Catalytic Conversion of Renewable Biomass Resources to Fuels and Chemicals

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Abstract

Lignocellulosic biomass is renewable and cheap, and it has the potential to displace fossil fuels in the production of fuels and chemicals. Biomass-derived carboxylic acids are important compounds that can be used as platform molecules for the production of a variety of important chemicals on a large scale. Lactic acid, a prototypical biomass derivative, and levulinic acid, an important chemical feedstock produced by hydrolysis of waste cellulosic materials, can be upgraded using bifunctional catalysts (those containing metal and acid sites), which allows the integration of several transformations (e.g., oxygen removal and C–C coupling) in a single catalyst bed. This coupling between active sites is beneficial in that it reduces the complexity and cost of the biomass conversion processes. Deoxygenation of biomass derivatives is a requisite step for the production of fuels and chemicals, and strategies are proposed to minimize the consumption of hydrogen from an external source during this process.

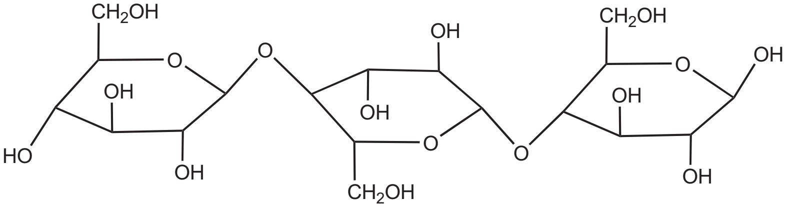
INTRODUCTION

Fossil fuels are the primary source of energy, chemicals, and materials for our modern society. It is estimated that almost 90% of the energy consumption in the world is currently derived from fossil fuel resources, such as petroleum, coal, and natural gas, and this percentage is even higher (96%) for the transportation sector (1). However, the use of fossil fuels for the generation of energy and the production of chemicals and materials is associated with several important issues. First, fossil fuel reserves are finite, and the current consumption rate is increasing yearly because of the higher demand of industrialized countries and the development of emerging economies, which will lead to inevitable depletion within a few decades (2). Second, the consumption of fossil fuels leads to net emissions of CO_2 into the atmosphere, which contribute to global warming and climatic issues (3). Third, the uneven geographical distribution of the fossil fuel reserves (4) is the origin of political, economic, and security issues worldwide. These important concerns require society to search for renewable sources of energy and chemicals. In this sense, aggressive government directives, both in the U.S. (5) and in the European Union (6), are stimulating a gradual shift of our current fossil fuel-based economy toward a more renewable energy-based one, and ambitious goals to produce 20% of fuels and 25% of chemicals from renewable sources by 2030 have been established (7).

Biomass as a Renewable Source of Carbon

Biomass, being renewable, is the only sustainable source of energy and organic carbon for our industrial society (8). The U.S. Department of Energy has estimated that more than 1 billion tons of dry biomass, enough to displace 30% of U.S. annual petroleum consumption, could be harvested annually from fields and forests without major agricultural changes and while still meeting the food, feed, and export demands of the U.S. (9). The production of fuels and chemicals from biomass has, among others, two unquestionable advantages. The main benefit is environmental, associated with the reduction of the net emissions of CO_2 (a greenhouse gas) into the atmosphere. Unlike fossil fuels, biofuels are considered to be carbon neutral because any CO_2 produced during fuel combustion is consumed by subsequent biomass regrowth (10). Additionally, the establishment of a new energy system based on biomass would improve the economy of those countries determined to accept the challenge. In this sense, economies would be (*a*) less sensitive to the strong fluctuations in the price of oil (11) and (*b*) stronger as a result of job creation in sectors such as the agricultural, forest management, and oil/chemical industries (12). However, important moral and ethical questions have arisen from the use of edible biomass (sugars, starches, and vegetable oils) for the large-scale production of fuels. These have driven researchers around the world to develop technologies to process nonedible biomass (lignocellulosic biomass), thereby permitting sustainable production of fuels (so-called second-generation fuels) and chemicals without affecting food supplies. Additionally, the lower cost and faster growth of lignocellulosic biomass compared with food crops (13) and its high availability (9, 14) make this resource an attractive raw material for substitution of petroleum. Consequently, this review will focus on lignocellulosic biomass.

Lignocellulosic biomass is a complex fibrous material that can be found in the cell walls of plants. It consists of three main structural units: cellulose, hemicellulose and lignin (15, 16). Cellulose is a polymer of glucose units (with a molecular weight ranging from 3×10^5 to 5×10^5) connected linearly by β-glycoside linkages (17) as shown in **Scheme 1**:



Scheme 1. Chemical structure of cellulose.

This arrangement allows a high degree of hydrogen bonding between different cellulose chains, conferring this material with superior stability and resistance to chemical attack (18), low surface area, and a high degree of crystallinity. Cellulose typically accounts for 40–50% of a particular lignocellulose source (16). Unlike cellulose, hemicellulose possesses a heterogeneous composition. It is a highly branched, amorphous polymer of five different C_5 and C_6 sugars that binds the cellulose chains together and usually accounts for 20–30% of the total mass of a lignocellulose source. Lignin is a three-dimensional polymer of propyl-phenol groups that forms the walls of lignocellulosic materials and provides structural rigidity. It is typically found in woody biomass and usually comprises approximately 15–25% of lignocellulose.

Methods for Converting Biomass to Fuels and Chemicals

Because of the structural and chemical complexity of lignocellulosic biomass, various processes have been employed to convert this resource into fuels and chemicals. Current technologies involve three major routes: gasification, pyrolysis/liquefaction, and hydrolysis (**Figure 1**). The first route is well-suited for the production of fuels, whereas pyrolysis/liquefaction and hydrolysis provide attractive paths for the production of biomass derivatives that can be subsequently upgraded to useful chemicals and/or fuels for the transportation sector.

Gasification of biomass requires high temperatures (e.g., >1100 K), which are necessary for the endothermic formation of synthesis gas, a valuable mixture of CO and H_2 (15). In the gasification process, cofeeding an oxidizing agent (e.g., oxygen, air, steam) in the gasifier causes partial combustion of the biomass. The synthesis gas obtained can be converted into a distribution of alkanes through well-established Fischer-Tropsch approaches (19–21) or can be used to produce methanol by methanol synthesis (22, 23). Moreover, the H_2/CO ratio of the synthesis gas can be adjusted by using a water gas shift (WGS) catalyst (24) or by in situ CO_2 absorption (25) to produce H_2-enriched streams. The patent literature contains a variety of gasifier designs (26). Even though gasification can be used to process the three components of lignocellulosic biomass, the low-purity and highly diluted synthesis gas stream (27), the negative influence of the high moisture content of the biomass on the thermal efficiency of the process (14), and the large amounts of biomass required (which lead to high costs for transporting the low–energy density biomass to a central location) (28, 29) are challenges for the development of this route.

Unlike gasification, pyrolysis and liquefaction involve the thermal decomposition of biomass under an inert atmosphere at lower temperatures (573–973 K) (15, 30). These processes convert biomass to a dark organic liquid, commonly known as bio-oil, which consists of a complex mixture of more than 300 highly oxygenated compounds, polymeric carbohydrates, and lignin fragments (10, 30), with the bio-oil having a water content of typically 25 wt%. When separated into their components, bio-oils are good sources of chemicals. However, the high oxygen content of the molecules present in bio-oils confers on this liquid a low energy content. Thus, to be used as a transportation fuel, the bio-oil requires further deoxygenation, which typically involves consumption of an external supply of H_2 (31, 32), or additional upgrading over zeolites to produce aromatic fuels (33). The simplicity of pyrolysis (usually requiring only one reactor and low capital

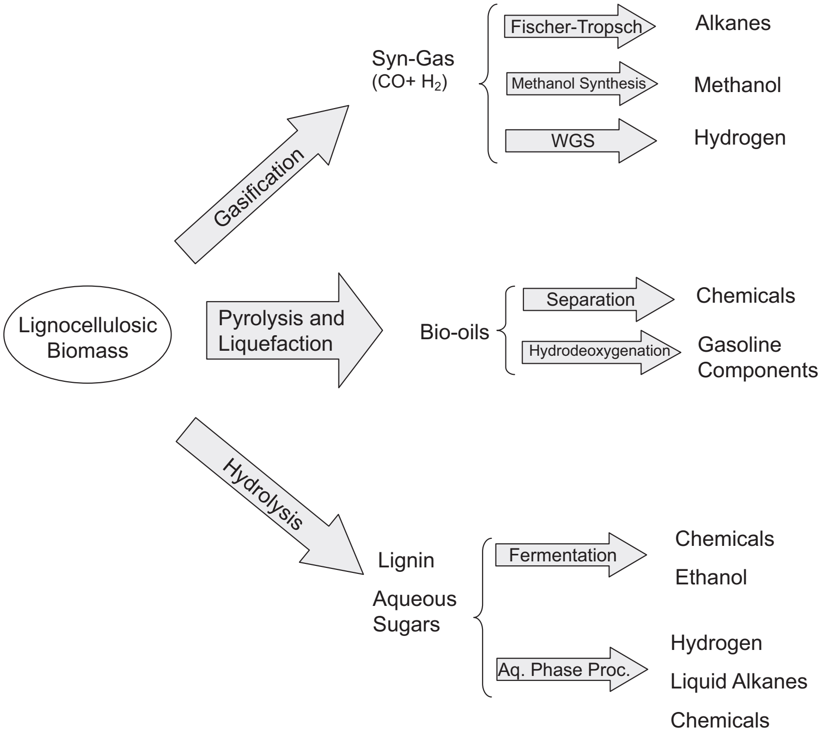


Figure 1

Routes for the conversion of lignocellulosic biomass into fuels and chemicals. WGS, water gas shift. Adapted from References 1 and 14.

costs) contrasts with the lack of selectivity that leads to additional costly separation and upgrading processes to convert the bio-oils into fuels and chemicals.

