

“Green” Chemicals from Renewable Agricultural Biomass - A Mini Review

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Abstract: Recently, utilization of renewable resources to replace petroleum as a primary feedstock for liquid fuels, chemicals and materials has become a topic of interest around the world. It is intriguing due to rising oil prices, the negative effects of petroleum on the environment and the advantages of renewable resources, such as their abundance and sustainability. Herein, the possibilities for biobased chemicals prepared from renewable resources are reviewed. The most popular feedstocks for commodity and specialty chemicals are carbohydrates as they account for approximately 95% of the biomass produced annually. The conversion routes, including chemical and biological routes, direct extraction, and selected technical advancements are discussed. Examples of select biochemicals, their conversion pathways from biomass, and their derivatives and potential applications are identified.

Keywords: Green chemicals, biomass, biomass conversion, biobased chemicals, renewable resources.

INTRODUCTION

Organic chemicals play important roles in our everyday lives. The United States is the largest producer of chemicals in the world, and represents approximately 25% of the worldwide chemical market [1]. Since the middle of the 20th century, fossil oil and natural gas have served as the main raw material resources for chemicals production [2]. Currently, almost all organic compounds can be derived from seven basic building blocks, including syngas from methane, ethylene, propylene, butanes, butylenes, butadiene, and BTX (which is a mixture of benzene, toluene, and xylene). These building blocks are obtained from natural gas, petroleum and coal [1]. Currently, in the United States, ~13% of the crude oil is used to produce nonfuel chemicals [3]. There is a growing interest in the replacement of fossil-based chemicals with biochemicals. Biochemicals refer to the chemicals produced from biomass. Several factors, including awareness of finite petroleum resources, availability of renewable resources, environmental imperatives and recent advances in processing technologies, are driving chemical industries to shift their feedstocks from petroleum to renewable counterparts for production of organic chemicals.

It is well known that the reserves of oil, natural gas and coal are vast but still limited. Fossil energy sources will be depleted with their continuous exploitation. In contrast, biomass is a reliable resource for fuels and chemicals in the long term [4]. Supplementing petroleum consumption with renewable biomass resources is of critical importance in sustaining the growth of the chemical industry. The advantages of using biomass rather than petroleum to manufacture chemicals include opportunities for less pollution, no net CO₂ contribution to the atmosphere, more biodegradable and sustainable products and, in some cases, lower cost [5]. It has been found that many biomass derived chemicals have economical advantages, particularly for some functionalized

chemicals [6]. In addition, recent advances in process technologies, especially in fermentation technologies such as enzymatic engineering, metabolic engineering and genetic manipulation, provide new opportunities for producing a wide variety of industrial products from renewable plant resources [7-8]. A key to the chemical industries gradual shift toward the use of renewable biomass resources for industrial chemical manufacturing is the implementation of the biorefinery concept [9]. Similar to a petroleum refinery, a biorefinery integrates a variety of processing technologies to produce multiple bioproducts from various biomasses. Such an approach will help maximize the value of the biomass and minimize low or no value byproducts [1, 10].

Production of green chemicals from renewable resources is a very broad topic. This mini-review focuses mainly on developments in the last couple decades in the areas of renewable biomass as a source of chemicals, possible conversion pathways and products.

POTENTIAL RENEWABLE RESOURCES

Renewable resources, generally known as biomass, refer to any material having recent biological origin, including plant materials, agricultural crops, and even animal manure [11]. As a naturally abundant resource, biomass is a desirable alternative to petroleum for production of chemicals because of its sustainability and often low cost. Further, biomass, comprised of C, H, O, and N, has a chemical composition similar to fossil feedstocks which contain C and H. As a consequence, products produced from petroleum can be produced from biomass [1]. Currently, the annual worldwide production of biomass is estimated to exceed 100 trillion kilograms. In the United States, the 250 billion kilograms of wasted plant biomass produced each year far exceeds the current total consumption of 100 billion kilograms for organic chemicals, plastic resins, and fibers [7]. However, presently, only 5% of chemicals are derived from renewable resources [12]. Therefore, there is huge potential for biobased chemicals to share markets with their fossil based counterparts.

