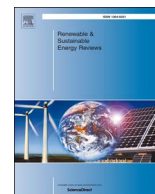




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Traversing the history of solid catalysts for heterogeneous synthesis of 5-hydroxymethylfurfural from carbohydrate sugars: A review

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ABSTRACT

5-Hydroxymethylfurfural (HMF) belongs to the group of “drop-in biofuels” and platform molecule of prime importance. Synthesis of HMF from various sugar sources has traversed a long span of time and has witnessed various modifications viz., use of heterogeneous catalysts over homogeneous catalysts, employment of organic phase over aqueous, introduction of biphasic systems to overcome side reaction limitations and still counting. Every modification has been carried out with the objective of improved selectivity and product synthesis, cost and energy optimization, and a shift towards greener process over existing methods. Use of lignocellulosic biomass instead of commercial sugars also finds applicability in direct HMF synthesis along with levulinic acid, furfural etc. However, low yields from these abundant, cheap and readily available sugar sources are still ideal for scale-up of the process strategies. Among large pool of studies available in this area, current review presents the advantages imparted towards HMF synthesis with the advent of heterogeneous catalysis over the course of time and various reaction systems evolved to meet the steeping demand of HMF, specifically from common carbohydrate sources. Special attention has been paid to understand the mechanism of modifications imparted to various solid catalysts for improved HMF synthesis.

1. Introduction

The prime concern of researchers for the past few decades is abating the dependence on fossil based energy sources. Concurrently, motivations to protect environment from disastrous carbon emissions from fossil based fuels has led to civilization as well as industrial sectors to be less energy-dependent compared to the past. However, the global energy demand is expected to increase upto 37% by 2040 [1]. Considering the extended time required for the replenishment of natural energy sources and predicted shortage to meet postulated global requirements has motivated the search for development of new renewable resource to substitute petroleum derivatives. 5-Hydroxymethylfurfural (HMF), one such identified energy source and is considered a versatile key value-added chemical (or platform molecule), receiving much attention in petroleum and chemical industries [2–4]. Because HMF is susceptible to many chemical reactions due to its excellent chemical reactivity enabling synthesis of variety of commercially important chemicals depending on the synthesis scheme, as proposed in Fig. 1 [5]. For example, hydrogenation reactions result in synthesis of 2,5-

dimethylfuran, which is a commonly used as transportation fuel (bio-derived), 2,5-bis(hydroxymethyl)furan (BHMF; used in manufacture of polyurethane foam), 2,5-dimethyltetrahydrofuran (used in polyester preparation) and so on. Also, HMF acts as an oxidative precursor to prepare FDCA (2,5-furandicarboxylic acid), an alternative to terephthalic acid in PET manufacturing, and adipic acid, which is extensively used in nylon preparations [2]. Also, 2,5-diformylfuran (DFF) finds application in synthesis of diamine and Schiff bases. The most advantageous property offered by the use of HMF-derivatives in plastic industries resulted better product biodegradability and thus, enabling a vision of low-carbon emission cycle. Similarly, 1,6-hexanediol produced by ring hydrogenation of HMF is considered as another most important additive in plastic and other chemical industries, and further trailing amination of which leads to formation of caprolactam, a monomer of nylon-6. Condensation reactions of HMF resulting in formation of long chain alkanes that could also be used as direct transportation fuel. Uncontrolled reaction conditions for instance, prolonged reaction, presence of surplus water molecule etc. during HMF hydrogenation reaction typically leads to equimolar synthesis of levulinic

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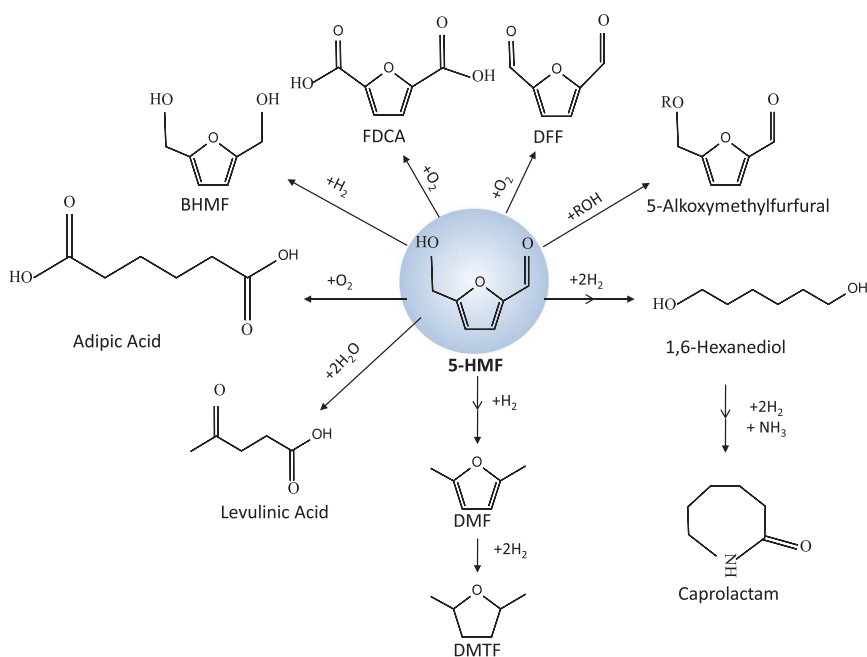


