

Chapter 2

Catalytic Production of Liquid Hydrocarbon Transportation Fuels

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Abstract Lignocellulosic biomass resources are abundant worldwide and have the potential to displace petroleum in the production of liquid fuels for the transportation sector of our society. Bioethanol, the dominant biofuel used today, suffers from low energy density and high solubility in water, properties that are undesirable for transportation fuels. The production, from lignocellulosic sources, of liquid hydrocarbon fuels that are chemically similar to those currently used in the transportation sector is a promising alternative to overcome the limitations of bioethanol. The transformation of highly functionalized biomass into oxygen-free liquid fuels can be carried out by gasification, pyrolysis, and aqueous-phase processing, as outlined in this chapter, with particular emphasis on the catalytic aspects of these processes.

Abbreviations

APD/H	Aqueous-phase dehydration/hydrogenation
APR	Aqueous-phase reforming
BTL	Biomass to liquids
CTL	Coal to liquids
DALA	δ -aminolevulinic acid
FTS	Fischer–Tropsch synthesis
GTL	Gas to liquids
GVL	γ -Valerolactone
HMF	Hydroxymethylfurfural
lge	Liter of gasoline equivalent
MTHF	Methyltetrahydrofuran

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Ppm	Parts per million
Syngas	Synthesis gas
WGS	Water–gas shift

2.1 Introduction

Fossil fuels (i.e., coal, natural gas, and petroleum) currently represent the primary source of energy for our modern society. According to the most recent statistics available, in 2008 these nonrenewable resources supplied about 85% of the total energy consumed in the USA [1] and almost 80% of the energy produced in the European Union [2]. This lower use of fossil fuels in the European Union is compensated by more extensive use of nuclear energy, since renewable energy accounted for the same fraction (8%) in both industrialized regions. The energy produced by fossil fuels is unevenly distributed among the different sectors (i.e., residential, commercial, industrial, transportation, and electrical power) of society. Thus, while coal supplies more than 50% of the energy for electricity production and natural gas prevails in the residential and commercial sectors, petroleum accounts for essentially all (96%) of the transportation energy [3]. On the other hand, renewable sources supply less than 10% of the energy to any single sector, with the transportation being the sector with the lowest contribution in this respect (2%). This contribution is expected to increase rapidly within the next few years. Thus, according to projections by the International Energy Agency, the world biofuel production will increase from 1.9 million of barrels per day (mbd) in 2010 to 5.9 mbd by 2030, which represents 6.3% of the world conventional fuel production [4].

The energy consumption data outlined above indicate that fossil fuels dominate the current global energy system. However, there are several important issues inherently associated with the usage of these nonrenewable resources. The first concern is related with availability. Fossil fuel reserves are finite and the current consumption rate increases yearly to meet the growing demand of industrialized countries and rapid development of emerging economies. In this respect, the US Energy Information Administration projects a 35% increase in the world energy consumption over the next 20 years [4], and recent analyses of proven reserves versus consumption rates indicate that oil, natural gas, and coal will be depleted within the next 40, 60, and 120 years, respectively [5]. The second important issue is environmental. The consumption of fossil fuels leads to net emissions of CO₂ into the atmosphere, contributing to global warming and the climatic issues [6]. Recent studies show that the burning of fossil fuels for energy production is responsible for 70% of the global warming problem [7]. The third important issue is derived from the geographical distribution of fossil fuel reserves. It is estimated that 60% of world proven oil reserves and 41% of natural gas supplies are situated in Middle-East countries, whereas USA, Russia, and China monopolize the 60% of the world recoverable coal reserves [4]. This uneven distribution of reserves can lead to political, economic, and security issues worldwide.

To address the above important concerns, governments, through aggressive directives [8, 9], are stimulating society to use renewable sources of energy (e.g., solar, wind, hydroelectric, geothermal, and biomass) to progressively displace oil, coal, and natural gas from the energy production system. Unlike fossil fuels, renewable resources are abundant and well distributed around the world. Additionally, they allow the development of zero-carbon or carbon-neutral technologies, thus contributing to mitigation of global warming effects.

In the same way that fossil fuels have different contributions to the various energy sectors of society, renewable technologies will also be implemented selectively in society. Recent studies indicate that solar, wind, geothermal, and hydroelectric power will be used to generate heat and electricity in stationary power applications, allowing the eventual substitution of coal and natural gas [10, 11]. On the other hand, biomass has been proposed as the only sustainable source of organic carbon currently available on earth [12] and thus, this resource is best suited as a potential substitute for petroleum for the production of fuels and chemicals [13, 14]. The petrochemical industry currently consumes a large fraction of the crude oil to generate liquid hydrocarbon fuels, whereas a minor fraction is used for chemicals production. Consequently, for biomass to effectively replace petroleum, new technologies for the production of liquid fuels from this resource, the so-called biofuels, are necessary. Unlike petroleum-based fuels, biofuels are conceptually carbon neutral, since CO_2 produced during fuel combustion is consumed by subsequent biomass regrowth [15]. However, CO_2 evolved during production and transportation of the biofuel must also be taken into consideration. Additionally, the large-scale production of biofuels can strengthen economies by reducing the dependence on the strong fluctuations in the price of the oil [16] and by creating new well-paid jobs in different sectors such as agricultural, forest management, and oil industries [7].

The liquid biofuels used most widely today for transport are ethanol and biodiesel. Ethanol is the predominant biomass-derived fuel at the present time, accounting for 90% of the total biofuel usage [17]. It is produced by anaerobic fermentation of corn and sugar cane-derived sugars, and only two countries (USA and Brazil) are responsible for 90% of the world production. The fermentation process produces a dilute aqueous solution of ethanol and thus, an expensive energy-consuming distillation step is necessary to completely remove water from the mixture. For ethanol to be used as a fuel in current spark ignition engines, only low-concentration (5–15%) blends with gasoline (i.e., E5–E15) are tolerated, and additional engine upgrades are required for ethanol-rich mixtures (E85). Utilization of edible biomass for its production, high miscibility with water, and the lower energy density compared to gasoline are also important limitations for the implementation of ethanol as a transportation fuel.

Biodiesel is a mixture of long-chain alkyl esters, typically derived from vegetable oils. It is produced by chemically combining the oil with an alcohol (such as methanol) in the presence of a basic catalyst, in a process known as transesterification. Glycerol, in the form of concentrated aqueous solutions, is the primary coproduct of biodiesel production and, as described below (Sect. 2.2.3), important

catalytic routes for the upgrading of this waste stream have already been developed. Similar to ethanol, biodiesel usage is currently limited to low-concentration blends with conventional diesel fuel (B5, B20), since pure biodiesel (B100) can cause rubber and other components in the engine or fuel lines to fail [17]. Additionally, the need for fossil fuel-derived methanol has led to research for utilization of renewable bioethanol as an esterification agent.

The transportation sector of society requires fuels that burn cleanly and have high energy densities for efficient storage at ambient conditions. These criteria are best fulfilled by petroleum-derived liquid hydrocarbon fuels, and infrastructure for the use of these fuels (e.g., engines, fueling stations, distribution networks, petrochemical processes) is already developed for these molecules. The effective and rapid implementation of ethanol and biodiesel has benefitted from this infrastructure, because these biofuels fit, although with several limitations, into the current hydrocarbon-based transportation system. The main limitations of ethanol and biodiesel alkyl esters as transportation fuels (e.g., need for low-concentration blends, lower energy density, miscibility with water in the case of ethanol) are, ultimately, derived from the different chemical composition of these molecules compared to hydrocarbon fuels. Thus, instead of using biomass to produce oxygenated fuels with new compositions, an attractive alternative to overcome these limitations would be to utilize biomass to generate liquid fuels chemically similar to those being used today, which are derived from oil [18]. When compared with ethanol, the production of hydrocarbon fuels from biomass has many important advantages, as outlined below:

- (a) *Compatibility with existing energy infrastructure.* Renewable hydrocarbon fuels would be essentially the same as those currently obtained from petroleum, except that they are made from biomass. Therefore, it would not be necessary to modify existing infrastructure for their implementation in the transportation sector. Additionally, the processes for the production of hydrocarbon biofuels could be coupled with the fuel production systems of existing and well-developed petroleum refineries.
- (b) *High-heating value.* The heating value (i.e., the heat released when a known quantity of fuel is burned under specific conditions) is an important quality of a fuel that finally determines the gas mileage of the vehicle. The oxygen content of the fuel negatively affects this parameter. For example, ethanol has only 66% of the heating value of gasoline and thus, cars running on ethanol-rich mixtures like E85 get a 30% lower gas mileage [19]. Biomass-based hydrocarbon fuels, in contrast, offer equivalent energy content and gas mileage performance to fuels derived from petroleum.
- (c) *Hydrophobicity.* Fuels that do not absorb water are highly desirable. The addition of oxygenates to regular gasoline, however, increases the water solubility of the mixture. In the case of ethanol/gasoline blends, water contamination can trigger a phase separation of both components which is an important concern especially in cooler climates. The hydrophobic character of biomass-derived hydrocarbons eliminates this problem since these molecules are

immiscible in water. Additionally, the ability of hydrocarbons to spontaneously separate from water is also beneficial in that it eliminates the need for an expensive energy-consuming distillation step required in the ethanol purification process.

- (d) *Smaller reactors.* The low energy density of biomass compared to fossil fuels is an intrinsic constraint of this resource. Thus, to process it into energy and fuels, a large amount of biomass will be required, leading to high cost (and probably use of fossil fuels) for transporting it from the biomass source to the processing location [20, 21]. Unlike ethanol, biomass-based hydrocarbon fuels can be produced at high temperatures and using concentrated water solutions [13], which allows for faster conversion reactions and smaller reactors. Thus, instead of having large central processing locations such as those required for ethanol production, these small units could be placed close to the biomass source, thereby avoiding transport of biomass over long distances. It has been suggested that this small-scale, geographically localized distribution of the biofuels industry would additionally benefit rural economies and reduce the vulnerability of infrastructure [15].

