

## Advanced Biofuels from Lignocellulosic Biomass

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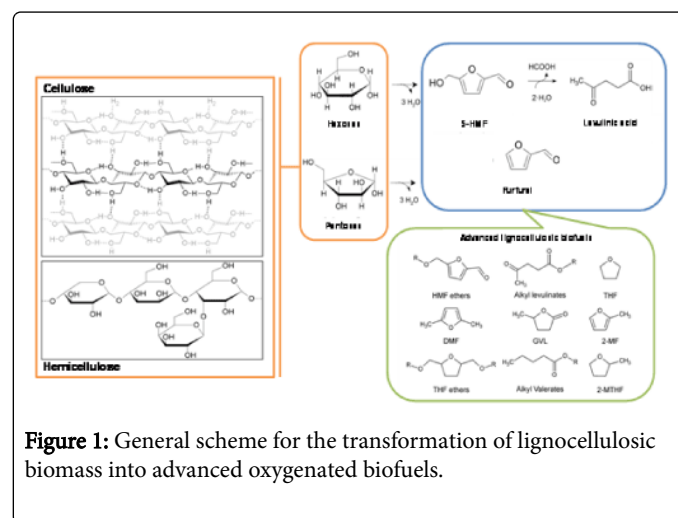
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### Introduction

The transport sector represents around 30% of total world primary energy consumption and currently depends predominantly on a single non-renewable source of energy, namely petroleum. Consequently, this sector is highly vulnerable to oscillations of oil market and responsible of high greenhouse gas emissions. Additionally, concerns about diminishing fossil fuel reserves along with global warming effects caused by increasing levels of CO<sub>2</sub> in the atmosphere are driving society towards the search for new renewable sources of energy for transport that can substitute fossil sources. In the long term, solar energy, sustainable electricity and fuel cells may have an impact in the transport sector technologies, but more research is necessary before these alternatives become economically and technically feasible. On the other hand, carbon-based biofuels serve as a promising short/medium-term alternative to oil-derived fuels. The applicability of biomass as renewable carbon source for transportation fuels has been demonstrated by the successful integration of first generation bioethanol and biodiesel into the current infrastructure, and their application has facilitated a reduced dependence from fossil fuels. However, first generation biofuels production technologies use easy accessible edible biomass, thereby impacting the supply of food for humans and animals. Furthermore, their availability is not sufficient to satisfy the demands presently met by petroleum.

These important limitations of conventional biofuels, together with new trends in legislation especially in the European Union, have stimulated the research for new technologies that allow high energy-density, infrastructure-compatible fuels (advanced biofuels) which could be easily implemented in the existing hydrocarbon-based transportation infrastructure (e.g. engines, fuelling stations, distribution networks and petrochemical processes) and, more importantly, not using edible-biomass for their production. Hence, as an alternative for a more sustainable production of biofuels, it is necessary to use widely available biomass feedstocks instead of edible starch and triglycerides. The best source for such alternative biofuels is lignocellulose, since it is the most abundant form of biomass in the planet and it is widely and easily available: as waste biomass, as conventional wood, and as fast rotation crops. However, lignocellulose is a complex biomass resource that must be first processed into simpler compounds (so-called *platform molecules*) which can be subsequently transformed into a number of valuable products (not only biofuels, but also a wide variety of chemicals) [1-3]. Therefore, lignocellulose must be separated into its constituents -lignin (15-30%), cellulose (35-50%) and hemicelluloses (25-30%) and depolymerized to their corresponding building blocks. The building blocks of lignin are aromatic alcohols, but controlled lignin depolymerization is rather difficult on a technical scale and this problem is still to be solved. Controlled cellulose depolymerization results in glucose, while the

hemicelluloses are depolymerized to a mixture of different sugars, including hexoses and pentoses. The resultant monosaccharides are key molecules for the production of the different identified platform molecules, i.e. 5-hydroxymethylfurfural (5-HMF), furfural and levulinic acid, which can be subsequently catalytically upgraded to biofuels (Figure 1).



**Figure 1:** General scheme for the transformation of lignocellulosic biomass into advanced oxygenated biofuels.

### Catalytic Conversion of Cellulose: 5-HMF and Levulinic Acid

#### 5-HMF

5-HMF is a promising platform chemical derived from cellulosic biomass because it offers strategies to produce various intermediates, polymer feedstocks, specialty chemicals, and transportation fuels. Large-scale production of HMF from C<sub>6</sub> sugars is a complex process, and several aspects still remain a challenge, one of which is the utilization of glucose as a sugar feedstock (inexpensive and highly available). Thus, HMF is typically produced from glucose with low yields, and current technologies include an additional isomerization step to fructose, since the dehydration of fructose to HMF takes place with better selectivity and higher rates [4]. Furthermore, the control over the undesired side reactions involving the reactant, intermediates and the final HMF product, is critical. It is particularly important to prevent HMF from overreacting in the aqueous phase, and utilization of biphasic reactors where HMF is continuously extracted into an organic solvent has shown promising results [5,6]. Most of the catalytic systems described in literature use mineral acids as catalyst which needs to be separated before downstream processing. The

