CHAPTER 12

Production of long-chain hydrocarbon biofuels from biomass-derived platform chemicals: Catalytic approaches and challenges

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Abbreviations
- 2-MF: 2-methylfuran
- AL: angelica lactone
- GVL: γ-valerolactone
- HAA: hydroxalkylation-alkylation
- HDO: hydrodeoxygenation
- HMF: 5-hydroxymethylfurfural
- LA: levulinic acid
- RO: ring-opening
- RS: ring-saturation
12.1 Introduction

Bioethanol and biodiesel are the most widely used liquid biofuels for a long time [1]. Bioethanol is usually produced from edible sugars via fermentation processes, while biodiesel is produced from triglycerides in the presence of alcohol (usually methanol or ethanol) via transesterification reaction. However, to reduce the consumption of edible biomass and proper utilization of nonedible biomass, modern biorefinery research has been dedicated to the exploitation of lignocellulosic biomass to obtain various organic chemicals and transportation fuels. Although the consumption of bioethanol and biodiesel has increased exponentially in the last few years due to their simple and well-known production technologies [2], these biofuels have several drawbacks such as low energy density, low oxidation stability, poor cold flow properties, and corrosive nature of biodiesel, which restrict their use as transportation fuels [3, 4]. Although a small amount of oxygen is acceptable in road fuels, aviation fuel must have a minimum gravimetric energy density of 42.8 MJ kg\(^{-1}\) (according to the properties of Jet A-1 fuel) and therefore, oxygen content has to be minimized as much as possible [5]. None of the currently commercialized biofuels have this minimum energy density due to their high oxygen content. Besides, the high water solubility of bioethanol is a big problem for its blending with gasoline as it increases the risk of engine damage. To mitigate these problems, it is important to find out new pathways for the synthesis of hydrocarbon biofuels with high energy content (e.g., gasoline, jet fuel, and diesel). These biofuels have properties similar to current transportation fuels and compatible with the present infrastructure of the transportation sector.

Conversion of biomass-derived platform molecules, such as furfural, 5-hydroxymethylfurfural (HMF), and levulinic acid (LA), into liquid hydrocarbon biofuels is an interesting approach. However, these platform molecules have multiple oxygen functionalities that need to be selectively removed to improve their fuel properties. Hydrodeoxygenation (HDO) is a well-known strategy to convert oxygenated precursors into hydrocarbon biofuel components with a higher H/C ratio. For example, partial or complete HDO of HMF gives 2,5-dimethylfuran or hexane, which have higher energy density. Since biomass-based platform chemicals usually contain five or six carbon units (as they are derived from pentose or hexose sugars), their final HDO products are C\(_5\) or C\(_6\) alkanes. These low-molecular-weight products cannot be used as road transportation fuels or fuel additives because of their low octane number and high volatility. Therefore, a new approach to increase the carbon numbers via the C–C coupling reaction is important to obtain hydrocarbon biofuels with high octane numbers.

This chapter summarizes the strategies for upgrading biomass-derived platform molecules into high carbon-number hydrocarbon biofuels developed in the past few years. The first section is focused on different C–C bond forming reactions for the synthesis of oxygenated fuel precursors. Suitable catalysts and reaction conditions for these reactions...
are briefly discussed. The subsequent section is focused on general strategies for oxygen removal from the oxygenated fuel precursors via HDO techniques, with a special emphasis on catalyst features and reaction mechanisms. For the details about HDO techniques, readers may refer to some excellent reviews published in the past on this topic [6–10]. This chapter briefly summarizes the C–C coupling and HDO reactions for the synthesis of long-chain hydrocarbon biofuels from different biomass feedstocks. General perspectives, associated challenges, and probable solutions are also discussed at the end of the chapter.

### 12.2 Strategies for C–C bond formation

The C–C coupling reaction is a prerequisite step to upgrade the platform molecules into liquid hydrocarbon biofuels with the desired carbon number. There are different strategies for C–C coupling reactions which include aldol condensation, hydroxyalkylation-alkylation (HAA), ketonization, pinacol coupling, Michael addition, Robinson annulation, and so on. In this section, catalytic strategies and reaction conditions of these reactions are discussed.

#### 12.2.1 Aldol condensation

This is one of the most often used techniques to increase the carbon chain length of small molecules. This type of reaction occurs between two carbonyl compounds having a reactive α-H on at least one of the carbonyl groups. The reaction usually requires acid or base catalysts to activate α-H. There are several reports on the aldol condensation of furfurals with carbonyl compounds, usually acetone, to synthesize the fuel precursors. Reactions can happen both in the presence and in the absence of solvents at a temperature ranging from room temperature to 100 °C. The solvent is usually not required when acetone is used because it can act as both reactant and solvent. Depending on the chain structure of targeted alkanes (e.g., branched or cyclic), oxygenated fuel precursors are synthesized by selecting appropriate substrates in aldol condensation. Scheme 12.1 shows the formation of targeted oxygenates of desired structures by selecting different substrates via both cross- and self-aldol condensation.

Both homogeneous and heterogeneous catalysts are reported for this reaction. Among homogeneous catalysts, an aqueous NaOH solution is very effective to form aldol products from the reaction between furfural (or its derivatives) and ketones [11]. To achieve high yield, an organic phase is usually used with the NaOH solution, which efficiently extracts the aldol adducts from the aqueous solution due to their low solubility in water. Sometimes, inorganic salts (e.g., NaCl) are also added to the aqueous solution to improve the partition coefficient of the aldol product. Product distribution can be tuned by changing the molar ratio of the furfural precursor to ketone and the amount of base.
For example, condensation between furfural and acetone gives both single- and double-condensation products in high yields. On the other hand, only single condensation products are observed when HMF is used. It is because the degradation of HMF generates acidic by-products that reduce the basicity of the solution and restrict the formation of the second condensation product.