Acid and enzymatic hydrolysis are effective for separating the carbohydrate and lignin fractions of lignocellulosic feeds at lower temperatures than those used in gasification and pyrolysis. In contrast to the starches present in edible biomass, the complex structure of lignocellulose, with its highly crystalline, low–surface area cellulose protected by lignin, confers this material with a high degree of recalcitrance, which makes its depolymerization into the corresponding monomer sugars a difficult task (34, 35). Consequently, to deconstruct lignocellulose into sugars, an effective pretreatment step must be employed to break the lignin protection so that the acids or enzymes can more easily access and hydrolyze the cellulose and hemicellulose fractions of the biomass. The morphology of the lignin network is modified in aqueous solutions at mild temperatures, which allows the hydrolysis of hemicellulose to occur under the same conditions in the presence of acids. The crystalline structure of cellulose protects its β-glycoside ether linkages from being accessed by the acid catalyst, so more severe conditions are required for full deconstruction of this polymer (15). Several pretreatment methodologies involving physical, chemical and biological treatments have been developed to depolymerize lignocellulosic materials (36, 37), and Wyman et al. have recently studied the effects of these pretreatments on the morphology and structure of biomass (38). The goal of these processes is to obtain an aqueous sugar monomer solution from lignocellulose at low cost. In this sense, it has been estimated that unrefined sugar solutions can be produced from corn stover at approximately 10¢ kg^{-1} of sugar (39), and future improvements in technologies could decrease the production cost of sugars to as low as 5¢ kg^{-1} (40).

Biomass Derivatives: Catalytic Strategies for Conversion to Fuels and Chemicals

Aqueous solutions of carbohydrates (derived from the cellulose and hemicellulose fractions of biomass) can serve as cheap feedstocks for the production of fuels through both chemical and biological processes. Presently the production of ethanol by bacterial fermentation of sugars is the primary technology for the generation of liquid fuels from biomass resources. The U.S. produced 15 billion liters of ethanol in 2005, of which 97% was generated from starch-based biomass, such as corn (41), and research is being conducted on how to use the more plentiful and inexpensive lignocellulose as the carbohydrate source (39). Ethanol blended with gasoline is currently used as a fuel in the U.S., although the low alcohol concentrations of the mixture (e.g., 10 vol%) and the high solubility of water in ethanol are limitations in its use as a transportation fuel. These limitations can be overcome by converting biomass-derived carbohydrates to hydrocarbon fuels chemically similar to those currently used in the transportation sector so that they can be processed and distributed by existing petrochemical technologies and infrastructure. However, the chemical composition of carbohydrates, which are C_5 or C_6 compounds with a high level of functionality (e.g., $-OH$, $-C{=}O$, $-COOH$), is different than that of transportation fuels, which are larger (e.g., C_5–C_{12} for gasoline, C_9–C_{16} for jet fuel, and C_{10}–C_{20} for diesel applications) and unfunctionalized. Consequently, various reactions involving oxygen removal (e.g., hydrogenolysis, dehydration, hydrogenation) combined with C−C bond formation steps (e.g., aldol condensation, ketonization, oligomerization) to increase the molecular weight are necessary to carry out the transformation of carbohydrates to hydrocarbon fuels (1, 42–44). As will be addressed below, the requisite deoxygenation of biomass derivatives ideally should be carried out with minimal use of an external source of hydrogen to make the process economically feasible, which is critical for large-scale biofuels production (10). Toward this goal, strategies for the complete reforming of sugars (by C−C bond breaking reactions) to produce renewable H_2, in combination with CO_2, have also been developed (45, 46).

Aqueous solutions of sugars obtained after hydrolysis of biomass can subsequently be converted to a variety of derivatives through chemical or biological processes, as depicted in **Figure 2** for glucose. Unlike the production of fuels from biomass, the conversion of sugars into chemicals takes place with partial removal of oxygen, leaving intact some functionalities that serve as reactive centers for subsequent upgrading. This strategy contrasts with that used in the petrochemical industry, which is based on the addition of oxygen to unfunctionalized feedstocks. In the same way as the entire petrochemical industry essentially can be constructed from a few building blocks (47), a recent study has identified (by screening approximately 300 substances) 12 of the most promising biomass derivatives for further research on the basis of their production costs and potential to serve as platform molecules for the development of biorefinery processes (48). The majority of these compounds can be derived from glucose by fermentation and/or chemical transformations (**Figure 2**). It is noteworthy that two-thirds of these potential renewable building blocks are organic acids, which is indicative of the importance of these compounds in the establishment of a renewable chemical industry (49, 50). In this review, we will explore different upgrading strategies for two of these renewable acids, one of them (lactic acid) obtained by fermentation and the other (levulinic acid) obtained by chemical dehydration of biomass.

The high oxygen content of biomass-derived compounds gives them low volatility, high solubility in water, high reactivity, and low thermal stability, properties that favor the processing of these resources by liquid-phase technologies at moderate temperatures (17, 51, 52). A variety of hydrocarbon fuels and chemical intermediates can be produced from biomass feeds by employing various types of reactions including dehydration, isomerization, C−C coupling, reforming, hydrogenation, oxidation, and hydrogenolysis (10). Some of these reactions (e.g., dehydration, hydrogenation, and hydrogenolysis) are especially useful for oxygen removal, which is necessary for the requisite deoxygenation of biomass derivatives, whereas other reactions (e.g., C–C coupling) allow conversion of low–added value compounds into chemicals with high demand and market. Because the chemical composition of biomass feedstocks is quite different from that of the final products, multiple processing steps are typically required in such transformations, which negatively affects the economy of the process. Consequently, the conversion of biomass-derived feedstocks to fuels and chemicals in a manner that is cost competitive with petrochemical-related technologies requires the development of new approaches that simplify the processing by reducing the number of reactors and purification/separation steps. In this sense, catalytic coupling at various length scales has been proposed as a useful approach for improving the efficiency of biomass conversion processes (53). In particular, four types of catalytic coupling have been examined, involving coupling between (*a*) multiple functions at an active site (functional coupling), (*b*) different types of active sites in a single catalyst bed (active site coupling), (*c*) multiple reactions (chemical reaction coupling), and (*d*) reactions and/or separations involving multiple phases (phase coupling). For example, our group has recently developed a two-step strategy for upgrading biomass oxygenates (glucose and sorbitol). This process is based on a reduction of the feed oxygen content in a first step to produce a stream of monofunctional compounds, followed by upgrading these compounds through C–C coupling reactions (43). The concept of functional coupling (e.g., the incorporation of different functions at the active site) is especially relevant for this strategy because the production of hydrogen and the removal of oxygen are achieved in the first step by incorporating both Pt and Re at the active sites, which leads to the production of targeted monofunctional compounds in a single reactor. Herein we will show how a related concept in catalytic coupling can be used to efficiently process two important biomass derivatives, lactic acid and levulinic acid. In particular, we employ active site coupling, in which two different types of catalytic sites are combined within the same reactor. Specifically, by using bifunctional catalysts containing metal and acid sites, it is possible to remove oxygen from the acids (by dehydration/hydrogenation reactions) and upgrade reactive intermediates (by C–C coupling reactions) in a single reactor, leading to the direct production of desired products. Additionally, the efficiency of these processes can also be improved using dual-bed systems in which different sites are situated in different catalytic beds, as previously employed for the conversion of glycerol to H_2/CO combined with Fischer-Tropsch synthesis (54).

LACTIC ACID

A Prototypical Biomass-Derived Molecule

Lactic acid (2-hydroxypropanoic acid) is the most widely occurring carboxylic acid in nature (55). The world's annual production was 1.2 × 10^5 tons per year in 2005 (56), 90% of which was produced by bacterial fermentation of biomass, with the remainder synthesized by hydrolysis of lactonitrile (57). Traditionally lactic acid has been used in food and food-related applications; however, since the early 1990s the lactic acid market has been expanding steadily at a rate of 4 × 10^4 tons per year as a result of the development and commercialization of new applications (55). These new uses are related to the industrial production of polymers and chemicals. In particular, lactic acid, because of its bifunctionality, can be converted through a variety of reactions (**Figure 3**) to such compounds as acetaldehyde (59) (via decarbonylation/decarboxylation), acrylic acid (58–61) (via dehydration), propanoic acid (62) (via reduction), 2,3-pentanedione (63) (via condensation), and polylactic acid (PLA) (64, 65) (via self-esterification to dilactide and subsequent polymerization).

