an 80% yield in each of the subsequent chemical steps. Given the number of steps involved, and the heavy use of auxiliary raw materials, this estimate is considered low. In comparison, the raw material cost contribution to vinyl phenol prepared from biomass is projected to be about \$0.50/lb, assuming a 10% yield of vinyl phenol from pyrolysis and only a 10% efficiency in its recovery from the other products present in the mixture. Comparing these results gives the ratio

$$4.82/0.5 = 9.64$$

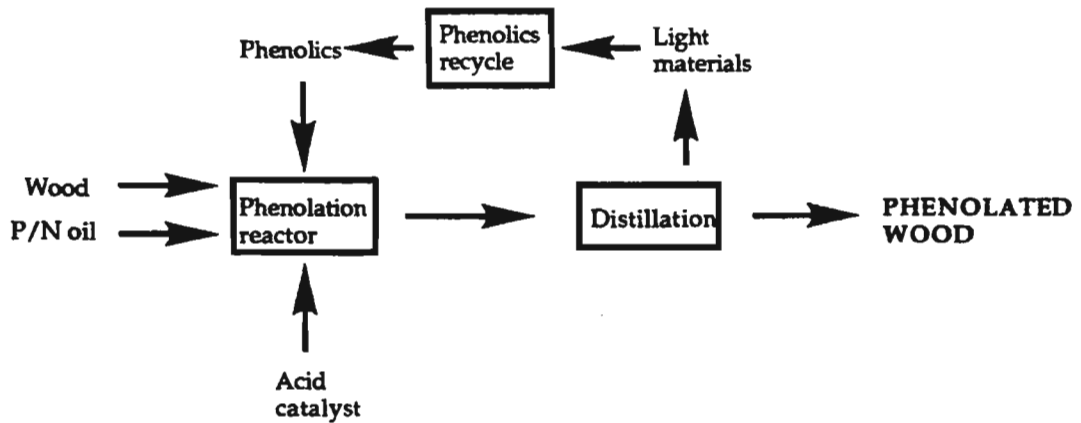
and when a risk factor of 1.3 is included, the ratio becomes

$$9.64/1.3 = 7.4.$$

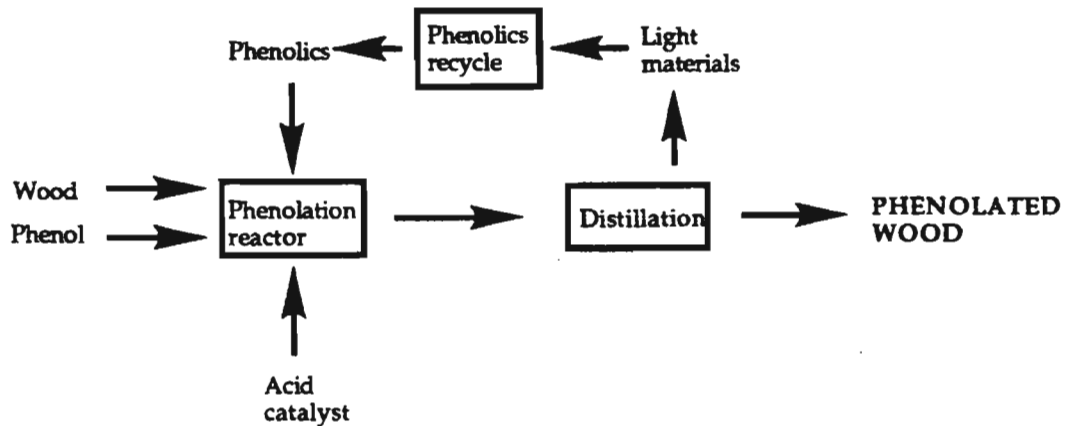
Future Projections: This high ratio indicates that further investigation into the recovery of vinyl phenol from biomass is warranted, especially in separating the vinyl phenol from the pyrolysis oil mixture.

5.1.9 Phenolics from Wood Phenolation

From biomass:



From petrochemicals:



Processes Compared: Phenolated wood can be made from phenol or a phenolics fraction from a pyrolysis P/N oil. This phenolic fraction has potential use in foams, adhesives, moldings and fibers.

Raw Material Cost Comparison: The raw materials cost of producing a phenolated wood is \$0.106/lb, assuming wood feedstock costs \$40/ton and P/N oils cost \$0.094/lb. Production of a phenolated wood using petrochemical derived phenol has a raw material cost of \$0.150/lb, again assuming wood costs \$40/ton and phenol costs of \$0.41/lb. Comparing these results gives the ratio

$$0.150/0.106 = 1.42$$

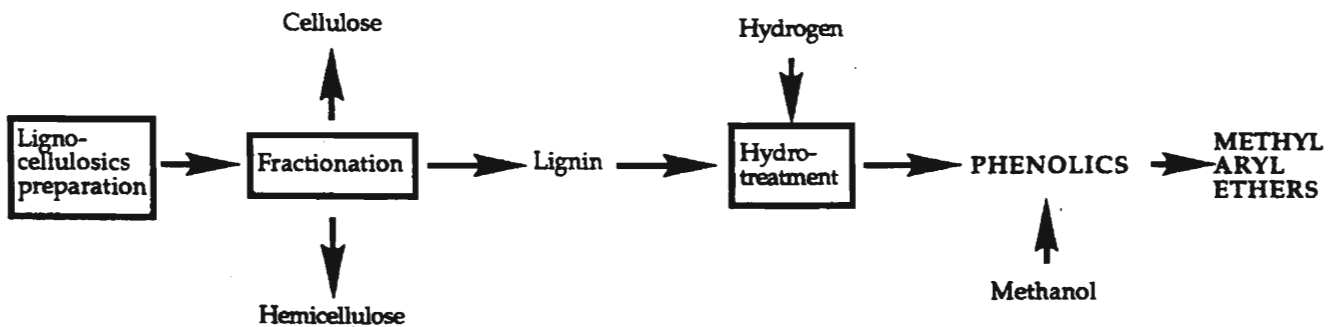
And when a risk factor of 1.3 is included, the ratio becomes

$$1.41/1.3 = 1.09.$$

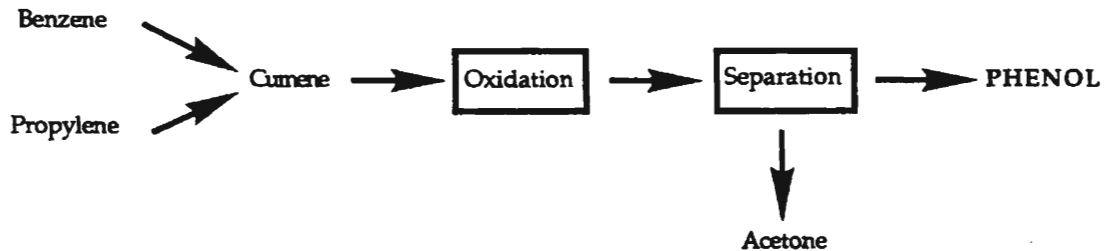
This ratio indicates that the biomass-based process could potentially compete with a process based on petrochemical derived phenol.

5.1.10 Phenolics (by hydrotreating of lignin)

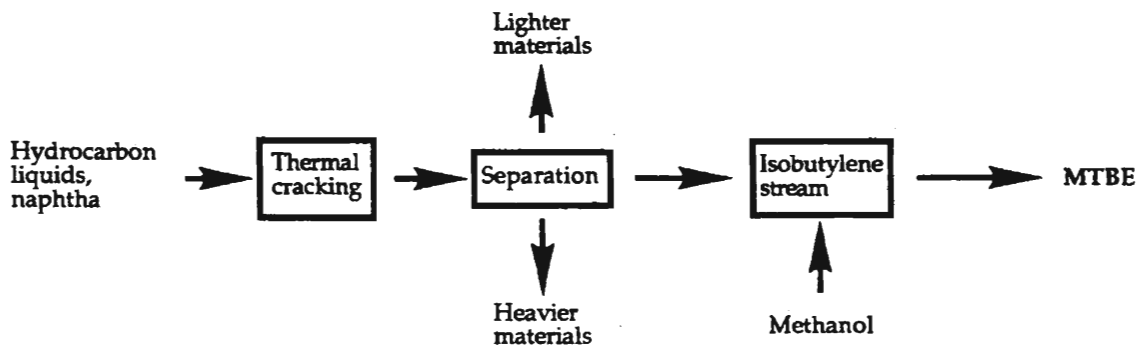
From biomass:



From petrochemicals:



Process for MTBE production:



Processes Compared: Hydrotreating of lignin, available from a variety of sources, affords a mixture of phenolic products. Treating the phenolics with methanol gives a mixture of methyl aryl ethers (MAE).

Two comparisons are made: a comparison of the cost of phenolics prepared by hydrotreatment of lignin to phenol prepared by the commercial cumene route, and a comparison of the cost of MAE to methyl *tert*-butyl ether (MTBE). MAE and MTBE are used as oxygenated gasoline additives. MTBE is prepared commercially from isobutylene and methanol.

Raw Materials Cost Comparison, Phenolics Production: The raw materials cost for producing a phenolic material by hydrotreating of lignin is \$0.085/lb, assuming that lignin (from NREL "clean fractionation") is available for \$0.032/lb, hydrogen is available at \$0.54/lb, and the hydrotreating process gives a 10% yield of phenolics. In comparison, phenol produced via the cumene process has a raw material cost of \$0.135/lb, calculated in section 5.1.6.

Comparing the costs of the petrochemical process to the biomass process gives the ratio

$$0.135/0.085 = 1.59$$

and when a risk factor of 1.3 is included, the ratio becomes

$$1.59/1.3 = 1.22$$

This ratio indicates that "clean fractionation" of lignocellulose (described in section 5.2.1) will give an inexpensive feedstock for producing phenolics that has a good opportunity to compete with material currently produced from petrochemicals.

Raw Materials Cost Comparison, MAE/MTBE Production: The raw materials cost for preparing MTBE from petrochemicals is \$0.06/lb, assuming that methanol is available at \$0.35/gal and ethane (the precursor to isobutylene from natural gas liquids) is available at \$0.25/gal. The cost of raw materials for the preparing mixed aryl ethers from lignin is \$0.12/lb, assuming that lignin is available at a value of \$0.025/lb, and methanol used in the process costs \$0.35/gal. The hydrocracker is assumed to give a total product yield of 48% with 23% conversion to mixed aryl ethers. Comparing the conventional process to the biomass process gives the ratio

$$0.06/0.12 = 0.5$$

and when a risk factor of 1.3 is included, the ratio becomes

$$0.5/1.3 = 0.38$$

The low value of this ratio indicates that producing mixed aryl ethers from hydrotreating will not compete with MTBE in the gasoline additive market under current feedstock assumptions and the low yield of MAE obtained from hydrotreating.

Future Projections: As in all of these evaluations, a sensitivity analysis can be performed. If the yield of the hydrotreating step rose to 72%, with 100% recovery of phenolics, the raw material cost drops to \$0.09/lb, giving a final ratio of 0.51 for producing MAE from phenolics derived by lignin hydrotreating. This ratio is still quite low, even using a highly optimistic projection of possible hydrotreating performance.

5.1.11 Syn Gas

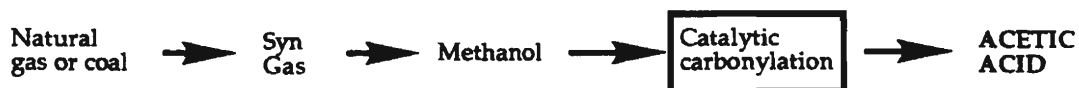
A direct comparison of the cost of syn gas produced from biomass versus petrochemicals is difficult, since "syn gas" is a generic term for a mixture of hydrogen and carbon monoxide. Different ratios of the component gases are possible from petrochemicals depending on the methodology employed. Of greater interest is comparing costs of products that can be derived from syn gas, for example, acetic acid (section 5.1.12).

5.1.12 Acetic Acid from Syn Gas

From biomass:



From petrochemicals:



Processes Compared: Both processes use syn gas as the starting material for acetic acid production. The key process feature is the higher level of carbon monoxide (CO) in syn gas produced by wood gasification. Conventional production of syn gas from natural gas gives a H₂/CO ratio of 3.0, and production from wood gives a ratio of 0.8 - 1.5. The presence of excess CO from wood gasification gives a process that uses part of the CO for methanol production (the precursor to acetic acid) and the excess CO for converting the methanol to acetic acid. Two different biomass gasifiers were evaluated: the IGT (direct) and the BCL (indirect) processes. Producing acetic acid from petrochemicals relies on a catalytic carbonylation of methanol, produced using the Monsanto acetic acid process.

Raw Materials Cost Comparison: Comparing the raw material costs of the petrochemical and biomass-based routes gives a ratio of 0.6, assuming natural gas costs \$1.66/Mft³. This number is based on actual performance results from an engineering unit operating on biomass gasification. A biomass-based process to acetic acid could compete with current petrochemical-based processes under several scenarios shown below in the sensitivity analysis.

Future Projections: A sensitivity analysis has been performed to show the effect of change in feedstock costs on the ratio of raw material costs for the processes and the results are shown below.

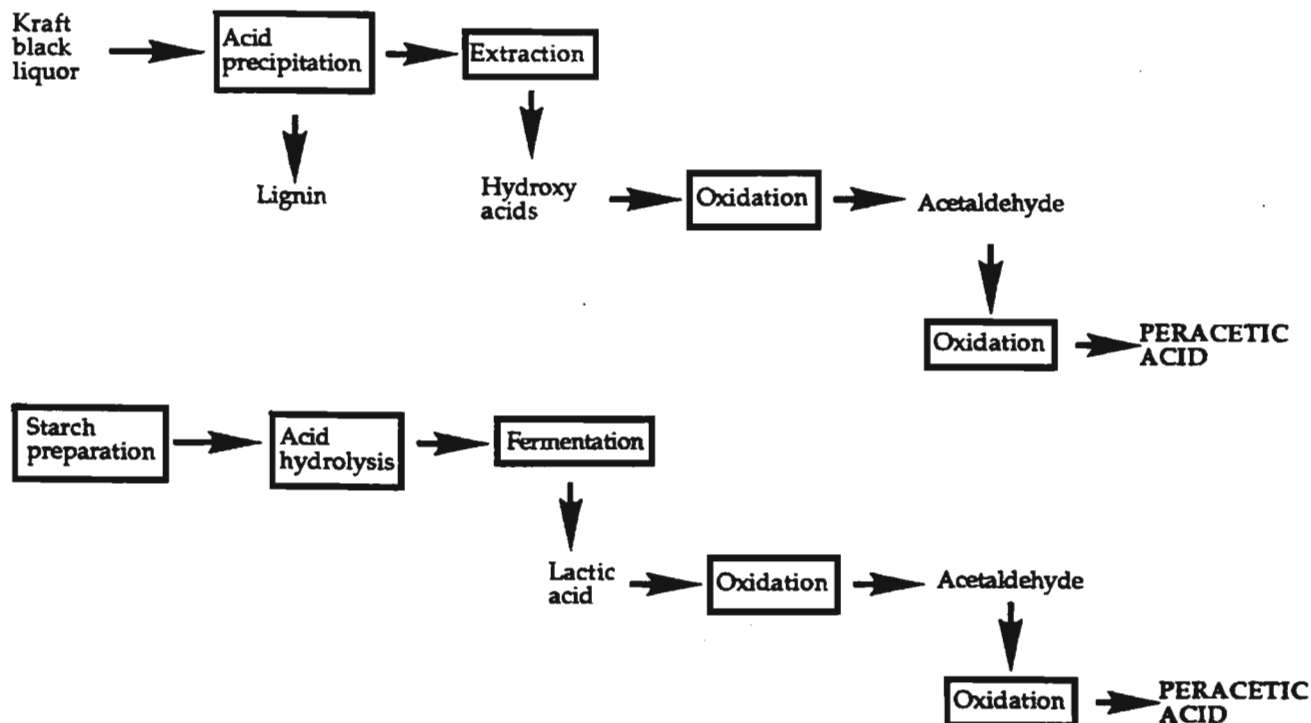
Cost of Biomass (\$/dry ton)

Cost of Methane (/Mft ³)	<u>\$30.00</u>	<u>\$40.00</u>	<u>\$50.00</u>	<u>\$60.00</u>
\$1.00	0.6	0.4	0.3	0.3
\$2.00	1.2	0.9	0.7	0.6
\$3.00	1.9	1.3	1.0	0.8
\$4.00	2.5	1.8	1.4	1.1

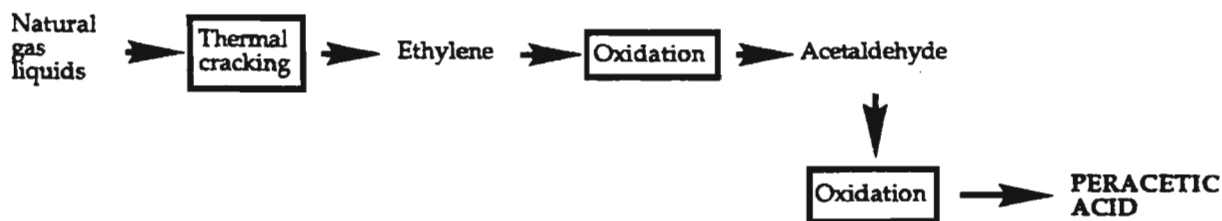
Note that either a drop in wood feedstock costs or an increase in methane costs by 20% can give ratios of unity, and suggest that acetic acid could be produced economically from wood gasification if methane costs about \$2.00/Mft³, and wood costs \$30-40/dry ton.

5.1.13 Peracetic Acid

From biomass:



From petrochemicals:



Processes Compared: Two biomass-based processes have been suggested for producing peracetic acid. The feedstocks are wastes from starch rich food processing streams or are compounds, such as lignin derived from pulping black liquor that are normally used for their fuel value. The first begins with mixed hydroxy acids available from fractionation of kraft black liquor. These acids, which are present in substantial amounts in black liquor, have a low heat content, limiting their fuel value. However, they could be used for peracetic acid production in this process by developing cost effective fractionation routes. The hydroxy acids are converted by oxidation to acetaldehyde, and then to peracetic acid. The second route converts glucose, derived from starch containing waste streams or corn starch, into lactic acid, followed by the same oxidation sequence to give peracetic acid. Peracetic acid is produced commercially from petrochemicals by the two-stage liquid phase oxidation of ethylene.

Raw Materials Cost Comparison: The projected raw material cost of peracetic acid from kraft black liquor is \$0.15/lb, assuming that the mixed hydroxy acids can be efficiently separated from the black liquor, and that the oxidation steps each proceed in 90% yield. A route from corn starch gives a raw material cost of \$0.20/lb, assuming starch costs \$0.07/lb and the same 90% yield performance in the oxidation steps. Producing peracetic acid from ethylene has a raw material cost of \$0.16/lb, assuming

an ethylene cost of \$0.20/lb. Comparing the cost of the petrochemical routes to those from biomass gives the ratios

(from kraft black liquor) $0.16/0.15 = 1.07$
 (from starch) $0.16/0.20 = 0.8$

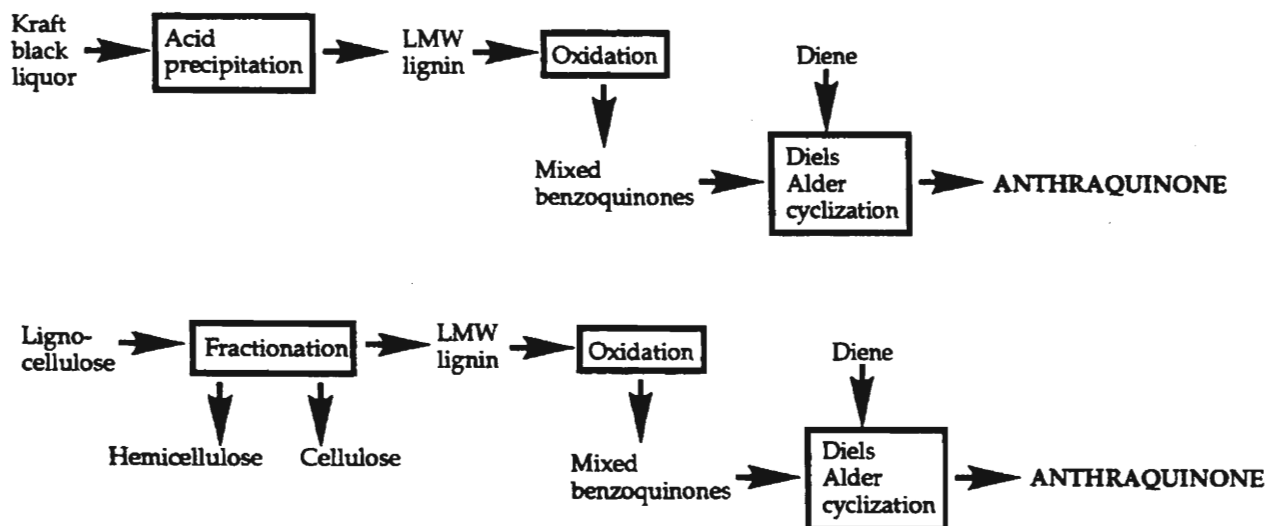
and when a risk factor of 1.3 is included, the ratios become

(from kraft black liquor) $1.07/1.3 = 0.82$
 (from starch) $0.8/1.3 = 0.61$.

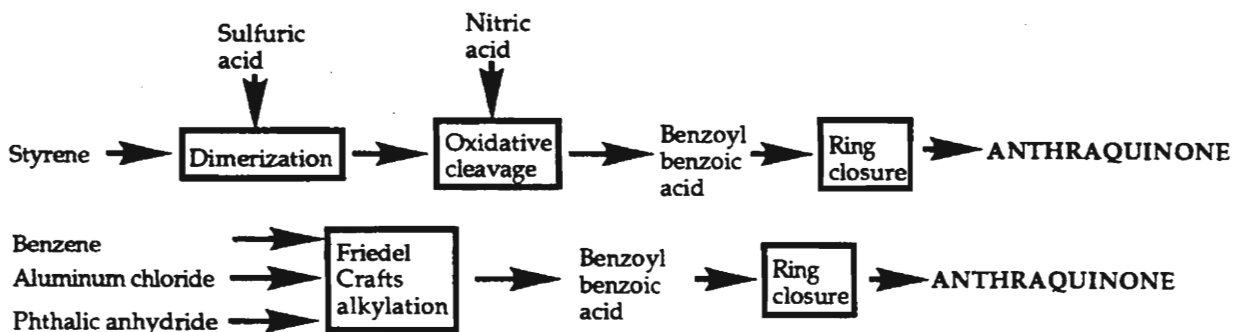
These ratios indicate that a route to peracetic acid starting from kraft black liquor has a chance to compete with the current petrochemical route, assuming certain levels of performance in both the fractionation and oxidation steps. A route beginning from corn starch will probably not be as competitive as a route using a starch containing waste stream. Peracetic acid is a reasonable candidate to consider for further research.

5.1.14 Anthraquinone

From biomass:



From petrochemicals:



Processes Compared: Anthraquinone, or anthraquinone-like products, can be produced from biomass derived low molecular weight lignin, available either from kraft black liquor or the organosolv "clean fractionation" process (section 5.2.1), by a two-step chemical sequence. The conversion proceeds with oxidation of the lignin to a mixture of benzoquinones, followed by addition of a diene. Commercially, anthraquinone is produced from phthalic anhydride and benzene, using aluminum chloride as a catalyst. Another process, starting from styrene is known, and has come close to commercialization. Other petrochemical-based routes to anthraquinone have much higher costs.

Raw Materials Cost Comparison: Two different sources of lignin, organosolv and kraft, were considered as starting materials for the biomass-based route to anthraquinone and were compared to the two petrochemical routes. The cost of raw materials for a process starting from organosolv lignin is \$0.592/lb, assuming yields of 40% and 50% in the two chemical steps, respectively. The cost using kraft black liquor as the starting material gives a raw material cost of \$0.836/lb, assuming yields of 30% and 90% in each of the two chemical steps respectively. The benzene-based route to anthraquinone has raw materials costs of \$1.98/lb, and the styrene-based route has similar costs of \$1.00/lb. Comparing these results gives the ratios

$$(\text{AQ from benzene/AQ from organosolv}) 1.98/0.592 = 3.34$$

$$(\text{AQ from benzene/AQ from kraft}) 1.98/0.836 = 2.37$$

$$(\text{AQ from styrene/AQ from organosolv}) 1.00/0.592 = 1.69$$

$$(\text{AQ from styrene/AQ from kraft}) 1.00/0.836 = 1.20$$

and when a risk factor of 1.3 is included, the ratios become

$$(\text{AQ from benzene/AQ from organosolv}) 3.34/1.3 = 2.57$$

$$(\text{AQ from benzene/AQ from kraft}) 2.37/1.3 = 1.82$$

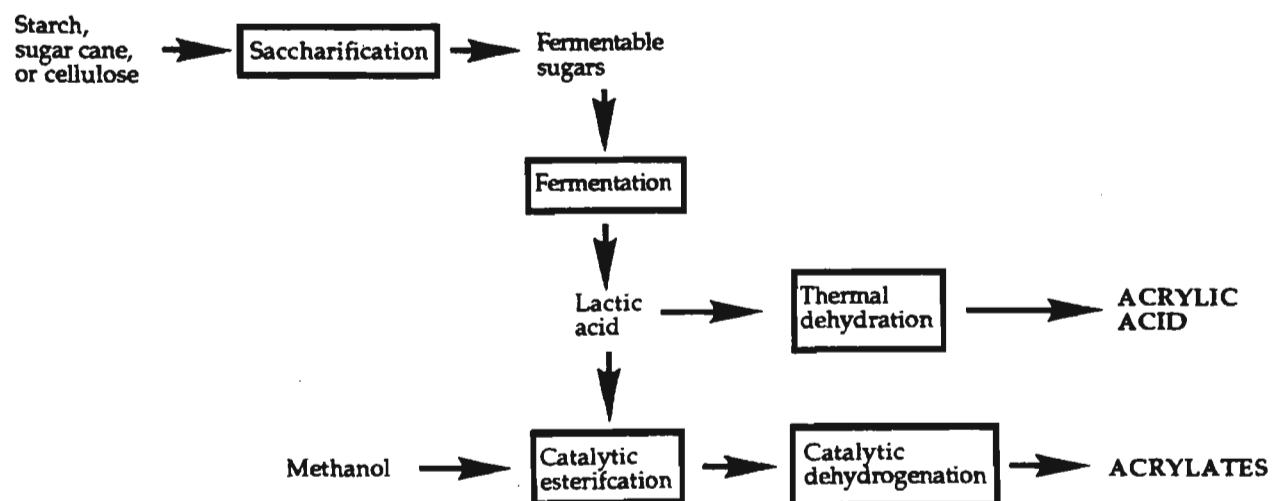
$$(\text{AQ from styrene/AQ from organosolv}) 1.69/1.3 = 1.30$$

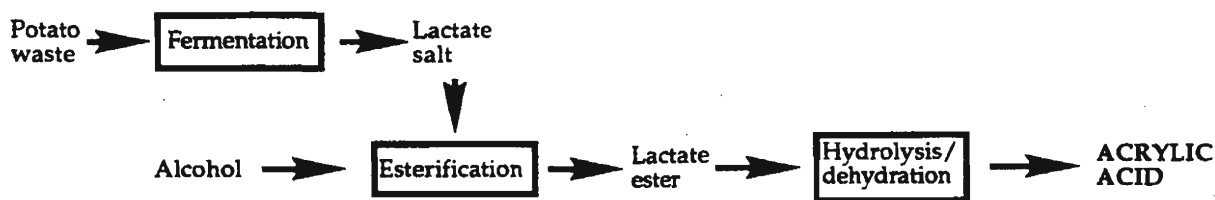
$$(\text{AQ from styrene/AQ from kraft}) 1.20/1.3 = 0.92.$$

These large ratios indicate that a biomass-based route to anthraquinone could compete successfully with current petrochemical routes. These results are based as closely as possible on actual laboratory results increasing the reliability of this evaluation. A more in-depth analysis of these routes has been carried out and is summarized in section 5.4.2 of the report.

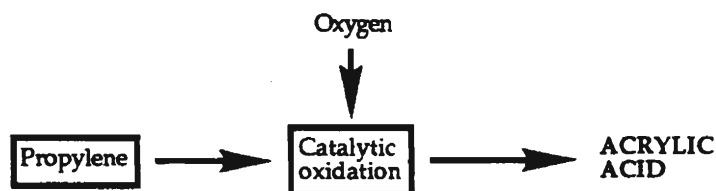
5.1.15 Acrylic Acid/Esters

From biomass:





From petrochemicals:



Processes Compared: A number of different biomass feedstocks have been suggested as possible starting materials for preparing acrylic acid, including potato waste, cheese whey, and blackstrap molasses. Each of these materials give varying amounts of fermentable sugars, the preferred starting material for acrylic acid production. The sugars can be fermented to lactic acid and thermally dehydrated to give acrylic acid (Antal, 1989). Alternatively, potato waste can be saccharified, and then fermented in the presence of ammonia to produce an ammonium lactate salt that is esterified with an alcohol to give a lactate ester. The ester can be hydrolyzed to give acrylic acid and recover the alcohol for reuse. Acrylic acid is produced commercially from propylene by a two-stage oxidation process.

Raw Materials Cost Comparison: The raw material cost for producing acrylic acid from petrochemicals is \$0.145/lb, assuming that propylene can be obtained for \$0.16/lb, and that the yield of the oxidation is 80%. Thermal production of acrylic acid from lactic acid has a raw material cost of \$0.366/lb because of the high cost of lactic acid. This cost assumes a 75% yield for the process. In contrast, the low feedstock cost of potato waste (assumed to be zero) gives a raw material cost for direct potato waste fermentation of \$0.053/lb, assuming 36% yield. Comparing the petroleum-based process to the two biomass routes gives the ratios

$$\begin{aligned} \text{(thermal route)} & 0.145/0.366 = 0.4 \\ \text{(from zero value potato waste)} & 0.145/0.076 = 1.91 \end{aligned}$$

and when a risk factor of 1.3 is included, the ratios become

$$\begin{aligned} \text{(thermal route)} & 0.4/1.3 = 0.30 \\ \text{(from zero value potato waste)} & 1.91/1.3 = 1.47 \end{aligned}$$

The results of the potato waste analysis indicate that producing acrylic esters in this method has a good chance of competing with acrylates currently produced by petrochemical means *if the cost and availability assumptions on potato waste can be verified*. Production from the thermal route would be less competitive, given current feedstock costs.

Future Projections: Acrylic acid and its esters have a wide range of applications in polymer markets. Further investigation of this methodology should be done to answer questions about the range of acrylate esters that can be produced from different alcohols, and whether the lactate esters can be converted into peroxy esters, compounds used as polymerization initiators and in other applications.

5.2 Improved Production

A number of chemicals and materials have been identified that are currently produced from renewable sources. These materials have the potential of serving as building blocks for end products that replace those currently derived from petrochemicals. The production levels of these materials are relatively low, either because markets for their use have not been identified or because their cost is too high to justify their use as starting materials for end products currently produced from petrochemical building blocks. This portion of the evaluation describes the potential cost of these materials if new methods of production could be developed. *Identifying new, lower-cost routes for producing these materials will suggest new applications of renewable starting materials in markets traditionally dominated by petrochemical derivatives. Recent work at NREL has resulted in a promising market opportunity for the Alternative Feedstocks program and producing these materials - the clean fractionation process.*

5.2.1 The NREL Clean Fractionation Process

Many of the chemicals or product families evaluated in the improved production category have a demonstrated use in the marketplace (section 4.3), although they are more specialty oriented than those materials in the direct substitution category. The common link between these chemicals is their derivation from glucose or xylose. Conventional production of these two monomeric carbohydrates normally uses corn starch as the starting material for glucose and the 5-carbon sugars in corn cobs as the starting material for xylose. Alternatively, these carbohydrates can be prepared from fractionating lignocellulose, followed by converting the cellulose fraction to glucose and the hemicellulose fraction to xylose (Figure 5.1 shows the derivation of different product families, from glucose and xylose, using lignocellulosics as the starting feedstock). However, the corn-based route has historically proven more economical.

Recent work at NREL has discovered a new process for the clean separation of wood into its constituents cellulose, hemicellulose, and lignin, at efficiencies approaching 100% for each component. Because the process is potentially proprietary, and patents are currently being filed, the results presented here will not reveal the specific conditions under which this "clean fractionation" is obtained other than to note that results have been obtained in small scale organosolv pretreatment experiments. However, the results could be of broad scope and offer a promising market opportunity for the Alternative Feedstocks program.

The most important result of this work comes out of a technoeconomic evaluation of its potential. This process could potentially offer glucose and xylose at a cost substantially lower than other routes, including the conventional corn starch-based process. These results have a cascade effect, lowering the costs associated with producing the related product families (Figure 5.1). The process also offers a low cost source of glucose (fermentable sugar) for use in bioprocessing, suggesting a solid opportunity to develop hybrid chemical/biochemical processes to products. Moreover, cellulose, the precursor to glucose, is used in large quantities by the chemical industry. An efficient and lower cost process for producing high purity cellulose would have an impact on a number of markets (section 4.3).

The most influential assumption in assessing clean fractionation is the availability of wood, delivered as chips on a large scale to a plant site at a cost of \$40/dry ton (discussed in more detail in section 3.1). The ratios in this section compare the conventional biomass-based routes to the materials with new, less expensive routes, based on the availability of cheaper raw materials. Of particular interest in this section are new, more cost-effective routes to a number of carbohydrates, materials available cheaply in large quantities, but possessing a high degree of functionality and structural complexity. The raw materials cost contribution analysis for producing glucose and xylose from clean fractionation is presented in sections 5.2.1.1 and 5.2.1.2, and a more detailed analysis, including projected operating and capital costs, is given in section 5.4.3.

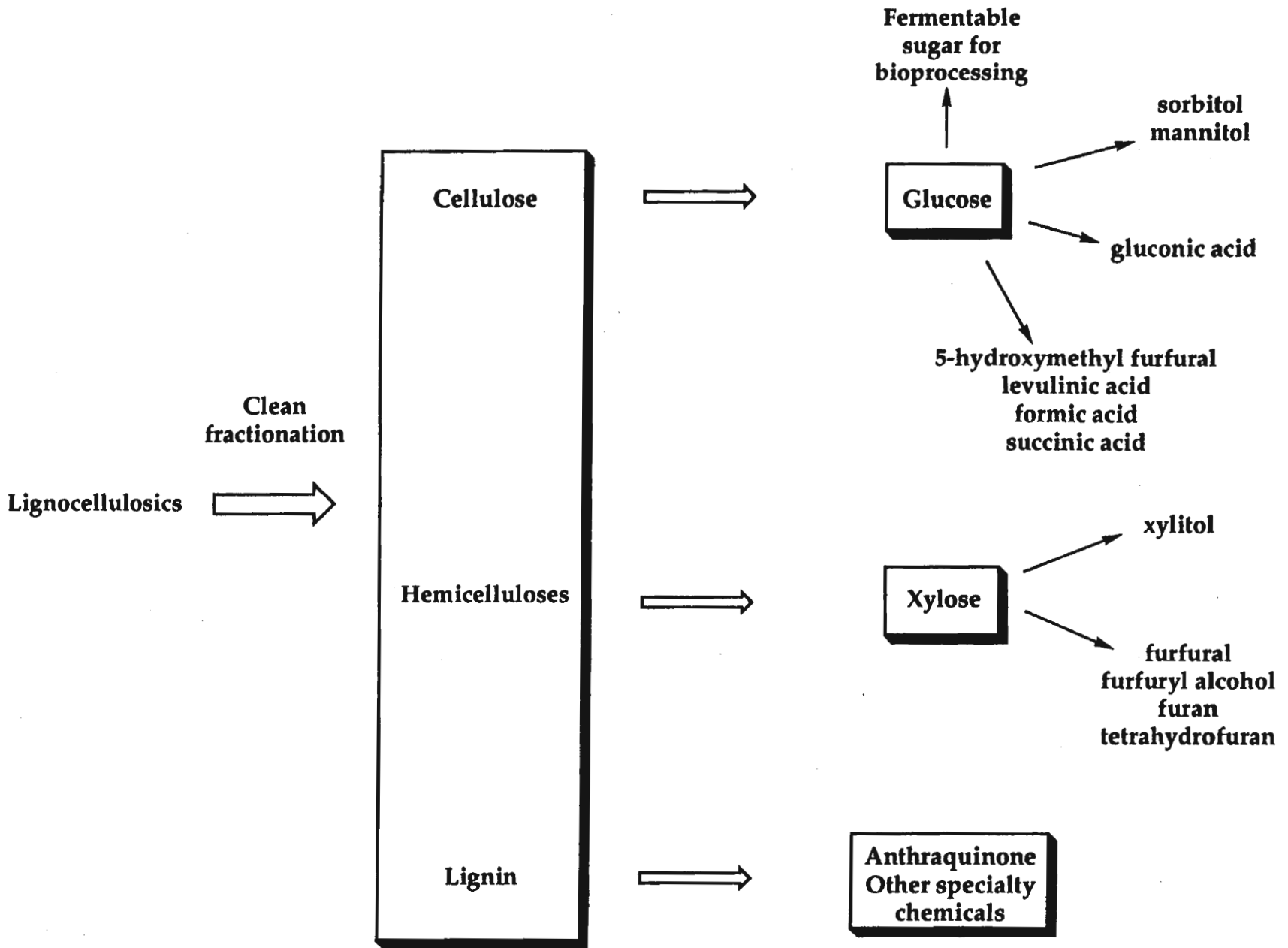
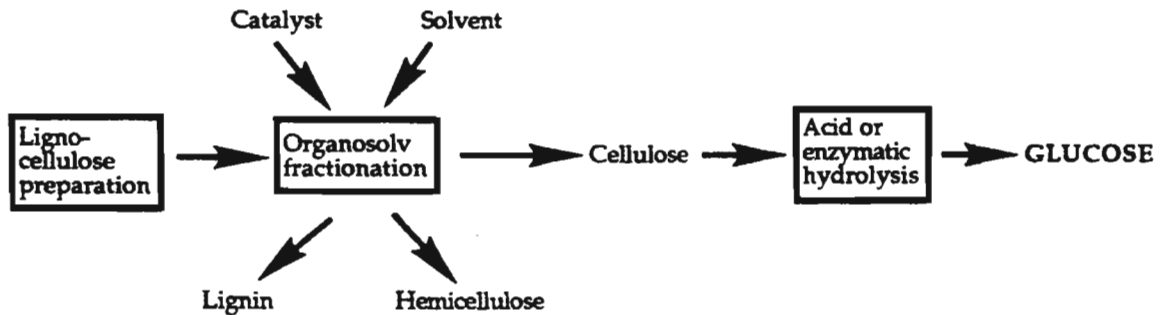


Figure 5.1 - Flowchart for Production of Chemical Families from Clean Fractionation

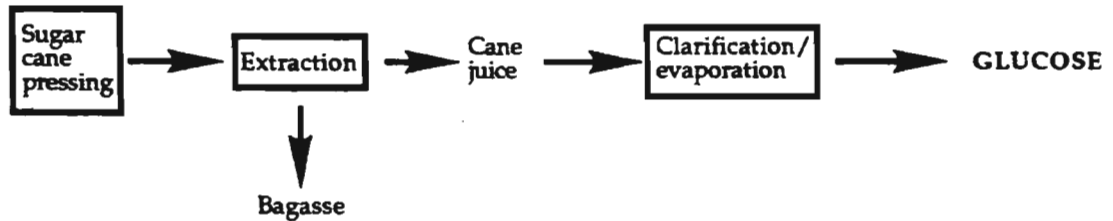
5.2.1.1 Glucose

Glucose is a renewable building block that serves as a precursor to a variety of materials. The evaluation compares the costs of producing glucose from four raw materials, lignocellulosic biomass, by means of the new NREL clean fractionation technology, sugar cane, corn starch, and wood by steam explosion.

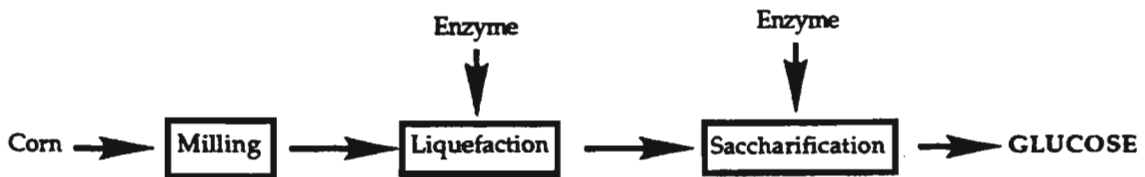
From lignocellulose:



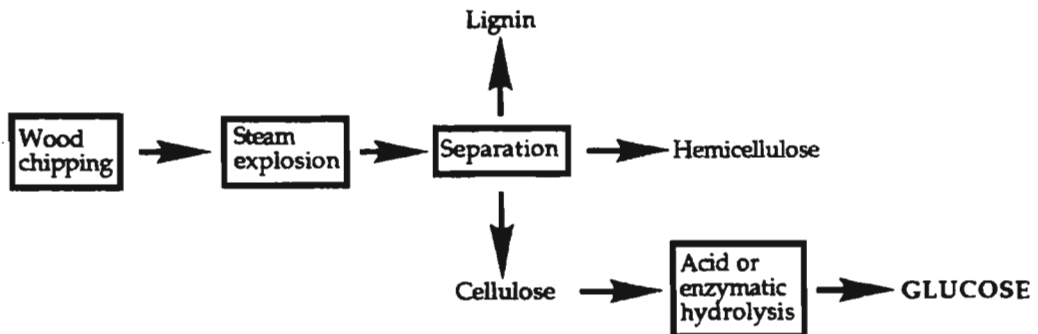
From sugar cane:



From corn:



From steam explosion of wood:



Glucose from lignocellulosic biomass

Glucose, in this case, is derived from hydrolysis of the cellulose fraction of the NREL clean fractionation technology for lignocellulosic biomass. The advantage to this process is that all three coproducts could be upgraded to commercial materials for use in different markets. The raw material cost contribution can be shared equally among the coproducts. A raw materials cost of \$0.032/lb for glucose results, assuming wood feedstock costs \$40/dry ton and a yield of glucose from cellulose of 90%.

Glucose from sugar cane

The cost of producing fermentable sugars (as glucose) was estimated by extrapolating information collected as part of a report on producing ethanol by fermentation of sugar cane. A raw materials cost of \$0.08/lb (corrected to 1992) was obtained based on a cost of growing and harvesting sugar cane of \$0.006/lb (1978), in a plant designed to produce 12.6 million gallons of ethanol per year. Sugar containing juice from sugar cane suffers from a short growing season and a limited shelf life, making a constant rate of operation through the year difficult. This would be less of a problem in Hawaii where harvesting can take place 10 months out of the year.

Glucose from corn starch

Again, the cost of fermentable sugars (as glucose) was estimated from a report describing an ethanol production facility designed to make 25 million gallons per year from dry milled corn. Assuming corn costs \$2.60/bushel, and a yield of 73% of sugars from corn starch saccharification, a raw materials cost of \$0.05/lb (corrected to 1992) for sugars from corn was obtained. In contrast to the sugar cane process, corn can be stored through the year, assuring a constant production level of fermentable sugars.

Glucose from wood by steam explosion pretreatment

Glucose can also be prepared by pretreating wood in a steam explosion process. The information for the calculations was provided from a series of engineering reports describing processes to produce glucose by steam explosion, followed by enzymatic or acid hydrolysis of the cellulose produced. Assuming wood feedstock costs \$40/dry ton, and a yield of 32-39% of cellulose from dried wood, a cost of \$0.056/lb can be calculated. This value is an average of two different economic evaluations (A. D. Little 1985, Stone and Webster 1987).

Comparative evaluation

From this information, a cost comparison similar to that used for direct substitution items can be derived. Comparing the cost of glucose derived from sugar cane or corn starch to that derived from lignocellulosics gives the ratios

$$(\text{glucose from sugar cane}/\text{glucose from lignocellulosics}) 0.08/0.032 = 2.50$$

$$(\text{glucose from corn starch}/\text{glucose from lignocellulosics}) 0.05/0.032 = 1.56$$

$$(\text{glucose from steam explosion}/\text{glucose from lignocellulosics}) 0.056/0.032 = 1.75$$

and when a risk factor of 1.3 is included, the ratios become

$$(\text{glucose from sugar cane}/\text{glucose from lignocellulosics}) 2.50/1.3 = 1.92$$

$$(\text{glucose from corn starch}/\text{glucose from lignocellulosics}) 1.56/1.3 = 1.20$$

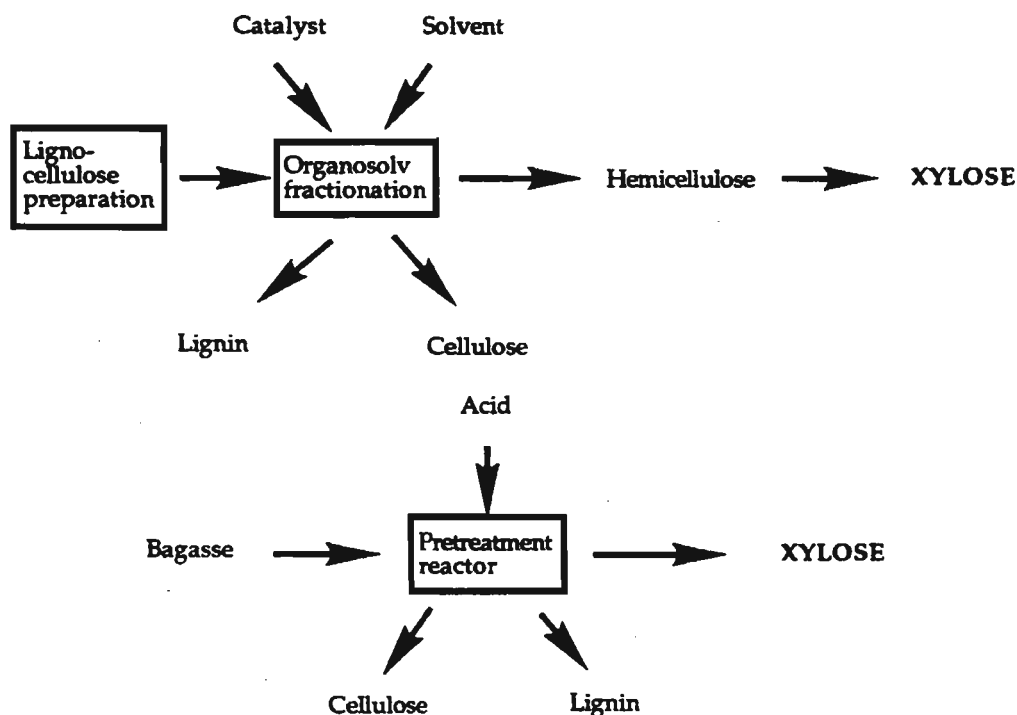
$$(\text{glucose from steam explosion}/\text{glucose from lignocellulosics}) 1.75/1.3 = 1.35.$$

Wood feedstock at \$40/dry ton is allocated on a weight basis to all three coproducts from the fractionation (cellulose, xylose, and lignin). This assumes that each of the coproducts can be upgraded to useful products that the market will consume.

The high value of these ratios, derived from actual laboratory results, indicates that clean fractionation could provide raw materials at a cost considerably lower than from conventional sources, providing that markets are found for consumption of all three coproducts. This process should be recommended for further investigation and application to synthesizing new materials, such as cellulose polymers such as acetates, propionates, rayons, etc., that require a high purity cellulose feed.

5.2.1.2 Xylose

Production Methods:



Xylose is produced by acid treatment of pentosans in lignocellulosics. Two processes were compared: converting the hemicellulose fraction derived from the NREL clean fractionation technology to xylose in a coproduct process with cellulose and lignin, and converting bagasse to xylose, using technology similar to that practiced by Quaker Oats in their process to make furfural.

Producing xylose from clean fractionation is projected to give xylose at a cost of \$0.032/lb, assuming all three coproducts (cellulose, xylose, and lignin) share costs on a pound basis, and can be upgraded to useful products. If only two of the coproducts can be consumed, the projected xylose cost rises to \$0.034/lb. By comparison, xylose produced from bagasse has a raw materials cost of \$0.09/lb, assuming bagasse is delivered at \$40/dry ton, and gives an overall yield of xylose of 75%. Comparing these results gives the ratios

$$\begin{aligned} &(\text{bagasse/lignocellulose, 3 coproducts}) 0.09/0.027 = 3.33 \\ &(\text{bagasse/lignocellulose, 2 coproducts}) 0.09/0.034 = 2.65 \end{aligned}$$

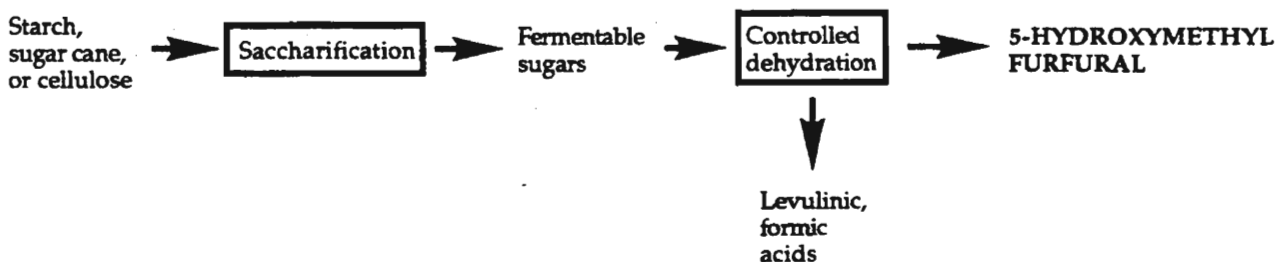
and when a risk factor of 1.3 is included, the ratios become

$$\begin{aligned} &(\text{bagasse/lignocellulose, 3 coproducts}) 3.33/1.3 = 2.56 \\ &(\text{bagasse/lignocellulose, 2 coproducts}) 2.65/1.3 = 2.04 \end{aligned}$$

These high values indicate that producing xylose by clean fractionation could compete very favorably with xylose prepared by conventional processes, and serve as a new low cost starting material for producing furfural, furfuryl alcohol, and tetrahydrofuran.

5.2.2 5-Hydroxymethylfurfural

Production method:



5-Hydroxymethylfurfural is a material that can be obtained by the controlled acidic dehydration of glucose or fructose. Further acid catalyzed dehydration leads to coproduction of levulinic and formic acids. A number of different materials could be derived from this functional monomer. Two sources of starting glucose (fermentable sugars) were considered in the comparison: glucose derived from corn starch, and glucose derived from the NREL clean fractionation. The raw material cost of 5-hydroxymethylfurfural from corn starch derived glucose is \$0.102/lb, assuming a 70% yield of 5-hydroxymethylfurfural from glucose dehydration, and a glucose cost of \$0.05/lb. In comparison, the cost of 5-hydroxymethylfurfural from clean fractionation glucose is \$0.065/lb, assuming a glucose cost of \$0.032/lb. Comparing the two glucose starting materials used gives the ratio

$$0.102/0.065 = 1.57$$

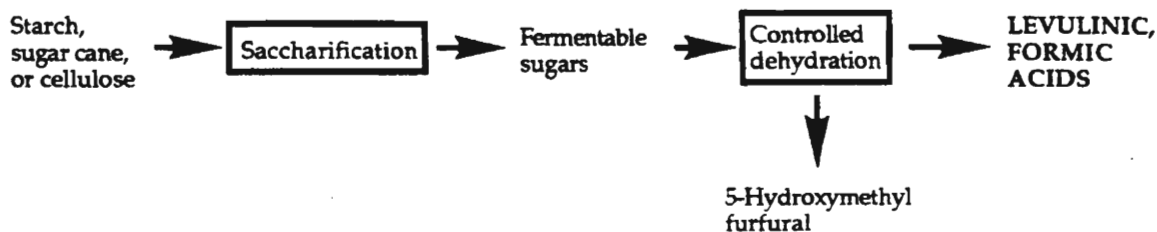
and when a risk factor of 1.3 is included, the ratio becomes

$$1.57/1.3 = 1.21.$$

This ratio indicates that glucose from clean fractionation can serve as a significantly lower cost feedstock for producing 5-hydroxymethylfurfural, and perhaps stimulate its consideration as a novel chemical building block.

5.2.3 Levulinic/Formic Acids

Production method:



Production method: Levulinic and formic acids can be produced as coproducts in a 72/28 mixture with 5-hydroxymethylfurfural from the controlled acidic dehydration of glucose or fructose.

Raw Material Cost Comparison: The comparison was made between producing levulinic and formic acids from corn starch derived glucose, and glucose prepared by the NREL clean fractionation process. Levulinic acid can be produced from corn starch derived glucose at a raw material cost of \$0.164/lb, assuming that glucose is available at \$0.05/lb, and a 70% yield in the conversion step. In comparison, levulinic acid prepared from clean fractionation glucose has a raw material cost of \$0.105/lb, assuming the same yield performance and a glucose cost of \$0.032/lb. Comparing these values gives the ratio

$$0.164/0.105 = 1.56$$

and when a risk factor of 1.3 is included, the ratio becomes

$$1.56/1.3 = 1.20.$$

This value indicates that producing levulinic acid from clean fractionation glucose could offer a lower cost product, increasing its use as a chemical feedstock.

