

# Catalytic conversion of biomass to biofuels

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Biomass has received considerable attention as a sustainable feedstock that can replace diminishing fossil fuels for the production of energy, especially for the transportation sector. The overall strategy in the production of hydrocarbon fuels from biomass is (i) to reduce the substantial oxygen content of the parent feedstock to improve energy density and (ii) to create C–C bonds between biomass-derived intermediates to increase the molecular weight of the final hydrocarbon product. We begin this review with a brief overview of first-generation biofuels, specifically bioethanol and biodiesel. We consider the implications of utilizing starchy and triglyceride feedstocks from traditional food crops, and we provide an overview of second-generation technologies to process the major constituents of more abundant lignocellulosic biomass, such as thermochemical routes (gasification, pyrolysis, liquefaction) which directly process whole lignocellulose to upgradeable platforms (e.g., synthesis gas and bio-oil). The primary focus of this review is an overview of catalytic strategies to produce biofuels from aqueous solutions of carbohydrates, which are isolated through biomass pretreatment and hydrolysis. Although hydrolysis-based platforms are associated with higher upstream costs arising from pretreatment and hydrolysis, the aqueous solutions of biomass-derived compounds can be processed selectively to yield hydrocarbons with targeted molecular weights and structures. For example, sugars can be used as reforming feedstocks for the production of renewable hydrogen, or they can be dehydrated to yield furfurals or levulinic acid. For each of the platforms discussed, we have suggested relevant strategies for the formation of C–C bonds, such as aldol condensation of ketones and oligomerization of alkenes, to enable the production of gasoline, jet, and Diesel fuel range hydrocarbons. Finally, we address the importance of hydrogen in biorefining and discuss strategies for managing its consumption to ensure independence from fossil fuels.

## 1. Introduction

An important current focus of research in chemistry, engineering, agriculture, and environmental policy is the development of clean technologies that utilize a sustainably produced feedstock to the largest extent possible.<sup>1</sup> This research is especially important in the transportation fuel sector which is strongly dependent on petroleum, a non-renewable fossil source of carbon. However as the worldwide supply of petroleum diminishes, it is becoming increasingly expensive and, accordingly, less attractive as a carbon source. Furthermore, the combustion of fossil fuels or their derivatives for the production of heat and power is associated with a net increase in greenhouse gas levels worldwide.<sup>2–4</sup> In contrast to the present situation, where the entirety of demand is met by a single source (i.e., petroleum), a more flexible system drawing from multiple energy sources should be an attractive long term solution. Vehicles powered by electricity, solar energy, hydrogen fuel cells, and biofuels are all being actively researched to reduce our dependence on petroleum as a source of energy. Nevertheless, these new technologies require time to be economically and technically viable. The situation is further exacerbated by the lack of

an infrastructure to support cutting-edge technologies like hydrogen fuel cells, and change will thus come slowly to a market currently governed by preferences and habits that are based on widespread availability of liquid hydrocarbon fuels. In this respect, liquid biofuels derived from renewable plant mass, are unique in their similarity to the currently preferred fuel sources. As such, their implementation does not require extensive changes to the transportation infrastructure and the internal combustion engine. Thus, the use of biomass as a renewable source of carbon for the production of transportation fuels is a promising alternative that is realizable on short time scales. For example, bioethanol and biodiesel are currently used commercially as blending agents for petroleum-derived gasoline and Diesel fuels.

Presently in the petrochemical industry, crude oil is fractionated and refined to produce various grades of liquid transportation fuel, and hydrocarbon feedstocks are functionalized to produce intermediates and speciality chemicals. The analogous concept of biorefining would be similar in scope, with the key difference being that biomass—rather than petroleum—would be utilized as a renewable source of carbon<sup>5,6</sup> that can be transformed into fuels and valuable chemicals within a single facility. Furthermore, in the production of heat and power, the utilization of biomass derivatives mitigates the release of greenhouse gas emissions through cycles of regrowth and combustion,<sup>2,7</sup> as illustrated in Fig. 1.

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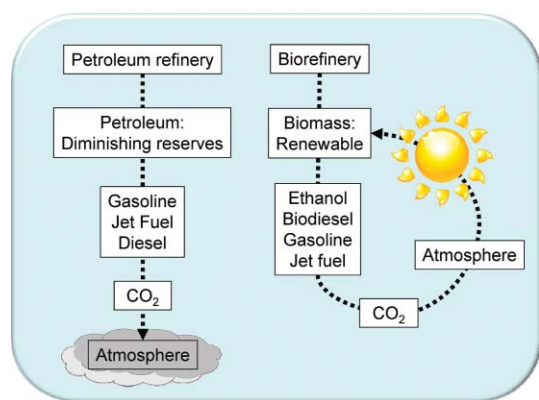


Fig. 1 CO<sub>2</sub> cycles for petroleum- and biomass-derived fuels.

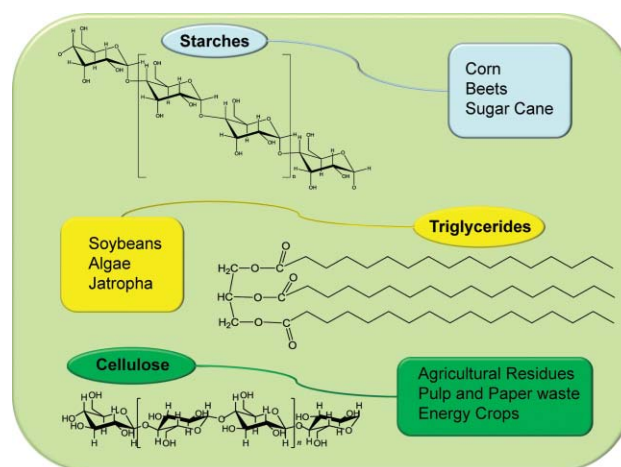


Fig. 2 Chemical structure of biomass feedstocks.

We can consider three general classes of feedstocks derived from biomass that are appropriate for the production of renewable fuels:<sup>8</sup> starchy feedstocks (including sugars), triglyceride feedstocks, and lignocellulosic feedstocks. In Fig. 2, representative chemical structures for starches and triglycerides are compared to that of cellulose—the predominate component of lignocellulosic biomass. Fig. 3 shows different biofuels that can be obtained with each of these feedstocks. Starchy feedstocks are those comprised of glucose polysaccharides joined by  $\alpha$ -glycosidic linkages, such as amylose and amylopectin, which are easily hydrolyzed into the constituent sugar monomers, making them easy to process such as in first generation bioethanol facilities. Triglyceride feedstocks are those comprised of fatty acids and glycerol derived from both plant and animal sources. Sources of triglycerides for the production of biodiesel include various vegetable oils, waste oil products (*e.g.*, yellow grease, trap grease), and algal sources.<sup>8</sup> Lignocellulosic biomass is the most abundant class of biomass. While starch and triglycerides are only present in some crops, lignocellulose contributes structural integrity to plants and is thus always present. In general, most energy crops and waste biomass considered for energy production are lignocellulosic feedstocks, with examples including

switchgrass, miscanthus, agricultural residues, municipal wastes, and waste from wood processing. Lignocellulose is comprised of three different fractions: lignin, hemicellulose, and cellulose.

In this review we consider various processes by which biomass can be transformed into biofuels, giving special attention to utilization of lignocellulosic biomass. Without underestimating the contributions of other possible feedstocks and processes, this review will focus primarily upon upgrading strategies for the production of fuels from aqueous solutions of lignocellulose-derived carbohydrates. With the examples discussed in this work, we hope to outline various alternatives for biomass processing, providing options such that each feedstock can be processed in the most efficient way possible.

## 2. Lignocellulosic biomass

While attractive as an inexpensive and abundant feedstock, lignocellulosic biomass must be broken into its constituent parts to be efficiently processed by specific refining strategies. Biomass fractionation is a difficult process and has contributed

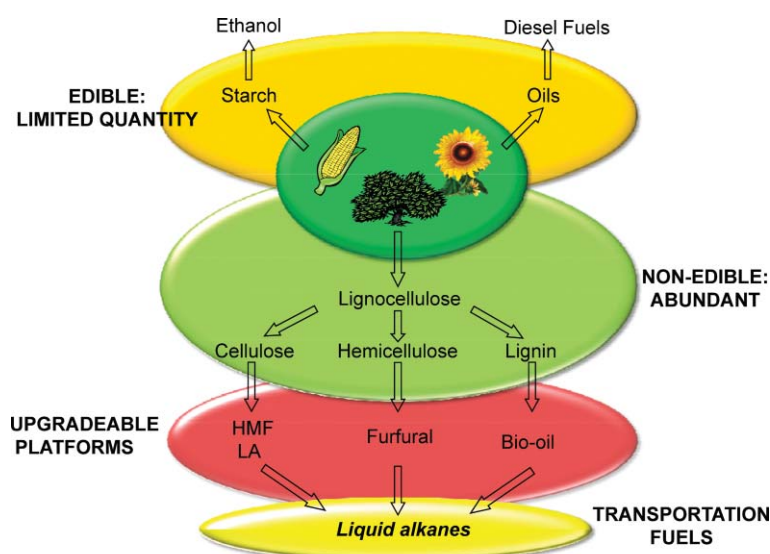


Fig. 3 Biomass-derived feedstocks and platforms for conversion to biofuels.

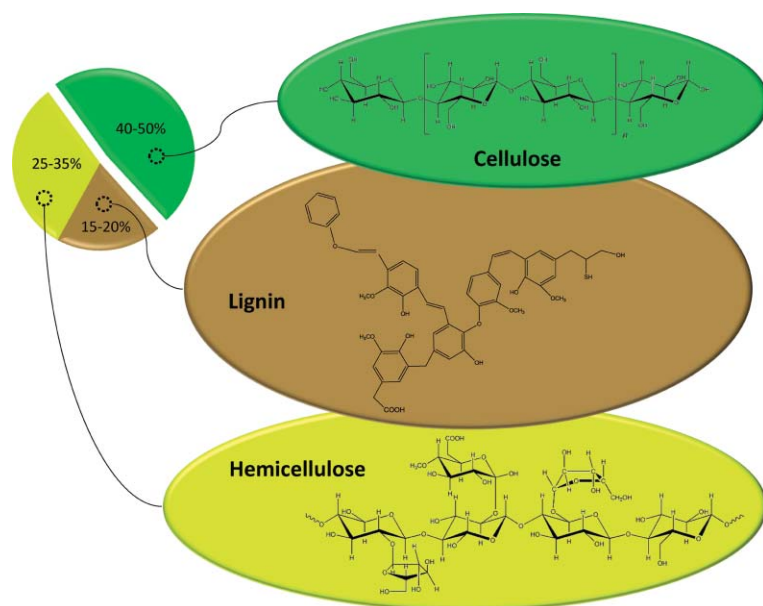


Fig. 4 Lignocellulose composition: cellulose, hemicellulose and lignin.

to the high cost of processes utilizing lignocellulosic feedstocks. For example, at present, the cost of cellulosic ethanol is approximately two times higher than the cost of corn ethanol, with the higher price being attributed to the complexity of the isolation of sugars from lignocellulosic biomass.<sup>9</sup> Lignocellulosic biomass is generally composed of hemicellulose (25–35%), cellulose (40–50%), and lignin (15–20%),<sup>10</sup> and these structures are illustrated in Fig. 4. The isolation of biomass fractions typically proceeds through pretreatment followed by hydrolysis. The pretreatment stage is comprised of both physical (*e.g.*, milling, comminuting, steam) and chemical (*e.g.*, acid or base hydrolysis) methods, and is intended as a means of increasing the susceptibility of crystalline cellulose to degradation in subsequent hydrolysis steps. Pretreatment achieves this objective by penetration/depolymerization of the lignin seal and extraction/preservation of the pentose (hemicellulose-derived) fraction of biomass.<sup>11</sup> In the following sections, we address briefly the composition of each biomass fraction and the potential application of each as a feedstock for biofuels.

### 2.1. Lignin

The lignin fraction of biomass is an amorphous polymer composed of methoxylated phenylpropane structures, such as coniferyl alcohol, sinapyl alcohol, and coumaryl alcohol,<sup>2,12</sup> which provide plants with structural rigidity and a hydrophobic vascular system for the transportation of water and solutes.<sup>13</sup> Lignin surrounds the hemicellulose and cellulose fractions, and one function of biomass pretreatment is to de-polymerize the lignin seal such that the carbohydrate portions can be accessed.<sup>2,11</sup> If desired, lignin can be removed from biomass to isolate the carbohydrate fraction through depolymerization/solubilization in alkaline-alcohol solutions, similar in effect to the Kraft paper pulping process.<sup>11,12</sup> Alternatively, residual lignin can be collected following pretreatment and acid or enzymatic hydrolysis for the extraction of pentose and hexose sugars

from hemicellulose and cellulose, respectively.<sup>14,15</sup> Although lignin can be isolated, it is not readily amenable to upgrading strategies. As such, one option for lignin utilization is to burn it directly for the production of heat and electricity. A report by the U.S. National Renewable Energy Laboratory (NREL) suggests that in an integrated biorefinery for the production of cellulosic ethanol, lignin and residual solids can be used to provide process heat and power at a rate in excess of the energy required to drive the process.<sup>16,17</sup> In addition, alternatives have been suggested that allow for the production of functional intermediates from lignin to make valuable chemicals. For example, given that it is rich in oxygenated aromatic species, lignin can be used as a feedstock in the production of phenolic resins,<sup>18</sup> and several studies report pyrolysis strategies for the production of bio-oils<sup>19</sup> and aromatics<sup>20,21</sup> from lignin.

