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A review on synthesis of alkoxymethyl furfural, a biofuel candidate

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ABSTRACT

Recently extensive efforts have been made to obtain drop-in fuel or fuel additives from renewable and sustainable resources. Alkoxymethyl furfurals synthesized from etherification reactions of aliphatic alcohols and 5-(hydroxymethyl)furfural (HMF) have been proposed as a diesel fuel additive and precursor of the drop-in fuel. Among the alkoxymethyl furfurals, 5-(methoxymethyl)furfural (MMF) and especially 5-(ethoxymethyl)furfural (EMF) have received much attention due to their superior prosperities including high energy density, low toxicity, high stability, and proper flow properties. Different acid catalysts have been tested for cost-effective production of EMF and MMF. Besides, broad ranges of feedstock from untreated lignocellulosic biomass and algae to carbohydrates and HMF have been used and their performances have been investigated. Production technologies for these fuel compounds and upgrading some of these compounds have been surveyed in many review papers. Therefore, making a concise overview on the production methodologies of all the relevant furan based fuel compounds, including long chain hydrocarbon alkanes from furfurals such as EMF and MMF is worthy of investigation. The current review summarizes the available technologies to help with further improvements and advancements of the production technologies of EMF and MMF. A special emphasis is placed on the state-of-the-art catalytic processes for EMF and MMF synthesis. Based on the review, the future direction is suggested.

1. Introduction

The main objective of this review is to compare the conversion yield of various feedstocks (e.g., HMF, carbohydrates, and biomass) to EMF and the applied reaction conditions. Moreover, the type of acid catalysts (e.g., homogenous or heterogeneous) and their performance are discussed as another objective. Reaction mechanisms are reported to provide a base for a reactor design. In order to highlight a major objective of this review, the EMF separation and isolation from various reaction media in different approaches are discussed.

Fossil fuels are the back bone of carbon-based economy. Fossil fuels and the chemicals derived from them have been produced from the limited natural sources. Due to the ever increasing demand for fossil fuels, their supply is often unstable. At the same time, the environment has been negatively affected by the carbon-based economy over the years. Thus, it is the consensus of general opinion that fossil fuels, or part of them, should be replaced by alternative and sustainable energy sources [1,2]. As one of the possible candidates, biomass is regarded as a very effective sustainable energy source. Indeed, biomass is the only sustainable source of organic compounds that has been proposed as the ideal equivalent to petroleum for the production of fuels and chemicals. Biomass is widely available as a proper feedstock, whose production estimates 1.0×10^{11} tons per year. Extensive research and studies have been conducted to produce biofuels and biodegradable products from biomass [3–5].

Carbohydrates are the major source of carbon in biomass. In order to produce fuel and chemicals from carbohydrates, the amount of oxygen within the molecular structure should be decreased. One way to do it is dehydration of carbohydrates, which results in furan formation, such as hydroxymethyl furfural (HMF) and furfural [6]. Bozell and Petersen [7] emphasized the important role of HMF and furfural in the recently updated DOE's top 10 list of bio-based chemicals. There are many reports on HMF chemistry, synthesis, and applications available in the literature [6,8–13]. In view of HMF and its derivatives' importance, Teong et al. [14] reviewed the timeline of HMF development in greater details.

HMF is an important platform molecule that connects carbohydrates to chemical and fuel precursors (see Fig. 1). HMF derivatives have various applications [6] and some of them have huge market potentials. For instance, one of the HMF oxidation products, 2,5-furandicarboxylic acid (FDCA), is a viable replacement for terephthalic acid in the polyethylene terephthalate (PET) production and adipic acid

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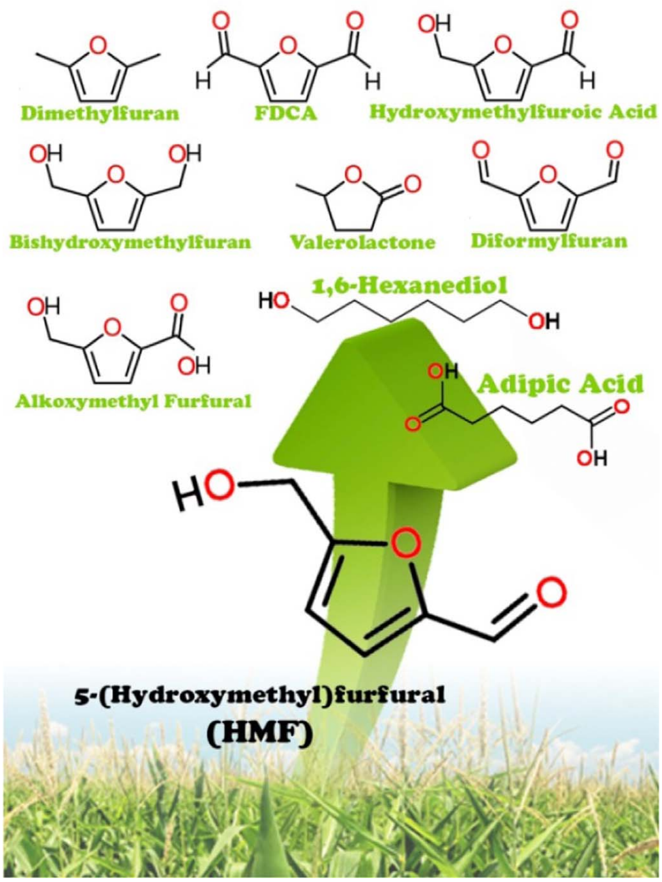

Fig. 1. HMF as a building block molecule.

production in nylon industry [15,16]. In another case, hydrogenation of HMF results in 2,5 dimethylfuran (DMF) which is often used as a fuel additive [17–19]. In addition, it is possible to produce drop-in fuel from hydro-deoxygenation of HMF condensation products [20–25].

