

# Hydrogen from Biomass

## State of the Art and Research Challenges

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# Table of Contents

Preface.....	i
Executive Summary.....	1
Routes to Hydrogen from Biomass.....	5
Introduction.....	5
Direct Production from Whole Biomass.....	7
Gasification.....	7
Thermal/Steam/Partial Oxidation.....	7
Direct Solar Gasification.....	11
Miscellaneous Gasification Processes.....	11
Biomass-Derived Synthesis Gas Conversion.....	12
Supercritical Conversion of Biomass.....	14
Biomass Pyrolysis to Hydrogen and Carbon or Methanol.....	17
Biological Conversion of Biomass to Hydrogen.....	17
Production of Storable Intermediates from Biomass Partial Conversion.....	18
Hydrogen from Biomass-Derived Pyrolysis Oils.....	18
Hydrogen from Biomass-Derived Methanol.....	19
Hydrogen from Biomass-Derived Ethanol.....	21
Methane and Natural Gas to Hydrogen or Methanol by Direct Thermolysis.....	23
Pyrolysis to Hydrogen and Carbon.....	25
Reforming of Methane (and Natural Gas) to Hydrogen.....	28
Technoeconomic and Life Cycle Analysis of Biomass to Hydrogen.....	28
Technoeconomic Assessments.....	28
Life Cycle Analyses.....	28
Overviews of Hydrogen Production Pathways.....	28
Information on Country Programs.....	29

Promising Areas for Research, Development and Demonstration..... 30

Appendix: A: References to Technical sections..... 33

Appendix: B: References to Major Sources of Biomass-to-Hydrogen Information..... 72

Acknowledgments..... 78

## Preface

This report is a review largely of thermochemical research studies for the formation of hydrogen from whole biomass and stable intermediate products from biomass. The purpose of this report is to serve as a baseline of the state of the art and to identify research opportunities that can be conducted within a new Task of the International Energy Agency's (IEA) Programme on the Production and Utilization of Hydrogen. This new Task, Task 16 – Hydrogen from Carbon Containing Materials, will begin work in early 2002. Subtask B addresses Biomass to Hydrogen. The Task Leader is Elisabet Fjermestad Hagen, Norsk Hydro ASA, N-0246, Oslo, Norway. Included in this report are references to the thermal gasification of biomass. These were reviewed in cooperation with the IEA Bioenergy Programme, specifically the Gasification Task - Suresh Babu, Task Leader. [Suresh.Babu@gastechnology.org](mailto:Suresh.Babu@gastechnology.org)

# Executive Summary

## OVERVIEW

Approximately 95% of the hydrogen produced today comes from carbonaceous raw material, primarily fossil in origin. Only a fraction of this hydrogen is currently used for energy purposes; the bulk serves as a chemical feedstock for petrochemical, food, electronics and metallurgical processing industries. However, hydrogen's share in the energy market is increasing with the implementation of fuel cell systems and the growing demand for zero-emission fuels. Hydrogen production will need to keep pace with this growing market.

In the near term, increased production will likely be met by conventional technologies, such as natural gas reforming. In these processes, the carbon is converted to CO<sub>2</sub> and released to the atmosphere. However, with the growing concern about global climate change, alternatives to the atmospheric release of CO<sub>2</sub> are being investigated. Sequestration of the CO<sub>2</sub> is an option that could provide a viable near-term solution.

Reducing the demand on fossil resources remains a significant concern for many nations. Renewable-based processes like solar- or wind-driven electrolysis and photobiological water splitting hold great promise for clean hydrogen production; however, advances must still be made before these technologies can be economically competitive. For the near- and mid-term, generating hydrogen from biomass may be the more practical and viable, renewable and potentially carbon-neutral (or even carbon-negative in conjunction with sequestration) option. Recently, the International Energy Agency's (IEA) Program on the Production and Utilization of Hydrogen launched its new Task 16, Hydrogen from Carbon-Containing Materials, to bring together international experts to investigate some of these near- and mid-term options for producing hydrogen with reduced environmental impacts. In addition to large-scale fossil-based production with carbon sequestration and production from biomass, small-scale reforming for distributed generation is included in the activity.

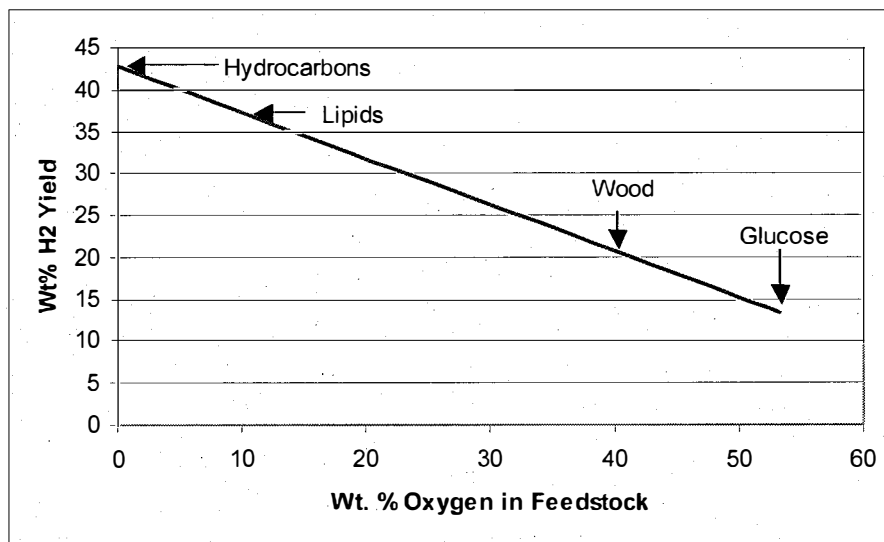
This review of the state of the art of hydrogen production from biomass was prepared to facilitate in the planning of work that should be done to achieve the goal of near-term hydrogen energy systems. We describe the relevant technologies that convert biomass to hydrogen, with emphasis on thermochemical routes. In evaluating the viability of the conversion routes, each must be put in the context of the availability of appropriate feedstocks and deployment scenarios that match hydrogen to the local markets. Co-production opportunities are of particular interest for near-term deployment since multiple products improve the economics; however, co-product development is not covered in this report.

We do not discuss the nature of the biomass feedstock, but any economically viable process must be closely linked to the characteristics of the locally available materials and appropriately sized for the supply. Relevant feedstock qualities are: cost, distribution, mass, and physical and chemical characteristics. All of these qualities must be considered when matching feedstock with conversion technology. Biomass feedstocks vary greatly in both composition and form. Both moisture and energy content are key parameters in the evaluation of biomass and also lead to a number of engineering considerations that must be addressed. Since biomass is low in density, the transportation costs for both the feedstock and the hydrogen must be balanced with the savings from employing economy of scale. The distribution of hydrogen production sites requires a decision on the transport of both the biomass and the hydrogen. These

characteristics will make it difficult to compete with natural gas steam reforming without credits and has inhibited the implementation of commercial biomass systems to date.

The first task in biomass hydrogen development is to identify the optimum match of feedstock, production technology, and end-use options. Technoeconomic comparisons are the only way to make rational selection of appropriate research and development paths in this complex and rich technical area. Regional perspectives will vary greatly and, hence, opportunities will be different for Europe, N. America, Asia, and the developing regions of the world. These items are not reviewed here, but they must guide the identification of research, development and demonstration (R,D&D) needs (a selection of recent references is given below). (See IEA Bioenergy Agreement Task 35, Technoeconomic assessments for Bioenergy Applications.)

Biomass has the potential to accelerate the realization of hydrogen as a major fuel of the future. Since biomass is renewable and consumes atmospheric CO<sub>2</sub> during growth, it can have a small net CO<sub>2</sub> impact compared to fossil fuels. However, hydrogen from biomass has major challenges. There are no completed technology demonstrations. The yield of hydrogen is low from biomass since the hydrogen content in biomass is low to begin with (approximately 6% versus 25% for methane) and the energy content is low due to the 40% oxygen content of biomass. Since over half of the hydrogen from biomass comes from spitting water in the steam reforming reaction, the energy content of the feedstock is an inherent limitation of the process. The yield of hydrogen as a function of oxygen content is shown in Figure 1.

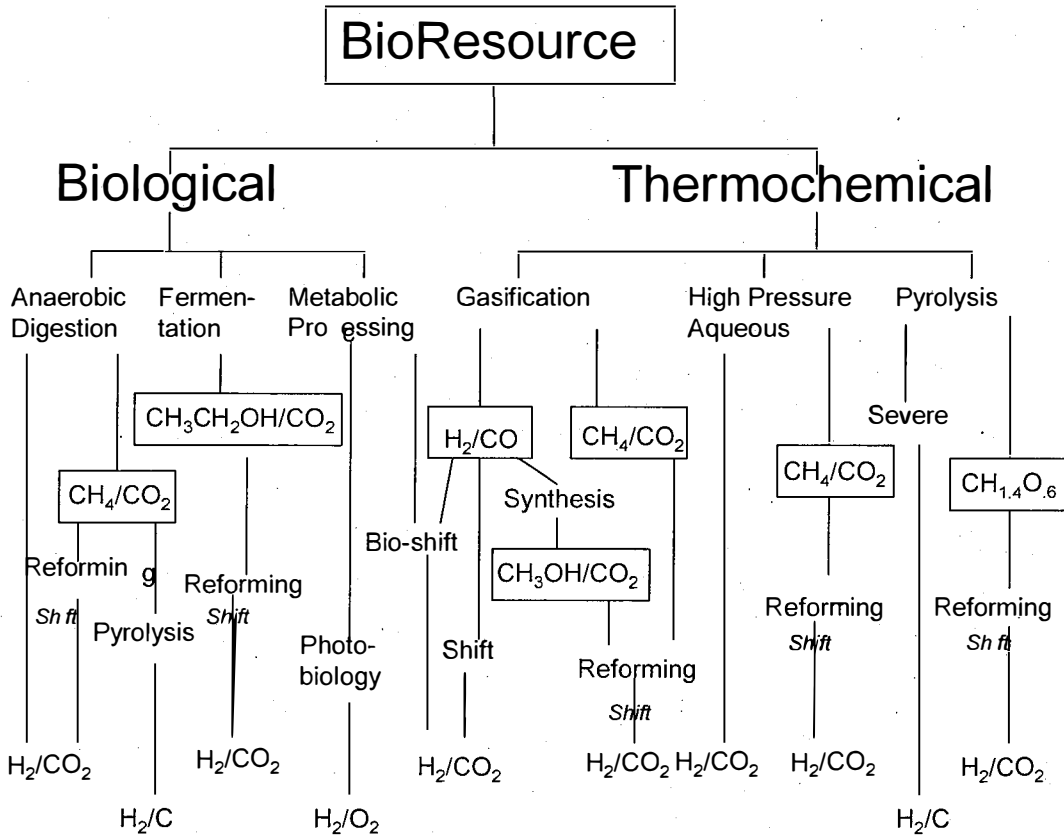


**Figure 1 - Theoretical yield of H<sub>2</sub> as a function of the oxygen content in the feed.**

The low yield of hydrogen on a weight basis is misleading since the energy conversion efficiency is high. For example, the steam reforming of bio-oil at 825°C with a five-fold excess of steam demonstrated in the laboratory has an energy efficiency of 56%.

However, the cost for growing, harvesting and transporting biomass is high. Thus, even with reasonable energy efficiencies, it is not presently economically competitive with natural gas steam reforming for stand-alone hydrogen without the advantage of high-value co-products. Additionally, as with all sources of hydrogen, production from biomass will require appropriate hydrogen storage and utilization systems to be developed and deployed.

Biomass conversion technologies can be divided into two categories: 1) direct production routes and 2) conversion of storable intermediates. Direct routes have the advantage of simplicity. Indirect routes have additional production steps, but have an advantage in that there can be distributed production of the intermediates, minimizing the transportation costs of the biomass. The intermediates can then be shipped to a central, larger-scale hydrogen production facility. Both classes have thermochemical and biological routes. Figure 2 shows the technologies that are reviewed in this report.



**Figure 2 - Pathways from Biomass to Hydrogen.**  
Storable intermediates are shown in boxes.

A third area of hydrogen from biomass is metabolic processing to split water via photosynthesis or to perform the shift reaction by photo biological organisms. The photo-biological production of hydrogen is only briefly cited since it is an area of long-term research and is covered in a separate IEA Task (IEA Hydrogen Agreement Task 15, Photobiological Production of Hydrogen). The use of microorganisms to perform the shift reaction is of great relevance to hydrogen production because of the potential to reduce carbon monoxide levels in the product gas far below the level attained using water gas shift catalysts and, hence, eliminate final CO scrubbing for fuel cell applications. The following serves as an introduction to the areas reviewed in this report.

## AREAS FOR FURTHER RESEARCH AND DEVELOPMENT

Promising areas for biomass to hydrogen conversion technology R,D&D are determined by the range of available low cost biomass feedstocks and the markets for hydrogen in areas where the feedstocks are available. The major areas for R,D&D are:

- **Feedstock preparation and feeding:** For biological routes, pretreatment to increase accessibility is an issue, and for thermochemical routes, there are major issues for the preparation of the variety and nature of the feeds for high temperature and pressure reactors.
- **Gasification gas conditioning:** The key to hydrogen utilization is fuel cell applications, so product purity requirements for the fuel cell will drive the gas purity requirements of all production systems. In gasification, the presence of hydrocarbons and trace levels of nitrogen, sulfur, and chlorine compounds must be addressed, not only for end use applications, but also for shift reaction catalysts and separation systems, such as pressure swing adsorption.
- **System integration:** The development of hydrogen technology depends on the integration of several key steps that must be practiced at appropriate scales of operation. Technical and economic analysis is required to match the optimum technology with available feedstock to produce a product of the necessary quality for the target application. Although biomass to hydrogen allows great flexibility in deployment, it also means a greater array of technical possibilities must be covered.
- **Modular systems development:** There is an opportunity for biomass systems to address small-scale and remote applications. These systems will require novel conversion and gas conditioning technologies and will also need to be designed appropriately for the resources and technical expertise available in that region.
- **Valuable co-product integration:** Appropriate systems for conversion of by-product streams from chemical and biological processing of biomass are the best prospects for near-term development.
- **Larger-scale demonstrations:** The most promising technologies will need to be selected at the larger-scale. These demonstrations will need to include successful utilization of the hydrogen (i.e. in a fuel cell, internal combustion engine, turbine, etc).

These are in addition to the challenges for any hydrogen process in storage and utilization technologies.