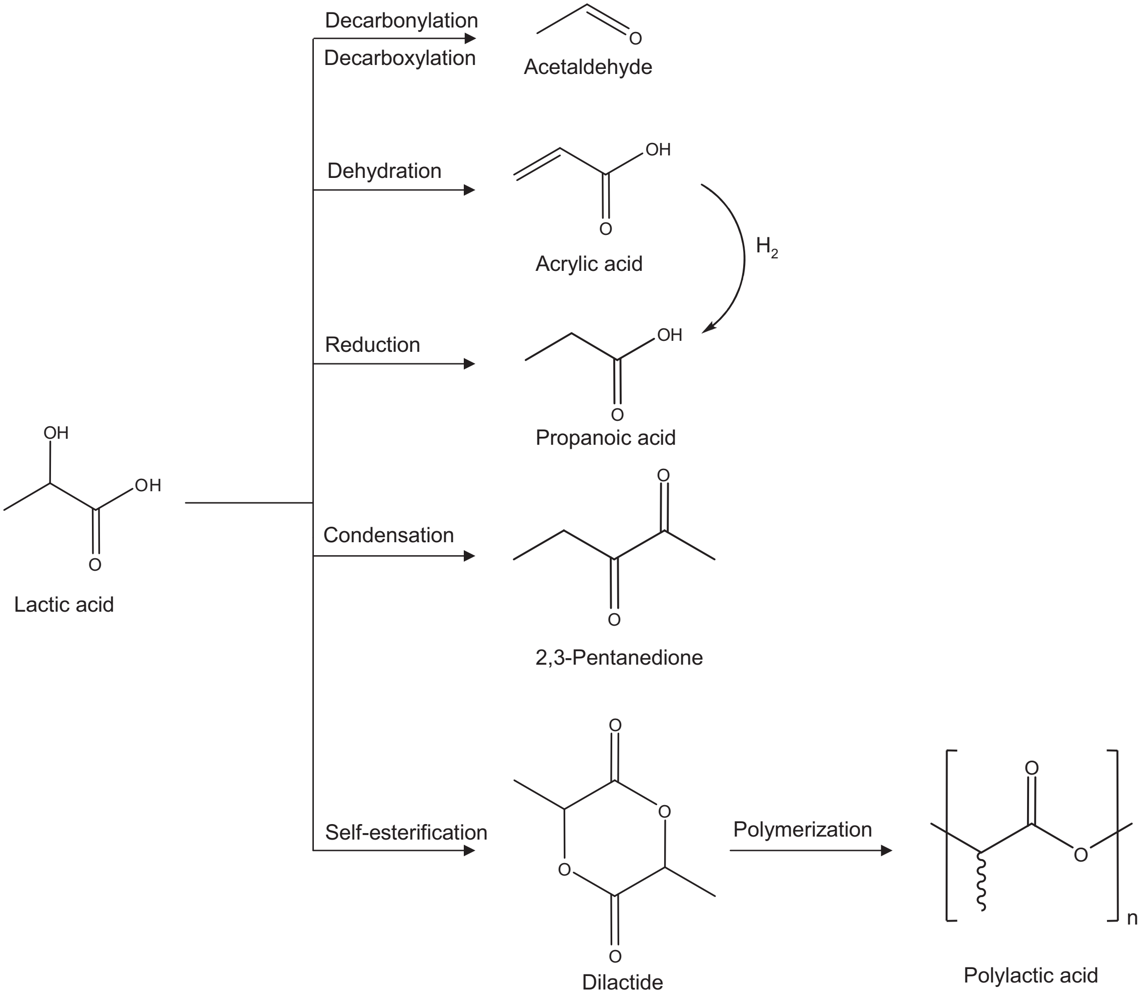


Figure 3

Lactic acid derivatives. Adapted from Reference 58.

First and foremost, lactic acid is an attractive feedstock for the renewable chemical industry (49). In addition, lactic acid has interest from a fundamental point of view because it can be considered as a prototype of an overfunctionalized biomass-derived molecule. Accordingly, studies of catalytic reactions involving lactic acid can provide relevant information for the upgrading of other more complex biomass derivatives. For example, it has been proposed that an effective strategy for the catalytic processing of renewable feedstocks involves a previous reduction of the oxygen content to control reactivity (66), which leads to the production of monofunctional intermediates that still possess some reactivity and can thus be subsequently upgraded to fuels and chemicals (43). In the case of lactic acid, the presence of two adjacent functional groups (−OH and −COOH) in a small molecule of only three carbon atoms clearly leads to its high reactivity as well as its tendency to decompose at elevated temperatures (67). Effective approaches for controlling the reactivity of this resource are thus required.

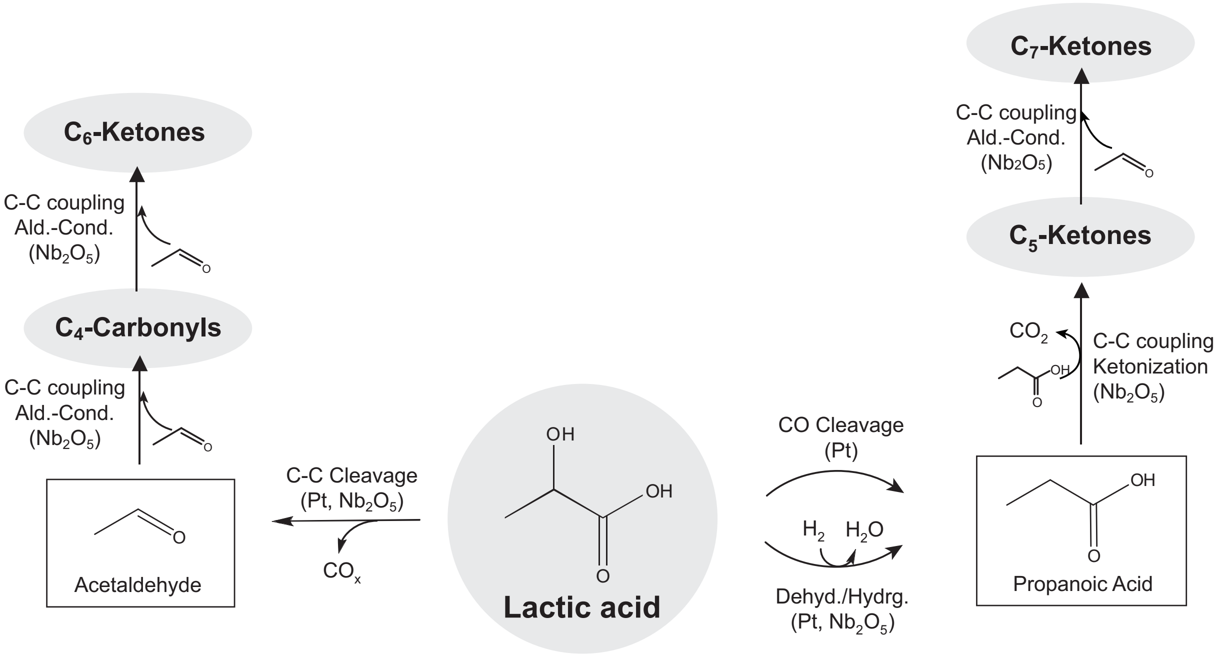


Figure 4

Reaction pathways for the catalytic upgrading of lactic acid over Pt/Nb_2O_5. Adapted from Reference 62.

Catalytic Strategies to Upgrade Lactic Acid to Fuels and Chemicals

Recently, coupling between active sites in a single reactor (53) has been applied to the catalytic upgrading of lactic acid (62). In this respect, a bifunctional Pt/Nb_2O_5 catalyst containing metal and acidic sites was used to control the high reactivity of lactic acid, directing the synthesis to the production of targeted compounds in a one-step process (**Figure 4**). The removal of oxygen from lactic acid is favored by the use of bifunctional catalysts through a cycle of dehydration (over the acid sites of Nb_2O_5) and hydrogenation (catalyzed by platinum) (44), which leads to the formation of propanoic acid, the first monofunctional intermediate. Simultaneously, lactic acid can be deoxygenated through decarbonylation/decarboxylation reactions, which lead to the formation of monofunctional acetaldehyde and the release of gaseous CO and CO_2. The acidity of Nb_2O_5 also favors the decarbonylation of lactic acid (59). This example of lactic acid conversion thus shows two possible strategies to deoxygenate biomass derivatives: (*a*) through dehydration/hydrogenation reactions that involve the removal of water but require the consumption of hydrogen from an external source and (*b*) through decarbonylation/decarboxylation reactions that take place without utilization of external hydrogen but involve the loss of carbon into the gas phase. The importance of the use of an external source of hydrogen for the deoxygenation of biomass-derived compounds will be discussed below.

