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Review

Review: Sustainable production of hydroxymethylfurfural and levulinic acid: Challenges and opportunities

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ABSTRACT

Hydroxymethylfurfural (HMF) and levulinic acid (LA) are two of the most promising chemicals derived from biomass owing to their convertibility into a large number of chemicals having applications in diverse industries. Their transition from niche products to mass-produced chemicals, however, requires their production from sustainable biomass feedstocks at low costs using environment-friendly techniques. In this review, the numerous reaction systems that have been developed to produce HMF and LA from various substrates have been looked at and their merits, demerits and requirements for commercialisation outlined. Special attention has been paid to microwave irradiation-heated systems due to their dual advantages of high product yields and low environmental footprint.

1. Introduction

The rapid depletion of fossil fuels has led to an increased international effort to augment the use of renewable energy. However, alongside being the predominant source of energy, fossil fuels are also the leading source of organic chemicals which are the backbone of modern life. The replacement for fossil fuels in this area can come from biomass, with biorefineries being presented as the future substitutes for the present day petroleum refineries. In the same way that petroleum refineries use certain chemicals as the building blocks for more complex molecules such as polymers, a biorefinery will use simple molecules that can be readily obtained from a variety of feedstock as a base for the synthesis of biopolymers and other large molecules [1,2]. Among the most promising building blocks are hydroxymethylfurfural (HMF) and levulinic acid (LA), which are the subject of this literature review.

HMF has been referred to as a 'sleeping giant' owing to the vast potential of this compound in the emerging bio-based economy due to the key position it holds in the production of biomass-derived intermediates [3]. It is said to be one of the few petroleum-derived chemicals that can also be readily synthesised from renewable resources, and is held to be a

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bridge between carbohydrate chemistry and industrial mineral oil-based organic chemistry [4]. While a vast number of chemicals can be produced from HMF, some of the most important ones are listed in Table 1 [5–10], along with their potential uses. Among the chemicals not listed in Table 1 is LA, the attributes of which are also of importance for discussion in this paper.

In addition to being an intermediate in the production of chemicals mentioned in Table 1, HMF also has some potential uses on its own, such as in fuel cells [11], the treatment of sickle cell disease [12], etc. Ultimately, however, the major potential of HMF is as a key platform chemical, and this depends on its availability and cost [13]. In 1993, it was estimated that the cost of producing HMF would be between Deutsche Mark (DM) 5000–10,000 per ton based on a fructose price of DM 2000 per ton or inulin price of DM 1000 per ton [14], which at 2002 prices would be comparable to 2500–5000 €/ton [15]. These prices are fairly similar to those obtained for the pilot plant operated by Südzucker AG in the Federal Republic of Germany, with the manufacturing price of HMF being 6000 DM/ton for a fructose price of 500 DM/ton [13], and also the price of 2000 €/ton predicted by Bicker et al. for a fructose price of 500 €/ton [16].

Some researchers have investigated whether HMF could be produced at reduced cost in order to be used as a substitute for certain target chemicals. Torres et al. estimated the cost of production of HMF using a semi-batch biphasic reactor and compared it with the price of p-xylene, for which HMF can act as a substitute in the production of polyethylene terephthalate (PET) [17]. They obtained a minimum HMF cost of 0.248–0.273 $/mol (1967–2165 $/ton) for a fructose cost of 550 $/ton, depending on the solvent used at the extraction stage. However, this was higher than the cost of p-xylene (0.109 $/mol or 1027 $/ton). Since the cost of fructose is the dominant factor in the HMF price, it was concluded that lower fructose costs are necessary alongside the development of more efficient processes for the HMF price to be competitive [17]. More recently, Kazi et al. estimated that a plant co-producing dimethylfuran (2,5-DMF) and HMF from 300 metric ton/day of fructose would yield HMF with a minimum selling price of $ 1.33/l, which translates into approximately $ 1100/ton. However, this is still too expensive for HMF to be used as a feedstock for the production of FDCA as a replacement for terephthalic acid, which sells for around $ 800/ton [18]. Recently, Liu et al. stated that HMF produced at $1210/ton would be cost competitive with the petroleum-derived para-xylene-terephthalic acid selling at $1440/ton, and state that this HMF price is achievable for a fructose price of 460 $/ton [19].

LA is a compound derived from HMF that is itself a promising chemical intermediate. It was listed among the top 12 most promising value added chemicals from biomass by the Biomass Program of the US Department of Energy in 2004 [1], and continues to rank highly in more recent reviews of most important biorefinery target products [20]. This recognition of the potential of LA is not a recent phenomenon. The compound was first identified in the 1870s, and in 1956 a detailed report outlining the many derivatives from LA and their potential applications were published [21]. Despite this, the

Table 1 – Chemicals produced from HMF and their applications [5–10].

Chemical	Potential markets/ applications
Formic acid	Commodity chemical Textiles Road salt Catalysts Fuel cells
Ethoxymethylfurfural	Biofuels
5-Hydroxymethylfuroic acid	Polymers
2,5-Furandicarboxylic acid (FDCA)	Polymers Pharmaceuticals
2,5-di(Hydroxymethyl)furan (DHMF)	Solvents Polymers
Furfuryl alcohol	Resins Solvents
Dimethylfuran (2,5-DMF)	Biofuels
2-Methylfuran	Biofuels
2,5-Diformylfuran (DFF)	Pharmaceuticals Fungicides
2,5-di(Hydroxymethyl)tetrahydrofuran (DHM-THF)	Solvents
2,5-Furandicarboxyaldehyde (FDC)	Polymers Resins

Table 2 – Potential applications for select chemicals produced from LA [8,23–26].

Chemical	Potential markets/ applications
Diphenolic acid	Epoxy resins Lubricants Adhesives Paints Polymers
Succinic acid	Polymers Solvents Pesticides
δ-Aminolevulinic acid (DALA)	Herbicides Insecticides Cancer treatment
Methyltetrahydrofuran	Fuel additive Solvents
Ethyl levulinate	Fuel additive Food flavouring
γ-Valerolactone (GVL)	Solvents Fuel additive Biofuels Polymers
Different esters of LA	Plasticisers Solvents
α-Angelicalactone	Fuel additive Solvents
Sodium levulinate	Antifreeze
Calcium levulinate	Antifreeze Pharmaceutical
1,4-Butanediol	Polymers Solvents Fine chemicals
Valeric (pentanoic) acid	Fuel additive
5-Nonanone	Paints Resins

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