Recent progress in the development of advanced biofuel 5-ethoxymethylfurfural

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Abstract

Biomass-derived 5-ethoxymethylfurfural (EMF) with excellent energy density and satisfactory combustion performance holds great promise to meet the growing demands for transportation fuels and fuel additives to a certain extent. In this review, we summarized the relative merits of the EMF preparation from different feedstocks, such as platform chemicals, biomass sugars and lignocellulosic biomass. Advances for EMF synthesis over homogeneous (i.e. inorganic acids and soluble metal salts), heterogeneous catalysts (i.e. zeolites, heteropolyacid-based hybrids, sulfonic acid-functionalized catalysts, and others) or mixed-acid catalysts were performed as well. Additionally, the emerging development for the EMF production was also evaluated in terms of the different solvents system (i.e. single-phase solvents, biphasic solvents, ionic liquids, and deep eutectic solvents). It is concluded with current challenges and prospects for advanced biofuel EMF preparation in the future.

Keywords: Biofuel, 5-ethoxymethylfurfural, Feedstocks, Homogeneous, Heterogeneous, Mixed acid, Solvent

Introduction

It is urgent to convert renewable biomass resources into advanced biofuels, and platform chemicals, such as polyhydric alcohol, furan compounds, short-chain alkanes, organic acids, and their esters derivatives [1–4]. Among these biofuels, 5-ethoxymethylfurfural (EMF), as a promising transportation fuel and fuel additive, has been in a center of attention [5–7]. The energy density of EMF (30.3 MJ/L) is closed to that of gasoline (31.3 MJ/L) and diesel (33.6 MJ/L), and higher than that of ethanol (23.5 MJ/L) [8, 9]. In addition, EMF as advanced biofuel can reduce the environmental pollution profiting from its high oxidation stability, accompanied by the reduction of soot emissions, sulfur oxides and nitrogen oxides [10, 11].

At present, EMF is usually synthesized from biomass sugars (i.e. glucose, fructose, inulin) over the acid catalyst in ethanol. In contrast with traditional hydrolysis, the most remarkable advantage in ethanol system is that it could minimize the wastewater treatment and discharge. Meanwhile, unreacted ethanol can be easily recovered, which accords with sustainable development. What’s more, the ethanol reactant is more conducive to the production of active groups in glycosyl and the reduction of side reactions. As shown in Fig. 1, the ethanolysis of biomass to EMF is a continuous multi-step reaction [12]. In brief, cellulose was firstly hydrolyzed to glucose in the presence of acidic catalysts, and then divided into two ways: (1) glucose was isomerized to fructose through Lewis acid sites, and then EMF was produced with dehydration of fructose followed by in-situ etherification of 5-hydroxymethylfurfural (HMF) in ethanol. (2) Glucose was easily converted into ethyl glucoside (EG) through Bronsted acid sites and then formed EMF. Although the preparation pathway undergoes a multi-step intermediate process, the reaction can be carried out continuously in the same reactor with the simple process and controllable conditions. Therefore, the preparation pathway is also

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called “one-pot” reaction. Given the above advantages, direct ethanolysis of biomass to prepare EMF is considered as a potential approach for biomass development and utilization.

Here, the progress of EMF preparation had been deeply analyzed in the sections of feedstocks, catalysts system and solvents. More importantly, the current challenges and future perspectives have also been prospected.

**Feedstocks**

The feedstocks of EMF preparation were mainly divided into three categories: (1) the platform chemicals were directly etherified to prepare EMF in acidic conditions, such as HMF, 5-chloromethylfurfural (CMF) and 5-bromomethylfurfural (BMF). (2) The biomass sugars (i.e. glucose), were sequentially subjected to the steps of isomerization, dehydration, and etherification to prepare EMF. (3) The lignocellulosic biomass was directly transformed into EMF. The summarization was listed in Table 1 and Fig. 2.