implementation of solid acid catalysts in this process may have several advantages over widely used liquid acid catalysts: (a) they facilitate the separation of product and can be recycled; (b) they can work at high temperatures, thus shortening the reaction time and favoring the formation of HMF instead of its decomposition during a prolonged reaction period; (c) they are capable of adjusting the surface acidity to improve the selectivity towards 5-HMF [7]. Hence, the near term challenges are the development of highly resistant and selective solid acid catalysts in appropriate solvent systems. Unfortunately, 5-HMF is still not produced on an industrial scale.

While HMF is not an attractive fuel component by itself due to its lack of chemical stability, it can be used as a starting point to produce a variety of furan derivatives and chemical intermediates with remarked potential to be used as energy-dense fuels [8]. Indeed, the processing of HMF into drop-in biofuel candidates has attracted much interest. For example, 5-(ethoxymethyl)furfural (EMF) and 2,5-dimethylfuran (DMF) are considered to be two of the most potential biofuel candidates, which can be obtained from the etherification and hydrogen reduction of HMF, respectively [9].

### DMF

2,5-dimethylfuran (DMF) can be obtained by the metal catalyzed hydrogenolysis of 5-HMF. As a biofuel, is considered superior to ethanol in several important ways: it has an energy content of 31.5 MJ L<sup>-1</sup>, similar to that of gasoline (35 MJ L<sup>-1</sup>) and 40% greater than that of ethanol (23 MJ L<sup>-1</sup>); DMF (bp 92-94°C) is less volatile than ethanol (bp 78°C); it blends more easily with petroleum; and, contrary to ethanol, it is immiscible with water, so it does not absorb water from the atmosphere. These attributes bode well for the use of DMF as an alternative liquid biofuel for transportation. However, it still has been difficult to be produced economically.

### EMF

The direct product of etherification of HMF with ethanol, 5-(ethoxymethyl)-furfural (EMF), is the main representative of the 5-alkoxymethylfurfural ethers family and it is considered to be an excellent additive for diesel. It has a high energy density of 8.7 kWh/L, which is similar to regular gasoline (8.8 kWh/L), nearly as good as diesel (9.7 kWh/L) and significantly higher than ethanol (6.1 kWh/L) [10]. With favourable blending properties, EMF has been used mixed with commercial diesel in engine tests, leading to promising results with a significant reduction of soot (fine particulates), and a reduction of the So<sub>x</sub> emissions [11,12].

### Levulinic acid

The production of levulinic acid has been demonstrated at the pilot scale by Biofine, which reported a yield of 75% from biomass (such as paper mill sludge, urban waste paper, and agricultural residues) using aqueous monophasic systems [13,14]. The main limitation in levulinic acid production is the separation of the product from the mineral acid and the formation of degradation products known as humins. Production of humins has been typically minimized by using low loadings of cellulose, which increases the purification cost of the levulinic acid due to the resulting low concentration. The use of biphasic systems is an option for the production of levulinic acid, since the levulinic acid can be concentrated into the organic phase. Alkylphenol compounds have shown to be effective solvents, extracting over 75% of the levulinic acid produced into an organic

phase, while leaving 100% of the mineral acid in the water phase. This water phase can be reutilized after the extraction to produce more levulinic acid [15]. Another advantage of using these solvents is that once the mineral acids have been separated, the levulinic acid can be processed without further purification. Likewise, other challenge of this process is the replacement of a mineral sulfuric acid by a solid acid catalyst. The catalytic processing of levulinic acid into advanced biofuel candidates has been mainly focused to the production of alkyl esters, e.g. Ethyl Levulinate (EL), and Gamma-Valerolactone (GVL).

### Ethyl Levulinate

Low-alkyl levulinates, and prominently Ethyl Levulinate (EL), can be advantageously used as fuels. EL can be used as octane booster for gasoline and fuel extender for diesel and biodiesel, while butyl levulinate and other higher alkyl levulinates are found to be good quality improvers for diesel and bio-diesel [16-18]. Although levulinates can be easily obtained by direct esterification of levulinic acid with a lower alcohol (e.g. ethanol), more appealing alternatives for their production from lignocellulosic biomass have also been envisioned, such as the direct production of levulinates from glucose or even cellulose.