### 2.2. Hemicellulose

The hemicellulose fraction of lignocellulosic biomass is an amorphous polymer that is generally comprised of five different sugar monomers, D-xylose, L-arabinose, D-galactose, D-glucose, and D-mannose, with xylose being the most abundant.<sup>3</sup> Hemicellulose is bound to lignin, and cellulose strands are interlaced with hemicellulose. Generally, it is preferable to remove the hemicellulose fraction of biomass during pretreatment, such that subsequent hydrolysis steps to recover glucose from cellulose are more effective. Ideally, the pretreatment process preserves the xylose obtained from hemicellulose, and conditions favoring the formation of degradation and dehydration products are not used.<sup>11</sup> Hemicellulose extraction can be achieved through either physical methods or a mixture of physical and chemical methods. In general, physical methods, such as steam explosion or hot water treatment, yield polymeric xylans that can be subsequently hydrolyzed under mild conditions to produce xylose monomers. Pretreatment methods that combine chemical treatments such as dilute acid hydrolysis typically produce xylose monomers

in good yield. In comparison to the digestion of crystalline cellulose, hemicellulose extraction/hydrolysis is regarded as a straightforward process that can be carried out with high yields of sugar. For example, hemicellulose is readily depolymerized to yield xylose monomers through dilute acid hydrolysis with  $\text{H}_2\text{SO}_4$  being the most commonly used acid.<sup>6,22</sup> Once extracted and hydrolyzed, xylose monomers are appropriate feedstocks for ethanol production *via* fermentation<sup>23,24</sup> or for preparation of furfural *via* dehydration.<sup>22</sup>

### 2.3. Cellulose

Cellulose is a polymer of glucose units linked *via*  $\beta$ -glycosidic bonds, imparting the structure with rigid crystallinity that impedes hydrolysis.<sup>3</sup> Cellulose is typically isolated within the complex lignin/hemicellulose matrix, and it is largely inaccessible to hydrolysis in untreated biomass. Biomass pretreatment *via* milling and physical/chemical treatments serves to permeate lignin and extract hemicelluloses, such that subsequent hydrolysis steps to isolate the glucose monomers of cellulose are more effective.<sup>2,11</sup> Once isolated, the hydrolysis of cellulose for the production of glucose is considered more difficult than the analogous production of xylose from hemicellulose. High glucose yields (>90% of theoretical maximum) are achieved *via* enzymatic hydrolysis of cellulose following biomass pretreatment.<sup>14,15</sup> Cellulose hydrolysis can also be achieved under harsher conditions using solutions of mineral acids ( $\text{H}_2\text{SO}_4$ ) at elevated temperatures; however, the harsh conditions required for non-enzymatic deconstruction of cellulose favor the formation of degradation products such as hydroxymethylfurfural (HMF), levulinic acid, and insoluble humins.<sup>25,26</sup> The selectivity for production of glucose can be optimized through proper selection of acid concentration and reaction temperature, and by operating reactors at short residence times.

### 3. Developed processes for conversion of biomass to fuels

Apart from burning wood as a source of heat, biomass-derived alcohols and oils have been used as liquid energy sources since 6000 BC.<sup>27</sup> Alcohols have been used as transportation fuels since the invention of the internal combustion engine in 1897,<sup>28</sup> while the Diesel engine was initially designed to work with oils.<sup>29</sup> However, the increased availability of inexpensive petroleum almost completely replaced these green alternatives. Presently, given the diminishing worldwide supply of petroleum, the interest in conversion strategies for the production of liquid fuels from biomass is receiving renewed attention, and many options are under consideration. First generation biofuels use conventional technologies to process food crops (*e.g.*, sugar, starch and oils) and consist mainly of alcohols (bioethanol) and oils (biodiesel). These fuels are readily available, because the processes to obtain them are well understood technologies and have been refined over many years of development. The main challenge in research involving first generation biofuels is not in the development of new technologies, but in the optimization of processes to reduce cost, such that green fuels can be competitive with those produced from petroleum.

Bioethanol is the most abundantly produced biofuel. With a production scale of 13.5 billion gallons in 2006, it accounts for more than 94% of total biofuel production,<sup>30</sup> and ethanol production continues to increase, with 17.2 billion gallons produced in 2008.<sup>31</sup> This fast growth is possible because blends of ethanol and gasoline can be used in modern gasoline engines without requiring any modifications.<sup>32</sup> The production of bioethanol, outlined in Fig. 5, begins with biomass pretreatment to produce sugar monomers, such as glucose, that can be converted to ethanol by fermentation using a variety of microorganisms (*e.g.*, yeast, bacteria and mold). The ethanol product is then purified by distillation, whereupon it is appropriate for direct use as a fuel or additive. Food crops, such as sugarcane in Brazil and

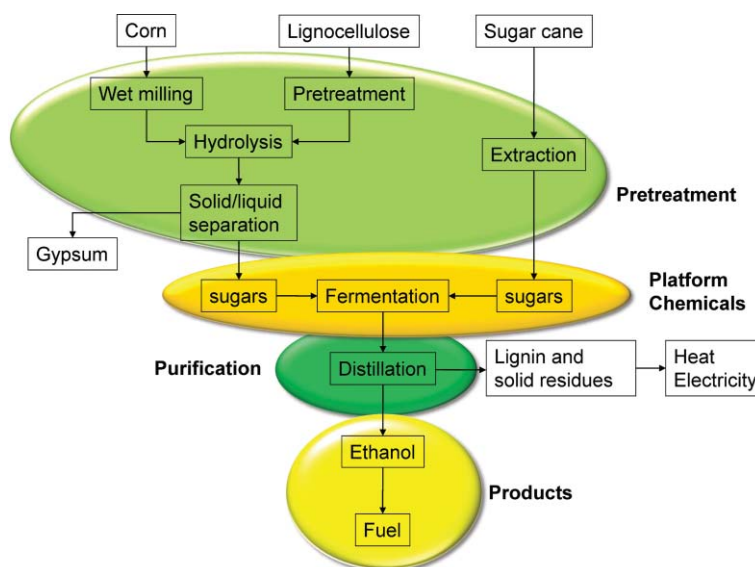


Fig. 5 Process schematic: bioethanol production.



corn in the USA, are the preferred feedstocks for bioethanol production, because they are rich in sugars and starches that are easily hydrolyzed (as compared to cellulosic feedstocks).

Lignocellulosic biomass has been considered an appropriate feedstock to produce sustainable, second generation bioethanol. Presently, one of the main challenges in the utilization of lignocellulosic biomass is pretreatment and hydrolysis for the production of sugars, and these steps are considered the greatest impediment to economic viability of strategies involving the production of sugars from lignocellulosic biomass. As such, an active area of research is the optimization of biomass pretreatment and hydrolysis to improve the suitability of this feedstock.<sup>16,33</sup> More recently algae crops have been considered as a sustainable source of feedstocks for bioethanol and biodiesel, and these algae-derived fuels are generally called third generation biofuels. However, these potential alternatives are still at an early stage of development, and more research on feedstock availability and process optimization is necessary. The energy balance of ethanol production depends strongly on the raw materials used, and some authors claim that the production of ethanol has a negative energy balance because more fossil energy is required in the process than the energy released by the ethanol produced.<sup>34,35</sup> Other authors defend that the energy balance is slightly positive considering the advances achieved in ethanol production in recent years.<sup>2,36</sup>

Biodiesel is the second most abundant renewable liquid fuel, with an annual production of 4.3 billion gallons in 2008.<sup>31</sup> Biodiesel can be used in current injection engines in a wide range of blends with petrol-diesel or as a pure fuel (without petrol-diesel), and its preparation is outlined schematically in Fig. 6. First generation biodiesel<sup>37,38</sup> is produced by esterification of fatty acids or transesterification of oils (triglycerides) with alcohols (normally methanol and ethanol) using a basic<sup>39-41</sup> or acidic catalyst.<sup>42,43</sup> The fatty esters are separated from glycerol by decantation and purified for direct use as fuels. Another alternative to process oil into biofuels is hydro-treating,<sup>44</sup> which can be carried out synergistically in the existing petroleum

refinery infrastructure through mixing and co-processing of vegetable oils with petroleum derived feedstocks.<sup>8,45</sup> The main drawback of oil-based processes is the availability of inexpensive feedstocks. Normally palm, sunflower, canola, rapeseed and soybean oils are used, but they are expensive and can otherwise be used as food sources. Challenges in biodiesel research are focused on the development of new catalytic processes that allow the use of low quality or waste oils (*e.g.*, used fryer oil), such that biodiesel production is less expensive and does not directly compete with the food supply. The use of these low quality oils has been proposed as an avenue for cost reduction; however, uncertainty regarding the composition of these used oils, which often contain large quantities of water and other impurities, can complicate their utilization. As an alternative, different non-edible oils have been proposed as appropriate feedstocks (*e.g.*, cynara,<sup>46</sup> *Jatropha*, *Karanja*<sup>47</sup>). Additionally, researchers are focusing on the production of third generation biodiesel, which is produced from triglycerides derived from algae.<sup>48</sup>

A drawback of using only the easily processed sugar and triglyceride fractions of a plant is that these fractions are only a small part of the biomass. Accordingly, the net energy yield that can be achieved using only these fractions is poor,<sup>49</sup> and only specific crops can be used. To improve energy yield of fuels from biomass, lignocellulosic feedstocks must be utilized despite their complexity. Additionally, it is preferable to utilize non-edible biomass as a feedstock for the production of fuels and chemicals, such that the production of transportation fuels does not interfere with either the food supply or disrupt land use unduly.<sup>3,50,51</sup> Accordingly, the following section will be devoted to an overview of various processing options currently available for lignocellulosic feedstocks.

#### 4. General approach for conversion of lignocellulosic biomass to liquid fuels

The overall goal of converting lignocellulosic biomass to hydrocarbon fuels is the removal of oxygen, combined with

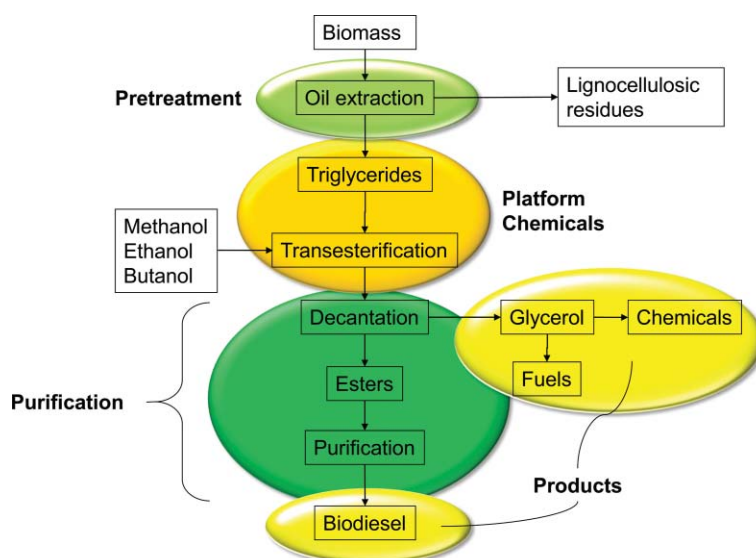


Fig. 6 Process schematic: biodiesel production.

the formation of C–C bonds to control the molecular weight of the final hydrocarbons, and requiring the least amount of hydrogen from an external source (such as the steam reforming of petroleum). The strategy for achieving this goal is typically comprised of two broad types of steps: (i) conversion of the solid lignocellulosic biomass feedstock to a gaseous or liquid-phase chemical platform, involving partial removal of oxygen; and (ii) catalytic upgrading of this chemical platform to the final hydrocarbon fuel by controlled C–C coupling reactions and removal of the remaining oxygen functionality. In the following sections we will illustrate this general strategy for various specific approaches.

