Review Article

Upgrading of Carbohydrates to the Biofuel Candidate 5-Ethoxymethylfurfural (EMF)

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5-Ethoxymethylfurfural (EMF), one of the significant platform molecular derivatives, is regarded as a promising biofuel and additive for diesel, owing to its high energy density ($8.7 \, \text{kWh·L}^{-1}$). Several catalytic materials have been developed for the synthesis of EMF derived from different feedstocks under relatively mild reaction conditions. Although a great quantity of research has been conducted over the past decades, the unsatisfactory production selectivity mostly limited to the range 50%–70%, and the classic fructose used as the substrate restricted its application for fuel manufacture in large scale. To address these production improvements, this review pays attention to evaluate the activity of various catalysts (e.g., mineral salts, zeolites, heteropolyacid-based hybrids, sulfonic acid-functionalized materials, and ionic liquids), providing potential research directions for the design of novel catalysts for the achievement of further improved EMF yields.

1. Introduction

Diminishing fossil reserves and growing environmental problems have determined research for sustainable, green, and environmentally benign resources for liquid fuels and chemicals [1–3]. Biomass is widely available, inexpensive, and a CO_2-neutral source of carbon, the catalytic conversion of which to platform chemicals has potential to substitute the products from nonrenewable fossil sources [4–6]. A large number of strategies have been investigated for the conversion of carbohydrates in lignocellulosic biomass into chemicals and fuels [7–9]. The choice of an appropriate catalyst plays a significant role in observing high conversion and selectivity to the target chemicals in a sustainable, green, and economic process [10].

The main purpose of this review is to evaluate the activity of various catalysts (e.g., mineral salts, zeolites, heteropolyacid-based hybrids, sulfonic acid group-functionalized materials, and ionic liquids) with different catalytic effects and functional groups for the production of EMF from HMF,

fructose, glucose, and other carbohydrates under the applied reaction conditions, providing potential research directions for the design of novel catalysts for the achievement of further improved EMF yields. Fossil fuels and the derived chemicals have been produced from the limited natural sources. Increasing demand for limited fossil fuels and environmental degradation is gradually severe. Thus, replacing the fossil fuels with alternative and sustainable energy sources is imperative [11, 12]. Biomass is regarded as the only sustainable source of organic carbon compounds that have been suggested as the ideal equivalent to petroleum for the synthesis of fuels and chemicals. Biomass is widely existing and 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 [13–15].

Among multiple furan derivatives derived from biomass, EMF is recognized as an excellent additive for regular diesel with promising properties as follows:

(i) With high boiling point (508 K) in comparison with diesel fuel.

(ii) High energy density $(30.3 \, MJ \cdot L^{-1})$ is similar to regular gasoline $(31.9 \, MJ \cdot L^{-1})$ and is compared to diesel fuel $(33.6 \, MJ \cdot L^{-1})$, which is notably higher than ethanol $(21 \, MJ \cdot L^{-1})$ [16].

(iii) Due to its low toxicity, EMF can be used as a flavor and aroma ingredient in the food beverage industries [17–21].

(iv) To blend EMF with diesel fuel in a diesel engine reduces the formation of particulate contamination, SO_2 emissions, and soot. Meanwhile, EMF-blended fuel can make the engine run smoothly for hours [11, 12, 22, 23].

(v) Ethers that included EMF have a high cetane number [16], which is a very important factor for combustion performance and emission.

(vi) No hydrogenation step is required in EMF production, which is an advantage over other fuel additives (e.g., DMF) obtained from HMF production.

Considering the fact that EMF plays a significant role as a fuel candidate, diesel fuel additive [24], FDCA, or cyclopentenones precursor [25, 26], it is vital to review their different production aspects with detailed attention. Thus, recent progress in EMF synthesis is summarized in this review.

2. Synthesis of EMF

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 in large scale because their price is considerably low compared to fructose and HMF. Production of EMF from disaccharides, polysaccharides, and biomass through a "one-pot" approach is economically desirable due to the fact that the costs of saccharification, sugar isolation, and purification can be eliminated. However, the yield of synthesized EMF decreases significantly when HMF or fructose has not been used as the feed, and the possible reaction pathways for the synthesis of EMF from carbohydrates are presented in Scheme 1. The proposed reaction mechanism of hexose conversion to EMF is shown in Scheme 2.

Another method to produce EMF from different feedstocks is to follow a multistep mechanism. In the first step of the mechanism, an intermediate is produced, and then the intermediate is converted to EMF at very high yield. A representative example of the multistep method is found in the preparation of halomethylfurfural, namely, 5-chloromethylfurfural (CMF), where the reaction of biomass, polysaccharides, or C6 sugars with HCl leads to the production of CMF, and then, EMF is produced by nucleophilic substitution of CMF with ethanol [27]. Herein, we reviewed and compared different acid catalysts and their efficacies on the production yields of EMF from various feedstocks. Optimal reaction conditions for the case were presented.

2.1. Homogeneous Mineral Salts. Soluble catalysts or the homogeneous catalysts possessed excellent catalytic performance and the fast reaction rate, the existent ions of which are highly dispersed through the medium to enhance the availability of active sites with reactants. Generally, mineral salts acted as Lewis acid in favor of converting the glucose-based substrates to synthesize EMF. However, the separation and recycle wasted energy are not catered to the green and sustainable development.