The technologies reviewed in this report will be discussed by international experts using the following criteria:

- Technical feasibility
- Interest of the participating countries
- Feedstock availability
- Potential use for the hydrogen
- Economic potential

Those identified by the experts as the most promising will be the subject of further review and/or research under the new IEA Hydrogen Agreement Task 16, Hydrogen from Carbon Containing Materials. Technoeconomic and life cycle analyses will be performed on select technologies in the context of regional perspectives and to identify opportunities for further R,D&D.



# Routes to Hydrogen from Biomass

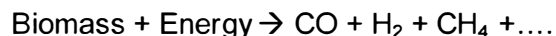
## INTRODUCTION

### *Direct Production of Hydrogen from Biomass*

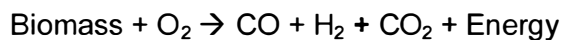
Gasification is a two-step process in which a solid fuel (biomass or coal) is thermochemically converted to a low- or medium-energy-content gas. Natural gas contains 35 MJ/Nm<sup>3</sup>. Air-blown biomass gasification results in approximately 5 mJ/M<sup>3</sup>; oxygen-blown in 15 mJ/m<sup>3</sup>. In the first reaction, pyrolysis, the dissociated and volatile components of the fuel are vaporized at temperatures as low as 600°C (1100°F). Included in the volatile vapors are hydrocarbon gases, hydrogen, carbon monoxide, carbon dioxide, tar, and water vapor. Because biomass fuels tend to have more volatile components (70-86% on a dry basis) than coal (30%), pyrolysis plays a larger role in biomass gasification than in coal gasification. Gas phase thermal cracking of the volatiles occurs, reducing the levels of tar. Char (fixed carbon) and ash are the pyrolysis by-products that are not vaporized. In the second step, the char is gasified through reactions with oxygen, steam, and hydrogen. Some of the unburned char may be combusted to release the heat needed for the endothermic pyrolysis reactions.

Gasification coupled with water-gas shift is the most widely practiced process route for biomass to hydrogen. Thermal, steam and partial oxidation gasification technologies are under development around the world. Feedstocks include both dedicated crops and agricultural and forest product residues of hardwood, softwood and herbaceous species.

Thermal gasification is essentially high severity pyrolysis although steam is generally present. An example of this is the Sylvagas (BCL/FERCO) low-pressure, indirectly heated circulating fluid bed.

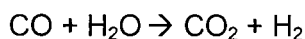


By including oxygen in the reaction gas the separate supply of energy is not required, but the product gas is diluted with carbon dioxide and, if air is used to provide the oxygen, then nitrogen is also present. Examples of this are the GTI (formerly IGT) High-Pressure Oxygen-Blown Gasifier, as well as the circulating fluid bed by TPS Termiska.



Other relevant gasifier types are bubbling fluid beds being tested by EneKem, and the high-pressure high-temperature slurry-fed entrained flow Texaco gasifier.

All of these gasifier examples will need to include significant gas conditioning, including the removal of tars and inorganic impurities and the conversion of CO to H<sub>2</sub> by the water-gas shift reaction:



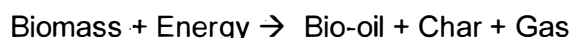
Significant attention has been given to the conversion of wet feedstocks by high-pressure aqueous systems. This includes the supercritical-gasification-in-water approach by Antal and coworkers as well as the supercritical partial oxidation approach by General Atomics.

Pyrolysis to hydrogen and carbon is being explored as a viable technology for carbon sequestration although most work is applied to natural gas pyrolysis. Biomass or biomass-derived intermediates could be processed in this way.

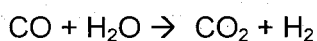
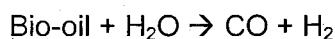
Biological conversion via anaerobic digestion is currently being practiced by workers around the world resulting in methane that can be processed to hydrogen by conventional steam reforming processes.

### ***Storable Intermediates***

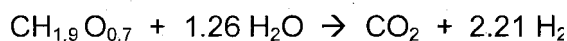
Pyrolysis produces a liquid product called bio-oil, which is the basis of several processes for the development of fuels, chemicals and materials. The reaction is endothermic:



The oil can be formed in 66 wt. % yields. Chornet and coworkers have developed the concept of using the residual fractions of the oil for hydrogen after co-products have been produced. Catalytic steam reforming of Bio-oil at 750-850°C over a nickel-based catalyst is a two-step process that includes the shift reaction:



The overall stoichiometry gives a maximum yield of 17.2 g H/100 g bio-oil (11.2% based on wood).



Regional networks of pyrolysis plants could be established to provide oil to a central steam reforming facility. The process is compatible with other organic waste streams such as aqueous-steam fractionation processes used for ethanol production and trap grease. Methanol and ethanol can also be produced from biomass by a variety of technologies and used for on-board reforming for transportation. Methane from anaerobic digestion could be reformed along with natural gas. Methane could be pyrolyzed to hydrogen and carbon if markets for carbon black were available.

Systems analysis has shown that biomass gasification / shift conversion is economically unfavorable compared to natural gas steam reforming except for very low cost biomass and potential environmental incentives. The pyrolysis with valuable co-product approach yields hydrogen in the price range of \$6 - \$8/GJ, which is promising for near term applications.

## DIRECT PRODUCTION FROM WHOLE BIOMASS

### *Gasification*

- **Thermal/Steam/Partial Oxidation**

This section briefly covers processes that will be addressed in detail in a new cooperative Task of the IEA Bioenergy Agreement. It is included here for completeness of the survey under the IEA Hydrogen Agreement Task 16, Hydrogen from Carbon-Containing Materials. [Dr. Suresh Babu (USA) at the Gas Technology Institute can be contacted for details of the IEA Bioenergy Agreement's gasification-to-hydrogen plans.]

Consideration of hydrogen from carbonaceous materials has a long history in the "hydrogen" literature. At the First World Hydrogen Energy Conference, Tsaros et al. (1976) (USA) reported on three routes to hydrogen using sub-bituminous coal. (Their ultimate goal was liquid fuels.) The processes considered were: (1) Koppers-Totzek; (2) U-Gas and (3) Steam-iron. Hydrogen yields of 93-96% of theoretical were predicted.

Soo et al. (1978) (USA) present calculations and experimental data on steam processes to convert coal to hydrogen. A large excess of steam (4 moles water to 1 mole carbon) at 1300°C produces up to 90% hydrogen without the need for shift conversion. It was claimed that their process is a better source of hydrogen than Hygas or Steam-iron. Eliminating the need for pure oxygen renders this process superior to the large, Totzek and Synthane processes. A technical note by Williams (1980) (USA) makes a case for efficient hydrogen production from coal using centrifuge separation of hydrogen from other gases following steam gasification at 1100-5000°C. Recent advances in new materials developed by the aerospace industry made it appear possible to develop such a gaseous centrifuge.

The U-Gas® process for producing hydrogen from coal is discussed by Dihu and Patel (1983) (USA). U-Gas® has been developed by IGT from over 50 years of coal-conversion research. It comprises a single-stage, non-slugging, fluidized-bed gasifier using oxygen or air. Pilot plant results and economic projections of the cost of hydrogen are given. Pilot-scale experiments in the steam gasification of charred cellulosic waste material are discussed in Rabah and Eddighidy (1986) (Egypt). The beneficial effects of some inorganic salts, such as chlorides, carbonates and chromates, on the reaction rate and production cost of hydrogen were investigated.

A large number of single research studies have appeared from 1981-2000, from researchers in many countries around the world. Brief notes follow. McDonald et al. (1981) (New Zealand) proposed extracting protein from grass and lucern and using the residue for hydrogen production (among other fuels). Saha et al. (1982, 1984) (India) reported using a laboratory-scale fluidized-bed autothermal gasifier to gasify carbonaceous materials in steam. Further studies with agricultural wastes were planned. Cocco and Costantinides (1998) (Italy) describe the pyrolysis-gasification of biomass to hydrogen.

More-or-less conventional gasification of biomass and wastes has been employed with the goal of maximizing hydrogen production. Researchers at the Energy and Environmental Research Center at Grand Forks have studied biomass and coal catalytic gasification for hydrogen and methane (Hauserman & Timpe, 1992, and Hauserman,

1992) (USA). A brief experimental effort is described to demonstrate that the pilot-scale research on hydrogen production by catalytic coal gasification can be extended to wood. The results show that the coal technology is fully transferable to wood, subject to minor substitutions in feeding and solids handling components. Continuing work relating coal and biomass gasification, gasification mechanisms, and plant operator costs are given in Hauserman, (1994a) (USA). Two processes were compared using bench-scale methods to predict the approach best suited to specific coals or biomass: 1) pyrolysis and subsequent cracking and 2) steam char gasification. Either process can be greatly enhanced by use of catalysts. Bench-scale methodology is given to determine proportions of hydrogen and methane from pyrolysis and gasification reactions. In Hauserman (1994b) (USA), gasification of coal or wood, catalyzed by soluble metallic cations to maximize reaction rates and hydrogen yields, are said to offer a potential for large-scale economical hydrogen production with near-commercial technology. Timpe et al. (1996) (USA) continued studies at the bench and pilot-scale of wood and coal. Catalyst screening shows that potassium-rich minerals and wood-ash provide the best rate enhancement. Conditions of 700-800°C and one atmosphere have produced 50 mole % of the gas as hydrogen. Dolomite and zeolites are effective in downstream cracking of aerosols and tar droplets. Catalysis increases gasification rates 10-fold. Relating catalytic coal or biomass gasification mechanisms to plant capital cost components through bench-scale methodology is further discussed in Hauserman (1997) (USA).

From 1994-1997, researchers at Lawrence Livermore National Laboratory pursued hydrogen production by gasification of municipal solid waste. Two government reports (Pasternak et al., 1994, and Rogers, 1994) (USA) use computer models based on actual Texaco coal plant design to predict economics and design for wastes. This cooperative development by Texaco and Lawrence Livermore National Laboratory explored physical and chemical treatment methods necessary for the Texaco gasifier. Lab focus was on pretreatment of municipal solid waste to prepare a slurry of suitable viscosity and heating value for efficient hydrogen production. Hydrothermal treatment at 300°C and mild dry pyrolysis with subsequent slurrying were considered. Demonstration of the process in the Texaco pilot facility was planned. In Richardson et al. (1995) (USA), initial laboratory-scale municipal solid waste (MSW) treatment results (e.g., viscosity, slurry solids content) over a range of temperatures and for newspaper and plastics are covered. Wallman et al. (1996) (USA) continued development of the Texaco gasification process with emphasis on feed preparation. An MSW hydrothermal treatment pilot plant was modified for batch operation. A slurry shearing pilot plant has been assembled for particle size reduction. Products from a treatment at 275°C were used at Lawrence Livermore National Laboratory for laboratory studies and proved acceptable as slurries. To date, pumpable slurries from an MSW surrogate mixture of treated paper and plastic have shown heating values in the range of 13-15 MJ/kg. Wallman and Thorsness (1997) (USA) extended process considerations to automobile shredder residues and other plastic/rubber wastes. No experimental results were shown for the complete process. The latest report on this approach available to us is Wallman et al. (1998) (USA), which summarizes most of the above work in a refereed journal. For MSW, it is predicted that thermal efficiency to hydrogen is 40-50%.

Pacific Northwest Laboratories studied the gasification of biomass to produce a variety of gaseous fuels by use of appropriate catalysts. An early paper gives bench and pilot-scale results for optimizing either methane or hydrocarbon synthesis gases from wood (Weber et al., 1980) (USA). Much later, Cox et al., 1995 (USA), portray a new approach

to thermochemical gasification of biomass to hydrogen. The process is based on catalytic steam gasification of biomass with concurrent separation of hydrogen in a membrane reactor that employs a permselective membrane to separate the hydrogen as it is produced. The process is particularly well suited for wet biomass and may be conducted at temperatures as low as 300°C. One study was conducted at 4000 psi and 450°C, though most were at 15-30 psi. The process was named SepR<sub>x</sub>. Optimal gasification conditions were found to be about 500°C, atmospheric pressure and a steam/biomass ratio equal to 10/1. In the presence of a nickel catalyst, hydrogen at 65% (volume) was produced under these conditions.

A study of almond shell steam gasification in a fluidized bed revealed that, over the range 500-800°C, smaller particle size yielded more hydrogen than did higher temperatures (Rapagna, 1996) (Italy). In a later report (Rapagna and Foscolo, 1998) (Italy) catalytic steam gasification of biomass was studied in a bench-scale plant containing a fluidized-bed gasifier and a secondary fixed-bed catalytic reactor. The catalytic converter, using different steam reforming nickel catalysts and dolomite, was tested over a range of 660-830°C. Fresh catalyst at the highest temperature yielded 60% by volume of hydrogen.

An assessment of hydrogen production technologies by McKinley et al. (1990) (USA) concludes that biomass gasification is the most economical process for renewable hydrogen production. In 1998, Turn et al. (USA) reported results from their bench-scale fluidized-bed non-catalytic gasifier. For sawdust, the highest yield was obtained at a reactor temperature of 825°C, an equivalence ratio of 0.0 (no added oxygen) and a steam-to-biomass ratio of 1.7. The yield was 78% of theoretical. Most recently Zhou et al. (1999) (USA) assessed the effect of steam addition to a catalytic reformer operating on biomass. It was found that adding steam to a nickel-catalyzed reactor downstream of the biomass gasifier has a greater effect on gas quality than adding steam to the gasifier. A commercial catalyst can be used to crack tar species and upgrade product-gas composition with the addition of steam.

Demirbas et al. (1996) (Turkey) give conversion data for black liquor in a steam gasification approach with and without catalysts. In Demirbas and Caglar (1998), biomass and heavy oil residues are discussed. Demirbas (2001) presents results from pyrolysis of several biomass samples. Pine sawdust is steam reformed in a fluid-bed with and without a Ni-Al<sub>2</sub>O<sub>3</sub> catalyst (Garcia et al. 1996, 1997) (Spain). Walcher et al. (1996) (Germany) describes a plan to provide clean energy for the town of Bad Bruckenau by steam reforming of natural gas and later by biomass. Production of hydrogen and other fuels are forecast. Experiments were conducted with wastes from vine, cotton and tobacco.

Kubiak et al. (1996) (Germany) report on the all-thermal gasification of biomass in a fluidized bed reactor that is activated by steam fed from the bottom. The necessary heat is delivered by a heat exchanger immersed into the fluidized bed. The temperature of the gasification is limited and no slag is formed. Tests with biomass were performed at the laboratory and kg-scale. Data are given for gasification of coke from biomass and lignites.