First, we will briefly explore gasification combined with Fischer–Tropsch synthesis, in which the first step in lignocellulosic biomass conversion is gasification to produce synthesis gas (*i.e.*, CO : H<sub>2</sub> gas mixtures), and the second step is the catalytic conversion of synthesis gas platform to linear hydrocarbons in the Diesel fuel range. Second, we will consider pyrolysis and liquefaction, where the first step involves anaerobic thermal treatment of lignocellulosic biomass to form liquid bio-oil, leading to the removal of ~80% of the oxygen in the feed, and the second step involves the catalytic upgrading of this bio-oil in the presence of H<sub>2</sub> to achieve C–C coupling and to remove the remainder of the oxygen moieties. Third, we will address aqueous-phase reforming, in which the lignocellulosic biomass must first undergo treatment to produce an aqueous solution of sugars or polyols. This platform of aqueous compounds having a C : O stoichiometry of 1 : 1 is then converted by a combination of C–C and C–O cleavage reactions to produce a mixture of mono-functional organic compounds (alcohols, ketones, carboxylic acids, heterocyclics). These mono-functional intermediates then undergo catalytic upgrading to hydrocarbon fuels by various routes to control C–C coupling and oxygen removal, such as dehydration, aromatization and alkylation over acid zeolite catalysts, aldol-condensation of alcohols and ketones over bifunctional catalysts containing metal and basic sites, and ketonization of carboxylic acids over basic oxides. Fourth, we briefly consider an approach in which aqueous solutions of sug-

ars formed by treatment of lignocellulosic biomass undergo catalytic dehydration to produce furan compounds, such as furfural and hydroxymethylfurfural (HMF). These furanic aldehydes can then be used as feedstocks for aldol-condensation reactions over basic catalysts to produce hydrocarbons suitable for Diesel fuel applications by achieving controlled C–C coupling reactions while minimizing undesirable branching processes. Finally, we consider the levulinic acid platform, in which lignocellulosic biomass first undergoes treatment in acid solutions to produce levulinic acid. The aqueous solution of levulinic acid (in the presence of formic acid) then undergoes catalytic reduction to  $\gamma$ -valerolactone (GVL), which serves as an intermediate for the production of nonane for Diesel fuel or the production of branched alkanes with molecular weights appropriate for jet fuel. In particular, GVL can undergo ring-opening and reduction to pentanoic acid, followed by ketonization to form 5-nonanone, and completed by hydrodeoxygenation to nonane. Alternatively, GVL can undergo catalytic conversion to butene and CO<sub>2</sub>, combined with butene oligomerization to form C<sub>8</sub> – C<sub>20</sub> alkenes.

## 5. General approaches for conversion of cellulosic biomass: thermochemical and hydrolysis pathways

Fig. 7 presents two of the most frequently considered strategies for biomass processing. The first approach involves thermochemical routes that process whole lignocellulose at high temperatures and/or pressures (*e.g.*, pyrolysis, gasification, liquefaction). The thermal deconstruction of biomass yields upgradeable intermediates such as bio-oils by pyrolysis and synthesis gas by gasification (CO : H<sub>2</sub> gas mixtures, denoted as syngas). Thermal processing is typically coupled with subsequent chemical/catalytic upgrading (Fischer–Tropsch synthesis, hydrodeoxygenation) to produce fuel range hydrocarbons. The second processing option for lignocellulosic biomass is fractionation/hydrolysis, an option by which sugars and lignin are isolated from lignocellulosic biomass and processed selectively through either biological or chemical pathways. In general,

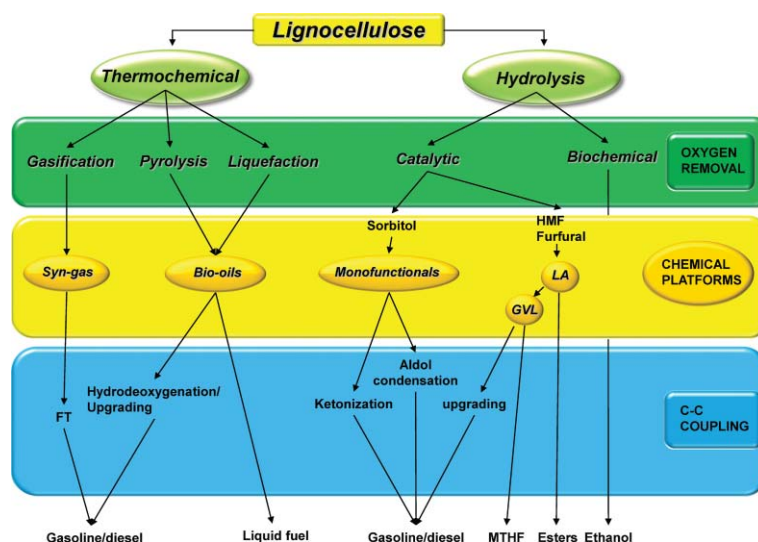


Fig. 7 Strategies for conversion of lignocellulosic biomass to liquid biofuels by thermochemical and hydrolysis routes.

biomass hydrolysis is more complex than thermochemical conversion and is carried out at higher cost. However, hydrolysis based strategies offer selective processing options and chemical platforms unavailable using thermochemical technologies. In this section, we examine both the predominate thermochemical pathways and general approaches for the hydrolytic conversion of biomass.

### 5.1. Gasification

Gasification is carried out through partial combustion of biomass to produce syngas or producer gas, which typically has some quantity of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> (producer gas).<sup>2</sup> Syngas can be upgraded to liquid fuels such as Diesel and gasoline by Fischer–Tropsch (FT) synthesis,<sup>52</sup> and large scale gasification-FT production facilities are in use in South Africa (SASOL). Gasification is normally carried out at temperatures over 1000 K, but recently it has been demonstrated that H<sub>2</sub> and CO can be produced through the aqueous phase reforming of glycerol at lower temperatures (<620 K),<sup>53,54</sup> at which integration of syngas production with FT upgrading is feasible.<sup>54</sup> The ratio of CO/H<sub>2</sub> can be modified by the water gas shift reaction (CO+H<sub>2</sub>O → CO<sub>2</sub>+H<sub>2</sub>). Fig. 8 shows a typical biomass gasification process. The advantage of gasification is that it is not constrained to a particular plant-based feedstock, and thus any lignocellulosic biomass can be considered appropriate. However, the amount of water in the biomass<sup>2</sup> and impurities in the gases produced<sup>55</sup> can be problematic in downstream FT processes, where a clean gas feed is required.

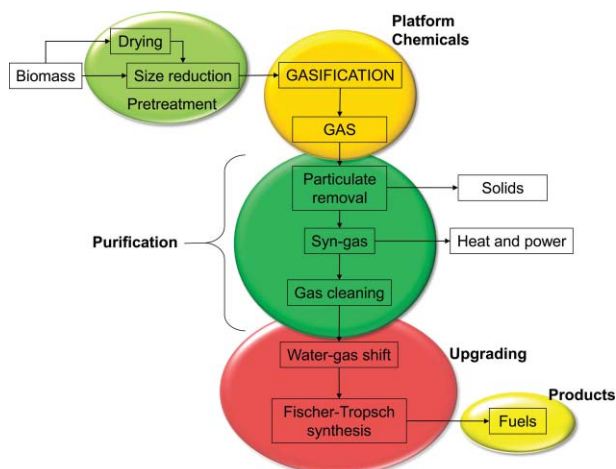


Fig. 8 Process schematic: biomass gasification and upgrading.

### 5.2. Pyrolysis

Pyrolysis takes place through thermal, anaerobic decomposition of biomass (at temperatures from 650 to 800 K). At these elevated temperatures, vapor phase products react and subsequently condense upon cooling to produce a liquid mixture of more than 350 compounds such as acids, aldehydes, alcohols, sugars, esters, ketones, and aromatics, which are collectively referred to as “bio-oil.” Yields of bio-oil up to 70% of the initial mass fed into the reactor have been reported.<sup>56</sup> Typically, short residence times (seconds) are necessary for the

production of liquid bio-oils. At longer reaction times, the main product of pyrolysis is solid coke (slow pyrolysis) that can be used to generate energy by combustion. Catalytic fast pyrolysis has recently been developed as a means for producing aromatic compounds, rather than bio-oil, from direct pyrolysis of lignocellulosic biomass, and yields of 20–30% aromatics have been reported when pyrolysis takes place in the presence of H-ZSM-5.<sup>57</sup> Pyrolysis has received considerable attention as an inexpensive processing option that allows for the total utilization of lignocellulosic biomass, and can be used for processing lignin after extraction of carbohydrates from lignocellulosic biomass.<sup>19,21</sup> Given that pyrolysis pathways, illustrated in Fig. 9, do not require the extensive pretreatment steps common to hydrolysis/sugar platforms, the cost of producing a bio-oil is considerably less than the cost of sugar-based products. However, the bio-oil product is not particularly well suited for use as a fuel and must be treated extensively before it can be used in internal combustion engines. The main limitations to direct bio-oil utilization are the high acidity and oxygenate content of the bio-oil, leading to a low energy density liquid and corrosive properties that are detrimental to equipment lifetime when used in existing engines.<sup>58</sup>

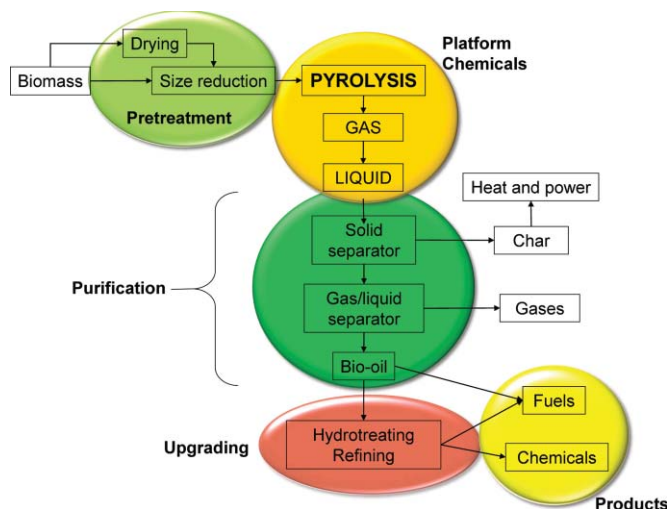


Fig. 9 Process schematic: biomass pyrolysis and upgrading.

### 5.3. Liquefaction

Liquefaction is an alternative pathway for the production of bio-oils, and this approach is summarized in Fig. 10. Liquefaction consists of the catalytic thermal decomposition of large molecules to unstable shorter species that polymerize again into a bio-oil. Biomass is mixed with water and basic catalysts like sodium carbonate, and the process is carried out at lower temperatures than pyrolysis (525–725 K) but higher pressures (5–20 atm) and longer residence times. These factors combine to make liquefaction a more expensive process; however, the liquid product obtained contains less oxygen (12–14%<sup>59</sup>) than the bio-oil produced by pyrolysis<sup>2</sup> and typically requires less extensive processing.

Bio-oils, in general, have been successfully tested in engines, turbines and boilers, that required small modifications.<sup>60</sup>



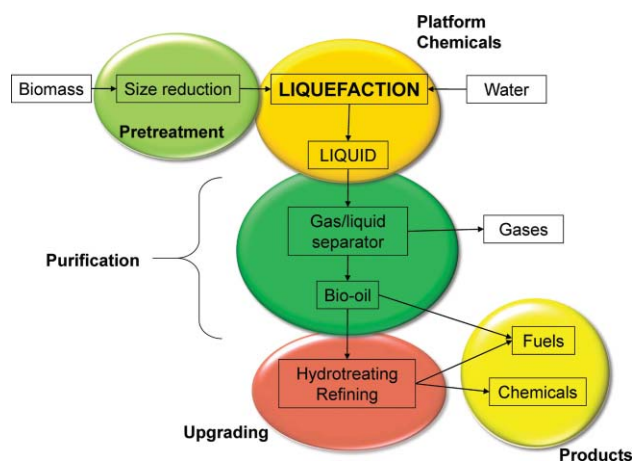


Fig. 10 Process schematic: biomass liquefaction and upgrading.

However, problems exist associated with the complexity of the bio-oil product, leading to unsuitability for long term storage.<sup>64</sup> Different approaches such as hydrodeoxygenation or steam reforming<sup>59</sup> have been proposed to upgrade the bio-oils and to solve the stability issues. The hydrogen required by these upgrading strategies can be obtained by aqueous reforming of biomass releasing CO<sub>2</sub>,<sup>62–64</sup> thereby decreasing the dependence on external sources of hydrogen. It has also been proposed that bio-oils can serve as appropriate feedstocks for co-processing in petroleum refineries, particularly as both hydrotreating and steam reforming are common practices in petroleum processing.<sup>8</sup>

#### 5.4 Hydrolysis

Hydrolysis pathways are appropriate for lignocellulose processing if higher selectivity is desired in biomass utilization, for example, in the production of chemical intermediates or targeted hydrocarbons for transportation fuel. Selective transformations require isolation of sugar monomers, a step which is complex and expensive for lignocellulosic feedstocks. Once sugar monomers are isolated, however, they can be processed efficiently at relatively mild conditions by a variety of catalytic technologies. Lignin utilization remains a challenge, although it makes a suitable feedstock for phenolic resins<sup>18</sup> bio-oil/aromatic production through pyrolysis or catalytic fast pyrolysis,<sup>21</sup> or heat and power production.<sup>16</sup> Aqueous phase processes for the conversion of carbohydrate-derived compounds are potentially attractive in that they do not require concentration of the aqueous solution and generally yield a gas phase or hydrophobic product that separates spontaneously from water, which reduces the cost of separation steps in the catalytic processing strategies. The primary motivation of the chemical route is the targeted reduction of the high oxygen content of carbohydrates (10 to 44%)<sup>27</sup> by different reactions such as hydrogenolysis, dehydration or hydrogenation to obtain hydrocarbons with increased energy density.<sup>65,66</sup> One of the main drawbacks of this alternative is that, as in the production of cellulosic ethanol, aqueous phase catalytic processing requires a pretreatment step to hydrolyze solid lignocellulose to soluble carbohydrates.<sup>56,67</sup> However, an advantage in using catalytic chemical approaches is decreased processing times compared to biological approaches.

