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Biomass to fuels: The role of zeolite and mesoporous materials ☆

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ABSTRACT

Biomass is an abundant and carbon–neutral renewable energy resource for the production of biofuels, moving the market dependence away from fossil-based energy sources. The main problem is how to efficiently remove the abundant oxygen content from biomass-derived products and convert it into a hydrophobic molecule with the appropriate combustion or chemical properties. Many efforts have been devoted to the search of heterogeneous catalytic systems, more selective, safe and environmentally friendly. In this scenario zeolites and mesoporous compounds may help chemists to develop new biofuel generation processes. The development of new catalysts in the field of conversion of biomass to biofuels requires knowledge of the complex nature of the substrates to be converted. Starting from the main chemical aspects of the different biomass platforms, an overview of some of the zeolite and mesoporous materials technologies currently used commercially or tested at pilot and laboratory scale, is presented in this paper.

1. Introduction

Expansion and progress, particularly in emerging countries, will boost the need for energy in all the end-use sectors, in particular in the transportation utilization [1].

As reported by 2009 Energy Outlook of Energy Information Administration of DOE, the world liquid fuel supply forecast is still increasing [2]. In 2030 106.6 million barrels per day is the expected demand of liquid fuel (Fig. 1).

The transportation sector accounts for the largest increment in total liquids demand, at nearly 80% of the total world increase. Unconventional liquids play an increasingly important role in meeting demand for liquid fuels over the course of the IEO2009 projections. Fuels derived from shale oils, oils sands, extra heavy oils, coal to liquids and gas to liquids processes, and biofuels are considered unconventional liquids. In the reference case, 12.6% of world liquids supply in 2030 comes from unconventional sources, including 1.5 million barrels per day from OPEC and 11.9 million from non-OPEC sources. As illustrated in Fig. 2, biofuels represent a significant part of unconventional supplies, i.e. increasing as absolute value and as percentage with respect to the other unconventional sources. Biofuels are liquids or gases for transport purposes that are produced from biomass.

The increasing demand of biofuels is due to several key issues, the first one is that bio-based resources are renewable and CO_2 neutral in contrast with fossil fuels. In fact, while electricity and heat can be generated from a wide spectrum of alternatives (sun, wind, hydro, geothermal heat, etc.) the production of transportation fuels can just rely on carbon-biomass, as only alternative carbon source to fossils ones. However, the main driver is the strong political focus on renewable biofuel alternatives together with the increasing severity of regulations everywhere in the World. The Renewable Energy Directive (RED) of European Union requires biofuels to reach 10% of total automotive fuel consumptions by the year 2020. Biofuels must contribute to CO_2 reduction of 35% at the introduction of the new Directive, till to reach 50% CO_2 reduction by 2017 (60% for the new production plants). US Renewable Fuel Standard (RFS) requires around 2.2 MBPD biofuels by 2022 (30% of the transport pool), with corn ethanol capped at 1 MBPD.

First-generation biofuels, produced primarily from agricultural crops, traditionally grown for food and animal feed purposes, are the initial step in this direction.

The main first-generation biofuels are bioethanol, used as a gasoline substitute, produced from sugar containing plants or cereals crops, and biodiesel, produced from vegetable oils after conversion into the corresponding fatty acid methyl esters.

However, most of first-generation biofuels have several drawbacks, including the competition with food crops, the competition for water, the potentially negative impact on biodiversity, the limited greenhouse gas emission reduction (with the exception of sugarcane ethanol) and the high production cost [3].

Many of these problems could be addressed by the production of the second generation biofuels, manufactured from agricultural

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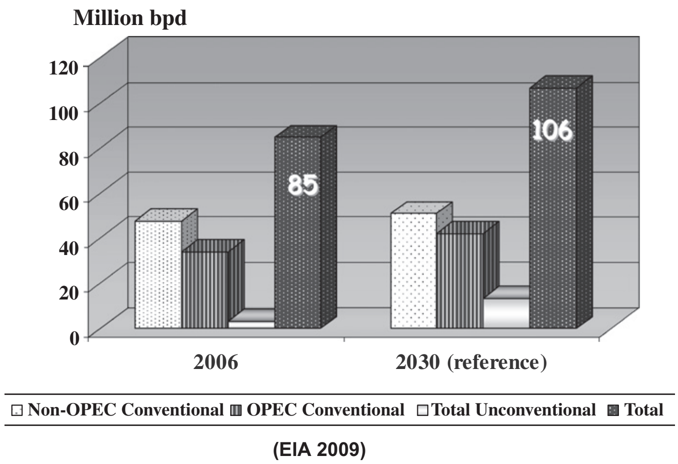

Fig. 1. World liquid fuel supply 2006–2030 by EIA.

and forest residues and from ligno-cellulosic non-food energy crops.