In a series of proceedings, Bakhshi and associates (1999) (Canada) present results from steam gasification of lignin, biomass chars and Westvaco Kraft Lignin to hydrogen and high and medium Btu gas. Three lignins, Kraft-1, Kraft-2 and Alcell, were gasified at 600-

800°C in a fixed bed with a steam flow rate of 10g/h/g of lignin. Hydrogen contents ranged from 30-50 mol %. (Igbal et al. 1998) (Canada). Srinivas et al. (1998) (Canada) applied the fixed-bed gasifiers to char from the bubbling fluidized-bed pyrolysis of biomass to liquids (70 wt % liquid, 15% char). During zeolite upgrading of the oils, another 10-20 wt % char is formed. These chars were gasified at 800°C producing 85-95% conversion. One char produced a high-hydrocarbon gas while the other produced a gas rich in hydrogen. Following this work, the same techniques and conditions were used on straw, rice straw, Danish wheat straw, pine sawdust, pine softwood, spruce/pine/fur mixtures, thermal, catalysts chars and Kraft-1 lignin from spruce wood. Hydrogen yields at 800°C ranged from 3 to 46.7 mole%. CH<sub>4</sub> ranged from 22 to 49% (Bakhshi et al., 1999). In the latest reports (Chaudhari et al., 2000 and 2001, and Ferdous et al 2001) (Canada) both pyrolysis in He and steam gasification were carried out in a fixed-bed at 650-800°C and with steam-flow ratios of 5, 10 and 15 g steam/g of Westvaco Kraft lignin. As expected, steam gasification yielded more hydrogen than pyrolysis alone (hydrogen ranged from 31-62 mol%) and higher total gas yields. Results for biomass-derived char are reported in Chaudhari et al. (2001) (Canada).

Gallin-Ast (1999) (Germany) has a patent entitled "Method and apparatus for production of hydrogen, particularly high-purity hydrogen, during gasification of biomass." Midilli et al. (2001) (U.K.) are studying the use of an air-blown, downdraft gasifier for hydrogen from hazelnut shells. Naushkin et al. (1988) (Russia) review the feasibility of producing hydrogen from biomass at temperatures of 700-800°C on a (Ni)(Fe)/Al<sub>2</sub>O<sub>3</sub> catalyst. Thermodynamic calculations are given for the process conditions.

Steam gasification was intensely studied by Corella and others at the University of Saragossa from 1984-1992 (Spain). Aznar et al. (1997) (Spain) discuss steam-oxygen gasification of biomass for hydrogen production. Hydrogen vol. % yields as high as 57% were reported using a secondary steam reformer. Results are reported in this paper for three different CO-shift catalysts that increase the hydrogen to 70 vol. %. The Waterloo Fast Pyrolysis Process technology carried out at 700°C is used for the steam gasification of pine sawdust. Using Ni-Al catalyst at a molar ratio of 1:2 showed catalyst reactivation and high steam-to-biomass ratios diminished the rate of deactivation.

Hofbauer (2000) (Austria) is the coordinator of a project to develop a fluidized-bed gasification process for a hydrogen-rich gas from biomass based on a dual bed with a gasification zone and a combustion zone. The aim is to couple these gasifiers with a phosphoric acid fuel cell. Lobachyov and Richter (1998) (USA) discuss integrating a biomass gasifier with a molten fuel cell power system. A study of the gasification of microalgae at 850°C-1000°C is described in Hirano et al. (1998) (Japan). Though the goal was methanol, it is relevant if hydrogen is to be maximized instead of converted with carbon monoxide to methanol. Caglar and Dimirbas (2001) (Turkey) use pyrolysis of tea waste to produce hydrogen while Abedi et al (2001) (USA), are looking at hydrogen and carbon from peanut shells. Finally, Hayashi et al. (1998) (Japan) discuss rapid steam reforming of volatiles from the flash pyrolysis of coal. A review of "tars" from biomass gasification is given in Milne et al (1998) (USA)

- **Direct Solar Gasification**

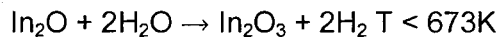
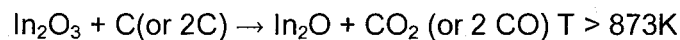
In 1976, Antal et al. (USA) examined the feasibility of using solar process heat for the gasification of organic solid wastes and the production of hydrogen. With a credit for the wastes used, the economic projections were thought to be surprisingly favorable. Epstein and Spiwak (1994) (Israel, Germany) give a detailed review, with many references, of the technology for solar gasification of carbonaceous materials to produce a syngas-quality intermediate for production of hydrogen and other fuels. Shahbazov and Usubov (1996) (Azerbaijan) show good hydrogen yields from agricultural wastes using a parabolic mirror reflector. Thermal decomposition samples were studied by the method of derivative chromatographic analysis. In 1998, Rustamov et al., (Azerbaijan) studied the thermo-catalytic reforming of cellulose and wood pulp using concentrated solar energy. The possibility of obtaining hydrogen and carbon monoxide with temperatures of 700-750°C on a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst is shown.

Midilli et al., (2000) (Turkey) present results of the use of a palladium diaphragm to achieve solar assisted hydrogen separations from the gases generated by pyrolysis of hazelnut shells at 500-700°C. It was concluded that pure hydrogen gas could be efficiently separated at membrane temperatures between 180-250°C. Walcher et al (1996) (Germany) mention a plan to utilize agricultural wastes in a heliothermic gasifier.

- **Miscellaneous Gasification Processes**

Several novel heat sources and chemistries have been explored for hydrogen from organic materials. Safrany (1971) (USA) proposed using a thermonuclear device to vaporize waste organic materials in an underground, large-scale plasma process. He predicted that hydrogen could be produced for considerably less than 1¢/lb. Needless to say, this was never implemented.

In the 80's, two novel processes for hydrogen from carbonaceous materials were presented. Thakur (1980) (India) tested the production of hydrogen by the electrolysis of a mixture of coal, lime and water. The process was thought to hold promise. In 1981, Otsuka and Takizawa (Japan) tested an open-cycle two-step process involving the reduction of In<sub>2</sub>O<sub>3</sub> by carbon (chars) and its reoxidation by water to produce hydrogen:



K<sub>2</sub>CO<sub>3</sub> was a good catalyst. Years later, Otsuka et al. (2001) (Japan) used indium and iron oxide to produce hydrogen from methane without CO<sub>2</sub> emissions. Epple (1996) (Germany) was issued a patent (in German) for the electrolytic hydrogen recovery from biomass using ultrasound

The Hüls plasma-reforming process can be combined with further known process steps for the production of hydrogen. The conditions and advantages are illustrated for coal. Electrical energy is coupled into a gas by means of an electric arc (Kaske et al. 1986) (Germany).

Antal (1974) (USA) proposed a set of biochemical reactions to decompose water into hydrogen and oxygen using nuclear heat and a carbon cycle. Municipal waste was suggested as a possible source of carbon. Algae could be a by-product.

Coughlin and Farooque (1979) (USA) showed that coals and other forms of solid carbonaceous fossil fuels could be oxidized to oxides of carbon at the anode of an electrochemical cell and hydrogen produced at the cathode. Gases produced are discussed as a function of coal slurry concentration and electrode potential.

Sato and White (1980) (USA) shows that, by using a physical mixture of powdered Texas lignite and platinized titania in the presence of water vapor and UV light, a catalytic reaction to produce  $H_2$  and  $CO_2$  at  $23^\circ C$  is achieved. Quantum yields were very low, but improvements were thought to be possible.

Hydrogen production from coal conversion under high-power electric beams has been studied with an 80 kW beam. Product formation rates, energy consumption and energy storage in products were determined. A comparison with traditional coal conversion methods was made (Yermakov et al., 1994) (Russia). Yermakov discussed preliminary results for coal using an electron accelerator as a radiation source (Yermakov et al., 1988) (USSR).

Belghit and El Issami (2001) (Morocco) developed a theoretical model of a chemical moving bed reactor for gasifying coal with steam. The heat is supplied by a high-temperature nuclear reactor.

Cypres (1987) (Belgium) discuss metallurgical processes for hydrogen production from coal and other carbonaceous materials, including coal gasification in a molten iron bath. An argument is made to place such gasifiers in the vicinity of steel manufacturing plants.

- **Biomass-Derived Synthesis Gas (Syngas) Conversion**

Many processes discussed in this report involve the non-storable intermediates CO and  $H_2$ . Examples include the sponge iron process and conversion of syngas, from whatever sources, to  $H_2$ ,  $CH_4$ ,  $CH_3OH$  and hydrocarbon liquids. We list here just a few examples and some general syngas references. The report by G. Mills, though it is aimed at conversion of syngas to liquid energy fuels, should be useful (Mills, 1993) (USA). Another major review of synthesis gas reactions is given in Wender, 1996 (USA). A biological approach to water gas shift to hydrogen is under study at NREL. [See references to Weaver, Maness and Wolfrum in the Biological section.]

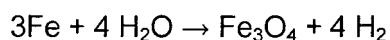
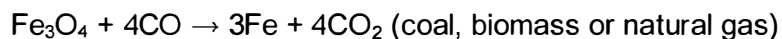
#### Sponge Iron and Related Processes

The steam-iron process is one of the oldest commercial methods for the production of hydrogen from syngas (patents in 1910 and 1913 are referenced). This study explores different types of oxides of iron. Neither chemical composition nor porosity of the ores was found to govern the efficiency. Potassium salts enhanced the activity of both natural and synthetic oxides (Das et al., 1977) (India).

A number of recent studies have looked at the classical steam-iron (sponge-iron) process for upgrading synthesis gas (mainly  $CO + H_2$ ) to pure hydrogen for use in fuel cells and other energy devices.



Friedrich et al. (1995) (Austria and Canada) looked at this purification of nitrogen containing "reduction" gas from a biomass gasifier using wood and wood wastes. The process involves two steps in one: (1) cleaning of gas from solid biomass, coal or methane and (2) energy storage in sponge iron. This study investigates woody biomass and commercially available sponge iron. The reactions are:



This approach is stated to have little risk. In Jannach et al. (1997) (Austria), the sponge iron process is extended to FeO, as well as Fe as the oxidant.

Further discussion of the sponge iron reaction, including thermogravimetric analysis of both the reduction and oxidation step kinetics is given in Hacker et al. (1998a) (Austria). This work is extended as reported in Hacker et al. (1998b) (Austria) with cyclic experiments in a tube-furnace device. A new sponge-iron reactor is being constructed at the Technical University Graz. Fankhauser et al. (1998) (Austria) discuss the first results from the tube reactor and present the schematic of a small-scale laboratory reactor. Reports in 2000 bring current activities up to date. In Hacker et al. (2000), previous studies are reviewed and the simulation of the whole process and design for a 10 MW system is carried out. Small-scale research showed that the sponge-iron approach yields hydrogen sufficiently pure for fuel-cell use ( $\text{CO} < 10$  ppm).

Biollaz et al., (2000) (Switzerland) are also exploring the iron redox process for production of clean hydrogen from biomass. In the first step, iron oxide in the form of  $\text{Fe}_3\text{O}_4$  reacts with the reducing components of wood-gas to produce FeO,  $\text{CO}_2$  and  $\text{H}_2$ . The kinetics of the second step,  $3\text{FeO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{Fe}_3\text{O}_4$ , could be improved by adding other transition metal oxides. They expect that up to 90% of the heating value of the low Btu gas (rice gas) can be transferred to hydrogen if suitable modified oxides can be found. Oxide materials have been tested with gas from a small gasifier. The reduction of iron oxide with biosyngas to sponge iron and later oxidation of the sponge iron with steam offers the potential of shifting and purifying biosyngas and storing and transporting its energy. The sponge iron is steamed to produce clean hydrogen on demand. A thermodynamic computer model is used (Werth and Straus) (1994) (USA). Such analysis was continued in Strauss and Terry (1995) (USA).

In studies from 1982 to 1990, Knippels et al. (1990) (Netherlands) present laboratory and pilot data showing the technical feasibility of hydrogen recovery from biomass gasification lean mixtures (e.g., producer gas). The new method uses metal hydrides (e.g.,  $\text{LaNi}_5$  and  $\text{LaNi}_{4.7}\text{Al}_{0.3}$ ) for continuous hydrogen recovery. In this way, continuous operation is possible and the disadvantages of the classical method that uses packed beds are avoided.

Bijetima and Tarman (1981) describe the steam-iron process for hydrogen production and operating results for a large-scale pilot facility. Economic advantages of the process are presented.

There is great interest in water-gas shift catalysts in the burgeoning field of fuel cells. Just one example is cited in Ruettinger et al. (2001) (USA).

## ***Supercritical Conversion of Biomass***

A number of researchers have investigated the aqueous conversion of whole biomass to hydrogen under low-temperature, but supercritical conditions.

The earliest report on supercritical gasification of wood is that of Modell (1977) (USA). In 1978, a patent was issued (Modell et al., 1978) (USA). He reported the effect of temperature and concentration on the gasification of glucose and maple sawdust in water in the vicinity of its critical state (374°C, 22 MPa). No solid residue or char was produced. Hydrogen gaseous concentrations up to 18% were seen. In later work, gasification and liquefaction of forest products was reported along with work on glucose. Results at critical conditions for glucose, cellulose, hexanoic acid and polyethylene are shown with and without metallic catalysts. In 1985, Modell (USA) gives a review of gasification and liquefaction of forest products in supercritical water.

In 1982, Labrecque et al. (Canada) looked at the pyrolysis of Aspen wood in supercritical methanol, though the emphasis was on maximizing pyrolysis liquids, not hydrogen. Elliott and co-workers (USA), in papers and patents from 1988 to 1997, present an approach to gasifying aqueous carbonaceous materials at conditions approaching the critical state for water (up to 25 MPa and 450°C). A continuous flow reactor process called TEES (Thermochemical Environmental Energy System) is studied for a variety of feedstocks and catalysts. The emphasis is on a high-methane content gas, but the results are relevant to hydrogen as a preferred product (Elliott et al.; 1988, 1990, 1991, 1994 and 1997). A patent was issued for conversion of lignocellulosic materials into a fuel gas (Sealock and Elliott, 1991) (USA). Elliott et al. (1997) (USA) patented a method for the catalytic conversion of organic materials into a product gas. The process involves a high-pressure reaction of water and liquid organic material in the presence of a reduced metal catalyst selected from the group consisting of ruthenium, rhodium, osmium, iridium or mixtures thereof. Reactor conditions from about 300-450°C and, at least, 130 atm pressure are covered.

