

**CONVERSION OF CELLULOSE AND HEMICELLULOSE
INTO PLATFORM MOLECULES: CHEMICAL ROUTES**

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Abstract

This contribution reviews the main thermochemical pathways currently under development for the transformation of cellulose and hemicellulose into valuable compounds, which could be further used for the production of both fuels and chemicals. The relevance of dehydration processes, followed by oxidation, hydrogenation and acid/base catalyzed reactions is clearly evidenced. Moreover, in order to improve the efficiency of these processes is important to avoid costly separation and purification steps, as well as to find routes for the one-pot transformation of the carbohydrates, or even better of the polysaccharides, into the final products. In this sense, the design of multifunctional catalysts suitable to work efficiently in water or biphasic media is a topic of great interest.

Introduction

First generation biofuels production technologies use easy accessible edible biomass, thereby impacting the supply of food for humans and animals, whereas their extensive and continued production does not seem to be a sustainable solution. Therefore, new alternatives for a more sustainable production of biofuels (and also chemicals according to the bio-refinery concept) must be developed, using widely available biomass feedstocks instead of edible starch and triglycerides. The best sources for such alternative biofuels is lignocellulose, since this polymer is the most

abundant form of biomass in the planet and it is widely available: as waste biomass, as conventional wood, and as fast rotation crops.

Two routes exist for the conversion of lignocellulose into biofuels: the thermochemical route and the sugar route [1]. The first approach involves thermochemical processing of lignocelluloses at high temperature and/or pressures (e.g. pyrolysis, gasification and liquefaction). The thermal deconstruction of biomass yields upgradeable intermediates such as bio-oils by pyrolysis and synthesis gas by gasification (CO:H₂ mixtures, denoted as syngas). Thermal processing is coupled with subsequent chemical/catalytic upgrading to produce fuel range hydrocarbons. In the sugar route, lignocellulose must be separated into its constituents lignin (15-30 %), cellulose (35-50 %) and hemicelluloses (25-30 %), which are then depolymerized to the corresponding building blocks. The sugars so obtained can be subjected to fermentation resulting mainly in the formation of bioethanol. However, this conversion involves drawbacks especially in view of the atom economy, the low energy density of ethanol and its relative low boiling point. Alternatively, fuel-type molecules and chemicals can be synthesized via a number of direct chemical catalytic conversion processes [2], which are next described.

Selective transformation of sugars into platform molecules

Conversion of biomass into functionalized targeted platform molecules is unique to hydrolysis-based methods and allows the production of a wide range of fuels components and also chemicals. Among the different platform molecules that can be obtained, furfural (2-furaldehyde), 5-hydroxymethylfurfural (5-HMF) and levulinic acid (LA) are of high interest for the production of industrial solvents, polymers and fuels additives, according to the following pathways [3]:

a) Dehydration of hexoses to furan compounds: 5-HMF and derivatives

Dehydration of hexoses in acid media leads to the formation of 5-(hydroxymethyl)furfural (5-HMF) which is a significant intermediate for the synthesis of a great variety of chemicals and biofuels. In this section, the different strategies of 5-HMF synthesis from hexoses will be discussed as well as their catalytic transformation in valuable biofuels and chemicals.

b) Dehydration of pentoses to furans: synthesis of furfural and derivatives

Hemicellulose is a rather heterogeneous polymer of pentoses (xylose, arabinose...), hexoses (mannose, glucose, galactose) and sugar acids. In contrast with cellulose, hemicellulose can be easily hydrolysed using dilute acids under moderate conditions to yield a mixture of sugars. Among them, xylose is one of the main products as it constitutes for about 30% of the hydrolyzate of corn stover. In a similar way to the formation of HMF from hexoses, dehydration of pentoses results in the production of furfural, which has been proposed as a viable platform chemical for biorefinery.

Catalytic routes for the aqueous-phase conversion of sugars and derivatives into liquid hydrocarbon for transportation fuels

In the last years new routes for the catalytically transformations of some biomass derivatives in the aqueous phase, such as sugars, into liquid fuels have been proposed [4]. The fundamental advantage of this route, in comparison with gasification and pyrolysis processing of biomass, is the mild reaction conditions used, which provides a better control of selectivity. However, catalytic treatments of aqueous solutions are relatively complex, they require a series of biomass pre-treatments and produces lignin residues, which can be energetically valorized by combustion.

The production of hydrocarbon from chemicals derived from biomass implies profound chemical transformations, in order to decrease the functionality provided by the high oxygen content of these products of biological origin. Another significant limitation is originated by the fact of sugar molecules being formed by five or six carbon atoms, but liquid hydrocarbons for transportation fuels have a larger chain (up to C₂₀ for diesel). Consequently, very efficient catalysts for deoxygenation and oligomerization processes in aqueous solutions must be developed. In addition, two aspects are crucial to ensure the economic feasibility of the aqueous phase route: (i) reduction of the number of processing steps and (ii) deoxygenation with minimal consumption of hydrogen from an external source.

In achieving these goals, it is foreseeable that these novel routes may become competitive alternatives to traditional processes for the transformation of biomass into biofuels and chemicals.

References

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