One of the main concerns when producing biofuels at large scale is the utilization of edible biomass as feedstocks (e.g., sugars, starches, and vegetable oils). Important moral and ethical questions arise because this practice creates a competition with food for land use. These issues have driven researchers around the world to develop technologies to process nonedible biomass (lignocellulosic biomass), thereby permitting sustainable production of a new generation of fuels (so-called second generation of fuels) without affecting food supplies. In this respect, lignocellulosic biomass is abundant [22] and can be grown faster and at lower price than food crops [23]. Lignocellulosic biomass consists of three major components (Fig. 2.1): cellulose, hemicellulose, and lignin [24, 25]. Cellulose is a linear polymer of glucose, connected linearly by β -1,4-glycoside linkages, that typically comprises about 40–50% of a given lignocellulosic source. As shown in Fig. 2.1, this arrangement allows a high degree of hydrogen bonding between different cellulose chains that confers this material with high stability and resistance to chemical attack [26], high crystallinity, and low surface area. Unlike cellulose, hemicellulose is amorphous and possesses a heterogeneous composition, since it is formed by polymers of five different C_5 and C_6 sugars. It surrounds the cellulose fibers and typically accounts for 20–30% of the total mass of a lignocellulose source. Lignin is a complex three-dimensional polymer of propyl-phenol groups bound together by ether and carbon-carbon bonds. It provides structural rigidity by holding the fibers of polysaccharides together. It is typically found in woody biomass and usually comprises 15–25% of lignocellulose depending on the source.

Two aspects currently limit the implementation of lignocellulose as a feedstock for transportation fuels: recalcitrance and complexity. The structure of lignocellulose, with lignin offering an extra protection to cellulose and hemicellulose, is naturally designed to provide stability and resistance to external attack. In contrast, edible biomass such as starch consists of glucose polymers with α linkages that

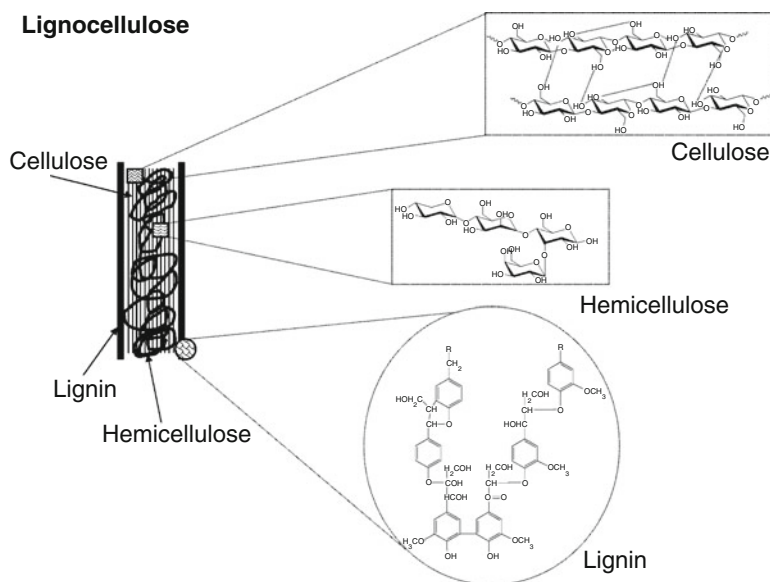


Fig. 2.1 Structure of lignocellulosic biomass and their components. Adapted from [47]

make the polymer highly amorphous and, consequently, more readily deconstructed into monomers [27]. This chemical structure of edible biomass allows simple and economic processing to take place. For example, while corn-derived ethanol can be generated at 0.6–0.8 \$/liter of gasoline equivalent (lge), recent economic studies indicate that the use of lignocellulose for ethanol production would increase the cost to the level of 1.0\$/lge [28]. Accordingly, research is being conducted worldwide on how to decrease recalcitrance of lignocellulosic biomass [29–31] in order to develop cost-competitive technologies for the generation of liquid fuels from nonedible sources. This latter aspect has been identified by experts as the key bottleneck for the large-scale implementation of lignocellulose-derived biofuel industry [32].

The structural and chemical complexity of lignocellulosic biomass suggests that a combination of different processes may be utilized to maximize yields. The most promising methodology used today for biomass processing resembles that used for oil in petroleum refineries, and involves the conversion of lignocellulosic feedstocks into simpler fractions that are subsequently converted into a variety of useful products. These transformations would be carried out in a facility, denoted as a biorefinery, that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from this resource [33–35]. Current technologies for conversion of lignocellulosic biomass into liquid hydrocarbon fuels involve three major primary routes: gasification, pyrolysis, and hydrolysis (Fig. 2.2), and they are described in separate sections of this chapter. The first technology (Sect. 2.2.1) allows biomass transformation into synthesis gas (syngas),

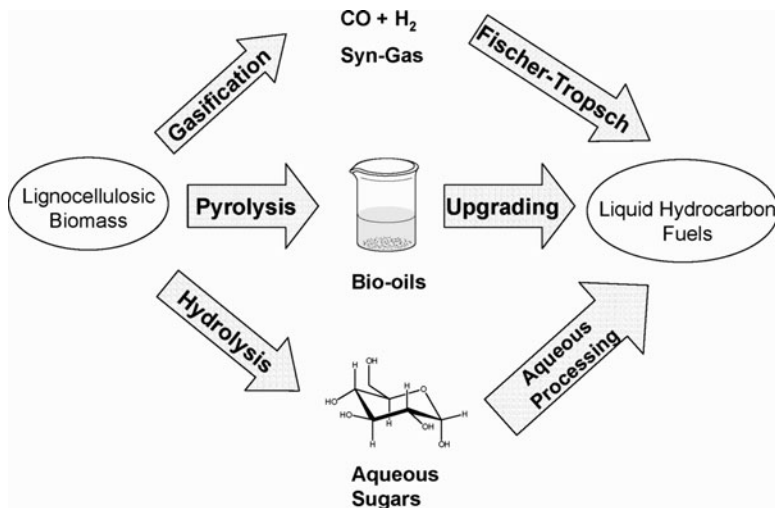


Fig. 2.2 Schematic representation of the different routes for the conversion of lignocellulosic biomass into liquid hydrocarbon transportation fuels

a valuable mixture of CO and H₂ which serves as a precursor of liquid hydrocarbon fuels. The second path (Sect. 2.2.2) converts solid biomass into a liquid fraction known as bio-oil, which can be further upgraded to gasoline and diesel components. Finally, the third route involves the hydrolysis of biomass to produce sugars and valuable intermediates that, as described in Sect. 2.2.3, can be catalytically processed in the aqueous phase to the full range of liquid hydrocarbon fuels including gasoline, diesel, and jet fuels.

2.2 Catalytic Routes for the Production of Liquid Hydrocarbon Transportation Fuels from Lignocellulosic Biomass

Solid biomass is converted by gasification and pyrolysis approaches to gas and liquid fractions, respectively, which are subsequently upgraded to the final fuel products. Gasification and pyrolysis are pure thermochemical routes, that is, biomass decomposition is carried out by increasing temperature and/or pressure under controlled atmosphere in the absence of catalysts, which are used downstream for syngas and bio-oil upgrading processes. Aqueous-phase processing of biomass derivatives, in contrast, involves a series of catalytic reactions to selectively convert water-soluble sugars (or molecules derived from these sugars) into liquid hydrocarbon fuels. A previous lignocellulose pretreatment (to break the lignin protection) and hydrolysis (to depolymerize cellulose and hemicellulose fractions) steps are necessary to generate the aqueous feeds used in this approach.

2.2.1 Biomass to Liquids

The biomass to liquids (BTL) route refers, similar to coal to liquids (CTL) or gas to liquids (GTL) technologies, to biomass conversion into liquid hydrocarbon fuels by the integration of two different processes: biomass gasification to syngas (H_2/CO) and subsequent Fischer–Tropsch synthesis (FTS) to hydrocarbon fuels. Individually, both technologies are relatively well developed. Biomass gasification resembles coal gasification, and FTS is an industrial process first developed in the early 1900s and is used extensively in countries like South Africa to produce liquid hydrocarbon fuels. The challenges of BTL arise when efficient integration of both technologies is required. Thus, the utilization of biomass for the production of syngas in substitution of classical feeds such as coal or natural gas introduces new difficulties that are outlined in this section.

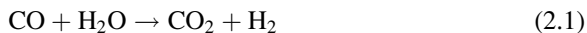
Gasification is defined as a thermal degradation in the presence of an externally supplied oxygen-containing agent (e.g., air, steam, oxygen). By controlling the reaction atmosphere, biomass can be partially combusted to produce a high-heating value gaseous stream composed of CO , H_2 , CO_2 , CH_4 , and N_2 (producer gas), or to generate mixtures enriched in CO and H_2 (syngas) [36]. While producer gas is generated with air as the oxidizing agent and is typically combusted to produce electricity and heat, syngas streams are produced when pure oxygen is used as the oxidizing agent and these streams are preferred as chemical feedstocks for fuels and chemicals. This latter route is the focus of this section.

Gasification of biomass to syngas is favored at high temperatures (e.g., 1,100–1,300 K) because the decomposition of carbohydrates to CO and H_2 is an endothermic reaction [37]. However, at such harsh conditions the control over the gas composition from the gasifier is difficult and depends on diverse factors such as biomass source and particle size, gasification conditions, and gasifier design. As indicated above, co-feeding oxygen below the stoichiometric regime allows mixtures enriched in CO and H_2 to be achieved by favoring partial oxidation reactions [24]. Biomass particle size is also an important factor affecting both gasification rate and gas stream composition. In order to maximize the amount of syngas in the outlet, the particle size of feedstocks should be small enough (lower than 1-mm diameter) for complete and efficient gasification to occur [38]. Regarding the gasifier type, the patent literature contains a large variety of designs depending on bed configurations (fixed or fluidized), feeding approaches (updraft, downdraft, or direct entrained), working pressure (atmospheric or pressurized), and heat supply (direct or indirect) [39]. Research indicates that direct air-blown gasifiers operated at atmospheric pressure are not suitable for BTL applications since the gas stream is obtained highly diluted in inert nitrogen. In contrast, direct entrained gasifiers allow processing at high pressures (10–60 bars), high temperatures (1,500–1,800 K), and short residence times, conditions that favor syngas production [40].