Additionally, the heterogeneous catalytic reaction caused lower corrosion for the environment and equipment. Therefore, much more researchers concentrated on solid acid catalysts and enhanced their performances and activities [28–30]. Reaction temperature plays a crucial role in carbohydrates transformation and EMF synthesis, and the temperature ranges from 70°C to 160°C. The major by-products existing in the system were EL, 5-(ethoxymethyl) furfural diethylacetal (EMFDEA) [17], and 5,5′(oxy-bis(methylene))bis-2-furfural (OBMF) [31].

Metal chloride always is a commercially available Lewis acid with low toxicity and a high catalytic activity for the conversion of hexoses. Series of metal chlorides have been introduced for the production of EMF (Scheme 3). Initially, Liu et al. [32] examined various inorganic salts to promote fructose into EMF with NH_4Br, $CuCl_2 \cdot 4H_2O$, and $NiCl_2 \cdot 6H_2O$ giving low yields of EMF. Among those mentioned above, NH_4Cl demonstrated superior catalytic activity with 42% total yield of HMF and EMF under optimum reaction condition. Simultaneously, Yang et al. [33] chose the $AlCl_3 \cdot 6H_2O$ as a catalyst for carbohydrates including glucose, sucrose, maltose, cellobiose, starch, and cellulose and converted to EMF in ethanol/water binary solvents. The higher total furans yield (included HMF and EMF) of 57% was obtained, and a moderate EMF yield of 40% was derived from sucrose. However, the conversion efficiencies of other carbohydrates to furan were low. The highest EMF yield through single step reaction from HMF was proved to be 92.9% catalyzed by $AlCl_3$ at 100°C for 5 h by Liu et al. [31]. With the same carbohydrates conversion system, Yu et al. [34] performed the use of large-scale common metal salts as catalysts for the preparation of EMF to understand the catalytic mechanism. According to the research, $AlCl_3$ gave good catalytic activity for producing EMF from fructose at 140°C, while $CuSO_4$ and $Fe_2(SO_4)_3$ provided comparable EMF yields at 110 to 120°C, and the latter favored the EL formation.