Due to the problems of environmental pollution and equipment corrosion, the use of heterogeneous catalysts has gained more attention these days. Basic metal oxides, basic zeolites, phosphates, and layered double hydroxides are generally used as heterogeneous catalysts. One big advantage of these catalysts is that the strength and number of basic sites can be easily adjusted according to the nature of the reaction. Apart from that, these solid catalysts can be used as supports to make bifunctional catalysts by introducing active metals (such as Pd, Pt, Ni, Ru, etc.), which perform both aldol condensation and HDO reaction simultaneously. However, one drawback of the solid base catalysts is their poor hydrothermal stability that causes the leaching of active sites in aqueous media, and therefore, they need organic solvents. Thus, the development of hydrothermally stable catalysts is critical to run the process in aqueous media. In this respect, mixed oxides such as MgO-Al₂O₃, MgO-ZrO₂, and CaO-ZrO₂ are highly promising as...
the extent of leaching is very low [16]. The basic strength of these mixed oxides generally depends on the combination and molar ratio of the two oxides. It is observed that the mixed metal oxides with medium strength and an optimal ratio of acid/base site (1:1.1) are suitable to obtain C_{15} adduct from HMF and acetone. On the other hand, stronger basic sites assist the retro-aldol condensation. The activity of mixed oxides can be further improved by grafting them on mesoporous carbon supports. For example, in the reaction between furfural and acetone, Mg—Zr mixed oxide supported on high-surface-area graphite achieved 96.5% furfural conversion with 87.8% selectivity for C_{8} and C_{13} adducts [17].

### 12.2.2 Hydroxyalkylation-alkylation (HAA)

This process is usually used to upgrade furan-based molecules to produce the precursors of branched alkanes. Furan and 2-methylfuran (2-MF) were mostly used by different groups. Huber’s group first reported that furan can act as a nucleophile to couple with electrophiles, such as HMF and other furfurals, via the HAA process in the presence of H_{2}SO_{4} to form different oxygenated intermediates with higher carbon number [18]. The reaction undergoes by the protonation of the alcohol or the carbonyl oxygen (in HMF or furfural) and the subsequent reaction with furan to form difurylmethane (C_{9}) that further reacts with another furan to yield trifurylmethane (C_{13}). Similarly, reaction with HMF produces C_{10}, C_{14}, and C_{18} precursors (Scheme 12.2).

![Scheme 12.2 Hydroxyalkylation-alkylation reaction of furan and 2-methylfuran (Sylvan).](image-url)
2-MF also undergoes a similar reaction with a carbonyl compound to form different precursor molecules for linear and branched-chain hydrocarbons. Compared to furan, the use of 2-MF is more promising in HAA reaction because of several reasons. First of all, it is more reactive and selective in the HAA reaction. Secondly, the methyl group protects one of the reactive α-positions and therefore, the reaction of 2-MF with carbonyl compounds restricts the formation of undesired polymers. Finally, the extra methyl group makes the molecule more hydrophobic which facilitates easy separation of products from the aqueous phase. Corma and coworkers developed a new technique named “Sylvan process” where three molecules of 2-MF (Sylvan) are involved in the HAA reaction to produce a C₁₅ precursor (Scheme 12.2) [19–21]. Under the acidic conditions, 2-MF undergoes the ring-opening reaction via hydrolysis to form 4-oxopentanal. It further reacts with two molecules of 2-MF through the HAA reaction to produce the C₁₅ precursor, which subsequently undergoes the HDO reaction to produce a C₁₅ branched alkane. One major problem with 2-MF is that currently there is no known process to produce 2-MF industrially. Therefore, the first step is to develop a cost-effective and efficient method for 2-MF production to make the Sylvan process industrially successful.

HAA reactions can undergo both in the presence and absence of solvents at a temperature ranging from room temperature to 120°C. Bronsted acidic catalysts are usually used for these reactions. Among homogeneous catalysts, both inorganic acids (e.g., HCl and H₂SO₄) and organic acids (e.g., p-toluenesulfonic acid) are used [19, 21]. Among solid acid catalysts, resins (e.g., Amberlyst-15, Amberlyst-36, Nafion-115, and Nafion-212), [19, 21–23], zeolites (e.g., H-Y, H-USY, and H-ZMS-5) [21, 23], phosphates (e.g., zirconium phosphate) [23], and acid functionalized carbonaceous materials (e.g., AC-SO₃H) [23] are reported by different groups. Collective results indicate that HAA reaction is dependent on the acid strength of the catalysts and strong acid sites are more effective for this process. Nafion-212 was found to be the best among all catalysts in terms of catalytic performance and stability.

12.2.3 Ketonization

Ketonization is usually applied to synthesize a ketone from two carboxylic acids via decarboxylation. The main goal of ketonization is to remove the oxygen from biofuels. The reaction has recently received increasing attention in biorefinery since it can increase the carbon number of biomass-derived small molecules and can remove the reactive acid groups. Self-condensation of LA is a very well-known example in biorefinery, where two molecules of LA give C₉ oxygenated precursor (nonane-2,5,8-trione, Scheme 12.3) for the production of 5-nonanone and finally nonane after HDO reaction [24, 25]. This reaction provides a new approach to directly transform LA to C₉ hydrocarbons by losing only one carbon. Ketonization is also an effective pathway to upgrade fatty acids to produce a heavy fatty ketone in the presence of a base catalyst. For example, ketonization of
lauric acid (C_{12}H_{24}O_{2}) over MgO catalyst at 400 °C can give the corresponding ketone (a precursor of diesel-range fuel) with an excellent selectivity of 97% at 95% conversion (Scheme 12.3) [26].

Among different metal oxide-based catalysts (acidic, basic, and amphoteric), the weakly basic and amphoteric CeO_{2} were found to be very efficient for the effective removal of acid functionalities of bio-oils via the ketonization reaction [27]. The catalyst also works well for acetic acid to produce acetone. Other amphoteric metal oxides including ZrO_{2} and TiO_{2} also show good performance. It may be noted that these metal oxides (CeO_{2}, TiO_{2}, and ZrO_{2}) are reducible in nature and have oxygen vacancy in their lattice, which is highly important for decarboxylation. Highly acidic zeolites are also known to catalyze the ketonization reaction efficiently. Most of the acid-catalyzed ketonization reactions are carried out in the gas phase at relatively higher temperatures (200–400 °C). High temperatures are specially required when alcohol groups containing molecules are also present in the reaction. Under the reaction condition, two parallel reactions are observed: (i) ketonization and (ii) reversible esterification. The esterification is more favorable at lower temperatures, while ketonization dominates at higher temperatures. However, high temperatures can be problematic in some cases. For instance, the ketonization product of LA (nonane-2,5,8-trione) is highly reactive at high temperatures, and therefore, it is difficult to achieve high selectivity to nonene [28]. Therefore, the design of new catalysts is essential, which can work in water at a lower temperature. This is particularly important for LA because of its low vapor pressure and high water solubility.