The main issue when biomass gasification is integrated with FTS is the gas cleaning between reactors. The gaseous stream obtained from the gasifier contains,

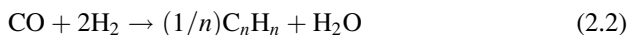
apart from CO and H₂, a number of contaminants that need to be removed before reaching the Fischer–Tropsch unit, which is highly sensitive to impurities. Tars (high molecular weight hydrocarbons produced by incomplete gasification of biomass) represent the main issue in any gasification technology [39]. They condense in the gasifier or in downstream processing equipment, causing blockages of pipelines and troublesome operations. The amount of tar can be reduced by proper choice of gasification conditions and reactor design [41], or by adding solid catalysts based on Pt, Ru, and Ni in the gasifier to assist in the gasification of heavy hydrocarbons [42–45]. Lignocellulosic biomass typically contains a variety of minor components such as proteins rich in sulfur and inorganic materials based on phosphorous, potassium, and halogens. Thus, the gas stream produced from biomass gasification carries alkali, HCl, NH₃, and volatile sulfur compounds that can corrode turbines used for electricity generation or, in the case of BTL technology, can poison the catalysts used in the Fischer–Tropsch downstream unit. Furthermore, the gasification stream, especially when small particle size is used as a feedstock, contains fine particles that can cause blockages and can clog filters.

For the reasons outlined above, BTL technologies must include a gas conditioning unit between the gasifier and the Fischer–Tropsch reactor. Sufficient gas cleaning has been noted as a key point for the development of effective BTL processes [46]. Because the cleaning includes a number of different contaminants (tars, particles, chemicals, etc.) which have to be removed to the ppm level [21], this unit typically comprises multiple steps and advanced technologies [47] that contribute significantly to the complexity and cost of the BTL plant. Another requirement in the gas composition for the Fischer–Tropsch units is related to the CO/H₂ molar ratio. Fischer–Tropsch processes to hydrocarbon fuels usually require syngas with a H₂/CO ratio close to 2 [48, 49], and, due to the high oxygen content of biomass, typical streams delivered from this resource contain a H₂/CO ratio of about 0.5 [50]. This ratio can be adjusted via water–gas shift (WGS) reactions, where CO reacts with steam to produce CO₂ and H₂:



This adjustment can be carried out in an additional WGS reactor between the gasifier and the Fischer–Tropsch unit or, alternatively, can be achieved without additional reactors by co-feeding extra water along with the biomass in the gasifier. This latter alternative, however, negatively affects the thermal efficiency of the gasification process.

After the syngas has been cleaned and “shifted,” it is introduced into the FTS reactor, the last unit of the BTL process. FTS is a well-known industrial process to produce alkanes (C_nH_n) from syngas using Co-, Fe-, or Ru-based catalysts [49]:



The WGS reaction also takes place over Fischer–Tropsch catalysts (especially those based on Fe) allowing the eventual adjustment of the H₂/CO ratio in the same

synthesis bed. One of the main limitations of Fischer–Tropsch technologies is the lack of selectivity in the final alkane product, with broad distributions that can range from C_1 to C_{50} . The Anderson–Schulz–Flory (ASF) polymerization model, which governs the alkane chain growth probability, indicates that neither gasoline nor diesel fuels can be produced selectively without generating a large amount of undesired products [47]. In order to overcome this limitation, indirect routes involving the initial production on heavy hydrocarbons (waxes) and subsequent controlled hydrocracking of these heavy compounds to gasoline and diesel [51], and utilization of active materials for cracking and isomerization such as ZSM-5 as supports of Co and Fe catalysts to produce gasoline components [52] are currently used for selective FTS reactions.

Current BTL activities are at research, development, and demonstration stages. One small demonstration plant in the Netherlands to produce diesel fuel from woody biomass [53], and a more recent plant to produce 15,000 tons per year of liquid fuels from multiple lignocellulosic feedstocks in Germany [54] are the most promising BTL projects at the present time. A challenge for the commercialization of BTL technology is the cost of producing the fuel, negatively affected by the complexity of the process. Thus, this route is only economical on the large scale, requiring the use of large centralized facilities with the corresponding expense of transporting the low energy density biomass. The coproduction, along with hydrocarbon fuels, of higher value chemicals like methanol [55] and hydrogen [56, 57] from biomass-derived syngas is an alternative to improve the economics of the BTL process.

2.2.2 Biomass Pyrolysis Integrated with Upgrading Processes

When biomass is treated under inert atmosphere at temperatures ranging 648–800 K it forms gaseous products which condense, forming a dark viscous liquid commonly known as bio-oil. This liquid consists of a complex mixture of more than 400 highly oxygenated compounds, including acids, alcohols, aldehydes, esters, ketones, aromatic compounds, polymeric carbohydrates, and lignin fragments [58, 59]. The control over the final composition of the bio-oil is difficult, since it is affected by a large number of factors such as feedstock type (wood, agricultural wastes, forest wastes), reaction conditions (temperature, pressure, residence time of vapors), reactor design, alkali content of feedstock, particle size, and storage conditions [60]. In a typical pyrolysis process, bio-oil contains about 25 wt% water (contributed by the water in the initial biomass feedstock and from the conversion process) and 10 wt% of suspended char which is separated for subsequent utilization of the bio-liquid.

Similar to gasification, a key advantage of pyrolysis is that it allows conversion of all the organic matter in lignocellulosic biomass, including the highly resistant lignin portion. Furthermore, a large fraction of biomass energy (up to 70%) is retained in the bio-oil [47] allowing strategies to concentrate the energy of biomass

in a liquid that can be more easily handled and transported. Unlike BTL, pyrolysis is simple and only requires one single reactor, which favors cost-effective conversions on small scale, allowing the use of small portable pyrolysis units easily distributed close to the biomass source [15]. Thus, several small facilities (10–100 tons of biomass per day) are currently in commercial operation in the USA, Canada, and the Netherlands [61]. Bio-oils are currently used as boiler fuels for stationary power and heat production, as well as for chemical production.

There are important barriers for the utilization of bio-oils as transportation fuels. As indicated above, pyrolysis oils are complex mixtures of oxygenated compounds, which confer this liquid with low energy density (typically 50% of conventional hydrocarbon fuels), low volatility, and low stability, characteristics that are undesirable for transportation liquid fuels. Additionally, their high acidity ($\text{pH} \sim 2.5$), viscosity, and water content could cause storage and engine issues. Therefore, bio-oils must be pretreated if they are to be used as transportation fuels. Thus, the main routes for upgrading bio-oils are described in the next sections.

2.2.2.1 Hydrodeoxygenation

The pyrolysis process does not involve deep chemical transformations in the feedstock and, consequently, the composition of the organic liquid resembles that of biomass rather than hydrocarbon fuels. Therefore, in the same way as petroleum feedstocks are refined to adjust their composition to that of conventional fuels, bio-oils must be chemically transformed to provide these liquids with characteristics of hydrocarbon fuels such as high energy density, volatility, and thermal stability. These changes can be accomplished through more extensive removal of oxygen, in contrast with removal of sulfur and nitrogen during refining of petroleum. One of the possibilities to reduce the oxygen content in bio-oils involves the utilization of hydrogen at elevated pressures and moderate temperatures in a process called hydrodeoxygenation [62, 63]. The hydrogenation of bio-oil components is typically carried out over sulfided CoMo- and NiMo-based catalysts, which are widely used for sulfur and nitrogen removal in the petrochemical industry. Precious metals like Pt and Ru have also been used for this purpose, although their high cost and low tolerance to sulfur impurities typically present in bio-oils are serious limitations for their commercial implementation. As a result of hydroprocessing, the oxygenated compounds in bio-oils are completely reduced and oxygen is removed in the form of water, which appears in the reactor as a separate phase. The resulting organic layer possesses hydrocarbon-like properties such as low viscosity, high stability, and high heating value required for fuel applications.

The hydrodeoxygenation of bio-oils has a number of drawbacks that must be addressed to make the process economically feasible. First, hydrodeoxygenation requires the consumption of high amounts of hydrogen, which is typically produced from fossil fuels. This limitation could be overcome by developing strategies to produce hydrogen from lignocellulosic biomass. In this approach, a fraction of the

biomass would be utilized to produce renewable hydrogen, which would be subsequently used for bio-oil deoxygenation. Several technologies for production of hydrogen are currently available and could be utilized for hydrodeoxygenation, including gasification-WGS routes (described in the previous section), steam reforming of water-soluble fractions of bio-oils [64], and aqueous-phase reforming (APR) of biomass-derived sugars [65, 66]. The second important issue of hydrodeoxygenation is derived from the complex composition of the bio-liquid, which includes a large number of compounds (e.g., acids, ketones, aldehydes, alcohols, aromatics) with very different reactivities toward hydrogenation. One of the challenges of this process is, thus, the control over the extent of hydrogenation. The objective is selectively remove oxygen versus hydrogenation of aromatic compounds (derived from lignin and useful as a gasoline components) to avoid unnecessary hydrogen consumption. Finally, the use of high hydrogen pressures (typically above 100 bars) for complete deoxygenation of bio-oils negatively affects the economics of the process by increasing the operational costs.

