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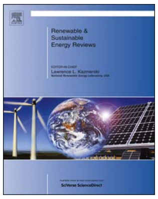

Chemoselective hydrogenation of biomass derived 5-hydroxymethylfurfural to diols: Key intermediates for sustainable chemicals, materials and fuels

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ABSTRACT

Biomass-derived 5-hydroxymethylfurfural (HMF) is hailed as an all-purposed platform molecule that holds great promise to address a number of high volume markets for chemicals, polymeric materials, and transportation fuels. HMF-derived diols, including 2,5-bishydroxymethylfuran (BHMF), 2,5-bishydroxymethyltetrahydrofuran (BHMTF), and 1,6-hexanediol (1,6-HD), are key intermediates for the catalytic upgrading of HMF in a biorefinery. These diols can be employed as renewable polymeric monomers, and among them BHMF and BHMTF are also attractive precursors for biofuels, such as 2,5-dimethylfuran (DMF), 2,5-bis(alkoxymethyl) furans (BAMFs), and 2,5-dimethyltetrahydrofuran (DMTHF). Hence, gaining more insights into the chemoseletive hydrogenation of HMF to these diols is of particular importance. In this review, we comprehensively summarize the advances in the selective hydrogenation of HMF into these diols in terms of the diversity of hydrogen sources, mainly including molecular H_2, alcohols, formic acid and water, over homogeneous or heterogeneous catalysts. Assessment of the relative merits of different hydrogen sources for the hydrogenation of HMF is performed as well. We also discuss challenges and opportunities in employing these HMF-derived diols for the production of polymeric materials and biofuels.

1. Introduction

The depletion of fossil resources alongside the deterioration of environment drives powerful momentum to develop green and renewable energy and resources to alleviate our overwhelming dependency on non-renewable fossil resources over the past decades [1]. Of well-known green energies like solar and wind energy, biomass is the only current renewable carbon source to extract liquid fuels, chemicals and polymeric materials produced conventionally from petroleum [2]. In this scenario, biomass holds great promise to afford the fascinating prospect of sustainable future. To this end, biorefinery, which is defined as the production processes that integrate numerous technologies and facilities to convert biomass resources (primarily the inedible parts) into a wide variety of chemicals, materials and energy, has been recently presented [3,4].

Platform chemicals stemmed from lignocellulose, the most abundant biomass resource on the Earth, are important intermediates during biorefinery, which is a bridge between raw biomass and end-products including value-added chemicals, materials and fuels [5]. To date, a large amount of research contributed to the chemical and/or biological transformation of lignocellulosic biomass into platform molecules, which include 5-hydroxymethylfurfural (HMF) [6], furfural [7], levulinic acid (LA) [8], γ-valerolactone (GVL) [9], and succinic acid [10], etc. Among these biomass-derived platform molecules, HMF is hailed as a “sleeping giant” thanks to a broad range of potential applications of HMF (as shown in Scheme 1) [6]. It is well-known that HMF can be readily prepared with high yields from hexoses in the presence of acid catalysts in various solvents, especially in ionic liquids [11]. Both oxidation and hydrogenation of HMF offer access to useful monomers for polymers and/or precursors for biofuels. HMF can be oxidized to 2,5-diformylfuran (DFF), 2,5-furandicarboxylic acid (FDCA), adipic acid, and 5-hydroxymethyl-2-furan carboxylic acid, which can be used as a new family of polymeric monomers [12,13]. The reduction of HMF gives diols, including 2,5-bishydroxymethyl furan (BHMF), 2,5-bishydroxymethyltetrahydrofuran (BHMTF), and 1,6-hexanediol (1,6-HD), which can be served as the building blocks for