The two monofunctional compounds, propanoic acid and acetaldehyde, along with gaseous CO and CO_2, are the primary products observed when aqueous solutions of lactic acid are processed over Pt/Nb_2O_5 at moderate temperatures (523 K) and hydrogen pressures (57 bar) (68). An increase in the conversion (by increasing temperature or decreasing space velocity) leads to the formation of an organic layer that spontaneously separates from water and is mainly composed of propanoic acid and ketones in the C_4–C_7 range. When optimum reaction conditions and concentrated solutions of lactic acid are used, approximately 50% of the carbon in the feed can be stored in this organic layer. In contrast, when a monofunctional control catalyst of Pt supported on inert carbon black (Vulcan) is utilized under the same conditions, no organic layer is produced. Instead, the majority of the carbon in lactic acid is lost into the gas phase as CO, CO_2, and methane, which indicates that niobia (Nb_2O_5) plays a key role in the generation of the organic phase. The chemistry involved in the formation of the C_4–C_7 ketones from the intermediates acetaldehyde and propanoic acid is depicted in **Figure 4**. Propanoic acid can be partially converted into 3-pentanone by ketonization reactions (69) that involve the condensation of two molecules of acid to produce a larger symmetric ketone. This reaction is of interest in the catalytic upgrading of biomass-derived acids (70) because the formation of a more hydrophobic, larger compound (2n-1 carbon atoms) takes place with the simultaneous reduction of the oxygen content of the acid (i.e., the reaction involves the removal of CO_2 and water). Total conversions of propanoic acid to pentanone can be achieved by using a second bed of ceria-zirconia (following the Pt/Nb_2O_5) at the same pressure and temperature conditions (62). Ceria-zirconia has also exhibited excellent properties for the selective ketonization of carboxylic acids and esters present in mixtures with other biomass-derived monofunctional compounds (43, 70). The remainder of the C_4–C_7 ketones detected in the organic phase are formed from acetaldehyde, which acts as a building block for the production of C–C bonds by means of aldol condensation reactions (**Figure 4**). Three reasons support this statement: (*a*) acetaldehyde is known to readily undergo self- or cross-condensation with ketones (71); (*b*) high concentrations of this compound are produced in the reactor because, as indicated above, the acidity of niobia favors the decarbonylation of lactic acid; and (*c*) niobia-supported metal catalysts have been previously reported to be appropriate materials for the condensation of carbonyls to larger compounds (72, 73). Niobia, as indicated above, plays a crucial role in directing the synthesis toward the formation of the larger ketones. Interestingly, by using a bifunctional catalyst (containing metal and acid sites), the series of reactions leading to the desired compounds (dehydration/hydrogenation and C–C coupling) are simply carried out in a single reactor, thereby reducing the potential operational and capital cost of the process. Additionally, its strong acidity and stability under high-water environments make niobia a suitable material for the deoxygenation of biomass derivatives (44, 74).

In addition to the fundamental information obtained, several applications can be anticipated for the catalytic processing of lactic acid over bifunctional Pt/Nb_2O_5 catalysts. For example, the organic layer produced from this processing can be separated into its components and serve as a source of valuable chemicals currently obtained exclusively from petroleum. Additionally, and without the need for separation, the oil can be treated with a Ru/C catalyst to transform the ketones into the corresponding alcohols, and this liquid mixture of alcohols in the C_4–C_7 range can be used as a high–energy density liquid fuel for the transportation sector (62).

Finally, as will be outlined in the next section, fundamental knowledge obtained from studies of lactic acid reactivity on different types of heterogeneous catalysts provides valuable information that can be applied to the processing of other overfunctionalized derivatives obtained from biomass, such as levulinic acid.

LEVULINIC ACID

An Important Biomass-Derived Feedstock

Levulinic acid (4-oxopentanoic acid) is a high–boiling point (520 K), water-soluble acid (pKa = 4.59) that crystallizes at room temperature (melting point 311 K) (75). As in the case of lactic acid, a molecule of levulinic acid contains two reactive functional groups (–C=O and –COOH) that provide the opportunity for a variety of synthetic transformations (76). Among the top 12 value-added chemicals available from biomass mentioned in the Introduction (48), only levulinic acid can be produced using exclusively acid-catalyzed chemical processing, e.g., dehydration (**Figure 2**). In contrast, the other top-value biomass derivatives require either a biological route, such as fermentation, or hydrogenation or oxidation in the production process. This attribute makes levulinic acid especially attractive because a variety of inexpensive lignocellulosic feeds can be used for the direct production of this thermodynamically stable molecule. Thus, cane sugar (77), corn starch (78, 79), rice straw (80), pulp slurry (81), woods (82, 83), newspapers (84), cellulose (85), and sugars (86, 87) in mixtures with mineral acids, such as HCl (78), HBr (85), and H_2SO_4 (86, 88, 89), or solid acids (87, 90), have been used to produce levulinic acid. The dehydration of C_6 sugars by acids generates levulinic acid with a maximum yield of 64.5% by weight because it is coproduced with equimolar amounts of formic acid (76). However, yields equal to approximately two-thirds of this maximum yield are typically obtained because of the formation of unwanted black, insoluble materials called humins.

Several technologies have been developed for the large-scale continuous production of levulinic acid. Dunlop & Wells (91) designed a plant for industrial production of levulinic acid from corncob furfural residue using dilute solutions of sulfuric acid (3 wt%) and elevated temperatures (442 K). The humins were separated from the reaction mixture by a filter unit, and the levulinic acid was separated from the aqueous sulfuric phase by extraction with an organic solvent. The levulinic acid yield obtained was 20% by weight. Improvements in levulinic acid yields were achieved more recently using reactive extrusion at variable temperatures (92). The levulinic acid yield attained was significantly increased (48% by weight) because of the use of easily hydrolysable corn starch as feedstock and of more concentrated sulfuric acid solutions (5 wt%). However, the most promising technology proposed for the industrial production of levulinic acid, patented by the Biofine Corporation (93, 94), eliminates many of the existing problems associated with its production. This approach uses a double-reactor system and minimizes the formation of by-products and the resulting separation problems (**Figure 5**). The carbohydrate feedstock and sulfuric acid catalyst solution are mixed, and the slurry is supplied continuously to a tubular reactor in which a mixture of C_5 and C_6 sugars is produced at high temperature (483–503 K) for short residence times (13–25 s) in the presence of 1–5 wt% mineral acid. This initial hydrolysis produces hydroxymethylfurfural (HMF), which is continuously removed and fed to a second reactor where HMF is further converted at lower temperatures (468–488 K) but longer residence times (15–30 min) to produce levulinic acid. Interestingly, the reaction conditions in the second reactor are adjusted to vaporize the furfural by-product (formed by dehydration of C_5 sugars) and formic acid (the coproduct of the dehydration of the hexoses), which are condensed and further collected. Solid humins are removed from the levulinic acid solution in a filter-press unit and collected as combustible wastes (**Figure 5**). The levulinic acid yield, based on the hexose content of the carbohydrate-containing feedstock, is one of the best reported in the literature (approximately 40 wt%). Additionally, this technology has been used successfully with diverse, inexpensive cellulose-containing waste materials including paper mill sludge, urban waste paper, agricultural residues, and cellulose fines from papermaking. As a result, levulinic acid can be produced at low cost (8–20¢ kg^{-1}) (95), which makes this compound suitable for use as a platform molecule. This price estimate should, however, be reevaluated in the current economic climate. Several plants have been constructed and operated with tons of waste cellulosic materials per day both in the U.S. (95) and in Europe (96).

Levulinic acid has been suggested as a platform molecule for the production of specific commodity chemicals (95, 97, 98). In particular, levulinic acid can be converted into methyltetrahydrofuran (MTHF) (99) and various levulinate esters (100, 101) that can be used as additives in gasoline (102) and biodiesel (103), respectively. The halogenation of the methyl group of