For example, following the pretreatment step, the time to convert cellulose to levulinic acid in the Biofine process (30 min) is shorter than the time to convert cellulose (7 days) and starch (2 days) to ethanol.<sup>68</sup> Finally, catalytic/chemical routes for aqueous phase processing can be targeted for the production of hydrophobic compounds that separate spontaneously from water not requiring distillation processes to purify the final products, compared to fermentation/distillation that accounts for approximately 67% of the ethanol production cost.<sup>69</sup>

Depending on the available feedstock and desired product, thermochemical and hydrolysis pathways may both be important in the production of sustainable fuels and chemicals. The advancement of both technologies reduces the dependence upon one process or one kind of biomass, and an integrated biorefinery must ultimately be more adaptable than an analogous petroleum refinery with its dependence on a single feedstock. Recently, studies have examined potential synergies between pyrolysis and hydrolysis pathways and concluded that there is little difference in carbon yields to upgradeable products.<sup>21</sup> The authors suggest that a combination of hydrolysis and pyrolysis pathways can, in fact, be more efficient provided that appropriate upgrading strategies are in place for hydrolysis products (*i.e.*, sugars such as glucose and xylose), and they conclude that there are potential applications for pyrolysis of lignins to produce value-added chemical intermediates or fuel additives.<sup>21</sup> In general, we anticipate that important contributions will be made by biological, hydrolysis, and thermal pathways in biorefineries of the future, where a combination of all these processes will be necessary to process 100% of the biomass with the maximum yield possible, though the remainder of this review shall focus upon hydrolysis based strategies for the production of fuels.

The following sections provide a discussion of various aqueous phase catalytic strategies available for processing a variety of biomass derivatives including sugars, polyols, furfurals, levulinic acid, and  $\gamma$ -valerolactone, to yield hydrocarbon fuels.

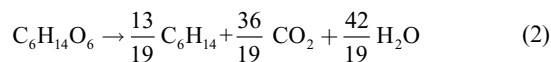
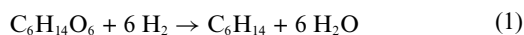
#### 6. Aqueous phase reforming and derivative technologies

Initially presented as a strategy for the production of renewable hydrogen,<sup>64</sup> aqueous phase reforming (APR) has branched into strategies for the production of light alkanes,<sup>70</sup> syngas<sup>53</sup> and monofunctional compounds.<sup>71</sup> Aqueous phase reforming and its derivatives have provided the various alternative strategies shown in Fig. 11.

It has been demonstrated that oxygenated feedstocks such as glucose, sorbitol, glycerol, ethylene glycol, and methanol can be processed to produce renewable hydrogen. This hydrogen can be used directly as energy, in hydrogen fuel cells for example, or indirectly, as an external source of hydrogen required in biomass upgrading processes (*e.g.*, aldol condensation, hydrodeoxygenation). The process is typically carried out in the presence of supported Pt catalysts.<sup>64</sup> The nature of both the metal and support has an important influence on APR reactions of aqueous solutions of oxygenates with C : O stoichiometric ratio equal to 1 : 1 (sorbitol, glycerol, ethylene glycol, methanol), and the product selectivity can be tuned depending on the metal, support, and promoter.<sup>72</sup> Pt-black and Pt supported on Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub><sup>73</sup> have been demonstrated to be active and



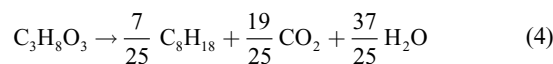
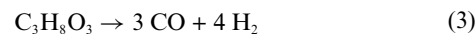
selective for the aqueous phase reforming of methanol and ethylene glycol to produce hydrogen. Catalysts based on Pd have shown similar selectivity, although lower activity compared to Pt analogs. It has also been observed that Rh, Ru, and Ni favor the production of alkanes from polyols as opposed to hydrogen.<sup>74</sup> The reason for this difference is that these metals favor cleavage of C–O bonds rather than C–C bonds. Acidity also has an important effect on reaction selectivity through the catalytic cleavage of C–O bonds by dehydration. The addition of specific promoters can also enhance reforming activity and selectivity for hydrogen production. For example, nickel supported on SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> was found to have low selectivity for hydrogen production; rather, it favored the formation of light alkanes. However, the addition of a Sn promoter to RANEY®-Ni based catalysts enhanced the production of hydrogen from sorbitol, glycerol, and ethylene glycol using low-cost catalysts.<sup>75</sup> As the acidity of the reaction system is increased, either through the use of solid acid catalyst supports (*i.e.*, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>) or the addition of mineral acids to the feed (HCl), the selectivity to alkanes increases<sup>73</sup> due to the increased rates of dehydration and hydrogenation pathways compared to hydrogenolysis and reforming reactions. This tendency can be exploited to selectively produce alkanes (butane, pentane, and hexane) from sorbitol over Pt–SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts<sup>70</sup> (eqn (1)). The formation of smaller alkanes is requisite without an external source of hydrogen, because at least a portion of the 6-carbon sorbitol feedstock must be reformed (by cleavage of C–C bonds) to provide the hydrogen necessary for complete deoxygenation (eqn (2)).



If desired, the selectivity to *n*-hexane can be improved through the introduction of an external hydrogen co-feed. However, the alkanes produced in this manner are limited to a maximum of six carbon atoms and are too volatile to be used in high concentrations as liquid fuels.

Advances in aqueous phase reforming of polyols using Pt-based catalysts have been made toward the low temperature production of syngas from glycerol feedstocks.<sup>53</sup> In this process, it is necessary to utilize a catalyst that favors the cleavage of C–C bonds over C–O bonds, with earlier studies supporting Pt as an appropriate noble metal for this requirement.<sup>64,76</sup> However, at the reaction conditions studied for the gas phase conversion of glycerol (498–548 K) the Pt surface is predominately covered by adsorbed CO molecules, which inhibits catalyst performance.<sup>77</sup> PtRu and PtRe were identified<sup>78,79</sup> as alloys that could offer the reforming activity of Pt but that bind CO less strongly, thus mitigating reaction inhibition in the presence of desired products. Results from experimental studies demonstrated that both of these alloys were active in the production of syngas from glycerol with less susceptibility to poisoning arising from adsorbed CO.<sup>80</sup> The production of syngas from aqueous solutions of glycerol differs in product selectivity from the reforming of glycerol (or other polyols) in that syngas production is carried out at low

system pressure, such that water gas shift is not equilibrated and production of CO and H<sub>2</sub> is favored (eqn (3)), whereas at the elevated pressures typical of APR, high partial pressures of water favor the formation of CO<sub>2</sub> and H<sub>2</sub>. Accordingly, by operating the reactor at lower system pressures, the selectivity can be tailored toward the production of syngas as opposed to the production of H<sub>2</sub> and CO<sub>2</sub>.<sup>80</sup>



Moreover, by producing a catalyst that is less susceptible to inhibition by CO at low temperatures, it is possible to integrate the production of syngas with Fisher–Tropsch synthesis with minimal intermediate processing<sup>54</sup> (eqn (4)).

In addition to decreasing the binding energy of CO on the catalyst surface, leading to higher rates of reforming at low temperatures, the addition of Re to carbon-supported Pt catalysts promotes the water gas shift reaction, as evidenced by an increase in the H<sub>2</sub>/CO ratio and a decrease in the CO/CO<sub>2</sub> ratio with increasing rhenium content of the catalyst.<sup>81</sup> Characterization studies of Pt–Re/C catalysts were carried out to determine that PtRe alloy particles were present on the carbon support.<sup>82</sup> Moreover, microcalorimetric studies indicate a lower binding energy for CO adsorption on Pt–Re alloy, consistent with results from DFT calculations.<sup>79,83–85</sup> Results from reaction kinetics studies of the vapor phase conversion of glycerol over Pt–Re catalysts show that increasing the system pressure shifts the product selectivity away from typical reforming products of H<sub>2</sub>, CO, and CO<sub>2</sub> and favors the production of alkanes and partially deoxygenated reaction intermediates,<sup>82</sup> such as alcohols and ketones, suggesting that it is possible to selectively deoxygenate polyols. Importantly, this result indicates that it is possible to couple biomass reforming strategies with those of hydrodeoxygenation to improve energy density without an external source of hydrogen.

By operating under conditions that favor C–O bond cleavage (*e.g.*, high oxygenate feed concentration, elevated system pressure, low temperature) a Pt–Re/C catalyst is able to partially deoxygenate polyols and produce monofunctional intermediates, which are predominately 2-ketones, secondary alcohols, heterocycles, and carboxylic acids. These monofunctional intermediates can be used as a feedstock for a variety of upgrading strategies that are not limited to the production of shorter alkanes (hexane) or syngas. In this respect, C–C coupling is employed along with oxygen removal to obtain larger hydrocarbons starting from biomass-derived C<sub>5</sub> and C<sub>6</sub> compounds,<sup>86</sup> as depicted in Fig. 12. Ketones can subsequently be coupled *via* aldol condensation using basic catalysts such as MgAlO<sub>x</sub>,<sup>69,87,88</sup> MgAl, Pd–MgO/ZrO<sub>2</sub>, Mg/ZrO<sub>2</sub>, La/ZrO<sub>2</sub>, Y/ZrO<sub>2</sub>, and Mg/TiO<sub>2</sub>.<sup>89,90</sup> Furthermore, introduction of bifunctional metal-basic catalysts allows for the coupling of secondary alcohols in the presence of H<sub>2</sub>. In particular, an equilibrium is established over the metal component of the catalyst between secondary alcohols and 2 ketones, the latter of which can react *via* acid or base catalyzed condensation with other ketones present in

the monofunctional products to yield larger methyl ketones (condensation products).<sup>91,92</sup> In addition, the presence of H<sub>2</sub> is employed in aldol condensation processes to drive the equilibrium toward condensation products by hydrogenation of C=C double bonds formed in dehydrated aldol-adducts. Another effective strategy for achieving C–C coupling between biomass-derived compounds is the ketonization of carboxylic acids, in which two C<sub>n</sub>OOH acids can be converted nearly quantitatively to ketones containing 2n–1 carbon atoms, plus CO<sub>2</sub> and water, in the presence of basic catalysts such as ceria and BaOH.<sup>93–95</sup> For example, CeZrO<sub>x</sub> has been shown to be an active catalyst for ketonization of propionic acid (derived from lactic acid).<sup>96</sup>

The monofunctional compounds produced by conversion of glucose or sorbitol over Pt–Re/C catalysts can also be converted to gasoline by fully hydrogenating these compounds to alcohols, which can subsequently be upgraded over H-ZSM-5, which has been demonstrated to be effective in the catalytic upgrading of bio-oil components.<sup>97</sup> Alternatively, alcohols produced by hydrogenation can be dehydrated over various solid acid catalysts<sup>98</sup> to produce olefins. Kunkes *et al.*<sup>71</sup> designed a cascade process where monofunctional oxygenates are first hydrogenated to form alcohols (*e.g.*, pentanol, hexanol) and then converted directly over H-ZSM-5 at 673 K, during which 40% of the carbon in the monofunctional products is transformed into C<sub>6+</sub> gasoline range components. In a two step process, the alcohols can be dehydrated over an acidic niobia catalyst and the resulting olefins coupled over H-ZSM-5, leading to branched olefins centered at C<sub>12</sub>. To produce less extensively branched compounds appropriate for Diesel fuels, the authors suggest a process by which monofunctional intermediates are condensed directly over CuMg<sub>10</sub>Al<sub>7</sub>O<sub>x</sub> catalysts to produce C<sub>8</sub>–C<sub>12</sub> ketones, accounting for 45% of the carbon in the monofunctional mixture. However, basic CuMg<sub>10</sub>Al<sub>7</sub>O<sub>x</sub> catalysts deactivate with time on stream, attributed to the poisoning of basic sites necessary for aldol condensation by organic acids present in the feed of monofunctional compounds derived from glucose and sorbitol. Neutralization of these acids represents an appropriate strategy for feedstocks with small quantities of acids (*i.e.*, those derived from processing of sorbitol); however, feedstocks derived from glucose were rich in carboxylic acids (30% of the monofunctional compounds), and neutralization of these acids represents both a large consumption of a non-renewable species (NaOH) and a loss of carbon. Accordingly, ketonization can be carried out to achieve C–C coupling and thereby remove the carboxylic acids prior to the aldol condensation step, in which the ketones subsequently undergo C–C coupling over basic sites. According to this strategy, a mixture of monofunctional compounds derived from either glucose or sorbitol would first be fed to a fixed bed reactor containing CeZrO<sub>x</sub> and operating at 573 K and 20 bar. Under these conditions, the acids present in the feed are converted quantitatively to larger ketones (C<sub>7</sub>–C<sub>11</sub>), CO<sub>2</sub>, and water. The C<sub>3</sub>–C<sub>6</sub> ketones present in the feed are not reactive over CeZrO<sub>x</sub> and remain unconverted. By operating at high pressures and low temperature, product vaporization can be minimized, and the effluent from ketonization can be fed to a reactor containing a bifunctional aldol condensation catalyst, such as Pd/CeZrO<sub>x</sub>, which shows good condensation activity and improved resistance to organic acids. Using a combination

of ketonization and aldol condensation, the authors report a yield of 63% to C<sub>7+</sub> oxygenates from a glucose-derived stream of monofunctional compounds. The production of liquid alkane fuels through similar avenues based on a monofunctional platform has also been reported elsewhere by Blommel *et al.*<sup>99</sup>