2.2.2.2 Zeolite Upgrading

An alternative route to achieve deoxygenation of bio-oils without using hydrogen is based on the catalytic cracking approach used in petroleum refining, and it involves the processing of the bio-liquid over acidic zeolites at atmospheric pressure and moderate temperatures [67–69]. As a result of this treatment, the oxygenates in bio-oil are converted, with modest yields, into a mixture of aromatic and aliphatic hydrocarbons, while oxygen is eliminated in the form of CO, CO₂, and water through a complicated set of reactions including dehydration, cracking, and aromatization. The distribution of aromatic and aliphatic hydrocarbons obtained is a function of the acidity and porous structure of the catalysts employed. Thus, while H-ZSM5 maximizes the aromatic to aliphatic ratio, amorphous silica–alumina achieves mostly aliphatic hydrocarbons. When compared with hydrodeoxygenation, zeolite upgrading offers significant processing and economic advantages, since no hydrogen is required and the reaction can be carried out at atmospheric pressure and moderate temperatures (623–773 K). Importantly, these temperatures are similar to those used in the production of bio-oil, which allows the integration of pyrolysis and zeolite upgrading in a single reactor [70]. The usefulness of zeolite upgrading is limited by two important aspects: the poor hydrocarbon yield and deactivation issues. The low hydrocarbon yield is caused by the large fraction of the organic carbon present in the bio-liquid (40–60 wt%) that is lost to the gas phase (in the form of light olefins, CO, and CO₂) and is deposited over the zeolite as coke. This coke deposition produces deactivation of the catalyst, although the initial activity can be recovered by burning off the carbonaceous material. Additionally, irreversible deactivation is observed, because zeolite structures undergo de-alumination at the water contents typically found in bio-oils and produced in situ through dehydration reactions.

2.2.2.3 Ketonization of Bio-oils

The main challenge associated with bio-oil upgrading is to achieve efficient deoxygenation while minimizing the consumption of hydrogen. In particular, the use of hydrogen during bio-oil upgrading allows clean processing without excessive coke formation, but, at the same time, its high cost increases the expense of the process. On the other hand, bio-oils typically contain a significant quantity (up to 30 wt%) of carboxylic acids [71], which provides these liquids with high acidity and corrosiveness. Furthermore, the high reactivity of acids leads to instability of the bio-oil. These undesired properties, along with the high amount of hydrogen consumed by carboxylic acids during hydrodeoxygenation to hydrocarbons, suggest that it would be desirable to develop techniques for effective removal of acidity from bio-oils. In this respect, an interesting route to process the acidic fraction of bio-oils without utilizing hydrogen involves catalytic ketonic decarboxylation or ketonization [72]. By means of this reaction, two molecules of carboxylic acids are condensed into a larger ketone ($2n-1$ carbon atoms) with the release of stoichiometric amounts of CO_2 and water:



This reaction is typically catalyzed by inorganic oxides such as CeO_2 , TiO_2 , Al_2O_3 , and ZrO_2 at moderate temperatures (573–773 K) and atmospheric pressure [73, 74]. Ketonization could find application for catalytic upgrading of bio-oils for several reasons. First, carboxylic acids present in the bio-oil can be selectively removed [75] (without affecting the rest of compounds) and transformed into a more hydrophobic, larger ketone at temperatures and pressures typically used in pyrolysis. Second, this transformation takes place with the simultaneous reduction of the oxygen content of the acid (in the form of water and CO_2) and without using hydrogen. Consequently, a pretreatment of the bio-oil over a ketonization bed could serve to reduce acidity and oxygen content, thereby reducing hydrogen consumption and leaving bio-oil more amenable for subsequent hydrodeoxygenation processing. Third, ketonization can be also applied to other compounds typically present in bio-oils like esters [76, 77], which are formed by reaction between acids and alcohols [78]. Finally, unlike zeolite upgrading, this reaction can be efficiently performed in the presence of moderate amounts of water [79], as typically found in bio-oils.

2.2.3 Aqueous-Phase Processing of Biomass Derivatives

As outlined earlier in this chapter, lignocellulosic biomass is composed of three units: cellulose, hemicellulose, and lignin. The first two units are polymers of C_5 and C_6 sugars which can be deconstructed by enzymatic or acid hydrolysis to yield

aqueous solutions of carbohydrates. However, to allow efficient depolymerization of cellulose and hemicellulose, the lignin protection must be previously broken or weakened. Several approaches, including chemical and physical treatments, have been developed for this purpose [29], and the effects of these pretreatments on the morphology and structure of biomass have been recently studied [31].

The aqueous solution of carbohydrates obtained after hydrolysis can then serve as a feedstock for the production of fuels like ethanol or, alternatively, can be used to produce a set of useful chemical derivatives through chemical and biological routes [80]. As outlined in this section, sugars, as well as some important chemicals derived from them, can also be catalytically processed in the aqueous phase to produce liquid alkanes chemically similar to those currently used in the transportation sector. Unlike the other two major routes for the conversion of lignocellulosic biomass to hydrocarbon fuels (i.e., gasification and pyrolysis), the aqueous-phase processing of biomass-derived compounds is carried out at mild temperatures, which potentially allows for better control of the catalytic chemistry and, with it, the possibility of achieving specific and well-defined liquid hydrocarbon fuels from biomass with high yields. However, the biomass must be previously treated to prepare the aqueous feeds for subsequent catalytic processing and, lignin fraction, once separated, cannot be utilized in this route. These factors represent disadvantages with respect to gasification and pyrolysis, which are designed to operate with raw biomass feedstocks including cellulose, hemicellulose, and lignin components.

Unlike petroleum feedstocks, biomass derivatives contain a high level of functionality (e.g., $-\text{OH}$, $-\text{C}=\text{O}$ and $-\text{COOH}$ groups). This chemical composition clearly determines the catalytic strategies used to upgrade these biomass-derived molecules into liquid hydrocarbon fuels. On one hand, the high oxygen content of these biomolecules has two important consequences: these molecules possess high chemical reactivity (with a natural tendency to decompose with temperature) and, in view of their high solubility in water, they will be typically be obtained from biomass in the form of aqueous solutions. These characteristics suggest that aqueous-phase processing at mild temperatures could be an effective approach for the catalytic treatment of these resources. Unfortunately, the chemical composition of the biomass derivatives, which is quite different from that of the targeted compounds (e.g., liquid alkanes), necessitates deep chemical transformations that typically require multiple processing steps. Consequently, various types of reactions are required, including dehydration, isomerization, C–C coupling, reforming, hydrogenation, and hydrogenolysis. Some of these reactions are especially useful to achieve the requisite deoxygenation of the biomass derivative (e.g., dehydration, hydrogenation, and hydrogenolysis) whereas other reactions (e.g., those of C–C coupling) allow adjustments in the molecular weight of the final hydrocarbon fuel.

Some of the most relevant biomass-derived molecules are discussed in the next subsections. They have been selected in view of their potential to produce liquid hydrocarbon fuels by means of aqueous-phase catalytic processing. Glycerol (Sect. 2.2.3.1) was selected because, as indicated in the Introduction, it is a waste stream of the important and growing biodiesel industry which, in addition, can be produced by bacterial fermentation of sugars [81]. Hydroxymethylfurfural (HMF)

is an important product of the dehydration of glucose and fructose, and it has been extensively studied as important intermediate for production of polymers [80], solvents [82], and fuel additives [83]. As outlined in Sect. 2.2.3.2, HMF can also serve as a platform molecule for the production of liquid hydrocarbon fuels suitable for diesel and jet fuel applications. Instead of using sugars to produce secondary products like glycerol and HMF, these molecules can be used directly as feeds for the production of liquid hydrocarbon fuels through a two-step cascade catalytic approach involving reforming and C–C coupling reactions. This important route, which allows flexible production of hydrocarbon fuels with different compositions for gasoline, diesel, and jet fuel, is the focus of Sect. 2.2.3.3. Deoxygenation of biomass to hydrocarbon fuels is a complicated process that should ideally be carried out with minimal utilization of external hydrogen to make the bio-process economically feasible and cost competitive with current petroleum-based technologies [84]. Thus, the development of catalytic routes for the production of hydrocarbon fuels from biomass without (or with minimal) hydrogen consumption is highly desirable, and recent advances in this respect are described in Sect. 2.2.3.4.

2.2.3.1 Glycerol Conversion Integrated with Fischer–Tropsch Synthesis

Glycerol (1,2,3-propanetriol) is a high boiling point (563 K), water-soluble hygroscopic compound. Glycerol contains three hydroxyl groups which are responsible for its physical properties and, additionally, provide this molecule with high versatility and high chemical reactivity. Thus, oxidation [85], dehydration [86, 87], reduction [88], hydrogenolysis [89, 90], acetalization [91], and etherification [92] reactions can be performed over this molecule to produce valuable chemicals.

Since the development of the biodiesel industry, the upgrading of glycerol into useful products has caught the attention of researchers around the world [88]. The reason for this interest is that significant amounts of glycerol (e.g., 100 kg of glycerol per ton of biodiesel [93]), in the form of concentrated aqueous solutions, are produced daily in biodiesel facilities and will be available in the market. Additionally, glycerol can also be obtained as a by-product of the conversion of lignocellulose into ethanol, which is expected to be an important industry in the near future [94]. Even though glycerol currently has a large number of applications in varied fields such as cosmetics, pharmaceuticals, foods, and drinks, the overproduction of biodiesel-derived glycerol exceeds the current demand of this compound for chemical production and, thus, new technologies for the large-scale usage of this feedstock will be required. The current production of glycerol has currently reached a plateau due to competition with food production, although the expected growth of biodiesel production levels both in Europe and in the US will stimulate researchers to find new applications for crude glycerol. One of the possibilities for large-scale consumption of glycerol would be to utilize glycerol as fuel for the transportation sector. Unfortunately, unlike ethanol, glycerol cannot be directly added to conventional fuels due to its low solubility in hydrocarbons. Additionally, the high viscosity and instability (at high temperatures) of this compound strongly discourage its use as an additive in

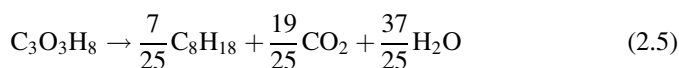
combustion engines. Therefore, glycerol must be chemically transformed (e.g., deoxygenated) to adjust its properties to those of liquid hydrocarbon fuels. In this respect, a promising route for glycerol conversion involves the production of syngas through APR processes [95]:



This reaction is typically carried out over platinum catalysts due to the ability of this metal to achieve C–C breaking reactions (leading to CO, H₂, and CO₂) versus C–O breaking reactions (leading to light hydrocarbons) [65, 96]. To selectively produce syngas, WGS processes [reaction (2.1)] must be avoided, for example, by using inert materials (e.g., carbon) as a catalyst support instead of using oxide supports that can activate water [95]. A combination of chemical inertness (which prevents acid-catalyzed polymerization reactions from occurring) and hydrophobicity (which provides stability under water environments) are probably responsible for the good stability of carbon catalysts in the aqueous-phase processing of glycerol to syngas.