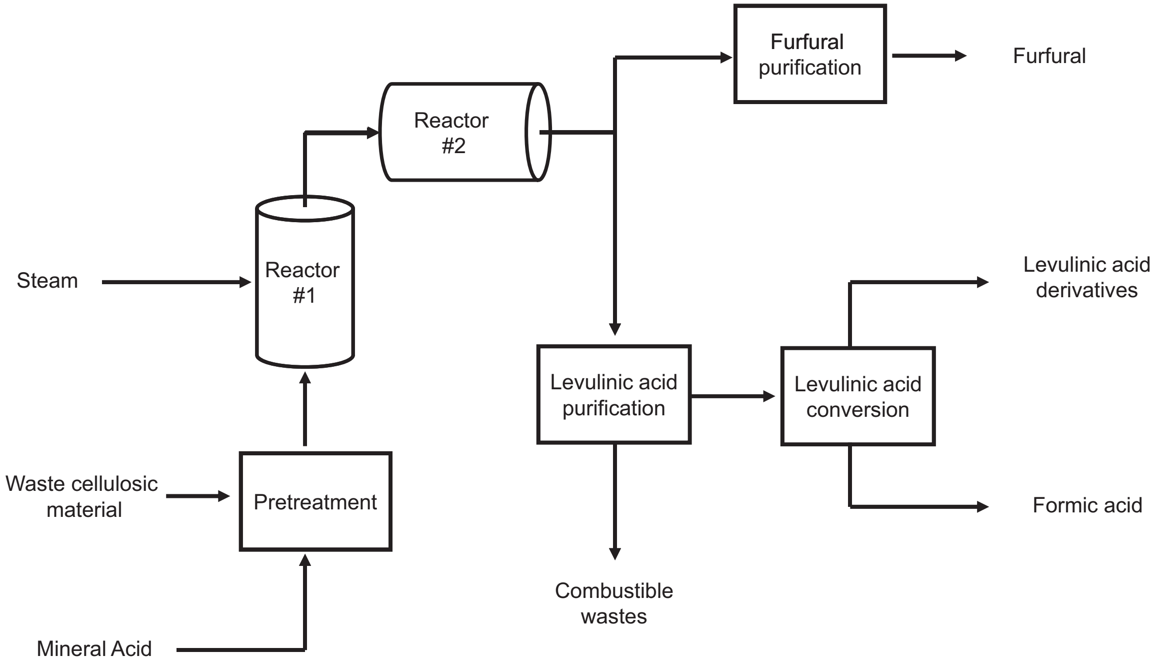


Figure 5

Schematic diagram of the Biofine process. Adapted from Reference 95.

levulinic acid (75) allows this compound to be converted to δ-aminolevulinic acid (DALA) (104), a biodegradable pesticide with a projected market of 100–200 million kg year^{-1} (95). An intermediate in the production of DALA is β-acetylacrylic acid. This material could be used in the production of new acrylate polymers for a market of 1.1 billion kg yr^{-1} (48). Through reaction of the carbonyl group in levulinic acid with aromatics or heterocyclic alcohols, it is possible to produce 4,4-diaryl-substituted valeric acids, such as diphenolic acid (DPA) (105), which has been proposed as a substitute for bisphenol A in the polymer market (95). The complete reduction of levulinic acid to 1,4-pentanediol (for the production of new polyesters) and its oxidation to succinic acid (1,4-butanedioic acid), a versatile compound for the production of important derivatives (106), are also significant routes to expand the market for levulinic acid as a chemical feedstock.

Reaction Pathways for Levulinic Acid Conversion: Thermodynamic Considerations

Figure 6 shows various reaction pathways (along with the thermodynamics involved) that our group has employed to upgrade levulinic acid into hydrocarbon fuels and chemicals. For each individual step the numeric value is the calculated standard Gibbs energy change at 523 K, whereas the value in parentheses is the standard enthalpy change at 523 K for the same step. This scheme considers four possible reactions of levulinic acid. In particular, levulinic acid can be decarbonylated to produce methyl-vinyl ketone, isomerized to form pseudolevulinic acid (76), hydrogenated to produce 4-hydroxy-pentanoic acid (97), and decarboxylated to form 2-butanone. Pseudolevulinic acid can dehydrate to form α-angelica lactone, which can isomerize to β-angelica lactone. Both lactones can decarbonylate to form methyl-vinyl ketone, as described elsewhere (107, 108),

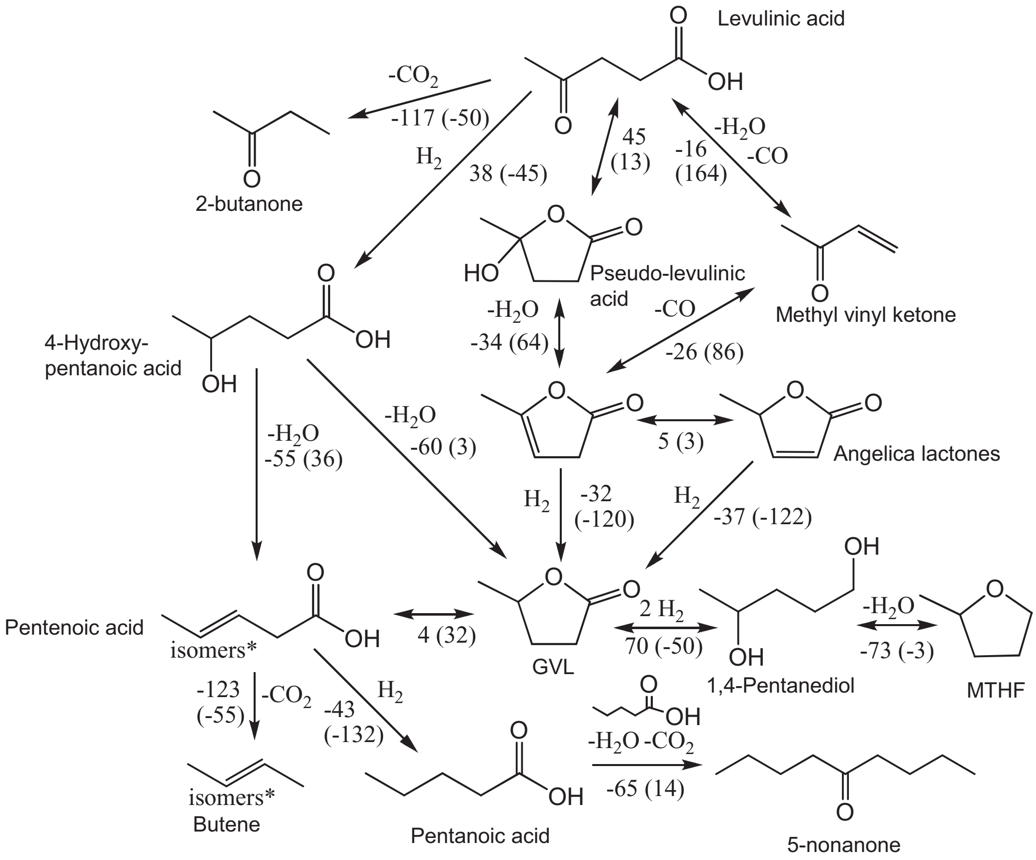


Figure 6

Reactive pathways for conversion of levulinic acid to several products. Numeric values indicate ΔG° (ΔH°) in kJ mol^{-1} at 523 K. *Thermodynamics were calculated from *trans*-3-pentenoic acid and *trans*-2-butene.

or they can be hydrogenated to form γ-valerolactone (GVL). The dehydration of 4-hydroxy-pentanoic acid can also yield GVL, or it can produce pentenoic acid isomers. As mentioned above, hydrogenation of GVL yields 1,4-pentanediol, which can be dehydrated to produce MTHF. Alternatively, GVL can be ring-opened to form pentenoic acid isomers (109), which can undergo decarboxylation to produce a mixture of butenes or can be hydrogenated to produce pentanoic acid. Lastly, pentanoic acid can be converted into 5-nonanone by means of a ketonization reaction (69). From data in **Figure 6** it is apparent that reactions releasing carbon dioxide (e.g., decarboxylation and ketonization) have large negative Gibbs energy changes and are thermodynamically favored. Consequently, the production of 2-butanone from levulinic acid ($\Delta G^\circ = -117$ kJ mol^{-1}), the formation of butenes from pentenoic acid ($\Delta G^\circ = -123$ kJ mol^{-1}), and the ketonization of two molecules of pentanoic acid to form 5-nonanone ($\Delta G^\circ = -65$ kJ mol^{-1}) are processes favored at 523 K. The total Gibbs energy changes from levulinic acid to these species are −117, −140, and −187 kJ mol^{-1}, respectively. The decarboxylation reactions are also exothermic, and although this usually implies that they should be more favored at lower temperatures, the large change in free energy renders these reactions essentially irreversible. Ketonization is an endothermic reaction ($\Delta H^\circ = 14$ kJ mol^{-1}) that takes place at higher temperatures (70).

All of the hydrogenation reactions considered here are exothermic, and they are more favorable for saturation of C=C double bonds than for C=O double bonds or C–O cyclic bonds. The hydrogenation of angelica lactones to GVL ($\Delta G° = -32$ kJ mol^{-1}) and of pentenoic acid to pentanoic acid ($\Delta G° = -43$ kJ mol^{-1}) contrasts with the hydrogenation of levulinic acid to 4-hydroxypentanoic acid ($\Delta G° = 38$ kJ mol^{-1}). The thermodynamics of ring opening hydrogenation depend on the C–O bond that is broken. Thus, the cyclic ester hydrogenation involved in the conversion of GVL to 1,4-pentanediol is not favorable at 523 K ($\Delta G° = 70$ kJ mol^{-1}), whereas the cyclic ether hydrogenation involved in the reaction of tetrahydrofuran to *n*-butanol is highly favorable, with a net change in free energy of -54 kJ mol^{-1} (110). Because all these hydrogenation reactions are exothermic, the above-mentioned reactions should be favored at lower temperatures.