The combined use of CeZrO<sub>x</sub> and Pd/CeZrO<sub>x</sub> catalysts to achieve ketonization and aldol-condensation of biomass-derived monofunctional compounds has been studied in detail.<sup>100</sup> In particular, CeZrO<sub>x</sub> demonstrated high activity for ketonization of carboxylic acids to form CO<sub>2</sub> and water, whereas Pd/CeZrO<sub>x</sub> demonstrated high activity for aldol-condensation of 2-hexanone, secondary alcohols, and other ketones introduced as co-feeds with 2-hexanone. Primary alcohols are detrimental to catalytic activity for aldol-condensation, which can be attributed to the formation of aldehydes. The presence of carboxylic acids (*e.g.*, butyric acid) in a 2-hexanone feed strongly inhibits the aldol condensation of the ketone over Pd/CeZrO<sub>x</sub>, thus requiring ketonization of the biomass-derived feedstock prior to aldol-condensation. However, the water and CO<sub>2</sub> products of ketonization may also potentially serve to inhibit the rate of aldol-condensation over Pd/CeZrO<sub>x</sub> in the downstream reactor, and experiments were designed to study the aldol-condensation of ketones over Pd/CeZrO<sub>x</sub> in a feed prepared to simulate the effluent from an upstream ketonization step over CeZrO<sub>x</sub>, thus containing water and CO<sub>2</sub>. Whereas aldol condensation over Pd/CeZrO<sub>x</sub> was weakly inhibited by water, the rate was strongly inhibited by the presence of CO<sub>2</sub>, which binds to the strong basic sites of CeZrO<sub>x</sub>. Accordingly, the coupling of ketonization/condensation processes to achieve C–C coupling of mixtures containing carboxylic acids and ketones is best achieved with an intermediate separation stage to remove water and CO<sub>2</sub> between the two catalyst beds.<sup>100</sup> Inhibition of aldol condensation by CO<sub>2</sub> was shown to be reversible at reaction conditions, and subsequent temperature programmed reaction studies demonstrated that Pd/CeZrO<sub>x</sub> catalyzes the reduction of surface bound CO<sub>2</sub> to form CO and methane.

In more recent studies, Gurbuz *et al.* studied the coupling between ketonization and aldol-condensation by varying the composition of the downstream aldol-condensation catalyst.<sup>101</sup> Importantly, they found that the inhibiting effects of both CO<sub>2</sub> and water can be suppressed by decreasing the amount of cerium in the ceria/zirconia mixed oxide aldol-condensation catalyst, such that a Pd/ZrO<sub>2</sub> catalyst (in which the strong basic functionality has been largely removed) was effective for aldol-condensation in the presence of CO<sub>2</sub> and water. Ketonization and aldol condensation can thus be achieved in a single reactor using stacked catalyst beds of CeZrO<sub>x</sub> followed by Pd/ZrO<sub>2</sub>, thus eliminating the need for an intermediate separation step between catalysts. Additionally, the acidic ZrO<sub>2</sub> support shows improved conversion of heterocyclic compounds present in the mixture of monofunctional compounds produced by conversion of glucose or sorbitol over Pt–Re/C catalysts. The overall conversion and yield to C<sub>7+</sub> products using a stacked bed system were comparable to those obtained using a two-reactor system with intermediate separation between reactors.

Studies of the acid/base properties of ceria/zirconia mixed oxide catalysts were carried out using temperature programmed desorption of ammonia and CO<sub>2</sub>. Catalysts with greater proportions of ceria adsorb larger amounts of CO<sub>2</sub> and also show sites

that adsorb CO<sub>2</sub> more strongly (leading to catalysts that display both strong and weak binding sites). Catalysts with greater proportions of zirconia adsorb larger amounts of ammonia. Pd/ZrO<sub>2</sub> catalysts show higher activity for aldol condensation of 2-hexanone compared to Pd/CeZrO<sub>x</sub> catalysts<sup>102</sup> (90% conversion of 2-hexanone *versus* 58% conversion, respectively). Additionally, because the ZrO<sub>2</sub>-rich catalyst binds CO<sub>2</sub> weakly, the extent of inhibition by CO<sub>2</sub> is lower compared to catalysts rich in CeO<sub>2</sub>. In particular, the introduction of 10 mol% CO<sub>2</sub> into a 2-hexanone feed decreases the conversion from 58% to 5% over a Pd/CeZrO<sub>x</sub> catalyst, while the conversion over the Pd/ZrO<sub>2</sub> catalyst decreases from 90% to 72%. Indeed, experiments using stacked beds of CeZrO<sub>x</sub> and Pd/ZrO<sub>2</sub> and a feed containing 20% butyric acid in 2-hexanone demonstrated that the upstream CeZrO<sub>x</sub> catalyst can achieve complete conversion of the butanoic acid, and the downstream Pd/ZrO<sub>2</sub> catalyst can convert the 2-hexanone feed (75%) to larger oxygenates.<sup>102</sup>

The aforementioned studies of APR have mainly been carried out using C<sub>6</sub> polyols and glucose. Blommel and coworkers suggest that APR processing is sufficiently robust to accommodate the processing of C<sub>5</sub> sugars, and that the inclusion of the hemicellulose fraction of biomass would improve the production capacity of hydrocarbons from sugar cane bagasse by approximately 30%.<sup>99</sup>

## 7. Selective transformations of platform chemicals

Given the chemical disparity that exists between feedstock and end product, the preparation of fuels or chemicals from biomass will typically occur through partially deoxygenated biomass derivatives, as outlined in section 4. In general, a greater degree of selectivity in the preparation of these intermediates—referred to here as platform chemicals—will afford a greater degree of flexibility in downstream processes. Conversion of biomass into functionalized, targeted platform molecules is unique to hydrolysis based methods and allows for the production of a wide range of fuels and chemicals. In the following sections, we describe methods for production and processing of several important platform molecules, furfural and hydroxymethylfurfural (HMF), levulinic acid (LA) and  $\gamma$ -valerolactone (GVL).

### 7.1. Furfural and hydroxymethylfurfural (HMF)

The use of furans, such as HMF and furfural, as precursors of liquid hydrocarbon fuels is an option for the production of linear alkanes in the molecular weight range appropriate for Diesel or jet fuel. Polysaccharides can be hydrolyzed to their constituent monomers, which can subsequently be dehydrated over an acid catalyst (HCl, 423 K<sup>103</sup>) to furan compounds with a carbonyl group such as HMF, 5-methylfurfural, or 2-furaldehyde (furfural). Furthermore, furans can be produced from both cellulose and hemicellulose fractions of biomass; thus, furan platforms utilize a large fraction of the available lignocellulosic feedstock. Furfural and HMF can be produced with good selectivity (*e.g.*, 90%) from xylose and fructose respectively in biphasic reactors,<sup>90,104</sup> whereas yields are lower for glucose (42% at low concentrations of 3 wt%).<sup>105</sup> The addition of aprotic solvents, such as DMSO, improves the selectivity to HMF from fructose, with final yields of over 90%.<sup>105</sup> Reducing the water concentration is critical to the selective preparation of HMF, because it is readily hydrated in water to form levulinic acid and formic acid.<sup>106</sup> To minimize the incidence of side reactions, such as condensation, furfural compounds can be extracted from the aqueous layer using organic solvents such as THF, butanol, and methyl isobutyl ketone<sup>103,107</sup> and by addition of salts to the aqueous phase,<sup>108</sup> which decreases the solubility of organic species in water. A potential drawback of this approach is that the use of solvents requires a downstream separation step, which increases the total cost of the process.<sup>109</sup> Roman-Leshkov *et al.* reported a process where they separate the HMF produced using 2-butanol and methyl isobutyl ketone (MIBK), thereby decreasing the energy requirements of downstream purification.<sup>107</sup> The use of DMSO and an extracting solvent can also be employed to increase HMF selectivity to 55% when glucose is used as the feed,<sup>110</sup> compared to 11% in water. Fig. 13 shows different strategies for upgrading HMF to liquid fuels. HMF can be transformed by hydrogenolysis to 2,5-dimethyl furan (DMF) with 76–79% yields over a Cu–Ru/C catalyst or over CuCrO<sub>4</sub> with 61% yield.<sup>108</sup> DMF is not soluble in water and can be used as blender in transportation fuels. To form larger hydrocarbons, HMF and

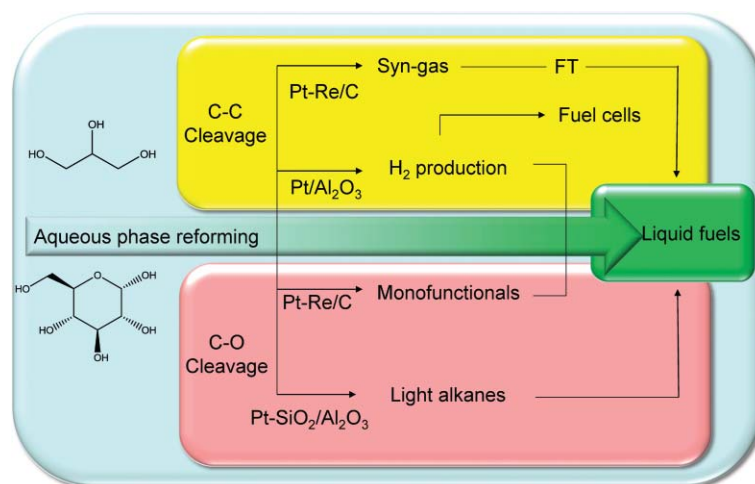


Fig. 11 Processing options to convert sugars and polyols to biofuels by aqueous phase reforming approaches.

other furfural products can be upgraded by aldol condensation with ketones, such as acetone, over a basic catalyst (NaOH) at 298 K.<sup>103</sup> Single condensation of HMF and acetone produces a C<sub>9</sub> intermediate, which can react with a second molecule of HMF to produce a C<sub>15</sub> intermediate. Condensation products can then undergo hydrogenation/dehydration over bifunctional catalysts with metal and acid sites (Pd/γAl<sub>2</sub>O<sub>3</sub> at 373–413 K and 25–52 bar; Pt/NbPO<sub>5</sub> at 528–568 K and 60 bar)<sup>69</sup> to produce linear C<sub>9</sub> or C<sub>15</sub> alkanes that are hydrophobic and separate spontaneously from water, reducing the cost of purification. Aldol condensation can be coupled with hydrogenation steps using a bifunctional catalyst like Pd/MgO–ZrO<sub>2</sub>, leading to high yields of condensation products (>80%) at 326–353 K.<sup>89</sup> By selective hydrogenation, HMF and furfural can be converted to 5-hydroxymethyltetrahydrofurfural (HMTHDA) and tetrahydrofurfural (THF2A) that after self-condensation and hydrogenation/dehydration steps produce C<sub>12</sub> or C<sub>10</sub> alkanes, respectively.

## 7.2. Levulinic acid

The Biofine process,<sup>111,112</sup> see Fig. 14, (which has been scaled to pilot level production) provides an interesting approach to convert lignocellulose to valuable platform chemicals, specifically levulinic acid (C<sub>6</sub> fraction) and furfural (C<sub>5</sub> fraction), that can subsequently be upgraded to liquid biofuels by different routes.<sup>113</sup> The biomass feedstock is mixed with sulfuric acid (1.5–3 wt%) and introduced into a first plug-flow reactor where hydrolysis of the carbohydrates to intermediates (HMF) takes place at 483–493 K and 25 bar with a short residence time (12 s) to minimize the formation of degradation products. Subsequently in a second reactor, the intermediates are converted to levulinic acid and formic acid at 463–473 K and 14 bar, with a residence time close to 20 min. These conditions have been optimized to remove formic acid, as well as remove the furfural arising from dehydration of the C<sub>5</sub> sugars present in biomass. Final yields to levulinic acid are around 70–80% of the theoretical maximum, and correspond to 50% of the mass of

the C<sub>6</sub> sugars. The remaining mass is collected as formic acid (20%) and a solid residue called humins (30%), produced by degradation reactions of the large number of intermediates<sup>114</sup> and Klason lignin. The properties and the amount of this solid residue depend on the feedstock used, and normally this solid is burned to produce heat and electricity. Optimization of the Biofine process for use with inexpensive raw materials could decrease the price of LA to 8–20 ¢/kg,<sup>115</sup> increasing the scope of its potential uses. Pilot plants in the United States and Italy have used paper waste, agricultural residues, and organic municipal wastes<sup>56,116</sup> with successful results. Fig. 15 shows the different pathways to upgrade levulinic acid into different liquid fuels, and the following sections expand upon these applications.