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The most popular biomass feedstock for commodity and specialty chemicals production are carbohydrates. Carbohydrates are, by far, the largest bulk of organic compounds on earth and account for approximately 95% of the biomass produced annually. Carbohydrates exist primarily in the form of polysaccharides, including starch and cellulose [13]. Traditionally, starch has been used as a basic organic raw material by chemical industries. Many bulk chemicals and polymers can be produced by chemical modification or fermentation of starch and its monosaccharide derivative (D-glucose) [14-16]. However, there is a concern about the competition between industrial and food applications of starch. Therefore, in the medium to long term, conversion of lignocellulosic biomass into glucose and xylose using microbes and other biological systems for fuel and biochemical production is more attractive. Cellulosic biomass, or lignocellulosics, refers to woody and herbaceous plants and major crop residues such as sugar cane bagasse, wheat straw, rice straw and corn stover [7]. Lignocellulosic materials are composed mainly of cellulose, hemicellulose and lignin. Most of the biomass on earth is in the form of lignocellulose. Theoretically, lignocellulosic material is an ideal source of raw sugars for industrial processes since it does not affect food supplies and price. Many efforts have been made to utilize biological, thermal, and chemical conversion technologies to convert lignocellulosic biomass to ethanol and chemicals [17-19]. In addition, lignocellulosic materials could be liquefied into chemical intermediates rich in hydroxyl groups [20]. However, different from its starch counterpart, the highly ordered crystalline structure of cellulose itself, together with the protective sheath (lignin and hemicellulose layers) around it, requires some form of pretreatment to open up the structure to effectively convert it to glucose. Pretreatment processing generally includes treating lignocellulosic materials with dilute sulfuric acid, followed by delignification with various organo-solvents, combined dilute alkaline treatment and homogenization, autohydrolysis, and steam explosion [21-25]. Recently, National Renewable Energy Laboratory researchers developed an advanced pretreatment technology that uses a mixture of an organic solvent and water to cleanly fractionate chemical-grade cellulose, hemicellulose sugars, and lignin [26]. Nevertheless, under current conditions, due to technological disadvantages and economic hurdles, including low specific activity and cost of current commercial cellulose enzymes, the use of lignocellulosic materials as a raw material for chemical production has been a distant second contender compared to its starch counterpart.

Besides the above mentioned carbohydrates, oils and fats of vegetable and animal origin are important renewable raw materials for "green" lubricants, surfactants, and alkyd resins in many industrial and pharmaceutical applications. Different non-ionic surfactants have been produced by changing the length of the hydrophobic fatty acid moiety and the degree of polymerization of the hydrophilic part [27]. In addition, a variety of plants, including some flowers such as poppies and rosemary which provide drugs, fragrances and flavors, have been used as a source of fine and specialty chemicals [28].

In order to expand the use of abundantly available renewable resources as the raw materials for chemical production, to reduce our dependence on foreign oil and environ-

mental pollution, a detailed examination of conversion pathways is required.

POSSIBLE CONVERSION PATHWAYS

Chemical Conversions

Chemical conversions refer to processes which directly convert biomass to chemicals at high temperature and pressure and in the presence of a catalyst. Some bulk chemicals, including levulinic acid and furfural, can be produced by treating biomass at high temperature for specific times in the presence of conventional mineral acid catalysts, such as hydrosulfuric, hydrochloric, and phosphoric acids [29-31]. However, low yield and significant volumes of side products, together with the use of corrosive chemicals, are challenging commercialization and environmental issues.

A thermochemical process, generally referred to as gasification, partially oxidizes biomass into syngas, a fuel gas mixture consisting of hydrogen, carbon dioxide, nitrogen and carbon monoxide [32]. The syngas can be converted to important chemical intermediates, including methanol, ammonia and oxy-alcohols [33]. However, this route is relatively slow and typically requires large, complicated and expensive equipment [34].