In spite of several studies on ketonization reaction to understand its mechanism, there are still some debates. An excellent review by Resasco et al. has summarized all the possible mechanisms of ketonization over different catalysts [28]. Briefly, ketonization activity can be related to several potential characteristics of a catalyst which include (i) oxygen
vacancies, (ii) acid sites, (iii) basic sites, (iv) redox properties, and (v) coordinatively unsaturated cations.

12.2.4 Pinacol coupling

In this route, furan derivatives with an aldehyde group on the α-position and aromatic aldehydes undergo the self- or cross-coupling reaction to form condensation products (Scheme 12.4). The reaction proceeds through a radical pathway in the presence of reductants under mild reaction conditions. Huang et al. reported the pinacol coupling of furanic aldehydes to produce C_{10}–C_{14} precursors using metallic powders (e.g., Al, Mg, and Zn) as reductants in different mediums including H_{2}O and aqueous solutions of NaOH, KOH, or NH_{4}Cl\[29\]. Using Zn in 10% aqueous solution of NaOH, 99% furfural conversion, and 96% selectivity for the targeted C_{10} product were achieved at 50°C. However, when the optimized conditions for furfural were used to convert HMF, polymerized products with molecular weights of 200–800 were obtained, which was probably due to the low stability of HMF. Alternatively, 5-methylfurural (5-MF) can be used instead of HMF as 5-MF is more stable. Using 5-MF as starting material, 85% yield of the corresponding C_{12} dimer was obtained.

Pinacol coupling can be successfully employed for upgrading varieties of aromatic aldehydes derived from lignin. Vanillin is an important example, which can undergo pinacol coupling to form an intermediate for C_{14} alkane\[30\]. The reaction is carried out both chemically and electrochemically using Zn powder and Zn electrode as catalysts, respectively. There are also examples of cross pinacol coupling between vanillin and other aldehydes (e.g., benzaldehyde) under different reaction conditions.
12.2.5 Other routes of C–C coupling

Apart from the above-discussed pathways, other reactions, such as Michael addition, Robinson annulation, olefin addition, and oligomerization, are also known as viable techniques to upgrade different platform molecules to hydrocarbon biofuels. Michael addition is an excellent technique to form highly branched ketones from a $\beta$-dicarbonyl compound and an $\alpha,\beta$-unsaturated carbonyl compound [31]. The main problem of this process is that the starting compounds cannot be directly obtained from biomass; rather they need to be synthesized by an aldol condensation reaction. Transition metal chlorides are known to work well as catalysts for Michael's addition reaction because of their ability to form chelate complexes with $\beta$-dicarbonyl compounds. For example, using CoCl$_2$·6H$_2$O as a catalyst, 82.9% conversion of 4-(2-furanyl)-3-butene-2-one (FA, the aldol condensation product of furfural and acetone) and 75.1% yield of furfural-acetone-diketone (FAD, Michael product of FA and 2,4-pentanedione) was achieved (Scheme 12.5) [31]. When the Michael addition product contains an active $\alpha$-H atom, an intramolecular aldol condensation can be performed to synthesize cyclic oxygenates. The consecutive process of Michael addition followed by intramolecular aldol condensation is named as Robinson annulation, which eventually gives a six-membered ring with a carbon chain (Scheme 12.5) [32]. The obtained high-quality alkylcyclohexanes (after HDO) can be easily mixed with traditional fuels to improve their combustion properties.

![Scheme 12.5 Michael addition and Robinson annulation of furfural with carbonyl compounds.](image-url)
Oligomerization is another approach to produce long-chain alkene precursors from low-molecular-weight alkenes. For upgrading LA to liquid hydrocarbon biofuels, oligomerization is a good pathway (Scheme 12.6) [33]. However, first LA needs to be converted into butenes via γ-valerolactone (GVL) and pentenoic acid. Production of GVL from LA is a well-established process, where hydrogenation catalysts (such as Pd, Ru, Ni, Cu, etc.) are successfully used [34]. GVL can undergo ring-opening reaction to give pentenoic acid, which is subsequently decarboxylated to give butenes. Oligomerization of butenes takes place usually in the presence of acidic catalysts, such as H-ZSM-5, Amberlyst resins, etc., at a temperature ranging from 170°C to 220°C.

**Scheme 12.6** Production of higher alkenes from GVL via oligomerization reaction.

### 12.3 Strategies for oxygen removal from oxygenated fuel precursors

The most important step in the synthesis of liquid hydrocarbon biofuels is the removal of oxygen from the oxygenated precursors via the HDO process. This process typically occurs via hydrogenolysis of C–O bonds and the subsequent elimination of oxygen in the form of water. The fuel precursors obtained from C–C coupling reactions usually contain different oxygen functionalities (such as C=O, C–OH, and C–O–C bonds) and unsaturation (C==C bond). Therefore, a series of reactions including dehydration, hydrogenation, and hydrogenolysis is necessary to improve the H/C ratio. HDO process is the most challenging part of the process of hydrocarbon biofuels production because the main goal of HDO is to achieve the effective removal of oxygen with minimum H₂ consumption. The catalyst design thus plays a crucial role in this process. Until now, several catalysts containing noble metals (e.g., Pd, Pt, Ru, Rh, Re, etc.) and non-noble metals (e.g., Fe, Ni, Cu, Mo, etc.) have been reported for the HDO process [6, 9]. Initially, HDO catalysts were designed by the formulation of hydrodesulfurization (HDS) catalysts that are mainly used in the petroleum industries for removing sulfur impurities. Traditional industrial catalysts based on sulfided Co–Mo–Ni supported on Al₂O₃ show good HDO performance but they suffer from the following serious problems. (i) The maintenance of stable catalytic activity needs the addition of sulfur, which results in sulfur contamination and H₂S emissions. (ii) An unavoidable by-product in the HDO process is
water that converts Al₂O₃ into boehmite (AlO(OH)). (iii) The high Lewis acidity of Al₂O₃ induces coke formation which results in the deactivation of the catalyst [8]. In this context, alternative supports, such as SiO₂, CeO₂, TiO₂, and mesoporous carbons, are of good choice due to their low acidity and coke-resistance ability [35]. Among sulfur-free HDO catalysts, metal carbides, metal phosphides, and metal nitrides are also widely used for their comparable activities [35]. The latter studies in this direction have focused more on investigating the reaction network and catalyst requirement in each step of the HDO process, with a special emphasis on understanding the substrate-catalyst interaction. It is important to mention here that most of the fundamental studies on HDO catalyst design use model compounds containing the functional group of interest because it is much easier to study the mechanism with model compounds rather than the real feedstocks.