To enhance the catalytic performance, Jia et al. [35] explored combinations of $AlCl_3$ with different cocatalysts such as $B(OH)_3$ and $BF_3 \cdot (Et)_2O$ or halide salts such as NaF, NaCl, and NaBr. The result of $BF_3 \cdot (Et)_2O/AlCl_3 \cdot 6H_2O$ proved to be significantly superior to other catalysts; 55.0%, 45.4%, and 23.9% high yields of EMF derived from fructose, inulin, and sucrose were achieved, respectively, under the optimized conditions. Later, Zhou et al. [36] studied the reactivity of $FeCl_3$, $CrCl_2$, $GeCl_4$, $IrCl_3$, and so on for the production of EMF. The presented toxicity, high price, and instability drawbacks of other metal chlorides affect the further exploration. In the presence of $FeCl_3$, a maximum EMF yield of 30.1% was obtained in the mixture solvent composed of [Bmim]Cl and ethanol.
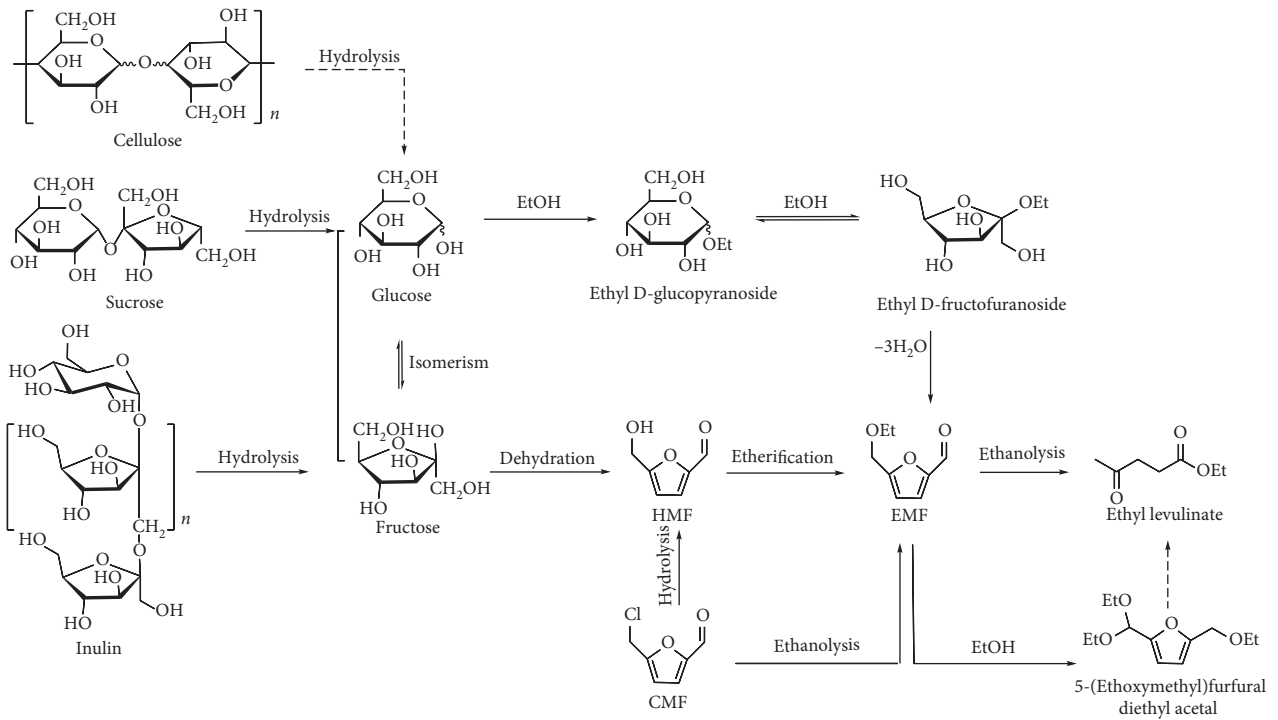
Scheme 1: Reaction pathways for the synthesis of EMF from carbohydrates.
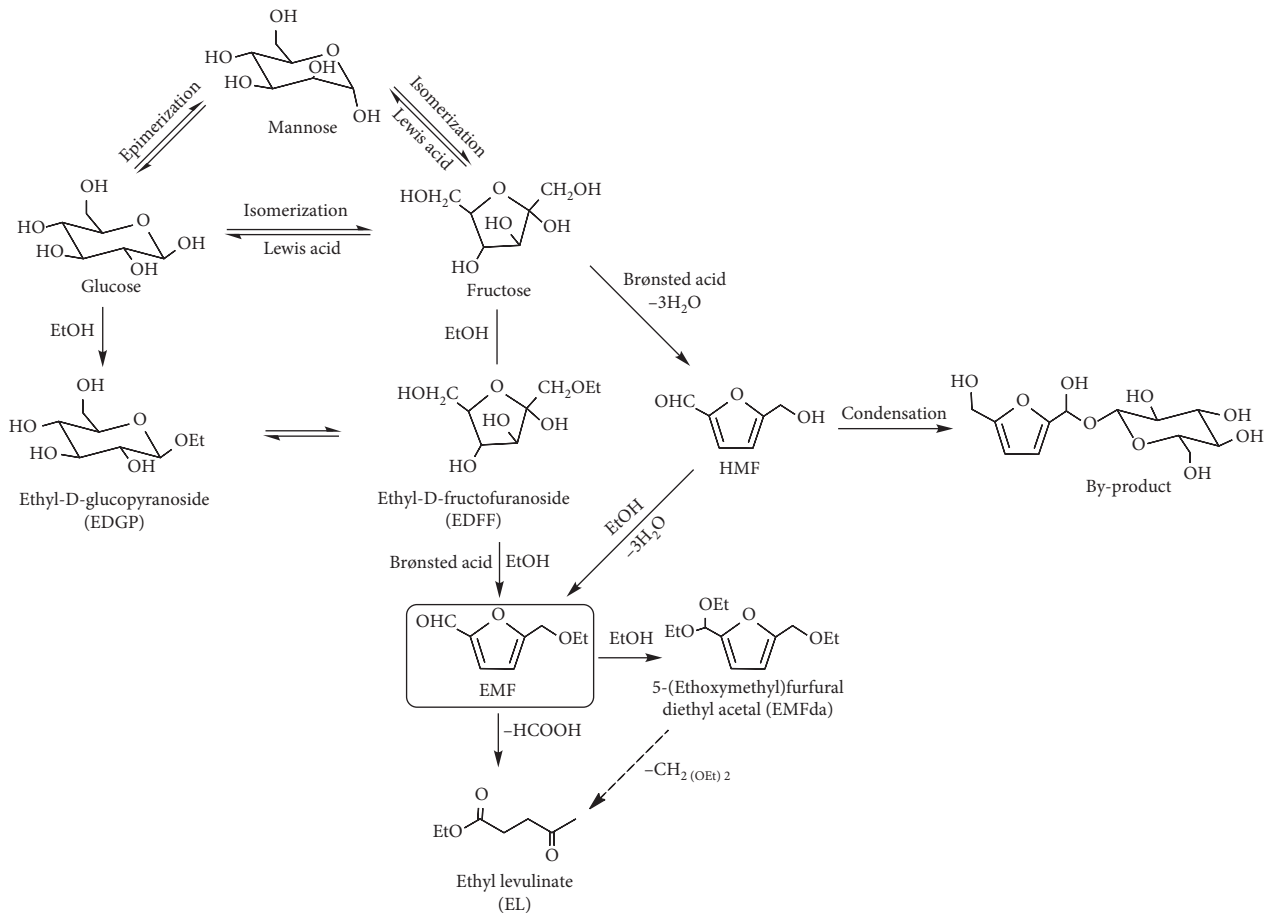
Scheme 2: Proposed mechanism for one-pot conversion of hexose to EMF.
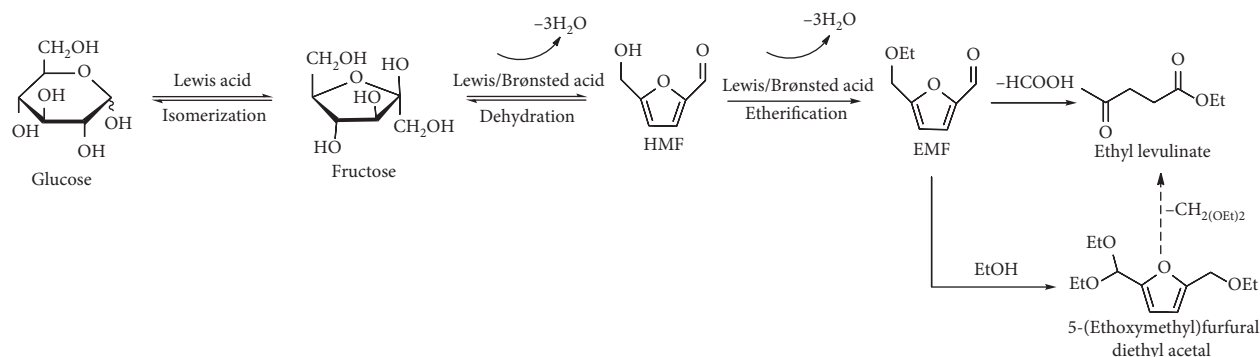
Scheme 3: Reaction pathways for the conversion of hexose to EMF catalyzed by Lewis acid.