Formic acid can be produced from corn starch derived glucose at a raw material cost of \$0.064/lb, given the same yield and cost assumptions as for levulinic acid. The cost from clean fractionation glucose is \$0.041/lb. Comparing these values gives the ratio

$$0.064/0.041 = 1.56$$

and when a risk factor of 1.3 is included, the ratio becomes

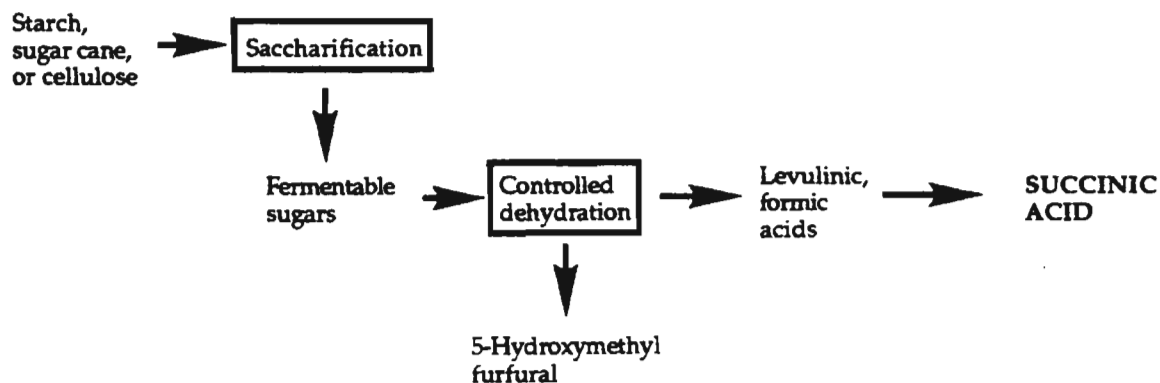
$$1.56/1.3 = 1.20.$$

The primary competition for formic acid will come from the petrochemical process. Current costs of petrochemical derived formic acid is about \$0.40 - 0.50/lb.

5.2.4 Succinic Acid

Production method:

From biomass:



From petrochemicals:



Production Methods: Succinic acid can be prepared from biomass from levulinic acid generated as a coproduct with formic acid and 5-hydroxymethylfurfural by dehydration of glucose. The commercial approach to succinic acid proceeds by reducing maleic anhydride (prepared by butane oxidation) to give succinic anhydride, followed by ring opening hydrolysis to give succinic acid.

Raw Material Cost Comparison: The cost of succinic acid prepared from biomass is projected to be \$0.09/lb, assuming an 83% yield for the oxidation of levulinic acid, and taking credit for the coproducts produced. The cost of succinic acid from petrochemicals is \$0.11/lb, assuming that maleic anhydride is available at \$0.125/lb, and the reduction and hydrolysis proceed in overall 95% yield. Comparing the biomass route to the petrochemical route gives the ratio

$$0.11/0.09 = 1.22$$

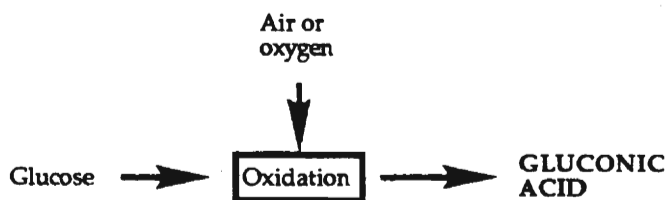
and when a risk factor of 1.3 is included, the ratio becomes

$$1.22/1.3 = 0.94.$$

This value indicates that producing succinic acid from biomass could compete with that derived from petrochemicals. Further investigation should be performed on the levulinic acid oxidation to verify the reported performance numbers.

5.2.5 Gluconic Acid

Production method:



Gluconic acid, produced by the oxidation of glucose, has its largest applications in the food and pharmaceutical industries. It has the potential of serving as a building block for a variety of materials if appropriate markets can be defined and a low cost source of glucose can be obtained.

Because of the technical simplicity and high yield (nearly quantitative) of the current route to gluconic acid, improvements will most likely be realized if a lower cost source of the glucose starting material is discovered. The clean fractionation of lignocellulosics being investigated at NREL holds the possibility of providing cellulose (the precursor to glucose) at a cost lower than other currently practiced methods. Thus, the costs of gluconic acid from two low cost glucose sources (corn starch and lignocellulose) were compared. The details for the cost contribution of glucose are given in section 5.2.1.

Glucose from Corn Starch

Glucose from corn starch is estimated to be available at \$0.049/lb. The raw material cost contribution to the cost of gluconic acid production is projected to be \$0.058/lb, assuming oxygen is available at \$0.10/lb, and the oxidation proceeds in 95% yield.

Glucose from Lignocellulosics

Producing glucose from the cellulosic fraction of lignocellulose derived from clean fractionation is projected to cost \$0.032/lb. The raw material cost contribution to the cost of gluconic acid production is projected to be \$0.040/lb, assuming oxygen is available at \$0.10/lb, and the oxidation proceeds in 95% yield.

Comparing the two costs gives the ratio

$$(\text{corn starch/lignocellulose}) 0.058/0.040 = 1.45$$

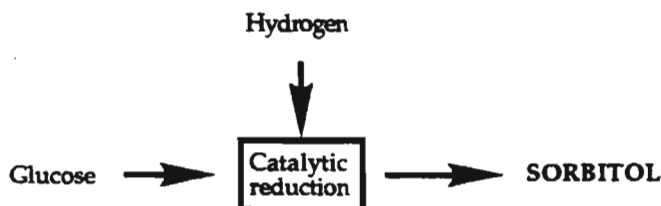
and when a risk factor of 1.3 is included, the ratio becomes

$$1.45/1.3 = 1.12.$$

This ratio suggests that changing the source of the glucose feedstock from corn starch to lignocellulose could result in a significant cost improvement in producing gluconic acid.

5.2.6 Sorbitol

Production method:



Sorbitol is currently made in very high yield from the catalytic hydrogenation of glucose. As in the case of gluconic acid, the technology for producing sorbitol is simple and affords product in high yield. The greatest chance for improving the technology resides in the identifying a less expensive source of glucose. Clean fractionation technology potentially offers the most inexpensive source of glucose of those studied. Two sources of glucose were compared for this evaluation.

Glucose from Corn Starch

Producing sorbitol from reduction of corn starch derived glucose is projected to give a raw material cost contribution of \$0.058/lb, assuming that hydrogen is available at \$0.54/lb, the reduction proceeds in 95% yield, and not including the cost of the catalyst.

Glucose from Lignocellulose

Producing sorbitol from reduction of lignocellulose derived glucose is projected to give a raw material cost contribution of \$0.034/lb, again assuming that hydrogen is available at \$0.54/lb, the reduction proceeds in 95% yield, and not including the cost of the catalyst.

A comparison of the two sorbitol costs gives the ratio

$$(\text{corn starch/lignocellulose}) 0.058/0.034 = 1.71$$

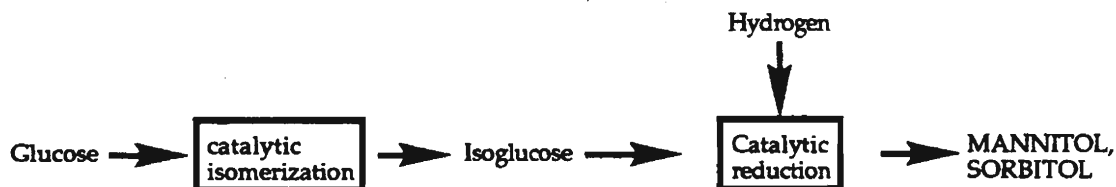
and when a risk factor of 1.3 is included, the ratio becomes

$$1.71/1.3 = 1.31.$$

This ratio suggests that changing the source of the glucose feedstock from corn starch to lignocellulose could significantly improve costs for producing sorbitol.

5.2.7 Mannitol

Production method:



Mannitol is available in about 30% yield from the catalytic hydrogenation of isoglucose derived by molybdate catalyzed isomerization of starch derived glucose. The remainder of the product mixture is sorbitol. Separation is normally not a problem because mannitol can be selectively crystallized from solution. The greatest opportunity for process improvement in mannitol production would arise from developing a more selective process (i. e., a lower proportion of sorbitol in the sucrose/fructose reduction mixture) along with a lower cost source of starting material, for example, glucose from cellulose derived from the NREL clean fractionation technology. The latter possibility has been examined by comparing the raw material cost for mannitol production from two different glucose sources.

Glucose from Corn Starch

Producing mannitol from reduction of corn starch derived glucose is projected to give a raw material cost contribution of \$0.065/lb, assuming that hydrogen is available at \$0.54/lb, a corn starch cost of \$0.05/lb, and not including the cost of the catalysts.

Glucose from Lignocellulose

Producing mannitol from reduction of lignocellulose derived glucose is projected to give a raw material cost contribution of \$0.043/lb, again assuming that hydrogen is available at \$0.54/lb, glucose is available from clean fractionation at \$0.032/lb, and not including the cost of the catalyst.

Comparing the costs of mannitol from the two different sources gives the ratio

$$(\text{corn starch/lignocellulose}) 0.065/0.043 = 1.51$$

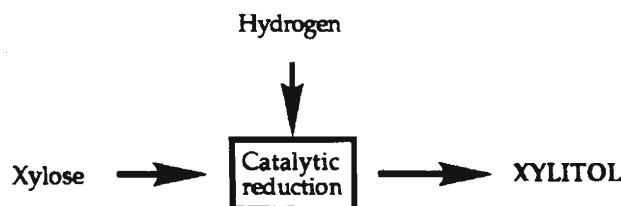
and when a risk factor of 1.3 is included, the ratio becomes

$$1.51/1.3 = 1.16.$$

This ratio suggests that changing the source of the glucose feedstock from corn starch to lignocellulose could significantly improve costs in producing mannitol.

5.2.8 Xylitol

Production method:



Xylitol can be produced in high yield by the catalytic reduction of xylose. As with other similar sugars, the process for its production is simple, and proceeds in high yield. Any improvements will come from reducing the costs of the starting material. A comparison of xylitol costs as a function of the method used for xylose production can be made. Two sources of xylose were compared: xylose prepared by conventional means from bagasse, and xylose prepared by acid treatment of the hemicellulose fraction of lignocellulose from the NREL clean fractionation technology.

Producing xylitol from reduction of bagasse derived xylose is projected to give a raw material cost contribution of \$0.103/lb, assuming that hydrogen is available at \$0.54/lb, and not including the cost of the catalyst. By comparison, xylitol produced by reduction of lignocellulose derived xylose will have a raw material cost contribution of \$0.037/lb. Comparing these results gives the ratio

$$(\text{bagasse/lignocellulose}) 0.103/0.037 = 2.78$$

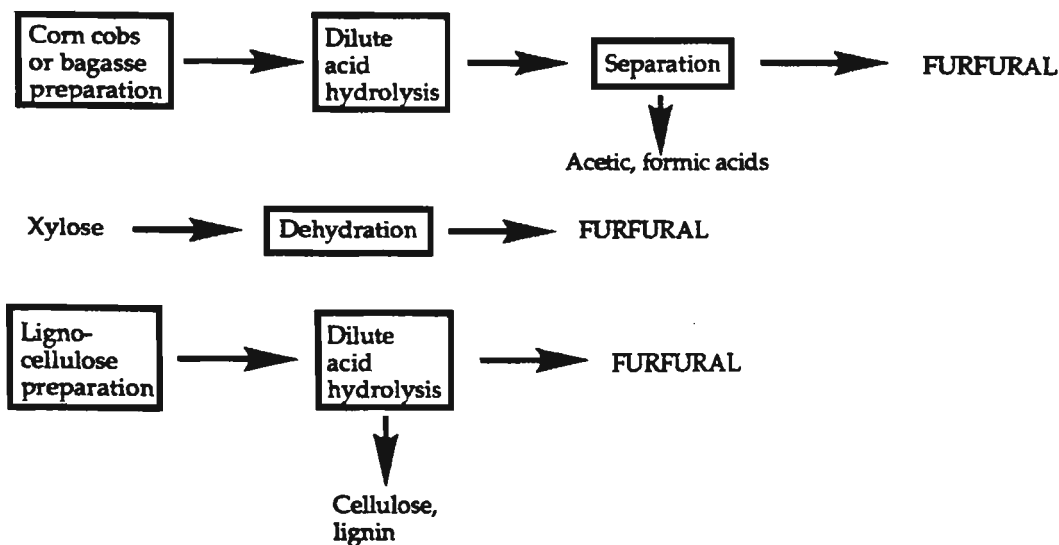
and when a risk factor of 1.3 is included, the ratio becomes

$$(\text{bagasse/lignocellulose}) 2.78/1.3 = 2.14.$$

This high value indicates that a significant cost advantage could be realized for producing xylitol from lignocellulose derived xylose.

5.2.9 Furfural

Production methods:



Furfural is produced commercially by the acid dehydration of corn byproducts, or similar lignocellulosics, and is a starting material for such high volume organics as adipic acid, maleic anhydride, and butanol. A coproduct fuels and chemicals process, generating ethanol and furfural from acid hydrolysis of lignocellulose, was investigated by NREL a number of years ago. The study estimated the potential future market for three commodity derivatives that could be competitively produced from furfural using existing technology. The results of the study are shown below.

<u>Chemical</u>	<u>Price (\$/lb)</u>	<u>Total Furfural Demand (tons/yr)</u>	<u>Total Revenue (millions of \$)</u>
Furfural	0.57	63,492	79.8
Adipic Acid	0.33	517,913	377
Maleic Anhydride	0.12	723,810	192
Butanol	0.09	1,521,088	302

The price of furfural was projected to drop over a period of about 10-15 years, as the volume of ethanol produced from the plant increased. As the price reached the levels shown, furfural would become a competing starting material for producing the chemicals shown in the first column, giving revenues as shown. A coproduct ethanol/furfural process could be an alternative source of adipic acid, maleic anhydride, and butanol and should be investigated further.

A raw material cost comparison can be made for furfural by comparing a furfural process based on xylose starting material derived from bagasse using conventional technology, versus xylose derived from the NREL clean fractionation process. Furfural can be produced from bagasse-derived xylose at a raw material cost of \$0.10/lb, assuming a feedstock cost of \$40/dry ton, and an 85% yield in the conversion. In comparison, the raw material cost for furfural derived from clean fractionation xylose is \$0.062/lb, assuming that xylose is available at \$0.032/lb and the conversion proceeds in 85% yield. Comparing these values gives the ratio

$$0.1/0.062 = 1.61$$

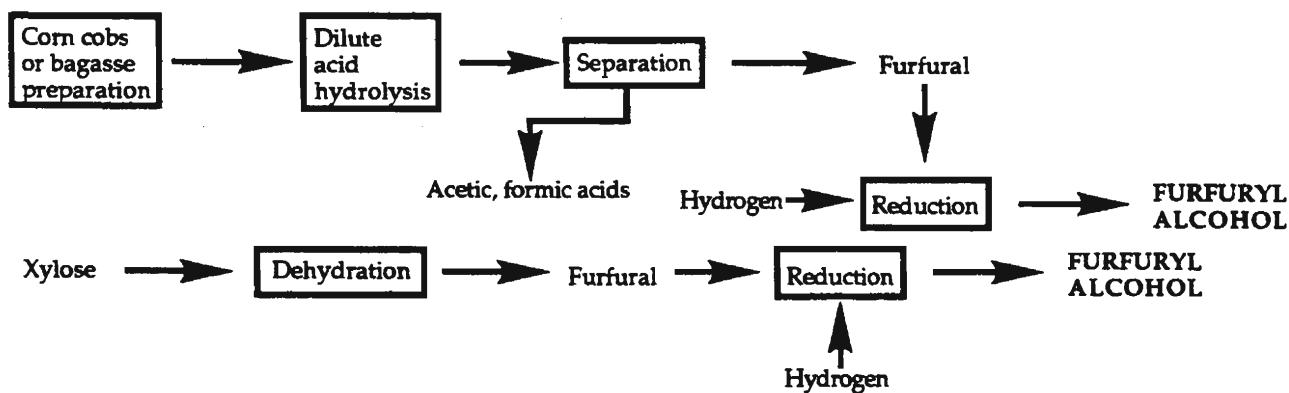
and when a risk factor of 1.3 is included, the ratio becomes

$$1.61/1.3 = 1.24.$$

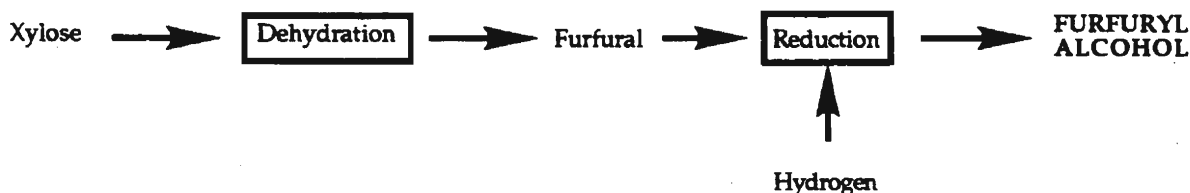
This value indicates that clean fractionation technology offers a lower cost source of furfural and could increase its value as a chemical feedstock for materials currently produced from petrochemicals.

5.2.10 Furfuryl Alcohol

Production methods, from corn or bagasse:



From Xylose:



Processes Compared: A major portion of the domestic furfural production is reduced in high yield to give furfuryl alcohol, an important component for the producing furan resins. The furfural market has been static for a number of years, but developing a new, cheaper starting material could give new impetus for its use. The NREL clean fractionation technology can provide inexpensive xylose, a starting material for furfural/furfuryl alcohol.

Raw Material Cost Comparison: The raw material cost for producing furfuryl alcohol from bagasse-derived furfural is \$0.116/lb, assuming furfural costs \$0.10/lb (including coproduct credits), and a yield in the reduction step of 95%. In comparison, the cost of furfuryl alcohol from clean fractionation xylose is \$0.066/lb, assuming furfural costs \$0.062/lb when produced from xylose, and a 95% yield in the reduction step. Comparing the bagasse route to the xylose route gives the ratio

$$0.116/0.066 = 1.76$$

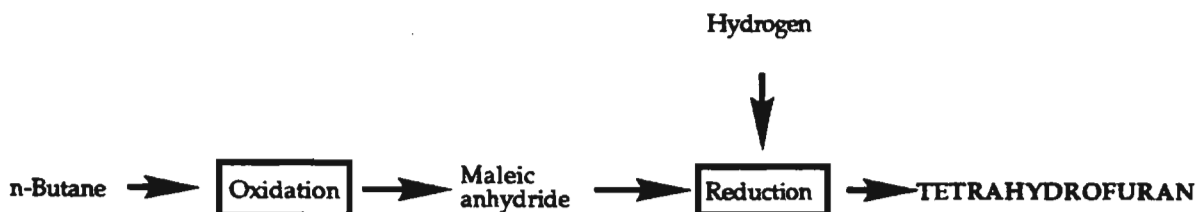
and when a risk factor of 1.3 is included, the ratio becomes

$$1.76/1.3 = 1.35.$$

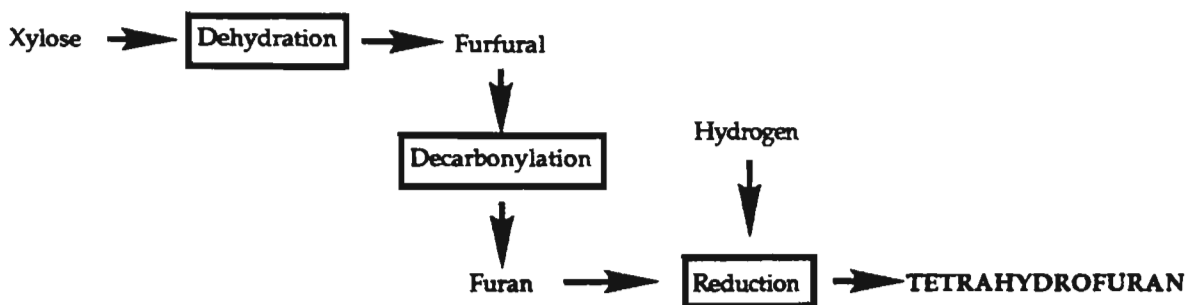
This value indicates that producing furfural would benefit by a change of starting material from bagasse to clean fractionation xylose.

5.2.11 Furan/Tetrahydrofuran (THF)

From petrochemicals:



From biomass:



Processes compared: Almost all THF is produced today from petrochemicals via 1,4-butanediol cyclization, acetylene/formaldehyde reaction (the Reppe process), and other processes. Successfully developing a process based on butane oxidation could potentially be a large scale producer of THF and was chosen for the comparison. The biomass-based route to THF begins with xylose, available from fractionation of lignocellulose. Tetrahydrofuran was once exclusively prepared from xylose, via converting and reducing furfural, available from agricultural wastes (corn cobs). Today, only about 10% of all THF production starts with furfural, since routes from 1,4-butanediol, and acetylene and formaldehyde cost less. However, the NREL clean fractionation technology has the potential to offer a low cost form of very pure xylose from lignocellulose. In addition, recent work at NREL has identified a high yield catalytic method for the converting furfural into furan.

Raw Materials Cost Comparison: The raw material cost for the producing THF from petrochemicals is projected to be \$0.108/lb, assuming that maleic anhydride is available at \$0.125/lb, hydrogen is available at \$0.54/lb, and the reduction proceeds in 90% yield. The raw material cost contribution for tetrahydrofuran produced using clean fractionation xylose as the starting material is \$0.117/lb,

assuming that the xylose is available for \$0.032/lb, converting to furfural proceeds in 85% yield, and subsequent conversion of furfural into tetrahydrofuran proceeds in 80% yield. Comparing these results gives the ratio

$$0.108/0.117 = 0.92$$

and when a risk factor of 1.3 is included, the ratio becomes

$$0.98/1.3 = 0.71.$$

This ratio suggests that THF produced from xylose could have a chance of competing with petrochemical derived THF, if the prices of the raw material feedstocks change, i. e., if the price of lignocellulosics drops or the price of petroleum rises.

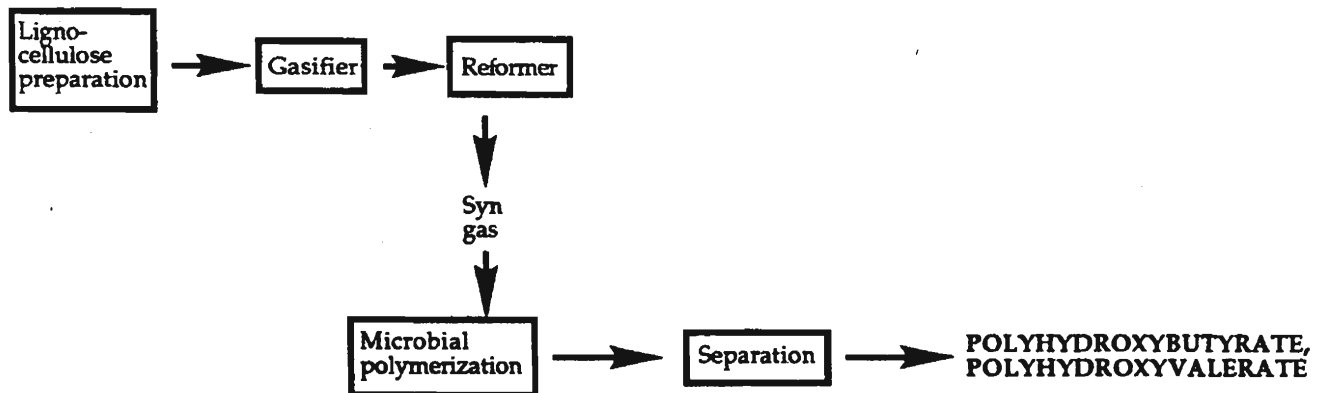
5.2.12 Polyhydroxybutyrate/Polyhydroxyvalerate (PHB/PHV)

Production Methods:

From glucose and propionic acid:



From synthesis gas:



Processes compared: PHB and PHV, thermoplastic polyesters, can be prepared microbiologically by reaction of glucose and propionic acid in an aqueous medium. More recently, a microbe has been identified that can produce PHB/PHV directly from synthesis gas. Biomass derived synthesis gas has been described as a cost effective starting material for producing acetic acid (section 5.1.12).

Raw Material Cost Comparison: The microbial polymerization produces about a 70/30 mixture of PHB/PHV, but for simplicity, the evaluation was performed assuming pure PHB would be produced. The raw materials for producing PHB/PHV were assumed to be glucose and purchased propionic acid. Assuming a cost of \$0.10/lb for glucose, \$0.40/lb for propionic acid, and a polymerization yield of 26 wt%, a raw material cost contribution of \$0.58/lb was derived. In comparison, the raw material cost for producing PHB/PHV from syn gas is \$0.10/lb, assuming wood feedstock costs \$40/dry ton, and a 32 wt% yield of PHB/PHV.

It is possible that conditions can be developed for *in situ* production of the propionic acid anaerobically from glucose. This possibility was not addressed. Comparing the glucose route to the syn gas route gives the ratio

$$0.58/0.10 = 5.8$$

and when a risk factor of 1.3 is included, the ratio becomes

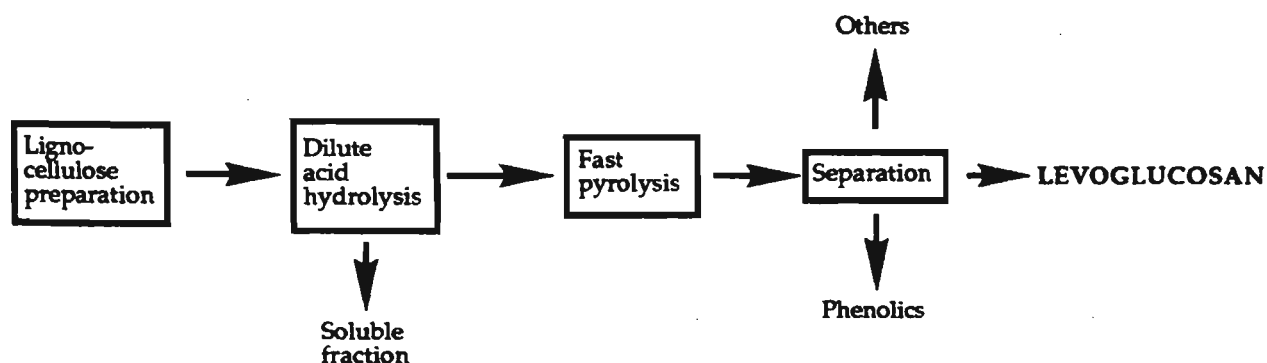
$$5.8/1.3 = 4.46.$$

If a less expensive source of glucose were used, the ratios would drop accordingly. This large value indicates that PHB/PHV could be produced much more economically from biomass derived synthesis gas than from a glucose/propionic acid starting material. Further investigation of this process is warranted, especially in separating the polymer from the microbial solution.

5.3 New Building Blocks/Products

5.3.1 Levoglucosan

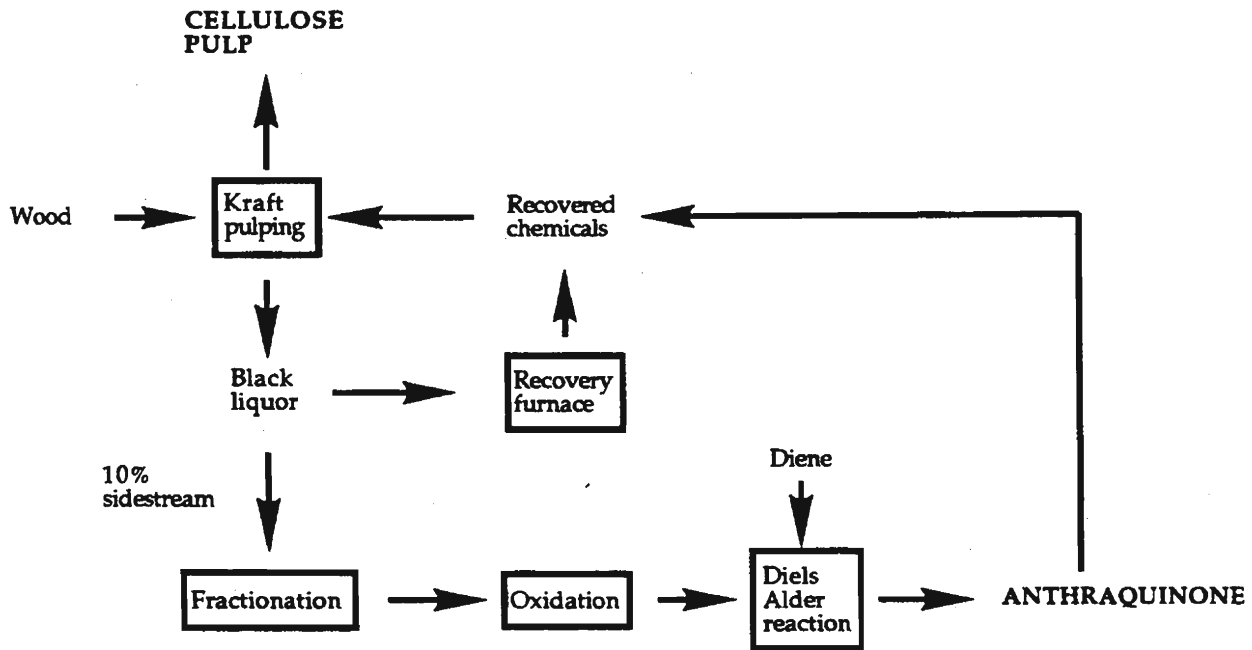
Production method:



Levoglucosan can be produced by the pyrolysis of acid treated lignocellulosics in 20-30% yield. Levoglucosan has traditionally been an expensive specialty material, but process improvements suggest that costs can be significantly reduced. Specific markets for using this new building block are being defined by industry (ACS Symposium on Levoglucosan and Levoglucosenone, 1992). If low cost levoglucosan can be obtained, it could serve as a starting material for producing new polymers or high value materials, and as a raw material for some of the sugar alcohols described above. A comparison of the raw materials cost for the production of levoglucosan from lignocellulosics versus starch has been carried out. Raw materials cost for producing levoglucosan from wood is estimated at \$0.054/lb, assuming wood feedstock costs \$40/dry ton, and a 22% yield. In contrast, producing levoglucosan from starch has a raw materials cost of \$0.38/lb, assuming corn starch to be available at \$0.08/lb. The lignocellulosic pyrolysis has a significant cost advantage that is aided by sharing the raw materials cost with coproduct phenolics. Levoglucosan is currently considered an important raw material for further investigation.

5.3.2 Cellulose (Kraft)/Anthraquinone

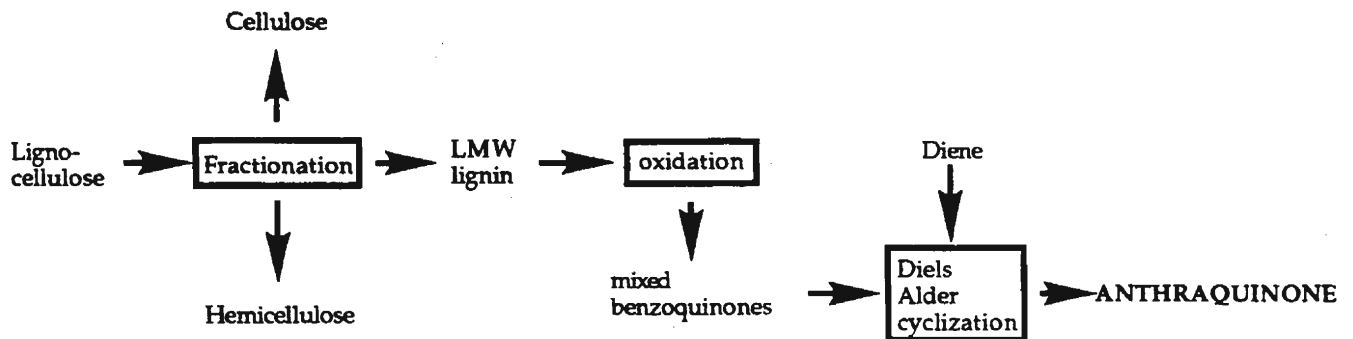
Production method:



An alternative method investigated for the production of anthraquinone from biomass derived lignin envisions building a small anthraquinone production facility on the site of an existing kraft mill. The operation would be supplied with a 10% sidestream of kraft black liquor and convert it to anthraquinone. The remaining black liquor would be treated as usual to provide fuel and recover pulping chemicals for the operation. The produced anthraquinone would be fed into the operation as a catalyst. Investigating the costs of such an operation reveal that the scale would be too small to be economical. An alternate scenario envisions building a single standalone anthraquinone plant in a location convenient to a number of pulp mills. The plant would receive black liquor and convert it not only to anthraquinone, but to other lignin derived products. This allows a much larger plant to be built and realize the economies of scale. The details of this evaluation are found in section 5.4.1.

5.3.3 Cellulose (Organosolv)/Anthraquinone

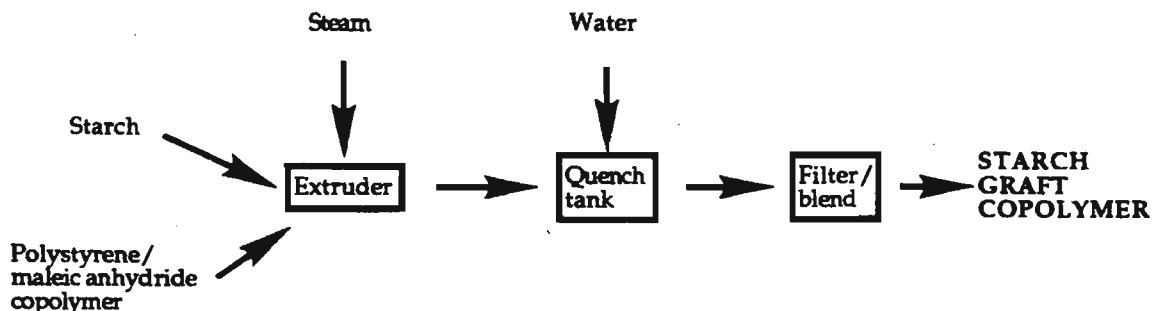
Production method:



As described in section 5.1.14, anthraquinone can be derived from organosolv fractionation of lignocellulosics by chemically transforming the lignin stream of the process. The process also offers two other product streams for use as chemical feedstocks. The cellulose fraction can be used as a feedstock for lower grade paper products, or blended with other celluloses, for example, from a conventional kraft operation. The ability of this clean fractionation process to provide three products that can be absorbed by the chemical market allows raw material costs to be shared between the products, resulting in a lower overall raw material cost. This process is described in greater detail in section 5.4.1.

5.3.4 Starch Plastics

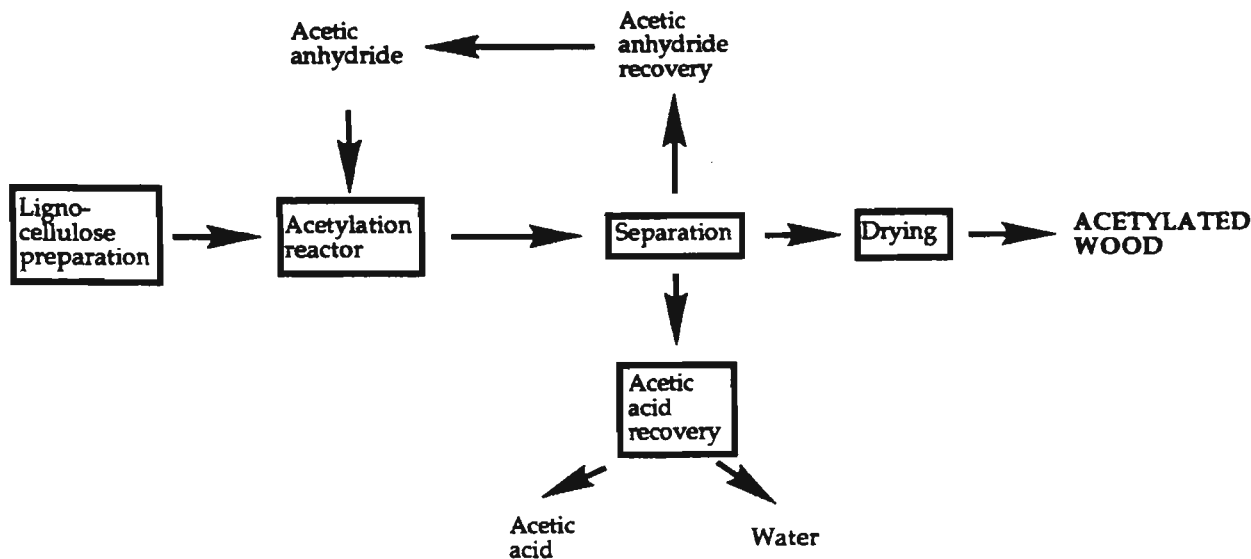
Production method:



A family of biodegradable graft copolymers can be prepared from the coextrusion of starch and a polystyrene/maleic anhydride copolymer. This product could be of use in producing new thermoplastic materials and compatibilizers for blends of cellulose and starch with plastics. The process evaluated was developed by Ramani Narayan and coworkers at the Michigan Biotechnology Institute. Because of proprietary information involved in the work, no details are presented here but overall costs are given in section 5.4.5.

5.3.5 Acetylated Wood

Production method:



Treating wood with acetic anhydride gives a material that shows much greater dimensional stability and resistance to biological degradation, properties that significantly broaden the potential market

applications of products made from acetylated wood. The process also produces acetic acid as a coproduct, the cost of which can be taken as a byproduct credit in calculating process economics. The details of the evaluation are described in section 5.4.4. Rowell describes wood acetylation in detail (Rowell 1992). The technoeconomic assessment of this concept was described by Chum and Power (H. L. Chum and A. J. Power in Rowell 1992) for two cases of particles and fibers.

5.4 Selected Detailed Production Cost Estimates

Evaluations based on raw materials cost contributions provide an initial screening method to determine whether a given chemical could be produced in a cost effective manner from renewable feedstocks. However, we have also carried out a more in-depth technoeconomic evaluation of the most promising candidates identified by raw materials cost comparison through preliminary plant design to estimate capital and operating costs. Combining these costs with the raw material costs of the process chemistry leads to a total amortized production cost of the material. This section summarizes the results of these more detailed screenings of several of the most promising candidates. A tabular summary of the major cost contributors to the amortized production cost of each is given in Table 5.2.

The choice of which chemicals or processes to evaluate in this section was based on several criteria, but two are most important. First, the ratio of the raw material cost contribution, petrochemical/biomass, needed to be favorable. As described in section 4., the screening, based on raw material costs, serves as a "pointer" to identify opportunities with particular promise. However, a favorable ratio also needs to be combined with sufficient process information, based on actual laboratory or development experience, to make the more detailed evaluation credible. For example, the petrochemical/biomass ratio for vinyl phenol (section 5.1.8) is 7.40, the highest of all the candidates evaluated. However, the process parameters for vinyl phenol production are only beginning to be defined. Considerable laboratory work is still needed before a reasonable projection of capital and operating costs can be made. Conversely, producing phenolics by pyrolysis had a much lower ratio, 1.17, but is considered an excellent candidate for a more detailed analysis. Many years of experience at NREL in running the process on a multipound scale has given process parameters that can be used with confidence in preparing a detailed economic projection.

The processes described in this section are listed according to category (direct substitution, improved production, new building blocks/products). We believe that each of these chemicals or processes represents a promising opportunity and no attempt is made to favor one over another. The reader is expected to bring his or her own criteria to these evaluations and decide if any of the processes fits their current needs.

5.4.1 General Information

Each of the evaluations summarized in this section followed the same general procedure:

- a. Drawing the flow diagram (for each new base case)
- b. Calculating the material balance
- c. Calculating the energy balance
- d. Estimating equipment sizes
- e. Estimating the capital costs
- f. Estimating the operating costs
- g. Evaluating economics and potential profitability
- h. Defining and evaluating of variations on the base cases
- i. Developing conclusions and recommendations

This group of tasks is commonly known as preliminary chemical process design; it is significantly more rigorous than "back-of-the-envelope" approaches, but is short of capital budget quality work. The degree of detail in each step can vary considerably, usually depending on the availability and quality

Table 5.2 - Summary of Key Economic Contributors to Amortized Production Costs from Phase II Analysis

<u>Process Evaluated</u>	<u>Capital Investment</u> (millions of dollars)	<u>Annual Production</u> (millions of pounds)	<u>Raw Materials (\$/lb)</u>	<u>Capital Costs (\$/lb)</u>	<u>Operating Costs(\$/lb)</u>	<u>Total Cost(\$/lb)</u>
Anthraquinone						
from kraft lignin	10.7	19.3	0.836	0.084	0.125	1.045
from organosolv	12.7	19.3	0.592	0.098	0.125	0.815
Phenolics from Fast Pyrolysis	34.0	140	0.094 ¹ 0.024 ²	0.037 0.032	0.034 0.042	0.165 0.098
Phenolics from Wood Phenolation	33.8	140	0.166 ^{1,3} 0.153 ^{2,3}	0.048 0.048	0.036 0.036	0.250 0.237
Clean Fractionation 3 coproducts, cellulose, hemicellulose, lignin	54.6	1,248	0.032	0.006	0.018	0.056
Acetylated Wood Particle Feedstock	30.1	500	0.089 ⁴	0.004	0.004	0.097
Fiber Feedstock	46.4	500	0.089 ⁴	0.005	0.017	0.111
Veneer Feedstock	44.4	500	0.089 ⁴	0.005	0.017	0.111
Starch Plastics						
Base case 1	17.2	10	0.62	0.22	0.63	1.47
Base case 2	7.7	10	0.62	0.13	0.16	0.91
Base case 3	2.8	10	0.71	0.04	0.084	0.83

Notes: ¹Wood chips purchased at \$40/dry ton

²Wood chips purchased at \$10/dry ton

³Phenolation agent is 20% distilled phenolics fraction (or phenolics/ neutrals oils) at \$20/ton transfer cost

⁴Includes byproduct credit of \$0.055/lb

of basic process chemistry information. Approximate, short-cut design and costing methods are used because they conserve time and are more than adequate to identify areas for further research or more detailed calculation. In addition, the type of preliminary design and economic analysis described here can direct research time and funding to those areas that have the most impact on the process economics.

Because process design is an iterative process, these evaluations are part of a continuing succession of increasingly refined, focused, and detailed designs. The results of this study could be used to convey most of the basic information industrial developers of chemicals from renewables need to make in-house studies of potential long-term profitability in terms of their proprietary business plans.

5.4.2 Detailed Process Analysis - Anthraquinone (AQ) from Low Molecular Weight Lignin

The first evaluation, a technoeconomic investigation of producing AQ from lignin, is presented in more detail *only* to give a sense of the process and the salient features used in developing these more detailed evaluations. AQ is of potential use as a pulping catalyst in the pulp and paper industry, but is not yet widely used because its cost is too high (about \$4.00-\$4.50/lb). The key features to note are the development of possible overall approaches to AQ (development of "base cases"), the assumptions necessary to prepare the base cases, and the economic data that arises from evaluating the base cases.

5.4.2.1 Definition of Process Chemistry

The most important portion of the evaluation is a clear definition of the process chemistry, because all projections depend on the yield, efficiency and number of steps required to transform a renewable feedstock into a given chemical. The block diagrams describing the process chemistry of the lignin-to-AQ process were presented in section 5.1.14. The following performance assumptions were made:

For the process based on organosolv lignin, it is assumed that:

1. The LMW lignin will be obtained directly from an extraction/solvent recovery system of an organosolv pulping mill (using the NREL clean fractionation technology) to give a net delivered cost of \$0.016/lb, after \$300/ton credit for pulp and \$0.025/lb credit (fuel) for hemicellulose and extractives.
2. A 40% chemical yield of benzoquinones will result in the first step of the process upon oxidation of LMW lignin.
3. The oxidation will proceed with 10% losses of NO_2 , the chosen oxidant for the evaluation.
4. A 50% chemical yield of AQ or AQ like materials will occur upon reaction of the benzoquinones with the chosen diene for the evaluation, isoprene.
5. The reaction of isoprene with the benzoquinone mixture will occur with 50 wt % efficiency.

For the process based on kraft lignin, it is assumed that:

1. The lignin raw material is obtained by diverting a 10% sidestream of concentrated black liquor from seven 1500 tpd kraft pulp mills.
2. LMW lignin will be recovered at each mill by ultrafiltration from concentrated kraft black liquor (35% total solids) to give a filtrate containing 25% of total solids fed, 72% of which is LMW lignin; the LMW lignin will be recovered as a dry product via flash drying and shipped to a central AQ plant at a total delivered cost, derived from approximation from past studies of about \$0.18/lb, that includes the various combinations of extraction (conventional and/or supercritical), acid precipitation, and drying operations that are required.
3. A 30% chemical yield of benzoquinones will result in the first step of the process upon oxidation of LMW lignin.
4. The oxidation will proceed with 10% losses of NO_2 , the chosen oxidant for the evaluation.
5. The benzoquinones will be converted to AQ or AQ like materials in 80% chemical yield.
6. Converting isoprene will proceed with 50 wt % efficiency.

5.4.2.2 Definition of Base Cases

Laboratory results obtained to provide information for this evaluation suggested defining two base cases for technoeconomic evaluation. The first is based on organosolv lignin and the other is based on using kraft lignin as a starting material. All base cases generally follow the two-stage process described in section 5.1.14. The primary difference between the black liquor and the organosolv case is in the lignin processing stage. The organosolv case proceeds by separating and using a LMW lignin fraction, produced directly using the NREL clean fractionation technology. Note that by definition each of these base cases offers broad foundations for further discussion.

Within each base case is the ability to manipulate the evaluation for different possible operating scenarios and give the answers to various "what-if" questions such as:

- a. What performance, i.e., efficiencies, rates, costs, etc., must this process achieve to be a commercial success?
- b. Can the required performance be accomplished without violating fundamental limitations, such as the laws of thermodynamics?
- c. What additional developments are needed to achieve the required performance?
- d. What are the prospects for improvements in the process?

All cases describe large-scale, stand-alone plants, sized to supply AQ by distribution to a significant part of the entire pulping industry, and are based on built-up process flow diagrams, principal stream material balances, and preliminary major equipment design.

A plant capacity basis of 19,300,000 lb/year of AQ was developed and used for each base case as a representative large capacity that would supply a significant part of the pulping industry. A capacity in the range of 19,300,000 lb/year of AQ was considered a reasonable basis because the ultimate AQ demand of the industry could be in the 100,000,000 lb/year range. The scale of 100,000,000 lb/year of AQ in a single plant located in the southeastern United States is based on the assumption that half of all Canadian and United States sulfate pulp production would convert to AQ, using 0.1% of AQ based on wood feed. The basis is projected to be 50,000,000 tons per year (tpy) of pulp in the late 1990s, with wood feed of 100,000,000 tpy, assuming 50% yield of pulp.

A number of other operating assumptions are necessary to complete this evaluation and are shown in Table 5.3. While certain specific values for these parameters may differ from evaluation to evaluation, the table gives a sense of the types of information used in these more detailed evaluations.

5.4.2.3 Results of Evaluation

Completing a more detailed process evaluation gives a number of useful pieces of information. Figure 5.2 shows a comparison of the projected raw materials costs (calculated in section 5.1.14) of the two base cases studied to the projected amortized production cost of AQ. Tables 5.4 and 5.5 summarize the overall projected raw material, capital, and operating costs for the base cases.

5.4.2.4 Evaluation of Competing Routes to AQ

A more detailed analysis can project the amortized production costs of competing routes to AQ and give an indication of how a biomass based route would fit into the market. Five potential petrochemical based competitors were identified from the open and patent literature and were subjected to the same detailed process analysis as AQ. The results of the evaluation are summarized in Figure 5.3, and the processes evaluated are shown in block form in Figure 5.4. Overall, this more detailed analysis indicates that AQ-from-lignin is a highly promising candidate for further R&D investigation. The process offers an approach to a potentially useful material at a projected cost substantially less than other routes.

Table 5.3- Additional Assumptions for Process and Capital Cost Evaluations

Zero time construction period.

Timing of investment	All investments occur at start of construction.
Interest rate during construction	Zero, because of zero construction time.
Plant capacity factor	Typically 0.9, although it may be set to suit the system.
Long-term return on investment	15% for all systems before taxes. Sensitivity of price to higher returns will be investigated later when process is better defined.
Equity	None; all capital is borrowed.
Source of financing	All money obtained at the same interest rate.
Income taxes	None; analyses are for production costs only.
Timing of costs	Operating expenses paid at end of year; payments to debt paid at end of year.
Working capital	Available at completion of construction, and recovered at end of project life; consisting of: <u>Feedstock Inventory</u> - one week's supply at cost; <u>Product Inventory</u> - two weeks supply at production costs, products, and by-products; <u>Accounts Receivable</u> - one month's production costs; <u>Cash</u> - one week's production costs less depreciation; less <u>Accounts Payable</u> - one month's supply raw materials at cost.
Debt recovery	Debt repaid in uniform series of annual payments of principal and interest.
Plant lifetime	20 years
Base rate, salary	Operating labor: \$28,700/year Foremen:\$32,500/year Supervisors:\$39,500/year
Labor burden (fringes)	45% operating labor plus supervision.
Administration and general overhead	65% total operating and supervisory labor including overhead.
<u>Utilities and Chemicals - Unit Costs</u>	
Electric power	\$0.035/kWh.
Steam, 100 psig	\$3.90/thousand pounds
Cooling water	\$0.06/thousand gallons
Process water	\$1.25/thousand gallons
LMW lignin, <u>Organosolv</u>	\$0.016/lb
LMW lignin, <u>Black Liquor</u>	\$0.18/lb
Methanol	\$0.10/lb
Nitrogen dioxide	\$0.30/lb
Oxygen	\$0.025/lb
Isoprene	\$0.285/lb
Residual organics (fuel)	\$0.025/lb

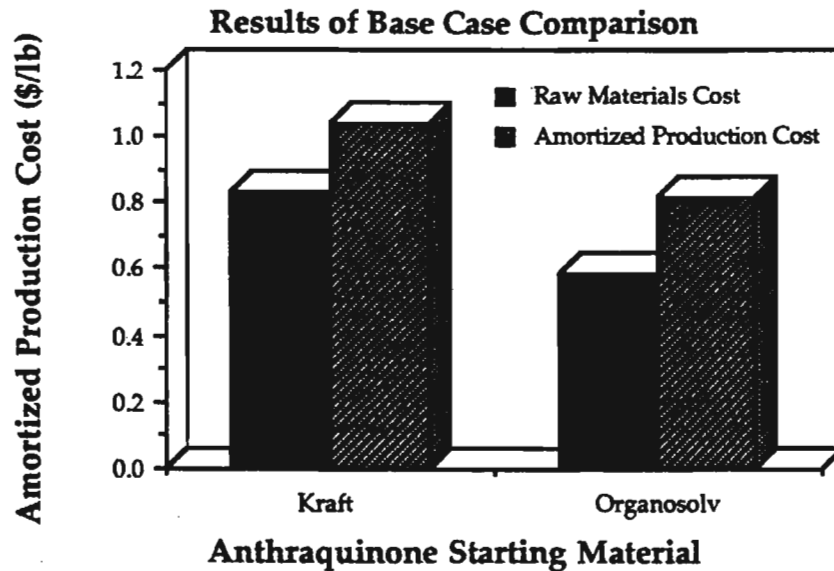


Figure 5.2 - Comparison of Costs; Base Cases for Anthraquinone Production

Table 5.4- Comparative Summary of Base Case Capital Investments (Millions of \$)

	<u>Organosolv</u>	<u>Kraft Black Liquor</u>
Major Equipment Cost	2.1	2.1
Installation Costs	0.3	0.3
Piping	1.0	1.0
Instrumentation	0.2	0.2
Buildings/Structures	0.2	0.2
Auxiliaries	0.5	0.5
Outside Lines	0.2	0.2
Engineering/Contingencies	2.3	2.3
Offsites	1.9	1.9
Total Fixed Investment	8.8	8.8
Working Capital	3.9	1.9
Total Utilized Investment	12.7	10.7

Table 5.5 - Comparative Summary of Base Case Costs of Production (\$/lb of Product)

	<u>Organosolv</u>	<u>Kraft Black Liquor</u>
Raw Materials	0.592	0.836
Utilities	0.028	0.028
Operating Costs/Expenses	0.097	0.097
Production Cost	0.718	0.958
Capital Charges	0.098	0.084
Amortized Production Cost	0.816	1.042

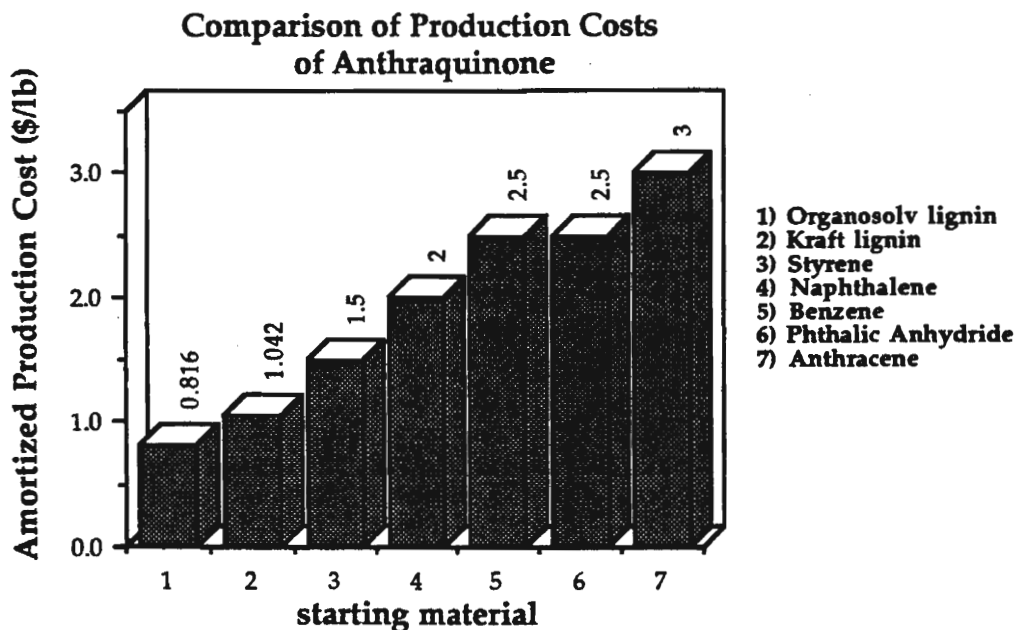


Figure 5.3- Amortized Production Costs of AQ from Different Starting Materials.