The glycerol-derived syngas can subsequently be used for the production of liquid hydrocarbon fuels and/or chemicals by means of Fischer–Tropsch and methanol syntheses, respectively. This new route would represent an interesting alternative for BTL (Sect. 2.2.1) that would overcome many of the limitations of this complex technology in the production of liquid alkanes from renewable resources, as outlined below:

- (a) In contrast to the high temperatures required for biomass gasification (1,100–1,300 K), glycerol reforming is typically carried out under relatively mild temperatures (498–620 K). These temperatures are within the range employed for FTS [reaction (2.2)] and, consequently, efficient combination of both processes is possible in a single reactor [97].
- (b) Concentrated aqueous solutions of glycerol (as produced in biodiesel facilities) can be reformed in a single reactor and, thus, there is no need for large biomass gasifiers and oxygen-production plants required for BTL. Additionally, the syngas obtained is undiluted and free of impurities, which decreases the capital costs associated with the expensive gas-cleaning unit (Sect. 2.2.1). Consequently, this route allows cost-competitive operations at small scale which is, as outlined in Sect. 2.2.2, advantageous for the processing of distributed biomass resources.
- (c) FTS processes suffer from low thermal efficiency [98]. The coupling of the endothermic glycerol processing to syngas with the exothermic FTS processing, as shown in reaction (2.5) for the case of octane, result in an energy-efficient route for the production of liquid hydrocarbon transportation fuels from a renewable resource.



2.2.3.2 Dehydration of Sugars: HMF and Furfural Platforms to Hydrocarbon Fuels

Biomass-derived sugars, obtained from cellulose, hemicellulose, or starches, can be dehydrated to form furan compounds such as furfural and HMF. These molecules have a large number of applications as chemical intermediates in the production of industrial solvents, polymers, and fuel additives. While industrial production of furfural, based on acid-catalyzed dehydration of C₅ sugars, is well developed [99], HMF generation on large scales is currently limited by the lack of cost-effective technologies, and two main challenges remain in this respect. The first challenge deals with the development of processes for effective production of HMF directly from glucose. In particular, current technologies require a glucose isomerization step to fructose, because dehydration of fructose to HMF takes place with better selectivity and higher rates [100, 101]. The second important issue is related to the control over unwanted side reactions involving the reactant, intermediates, and the final HMF product. In this latter case, the use of biphasic reactors has shown promising results, where fructose is dehydrated to HMF in the aqueous phase and the HMF is subsequently extracted by an organic solvent to avoid further degradation reactions [102].

Apart from the applications noted above, furfural and HMF form the building blocks for the production of liquid hydrocarbon transportation fuels from biomass-derived carbohydrates by means of a cascade process involving dehydration, hydrogenation, and aldol-condensation reactions [103, 104] (Fig. 2.3). The multi-step process starts with acid hydrolysis of polysaccharides such as cellulose, hemicellulose, and starch to produce monosaccharides such as glucose, fructose, and xylose. These sugars can be further dehydrated in the same acid environment to form carbonyl-containing furan compounds such as furfural and HMF. In a subsequent step, these furfural compounds can be converted into larger molecules through aldol-condensation reactions with carbonyl-containing molecules such as acetone. Condensation reactions are typically carried out at low temperatures in polar solvents like water, and are catalyzed by basic solids such as Mg–Al oxides or homogenous base catalysts such as NaOH. The aldol adducts formed contain a higher number of carbon atoms and unsaturated C=C bonds and, consequently, these compounds display low solubility in water and precipitate out of the aqueous phase. Alternatively, the aldol condensation can be carried out in a biphasic reactor where furfural compounds (previously extracted in an organic solvent such as THF) are contacted with an aqueous phase containing NaOH [104]. This process represents an improvement, since the aldol adducts are extracted in situ into the organic phase. Interestingly, the aldol adducts can undergo a second condensation with initial furfural compounds thereby allowing the production of larger molecules (Fig. 2.3). The third step of the process involves the hydrogenation of the C=C and C=O bonds of the aldol adducts in the presence of a metal (typically Pd), thereby increasing the solubility and making large water-soluble organic compounds. Interestingly, aldol condensation and subsequent hydrogenation steps can be carried out in a single reactor by using a bifunctional (metal and basic sites) and

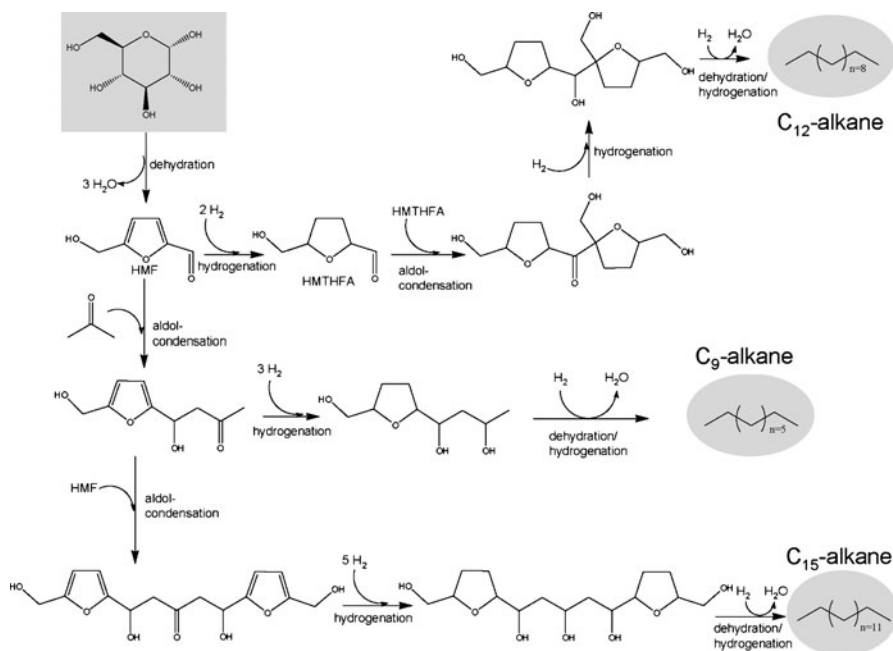
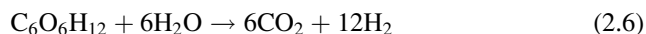


Fig. 2.3 Reaction pathways for the conversion of biomass-derived glucose into liquid alkanes via HMF. Adapted from [103]

water-stable Pd/MgO–ZrO₂ catalyst [105]. In the last step, hydrogenated aldol adducts are converted into liquid alkanes through aqueous-phase dehydration/hydrogenation (APD/H) reactions [106]. This process achieves oxygen removal from the water-soluble adduct by means of continuous cycles of dehydration and hydrogenation reactions over a bifunctional catalyst (Pt–SiO₂–Al₂O₃) containing metal and acid sites. This last step is carried out in a four-phase reactor containing an aqueous solution of adducts, a hydrogen gas inlet stream, a hexadecane sweep stream, and the solid catalyst [103]. As oxygen is removed from the hydrogenated adducts in the form of water, they become more hydrophobic and the hexadecane sweep stream assists the removal of these species from the catalysts surface avoiding overreaction to coke. A recent improvement in the ADP/H step allowed elimination of the hexadecane sweep stream by using water-stable bifunctional Pt/NbPO₄ catalysts [104], in which the niobium-based support presents superior dehydration activity and stability properties under water environments [107]. As a result of this improvement, the final products, liquid hydrocarbon fuels with targeted molecular weights (C₉–C₁₅ for HMF and C₈–C₁₃ for furfural), are obtained in the form of a pure organic stream that spontaneously separates from water and retains about 60% of the carbon of the initial sugar feed.

2.2.3.3 Reforming/Reduction of Sugars Over Pt–Re Catalysts

Biomass-derived carbohydrates (obtained from cellulose and hemicellulose) are typically C₅ or C₆ molecules with a high oxygen content (C:O stoichiometry of 1:1). This chemical composition contrasts with that of transportation fuels, which are larger (e.g., C₅–C₁₂ for gasoline, C₉–C₁₆ for jet fuel, and C₁₀–C₂₀ for diesel applications) and do not contain oxygen. Consequently, the production of liquid hydrocarbon fuels from biomass-derived carbohydrates must involve reactions for oxygen removal (e.g., C–O hydrogenolysis, dehydration, hydrogenation) combined with C–C bond formation steps (e.g., aldol condensation, ketonization, oligomerization) to increase molecular weight. To ensure economic feasibility of the process, this deep chemical transformation should ideally be carried out (a) with minimum use of hydrogen from an external source and (b) with a limited number of reactors and purification/separation steps. Several approaches have been proposed to address these points. First, hydrogen necessary for deoxygenation processes can be provided by a fraction of the same sugar feedstock, utilizing APR reactions to produce hydrogen in situ [65], as indicated in the following equation for the case of glucose:



Second, multifunctional catalysts, able to carry out different reactions in the same reactor, can be used to reduce the complexity of biomass upgrading processes [108].

Recently, a new technology that combines both approaches (e.g., in situ generation of hydrogen and use of multifunctional catalysts) has been used to transform aqueous solutions of sugars and sugar alcohols into liquid hydrocarbon fuels by means of a simple two-step process [75] (Fig. 2.4). In the first step, sugars and polyols are partially deoxygenated over a Pt–Re/C catalyst at temperatures near 500 K to yield a mixture of monofunctional hydrocarbons in the C₄–C₆ range (including acids, alcohols, ketones, and heterocycles) which are stored in an organic phase that spontaneously separates from water. The Pt–Re/C catalyst achieves partial deoxygenation of the sugar feedstock (up to 80% of the oxygen in the initial sugar is removed) by the proper control of the rates for C–C cleavage (leading to CO₂ and H₂) and C–O cleavage (leading to alkanes). The cleavage of C–O is accomplished by reaction with hydrogen (e.g., hydrogenolysis) and is promoted by Re [109, 110]. As oxygen is progressively removed from the intermediates in the form of water, their interaction with the surface of the catalyst becomes weaker, facilitating desorption and resulting in the formation of acids, alcohols, ketones, and heterocycles (Fig. 2.4). Interestingly, this process represents an improvement over pyrolysis (Sect. 2.2.2) since, unlike bio-oils, the monofunctional stream contains a well-defined mixture of hydrophobic compounds in an organic phase completely free of water.