The first report of Antal's (USA) extensive work on supercritical conversion of biomass-related organics is in Manarungson et al., 1990 (USA), where glucose at 550°C and 5,000 psig was converted largely to H<sub>2</sub> and CO<sub>2</sub>. Mok and Antal (1992) (USA) followed with a study of the uncatalyzed solvolysis of whole biomass and hemicellulose in hot, compressed liquid water. First studies show that complete gasification of glucose can occur at 600°C, 34.5 MPa and a 30-second residence time. Inconel strongly catalyzes the water-gas shift reaction (Yu et al., 1993) (USA). Following this work, a flow reactor was used with newly discovered carbon-based catalysts to convert water hyacinth, algae, pithed bagasse liquid extract, glycerol, cellobiose, whole biomass feedstocks and sewage sludge to hydrogen. Spruce wood charcoal, macadamia shell charcoal, coal activated carbon and coconut carbon serve as effective catalysts. Temperatures above about 600°C and pressure above about 25 MPa are adequate for high gasification efficiencies. Thermodynamic calculations predict low carbon monoxide formation (Antal et al., 1994a; Antal et al., 1994b; Antal et al., 1995; Xu et al., 1996); Nuessle et al., 1996) (USA). Also in 1996 (Antal et al., 1996) (USA), the research team developed a method to extend the catalyst life; began studies of the water-gas shift reaction; completed studies of CO<sub>2</sub> absorption in high-pressure water; measured the rate of carbon catalyst gasification in supercritical water; and measured the pumpability of oil-biomass slurries.

In Antal and Xu (1997) (USA) it was shown that wood sawdust, dry sewage sludge or other particulate biomass could be mixed with a cornstarch gel to form a viscous paste. This paste

can be delivered to a supercritical flow reactor with a cement pump. Ongoing work indicates that the starch can be reduced to 3 wt % and the particulate biomass increased to 10 wt %. At the critical pressure of water (22 MPa) the paste vaporizes without the formation of char. A packed bed of carbon catalyst, at 650°C, causes the tarry vapors to react with water to produce hydrogen, carbon dioxide, some methane and only a trace of carbon monoxide. In the same year, Antal and associates (Matsumara et al., 1997a) (Japan) (USA) demonstrated the use of high-pressure water to separate H<sub>2</sub> from CO<sub>2</sub>. A hydrogen purity of 90% has been achieved. Matsumura et al. (1997b) (Japan, USA) has published a review of the University of Hawaii work on glucose conversion in supercritical water. In 1997, Matsumara et al. (1997c)(Japan, USA) studied the gasification of an activated carbon in supercritical water. Matsumara (2000) (Japan) discusses gasification of liquified biomass in supercritical water using partial oxidation.

Two reports in 1998 (Antal and Xu and Xu and Antal) (USA) present data on the starch-biomass paste approach to water gasification under supercritical conditions. Sewage sludge turns out to be a very problematic feed and is difficult to gasify. In contrast, the waste product from the commercial production of bio-diesel appears to be a perfect feedstock. Gas composition from poplar wood, cornstarch, glycerol, and glycerol/methanol experiments are shown. Antal et al. (1999) (USA) report further results with pastes of potato wastes, wood sawdust and various starch gels. Finally, in Antal et al. (2000) (USA), much of the above work is summarized and reactive plugging and reactor materials corrosion is discussed. Nickel-alloy tubes are not suitable. Reactor walls are required that do not suffer corrosion and do not catalyze the reactions of interest. The Hydrogen Program plan (2000) (USA) continues work by Combustion Systems, Inc., to develop the engineering tools necessary to bring the supercritical water pyrolysis process to commercial status. One task is to develop slurry pumps that will handle 20 wt % biomass. The other is to develop a new reactor design that substantially increases the heating rate of the wood paste.

Work by Combustion Systems, Inc., (Divilio, 1998, and Divilio, 1999) (USA) is given in some detail in the annual DOE Hydrogen Program review meetings. In 1998, it was reported that a heat transfer model has been developed to predict temperature profiles inside the University of Hawaii's supercritical water reactor. Heat transfer tests were conducted on the Hawaii apparatus to calibrate the model. A literature review is presented for pyrolysis of biomass in water at temperatures up to the supercritical range. Equilibrium calculations also were performed. Data from the reactor fell both below and above predictions depending on test conditions. Fast heating rates may be beneficial to the hydrogen yield. In the 1999 work, a high-pressure gas cleanup process and a model were developed to predict the formation of char at the entrance to the reactor. Fast heating rates decreased the amount of char predicted by the model. A mass transfer model was developed for the water-gas shift reaction. Finally, a global model for the supercritical water pyrolysis process was developed and the model was calibrated using the glucose pyrolysis data from the studies by Holgate et al. (1995).

Minowa, Yokoyama and Ogi (Japan) have carried out studies on the high-pressure steam gasification of cellulose and lignocellulose materials using a reduced metal catalyst. At a temperature of 200-374°C and pressure of 17 MPa, hydrogen was formed that, under many conditions, was converted to methane. Methane formation was prevented at subcritical conditions (Minowa et al. 1995a; Minowa et al., 1997; Minowa and Fang, 1998; Minowa and Ogi, 1998; Minowa and Inoue, 1999). Patents related to hydrogen by this means are held by Yokoyama et al., (1997a and 1997b) (Japan). The most recent report on biomass to hydrogen under the above conditions is in Minowa and Fang (2000). The reaction mechanism is discussed, based on the products other than hydrogen. (In 1994 and 1995b, Minowa et al. looked at methane production from cellulose.) Most recently, Minowa (2000) has presented

reaction mechanisms of the low temperature catalytic gasification reported by Elliott et al. in 1990 (USA).

A supercritical process to produce hydrogen while absorbing CO<sub>2</sub> in CaO is described in four recent publications and a patent. The process goes by the name Hy Py-RING (Hatano et al., 1999) (Japan). A thermodynamic analysis is presented for coal under conditions such as 20 MPa and 1000°K. Experiments show the process can be used with heavy oil, biomass and plastics (Lin et al., 1999a, and Lin et al., 1999b) (Japan). The process is also reviewed in Lin (2000) and a patent was issued (Lin et al., 2000 a,b).

A basic study of the decomposition behavior of the main components of wood is given in Ando et al., (2000) (Japan). Bamboo, chinquapin (hardwood) and Japan cedar (softwood) were examined in a hot-compressed-water flow reactor at 9.8 MPa and stepped temperatures from 180°C to 285°C. Other recent publications discuss supercritical treatment of whole biomass. Boukis et al., (2000) (Germany) present behavior of biomass and organic wastes at 30 MPa and 600°C. At these operating conditions, water exhibits properties of a dense gas, including high solubility of organic substances and gases like oxygen. The two major problems are plugging of the reactor with precipitated salts and, in some cases, corrosion. The process can be tuned to produce methane or hydrogen.

Supercritical water gasification of biomass/coal slurries, as well as composted municipal refuse, sewage sludge, crumb rubber and pulp and paper wastes, is carried out in HRSG tubes at up to 25% solids (Tolman, et al, 2000) (USA). Pilot-scale data on sewage sludge have been obtained by General Atomics (1997) (USA). A feasibility study was followed by tests of sewage sludge feed preparation, pumping and gasification in a pilot plant facility. This helped define a base-line complete system. Technical and business plans were developed resulting in a 3-year plan culminating in a follow-on demonstration test of a 5 GT/day system at a local wastewater treatment plant.

General Atomics (2001; Spritzer, et al, 2001; Johanson, et al, 2001) (USA) is studying supercritical water partial oxidation of biomass for hydrogen. Bench-scale tests are planned as is pilot-scale design and analysis. Collaborators are Environmental Energy Systems, Inc., and Combustion Systems, Inc.

Penninger (1999) (Netherlands) has carried out a feasibility study of wet biomass conversion in supercritical water ( $T > 374^{\circ}\text{C}$  and  $P > 22$  MPa). A survey shows that biomass is abundantly produced throughout the EU countries, and could replace as much as 10% of the natural gas use. Kruse et al. (2000) (Germany) studied the gasification of pyrocatachol in supercritical water as part of a fundamental look at hydrogen production from high moisture biomass and wastewater. Batch and tubular reactors were used.

A pilot-scale apparatus for continuous supercritical and near-critical reaction of cellulose at temperatures up to 600°C, pressures up to 40 MPa and residence times of 24s to 15 min, was used. A three-step pathway for cellulose hydrolysis was proposed (Lu et al., 2000) (Japan).

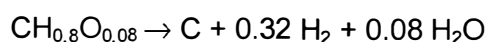
In assessing the supercritical approach for hydrogen from biomass and waste, two fundamental reviews can be consulted. Savage et al. (1995) (USA) notes that such conditions may be advantageous for reactions involved in fuels processing and biomass conversion. (Some 180 references are included). A more recent review of organic chemical reactions in supercritical water is also given by Savage (1999) (USA). A soon-to-appear review of organic compound reactivity in superheated water is given in Siskin and Katritzky (2001). Finally, projects

underway in the Netherlands are shown in van de Beld (2001) (Netherlands) [Contact van de Beld at [vandeBeld@btg.ct.utwente.nl](mailto:vandeBeld@btg.ct.utwente.nl)]

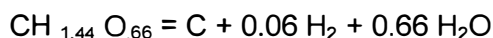
### ***Pyrolysis to Hydrogen and Carbon or Methanol***

Steinberg and associates at Brookhaven National Laboratory have long considered processes based on high-temperature pyrolytic conversion of coal, biomass and other carbonaceous materials to hydrogen, carbon, methanol and light hydrocarbons.

In the 'Hydrocarb' process, Steinberg (1987a, 1989) (USA) describes a two-step process involving (1) the hydrogenation of carbonaceous materials like coal and biomass to methane, followed by (2) thermal decomposition of the methane to hydrogen and a clean carbon-black fuel. For coal, a typical overall reaction would be:

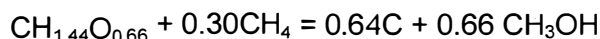


For biomass, the 2-step reaction is:



Preliminary pyrolysis experiments related to the Hydrocarb reactions are discussed in Steinberg et al. (1986), Steinberg (1986), and Steinberg (1987b).

In later work, Steinberg (1990) (USA) describes a process in which biomass and methane are converted to methanol plus carbon (Carnol). The overall stoichiometry is:



As the names imply, Hydrocarb and Carnol processes emphasize the minimization of CO<sub>2</sub> and the production of elemental carbon.

In 1994, Dong and Steinberg (USA) introduced the biomass conversion process they called 'Hynol'. Its aim is to produce economical methanol with reduced CO<sub>2</sub> emissions. Three process steps are involved:

1. Hydrogasification of biomass;
2. Steam reforming of the produced gas with additional natural gas feedstock; and
3. Methanol synthesis from the hydrogen and carbon monoxide produced.

The process is proposed for any condensed carbonaceous material, including municipal solid waste and coal. The process is further elaborated, including techno-economic analysis, but no experimental data, in Borgwardt (1995) (USA), Steinberg and Dong (1996) (USA), Steinberg (1997) (USA), Dong and Steinberg (1997) (USA) Dong and Borgwardt (1998) (USA) and Sethi et al. (1999) (USA).

### ***Biological Conversion of Biomass to Hydrogen***

The emphasis of this report is on thermo-chemical conversion of whole biomass and stable products presently formed from biomass. A separate IEA activity, IEA Hydrogen Agreement Task 15, is addressing the photobiological production of hydrogen (see Zaborsky, 1998); thus, the subject is not included here.

There are several interfaces with the main scope of this review that use non-photobiological processes. The best knowns are the anaerobic digestion routes from biomass to methane and the fermentation routes to ethanol. No attempt to cite this literature is made. Another biological step that interfaces with thermo-chemical conversion (gasification) is the use of biological organisms for the water-gas shift for  $\text{CO} + \text{H}_2$  from  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . References to this approach follow, as well as a sampling of non-photo biological research involving biomass.

## **PRODUCTION OF STORABLE INTERMEDIATES FROM BIOMASS PARTIAL CONVERSION**

### ***Hydrogen from Biomass-Derived Pyrolysis Oils***

Laboratory work using this approach has been conducted at NREL (USA), starting in 1993 (see Chornet et al., 1994; Wang et al., 1994; Wang et al., 1995; Chornet et al., 1995; and Chornet et al., 1996 a, b, c). Early papers present the concept of fast pyrolysis for converting biomass and wastes to oxygenated oils. These oils are subsequently cracked and steam-reformed to yield hydrogen and CO as final products (Mann et al., 1994). The 1995 Wang report presents the chemical and thermodynamic basis of this approach, the catalysis related to steam reforming of the oxygenates, and the techno-economic integration of the process. In first experiments, Ni-based catalysts were favorable (80% of theoretical maximum hydrogen yield has been obtained), but enough CO remained to require the addition of a water-gas shift step. Low biomass costs are needed to produce hydrogen economically since feedstock cost is a major component of production cost. In Wang et al. (1995) laboratory and bench-scale studies of model compounds of oxygenates known to be present in pyrolysis oil were presented. Ni-based catalysts were used in microscale laboratory tests to identify the conversion products. All model compounds were successfully steam reformed. Bench-scale, fixed-bed tubular reactor experiments indicate that control of coke formation was a key aspect of the process. Loss of activity of the nickel catalysts after a few hours forced periodic regeneration. It was shown that  $\text{CO}_2$  from a pressure swing absorption step effectively removed the coke.

Six progress reports in 1996 and 1997 document the systematic exploration of the pyrolysis oil-to-hydrogen process. In Chornet et al. (1996a) bench-scale experiments determined the performance of nickel-catalysts in steam reforming of acetic acid, hydroxyacetaldehyde, furfural, and syringol. All proceeded rapidly. Time-on-stream experiments were started. In Chornet et al., (1996b), Czernik et al., (1996), and Wang et al. (1997a), the approach of using extractable, valuable co-products with the balance of the oil converted to hydrogen is explored. Depending on biomass feedstock costs, the selling price for steam reforming hydrogen is predicted to fall within the then current market price of hydrogen (\$5-\$15/GJ). One of the most promising co-products from whole bio-oil is an adhesive. In Chornet et al., (1996c) economics and plant design are summarized.

The initial refereed journal reports of the above work are in Wang et al. (1996), and Wang et al. (1997b). The first paper documents the catalytic steam reforming results for acetic acid and hydroxyacetaldehyde using a micro-reactor and molecular-beam mass spectrometry. The second paper consolidates the early work on model compounds, nickel-catalysts and reforming of both whole bio-oils and oils after extraction of valuable chemicals. Economics, process designs and thermodynamics are discussed.

In 1998, the NREL group published data on bench-scale reforming results from model compounds, the aqueous-fraction of poplar pyrolysis oil and whole pyrolysis oil with commercial nickel-based steam reforming catalysts. Hydrogen yields as high as 85% were obtained

(Czernik et al., 1998) (Wang et al., 1998). A 2-inch diameter fluidized-bed reformer is described in the Czernik report.