Many efforts have been made to design innovative alternative pathways to effectively convert biomass to chemicals. One area of research has focused on improving the efficiency of catalysts. A novel aqueous phase catalysis process uses robust catalysts and modified carbon supported catalysts developed to convert sugar and organic acids to industrial chemicals at the Pacific Northwest National Laboratory [35-36]. McKoon *et al.* [37] investigated the stability of silica-support Ru catalysts in an aqueous phase conversion of glucose to sorbitol. Size and shape-selective zeolites were found to be very valuable catalysts in conversion of biomass to numerous chemicals [38]. These catalysts significantly increase the efficiency of reactions by immobilizing reactants in their matrix structure. Besides research on catalysts, advancement of efficient conversion processes have been reported. A cost-effective two-phase route for the selective dehydration of fructose to remove excess functional groups, and thereby produce hydroxymethylfurfural, a valuable chemical intermediate, were reported by Roman-Leshkov *et al.* [39].

Jin *et al.* [40] found that hydrothermal processing was the most promising for the conversion of biomass into acetic acid using supercritical water as a reaction medium. In addition, chemical conversions have been used to convert the chemical intermediates, which were produced from biological conversion, to final chemical products, including tetrahydrofuran and gamma-butyrolactone from 1, 4-diacids (succinic, fumaric, and malic), and 1,3-propanediol from 3-hydroxypropionic acid [41-42].

Biological Conversions

Biological conversions involve the utilization of biological enzymes or living organisms to catalyze the conversion of biomass into specialty and commodity chemicals. Overall, it is considered to be the most flexible method for conversion of biomass into industrial products [7]. Compared to chemical conversions, where high temperatures and pressures are

involved, operating conditions for biological conversions are relatively mild. Actually, biological conversions are not a new topic, but rather some commercial bulk chemicals, such as ethanol, lactic acid, citric acid and acetone-butanol, have been produced *via* yeast and bacterial fermentation processes [43-45]. Recently, there has been growing interest in utilization of biocatalysts to convert renewable resources into chemicals, due to high yield and selectivity, and fewer by-products. However, because of the metabolic restriction in microorganisms, only a few bulk products currently are produced *via* fermentation [8]. Therefore, development of new technologies to broaden the product spectrum is necessary. Genetic engineering has emerged as a powerful tool for genetic manipulation of multistep catalytic systems involved in cell metabolism [46]. Recombinant DNA technology is used to clone and manipulate gene encoding enzymes in organisms. Recombinant microorganisms, with altered sugar metabolism, are able to ferment sugar to some specialty chemicals, which cannot be produced by the corresponding original strain [8]. For example, catechol and adipic acid were produced from glucose using genetically modified *Escherichia coli*. Both glucose and xylose, in cellulosic biomass, have been converted into ethanol by recombinant *Saccharomyces* yeast [47]. In addition, immobilized enzyme and whole cells have been used to produce biomass-derived chemicals. Huang and Yang [48] produced fumaric acid from glucose and cornstarch by immobilizing *Rhizopus Oryzae* cells on a rotating fibrous matrix. Hames *et al.* [49] patented a microbial process for converting biomass hydrolyzate into fuels and chemicals by absorbing biomass hydrolyzate on solid metal oxide support to fractionate it with fermentation inhibitors, such as lignin-derived compounds, thus improving the products yield. Currently, efforts are continuing to identify, characterize, and even modify enzymes and living organisms and processes so they can better utilize renewable resources to produce structurally diverse and complex chemicals. High yield and selectivity, as well as minimum waste streams, favor biological conversions as pathways to transform biomass to higher-value chemicals. However, there are still problems with current biological conversion technologies. Sterilization, fermentation stirring, and separation of target products from aqueous systems with low production concentration entail high energy requirements [8]. Further, considerable investment is required to make processes highly efficient and continuous [3]. Therefore, there are research opportunities in the development of new low cost biological conversion technologies to effectively transform biomass into chemicals.

Direct Extraction

Some commodity and fine chemicals can be extracted directly from biomass. Ferulic acid, a precursor for vanillin, occurs in a relatively high concentration in the form of xylan polysaccharide ester in corn fiber. Shin *et al.* [50] extracted ferulic acid from corn fibers using novel fungal and bacterial feruloyl esterases. Arabinogalactan and quercetin dehydrate were isolated from larch wood [51]. Vanillin, used in the flavor and fragrance industries, can be recovered by alkaline oxidation of lignin in the presence of a copper catalyst [52-53]. Derouane and Powell [54] patented a novel extraction process that used large pore, high silica/alumina ratio zeolites as selective sorbents to remove vanillin from various

liquid solutions. Eckert *et al.* [55] explored a more benign and cost-efficient way to extract vanillin from lignin using a gas-expanded liquid. Gas, typically CO₂, was added to an organic solvent, providing the solvent with different and tunable properties such as solubility, transportability and polarity. Compared to traditional solvents, the advantages of using gas-expanded liquids include low operating cost, ease of separation and reduction of the amount of solvent needed. Direct extraction is a promising pathway for utilizing renewable resources, irrespective of scale [2]. From an economic point of view, the extraction of high-value added chemicals from biomass can be the most profitable, but the availability and variety of chemicals are limited.