The monofunctional compounds are not completely deoxygenated and they thus contain functionalities that can be used for subsequent upgrading processes.

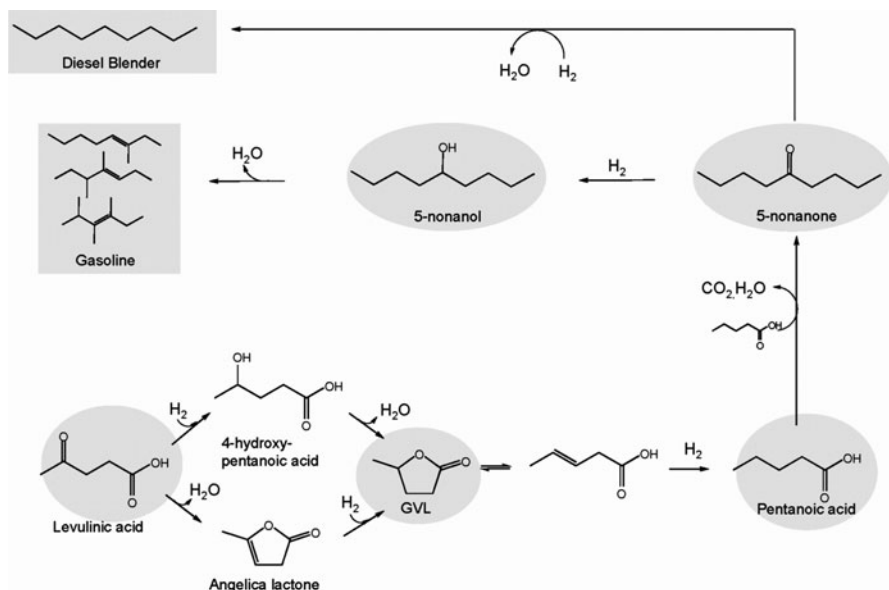


Fig. 2.5 Catalytic routes for the production of liquid hydrocarbon fuels from biomass-derived levulinic acid. Adapted from [84]

2.2.3.4 Levulinic Acid and γ -Valerolactone Platforms to Hydrocarbon Fuels

Levulinic acid (4-oxopentanoic acid) is an important biomass-derived acid that can be obtained in high yields via acid hydrolysis of cellulosic wastes, such as paper mill sludge, urban waste paper, and agricultural residues [112]. Additionally, levulinic acid is considered to be one of the 12 most promising biomass derivatives in view of its potential to serve as a building block for the development of biorefinery processes [80]. Levulinic acid contains two functional groups (C=O and COOH) which gives this molecule a variety of synthetic transformations [113] to generate value-added chemicals such as methyltetrahydrofuran (MTHF) (a gasoline additive) and δ -aminolevulinic acid (DALA) (a biodegradable pesticide) [114].

Recently, our group has developed a catalytic route to upgrade concentrated aqueous solutions of levulinic acid into liquid hydrocarbon fuels (gasoline and diesel) [115]. The catalytic approach involves dehydration/hydrogenation (to reduce the oxygen content of the molecule) and ketonization (to increase the molecular weight) reactions (Fig. 2.5). Interestingly, the use of a bifunctional (metal and acid sites) Pd/Nb₂O₅ catalyst allows these reactions to be carried out with a minimum number of reactors and separation steps. Levulinic acid is first hydrogenated at low temperatures (e.g., 423 K) to form γ -valerolactone (GVL) over a Ru/C catalyst. This hydrogenation step is requisite to prevent the catalytic route from passing through high concentrations of angelica lactone, a known coke

precursor [116] which is produced by dehydration at higher temperatures (e.g., 573–623 K). Aqueous GVL is subsequently transformed into hydrophobic pentanoic acid with high yields over Pd/Nb₂O₅ by means of ring opening (on acid sites) and hydrogenation reactions at moderate temperatures and pressures. Remarkably, when the space velocity is sufficiently low, pentanoic acid is upgraded to 5-nonanone over the same Pd/Nb₂O₅ bed with a 70% carbon yield, allowing the direct production of 5-nonanone from GVL in a single reactor [115]. 5-nonanone, which is obtained in an organic layer that spontaneously separates from water, serves as a platform molecule for the production of liquid hydrocarbon fuels for the transportation sector (Fig. 2.5). For example, the organic C₉-ketone stream can be processed (through hydrogenation/dehydration cycles) over a bifunctional metal–acid catalyst such as Pt/Nb₂O₅ [104] into linear *n*-nonane, with excellent cetane number and lubricity to be used as a diesel blender agent. Alternatively, 5-nonanol, obtained by the hydrogenation of the C₉-ketone, can be dehydrated and isomerized in a single step over an USY zeolite catalyst to produce a mixture of branched C₉ alkenes with the appropriate molecular weight and structure for use in gasoline after hydrogenation to the corresponding alkanes.

GVL is an interesting biomass derivative that has been proposed to be a potential gasoline additive [117] as well as a precursor of polymers [118] and fine chemicals [119]. It is typically produced by catalytic hydrogenation of levulinic acid. This reduction is normally carried out at low temperatures to avoid GVL over reduction to MTHF. However, what makes GVL a very interesting biomass feedstock is the potential to produce it without using any external source of hydrogen. In particular, as a result of the dehydration of C₆ sugars, levulinic acid is produced along with stoichiometric amounts of formic acid, which can be converted to CO₂ and H₂ at the same temperatures used for levulinic acid reduction to GVL. Consequently, formic acid can be utilized as a renewable source of hydrogen for levulinic acid reduction to GVL [120].

Recently, a new catalytic route has taken advantage of this important characteristic of GVL to develop a process that converts aqueous solutions of GVL into liquid hydrocarbon fuels without the need of an external source of hydrogen [121]. In this process, the GVL feed undergoes decarboxylation at elevated pressures (e.g., 36 bar) over a silica/alumina catalysts, producing a gas stream composed of butene isomers and CO₂. This gaseous stream is then passed over an acidic catalyst (H-ZSM5, Amberlyst) that achieves oligomerization of butenes yielding alkenes with molecular weights suitable for gasoline and jet fuel applications. Prior to oligomerization, liquid water must be removed from the gas stream in a separator to achieve effective oligomerization of butene in the second reactor. This technology presents important economic and environmental advantages: (a) no external hydrogen is required in the process, (b) precious metal catalysts are not required, and (c) a gas stream of pure CO₂ is produced at the elevated pressures, thereby permitting effective utilization of sequestration or capture technologies to mitigate greenhouse gas emissions.

2.3 Conclusions

Our society is highly dependent on fossil fuels, which are nonrenewable and contribute to global warming. The production of liquid hydrocarbon transportation fuels from nonedible lignocellulosic biomass is an interesting alternative that can mitigate these issues and overcome many of the limitations of ethanol and biodiesel as biofuels. Recalcitrance and complexity are the two main barriers for the large-scale utilization of lignocellulose as a source of liquid hydrocarbon fuels. Several routes exist for achieving the deep chemical transformations required to convert biomass into liquid hydrocarbon fuels (e.g., BTL, pyrolysis integrated with upgrading processing, and aqueous-phase processing of biomass derivatives), and all of these routes involve the judicious use of heterogeneous catalysts to control the specifications of the final fuel.

References

1. EIA Annual Energy Review (2008) <http://www.eia.doe.gov/aer/pdf/aer.pdf>. Accessed 7 Jul 2010
2. Eurostat (2009) Statistical aspects of the energy economy in 2008, issue number 55/2009. http://epp.eurostat.ec.europa.eu/cache/ITY_OFFPUB/KS-SF-09-055/EN/KS-SF-09-055-EN.PDF. Accessed 7 Jul 2010
3. Simonetti D, Dumesic JA (2008) Catalytic strategies for changing the energy content and achieving C–C coupling in biomass-derived oxygenated hydrocarbons. *ChemSusChem* 1:725–733
4. Energy Information Administration, International Energy Outlook (2009) <http://www.eia.doe.gov/oiar/ieo/pdf/0484%282009%29.pdf>. Accessed 7 Jul 2010
5. BP (2009) Statistical review of world energy. <http://bp.com/statisticalreview>. Accessed 7 Jul 2010
6. Intergovernmental Panel on Climate Change (2007) Climate change 2007: synthesis report. http://www.ipcc.ch/publications_and_data/ar4/syr/en/contents.html. Accessed 7 Jul 2010
7. Worldwatch Institute Center for American Progress (2006) American energy: the renewable path to energy security. <http://www.worldwatch.org/files/pdf/AmericanEnergy.pdf>. Accessed 7 Jul 2010
8. White House (2007) President Bush state on the union address. <http://usgovinfo.about.com/b/2007/01/23/bush-delivers-his-seventh-state-of-the-union-address.htm>. Accessed 7 Jul 2010
9. Official Journal of the European Union (2003) Directive 2003/30/EC of the European Union Parliament. http://ec.europa.eu/energy/res/legislation/doc/biofuels/en_final.pdf. Accessed 7 Jul 2010
10. Kreith F, Goswami DY (2007) Handbook of energy efficiency and renewable energy. CRC Press, Boca Raton
11. Graziani M, Fornasiero P (2007) Renewable resources and renewable energy: a global challenge. CRC Press, Boca Raton
12. Klass DL (1998) Biomass for the renewable energy, fuels and chemicals. Academic, London
13. Chheda J, Huber GW, Dumesic JA (2007) Liquid-phase catalytic processing of biomass-derived oxygenated hydrocarbon to fuels and chemicals. *Angew Chem Int Ed* 46:7164–7183
14. Ragauskas AJ et al (2006) The path forward for biofuels and biomaterials. *Science* 311:484–489

