



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Catalytic insights into the production of biomass-derived side products methyl levulinate, furfural and humins

Layla Filiciotto^a, Alina M. Balu^{a,*}, Jan C. Van der Waal^b, Rafael Luque^a^a Departamento de Química Orgánica, Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie (C-3), Ctra Nnal IV-A, km 396, Córdoba, Spain^b Avantium Chemicals, Zekeringstraat 29, 1014 BV, Amsterdam, The Netherlands

ARTICLE INFO

Article history:

Received 2 December 2016

Received in revised form 15 February 2017

Accepted 4 March 2017

Available online xxx

Keywords:

Biomass valorization

Side-products

Methyl levulinate

Furfural

Humins

ABSTRACT

Biomass conversion into useful chemicals, materials and fuels emerged as a promising alternative toward replacing the current production of most of these commodities and specialty products from petroleum feedstocks. Interestingly, not only end products but also side-products from biomass valorization have a significant potential for future research and further conversion into novel families of useful derivatives. Based on such potential, the proposed contribution has been aimed to focus on catalytic insights into the production of three particular biomass-derived side products from the hemicellulosic fraction, namely methyl levulinate (MeL), Furfural and Humins using both homogeneous and heterogeneously catalyzed processes.

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1. Introduction

Fossil-based resources currently used for energy and material production are not endless and will run out in due time. This ongoing depletion together with the detrimental augmentation of greenhouse effects have driven the worldwide scientific community to find economically valid, environmental-friendly, sustainable alternatives to current petroleum-based industry. Novel routes employing sustainable C-sources will need to be sought, especially in the case of materials and for some types of transportation fuels.

The development of high-output technologies in agronomics [1] has yielded a surplus of one of the most promising undepletable sources: vegetable biomass. In fact, plant-derived feedstocks have been proposed as the major renewable C-source alternative that can match fossil resources in the chemicals and specific fuels production [2]. The variety of biological and/or chemocatalytic conversion strategies to drop-in fuels, high added value chemicals and novel materials make biomass an attractive and versatile resource [1–5]. In particular, the plentiful abundance of lignocellulosic biomass, along with its potential fast renewability, accommodate the need to find a cheap and readily available green resource.

Lignocellulose is the main structural constituent of all land-based plants [4], found in agricultural and forestry residues,

herbaceous and woody crops alike. This makes lignocellulosic biomass a readily available non-fossil carbon source without being in competition with the food and feed industries [6]. A clear challenge in the conversion of lignocellulose into valuable-added chemicals relates to its structural complexity. In part, this is due to the nature of the three major components in biomass, namely: (i) lignin (15–30%) which confers structural rigidity to the plant, comprising a recalcitrant polyaromatic/phenolics polymer; (ii) cellulose (35–50%), an insoluble, crystalline, linear glucose polymer linked by β -1,4 glycosidic bonds whose crystallinity gives tensile strength to the plant cell walls; and (iii) hemicellulose (20–35%), a cross-linked fibrous amorphous polymer, mostly comprised of different pentoses with some hexoses and uronic acids sugar monomers often functionalized with methoxy and acetoxy groups. As a whole feedstock, lignocellulosic biomass can be directly converted into syngas and bio-oil by gasification and pyrolysis [7]. However, more promising routes seem to be the fractionation of lignocellulose into its individual constituents by the means of chemical and/or enzymatic hydrolysis [2,4].

Lignocellulosic biomass can be converted into a plethora of possible compounds, ranging from biofuels to fine chemicals and specialty materials, which include both commercial and unknown compounds [2]. In order to limit the research's targeted molecules, the 2004 US DOE report [8] listed the top biomass-derived chemical compounds (later revisited by Bozell and Petersen [9]), which comprised of the 10 most promising compounds that could achieve mass production with the current biorefinery tech-

* Corresponding author. Tel.: +34 957211050.

E-mail addresses: qo2balua@uco.es, q62alsor@uco.es (A.M. Balu).

nologies. Several new industrial scale productions of biomass derivatives have already been achieved, for example with the two-step acid-catalyzed production of Levulinic Acid (LA) in the so-called *Biofine Process* [10], which recently has been revitalized by GFBiochemicals. Advancements of Avantium's *YXY technology* [11] have further plans for large scale production in Antwerp, Belgium for the sustainable conversion of plant-based feedstocks into 2,5-furandicarboxylic acid (FDCA), platform chemical for the complete substitution of polluting terephthalate plastics. It is, however, clear from the DoE report and exemplified by these processes that the preferred feedstock for selective chemical production are sugars from the (hemi-)cellulosic fraction of biomass.

Chemocatalytic sugar conversions often leads to numerous side-products which limit targeted product yields, increase separation costs and renders overall production uneconomical. Fine-tuning of the current processes with the aim to minimize waste has so far proven difficult, and thus, the valorization of side-products and waste streams has to be studied in depth.

The present contribution aims to provide a general overview of the production of three major products from acid catalyzed sugar conversion processes: Levulinic acid and its Methyl ester (LA, resp., MLA), Furfural (FF), and Humins (HUM). Exploring new ways of their utilization as a feedstock for novel process may lead to improved efficiencies in new biorefinery concepts.