Fig. 1. Proposed end use of HMF as value added commodity.

acid (LA) and formic acid; nevertheless, LA itself exhibits as a valuable building block. Recent survey estimated that global consumption of HMF is around 100 t per year (Business Analytic Center report, BAC-2015) and therefore, in postulation, HMF shall be a bulk energy source in the near future by keeping in view of the potential applications [6,7]. Till date, extensive studies have reported for HMF preparation using variety of carbohydrate sources including fructose [4,7,8], glucose [9], cellulose, starch [10], sucrose [11], inulin [7] etc. But majority of the studies have used fructose as the starting substrate owing to ease of conversion and high selectivity through simple dehydration reaction by adapting either acyclic or cyclic mechanism, as depicted in Fig. 2a & b. Overall, in line, numerous pathways towards HMF synthesis are proposed but many are still poorly defined depending on the catalyst employed. However, the simplicity of the process is abated by the inherent disadvantages posed by high cost and limited availability of fructose sugar.

1.1. HMF production strategies

On the other hand, advent of production schemes using glucose appeared to have opened the golden gates in terms of low inventory cost as well as uninterrupted supply, demonstrating more sustainable synthesis of HMF. Glucose (six carbon membered molecule) can be obtained from various oligosaccharide sources like maltose, sucrose, cellobiose, as well as certain biogenic polysaccharides, such as cellulose and starch. Synthesis of HMF from glucose is principally a two-step process, where a base or Lewis acid catalyzed reaction for isomerization of glucose to fructose and followed by, Brønsted acid mediated catalysis to the end product. However, the commonly facing hurdles associated with the use of glucose as substrate include reduced overall yields mainly attributed to the participation of obtained reaction intermediates and/or the main synthesis product; HMF itself leading to increased formation of insoluble humins via self-polymerization, as depicted in Fig. 3. Several evident studies have revealed the superlative performances of fructose over glucose during heterogeneous HMF preparation under the modest reaction conditions, as data presented in Table 1. However, water-compatible Lewis acid possess low catalytic activity in aqueous environment due to rigorous effect of their progressive deactivation as well as coordinating polar environment offered by water. This renders their complex formation with low-coordinate metal species impossible, resulting ruling out the possibility of HMF

synthesis in good yields. Although traditional aqueous based systems established cost-effective owing to use of water as solvent along with some cheap alternate sources like corn starch [12] and wood chips [13], it is restricted by meager selectivity towards HMF. For instance, initial studies on HMF production from fructose in aqueous systems yielded < 50% wt. and later explained as being related to instability of HMF in water under acidic conditions and also, attributed to high yield of levulinic acid and formic acid following rehydration of HMF under the same prevailing reaction conditions. Since, the first report on HMF synthesis from inulin under aqueous acidic conditions, synthesis reaction has mapped large longitudes and latitudes with respect to sustainability achieved through high yields and selectivity, cost economics, ease of operation etc. [14]. This is owing to the following factors, such as introduction of continuous extraction, polar solvents in single phase systems, biphasic systems, heterogeneous acid catalysis, ionic liquids (IL), advanced heterogeneous catalysis (solid acid-base catalysts) etc. In pioneering work, Kuster and van der Steen [15] demonstrated HMF synthesis in organic solvent medium and claimed appreciable synergistic effects on HMF's rate of formation along with limited decomposition to humins and other side products. In support, several favorable studies postulated that aprotic solvents inhibit levulinic acid and humic substances formation [16]. Till date, popularly dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), dimethyl acetamide (DMA), N-methyl pyrrolidone (NMP), sulfolane etc. have been tested for HMF synthesis and accompanied higher yields. Nevertheless, overall cost economics of such processes is lavish owing to complex recovery itinerary of high boiling point solvents. In larger interest of affordable production of the versatile platform compounds, research has been focused on use of readily separable solvents, for example 1,4-dioxane, tetrahydrofuran (THF), *sec*-alcohols etc. However, use of alcohols in combination with acidic catalysts are detrimental on account of formation of HMF under the prevailing conditions [17]. Fascinatingly, THF exhibit prominent during HMF synthesis due to its excellent extraction property.

Numerous advanced studies have evaluated HMF production in co-solvent systems consisting combined solvent mixtures, for example methanol-THF, water-methyl isobutyl ketone (MIBK), water-2-butanol etc. in one-pot reactor setup and reported comparatively improved product yields [18]. This is mainly attributed to continuous extraction of furanic compounds as soon as it is formed, which prohibits from further degradation that inturn improve HMF yield, as in the case of

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