HMF, as the most common platform chemical, has a furan ring, a hydroxymethyl and an aldehyde group, which made it has many active chemical properties. Therefore, many derivatives could be obtained by condensation, oxidation, hydrogenation, or by directly etherification in the ethanol system [31, 32]. Much research on the etherification of HMF to EMF has been reported, and the results almost had superior conversion and
selectivity in various reaction processes [13–18]. Kumari et al. [13] conducted HMF etherification over Ta exchanged tungstophosphoric acid with SnO$_2$ support as the catalyst, the EMF yield was 90.2%. A 91% of EMF yield was reached from HMF used Cs$_2$STA as the catalyst in ethanol by Raveendra et al. [18] as well. However, the industrial production of EMF was limited by the high price of HMF.

Biomass sugars, as raw materials, were usually divided into fructose-based carbohydrates and glucose-based carbohydrates [33]. According to previous study, the EMF yield could go as high as 60%~90% when fructose was used as substrate [19–21], while it was 30%~60% with sucrose [22–24]. However, the EMF yield was almost as low as 40% due to the speed limit of glucose isomerization to fructose [25]. Furthermore, the yields of EMF from inulin

Table 1 Valorization of various biomass into EMF

| Entry | Feedstock | Catalyst | Solvent | Temp./°C | Time/h | Yield/% | Ref. |
|-------|-----------|----------|---------|----------|--------|---------|------|
| 1     | HMF       | 30% TaTPA/SnO$_2$ | EtOH$^a$ | 120      | 0.75   | 90.2    | [13] |
| 2     | Fructose  | 30% TaTPA/SnO$_2$ | EtOH     | 120      | 8      | 68      | [13] |
| 3     | HMF       | (MIMB)$_2$PW$_{12}$O$_{40}$ | EtOH | 70       | 24     | 90.7    | [14] |
| 4     | HMF       | Fe$_3$O$_4$@SiO$_2$-HPW | EtOH  | 100      | 11     | 84      | [15] |
| 5     | Fructose  | Fe$_3$O$_4$@SiO$_2$-HPW | EtOH  | 100      | 24     | 55      | [15] |
| 6     | HMF       | Cs$_2$STA  | EtOH     | 110      | 4      | 80      | [16] |
| 7     | HMF       | C/MCF(63)  | EtOH     | 110      | 4      | 78      | [16] |
| 8     | HMF       | K-10 clay-Al | EtOH | 100      | 8      | 89.5    | [17] |
| 9     | HMF       | Cs$_2$STA  | EtOH     | 120      | 2.5    | 91      | [18] |
| 10    | Fructose  | Poly (VMPS)-PW | EtOH     | 110      | 10     | 72.5    | [19] |
| 11    | Fructose  | [C$_6$N$_3$][SO$_3$CF$_3$]-HCSs-1 | EtOH | 140     | 2      | 67.2    | [20] |
| 12    | Fructose  | HReO$_4$ (10 mol%) | EtOH | 140      | 1      | 63      | [21] |
| 13    | Fructose  | HReO$_4$ (10 mol%) | EtOH/THF | 140 | 1     | 73      | [21] |
| 14    | Inulin    | HReO$_4$ (10 mol%) | EtOH/THF | 140 | 1     | 51      | [21] |
| 15    | Sucrose   | HReO$_4$ (10 mol%) | EtOH/THF | 140 | 1     | 36      | [21] |
| 16    | HMF       | S-PANI     | EtOH     | 90       | 6      | 83.8    | [22] |
| 17    | HMF       | S-PANI-FeVO$_4$(11) | EtOH | 90       | 6      | 80      | [22] |
| 18    | Sucrose   | S-PANI-FeVO$_4$(11) | EtOH | 90       | 24     | 57.2    | [22] |
| 19    | Fructose  | S-PANI-FeVO$_4$(11) | EtOH | 90       | 24     | 72.5    | [22] |
| 20    | Fructose  | PSDVB-SO$_3$H | EtOH     | 120      | 2      | 67.5    | [23] |
| 21    | Sucrose   | PSDVB-SO$_3$H | EtOH     | 120      | 2      | 31.1    | [23] |
| 22    | Fructose  | MCC-SO$_3$H | EtOH     | 120      | 16     | 63.2    | [24] |
| 23    | Inulin    | MCC-SO$_3$H  | EtOH     | 120      | 16     | 51.3    | [24] |
| 24    | Sucrose   | MCC-SO$_3$H  | EtOH     | 120      | 16     | 32.5    | [24] |
| 25    | Glucose   | MCC-SO$_3$H  | EtOH     | 120      | 16     | 86.5$^c$ | [24] |
| 26    | Glucose   | Sn-BEA and Amberlyst-13 | EtOH     | 90       | 24     | 31      | [25] |
| 27    | Fructose  | H$_3$PW$_{12}$O$_{40}$ | EtOH/THF (5:3) | 130 | 0.5 | 76      | [26] |
| 28    | Fructose  | H$_3$PW$_{12}$O$_{40}$ | EtOH     | 130      | 0.5    | 65      | [26] |
| 29    | Sucrose   | H$_3$PW$_{12}$O$_{40}$ | EtOH/THF (5:3) | 130 | 0.5 | 33      | [26] |
| 30    | Inulin    | H$_3$PW$_{12}$O$_{40}$ | EtOH/THF (5:3) | 130 | 0.5 | 62      | [26] |
| 31    | Fructose  | MIL-101-SO$_3$H(H100) | EtOH/THF (5:4) | 130 | 15 | 67.7    | [27] |
| 32    | Inulin    | MIL-101-SO$_3$H(H100) | EtOH/THF (5:4) | 130 | 15 | 54.2    | [27] |
| 33    | Cellulose | H$_2$SO$_4$ | EtOH     | 200      | 1.25   | 14.93   | [28] |
| 34    | Corn stover | USY/H$_2$SO$_4$ | EtOH | 210      | 2.05   | 23.9    | [12] |
| 35    | Cassava   | NISO$_4$ | EtOH     | 200      | 2      | 11.4    | [29] |
| 36    | Bagasse   | Zr(O)Cl$_2$/CrCl$_3$ | EtOH/(Bmim)Cl | 120 | 15 | 21.6$^d$ | [30] |