Second generation biofuels are expected to be superior to many of the first-generation biofuels in terms of energy balances, greenhouse gas emission reduction, land requirement and competition for land, food, fiber and water. The main reason they have not yet been taken up commercialization, despite their potential advantages, is that the involved production technologies are not technically proven at a commercial scale and their costs are at the moment estimated to be significantly higher than that of most first-generation biofuels.

Therefore, there is still much work to be done for the improvement of the existing processes and for the development of new efficient technologies. Acid and base catalysis plays a crucial role in most of the processes currently used for the production of biofuels, such as the transesterification of vegetable oils with methanol in the biodiesel process (catalysed by alkali, i.e. NaOH, MeONa, KOH) and the hydrolysis of cellulose to fermentable sugars for bioethanol production (catalysed by H_2SO_4). The homogeneous catalysts, used in both these processes, have some drawback, mainly due to the neutralization step needed at the end of the reaction.

In order to avoid these problems, many efforts have been devoted to the search of solid catalysts, more selective, safe and environmentally friendly. In this scenario zeolites and mesoporous compounds may help chemists to develop new biofuel generation processes, due to their important properties, namely, high concentration of active sites, high thermal/hydrothermal stability and enhanced shape selectivity. The aim of this contribution is to summarise some challenges facing zeolite and mesoporous catalysts in new industrial processes.

2. The role of zeolite catalyst in biomass conversion

Zeolites have found wide application as solid acid catalysts or catalyst carriers in the oil refining and petrochemical industries, where they have been gradually replacing conventional homogeneous and heterogeneous catalysts (e.g. free liquid acids; amorphous mixed oxides). In most of the processes, zeolite and mesoporous materials are involved in acid-catalyzed reactions that proceed through the formation of carbocation-like intermediates. Therefore the chemistry of the catalytic transformations is closely related to the chemistry of the carbocations in the restricted microporous environment. Normally, the reactions are performed in apolar gas or liquid phases where the substrate to be converted is an hydrocarbon oil or an hydrocarbon-like molecule. To produce biofuels, we should take in account that the composition and the structure of biomass raw materials are totally different from petroleum. Lignocellulose (wood and its derivatives) is the cheapest and most abundant source of biomass and is essentially composed of cellulose (38–50%), hemicelluloses (23–32%) and lignin (15–25%) [4]. All these compounds are polymeric molecule insoluble in most of conventional organic solvents. The transport of heavy biomass molecules into catalyst pores is very cumbersome and severe mass transfer limitations should be expected. To be transformed the biomass require a dispersant as reaction medium and the so obtained

Table 1
Chemical composition of various biomass feedstock.

Biomass substrate (dry base)	Elemental analysis (%)				
	C	H	O	N	S
Sawdust	45.8	6.1	42.7	<0.1	<0.1
Switchgrass	47.8	5.8	45.0	1.1	0.1
Arundo donax	47.1	5.8	46.4	0.6	0.1
Algae	46.1	7.4	41.3	4.8	0.4
Organic urban waste	44.3	6.7	44.5	3.5	0.9
Fossil heavy oil	86.1	11.8	<0.1	0.1	2.0

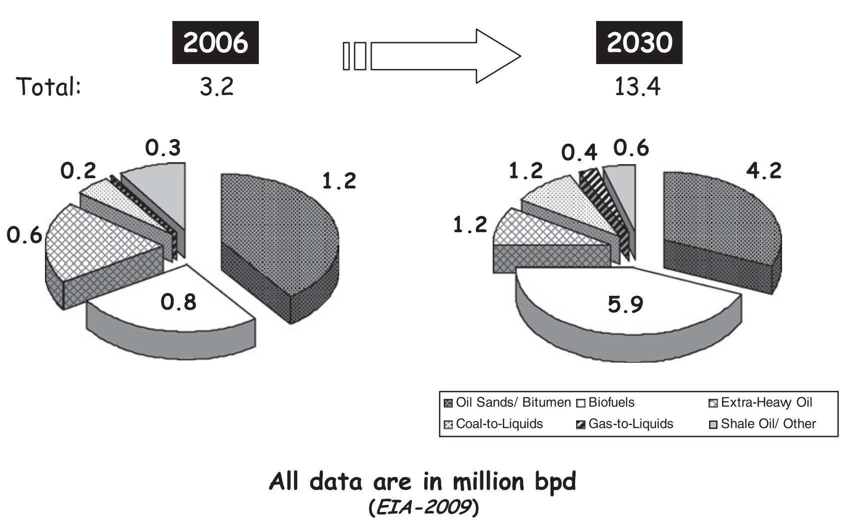

Fig. 2. World production unconventional liquid fuels 2006–2030 by EIA.