POTENTIAL PRODUCTS

Werpy *et al.* (2004), at the Pacific Northwest National Laboratory and National Renewable Energy Laboratory, identified the potential top 12 value added building-block chemicals from biomass, actually from sugar [56]. They are 1,4-diacids (succinic, fumaric and malic acids), 2,5-furan dicarboxylic acid, 3-hydroxy propionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutyrolactone, glycerol sorbitol, and xylitol/arabinitol. Based on the different conversion pathways, these building-block chemicals, and their derivatives and potential applications, are summarized in Tables 1 and 2. From the tables, the 12 building-blocking chemicals were converted either biologically or chemically from sugar. All building-block chemicals were further converted to a wide spectrum of derivatives through chemical processes, such as reduction, oxidation, dehydration, hydrogenolysis and direct polymerization. Those chemicals can be used widely as solvents, fiber, antifreeze, and new polymers (such as polyesters, polyamides, and polyurethane) with better polymeric properties, than those currently derived from petroleum.

Further, Frost's group at the Michigan State University conducted research on synthesis of benzene-free aromatic chemicals and their derivatives from glucose, which traditionally have been derived from benzene. These aromatic chemicals include phenol [57], catechol [58], quinic acid and hydroquinone [59], pyrogallol [60], hydroxyhydroquinone [61], phloroglucinol [62], caprolactam [63] and (derivative) adipic acid [64]. Fig. (1) summarizes the synthesis routes of these chemicals from glucose and their possible derivatives. It was found that two steps were involved in preparation of aromatic chemicals from glucose. Typically, glucose first was converted to chemical intermediates by microbial synthesis, followed by chemical conversion of these intermediates into ideal end chemicals.

It is worthy of note that many of the intermediates, whose syntheses generally require some special enzymes which cannot be found in conventional microbes, can be synthesized at this point because DNA recombinant technology allows the transfer of genes for specific chemical forming enzymes in traditional microbial strains.

Beside synthesis of aromatic chemicals from glucose, as discussed above, Haveren *et al.* [4] discussed the possibility of production of aromatic chemicals from lignin due to the presence of large quantities of aromatic structures in its molecule as well as it being a simple and economic process. A complex mixture of polyhydroxylated and alkylated phe-

Table 1. Biological Conversion for Chemical Building Blocks, and their Derivates and Potential Application¹

Building Block Chemicals	Pathway from Sugar	Derivatives or Derivative Family	Pathways to Derivatives	Potential Application
1,4-diacids (Succinic, fumaric, malic)	Fermentation from Krebs cycle pathways	Butanediol Tetrahydrofuran (THF) γ-butyrolactone (BL)	Reduction	Solvents Fiber
		Pyrrolidinone N-methylpyrrolidinone (NMP)	Reductive aminations	Green solvent Water soluble polymers
		Straight chain polymers	Direct polymerization	Fiber
3-Hydroxypropionic acid	Fermentation	1,3-propane diol	Reduction	Sorona Fiber
		Acrylate Family acrylic acid, acrylamide	Dehydration	Contact lenses Diapers
Aspartic acid*	Fermentation or Enzymatic conversion of oxaloacetate in the Krebs cycle	Amine butanediol Amine tetrahydrofuran Amine-γ-butyrolactone	Reduction	Amino analogs of C4 1,4 dicarboxylic acid
		Aspartic anhydride	Dehydration	New area
		Polyaspartic	Direct polymerization	New area
Glutamic acid	Fermentation	Diols (1,5-pentandiol) Diacids (Glutaric acid) Aminodiols (5-amino-1-butanol, glutaminol ect)	Reduction	Monomers for polyesters and polyamides
Itaconic acid	Aerobic fungal fermenta- tion	Methyl butanediol Methyl THF Methyl- γ-BL Methyl Pyrrolidinone Methyl NMP	Reduction	New useful properties for butanediol, THF, and butyrolactone
		Polyitaconic	Direct polymerization	New Polymers
Glycerol*	Enzymatic transesterifi- cation	Glyceric acid PLA analogs	Oxidation	Polyester fibers with new properties PLA with better polymeric properties
		Propylene glycol 1,3-propanediol	Hydrogenolysis	Antifreeze, humectant Sorona fiber
		Branched polyesters and polyols	Direct polymerization	Unstaturated polyure- thane resin for Insulation