Since various types of reactions are involved in an HDO process, the catalyst requirement is also different for each reaction. Therefore, the choice of a suitable catalyst should consider the optimization of several factors to achieve higher selectivity of the targeted products. From Table 12.1, it is clear that a bifunctional catalyst containing an acidic site and a metallic counterpart is essential for all the necessary steps to perform together.

### Table 12.1 Reactions involved in the HDO process and their corresponding catalysts.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Example</th>
<th>Catalyst requirement</th>
</tr>
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<tbody>
<tr>
<td>Dehydration of alcohols</td>
<td></td>
<td>Bronsted acidic catalysts including inorganic acids. Activity increases with the acidity</td>
</tr>
<tr>
<td>Hydrogenation</td>
<td></td>
<td>Bifunctional catalysts consisting of metals (Pd, Ru, Pt, Ni, Cu, etc.) and acid sites</td>
</tr>
<tr>
<td>Conversion of ethers</td>
<td></td>
<td>Combination of metal catalyst and acid under harsh conditions</td>
</tr>
<tr>
<td>C–O hydrogenolysis</td>
<td></td>
<td>Bimetallic catalysts containing noble metal and group 6 or 7 metals (e.g., Pt—Re, Pt—W, Pd—W, Rh—Mo, Rh—Re, Ir—Re, etc.)</td>
</tr>
<tr>
<td>C–C dissociation and isomerization</td>
<td></td>
<td>Combination of metal (e.g., Ru, Ir, and Rh) and acid</td>
</tr>
<tr>
<td>Decarboxylation and decarbonylation</td>
<td></td>
<td>Transition metals are typically used, but acid or base can also promote this reaction</td>
</tr>
</tbody>
</table>
Important reactions including hydrogenation of different functional groups (such as C= C, C=O, and –COOH), C–C dissociation, decarboxylation, and decarbonylation occur on metal sites. On the other hand, acid sites promote different reactions, such as dehydration, isomerization, hydration, and hydrolysis. It is important to note here that the HDO process often requires high H₂ pressure that can also cause overhydrogenation or carbon loss by C–C bond cleavage. Bifunctional catalysts can perform the C–O bond cleavage at a lower H₂ pressure than those required for standalone metal nanoparticles, which is a significant advantage [36].

Bifunctional catalysts can be formulated in two different ways. The most common strategy is dispersing the metal components on solid acid support (e.g., Al₂O₃, zeolite, Nafion, etc.). In this case, the major focus is given on the textural, electronic, and acid–base properties of the support, which can influence the overall catalyst design. Importantly, the type of acidic sites determines the reaction pathway since different acid sites have different roles in the HDO process. For example, the Lewis acid site binds electron-rich species to the catalyst surface whereas the Brønsted acid site provides protons to the intermediates [8]. It is worth mentioning that although the acidic supports are of immense importance for some of the reactions, they also trigger the coke formation and catalyst deactivation. In this regard, oxophilic supports, such as ZrO₂, TiO₂, and Nb₂O₅, exhibited less susceptibility for carbon deposition and higher selectivity to aromatic compounds in the phenolics HDO process [37]. Another type of bifunctional catalyst is the bimetallic catalyst, which is composed of a reducing metal (such as Pd, Pt, Rh, etc.) and an oxophilic metal (such as Re, W, etc.) [7]. The acidic –OH groups strongly attached to the oxophilic metals provide protons to the reactants to form carbenium ions [38]. Close proximity of these two types of metal sites can give high activity for hydrogenolysis. Experimental studies proved that ReOₓ species cover reducible metals (e.g., Pt), resulting in the direct interaction of both sites with each other [39].

Among several catalysts explored in HDO processes, niobium-supported solid acid catalysts have attracted immense attention because of their better activity under mild conditions as compared to the other catalysts supported on Al₂O₃, SiO₂, or H-ZSM-5. For example, Pd/NbOPO₄ shows almost full conversion of furfural-acetone aldol adduct into octane with 94% yield at 170°C and 20 bar H₂ [40]. Combined experimental and DFT calculation results indicate that the Nb–O–Nb chains in both NbOₓ and NbOPO₄ are very efficient to break the C–O bond on the tetrahydrofuran ring. It is also observed that different states of NbOₓ have a different activity, where NbOₓ with a lower coordination number of Nb is suitable for the HDO of furanics [41]. Briefly, Nb-based catalysts have the following features: (i) high mesoporosity and surface areas for homogeneous metal dispersion, (ii) high oxygen affinity to activate C–O bonds, (iii) synergistic effect between NbOₓ and metal for effective oxygen removal, (iv) desired acidity of NbOₓ to assist the necessary acid-catalyzed reactions, and (v) high stability and water resistance ability.
It is often seen that the furan ring is a part of the structure of many fuel precursors since furanic platform chemicals are used as the main carbon sources. To achieve open-chain alkanes, the furan ring needs to be opened and it is very important to know the ring-opening (RO) mechanism in the reaction network and its impact on the total HDO process. Another event associated with the ring-opening process is ring-saturation (RS) and it is also important to know the sequence of these two events in order to determine the selectivity of final products. There are several reports on the catalytic hydrogenolysis of lignocellulose-derived aromatics to linear alcohols/polyols. However, the sequence of RO and RS steps remained a controversial topic [21, 42]. Sutton et al. experimentally proved that it is hard to open the ring once it is fully saturated [43]. As can be seen in Scheme 12.7, the formation of 3 by the full hydrogenation of the furan ring is a dead-end for the production of alkanes under mild conditions. However, RO of 2 to a polyketone (4) prior to RS can produce nonane (5) in high yield via a lower energy route. In support of this result, Chen and Vlachos performed combined studies based on DFT and high-resolution electron energy loss spectroscopy (HREELS) analysis to study the hydrogenolysis of saturated (e.g., furan, furfural, and furfuryl alcohol) and unsaturated (e.g., tetrahydrofurfuryl alcohol) heterocyclic compounds on iridium, which also revealed that unsaturation promotes RO, while full saturation causes slower kinetics and hinders the