2.2. Heterogeneous Catalysts

2.2.1. Zeolitic Catalysts.
Zeolites with the highly dispersed and uniform channel microporous structure typically restrict the formation of large and unwanted by-product for the EMF preparation system. Meanwhile, the micropores also limit the effective diffusion of HMF and EMF due to the molecular sizes and small pore openings of zeolites [37, 38]. Expansion of the pore sizes needed to be further explored for the application in more areas.

The enlarged pore sizes play an important role for these materials. For instance, Lanzafame et al. [29] conducted the efficient etherification of HMF catalyzed by mesoporous Al-MCM-41 (with different Si/Al ratios), zirconia, or sulfated zirconia immobilized on SBA-15. Strong Lewis acid sites ZrO_2 and isolated Al^{3+} sites were explained to be beneficial for EMF production. In addition, strong Brønsted acid sites led to the formation of ethyl 4-oxopentanoate. Investigation on mesoporous aluminosilicates by further introducing aluminum into the framework Al-TUD-1 (Si/Al ratio: 21) was carried out by Neves et al. [39]. Based on the unique and regular channel of MCM-41, Che et al. [30] illustrated a nanosphere catalyst with highly dispersed $H_4SiW_{12}O_{40}$/MCM-41 for the etherification of the hydroxyl group of HMF. Comparing the catalytic performance with p-TSA, H_2SO_4, Amberlyst-15, and H_3PO_4, $H_4SiW_{12}O_{40}$/MCM-41 showed 84.1% selectivity to EMF with 92.0% conversion of HMF under mild conditions. Meanwhile, the intermediate 5,5'(oxybis(methylene))bis-2-furfural could also be converted to target product EMF. They found that, with the strength of acids and heteropoly anion effects, the effective catalytic performance of $H_4SiW_{12}O_{40}$/MCM-41 was obtained. In this regards, Liu et al. [40] developed MCM-41-HPW with different dosages of phosphotungstic acid (HPW) supporting on MCM-41. The optimal 40 wt.% MCM-41-HPW achieved a high EMF yield of 83.4%, converted from HMF at 100°C for 12 h.

Inspired by the published results that tin-containing zeolite (Sn-BEA) was effective for the glucose-fructose-HMF conversion, Lew et al. [41] further employed Sn-BEA combined with Amberlyst-131 for one-pot glucose-to-fructose-to-HMF-to-EMF conversion, giving 31% yield of EMF. Li et al. [42] found DeAl-H-beta could provide a moderate EMF yield (43%) from sucrose, and the EMF yield was improved up to 50% by a one-pot two-step method. However, poor catalytic performance was achieved using cellobiose as a substrate for EMF. Lewis et al. [43] explored a series of zeolites including Hf-, Zr-, Ti-, Ta-, Nb-, and Sn-Beta that could promote the etherification reaction of HMF. Under batch conditions, Ta-Beta and Al-Beta showed comparable EMF yields of 56% and 41%, respectively.

Product selectivity depends on the control of active sites strength. Barbera et al. [44] introduced NH_4-exchanged zeolites, and the NH_4 was used to block the strong sites, thus preventing the secondary reactions. The results proved that NH^{4+} effectively increased the product selectivity of NH_4-BEA catalyst for HMF etherification reaction. Recently, Bai et al. [45] exhibited the glucose conversion to EMF catalyzed by multifunctional MFI-Sn/Al zeolite with dual meso-/microporosity and dual Lewis and Brønsted acidity. Combination of Lewis acidic Sn and Al sites and Brønsted acidic Al-O(H)-Si sites was efficient for the cascade isomerization-dehydration-etherification reaction, affording 44% EMF yield.

2.2.2. Heteropolyacid-Based Hybrid Catalysts.
Heteropolyacids have several advantages such as strong Brønsted acidity, tunable acid-base properties, and high proton mobility. But, they tend to dissolve in water and polar solvents and possess low surface area and low thermal stability, which limits their application in catalytic conversion. Supporting a solid support is a method that has been used by different groups.