Work on this long-range project continued in 1999 and was reported in three publications. Czernik et al. (1999 a and b) give steam reforming results of the aqueous fraction of bio-oil. The non-volatile compounds, such as sugars and lignin-derived oligomers, tend to decompose thermally and to form carbonaceous deposits on the catalyst surface and in the reactor freeboard. To minimize these, a fluidized-bed reformer with fine-mist feed injection was used and gave hydrogen yields of 80% of stoichiometric. 90% of the feed carbon was converted to CO and CO<sub>2</sub>, but carbon deposited on the catalyst gradually decreased its activity. The catalyst was easily regenerated by steam or CO<sub>2</sub> gasification of the deposits. At 850°C, with a steam-carbon ratio of 9, the hydrogen yield was 90% of stoichiometric during 8 hours of on-stream reforming of the aqueous fraction of bio-oil. Hydrogen yield from a hemicellulose fraction was about 70% of stoichiometric, due to the higher content of oligomeric material.

Steam reforming of model compounds of fast pyrolysis oil and of sunflower oil, is discussed in Marquevich et al. (1999), (2001) (Spain, USA; Canada). Acetic acid, m-cresol, dibenzyl ether, glucose, xylose and sucrose were steam reformed with two commercial nickel-based catalysts used for naphtha steam reforming. The sugars were difficult to reform because they readily decomposed via pyrolysis in the freeboard.

The latest publications are a reprise of the fluid-bed studies of the carbohydrate fraction of pyrolysis oil (Czernik et al., 2000 a,b) and a study of the hydrogen yield from "crude glycerin." It was also suggested that residual fractions derived from pulping operations and from ethanol production could be attractive feeds (Czernik et al., 2000c).

The final studies reported in 2000 are a look at the effects of catalyst composition on steam reforming of bio-oils (Garcia et al., 2000 a,b) (Spain, USA) and an overview of the method (Feik et al., 2000) (USA). Aqueous fractions of bio-oil were steam-reformed at 825° and 875°C, high space velocity (up to 126,000 h<sup>-1</sup>) and low residence time (26 ms.), using a fixed-bed micro-reactor interfaced with a molecular-beam mass spectrometer. A variety of research and commercial catalysts were tested. Since the main constraint in reforming bio-oils is catalyst deactivation caused by carbon deposition, two approaches were tested: 1) enhanced steam adsorption to facilitate coke gasification and 2) to slow down the surface reactions that led to coke precursors. Commercial catalysts that were developed for steam reforming of natural gas and crude oil fractions proved to be more efficient for bio-oil than most of the research catalysts, mainly due to higher water-gas-shift activity.

Evans et al (2001) (USA) describes scale-up work planned using peanut shells as feed. Information on Operating Plans for 2000 and 2001 are given in *Hydrogen Program 2000, 2001* and in Yeboah et al. (2000 & 2001) (USA) and in Abedi et al. (2001) (USA). Lathouwers and Bellan (2001) (USA) update their extensive work on modeling biomass pyrolysis. Chornet (2001) contains his group's latest work on oils to hydrogen. French et al. (2001) (USA) looked at co-reforming of pyrolysis oils and natural gas while Czernik et al. (2001) (USA) extended the approach to "trap grease."

### ***Hydrogen from Biomass-Derived Methanol***

Steam reforming of methanol and ethanol with catalysts has a long history. For example, the mechanism of methanol over Cu-Si catalysts to hydrogen is discussed in Takahashi et al. (1982) (Japan) who references work back to 1971. In 1989, Seifritz makes the case for

converting fossil fuels to methanol as a logistically ideal energy carrier for transoceanic transportation, with concentrated CO<sub>2</sub> for easier disposal. The methanol can be converted to hydrogen for decentralized applications. Jiang et al. (1993) (Australia) continues mechanistic studies using Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> catalysts.

There has been recent and continuing interest in the conversion of methanol to hydrogen with a dominant interest in methanol use in fuel cells. Cheng (1996) (Taiwan) addressed the development of active and stable catalysts for this purpose. The Cu-ZnO-based methanol synthesis catalysts behaved poorly for the decomposition reaction. Highly active copper-containing catalysts, comprising Cu, Si, O and Ba or Mn, were developed. Copper is the active species. Adding CO<sub>2</sub> to the methanol feed greatly increases the catalyst stability. Decomposed methanol, using exhaust heat for the endothermic dissociation, could be up to 60% more efficient than gasoline and up to 34% better than methanol. Results for nine copper-containing catalysts, operating at 250°C, show the best (Cu, Cr, Mn, Si) to achieve 60-92% conversion. Amphlett et al. (1994, 1995) (Canada) have developed a semi-empirical model of the kinetics of the catalytic steam reforming of methanol over CuO/ZnO/Al<sub>2</sub>O<sub>3</sub>. The end use is hydrogen in a polymer electrolyte membrane fuel cell. The problem of carbon monoxide removal is most significant. The 1995 paper presents some of their experience with deactivation over time and temperatures as high as 300°C.

The use of zeolites as catalysts for hydrogen generation and hydrogen storage has received only limited attention. (Laniecki, M. and Kazmierczak-Rozik, K.1998) (Poland). In this study, narrow pore (A, ZSM-5), medium pore (mordenite) and large pore (X,Y) zeolites were applied to steam reforming of methanol. Conversion results with time are shown for five types of zeolites with Cu, Ni and Cr ion exchanged and Y zeolites consisting of nickel and cobalt solid-state exchanged catalysts. The results presented show that zeolites can be applied in steam reforming, but further investigations were stated to be needed.

Lelewer (1999) (USA) gives an overview of the options for conversion of landfill gas, methanol or natural gas to hydrogen for a hydrogen refueling station. They propose to use the "innovative" UOB™ process, which utilizes Hydrogen Burner Technology's system for landfill gas, methanol and/or natural gas (UOB™ uses a non-catalytic partial oxidation reformer.) Antonyak et al. (2000) (Russia) studied methanol decomposition in a water-methanol equimolar mixture in the presence of a nickel-promoted, copper-zinc-cement catalyst. The catalyst was highly active at 200-300°C.

Other recent reports are by Yalin et al. (2000) (China) and Yang et al. (2000) (China). The Yalin paper presents results for a "99.999% hydrogen by methanol pyrolysis-PSA technique." A catalyst named ALC-AIA, based on a copper-based methanol synthesis catalyst, it tested as a function of temperature and pressure. Yang et al. report on a novel palladium catalyst for methanol decomposition. Qi et al. (2000) (China) identify key factors in hydrogen generation from methanol by partial oxidation. The mole ration of O<sub>2</sub>/CH<sub>3</sub>OH is the most sensitive factor; the ratio of H<sub>2</sub>O/CH<sub>3</sub>OH is the second; the third is the pressure. Newson et al. (2000) (Switzerland) give catalyst screening results for partial oxidation methanol reforming with copper-containing catalysts. A system analysis predicts a "well-to-wheel" efficiency of 24% for methanol-to-hydrogen with a PEM fuel cell, compared to 18% for a gasoline internal combustion engine. Methanol from biomass is mentioned for a sustainable source.

Innovatek is combining microtechnology with advanced catalysts and separation technology for clean hydrogen from methanol for use in a PEM fuel cell (Irving et al., 2000 and Hydrogen Program, 2000) (USA). The reformer can be used to convert methane or methanol produced



through the thermochemical processing of biomass. Advanced membrane separation technology will be tested and the system evaluated. Work continues apace on methanol reforming for fuel cell use. Fuel cells manufactured by H Power Enterprises Canada, Inc. require a suitable hydrogen source. This paper gives experimental data for the Northwest Power Systems reformer, which yielded hydrogen with less than 5 ppm CO (Bateman et al., 1999) (Canada and USA).

DeWild and Verhaak (2000) (Netherlands) report on results for metal-supported catalyst systems for steam reforming of methanol for fuel cell application. Such catalysts overcome the slow heat transfer of packed-bed systems by integrating endothermic steam reforming with exothermic hydrogen combustion. A wash-coated aluminum heat exchanger showed the best performance using a suspension of commercial reforming catalysts. By proper temperature control, 450 hours of continuous operation have been achieved from an aluminum foam with greater than 90% methanol conversion.

A recent paper by Andrian and Mensinger (2000) (Germany) presents an analysis of a direct, liquid-feed, methanol fuel system for solid polymer electrolyte fuel cells. Advantages over a steam-reforming-to-hydrogen fuel-cell system are cited such as the avoidance of complex fuel processing and gas treatment in the indirect (hydrogen) methanol fuel cell systems. Murcia-Mascaros et al. (2001) (Spain, Italy), look at an oxidative methanol reformer on CuZnAl catalysts. Agrell et al. (2001) (Sweden) find the microemulsion catalysts are better than conventional co-precipitation catalysts. Lindstrom and Petterson (2001) (Sweden) are studying methanol reforming over copper-based catalysts for fuel-cell applications. Work in methanol to hydrogen should accelerate with the growing interest in fuel cells for vehicles. Mizsey et al. (2001) (Switzerland) and Avci et al (2001) (Turkey, Australia) are looking at on-board conversion of methane, propane, octane and methanol for fuel cells. [See also Moon et al (2001) (South Korea) and Trimm and Onsan (2001) (Australia, Turkey).]

### ***Hydrogen from Biomass-Derived Ethanol***

Ethanol, likely produced from lignocellulosics in the future, has been considered by researchers in a number of countries for hydrogen production. The advantages of both methanol and ethanol in ease of steam reforming to hydrogen, vis-à-vis methane, are stressed, as is the storage aspect of liquids for vehicle and fuel cell application. Ethanol's lack of toxicity compared to methanol is also mentioned.

Garcia and Laborde (1991) (Argentina) examined the thermodynamic equilibrium in the steam reforming of ethanol to produce hydrogen, pointing out that the literature on ethanol reforming was scarce. The calculations cover pressures of 1-9 atm, temperatures of 400-800K and water-to-ethanol feed ranges of 0.1 to 10.0. The best conditions for hydrogen production are at  $T > 650\text{K}$ , atmospheric pressure and water in excess in the feed. In this condition,  $\text{CH}_4$  is minimized and carbon formation is thermodynamically inhibited. Higher temperatures and higher water-to-ethanol ratios (2.0) are needed, compared to methanol, for best hydrogen production. A catalyst must be found to achieve adequate production and selectivity. Some five years after the Garcia and Laborde study, Vasudeva et al. (1996) (India) carried out another equilibrium study of ethanol steam reforming under conditions conducive to carbon formation. Equilibrium hydrogen yields as high as 5.5 moles per mole of ethanol in the feed are attainable. The approach adopted permits estimation of the carbon formed. The results differ from Garcia and Laborde under conditions conducive to carbon formation. Most recently, a third thermodynamic analysis of ethanol steam reforming has appeared (Fishtik et al., 2000) (USA, Romania). In this approach, the reforming is considered in terms of "response reaction (RERs)" that have the

property of being independent of the usually arbitrary initial choice of a set of independent reactions. A simple algorithm is proposed for deriving a unique set of RERs to rationalize the effect of process variables on the steam reforming of ethanol to produce hydrogen. At, or above, 700-800K and with high water-ethanol ratios, the desired reaction of ethanol to hydrogen can be made predominant. In the latest of such thermodynamic analyses, Ioannides (2001) (Greece) gives a thermodynamic analysis of hydrogen from ethanol with respect to solid-polymer-fuel-cell applications. Both steam reforming and partial oxidation reactors connected to water-gas-shift and CO-oxidation reactors were considered to assess the effect of operating parameters on hydrogen yields.

Besides these thermodynamics studies, a number of experimental catalytic studies have been reported from researchers around the world. (Argentina, Switzerland, India, Italy, Sweden, Greece, and Germany). Luengo et al. (1992) (Argentina) used nickel-copper-chromium on  $\alpha$ - $\text{Al}_2\text{O}_3$  in a fixed-bed reactor to steam reform ethanol. Operating temperatures ranged from 573-823K, steam-ethanol mole ratios varied from 0.4-2.0 and space velocities from  $2.5\text{-}15\text{h}^{-1}$ . The catalyst showed high activity for ethanol gasification. Comparison with thermodynamic predictions showed that catalyst activity is more pronounced at lower temperature. The 4.0% Ni/O, 79% Cu/O and 25% Cr, supported on  $\alpha$ - $\text{Al}_2\text{O}_3$ , is both active and selective for ethanol. Studies are planned at higher metallic concentrations. In later work, Marino et al. (1998, 2001) (Argentina) looked at the effect of copper loading and calcination temperature on the structure and performance of Cu/Ni/K<sub>y</sub>- $\text{Al}_2\text{O}_3$  catalysts.

Highfield et al. (1994) (Switzerland) present a scheme for hydrogen energy storage in the form of biomass-derived alcohols in which the hydrogen release step is by steam reforming. Promising catalysts consist of Cu, Co and Ni, acting on basic, high-area supports like magnesium oxide. Preparation, characterization and testing are described. Acetic acid, originating from acetaldehyde disproportionation, is identified as a key intermediate. Beneficial effects of promotion with alkali-metal ions on coking control and selection are reported. Future studies will investigate the reverse reaction to form ethanol.

Ethanol steam reforming in the context of a molten carbonate fuel cell is studied kinetically with a CuO/ZnO/ $\text{Al}_2\text{O}_3$  catalyst, (Cavallaro and Freni, 1996, 1998) (Italy). The process appears feasible between temperatures of 800 and 1000K and pressure up to 100 bars, based on predictions from a kinetic model. At temperatures above 630°K, equilibrium is approached for CaO/ZnO/ $\text{Al}_2\text{O}_3$  and NiO/CuO/ $\text{SiO}_2$  catalysts and no appreciable quantities of coke or unexpected oxygenates are formed even with  $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$  lower than 3 mol/mol. In later work (Cavallaro, 2000) (Italy), ethanol steam reforming on Rh/ $\text{Al}_2\text{O}_3$  catalysts was explored.  $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$  ratios of 8.4 mol/mol were used to simulate the composition of the ecological fuel product from vegetable biomass fermentation. Studies were from 323-923K. (The molten carbonate fuel cell standard temperature is 923°K.) The acid support ( $\text{Al}_2\text{O}_3$ ) promotes the dehydration of the alcohol while all other reactions are catalyzed by the rhodium. At 923K, coking does not occur and the catalyst maintains its activity for several hours.

A program to use stored crops grown on fallow land in the European Community and to convert them to ethanol by fermentation is reported by Rampe et al. (2000, 2001) (Germany). The aim is to reform the ethanol to hydrogen for use in polymer electrolyte fuel cells (PEFC). A catalyst screening program is under way together with the planned use of pressure swing absorption to lower the CO to a tolerable level of 20 ppm. The operation pressure for the reforming is varied from 2-9 bar, the temperature from 600 to 800°C and the steam-to-carbon ratio between 2-4 moles carbon to moles water. A minimum pressure of 6 bar is needed for the absorption step,

giving an advantage to a liquid feed like ethanol, compared to gaseous fuels, in the energy required for the pressurization step.