Scheme 12.7 The divergent pathway leads to different products during the HDO of HMF-acetone adduct.
Contradictory results were reported by Song et al. where it was shown that RO is possible even after full saturation of the furan ring in presence of a metal triflate promoter $(\text{M(OTf)}_x$, where $\text{M} = \text{La, Ce, Sm, Yb, Sc, Fe, Al, and Hf})$. However, the RO step is observed to be successful only in the case of metal triflate with strong Lewis acidity. The entire process proceeds through two main steps: (i) Pd/C-catalyzed saturation of the furan ring and exocyclic double bond at low temperatures, and (ii) triflate-catalyzed HDO of saturated furan intermediate at high temperatures. Up to 92% of nonane was obtained from HMF-acetone adduct using Pd/C–Hf(OTf)$_4$ combination. The high activity of Hf(OTf)$_4$ is related to the high charge density at Hf$^{4+}$ center that facilitates RO by activating the C–O bonds. Followed by this work, Dutta and Saha also used Hf(OTf)$_4$ promoter for the HDO of furylmethanes to produce alkanes [47]. For example, in the case of C$_{15}$ trifuran (1), the furan rings can be first hydrogenated by Pd/C to fully saturated cyclic ethers, which can then undergo facile RO and deoxygenation to form the alkanes (Fig. 12.1). The RO step is believed to be assisted by the formation of an intermediate between nucleophilic ethereal O and Hf$^{4+}$ center. Additionally, O atoms of the $\text{SO}_3$ group can form a cyclic intermediate (4) to cleave the $\beta$-C–H bonds, which facilitates the RO of Hf-bonded ether to form Hf-bonded alcohol (5). It is observed that the furan ring without $\text{CH}_3$ group first undergoes RO, which could be due to the formation of a stable adduct between Hf$^{4+}$ and furan O in absence of steric hindrance.

![Fig. 12.1 Reaction pathways for the synthesis of alkanes from C$_{15}$ trifuran using Pd/C–Hf(OTf)$_4$ as catalyst.](image-url)
Marks et al. also established a similar mechanism for the hydrogenolysis of 2-methyltetrahydropyran to \( n \)-hexane using metal triflates [48]. From all these results, it is clear that the whole HDO process of furan compounds involving ring hydrogenation, RO, and deoxygenation depends on various factors including ring substitution, catalyst nature (e.g., charge density on the metal sites, acidity, etc.), and reaction conditions.

**12.4 Examples of long-chain hydrocarbon biofuels derived from different feedstocks**

**12.4.1 Hydrocarbon biofuels from furan-based compounds**

Among furan-based feedstocks, furfural and HMF are widely used monomers to produce liquid hydrocarbon biofuels. Aldol condensation is one of the most effective routes to upgrade these monomers into long-chain hydrocarbon biofuels, where acetone is mainly used as a reactive \( \alpha \)-H containing unit. Several studies have reported the synthetic strategy of hydrocarbon biofuels via aldol condensation of furfural and HMF with acetone and other ketones [49–55]. In 2005, Dumesic et al. first reported the production of \( C_7-C_{15} \) alkanes from biomass-derived carbohydrates using a multistep process (Fig. 12.2) [49–51]. According to the protocol, the first step is the conversion of sugars to furfural and HMF, which undergo aldol condensation in the next step with acetone to form long-chain oxygenated fuel precursors. Improved yield of aldol adducts can be achieved by using a biphasic reactor, where the organic solvent continuously extracts the products from the aqueous phase. To perform the HDO of these precursors, they designed a four-phase reactor system made of (i) an aqueous inlet stream containing the water-soluble large organic reactant, (ii) a hexadecane alkane inlet stream, (iii) a hydrogen inlet gas stream, and (iv) a solid HDO catalyst (Pt/SiO\(_2\)-Al\(_2\)O\(_3\)). As the oxygenated precursors undergo dehydration/hydrogenation reactions, they become more hydrophobic, and the hexadecane alkane stream removes them from the catalyst before they further react to form coke. Both single and double condensation products were obtained when acetone was used. Product distribution can be tuned by changing the ratio of furfural to acetone. Different bifunctional catalysts, such as Pd/Al\(_2\)O\(_3\) (at 100–140 °C and 25–52 bar H\(_2\)) and Pt/NbOPO\(_4\) (at 255–295 °C and 60 bar H\(_2\)), were used to obtain a mixture of linear alkanes. For HMF-acetone systems, 58%–69% yield of \( C_7-C_{15} \) alkanes (based on carbon) was achieved from fructose, while 79%–94% carbon yield was achieved from various furfurals.

Furfural can be condensed with LA (or its ester) to produce precursors for diesel-range hydrocarbon biofuels. For example, Olson and Heide patented a process to convert cellulose into fuel components, where furfural and ethyl levulinate are converted into \( C_9-C_{15} \) alkanes [56]. Following this work, Li and coworkers reported an energy-efficient tandem three-step process to directly convert raw lignocellulosics (e.g., corncob) into long-chain branched alkanes (Fig. 12.3) [57]. In the first step, hemicellulose and cellulose...
Fig. 12.2 Step-wise synthesis of liquid hydrocarbon biofuels from biomass-derived carbohydrates.

Fig. 12.3 Production of branched alkanes from corncob biomass.
fractions are converted into furfural and isopropyl levulinate through an acid-catalyzed hydrolysis-dehydration-hydration reaction in a water/toluene biphasic system with added isopropanol. The addition of isopropanol enables the spontaneous formation of LA ester and its transfer into the organic phase. As a result, LA ester coexists with furfural in the same phase, which makes their double aldol condensation (the second step) effective in the toluene phase. In the third step, HDO of double condensation adduct was performed in an organic solvent (e.g., cyclohexane) using Pd/NbOPO₄ catalyst to produce 91.4% C₁₅ alkane along with 5.6% C₁₄ alkane at 220°C and 60 bar H₂.