Originally, Yang et al. [46] investigated the fructose-EMF transformation in a mixed ethanol/THF (tetrahydrofuran) medium catalyzed by $H_3PW_{12}O_{40}$ (HPW). The microwave offered EMF in yield of 76% under the optimum reaction condition, and the cosolvent THF significantly increased fructose conversion. Wang et al. [47] compared the activity of HPW, phosphomolybdic acid (HPM), $AlCl_3$, H_3PO_4, and Amberlyst-15 for production of EMF from fructose in an ethanol/DMSO mixture. Results indicated that HPW and HPM exhibited superior catalytic activities than $AlCl_3$, H_3PO_4, and Amberlyst-15, and the former formed 64% EMF within 130 min at 140°C. In this regard, Ren et al. [48] exchanged H^+ ion of HPW with Ag^+ and achieved Ag_1H_2PW, which presented a high activity and EMF yield of 88.7%. Further replacing another H^+ in the

Ag_1H_2PW, the acid strength of the catalyst decreased. Ren et al. used Ag_1H_2PW catalyst for fructose dehydration and HMF etherification, and a relatively high yield of EMF (69.5%) was obtained.

Stability and efficient separation are crucial criteria to be the catalyst support. Addition of heteropolyacid into $Fe_3O_4@SiO_2$, simultaneously with the introduction of the silica layer could modify the MNPs-formed inert surface. $Fe_3O_4@SiO_2$-HPW catalyzed the reaction of HMF with ethanol, and therefore, the activity increased dramatically and the production of EMF yield reached 83.6% [49]. Wang et al. [50] also applied $Fe_3O_4@SiO_2$-HPW for EMF production from HMF to obtain the same effect, which was in accordance with the results of Liu and Zhang [51]. Besides, $Fe_3O_4@SiO_2$-HPW achieved an EMF yield of 54.8% derived from fructose.

Organic-inorganic hybrid materials become the hotspot to be the catalyst, for instance, HPA-based $[MIMBS]_3PW_{12}O_{40}$ hybrid catalyst reported by Liu et al. [52] for the preparation of EMF. Combination of IL with $H_3PW_{12}O_{40}$ enhanced the EMF yield to 90.7% with 98.1% conversion of HMF under the optimum reaction condition at 70°C within 24 h. Wang et al. [53] studied the uniform nanospheric hybrids by controlling the molar ratio of phosphotungstic acid (HPW) and pyridine (PY) or trimethylamine (TEA) in different nanosizes. Particularly, PY-PW-1 showed an excellent catalytic activity with 90% of EMF, which attribute to the relatively strong acidity and regular pore size. With the prepared nanosphere PY-PW-1, fructose was also converted to EMF in one-pot reaction process and obtained a moderate yield of 55% with the enhanced temperature at 120°C.

The synthesized K-10 clay-HPW not only avoided the HPW being dissolved into polar organic solvents and expressed the high activity. Liu et al. [54] used 30 wt.% of K-10 clay-HPW for HMF-EMF transformation. Under the optimum reaction conditions (100°C, 10 h), catalytic activity was increased to 91.5% yield, whereas for one-pot fructose conversion to EMF, 61.5% yield of EMF was gained. The prepared catalyst with high stability could be reused several times without loss of catalytic performance. MCM-41 with uniform channel structure and pore size was suitable to support 12-tungstophosphoric acid that allowed the one-pot conversion of fructose directly into EMF, leading to 42.9% EMF by 40 wt.% MCM-41-HPW [40].

Apart from K-10 clay and MCM-41, MOF-based [Cu-BTC][HPM] (NENU-5) was also efficient for the etherification of HMF to EMF with up to 68.4% yield under normal pressure and optimized conditions (Figure 1). Benefiting from the unique structure, MOFs can provide adsorption sites for HPM to avoid HPM dissolving into solvents, making the catalysts be recyclable with 55% EMF yield [55].

The addition of cosolvent exhibits improvement in EMF yield as compared with the single solvent, and enhanced yield of EMF ranges from 5 to 20 percentages. Xu et al. [56] explored the ethanol/n-hexane mixture solvent indicating that the introduction of n-hexane could enhance the yield of EMF to 66.3% with optimum volume ratio (ethanol : n-

hexane, 6 : 4), conducted at 120°C within 180 min. With the ethanol-DMSO mixture, Li et al. [57] also developed acid-base bifunctional hybrid nanosphere catalyst Lys/PW that possessed an optimal reaction activity of 76.6% EMF yield from fructose, implying that the base sites of the catalysts play an important role in increasing EMF stability.

Combination of Lewis acid $AlCl_3 \cdot 6H_2O$ and Brønsted solid acid PTSA-POM proved cooperative effect for glucose transformation into EMF and generated 30.6% EMF under the ethanol-water (9 : 1) system. [58].

The appropriate supports play a vital role in heteropolyacid as the active center producing EMF. Partial substitution of protons is another effective approach to change the property of heteropolyacid for better catalytic activity. Raveendra et al. [59] reported the cesium-exchanged silicotungstic acid to enhance the surface area and acidity and finally obtained 91% EMF yield with Cs_2STA at 120°C for 2.5 h.

2.2.3. Sulfonic Acid-Functionalized Catalysts.

The strong acidity of sulfonic acid groups can be immobilized onto the diverse supporter by sulfonation reactions and hence gain multiple sulfonic acid-functionalized catalysts. Simultaneously, the acidic density can be flexibly controlled by the dosage of sulfonic sources. Considering the green and sustainable development request, loss of element S was not catered for the present development.