From Styrene



From Phthalic Anhydride



From Naphthalene/Butadiene



From Anthracene



From Benzene/Phthalic Anhydride



Figure 5.4 - Alternative Routes to Anthraquinone

5.4.3 Detailed Process Analysis - Phenolics from Biomass by Pyrolysis and Wood Phenolation

Pyrolysis of lignocellulosic feedstock has been demonstrated at NREL to be effective for producing a number of different materials. Fast pyrolysis processes offer the advantage of high yields of liquid products from different feedstocks (Bridgewater 1988; Soltes 1988; Hogan 1990; Overend 1985). In these processes, pyrolysis temperatures are 450°-600°C, and residence times are on the order of seconds.

Solvolytic of wood is an alternative route to substituted phenolics. If carried out in a range of high severities, at moderate temperatures, and long residence times, solvolysis yields reactive wood tars or pastes, principally if phenol is used as a solvent. Lower severities give a phenol pulping process (Lipinsky 1983), and at high severities, wood liquefaction occurs (Shiraishi 1986, 1987). These processes both introduce phenols into the α - or β -position of the side chains of the phenylpropane units, in addition to acid-catalyzed ether cleavages at both α - and β -aryl ether linkages of the lignin units.

A more detailed process analysis of this process based on some of the published results, and also on some more recent experimental findings (Johnson 1990), has been carried out. A definition of the process chemistry in the literature was found to be sketchy. The following conditions were assumed: the plant was sized to consume 1000 tons/day of wood feedstock. Wood phenolation is operated with a mixture of 20% of the low-molecular-weight phenolics recovered from the pyrolysis/fractionation process, instead of the more expensive purchased phenol. The liquor-to-wood ratio is 5:1; water is found to be necessary for the reaction to occur. The temperature is 250°C for 120 min (600 psi steam). About 70% soluble oils are obtained. The incorporation of phenolics is assumed at about 60%. An alternative would have been to use the low-molecular-weight phenolics fraction distilled from the phenolation process. This technology was then compared to producing phenols by fast pyrolysis.

The amortized production cost of this wood phenolation product is estimated at \$0.25/lb (see Table 5.2). This estimate is approximate because the published data do not contain sufficient detail for a more complete technoeconomic assessment at this point. However, this production cost value, with an uncertainty of about 40%, is close enough to that of the products derived from the fast pyrolysis and fractionation above to indicate that the phenolation process is potentially competitive. The published data on the reactivity and resin formulations suggest that the process has economic promise.

This analysis for the producing phenolics by fast pyrolysis indicates that waste sawdust can be converted into phenol replacements at \$0.10-\$0.27/lb. In this evaluation, feed cost varied from \$10-\$40/dry ton, plant life from 10-20 years, and return on investment from 15%-30%. The evaluation was performed assuming a plant would use 1000 tons/day of feedstock, producing 140,000,000 lb/yr of pyrolysis oils. This plant size corresponds to a relatively large resin production plant. The procedure followed for the evaluation was described in section 5.4, and the process chemistry described in section 5.1.6. The results of the evaluation are shown in Tables 5.6 and 5.7.

Considering the range of phenol costs (\$0.3-0.4/lb), depending on economic conditions and oil prices, these results indicate that phenolics from these processes could be inexpensive substitutes for a portion of phenol currently derived from petrochemicals. Smaller scale plants are possible but the amortized production costs double. The process is attractive when wood feedstock is available at \$40/ton.

5.4.4 Detailed Process Analysis - Clean Fractionation of Lignocellulosics

NREL is developing a process to cleanly fractionate wood into its three major components: cellulose, hemicellulose, and lignin for use in producing a number of chemicals evaluated in the raw materials cost comparison. This summary describes the projected amortized production cost for the three components. Since the patent protection is currently being filed for the process, fewer details can be revealed than in other processes. The plant evaluated is projected to produce 660,000,000 lb/yr of cellulose, 256,200,000 lb/yr of hemicellulose (as xylose) and 332,700,000 lb/yr of lignin. The process chemistry is shown in block form in section 5.3.2. A summary of the amortized production costs is given in Tables 5.8 and 5.9.

Table 5.6 - Summary of Base Case Capital Investments (Millions of \$)

Major Equipment Cost	7.4
Installation Costs	1.1
Piping	3.3
Instrumentation	0.8
Building and Structures	0.8
Auxiliaries	1.8
Outside Lines	0.8
Total Direct Cost	16.0
Engineering/Contingencies	7.9
Offsites	6.6
Total Fixed Investment	30.5
Working Capital	3.5
Total Utilized Investment	34.0

Table 5.7 - Summary of Base Case Costs of Production (\$/lb of Product)

Raw Materials (wood waste @ \$40/ton)	0.094
Utilities	0.007
Operating Costs/Expenses	0.027
Production Cost	0.128
Capital Charges	0.037
Amortized Production Cost	0.165

Table 5.8 - Summary of Base Case Capital Investments (Millions of \$)

Costs Inside Battery Limits	37.3
Offsites	11.2
Total Fixed Investment	48.5
Working Capital	6.1
Total Utilized Investment	54.6

Table 5.9 - Summary of Base Case Costs of Production (\$/lb of Product)

Raw Materials	0.032
Utilities	0.014
Operating Costs/Expenses	0.004
Production Cost	0.05
Capital Charges	0.006
Amortized Production Cost	0.056

5.4.5 Detailed Process Analysis - Acetylated Wood

Acetylation of wood imparts added chemical and biological resistance to wood fibers. Products made from acetylated wood show:

- 1) high dimensional stability both in the thickness and lineal directions
- 2) a high level of rot resistance
- 3) a low degree of thermal expansion
- 4) smooth surfaces that do not require further sanding
- 5) a uniform density throughout the product wall
- 6) no increase in toxicity of the wood
- 7) high strength—both wet and dry
- 8) a high degree of UV radiation stability
- 9) no change in flammability.

Acetylated veneers can be pressed along with the acetylated fiber mat to yield veneer-faced fiber-backed products (Rowell, in Chum 1989).

A more detailed assessment of the acetylation of wood process was made using the methodology described for anthraquinone. The financial results of the study are summarized in Tables 5.10 and 5.11 that present the estimated capital and processing costs for each of the three general classes of feedstocks. The plant evaluated was projected to produce 500,000,000 lb/yr of acetylated wood. The evaluation considered treating three different materials: wood particles, fibers, and veneers. Note that a byproduct credit can be taken for the acetic acid produced. The process based on particles has the lowest fixed investment, about 50% of the level required for processing fibers. Particles processing is simpler in the solids-handling operations and requires less specialized equipment.

Processing costs are dominated by the net cost of the acetic anhydride raw material, that corresponds to the total acetic anhydride cost minus the acetic acid by-product cost ($14.4 - 5.5 = 8.9$ cents per pound of the product), that is assumed to be the same for these feedstocks. This element of cost is 96% in the case of fibers. The latter case is higher-cost principally because it requires more operators in the more-complex solids-handling systems, with their expensive equipment. In both cases, acetic anhydride was assumed to be purchased at \$0.22 per pound and acetic acid was credited at \$0.10 per pound. The process description is given in section 5.3.6, and the results of the evaluation are given in Tables 5.10 and 5.11.

Table 5.10 - Comparative Summary of Base Case Capital Investments (Millions of \$)

	<u>Particles</u>	<u>Fibers</u>	<u>Veneers</u>
Major Equipment Cost	3.8	7.7	8.2
Installation Costs	0.6	1.1	1.0
Piping	1.7	3.4	2.9
Instrumentation	0.4	0.8	0.6
Buildings/Structures	0.4	0.8	0.6
Auxiliaries	0.9	1.9	1.6
Outside Lines	0.6	1.1	1.0
Engineering/Contingencies	4.2	8.4	7.9
Offsites	3.5	7.0	6.6
Total Fixed Investment	15.9	32.3	30.3
Working Capital	14.1	14.1	14.1
Total Utilized Investment	30.0	46.4	44.4

Table 5.11 - Comparative Summary of Base Case Costs of Production (\$/lb of Product)

	<u>Particles</u>	<u>Fibers</u>	<u>Veneers</u>
Raw Materials	0.14	0.14	0.14
Utilities	0.0	0.009	0.008
Operating Costs/Expenses	0.004	0.008	0.009
Byproduct Credits	(0.055)	(0.055)	(0.055)
Production Cost	0.093	0.106	0.106
Taxes/Depreciation	0.004	0.005	0.005
Amortized Production Cost	0.097	0.111	0.111

5.4.6 Detailed Process Analysis - Starch Plastics

Starch acetate and a maleic anhydride/styrene copolymer can be extruded to give a new biodegradable material. Since portions of this work are proprietary, some details cannot be revealed in this evaluation. Three base cases were evaluated in this study to give a comparison of the projected amortized production costs. The plant was projected to produce 10,000,000 lb/yr of graft copolymers. The results of the evaluation are shown in Tables 5.12 and 5.13.

Table 5.12 - Comparative Summary of Base Case Capital Investments (Millions of \$)

	<u>Base Case 1</u>	<u>Base Case 2</u>	<u>Base Case 3</u>
Cost Inside Battery Limits	14.3	4.8	2.3
Offsites	2.9	2.9	0.5
Total Fixed Investment	17.2	7.7	2.8

Table 5.13 - Comparative Summary of Base Case Costs of Production (\$/lb of Product)

	<u>Base Case 1</u>	<u>Base Case 2</u>	<u>Base Case 3</u>
Raw Materials	0.62	0.62	0.71
Utilities	0.38	0.04	0.004
Operating Costs/Expenses	0.25	0.13	0.08
Production Cost	1.25	0.78	0.79
Taxes/Depreciation	0.22	0.13	0.04
Amortized Production Cost	1.47	0.91	0.83

6.0 BIOPROCESSING ROUTES TO CHEMICALS AND MATERIALS

6.1 Introduction and Rationale

Harnessing the activities of microorganisms has been one of humanity's greatest scientific and technical achievements. Microbial fermentations have been used for millennia to enhance food products (consider bread, wine, and cheese) and early in this century, microbial fermentations were a major source of commodity chemicals and fuels such as butanol and acetone. Increases in the cost of biological feedstocks and the evolution of the petrochemical industry after World War II rendered these latter processes economically uncompetitive (Jones and Woods 1986).

In the past decade, researchers have made many technological advances that promise, in concert, to significantly improve the economic competitiveness of biobased processes. Evaluation of this window of opportunity focuses on the inherent attributes of biological processes, the application of new technology to overcome past limitations, and integration with nonbiological process steps.

Fermentation processes involve chemical reactions carried out by living microorganisms that convert certain organic compounds to other compounds. The process may or may not occur in the presence of air. Microorganisms also produce enzymes that can themselves serve as catalysts for chemical reactions. A common characteristic of fermentation and of most biological processes is that the end product of the process is in dilute aqueous solution.

Bioprocesses include fermentations and biotransformations. In fermentations, a population of microbes converts a feedstock (e.g., a simple sugar) into an end product through a series of reactions known as a metabolic pathway. Biotransformations are processes in which a compound is converted into a structurally related product in one or a small number of reactions. The biotransformations can be carried out with growing or nongrowing cells, or by cell-free enzyme systems.

Fermentations and biotransformations have a number of beneficial attributes. Cells and enzymes can carry out most of the central classes of reactions used in the chemical industry (e.g., hydroxylations, condensations, oxidations, esterifications, acylations, and halogenations), and they do so with much greater specificity. Biobased processes often yield a single product, and in general, give much simpler product mixtures than thermochemical processes. Other advantages of fermentations and biotransformations, compared to thermochemical processes, include:

- Mild reaction conditions that permit converting substances labile to the extremes of heat, pressure, and chemical conditions inherent to thermal processes and that allow less expensive materials to be used in reactors
- Reactions at positions in molecules that are not ordinarily reactive, or at positions not favored by thermal processes
- Coupling long sequential series of specific chemical reactions by a microorganism containing several enzymes (a metabolic pathway)
- Producing fewer toxic byproducts than many thermal reactions, thereby greatly reducing the environmental cost of a given conversion.

Until recently, however, the economic competitiveness of biobased processes for the producing low- or moderate-value chemicals has been limited by a number of technical obstacles. Bioprocesses tend to yield dilute aqueous solutions of product, and it is often the cost of product purification that prevents commercialization. In other cases, product yield, the feedstock cost, or an insufficient reaction rate create barriers to commercialization. A series of technological advances, summarized in section 6.3,

should allow research and development to overcome these obstacles, making biobased production of chemicals economically attractive.

The establishment of a biobased processing industry for making chemicals from renewable feedstocks will enhance the chemical industry. In addition, biobased and thermal processes can be tailored to produce chemicals that themselves serve as intermediate-volume feedstocks for the existing petrochemicals industry.

As part of the Alternative Feedstocks program effort to integrate biobased and thermal processes, we will give attention to a new and developing class of catalysts — biomimetic catalysts. Biomimetic catalysts stand at the interface between biobased and thermal processes. These catalysts, which are only now beginning to be developed, are nonenzyme catalysts that carry out reactions using mechanisms discerned for enzymatic reactions. They tend to retain the attributes of biobased conversions (listed above) and they also offer greater stability and flexibility. Evaluating the evolution of this class of catalyst will be monitored and developments will be incorporated into the analysis of longer term opportunities.

6.2 Target Products and Markets for Chemicals

Currently, on the order of 5.0 quads of fossil fuel are used annually to produce chemicals. Of this, approximately 3.9 quads are derived from petroleum. Of the vast number of chemicals produced by this industry, approximately 90% can, in principle, be produced from renewable biomass feedstocks (Busche 1989). The Alternative Feedstocks program will attempt to define the most economical chemical candidates that might be produced from biomass in order to provide feedstock flexibility to the chemical industry and to accrue the multiple benefits to the United States economy of energy security, economic growth, and environmental stewardship.

6.2.1 Direct Substitution for Existing Chemicals

Two classes of products can be made from renewable feedstocks. The first class includes existing commodity chemicals not currently produced from biomass. Examples include acetaldehyde, acetic acid, acetone, n-butanol, glycerol, and isopropanol. Such products have an advantage in that the market is already established and thus they require less effort to sell. On the other hand, competition will be strictly on the basis of price because no product performance advantages are possible for products derived through biotechnology over those produced from petroleum. Because established products are manufactured in plants for which the capital investment is all or partially paid off, economics often favor the incremental expansion of existing petrochemical-based facilities. In this area, we have attempted to define processes or pathways that can yield a family of products rather than a single chemical.

6.2.2 Development of New Chemicals, Materials, and Feedstocks

The second class of products is new materials that can be derived through biotechnology. These are products that are unique to bioprocessing. Examples include new adhesives, biodegradable plastics, biocompatible solvents, degradable surfactants, and enzymes for various applications. New materials can also lead to an increased demand for existing chemicals such as the anticipated demand for lactic polymers based on lactic acid. For such products, competition would probably be based on performance, and the advantages of the bioproducts might provide unique niches for initial introduction into the marketplace. Therefore, less price pressure is possible initially for such new products. However, to have a substantial impact on petroleum consumption, large markets must eventually develop. An alternative way to open markets for biobased chemicals is to establish new uses for biobased products as feedstocks for producing high-volume chemicals. Thus we have sought to identify biobased processes that can be integrated with thermal processes to produce a spectrum of chemicals.

We began the study with 40 promising chemicals and materials identified by initial screening that can be produced from renewable feedstocks through bioprocessing. Next, we identified key process areas applicable to a multiplicity of promising products. This strategy was designed to promote developing a directed technology base that is balanced, with a portfolio of key processes and product families with representative target products. Since it is always desirable to build on the existing technological base, a thorough review of public and private sector data was initiated. A more synergistic database of information is needed for a less fragmented approach to this new industrial opportunity, allowing more in-depth comparisons with other chemical process investment opportunities by industry. This evaluation will enable the Alternative Feedstocks Program to take advantage of the existing cadre of experts, thereby avoiding duplicating analysis and promoting a synergistic information base.

6.3 Opportunities for Technology Improvement

Large quantities of alcohol fuels, some organic acids, and amino acids are currently produced by biological systems; nevertheless, most of the other potential bioprocessing routes are not being exploited because of poor economic performance that results from inefficient metabolic pathways, low yields, unacceptable or unknown kinetics, or inefficient processing techniques. In the past decade, researchers have made tremendous advances in techniques for improving both biocatalysts and processing systems. Increased metabolic understanding and new genetic manipulation techniques offer the likelihood that the intrinsic metabolism of a microbe may be altered to improve its product yield, bioconversion rates, and product tolerance. There is strong evidence that significant improvements can be made by developing and using technology that takes advantage of advanced processing concepts. For example, a common bioprocessing issue is that most products are formed only in dilute aqueous solution because of the autoinhibitory nature of the desired product. It is now possible to remove the inhibitory product from the ongoing fermentation as well as to develop a microbe that is able to tolerate higher product concentrations. Areas where advanced technology could have an important impact are outlined and the requirements for innovative RD&D are defined below.

A focused research and development effort is needed to improve both the process and the microbial metabolism. Six primary criteria will be used to evaluate possible advanced bioprocessing concepts and the potential of metabolic pathways modifications. Each of the possible innovations will be considered on the basis of

- volumetric productivity,
- yield as a fraction of theoretical yield,
- the product quality in purity and concentration,
- the energy use inherent in the process,
- the potential environmental impact, and
- the operability.

All of these criteria are considered to be important, but productivity and yield are of particular interest because these parameters have the most direct bearing on economic viability. We can estimate the maximum improvement in yield from the theoretical stoichiometry to determine the potential maximum impact from a program in that area. For example, *Lactobacillus* already produces lactic acid from glucose at near 1 g lactic acid/g glucose, the stoichiometric limit; thus, further yield improvements are unlikely to have an impact. On the other hand, butanol is produced by *Clostridium acetobutylicum* with a maximum yield of less than 0.3 g/g with significant amounts of coproducts; thus, metabolic improvements might increase the yield by more than 50%. Similar assessments can be made for other proposed process and metabolic improvements. These potentials will be evaluated in a process economic model for a base-case technology to determine if the potential for improvement is sufficient to alter the economics and create a new opportunity.

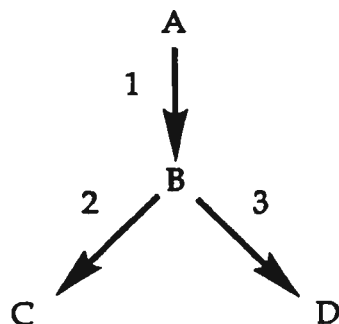
6.3.1 New Technologies in Genetic and Metabolic Engineering

Metabolic engineering is the deliberate alteration of an organism's metabolism, the chemical steps by which it converts feedstocks to products, through genetic manipulations. In the case of bioprocessing for producing chemicals, the objective of this engineering would be to improve the aspects of microbial physiology that tend to limit the commercial viability of bioprocesses:

- Poor tolerance to high concentrations of the desired product
- Production of byproducts
- Moderate or low conversion rates
- Requirements for expensive nutrients
- Instability of the microbial culture
- Need to utilize additional renewable feedstocks.

The relevance and importance of these items vary for each process considered, and depends on the organism involved, its metabolism, and the targeted compound.

The potential to channel material into desired products is illustrated schematically in Figure 6.1. The most straightforward types of alterations possible are removing competitive pathways that divert material from the desired product and enhancing the activity of a rate-limiting enzyme. Indirect effects that can affect energy use or product tolerance can also significantly improve product yield. In addition, novel technology developments enable one to alter the specificity of enzymes to create biological catalysts that give new products distinct from those originally produced. Research has demonstrated the potential of these approaches for improving bioprocessing. Examples of metabolic engineering include the introduction into *E. coli* of the ability to produce primarily ethanol, normally a minor product (Roy 1992), and addition of a multistep pathway for colorant production into brewer's yeast (Ausich et al. 1992). Examples of enzyme engineering include alterations of the enzyme that produces lactic acid to give new enzymes that produce malic acid or various derivatives of lactic acid (Wilks et al. 1992). Genetic manipulations can be directed to altering product distribution, improving productivity and product quality, minimizing energy use and environmental impact, or improving the operability of the overall process.



Metabolic Engineering can alter the activity or regulation of enzymes.

Examples: Enzyme 1 is the rate-limiting step of a pathway; increase its production or activity
Enzyme 2 gives the undesired side product C; eliminate its production or activity
Enzyme 3 generates the desired product D; enhance its production or activity

Figure 6.1 - Metabolic Engineering

Results such as these have occurred largely because of new or recently improved genetic technologies. These advances greatly enhance our ability to manipulate the metabolism of various organisms and include the following:

- PCR (the polymerase chain reaction). This technique generates large quantities of a gene and can simultaneously introduce precise changes in the gene's DNA sequence. The changes introduced can be designed to alter the activity, stability, or regulation of the activity of the protein produced by the gene.
- Physical methods for DNA introduction. One new method, electroporation, uses cells temporarily permeable to DNA outside the cell. Another new approach literally shoots small particles coated with DNA into cells, circumventing the need to develop specific biological methods.
- Technologies for control of genes. Introduction of DNA antagonistic to a cell's DNA, called antisense DNA, causes malfunction of the specific gene targeted. This method permits alteration of the regulation or activity of native genes, thereby affecting metabolism.

To date, the full potential of these methods has not been applied to metabolic engineering for the production of industrial chemicals. Manipulations of metabolic pathways and of individual enzymes that were not reasonable to attempt a few years ago are now realistic possibilities.

6.3.1.1 Future Technological Advances

The advances described above create immediate, specific opportunities for improving the economics of producing chemicals from renewable feedstocks. Additional technological developments can be anticipated that should affect these processes significantly, and these areas of technology provide targets for mid- and long-term research activities.

- Microbiology and metabolic engineering. Low product tolerance is recognized within the biotechnology industry as a major barrier to favorable process economics. Organisms tolerant of extreme concentrations of products or of low pH should be investigated as potential agents for biomass processing. New organisms, genetic systems for tolerant organisms, and directed selection for increased tolerance could provide valuable improvements. Metabolic pathways should be engineered into more tolerant organisms.
- Bioprocessing materials. Near-term efforts exploit new materials originally developed for applications other than bioprocessing. Materials science research into the discovery of novel membranes, ceramics, adsorbents, and reactors can be expected to provide new technologies that can be adapted for use in bioprocessing.
- Protein engineering. Future advances in understanding protein structure and function relationships, derived in part from analyzing the effects of structural changes introduced by genetic engineering, promise to allow the predictable alteration of a protein's properties to generate enzymes with enhanced capabilities for bioprocessing, such as increased stability, tolerance of organic solvents, or novel catalytic activity.
- Biomimetic catalysis. Biomimetic catalysts attempt to mimic the active site of enzymes in low molecular weight, synthetic catalysts to unite the favorable properties of enzymes (efficiency, specificity, and selectivity) with the small size, stability, and low cost of synthetic catalysts. This research could produce a new generation of catalysts for converting biomass or biomass-derived products to industrial chemicals.

Ideally, mid- and long-term research priorities should evolve in parallel with near-term activities that seek to commercialize existing technology, rather than as isolated efforts. Coordinating these activities will ensure that the technology areas addressed truly have potential to overcome the barriers which still exist to producing chemicals from renewable resources. Systems analysis and input from industrial advisors should be used to help set research priorities.

Page 136 is missing from all existing copies of this report.

must be produced and then introduced and maintained with high activity within the bioconversion reactor. Conventionally, this requires aseptic conditions with steam sterilization of all inlet streams. Improvements that decrease or eliminate the need for strict sterility will decrease both capital and operating costs; these improvements could include the use of extremophiles (microbes working at low pH or high temperature), high-product-tolerant microbes, or the selective retention of the desired microbes by immobilization. The stirred tank batch reactor is the conventional technology for bioconversion. Large increases (5 x to 500 x) in volumetric productivity are achievable by adding cell retention of some form in a continuous operation. Cell retention (either recycle or immobilization) will be a key in reaching the largest improvements and must be investigated for the particular system. The issues of mass and heat transfer must be addressed for the large scale operation of these technologies.

Bioconversion steps are generally inhibited by the desired product. This introduces the broad strength of combined processes. SSF combines enzymatic hydrolysis and fermentation to decrease inhibition caused by the intermediates. Several other processes have been proposed for simultaneous fermentation and separation. The separation can be accomplished by adsorption, extraction, membrane-based processes, or precipitation. Adsorption and precipitation are particularly relevant to producing organic acids such as succinic acid. With adsorption, more than 4-fold rate increases are possible; equivalent increases have been observed with precipitation. A completely different long-term approach involves using biocatalysts in nonaqueous systems such as organic solvents, biphasic liquids, or supercritical CO₂.

Downstream processing encompasses separation, purification, and waste use. Separating the desired product from these dilute, generally aqueous solutions is frequently the second most costly part of the process (raw material cost is often first) and is usually the largest energy consumer. Conventional separation technology for most bioproducts is either distillation (with high energy costs) or precipitation (with large amounts of waste salts produced). Replacing these separation methods is a critical area deserving near-, mid- and long-term programs. Adsorption, liquid-liquid extraction, pervaporation, and other membrane processes such as electrodialysis are the most promising alternatives. Adsorption should be investigated as a near- to mid-term replacement for precipitation of organic acids. Electrodialysis with bipolar membranes may be effective in recovering organic acids. Extraction and pervaporation have advantages for producing neutral solvents or volatiles.

In the near term, conventional waste treatment technologies are adequate; however, they must be robust and forgiving of a variety of streams and transients. The long-term emphasis must be on approaching a closed system through waste use, reuse, minimization or recycle. In the broadest sense, the total product and process life cycle needs to be considered. In particular, the proposed processes should not generate any hazardous waste. Bioconversions also produce large volumes of dilute streams with surplus nutrients. The biocatalysts should be studied to minimize or reduce their fee requirements. These technologies have enormous potential in overcoming the barriers to commercialization. Development and demonstration of improved technology will be critical for this program.

6.4 Product/Process Selection

A wide variety of chemicals and materials can be produced through fermentations and bioconversions. These products could be classified into the following groups:

- Amino Acids
- Antibiotics
- Biopolymers
- Enzymes
- Nucleic-acid-related compounds
- Organic acids
- Steroid hormones
- Foods and alcoholic beverages
- Miscellaneous organic chemicals

A set of criteria was defined to select, from the thousands of potential candidates, those candidates that would be evaluated in the initial development of a product portfolio. These criteria were developed to be consistent with the overall goal of the program. No single criterion was the most important for selecting candidates into the portfolio. Additional candidates will be added to the portfolio on a regular basis. The criteria for selecting additional candidates may be the same as for the original selection and will continue to be impacted by industrial interest.

The original set of selection criteria is as follows:

- High theoretical product yields from substrate
- Market interest in the product as an end product or as an industrial-important intermediate
- High production volume (current or potential)
- Nonfood use
- Ability to be biologically synthesized from the common sugars derived from various forms of biomass.

Given the scope of candidates in the portfolio, a methodology was devised to rank the candidates into near-, mid-, and long-term opportunities. The time scale for these opportunities is defined as 0-5 years, 5-10 years, and 10 or more years, respectively.

The ranking methodology consists of three stages. The first stage, referred to as the initial product screening, evaluates products using very approximate economic analysis based only on the prices of the products, byproducts, and starting materials.

The second stage of the analysis compares, where possible, the proposed bioprocess route to the current conventional petrochemical route. This again is a very approximate analysis that compares only the raw material costs for each process. The methodology used is similar to that used for products from thermal/chemical routes, described in section 4.2.1.

The third stage of the analysis, referred to as the integrated product/process screening, takes into account more specific process economic characteristics needed to estimate production costs and return on investment to predict the selling price of the product. The difference between the predicted selling price and the current or projected market value, together with the set of technical and economic assumptions used in the analysis, is used to classify the products into one of the three portfolio categories, near-, mid-, and long-term opportunities. Figure 6.2 illustrates the overall selection and ranking scheme used. This strategy will allow development of a concurrent research and development approach involving basic research, enabling technology (bridging research), and applied pre-commercial development.

6.4.1 Initial Product Screening Methodology

Many diverse products could be produced by biological routes from renewable feedstocks such as starch crops (e.g., corn) and lignocellulosic biomass (e.g., grasses and wood). However, not all these products can be produced in sufficient yields to be economically viable. The merits of each product can be estimated simply by determining the quantity and cost of feedstock required to generate a given amount and value of product. If the revenue generated from the sale of the products is insufficient to cover the cost of the substrate, a lower cost feedstock or one with a more favorable composition must be devised.

The purpose of the initial product screening is to rank the candidates based on a simple economic criterion, the fraction of revenue for feedstock (FRF); i.e., the ratio of the cost of the feedstock to the value of the products derived from the feedstock. The FRF can be calculated for each of the candidates using a number of different feedstocks. The FRF values can be determined for established experimental yields and theoretical maximum yields to determine the merits of the products now and their maximum

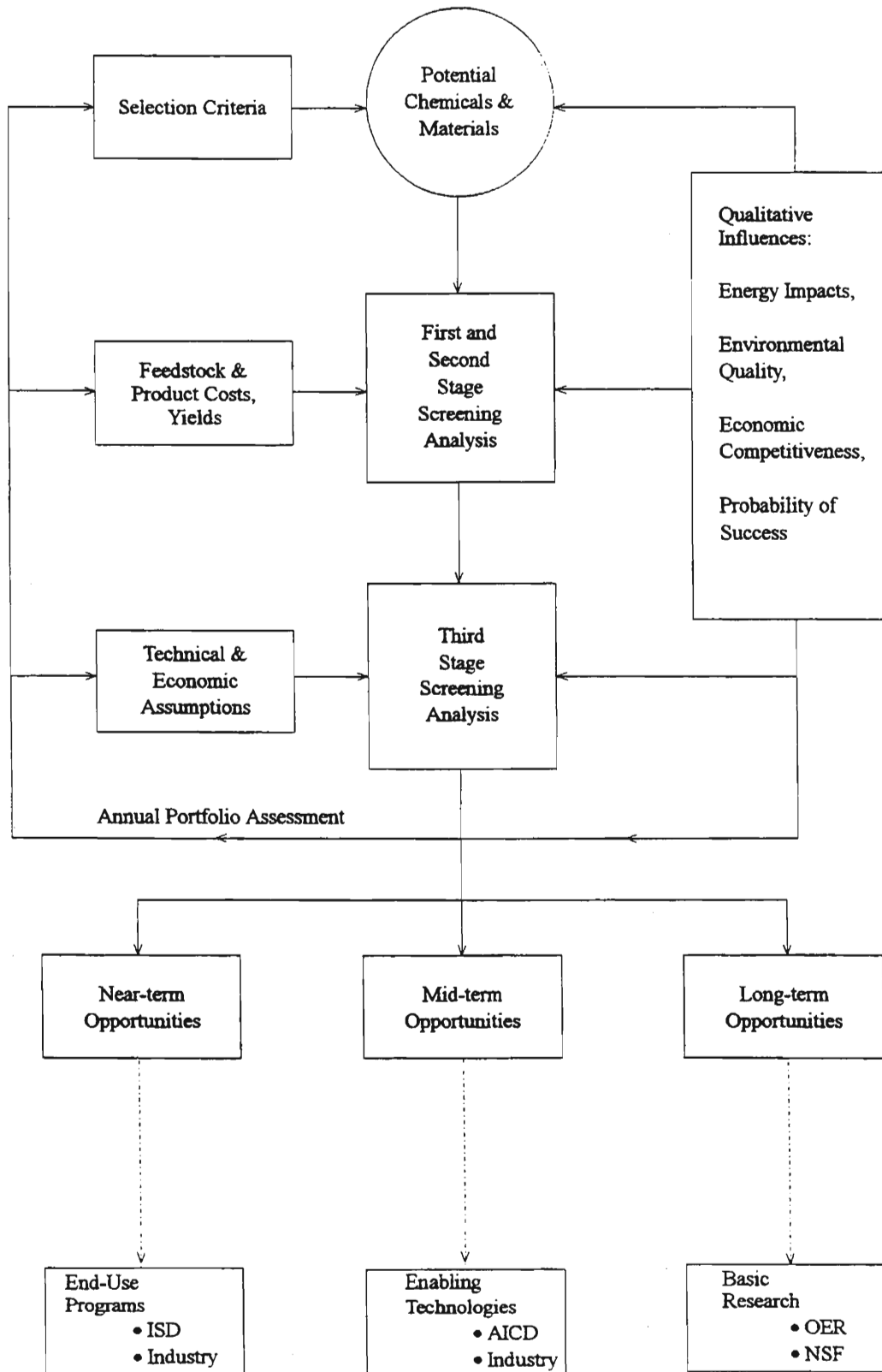


Figure 6.2 - Screening and Ranking Methodology

future potential based on this simple methodology. Because such an analysis does not consider other factors such as the cost of product recovery, it should be viewed as a first step to rapidly identify products that show limited promise based on stoichiometry alone. The results of the FRF analysis are given in section 7.0.

6.4.1.1 Fraction of Revenue for Feedstock

Calculating the FRF requires knowing the cost and composition of the feedstock, the yield of the product and any byproducts, and the market values of the products and byproducts. The FRF is calculated using equation (1).

$$\text{Fraction of Revenue for Feedstock} = \left[\frac{\text{Cost of Feedstock}}{\text{Value of Products}} \right] = \frac{C_f}{\sum \alpha_i y_i V_i x_i \beta_i} \quad [1]$$

where

i	=	Component i of the feedstock
C_f	=	Unit cost of the feedstock, dry weight
α_i	=	Fraction of maximum theoretical yield of product derived from component i
y_i	=	Theoretical yield of product derived from component i
V_i	=	Value of the product derived from component i
x_i	=	Fraction of component i in the feedstock
β_i	=	Hydrolysis weight gain conversion factor (if applicable, section 6.4.1.2)

Note that the FRF must be less than unity for a process to be economically feasible; i.e., the value of the products must be greater than the cost of the feedstock. The lower the FRF, the more promising the process looks for further investigation.

6.4.1.2 Feedstocks Evaluated

Three feedstocks were evaluated: glucose syrup, corn, and hybrid poplar. The prices used for each of these feedstocks are given in Table 6.1. The price of glucose syrup was obtained from a large corn wet-milling company. The price for corn was obtained from the USDA's Market News Service. The price for hybrid poplar is from the U.S. DOE Biofuels and Municipal Waste Technology Multiyear Plan (unpublished).

Glucose syrup is directly fermentable. Corn and hybrid poplar will yield glucose upon pretreatment and hydrolysis; they yield other byproducts as well whose values are known or can be estimated (section 6.4.1.5).

Table 6.1 - Feedstocks Evaluated and Current Prices

<u>Feedstock</u>	<u>Price(\$/lb)</u>
Glucose Syrup (99 DE)	0.102
Corn	0.052
Hybrid Poplar	0.021

Glucose syrup, corn, and hybrid poplar were chosen as representatives of the types of feedstocks that could be used in near-, mid-, and long-term opportunities. Corn as a feedstock can be further differentiated by the method used to convert its starch fraction into glucose. Both the wet-milling and dry-milling process were considered. These processes yield a substantial fraction of starch as a percentage of the starting material, however, the byproducts are quite different. The wet-milling fractionation process produces a starch slurry, crude corn oil, corn steep liquor, corn gluten meal, and corn gluten feed. The starch slurry can be hydrolyzed to glucose by chemical, enzymatic, or chemical and

enzymatic hydrolysis processes. The corn-to-ethanol dry-milling process produces a stillage called distillers dried grain and solubles (DDGS) and carbon dioxide. The DDGS is sold as an animal feed; the carbon dioxide is not usually recovered. The byproducts from the dry-milling process could be different from those resulting from ethanol production if a different product is produced in the fermentation. For example, the fermentation stillage may have no value as an animal feed if the organism used to produce the chemical of interest is *E. coli*. In this case, a protein extraction process might be required to recover a salable byproduct. Similarly, an aerobic fermentation would produce little, if any, carbon dioxide. When performing the FRF calculations using dry-milled corn as the feedstock, DDGS and carbon dioxide are assumed to be the only byproducts produced. The current market value of DDGS is taken as its byproduct credit; no credit is taken for the carbon dioxide.

For the FRF analysis, each feedstock is arbitrarily assumed to include up to six constituents, including cellulose, hemicellulose, starch, and possibly three other components. The compositions of the feedstocks evaluated are given in Table 6.2.

Table 6.2 - Feedstock Compositions

Glucose Syrup		Wet-Milled Corn		Dry-Milled Corn		Hybrid Poplar	
Constituent	Wt %	Constituent	Wt %	Constituent	Wt %	Constituent	Wt %
Cellulose	0.00	Cellulose	0.00	Cellulose	0.00	Cellulose	48.64
Hemicellulose	0.00	Hemicellulose	0.00	Hemicellulose	0.00	Hemicellulose	16.84
Starch	0.00	Starch	67.62	Starch	71.85	Starch	0.00
Glucose	97.50	Corn Oil	3.70	DDGS	28.15	Lignin	24.25
Other Sugars	2.50	Gluten Feed	24.47			Extractives	5.49
		Gluten Meal	4.21			Ash, Proteins	4.78

Corn and hybrid poplar have starch or cellulose as major constituents. Cellulose and starch are polymers of glucose units, which upon hydrolysis yield the glucose monomer (equation 2).



Depolymerizing the polymer to n monomeric units requires the addition of n water molecules. The molecular weight of the polymeric unit is 162, while the molecular weight of glucose is 180. The percentage weight increase upon hydrolysis is $180/162 = 111.1\%$. This correction factor is applied to the cellulose and starch mass fractions to account for the weight gain when the polymer is hydrolyzed to glucose.

Similarly, hemicellulose can, as an approximation, be described as a polymer of xylose units (mol wt = 132), which upon hydrolysis become xylose or related five-carbon sugars (mol wt = 150). The weight gain upon hydrolysis in this case is $150/132 = 113.6\%$. The hemicellulose mass fraction is multiplied by this correction factor to get the xylose mass fraction available for conversion. For this analysis, the hemicellulose fraction of the feedstock is assumed to be completely hydrolyzed to xylose and subsequently converted to ethanol (Section 6.4.1.3).

6.4.1.3 Byproducts

As much revenue as possible should be derived from the feedstock for any process to be economically viable. Therefore, it is important to consider converting the other fractions of the feedstocks listed in Table 6.3 into useful byproducts. In the corn wet milling process, the corn oil is extracted early for sale as food and the protein is recovered prior to processing the starch for sale as animal feed coproducts (called corn gluten meal and corn gluten feed). For dry milling of corn, the solid residue left after conversion of the starch into products is dried for sale as DDGS, an animal feed coproduct. For lignocellulosic biomass, the xylose derived from the hemicellulose is assumed to be converted into

ethanol while the lignin is burned as boiler fuel. The yield factor used in the calculations is the theoretical conversion of xylose to ethanol (0.511 lb ethanol/lb xylose). Table 6.3 summarizes the values of the coproducts.

Table 6.3 - Feedstock Coproduct Values

<u>Coproduct</u>	<u>Coproduct Value (\$/lb)</u>
Lignin - Boiler Fuel	0.020
Crude Corn Oil*	0.132
Gluten Feed**	0.053
Gluten Meal**	0.150
DDGS**	0.058
Ethanol	0.091
Extractives	0.000
Ash, Protein	0.000

* Chemical Marketing Reporter, December 20, 1991

** Alcohol Week's New Fuels Report, November 11, 1991

Processes resulting in coproducts with higher values would be desirable. This analysis considers only coproducts that are currently being produced economically; thus, this stage of the analysis could be viewed as a worst-case scenario. Future analyses will consider other value-added co-products. Significant economic benefit would be achieved if the lignin fraction of lignocellulosic biomass could be converted economically to useful higher-value products, rather than used as boiler fuel. This conversion most likely would be by thermal or chemical methods.

6.4.1.4 Experimental Yields

The literature was thoroughly searched to find current values for product yields. The experimental yields selected from the literature are based on glucose as the substrate. In most cases, the literature does not specify whether the yield was based on substrate consumed or substrate fed. The assumption is that the unit for the experimental yield is mass of product formed per unit mass of substrate consumed.

6.4.1.5 Theoretical Yields

The maximum theoretical yield of product on substrate, $Y_{p/s}$ (carbon equivalents of product formed per carbon equivalent of substrate consumed), is the minimum of the three yields discussed below (Andrews 1989). These yields are defined as the maximum yield that could be obtained if all the substrate were used to make a single product.

- Y_C : Yield based on carbon availability
- Y_H : Yield based on reducing potential
- Y_E : Yield based on energy availability

The stoichiometric coefficient for product formation written in terms of carbon equivalents provides Y_C . As an example, the stoichiometric equation, written in terms of carbon equivalents, for the biosynthesis of ethanol from glucose can be written as shown in equation 3.



One carbon equivalent of glucose produces 0.667 carbon equivalents of ethanol and 0.333 carbon equivalents of carbon dioxide. Thus, $Y_C = 0.667$.

The yield of product based on available reducing power, Y_H , is defined as the ratio of the generalized degree of reduction of the substrate to the generalized degree of reduction of the product. The generalized degree of reduction of a compound can be thought of as the number of available electrons per carbon equivalent (equation 4).

$$Y_H = \frac{\gamma_s}{\gamma_p} \quad [4]$$

The generalized degree of reduction of any compound, represented by the chemical formula $CH_aO_bN_c$ is calculated using equation 5.

$$\gamma = 4 + a - 2b - 3c \quad [5]$$

Returning to the ethanol-from-glucose example, the generalized degree of reduction of glucose (CH_2O) is shown in equation 6.

$$\gamma_s = 4 + 2 - (2) 1 = 4 \quad [6]$$

The generalized degree of reduction of ethanol ($CH_3O_{0.5}$) is given in equation 7.

$$\gamma_p = 4 + 3 - (2) 0.5 = 6 \quad [7]$$

Thus, the maximum yield of ethanol from glucose based on available reducing power, Y_H , is $4/6 = 0.667$, the same value as Y_C determined from the product formation reaction stoichiometry.

Calculation of the yield based on energy availability, Y_E , requires knowledge of the metabolic pathway used by a particular organism to synthesize the product from the substrate. Specifically, one needs to know:

- The amount of ATP generated during the catabolic breakdown reaction, per carbon equivalent of substrate, by substrate level and oxidative phosphorylation
- The amount of ATP generated per carbon equivalent of substrate by substrate level phosphorylation before the product formation pathway diverges from the catabolic pathway
- The amount of ATP required per carbon equivalent of substrate to synthesize the product from the precursors diverted from the catabolic pathway.

For products formed anaerobically, $Y_E > Y_C$, and energy limitation is impossible. Also, simple products formed aerobically are either carbon- or reduction-limited; energy limitation is impossible because the product synthesis requires no additional ATP beyond that generated from the catabolic breakdown reactions. Values for Y_E are not calculated because of the complexity involved in the determination and because the synthesis of most products would not be energy limited.

The minimum value of Y_C and Y_H is used as the maximum theoretical yield, $Y_{p/s}$, on a carbon-equivalent basis. Because all product and feedstock price information is on a weight basis, the desired unit for the yield factor is mass of product formed per mass of substrate consumed. The transformation of

the yield unit is achieved by multiplying $Y_{p/s}$ by the weight fraction of carbon in the substrate, then dividing by the weight fraction of carbon in the product (equation 8).

$$Y_{p/s} = \left[\frac{c - \text{equivalent product}}{c - \text{equivalent substrate}} \right] \left[\frac{\text{substrate wt \% carbon}}{\text{product wt \% carbon}} \right] = \frac{\text{amount of product}}{\text{amount of substrate}} \quad [8]$$

6.4.1.6 Product Values

The current prices of the product candidates were obtained from the *Chemical Marketing Reporter* (CMR), November 4, 1991; these are given in section 7.0, Table 7.1. For chemicals not listed in the CMR, the prices were obtained directly from a manufacturer or from the SIGMA Chemical Company 1991 catalog.

Prices from the SIGMA catalog were adjusted using a factor determined as follows. Prices for six chemicals listed in the CMR also were obtained from the SIGMA catalog. The ratio of the CMR price to the SIGMA price was calculated for each of the six chemicals. The average of these ratios, R_{SIGMA} was used to adjust the prices of the chemicals given by the SIGMA catalog. The value of R_{SIGMA} was 0.11.

For some candidates the corrected R_{SIGMA} price still was too high for a commodity chemical or even a large-volume specialty chemical. For example, the price information of polyhydroxybutyric acid was given in the SIGMA catalog as \$2,812/lb. The R_{SIGMA} corrected price is still \$312/lb. For this compound to compete as an intermediate for the production of biodegradable plastics, its price would have to be in the vicinity of \$0.50/lb. Therefore, the price of polyhydroxybutyric acid was arbitrarily set at \$0.50/lb for this analysis. This arbitrary valuation was exercised for a number of the candidates whose current prices seemed too high for estimates of their future market value.

6.4.1.7 Summary

The objective of the initial product screening stage was to provide a simplified quantitative assessment of the economic feasibility of a project. This assessment can be used together with qualitative input to rank the order of more detailed analyses of the projects under consideration. The methodology developed is iterative in nature. Demonstrated yields for various candidates will undoubtedly improve and estimates of the costs of dedicated feedstocks and market values of the candidates will be periodically revised. These changes will necessitate a periodic review of the portfolio of candidates and revision of the FRF calculations to reflect the current data and prevailing set of qualitative assumptions. Figure 6.3 illustrates the Initial Product Screening methodology and its iterative design.

6.4.2 - Comparative Evaluations

Comparative analyses of proposed bioprocessing routes with current petrochemical routes were performed at an early stage of process evaluation to help determine the order in which candidates are investigated in more detail. The basis for this comparison is the estimated raw material costs for each of the processing routes. The raw material costs are a significant fraction (50-80% or more) of the production cost for a majority of commodity chemicals. A preliminary economic comparison can be made between the bioprocessing route and the current petrochemical route assuming the raw material costs are an approximately equal fraction of the total production costs of each route.

The parameter of interest here is the ratio of the raw material costs. The ratio is modified by a risk factor of 1.3 to take into account possible problems, unknowns, and intangibles in a given bioprocess. One might also view this factor as accounting for the fact that in most situations the capital required for

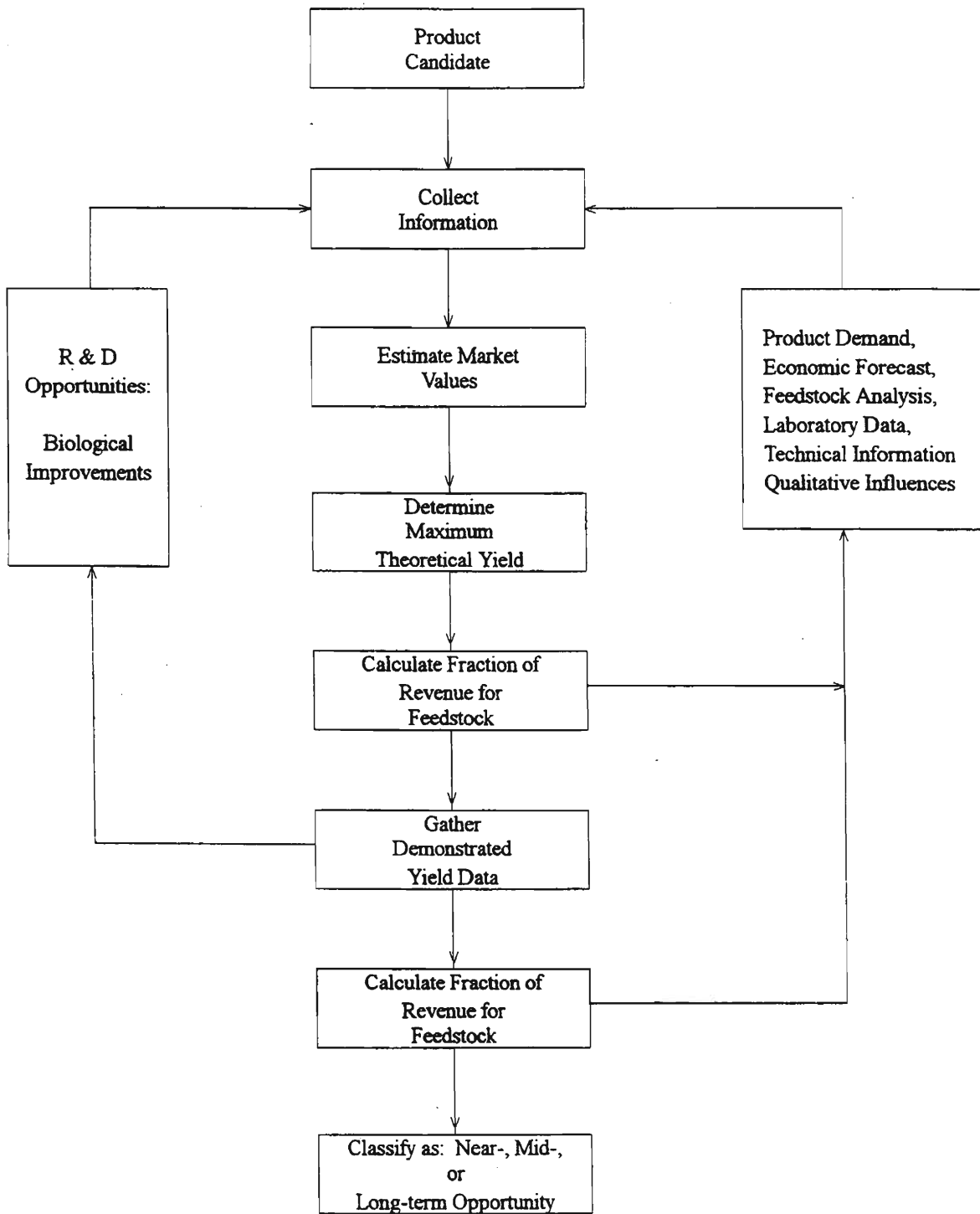


Figure 6.3 - Initial Product Screening Methodology

the existing petrochemical-based process is partially or completely paid-off. Thus, any competitive process would have to have substantially lower production costs.

$$\text{Raw Material Cost Ratio} = \frac{\text{Estimated Cost of Raw Materials for Petrochemical Process}}{\text{Estimated Cost of Raw Materials for Bioprocess}} \times \frac{1}{\text{Risk Factor}}$$

If the raw material cost ratio (RMCR) is greater than unity, then the proposed bioprocess shows potential, based on raw material costs alone, for being competitive with the existing petrochemical process. A ratio considerably less than unity indicates that the bioprocess could have difficulty competing with the current petrochemical route.

Similarly to the FRF calculations, both a currently achievable bioprocess and a theoretical achievable bioprocess can be considered. The basis for determining the raw materials costs for the currently achievable bioprocess portion of this analysis is the demonstrated yield factor, based on glucose, multiplied by 0.5 to adjust for unaccounted raw materials and the uncertainty in translating bench- or pilot-scale yield data to production scale. In some cases, this adjustment factor overpenalizes the bioprocess because some yields have been demonstrated at large scale, and additional raw material costs are negligible. Nevertheless, it has been kept in all cases for consistency. The basis for determining the raw materials costs for the theoretically achievable bioprocess part of this analysis is the theoretical yield factor, based on glucose, multiplied by 0.95. The adjustment factor in this case is applied to account for the inability of a full-scale process to achieve 100% of the theoretical yield. No adjustment is made to account for additional raw materials because, in theory, processes could be developed in which they would no longer be required or would be negligible.