### GVL

$\gamma$ -valerolactone (GVL) is considered an interesting levulinic acid derivative with potential applications in distinct fields, such as solvents or food additives. But more importantly, it also exhibits very attractive physical and chemical properties to be used as a sustainable liquid for global storage and transportation. It is typically obtained by catalytic hydrogenation of levulinic acid, and subsequent ring-closure of the intermediate 4-hydroxypentanoic acid [19]. Specifically, in terms of fuel properties, the comparative evaluation of GVL and ethanol, performed on a mixture of 10 v/v% GVL or EtOH and 90 v/v% 95-octane gasoline, showed very similar properties. Since GVL does not form an azeotrope with water, the latter can be readily removed by distillation, resulting in a less energy demanding process for the production of GVL than that of absolute ethanol [20].

### Catalytic Conversion of Hemicellulose: Furfural

Furfural can be obtained through the formation of C5 sugars (mainly xylose), and this furan compound is a key platform chemical for both chemical and fuel industries [21,22]. The first commercial process for furfural production was achieved in 1921 by Quaker Oats [23]. This process uses aqueous sulfuric acid in a batch mode at 443-458 K to achieve only limited (40-50%) furfural yield. Following the Quaker Oats process, other furfural production processes were developed in batch or continuous operation in a single step furfural production. However, all these commercial processes utilize mineral acids in single phase operation, which complicates the recovery of the furfural as well as the mineral acid. Moreover, in addition to dehydration of the sugar, several other side reactions take place, limiting the furfural yields. Hence, the reaction conditions need to be optimized to maximize furfural yield while minimizing humins production. As an improvement on the current furfural production processes, the use of solid acid catalysts [22] as well as biphasic systems have been studied. Even though biomass derived sugars are typically produced in aqueous solutions, many solid acid catalysts, such as zeolites, do not function well in liquid water, and leaching of acid functionalities at high reaction temperatures in aqueous environments is unavoidable. In addition, water has been found to accelerate side-

reactions, decreasing furfural selectivity. Therefore, different organic compounds such as toluene, acetone, Dimethyl Sulfoxide (DMSO) and Methyl Isobutyl Ketone (MIBK) have been studied as solvents for the formation of furfural over solid acid catalysts. Another approach for achieving high yields of furfural in the presence of water is to employ biphasic reactor systems. In this way, furfural is continuously removed from the aqueous acidic phase during reaction, avoiding its acid catalyzed consecutive reactions, including reactions with water. In the presence of an organic phase, homogenous mineral acids can be used to catalyze the reaction in the aqueous phase, and they can be recovered and recycled by separating the aqueous and organic phases after reaction. Xylose dehydration to furfural has been demonstrated with high yields (~90%) in several previous studies using mineral acids and salts in biphasic systems with organic solvents, such as MIBK, 2-butanol and tetrahydrofuran (THF) [6]. Moreover, furfural can be obtained as a co-product of levulinic acid and 5-HMF production when the feedstock contains pentoses [21]. Nevertheless, despite all the above-described developments, the cost and energy intensity of furfural production and recovery still requires significant improvements.

Regarding the production of advanced biofuels from furfural, most of the reported applications are devoted to the synthesis of energy dense oxygenated chemicals, showing good miscibility and compatibility with hydrocarbons, since the preparation of fuels and fuel additives is one of the most interesting final destination for furfural [21]. In this way, several chemical transformations have been described, looking for the deoxygenation of the starting furfural, and leading to the enhancement of the energy density of the final products. The hydrogenation of furfural, as it has been thoroughly reported in literature, leads to the formation of several important intermediates, for instance furfuryl alcohol. This chemical depicts a higher energy density than the furfural from which it is obtained, and thus, it is suitable to be used as a fuel additive. Nevertheless, its intrinsic energy density can be upgraded by means of different techniques, for instance by esterification with short alkyl chain carboxylic acids, etherification with short chain alcohols or by its rearrangement to alkyl levulinates.

In summary, a huge variety of potential advanced oxygenated biofuels for the formulation of conventional fuels is evidenced. As herein commented, the key is the economic and sustainable production of platform molecules which can be subsequently upgraded to a great variety of fuel components by means of, for example, hydrogenation combined with acid-catalyzed reactions such as esterification and etherification. The resultant oxygenated compounds have shown attractive properties as blending components for gasoline, diesel and even biodiesel. However, the overall manufacturing chain still presents major challenges for the cost-effective production and recovery of such platform molecules. Additionally, mineral acid-catalyzed processes should be replaced by more environmentally friendly processes based on the use of active and stable solid catalysts able to work in organic solvents. Therefore, the direct transformation of lignocellulosic biomass in presence of suitable catalytic systems and adequate reaction conditions (alcoholic medium) is of great interest in order to minimize wastewater discharges and lead to higher-grade products. Hence, much catalysis and engineering research is still needed to achieve the potential of these platform molecules for manufacturing advanced lignocellulosic biofuels. And last, but not least, the deployment of such advanced biofuels will require a great effort in the areas of specification and legislation.

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