Magnetic carriers to load sulfonic acid groups can be easily separated by a permanent magnet and recycled for times without loss of activity attracting much attention of scientists. Zhang et al. [60] chose $Fe_3O_4@SiO_2$ for preparation supporting a high yield (up to 89.3%) of EMF converted from HMF. Magnetic nanoparticles (MNPs) and amorphous carbon were selected to immobilize sulfonic acid groups ($-SO_3H$) which act as a solid acid catalyst for EMF production [61]. Successfully, $Fe_3O_4@C-SO_3H$ shared active catalytic properties in HMF-EMF, fructose-EMF, sucrose-EMF, and inulin-EMF systems, and considerable yields of 88.4%, 67.8%, 33.2%, and 58.4% were obtained, respectively. Among those, the low yield of EMF was produced from sucrose owing to the composition of sucrose, which contains one fructose and glucose unit, and glucose cannot be converted to EMF directly. The more deep-seated research was carried out by $Fe_3O_4@SiO_2$-SH-Im-HSO_4 [62] and facilitated by it, indicating that EMF yields derived from inulin (56.1%) and fructose were consistent while glucose always promoted to ethyl glucoside. Soon afterward, Wang et al. [63] illustrated the smooth conversion of sucrose and inulin with superior catalytic performance offering 53.6% and 26.8% EMF yields, respectively, at 140°C for 24 h. Excellent catalytic performance of OMC-SO_3H indicated its promising application for biomass conversion into value-added chemicals and liquid fuels.

Considering the sustainable and green development trend, the same magnetic $Fe_3O_4@C-SO_3H$ prepared from wheat straw biomass afforded comparable EMF yield of 64.2% in DMSO-ethanol binary solvent. Bearing multiple
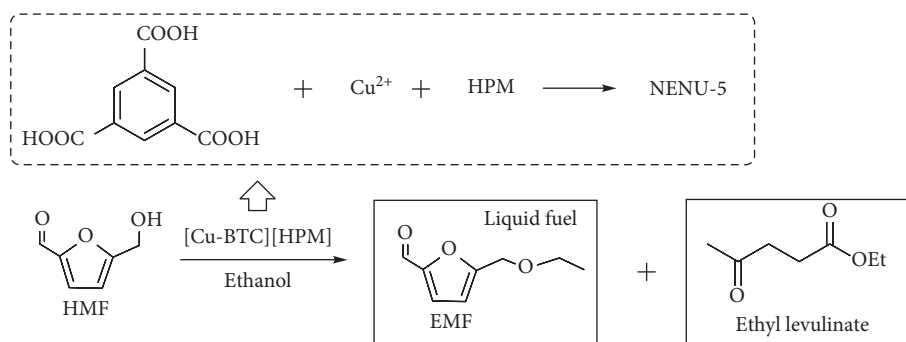
Figure 1: Schematic of the catalyst preparation and catalytic procedure.

-COOH, -SO$_3$H, and -OH groups, the authors described the progress of fructose or HMF to EMF in relatively high yields with 64.2% and 85.6% [64].

Grafting sulfonic acid onto the inorganic insoluble supports is a technique to prepare high-performance heterogeneous solid acidic catalysts. Liu and Zhang [51] studied the grafting of sulfonic acid onto the mesoporous silica and utilized for effective etherification of HMF for EMF with 83.8% under the optimal conditions (100°C, 10 h), while the high yields of 63.1% and 60.7% were synthesized by one-pot transformation of fructose and inulin. However, the aldose-based carbohydrates such as glucose were mainly turned to ethyl D-glucopyranoside with a high yield of 91.7%. The unique properties such as 2D structure, high stability, and high surface areas decided GO as a promising catalytic material that was oxidized by Hummers' method clarified the engineered catalytic performance for the conversion of HMF into EMF with high yield of EMF (92%), while EMF yield was decreased when fructose replaced HMF as a starting material [65] (Figure 2). Under mixture solvent ethanol-DMSO in 3 : 7, furan selectivity enhanced to 71% EMF yield and 34%, and 66% EMF yields were achieved when sucrose and inulin were used as the substrates. Partially reducing GO, amorphous carbon black (CB), and carbon nanotubes (CNTs) by sulfuric acid (S-RGO) were conducted for the synthesis of EMF converted from HMF. The catalytic activity of S-RGO proved to be superior to S-CB, S-CNTs, and even the classic Amberlyst-15 [66].

Besides, new solid acid catalysts obtained by sulfonating natural biopolymers met the green trend for biomass conversion to high value-added chemicals. Liu et al. [67] developed the cellulose sulfuric acid for the etherification of HMF for the synthesis of EMF and observed high yield (84.4%) under optimized condition. Similarly, application of glucose-derived magnetic solid acid, glu-Fe$_3$O$_4$-SO$_3$H, also acted as an etherification catalyst and generated 92% isolated yield EMF [68]. With the optimal 50 wt.% loading rate of glu-Fe$_3$O$_4$-SO$_3$H, EMF from fructose was effectively produced by 81% yield.