For example, one proposed bioprocess to produce succinic acid requires the addition of base to the fermentor to maintain an economical volumetric productivity and concentration of succinate. The resulting succinate salt is then acidified to recover succinic acid. These two raw materials alone contribute approximately \$0.05 to \$0.07 per pound of succinic acid produced. An alternative process has been developed that uses water-splitting electrodialysis to form an aqueous succinic acid solution and a base that can be recycled back to the fermentor, thereby eliminating the acid and base raw material costs.

Only the currently achievable petrochemical processes were considered. Assuming that these processes have already been fully optimized and that additional process improvements would not be cost-effective. The basis for determining the raw material costs for the petrochemical processes is the current demonstrated yield factor, based on the primary precursor. This data was obtained from the literature, the majority from the Stanford Research Institute's Chemical Economic Handbook. No adjustment factor was applied to the yield factor because all raw material costs are assumed to be known and the yield is clearly demonstrated at full scale. A point to keep in mind is that true yield and raw material cost data for many commercial processes are proprietary and thus unavailable. Therefore, these numbers could be significantly different than the data used in the comparative analyses.

Rather than examining various feedstocks, as was done for the FRF calculations, a range of glucose costs was used to determine the raw material costs for the bioprocesses. The source of this glucose could be, for example, from corn (hydrolyzed starch), from lignocellulosic biomass (hydrolyzed cellulose), or from an industrial waste stream containing recoverable amounts of starch, cellulose, or their hydrolysates. The range of glucose costs evaluated was from \$0.05 to \$0.13 per pound, although the cost could be lower, conceivably even negative for some waste streams. Thus, two RMCR curves were generated for each product, one for current yield and one for theoretical yield, both versus the cost of glucose.

Most bioprocesses require the addition of various nutrients, such as corn steep liquor as a nitrogen source or air as an oxygen source for aerobic organisms. The cost of these nutrients is usually small compared to the feedstock cost. However, rather than omit these costs, they have been estimated and included as 20% of the feedstock cost.

These comparative analyses should be viewed only as a first attempt to compare the competitiveness of bioprocesses with the current petrochemical-based processes, and will be used only to help identify the order in which more detailed engineering economic analyses will be performed. A comparison of the more detailed engineering analyses will provide a better measure of the competitiveness of the bioprocessing route. These detailed engineering analyses also will be used to identify key research opportunities for bridging the competitiveness gap between bioprocesses and petrochemical processes.

6.4.3 Integrated Product/Process Screening Methodology

The effort required to complete this stage of screening is significantly greater than that for the initial product screening. The ranked results from the initial product screening stage can be used to rank the order in which candidates undergo the more rigorous integrated product/process screening. In the second stage of the analysis, as in the first stage, the objective is to classify the candidates and associated process technologies as near-, mid-, or long-term opportunities.

The second stage of the screening analysis requires a complete process design. During this phase of the analysis, an order-of-magnitude level of detail is sufficient. In other words, the actual fixed capital investment for a project is assumed to be within $\pm 30\%$ of the estimated value. The factoring method is used to determine the various fixed and variable costs from independently determined purchased equipment, raw material, and operating labor costs. A reasonable allowance for return on investment must also be made.

A discounted-cash-flow analysis is used to predict the selling price of the product. The processes then are ranked based on the difference between the estimated market value and the predicted selling price. The rankings from the three screening stages will likely be different. The ranking from the third screening stage will be the most accurate because many more details are considered. However, the results of all rankings, together with qualitative input, will be used to determine the final project classifications into near-, mid-, and long-term opportunities.

It is important to point out that the screening methodology in general is an iterative process. As biological and process improvements unfold, and the screening methodology and criteria evolve, the rankings of the candidates and technologies will change.

6.4.3.1 Process Design

The first step in performing the integrated product/process screening analysis for a project is completing a process design. A number of plant designs and design assumptions can be considered for each candidate in this stage of screening. The proper choice will depend on a number of factors including the process technology, the projected product demand, and the intended purpose for the results of the analysis.

The first and simplest design basis is an independent bioconversion plant. A wide variety of feedstocks could be considered for this type of design, such as sugar syrups, whey and whey hydrolyzates, and industrial wastes. These feedstocks require little or no pretreatment to convert them to fermentable substrates. The assumed cost of the feedstock could be its current market or contract value, an estimated transfer price, or its tipping fee in cases of waste streams.

A second design basis is a bioconversion facility integrated with a plant that produces one or more streams of fermentable substrates and perhaps other nonfermentable products or byproducts. An example of such a plant is a corn milling facility. A wet-milling facility produces a hydrolyzed starch

slurry as the fermentation feedstock. Some of the light steep water is used as a nutrient source for the fermentation process. The remaining light steep water is concentrated and sold as corn steep liquor or added to the gluten feed, another process coproduct. Other coproducts from the wet-milling operation are crude corn oil and corn gluten meal.

Another integrated plant example is a bioconversion facility integrated with a lignocellulosic processing plant. The feedstock to this plant could be any form of lignocellulosic biomass. A variety of process technologies exist to convert the cellulose and hemicellulose fractions of biomass to fermentable sugars.

The process design includes performing material and energy balances and specifying and sizing the process equipment. When all of the equipment is specified, the purchase price is estimated using ICARUS' Questimate PC-based process equipment costing software, estimated from historical data updated to the reference year, or obtained through equipment vendors. Various cost multiplication factors are applied when necessary; for example, when specialized construction materials or construction for high-pressure conditions are required.

The initial process designs, material and energy balances, and profitability analyses are performed using PC-based spreadsheet software (Microsoft Corporation's Excel 4.0). More rigorous material and energy balances can be performed using an ASPEN process simulator.

6.4.3.2 Profitability Analysis

An economic model was developed to perform the profitability analyses. The model uses the discounted-cash-flow method to calculate the profitability of the process. This method is most frequently used in the chemical process industry for the initial assessment of a project's economic potential. The method is predominant because it takes into account the time value of money. According to this principle, receiving a dollar in income today is worth more than receiving a dollar next year because today's dollar could be invested and next year be worth one dollar plus the interest earned.

With any project the investment may be made over a period of time; the income will be generated over a longer period of time and often will be quite variable. The discounted cash flow method relates all aspects of the cash flow to a common time basis. The basis used for this model is the time at which the plant starts operation after an assumed 1-, 2-, or 3-year period of construction.

Specifically, the discounted-cash-flow rate of return is a hypothetical interest rate such that, when it is used to calculate the present value of all of the income cash flow for each year plus all of the capital expenditure, the present value is zero. In other words, it is the interest rate that would be received if the same capital investment funds were to be placed in a bank for a given period (the life of the plant) and earned the same amount in interest as the cash flow produced by the plant.

The standard procedure for calculating discounted cash flow is to first tabulate all the cash flows involved with the project and then discount them to the reference time value by an assumed interest rate. These discounted present values are added together and the process is repeated with different interest rates until the sum of the discounted cash flows is zero. That interest rate is the discounted cash flow (DCF) or internal rate of return (IRR) for the project. This trial-and-error calculation is based on establishing appropriate compound interest discount factors for each cash flow to bring its value to the reference time value.

This approach is based on the assumption that all the cash flows, including the revenue, can be determined. However, the revenue can be calculated only if the product selling price is known. If the selling price is to be determined, the DCF is set to the minimum acceptable rate and trial-and-error calculations are performed with product selling price as the variable. Once the product selling price is

determined, all the discounted cash flows sum to zero. This price is compared to the current or estimated market value in order to classify the project as a near-, mid-, or long-term opportunity.

6.4.3.3 Economic Assumptions

A set of economic parameters was defined to be used as the basis for the base-case process designs. Applying this set of assumptions to all of the process designs ensures that all the projects are evaluated on a common ground. Table 6.4 lists the most important of these parameters. Note that most of these parameters can be varied in sensitivity studies, (Section 6.4.3.4).

Table 6.4 - Technical and Economic Assumptions

<u>Parameter</u>	<u>Assumption</u>
Plant Location	Midwest
Plant Type	"Grass Roots"
Effective Date	1992
Plant Life, years	10
Materials of Construction	Stainless Steel, 316L
Equipment Depreciation MACRS Service Life	5 years
Building Depreciation (straight-line)	30 years
Combined Federal and State Tax Rate	37%
Equipment Salvage Value (percent of purchase cost)	0%
Discounted-Cash-Flow Rate of Return	15%
Inflation Rate	3.5%
Percent of Capital Investment Spent in the 1st year of Construction	30%
Percent of Capital Investment Spent in the 2nd year of Construction	50%
Percent of Capital Investment Spent in the 3rd year of Construction	20%
Percent of Start-up Costs Spent in the 3rd year of Construction	30%
Plant Capacity, as a percentage of nameplate capacity, in year 1	60%
Plant Capacity, as a percentage of nameplate capacity, in year 2	80%
Plant Capacity, as a percentage of nameplate capacity, in years 3-life	100%

6.4.3.4 Sensitivity Analyses

Various sensitivity analyses can be performed to determine where the economics of the process might be improved. The predicted product selling price is determined for distinct values in some range of process parameter variations around the base-case value. Examples of the general parameters most often varied in sensitivity studies include plant size, plant cost, raw material costs, working capital, sales volume, sales price, and return on investment. Examples of case-specific parameters that might be varied in sensitivity studies include process stream concentrations, reaction rates, conversion yields, nutrient requirements, energy requirements and costs. The results of sensitivity studies are most often displayed graphically in Figure 6.4.

6.4.3.5 Summary

The objective of the integrated product/process screening stage is to provide a more rigorous assessment of both the technical and economic feasibility of a project. Like the initial product screening stage, it is an as-simplified-as-possible methodology to give the desired results. The purpose is not to prepare extremely detailed and costly process designs, but to provide another quantitative measurement by which projects can be ranked. Detailed designs and rigorous profitability analyses are future activities performed on portfolio candidates whose manufacturing technology becomes ripe for commercialization.

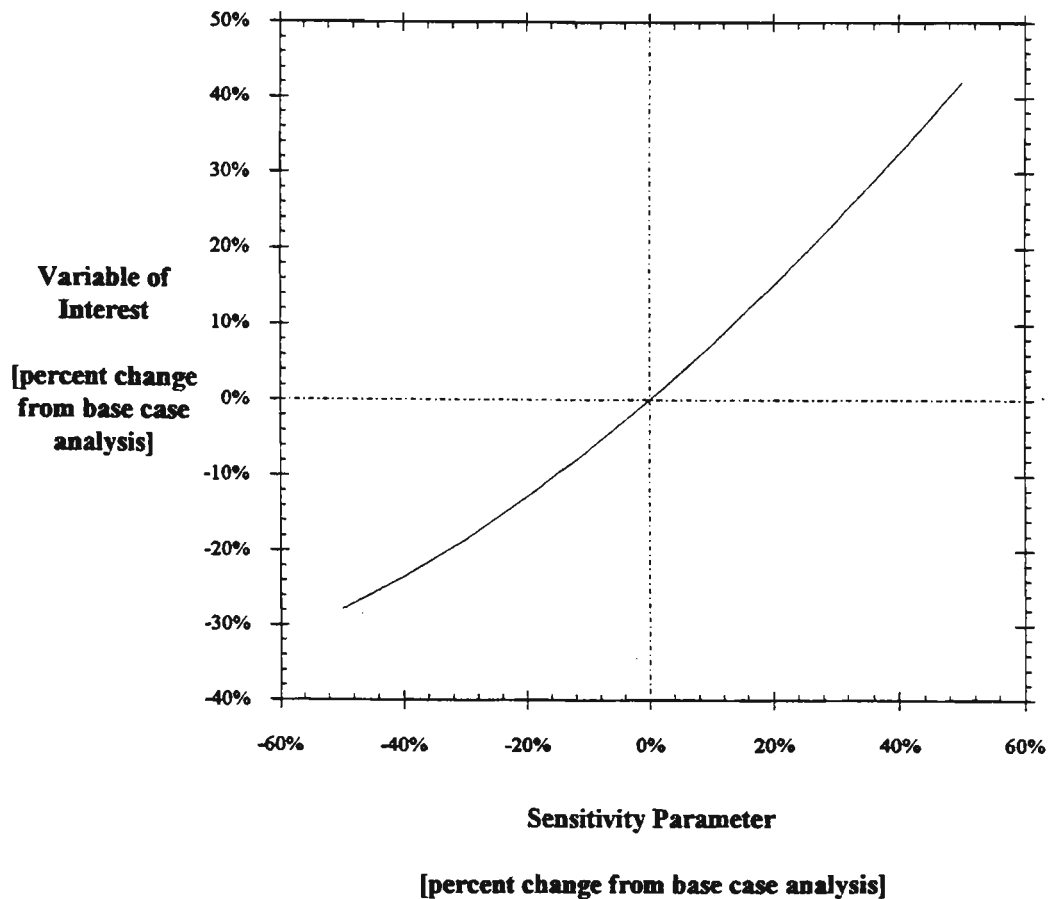


Figure 6.4 - Generic Example of Sensitivity Analysis

Also in common with the initial product screening stage is the iterative nature of the integrated product/process screening stage. In addition to factors that influenced the calculation of the FRF, a number of other factors come into consideration during this stage of the analysis. Parameters that affect the manufacturing costs will change periodically, some much more rapidly than others. Demonstrated new technology concepts for bioconversion systems and product purification and recovery operations may catapult a process from the ranks of a long-term opportunity to those of mid- or near-term opportunities. Constantly changing technologies, and revised economic forecasts, will necessitate continual re-evaluation of the projects at this level of analysis.

Figure 6.5 illustrates the integrated product/process screening methodology and its iterative design.

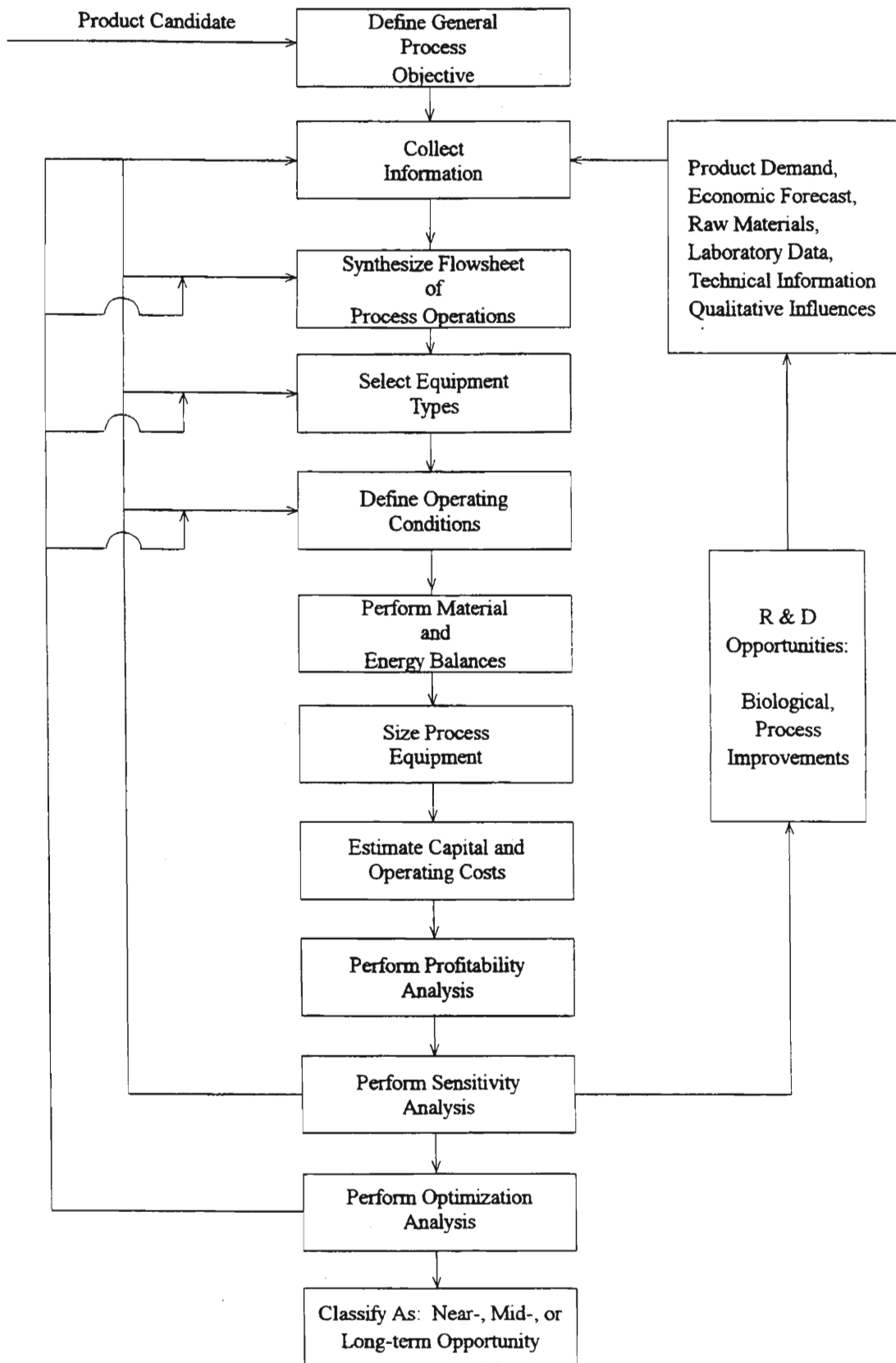


Figure 6.5 - Integrated Product/Process Screening Methodology

7.0 RESULTS OF INITIAL ANALYSIS

7.1 Initial Targets

The initial bioprocessing program portfolio is made up of 40 chemicals and materials. They are listed in alphabetical order in Table 7.1 along with their market values and consumption (where known). Note that the market values are based on demand and may be significantly higher than the actual cost of production.

As mentioned in sections 6.4.1.4 and 6.4.1.5, experimental yields were obtained from the literature and theoretical yields were calculated. Table 7.2 compares the experimental yield with the theoretical yield. The units of the yield are mass of product formed per mass of substrate consumed.

7.2 Applying Prioritization Methodology

The FRF was calculated for the 40 candidates for a number of feedstocks. The results of the calculations using wet-milled corn and hybrid poplar are reported below. These calculations were done once using demonstrated yields and once using the maximum theoretical yields.

Again, the lower the FRF, the greater the value of the products compared to the cost of the feedstock. If the FRF is unity, the value of the products just equals the value of the feedstock used. If the FRF is greater than unity, the products are worth less than the feedstock. Arbitrary project classifications into one of the time-frame opportunity categories can be made based on the FRF. For example, if the FRF using demonstrated yield data with corn as the feedstock is below a certain value, then that candidate might be classified as a near-term opportunity. Similarly, if the FRF is below the cut-off value using the theoretical yield data with corn as the feedstock, or using demonstrated yield data with hybrid poplar as the feedstock, the candidate might be classified as a mid-term opportunity. Candidates whose FRF is below the cut-off when using theoretical yield data with hybrid poplar as the feedstock might be classified as long-term opportunities. All other candidates would be classified as very long-term opportunities.

	Demonstrated Yield	Theoretical Yield
Corn	Near-Term Opportunity if FRF less than θ	Mid-Term Opportunity if FRF less than θ
Hybrid Poplar	Mid-Term Opportunity if FRF less than θ	Long-Term Opportunity if FRF less than θ

The preceding classification scheme could be generalized to have broader biological and process improvements as its bases. The cut-off criterion may be a parameter such as the difference between the estimated product selling price and the estimated market value, or perhaps the ratio of these two estimates. This is the kind of analysis that will be performed during the third screening stage.

	Current Biological Performance	Theoretical Biological Performance
Current Process Performance	Near-Term Opportunity if Criterion is Satisfied	Mid-Term Opportunity if Criterion is Satisfied
Theoretical Process Performance	Mid-Term Opportunity if Criterion is Satisfied	Long-Term Opportunity if Criterion is Satisfied

Table 7.1 - Bioprocessing Element Product Portfolio Candidates and Market Values

<u>Candidate</u>	<u>Price (\$/lb)</u>	<u>Domestic Consumption^a</u>	<u>Candidate</u>	<u>Price (\$/lb)</u>	<u>Domestic Consumption^a</u>
Acetaldehyde	0.46	561	Isopropanol	0.36	1,209
Acetic Acid	0.33	3,410	Itaconic Acid	1.00	
Acetone	0.34	2,178	Lactic Acid	0.35	40
Acrylic Acid	0.69	1,000	Lysine	1.20	37
Adipic Acid	0.65	1,567	Malic Acid	0.81	14
Alginate	1.00	14	Oleic Acid	0.62	30
Ascorbic Acid	1.00	32	Polyhydroxybutyric Acid	0.50	
Azelaic Acid	0.69		1,3-Propanediol	0.60	
Bacterial Cellulose	1.00		Propionic Acid	0.41	100
2,3-Butanediol	0.90		Propylene Glycol	0.58	621
Butanol	0.41	1,016	Protease	1.00	
Butyraldehyde	0.43	2,063	Pullulan	1.00	
Butyric Acid	0.48	30	Rhamsan	1.00	
Cellulase	1.00		Scleroglucan	1.00	
Citric Acid	0.82	332	Sorbitol	0.36	400
Dextran	1.00		Succinic Acid	0.35	
Fumaric Acid	0.67	33	Surfactin	0.75	
Gluconic Acid	0.90	5	Tartaric Acid	1.00	4
Glycerol	0.58	340	Xanthan Gum	1.00	25
Hyaluronic Acid	0.50		Xylitol	0.40	

^aDomestic consumption in millions of pounds/year.

Table 7.2 - Portfolio Candidate Yields: Demonstrated and Theoretical

<u>Candidate</u>	<u>Y_{ex}</u>	<u>Y_{th}</u>	<u>Candidate</u>	<u>Y_{ex}</u>	<u>Y_{th}</u>
Acetaldehyde	N/A	0.59	Isopropanol	0.12	0.33
Acetic Acid	0.50	0.67	Itaconic Acid	0.65	0.72
Acetone	0.12	0.48	Lactic Acid	0.95	1.00
Acrylic Acid	N/A	0.80	Lysine	0.50	0.70
Adipic Acid	N/A	0.75	Malic Acid	0.56	1.12
Alginate	0.52	0.90	Oleic Acid	0.05	0.37
Ascorbic Acid	0.01	0.98	Polyhydroxybutyric Acid	0.40	0.47
Azelaic Acid	N/A	0.52	1,3-Propanediol	0.80	0.42
Bacterial Cellulose	0.25	0.90	Propionic Acid	0.46	0.55
2,3-Butanediol	0.33	0.50	Propylene Glycol	0.27	0.42
Butanol	0.25	0.41	Protease	0.10	N/A
Butyraldehyde	N/A	0.40	Pullulan	0.43	0.90
Butyric Acid	0.38	0.49	Rhamsan	0.40	0.90
Cellulase	0.27	N/A	Scleroglucan	0.36	0.90
Citric Acid	0.87	1.07	Sorbitol	0.36	0.93
Dextran	0.30	0.53	Succinic Acid	0.87	0.98
Fumaric Acid	0.72	0.97	Surfactin	0.02	N/A
Gluconic Acid	0.90	1.09	Tartaric Acid	0.05	0.83
Glycerol	0.50	0.88	Xanthan Gum	0.60	0.90
Hyaluronic Acid	0.25	0.65	Xylitol	0.12	0.84

Tables 7.3 and 7.4 give the results of the FRF calculations for the 40 candidates. If a demonstrated yield was not currently available in the literature, the FRF calculation was not performed. In the cases of protease and cellulase, the theoretical yield was not calculated because these products are enzyme complexes, not single species, and no single product formation reaction can be written. Thus, the FRF calculation could not be performed for these candidates using a theoretical yield. Table 7.5 gives the results of an initial classification based on the FRF alone. Arbitrary FRF cut-off limits of 0.15, 0.20, and 0.25 were chosen. These results, when combined with various other qualitative factors and comparative analyses with existing processes, can be used to determine the order in which the processes are investigated in more depth.

Table 7.3 - FRF Results using Wet-Milled Corn as the Feedstock

<u>Candidate</u>	<u>FRF_{ex}</u>	<u>FRF_{th}</u>	<u>Candidate</u>	<u>FRF_{ex}</u>	<u>FRF_{th}</u>
Acetaldehyde	N/A	0.20	Isopropanol	0.73	0.38
Acetic Acid	0.30	0.24	Itaconic Acid	0.09	0.08
Acetone	0.75	0.30	Lactic Acid	0.16	0.16
Acrylic Acid	N/A	0.10	Lysine	0.09	0.07
Adipic Acid	N/A	0.11	Malic Acid	0.13	0.06
Alginate	0.11	0.06	Oleic Acid	0.86	0.23
Ascorbic Acid	1.15	0.06	Polyhydroxybutyric Acid	0.25	0.22
Azelaic Acid	N/A	0.15	1,3-Propanediol	0.12	0.21
Bacterial Cellulose	0.21	0.06	Propionic Acid	0.27	0.23
2,3-Butanediol	0.18	0.12	Propylene Glycol	0.31	0.21
Butanol	0.43	0.29	Protease	0.43	N/A
Butyraldehyde	N/A	0.28	Pullulan	0.13	0.06
Butyric Acid	0.28	0.22	Rhamsan	0.14	0.06
Cellulase	0.19	N/A	Scleroglucan	0.15	0.06
Citric Acid	0.08	0.07	Sorbitol	0.36	0.16
Dextran	0.18	0.11	Succinic Acid	0.18	0.16
Fumaric Acid	0.12	0.10	Surfactin	1.17	N/A
Gluconic Acid	0.07	0.06	Tartaric Acid	0.67	0.07
Glycerol	0.18	0.11	Xanthan Gum	0.09	0.06
Hyaluronic Acid	0.37	0.17	Xylitol	0.70	0.16

Table 7.4 - FRF Results using Hybrid Poplar as the Feedstock

<u>Candidate</u>	<u>FRF_{ex}</u>	<u>FRF_{th}</u>	<u>Candidate</u>	<u>FRF_{ex}</u>	<u>FRF_{th}</u>
Acetaldehyde	N/A	0.13	Isopropanol	0.57	0.27
Acetic Acid	0.20	0.16	Itaconic Acid	0.06	0.05
Acetone	0.58	0.20	Lactic Acid	0.11	0.10
Acrylic Acid	N/A	0.07	Lysine	0.06	0.04
Adipic Acid	N/A	0.08	Malic Acid	0.08	0.04
Alginate	0.07	0.04	Oleic Acid	0.69	0.15
Ascorbic Acid	1.01	0.04	Polyhydroxybutyric Acid	0.17	0.15
Azelaic Acid	N/A	0.10	1,3-Propanediol	0.08	0.14
Bacterial Cellulose	0.14	0.04	Propionic Acid	0.18	0.15
2,3-Butanediol	0.12	0.08	Propylene Glycol	0.21	0.14
Butanol	0.30	0.20	Protease	0.31	N/A
Butyraldehyde	N/A	0.20	Pullulan	0.09	0.04
Butyric Acid	0.19	0.15	Rhamsan	0.09	0.04
Cellulase	0.13	N/A	Scleroglucan	0.10	0.04
Citric Acid	0.05	0.04	Sorbitol	0.25	0.11
Dextran	0.12	0.07	Succinic Acid	0.01	0.01
Fumaric Acid	0.08	0.06	Surfactin	1.04	N/A
Gluconic Acid	0.05	0.04	Tartaric Acid	0.52	0.05
Glycerol	0.12	0.07	Xanthan Gum	0.06	0.04
Hyaluronic Acid	0.26	0.11	Xylitol	0.54	0.11

Table 7.5 - Initial Candidate Classification

FRF Cut-OFF

Candidate	0.15	0.20	0.25
Acetaldehyde	Very Long	Mid	Mid
Acetic Acid	Very Long	Very Long	Mid
Acetone	Very Long	Very Long	Very Long
Acrylic Acid	Mid	Mid	Mid
Adipic Acid	Mid	Mid	Mid
Alginate	Near	Near	Near
Ascorbic Acid	Mid	Mid	Mid
Azelaic Acid	Very Long	Mid	Mid
Bacterial Cellulose	Mid	Mid	Near
Butanediol, 2,3-	Mid	Near	Near
Butanol	Very Long	Very Long	Very Long
Butyraldehyde	Very Long	Very Long	Very Long
Butyric Acid	Very Long	Long	Mid
Cellulase	Long	Near	Near
Citric Acid	Near	Near	Near
Dextran	Mid	Near	Near
Fumaric Acid	Near	Near	Near
Gluconic Acid	Near	Near	Near
Glycerol	Mid	Near	Near
Hyaluronic Acid	Very Long	Mid	Mid
Isopropanol	Very Long	Very Long	Very Long
Itaconic Acid	Near	Near	Near
Lactic Acid	Long	Near	Near
Lysine	Near	Near	Near
Malic Acid	Near	Near	Near
Oleic Acid	Very Long	Very Long	Mid
Polyhydroxybutyric Acid	Very Long	Long	Mid
Propanediol, 1,3-	Near	Near	Near
Propionic Acid	Very Long	Long	Mid
Propylene Glycol	Very Long	Very Long	Mid
Protease	Very Long	Very Long	Very Long
Pullulan	Near	Near	Near
Rhamsan Gum	Near	Near	Near
Scleroglucan	Mid	Near	Near
Sorbitol	Very Long	Mid	Mid
Succinic Acid	Long	Near	Near
Surfactin	Very Long	Very Long	Very Long
Tartaric Acid	Mid	Mid	Mid
Xanthan Gum	Near	Near	Near
Xylitol	Very Long	Mid	Mid

7.3 Comparative Evaluations

This section contains a series of comparative analyses of proposed bioprocessing routes and current petrochemical routes. Although there are 40 product candidates in the bioprocessing element portfolio, only 12 were evaluated in this comparative analysis. Many candidates in the portfolio are produced solely through bioprocessing routes; for example lysine or pullulan gum. Others are currently produced through bioprocessing, although a petrochemical process is available, for example, citric acid. Some candidates, though theoretically possible to produce through bioprocesses, have no proposed bioprocess, and thus yields and raw material costs for these processes cannot be determined.

These comparative analyses should be viewed as a first attempt to compare the competitiveness of bioprocesses with the current petrochemical-based processes.

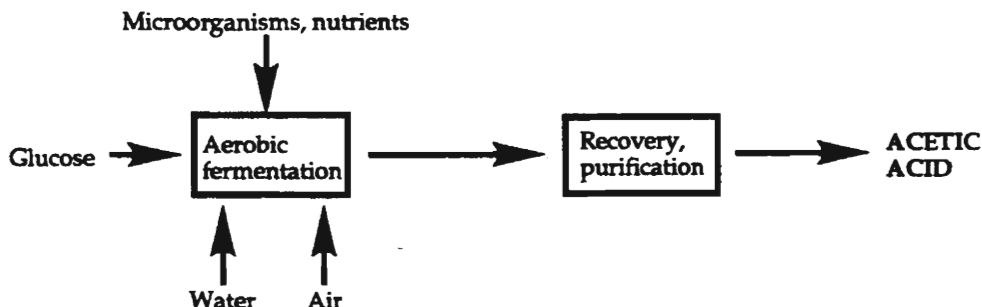
Preliminary evaluations of the bioprocesses compared to the conventional petrochemical-based processes were performed slightly differently than the comparative evaluations of thermal/chemical biomass-based processes and petrochemical-based alternative processes. The main difference is that the raw material costs were estimated and used in the calculations rather than the raw material cost contribution. Another difference is that a range of bioprocessing feedstock costs were considered.

An example of the raw material cost ratio is given for two cases. Both cases assume the glucose cost to be \$0.075/lb. This is an estimated transfer price of glucose from a corn wet-milling facility. The first case is for currently achievable bioprocess technology. The second case is for theoretically achievable bioprocess technology.

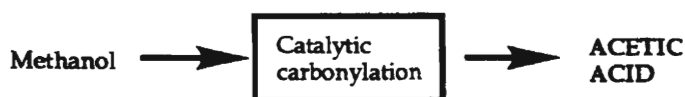
Also included in each analysis is a chart showing the sensitivity of the raw material cost ratio of each product to the cost of the glucose. Both currently achievable and theoretically achievable bioprocess technology scenarios are shown on these charts.

7.3.1 Acetic Acid

Bioprocess:



Petrochemical process:



Processes Compared: The bioprocess is an aerobic fermentation of glucose, with about 50% conversion to acetic acid. The process is economically favorable if the cost of glucose is sufficiently low.

In the hydrocarbon-based route, the currently predominant acetic acid process is direct carbonylation of methanol, which is manufactured from natural gas-derived syn gas (carbon monoxide plus hydrogen). The conversion of methanol is essentially 100%.

Raw Materials Cost Comparison: In the bioprocess, with a glucose raw materials cost of \$0.075/lb and 95% conversion, the raw materials cost is \$0.300/lb of acetic acid.

In the manufacture of acetic acid from methanol, with 100% conversion of methanol, the raw material cost is \$0.131/lb of acetic acid. This estimate is based on \$1.60/million BTU natural gas.

Comparison of the costs of the hydrocarbon and bioprocess routes gives the ratio

$$(\$0.131)/(\$0.300) = 0.44$$

and when a "risk" factor of 1.3 is included, the ratio becomes

$$0.44/1.30 = 0.34.$$

Therefore, the bioprocess route does not pass the screening test.

Future Projections: Potential biological and process improvements could reduce the raw materials cost for the bioprocess to \$0.118/lb of acetic acid. Recombination of the costs of the hydrocarbon and bioprocess routes gives the ratio

$$(\$0.131)/(\$0.118) = 1.11$$

and when a "risk" factor of 1.3 is included, the ratio becomes

$$1.11/1.30 = 0.86.$$

Acetic acid from glucose comes close to passing the screening test and might compete in future capacity expansions if the glucose raw material cost can compete with natural gas-derived syn gas, and/or if the necessary process improvements can be realized (see Figure 7.1).

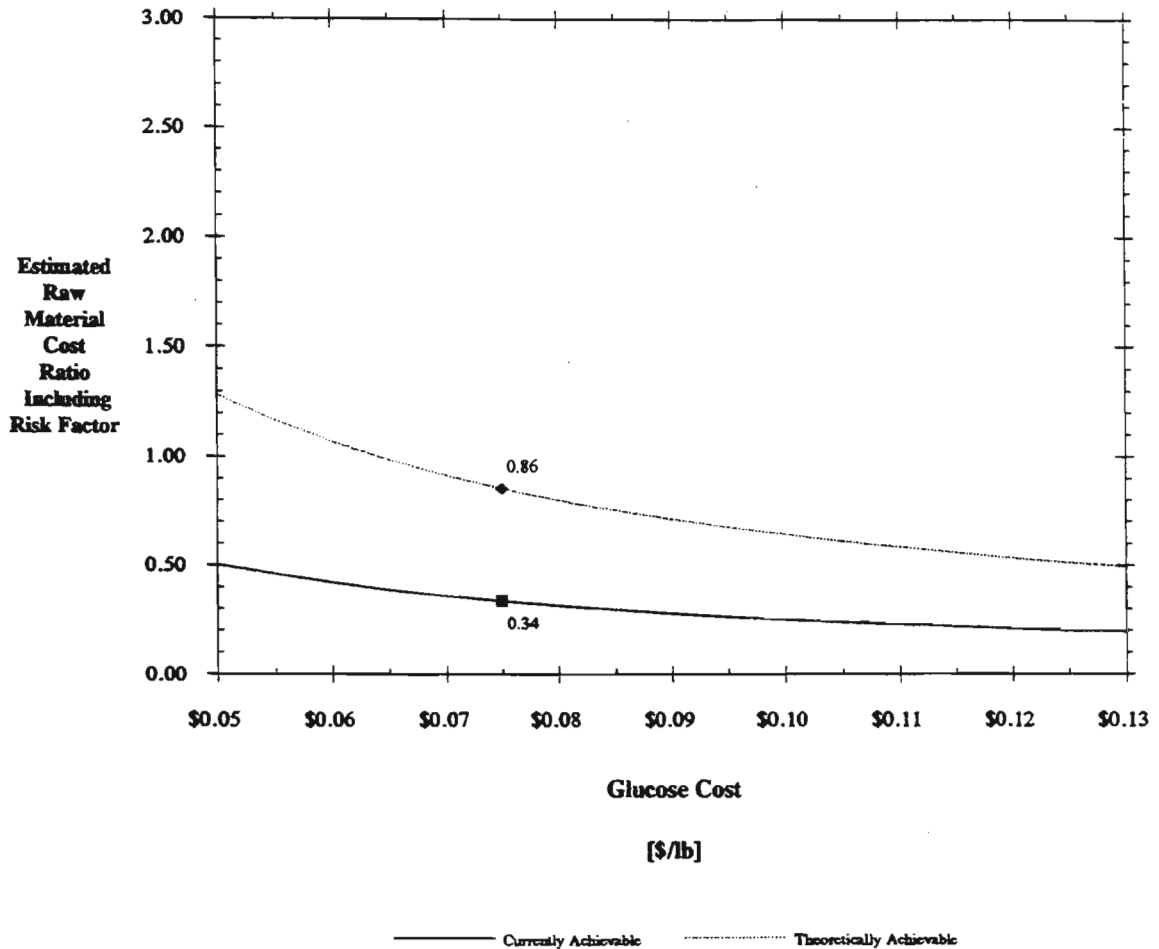
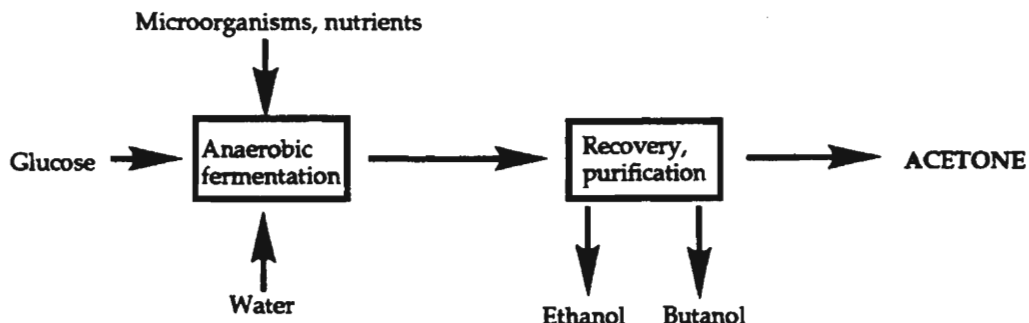


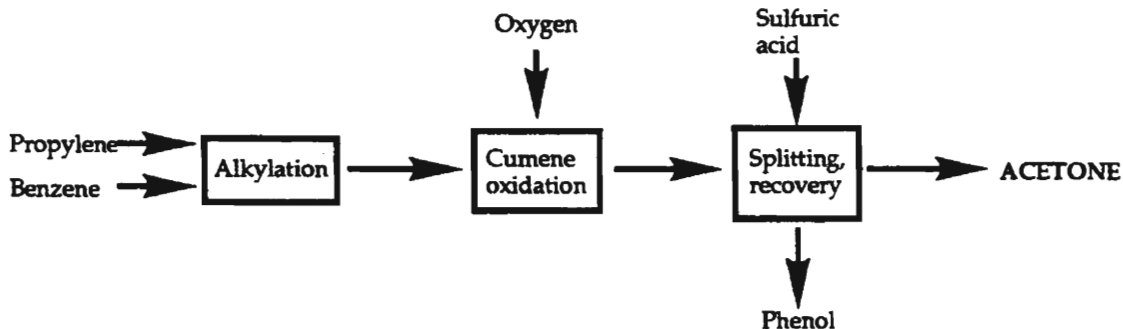
Figure 7.1 - Estimated Raw Material Cost Ratio versus Glucose Cost, Acetic Acid Production

7.3.2 Acetone

Bioprocess:



Petrochemical process:



Processes Compared: In the bioprocess, acetone, butanol and ethanol are coproduced by fermentation of glucose in wt% yields of 9%, 23% and 2%, respectively, for a total coproduct yield of 34%, based on glucose. If glucose is valued at a cost of \$0.075/lb, the raw materials cost is \$1.25/lb of the acetone, butanol, and ethanol mixture.

Acetone is a coproduct, with phenol, of the oxidation of isopropyl benzene (cumene), which is made in a highly efficient alkylation of benzene with propylene. If all the propylene is assumed to be converted to acetone, the raw materials cost is \$0.129/lb of acetone, with propylene valued at \$0.135/lb.

The ratio of the hydrocarbon-based process and bioprocess raw materials cost is then

$$(\$0.129)/(\$1.25) = 0.10,$$

and when a "risk" factor of 1.3 is included, the ratio becomes

$$0.10/1.3 = 0.08.$$

It would be difficult for the bioprocess to compete with the existing petrochemical route, primarily because of the low yield of useful fermentation coproducts and the relatively much lower cost of the hydrocarbon feedstocks. Any RD&D effort must address these yield differences between the two routes.

Future Projections: Potential biological and process improvements could reduce the raw materials cost for the bioprocess to \$0.164/lb of acetone. Recombination of the costs of the hydrocarbon and bioprocess routes gives the ratio

$$(\$0.129)/(\$0.164) = 0.79$$

and when a "risk" factor of 1.3 is included, the ratio becomes

$$0.79/1.30 = 0.61.$$

Acetone via fermentation of glucose will have difficulty competing in future capacity expansions unless a low-cost source of glucose is available (see Figure 7.2).

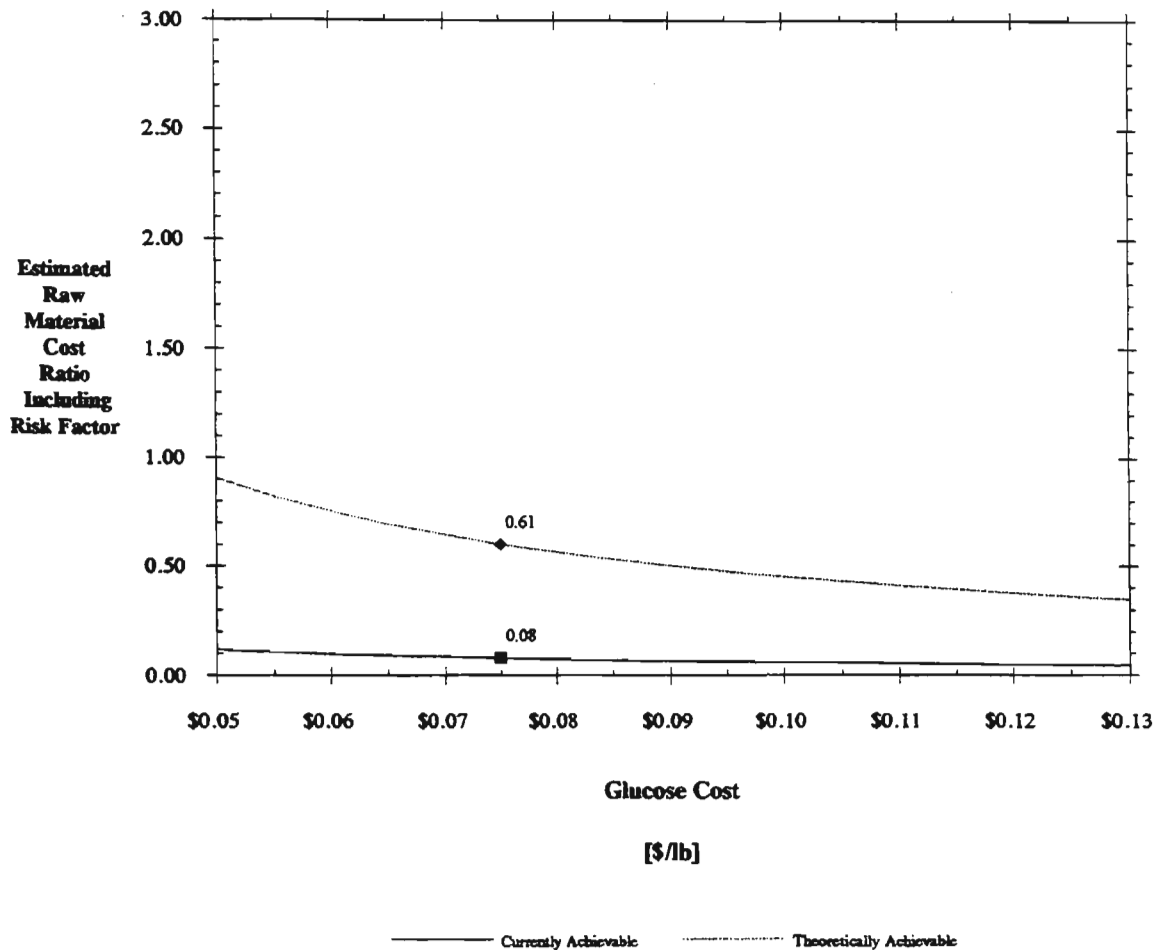
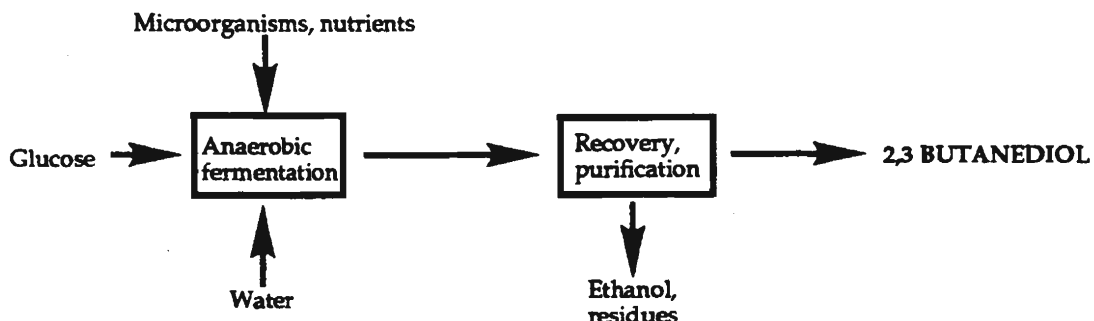


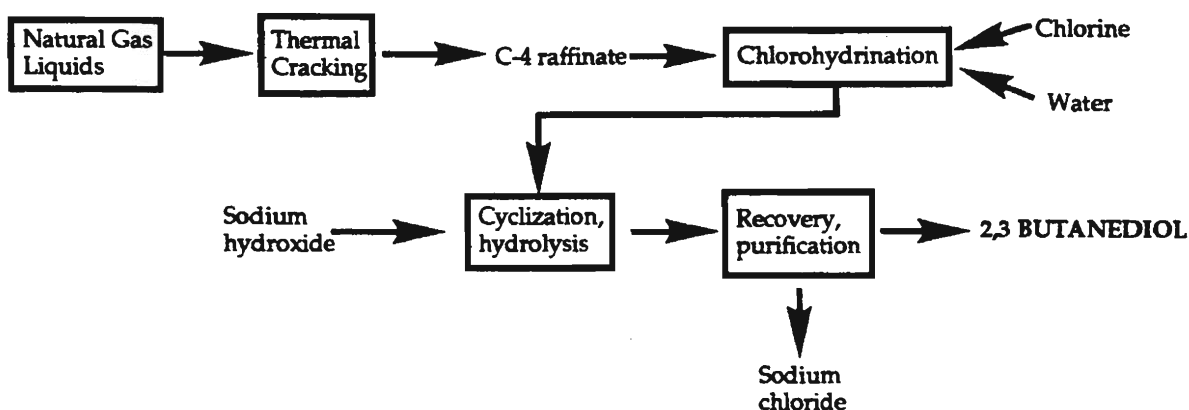
Figure 7.2 - Estimated Raw Material Cost Ratio versus Glucose Cost, Acetone Production

7.3.3 2,3-Butanediol

Bioprocess:



Petrochemical process:



Processes Compared: 2,3-Butanediol is a small-volume, specialty chemical that is used as a resin crosslinking agent and as a precursor to insecticides and pharmaceutical products; its future as a commodity is unclear.

The bioprocess is a fermentation of glucose with coproduction of 2,3-butanediol and ethanol.

The hydrocarbon-based process is based on a 4-step conversion of the "C-4 raffinate" from hydrocarbon cracking (ethylene process) and consists of: (1) chlorohydration (90% yield); (2) cyclization with caustic (90% yield); (3) hydrolysis (90% yield); and (4) vacuum fractionation (90% yield). The major raw materials consumed are butenes, chlorine and caustic.

Raw Materials Cost Comparison: In the glucose fermentation process, there is an estimated 75% yield of coproduct ethanol and 2,3-butanediol. Using a glucose raw materials cost of \$0.075/lb and a recovery yield of 85%, and spreading costs over the two coproducts, the raw materials cost is \$0.455/lb of 2,3-butanediol and ethanol.

In the hydrocarbon-based process, the raw materials costs for butenes, chlorine, and caustic are \$0.087, \$0.08 and \$0.19, respectively, per lb of 2,3-butanediol, for a total raw materials cost of \$0.357/lb, based on the reported yields of the process. The ratio of the hydrocarbon-based and bioprocess raw materials cost is then

$$(\$0.357)/(\$0.455) = 0.78,$$

and when a "risk" factor of 1.3 is included, the ratio becomes

$$0.78/1.3 = 0.60.$$

Future Projections: Potential biological and process improvements could reduce the raw materials cost for the bioprocess to \$0.158/lb of 2,3-butanediol. Recombination of the costs of the hydrocarbon and bioprocess routes gives the ratio

$$(\$0.357)/(\$0.158) = 2.26$$

and when a "risk" factor of 1.3 is included, the ratio becomes

$$2.26/1.30 = 1.74.$$

A low-cost source of glucose together with biological and process improvements could make the 2,3-butanediol bioprocess a viable alternative to the petrochemical route (see Figure 7.3).

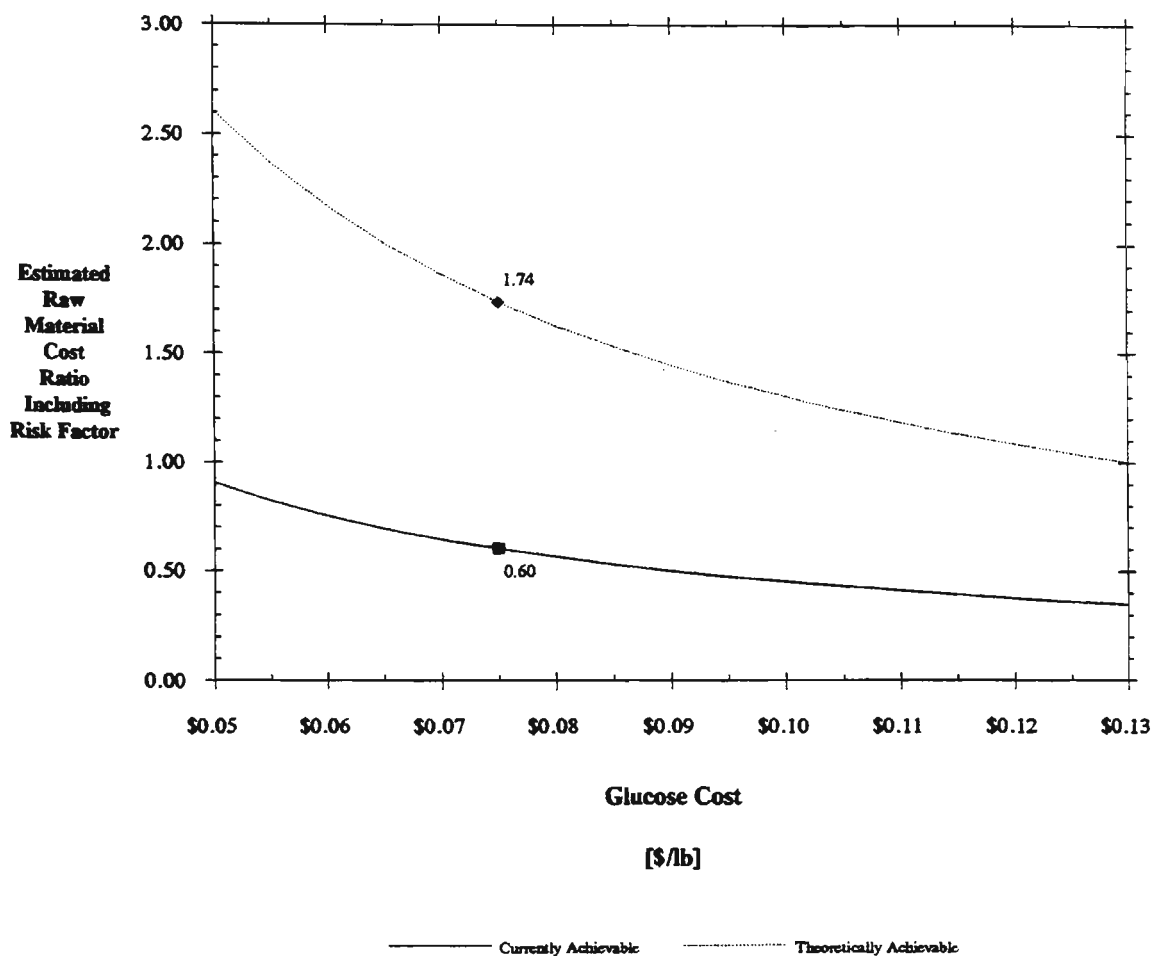
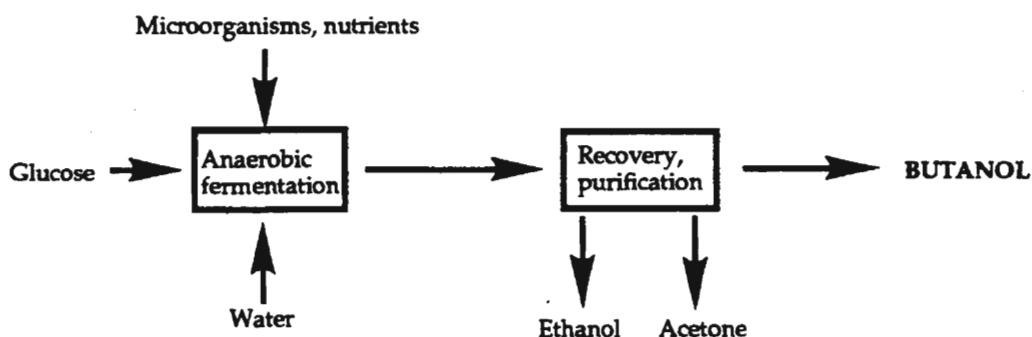


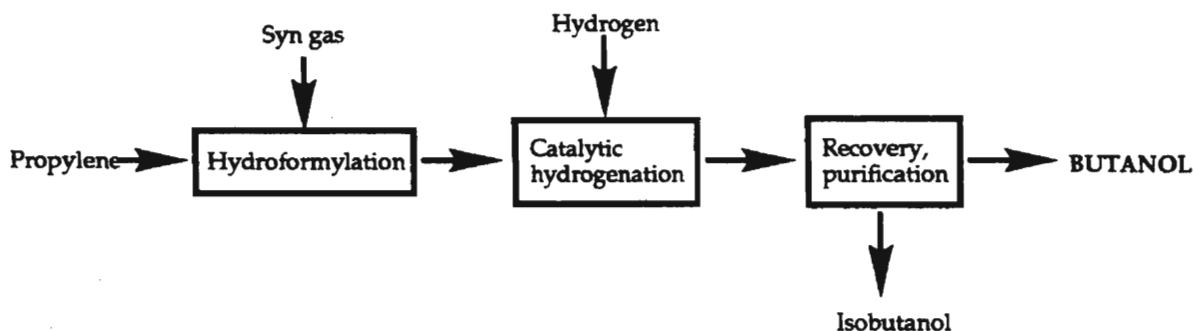
Figure 7.3 - Estimated Raw Material Cost Ratio versus Glucose Cost, 2,3-Butanediol Production

7.3.4 Butanol

Bioprocess:



Petrochemical process:



Processes Compared: Hydrocarbon-based n-butanol is made in two steps: (1) hydroformylation (oxo) of propylene with syn gas to mixed butyraldehydes, and (2) catalytic hydrogenation of the aldehydes to mixed coproduct iso- and n-butanol; n-butanol is recovered and purified by distillation. The raw materials cost is \$0.323/lb of n-butanol, with propylene valued at \$0.135/lb and syn gas at \$2.29/thousand standard cubic feet.