$^a$EtOH is ethanol; $^b$THF is tetrahydrofuran; $^c$ The yield is EG yield; $^d$ The yield is mass yield
were slightly lower compared to the case that fructose was used as feed \[26, 27\]. This was because that one unit of inulin consists of one unit of glucose and 1–59 units of fructose. Cellulose is the most widely distributed and abundant polysaccharide in nature \[34\]. Presently, there are two processes for preparing EMF from cellulose. Cellulose was directly converted into BMF in dichloroethane medium and then EMF with a yield of 40% could be obtained after reflux, evaporation, extraction, and washing processes. Although highly considerable yield could be reached, long reaction time (4 h) and complexed subsequent extraction process still existed in this process \[35\]. In the other case, low sulphuric acid acted as the homogeneous catalyst for the synthesis of EMF by one pot with the simple preparation process and short reaction time (1.25 h), resulting in a low yield (14.93%) \[28\]. Therefore, when biomass sugars were used as raw materials by one pot method, the general trend of EMF yield showed as follows: fructose > inulin > sucrose > glucose > cellulose.

A large amount of biomass waste was produced in the world every year, which would improve its utilization rate if it was used reasonably. Corn stover was employed for the synthesis of EMF, and the yield could reach 23.9% over mixed acid catalyst by author’s group \[12\]. Tian et al. \[29\] prepared EMF from waste cassava by NiSO$_4$ with a yield of 11.4%. In addition, 21.6% mass yield of EMF could be obtained from bagasse with Zr(O)Cl$_2$/CrCl$_3$ after 15 h \[30\]. In general, EMF yield was very low due to the complex of biomass structure. Therefore, in order to achieve the goal of sustainable development, the inexpensive biomass resources should be focused on the development of direct transformation and synthesis technology of EMF as well as hierarchical utilization of biomass resources.

**Catalytic system**

Catalysts played a crucial role in the conversion of biomass to EMF, which mainly promoted the isomerization of glucose and assisted the reaction of fructose to EMF \[36\]. By now, the reported catalysts for the synthesis of EMF mainly included inorganic liquid acids, metal salts, molecular sieves, sulfonated solid acids, functionalized ionic liquids, heteropoly acids, etc. The catalytic system would be divided into homogeneous catalytic system, heterogeneous catalytic system, and mixed-acid catalytic system, according to the reaction characteristics of the synthesis of EMF.