Other than aldol condensation, furfural can undergo reductive self-condensation via pinacol coupling reaction in presence of a base and a metal, such as Al, Zn, or Mg (in powder form) to produce C₁₀ fuel precursor (Scheme 12.8) [29]. Subsequent HDO of this dimer over Pt/AC and Pd/C catalysts gives C₈–C₁₀ alkanes and the yield depends on the nature of the acidic counterpart (NbOPO₄, TaOPO₄, and WO₃) of the catalysts. Using Pt/AC–TaOPO₄ as the catalyst, a maximum molar yield of 83.6% was achieved from an aqueous solution of the dimer at 300°C. This strategy can also be applied to other substrates (such as 5-methylfurfural, anisaldehyde, and vanillin) to obtain C₁₂ and C₁₄ alkanes. Similar to pinacol coupling, HMF can be upgraded to C₁₂ alkane through a self-coupling reaction via organocatalysis and subsequent HDO via metal-acid tandem.

Scheme 12.8 Different routes for the conversion of furfural into liquid hydrocarbon biofuels.
catalysis [58]. In the first step, HMF is converted to 5,5'-dihydroxymethyl-furoin (DHMF) in 91% yield using N-heterocyclic carbenes at 60°C. In the second step, DHMF is converted to linear alkanes with 78% carbon yield and 64% selectivity to n-C_{12}H_{26} using a bifunctional catalyst containing Pd/C, acetic acid, and La(OTf)_{3} at 250°C.

Huber et al. developed a method to form C–C bond between furfural and furan to obtain linear and branched C_{9–13} alkanes (Scheme 12.8) [18]. Corma et al. established the Sylvan process for the conversion of 2-MF (Sylvan) into diesel-range branched alkanes via a two-step process, i.e., HAA followed by HDO [19–21]. In their initial study, 2-MF was trimerized in the presence of an acid (e.g., H_{2}SO_{4}) to form 5,5-bis(sylvyl)-2-pentanone at 60°C (Scheme 12.8) [19]. Subsequent HDO with Pt/C–Pt/TiO_{2} catalyst at 350°C and 50 bar H_{2} resulted in 87% overall yield of diesel from Sylvan. This strategy can be further extended to the reactions between 2-MF and other carbonyl compounds (such as butanal, furfural, HMF, 5-methylfurfural, acetone, hydroxyacetone, and cyclopentanone) to obtain branched alkanes with different carbon numbers [20, 23, 59–62].

12.4.2 Hydrocarbon biofuels from levulinic acid and its derivatives

The United States Department of Energy identified LA as 1 of the 12 important biomass-derived building blocks with a wide range of potentials in chemical production [63]. LA has two main functional groups, i.e., carboxylic acid and ketone, which make LA highly reactive for multiple transformations. LA can be converted into hydrocarbon biofuels by a number of catalytic routes involving ketonization, condensation, lactonization, and other reactions.

12.4.2.1 Direct route

Since LA contains five carbons, the coupling of two or more LA can give rise to the precursors of long-chain hydrocarbon biofuels. For example, acid-catalyzed ketonization of LA via decarboxylation is a promising route to generate nonane-2,5,8-trione, which can be further converted into nonane by HDO reactions [25]. Karimi et al. reported aqueous phase conversion of LA to nonane using Red Mud as a catalyst [25]. Since Red Mud contains an alkaline mixture of Fe_{2}O_{3}, TiO_{2}, and various complex sodium alumino–silicates, it can be used as a multifunctional catalyst for different reactions including reductions, oxidations, and acid/base mediated transformations. The active phase of the catalyst is made of reduced FeO_{x}, aluminate, silicate, and carbide phases that are generated by either prereduction of the Red Mud in the presence of formic/acetic acid or in situ reduction with H_{2}. At 365°C, the total conversion of LA could be achieved with a 76% yield of alkanes with high selectivity for C_{9} alkanes. Due to the presence of active α–H, LA can undergo self-aldol condensation catalyzed by either base or acid to form C_{10} fuel precursors. For example, mixed MgZr oxide can
form two condensation products of LA. The first one is from the self-condensation of LA, while the other one is from the condensation between LA and its lactone obtained via cyclization [64]. However, a maximum of 30% LA conversion could be achieved with a 21% yield of C\textsubscript{10} adduct. This is because the $-\text{COOH}$ group competes with the $-\text{C}=\text{O}$ group for the basic sites and deactivates the catalyst by neutralizing the basicity. As an alternative, Brønsted acid (e.g., trichloroacetic acid) and Lewis acid (e.g., ZnCl\textsubscript{2}) can promote the reaction with C\textsubscript{10} yield of 50.9\% (Scheme 12.9) [65].

![Scheme 12.9](image)

**Scheme 12.9** Transformation of levulinic acid into liquid hydrocarbon biofuels via different routes.

**12.4.2.2 Conversion via angelica lactone**

Angelica lactone (AL) is obtained via intramolecular dehydration of LA in the presence of acids. It is more reactive than LA due to the ring unsaturation. Under relatively mild conditions and in the presence of alkali catalysts, AL can be quantitatively converted to C\textsubscript{10} or C\textsubscript{15} intermediates, which are the precursors of branched alkanes (Scheme 12.9) [66–68].
Several catalysts including Pt-ReO\(_x\)/C, Ir-ReO\(_x\)/SiO\(_2\), Pd/Al\(_2\)O\(_3\), and Pd/C can be used for the HDO reaction. The advantages of this process are as follows. (i) It requires relatively low H\(_2\) pressure to achieve an almost quantitative yield of hydrocarbons. (ii) The process does not require any organic solvent. (iii) The number of steps involved in the production of liquid alkanes is less. (iv) The atom efficiency of this process is about 90% as the catalyst can be easily recovered from the reaction medium and regenerated. Besides self-condensation, AL can also undergo a cross-coupling reaction with other carbonyl-containing compounds (e.g., furfural) to produce C\(_9\) and C\(_{10}\) alkanes [69]. Various metal oxides (both acidic and basic) including Mn\(_2\)O\(_3\), La\(_2\)O\(_3\), MgO, ZnO, Fe\(_2\)O\(_3\), Cr\(_2\)O\(_3\), Nb\(_2\)O\(_5\), and TiO\(_2\) are used for the solvent-free condensation reaction, among which Mn\(_2\)O\(_3\) showed the highest activity and stability. The obtained C\(_{10}\) oxygenate was hydrogenated and hydrodeoxygenated over Pd-based catalysts (Pd/C and Pd-FeO\(_x\)/SiO\(_2\)) with up to 96% carbon yield of C\(_9\) and C\(_{10}\) alkanes. The addition of iron in the Pd/SiO\(_2\) catalyst avoids undesired decarboxylation and decarbonylation reaction and increases the HDO activity.