The raw materials cost for the bioprocess is \$0.60/lb of n-butanol (see section 7.3.2). The ratio of the hydrocarbon-based and biomass raw materials cost is then

$$(\$0.323)/(\$0.60) = 0.54,$$

and when a "risk" factor of 1.30 is included, the ratio becomes

$$0.54/1.30 = 0.41.$$

The biomass process would have difficulty competing with the existing petrochemical route, primarily because of the low yield of useful fermentation coproducts and the relatively much lower cost of the hydrocarbon feedstocks. RD&D must address these yield differences between the routes.

Future Projections: Potential biological and process improvements could reduce the raw materials cost for the bioprocess to \$0.193/lb of n-butanol. Recomparison of the costs of the hydrocarbon and bioprocess routes gives the ratio

$$(\$0.357)/(\$0.193) = 1.67$$

and when a "risk" factor of 1.3 is included, the ratio becomes

$$1.67/1.30 = 1.29.$$

Lower glucose costs and biological and process improvements could make the acetone-butanol-ethanol bioprocess economically viable (see Figure 7.4).

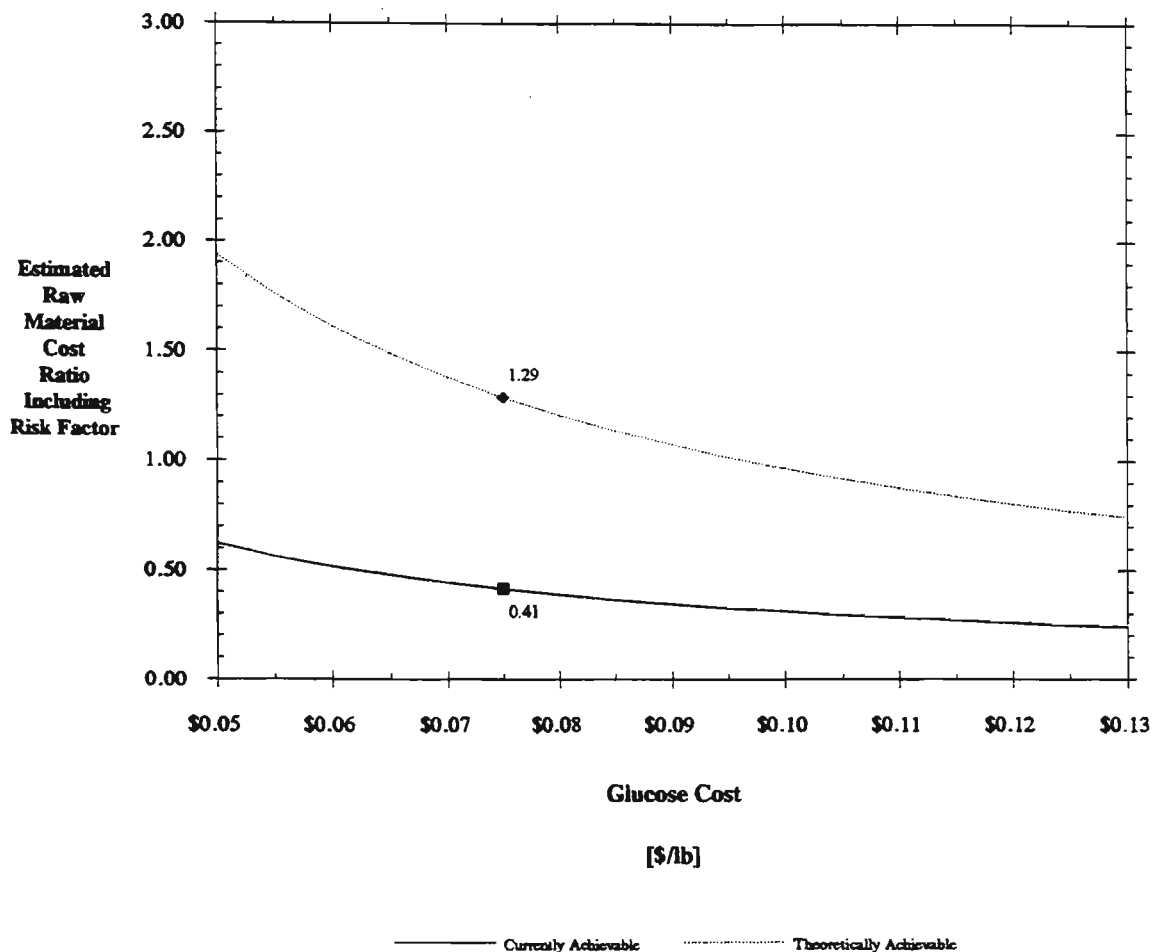
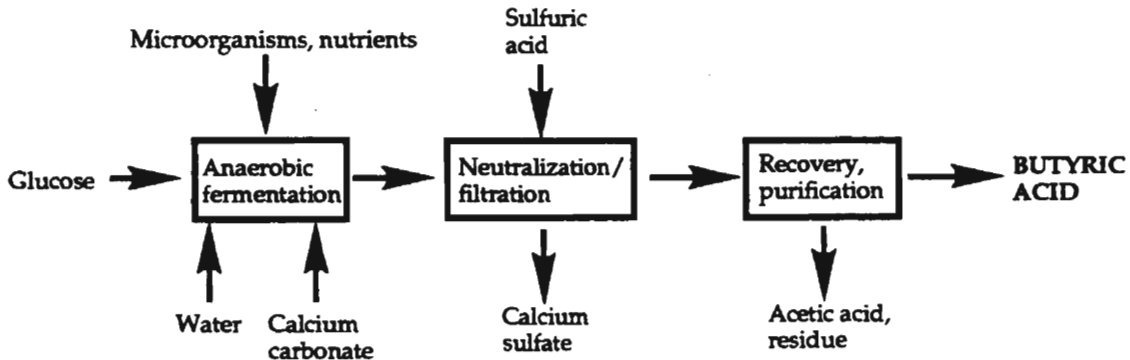


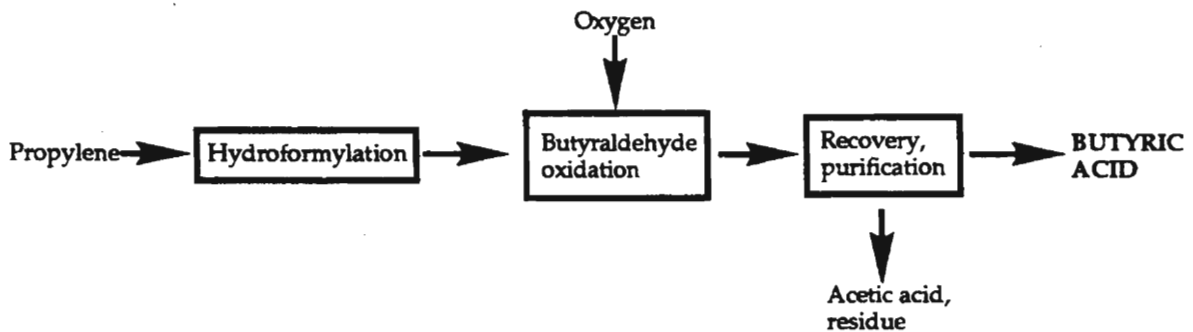
Figure 7.4 - Estimated Raw Material Cost Ratio versus Glucose Cost, Butanol Production

7.3.5 Butyric Acid

Bioprocess:



Petrochemical process:



Processes Compared: In the bioprocess, an anaerobic fermentation of glucose, using limestone for pH control and sulfuric acid for neutralization, gives an overall 46% yield of butyric acid, based on glucose feedstock. Acetic acid is a coproduct.

Hydrocarbon-derived butyric acid is manufactured by oxidation of butyraldehyde, with propylene as the principal raw material. The yield is 90% to butyric acid, based on butyraldehyde.

Raw Materials Cost Comparison: In the bioprocess, raw materials cost based on the yield of the reaction is \$0.395/lb of butyric acid. In the butyraldehyde oxidation process, total raw materials cost is \$0.215/lb of butyric acid. Assumed basic raw materials costs include \$0.135/lb for propylene and \$2.29/thousand standard cubic feet for synthesis gas. The ratio of raw materials costs is then

$$(\$0.215)/(\$0.395) = 0.54$$

and when a "risk" factor of 1.3 is added, the ratio becomes

$$0.54/1.3 = 0.42.$$

The bioprocess would have difficulty competing with the existing petrochemical route, primarily because of the low yield of useful fermentation coproducts and the relatively much lower cost of the hydrocarbon feedstocks. Any RD&D effort must address these yield differences between the two routes.

Future Projections: Potential biological and process improvements could reduce the raw materials cost for the bioprocess to \$0.161/lb of butyric acid. Recomparison of the costs of the hydrocarbon and bioprocess routes gives the ratio

$$(\$0.215)/(\$0.161) = 1.34$$

and when a "risk" factor of 1.3 is included, the ratio becomes

$$1.34/1.30 = 1.03.$$

Biological and process improvements could make the butyric acid bioprocess competitive with the petrochemical process. A low-cost source of glucose would widen the competitive gap in favor of the bioprocess (see Figure 7.5).

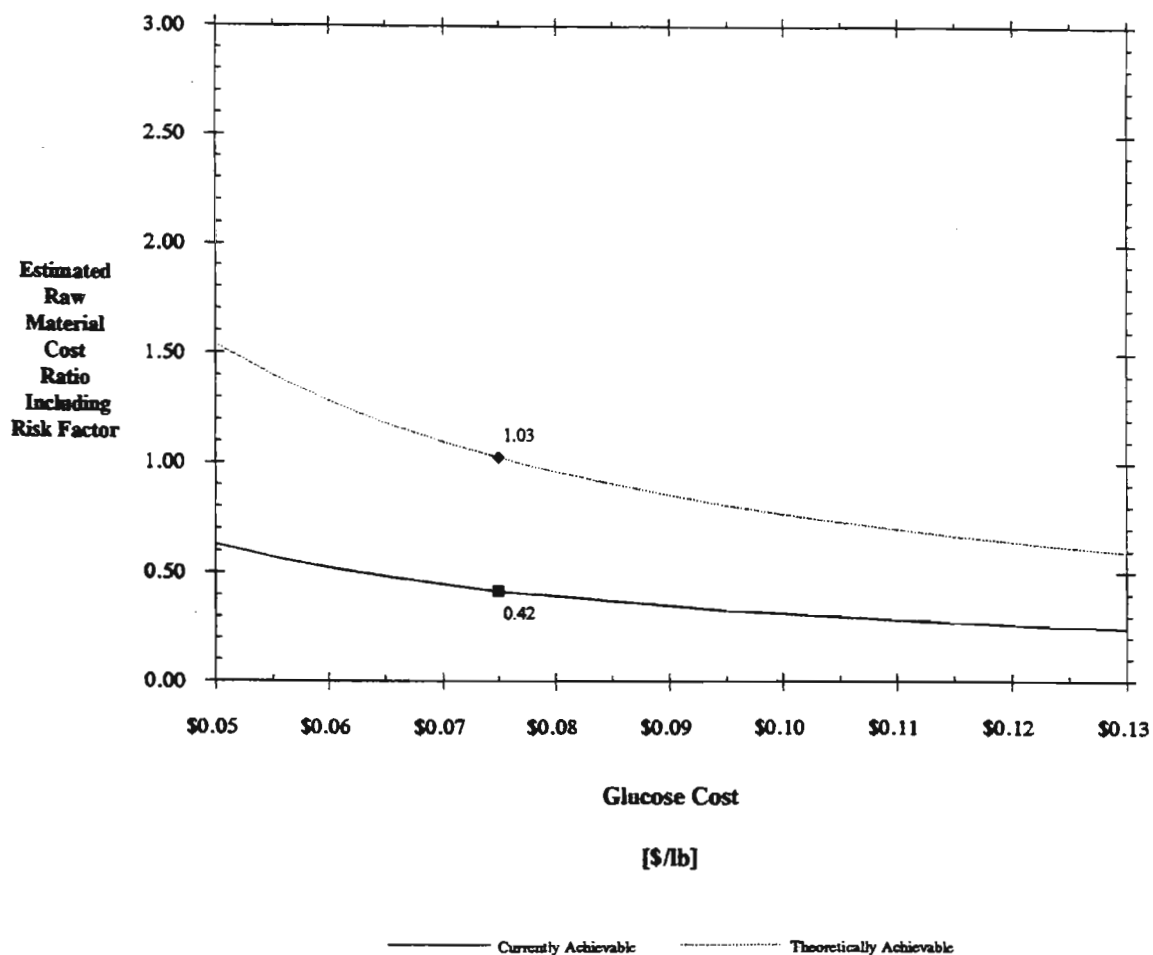
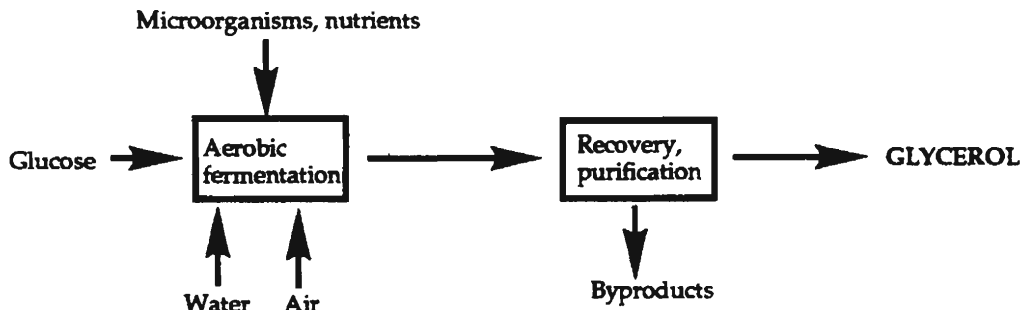


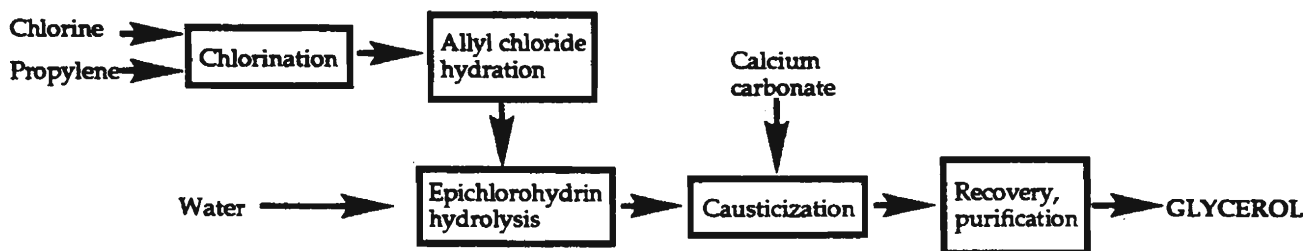
Figure 7.5 - Estimated Raw Material Cost Ratio versus Glucose Cost, Butyric Acid Production

7.3.6 Glycerol

Bioprocess:



Petrochemical process:



Processes Compared: Glycerol is now manufactured from "natural" sources (mostly animal fats) or by one of several existing synthetic routes. End uses determine the split. Because "natural" glycerol is a by-product of soap, fatty acid, and detergent alcohol production, its availability is dependent on demand for those products rather than on total glycerol demand. Thus, historical fluctuations in natural glycerol production mainly reflect demand for detergent alcohol (from natural sources), soap, and fatty acid in those years. Because natural glycerol is a by-product, it is sold at the highest price that will ensure its total disposition. Consequently, the market available to synthetic glycerol is determined by the total glycerol demand minus the supply of natural glycerol. Fluctuations in synthetic glycerol production for the most part reflect this demand differential. The proposed production of glycerol from glucose would compete as "synthetic" material.

In the aerobic fermentation process, there would be a projected 50% yield of glycerol from glucose, with no credits for possible coproducts. In the most common synthetic glycerol process, propylene is processed in five conversion steps: (1) propylene to allyl chloride; (2) allyl chloride to dichlorohydrin; (3) dichlorohydrin to epichlorohydrin; (4) epichlorohydrin to α -monochlorohydrin; and (5) α -monochlorohydrin to glycerol, using limestone.

Raw Materials Cost Comparison: For the glucose-based fermentation process, a glucose raw materials cost of \$0.075/lb of glucose, results in a total raw materials cost of \$0.300/lb of glycerol, given the known yield of the process.

For the propylene-based synthetic process, the principal raw materials costs are propylene at \$0.122/lb, chlorine at \$0.203/lb, and limestone at \$0.027/lb, for a total of \$0.352/lb of glycerol, based on the yields of the commercial process. The ratio of the hydrocarbon-based and bioprocess raw materials costs is then

$$(\$0.352)/(\$0.300) = 1.17,$$

and when a "risk" factor of 1.3 is included, the ratio becomes

$$1.17/1.3 = 0.9.$$

Future Projections: Potential biological and process improvements could reduce the raw materials cost for the bioprocess to \$0.09/lb of glycerol. Recomparison of the costs of the hydrocarbon and bioprocess routes gives the ratio

$$(\$0.352)/(\$0.09) = 3.91$$

and when a "risk" factor of 1.3 is included, the ratio becomes

$$3.91/1.30 = 3.01.$$

The glucose fermentation process to glycerol appears to be a highly promising approach, provided all the assumptions on yield and glucose cost are realized.

Biological and process improvements could make the glycerol bioprocess competitive with the petrochemical process. A low-cost source of glucose would widen the competitive gap in the favor of the bioprocess. Glucose-based glycerol should find a place in the market, provided the projected low feedstock costs are realized. It also might qualify for special uses as "natural" glycerol because it would be derived from biomass rather than hydrocarbons (see Figure 7.6).

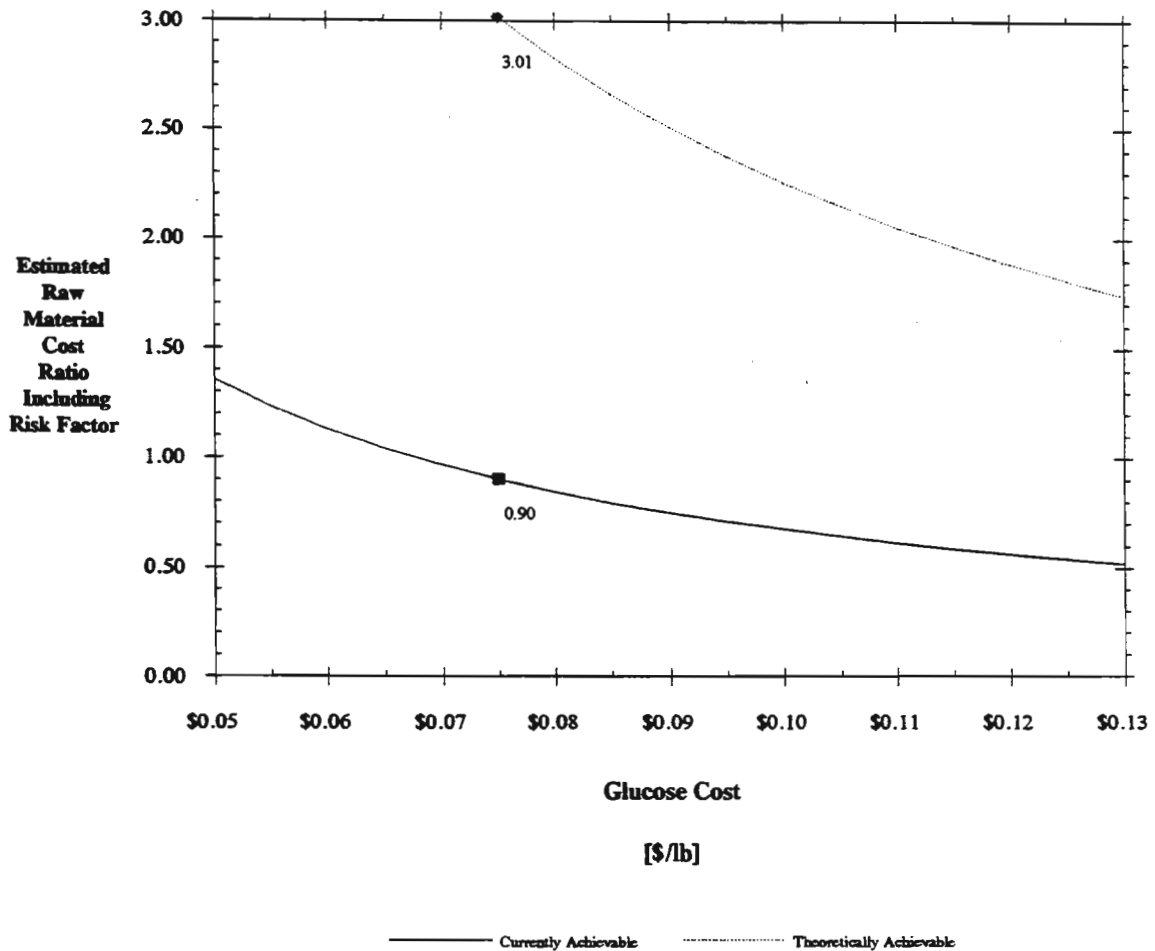
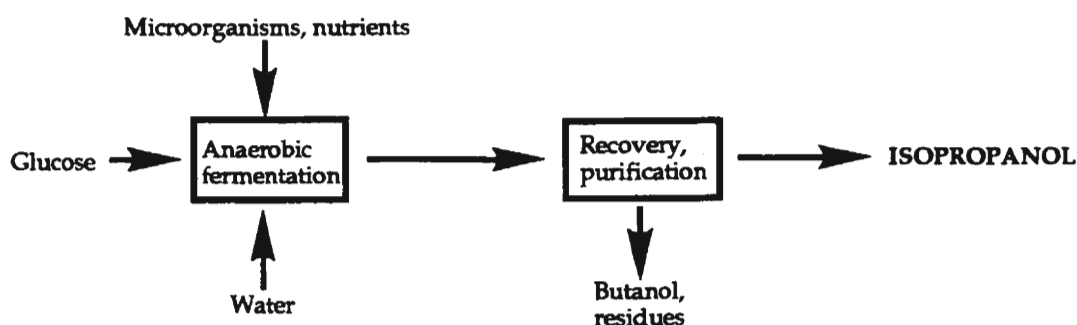


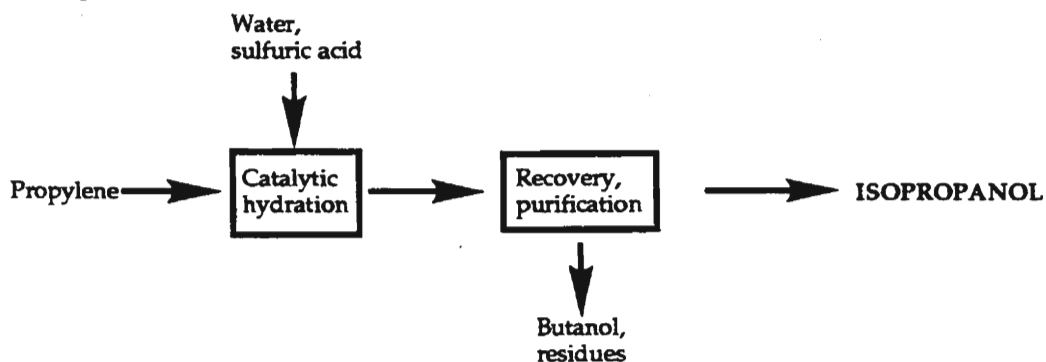
Figure 7.6 - Estimated Raw Material Cost Ratio versus Glucose Cost, Glycerol Production

7.3.7 Isopropanol

Bioprocess:



Petrochemical process:



Processes Compared: The proposed glucose fermentation route yields the coproducts butanol and isopropanol, with a yield to total products of 35%, based on glucose. The product split is assumed to be 43% isopropanol and 57% butanol.

In the existing hydrocarbon-based process, propylene is hydrated, either directly, at 1500-2000 psig, or indirectly, through isopropyl sulfate, with recycle of sulfuric acid, to isopropanol. Yield based on propylene is about 90% by either route.

Raw Materials Cost Comparison: In the glucose fermentation process, assuming a glucose cost of \$0.075/lb, the raw materials cost is \$1.25/lb of isopropanol.

In the propylene hydration process, the raw materials cost is \$0.105/lb of isopropanol, based on propylene valued at \$0.135/lb. The ratio of hydrocarbon-based and bioprocess raw materials cost is then

$$(\$0.105)/(\$1.25) = 0.08,$$

and when a "risk" factor of 1.3 is included, the ratio becomes

$$0.08/1.3 = 0.06.$$

The bioprocess would have difficulty competing with the existing petrochemical route, primarily because of the low yield of useful fermentation coproducts and the relatively much lower cost of the hydrocarbon feedstocks. Any RD&D effort must address these yield differences between the two routes.

Future Projections: Potential biological and process improvements could reduce the raw materials cost for the bioprocess to \$0.239/lb of isopropanol. Recomparison of the costs of the hydrocarbon and bioprocess routes gives the ratio

$$(\$0.105)/(\$0.239) = 0.44$$

and when a "risk" factor of 1.3 is included, the ratio becomes

$$0.44/1.30 = 0.34.$$

The bioprocess still would have difficulty competing with the existing petrochemical route, primarily because of the low yield and the relatively much lower cost of the hydrocarbon feedstocks (see Figure 7.7).

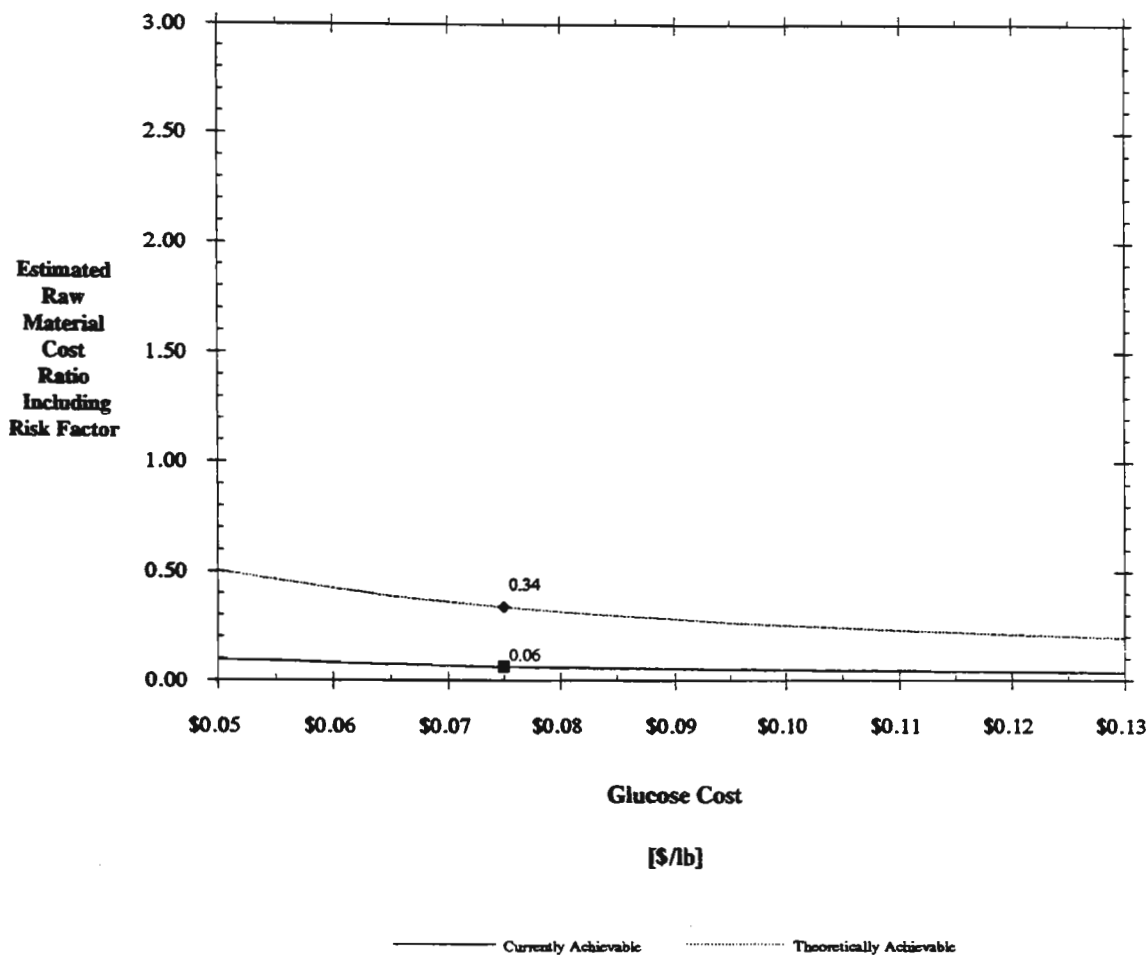
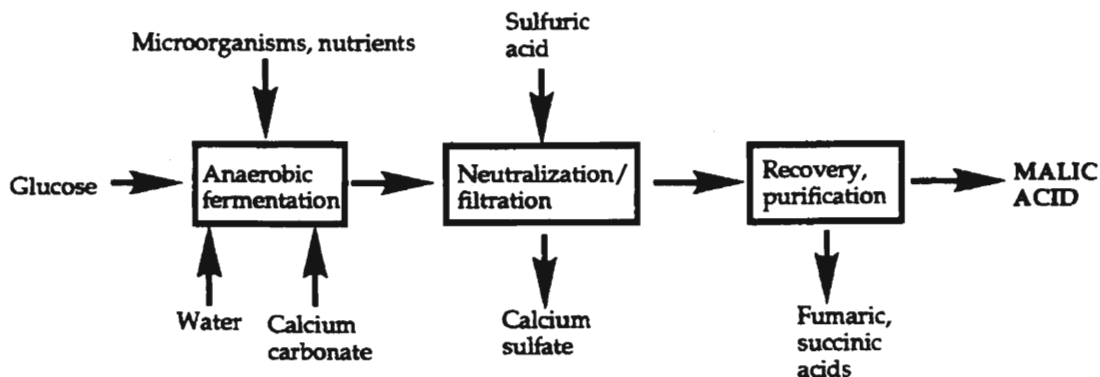


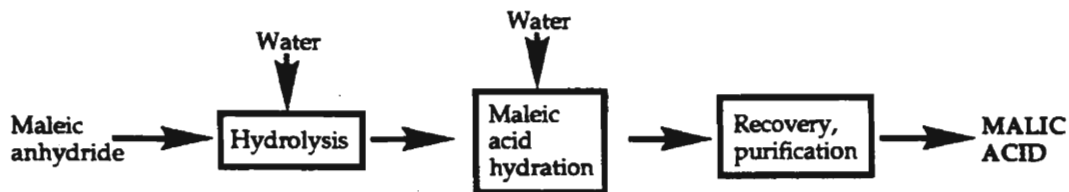
Figure 7.7 - Estimated Raw Material Cost Ratio versus Glucose Cost, Isopropanol Production

7.3.8 Malic Acid

Bioprocess:



Petrochemical process:



Processes Compared: In the glucose fermentation process, there is coproduction of malic, succinic and fumaric acids. For this appraisal an overall yield of 75%, glucose to malic acid, was used, with an 85% recovery efficiency.

In the hydrocarbon-based route, malic acid is manufactured in a two-step process: (1) hydration of maleic anhydride to maleic acid, and (2) addition of another mole of water to produce malic acid. The sole U.S. manufacturer is Alberta Gas, with an annual capacity of 10,000,000 pounds to supply specialty uses in the pharmaceutical industry. The potential utility of malic acid as a commodity is currently unclear.

Raw Materials Cost Comparison: In the bioprocess, the raw materials cost is \$0.268/lb of malic acid, based on a glucose cost of \$0.075/lb.

In the hydrocarbon-based process, net raw materials cost is \$0.269/lb of malic acid. The ratio of raw materials cost is then

$$(\$0.269)/(\$0.268) = 1.00$$

and when a "risk" factor of 1.3 is added, the ratio becomes

$$0.77/1.3 = 0.77.$$

The bioprocess would have difficulty competing with the existing petrochemical route, primarily because of the low yield of useful fermentation coproducts and the relatively much lower cost of the hydrocarbon feedstocks. Any RD&D effort must address these yield differences between the two routes.

Future Projections: Potential biological and process improvements could reduce the raw materials cost for the bioprocess to \$0.081/lb of malic acid. Recomparison of the costs of the hydrocarbon and bioprocess routes gives the ratio

$$(\$0.269)/(\$0.081) = 3.32$$

and when a "risk" factor of 1.3 is included, the ratio becomes

$$3.32/1.30 = 2.55.$$

The malic acid bioprocess looks favorable compared to the petrochemical process based on the raw material cost comparison alone. The future of a malic acid bioprocess is dependent on the development of markets for its use as a precursor to other value-added intermediates and end products (see Figure 7.8).

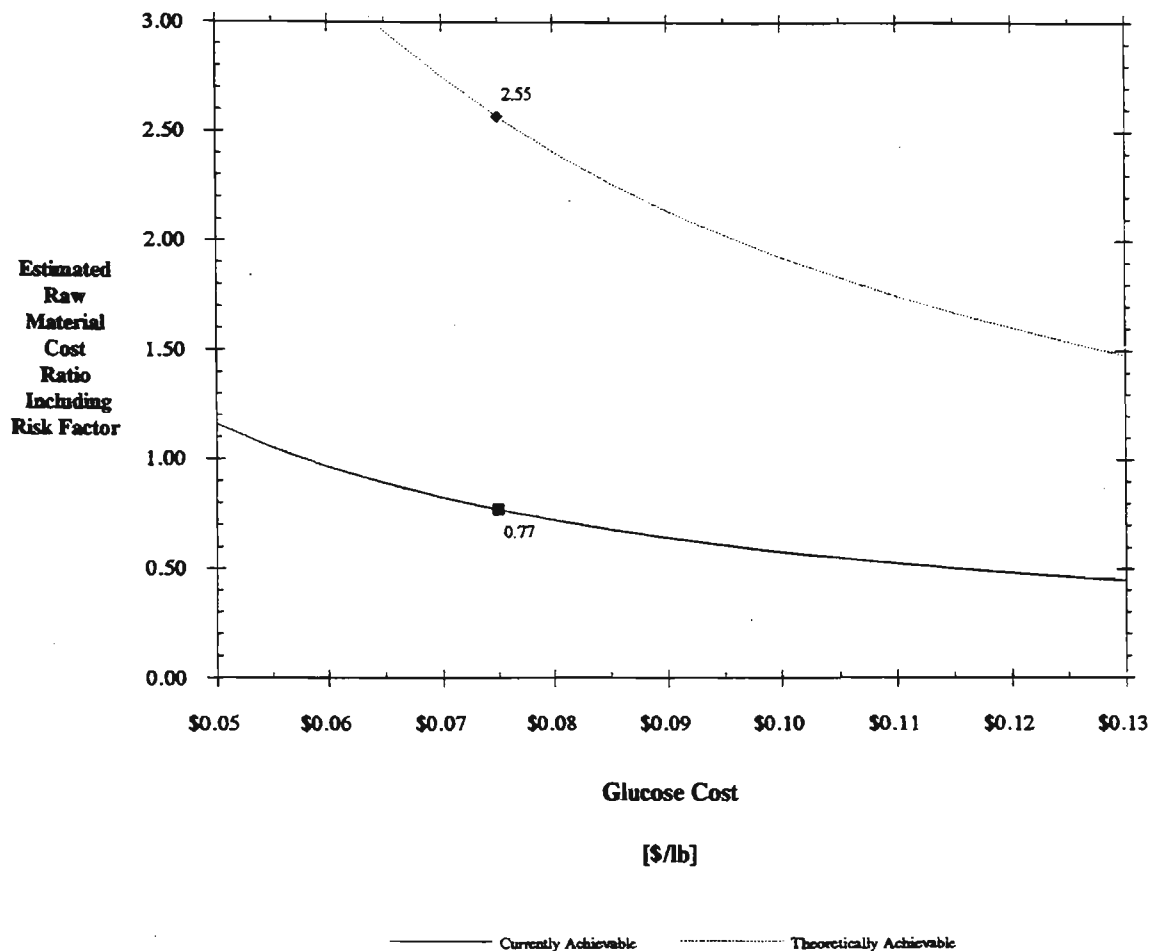
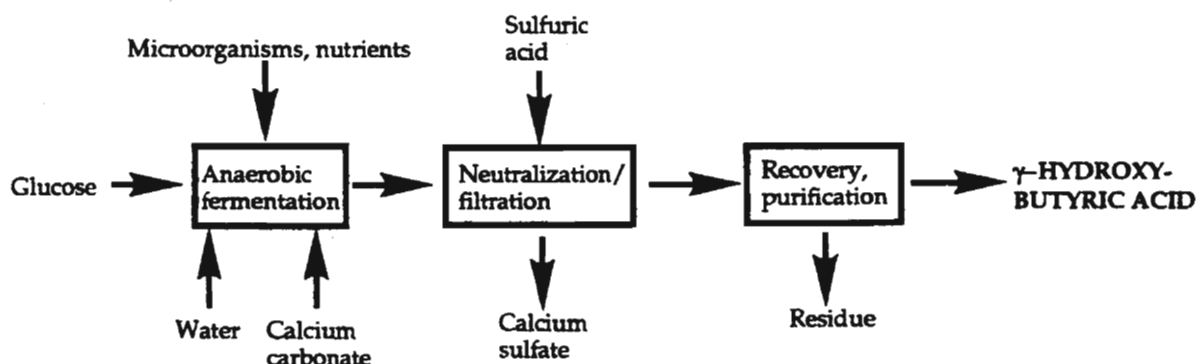


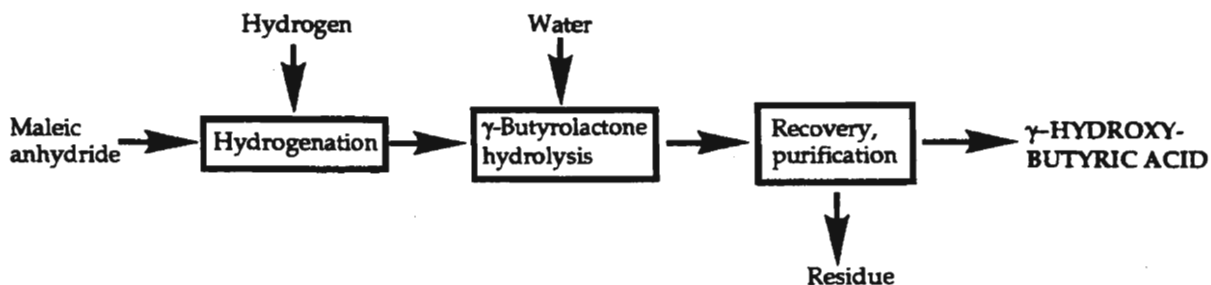
Figure 7.8 - Estimated Raw Material Cost Ratio versus Glucose Cost, Malic Acid Production

7.3.9 Polyhydroxybutyric Acid

Bioprocess:



Petrochemical process:



Processes Compared: To simplify this comparison, and to make best use of available literature information, the comparison is based on the monomer γ -hydroxybutyric acid. This is a specialty chemical produced in limited quantities and used for plasticizer and pharmaceutical precursor applications.

In the bioprocess, a glucose fermentation with an overall yield of 40% is assumed, based on limited process information.

In the hydrocarbon-based process, developed and used by ICI, maleic anhydride is first hydrogenated to γ -butyrolactone. The lactone then is hydrolyzed to γ -hydroxybutyric acid. There is a 90% yield in each step.

Raw Materials Cost Comparison: In the bioprocess, the raw materials cost, based on the process yields and an assumed glucose cost of \$0.075/lb, is \$0.375/lb of γ -hydroxybutyric acid.

In the ICI process, the total raw materials cost is \$0.340/lb of γ -hydroxybutyric acid, using a raw materials cost, previously described, of \$0.269/lb of n-butane derived maleic anhydride. The raw materials cost ratio is then

$$(\$0.340)/(\$0.375) = 0.91$$

and when a "risk" factor of 1.3 is added, the ratio is

$$0.91/1.3 = 0.70.$$

Future Projections: Potential biological and process improvements could reduce the raw materials cost for the bioprocess to \$0.168/lb of γ -hydroxybutyric acid. Recombination of the costs of the hydrocarbon and bioprocess routes gives the ratio

$$(\$0.340)/(\$0.168) = 2.02$$

and when a "risk" factor of 1.3 is included, the ratio becomes

$$2.02/1.30 = 1.56.$$

The biomass-based process has the potential to compete with existing processes, if RD&D can improve the performance of the bioprocess (see Figure 7.9).

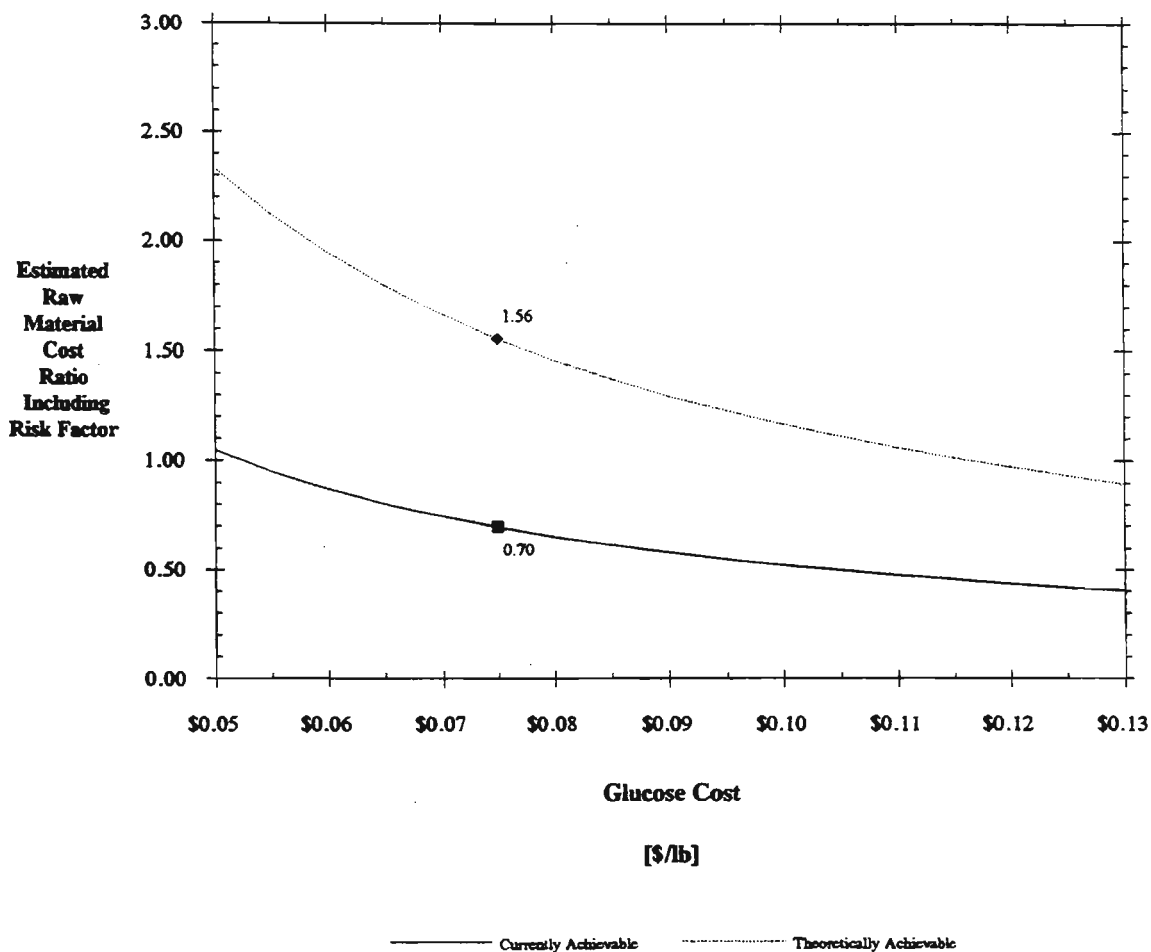
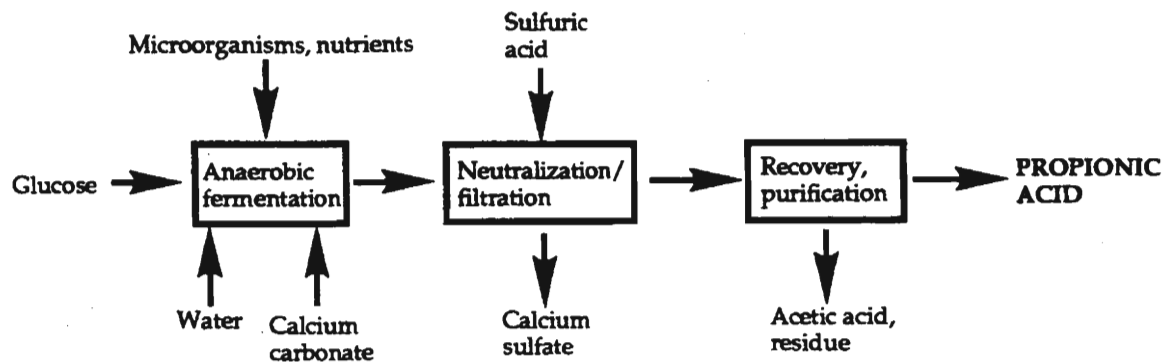


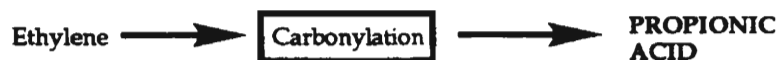
Figure 7.9 - Estimated Raw Material Cost Ratio versus Glucose Cost, Polyhydroxybutyric Acid Production

7.3.10 Propionic Acid

Bioprocess:



Petrochemical process:



Processes Compared: The bioprocess is an anaerobic fermentation of glucose, using limestone to control pH and sulfuric acid for neutralization. Overall yield from glucose is 60% to mixed propionic and acetic acids, with a 2:1 ratio of propionic to acetic. Coproduct acetic acid is assumed to share costs.

The hydrocarbon-based process starts with the hydroformylation of ethylene to propionaldehyde, which is then oxidized to propionic acid. Almost 90% of the domestic propionaldehyde supply is produced by this process, principally by Tennessee-Eastman and Union Carbide. The overall yield, based on ethylene, is 90%. Total existing capacity is 225,000,000 pounds per year.

Raw Materials Cost Comparison: In the bioprocess, the raw materials cost is \$0.326/lb of propionic acid. In the hydrocarbon-based process, the total raw materials cost is \$0.200/lb of propionic acid, based on an ethylene raw materials cost of \$0.225/lb of ethylene, which is a current average value between atmospheric gas oil and naphtha feedstocks. The ratio of raw materials costs is then

$$(\$0.200)/(\$0.326) = 0.61,$$

and when a "risk" factor of 1.3 is added, the ratio becomes

$$0.61/1.3 = 0.47.$$

Future Projections: Potential biological and process improvements could reduce the raw materials cost for the bioprocess to \$0.144/lb of propionic acid. Recombination of the costs of the hydrocarbon and bioprocess routes gives the ratio

$$(\$0.200)/(\$0.144) = 1.39$$

and when a "risk" factor of 1.3 is included, the ratio becomes

$$1.39/1.30 = 1.07.$$

The biomass-based process has the potential to compete with existing processes if RD&D can improve the performance of the bioprocess (see Figure 7.10). Propionic acid is not a large-scale commodity, and opportunities for investment in new capacity will be limited.