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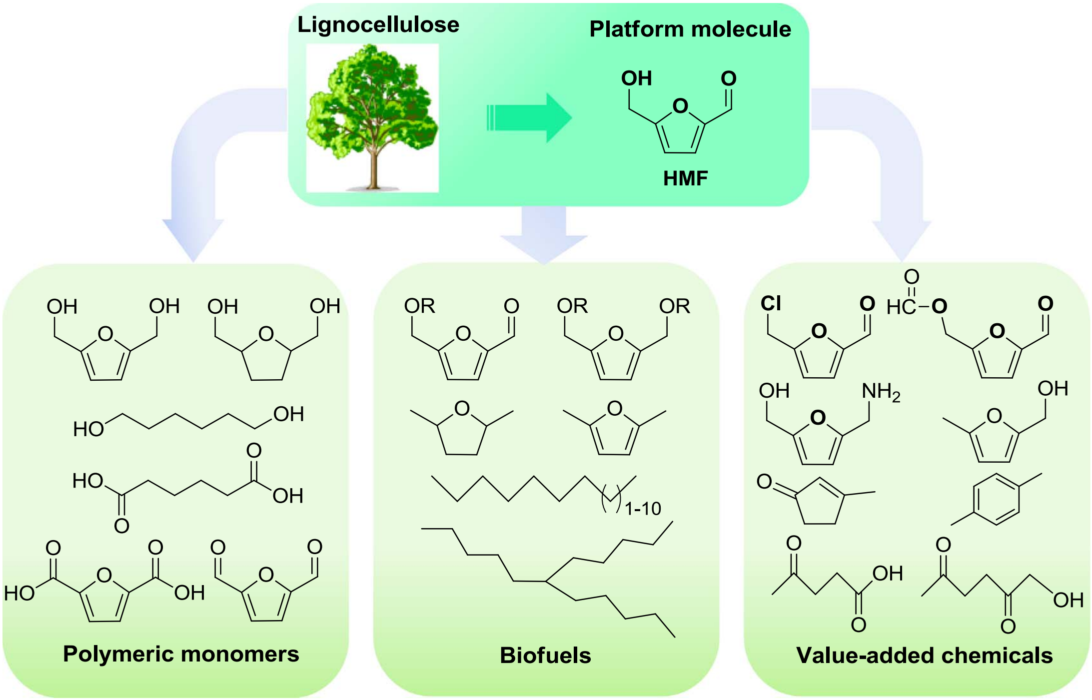
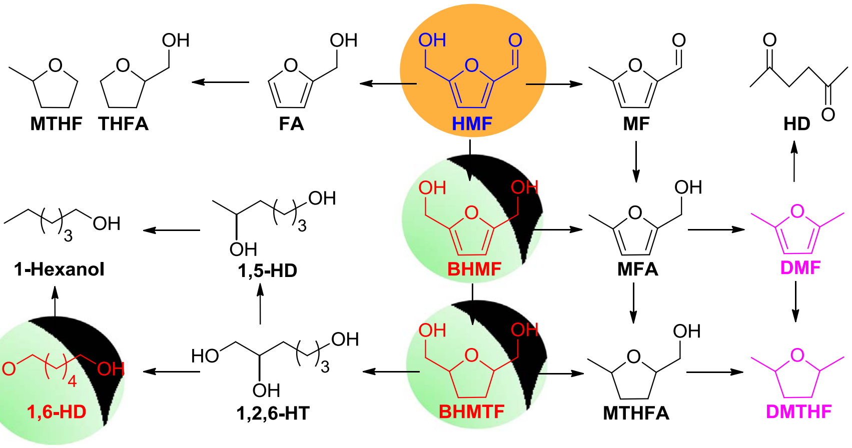


Scheme 1. Valorization of biomass-derived HMF into value-added chemicals, polymeric monomers, and biofuels.



Scheme 2. The possible products formed by the hydrogenation of HMF.

biobased polyesters [12]. Furthermore, these diols can also be converted to potential biofuel candidates. For instance, the hydrogenolysis of BHMF and BHMTF give 2,5-dimethylfuran (DMF) and 2,5-dimethyltetrahydrofuran (DMTHF), which are a new-fashioned liquid biofuel due to their similar properties (such as energy density, boiling point, and water solubility) to commercial gasoline and high octane number [14–16]. 2,5-Bis(alkoxymethyl)furans (BAMFs) derived from the etherification of BHMF and alcohols have much higher cetane number than that of commercial diesel and are completely miscible with commercial diesel at blend rates below 40 vol% [17–19]. HMF also can be applied as the precursor for the production of “drop-in” liquid fuels (C9–C15 alkanes) by aqueous-phase processing [20]. In addition, HMF can be converted into value-added chemicals used in pharmaceuticals, flavors and fragrances, through these above mentioned diols [12].

Van Putten et al. have comprehensively reviewed the general mechanistic aspects of the formation of HMF by the dehydration reaction of carbohydrates as well as the catalytic upgrading of HMF [12]. However, the catalytic valorization of HMF into a wide spectrum of useful products has already become a booming topic of research in biorefinery, and relevant references published are growing exponentially in recent years. The hydrogenation of HMF is of particular interest to provide polymeric monomers. On the other hand, biomass-derived molecules are extensively oxygenated in comparison to petroleum-derived chemicals; therefore, the removal of oxygen from these molecules by hydrogenation is the crucial step for the upgrading of biomass-derived chemicals to produce fuels. At this point, gaining more insights into the chemoseletive hydrogenation of HMF to these diols is of particular importance for the catalytic upgrading of HMF. However, it is challenging to control the degree of the reduction of HMF, since HMF has several highly active moieties containing furan ring, hydroxyl and carboxyl groups. In this review, the latest advances in the catalytic conversion of HMF to diols, including BHMF, BHMTF and 1,6-HD, are selectively summarized in terms of the diversity of hydrogen sources and catalysts. We also discuss challenges and opportunities in addressing a number of high volume markets for biofuels and polymeric materials through HMF-derived diols.