¹From Werpy *et al.* (2004).

*Indicates the building block chemicals also are produced by chemical conversion shown in Table 2.

nol compounds were formed by cracking lignin with a high temperature thermal process. Although currently there is a challenge in upgrading these mixtures to a higher content of phenol, production of phenol from lignin still is a long-term option.

Currently, there is also a growing interest in synthesis of ethylene from renewable resources. Arenamart and Trakarnpruk [65] and Takahara *et al.* [66] converted ethanol to ethylene using dealuminated mordenite, zeolites and silica-alumina catalysts. Further, photosynthetic conversion of carbon dioxide to ethylene by recombinant cyanobacterium *Synechococcus* sp. PCC 7942 was reported by Sakai *et al.* [67].

The products listed here represent only a small portion of the biochemicals made by different research groups around

the world. Efforts to expand the spectrum of chemicals derived from renewable resources are continuing.

CONCLUSIONS

The fossil fuel crisis and environmental concerns have encouraged scientist to explore new resources and pathways for chemicals production. Low cost and sustainability, together with chemical compositions similar as fossil feedstocks, render biomass a promising raw material for production of biochemicals. Technological advancements, including biorefineries, heterogeneous catalysts and genetic engineering, guarantee development of green chemicals from biomass. In the mid- to long- term, biochemicals will share markets with petroleum-based chemicals and ultimately replace them as biochemicals become price competitive.

Table 2. Chemical Conversion for Building Blocks Chemicals, their Derivates and Potential Application¹

Building Block Chemicals	Pathway from Sugar	Derivatives or Derivative Family	Pathways to Derivatives	Potential Application
2,5-furan dicarboxylic acid (FDCA)	Oxidative dehydration of C6 sugars	Diols and aminations Levulinic and succinic acids Polyethylene Terephthalate analogs Furanoic polyamines	Reduction Direct polymerization	New polyester and nylon All uses of succinic and levulinic Furanoic polyesters for bottles and films Polyamide for nylons
Glucaric acid	Nitric acid oxidation of starch Catalytic oxidation of starch with bleach	Lactone Polyglucaric ester and amides	Dehydration Direct polymerization	Solvents Nylons or different properties
Aspartic acid*	Amination of fumaric acid with ammonia	Same as Table 1	Same as Table 1	Same as Table 1
Levulinic acid	Acid catalyzed dehydration and decomposition of celluloses and sugars	Methyl tetrahydrofuran γ -butyrolactone Acetyl acrylates Acetic-acrylic succinic acids Diphenolic acid	Reduction Oxidation Condensation	Fuels oxygenates Solvents Copolymerization with other monomers Replacement of bisphenol for polycarbonate
3-Hydroxy-butyrolactone	Oxidative degradation of starch	Furans, Analogs of pyrrolidones Amino analogs to tetrahydrofuran	Reduction Direct polymerization	Solvents Amino analogs to lycra fibers
Glycerol*	Transesterification of oils	Same in Table 1	Same in Table 1	Same in Table 1
Sorbitol	Hydrogenation of glucose	Isosorbide, anhydrosugars Propylene glycol, lactic acid Branched polysaccharides	Dehydration Hydrogenolysis Direct polymerization	PET like polymers Antifreeze, PLA Water soluble polymers
Xylitol/arabinitol	Hydrogenation of sugars or extraction from biomass pre-treatment processes	Xylaric and xylonic acids Arabonic and Arabinoic acids Polyols (propylene and ethylene glycols), lactic acid Xylitol, xylaric, xlyonic, polyesters and nylons	Oxidations Hydrogenolysis Direct polymerization	New uses Antifreeze, UPRs New polymer

From Werpy et al. (2004).