**Homogeneous catalytic system**

Homogeneous catalysts are attractive choices because of their uniform distribution of catalytic sites in solvents, which could adequately mix reaction substrates for catalytic

![Fig. 2 Preparation of EMF from various feedstocks](image-url)
reactions [37]. Homogeneous catalysts used for the preparation of EMF from biomass had been summarized and listed in Table 2, within mainly inorganic acids and soluble metal salts.

In general, H_2SO_4 [38] and HCl [39] were employed for the preparation of EMF from fructose, the results indicated that the yield of EMF was much higher with H_2SO_4 (70%) than that of with HCl (40%). In addition, the amount of HMF was almost not detected with H_2SO_4 as the catalyst while that of was significant (24%) with HCl as the catalyst. However, it was also noted that the longer reaction time (24 h) was needed with sulfuric acid as the catalyst, while only 2 h of the reaction was performed in the case of HCl. The effects of H_2SO_4 and H_3PO_4 on HMF etherification were investigated as well by Che et al. [40], and only 1.7% EMF yield was detected in the presence of H_3PO_4 when the yield of EMF was up to 79% with H_2SO_4 as the catalyst. They claimed that strong acids could provide enough acidic sites for EMF production. Flannely et al. [41] also found that H_2SO_4 had relatively high catalytic activity and the mass yield was 63% from fructose. However, the equipment was seriously corroded due to the H_2SO_4 used as the catalyst. To overcome this problem, extremely low sulphuric acid (0.1 wt.% H_2SO_4) was implemented as the catalyst for the synthesis of EMF from fructose by Xu et al. [42], and the EMF yield was 66% at 120 °C. Although the yield was decreased, it could effectively reduce the negative impact on equipment corrosion and environment. Sulphuric acid, as a representative of inorganic acids, has great catalytic activity and is a commercial product. However, the higher concentration of H_2SO_4 would lead to the formation of humins and the tedious post-process while the lower concentration of H_2SO_4 needs higher temperature and pressure to reach a better catalytic activity.

Metal chloride has been in the spotlight as a commercially available Lewis acid for the transformation of hexoses. Various metal salts were investigated for the production of EMF with fructose as feed by Liu et al.