Toci and Modica (1996) (Italy and Sweden) describe an innovative process for hydrogen production by “plasma reaction cracking” of vaporized ethanol solutions in the presence of a nickel-based catalyst. The approach is the “cold-plasma-chemical-processing” developed at Stuttgart University. Results on the separation and purification of the hydrogen as well as project scale up are presented. A process for the production of hydrogen and electrical energy from reforming of bio-ethanol is described by Verykios in International patent C01B 3/32, H01M 8/06 (1998) (Greece). Partial oxidation reforming of ethanol produces hydrogen that is fed to a fuel cell. The ethanol is in an aqueous solution of 40-70% ethanol originating from fermentation of biomass. Moles of oxygen to moles of ethanol are between 0 and 0.5. The mixture is fed to a reactor with a suitable catalyst-containing metal of the Group VII or metal oxides of the transition metals.

Amphlett et al. (1999) (Canada) present a comparative evaluation of ethanol versus methanol for catalytic steam reforming to hydrogen for fuel cells. Galvita et al. (2001) (Russia, Greece) discuss synthesis gas production from steam reforming ethanol.

### ***Methane and Natural Gas to Hydrogen or Methanol by Direct Thermolysis***

No attempt is made to cover the old and extensive literature involving steam reforming of natural gas and other gaseous and liquid fossil fuels. Recent examples are cited that involve renewable feedstocks (e.g., methane from anaerobic digestion), natural gas for fuel cells or an attempt to minimize greenhouse gases (mainly CO<sub>2</sub>).

- **Methane Pyrolysis to Hydrogen and Carbon**

Fulcheri and Schwab (1995) (France) present, from simple hypotheses and physical considerations related to existing processes, a theoretical study whose conclusions could open the way to a new carbon black plasma-assisted process. Cracking methane, with no oxygen, into carbon and hydrogen has the potential to be no more energy intensive than existing processes. Such thermolysis needs a very high temperature reaction, which is now accessible through improvements in plasma technology. The process for hydrogen may be favorable for carbon-black production.

A continuing series of studies by Muradov (1993-2000) (USA) at the Florida Solar Energy Center (2001) rests on the premise of producing hydrogen from hydrocarbons without CO<sub>2</sub> production. The capture of CO<sub>2</sub> from the steam reforming process and its sequestration (underground or ocean disposal) is actively discussed in the literature. It is noted that this method is energy intensive and poses uncertain ecological consequences. His approach is to thermo-catalytically decompose the hydrocarbon to hydrogen and carbon over metal-oxide and carbon-based catalysts. This work is planned to continue (Hydrogen Program, 2001) (Muradov, 2001a,b,c.).

A surprising number of studies of hydrocarbons to H<sub>2</sub> and C are reported around the world. Czernichowski et al. (1996) (France) show results for hydrogen and acetylene (not carbon) using the so-called Gliding Arc, a relatively cold, powerful electrical discharge in a non-equilibrium state. Up to 34% of natural gas has been converted to hydrogen and assorted hydrocarbons. Kuvshinov et al. (1996) (Russia) have applied low-temperature catalytic pyrolysis of hydrocarbons to produce a new graphite-like porous material and

hydrogen. Results are shown for methane decomposition on Ni-containing catalysts. Babaritskiy et al. (1998) (Russia) use their version of plasma catalysis to produce carbon and hydrogen from methane. The plasma accelerates the process due to specific influence of the plasma-active particles (ions, radicals), making temperatures as low as 500°C effective. The pre-heated methane (400-600° C) at atmospheric pressure enters a plasmatron in which the gas is exposed to a pulse-periodic microwave discharge. Methane conversions up to about 30% are shown at temperatures from 250-600°C.

In four more studies from Russia, natural gas thermal decomposition is studied using a hot matrix in a regenerative gas heater. Concerns arise due to ecological issues and low efficiency. Special conditions that could prevent pyrocarbon in the zone of the reaction need to be developed. The goal was to produce hydrogen plus carbon black (Popov et al. 1999a) (Russia). In a companion paper (Popov et al., 1999b) conditions are shown that produce carbon in methane almost completely as black carbon without pyrocarbons being produced. Finally, Shpilrain et al. (1998 and 1999) (Russia) show results from a comparative analysis of different methods of natural gas pyrolysis.

Hydrogen from natural gas without release of CO<sub>2</sub> is the subject of a systems and economic comparison by Gaudernack and Lynum (1996 and 1998) (Norway). The two main options for this are: (1) conventional technology (e.g., steam reforming) with CO<sub>2</sub> sequestration and (2) high-temperature pyrolysis yielding pure hydrogen and carbon black. Technologies for industrial-scale realization of these options have been developed and tested in Norway, but could not yet compete using costs of methane from renewables. Lynum et al. (1998) (Norway) discuss two processes developed by Kvaerner Oil and Gas A.S. One, called the Kvaerner CB&H process, decomposes a wide spectrum of hydrocarbons into carbon black and hydrogen by use of a high-temperature plasma process. The energy for decomposition of hydrocarbons comes from a plasma generator that converts electric power to heat. A pilot plant, situated in Sweden, has been operated since 1992. The PyroArc process utilizes waste and hydrocarbons as feedstock. The process is a two-stage gasification and decomposition process that converts feedstock into pure fuel gas, steam, slag and metals. The fuel-gas, which consists of H<sub>2</sub> and CO, can be separated for hydrogen use. The PyroArc pilot plant is also cited in Sweden and has been operating since 1993. Steinberg and associates have applied their processes for direct biomass conversion to hydrogen and carbon (Hydrocarb) to hydrogen and methanol (Hynol), and to conversion of methane to carbon and methanol (Carnol). Studies of methane in a tube reactor are given in Steinberg (1996a) (USA). Designs and economics plus advanced Carnol processes are given in Steinberg (1996b). A patent was issued for the process in 1998 (Steinberg and Dong). An overview is published in Steinberg (1999a). Finally, Steinberg (1999b, 1998) argues for thermal decomposition or pyrolysis of methane or natural gas (TDM) to hydrogen and carbon. The energy sequestered in the carbon, if buried, amounts to 42% of that of the natural gas. He notes that it is much easier to sequester carbon than CO<sub>2</sub>.

Li et al., (2000) (China) discuss the simultaneous production of hydrogen and nanocarbon from the decomposition of methane without carbon oxide formation. Catalysts based on nanometer-scale nickel particles prepared from a hydrocalcite-like anionic clay precursor have been designed and tested. The process is best at temperatures above 1073K. Copper-doping raises the nickel catalyst activity above 923K — the maximum activity temperature for the pure nickel. Takenaka et al (2001) (Japan) looked at methane decomposition over nickel catalysts and the effect of supports on lifetime. See Otsuka et al. (2002) for studies on gasoline-range alkanes.

One study of the thermal dissociation of methane in a solar furnace has been described (Weimer et al., 2000 and Dahl et al., 2001 a,b.) (USA). Approximately 90% of methane was dissociated to produce hydrogen and carbon black under a solar flux of 2400 kW/m<sup>2</sup> (or suns). The economies of the process are discussed and show promise for the concept. This work is to continue (Hydrogen Program 2001) (Weiner and Lewandowski, 2001). [See also Hirsch et al (2001) (Israel, Switzerland) for their latest and previous work on solar production of carbon and hydrogen from natural gas.]

- **Reforming of Methane (and Natural Gas) to Hydrogen**

The conversion of methane, natural gas and higher hydrocarbons to hydrogen has an extensive history in petroleum refining and hydrocarbon processing in general. This review is restricted to recent studies in the hydrogen literature, related to H<sub>2</sub> production as a neat fuel, often for use in fuel cells.

Karim and Metwally (1978, 1980) (Canada) have published a thermal-kinetic analysis of steam-methane reforming at temperatures of 1400-3000°K, pressures of 0.5-10 atm and steam-methane ratios of 1-5. The reaction is attractive at temperatures over 1800°K where near-equilibrium is obtained in 10 seconds. The conversion is not sensitive to pressure change but is sensitive to the steam-methane ratio. The addition of about 5% oxygen has only a small effect on hydrogen yield, but significantly reduces the heat required. In 1992 and 1993, Karim and Zhou (1992, 1993) present a detailed kinetic scheme for partial oxidation to hydrogen. Balthasar and Hambleton (1978) (Netherlands) review three major routes for the production of hydrogen from fossil fuels. At that time, they stated that steam reforming of light hydrocarbons was the most widely used due to better economics.

A decade later, Bulanov et al. (1988) (USSR) explored the catalytic steam reforming of natural gas using solar energy to increase the heating value of the resulting gas. The process accomplishes storage of solar energy. The heat of combustion of the resultant gas, rich in hydrogen, was increased 25%.

In the same year, Nazarov et al. (1988) (USSR) presented heat-exchanger design to use a gas-cooled nuclear reactor to steam reform natural gas. Brun-Tsekhovoi et al. (1988) (USSR) note that hydrogen production is one of the most energy-intensive industrial processes. They present data on steam reforming of methane in a fluidized bed of catalyst that contains CaO to bond CO<sub>2</sub> as CaCO<sub>3</sub>. A fourth paper at the World Hydrogen Energy Conference in Moscow, Akhundov et al. (1988) (USSR), present their version of using solar heat to decompose methane to hydrogen. The papers contain many references to not-commonly-cited work in Western literature. Petit et al. (1992) (France) reported on partial oxidation of methane for hydrogen production.

Rosen and Scott (1988) (Canada) carried out a computer analysis of the thermodynamics of the steam-methane-reforming (SMR) process. The analysis showed that the principal energy losses occur in the reformer due to irreversibilities in combustion and heat transfer across large temperature differences. [See also Rosen (1991) for similar information.]

A mathematical simulation of steam reforming of methane in a tabular catalytic reactor with a hydrogen-permeable wall is described in Prokopiev, et al (1992) (Russia, Italy).

The influence of temperature, pressure and thickness of a palladium membrane are studied. Improvements over conventional steam reforming are claimed. Astanovsky et al. (1992, 1994) (USSR) present yet another new reactor design for steam catalytic hydrocarbon conversion. Reactor characteristics for natural gas and CO conversion are given. Li Qiyvan (1992a,b) presents results for a new kind of methane reforming catalyst containing nickel. Chawla and Ghosh (1992) (India) present the thermodynamics of steam reforming, shift and carbon deposition of a typical digester biogas feed (60% CH<sub>4</sub>, 40% CO<sub>2</sub>) and pure methane.

A novel catalytic approach to hydrogen from methane and other light hydrocarbons via direct electro-steam reforming is given in Spagnolo et al. (1992) (Canada). The report notes that conventional steam reformers suffer from three major drawbacks: 1) inefficient reactor heat transfer, 2) high maintenance costs and 3) high methane fuel consumption. Heat is supplied directly to a nickel catalyst surface through resistance electrical heating. Methane conversions to hydrogen of 50-80% were achieved. At temperatures above 800°C, conversions were nearly independent of temperature, space-velocity, steam-methane feed ratio and nickel metal content, implying diffusion as the rate-limiting mechanisms. Research needs are itemized.

A pioneering power project, using natural gas initially and biomass later, to produce hydrogen for fuel cells is described in Walcher et al. (1996) (Germany). The system is designed to supply 6 GWh per annum of electrical energy. Poirier and Sapundzhiev (1997) (Canada) present a concept in which natural gas is decomposed on a catalyst with carbon deposition and hydrogen production. Periodically, the carbon is burned off in a dual-reactor system. The advantages are production of a hydrogen stream of greater than 95% purity and with less than 5 ppm CO. No experimental results were reported, but a variety of possible catalysts are listed.

Babaritsky et al. (2000) (Russia) extended their plasma catalysis process for methane to hydrogen and carbon to the steam reforming of methane, ethane and ethanol to hydrogen. Shu-Ren (1998) (China) describes the activities in China to produce hydrogen by catalytic steam reforming of natural gas, refinery off-gases, LPG, naphtha and industrial methanol. Pruden (1999) (Canada) looks at the technical and economic aspects of steam reforming of natural gas for hydrogen. The technologies of electrolysis and partial oxidation appear to be more economic in small sizes. Yokota et al. (2000) (Japan) studied the stoichiometry of the steam reforming of methane under the radiation from a concentrated Xe-lamp (solar simulator) at 650°C. The methane-steam ratio was 1.0 and a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was used. Hydrogen yields were about 70%. The products at 690°C were near equilibrium.

Thermal plasma technology applied to methane has been reported in Bromberg et al. (1997a&b;1998;and 1999a) (USA). These papers describe experiments and calculations of high temperature conversion of methane using both homogeneous and heterogeneous processes. The thermal plasma is characterized by extremely high temperatures (several thousand degrees C) and large amounts of ionization. Hydrogen-rich gases (50-75% H<sub>2</sub> and 25-50% CO) can be efficiently produced in compact plasma reformers. A system has been demonstrated for hydrogen production with a CO content of only about 2%. A nickel-based catalyst on alumina was used. Air-methane and water-methane ratios were varied as well as plasma input power. With steam injection it was possible to combine reforming and water-shift reactions in a single stage with no soot buildup on the catalyst surfaces of the reactor. Plasmatron generation has possible

applications for decentralized energy production with fuel cells, for hydrogen refueling stations and "hard to use fuels such as raw biomass." In Bromberg et al. (1999b), application of the plasma technologies to natural gas are explored. Development of plasma hydrogen from natural gas is continuing in the DOE Hydrogen FY2001 program. Included will be operation with biofuels and decreasing problems of catalyst sensitivity and deterioration (Bromberg, et al., 2001 a). A very recent discussion of hydrocarbon conversion is found in Bromberg et al (2001b)

In four recent project reports for the U.S. DOE, Sircar et al. (1995) (USA), Hufton et al. (1998) (USA) and Hufton et al. (1999;2000) present progress on the sorption enhanced reaction process (SERP) for the production of hydrogen by steam-methane reforming. This involves the reaction of steam with methane in the presence of an admixture of a catalyst and a selective absorbent for CO<sub>2</sub>. Reforming and CO<sub>2</sub> separation are accomplished in one reactor. Initial reactor results, using K<sub>2</sub>CO<sub>3</sub> promoted hydrotalcite in a non-cyclic mode, gave a gas containing 90+ %H<sub>2</sub>, the balance is CH<sub>4</sub> and only trace levels (<5 ppm) of carbon oxides. In the 1999 work, a new method of promoting the absorbent with carbonate spray injection was reported. Scale-up designs and an alternate method for providing heat by indirect gas heating was developed. Reactor temperatures of 400-500° can, thus, be achieved. This work is continuing in FY2000 under the U.S. DOE Hydrogen Program with consideration of a process development unit.