15. NSF (2008) Breaking the chemical and engineering barriers to lignocellulosic biofuels: next generation hydrocarbon biorefineries. <http://www.ecs.umass.edu/biofuels/Images/Roadmap2-08.pdf>. Accessed 7 Jul 2010
16. US Energy Information Administration (2009) Petroleum navigator. <http://tonto.eia.doe.gov/dnav/pet/hist/wtotworldw.htm>. Accessed 7 Jul 2010
17. Worldwatch Institute (2007) Biofuels for transport. Earthscan, London
18. Regalbuto JR (2009) Cellulosic biofuels—got gasoline? *Science* 325:822–824
19. EPA/DOE sponsored web site. <http://www.fueleconomy.gov/feg/flextech.shtml>. Accessed 7 Jul 2010
20. Hamelinck CN, Suurs RAA, Faaij APC (2005) International bioenergy transport costs and energy balance. *Biomass Bioenergy* 29:114–134
21. Spath PL, Dayton DC (2003) Preliminary screening-technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomass-derived syngas. United States Department of Energy, National Renewable Energy Laboratory. <http://www.nrel.gov/docs/fy04osti/34929.pdf>. Accessed 7 Jul 2010
22. Perlack RD, Wright LL, Turhollow AF, Graham RL, Stokes BJ, Erbach DC (2005) Biomass as feedstock for a bioenergy and bioproducts industry: the technical feasibility of a billion-ton annual supply. DOE/GO-102005-2135, Oak Ridge National Laboratory. http://feedstockreview.ornl.gov/pdf/billion_ton_vision.pdf. Accessed 7 Jul 2010
23. Klass DL (2004) Biomass for the renewable energy and fuels. In: Cleveland CJ (ed) *Encyclopedia of energy*. Elsevier, London
24. Lange JP (2007) Lignocellulose conversion: an introduction to chemistry, process and economics. *Biofuels, Bioprod Biorefin* 1:39–48
25. Stocker M (2008) Biofuels and biomass-to-liquid fuels in the biorefinery: catalytic conversion of lignocellulosic biomass using porous materials. *Angew Chem Int Ed* 47:9200–9211
26. US Department of Energy (2005) Feedstock composition glossary. http://www1.eere.energy.gov/biomass/feedstock_glossary.html#C. Accessed 7 Jul 2010
27. US Department of Energy (2005) Feedstock composition glossary. http://www1.eere.energy.gov/biomass/feedstock_glossary.html#S. Accessed 7 Jul 2010
28. International Energy Report (2007) Energy technology essentials, biofuel production. <http://www.iea.org/techno/essentials2.pdf>. Accessed 7 Jul 2010
29. Kumar P, Barrett DM, Delwiche MJ, Stroeve P (2009) Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. *Ind Eng Chem Res* 48:3713–3729
30. Carrol A, Somerville C (2009) Cellulosic biofuels. *Annu Rev Plant Biol* 60:165–182
31. Kumar R, Mago G, Balan V, Wyman CE (2009) Physical and chemical characterizations of corn stover and poplar solids resulting from leading pretreatment technologies. *Bioresour Technol* 100:3948–3962
32. Bozell JJ (2008) Feedstocks for the future: biorefinery production of chemicals from renewable carbon. *Clean Soil Air Water* 36:641–647
33. Lynd LR, Wyman C, Laser M, Johnson D, Landucci R (2002) Strategic biorefinery analysis: analysis of biorefineries, technical report. US National Renewable Energy Laboratory. <http://www.nrel.gov/docs/fy06osti/35578.pdf>. Accessed 7 Jul 2010
34. Kamm B, Gruber PR, Kamm M (2006) Biorefineries-industrial processes and products: status quo and future directions. Wiley-VCH, Weinheim
35. Kamm B (2007) Production of platform chemicals and synthesis gas from biomass. *Angew Chem Int Ed* 46:5056–5058
36. Bridgwater AV (2001) Progress in thermochemical biomass conversion. Blackwell Science Ltd, Oxford
37. Lange JP (2007) Lignocellulose conversion: an introduction to chemistry, process and economics. In: Centi G, van Santen RA (eds) *Catalysis from renewables: from feedstock to energy production*. Wiley, Weinheim

38. Kavalov B, Peteves SD (2005) European commission joint research centre. Status and perspectives of biomass-to-liquid fuels in the European Union. <http://www.mangus.ro/pdf/Stadiul%20actual%20si%20perspectivele%20bio-combustibililor%20in%20Europa.pdf>. Accessed 7 Jul 2010
39. Milne TA, Evans RJ, Abatzoglou N (1998) Biomass gasifier tars: their nature, formation and conversion; Report No. NREL/TP-570-25357. National Renewable Energy Laboratory. <http://www.nrel.gov/docs/fy99osti/25357.pdf>. Accessed 7 Jul 2010
40. Boerrigter H, Van Der Drift A (2004) Biosyngas: description of R&D trajectory necessary to reach large-scale implementation of renewable syngas from biomass. Energy Research Centre of the Netherlands. <http://www.ecn.nl/docs/library/report/2004/c04112.pdf>. Accessed 7 Jul 2010
41. Devi L, Ptasinski KJ, Janssen FJJG (2003) A review of the primary measures for tar elimination in biomass gasification processes. Biomass Bioenergy 24:125–140
42. Rapagna S, Jand N, Kiennemann A, Foscolo PU (2000) Steam-gasification of biomass in a fluidised-bed of olivine particles. Biomass Bioenergy 19:187–197
43. Tomishige K, Asadullah M, Kunimori K (2004) Syngas production by biomass gasification using Rh/CeO₂/SiO₂ catalysts and fluidized bed reactor. Catal Today 89:389–403
44. Sutton D, Kelleher B, Ross JRH (2001) Review of literature on catalysts for biomass gasification. Fuel Process Technol 73:155–173
45. Mudge LK, Baker EG, Mitchell DH, Brown MD (1985) Catalytic steam gasification of biomass for methanol and methane production. J Solar Energy Eng 107:88–92
46. Stahl K, Waldheim L, Morrim M, Johnsson U, Gardmark L (2004) Biomass IGCC at Värnamo, Sweden: past and future, GCEP Energy Workshop. http://gcep.stanford.edu/pdfs/energy_workshops_04_04/biomass_stahl.pdf. Accessed 7 Jul 2010
47. Huber GW, Iborra S, Corma A (2006) Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. Chem Rev 106:4044–4048
48. Caldwell L (1980) Selectivity in Fischer-Tropsch synthesis: review and recommendations for further work. http://www.fischer-tropsch.org/DOE/DOE_reports/81223596/pb81223596.pdf. Accessed 7 Jul 2010
49. Dry ME (2002) The Fischer–Tropsch process: 1950–2000. Catal Today 71:227–241
50. Boerrigter H, Zwart R (2004) High efficiency co-production of Fischer-Tropsch (FT) transportation fuels and substitute natural gas (SNG) from biomass. Energy Research Centre of the Netherlands. <http://www.biosng.com/fileadmin/biosng/user/documents/reports/rx04042.pdf>. Accessed 7 Jul 2010
51. Steynberg A, Dry M (2004) Fischer-Tropsch technology. In: Steynberg A, Dry M (eds) Studies on surface science and catalysis, vol 152. Elsevier, New York
52. Martinez A, Lopez C (2005) The influence of ZSM-5 zeolite composition and crystal size on the in situ conversion of Fischer–Tropsch products over hybrid catalysts. Appl Catal A Gen 294:251–259
53. Boerrigter H, Calis H, Slort D, Bodestaff H, Kaandorp A, Den Uil D, Rabou L (2004) Gas cleaning for integrated biomass gasification (BG) and Fischer-Tropsch (FT) synthesis. Energy Research Centre of the Netherlands and Shell Global Solutions International. <http://www.ecn.nl/docs/library/report/2004/c04056.pdf>. Accessed 7 Jul 2010
54. Choren Industries Press Release. http://www.choren.com/en/choren_industries/information_press/press_releases/?nid=195. Accessed 7 Jul 2010
55. Lange JP (2001) Methanol synthesis: a short review of technology improvements. Catal Today 64:3–8
56. Zhang R, Cummer K, Suby A, Brown RC (2005) Biomass-derived hydrogen from an air-blown gasifier. Fuel Process Technol 86:861–874
57. Koppatz S, Pfeifer C, Rauch R, Hofbauer H, Marquard-Moellenstedt T, Specht M (2009) H₂ rich product gas by steam gasification of biomass with in situ CO₂ absorption in a dual fluidized bed system of 8 MW fuel input. Fuel Process Technol 90:914–921