12.4.2.3 Conversion via \(\gamma\)-valerolactone

LA can be converted to \(\gamma\)-valerolactone (GVL) by hydrogenation via either AL intermediate or 4-hydroxypentanoic acid intermediate [70]. GVL is considered a fuel additive because of its high energy density, calorific value similar to ethanol, and low vapor pressure. But the use of GVL as a fuel additive is restricted by some limitations, such as high water solubility and relatively lower energy density as compared to traditional fossil fuels. Two possible routes are reported for upgrading GVL into liquid hydrocarbon biofuels. The first route proceeds through the formation of butenes, which is designated as the C\(_4\) route (Scheme 12.9). Bond et al. developed a combined catalytic route for the conversion of GVL to liquid hydrocarbon biofuels using a dual reactor system [33]. In the first reactor, GVL is converted to pentenoic acid via acid-catalyzed RO and then decarboxylated in the presence of solid acid catalysts (e.g., SiO\(_2\)–Al\(_2\)O\(_3\)) to form butenes. Over 99% yield of butenes was obtained from an aqueous solution of GVL at 375 °C and 35 bar H\(_2\). The gas mixture produced in the first reactor was then transferred into the second reactor to form C\(_8\)–C\(_{16}\) hydrocarbons via oligomerization over an acid catalyst (e.g., H-ZSM-5 or Amberlyst-70). The temperature of the second reactor was kept relatively low (150–170 °C) to avoid the undesired cracking reactions and improve the yield of higher alkenes.

The second route follows the reductive RO of GVL to pentanoic acid, which undergoes ketonization to produce 5-nonanone. Hydrogenation of 5-nonanone followed by dehydration produces C\(_9\) alkene (nonene). This route is designated as C\(_9\) route (Scheme 12.9). Nonene can be further converted to \(n\)-nonane or other branched C\(_9\) alkanes via isomerization. Dumesic group developed a method to produce 5-nonanone in high yields (90%) from a concentrated aqueous solution of GVL by using
a dual catalyst bed in a single reactor [24, 71]. In the first catalyst bed, pentanoic acid is produced from GVL via RO and hydrogenation over the bifunctional Pd/Nb$_2$O$_5$ catalyst at 325 °C. In the second catalyst bed, ketonization of pentanoic acid is carried out over Ce$_{0.5}$Zr$_{0.5}$O$_2$ catalyst at 425 °C. The hydrophobic nature of 5-nonanone makes its separation from water spontaneous. 5-Nonanone can be transformed into $n$-nonane via hydrogenation/dehydration using a bifunctional catalyst such as Pt/Nb$_2$O$_5$. Alternatively, the carbon number of alkanes can be increased via oligomerization of nonene using an acid catalyst, which produces a mixture of C$_{18}$–C$_{27}$ alkenes that can be eventually hydrogenated to diesel-range fuels [72]. It was estimated that 100 kg of GVL can produce about 50 kg of liquid hydrocarbon biofuels retaining more than 90% of its initial energy content.

12.4.3 Hydrocarbon biofuels from lignin

The lignin has a higher C/O ratio and energy density compared to cellulose and hemicellulose. This factor makes it a perfect candidate for the production of hydrocarbon biofuels. The depolymerized monomers and dimers of lignin generally contain 7–18 carbon, which makes them appropriate precursors for the production of aviation fuel [73]. However, the stable polymeric structure and irregular arrangement of lignin prevent its chemical depolymerization and selective conversion challenge.

Lignin structure has a high content of the methoxy group. The removal of the methoxy group is thus essential for its full conversion. But the presence of a methoxy group is sometimes advantageous if the methyl group is transferred to the aromatic ring. This can be easily done through transalkylation or disproportionation reaction, which produces alkyphenols or alkylbenzenes [74]. In this way, both carbon loss and H$_2$ consumption can be reduced. Additionally, the HDO products of these alkyphenols and alkylbenzenes have high octane numbers, which are suitable for fuel blend.

Apart from transferring a methyl group to the aromatic ring, two lignin-degraded monomers can be coupled to obtain hydrocarbon biofuels with increased carbon number [73, 75–78]. For example, vanillin can be converted to vanillin alcohol and $p$-cresol, which are condensed to form high carbon number cycloalkanes using Ru@Al catalyst [77]. Compared to lignin model compounds, the structure of real lignin is more complicated and its conversion is thus challenging. The dissociation energy of the C–O bond ($\sim$218–314 kJ mol$^{-1}$) is lower than that of the C–C single bond ($\sim$384 kJ mol$^{-1}$). Therefore, it is theoretically possible to selectively cleave C–O–C bonds in the lignin structure by keeping C–C bonds intact [73]. However, the selection of proper catalysts and reaction conditions is necessary. Wang et al. used a highly concentrated aqueous solution of ZnCl$_2$ (63%) to depolymerize softwood technical lignin at 120–200 °C (Scheme 12.10) [75]. Zn$^{2+}$ ions in such a concentrated solution selectively coordinate with oxygen atoms of C–O–C bonds to cause easier cleavage of key linkages of lignin under mild conditions.

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Alkylphenols (both monomeric and dimeric) are obtained as major products that can be converted into cycloalkanes using Ru/C catalyst. Some linear alkanes are also found, indicating that Ru/C can assist RO through hydrogenolysis. Other dimers different from lignin subunits are also obtained, confirming the occurrence of coupling reactions. Under certain conditions, the cleavage of ether bonds releases benzylic carbonium ions that subsequently react with aromatic species to give coupling products.

Scheme 12.10 Conversion of lignin to hydrocarbon biofuels using ZnCl₂ solution and Ru/C catalyst.