Figure 6 shows that dehydration reactions to form unsaturated compounds and water are favored at 523 K. The enthalpy change, however, depends upon the type of unsaturated compound that is formed. Dehydrations to form C=C bonds, such as those involved in the dehydration of pseudolevulinic acid to α-angelica lactone ($\Delta H° = 64$ kJ mol^{-1}) or in the dehydration of 4-hydroxypentanoic acid to pentenoic acid ($\Delta H° = 36$ kJ mol^{-1}), are endothermic. However, dehydration reactions to form ring structures, such as those involved in the conversion of 4-hydroxypentanoic acid to GVL ($\Delta H° = 3$ kJ mol^{-1}) or in the dehydration of 1,4-pentanediol to MTHF ($\Delta H° = -3$ kJ mol^{-1}), are close to thermoneutral.

Finally, the last reactions to be considered are isomerization and decarbonylation. Isomerization processes typically involve a small change in free energy between species, such as 5 kJ mol^{-1} between the angelica lactones and 4 kJ mol^{-1} between GVL and pentenoic acid, and interconversion between these species is easily accomplished owing to low barriers. Decarbonylation, although favored (-26 kJ mol^{-1} for α-angelica lactone to methyl-vinyl ketone), is highly endothermic (86 kJ mol^{-1} for this same reaction), necessitating high temperatures for reaction.

Production of Fuels from Levulinic Acid: Catalytic Coupling

We have employed some of the routes described above to upgrade concentrated aqueous solutions of levulinic acid into hydrocarbon fuels for use in diesel and gasoline applications. Levulinic acid, as is common for biomass derivatives, suffers from an excess of functionality that makes it difficult to control reactivity and direct the conversion to targeted compounds. However, as for the case of lactic acid, this difficulty can be overcome by means of a two-step strategy (involving oxygen removal and upgrading of intermediates) that is simplified by the utilization of active site coupling (53). Thus, by using a bifunctional Pd/Nb_2O_5 catalyst it is possible to upgrade levulinic acid to fuels with a limited number of reaction and separation steps (**Figure 7**). Levulinic acid, in the presence of strong mineral or solid acids, dehydrates readily at moderate temperatures (573–623 K) to yield the corresponding cyclic product, α-angelica lactone (75, 97). This compound is a well-known coke precursor (109), and we have observed that all upgrading routes through this intermediate lead to deactivation of the catalyst and/or loss of carbon. Consequently, to avoid the formation of this compound, an alternative path can be employed to initiate the synthesis through the formation of the saturated lactone, GVL, which is stable and water-soluble (111). Accordingly, by operating at lower temperatures (423 K) and without the presence of acidic catalysts (Ru/C), concentrated aqueous solutions of levulinic acid are almost quantitatively converted to GVL through the intermediate 4-hydroxypentanoic acid (**Figure 7**). The catalytic upgrading of GVL requires the use of harsher conditions and different catalysts. Thus, by combining ring-opening reactions (on acid sites) and hydrogenation reactions (on metal sites), aqueous solutions of GVL can be converted to pentanoic acid over a water-stable bifunctional Pd/Nb_2O_5 catalyst at moderate temperatures (600 K) and pressures (35 bar). When conditions and catalysts are optimized, pentanoic acid is obtained in an organic layer that spontaneously separates from water and has a 92% carbon yield (*n*-butane and *n*-pentane were the main by-products). Interestingly, when the space velocity was decreased by a factor of 10, pentanoic acid was upgraded to 5-nonanone over the same Pd/Nb_2O_5 bed with a 70% carbon yield, allowing the direct production of 5-nonanone from GVL in a single reactor. These results indicate the beneficial effects of operating with multifunctional catalysts (where niobia catalyzes ring-opening of GVL and ketonization of pentanoic acid) for reduction of complexity in biomass conversion processes. Similar to lactic acid conversion, the use of a dual bed of Pd/Nb_2O_5 followed by ceria-zirconia improved the yield of 5-nonanone to values close to 90%. As depicted in **Figure 7**, this 5-nonanone product can be completely reduced by hydrogenation/dehydration/hydrogenation cycles (44) to *n*-nonane, which possesses excellent lubricity and cetane number properties, to be used in diesel fuel. Alternatively, 5-nonanone can be hydrogenated to the corresponding alcohol, which serves as precursor of gasoline compounds by means of dehydration/isomerization over an ultra-stable Y (USY) zeolite catalyst.

HYDROGEN INTEGRATION IN THE CONVERSION OF SUGARS TO TRANSPORTATION FUELS

The conversion of sugars to high–energy density liquid fuels for the transportation sector requires the removal of oxygen, typically as a combination of CO_2 and H_2O. This conversion can be imagined to take place in two steps: hydrogen production by reaction of the sugar with water, and hydrogen consumption by reduction of the sugar to form an alkane. These two processes are illustrated below for the conversion of glucose to hexane:

$$\frac{7}{12}[C_6O_6H_{12} + 6H_2O \longrightarrow 6CO_2 + 12H_2] \qquad 1.$$

$$+ [C_6O_6H_{12} + 7H_2 \longrightarrow C_6H_{14} + 6H_2O] \qquad 2.$$

$$\frac{19}{12}C_6O_6H_{12} \longrightarrow C_6H_{14} + \frac{7}{2}CO_2 + \frac{5}{2}H_2O. \qquad 3.$$

The hydrogen production reaction is endothermic by 95 kcal mol^{-1}, and the sugar reduction reaction is exothermic by 166 kcal mol^{-1}, such that the overall conversion of glucose to hexane is exothermic by 71 kcal mol^{-1}. Accordingly, a process that integrates hydrogen generation with hydrogen consumption produces a fuel (i.e., hexane in this case) that contains 93% of the energy content of the sugar reactant. Moreover, the hexane fuel contains only 30% of the mass of the sugar reactant, leading to high energy density. In cases in which it is not possible to integrate the energy requirement of the hydrogen generation step with the hydrogen consumption step, an additional 9% of the sugar must be combusted to provide process heat, such that the hexane fuel would now contain 84% of the original sugar feed.

The above thermodynamic analysis points to a significant energy advantage in integrating hydrogen production and utilization steps in the conversion of sugars to high–energy density fuels. In addition, as outlined in the Introduction, combining at least a portion of the hydrogen production and utilization steps in a single reactor simplifies the process flow sheet (e.g., fewer reactors and/or separation steps), leading to savings in capital and operating costs. This strategy for process intensification requires a combination of different reaction chemistries for cleavage and/or formation of C–C and C–O bonds in oxygenated hydrocarbons. For example, cleavage of C–C bonds in a highly oxygenated molecule (e.g., a sugar or a polyol) over a metal catalyst leads to the formation of H_2 and CO, the latter being converted with water to CO_2 and H_2 by the WGS reaction. In tandem with these hydrogen production processes, cleavage of C–O bonds in the presence of hydrogen (i.e., hydrogenolysis) leads to the formation of alkyl moieties and ultimately to the formation of alkanes. The combination of C–C and C–O bond cleavage steps in the same sugar molecule leads to the formation of light alkanes (e.g., methane, ethane, propane), whereas the cleavage of C–C bonds in one molecule combined with the cleavage of C–O bonds in another molecule leads to the formation of a heavier alkane, such as hexane. A strategy for enhancing the rate of C–O bond cleavage in this scenario is to combine an acid catalyst with a metal catalyst, leading to dehydration/hydrogenation processes. In particular, the acid catalyst carries out dehydration of the oxygenated hydrocarbon, which leads to the formation of C=C and/or C=O bonds and is followed by hydrogenation of these reactive intermediates over the metal catalyst. Alternatively, another option for combining the cleavage and/or formation of C–C and C–O bonds in an oxygenated hydrocarbon is the formation of a carboxylic acid, which leads to the formation of a –COOH group and a $-CH_2-$ moiety, which upon decarboxylation forms CO_2 and a $-CH_3$ group. These processes can take place over acidic and/or basic catalysts and do not necessarily require the presence of metal sites. This strategy for oxygen removal involves hydrogen transfer within a single molecule, without the intermediate formation of H_2 in the gas phase. We thus see that a variety of options are available for the removal of oxygen from sugar to form CO_2 and/or H_2O, and an important goal of catalytic processing is to find combinations of these options to achieve as completely as possible the integrated conversion of sugars to high–energy density fuels, as depicted above in Equation 3.

It is now important to address the energy changes involved in reactions employed to increase the length of the alkane chain. These reactions are necessary for the production of alkanes for transportation fuels. In particular, the reduction processes considered in the above examples would lead to the conversion of glucose to hexane, whereas larger alkanes are required for gasoline, jet, and diesel fuel applications. Again, we begin with simple thermodynamic arguments. We consider the scenario in which we first produce an alkane, then carry out C–C coupling reactions to increase the molecular weight. For example, the conversion of ethane to butane by the following stoichiometric reaction is an endothermic process (10 kcal mol^{-1}):

$$2C_2H_6 \longrightarrow C_4H_{10} + H_2. \qquad 4.$$

Accordingly, the equilibrium constant for this reaction would be low, and it would not be possible to achieve high conversions in a single-pass reactor. In contrast, the oxidative coupling of ethane to produce butane and water is exothermic (−47 kcal mol^{-1}):

$$2C_2H_6 + \frac{1}{2}O_2 \longrightarrow C_4H_{10} + H_2O. \qquad 5.$$

Although this C–C coupling reaction has a favorable equilibrium constant, it is difficult to achieve in practice at high yields because of the high reactivities of alkanes to undergo combustion reactions with O_2.