Table 2: Preparation of EMF from biomass by homogeneous catalysts

| Entry | Feedstock | Catalyst | Solvent | Temp./°C | Time/h | Yield/% | Ref. |
|-------|-----------|----------|---------|----------|--------|---------|------|
| 1     | Fructose  | H_2SO_4(10 mol%) | EtOH     | 100      | 24     | 70 [38] |      |
| 2     | HMF       | H_2SO_4(5 mol%)  | EtOH     | 75       | 24     | 81 [38] |      |
| 3     | Fructose  | HCl(5 mol%)      | EtOH     | 120      | 2      | 40 [39] |      |
| 4     | HMF       | H_3PO_4        | EtOH     | 90       | 2      | 1.7 [40]|      |
| 5     | HMF       | H_2SO_4        | EtOH     | 90       | 2      | 79 [40]|      |
| 6     | Fructose  | H_2SO_4        | EtOH     | 100      | 24     | 63* [41]|      |
| 7     | Fructose  | H_2SO_4(0.1 wt.%) | EtOH/n-hexane | 120     | 3      | 66 [42]|      |
| 8     | Fructose  | CuCl_2·2H_2O   | EtOH     | 100      | 12     | 12 [43]|      |
| 9     | Fructose  | NiCl_2·6H_2O   | EtOH     | 100      | 12     | 5 [43]|      |
| 10    | Fructose  | SnCl_2·SH_2O   | EtOH     | 100      | 12     | 23 [43]|      |
| 11    | Fructose  | FeCl_3        | EtOH     | 100      | 12     | 28 [43]|      |
| 12    | Fructose  | CrCl_3·6H_2O  | EtOH     | 100      | 12     | 33 [43]|      |
| 13    | Fructose  | FeCl_3        | EtOH/[Bmim]Cl | 100    | 4      | 30.1 [44]|      |
| 14    | Glucose   | AlCl_3       | EtOH/water | 160    | 0.25   | 33 [45]|      |
| 15    | HMF       | AlCl_3        | EtOH     | 100      | 5      | 92.9 [46]|      |
| 16    | Fructose  | AlCl_3        | EtOH     | 100      | 11     | 71.2 [46]|      |
| 17    | Inulin    | AlCl_3        | EtOH     | 100      | 11     | 58.2 [46]|      |
| 18    | Glucose   | AlCl_3        | EtOH     | 100      | 11     | 38.4 [46]|      |
| 19    | Starch    | AlCl_3        | EtOH     | 100      | 11     | 27.2 [46]|      |
| 20    | Fructose  | AlCl_3·6H_2O/ BF_3·(Et)_2O | EtOH | 110 | 3 | 55 [47]|      |
| 21    | Fructose  | AlCl_3·6H_2O/ NaF | EtOH | 110 | 3 | 22 [47]|      |
| 22    | Fructose  | AlCl_3·6H_2O/ NaCl | EtOH | 110 | 3 | 28.9 [47]|      |
| 23    | Fructose  | AlCl_3·6H_2O/ NaBr | EtOH | 110 | 3 | 26.3 [47]|      |
| 24    | Sucrose   | AlCl_3·6H_2O/ BF_3·(Et)_2O | EtOH | 110 | 3 | 23.9 [47]|      |
| 25    | Inulin    | AlCl_3·6H_2O/ BF_3·(Et)_2O | EtOH | 110 | 3 | 45.4 [47]|      |

*Mass yield
AlCl₃ as a homogeneous catalyst in ethanol medium, further studied the conversion of glucose-to-EMF over exploration. The concept of green chemistry, which also limits the further price, instability, and toxicity, are not catered to the commercialization of EMF production. Such as the difficulty of separation and recycle, high price, instability, and toxicity, are not catered to the concept of green chemistry, which also limits the further exploration.

Accordingly, the disadvantages of the metal chloride, such as the difficulty of separation and recycle, high price, instability, and toxicity, are not catered to the concept of green chemistry, which also limits the further exploration.

**Heterogeneous catalytic system**
Heterogeneous catalysts have some special properties in the reaction process, such as insoluble in reaction solvents, easy to separate, recyclable and high catalytic activity, which have attracted many great attention than homogeneous catalysts [48]. Meanwhile, heterogeneous catalysts have superior controllability and can be used in the catalytic conversion of biomass due to adjustable specific surface area and acidic sites [49]. As listed in Table 3, heterogeneous catalysts for preparing EMF have been summarized.

**Zeolite catalysts**
Zeolite catalysts, as porous and green catalysts, play an important role in many fields, especially in the petrochemical industry [66, 67]. In recent years, Zeolite catalysts have also been applied to synthesize EMF. Che et al. [40] and Liu et al. [50] successfully supported H₄SiW₁₂O₄₀ and H₃PW₁₂O₄₀ (HPW) on mesoporous MCM-41 with high catalytic activity, respectively. A series of mesoporous Al-MCM-41 molecular sieves with different Si/Al ratios were synthesized by Lanzafame et al. (2011) [51], and the yield of EMF was up to 68% from HMF. These catalysts had a high specific surface area (over 1000 m²/g) and uniform mesoporous structure, and the introduction of Al³⁺ could obviously improve the catalytic activity and increase the selectivity of EMF synthesis. Bai et al. [52] reported a hierarchical lamellar multi-functional MFI-Sn/Al zeolite recently. The highlight is that the one-step crystallization zeolite was successfully synthesized with both Lewis acidic sites (Sn) and Bronsted acidic sites (Al-O(H)-Si), which enabled a three-step reaction cascade for the glucose to fructose (isomerization) over Lewis acidic sites and fructose to HMF (dehydration) and then HMF to EMF (etherification) in ethanal medium over Bronsted acidic sites. The EMF yield was 44% from glucose through cooperative catalysis.