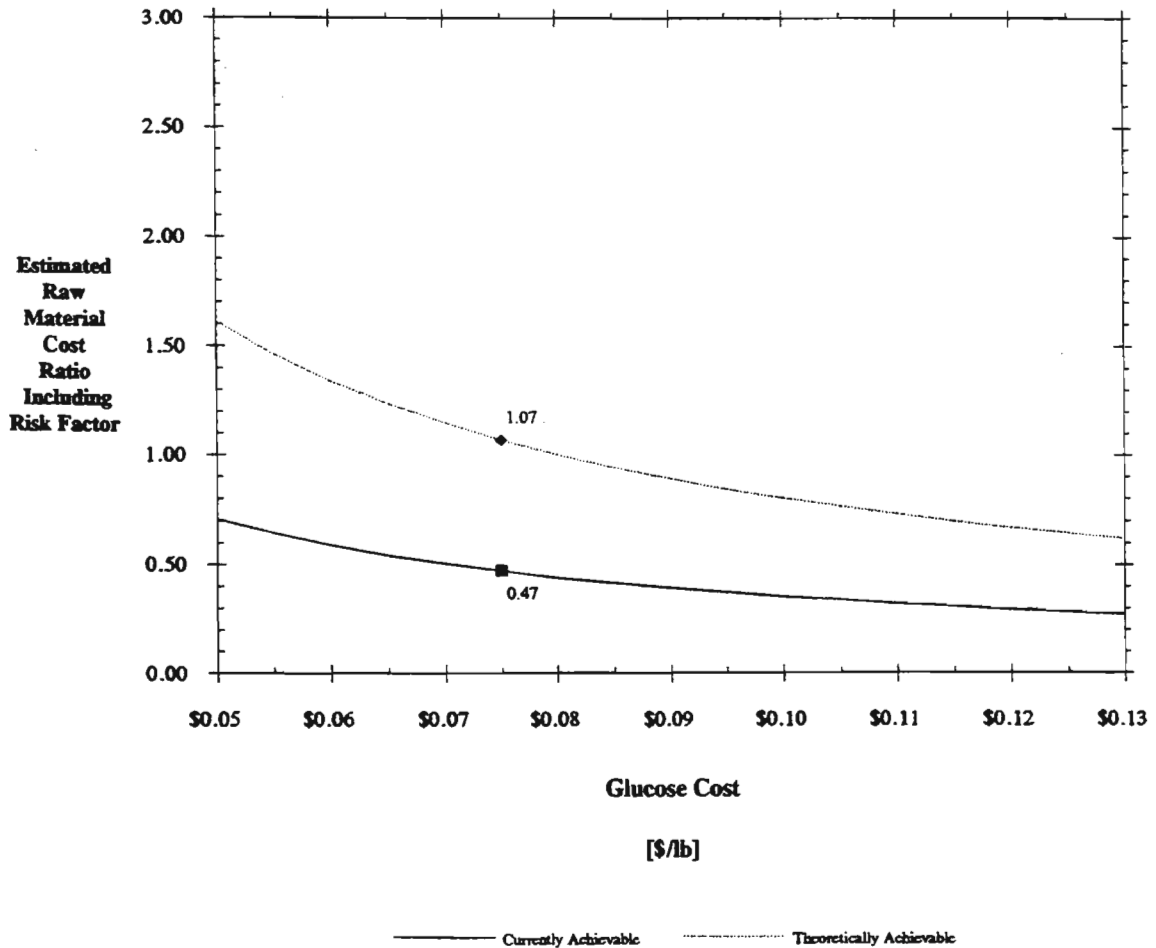
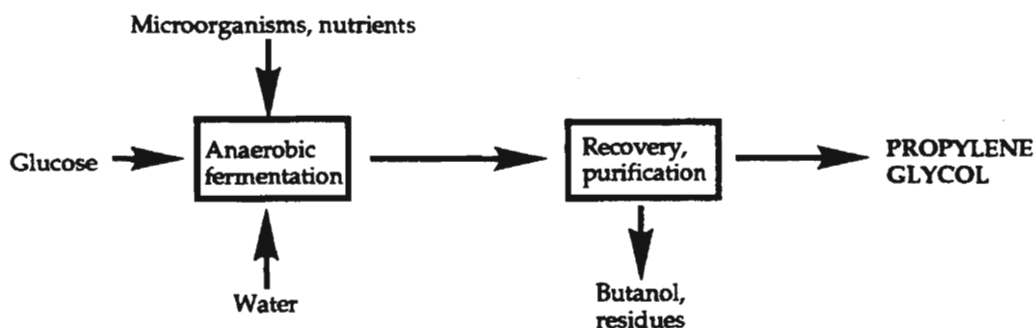


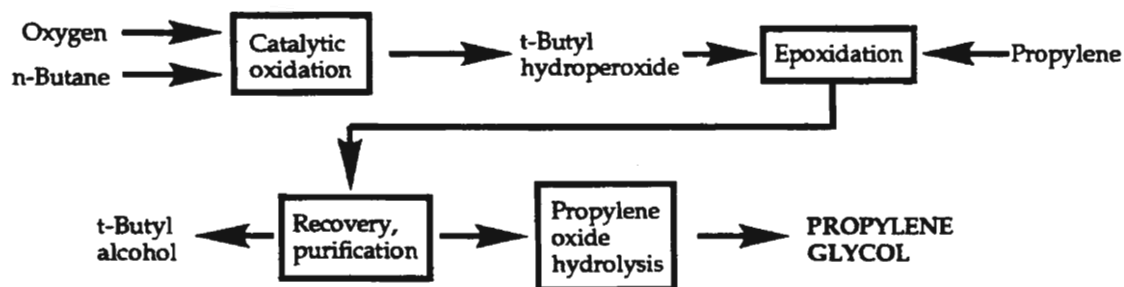
Figure 7.10 - Estimated Raw Material Cost Ratio versus Glucose Cost, Propionic Acid Production

7.3.11 Propylene Glycol

Bioprocess:



Petrochemical process:



Processes Compared: In the fermentation of glucose, the best reported experimental yield is 27%, based on glucose; the theoretical yield is 42%. For this evaluation, 35% yield was used.

In the hydrocarbon-based route, propylene oxide is hydrated in 85% yield to propylene glycol. Propylene oxide is coproduced with t-butyl alcohol in a two-step process consisting of: (1) oxidation of isobutane to t-butyl hydroperoxide and t-butyl alcohol, and (2) reaction of propylene with t-butyl hydroperoxide to yield the coproducts, propylene oxide and t-butyl alcohol. The propylene oxide yield is about 93% of theoretical, and 0.77 unit of propylene is consumed per unit of propylene oxide.

Raw Materials Cost Comparison: In the fermentation process, the raw materials cost is \$0.556/lb of propylene glycol, based on a glucose cost of \$0.075/lb of glucose.

In the propylene-based process, the raw materials cost is \$0.285/lb of propylene glycol, based on propylene valued at \$0.135/lb. The ratio of raw materials costs is then

$$(\$0.285)/(\$0.556) = 0.51,$$

and when a "risk" factor of 1.3 is included, the ratio becomes

$$0.76/1.3 = 0.39.$$

The bioprocess would have difficulty competing with the existing petrochemical route, primarily because of the low yield of useful fermentation coproducts and the relatively much lower cost of the hydrocarbon feedstocks. Any RD&D effort must address these yield differences between the two routes.

Future Projections: Potential biological and process improvements could reduce the raw materials cost for the bioprocess to \$0.188/lb of propionic acid. Recombination of the costs of the hydrocarbon and bioprocess routes gives the ratio

$$(\$0.285)/(\$0.188) = 1.52$$

and when a "risk" factor of 1.3 is included, the ratio becomes

$$1.52/1.30 = 1.17.$$

The bioprocess has a possibility of competing with existing processes if RD&D can improve the performance of the bioprocess (see Figure 7.11).

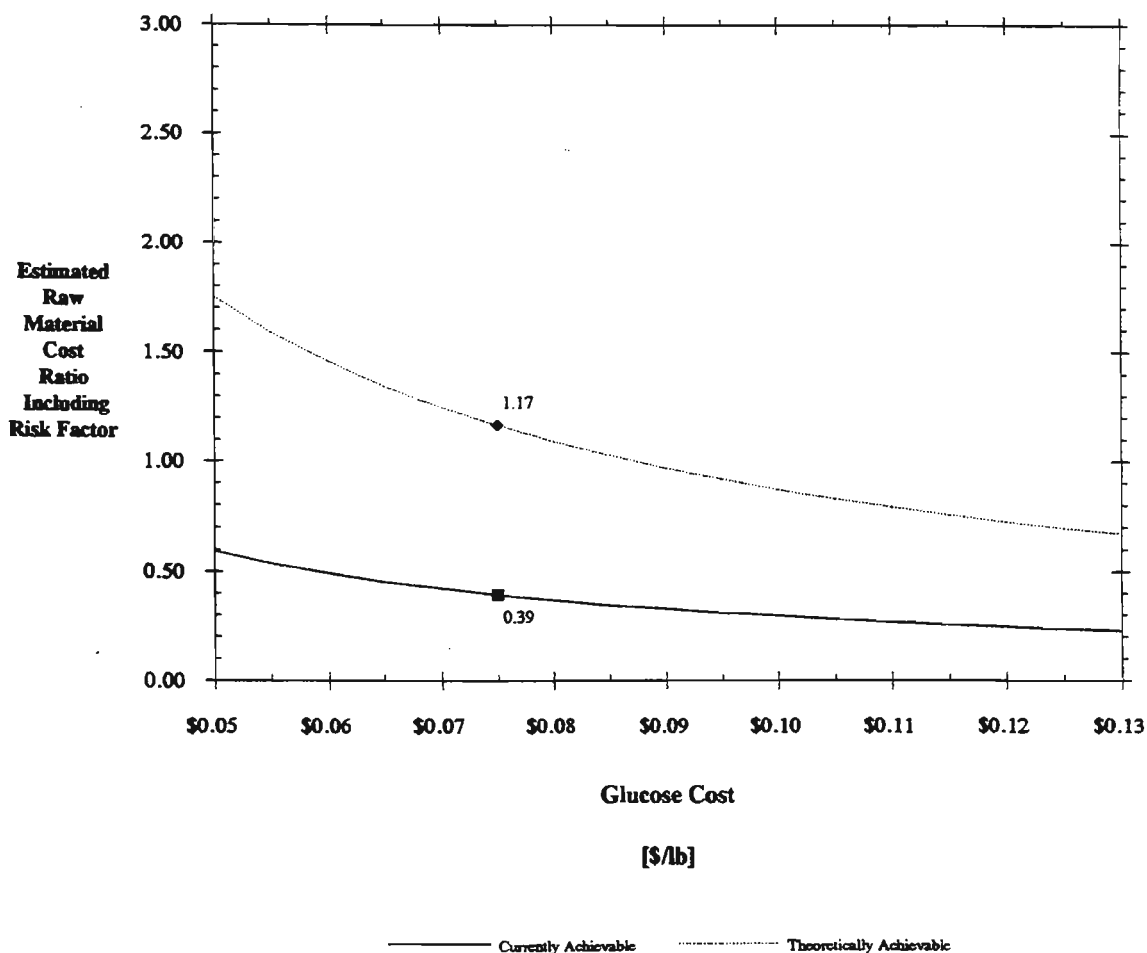
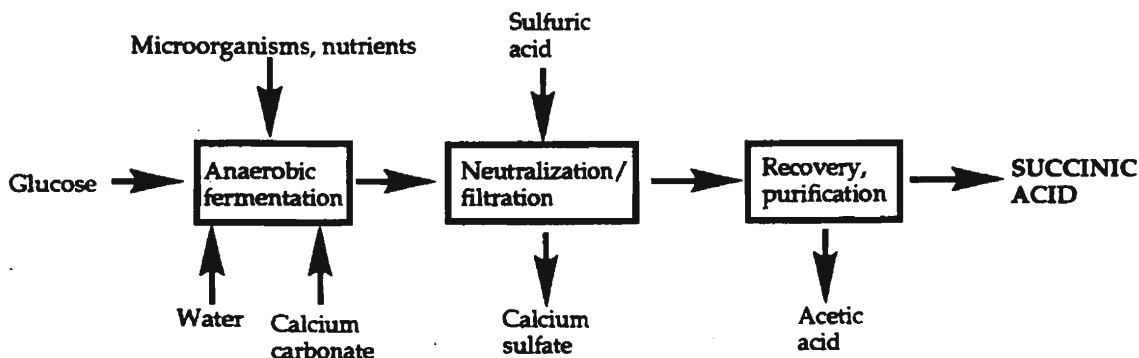


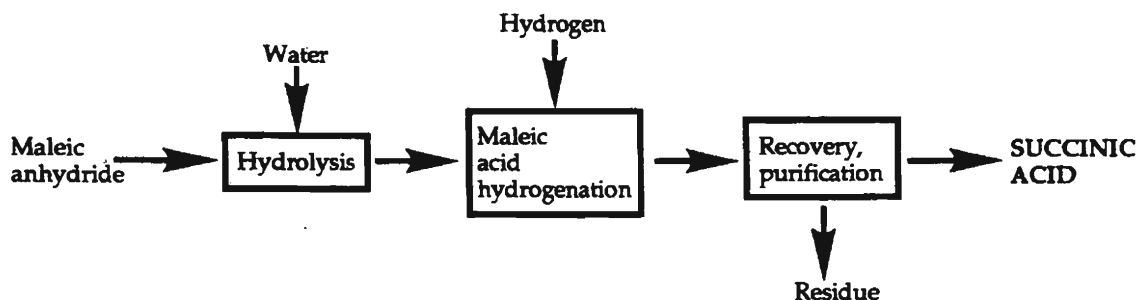
Figure 7.11- Estimated Raw Material Cost Ratio versus Glucose Cost, Propylene Glycol Production

7.3.12 Succinic Acid

Bioprocess:



Petrochemical process:



Processes Compared: The bioprocess is an anaerobic fermentation in the presence of hydrated lime, with intermediate calcium succinate recovered by acidification with sulfuric acid, and succinic acid recovered as a water solution. Major raw materials are glucose, limestone, and sulfuric acid. Minor raw materials are carbon dioxide, ion exchange resins, nutrients, corn steep liquor, tryptophan, and sodium carbonate. The fermentation yield is reported as 87% to calcium succinate; recovery yield is assumed to be 80%.

In the hydrocarbon-based process, n-butane is first oxidized to maleic anhydride. This well-established process is used by five U.S. companies, four in Western Europe, and two in Japan. Reliable manufacturing cost data is reported in the SRI Chemical Economics Handbook. Maleic anhydride is then hydrated to maleic acid, and in a second step the double bond is hydrogenated to yield succinic acid. Overall yield of maleic anhydride to succinic acid is 95%.

Raw Materials Cost Comparison: In the bioprocess, the raw materials cost is \$0.187/lb of succinic acid. In the hydrocarbon-based process, total raw materials cost is \$0.269/lb of succinic acid. The ratio of raw materials costs is then

$$(\$0.269)/(\$0.172) = 1.56,$$

and when a "risk" factor of 1.3 is added, the ratio becomes

$$1.56/1.3 = 1.20.$$

Future Projections: Potential biological and process improvements could reduce the raw materials cost for the bioprocess to \$0.081/lb of succinic acid. Recomparison of the costs of the hydrocarbon and bioprocess routes gives the ratio

$$(\$0.269)/(\$0.081) = 3.32$$

and when a "risk" factor of 1.3 is included, the ratio becomes

$$3.32/1.30 = 2.55.$$

The succinic acid bioprocess looks favorable compared to the petrochemical process based on the raw material cost comparison alone. The future of a succinic acid bioprocess is dependent on the development of markets for its use in food products and as a precursor to other value-added intermediates and end products (see Figure 7.12).

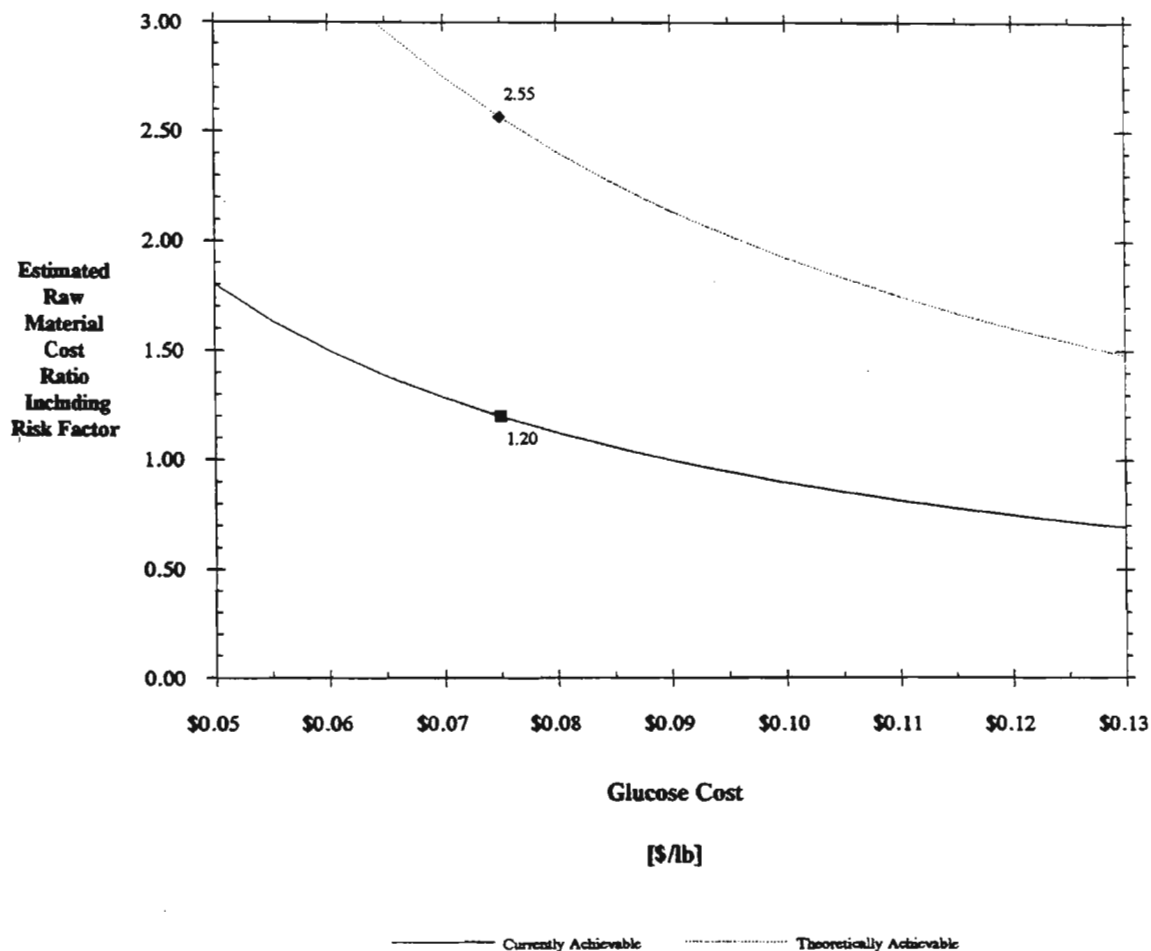


Figure 7.12 - Estimated Raw Material Cost Ratio versus Glucose Cost, Succinic Acid Production

7.4 Qualitative Influences

The qualitative influences considered in the selection of the first two candidates for the integrated product/process screening are listed under four broad categories. The current set of influences are:

- **Energy Impacts**
 - Process energy savings
 - Vulnerability to oil supply disruptions
 - Feedstock displacement
- **Environmental Quality**
 - Air emissions
 - Water pollution
 - Solid waste generation
 - Regulatory impacts
 - Cost of Remediation
- **Economic Competitiveness**
 - Current cost of production
 - Future cost of production
 - Current market price
 - Future market price
 - Consumer interest
- **Probability of Success**
 - Potential domestic production

Each of the candidates is assessed with respect to the criteria listed above. The current assessment is given in two parts as Table 7.6. The nomenclature for this table is as follows:

- + favorable impact
- unfavorable impact
- o little or no impact
- blank unable to assess impact at this time

Table 7.6, part 1 - Qualitative Influences on Selection Process

Energy Impacts			Environmental Quality				Economic Competitiveness				Probability of Success			
Feedstock Displacement	Supply Disruptions	Vulnerability to Oil	Process Energy Savings	Regulatory Impacts	Solid Waste Generation	Water Pollution	Air Emissions	Future Market	Current Market	Future Cost	Current Cost		Potential Domestic Production	
+	0	+						0	0	0	0		+	Acetaldehyde
+	+	+		+			0	+	0	+	0		+	Acetic Acid
+	+	+				0	0	+	0	+	0		+	Acetone
+	+			+				+	0	+	0		+	Acrylic Acid
+	+	+					+	+	0	+	0		+	Adipic Acid
0	0	0						0	0	0	0			Alginate
0	0	0				+		+	0	+	0			Ascorbic Acid
														Azelaic Acid
0	0			+	+	+		+		+	+		+	Bacterial Cellulose
0	0	-												Butanediol, 2,3-
+	+	+		+	0	0	0	+	0	+	+		+	Butanol
+	+	+		0	0	0	0	0	0	+	0			Butyraldehyde
0	0	0		0	0	0	0	+	0	+	+			Butyric Acid
														Cellulase
0	0	0		0	+	0	0	+	+	+	+		+	Citric Acid
0	0	0		0	0	0	0							Dextran
0	0				-	0	0	0	0	+	0			Fumaric Acid
0	0	0			+	0	0							Gluconic Acid
0	0	0						0	0	+	0			Glycerol
0	0	0						+	0	+	0		+	Hyaluronic Acid

Table 7.6, part 2 - Qualitative Influences on Selection Process

Energy Impacts			Environmental Quality					Economic Competitiveness				Probability of Success			
Feedstock Displacement	Vulnerability to Oil Supply Disruptions	Process Energy Savings	Regulatory Impacts	Solid Waste Generation	Water Pollution	Air Emissions	Future Market	Current Market	Future Cost	Current Cost	Potential Domestic Production				
+	+						0	0	+	0	0			0	Isopropanol
0	0	0													Itaconic Acid
+	0	+	+	+	+		+	0	+	+				+	Lactic Acid
0	0	+		+	+		+	0	+	0				+	Lysine
		0					0	0	+	0					Malic Acid
0	0	0					0	0	0	0					Oleic Acid
+	0	+		+			+	0	+	0				+	Polyhydroxybutyric Acid
0	0	0					0	0	+	0					Propanediol, 1,3-
+	0	0	+				0	0	0	0					Propionic Acid
+	+	+		0	+	+	0	0	+	0				+	Propylene Glycol
															Protease
0	0	0	+				+	0	+	0				+	Pullulan
0	0	0													Rhamsan Gum
							+	0	+	0					Scleroglucan
0	0	0	0	0	0	0	0	0	0	0					Sorbitol
+	+	+	0	+	+	+	+	0	+	+				+	Succinic Acid
0	0	0	+	-	+		0	0	0	0					Surfactin
0	0	0					0	0	0	0					Tartaric Acid
+	0	+	0	0	0	0	+	0	+	0					Xanthan Gum
0	0	0													Xylitol

7.5 Initial Candidates for Process Evaluation

The methodology described above led to the selection of initial target candidates for more detailed evaluation. Each of these specific targets, an industrial chemical, is also representative of a product family to allow a potential greater developmental impact while focusing on commercializing a specific chemical process. The continuing, iterative RD&D will require reevaluation as new information is discovered; this will influence future targets and help to place current targets in order of priority. This approach also will provide a framework for future decision points while allowing commercialization to take advantage of current opportunities. Generic process flowsheets were created as a tool for identifying potential areas where cross-cutting advanced technologies and genetic techniques can have an impact. For example, in feed material processing, fractionation and hydrolysis are two key processes in the conversion of lignocellulosics. The initial feedstocks are starch from corn grain and cellulose from wood.

7.5.1 Organic Acids (Succinic/Malic/Fumaric)

Many industrial organic acids, such as acetic, citric, and lactic acids, can be produced by fermentation. Citric acid is made by fermentation, new processes are being developed and plants are being built for lactic acid, and acetic acid is still produced by fermentation for food use (vinegar). Another group of organic acids includes succinic, malic, and fumaric acids, which are four-carbon dicarboxylic acids that are interconvertible chemically or enzymatically. Microbially, these acids are often produced by similar metabolic pathways and often as by-products. They have ultimate uses in manufacturing polymers, resins, antioxidants, and other commercial products described below.

7.5.1.1 Market Definition

Succinic acid (SA) and succinic anhydride (SAH) currently are produced from petrochemical feedstocks, as are all of the prospective derivatives of these two chemicals (see Table 7.7). Most or all commercial production of SA and SAH is non-domestic.

The production levels for SA and SAH are low at present, but the industry is stable. If the proposed derivatives (which include 1,4-butanediol, gamma-butyrolactone, tetrahydrofuran, and adipic acid) were to be produced using succinic acid as a feedstock chemical (in place of the currently used feedstock chemicals), the market demand would rise dramatically. For example, if 50% of current 1,4-butanediol production was based on a succinic acid feedstock, the market demand for succinic acid would increase approximately 200-fold, i.e., from 0.00045 million metric tons/year (0.001 billion lbs/year) to 0.09 million metric tons/year (0.2 billion lbs/year). Because all of the proposed derivatives are commodity chemicals, this reasoning can be applied to all examples of potential displacement by succinic acid, i.e. a change to a succinic acid feedstock for the production of gamma-butyrolactone, tetrahydrofuran, or adipic acid will substantially increase succinic acid market demand. An important consideration in proposing such a scale-up of market demand is that the market price should become significantly lower.

The markets for the materials produced from the proposed derivatives, i.e., polybutylene terephthalate (PBT) resins (used for automotive and electrical parts), polyvinyl chloride (PVC, used for many plastics applications), and nylon, are all stable and are expected to continue to grow (Chemical Marketing Reporter, 1990-1992).

Of interest is the historical tightness of the adipic acid and 1,4-butanediol markets in recent years that has resulted in increased imports of these chemicals. This market tightness indicates a need for increased U.S. production capacity, which may encourage development of a new synthesis methodology, i.e., utilization of a succinic acid feedstock.

Table 7.7 - Market Information for Succinic Acid/Succinic Anhydride and Potential Derivatives.¹

Chemical	Growth ²	Production ³	Price ⁴	Price Stability ⁵	Usage ⁶	Feedstock ⁷
Succinic Acid (SA)	S	0.00045 (0.001) ⁸	957 (435)	+	Multiuse ⁹	Succinic Anhydride
Succinic Anhydride (SAH)	S	0.00045 (0.001) ⁸	376 (171)	+	Multiuse ⁹	Maleic Anhydride
1,4-Butanediol	S (3.5)	0.2 (0.45)	220 (100)	+	Feedstock for tetrahydrofuran, PBT resins, and gamma-butyrolactone	Acetylene, Formaldehyde
Gamma-Butyrolactone	S	-	301 (137)	+	Feedstock for pyrrolidone derivatives	Tetrahydrofuran or 1,4-Butanediol
Tetrahydrofuran	S	-	282 (128)	+	Feedstock and solvent for polymers including PVC and PTMEG	1,4-Butanediol
Adipic Acid	S (2.5)	0.77 (1.7)	145 (66)	+	Feedstock for nylon and nylon resins	Cyclohexane or phenol

¹Sources of information are: *Chemical Marketing Reporter* 1990-1992; *Encyclopedia of Chemical Technology* 1982; Szmant 1989.

²Predicted growth of industry over next two to four years. (S) indicates stable growth predicted. Numerals indicate predicted percentage growth increase/year.

³Current annual production for United States, metric tons x 10⁶/yr (billion lb/yr). (-) indicates current production not known at this time.

⁴Current market price, bulk quantities, \$/kg (\$/lb).

⁵(+) indicates that the market price has remained stable over the last 1.5 years.

⁶Current primary utilization for chemical.

⁷Current petrochemical feedstocks used to produce chemical.

⁸Current combined total production of SAH and SA for world.

⁹SA and SAH are currently used in unmodified and derivatized forms as additives for several industries including pharmaceuticals, food, and cosmetics.

Another important consideration is the relatively innocuous nature of succinic acid when compared to the other chemical feedstocks listed in Table 7.7. Minimization of hazardous waste generation in any prospective chemical process is imperative in the designing stage of that process, primarily because it improves the process economics (Stavins and Whitehead, 1992; Russell et al., 1992).

Domestic producers of derivatives include Allied Signal (adipic acid), Arco (1,4-butanediol), BASF (1,4-butanediol), DuPont (adipic acid, 1,4-butanediol), ISP (1,4-butanediol), and Monsanto (adipic acid) (Chemical Marketing Reporter, 1990-1991). There are thirteen domestic producers of PVC: Borden, CertainTeed, Formosa, Georgia-Gulf, Goodrich BF, Goodyear, Keysor-Century, OxyChem, Shintech, Union Carbide, Vista, Vygen, and Westlake (Chemical Marketing Reporter, 1992).

7.5.1.2 Process Evaluation

7.5.1.2.1 Process Concept

The base-case process concept for the bioproduction of succinic acid (Datta 1991) is illustrated in Figure 7.13. The process is modeled as a continuous operation and is sized at a scale equivalent to processing all of the hydrolyzed starch from a 15,000 bushel/day corn wet-milling plant. The productivity and yield data used in this design were translated from batch- and small-scale continuous fermentation data.

Glucose syrup is the feedstock used in the proposed process. This feedstock is diluted with process water and a recycle stream from the product recovery operations and is sterilized in a steam injection sterilizer. The glucose concentration of the feed stream leaving the sterilizer is slightly greater than 50 g/L. Corn steep liquor and the additional required nutrients and salts are batched and sterilized separately and then continuously combined with the glucose feed stream prior to its addition to the fermentor. A portion of the feed stream is diverted to the seed train as required for inoculum growth for the production fermentors.

A sterile calcium hydroxide slurry is added to the fermentors on demand for pH control. The addition of the calcium hydroxide simultaneously neutralizes the fermentor broth and precipitates the succinate as calcium succinate. An overall fermentor productivity of 2.0 g/L-h was used to size the production fermentors. The yield of succinate on glucose was assumed to be 0.88 gram of succinate produced per gram of glucose consumed. Nine 150,000 gal fermentors in series are required to complete the fermentation; i.e., the glucose concentration leaving the final fermentor is less than 0.1% (< 1.0 g/L).

The calcium succinate is recovered from the fermentor broth by first concentrating the slurry using hydrocyclones, then pressing the slurry in two belt press filters in series. A wash step is included between the belt press filters. The cake from the second filter is rewashed and the slurry is acidified to convert the calcium succinate to succinic acid and insoluble calcium sulfate (gypsum), which precipitates. Concentrated sulfuric acid is used for this acidification process. The succinic acid/calcium sulfate slurry is neutralized in a subsequent vessel using sodium hydroxide as the base. The calcium sulfate is recovered in another series of two belt press filters, again with a wash step after each press. The calcium sulfate slurry is fed to a screw press to remove most of the water. Part of the pressate from the screw press is sent to waste treatment and the rest is recycled to the front of the process.

The filtrate from the belt press filters containing the succinic acid is sent through a series of ion exchangers. The first is a strongly acidic cation exchanger, which removes the calcium and other cation impurities. The second is a weakly basic anion exchanger, which removes the sulfate and other strong anionic contaminants. The highly purified succinic acid is concentrated in a multi-effect evaporator to give a product stream that is approximately 50% succinic acid. A plant this size could produce approximately 150 million pounds of succinic acid annually. This base-case process for the bioproduction of succinic acid is intended to show the economic potential with existing technology. Multiple improvements and modifications are intended and are described in sections 7.5.1.3 and 7.5.1.4.

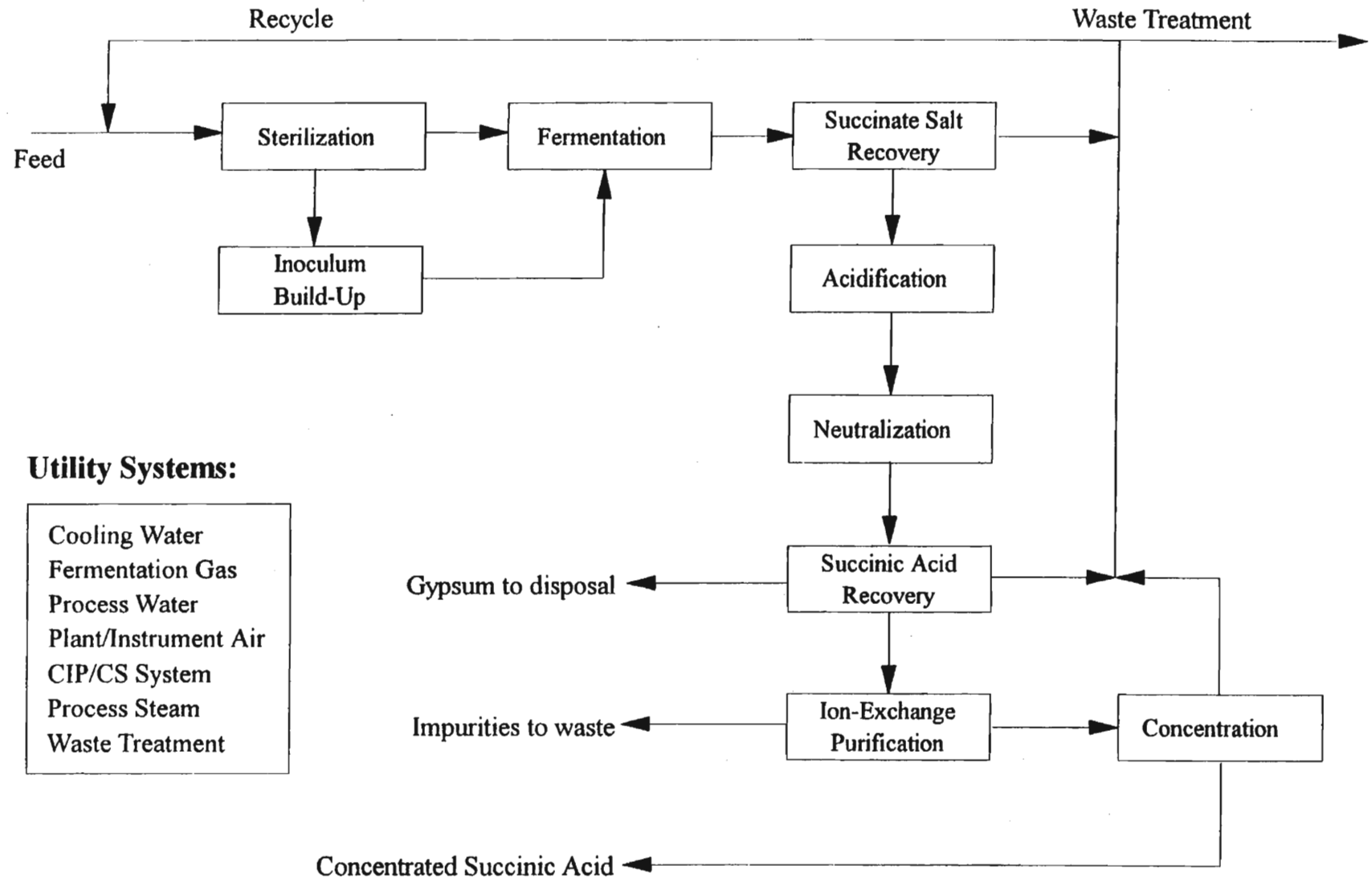


Figure 7.13 - Base Case Process Concept for Bioproduction of Succinic Acid

7.5.1.2.2 Profitability Analysis

The first step in completing the profitability analysis was to estimate the cost of the purchased equipment. Most of the equipment was assumed to be constructed of stainless steel; however, some of the equipment was costed assuming it was constructed from carbon steel, and some had specialized materials of construction factors applied to the stainless steel construction cost. An equipment schedule spreadsheet was created with links to the key flow rates used to size each of the major pieces of equipment in the material balance spreadsheet. The cost of the equipment was estimated for the base-case plant size using historical data updated to the reference year (1992). These data were combined with individual cost exponent factors for each type of equipment and the linked process flow rates to determine the purchased equipment cost for plants smaller and larger than the base-case plant size.

Once the purchased equipment price was estimated, the factoring method was used to estimate the costs of shipping, piping, electrical, instrumentation, foundations, insulation, and so on. The total installed purchased equipment price for the base case was estimated to be \$15,000,000 from an estimated purchased equipment price of \$6,600,000.

The total fixed capital investment was determined, again using a factoring method, from the installed purchased equipment cost. Examples of items included in the total fixed capital investment include land, yard improvements, service facilities, engineering and supervision, contractor's fee, and contingency. The total fixed capital investment for the plant was determined to be \$27,400,000.

The annual costs of raw materials and utilities was determined from the material and energy balances. A stream factor of 0.9 was used to calculate these costs. Table 7.8 summarizes the unit costs used in the analysis.

Table 7.8 - Unit Raw Material Costs

<u>Item</u>	<u>Source of Estimate</u>	<u>Cost [\$/lb]</u>
Glucose Syrup, 95DE	ANL, NREL Estimate	0.0750
Corn Steep Liquor	ANL, NREL Estimate	0.0250
Calcium Hydroxide	CMR, 1/7/91	0.0260
Sulfuric Acid, 100%	CMR, 1/7/91	0.0430
Carbon Dioxide, liquid, 99.5% purity	Air Products	0.0400
Tryptophan	ANL Estimate	10.9000
Cysteine HCl	NREL Estimate	3.2000
Sodium Hydroxide	CMR, 1/7/91	0.1130
Hydrochloric Acid	CMR, 1/7/91	0.0350
Sodium Carbonate	CMR, 1/7/91	0.1960
Cation Resin, Dowex 50 WX8	Dow Chemical	30.4000
Anion Resin, Amberlite IRA-94, Rohm & Hass	NREL Estimate	30.0000

The unit costs of the utilities are given in Table 7.9, and are all ANL, NREL estimates.

Table 7.9 - Unit Utility Costs

<u>Item</u>	<u>Unit Cost [\$/unit listed]</u>
Steam, 50 psig, [klb]	2.000
Electricity, [kWh]	0.045
Cooling Water, [klb]	0.012
Process Water, [klb]	0.042
Waste Treatment, [klb]	0.511
Solid Waste Disposal, [ton]	20.000

The operating labor costs were determined using estimates of man-hours required per unit operation per shift. The total annual operating labor costs were determined to be \$1,200,000. Labor-related expenses such as supervisory labor, payroll overhead, and laboratory charges were estimated as percentages of the operating labor. These total labor-related costs were estimated to be \$800,000 annually.

Capital-related costs were estimated as percentages of total plant cost. These costs include items such as maintenance, operating supplies, local taxes and insurance, and plant overhead costs. The capital-related costs were estimated to be \$2,100,000 annually.

Finally, costs indexed to sales, such as packaging and storage, administrative costs, distribution and sales, and RD&D, were estimated as percentages of total sales. The sales-related costs were estimated to be \$1,000,000 annually.

The discounted-cash-flow method was applied to determine the product selling price necessary to satisfy all the constraints. The product selling price for the base-case design was determined to be \$0.354/lb of succinic acid. This corresponds to a production level of approximately 150 million pounds per year. A lower net selling price is expected when process improvements described in the next two sections are incorporated into the process design.

The manufacturing cost summary for the base-case design is given in Table 7.10.

Table 7.10 - Manufacturing Cost Summary, Succinic Acid from Glucose Syrup

Succinic Acid Production from Glucose Syrup; Basis = 15000 bu/day Corn Wet-Milling Plant

Location Midwest Annual Capacity 153,300,000 lbs succinic acid
 Effective Date to Which Estimate Applies Oct-91 Cost Index Type CE Plant Index

Predicted Selling Price: \$0.354 Cost Index Value 357.7

Fixed Capital \$27,400,000

Working Capital \$5,800,000

Total Capital Investment \$33,200,000

Assumptions			
Plant Life	10 years	Investment Tax Credit, First Year	0.0%
DCF Rate-of Return	15.00%	Working Capital, (determined independently)	N/A
Equivalent Return on Investment	27.18%	Assumed Inflation Rate	3.5%
Equipment Service Life, MACRS Depreciation	5 years	Percent of Total Fixed Capital Investment Spent in Year -3	30.0%
Building Service Life, Straight-Line Depreciation	30 years	Percent of Total Fixed Capital Investment Spent in Year -2	50.0%
Combined Federal and State Tax Rate	37.0%	Percent of Total Fixed Capital Investment Spent in Year -1	20.0%
Equipment Salvage Value	0.0%	Percent of Start-Up Costs Spent in Year -1	30.0%

Production Cost		
	\$ per yr	\$ per lb product
Raw Materials, (itemized on page 3)	\$27,900,000	\$0.182
By-Product Credits	\$0	\$0.000
Utilities, (itemized on page 3)	\$10,100,000	\$0.066
Ion Exchange Resins	\$500,000	\$0.003
Operating Labor	\$1,200,000	\$0.008
Labor Related Costs	\$800,000	\$0.005
Capital Related Costs	\$2,200,000	\$0.014
Sales Related Costs	\$1,100,000	\$0.007
Total Expense at 100% Capacity, proof year: 5	\$43,300,000	\$0.282

Revenue		
Revenue from Sales	\$54,300,000	\$0.354
Net Annual Profit	\$11,000,000	\$0.072
Annual Income after Taxes	\$7,900,000	\$0.052

Raw Material Costs			
			\$ per lb raw material
Glucose Syrup	95 DE	ANL, NREL Estimate	\$0.0750
Corn Steep Liquor	50 % Solids	ANL, NREL Estimate	\$0.0250
Calcium Hydroxide		CMR, 12/25/92	\$0.0260
Sulfuric Acid	100%	CMR, 12/25/92	\$0.0430
Carbon Dioxide	liquid, 99.5% purity	Air Products	\$0.0400
Tryptophan		ANL Estimate	\$10.9000
Cysteine HCl		NREL Estimate	\$3.2000
Sodium Hydroxide		CMR, 1/7/91	\$0.1130
Hydrochloric Acid		CMR, 1/7/91	\$0.0350
Sodium Carbonate		CMR, 1/7/91	\$0.1960
Cation Resin	Dowex 50 WX 8, Dow Chemical	Dow Chemical	\$30.4000
Anion Resin	Amberlite IRA-94, Rohm & Haas	NREL Estimate	\$30.0000

Manufacturing Cost Summary continued

Succinic Acid Production from Glucose Syrup; Basis = 15000 bu/day Corn Wet-Milling Plant

Labor		
8 Operators per shift @ \$15 per hr	1.5 Overtime Multiplier	
21 shifts per week per position		
3 weeks vacation per operator		
Total Operating Labor		\$1,200,000 / year 5
Labor Related Costs		
	Percentage of Operating Labor	
Payroll Overhead	32.50%	\$400,000
Supervisory & Miscellaneous Labor	25.00%	\$300,000
Laboratory Charges	10.00%	\$100,000
Total Labor Related Costs		\$800,000 / year 5
Capital Related Costs		
	Percentage of Plant Cost	
Maintenance	1.50%	\$500,000
Operating Supplies	1.50%	\$400,000
Environmental	1.50%	\$400,000
Local Taxes	1.00%	\$300,000
Insurance	0.50%	\$100,000
Plant Overhead Costs	1.50%	\$400,000
Total Capital Related Costs		\$2,100,000 / year 5
Sales Related Costs		
	Percentage of Annual Sales	
Patents & Royalties	0.00%	\$0
Packaging & Storage	0.25%	\$100,000
Administrative Costs	1.00%	\$500,000
Distribution & Sales	0.25%	\$100,000
Research & Development	0.50%	\$300,000
Total Sales Related Costs		\$1,000,000 / year 5
Equipment		
	Percentage of Purchased Equipment Cost	
Purchased Equipment Cost		\$6,600,000
Shipping	5.0%	\$300,000
Piping	40.0%	\$2,700,000
Electrical	10.0%	\$700,000
Instrumentation	30.0%	\$2,000,000
Utilities and Service Facilities ISBL	15.0%	\$1,000,000
Foundations	7.5%	\$500,000
Insulation	5.0%	\$300,000
Painting	5.0%	\$300,000
Installation	10.0%	\$700,000
Total Purchased Equipment Installed		\$15,100,000
Fixed Capital		
	Percentage of Fixed Capital Investment	
Yard Improvements	1.0%	\$300,000
Utilities and Service Facilities OSBL	7.5%	\$2,100,000
Land	0.5%	\$100,000
Engineering and Supervision	7.5%	\$2,100,000
Construction Expenses	5.0%	\$1,400,000
Contractor's Fee	3.5%	\$1,000,000
Contingency	10.0%	\$2,700,000
Buildings	2.5%	\$700,000
Start-Up Costs	7.5%	\$2,100,000
Total Fixed Capital Investment		\$27,400,000

Manufacturing Cost Summary continued

Succinic Acid Production from Glucose Syrup; Basis = 15000 bu/day Corn Wet-Milling Plant

Raw Material Costs		lb/lb succinic acid	\$ per yr	\$ per lb product
Glucose Syrup	95 DE	1.13	\$13,000,000	\$0.0845 /lb product
Corn Steep Liquor	50 % Solids	0.20	\$800,000	\$0.0050 "
Calcium Hydroxide		0.70	\$2,800,000	\$0.0183 "
Sulfuric Acid	100%	0.91	\$6,000,000	\$0.0393 "
Carbon Dioxide	liquid, 99.5% purity	0.18	\$1,100,000	\$0.0071 "
Tryptophan		0.001	\$1,700,000	\$0.0108 "
Cysteine HCl		0.002	\$1,200,000	\$0.0079 "
Sodium Hydroxide		0.02	\$400,000	\$0.0028 "
Hydrochloric Acid		0.02	\$100,000	\$0.0008 "
Sodium Carbonate		0.01	\$300,000	\$0.0019 "
				\$0.1785 /lb product
Ion-Exchange Resins				
Cation Resin	Dowex 50 WX 8, Dow Chemical		\$300,000	\$0.0018 /lb product
Anion Resin	Amberlite IRA-94, Rohm & Haas		\$300,000	\$0.0018 "
				\$0.0035 /lb product
Utilities				
Steam, 50 psig @ \$2 /1000 lb		11.546	\$3,500,000	\$0.0228 /lb product
Electricity @ \$0.045 /kW-hr			\$300,000	\$0.0020 "
Cooling Water @ \$0.012 /1000 lb		207.205	\$400,000	\$0.0026 "
Process Water @ \$0.042 /1000 lb		11.050	\$100,000	\$0.0007 "
Waste Treatment @ \$0.511 /1000 lb		13.123	\$1,000,000	\$0.0065 "
Solid Waste Disposal @ \$20/ ton		3.163	\$4,800,000	\$0.0316 "
				\$0.0662 /lb product
Cost Contributions				
		% of Predicted Selling Price		
Raw Materials:		50.4%		\$0.1785 /lb product
Utilities:		18.7%		\$0.0662 "
Operating Labor:		2.2%		\$0.0078 "
Labor Related Costs:		1.5%		\$0.0052 "
Capital Related Costs:		4.1%		\$0.0144 "
Sales Related Costs:		2.0%		\$0.0072 "
Capital Equipment:		4.9%		\$0.0172 "
Taxes:		4.3%		\$0.0151 "
Interest on Investment:		0.0%		\$0.0000 "
Return on Investment:		12.0%		\$0.0425 "
Total:		100.0%		\$0.3540 /lb product

 50.4%	 18.7%	 2.2%	 1.5%	 4.1%	 2.0%	 4.9%	 4.3%	 0.0%	 12.0%
--	---	--	--	--	---	---	---	--	--

Manufacturing Cost Summary continued

Succinic Acid Production from Glucose Syrup; Basis = 15000 bu/day Corn Wet-Milling Plant

Design Basis	
Plant Type	Grass Roots, Nth plant
Stream Factor	0.9
Nominal Capacity	150 million pounds of succinic acid
<i>Fermentation</i>	
Type	Continuous with Batch Finish
Number of Stages	9
Nominal Volume of each Stage	150,000 gallons
Initial Glucose Concentration	50 grams / liter
Initial Corn Steep Liquor Concentration	5.0 grams / liter (dry-basis)
Overall Productivity	2.0 grams succinate / liter / hour
Overall Yield of Succinate on Glucose	0.88 pounds produced / pounds utilized
Overall Yield of Acetate on Glucose	0.10 pounds produced / pounds utilized
Gas Flow Rate (carbon dioxide)	1 volume / volume / hour
<i>Downstream Recovery</i>	
Acid Used to Recover Succinic Acid	Sulfuric Acid
Percent Excess Acid Used	10%
Neutralizing Base	Calcium Hydroxide
Percent Excess Base Used	0%
Fraction of Effluent Recycled	50%
<i>Purification</i>	
Loading Time of Cation Resin	24 hours
Regenerant	Hydrochloric Acid, 1 Molar
Regeneration Time	6 hours
Ratio of Flows: Regeneration:Loading	0.2
Life of Resin	2 years
Loading Time of Anion Resin	24 hours
Regenerant	Sodium Hydroxide, 1 Molar
Regeneration Time	6 hours
Ratio of Flows: Regeneration:Loading	0.2
Life of Resin	2 years
<i>Concentration</i>	
Method	Triple-Effect Evaporator
Resulting Succinic Acid Concentration	50.0%
Total Production	306.6 million pounds 50% Succinic Acid

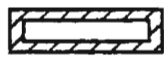
7.5.1.3 Application of New Technologies in Genetic and Metabolic Engineering to Succinic Acid

New technological advances greatly enhance our ability to manipulate the metabolism of a variety of organisms. The polymerase chain reaction (PCR; Arnheim et al., 1990) generates large quantities of a gene and can simultaneously introduce precise changes in the gene's DNA sequence. Consequently, it has become much easier to manipulate genes, tailoring them for expression in different organisms or for production of proteins with altered properties. New physical methods have arisen that permit introduction of foreign DNA into microbes without the development of specialized biological gene carriers. Electroporation employs an electrostatic discharge to briefly permeabilize bacteria, allowing uptake of DNA (Dower, 1990). Particle acceleration methods literally shoot microspheres coated with DNA into cells, and have recently been used successfully on bacteria (Klein et al., 1992; Sanford et al., 1992). Another new approach, called antisense technology, allows the introduction of nucleic acids antagonistic to the native nucleic acids of an organism, thereby allowing controlled alterations of the organism's internal metabolism (Cohen, 1989). It is possible not only to shut down a pathway, but to alter the regulation of pathways in order to divert the flow of material into one particular arm of a branched pathway, thereby increasing the yield of a desired product. Similarly, these new technologies offer the ability to alter other properties, not directly related to the pathway of interest but related to bioprocessing, such as shifting the distribution of membrane components to increase the tolerance of the strain to the products of metabolism. Thus, it is possible to specifically address several major impediments to a commercially viable bioprocess: poor tolerance to high concentrations of the desired product, requirements for expensive nutrients, production of by-products, and moderate conversion rates.

With regard to succinic acid, near-term opportunities for metabolic engineering exist. The metabolic pathway for production of succinic acid (also called succinate) and the related dicarboxylic acids fumarate and malate in the bacterium *A. succiniciproducens* is shown in Figure 7.14. The desired pathway to succinate is the branch to the left in Figure 7.14. Genes of the final steps of this pathway have been cloned from a variety of organisms, and mutants of these genes exist in *E. coli*, which facilitates their manipulation by allowing detection of the enzyme when introduced into *E. coli*. Because *A. succiniciproducens* is a gram-negative bacterium, it is likely that its genes will function in *E. coli*, facilitating their characterization and the ability to exploit antisense technology for regulation of metabolism in *A. succiniciproducens*. Potentially, reducing the flow of carbon into acetic acid could increase the yield of succinic acid up to 50%. This goal could be accomplished by reducing or eliminating the activity of the enzyme on the right side of Figure 7.14 that converts acetyl CoA to acetyl phosphate (some acetyl CoA is needed for biosynthetic purposes). Alternatively, increasing the activity of the enzyme at the branch point that adds CO₂ to phosphoenolpyruvate and directs carbon toward succinate, on the left, could serve to compete more effectively for phosphoenolpyruvate. Finally, adding genes that produce enzymes for the use of other sugars (e.g., xylose) could expand the range of feedstocks suitable for producing succinic acid, improving the process flexibility and economics. Currently, there are no examples of the introduction of DNA into *A. succiniciproducens*, but newer methods have not yet been attempted on this strain. Regulation of the succinate pathway in *A. succiniciproducens* is only partially understood (Samuelov et al. 1991), and investigation of the genetics that regulate the incorporation of CO₂ should suggest additional possibilities for genetic engineering. Activities should be prioritized to reflect the potential value of effort, the amount of time required, and the chance of success.

7.5.1.4 Advanced Bioprocessing Concepts

The product family of organic acids has been chosen as the initial candidate for developmental research for a chemical feedstock. These include acetic, citric, lactic, and the cluster of dicarboxylic acids (succinic, fumaric and malic acids) (Wise 1983). All are produced in relatively dilute form because of their high level of inhibition of the microorganism. This inhibition is due both to the chemical itself and to the lowered pH from acid production. Methods to decrease this inhibition and increase the rate of production are needed to improve the process.

 pH 6.2, HIGH CO₂

 pH 7.2, LOW CO₂

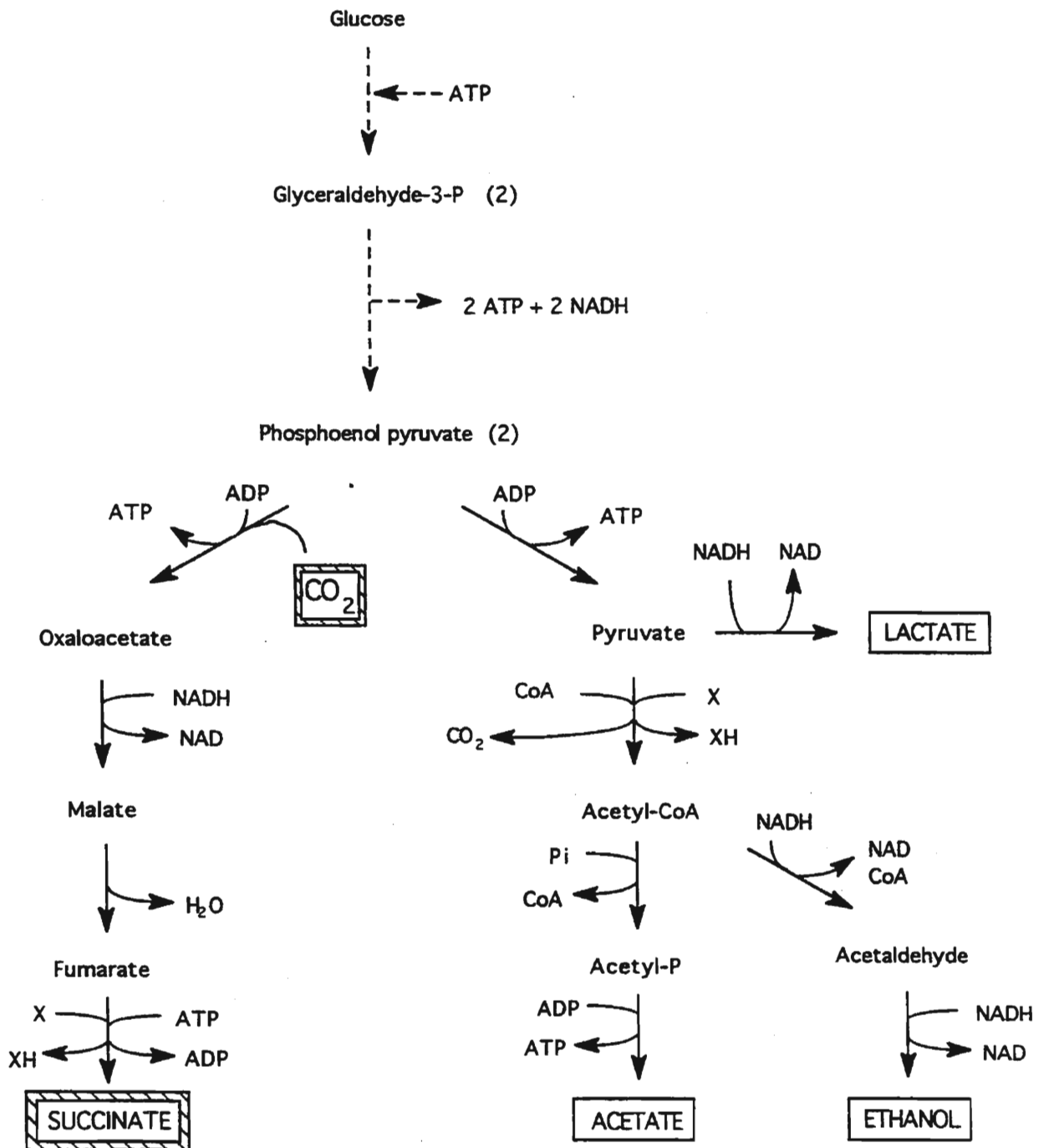


Figure 7.14 - Metabolic Pathway for Production of Succinic Acid

Improvements in production rate have been observed using various means of cell retention, including cell recycle, membranes, and immobilization (Vickroy, 1985; Ghose and Bhadra, 1985). These methods can lead to additional problems with mass transfer, especially if oxygen is a required co-substrate. Even with the increased rates, the final product concentration is comparable to batch reactions because of inhibition. Conventionally, the fermentation broth is neutralized to control the pH. This yields the product in its salt form, which requires additional processing to produce the desired acid. Several processes have been proposed to remove the inhibitory product from the ongoing fermentation (Busche, 1985). Extraction by solvents has been proposed, both a direct removal of the acid and a reactive removal by forming an ester in the organic solvent phase. Extraction configurations have included stirred tank reactors and membrane reactors. Adsorption has been proposed in various forms to remove the acid from the broth. This has included direct addition into the batch stirred tank (with problems of attrition and power) (Wang, 1981; Wang and Sobnosky, 1985); passing a broth recycle stream through a side adsorbent bed (Gaillot et al., 1990); and a direct addition and removal of the adsorbent to a fluidized bed of immobilized biocatalysts (Davison, 1992a; Davison, 1992b). The biparticle fluidized bed was referred to above as a combined bioconversion and separation process.