Amberlyst-15 as one of the standard solid acid catalysts was applied in various reaction systems and first explored by Zhu et al. [69] for the HMF-5-methoxymethylfurfural (MMF) conversion in low-boiling point solvent. The presence of cosolvent THF enhanced the contact of -SO$_3$H of Amberlyst-15 leading to promoting the catalytic progress
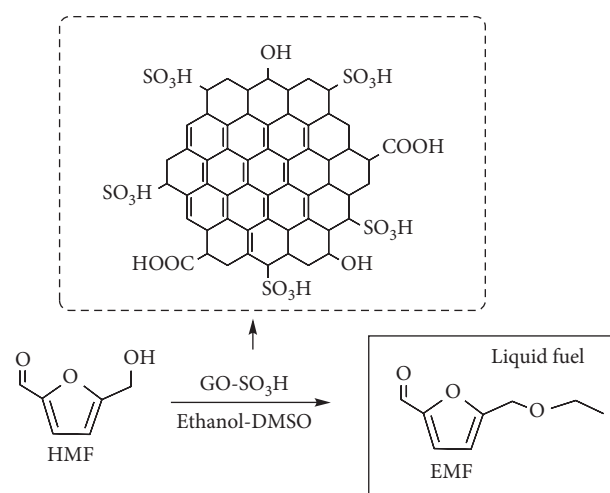

Figure 2: The conversion of HMF to EMF catalyzed by GO-SO$_3$H.

and accumulating the target molecules. Because of short of the high surface area and the limited contact of active sites and substrate, the catalytic performance of Amberlyst-15 was dissatisfactory. MOF provided large enough specific surface area and acidic density, and MIL-101-SO$_3$H(100) showed a better catalytic performance with 89.2% conversion of fructose and 67.7% EMF yield in the ethanol and THF mixture.

Well-defined structure and uniform distribution of active sites catalyst arenesulfonic acid-modified SBA-15 Ar-SO$_3$H-SBA-15 was studied for the conversion of fructose to EMF in binary ethanol-DMSO solvent in optimizing reaction conditions (e.g., temperature, catalyst loading, and DMSO concentration), demonstrating the maximum EMF yield of 63.4% [70]. Li et al. [71] generated a series of SO$_3$H-functionalized polymer solid acid catalysts for successive fructose dehydration and HMF etherification, and an EMF yield of 72.8% was achieved with the optimal catalyst poly(VMPS)-PW at 110°C within 10 h.

2.2.4. Ionic Liquid Catalysts. Due to the tailored design, good thermal and chemical stability, low melting point, and good solubility of acidic ionic liquids, the investigation of
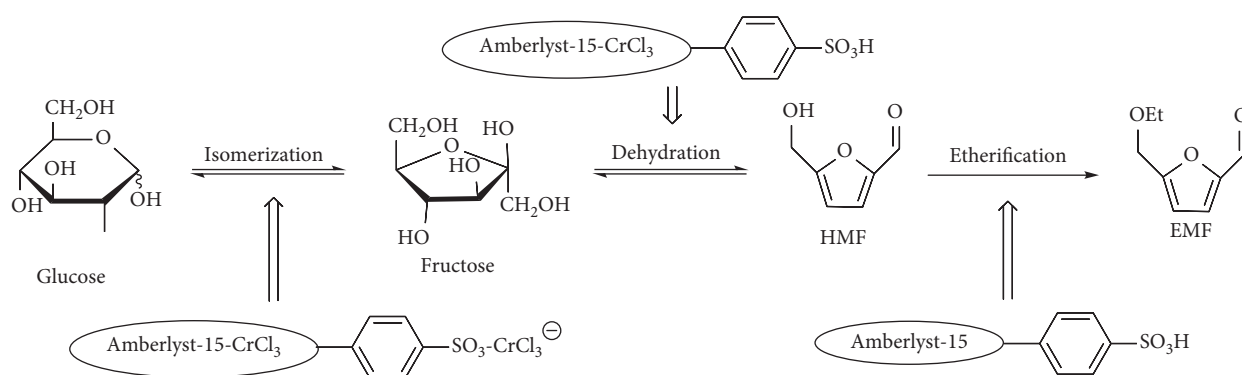
FIGURE 3: Schematic illustration of the catalysis progress.

them attracts much attention. The problem of high cost and recycle is urgently to be solved.

Kraus and Guney [72] appointed the sulfonic acid-functionalized IL to catalyze the conversion of fructose for the EMF fabrication in a one-pot procedure without the addition of solvent or acid catalysts. The application of 1-butyl-3-(3-sulfopropyl)-imidazolium chloride (4) and 1-methyl-3-(3-sulfopropyl)-imidazolium chloride (5) for EMF provided comparable 55% and 54% yields under the mild condition (100°C, 80 min), and the novel biphasic medium assembly of hexanes and IL enhanced the EMF yields to a certain extent.

The Brønsted acidic IL $[DMA]^+[CH_3SO_3]^-$ was effective for fructose-EMF conversion with a relatively high yield of 64%, while one-pot cellulose transformation gave 22% yield of EMF [73]. Alam et al. [37] further showed EMF production directly from Foxtail and Red nut sedge weeds in presence of $[DMA]^+[CH_3SO_3]^-$, which was better than $[NMP]^+[CH_3SO_3]^-$ when converting foxtail to EMF.

Except the ionic liquid catalysts, functionalized ionic liquids can also act as the reaction medium to afford efficient EMF yield. Guo et al. [74] chose hydrogen sulfate ionic liquid as a homogeneous catalyst and mixed with ethanol as a reaction solvent for efficient preparation of EMF. Catalyzed by the $[C_4mim][HSO_4]$-ethanol system, high yield of 83% EMF was observed from fructose at 130°C within 20 min, which could be attributed to the acidity of $[C_4mim]$ $[HSO_4]$, the viscosity of the mixture system, and the formed hydrogen bonds between $[C_4mim][HSO_4]$, ethanol solvent, and fructose.