58. Elliott DC, Beckman D, Bridgwater AV, Diebold JP, Gevert SB, Solantausta Y (1991) Developments in direct thermochemical liquefaction of biomass: 1983–1990. *Energy Fuel* 5:399–410
59. Mohan D, Pittman CU, Steele PH (2006) Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy Fuel* 20:848–889
60. Diebold JP (2000) A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils, Report No. NREL/SR-570-27613. National Renewable Energy Laboratory: Golden, CO. <http://www.p2pays.org/ref/19/18946.pdf>. Accessed 7 Jul 2010
61. Czernik S, Bridgwater AV (2004) Overview of applications of biomass fast pyrolysis oil. *Energy Fuel* 18:590–598
62. Elliott DC (2007) Historical developments in hydroprocessing bio-oils. *Energy Fuel* 21:1792–1815
63. Furimsky E (2000) Catalytic hydrodeoxygenation. *Appl Catal A Gen* 199:147–190
64. Czernik S, French R, Feik C, Chornet E (2002) Hydrogen by catalytic steam reforming of liquid byproducts from biomass thermoconversion processes. *Ind Eng Chem Res* 41:4209–4215
65. Cortright RD, Davda RR, Dumesic JA (2002) Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water. *Nature* 418:964–967
66. Davda RR, Dumesic JA (2004) Renewable hydrogen by aqueous-phase reforming of glucose. *Chem Commun* 36–37
67. Ramesh K, Sharma N, Bakhshi N (1993) Catalytic upgrading of pyrolysis oil. *Energy Fuel* 7:306–314
68. Adjaye JD, Katikameni SPR, Bakhshi NN (1996) Catalytic conversion of a biofuel to hydrocarbons: effect of mixtures of HZSM-5 and silica-alumina catalysts on product distribution. *Fuel Process Technol* 48:115–143
69. Gayubo AG, Aguayo AT, Atutxa A, Aguado R, Bilbao J (2004) Transformation of oxygenate components of biomass pyrolysis oil on a HZSM-5 zeolite. *Ind Eng Chem Res* 43:2610–2618
70. Carlson TR, Vispute TP, Huber GW (2008) Green gasoline by catalytic fast pyrolysis of solid biomass derived compounds. *ChemSusChem* 1:397–400
71. Milne TA, Aglevor F, Davis MS, Deutch D, Johnson D (1997) Development in thermal biomass conversion. Blackie Academic and Professional, London
72. Renz M (2005) Ketonization of carboxylic acids by decarboxylation: mechanism and scope. *Eur J Org Chem* 6:979–988
73. Dooley KM, Bhat AK, Plaisance CP, Roy AD (2007) Ketones from acid condensation using supported CeO₂ catalysts: effect of additives. *Appl Catal A Gen* 320:122–133
74. Hendren TS, Dooley KM (2003) Kinetics of catalyzed acid/acid and acid/aldehyde condensation reactions to non-symmetric ketones. *Catal Today* 85:333–351
75. Kunkes EL, Simonetti DA, West RM, Serrano-Ruiz JC, Gartner CA, Dumesic JA (2008) Catalytic conversion of biomass to monofunctional hydrocarbons and targeted liquid-fuel classes. *Science* 322:417–421
76. Klimkiewicz R, Fabisz E, Morawski I, Grabowska H, Syper L (2001) Ketonization of long chain esters from transesterification of technical waste fats. *J Chem Technol Biotechnol* 76:35–38
77. Gliniski M, Szymanski W, Lomot D (2005) Catalytic ketonization over oxide catalysts: transformations of various alkyl heptanoates. *Appl Catal A Gen* 281:107–113
78. Gaertner CA, Serrano-Ruiz JC, Braden DJ, Dumesic JA (2009) Catalytic upgrading of bio-oils by ketonization. *ChemSusChem* 2:1121–1124
79. Serrano-Ruiz JC, Dumesic JA (2009) Catalytic upgrading of lactic acid to fuels and chemicals by dehydration/hydrogenation and C–C coupling reactions. *Green Chem* 11:1101–1104
80. Werpy T, Petersen G (2004) Top value added chemicals from biomass. US Department of Energy, Office of Scientific and Technical Information. <http://www.nrel.gov/docs/fy04osti/35523.pdf>. Accessed 7 Jul 2010

81. Gong CS, Du JX, Gao NJ, Tsao GT (2000) Coproduction of ethanol and glycerol. *Appl Biochem Biotechnol* 84:543–559
82. Lichtenthaler FW, Peters S (2004) Carbohydrates as green raw materials for the chemical industry. *C R Chimie* 7:65–90
83. Paul SF (2001) US patent 6309430
84. Serrano-Ruiz JC, West RM, Dumesic JA (2010) Catalytic conversion of renewable biomass resources to fuels and chemicals. *Annu Rev Chem Biomol Eng* 1:79–101
85. Gulen D, Lucas M, Claus P (2005) Liquid phase oxidation of glycerol over carbon supported gold catalysts. *Catal Today* 102–103:166–172
86. Chiu CW, Dasari MA, Suppes GJ, Sutterlin WR (2006) Dehydration of glycerol to acetol via catalytic reactive distillation. *AIChE J* 52:3543–3548
87. Katryniok B, Paul S, Capron M, Dumeignil F (2009) Towards the sustainable production of acrolein by glycerol dehydration. *ChemSusChem* 2:719–730
88. Pagliaro M, Rossi M (2008) Future of glycerol, new usages for a versatile raw material. RSC publishing, London
89. Wang H, Liu H (2007) Selective hydrogenolysis of glycerol to propylene glycol on Cu–ZnO catalysts. *Catal Lett* 117:62–67
90. Maris EP, Davis RJ (2007) Hydrogenolysis of glycerol over carbon-supported Ru and Pt catalysts. *J Catal* 249:328–337
91. Ruiz VR, Veltz A, Santos LL, Leyva-Perez A, Sabater MJ, Iborra S, Corma A (2010) Gold catalysts and solid catalysts for biomass transformations: valorization of glycerol and glycerol–water mixtures through formation of cyclic acetals. *J Catal* 271:351–357
92. Karinen RS, Krause AOI (2006) New biocomponents from glycerol. *Appl Catal A Gen* 306:128–133
93. Wiinikainen TS, Karinen RS, Krause AOI (2007) Conversion of glycerol into traffic fuels. In: Centi G, Van Santen RA (eds) *Catalysis for renewables: from feedstocks to energy production*. Wiley-VCH, Weinheim
94. Carbohydrate Economy Bulletin (2000) http://www.carbohydrateeconomy.org/library/admin/uploadedfiles/Carbohydrate_Economy_Bulletin_Volume_1_Numb_3.htm. Accessed 7 Jul 2010
95. Soares RR, Simonetti DA, Dumesic JA (2006) Glycerol as a source for fuels and chemicals by low-temperature catalytic processing. *Angew Chem Int Ed* 45:3982–3985
96. Alcala R, Mavrikakis M, Dumesic JA (2003) DFT studies for cleavage of C–C and C–O bonds in surface species derived from ethanol on Pt(111). *J Catal* 218:178–190
97. Simonetti DA, Rass-Hansen J, Kunkes EL, Soares RR, Dumesic JA (2007) Coupling of glycerol processing with Fischer–Tropsch synthesis for production of liquid fuels. *Green Chem* 9:1073–1083
98. Bartholomew CH, Farrauto RJ (2006) *Fundamental of industrial catalytic processes*. Wiley, Hoboken
99. Zeitsch KJ (2000) The chemistry and technology of furfural and its many by-products. Elsevier, Amsterdam, pp 34–69
100. Chheda J, Roman-Leshkov Y, Dumesic JA (2007) Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and poly-saccharides. *Green Chem* 9:342–350
101. Moreau C, Belgacem M, Gandini A (2004) Recent catalytic advances in the chemistry of substituted furans from carbohydrates and in the ensuing polymers. *Top Catal* 27:11–30
102. Roman-Leshkov Y, Chheda J, Dumesic JA (2006) Phase modifiers promote efficient production of hydroxymethylfurfural from fructose. *Science* 312:1933–1937
103. Huber GW, Chheda JN, Barrett CJ, Dumesic JA (2005) Production of liquid alkanes by aqueous-phase processing of biomass-derived carbohydrates. *Science* 308:1446–1450
104. West RM, Liu ZL, Peter M, Dumesic JA (2008) Liquid alkanes with targeted molecular weights from biomass-derived carbohydrates. *ChemSusChem* 1:417–424

105. Barret C, Chheda J, Huber GW, Dumesic JA (2006) Single-reactor process for sequential aldol-condensation and hydrogenation of biomass-derived compounds in water. *Appl Catal B Environ* 66:111–118
106. Huber GW, Cortright RD, Dumesic JA (2004) Renewable alkanes by aqueous-phase reforming of biomass-derived oxygenates. *Angew Chem Int Ed* 43:1549–1551
107. West RM, Braden DJ, Dumesic JA (2009) Dehydration of butanol to butene over solid acid catalysts in high water environments. *J Catal* 262:134–143
108. Simonetti DA, Dumesic JA (2009) Catalytic production of liquid fuels from biomass-derived oxygenated hydrocarbons: catalytic coupling at multiple length scales. *Catal Rev* 51:441–484
109. Pallassana V, Neurock M (2002) Reaction paths in the hydrogenolysis of acetic acid to ethanol over Pd(111), Re(0001), and PdRe alloys. *J Catal* 209:289–305
110. Kunkes EL, Simonetti DA, Dumesic JA, Pyrz WD, Murillo LE, Chen JG, Buttrey DJ (2008) The role of rhenium in the conversion of glycerol to synthesis gas over carbon supported platinum–rhenium catalysts. *J Catal* 260:164–177
111. Kunkes EL, Gurbuz E, Dumesic JA (2009) Vapour-phase C–C coupling reactions of biomass-derived oxygenates over Pd/CeZrO_x catalysts. *J Catal* 266:236–249
112. Fritzpatrick SW (1997) World patent 9640609
113. Leonard R (1956) Levulinic acid as a basic chemical raw material. *Ind Eng Chem* 48:1330–1341
114. Bozell JJ, Moens L, Elliott DC, Wang Y, Neuenschwander GG et al (2000) Production of levulinic acid and use as a platform chemical for derived products. *Resour Conserv Recycl* 28:227–239
115. Serrano-Ruiz JC, Wang D, Dumesic JA (2010) Catalytic upgrading of levulinic acid to 5-nonanone. *Green Chem* 12:574–577
116. Ayoub P, Lange JP (2008) World Patent WO/2008/142127
117. Horvath IT, Mehdi H, Fabos V, Boda L, Mika LT (2008) γ -valerolactone—a sustainable liquid for energy and carbon-based chemicals. *Green Chem* 10:238–242
118. Lange JP, Vestering JZ, Haan RJ (2007) Towards bio-based Nylon: conversion of γ -valerolactone to methyl pentenoate under catalytic distillation conditions. *Chem Commun* 3488–3490
119. Manzer LE (2004) Catalytic synthesis of α -methylene- γ -valerolactone: a biomass-derived acrylic monomer. *Appl Catal A Gen* 272:249–256
120. Heeres H, Handana R, Chunai D, Rasrendra CB, Girisuta B, Heeres HJ (2009) Combined dehydration/(transfer)-hydrogenation of C₆-sugars (D-glucose and D-fructose) to γ -valerolactone using ruthenium catalysts. *Green Chem* 11:1247–1255
121. Bond JQ, Martin-Alonso D, Wang D, West RM, Dumesic JA (2010) Integrated catalytic conversion of γ -valerolactone to liquid alkenes for transportation fuels. *Science* 327:1110–1114

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