We now consider the option of achieving C–C coupling reactions in partially oxygenated intermediates. For example, the coupling between ethane and ethanol to form butane and water is an exothermic reaction (−12 kcal mol^{-1}):

$$C_2H_6 + C_2OH_6 \longrightarrow C_4H_{10} + H_2O. \qquad 6.$$

In a similar fashion, the coupling between two ethanol molecules leads to butanol and water in another exothermic reaction (−16 kcal mol^{-1}):

$$2C_2OH_6 \longrightarrow C_4OH_{10} + H_2O. \qquad 7.$$

This butanol product can then undergo dehydration to butene, leading to a small increase in enthalpy (9 kcal mol^{-1}):

$$C_4OH_{10} \longrightarrow C_4H_8 + H_2O. \qquad 8.$$

This dehydration reaction can be carried out with high conversion at moderate temperatures (e.g., 470 K) owing to the positive value for the entropy change of the dehydration process. It is noteworthy that alkenes serve as reactive intermediates for subsequent C–C coupling reactions. For example, the dimerization of ethylene to butene is exothermic by 28 kcal mol^{-1}:

$$2C_2H_4 \longrightarrow C_4H_8. \qquad 9.$$

Alkene oligomerization reactions can be carried out with high conversion at moderate temperatures (e.g., 470 K) because the favorable enthalpy change compensates for the unfavorable entropy change caused by the decrease in the number of moles upon reaction.

We now reach the important conclusion that a useful strategy for the conversion of sugars to high–energy density transportation fuels involves the integrated removal of oxygen to form reactive intermediates (e.g., alcohols, ketones, carboxylic acids, heterocyclic species, alkenes) that subsequently undergo C–C coupling reactions, which are potentially followed by further catalytic processing (e.g., complete removal of oxygen, hydrogenation of C=C bonds) to form hydrocarbon species with the appropriate structures and molecular weights for use in gasoline, jet, and diesel fuels.

We next address the extent to which hydrogen production and utilization can be combined, or internal hydrogen transfer can be employed, to produce reactive intermediates that can undergo C–C coupling reactions to control the molecular weight of the final fuel components. The following two equations represent the reduction of glucose to a partially oxygenated intermediate with stoichiometry $C_xO_yH_z$, combined with aqueous-phase reforming of glucose to produce the requisite amount of H_2 for the reduction process:

$$\left[\frac{nz}{2} - ny\right] H_2 + C_6O_6H_{12} \longrightarrow nC_xO_yH_z + [6 - ny]H_2O \qquad 10.$$

and

$$\left[\frac{nz}{24} - \frac{ny}{12}\right] [C_6O_6H_{12} + 6H_2O \longrightarrow 6CO_2 + 12H_2], \qquad 11.$$

where $n = 6/x$.

Combination of these two processes leads to the following stoichiometric equation for the integrated conversion of glucose to a reactive intermediate $C_xO_yH_z$:

$$\left[\frac{24 + nz - 2ny}{24}\right] C_6O_6H_{12} \longrightarrow nC_xO_yH_z + \left[6 - \frac{ny}{2} - \frac{nz}{4}\right] H_2O + \left[\frac{nz}{4} - \frac{ny}{2}\right] CO_2. \qquad 12.$$

According to Equation 12, the production of a reactive $C_xO_yH_z$ intermediate requires the formation of a stoichiometric amount of CO_2, which is produced by the combination of hydrogen production and utilization or by internal hydrogen transfer. Thus, the extent to which an external source of hydrogen is required to produce a given compound from a sugar can be assessed by the amount of CO_2 produced in the formation of this compound. A useful metric in this analysis is the ratio, R, of the number of moles of CO_2 produced according to Equation 13 per mole of carbon generated in the reaction intermediate (or product):

$$R = \left[\frac{nz}{4} - \frac{ny}{2}\right] \Big/ (nx) = \frac{z - 2y}{4x}. \qquad 13.$$

The value of R is a property of the reaction for production of a given species, and it represents the extent to which hydrogen production and utilization or internal hydrogen transfer (i.e., denoted as hydrogen integration) has been accomplished in the process.

We consider first the conversion of glucose to ethanol, for which the value of R is 0.5. Ethanol can be dehydrated to ethene with no change in the value of R. The conversion of glucose to ethane would thus correspond to a value of R equal to 0.75. Thus, if we imagine a scenario in which glucose would be converted to ethane (an alkane), and if we have a process in which glucose can be converted to ethene (an alkene) without the need for an external source of hydrogen, then the overall conversion of glucose to ethane by this route would represent 67% ($= 0.5/0.75 \times 100$) hydrogen integration; the external hydrogen required to hydrogenate ethene to ethane is 33% of the total hydrogen.

In another example, we consider the conversion of glucose to octane, a representative alkane in gasoline. We could imagine a scenario involving the conversion of glucose to ethanol, followed by dehydration to ethene and oligomerization to octene. The value of R for this integrated conversion of glucose to octene is 0.5. For comparison, the value of R for the conversion of glucose to octane is 0.56. Thus, the overall conversion of glucose to octane by this route would represent 89% ($= 0.5/0.56 \times 100$) hydrogen integration; the external hydrogen required to hydrogenate octene to octane is only 11% of the total hydrogen. The main conclusion from the above two examples is that the conversion of sugars to alkenes without the need for an external source of hydrogen represents an attractive route for the subsequent production of alkanes, and the extent of hydrogen integration by this approach becomes higher as the molecular weight of the alkane increases.

A useful reaction for hydrogen integration in the conversion of sugars to fuels is ketonization between two carboxylic acid molecules, which involves bimolecular coupling to produce a larger ketone molecule plus CO_2 and H_2O (69). As an example, we consider the conversion of glucose to acetic acid, which has a value of R equal to 0. In this respect, acetic acid is not an effective intermediate for hydrogen integration if it is simply reduced with an external source of hydrogen to ethane. In contrast, two acetic acid molecules can undergo ketonization to produce acetone, with a value of R equal to 0.33, plus CO_2 and H_2O. If acetone is then reduced with an external source of hydrogen to propane, with a value of R equal to 0.67, then the ketonization reaction would provide 50% of the hydrogen required for the conversion of glucose to propane that passes through acetic acid.

The conversion of sugars to ketones represents a useful intermediate process for the subsequent production of transportation fuels because these ketone intermediates can undergo C–C coupling reactions to increase the molecular weight by aldol condensation. For example, the value of R is equal to 0.42 for the production of hexanone from glucose, and aldol condensation of two hexanone molecules followed by hydrodeoxygenation leads to the production of dodecane, which has a value of R equal to 0.54. Thus, the conversion of glucose to hexanone represents 77% of the hydrogen required for the overall conversion of glucose to dodecane. One means to produce ketones from sugars is to balance C–C cleavage reactions versus C–O cleavage processes over bimetallic catalysts containing combinations of noble metals (e.g., Pt) with oxophilic metals (e.g., Re) (43). Another strategy for the production of ketones is to convert glucose to equimolar amounts of levulinic acid and formic acid, followed by hydrogen transfer between these two acids to form GVL, which has a value of R equal to 0.20. The GVL intermediate can undergo ring opening and hydrogenation to pentanoic acid, with a value of R equal to 0.30, followed by ketonization to 5-nonanone, with a value of R equal to 0.44, plus CO_2 and H_2O (**Figure 7**). If all of these steps can be carried out without the need for an external source of hydrogen, then the conversion of glucose to 5-nonanone represents 80% of the hydrogen required for the overall conversion of glucose to nonane, with a value of R equal to 0.55. At present, we have not yet integrated the conversion of GVL to pentanoic acid with an internal source of hydrogen, and thus our process for the conversion of glucose to nonane, passing through 5-nonanone, has achieved 60% hydrogen integration. We have demonstrated that GVL can undergo decarboxylation to CO_2 and butene, the latter of which can be converted to octene by dimerization. Accordingly, the conversion of glucose to octene, passing through the intermediate formation and conversion of levulinic acid, formic acid, GVL, and butene, represents 89% of the hydrogen required for the overall conversion of glucose to octane, which has a value of R equal to 0.56.

The above examples have targeted the conversion of sugars to alkanes in view of the high stability of these saturated hydrocarbons for storage under a wide range of conditions. Another option, however, is to employ alkenes and aromatics as fuel components, which means that smaller amounts of hydrogen will be incorporated in the final products. Thus, whereas the conversion of glucose to octane, passing through butene and octene, represents 89% hydrogen integration, the production of octene as a fuel component by this approach represents 100% hydrogen integration. Another approach is to convert sugars to a mixture of aromatics and alkanes. For example, it was noted above that glucose can be converted in a single catalytic reactor to hexanone, which has a value of R equal to 0.42. The subsequent conversion of hexanone to a mixture of benzene and hexane, which have values of R equal to 0.25 and 0.58, respectively, would lead to a mixture of compounds having an overall value of R equal to 0.42, which is equal to the value for hexanone. Thus, the conversion of glucose to a mixture of aromatics and alkanes that passes through the intermediate formation of ketones represents an approach leading to 100% hydrogen integration for the overall conversion of sugars to transportation fuel components.