12.5 Perspectives and challenges

Traditional aviation fuel typically consists of $n$-alkanes (20%), isoalkanes (40%), cycloalkanes (20%), aromatic hydrocarbons (20%), small amounts of olefins (<5%), and sulfur (<3000 ppm) [79]. Each component plays an important role in aviation fuel. Therefore, to replace the existing aviation fuel with 100% biomass-derived aviation fuel, we need to produce a mixture of $n$-, iso-, and cycloalkanes along with aromatics from biomass. This can be achieved by converting all three components of lignocellulose (hemicellulose, cellulose, and lignin) to aviation fuel. At the same time, achieving a high atom economy is equally important. Several strategies have been developed to utilize cellulose and hemicellulose to produce plenty of $n$- and isoalkanes. On the other hand, lignin is converted into cycloalkanes and aromatics. But the catalytic technologies for the clean conversion of raw lignin still lack fundamental understanding.

Another goal is to make biofuels economically competitive with conventional aviation fuel. The development of a highly integrated process is thus required, that can avoid expensive biomass pretreatment steps and allow “one-pot” conversion. The design of robust, recyclable, and multifunctional catalysts is required to combine many reactions in one step. A well-known multifunctional catalyst, Pd/NbOPO₄, can perform HAA and HDO steps efficiently to produce C₁₅ alkanes from 2-MF and furfural [62]. However, the catalyst undergoes phase transformation, and sintering of Pd particles is observed when the reactions are operated in batch mode (80 °C for HAA and 200 °C, 40 bar H₂ for HDO). The catalyst deactivates by the carbon deposition resulted from the severe
polymerization of large oxygenated HAA products due to their low solubility in alkane solvent (cyclohexane). Therefore, a suitable catalyst that can operate at mild conditions without compromising catalytic activity is required. In this regard, transition metal carbides based on molybdenum and tungsten exhibit high selectivity toward C–O bond scission in HDO reactions under relatively mild conditions [80, 81]. In addition, they are highly resistant to metal sintering, which keeps the active metals well-dispersed under the reductive environment. One problem of transition metal carbides is their high sensitivity toward water and oxygen that causes catalyst deactivation through the formation of metal oxides or oxycarbides. The deactivation by oxygen-poisoning can be prevented by using metal modifiers, which are deposited on transition metal carbide surfaces to lower the binding energy for oxygen. Alternatively, modification of the carbide surface to be hydrophobic and spatial confined carbides are also proposed to stabilize the carbide catalysts [81]. The solvent is another crucial component of the process. Therefore, it will be highly economical if the reactions are performed without a solvent or in the presence of a reusable solvent.

A big obstacle in implementing the HDO process at a commercial level is the high demand for external H₂. Consumption of H₂ can be minimized in many ways. For example, combined metal hydrolysis and HDO, combined in situ reforming and HDO, water-assisted in situ HDO, catalytic transfer hydrogenation/hydrogenolysis, and nonthermal plasma technology are gaining increased attention, which can successfully avoid the use of external H₂ [82]. Considering the low price and high availability of organic by-products (e.g., alcohols, polyols, and acids) produced from thermal conversion of biomass, they can serve as promising H₂ sources for in situ HDO reactions. Recently, an excellent strategy of avoiding external H₂ has been reported, where water provides the required H₂ during the in situ HDO of guaiacol [83]. Ni supported on CeO₂/carbon was used as a catalyst for multiple advantages. First, CeO₂ provides oxygen adsorption sites and facilitates H₂ release from the water. Second, activated carbon has an extremely high surface area to support and stabilize cluster-range Ni species. Finally, the hydrophobic nature of activated carbon can avoid the possibility of catalyst deactivation by water poisoning. Activation of water is believed to occur on CeO₂ oxygen vacancies, while the C–O bond cleavage is facilitated by Ni clusters, and the subsequent steps take place on the Ni–CeO₂ interface. The dispersion of CeO₂ on carbon reduces the particle size of CeO₂ and maximizes the Ni–CeO₂ interface, which eventually increases the activity. Another effective way of minimizing H₂ consumption is magnetic heating by using ferromagnetic nanoparticles, which release heat through hysteresis losses by exposing them to high-frequency alternative magnetic fields [84]. The close contact between the catalyst and the heating agent significantly increases the catalytic activity. Selective HDO can be performed using FeC@Ru nanoparticles at a low catalyst loading and a very low pressure of H₂ (3 bar). The process is benefited from the high heating power of the Fe₂C nanoparticles and the high activities of Ru. In most cases, all these new techniques are applied...
to model oxygenated compounds, which is pivotal to design working catalysts rationally. Now, a major question arises—are these new strategies applicable to raw biomass feedstocks? To find the solution, we need more case studies of these techniques using the open literature already available on complex feedstocks.

12.6 Conclusions

This chapter discussed different routes for the production of hydrocarbon biofuels from important platform chemicals derived from three major components of lignocellulose biomass. The catalyst development is one of the main tasks for future biorefineries to effectively utilize the abundant biomass resources. Remarkable efforts have been made in the last two decades to develop new catalytic routes for the conversion of highly oxygenated biomass feedstocks, where HDO is a key technique. Several fundamental studies were done using model compounds to understand the role of catalysts and the HDO reaction mechanism. Successful efforts were also made for real biomass precursors. However, the complex nature of biomass remains a major hurdle for the selective transformation of raw feedstocks into desired products. Another major concern is the cost of hydrocarbon biofuels that directly depends on the cost of hydrogen production. Therefore, the search for cheap technologies and resources for hydrogen production is an important task to commercialize the biomass conversion processes.

References

Production of longchain hydrocarbon biofuels


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Hydrocarbon biorefinery


Production of longchain hydrocarbon biofuels


Abstract
The rapid decrease of easily accessible fossil fuels has forced the research community to search for an alternative energy source. In this regard, lignocellulosic biomass can be an excellent source of renewable carbon-neutral fuels because of its abundance and no competing issues with food crops. Among the different classes of biofuels reported to date, long-chain hydrocarbons are of special interest because they have fuel properties similar to the existing fossil fuels-based transportation fuels. This chapter discusses the recent development of the production strategies of hydrocarbon biofuels from biomass-derived feedstocks. Two main reactions associated with this transformation, namely, C–C bond formation and hydrodeoxygenation, are discussed in this chapter. The catalyst development, reactor configuration, and mechanistic aspects of these reactions are covered in detail. Catalytic features required for each type of reaction are discussed to provide guidance for designing better catalysts. The specific future challenges are also listed with their probable solutions.

Keywords: Hydrocarbon biofuels, Biomass, Furanics, C–C coupling reaction, Hydrodeoxygenation, Cascade reactions, Bifunctional catalysts.