**Heteropolyacid-based hybrids catalysts**
Heteropoly acids (HPA) catalysts are regarded as a kind of multi-functional catalysts due to considerably stable structure and adjustable acidity and alkalinity [68, 69]. Li et al. [53] synthesized a series of nano-catalysts functionalized catalyst with basic amino acids and HPW as materials, the results showed that the most active catalyst combination consisted of lysine and HPW, the yields of EMF were 76.6, 58.5, 42.4, and 36.5% from fructose, inulin, sorbose, and sucrose, respectively. HPA supported on K-10 clay was prepared for efficient synthesis of EMF from HMF and fructose by Zhang and co-authors [54], which made the EMF yield as high as 91.5 and 61.5%, respectively. In addition, Zhang’s group [55] also utilized the Ag₁H₂PW catalyst via an Ag⁺ exchange between HPW and AgNO₃. Their findings showed that the catalyst was most active when Ag⁺ exchanged 1 H⁺ with HPW, and a high EMF yield of 88.7 and 69.5% could be reached when HMF and fructose were chosen as starting materials, respectively.

**Sulfonic acid-functionalized catalysts**
Not only do the solid acid catalysts supported acidic functional groups (such as SO₃H group) have high catalytic performance, but also they are easy to separate and recover, non-corrosive equipment, and green environmental protection [70, 71]. Immobilization of sulfonic acid on the surface of Silica (Silica-SO₃H) was designed by Zhang’s group [56], which could efficiently transform HMF, fructose, inulin, and sucrose utilized as feedstocks
| Entry | Feedstock | Catalyst | Solvent | Temp./°C | Time/h | Yield/% | Ref. |
|-------|------------|----------|---------|----------|--------|---------|------|
| 1     | HMF        | 20%H5SiW/M-Ns | EtOH    | 90       | 2      | 82.7    | [40] |
| 2     | HMF        | 40%H5SiW/M-Ns | EtOH    | 90       | 2      | 85.8    | [40] |
| 3     | HMF        | 40%H5SiW/M-Ns | EtOH    | 90       | 4      | 84.1    | [40] |
| 4     | HMF        | 60%H5SiW/M-Ns | EtOH    | 90       | 2      | 83.2    | [40] |
| 5     | HMF        | 40 wt.%MCM-41-HPW | EtOH    | 100      | 12     | 83.4    | [50] |
| 6     | Fructose   | 40 wt.%MCM-41-HPW | EtOH    | 100      | 12     | 42.9    | [50] |
| 7     | HMF        | Al-MCM-41 (25) | EtOH    | 140      | 5      | 67      | [51] |
| 8     | HMF        | Al-MCM-41 (50) | EtOH    | 140      | 5      | 68      | [51] |
| 9     | HMF        | Al-MCM-41 (75) | EtOH    | 140      | 5      | –       | [51] |
| 10    | Glucose    | MFI-Sn/Al zeolite | EtOH    | 140      | 9      | 44      | [52] |
| 11    | Fructose   | Lys/PW   | EOH/VMSO(7:3) | 200   | 15     | 76.6    | [53] |
| 12    | Inulin     | Lys/PW   | EOH/VMSO(7:3) | 200   | 15     | 58.5    | [53] |
| 13    | Sorbose    | Lys/PW   | EOH/VMSO(7:3) | 200   | 15     | 42.4    | [53] |
| 14    | Sucrose    | Lys/PW   | EOH/VMSO(7:3) | 200   | 15     | 36.5    | [53] |
| 15    | HMF        | K-10 clay-HPW | EtOH    | 100      | 10     | 91.5    | [54] |
| 16    | Fructose   | K-10 clay-HPW | EtOH    | 100      | 10     | 61.5    | [54] |
| 17    | HMF        | Ag,H2PW  | EtOH    | 100      | 10     | 88.7    | [55] |