Levulinic acid (LA) can be converted to methyltetrahydrofuran, a fuel extender and part of P-series fuels. MTHF can be blended up to 70% with gasoline without modification of current internal combustion engines. The lower heating value of MTHF compared with gasoline is compensated by its higher specific gravity, which results in similar mileage to that achieved with gasoline. Direct conversion of levulinic acid to MTHF is possible; however, improved yields can be achieved through indirect routes, which proceed through the production of γ-valerolactone as an intermediate. γ-valerolactone can be reduced to 1,4-pentanediol and subsequently dehydrated to MTHF<sup>115</sup> with a total consumption of 3 moles of external H<sub>2</sub> from LA to MTHF.<sup>68</sup> High yields (approximately 63 kg of MTHF for 100 kg of LA at 513 K and 100 bar) have been reported by the U.S. Pacific Northwest National Laboratory using a bimetallic catalyst (Pd(5%)Re(5%)/C).<sup>117</sup>

Another processing option for LA is the production of methyl and ethyl esters that can be blended with Diesel fuel. This esterification can be carried out at room temperature during LA storage in the presence of methanol or ethanol. Various acid catalysts have been studied to increase yields and reaction rates.<sup>118</sup> Studies conducted by Biofine and Texaco<sup>119</sup> have demonstrated that the 21 : 79 formulation, a mixture containing 20% ethyl levulinate, 79% Diesel and 1% of other co-additives, can be used in Diesel engines. The blend is a cleaner burning Diesel fuel (improved

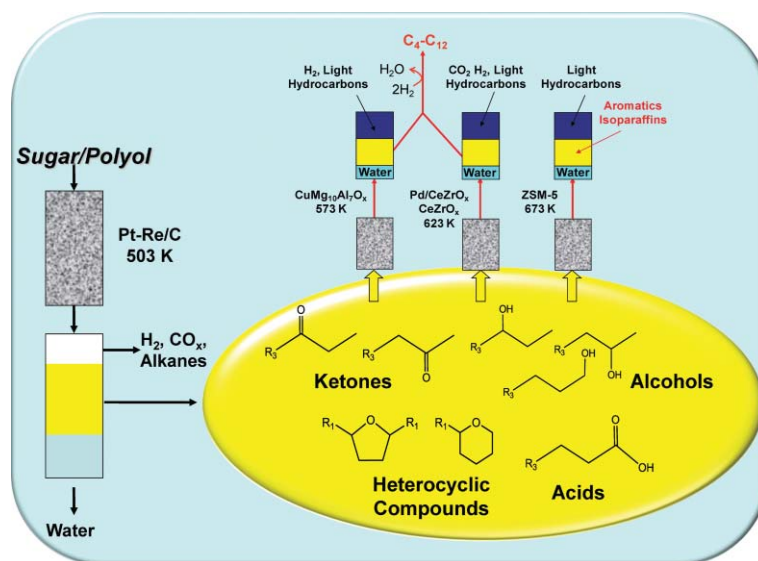


Fig. 12 Schematic pathways to convert sugars and polyols to biofuel through production of monofunctional intermediates. Adapted from ref. 71.



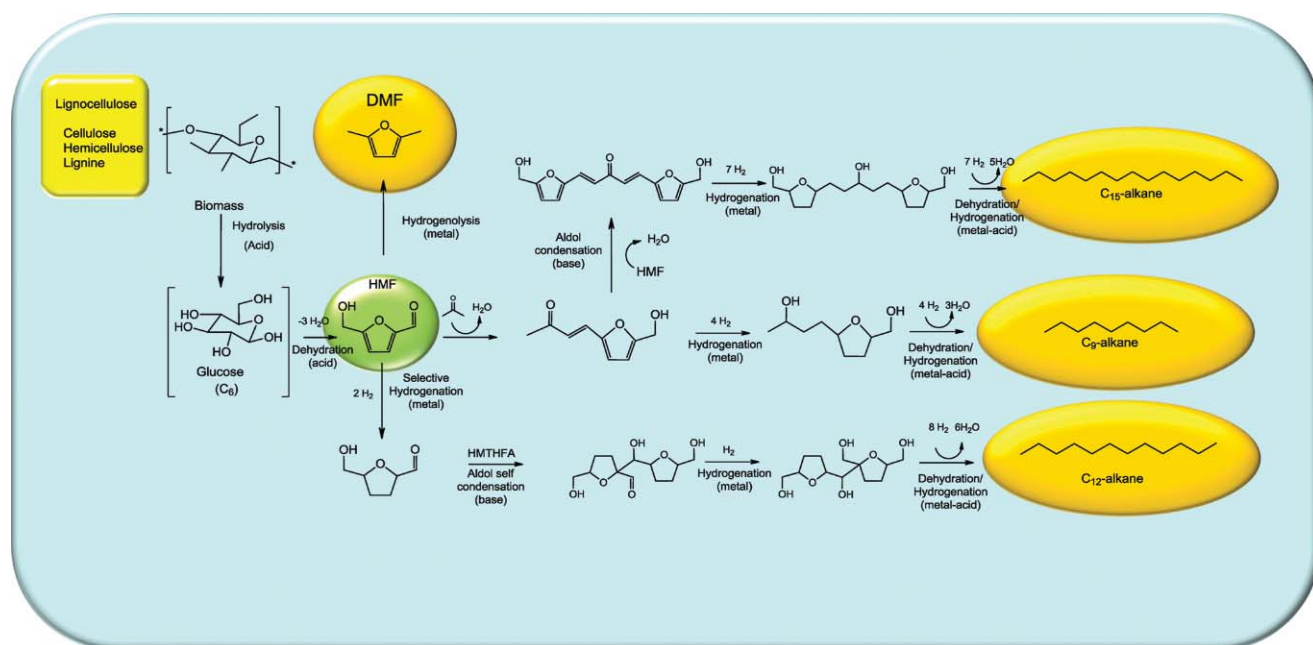


Fig. 13 Reaction pathways to upgrade HMF by aldol-condensation to liquid alkanes. Adapted from ref. 69.

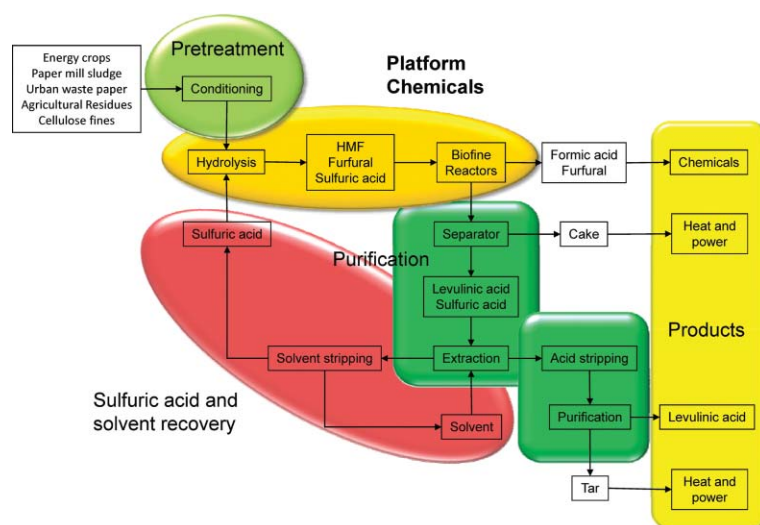


Fig. 14 Levulinic acid production. Biofine process.

by the increased oxygen content of the blend (6.9% w/w) that results in reduced sulfur emissions.<sup>120</sup>

LA can be converted to  $\gamma$ -valerolactone by dehydration to angelica lactone and subsequent reduction, or by reduction to 4-hydroxy-pentanoic acid and subsequent dehydration. These reactions are carried out at relatively low temperatures (373–543 K) and high pressures (50–150 bars), and both homogeneous and heterogeneous catalysts have been studied for this process.<sup>121</sup> LA is solid at room temperature (melting point = 303 K) and different solvents, such as ethylether, dioxane and water, have been used to facilitate pumping. The highest yields of GVL (97%) have been obtained using Ru/C catalysts at 423 K and 34.5 bar using dioxane as solvent.<sup>122</sup> This reduction is normally carried out using external H<sub>2</sub>; however, *in situ* hydrogen production through decomposition of the formic acid, produced

as a by-product in the production of levulinic acid, is a promising alternative. The use of formic acid as a hydrogen donor in aqueous solutions reduces the need for external H<sub>2</sub> in the production of GVL and eliminates the need for LA purification strategies. Both effects ultimately contribute to a lower overall cost for the production of GVL. The mechanism of the hydrogen transfer has not been definitively established. One alternative is that a metal-formate is formed which decomposes into CO<sub>2</sub> and a metal-hydride that reacts with LA to form 4 hydroxypentanoic acid, which then forms GVL by cyclisation. A second alternative is that formic acid is decomposed into CO<sub>2</sub> and molecular H<sub>2</sub>, the latter of which then carries out the hydrogenation.<sup>123</sup>

Recently, several works report a simple process for the production of GVL which integrates hydrolysis/dehydration of the carbohydrates to form LA and the subsequent hydrogenation

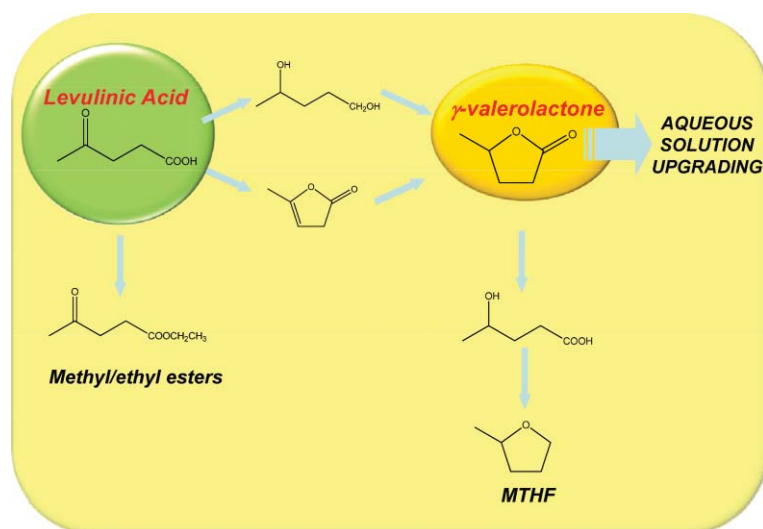


Fig. 15 Schematic pathways to upgrade levulinic acid to liquid fuels.

to GVL in a single vessel.<sup>121,123</sup> It has been reported that sulfuric acid (commonly used in cellulose hydrolysis) poisons the Ru catalyst (used in levulinic acid hydrogenation). Thus, to allow the integration of both reactions in the same vessel, other acids for cellulose hydrolysis have been investigated, such as trifluoroacetic acid. Heeres *et al.*<sup>121</sup> have worked extensively in this area using Ru/C as a catalyst. They report that the overall reaction rate is limited by the hydrogenation of LA to GVL. Using fructose as a raw material, a final yield of 39% for LA and 32% for GVL is achieved in 8 h at 453 K and 50 bars. The yield of GVL can be increased to 43% with 17% yield to LA by increasing the reaction time to 16 h, which indicates that the final products are stable at these reaction conditions. Further improvement to 52% and 11%, respectively, can be achieved if external formic acid is added at the beginning of the reaction. These numbers are close to the maximum yield of LA from fructose reported in the literature, indicating that the reaction rate of fructose hydrogenation to sorbitol/mannitol is slower than dehydration, and the presence of H<sub>2</sub> at the beginning of the reaction does not increase by-product formation. The yields are limited by the maximum yields in LA dehydration, 46% for glucose,<sup>122</sup> 40% for sucrose<sup>113</sup> and 29% for cellulose.<sup>124</sup> When comparing different feeds using formic acid and additional external hydrogen to increase reaction rates, they observe that the maximum yield is reached using fructose (62% GVL, 4% LA) and sucrose (52% GVL, 9% LA), and the yields are lower when using glucose (38% GVL, 4% LA) and cellulose (29% GVL, 6% LA). At low temperatures, the rate of glucose hydrogenation to sorbitol is higher than the rate of dehydration, which results in increased by-product formation. This problem can be addressed through optimization of heat transfer to the reaction medium. Better results have recently been reported using only formic acid as a hydrogen donor, HCl for sugar degradation, and a mixture of RuCl<sub>3</sub>·3H<sub>2</sub>O and PPh<sub>3</sub> as hydrogenation catalyst.<sup>123</sup> The authors observed that using a stronger base as a ligand increases the reaction rate at 423 K, and they suggest that the presence of specific concentrations of water and CO<sub>2</sub> have a positive effect on the final yield to GVL. They observed that with

less than 25% water, the conversion of LA during hydrogenation increased from 78% to 100% when CO<sub>2</sub> was added at 4 MPa. A similar but more pronounced effect is observed at 50% water. However, the positive effect of water is no longer observed at concentrations above 75%. The mechanism of rate enhancement in the presence of CO<sub>2</sub> and water remains unclear.