In general, the product streams for organic acids vary from 1 to 10 wt % in aqueous solution as provided by the fermentation step. Hence, the problem is one of dilute solution processing to recover the product. Typically, the acid is recovered in salt form via addition of base and then purified with several washings over activated carbon to remove impurities before final recovery. Several of the aforementioned technologies have potential for both product separation and purification and waste stream treatment. These approaches are extraction, adsorption, and membrane processing. In each of these cases, the objective is to selectively remove the acid from aqueous solution. Several process flowsheets exist for the recovery of acetic acid from dilute aqueous solution (Rousseau, 1987). In particular, several amine-based extractants show remarkable selectivity for acetic acid over water with distribution coefficients of greater than 10 as the acetic acid concentration goes below 0.5 wt % (Wardell and King, 1978). In addition, data have been gathered for the distribution properties of many fermentation product carboxylic acids, including acetic, lactic, and citric acids (Kertes and King, 1986). One could also envision placing these same types of functional groups on solid adsorbents to carry out separations and recovery.

Although in principle structural membranes could be made to distinguish between organic acids and water, ultrafiltration or reverse osmosis currently are not able to carry out an acceptable separation. In principle, one could use ion exchange membranes, which use functional groups similar to the ones considered for extraction and/or adsorption. Electrodialysis with bipolar membranes can purify organic acids with low power requirements (Berglund et al., 1991). Electrodialysis is the most attractive of the membrane methods (Datta, 1989) and is being developed commercially for lactic acid. Pervaporation membranes are able to carry out some degree of separation but are not selective enough to warrant use in either the recovery or dehydration of organic acids.

There is no existing commercial biological process for the production of succinic acid. The acid is currently synthesized from maleic anhydride for use in making coatings, dyes, esters, and polymers. Key process-related problems have been identified and put in the following order of priority: (1) the formation of dilute product streams and the cost of recovery; (2) the elimination of the salt waste from the current purification process; (3) the reduction of inhibition caused by the product succinic acid on the fermentation of itself; (4) the interference in slowing the reaction and complicating the separations caused by other by-products; (5) the reduction in the use of expensive nutrient supplements (e.g., vitamins) for the microbes; (6) the enhancement of the overall conversion rates; and (7) the need to increase the feedstock flexibility beyond glucose.

Succinic acid is an intermediate component in the citric acid cycle (or Krebs' cycle) common to all respiratory organisms. Therefore, many organisms produce small quantities of this acid along with their primary metabolic products. It is more difficult to find a single organism and process that accumulates succinic acid. The anaerobic *Anaerobiospirillum succiniciproducens* will ferment sugars and

carbon dioxide to more than 40 g/L succinic acid in the form of calcium succinate (Datta, 1991). *Candida brumptii* will produce up to 24 g/L succinic acid per liter from 80 g/L paraffin but not from glucose (Sato et al., 1972). Under a limited range of partial oxygen deprivation, *Brevibacterium flavum* will make up to 30 g/L succinate instead of its primary product L-glutamate (Okada et al., 1961). Two-stage approaches are more common. In these, first the sugar or starch is converted by one microbe into an organic acid such as fumaric, malic, or citric acid (Ling and Ng, 1989). Then a second microbe transforms this acid into succinic acid. Different pairs of microbes have been used, including the fungi *Rhizopus* to produce fumaric acid and *Enterobacter aerogenes* to convert fumaric into succinic acid (Takao et al., 1973; Hotta and Takao, 1973). *Aspergillus oryzae* has been used to produce a mixture of acids, and *Lactobacillus fermentum* to convert these to succinic acid. Citric acid also can be converted anaerobically into stoichiometric quantities of succinate and acetate (Cselovsky et al., 1992). These studies have been performed largely in batch culture, but there have been limited attempts at continuous culture.

Approaches to succinic acid overproduction will rely, first, on the selection of the microbial system (pure culture or a synergistic association of a mixed culture). There is potential for improvement of the yields by genetic manipulation, (see section 7.5.1.3). Also the optimization of production due to culture conditions will be needed. Some apparent waste materials, such as whey, may also have potential as feedstocks (Compere and Griffith, 1976). Because at least one organism (*C. brumptii*) can ferment hydrocarbons (paraffin) into succinate, it is possible that thermal/chemical processing of biomass into hydrocarbons may form a feedstock for this bioconversion, which might be coordinated with the thermal/chemical processing effort of the Alternative Feedstocks Program. The choice of feedstocks is important because carbon dioxide also is required for good yields in the anaerobic systems. The carbon dioxide is incorporated into the succinate product. Cell retention methods such as immobilization will need to be tested to increase overall rates and to decrease sterilization requirements.

One of the major reasons for the low succinic product concentration is the inhibitory nature of the organic acids. Protonated organic acids (as opposed to the ion "salt") freely cross the cell membrane and thus are able to deplete the necessary proton gradient and weaken the cell metabolism. Succinate appears to be more inhibitory than either acetic or lactic acids. This makes this fermentation a strong candidate for some form of *in situ* product removal. This removal might be possible using adsorbents in the biparticle fluidized bed, as suggested for lactic acid. Another possibility is precipitation of calcium succinate directly in the fermentor (Datta, 1991), but this is not ideal due to the production of a salt waste. The adsorption of succinic acid or electro dialysis from a recycled sidestream may allow better optimization of both the bioconversion and the separation steps. Datta et al. (Datta, 1991) found that recycling of part of their "spent" media improved their overall process economics. A major disadvantage of the precipitation method is the production of gypsum as a waste by-product. Precipitation is expected to require less energy than adsorption-based methods if the energy required to treat and produce the acids and salts is not considered. Downstream processing may be greatly improved by the use of adsorbents, ion exchangers, or membranes. The technologies described here are listed in Table 7.11 with a qualitative criteria evaluation. The base case is a standard free-cell batch fermentation for organic acids with production recovery by subsequent precipitation and purification. Productivity or rate is improved and product inhibition is reduced by removing the inhibitory succinate in the biparticle fluidized bed reactor (FBR), the precipitation/fermentor, and the sidestream absorber. The two-stage fermentation process is expected to decrease productivity because an additional vessel is required. A single-stage mixed culture was seen to improve productivity. Yields were improved in these processes. Separation development to deal with the dilute products will focus on adsorption methods that are low energy; however, precipitation is generally a lower energy process but it produces a substantial waste product. The use of membrane electro dialysis shows value for the near- or mid-term. The use of adsorption or membranes would reduce the production of a salt waste.

Table 7.11 - Performance Criteria Comparisons for Advanced Technologies Succinic Acid Production

Advanced Technology	<u>Impact on Criteria</u>						
	Productivity	Yield	Product Quality	Energy Use	Environmental Impact	Operability	Time frame
Simultaneous Fermentation & Separation							
Biparticle FBR	+	+	+	-	+	o	mid
Precipitation & Fermentation	+	+	+	o	-	o	near
Fermentation Sidestream Adsorption	+	+	+	-	+	+	long
Separations							
Separation by Adsorption	o	o	+	-	+	+	near
Membrane Electrodialysis	+	o	-	o	+	o	mid
Other Processes							
Use of Thermochemically Treated Feedstocks				-			long
Two-stage Fermentation	-	+		o	o	-	mid
Combined Mixed Culture	+	+	o	o	o	-	mid

The base case here is a standard free-cell batch fermentation for organic acids with production recovery by subsequent precipitation and purification. In the criteria comparison tables, "+" indicates an improvement, "-" a disadvantage, "o" neither an advantage or disadvantage, and a blank insufficient knowledge to evaluate at this time.

7.5.2 Neutral Solvents (Butanol)

Another class of chemical feedstocks that potentially can be manufactured by biotechnology is the neutral solvents such as butanol, acetone, and acetaldehyde.

Butanol is a commodity chemical feedstock and solvent that, early in this century, was primarily made by industrial fermentation (see reviews) (Jones and Woods, 1986; Linden et al., 1986). The fermentation process declined after World War II due to both the rise of the petroleum industry and the increase in raw material costs (molasses). Butanol is now synthesized chemically from petroleum-derived ethylene and triethylaluminum or carbon monoxide and hydrogen. Continued research in bioconversion of renewable resources and the actual and potential increases in petroleum costs have encouraged renewed interest in butanol fermentation. Butanol may have an additional market as an oxygenated fuel additive (Ladisich, 1991).

Butanol is the primary product of the fermentation of sugars by various bacteria, in particular *Clostridium acetobutylicum*. This is a complex fermentation, with, first, an acidogenic phase producing butyric and acetic acids and, then, a solventogenic phase producing butanol, acetone, and ethanol. Both the products and the lowered pH can be inhibitory to the continued fermentation. This has limited final butanol concentrations to a maximum of 15 g/L in batch culture, with generally much lower yields.

7.5.2.1 Market Definition

Butanol is used for a wide variety of applications and many derivatives are produced from it (see Table 7.12). Butanol and its derivatives are currently produced from petrochemical feedstocks; commercial production of butanol and some derivatives is sufficiently high to qualify them as commodity chemicals.

The industries that currently produce those chemicals listed in Table 7.12 are stable, and all expect growth. Stable growth in production of butanol and some of its derivatives is partly due to the lower environmental risk posed by the usage of these chemicals compared to other more hazardous chemicals used in the past (Chemical Marketing Reporter, 1991; Chemical Economics Handbook, 1990). This aspect of the future marketing potential for butanol cannot be overstated, as hazardous waste issues have become very important to industry for economic reasons (Russell et al., 1992; Stavins and Whitehead, 1992).

A primary consideration in terms of marketing new production processes for these chemicals is the low market price for most of them. Any new process involving butanol or its derivatives will have to be strongly competitive in terms of product selling price (which is not necessarily equal to the market price, but certainly is strongly related to that price).

The markets for the materials produced from butanol and its derivatives (i.e., paints, resins, textiles, polyvinyl chloride (PVC), and plastics) are stable, and continued growth of these materials is likely (Chemical Marketing Reporter, 1991, Chemical Economics Handbook, 1990).

Two major concerns that have always existed for butanol producers are propylene price fluctuations due to irregular petroleum prices and dependence on housing and automotive markets (Chemical Economics Handbook, 1990). In the recent past, some tightness of butanol production has been experienced due to limited petrochemical feedstocks (Chemical Economics Handbook, 1990); this type of situation represents an opportunity for the introduction of a new process technology based on an alternative feedstock whose supply is not limited, i.e., biomass.

Domestic producers of butanol and its derivatives include BASF (butanol, butyl acetate, butyl acrylate/methacrylate); Chem Service, Inc. (butyl acrylate/methacrylate); Dow Chemical

Table 7.12 - Market Information for Butanol and Potential Derivatives¹

Chemical	Growth ²	Production ³	Price ⁴	Price Stability ⁵	Usage ⁶	Feedstock ⁷
N-Butanol	S (2.5)	0.6 (1.3)	90 (41)	+	Solvent for coatings and resins, feedstock chemical	Propylene, butyraldehyde, ethylene
N-Butyl Acetate	S (1)	0.1 (0.23)	110 (50)	+	Solvent for coatings	N-Butanol
N-Butyl Acrylate	S (2) ⁸	0.3 (0.7)	158 (72)	+	Paint polymers, textile emulsions, PVC impact modifiers	N-Butanol
N-Butyl Methacrylate	S (2) ⁸	-	211 (96)	+	Resins, coatings	N-Butanol
Butyl Glycol Ethers	S (2)	-	81-194 (37-88) ⁹	+	Coatings solvent, plasticizer, feedstock chemical	N-Butanol, ethylene oxide

¹Sources of information are: *Chemical Marketing Reporter* 1991; *Encyclopedia of Chemical Technology* 1982; *Chemical Economics Handbook* 1990.

²Predicted growth of industry over next one to three years. (S) indicates stable growth predicted. Numerals indicate predicted percentage growth increase/year.

³Current annual production for U.S., metric tons x 10⁶/yr (billion lb/yr). (-) indicates current production not known at this time.

⁴Current market price, bulk quantities, ¢/kg (¢/lb).

⁵(+) indicates that the market price has remained stable over the last 1.5 years.

⁶Current primary utilization for chemical.

⁷Current petrochemical feedstocks used to produce chemical.

⁸Combined growth rate for butyl acrylate and butyl methacrylate.

⁹Price range is for four different butyl glycol ethers; low end = ethylene glycol monobutyl ether, high end = diethylene glycol monobutyl ether acetate.

U.S.A. (butyl glycol ethers); Eastman (butanol, butyl acetate, butyl glycol ethers); Hoechst Celanese (butanol, butyl acetate, butyl acrylate/methacrylate); Rohm and Haas Co. (butyl acrylate/methacrylate); Shell (butanol, butyl glycol ethers); Union Carbide (butanol, butyl acetate, butyl acrylate/methacrylate, butyl glycol ethers); and Vista (butanol) (Chemical Marketing Reporter, 1991; Chemical Economics Handbook, 1990).

7.5.2.2 Process Evaluation

The base-case process concept for the bioproduction of butanol (Glassner, 1991) is illustrated in Figure 7.15. The process is modeled as a two-stage fermentation. The first stage is a series of continuous fermentors. The second stage is a batch fermentation. The size of the base-case plant is at the scale equivalent to processing all of the hydrolyzed starch from a 70,000 bushel per day corn wet-milling plant. The productivity and yield data used in this design were translated from small-scale batch and continuous fermentation data.

Glucose syrup is the feedstock used in the simulated process. This is a readily available feedstock, requiring little pretreatment other than sterilization for its use as a fermentable substrate. If the economics of this acetone-butanol-ethanol (ABE) process were favorable using glucose syrup, then this process would be considered a near-term opportunity. However, the FRF for butanol from glucose syrup is quite close to one, meaning that the value of the products obtained is only slightly greater than the cost of the feedstock. For this reason a restrained approach to the engineering and economic analysis was used. The economics of the process were assessed after various stages of completion of the engineering analysis.

The first assessment of the economics was performed after all of the plant equipment associated with production had been sized and costed. This, of course, required that a complete material and energy balance be performed for this section of the plant. The equipment in this section includes the feedstock and nutrient storage vessels, the continuous sterilizers, the seed train fermentors, the production fermentors, and the miscellaneous pumps and heat-exchangers.

The predicted selling price for this broth was determined without taking into account any of the utility costs. Operating labor and labor related costs likewise were not considered. The only raw material cost considered at this stage was for the glucose syrup. A by-product credit was taken for the acetone and the ethanol in the fermentor broth. The predicted selling price of the butanol in the fermentor broth was determined to be \$0.54 per pound; the current market value of butanol is approximately \$0.41 per pound.

It is clearly a longer term opportunity to complete the design of this process, as it stands, using glucose syrup as the feedstock. Additional engineering analyses of the ABE process will be performed in the future using the other plant designs described in section 6.4.2.1. In these subsequent designs, consideration will also be given to the various advanced technologies that could improve the fermentor volumetric productivity and to the advanced feedstock pretreatment and product separations technologies.

Butanol is a candidate that will benefit from the iterative nature of the screening process. The current analysis, however, suggests that the ABE process be placed in the long-term or mid-term opportunity category. Attention can then be shifted to another candidate whose "window of opportunity" may be more near term.

The manufacturing cost summary for the base-case design is given in Table 7.13. Again, this summary is for an incomplete engineering analysis.

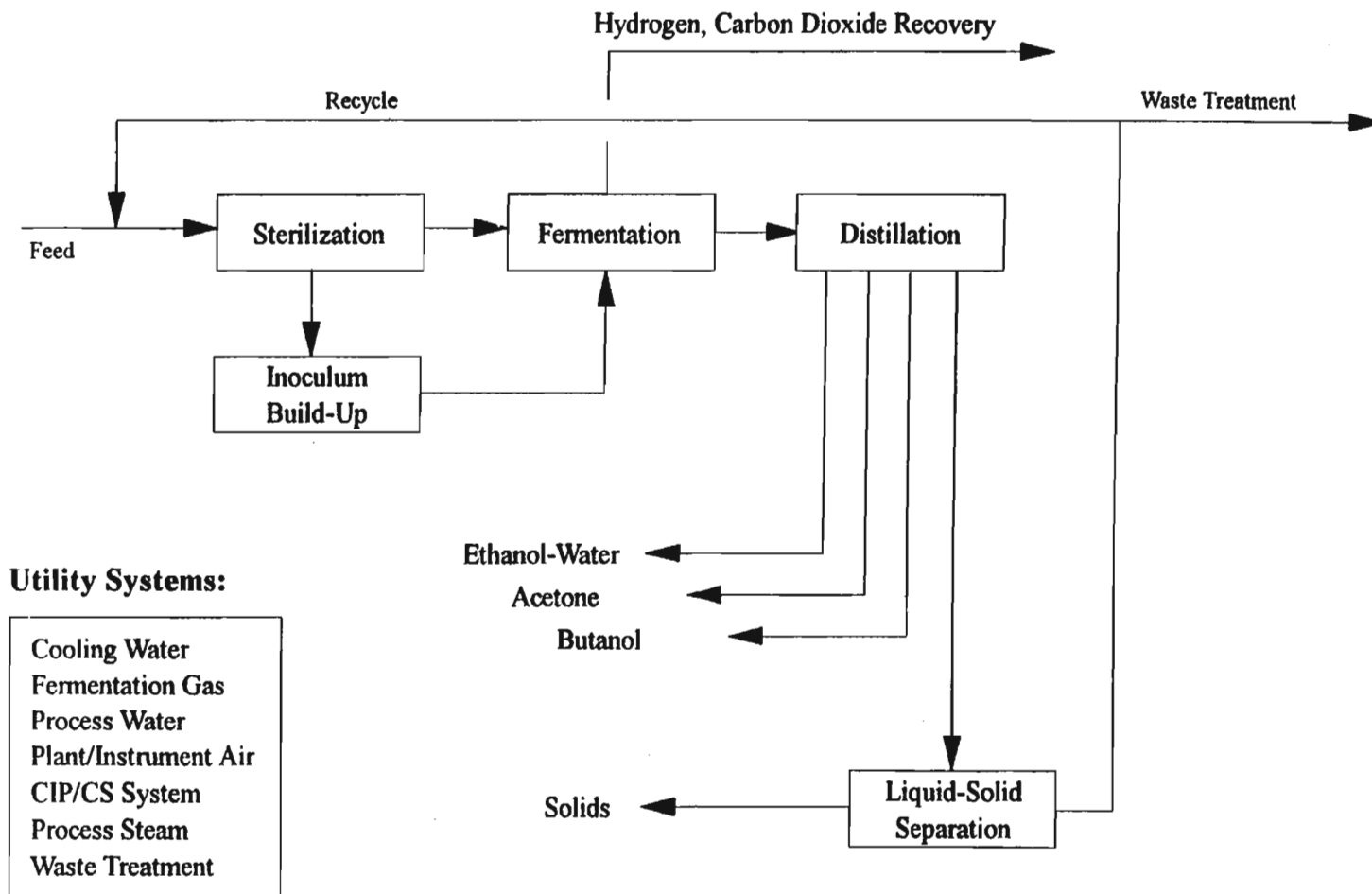


Figure 7.15 - Process Concept for Bioproduction of Butanol

Table 7.13 - Manufacturing Cost Summary for Butanol Production from Glucose Syrup

Butanol Production from Glucose Syrup; Basis = 70,000 bu/day Corn Wet-Milling Plant

Location: Midwest Annual Capacity: 175,000,000 lbs butanol
 Effective Date to Which Estimate Applies: 1990 Cost Index Type: CE Plant Index

Predicted Selling Price: \$0.54 Cost Index Value: 357.7

Fixed Capital: \$50,809,312

Working Capital: \$5,080,931

Total Capital Investment \$55,890,243

Production Cost	k\$/yr	\$/lb
Raw Materials	\$76,014	\$0.434
By-Product Credits	\$31,000	\$0.177
Operating Labor	\$0	\$0.000
Labor Related Costs	\$0	\$0.000
Capital Related Costs	\$8,881	\$0.051
Sales Related Costs	\$25,929	\$0.148
Steam, 50 psig @ \$0.006/lb	\$0	\$0.000
Electricity @ \$0.045/kW-hr	\$0	\$0.000
Cooling Water @ \$0.10/kGal	\$0	\$0.000
Process Water @ \$0.10/kGal	\$0	\$0.000
Waste Treatment @ \$4.16/kGal	\$0	\$0.000
Total Expense	\$79,825	\$0.000
Revenue from Sales	\$95,485	\$0.546
Net Annual Profit	\$15,660	\$0.089
Annual Income after Taxes	\$11,476	\$0.066
Assumptions		
Plant Life, yrs	20	Investment Tax Credit, First Year 0.0%
DCF Rate-of Return	10.00%	Working Capital, Percent of Total Fixed Capital Investment 10.0%
Capital Charge Factor	20.53%	
Equipment Depreciation, (straight-line), yrs	10	Percent of Total Fixed Capital Investment Spent in Year -3 30.0%
Buildings Depreciation, (straight-line), yrs	30	Percent of Total Fixed Capital Investment Spent in Year -2 50.0%
Federal Tax Rate	37%	Percent of Total Fixed Capital Investment Spent in Year -1 20.0%
Equipment Salvage Value	0.0%	Percent of Start-Up Costs Spent in Year -1 30.0%
Raw Material Costs		
Glucose Syrup	Cerelose 2617	Corn Products \$0.1025 /lb

Labor			
Operators	@	\$30,000 yr	/yr
Foreman	@	\$35,000 yr	/yr
Supervisor	@	\$40,000 yr	/yr
Total Operating Labor			/yr
Labor Related Costs			
Supervisory & Miscellaneous Labor, Percent of Operating Labor	20.00%		/yr
Payroll Overhead, Percent of Operating Labor	32.50%		/yr
Laboratory Charges, Percent of Operating Labor	15.00%		/yr
Total Labor Related Costs			/yr
Capital Related Costs			
Maintenance, Percent of Plant Cost	7.50%	\$3,505,843	/yr
Operating Supplies, Percent of Plant Cost	1.75%	\$818,030	/yr
Environmental, Percent of Plant Cost	2.75%	\$1,285,476	/yr
Local Taxes, Percent of Plant Cost	2.00%	\$934,891	/yr
Insurance, Percent of Plant Cost	2.00%	\$934,891	/yr
Plant Overhead Costs, Percent of Plant Cost	3.00%	\$1,402,337	/yr
Total Capital Related Costs			\$8,881,468 /yr
Sales Related Costs			
Patents & Royalties, Percent of Sales	0.00%	\$0	/yr
Packaging & Storage	3.50%	\$4,426,977	/yr
Administrative Costs	6.00%	\$7,589,104	/yr
Distribution & Sales	6.00%	\$7,589,104	/yr
Research & Development	5.00%	\$6,324,253	/yr
Total Sales Related Costs			\$25,929,438 /yr
Equipment			
Purchased Equipment Cost		\$8,431,826	
Shipping, Percent of Purchased Equipment Cost	10.0%	\$843,183	
Piping, Percent of Purchased Equipment Cost	45.0%	\$3,794,322	
Electrical, Percent of Purchased Equipment Cost	12.5%	\$1,053,978	
Instrumentation, Percent of Purchased Equipment Cost	35.0%	\$2,951,139	
Utilities, Percent of Purchased Equipment Cost	80.0%	\$6,745,461	
Foundations, Percent of Purchased Equipment Cost	10.0%	\$843,183	
Insulation, Percent of Purchased Equipment Cost	5.0%	\$421,591	
Painting, Etc., Percent of Purchased Equipment Cost	5.0%	\$421,591	
Total Purchased Equipment Installed			\$25,506,275
Fixed Capital			
Yard Improvements, Percent of Fixed Capital Investment	1.5%	\$762,140	
Service Facilities, Percent of Fixed Capital Investment	7.0%	\$3,556,652	
Land, Percent of Fixed Capital Investment	3.0%	\$1,524,279	
Engineering & Supervision, Percent of Fixed Capital Investment	10.0%	\$5,080,931	
Construction Expenses, Percent of Fixed Capital Investment	4.8%	\$2,438,847	
Contractor's Fee, Percent of Fixed Capital Investment	3.0%	\$1,524,279	
Contingency, Percent of Fixed Capital Investment	7.5%	\$3,810,698	
Start-Up Costs, Percent of Fixed Capital Investment	8.0%	\$4,064,745	
Buildings, Percent of Fixed Capital Investment	5.0%	\$2,540,466	
Total Fixed Capital Investment			\$50,809,312

7.5.2.3 Application of Genetic and Metabolic Engineering to Butanol Production

The pathway for butanol production is shown in Figure 7.16. This pathway is composed of two distinct, regulated phases: an early phase of acid production followed by a phase of solvent production. In the upper portion of the pathway, one-third of the carbon from glucose is lost as carbon dioxide. During the acidogenic phase, butyric and acetic acids are produced in a ratio of about 2:1; they are then reassimilated in the solventogenic phase and reduced to butanol and ethanol, respectively (Jones and Woods, 1989). The final distribution of solvents on a molar basis is approximately six parts butanol to three parts acetone to one part ethanol. The regulation of solvent production is becoming fairly well understood (Gottschalk and Grupe, 1992), and the molecular biology of the favored organism, *C. acetobutylicum*, is fairly well developed. Several genes of the butanol pathway have been cloned, and stable introduction of DNA into this strain has been reported (Mermelstein et al., 1992). In principle, elimination of the acid-producing phase and deregulation of the solvent-producing enzymes through genetic engineering could give a two-fold increase in the molar yield of butanol. Alternatively, in a less technically ambitious task, elimination of enzymes that produce acetic acid in the acidogenic phase and ethanol in the solventogenic phase could increase the molar yield of butanol by 15%. Mutation of enzymes that affect the production of H₂ should also favor solvent production. Alterations of the membrane of the host strain to give greater tolerance toward butanol could have even more economic impact because the toxicity of butanol, which is mediated through membrane effects, severely limits the final concentration of butanol that can be achieved.

7.5.2.4 Advanced Bioprocessing Concepts

As discussed earlier, key processing issues for butanol production are the dilute product and its separation, inhibition of rates caused by butanol, and the low yields. Removal of the inhibitory product from the ongoing fermentation process has been suggested by many researchers as a method to alleviate product inhibition and improve the process. Roffler et al. (1991) and Groot et al. (1992) review several possibilities for extractive bioconversions. The key advantages suggested for extractive bioconversion are higher feed concentrations leading to fewer process wastes and reduced product recovery costs compared to distillation.

Possibilities for *in situ* product removal include pervaporation (Friedl et al., 1991), the use of hollow-fiber reactors (Shukla et al., 1989; Kang et al., 1990); the use of solid adsorbents (Ennis et al., 1987; Davison, 1992; Gaillot et al., 1990; Wang and Sobnosky, 1985); and the use of an immiscible extractive solvent. Key issues are the extractant toxicity and capacity as well as the actual contacting scheme and its operability (Bruce and Daugulis, 1991). Many solvents have been tested for the acetone-butanol fermentation (Shukla et al., 1989; Ishii et al., 1985; Evans and Wange, 1988; Wayman and Parekh, 1987). Oleyl alcohol is commonly used because of its low toxicity, reasonable distribution coefficient, and selectivity for butanol.

Most studies of extractive acetone-butanol fermentation have been performed in a batch reactor (Ishii et al., 1985; Evans and Wang, 1990) with free cells. Wayman and Parekh (1987) performed a sequential batch extractive fermentation with cell recycle. Another approach is to continuously extract the butanol in a side stream of the fermentor. Roffler et al. (1988) performed a fed-batch fermentation with a concentrated glucose feed using an extraction column on a recycled side stream and achieved a butanol productivity of 1 g/L-h. Eckert and Schugerl (1987) used a continuous stirred fermentor with a membrane filter to recycle the cells and provide a cell-free broth to an extraction cascade. The lack of direct contact between the cells and the organic extractant allowed the researchers to use the more toxic extractant, decanol. Allen and coworkers have proposed using a immobilized-cell fluidized bed bioreactor with a concurrent immiscible liquid extractant (Busche and Allen, 1989); promising experimental results of this system have been obtained by Davison and Thompson (1992).

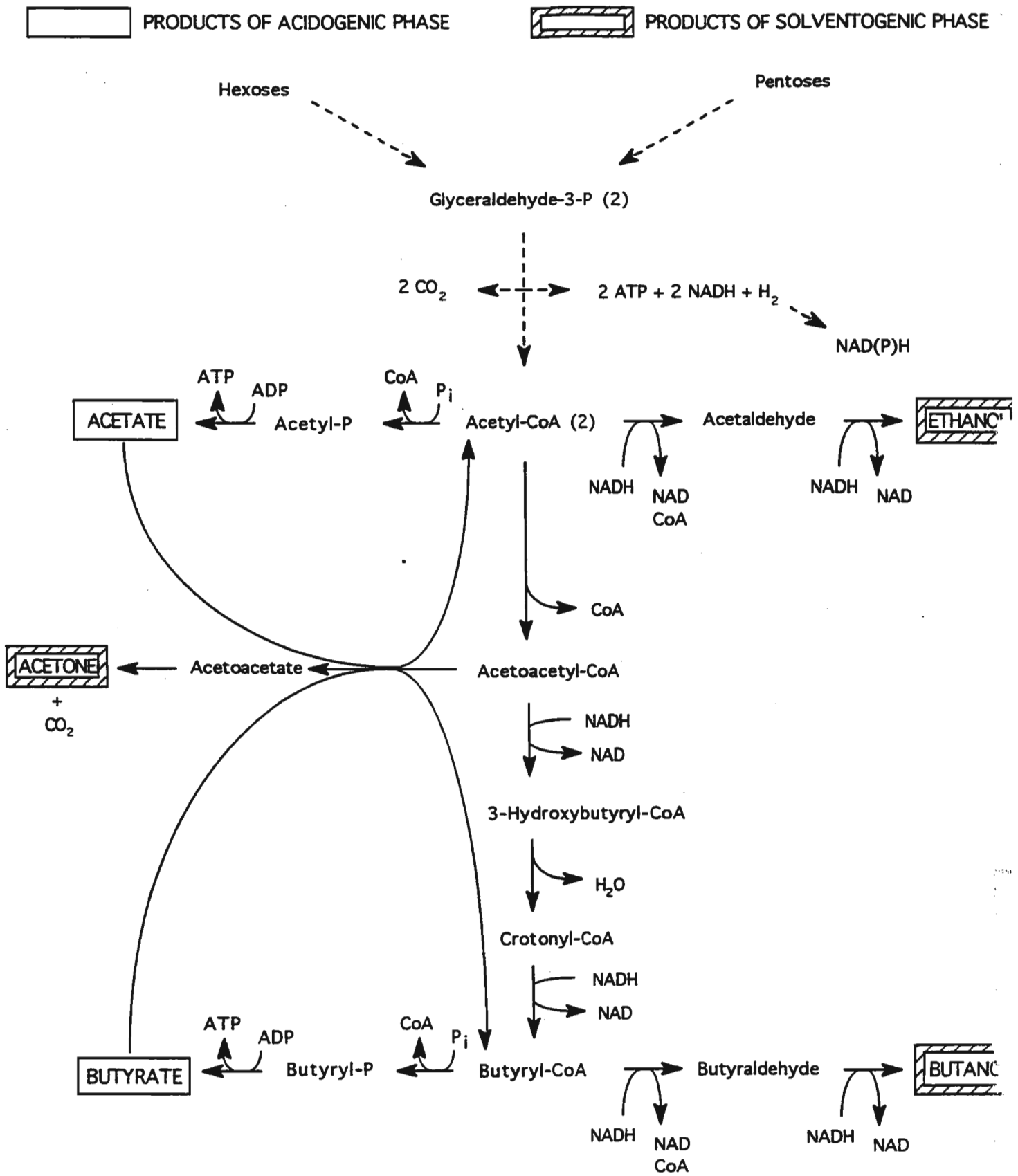


Figure 7.16 - Metabolic Pathway for Butanol Production

C. acetobutylicum can ferment both glucose and xylose and thus can improve the yield from lignocellulosic hydrolyzates. Simultaneous saccharification and fermentation (SSF) also has been tested preliminarily for the production of butanol (Shah et al 1991). This is an anaerobic fermentation with an inhibitory product, butanol; therefore, the need for strict sterilization requirements is likely to be reduced.

The economics of extraction in a free-cell, fed-batch butanol fermentation as well as in a continuous immobilized-cell reactor have been examined (Roffler et al., 1987) and compared to conventional fermentation (Busche, 1991). Several of these concepts are evaluated against the six criteria, drawing heavily on the references (Roffler et al., 1991; Bruce and Daugalis, 1991; Busche, 1991) in Table 7.14. The base-case here is a batch fermentation of biomass-derived sugars followed by distillation. Most of these extraction-based technologies have shown improvements in productivity, resulting from the advantages of continuous operation. Several liquid-extraction reports have shown improvements in yield as well. Perstraction has major operational difficulties and will not be considered initially. Adsorption also has difficulties *in situ*, and the current adsorbents are poor for neutral solvents. Pervaporation and extractive fermentation are seen as the most promising processes for further research. These technologies also can be considered as a distinct separation process with similar conclusions.

Table 7.14 - Performance Criteria Comparisons for Advanced Technologies Butanol Production

Advanced Technology	<u>Impact on Criteria</u>						
	Productivity	Yield	Product Quality	Energy Use	Environmental Impact	Operability	Time frame
Pervaporation (<i>in situ</i>)	++	o	++	++	+	o	mid
Gas Stripping (<i>in situ</i>)	+	o	o	+	o	o	near
Adsorption (<i>in situ</i>)	o	o	o	+	o	o	mid
Perstraction (<i>in situ</i>)	+	o	+	+	+	-	long
Liquid Extraction (<i>in situ</i>)							
- fed batch	+	+	+	++	o	o	near
- sidestream extraction and recycle	+	+	+	++	o	o	mid
- continuous FBR	++	+	+	++	o	o	mid
Simultaneous Saccharification and Fermentation	o	+	+	o	o	o	mid

The base case here is a batch fermentation of biomass-derived sugars followed by distillation. In the criteria comparison tables, "+" indicates an improvement, "-" a disadvantage, "o" neither an advantage or disadvantage, and a blank insufficient knowledge to evaluate at this time.

8.0 RECOMMENDATIONS

The qualitative background and market information and quantitative assessment methodology presented in this report are an attempt to identify RD&D opportunities for converting biomass to useful chemical products. Such a process should have some predictive power, and the ability to answer the question first posed in section 1.1.2: *Given a wide range of possibilities, how can an informed decision be made as to which materials to investigate more thoroughly?* However, because a broad spectrum of readers is expected to use this report, developing a single set of recommendations to apply to all situations is not reasonable. Therefore, this section will outline our own general criteria thought important to an informed decision, with the understanding that each reader will bring additional criteria to the decision making process, developed to reflect the needs and realities of their own situations. These unique and individual criteria could lead to completely different recommendations than those listed in this section. The decision making process and the logic behind it as described in this section will reflect the authors' original task to use this methodology to recommend promising RD&D areas most appropriate to the different research charters of certain DOE offices. Those recommendations are summarized in section 8.6.

8.1 Criteria for Recommendations

Figure 8.1 summarizes the chemicals and processes assessed for the thermal/chemical portion of the report. A similar summary for bioprocesses is shown in Figure 8.2. No single criterion was used to identify a chemical or process as a promising opportunity. Rather, the combination of a number of favorable features was most important to the final decision. These criteria included:

- *Comparative evaluation of raw material cost contribution*

This simple comparative assessment methodology, whose development and use are described in detail in sections 4.0 and 5.0, helps determine which of the chemicals or processes in the original portfolio offered the greatest opportunity from an economic standpoint. The value of the ratios from this evaluation, summarized in table 5.1, give a rough "performance index" by which a new biomass-based process can be judged. In some cases (e. g., acetylated wood or starch plastics, see section 8.2.1), sufficient information was available to perform a more detailed analysis of costs (section 5.4). These results can also be used to compare a new chemical or process to existing technology.

- *Relative maturity of new processes*

Although a favorable raw materials cost ratio is important, the amount of knowledge about the actual performance of a given process is also important to the final decision. Some chemicals or processes may exhibit high ratios from the raw materials cost comparison, but the actual process chemistry may not be clearly defined.

A number of the chemicals or processes evaluated have data from operation near 50 kg/h. However, in others, technical data was generated at considerably smaller scale. Because the different technologies investigated are at various levels of maturity, a final recommendation should consider if a process is at engineering scale and perhaps ready for pilot scale tests, requires scaleup to engineering level for confirmation of their initial promise from the simple screening results, or is at a more conceptual, and hence, smaller scale that would require longer term development. These considerations help both to identify specific product opportunities and give indications of general areas of RD&D that could lead to useful chemicals and materials of commercial interest.

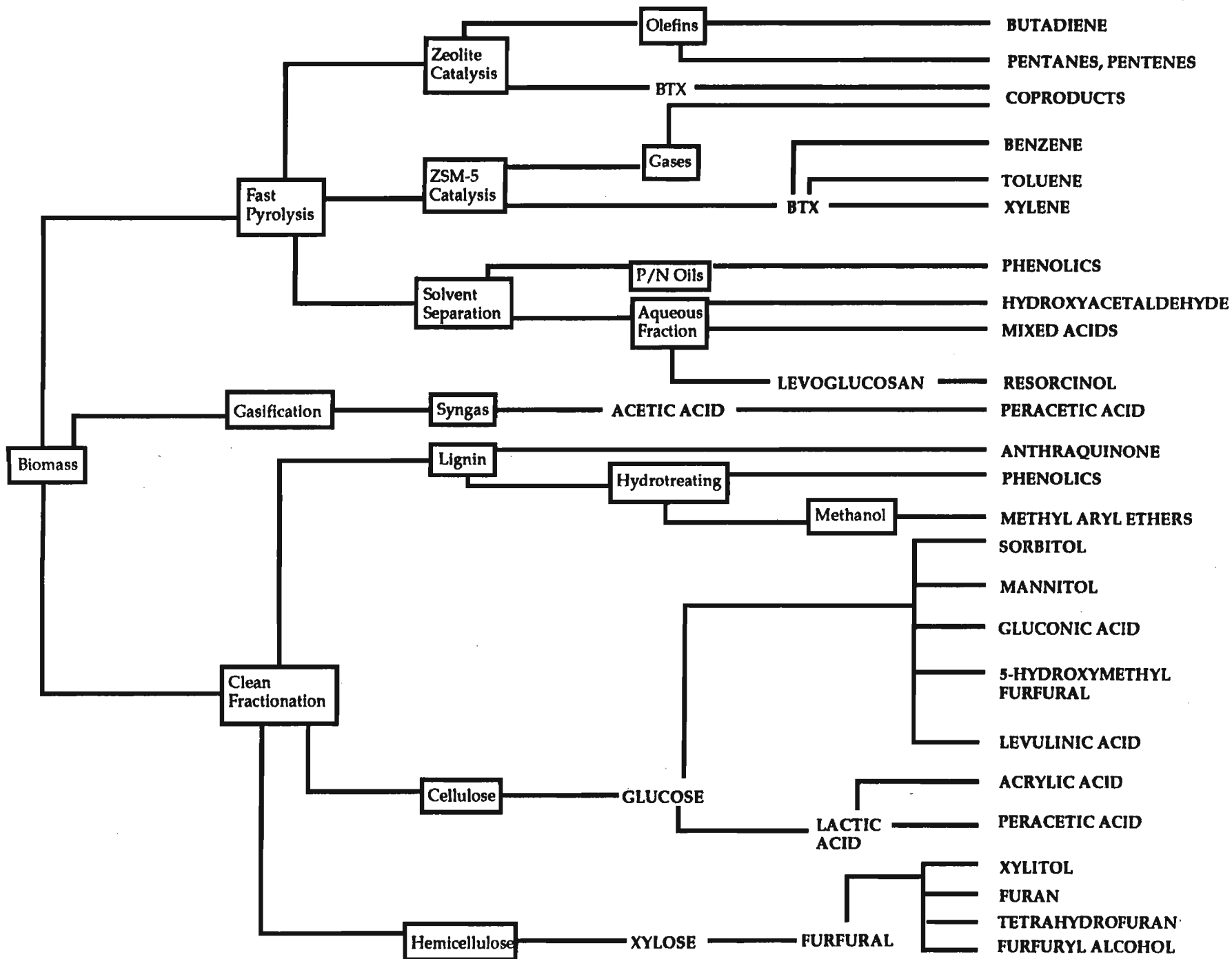


Fig. 1.1 - Chemical Products from Biomass

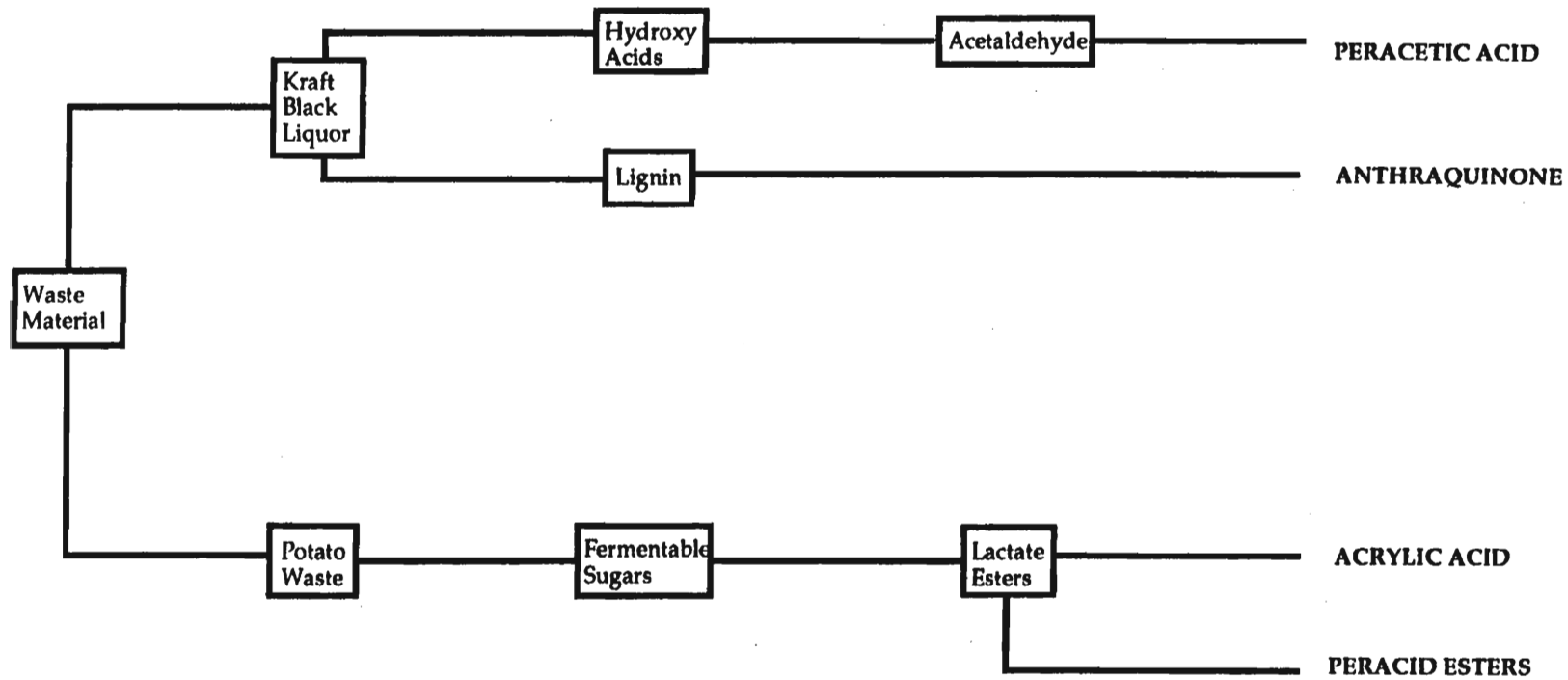


Figure 8.1 - continued

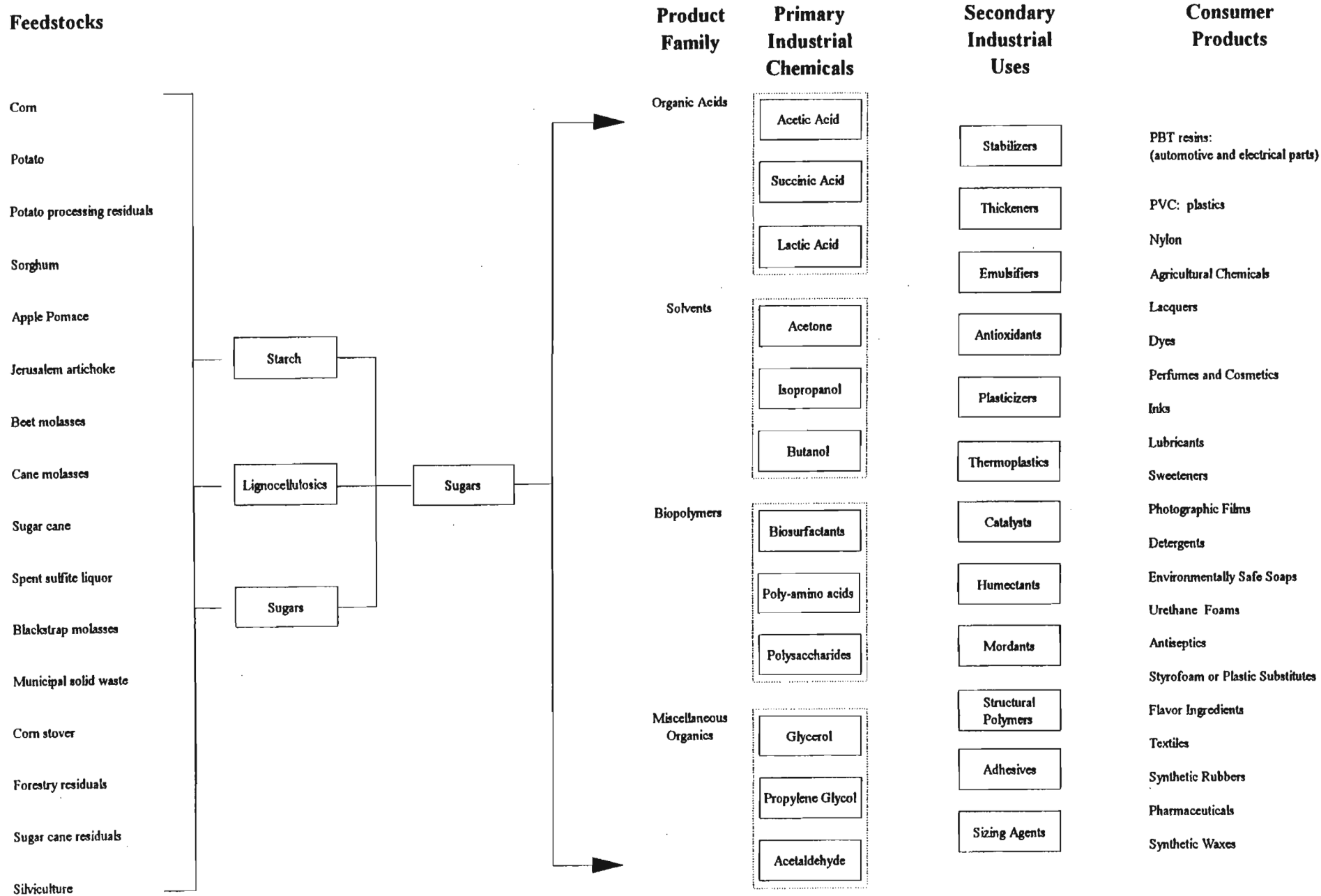


Figure 8.2 - Production of Consumer Products from Renewable Feedstocks

- *Market and environmental impact*

In addition to the technoeconomic aspects, one must also consider the markets of existing products and the potential impact of new products on markets, and attempt to answer questions such as: what is the competition for a selected material? Does it make sense to develop a small volume process when efficient high volume processes already exist to the same material? An evaluation should also overlay the environmental impact of both current processes and the emerging technologies. This approach takes the market, economic, environment, and energy impact of the route from the start, and allows a better selection of candidates of industrial relevance for potential near-term commercialization, mid-term promise, and long-term RD&D of relevant interest to the industry's needs.

- *Potential scope of process*

The possible range of applications from a given RD&D area should be considered. A chemical/process that could have a "cascade" effect on the costs and use of a number derivative chemicals and materials could offer a greater range of opportunities than focusing all attention on a single process to a single material.

Sections 8.3-8.5 list RD&D opportunities that have been identified through use of these criteria and have been separated roughly into near-, mid-, and long-term categories. Note that not all materials evaluated in sections 4.0 - 7.0 show up in the recommendations section. However, the failure to include a certain material does not mean that it is not worthy of consideration. Instead, it reflects the possibility that it might not compete with current existing routes. Alternatively, its absence could suggest research possibilities that, if realized, would make a new proposed process from biomass more viable.

8.2 Crosscutting Technical Barriers

Many technical issues have been discussed in this report, both generically and specifically for certain target products. Although this program will focus on commercialization of specific representative of chemical product families, there are barriers that are common to many of the potential products from renewables. It is clear that improvements in a specific production scheme could have applicability to other products. For convenience, the barriers can be considered in the areas of the process scheme, the intrinsic biocatalyst itself, and infrastructure issues.

A key barrier in most bioprocesses is that fermentations produce dilute aqueous products. Techniques to improve separations of these dilute chemicals are important and necessary to make purification more energy efficient and environmentally sound. Processing yields can be increased to eliminate by-products; this will improve the direct costs and make the separations easier. Conversion rates need to be increased by improved process design to decrease capital costs. The feedstocks and their pretreatments must be evaluated and improved to improve feedstock flexibility and to reduce the need for nutrient supplements such as vitamins. Some of these process concerns can also be addressed by modifying the existing biocatalysts through genetic manipulation. These manipulations could improve yield by decreasing by-product formation, improve the tolerance of higher levels of product, lower the need for added supplemental nutrients, and increase the intrinsic rate.

Other process barriers are the determination of the final end product or end use of the intermediate chemical. Subsequent conversion may be by thermal/chemical or biological means. There are additional purity and product quality issues that must be addressed for subsequent conversion. This program must also demonstrate the technology at sufficient scale to show the actual economics and capitalization risk involved. The optimum scale for a pre-commercial bioconversion plant from renewables has not been determined and will be influenced by feedstock transportation costs as well as direct process costs.

Broader infrastructure barriers that must be examined for the larger industry and for specific products included which will need to be developed include: the interface between the agribusiness and the chemical processing industry, the presence of a qualified pool of trained personnel for this new industry (National Academy of Sciences 1992); and the consumer acceptance or awareness of "green" products from renewables. Much of this discussion parallels conclusions reached by others such as the National Academy of Sciences (1992).