Due to the superior physical and chemical properties and benefits of acidic ILs, an effective progress for EMF derived from carbohydrates by deep eutectic solvent (DES) mixture as a solvent was proposed [75]. 77.3% EMF yield was gained with fructose as substrate catalyzed by Amberlyst-15, and more excellent catalytic performance afforded a high EMF yield of 46.7% obtained from glucose with $CrCl_3$-modified Amberlyst-15 (Figure 3).

2.2.5. Others. Except for the mentioned catalysts in the previous section, there exist many other effective materials such as Zr-Mont, Co(*x*)Pc, $MoO_2Cl_2(H_2O)_2$, and a combination of metal chloride with resins which could be also used for carbohydrates transformation to EMF.

Acidic Zr-montmorillonite (Zr-Mont) catalyst was utilized for synthesis mixture of EMF and 2-(diethoxymethyl)-5-(ethoxymethyl)furan by Shined and Rode [76], and the latter can turn into EMF by conducting in water with the same Zr-Mont. Under the optimized reaction conditions, EMF was observed in the highest yields of 91% by etherification HMF with ethanol. Yadav et al. [77] investigated the use of cobalt (I, II, III) phthalocyanine (Co(*x*)Pc) for the isomerization of glucose to fructose, for fructose dehydration, and in the subsequent etherification. It was noted that Co(*x*)Pc was effective for the direct conversion of carbohydrates to EMF in [EMIM]Cl ionic liquid, and Co(III) Pc exhibited much higher catalytic activity. The levulinate could be reduced by the waste and basic additive oil shale ash, which is formed by burning oil shale in power plants, while it was efficient for the preparation of EMF with high yield and purity [78]. The final product EMF syntheses starting from 5-bromomethylfurfural (BMF) afforded 88% yield without further purification which reacted under room temperature for 17 h in 96% ethanol.

Considering the excellent catalytic property for the reduction reaction, high valent oxomolybdenum complexes were investigated for the synthesis of EMF by one-pot fructose conversion in ethanol/THF (5 : 2) mixture and optimal yield of 53% was achieved within 17 h at 120°C. With the efficient catalyst, 40% and 23% yield of EMF were produced from inulin and sucrose, respectively [79].

Marine carbohydrate agar derived from red algae was reported for production of EMF in the presence of [EMIM] Cl, $CrCl_2$, and Dowex resin mixture, afford isolate 3.9 g of EMF and EL (EMF to EL mole ratio: 5 : 2) from 10 g of agar [80]. Similarly, biomass wheat straw was directly converted by alcoholysis reaction in 94% (w/w) ethanol with 30 mM H_2SO_4 at 200°C, and yields for EMF and by-product EL were 20% and 25%, respectively [81].

3. Conclusions

As mentioned above, various Lewis and Brønsted acid catalysts have been conducted to convert HMF, fructose, and inulin in high yields without extra costs for isolation and purification. It is worth noting that HMF is not affordable as

a feed for EMF production regardless of the high yields of 70%–95% reported for HMF etherification to EMF by different groups. The technoeconomic analysis carried out by Torres et al. [82] estimated the HMF price of 2.16 $/kg based on the process proposed by Roman-Leshkov et al. [83]. EMF synthesis from fructose at a desirable yield of 50%–70%, but high reaction temperature (90–130°C) and retention time (6–24 h), is needed compared to the HMF cases. In general, EMF production derived from sucrose did not gain high yields, because of the fact that glucose obtained from sucrose conversion was not converted to EMF in good yields. Nevertheless, the fructose polymer inulin exhibited better performance and produced EMF at high yields. One-pot transformation of cellulose or biomass to EMF led to low yields, due to their complex structures with the low glucose conversion to EMF. Ethanol/THF or ethanol/DMSO mixture is applied as a reaction medium for EMF synthesis from fructose. In a series of reactions, EMF may also participate in the rehydration reaction to produce EL.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.
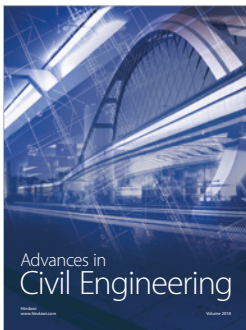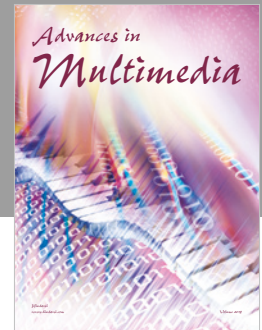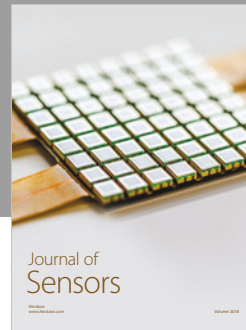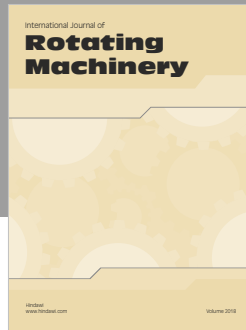
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