### 7.3. $\gamma$ -valerolactone

As depicted in Fig. 16,  $\gamma$ -valerolactone can be used in a number of applications, ranging from direct use as a fuel additive or solvent to diverse upgrading strategies for the production of fuels and chemicals.<sup>126</sup> There are limitations to its direct application as a transportation fuel in the present infrastructure, such as low energy density, blending limits, and high solubility in water. Because GVL is derived from levulinic acid in aqueous media, the direct use of GVL as a fuel necessitates purification of the GVL, by separation/purification steps and distillation/extraction methods that remove water and increase the overall cost of the process. The use of solvents, such as ethyl acetate<sup>113</sup> or supercritical CO<sub>2</sub><sup>127</sup> have been proposed to extract GVL, although they can be difficult to operate on large scales. Another alternative is to directly process the aqueous solutions of GVL to produce hydrophobic liquid alkanes with the appropriate molecular weight to be used as liquid fuels. Fig. 17 presents some of the alternatives for converting GVL to liquid hydrocarbons.

Serrano-Ruiz *et al.*<sup>128</sup> have demonstrated that aqueous solutions of GVL (50 wt%) can be upgraded to C<sub>9</sub> hydrocarbons using a flow reactor. GVL can be converted by ring opening to pentenoic acids,<sup>129</sup> and this mixture of pentenoic acids can subsequently be hydrogenated to produce pentanoic acid. Pd/Nb<sub>2</sub>O<sub>5</sub> has been identified as a water stable catalyst that is able to carry out both of these reactions. The yield to pentanoic acid is controlled by the amount of metal incorporated in the catalyst and the partial pressure of H<sub>2</sub>. Increased metal loadings and high partial pressures of H<sub>2</sub> favor the formation of byproducts, such as butane and CO<sub>x</sub> species, that form through

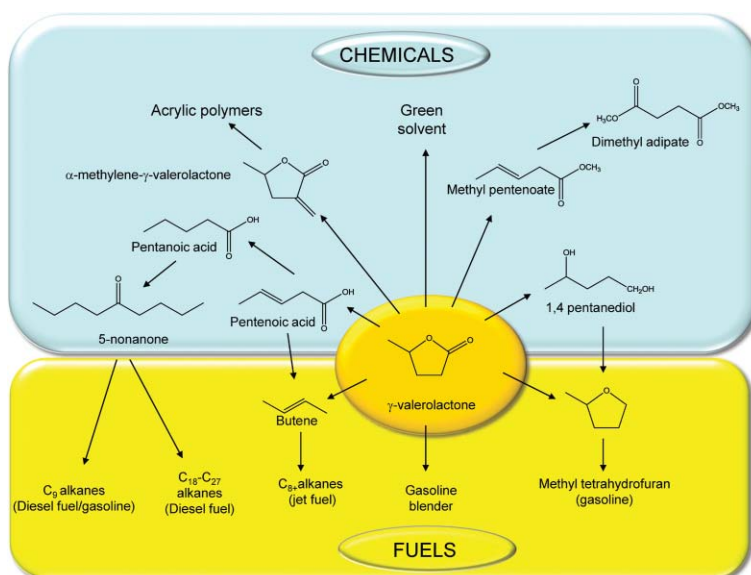


Fig. 16  $\gamma$ -valerolactone applications. Adapted from ref. 125.

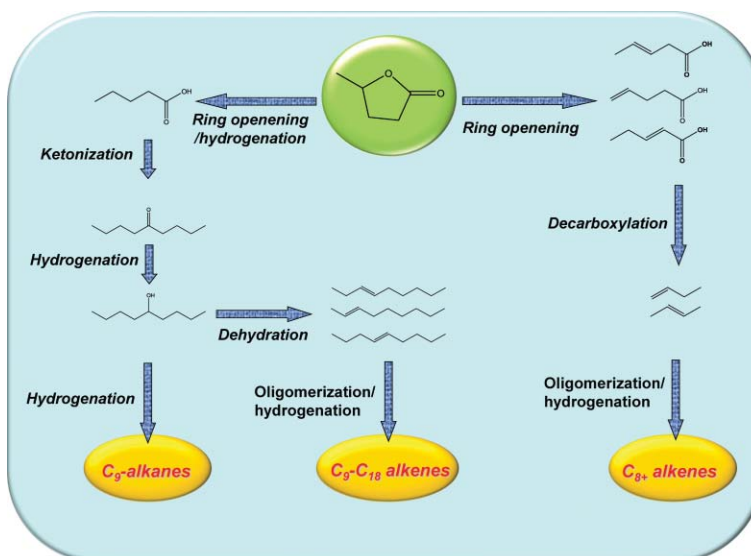


Fig. 17 Reaction pathways to convert  $\gamma$ -valerolactone to liquid fuels.

pentanoic acid decarboxylation/decarbonylation, and pentane, which forms through hydrogenation/dehydration of pentanoic acid. The best yields to pentanoic acid (92%) were obtained with 0.1% Pd at 598 K and 35 bars (50% H<sub>2</sub>, 50% He). Pentanoic acid can be upgraded to 5-nonanone by ketonization<sup>93</sup> over CeZrO<sub>x</sub> at 698 K and pressures from 1 to 20 bar. The ketonization of two molecules of pentanoic acid releases CO<sub>2</sub> and water, and this reaction is thermodynamically favored ( $\Delta G = -65 \text{ kJ mol}^{-1}$ ) at 523 K.<sup>130</sup> At 623 K the yield to 5-nonanone is approximately 60% and the authors report formation of other ketones of lower molecular weight (2-hexanone and 3-heptanone), which form by  $\alpha$  and  $\beta$  scission of 5-nonanone. Ceria-zirconia is an active catalyst for ketonization of organic acids.<sup>96</sup> Accordingly, using a dual catalyst bed system, it is possible to employ the best conditions reported for 0.1%Pd/Nb<sub>2</sub>O<sub>5</sub> to produce pentanoic acid in the first catalytic bed at 698 K, and to employ the best

conditions for ceria-zirconia in the second bed to produce 5-nonanone (698 K and 20 bars). The authors report a final yield of 84% to 5-nonanone with 6% yield to other lower ketones. This 5-nonanone can be hydrogenated/dehydrated to nonane over Pt/Nb<sub>2</sub>O<sub>5</sub> at 528 to 568 K and 60 bar.<sup>103</sup> Lower ketones are converted to C<sub>6</sub>–C<sub>7</sub> alkanes that can be removed in the gas phase and nonane remains in the liquid phase to be used as a blender in Diesel fuels. Another alternative is to hydrogenate the ketones over Ru/C at 423 K and 50 bar to produce alcohols which can be subsequently dehydrated over an acid catalyst, such as Amberlyst 70 (423 K), to produce nonene, which can be coupled by acid catalyzed oligomerization.<sup>131</sup> In this case, smaller ketones would also be converted to alkenes that would undergo oligomerization along with nonene to produce C<sub>6</sub>–C<sub>27</sub> alkenes that can be hydrogenated over Pt/Nb<sub>2</sub>O<sub>5</sub> to liquid alkanes to be used as a jet fuel or Diesel blenders. The molecular

weight range for the final alkanes can be modified by varying reaction conditions of temperature, pressure or WHSV.<sup>131</sup>

A recent alternative approach to upgrade aqueous solutions of GVL to liquid hydrocarbon fuels is based on a dual reactor system reported by Bond *et al.*<sup>132</sup> In the first catalytic reactor, GVL undergoes ring opening to pentenoic acid isomers which subsequently undergo decarboxylation to produce an equimolar mixture of butenes and CO<sub>2</sub>. Both reactions take place over a solid acid catalyst, with good butene yields (*e.g.*, 95%) reported for SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. This reaction proceeds selectively to butene and is thermodynamically favored ( $\Delta G = -123 \text{ kJ mol}^{-1}$ ) at 523 K.<sup>130</sup> In a second reactor connected in series, butene monomers can be coupled by oligomerization over an acid catalyst to form C<sub>8+</sub> alkenes that can be used as jet fuel upon hydrogenation. Excellent yields for butene oligomerization have been reported in the presence of CO<sub>2</sub> and trace quantities of water using Amberlyst 70 as a catalyst. There are several advantages to this processing option. One advantage is that, except for the last mole of H<sub>2</sub> required for alkane production, the process does not require an external source of H<sub>2</sub>. This advantage is unique when compared to other biomass processing options that require significant amounts of external hydrogen, such as hydrotreating of bio-oils or aldol condensation/dehydration-hydrogenation pathways for the production of alkanes. Another interesting advantage that can be leveraged for mitigation of greenhouse gas emissions is the production of a high pressure stream of pure CO<sub>2</sub>, produced through the combination of GVL decarboxylation and butene oligomerization.

Butene oligomerization is favored at elevated pressures, and good yields (*e.g.*, 90%) are reported over Amberlyst 70 at 35 bar. In an integrated, two-reactor process for conversion of GVL to alkene oligomers, it would be desirable to produce butene in the first reactor at the same pressure employed for olefin oligomerization in the second reactor. GVL ring opening is not affected by pressure; however, pentenoic acid decarboxylation is hindered at elevated pressures. For example, at 648 K using a 30% solution of GVL in water, the yield of butene is 75% at 1 bar and only 35% at 35 bars. Working at 673 K, 60% yield of butene can be reached, but catalyst deactivation is observed. Higher rates of GVL conversion can be achieved at higher GVL concentrations in the feed, and the yield of butene increases to 67% for an aqueous feed solution containing 60 wt% GVL. Further increases in the concentration of GVL cause catalyst deactivation, indicating that the presence of water is necessary to maintain catalyst stability in the first reactor.

The butene produced by the decarboxylation of an aqueous solution of GVL contains an equimolar quantity of CO<sub>2</sub> and a significant amount of water (40 wt%). Whereas the presence of CO<sub>2</sub> leads to a decrease in the rate of olefin oligomerization, this decrease is caused simply by a dilution effect, leading to a decrease in the butene partial pressure. For example, using HZSM5 as a catalyst for olefin oligomerization at 498 K and total pressure of 36 bar, the introduction of an equimolar amount of CO<sub>2</sub> decreases the butene conversion from 87% to 64%. Water has a far more pronounced effect on butene oligomerization, and an equimolar co-feed of water is sufficient to decrease the butene conversion to ~50% over H-ZSM-5 and to 0% over Amberlyst 70. However, more than 98% of the water can be removed prior to the butene oligomerization reactor using a

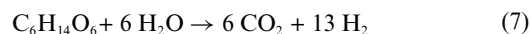
gas-liquid separator operating at the reaction pressure (36 bar) and at temperatures near 373–398 K. Amberlyst 70 is an active catalyst for olefin oligomerization at relatively low temperatures (423 K), a feature that leads to minimal selectivity to undesired cracking products. Using this catalyst for olefin oligomerization, combined with a silica/alumina catalyst for decarboxylation of GVL, an overall yield of approximately 75% can be achieved for the production of C<sub>8+</sub> liquid alkenes from GVL.

## 8. Hydrogen management in the production of biofuels

Hydrogen is broadly utilized in the deoxygenation of biomass derived feedstocks; however, it is desirable to minimize the extent that external H<sub>2</sub> is required for biofuels production, especially if this H<sub>2</sub> is produced from petroleum feedstocks. The initial phase of converting biomass to fuels (the production of an upgradeable platform as outlined in section 4) can proceed in all cases (gasification, pyrolysis, liquefaction, and hydrolysis) without the input of hydrogen. Hydrogen management becomes a more critical issue in the second stage of biofuel production wherein the upgradeable platforms are transformed to liquid hydrocarbon fuels. In the previous sections, we have outlined multiple strategies for each platform and elucidated the underlying chemical transformations. In this section, we outline topics that are important when considering the management of hydrogen in these processes. Generally, the strategies we have presented can be classified as hydrogen producing, hydrogen consuming, and hydrogen neutral.

### 8.1. Hydrogen producing processes

In general, two catalytic options can be employed for the production of renewable hydrogen from biomass. The most basic option is from the gasification platform, which can be combined with the water-gas shift reaction to favor hydrogen production from CO and H<sub>2</sub>O (eqn (5)). The second option is aqueous phase reforming of oxygenates, such as polyols<sup>62–64</sup> (eqn (6) and (7)). These strategies can be considered analogs to the production of hydrogen by steam reforming of petroleum derived feedstocks.