2. Methyl levulinate

Levulinate esters are a promising class of biomass derivatives with low toxicity, high lubrication and moderate flow properties at low temperatures [12–15]. Due to their relative simple production, they possess wide application potential as fragrances [16], herbicides [17], cancer therapeutics [18], and as oxygenated additives for gasoline and diesel transportation fuels. In their production, humin formation via polymerization of formed furanic compounds upon hemicellulose dehydration is suppressed at high alcohol/water ratios, making alkyl levulinates a more attractive platform chemical as compared to its hydrolyzed counterpart, levulinic acid.

Methyl levulinate, in particular, is employed as a flavoring agent, and, more importantly, possesses great potential as platform molecule, due to its transformable keto and ester group. Alkyl levulinates may be produced by (i) alcohol esterification of levulinic acid [19], (ii) conversion of furfuryl alcohol and its ethers [20], (iii) alcohol reactive extraction [21–23], (iv) carbohydrates conversion in alcohol media [24], or (v) as a co-product by direct synthesis from biomass (Scheme 1).

For example, methyl levulinate is a side-product to Avantium's methanolic fructose dehydration to 5-methoxymethylfurfural (MMF) [11], as well as a by-product in the aromatic production from liquefaction and fractionation of lignocellulosic biomass under sub-critical methanol conditions [25].

2.1. Homogeneously catalyzed MeL production

Producing levulinic esters from levulinic acid has been attempted by esterification of levulinic acid, produced from an aqueous product mixture of homogeneously acid-catalyzed conversion of biomass [19] which comprises also furfural, formic acid and the mineral acid catalyst (the latter two catalyze the esterification as well). A summary of the different employed homogeneous catalytic systems for MeL production from various substrates is given in Table 1.

Homogeneous acid catalysts have been extensively used in the synthesis of methyl levulinate. Brønsted acids are known to catalyze fructose dehydration, while aldose isomerization, required

Table 1
Overall comparison of homogeneous catalysts employed in methyl levulinate production.

Catalyst	Substrate	T (°C)	t (min)	Yield (%)	Refs.
HCl	Glucose	160	150	12	[31]
H ₂ SO ₄	Glucose	160	150	13	[31]
H ₂ SO ₄	Fructose	160	150	73	[31]
H ₂ SO ₄	Cellulose	183	12	38	[32,33]
H ₂ SO ₄	Cellulose	190	300	55	[34]
H ₂ SO ₄	Glucose	200	120	49	[32]
Al ₂ (SO ₃) ₄	Glucose	160	150	64	[36]
Al ₂ (SO ₃) ₄	Glucose	200	120	54	[35]
PTSA	Cellulose	180	300	20	[42]
In(OTf) ₃	Cellulose	180	300	52	[42]
In(OTf) ₃ + PTSA	Cellulose	180	300	70	[42]
In(OTf) ₃ + 2-NSA	Cellulose	180	300	75	[42]

when using glucose, is catalyzed by bases or Lewis acids [26–30]. For this reason, mineral acids such as H₂SO₄ and HCl yielded >70% methyl levulinate from fructose, but low yields (ca. 12%) were observed from glucose [31] (Table 1).

As for cellulose, yields of 46% [32,33] and 55% of methyl levulinate [34] were obtained in the presence of concentrated sulfuric acid at 179 °C and in near-critical conditions, respectively. Garves et al. [33] investigated the efficiency of extremely low acid (ELA) concentrations (up to 0.01 mol L⁻¹), obtaining 49% methyl levulinate from glucose after 2 h at 200 °C at the highest ELA. ELAs were also investigated in the methanolysis of cellulose, yielding 50% methyl levulinate at 210 °C using 0.01 mol L⁻¹ sulfuric acid.

Homogeneous mixed acids, particularly Al₂(SO₄)₃, sparked scientific interest thanks to the co-presence of both Lewis and Brønsted acidity. Yields of 54% [35] and of 64% [36] from glucose were reported due to the metal cation ability to catalyze the isomerization of glucose to fructose, and the latter consequent dehydration.

Although high yields might be achieved, homogeneous acid catalysts present major processing drawbacks (e.g. equipment corrosion, inefficient separability and reusability, polluting waste) as well as alcohol dehydration to its diether. A preferential focus was shifted toward heterogeneous catalytic systems.

2.2. Heterogeneously catalyzed MeL production

For instance, methyl levulinate yields of 88% were obtained over a methylated polymer-supported triazene (Me-PST) [36], while >95% methyl levulinate yields were achieved in mesoporous structures. In particular, Melero et al. [38] reported a 95% yield of the levulinate ester in methanol at 117 °C over SBA-15-(CH₂)₃-SO₃H, which decreased to only 93% after four consecutive runs. This was attributed to an enhanced mass diffusion of levulinic acid and relative ester in the mesopores. Similar trends were also observed in the use of solid heteropolyacids (HPA). HPA possess higher intrinsic acidity comparable to H₂SO₄ but these catalytic systems often display limited surface area and often high solubility in water and/or polar solvents, which leads to leaching of the active phase. The use of a porous catalyst support is often employed in order to avoid these problems. Yields of 73 to 99% of methyl levulinate were reported for levulinic acid conversion for H₄SiW₁₂O₄₀ incorporated on mesoporous SiO₂ [39] and H₃PW₁₂O₄₀-ZrO₂ with benzene moieties [40]. The remarkable activity of these catalysts is given by (i) the presence of hydrophobic moieties facilitating faster formation of methyl levulinate thanks to their capacities of facilitating levulinic acid adsorption over H₂O, and (ii) the larger pore structure, rather than acid sites density, type, and activity, factors that in non-porous catalysts (e.g. sulfonated oxides) are key for the observed activity [41].

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