Other work at Air Products and Chemicals Inc., the world leader in merchant hydrogen production, involves ceramic membrane reactor systems for converting natural gas to hydrogen and synthesis gas (Dyer et al., 1999; Dyer and Chen, 2000,USA; and Dyer, 2001). These Ion Transport Membranes (ITM) are non-porous, multi-component metallic oxides that operate at high temperatures and have exceptionally high oxygen flux and selectivities. The membranes incorporate the non-porous ITM with reduction and reforming catalysts. Oxygen from a hot air stream is reduced to oxygen ions that flow through the membrane where, in combination with a reforming catalyst, they partially oxidize a combination of hot natural gas and steam, thereby forming CO and H<sub>2</sub>. The amount of steam determines the H<sub>2</sub>/CO ratio. Studies from bench-scale to commercial plants are projected over the next 10-15 years. Collaborators with Air Products include Chevron, McDermott, Norsk Hydro, Ceramatec and Eltron. (Hydrogen Program, 2001). Work on sorption-enhanced reactions in methane reforming will appear in *Industrial and Eng. Chemistry* shortly (Ortiz and Harrison, 2001) (USA)

New aspects of conversion of hydrocarbons to syngas and hydrogen are reviewed with an emphasis on the catalysts used. Fundamental, as well as applied catalyst studies, are warranted (Rostrup-Nielsen, 2000). There is a great deal of activity at present, worldwide, on hydrogen from methane and natural gas; a sampling follows. Jarosch et al. (2001) (Canada) describes a novel process for steam reforming methane based on the use of a fast-fluidized membrane reactor (catforming). In the catformer-reactor concept, methane and steam contact regenerated catalyst and the resulting gas-solid suspension enter the downflow section where reforming and water gas shift occur. The hydrogen is removed continuously via permeation through a palladium membrane. Zeolite catalysts impregnated with Ni were tested. Lundsford (2000) (USA) gives a current review of the catalytic conversion of methane to more useful chemicals and fuels, including hydrogen.

Shah, M.M. et al. (2000) (USA) describe a new technology development program that will integrate ceramic membrane based syngas production and hydrogen separation technologies. Technoeconomic feasibility and membrane testing are the initial activities. For a further sampling of research on catalytic steam-reforming of methane, see: Coursen et al. (2000) (France); Specht et al. (2000) (Germany); Koenig et al., (2000) (Germany); Kumar et al. (2000) (USA); Heinzl et al. (2000) (Germany). See also: Hummel & Lelewer (2001) (USA); Astanovsky and Astanovsky (2001) (Russia); Gordon et al. (2000) (USA), Lelewer et al. (2000) (USA), Galli et al., (2000); (Italy) Parmon et al. (2000) (Russia); Bradshaw, (2001a&b) (USA); Choudhary et al. (2001a) (USA); Naito (2000) (Japan) and Choudhary et al. (2001b) (USA).

Kodama et al. (2001) (Japan) carry out CO<sub>2</sub> reforming of methane in a molten carbonate salt bath. Metal catalyst particles are suspended in the molten salt. K, Ni, Fe, Cu or W metals supported on Al<sub>2</sub>O<sub>3</sub> were tested at 1223K. Another recent paper (Tanner, et al, 2001) (Canada, USA) uses microwave-promoted carbon-catalyzed conversion of methane to produce ethylene, ethane, acetylene and hydrogen. A selection of C<sub>1</sub>-C<sub>4</sub> hydrocarbons was also tested. Innovatek, Inc. (USA) is planning to study a novel catalytic-fuel-reforming technique (Hydrogen Program, 2001 (USA); Irving, 2001)(USA). Diesel fuel and natural gas will be tested in a system applying the advantages of microtechnology in the development of catalytic fuel reforming. Also planned in 2001 are studies of the production of hydrobromic acid from bromine and methane for hydrogen production (Hydrogen Program 2001) (USA)(Bradshaw, 2001b). Very recent reports on methane and other hydrocarbon reforming are given in Panjala et al. (2001) (USA), Mirodatus et al. (2001) (France); Srimat et al. (2001) (USA); Witmer (2001) (USA); Manns and Taylor (2001) (USA); Zhu et al. (2001) (Australia); Ahmed & Krumpelt (2001) and Nagoka et al. (2001) (Japan). Song (2001)(USA) discusses catalytic processes for fuel cells. As with methanol, much more research on methane to hydrogen can be expected. A recent paper by Yanhui and Diyong (2001) (China), while treating n-octane for hydrogen production, may be relevant to lighter hydrocarbon. [See also Galvita et al (2001) (Russia), Moon et al (2001) (South Korea), Raman (2001) (USA) and Shah et al (2001) (USA).]

## **TECHNOECONOMIC AND LIFE CYCLE ANALYSIS OF BIOMASS TO HYDROGEN**

### ***Technoeconomic Assessments***

Many technoeconomic assessments of hydrogen from renewables have been published from 1992 (and probably earlier) to the present. These papers are not discussed individually, since the emphasis of the report is on research, development and demonstration of biomass-to-hydrogen technologies. However, citations to these sources follow, since many contain discussions, insights, and recommendations on biomass-to-hydrogen feasibility and research.

### ***Life Cycle Analyses***

A few such analyses are starting to appear and, like the above economic studies, can alert researchers to priority areas for RD&D. The bibliography of some of these reports follows.

## **OVERVIEW OF HYDROGEN PRODUCTION PATHWAYS**

The reader is encouraged to consider these broad overviews of energy from biomass and other sources to help put hydrogen from biomass into perspective.



## **INFORMATION ON COUNTRY PROGRAMS**

The Appendix provides a sampling of recent publications related to the programs of the member countries of the IEA. The IEA Web site (<http://www.iea.org>) gives more details on the Hydrogen and Bioenergy Programs and the countries participating in those activities.

## **Promising Areas for IEA Cooperative Programs in Research, Development and Demonstration**

The chief purpose of this review of biomass to hydrogen is to bring to the attention of researchers, developers, policy makers and energy managers in the participating IEA countries the very extensive activities around the world over the last several decades. In this brief section, we give our general impressions of areas where further R,D&D would lead to earlier introduction of hydrogen from biomass into the renewable economy. Specific research priorities can, of course, only be chosen by the technologists and managers in each county, hopefully finding guidance from this review of what has been tried in the past.

In the above review, we found it logical to divide the approaches from biomass (or its intermediate, stable derivatives like ethanol) into twelve categories. These are:

### **Thermal/Steam/Oxygen Gasification**

This report includes only a brief section on gasification although it is clearly a major thermochemical route to hydrogen. The IEA Hydrogen Agreement Task 16 Biomass to Hydrogen Subtask will work with the IEA Bioenergy Gasification Task to summarize the state of the art in gas separation and processing technologies. Of particular interest will be to analyze needs in relation to fuel-gas specifications for fuel cells. R,D&D needs will be defined in a summary report that will include techoeconomic evaluations.

Production of hydrogen from carbonaceous materials has a long history, with many studies still appearing in the 80s and 90s. Our general observation is that several types of gasifiers have been proven for both coal and biomass. One area needing more work, for all but direct fuel combustion, is gas cleanup. Issues of "tar" cleanup, alkali and sulfur effects, and shifting the syngas to maximize hydrogen still remain.

### **Direct Solar Gasification**

Only a few papers have explored the use of solar heat to gasify solid organic materials. Two studies, 1976 and 1994, examined the idea, while Russian studies (1996, 1998) report experimental data for a parabolic mirror. Midilli et al.(2000) are currently studying hydrogen separation from gasified biomass. There would appear to be long-range, high-risk research opportunities at all scales to achieve the maximum hydrogen yield possible from given biomass feedstocks.

### **Miscellaneous Gasification Processes**

A sprinkling of studies of novel sources of heat or chemistry to convert biomass to hydrogen has appeared, but none has been followed up. The nuclear heat approaches probably face much higher barriers than proposed in the 1970's. However, electrochemical and redox processes have only been touched upon. Good areas for basic, proof-of-concept research should exist.

### **Biomass-derived Syngas Conversion to Hydrogen**

No attempt was made to cover the vast literature on syngas manipulation for optimization of specific gases or liquids. One very old approach for hydrogen from syngas goes back to the early 20th century. The "steam-iron" process and its variations have been studied for application

to biomass, and studies continue to this day. A great deal of syngas conversion research is bound to occur with the current interest in storable fuels for on-board hydrogen fuel cells for transport. This may lessen its priority for the IEA Hydrogen Agreement Task 16 emphasis on biomass to hydrogen.

### **Supercritical Conversion of Biomass**

Unlike some of the above areas, there has been a lot of research on supercritical conversion to hydrogen of a variety of types of biomass. Some of this work has had about ten years of continuous funding, allowing laboratory results to be validated, scale-up to proceed and techno-economic studies to be launched. A close study of the work in the USA and Japan, mainly, will be needed to see if novel conditions or approaches have been missed. As with all the approaches mentioned so far, when economics approach competitiveness with fossil-based hydrogen, long-term pilot-scale demonstrations will be needed.

### **Biomass Pyrolysis to Hydrogen and Carbon or Methanol.**

Steinberg and Associates have published extensively on the "Hydrocarb" and "Hynol" processes, each of which produces solid carbon or methanol rather than CO<sub>2</sub> as the final product. There has been very little experimental data supporting the proposed routes to hydrogen and methanol. No laboratory study of the integrated process has come to our attention. Research is needed to validate the techno-economic arguments of Steinberg.

### **Biological Conversion of Biomass to Hydrogen**

Though a few references are listed earlier, this subject is left for the IEA Hydrogen Agreement Task 15, Photobiological Production of Hydrogen, to address. Biological routes are certainly of importance in that they produce storable intermediates like methane and ethanol from solid biomass, as well as hydrogen directly.

### **Hydrogen from Biomass-Derived Pyrolysis Oil**

The group at NREL, along with collaborators from Spain, has studied this approach to hydrogen for over eight years. The emphasis has been on the conversion of oxygenated fractions of whole oil after adhesive-forming elements have been extracted. Research opportunities exist in the less-studied pyrolysis and reforming of other fractions of the whole oil left over when valuable fractions have been extracted or converted, such as the non-fermentable fractions from bioethanol production.

### **Hydrogen from Biomass-Derived Methanol and Ethanol**

Many studies have been carried out on methanol, whose likely source for the near-term is from fossil fuels. Much of this work is of very recent origin and is being fostered by fuel-cell applications. Long-term tests appear to be lacking.

Ethanol studies are much more germane to biomass-to-hydrogen, again driven by interest in ethanol for a liquid transportation fuel, as well as for fuel cells. Interest and research activities accelerated in the 90's. Research and demonstration opportunities exist, particularly in long-term catalyst testing and impurity effects.

## **Methane and Natural Gas - Pyrolysis to Hydrogen and Carbon**

As with biomass pyrolysis to hydrogen and carbon, many system studies have appeared along with a few reports of preliminary experiments. Muradov has carried out catalytic pyrolysis studies for almost a decade. Research and development opportunities using approaches such as plasma catalysis, gliding arc reactors, direct solar, the Carnol process, etc., could move these processes forward.

## **Reforming of Methane (and Natural Gas) to Hydrogen**

In this review, reforming of  $\text{CH}_4$  to  $\text{H}_2 + \text{CO}_2$  was perhaps the most actively studied approach to hydrogen. Much of this work is aimed at fossil-derived natural gas and research and development will probably be adequately promoted by the natural gas community.

## **Techoeconomic and Life-Cycle Analysis**

This has been an active field and continued analysis opportunities will arise as new processes, sources of biomass-derived feeds and product slates are suggested for experimental demonstration.

## **Overviews of Hydrogen Production Pathways**

This section contains overviews of programs on hydrogen from biomass and other routes and is included to suggest fruitful ideas for continuing research

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## Appendix B

### References to Major Sources of Biomass-to-Hydrogen Information

The following lists major sources of papers and reports used in the preparation of this review. Also listed are major web-based sites that also uncovered many research papers on hydrogen from biomass.

#### A. Sites Focused on Hydrogen

- The American Hydrogen Association is dedicated to the advancement of inexpensive, clean and safe hydrogen energy systems. (<http://www.clean-air.org>)
- The National Hydrogen Association holds annual U.S. Hydrogen meetings (1990-2001). Reports are mainly from the USA, but occasional papers from around the world are included (<http://www.hydrogenus.com>).
- The Canadian Hydrogen Association holds annual conferences covering a broad range of topics. The latest is the 10<sup>th</sup> Canadian Hydrogen Conference (See CHA at <http://www.h2.ca/en/main.html>). Reports are presented from North American and World researchers.
- Norsk H<sub>2</sub> Forum (<http://www.hydrogen.no>).
- Swedish Hydrogen Forum (<http://www.h2forum.org>).
- German Hydrogen Association (<http://www.dwv-info.de/indexe.htm>).
- Association Francaise De L'Hydrogene, member of the European Hydrogen Association (<http://www.afh2.org/htm>).
- The European Hydrogen Association (EHA) (<http://www.h2euro.org>).
- International Energy Agency (IEA) Hydrogen Program (<http://www.eren.doe.gov/hydrogen/iea>). Task 12: H<sub>2</sub> Storage in Carbon; Task 13: Design and Optimization of Integrated Systems; Task 14: Photoelectrolysis Production of H<sub>2</sub>; Task 15: Photobiological Production of H<sub>2</sub>; Task 16: H<sub>2</sub> from Carbon Containing Materials.
- Hyforum 2000. The International Hydrogen Energy Forum 2000, Policy – Business – Technology. 11-15 Sept., 2000. (<http://www.hyforum2000.de/english/events/hyforum2000>)
- The International Association for Hydrogen Energy (P.O. Box 248266, Coral Gables, Florida 33124, (USA) publishes proceedings as: "Hydrogen Energy Progress, Vol. I (1976) to Vol. XIII (2000). These bi-annual conferences present papers on a broad range of pathways to hydrogen, from researchers around the world. The reports are under the editorship of T.N. Veziroglu et al. The XIV World Hydrogen Energy Conference (2002) is scheduled for June 9-14 in Montreal, Canada (IRH @ [uqtr.u.quebec.ca](mailto:uqtr.u.quebec.ca)). Another major source of biomass-to-hydrogen papers is the International Journal of Hydrogen Energy, also published by the International Hydrogen Energy Association, Vol. 1 (1976) through Vol. 26 (2001).
  - 1<sup>st</sup> World Hydrogen Energy Conference, Conference Proceedings, 1-3 March 1976, Miami Beach, Florida, USA, Ed. T. Nejat Veziroglu, International Association of Hydrogen Energy.
  - Hydrogen Energy Systems, Proceedings of the 2<sup>nd</sup> World Hydrogen Energy Conference, 21-24 August 1978, Zurich, Switzerland, Eds. T. Nejat Veziroglu and Walter Seifritz, Pergamon Press.
  - Hydrogen Energy Progress, Proceedings of the 3<sup>rd</sup> World Hydrogen Energy Conference, 23-26 June 1980, Tokyo, Eds. T.N. Veziroglu, K. Fueki and T. Ohta, Pergamon Press.