CONCLUSIONS

The conversion of biomass and biomass-derived compounds into fuels and chemicals can ameliorate many of the current issues associated with the use of fossil fuels. To accelerate the partial replacement of fossil fuels with renewable biomass resources, technologies for the production of renewables should be economically competitive with those used today in the petrochemical industry. Two aspects are critical in this sense: reducing the complexity of processes employed to convert biomass to fuels and chemicals and achieving biomass deoxygenation with minimal use of external hydrogen. This review has outlined strategies and given examples that address these issues, and we hope that the concepts described herein relating to catalytic coupling at multiple length scales might be useful for future development of new, economically viable routes for catalytic conversion of biomass to fuels and chemicals.

DISCLOSURE STATEMENT

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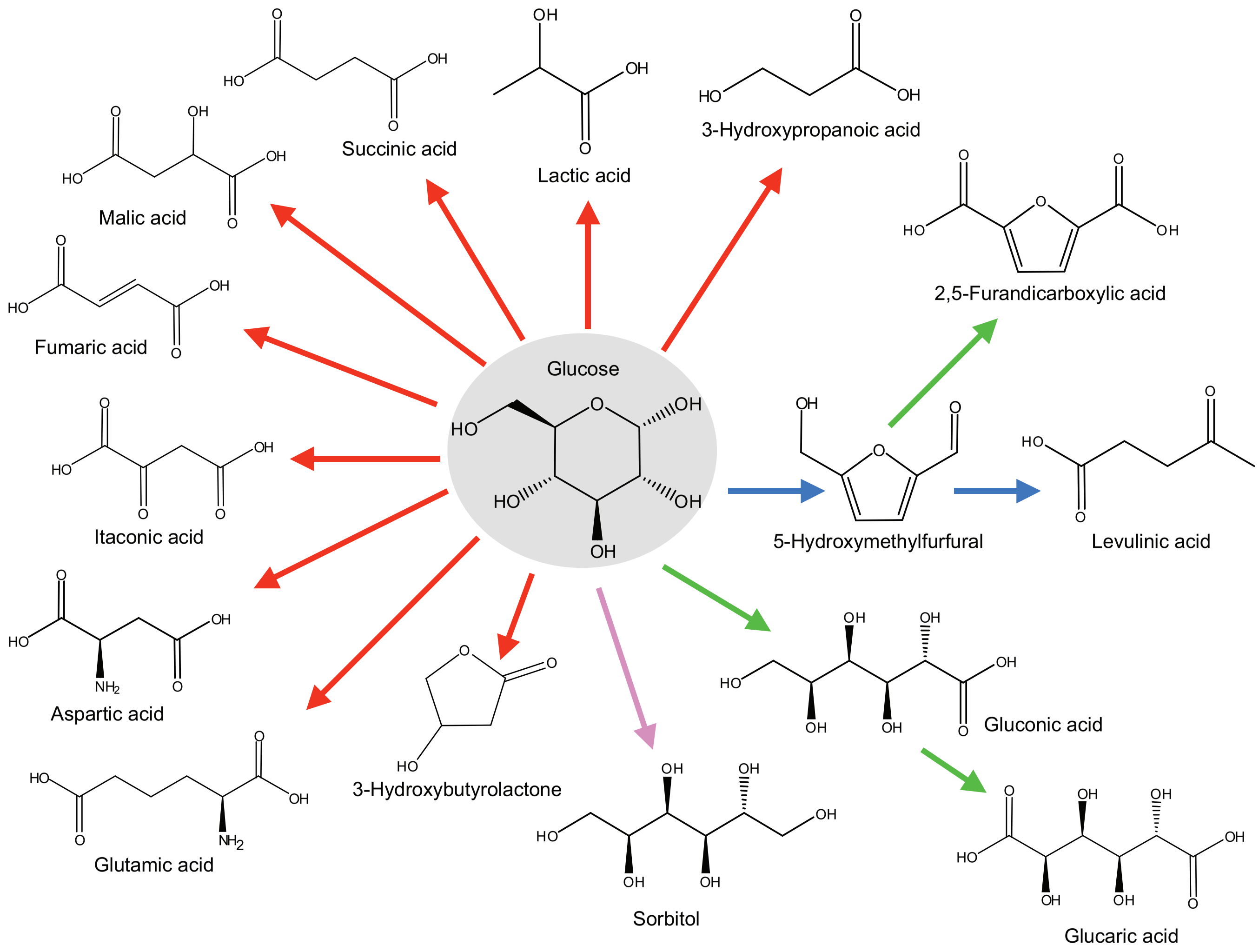

Figure 2

Value-added chemicals derived from glucose by means of dehydration (*blue arrows*), oxidation (*green arrows*), hydrogenation (*pink arrow*), and bacterial fermentation (*red arrows*) routes. Adapted from Reference 8.

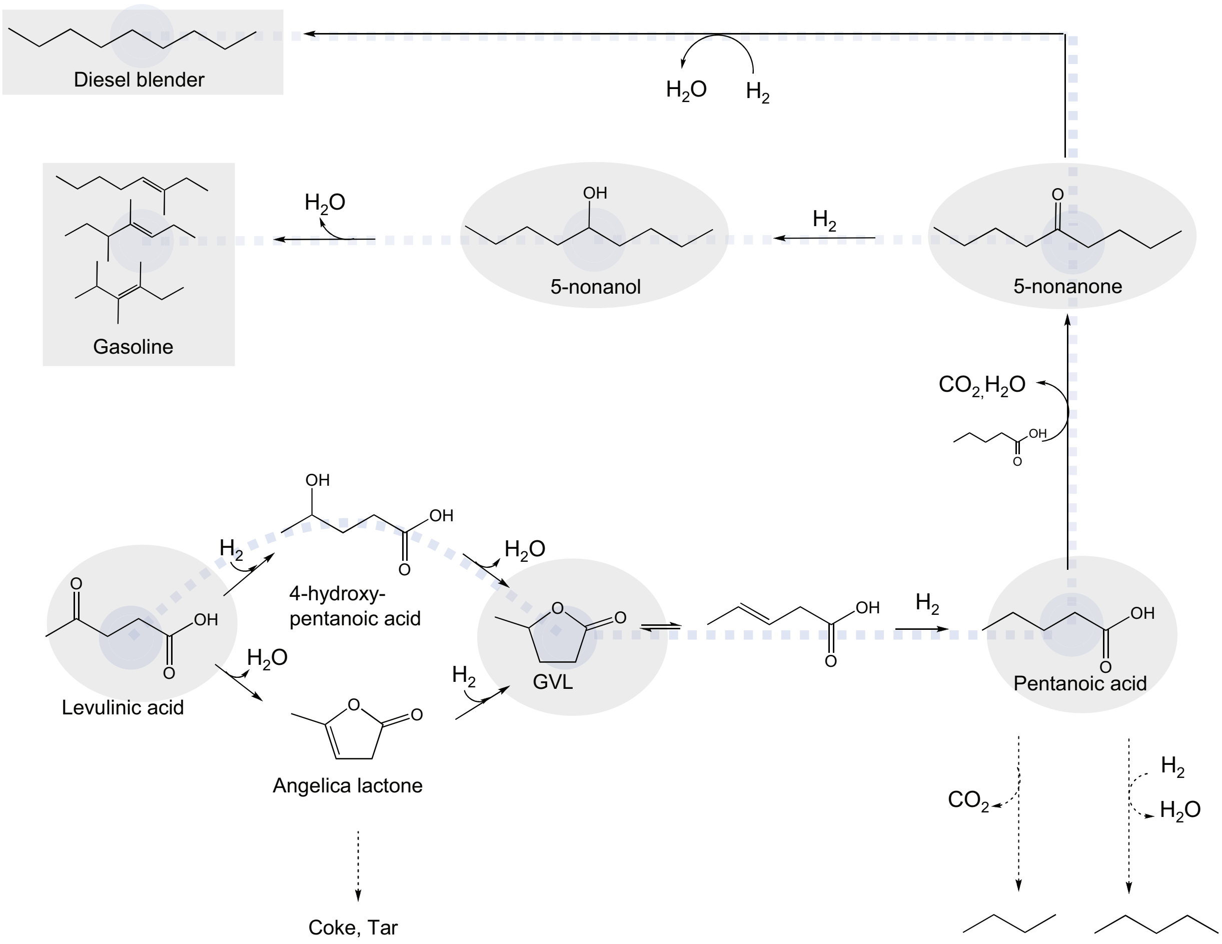

Figure 7

Catalytic routes for the upgrading of levulinic acid to hydrocarbon fuels.

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Contents

Errata

An online log of corrections to *Annual Review of Chemical and Biomolecular Engineering* articles may be found at http://chembioeng.annualreviews.org/errata.shtml