8.3 Near Term Opportunities

The evaluation process identified several possible RD&D opportunities that fall roughly into the near term timeframe. For bioprocesses, one opportunity was identified among organic acids, succinic acid production. For thermal chemical processes, two near term targets were also identified which will need some further evaluation prior to actual development: cellulose/lignin/hemicellulose production from clean fractionation processes and acrylic acid production. Additional near-term targets in thermal chemical processing are also listed and additional bioprocessing options were discussed in sections 6.0 and 7.0, and specifically in Table 7.5 .

1. **Succinic acid.** The emphasis in succinate-specific RD&D will focus on the bioconversion and separation steps with additional emphasis on market and infrastructure issues. As stated earlier, near-term development will use glucose syrup from corn wet milling in the near-term and encourage mid-term development of hydrolysis of lignocellulosics. However, this will depend on a suitable carbohydrate media from inexpensive bioresources. Immediate efforts will be needed to choose the best currently available organism (most likely *A. succiniciproducens*). More complete bioconversion processing data will be needed for succinic acid in the near-term.

The selection or creation of a better succinic acid organism (or mixed culture) is a near-term goal. Short-term research with genetic engineering techniques can determine the amenability of the succinic producer to genetic manipulation. Then, a near-term goal would be to improve the yield of succinic acid from sugars. Genetic alterations to improve the tolerance of the microbe to low pH and succinic acid would follow as a mid-term goal.

For *in situ* product removal to alleviate the problem of product inhibition, the precipitation and fermentation process is nearly available. However, the adsorption-based methods (biparticle FBR and the sidestream absorber with recycle) appear to be the most promising. Separations development will emphasize adsorption in the near term and membrane electrodialysis in the near- or mid-term. RD&D in the genetic and process areas will address the highest priority barriers discussed earlier. In addition, the subsequent conversion of succinic acid into other chemical products must be examined both in terms of the purity needed for the next process and the biological or thermal/chemical route to be used. Markets studies will continue to estimate future trends in potentially competitive technology and consumer acceptance and awareness of new "green" products.

2. **Clean fractionation of biomass.** Throughout this assessment of chemicals and materials from biomass, the past literature and commercial practice for separating the three components of lignocellulosics (cellulose, hemicelluloses, and lignin) has met with difficulty. Cross contamination of one fraction with traces of various components of other fractions reduces its value. The subsequent purification step necessary to high purity individual components also reduces the yield and thus increases the cost of the product.

The key to the effective and economic conversion of lignocellulosic biomass to chemicals is using of all three biomass fractions as sources of valuable chemicals and materials. Thus developing a technology that fractionates the three key biomass polymeric components in a clean manner,

that is cost-effective and environmentally safe is required. An assessment of the new NREL clean fractionation process indicates that it offers conditions that meet these requirements.

Several research needs can be identified as part of this analysis:

- The process needs to be investigated at larger scales and the individual product streams assessed for their value as feedstocks for chemicals and materials production.
 - By virtue of their lower cost, it is envisioned that these fractions could be used for manufacturing a large number of chemicals or materials, from either chemical or thermal processing or bioprocessing. As an example, the impact of clean fractionation is reflected on all monomeric carbohydrate derived chemicals derived from cellulose and hemicelluloses. It spans conventional products such as xylose, xylitol, furfural, furan resins, tetrahydrofuran and glucose, gluconic acid, sorbitol, mannitol, levulinic acid, succinic acid, as well as all the potential chemicals that can be derived from bioprocessing sugars, as described in sections 6.0 and 7.0 of this report. The raw materials cost ratio for each of these products is favorable when prepared from one of the primary products of the clean fractionation process. Essential for the success of the derivatives is the efficient hydrolysis of the cellulosic/hemicellulosic fractions. High-yield routes will be able to decrease the costs from those projected in this report.
 - In our view, this or other cost effective technologies that accomplish a clean separation of biomass polymers need to be developed before commercially attractive, environmentally sound and energy efficient technologies can be developed for producing chemicals and materials.
 - Polymeric properties of these cellulosic materials should be investigated as well as the ability to carry out the chemical modifications of these fractions into current and new products. The lignin fraction yields two types of products with different molecular weight ranges. The high molecular weight lignin fraction could be employed in a number of polymeric applications. A possible commercial application for the low molecular weight lignin fraction is manufacturing anthraquinone, described in section 8.4.
3. **Acetylated wood.** The inclusion of this technology as a near-term opportunity is based on the results of the detailed technoeconomic evaluation of the process described in section 5.4, that showed acetylated wood to be an inexpensive way to upgrade lignocellulosic biomass to a useful product. Wood acetylation imparts significant improvements in properties on wood fibers and waste fibers. The costs of wood acetylation appear to be acceptable for use in composite products, principally if the starting fibers have low cost, as is the case with wood waste, recycled fibers, and agricultural residues. There remains to be demonstrated in longer term testing that the compatibility of the acetylated wood fibers with the other components of composites is acceptable and reproducible.

The process appears to fulfill the criterion of broad potential scope. Although there has been an interest in the United States in government, universities, and industry, only in Japan are substantial inroads being made into starting the testing required for commercialization. For instance, Daiken Trade and Industry Co., Ltd. is beginning to commercialize acetylated wood under the name of α -wood for a number of higher value applications such as flat plate for large speaker systems, bath tubs and bathroom doors, kitchen applications, and wood plastic composites for heavy traffic walkways.

Whether additional substantial niche markets can be found remains to be seen; this market-driven research is largely in the hands of the private sector, but there may be an opportunity for a government-industry partnership in this area for acetylated wood, or perhaps, the broader area of chemical modification of wood with other chemical derivatives, from which a number of market niches or higher volume markets could be developed. It is necessary to

continue to assess the raw materials contribution costs of the other chemical modifications and to establish appropriate areas for future partnerships.

4. **Starch plastics.** This technology was also included because of the results of the more detailed economic projections of section 5.4. These are materials that could find use in producing biodegradable plastic packaging or other applications. Further evaluation of their production will be important, especially where chemical modification is used to impart specific properties.

We analyzed one case developed at Michigan Biotech for certain plastics packaging that combines synthetic plastics (ARCO's Dylark Resins) and inexpensive starch. It is an area that has significant industrial and university research. The concept analyzed is deemed promising and should be verified at a larger scale so that the properties of the end-use products can be assessed more completely.

It is also necessary to continue screening a number of other starch chemicals and polymers to uncover the most effective options for continued RD&D. Recent commercial developments using starch-based plastics confirm that the area is poised for additional product development.

5. **Fast pyrolysis of wood.** Replacing phenol with pyrolysis phenolics is undergoing engineering development and demonstration with industry. It shows a significant promise at the screening level and at the more detailed flow sheet level. It also shows significant industrial interest with the activities of the Pyrolysis Materials Research Consortium and the various companies dedicated to fast pyrolysis worldwide. The field is poised for engineering development and demonstration.

If the biomass pyrolysis refinery concept is to be developed to a significant industry, it is important to obtain higher yields of products from all fractions, just like the oil industry achieves use of more than 90% of its starting feedstocks.

A modification of fast pyrolysis for producing a high quantity of the oxygenated monomer levoglucosan looks extremely promising (section 8.5). The process modification from the conventional pyrolysis for phenolics has the potential to make two types of high volume chemicals that should be explored. The phenolics from the process modified route have not been assessed to the same level as those from straight pyrolysis. This modification should be examined further because it could lead to product diversification and use of 50-60% of the feedstock instead of 20-25%.

6. **Wood Phenolation.** The process involves the reaction of phenol and wood in the presence of sulfuric acid catalyst to liquefy wood. The neutralized oil is distilled to recover the product and some recycled phenolics that can be used along with more phenol to liquefy wood. Research in Japan at Kyoto University explores wood phenolation (and a number of other wood chemical modifications) for use in replacing phenol in phenol-formaldehyde thermosetting resins. Testing is proceeding at that University and with industry on products that can be made from this process. Replacing black shellac (insect derived plastic material) has been studied. Thermosetting resins prepared by this process have been reported to have excellent product performance, perhaps superior to conventional phenol-formaldehyde formulations.
7. **Benzene, Toluene, Xylene from Wood:** The process has a good potential for competing with conventional sources, based on the raw materials cost ratio of 0.97 (section 5.1.3) and the level of knowledge of how the process performs. However, at present, the U. S. markets for these chemicals are not expected to increase.

This process could be developed in countries and regions that need these chemicals and cannot import or produce them. It is a process option that needs to be developed and that could be very valuable for countries without major petroleum resources, but with significant biomass resources, and with a plastics industry in infancy or early development.

The U.S. can continue to participate in this type of technology development by sharing the intellectual property and knowhow accumulated over years of RD&D. The government investment could be leveraged by appropriate partnership with other countries through which the learned joint development results would become available to the U.S.. The technology might be needed in the United States when oil prices increase substantially, and principally if continued coal technologies development meet with environmental constraints that cannot be surmounted.

8. **Acrylic Acid.** A combination of bioprocessing and chemical processing produces acrylic acid. Lactic acid produced by fermentation of a starch waste (e.g., potato waste) can be esterified and catalytically dehydrated into the corresponding low boiling point acrylate ester. By hydrolysis, the acid is recovered and the alcohol used in the esterification can be recycled into the process. The raw materials cost ratio for this process was 1.47, for a process starting with potato waste. The chemistry and process performance of this technology has been investigated by workers at PNL and appears to be an interesting way for processing potato wastes. However, the economics need to be more carefully evaluated as a function of the cost of the potato waste, currently assumed to be negligible. "Zero value" waste materials necessarily rise to their market value when a use is discovered, and the effect of such a price increase on the ratio is not yet known (see discussion in section 3.0).

8.4 Mid Term Opportunities

The evaluation process identified several possible RD&D opportunities that fall into the mid-term time frame. These are generally processes or products that require some additional research and development to improve market acceptability or process economics. They are likely candidates for the next generation of products for the program. The bioprocessing target has been identified as butanol, an example of a neutral solvent. For thermal and chemical processes, two potential candidates were identified, anthraquinone and peracetic acid. Additional thermal and chemical examples are identified here and additional bioprocessing opportunities are discussed in sections 6.0 and 7.0, and specifically in Table 7.5.

1. **Butanol.** The secondary process evaluation indicated some economic uncertainty in the proposed butanol process. This, combined with insight from the industrial panel, indicated that butanol production should be considered a secondary priority because of limited funds and should be reexamined for mid-term research needs. These needs should focus on the improvement of yields and rates both by genetic manipulation and by simultaneous fermentation and separation. Extraction should be emphasized as the separation technology to be developed. Feedstock flexibility is another key mid-term issue.
2. **Xylose, xylitol, furfural, tetrahydrofuran, glucose, gluconic acid, sorbitol, mannitol, levulinic acid, and succinic acid.** Each of these materials, derived from glucose, could have greater importance as products in their own right, or as starting materials for other chemicals as a result of the advent of the clean fractionation process. These materials are examples of the "cascade" effect that could result from successful development of an efficient clean fractionation process. RD&D into new uses of these materials would help establish their position as viable feedstocks. Processes exhibit favorable raw materials cost ratios as high as 2.56 (xylose).
3. **Anthraquinone.** This process uses low-molecular-weight lignins that are converted to anthraquinones by a two step chemical process. The laboratory research (NREL and the

Institute of Paper Science and Technology) results indicate that the amortized production costs would be lower than all conventional processes published in the patent and open literature. This is a high value chemical with the potential to reduce the need for sulfur-pulping chemicals, increase the capacity of conventional kraft pulping thus helping the current industry, and eventually replace some of the mills in which environmental compliance could be more expensive than operation as a soda-AQ pulping in a retrofitted mode. Significant resource and energy savings are accrued by virtue of the higher yield. Additionally, because pulping can be carried out to a higher extent of delignification, bleaching chemicals requirements are lower. Producing this chemical in the United States could recapture a market from imports and the industry could become a significant exporter of catalysts to other countries.

An evaluation of this process gives a very favorable raw material cost ratio of up to 2.57, depending on the source of lignin used as the starting material. It falls more into the mid-term category because the research to date has been performed on a small laboratory scale. The process appears viable at this scale, but larger scale experimentation is necessary to verify these observations.

Recommended research includes screening process improvements and engineering scaleup of the best conditions to date. The parallel development of the best chemical process with the production of 100-500 g of pulping catalyst could allow its testing under "real world" pulping conditions. The process should be scaled up with industry if the results above justify the continued RD&D investment.

4. **Butadiene and Pentane/Pentenenes from Wood.** This process involves biomass fast pyrolysis followed by catalytic upgrading on zeolite-type catalysts. To date, the yields obtained from wood are not high enough to justify their cost-effectiveness (the ratio for butadiene is 0.47 and for pentanes/pentenenes is 0.43). However, if the feedstock is changed from wood into refuse-derived fuel from municipal solid waste, the route becomes an important route for producing four and five carbon hydrocarbons because of the much lower cost of the feedstock. Also, continued development of appropriate catalysts may increase the yield and thus decrease the costs of production.
5. **Acetic acid** can be produced from syn gas, a route that appears to be an interesting match given the unique composition of synthesis gas available from biomass, and makes possible a balanced process (through intermediate methanol) without the costs of syn gas reforming. The lack of a reforming step can decrease capital costs significantly.
6. **Peracetic acid:** This oxidant is a good non-chlorine containing pulp bleaching agent. Its high cost is the key impediment to a more widespread use. Alternative routes to peracetic acid through biomass-derived chemicals may offer lower costs. They require innovative separations solutions as well as the development of cost-effective oxidation processes. Using inexpensive lactic acid (or acetaldehyde) as a starting material could be a good way to decrease the cost of this chemical.

8.5 Long Term Opportunities

Long-term RD&D opportunities can also be suggested at this time. Several interesting candidates were noted during the analysis process as having potential promise. They are generally characterized as needing significant RD&D prior to developmental considerations as potential product lines.

1. **Levoglucosan.** This material can be prepared from fast pyrolysis of biomass and is a complex starting material for producing high value materials and specialty polymers. A specific levoglucosan derivative is resorcinol, a cold setting adhesive that would find additional

markets at lower cost. Markets for these products will be developed as current research emphasis in Japan, Canada, and the United States increases.

As this anhydro sugar becomes available from fast pyrolysis markets for its use need to be developed. Chemically, it can be the source of a number of useful chemicals and materials. The companion product, the unsaturated levoglucosenone, can also be obtained from cellulose or wood pyrolysis. Recent progress on biomass fast pyrolysis will enable the monomers to become available at very low cost. This inexpensive feedstock needs to be developed into products for this part of the biomass refinery to achieve as high a volume as the phenolic applications. Polymeric products with a high degree of chirality and special properties can be and are being developed.

2. **Vinylphenol:** This high-value specialty monomer used in coatings and microlithography can be made from biomass pyrolysis. With suitable biomass feedstocks, NREL research has shown that significant yields of this monomer can be produced. Technoeconomic projections for this process reveal a raw material cost ratio of 7.4, one of the highest calculated for any of the chemicals in the portfolio. However, process parameters for vinyl phenol production are not clearly defined, thus resulting in categorization of this material as a long-term opportunity. If this monomer can be isolated and purified, it could transcend the specialty area and become a precursor to biodegradable polystyrenes and other styrenic plastics. It should be explored both from the viewpoint of selecting the biomass type for higher yields of this product to improving the pyrolysis and separation processes. The process needs to be validated.
3. **Hydroxyacetaldehyde.** This material is a by-product of fast pyrolysis of wood, that could be a replacement for glyoxal as a crosslinking agent for resins. The raw material cost ratio, comparing hydroxyacetaldehyde to glyoxal, is calculated at 1.25. However, a process for separating the product needs to be developed to verify that this material could be produced efficiently from biomass.
4. **Polyhydroxybutyrate/valerate.** This material, prepared directly from syn gas or from glucose and propionic acid, could be important as a new biodegradable polymer with valuable properties for a variety of applications, but is included as a long-term opportunity because the data are not yet available at the level necessary to conduct a more detailed preliminary technoeconomic assessment. The final answer to the critical question — whether syn gas would be a cheaper precursor for a biological process than glucose — remains unanswered with data available. The preliminary assessment indicates that the syn gas route is less expensive based only on raw materials costs. The glucose plastics manufactured to date are indeed more expensive than equivalent polyesters. It is possible that if the raw materials cost contributions are reasonable and a simple engineering is achieved, that the syn gas derived polyesters could become more cost effective. Significant research, engineering, and development are necessary to demonstrate this concept.

8.6 Recommendations in Other DOE Program Areas and in Other Federal Agencies

One of the goals of this report is identifying potential RD&D roles for different offices within DOE. This information is intended to help determine the most appropriate use of RD&D funding to move the Alternative Feedstocks program forward. Also listed in this section are RD&D opportunities not directly linked to an evaluated chemical or process, but whose followup could provide important information to the program as a whole.

Note that some opportunities overlap different offices. This overlap results from recommended chemicals or processes that are made up of a mix of near-, mid-, and long-term research components. A schematic summary of these recommendations is given in Figure 8.3. This figure is a sketch of the past, current, and potential research and development efforts that have bearing on the use of alternative

Figure 8.3 - Coordination of research and development opportunities across federal agencies

DOE Basic Energy Sciences (BES) and the National Science Foundation (NSF)	Advanced Industrial Concepts Division (AICD)	Separations Division (SD)	Office of Waste Reduction (OWR)	Other DOE offices and federal agency efforts complementing AFP efforts	
	Biological and Chemical Technologies Research (BCTR)	AFP, Pulp & Paper, Separations	Waste Utilization Conversion (WUC)	U.S. Dept. of Agriculture	DOE office or federal agency
	Identifying and isolating new products from wood pyrolysis processes - N (see WUC)	Separation processes research for bioprocesses - N (Separations)	Design for recycle of products from wastes (wood, plastics, etc) - N	Citrus wastes to chemicals - O	
Metabolic and genetic engineering of new organisms - O	Microbial PHB/V (polyhydroxybutyrate valerate) from CO ₂ or syngas - P		Microbial PHB/V from syngas - R		
	Engineering enzymes and biocatalysts for unnatural/extreme environments - O (see Other)	Expanding the portfolio of potential commercial products - O (AFP -see BCTR)	Isolating new products from fast pyrolysis technologies - O & N		Enzymes in organic solvents - DOE Fossil Energy - O
Developing new chemical and biocatalysts, including biomimetic catalysts - O	Modeling biocatalysts, including biomimetic catalysts, for industrial applications - O	Developing bioprocessing for organic acids - O (AFP)			Simultaneous Saccharification Fermentation RD&D - O (Office of Transportation Technologies - OTT/ Biofuels)
New methods for transferring genetic information between organisms - O Understanding genetic control of microbial metabolism - O	Metabolic and genetic engineering of industrial bioprocesses including strict anaerobic systems - O Overcoming instabilities in genetically engineered microbial cultures - R	Providing industry with capabilities for a broad swing of products - N (AFP)			Sequencing various large genomes provide methods for transferring genetic information - O (DOE, NIH, NSF)
Bioreactor design and operation - O	Bioreactor design for continuous operation, reducing product feedback inhibition, and increasing conversion rates (organic acids, neutral solvents, etc.) - R & O	Implementing bioreactor design in pilot scale operation - O (AFP)			

Key: O = Ongoing or currently supported work in this area; P = preliminary ongoing or currently supported work; N = New opportunity for research or R&D; R = Previous work in this area; LCS - Lignocellulosics; RN - Renewables

Figure 8.3 - continued

DOE Basic Energy Sciences (BES) and the National Science Foundation (NSF)	Advanced Industrial Concepts Division (AICD)		Separations Division (SD)	Office of Waste Reduction (OWR)			Other DOE offices and federal agency efforts complementing AFP efforts	
	Biological and Chemical Technologies Research (BCTR)	Materials (AIM)	AFP, Pulp & Paper, Separations	Waste Utilization Conversion (WUC)	Industrial Waste Reduction (IWRP)	Municipal Solid Waste (MSW)	U.S. Dept. of Agriculture	DOE office or federal agency
Catalysts for LCS - N (see BCTR)	Catalyst models and catalyst testing for LCS derived feedstocks - N (see BES/NSF)		Developing bioprocessing for neutral solvents - O (AFP)	Hydroxyacetaldehyde from wood pyrolysis - N			AARC initiative development opportunities	Fermentable sugars from clean fractions of cellulose and hemicellulose - P (OTT/Biofuels)
	Clean fractionation for cellulose, lignin, hemicellulose - R & N	Acetylated or modified wood - P & R	Anthraquinone and other sulfur free pulping catalysts - R & N (Pulp/paper)	Lactic acid from renewables - O	Acetic acid from syngas - O		Uses for starch: plastics, etc. - O	
Photosynthesis research to enhance energy crop productivity - O	Clean fractionation to new products (xylose, glucose, gluconic acid, sorbitol, etc.) - N	Bio & chemical processing for new materials or uses of current materials: starch, plastics, etc. - R & N	Developing chemical processes for producing cellulose/lignin/hemicellulose feedstocks for chemicals and materials (cellulose acetate, etc.) - O (AFP)	Photosynthesis Research for crop productivity - O	Total life-cycle energy/environmental costs for commodities - O (can use AFP/BCTR data)	Butadiene and C5 chemicals from municipal solid waste streams - N (see BCTR)		Benzene, toluene, xylene from wood - N (viz. Techn. development in third world countries through U.S. Agency for International Development)
	Catalysts for butadiene, C5 compounds - N (see OWR/MSW)		Peracetic acid - N (Pulp/paper)	Pyrolysis of wood wastes to chemicals - O		High solids anaerobic digestors - O	Developing energy crops - O	Dedicated feedstock supplies - O (OTT/Biofuels)
	Levoglucosan monomers for polymers - P		Acetylated wood - N	Levoglucosan production - N (see BCTR)				Controlled environmental agriculture - O (NASA)

Key: O = Ongoing or currently supported work in this area; P = preliminary ongoing or currently supported work; N = New opportunity for research or R&D; R = Previous work in this area; LCS - Lignocellulosics; RN - Renewables

Figure 8.3 - continued

DOE Basic Energy Sciences (BES) and the National Science Foundation (NSF)	Advanced Industrial Concepts Division (AICD)	Separations Division (SD)	Office of Waste Reduction (OWR)		Other DOE offices and federal agency efforts complementing AFP efforts	
	<i>Biological and Chemical Technologies Research (BCTR)</i>	<i>AFP, Pulp & Paper, Separations</i>	<i>Waste Utilization Conversion (WUC)</i>	<i>Industrial Waste Reduction (IWRP)</i>	<i>U.S. Dept. of Agriculture</i>	<i>DOE office or federal agency</i>
	Developing uses of vinyl phenol as a feedstock - N		Vinyl phenol from bagasse - O			
New chemistries for use of carbohydrates for synthesis - O	New uses of carbohydrates derived from renewables for polymers, reagents, etc. - N	Integration of RN into existing processes - N (AFP)		CO ₂ and syngas: feedstocks for alcohols & other chemicals - O & N	New uses of carbohydrates for polymers, reagents, etc. - O & N	Protein engineering for new materials - R (U.S. Army Res.)
	Databases for potential new products from RN - O (AFP activity should be augmented with BCTR work) Data bases of pretreatment options - O	Databases for potential new products from RN - O (AFP)	Acrylic Acid from food wastes - N			Processing of LCS for fermentation processes - O (OTT/Biofuels)
Analytical tools for assaying RN processes - N	Analytical tools for assaying RN processes - N	Acrylic acid from waste streams - N				LCS characterization standards - O (OTT/Biofuels)
	Novel processing of fermentation broths for "product-by-design" - P		LCS characterization standards - O			LCS preparation for processing - O (OTT/Biofuels)
	Reverse chemical complexation to reduce energy consumption in isolating fermentation products - O	Electrodialysis, extraction, pervaporation for isolating fermentation products - O (AFP)	LCS preparation for thermal & biological processing - O			
CO ₂ as a feedstock for fuels production - O	CO ₂ as a feedstock for chemicals production - O & N					

For AFP, BCTR, IWRP, WUC programs: R&D in the development of better integrated decision making models. Would combine ongoing work in BCTR, AFP, IWRP, and WUC programs to take into account technical, economic, and environmental processing factors. Would be of value to industry. Can employ model development pursued by DOE's environmental restoration programs.

Key: O = Ongoing or currently supported work in this area; P = preliminary ongoing work; N = New opportunity for research or R&D; R = Previous work in this area; LCS - Lignocellulosics; RN - Renewables

feedstocks in the production of chemicals. The organization of the figure is intended to convey an ongoing and continuous process that progresses from early research findings, to bench scale demonstrations of technology, followed by precommercialization RD&D. The last two columns of Figure 8.3 show relationships to other DOE offices and federal agencies that complement the Alternative Feedstocks program. The examples depicted there range from basic research findings to precommercialization efforts. Defining the potential interactions between other DOE offices and other federal agencies will be included in future updates of this report.

8.7 Timeframe for Completion

The initial emphasis of the Alternative Feedstocks program has been on the evaluation of the potential and economic opportunity of biobased products. This ongoing product/process screen is supplemented by surveys on feedstock availability, market potential, improved pathways, and advanced chemical, thermal and bioprocessing concepts. Literature surveys and evaluations have been done in consultation with an industrial panel.

The program will take basic concepts, initiated under other programs, which show potential of marketability for biobased products. These concepts will be economically evaluated to estimate the impact. The best concepts for the target compounds will generally be taken directly to the developmental stages. Industrial involvement will be actively sought in the early phases of the development efforts. Often, it will be apparent that additional research is necessary to utilize the process. Research support will be sought from other DOE offices or other federal agencies to address these research issues.

A laboratory demonstration of the process components will be performed for the target compound. This work may be carried out at various sites. Results from this demonstration will be used to design a complete demonstration unit for testing. The results will also be used to refine the economic model. It is expected that industrial participant(s) will have an increased role at each stage of development. The final stage will be a pilot plant constructed through cost-sharing with the industrial participant.

Projects in the program will be market driven. However much of the RD&D may have generic applicability to an entire class of materials, such as improved separation for organic acids or improved pretreatment of lignocellulosics. The projects will tend to focus on the actual developmental demonstration and economic evaluation of real products and processes. Near-term projects are preferred, with an impact seen in 1 to 5 years; but mid-term (5 to 10 years) projects may also be considered. For a project, advanced techniques will be employed when they enhance process economics.

A typical time frame for demonstration and commercialization is shown in Figure 8.4.

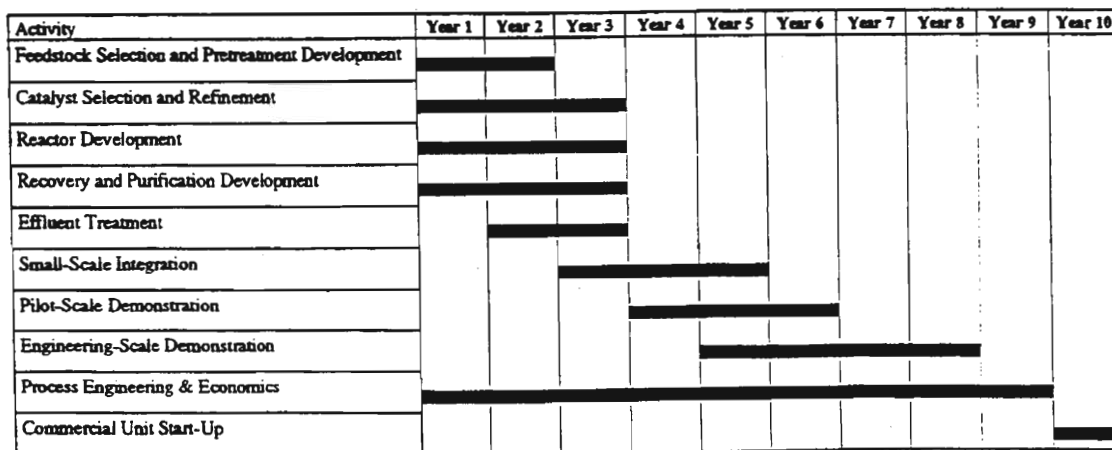


Figure 8.4 - Typical Demonstration and Commercialization Time Frame

9.0 REFERENCES AND SELECTED BIBLIOGRAPHY

General Documents and References

- 1) "Symposium on Levoglucosan and Levoglucosenone", Abstracts of the 204th National Meeting of the American Chemical Society, Washington, D. C., 1992.
- 2) "Annual Energy Outlook 1992 with Projections to 2010", Energy Information Administration, U.S. Department of Energy, publication number DOE/EIA-0383(92).
- 3) A. D. Little, "Technical and Economic Feasibility of Enzyme Hydrolysis for Ethanol Production from Wood", Arthur D. Little, Inc., Cambridge, MA, 1985.
- 4) Technical Insights, Inc., 1980, "Biomass Process Handbook - A Production/Economic Guide to 40 Chemical Processes that use Biomass as a Raw Material; Fort Lee, NJ.
- 5) Stone and Webster Engineering, "Economic Feasibility Study of an Enzyme-based Ethanol Plant", SERI/STR-231-3138, Solar Energy Research Institute, Golden, CO, 1987.
- 6) "Pulp and Paper 1992 North American Factbook", Miller Freeman Inc., San Francisco, 1991.
- 7) U.S. Department of Commerce, International Trade Administrative, U.S. Industrial Outlook 1992, Chapter 11, 1992
- 8) Browning, B. L., ed., "The Chemistry of Wood", New York: Interscience, 1963.
- 9) Browning, B. L., "Methods of Wood Chemistry", Vol. I and II, New York: Interscience, 1967.
- 10) Kollman, F. F. P., and W. A. Cote, Jr., "Principles of Wood Science and Technology," Vol. 1, New York: Springer-Verlag, 1968.
- 11) Panshin, A., and J. C. de Zeeuw, "Textbook of Wood Technology", 4th edition, New York: McGraw-Hill, 1980.
- 12) Rydholm, S. A., "Pulping Processes", New York: Interscience, 1965.
- 13) Sarkanen, K. V., and C. H. Ludwig, editors, "Lignin: Occurrence, Formation, Structure and Reactions", New York: Wiley-Interscience, 1971.

General References Used in Compiling Market Information

- 1) Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., John Wiley, New York, 1984.
- 2) Chemical Economics Handbook, SRI International, Menlo Park, CA, 1992.
- 3) Ullmann's Encyclopedia of Industrial Chemistry, 5th ed., VCH, Weinheim, 1986

Other References

- 1) Agricultural Statistics, (1991), Washington, D.C.: USDA.
- 2) "Agriculture 2000: A Look at the Future", Richland, WA: Columbus Division of Battelle Memorial Institute, Battelle Press, (1983).
- 3) Almosnino, A. M., and J. M. Belin, Biotechnol. Lett., 1991 13, 893.
- 4) Andrews, G., Biotech. Bioengin., 1989, 33, 256.
- 5) Arnheim, N., and C.H. Levenson, Chemical & Engineering News, October 1, 1990, 35.
- 6) Ausich, R., F. Brinkhuis, M. Donnelly, L. Hardin, E. Hatch, W. Hunsaker, L. Hunt, J. Kauth, I. Mukharji, M. Ratag, and B. Yen, "Production of Carotenoids by Recombinant DNA Technology", Society of Industrial Microbiology Annual Meeting, San Diego, CA, August 1992.
- 7) Battelle Memorial Institute, "Agriculture 2000: A Look at the Future", Battelle Press, Columbus/Richland, Washington (1983).
- 8) Bergez, J.-E., L. Bouvarel, and D. Auclair, Biores. Technol., 1991, 35, 41.
- 9) Berglund, K. A., et al., U.S. Patent 5,034,105 (1991).
- 10) "Biomarkets: 43 Market Forecasts for Key Product Areas", Fort Lee, NJ: Technical Insights, Inc., (1991).
- 11) Bond, G.E., in "Competitiveness of the U.S. Chemical Industry in International Markets", AIChE Symposium Series 274, (1990).
- 12) Bridgwater, A. V., J. Kuester, Eds. "Research in Thermochemical Biomass Conversion", Elsevier Applied Science: London, 1988; and references therein.

- 13) Bruce, L. J., and A. J. Daugulis, Biotechnol. Prog., 1991, 7, 116.
- 14) Busche, R. M., in "Biotechnology: Applications and Research", Lancaster, PA: Technomic Publishing, Inc., chapter 9 (1985).
- 15) Busche, R. M., "Technoeconomic Evaluation of the Extractive Fermentation of Butanol", ORNL/TM Report #11851, Oak Ridge, TN: Oak Ridge National Laboratory (1991); Busche, R. M., and B. R. Allen, Appl. Biochem. Biotechnol., 1989, 20/21, 357-374.
- 16) Chemical and Engineering News, June 29, 1992.
- 17) Chemical Marketing Reporter, July 24, 1992.
- 18) Chum, H. L., S. K. Parker, D. A. Feinberg, J. D. Wright, P. A. Rice, S. A. Sinclair, and W. G. Glasser, May 1985, "The Economic Contribution of Lignins to Ethanol Production from Biomass", SERI/TR-231-2488, Golden, CO: Solar Energy Research Institute.
- 19) Chum, H. L., L. J. Douglas, D. A. Feinberg, and H. A. Schroeder, SERI/TR 231-2183 (1985)
- 20) Chum, H. L., J. P. Diebold, J. W. Scahill, D. K. Johnson, S. Black, H. A. Schroeder, and R. Kreibich, 1989, in "Adhesives from Renewable Resources", R. Hemingway and A. Conner, Eds., ACS Symp. Series, 385, 135-151.
- 21) Chum, H. L., editor, "Assessment of Biobased Materials", SERI/TR-234-3610, Solar Energy Research Institute, Golden, CO, 1989, Chapter 2 and references therein.
- 22) Chum, H. L., J. P. Diebold, S.K. Black, J.W. Scahill, D.K. Johnson, and R.J. Evans "Inexpensive Phenol Replacements from Biomass" Energy from Biomass and Wastes XV, Washington, D.C., March 25-29, 1991.
- 23) Chum, H. L. and S. K. Black, U.S. Patent 4,942,269, (1990).
- 24) Cohen, J. C. (ed.), "Topics in Molecular and Structural Biology", p. 12 (1989).
- 25) Compere, A. L., and W. L. Griffith, Dev. Ind. Microbiol., 1976, 17, 247-52.
- 26) "Corn Annual", Corn Refiners Association, Inc., (1992).
- 27) Cselovszky, J., et al., Appl. Microbiol. Biotechnol., 1992, 37, 94.
- 28) Datta, R., "Technological Advances and Needs for Large Scale Bioprocessing and Separations," presented at National Corn Utilization Conference, St. Louis, MO, June 24-26, 1992.
- 29) Datta, R., U.S. Patent 4,885,247 (1989).
- 30) Datta, R. et al., Eur. Patent Appl. EP 405707 (1991).
- 31) Davison, B. H. and J.E. Thompson, Appl. Biochem. Biotech., 1992, 34/35, 431.
- 32) Davison, B. H. and C.D. Scott, Appl. Biochem. Biotech., 1988, 18, 19.
- 33) Davison, B. H. and C. D. Scott, Biotech. Bioengr., 1992, 39, 365.
- 34) Davison, B. H., and J. E. Thompson, Appl. Biochem. Biotechnol., in press.
- 35) Diebold, J. P. and A. J. Power, 1988, "Research In Thermochemical Biomass Conversion", A. V. Bridgwater and J. Kuester Eds., London: Elsevier Applied Science, pp. 609-628.
- 36) Diebold, J. P. and J. W. Scahill, 1988, in "Pyrolysis Oils from Biomass - Producing, Analyzing, and Upgrading", E. Soltes and T. Milne, Eds., ACS Symp. Series, 376, 21-28; Diebold, J. P. and J. W. Scahill, 1988, ibid., 31-40.
- 37) Diebold, J., in "Biomass Pyrolysis Liquids Upgrading and Utilisation", A.V. Bridgwater and G. Grassi, eds., Elsevier Applied Science, 1991, pp. 341-351.
- 38) Dower, W. J., "Genetic Engineering", J. K. Setlow, ed., p. 12, (1990).
- 39) Eckert, G., and K. Schugerl, Appl. Microbiol. Biotechnol., 1987, 27, 221.
- 40) EG&G Idaho, Inc., "Assessment of Biomass as an Alternate Energy Source", Idaho National Engineering Laboratory, Idaho Falls, Idaho (1981).
- 41) Elliott, D.C., D. Beckman, A.V. Bridgwater, J.P. Diebold, S.B. Gevert, and Y. Solantausta, Energy and Fuels, 1991, 5.
- 42) Elshafei, A. M., J. L. Vega, K. T. Klasson, E. C. Clausen, and J. L. Gaddy, Biores. Technol., 1991, 35, 73.
- 43) Electric Power Research Institute, "Biomass State-of-the-Art Assessment", Research Triangle Institute, Research Triangle Park, NC (1991).
- 44) "Encyclopedia of Chemical Technology", 3rd ed., (1982), New York, NY: John Wiley and Sons.
- 45) Ennis, B. M., N. Qureshi, and I. S. Maddox, Enzyme Microb. Technol., 1987, 9, 672.
- 46) Evans, P.J. and H. Y. Wang, Appl. Microbiol. Biotechnol., 1990, 32, 393.
- 47) Evans, P.J. and H. Y. Wang, Appl. Environ. Microbiol., 1988, 54, 1662.

- 48) Evans, R. J. and T. A. Milne, 1988, in "Pyrolysis Oils from Biomass - Producing, Analyzing, and Upgrading", E. Soltes and T. Milne, Eds., ACS Symp. Series, 376, 311-327.
- 49) Evans, R. J., T. A. Milne, in "Research in Thermochemical Biomass Conversion", Bridgwater, A. V.; Kuester, J., Eds., London: Elsevier Applied Science, 1988; p 264.
- 50) Evans, R. J. and T. A. Milne, "Energy from Biomass and Wastes XI", D. Klass, Ed., Chicago: Institute of Gas Technology, pp. 807-838, 1988; Evans, R. J. and T. A. Milne, "Research in Thermochemical Biomass Conversion", A. V. Bridgwater and J. Kuester, Eds., London: Elsevier Applied Science, pp. 264-279, 1988.
- 51) Frank, J.R., in "Fossil Energy Biotechnology: A Research Needs Assessment Final Report", W.R. Finnerty, ed., DOE Contract 01-91 ER 30156, Washington, DC: U.S. Department of Energy, chapter 8, (1992).
- 52) Frank, J.R., and W.H. Smith, in "Methane from Biomass: A Systems Approach", W.H. Smith and J.R. Frank (eds.) London: Elsevier Applied Science (1988).
- 53) Friedl, A., N. Qureshi, and I.S. Maddox, Biotechnol. Bioengr., 1991, 38, 518.
- 54) Gaillot, F. P., C. Gleason, J. J. Wilson, and J. Zwarick, Biotechnol. Prog., 1990, 6, 370.
- 55) Ghose, T. K. and A. Bhadra., in "Comprehensive Biotechnology", M. Moo-Young (ed.), New York, NY: Pergamon, chapter 38 (1985).
- 56) Glassner, D., and R. Datta, Eur. Pat. Appl. 0393 818 (1990).
- 57) Glassner, D., and R. Datta, Eur. Pat. Appl. 0389 103 (1990).
- 58) Gottschalk, G. and H. Grupe in "Harnessing Biotechnology for the 21st Century", Ladish, M. R. and A. Bose, (eds.), Washington, D.C.: American Chemical Society, 102 (1992).
- 59) Graham, R. G., B. A. Freel, and M. Bergougnou, in "Research in Thermochemical Biomass Conversion", A. V. Bridgwater and J. Kuester, Eds., London: Elsevier Applied Science, pp. 1988, pp. 629-641.
- 60) Groot, W. J., R.G.J.M. van der Lans, and K. Ch. A.M. Luyben, Process Biochem., 1992, 27, 61.
- 61) Gruy Engineering Corporation, "Estimates of RCRA Reauthorization Economic Impacts on the Petroleum Industry", prepared for American Petroleum Institute, July 20, 1991.
- 62) Hawaii Sugar Planters' Association, "Hawaii Sugar Manual 1991", ISSN 1048-9428.
- 63) Hickey, R.F. and R.W. Owens, Biotech. Bioeng. Symp. Ser., 1981, 399.
- 64) Holtberg, P.D., T.J. Woods, M.L. Lihn, and N.C. McCabe, in "Gas Research Insights" (1991).
- 65) Hogan, E. N., Ed., Proc. 7th Canadian Bioenergy Seminar, National Research Council of Canada: Ottawa, Ontario, Canada, 1990, pp 669-720.
- 66) Hotta, K. and S. Takao, Hakko Kagaku Zasshi, 1973, 51, 19.
- 67) HRA, Inc., "A Commercial and Technical Assessment of Lactic Acid, Selected Salts of Lactic Acid, and Polylactic Acid", prepared for Argonne National Laboratory (1991).
- 68) Ingram, L.O. et al., U.S. Patent 5,000,000 (1990).
- 69) Ishii, S., T. Masahito, and T. Kobayashi, J. Chem. Eng. Japan, 1985, 18, 125.
- 70) James, R. W., "Industrial Starches", Noyes Data Corp., Park Ridge, NJ, 1974.
- 71) Johnson, D. K., unpublished results at SERI, 1990.
- 72) Jones, D. T. and D. R. Woods, Microbiol. Rev., 1986, 50, 484.
- 73) Jones, D. T. and D. R. Woods in "Clostridia", N. P. Minton and D. J. Clarke (eds.), Plenum Press, 105 (1989).
- 74) Kang, W., R. Shukla, and K. K. Sirkar, Biotech. Bioengr., 1990 36, 826.
- 75) Kertes, A. S. and C. J. King, Biotech. Bioeng., 1986, 28, 269.
- 76) Klein, T. M., et al., Bio/Technology, 1992, 10, 286.
- 77) Ladisch, M. R., Enzyme Microb. Technol., 1991, 13, 280.
- 78) Lee, A.K.K. and A.M. Aitans, Oil and Gas Journal, September 10, 1990.
- 79) Leeper, S. A., J. H. Wolfram, M. L. Chow, and L. J. Dawley, "Municipal Solid Waste Bioconversion Techniques", EG&G Idaho, Inc., Idaho National Engineering Laboratory, Idaho Falls, Idaho (1982).
- 80) Leeper, S. A., T. E. Ward, and G. F. Andrews, "Production of Organic Chemicals via Bioconversion: A Review of the Potential", EG&G Idaho, Inc., Idaho National Engineering Laboratory, Idaho Falls, Idaho (1991).

- 81) Levy, P. F., A. P. Leuschner, and J. H. Stoddart, Jr., "Biorefining of Selected Industrial Wastes to Liquid Fuels and Organic Chemicals", Department of Energy, DOE/CE/40556-T2 (DE83013910) (1983).
- 82) Linden, J. C., A. R. Moreira, and T. G. Lenz, in "Comprehensive Biotechnology", M. Moo-Young, (ed.), Oxford: Pergamon Press, chapter 44, 915-931 (1986).
- 83) Ling, L. B., and T. K. Ng, U. S. Patent 4877731 (1989).
- 84) Lipinsky, F. S. Tappi J. 1983, 66(10), 47.
- 85) List, H.L., "Petrochemical Technology: An Overview for Decision Makers in the International Petrochemical Industry", Prentice-Hall, NJ (1986).
- 86) Lynd, L. R., J. H. Cushman, R. J. Nichols, C. E. Wyman, Science, 1991, 251, 1320.
- 87) Manzoni, M., and V. Cavazzoni, J. Chem. Tech. Biotechnol., 1992, 54, 311.
- 88) Maiorella, B. L. in "Comprehensive Biotechnology", vol. 3, M. Moo-Young, ed., Pergamon Press, New York (1985).
- 89) Mermelstein, L. D., et al., Bio/Technology, 1992, 10, 190.
- 90) Mok, W. S., M. J. Antal, M. Jones, J. Org. Chem., 1989, 54, 4596
- 91) Morris, D. and I. Ahmed, 1992, "The Carbohydrate Economy - Making Chemicals and Industrial Materials from Plant Matter," The Institute for Local Self Reliance, In press.
- 92) National Academy of Sciences, "Putting Biotechnology to Work: Bioprocess Engineering", Washington, D.C., National Academy of Sciences (1992).
- 93) Narayan, R., T. Kiessling, and G. T. Tsao, Appl. Biochem. Biotechnol., 1988, 17, 45.
- 94) Oak Ridge National Laboratory (1992), L. L. Wright, personal communication.
- 95) Office of Technology Assessment, "Commercial Biotechnology: An International Analysis", Congress of the United States, OTA-BA-218 (1984).
- 96) Office of Technology Assessment, "Agricultural Commodities as Industrial Raw Materials", Congress of the United States, OTA-F-476 (May, 1991).
- 97) Office of Technology Assessment, "Biotechnology in a Global Economy", Congress of the United States, S/N 052-003-01258-8 (1991).
- 98) Okada, H., et al., J. Gen. Appl. Microbiol., 1961, 7, 177.
- 99) "Organic Chemicals From Biomass", D. L. Wise (ed.), Benjamin/Cummings Publ. Co. (1983).
- 100) Osten, J. and W. Veno, "U.S. Refining Model Methodology Report. Final Report". Ga Research Institute Contract #5089-800-1796 (1991).
- 101) Overend, R. P., and H. L. Chum, Biologue, 1991, 8, 10.
- 102) Overend, R. P., T. A. Milne; L. K. Mudge, Eds., "Fundamentals of Thermochemical Biomass Conversion", Elsevier Applied Science: London, 1985.
- 104) Parker, S. K., M. Calnon, D. A. Feinberg, A. J. Power, and L. Weiss, 1983, "The Value of Furfural/Ethanol Coproduction from Acid Hydrolysis Processes", TR-231-2000, Golden, CO Solar Energy Research Institute.
- 105) Perlack, R.D., J. W. Ranney, and L. L. Wright, "Environmental Emissions and Socioeconomic Considerations in the Production, Storage, and Transportation of Biomass Energy Feedstocks", Oak Ridge National Laboratory, Report #ORNL/TM-12030 (1992).
- 106) Ransom, K. M., Editor, "Markets 90-94. The Outlook for North American Forest Products", Widman Management Ltd., Miller Freeman Publications, San Francisco, (1990).
- 107) Rejai, B., R. J. Evans, J. P. Diebold, and J. W. Scahill, in "Energy from Biomass and Wastes XV", Washington, D.C., (March 25-29, 1991).
- 108) Roffler, S. R., H. W. Blanch, and C. R. Wilke, Biotech. Bioengr., 1988, 31, 135.
- 109) Roffler, S. R., T. W. Randolph, D. A. Miller, H. W. Blanch, and J. M. Prausnitz, Chap 6 p. 133-172 in "Extractive Bioconversions", B. Mattiasson and O. Holst, (eds.), New York, NY: Marcel Dekker, Inc, chapter 6 (1991).
- 110) Roffler, S. R., H. W. Blanch and C. R. Wilke, Biotechnol. Prog., 1987, 3, 131.
- 111) Roger, E.W., in "Competitiveness of the U.S. Chemical Industry in International Markets", J.J. Ulbrecht, AIChE Symposium Series, 1990 274, 86.
- 112) Rousseau, R. W. (ed.), "Handbook of Separation Process Technology", New York, NY: John Wiley & Sons (1987).

- 113) Rowell, R. M., T. P. Schulz, and R. Narayan, Editors, "Emerging Technologies for Materials and Chemicals from Biomass", ACS Symposium Series, 476, (1992).
- 114) Roy, K. A., Hazmat World, 1992 (July), 32.
- 115) Russell, M., E. W. Colglazier, and B. E. Tonn, Environment, 1992, 34, 12-39.
- 116) Salunkhe, D. K., S. S. Kadam, and S. J. Jadhav, "Potato: Production, Processing, and Products", CRC Press, Boca Raton, Florida (1991).
- 117) Samuelov, N. S., et al., Appl. Env. Microbiol., 1991, 57, 3013.
- 118) Sato et al., Agr. Biol. Chem., 1972, 36, 1969.
- 119) Scott, D., J. Piskorz, and D. St. Radleinn in "Emerging Technologies for Chemicals and Materials from Renewables", R. M. Rowell, T. P. Schultz, and R. Narayan, Editors, ACS Symposium Series, 1992, 476, 422.
- 120) Shah, M. M., S.K. Song, Y.Y. Lee and R. Torget., Appl. Biochem. Biotechnol., 1991, 28/29, 99.
- 121) Shiraishi, N. in "Lignin: Properties and Materials"; Glasser, W. G.; Sarkanen, S., Eds.; ACS Symposium Series 1989, 397; 488.
- 122) Shiraishi, N. I. Appl. Polym. Sci. 1986, 32, 3189.
- 123) Shiraishi, N., H. Ito, S. V. Lonikar, N. Tsujimoto, I. Wood Chem. Technol., 1987, 7, 405.
- 124) Shukla, R., W. Kang, and K. K. Sirkar, Biotech. Bioengr., 1989, 34, 1158.
- 125) Soltes, E., T. A. Milne, Eds., Pyrolysis Oils from Biomass - Producing, Analyzing and Upgrading; ACS Symposium Series 376; American Chemical Society: Washington, D.C., 1988.
- 126) Spitz, P. H., "Petrochemicals - The Rise of an Industry", Wiley, New York (1988).
- 127) Stavins, R. N., and B. W. Whitehead, Environment, 1992, 34,, 7.
- 128) Szmant, H. H., "Industrial Utilization of Renewable Resources", Technomic Publishing Co., Lancaster, (1986).
- 129) Szmant, H.H., "Organic Building Blocks of the Chemical Industry", New York, NY: John Wiley & Sons (1989).
- 130) Takao, S., et al., Hakko Kogaku Zasshi, 1973, 51, 19.
- 131) Technical Insights, Inc., "Biomarkets: 43 Market Forecasts for Key Product Areas", Fort Lee, New Jersey (1991).
- 132) Teunissen, M. J., and G. D. Vogels, , "Cellulolytic and Xylanolytic Enzymes of Anaerobic Fungi." Presented at 14th Symposium on Biotechnology for Fuels and Chemicals, Gatlinburg, Tennessee, May 1992.
- 133) USDA, "Proceedings: Whey Products Conference", Eastern Regional Research Center, Philadelphia, Pennsylvania (1980).
- 134) USDA, "New Farm and Forest Products: Responses to the Challenges and Opportunities Facing American Agriculture", New Farm and Forest Products Task Force, Washington, D.C. (1987) .
- 135) USDA, "Costs of Production – Major Field Crops, 1990", Economic Research Service, ECIFS 10-4 (1990).
- 136) USDA, "Agricultural Statistics", Washington, D.C. (1991).
- 137) USDA, "Oil Crops Situation and Outlook Report", Economic Research Service, OCS-32 (January 1992).
- 138) USDA, "Feed Situation and Outlook Report", Commodity Economics Division, FDS-322 (May 1992).
- 139) USDA, "Agricultural Resources: Agricultural Land Values and Markets Situation and Outlook Report", Economic Research Service, AR-26 (June 1992a).
- 140) USDA, "Sugar and Sweetener Situation and Outlook Yearbook", Economic Research Service, SSRV17N2 (June 1992b).
- 141) USDA, "New Industrial Uses, New Markets for U.S. Crops: Status of Technology and Commercial Adoption", Hudson and Harsch, Maumee, OH (October 1992).
- 142) USDA, "Agricultural Resources: Crop, Plant, Water, and Conservation Situation and Outlook Report", Economic Research Service, AR-27 (September 1992).
- 143) U. S. Department of Energy, "Electricity from Biomass. National Biomass Power Program, Five Year Plan 1994-98" (1993)
- 144) Vickroy, T. B., in "Comprehensive Biotechnology," vol. 3. New York, NY: Moo-Young, M., (ed.), Pergamon, chapter 38 (1985).

- 145) Wang, H. Y. and K. Sobnosky, ACS Symp. Ser., 1985, 271, 123.
- 146) Wang, H. Y., F. M. Robinson, and S. S. Lee, Biotech. Bioengr. Symp. Ser., 1981, 11, 555.
- 147) Wardell, J. M. and C. J. King, I. Chem. Eng. Data, 1978, 23, 144.
- 148) Watson, S. A., and P. E. Ramstad, "Corn: Chemistry and Technology", American Association of Cereal Chemists, Inc. St. Paul, MN (1987).
- 149) Wayman, M., and R. Parekh, I. Ferment. Technol., 1987, 65, 295.
- 150) Wayman, M., S. Chen, and K. Doan, Proc. Biochem., 1992, 27, 239.
- 151) Wilks, H.M., et al. in 9th Proceedings of the International Biotechnology Symposium, 1992, 150.
- 152) Wright, L. L., J. H. Cushman, A. R. Ehrenshaft, S. B. McLaughlin, W. A. McNabb, J. W. Ranney, G. A. Tuskan, and A. F. Turhollow, "Biofuels Feedstock Development Program: Annual Progress Report for 1991", Oak Ridge National Laboratory, Report #ORNL-6742 (1992).
- 153) Yergin, D., The Prize, New York: Simon & Schuster, (1991).