- Hydrogen Energy Progress IV, Proceedings of the 4<sup>th</sup> World Hydrogen Energy Conference, 13-17 June 1982, Pasadena, California, USA, Eds. T.N. Veziroglu, W.D. Van Vorst and J.H. Kelley, Pergamon Press.
- Hydrogen Energy Progress V, Proceedings of the 5<sup>th</sup> World Hydrogen Energy Conference, 15-20 July 1984, Toronto, Ontario, Canada, Eds. T.N. Veziroglu and J.B. Taylor, Pergamon Press.
- Hydrogen Energy Progress VI, Proceedings of the 6<sup>th</sup> World Hydrogen Energy Conference, 20-24 July 1986, Vienna, Austria, Eds. T.N. Veziroglu, N. Getoff and P. Weinzierl, Pergamon Press.
- Hydrogen Energy Progress VII, Proceedings of the 7<sup>th</sup> World Hydrogen Energy Conference, 25-29 September 1988, Moscow, USSR, Eds. T.N. Veziroglu and A.N. Protsenko, Pergamon Press.
- Hydrogen Energy Progress VIII, Proceedings of the 8<sup>th</sup> World Hydrogen Energy Conference, 22-27 July 1990, Honolulu and Waikoloa, Hawaii, USA, Eds. T.N. Veziroglu, N. Getoff and P. Weinzierl, International Association of Hydrogen Energy.
- Hydrogen Energy Progress IX, Proceedings of the 9<sup>th</sup> World Hydrogen Energy Conference, 22-25 June 1992, Paris, France, Eds. T.N. Veziroglu, C. Derive and J. Pottier, International Association of Hydrogen Energy.
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- Hydrogen Energy Progress XI, Proceedings of the 11<sup>th</sup> World Hydrogen Energy Conference, 23-28 June 1996, Stuttgart, Germany, Eds. T.N. Veziroglu, C.-J. Winter, J.P. Beselt and G. Kreysa, International Association of Hydrogen Energy.
- Hydrogen Energy Progress XII, Proceedings of the 12<sup>th</sup> World Hydrogen Energy Conference, 21-26 June 1998, Buenos Aires, Argentina, Eds. J.C. Bolcich and T.N. Veziroglu, International Association of Hydrogen Energy.
- Hydrogen Energy Progress XIII, Proceedings of the 13<sup>th</sup> World Hydrogen Energy Conference, 12-15 June 2000, Beijing, China, International Association of Hydrogen Energy.
- Proceedings of the U.S. DOE Hydrogen Program Reviews (1991-2001) Annual Meeting papers. This series covers research and analysis of the extensive team of contractors in the DOE portfolio. These reports are available from the National Renewable Energy Laboratory, Golden, CO, USA in a series of NREL Technical Reports. Contact NREL Document Distribution Center, 1617 Cole Blvd., Golden, CO, 80401, for information on availability.
  - 1992, May 6-7, Honolulu, Hawaii. July. NREL/CP-450-4972
  - 1993, May 4-6, Cocoa Beach, Florida. August. NREL/CP-470-5771
  - 1994, April 18-21, Livermore, California. July. NREL/CP-470-6431.
  - 1995, April 18-21, Coral Gables, Florida. September. NREL/CP-430-20036
  - 1996, May 1-2, Miami, Florida. October. NREL/CP-430-21968
  - 1997, May 21-23, Herndon, Virginia. October. NREL/CP-430-23722
  - 1998, April 28-30, Alexandria, Virginia. August. NREL/CP-570-25315
  - 1999, May 4-6, Lakewood, Colorado. January, 2000. NREL/CP-570-26938

- 2000, May 9-11, San Ramon, California. NREL/CP-570-28890
- 2001, April 17-19, Washington, D.C. NREL/CP 570-30535. (Also available at <http://www.eren.doe.gov/hydrogen/docs/30535toc.html>)
- HyWEB – The Hydrogen and Fuel Cell Information System (<http://www.hydrogen.org/welcome/intro.html>). This network, started in 1997 under funding by the European Commission, presents comprehensive, detailed and up-to-date information on hydrogen as an energy carrier and on fuel cells (in German and English language versions). The cite includes a “Hydrogen Gazette” (<http://www.hydrogen.org/news/gazette.html>) and a “Hydrogen Compendium” section. The latter present detailed knowledge on hydrogen production, transportation, distribution, storage, conditioning and applications, especially in fuel cells. There are also sections on “Company and Products” databases, and on “Politica” (See <http://www.HyWeb.de/index-e.html>) (See Altman and Wurster below, 1998).
- WE-NET maintains a listing of hydrogen research organizations among other activities (<http://www.ena.or.jp/WE-NET/>).
- United States Hydrogen and American Hydrogen Association-Midwest Division (<http://www.USH2.com>).
- The Institute for Energy Technology in Norway conducts analyses of hydrogen systems as well as hydrogen production from fossil fuels. Contact D. Solberg Kjell, P.O.Box 40, N-2007, Kjeller, Norway.
- NEDO Sydney Representative Office. Promotes cooperative projects between Japan and Australia, New Zealand and South Pacific countries. Includes programs in hydrogen, alcohol and biomass technology (<http://www.nedo-sydney.org.au/main/default.htm>).
- Hydrogen and Fuel Cell Letter. This “publication is the voice of the international hydrogen and fuel cell communities, covering events and developments in this emerging field as they occur.” (<http://www.hfcletter.com>).
- The Hydrogen Energy Center offers links to companies and organizations who are contributing to the advancements of hydrogen or other renewable and sustainable energies (<http://www.h2eco.org/links.htm>).
- The DOE Hydrogen Energy Research (HYD) online document database (<http://www.osti.gov/hyd/hyhome.html>).
- Hydrogen Research Institute at the University of Quebec (<http://www.uqtr.quebec.ca/IRH/en/Main/welcome.htm>).
- Florida Solar Energy Center, Hydrogen Research and Applications Center addresses hydrogen from renewable resources among other topics (<http://www.fsec.ucf.edu>).
- California Hydrogen Business Council. Maintains a Hydrogen Resource Link database (<http://www.ch2bc.org/links.htm>).
- Shell Hydrogen and Shell Renewables sites are available at (<http://www.shellhydrogen.com/hydrogen-en/0,6011,,oo.html>).
- Makoto, Akai (1993). Hydrogen Based Global Renewable Energy Network. 2. *US/Japan Workshop on Global Change Research: Environmental Response Technologies, Honolulu, HI, 1-3 Feb 1993*:pp. 203-209.
- Altmann, M.; Wurster, R. (1998). HyWeb – The Hydrogen and Fuel Cell Information System Publication of a Hydrogen Acceptance Study in HyWeb as an Example of the Dissemination

of Hydrogen Information via the Internet. *Proceedings of the 12<sup>th</sup> World Hydrogen Energy Conference, Buenos Aires, Argentina, 21-26 June 1998*, Vol. 1:pp.281-290.

- Environment Institute, Renewable Energies University, European Commission's Joint Research Centre, Ispra, Italy. Activities in hydrogen from bio-ethanol for use in fuel cells and hydrogen production from biomass (<http://www.eurec.be>).
- Rocky Mountain Institute (<http://www.rmi.org/>)
- Sandia National Laboratories, California has a program on hydrogen reformation (<http://www.ca.sandia.gov/CRF/03-hydrogen.html>)
- U.S. Department of Energy (DOE) Hydrogen Program (<http://www.eren.doe.gov/hydrogen/program.html>)
- Alternative Fuels Data Center (AFDC) operated by DOE ([http://www.afdc.doe.gov/altfuel/hyd\\_general.html](http://www.afdc.doe.gov/altfuel/hyd_general.html))
- Hydrogen Now <http://www.hydrogennow.org/>

## **B. Sites Focused on Biomass**

- dk-TEKNIK ENERGY and ENVIRONMENT Center for Biomass Technology. A Danish biomass information network of four technological institutes working with biomass (<http://www.dk-teknik.dk/>).
- Renewable Energy Technologies, the Australian renewable energy Web Site. Contains information on biomass conversion technologies (<http://renewable.greenhouse.gov.au/technologies/biomass/bioconversion.html>).
- U.S. Department of Energy's National Biofuels Program (<http://www.biofuels.nrel.gov>).
- IEA Bioenergy – a listing of current tasks 28-39 and leader contacts (2001–2003) (<http://www.ieabioenergy.com>).
- Green Energy News (<http://www.nrglink.com/>).
- British Bio Gen (<http://www.britishbiogen.co.uk>)
- American Bioenergy Association (<http://www.biomass.org>)
- Bioenergy: Biobib and Other Databases (<http://www.bioenergy.ornl.gov>)
- EPA-Atmospheric Protection Branch (<http://www.epa.gov/docs/crb/apb/biomass.htm>)
- Canadian Renewable Fuels Association (<http://www.greenfuels.org/>)
- International Gas Turbine Institute. Coal, Biomass and Alternative Fuels Committee (<http://www.asme.org/igti/community/committees/cbaf/>)
- Australian Renewable Energy Website, Renewable Energy Technologies (<http://renewable.greenhouse.gov.au/technologies/biomass/bioconversion.html>)
- Biomass Research & Development Initiative. (U.S.) Involves some eleven government agencies (<http://www.bioproducts-bioenergy.gov/agencies.html>)
- ETC Energy Technology Center in Pitea. (Email: [info@etc.pitea.se](mailto:info@etc.pitea.se))
- European Forum for Renewable Energy Sources (EUFORES) (<http://www.eufores.org>)
- IEA Bioenergy, Task 27-Liquid Biofuels (<http://www.joanneum.ac.at/>)
- Renewable Fuels Association, RFA. (<http://www.ethanolrfa.org>)

- A new Web site combines the PyNe and GasNet sites at: <http://www.thermonet.co.uk>
- GasNet can be found at: <http://www.gasnet.uk.net>
- The Biomass Technology Group B.V. can be accessed at: <http://btgs1.ct.utwente.nl/home.html>

### C. General Renewable Energy Information

- The International Energy Agency (IEA) Web site: <http://www.iea.org/> provides lists of IEA implementing agreements such as: CADDET Renewable Energy; (<http://www.caddet-re.org>) Energy Technology Data Exchange (ETDE) (<http://www.etde.org/etdeweb/>); Energy Technology Systems Analysis (ETSAP) ([http://www.ecn.nl/unit\\_bs/etsap/](http://www.ecn.nl/unit_bs/etsap/)).
- OSTI – U.S. Office of Scientific and Technical Information (<http://www.osti.gov/bridge>). A public site requiring no registration or password.
- ECN (Netherlands Energy Research Foundation) provides energy information in the Internet (EII) database of energy-related information sources (<http://www.ecn.nl/eii/main.html>). Also (<http://www.ecn.nl>).
- ETDWEB at <https://www.osti.gov/infobridge/etde/search.easy.jsp> includes bibliographic records of international scientific and technical literature in the field of energy. The collection is approaching 800,000 records.
- Pub Science, maintained by DOE Office of Scientific and Technical Information, is providing access to a growing collection of scientific and technical publishers and peer-reviewed journal literature (<http://pubsci.osti.gov/>).
- Google™ provides searches based on keywords, e.g., hydrogen and biomass (<http://www.google.com>).
- Canadian Sustainable Energy Web Site. Renewable Energy and Sustainable Energy in Canada (<http://www.newenergy.org/>).
- Canadian Renewable Fuels Association (CRFA) (<http://www.greenfuels.org>)
- Canadian Associations for Renewable Energies. (<http://www.renewables.org>)
- Nordic Energy Index (NEI). Contains descriptions of ongoing and completed energy research, development and demonstration projects in Denmark, Finland, Norway and Sweden (<http://www.risoe.dk/nei>).
- Agores—A Global Overview of Renewable Energy Sources. Designed to be the European information center for renewable energy and the official European Commission Web Site for renewable energy (<http://www.agores.org>).
- Union of Concerned Scientists (<http://www.ucsusa.org/index.html>).
- Australian Institute of Energy (<http://www.aie.org.au/index.htm>).
- Joanneum Research, Austria. Has an Institute of Energy Research, among others (<http://www.joanneum.ac.at>).
- American Solar Energy Society (<http://www.ases.org>)
- Greenpower Mailing List (<http://www.solstice.crest.org/renewables/green-powe-archive/>)
- IEA Greenhouse Gas R&D Programme (IEAG) (<http://www.ieagreen.org.uk/test2b.htm>).
- Source Guides. Renewable Energy Nonprofit Organizations in the World by Business Name (<http://energy.sourceguides.com/businesses/byN/byName.shtml>)



- Pan-European Coalition of Environmental Citizens Organizations – European ECO-Forum (<http://www.eco-forum.org/top.htm>)
- REPP – Renewable Energy Policy Project (CREST) (<http://www.repp.org/repphome.html>)
- Solar Energy Society of Canada, Inc. (<http://www.solarenergysociety.ca/>)
- California Energy Commission. Programs and funding etc. (<http://www.energy.ca.gov/>)
- U.S. Export Council for Renewable Energy (US/ECRE) (<http://solstice/crest.org/renewables/usecre>)
- EPRI energy search (<http://www.energysearch.com/>)
- Joint Research Centre-Environmental Institute, Renewable Energies Unit. EUREC member (<http://www.jrc.org/>)
- Solstice – Online source for sustainable energy information from CREST (<http://solstice.crest.org/index.shtml>)
- INFORSE - Europe. International network for sustainable energy (<http://orgve.dk/inforse-europe>)
- WIRE - World Wide Information System for Renewable Energy (<http://www.wire.ises.org>)
- The Scientific World - a personal portal to science (<http://www.thescientificworld.com/>)
- The NREL Library (<http://www.nrel.gov>)
- U.S. DOE, Energy.gov (<http://www.energy.gov/sources/index.html>)
- World Energy Council. Addresses renewable among other energy sources. Member committees in over 90 countries (<http://www.worldenergy.org/wec-geis/>)
- American Bioenergy Association. (<http://www.biomass.org>)
- Business Council for Sustainable Energy. (<http://www.bcse.org>)
- ECO – Forum Energy and Climate Group. (<http://www.eco-forum.org> )
- Energy Efficiency and Renewable Energy Network (EREN) (<http://www.eren.doe.gov> )

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