HMF is an active molecule, which reacts with alcohols in the presence of an acid catalyst, and consequently produces its corresponding ether [26–28]. In other studies, HMF etherification products are reported when aliphatic alcohols are used as an extracting solvent during hexoses sugars conversion to HMF in aqueous media [28–30]. The ethers are more stable molecules than HMF [31], and their isolation from reaction media can be conducted more easily than HMF. For instance, distillation and crystallization can be used for separation of lower alkyl ethers and di-HMF-ethers, respectively [10]. A common etherification example is the HMF reaction with a simple alcohol such as methanol or ethanol that leads to the production of 5-(methoxymethyl)furfural (MMF) and 5-(ethoxymethyl)furfural (EMF). Although alkoxymethyl furfurals have been known for a long time, and patented as the tobacco flavor in early 1960s [32], they have been remained largely unexplored until recently reported as diesel fuel additives [33]. Among alkoxymethyl furfurals, EMF is recognized as an excellent additive for diesel fuel with promising properties as follows:

- A high boiling point (508 K) comparable to diesel fuel.
- A high energy density of 8.7 kWh/L, which is significantly higher than ethanol (6.1 kWh/L). EMF energy density is only 3% less than regular gasoline (8.8 kWh/L) and comparable with diesel fuel (9.7 kWh/L) [34,35].
- Low toxicity concerns. EMF has been used as a flavoring agent in the beverage industries [36–40].
- The presence of EMF in a blend with regular diesel in a diesel engine results in lower formation of fine particle and SO_2 emissions [1,41]. In recent years, a particular attention has been paid to the reduction of fine particulate matter from diesel combustion, because they have carcinogenic characteristics [2,42].
- EMF hydrogenation products are also considered as a potential fuel candidate [43,44].
- Ethers included EMF have high cetane number [45], which is a very important factor for combustion performance and emission.
- Ethyl levulinate (EL), a major byproduct of EMF synthesis, has been reported as a diesel fuel additive [46–49].
- No hydrogenation step is required in EMF production, which is an advantage over other fuel additives (e.g., DMF) obtained from HMF production.

Due to these significant properties of EMF, its syntheses from renewable sources have been attracted by many researchers and commercial companies. Sanborn [50] filed a patent on the processes for the preparation and purification of EMF from either HMF or fructose. Avantium company also filed a patent in 5-(alkoxymethyl) furfural production from either glucose or fructose [51]. The patent claimed the simultaneous production technology for 5-(alkoxymethyl) furfural and furfural from C5 and C6 sugars in the presence of acid catalysts. In the other patents [52,53], they claimed ether production technologies from etherification of branched C3-C20 alcohols with HMF. The same group performed synthesis of a mixture of furfural and 5-(alkoxymethyl)furfural derivatives through sugars dehydration and in-situ etherification of HMF in a mixture of various alcohols, namely, methanol, ethanol, and n-butanol [54]. These reactions resulted in the corresponding ethers, which led to productions of MMF, EMF and 5-n(butoxymethyl)furfural (nBuMF), respectively. They proposed another pathway for HMF ether production through hydroxyl-alkoxy addition. In this regard, they conducted an HMF reaction with an olefin using an acid catalyst [55].

Considering the fact that EMF or MMF plays an important role as a fuel candidate, diesel fuel additive [56], FDCA or cyclopentenones precursor [57,58], it is vital to review their different production aspects with detailed attention. Thus, recent developments in EMF and MMF synthesis are summarized in this review.

2. EMF synthesis

In order to produce EMF, HMF should participate in the etherification reaction with ethanol in the presence of an acid catalyst. Fructose or glucose may also be used as an initiator feed because their conversions to HMF occur in an acidic environment in parallel with HMF etherification reaction with ethanol. This "one-pot" approach can convert disaccharides, polysaccharides, and biomass to EMF by providing HMF as an intermediate (Fig. 2). The one-pot EMF synthesis

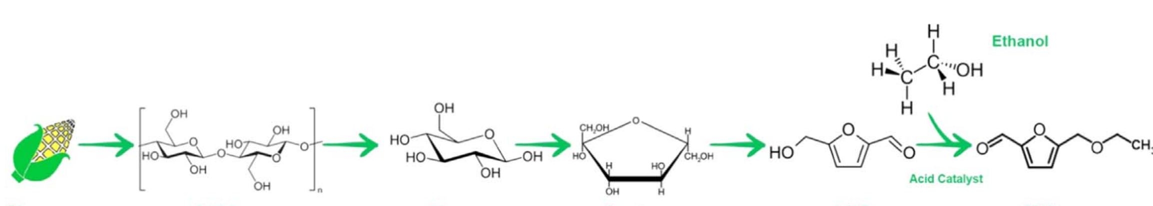

Fig. 2. Schematic of one-pot EMF production from different feedstocks.