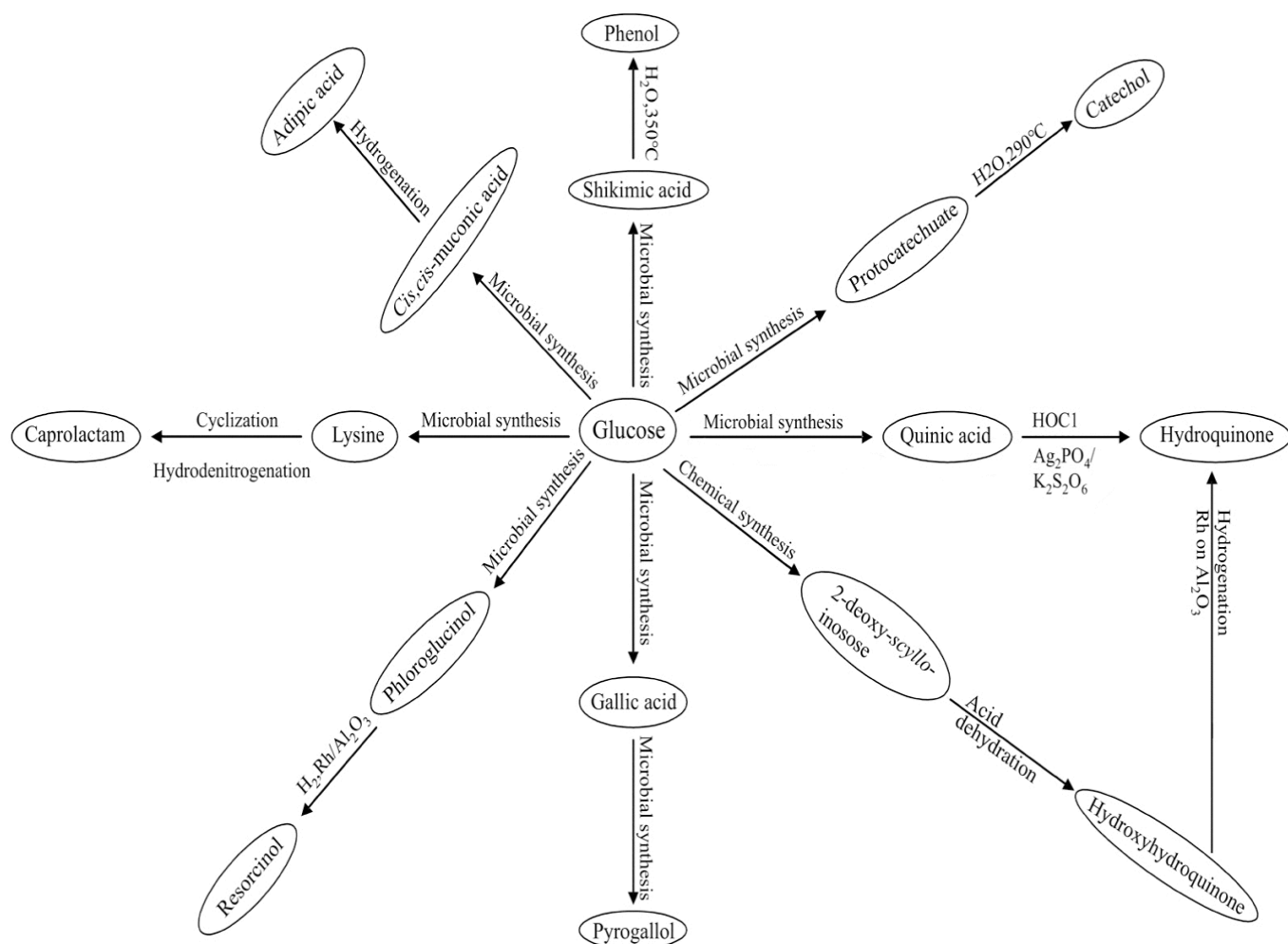


Fig. (1). Benzene-free aromatic chemicals and their synthesis route from glucose.

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