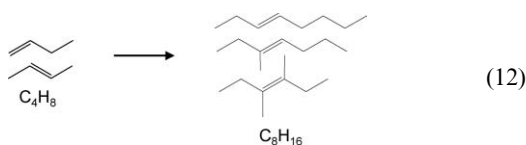
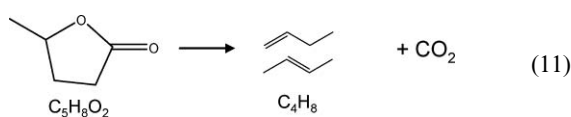
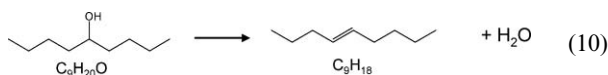
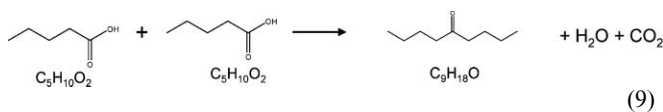
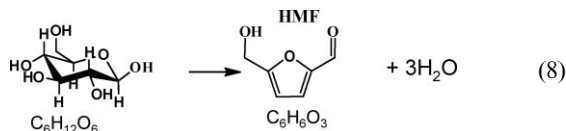


### 8.2. Hydrogen neutral processes

In the conversion of biomass, many important reactions proceed without the input of hydrogen. Dehydration strategies for the production of HMF and furfural are acid catalyzed reactions that lead to removal of oxygen and produce condensation feedstocks without hydrogen consumption (eqn (8)). Ketoneization is a highly selective strategy for the coupling of carboxylic acids, which are readily obtained from biomass derived sources. Ketoneization achieves deoxygenation (formation of CO<sub>2</sub>) and C–C coupling simultaneously in the absence of hydrogen (eqn (9)).



Alcohols are important intermediates in several biomass derived platforms. In the presence of an acid catalyst, the C–O bond of an alcohol is readily cleaved to produce alkenes (eqn (10)). Additionally, alkenes can be produced through decarboxylation of cellulose derived lactones (e.g., GVL) eqn (11). Neither of these strategies for alkene production consume hydrogen.



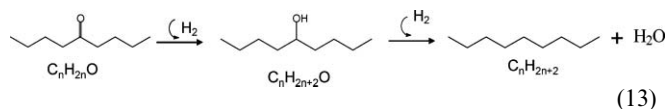
Furthermore, alkenes can be coupled by oligomerization over acidic catalysts without hydrogen input (eqn (12)). Thus, alkene platforms for biomass conversion are particularly attractive from the standpoint of hydrogen management, as the alkenes can be both produced and coupled without hydrogen. Additionally, as the molecular weight of the alkene product is increased by oligomerization, the quantity of hydrogen required per mole of carbon for the production of the final alkane fuel is smaller.<sup>130</sup> Finally, the product of olefin oligomerization is typically a broadly distributed mixture of branched hydrocarbons, which is an important component of jet fuels that is difficult to produce by existing methods such as Fischer–Tropsch synthesis or hydrodeoxygenation of triglycerides. Thus, oligomerization of renewable olefins provides an excellent complementary strategy for the preparation of surrogate jet fuels.

Aldol condensations can be either catalyzed by acid or base, serving to couple ketones, aldehydes, and alcohols, forming large oxygenates. The initial condensation does not consume an equivalent of hydrogen; however, condensation products typically require extensive hydrogenation and hydrodeoxygenation. Thus, condensations are considered again in the following section.

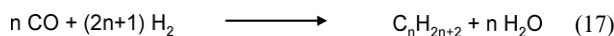
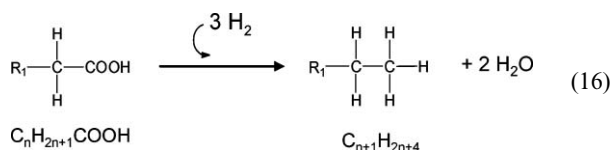
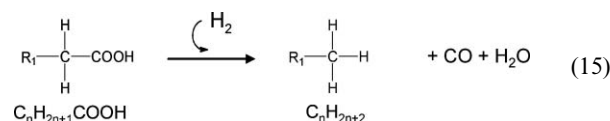
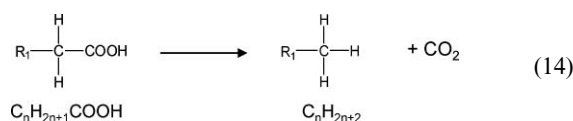
### 8.3. Hydrogen consuming processes

Coupling strategies of sugar derived intermediates (C<sub>3</sub>–C<sub>6</sub>) to form larger hydrocarbons typically rely on the formation of reactive intermediates having a functional group (ketone, alcohol, olefin) that can elicit the formation of new C–C bonds, and the product of C–C bond formation retains some degree of functionality. Thus, the final stage in the production of liquid alkanes is typically the hydrogenation of large, functionalized

species, most commonly ketones, alkenes, or some combination thereof, requiring 2 moles of H<sub>2</sub> for each C–O group and 1 mole of H<sub>2</sub> for each C–C bond (eqn (13)).

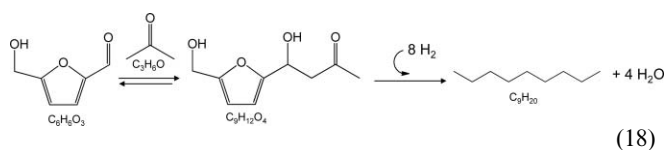


Strategies for the production of *n*-alkanes based on triglycerides achieve hydrodeoxygenation by decarboxylation (eqn (14)), decarbonylation (eqn (15)) and reduction (eqn (16)) and consume large quantities of hydrogen (10–15 moles H<sub>2</sub>) for each equivalent of triglyceride.<sup>44</sup> Pyrolysis and thermochemical processes are attractive, low cost strategies for the production of upgradeable liquid feedstocks (bio-oils) from lignocellulose. They do not require biomass pretreatment and fractionation, and they offer potential for lignin utilization. However, bio-oils require extensive hydrodeoxygenation before use in internal combustion engines or selective upgrading to larger hydrocarbons. Fischer–Tropsch (eqn (17)) is another strategy for the production of linear alkanes which has a large demand for hydrogen as (2*n*+1) moles are required per mole of carbon in the final alkane; however, this H<sub>2</sub> is provided as synthesis gas from biomass gasification, such that gasification combined with FT synthesis is hydrogen neutral.



Aldol condensation reactions are used in the formation of C–C bonds to increase the molecular weight of the final hydrocarbons, for example in the conversion of sugar-derived furans (HMF, furfural) and monofunctional species (alcohols, ketones) to Diesel fuel components. Although aldol condensation is not itself a hydrogen consuming reaction, it is typically equilibrium limited and products are generally hydrogenated to achieve high yields. Thus, aldol condensations utilize high pressures of hydrogen and bi-functional (metal/base) catalysts. Additionally, biomass derived condensation products, particularly those derived from furfural or HMF, are extensively oxygenated and require a large input of hydrogen to produce alkane fuels. It is estimated that the production of C<sub>9</sub> alkanes through condensation of HMF and acetone, for example requires 8 moles of hydrogen per mole of alkane product<sup>69</sup> (eqn (18)). A major benefit accompanying this large consumption of hydrogen, however, is that strategies based on aldol condensation allow for selective production of jet fuel and Diesel range linear alkanes

with minimal carbon branching, which is not possible with hydrogen-neutral strategies such as oligomerization.



## 9. Summary and conclusions

Biomass is a renewable carbon source that can be processed in an integrated biorefinery, in a manner similar to petroleum in conventional refineries, to produce fuels and chemicals. While commercial scale biofuel production has been established with bioethanol (corn, sugar cane) and biodiesel (canola, soybeans), these first generation processes utilize only the edible fraction of certain food crops, thereby decreasing their widespread applicability. The development of second and third generation biofuels that utilize lignocellulosic biomass and algae could allow for the large scale production of sustainable fuels and chemicals. The conversion of biomass to hydrocarbon biofuels faces two general chemical challenges: increasing the energy density of renewable feedstocks by reducing their high oxygen content, and the formation of C–C bonds such that parent monomers (generally limited to 6 carbon atoms) can be coupled to form hydrocarbons of appropriate molecular weight and volatility for use as transportation fuels.

The process of refining lignocellulosic feedstocks to hydrocarbon biofuels can be subdivided into two general portions. First, whole biomass is deconstructed to produce upgradeable gaseous or liquid platforms. This step is typically carried out through thermochemical pathways to produce synthesis gas (by gasification) or bio-oils (by pyrolysis or liquefaction), or by hydrolysis pathways to produce sugar monomers which are then deoxygenated to form upgradeable intermediates. Functional species from each platform are subsequently upgraded by C–C coupling reactions and finally reduced (if necessary) to form the desired liquid hydrocarbon fuel. For example, in strategies based on aqueous phase reforming, sugars/polyols are partially deoxygenated to form monofunctional compounds that are then upgraded by C–C bond forming strategies such as aldol condensation or ketonization to form targeted alkanes. Aqueous solutions of sugars can alternatively be dehydrated to form furfurals that can be coupled using aldol condensation strategies to form larger oxygenates that yield linear C<sub>9</sub>–C<sub>15</sub> alkanes upon dehydration/hydrogenation. Finally, cellulose can be converted into levulinic acid and subsequently into GVL which can be upgraded by ring-opening/ketonization or decarboxylation/oligomerization into targeted alkenes. In each of these strategies, the management of hydrogen plays a key role in eliminating the dependence upon external fossil fuels. In this respect, biorefining steps can be divided into those processes that generate H<sub>2</sub>, such as aqueous phase reforming, those that consume no hydrogen, such as ketonization or oligomerization, and those that consume hydrogen, such as hydrodeoxygenation. Frequently, it is possible to couple strategies that consume hydrogen with those that produce hydrogen such that the net demand of a process is reduced, affording strategies by which lignocellulosic biomass can be utilized efficiently in the

production of fuels, chemicals, hydrogen, and any necessary process heat and power.

## 10. Future perspectives

Currently, the transportation fuel sector depends predominately on a single non-renewable source of energy, namely petroleum. The present situation is not sustainable, and global energy concerns would be greatly alleviated by the adoption of a more flexible system that draws upon multiple resources and technologies. In the long term, solar energy, sustainable electricity, and hydrogen fuel cells may have an impact in the transportation sector as technologies whose efficiencies and environmental impact surpass those of the current combustion engine. However, more research and development are necessary before such alternatives become economically and technically viable. In addition, the current availability and relatively low cost of petroleum, the existing transportation infrastructure, and general consumer preferences all favor continued reliance on liquid alkane fuels.

Carbon-based biofuels serve as a promising short term alternative to petroleum-derived fuels. These biofuels can be derived from renewable carbon sources to mitigate greenhouse gas emissions, and the end products can be employed as drop-in replacements for petroleum fuels. The applicability of biomass as a renewable resource for transportation fuels has been demonstrated by the successful integration of first generation bioethanol and biodiesel into the current infrastructure, and the application of these biofuels has facilitated a reduced dependence upon fossil fuels. However, first generation technologies have drawbacks in that they rely on feedstocks that are not sufficiently available to satisfy the demands presently met by petroleum, and they rely on easily accessible edible biomass fractions, thereby impacting the supply of food for humans and animals. A more sustainable biofuels strategy would utilize widely available biomass feedstocks to the largest extent possible, ultimately drawing upon lignocellulosic biomass instead of only the sparse, edible starch and triglyceride fractions. However, as described thoroughly in this review, lignocellulose processing is less straightforward, owing to its inherent complexity and the diversity of lignocellulosic feedstocks available.

We believe that a successful lignocellulosic biorefinery can be realized through a combination of different technologies and biomass processing strategies for the flexible production of varied fuel and chemical products. As such, catalysis research should focus on (a) continued development of robust strategies for the production of flexible chemical platform molecules, such as levulinic acid and  $\gamma$ -valerolactone, (b) applications for interesting platform chemicals, specifically for the production of speciality chemicals and hydrocarbon fuels, (c) facile strategies for biomass deconstruction, such as fast pyrolysis, (d) methods for the synergistic coupling of hydrolytic and thermochemical methods into a fully integrated biorefinery, (e) implementation of cascade processes combined with the development of straightforward separation and purification schemes, and (f) strategies for lignin utilization. Ideally, advances made toward renewable transportation fuels through catalytic chemistry will be complemented by continuing development in biological

arenas as well, such that future biorefineries can call upon multiple technologies for biomass conversion.

The best strategies are likely to be a combination of technologies that may currently be viewed as competing. Biomass hydrolysis is best suited to the production of targeted fuels or chemicals. For example, levulinic acid and  $\gamma$ -valerolactone are readily prepared in a hydrolysis based system, and they are building blocks that introduce a high degree of flexibility in the system. However, hydrolytic strategies are not well suited to all types of biomass, particularly those containing large fractions of triglycerides and/or lignin. When processing fractions with a low carbohydrate content, other technologies such as hydrotreating, pyrolysis, and gasification can be used to create value. Finally, the development of more robust biological processing options could allow for straightforward production of alcohols and speciality chemicals, both of which could add flexibility and value to an integrated biorefinery. Ultimately, we hope to see a holistic utilization of lignocellulosic biomass through the most efficient processes available, resulting in a cleaner, more sustainable basis for the production of fuels and chemicals.

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