| 18    | Fructose   | Ag,H2PW  | EtOH    | 100      | 10     | 69.5    | [55] |
| 19    | HMF        | Silica-SO,H | EtOH    | 100      | 10     | 83.8    | [56] |
| 20    | Fructose   | Silica-SO,H | EtOH    | 100      | 10     | 63.1    | [56] |
| 21    | Inulin     | Silica-SO,H | EtOH    | 100      | 10     | 60.7    | [56] |
| 22    | HMF        | Fe,Fe@SiO2-SO4H | EtOH    | 100      | 10     | 89.3    | [57] |
| 23    | Fructose   | Fe,Fe@SiO2-SO4H | EtOH    | 100      | 10     | 72.5    | [57] |
| 24    | Inulin     | Fe,Fe@SiO2-SO4H | EtOH    | 100      | 10     | 63.3    | [57] |
| 25    | HMF        | Fe,Fe@SiO2-SH-Im-HSO4 | EtOH    | 100      | 12     | 89.6    | [58] |
| 26    | Fructose   | Fe,Fe@SiO2-SH-Im-HSO4 | EtOH    | 120      | 24     | 60.4    | [58] |
| 27    | Sucrose    | Fe,Fe@SiO2-SH-Im-HSO4 | EtOH    | 120      | 24     | 34.4    | [58] |
| 28    | Inulin     | Fe,Fe@SiO2-SH-Im-HSO4 | EtOH    | 120      | 24     | 56.1    | [58] |
| 29    | HMF        | Cellulose sulfonic acid | EtOH     | 100      | 10     | 84.4    | [59] |
| 30    | HMF        | Cellulose sulfonic acid | EtOH     | 100      | 10     | 72.5    | [59] |
| 31    | Fructose   | Cellulose sulfonic acid | DMSO     | 100      | 0.75   | 93.8<sup>a</sup> | [59] |
| 32    | Fructose   | Am-CMSs-SO,H | EtOH     | 100      | 12     | 68      | [60] |
| 33    | HMF        | C-SO,H | EtOH     | 100      | 6      | 71      | [61] |
| 34    | HMF        | C-SO,H | EtOH     | 140      | 8      | 81<sup>b</sup> | [61] |
| 35    | HMF        | 30% Glu-Fe2O3-SO,H | EtOH    | 80       | 2      | 92      | [62] |
| 36    | Fructose   | 50% Glu-Fe2O3-SO,H | EtOH    | 80       | 24     | 81      | [62] |
| 37    | Glucose    | 50% Glu-Fe2O3-SO,H | EtOH     | 140      | 48     | 27      | [62] |
| 38    | Inulin     | 50% Glu-Fe2O3-SO,H | EtOH/VMSO | 100   | 24     | 85      | [62] |
| 39    | Fructose   | Fe,Fe@C-SO,H | EtOH     | 100      | 10     | 64      | [63] |
| 40    | Fructose   | OMC-SO,H | EtOH     | 140      | 24     | 55.7    | [64] |
| 41    | Inulin     | OMC-SO,H | EtOH     | 140      | 24     | 53.6    | [64] |
| 42    | Sucrose    | OMC-SO,H | EtOH     | 140      | 24     | 26.8    | [64] |
| 43    | HMF        | LS-SO,H | EtOH     | 80       | 11     | 85.5    | [65] |
| 44    | Fructose   | LS-SO,H | EtOH     | 110      | 11     | 57.3    | [65] |
| 45    | Glucose    | LS-SO,H | EtOH     | 110      | 15     | 77<sup>c</sup> | [65] |
| 46    | Inulin     | LS-SO,H | EtOH     | 110      | 15     | 46.8    | [65] |

<sup>a</sup>The yield is HMF yield; <sup>b</sup>The yield is ethyl levulinate (EL) yield; <sup>c</sup>The yield is EG yield
into EMF while the yield of EMF was extremely low for glucose. The results showed that Silica-SO$_3$H had little activity for the isomerization of glucose to fructose, but the catalyst was much conducive to the reaction of dehydra-
tion and etherification. Subsequently, the sulfonic acid functionalized catalyst was further improved by silica-encapsulated Fe$_3$O$_4$ nanoparticles supported sul-
fonic acid catalyst (Fe$_3$O$_4$@SiO$_2$-SO$_3$H) [57]. In addition, the catalyst was also 
synthesized and it was used in the preparation of EMF by Zhang’s group [58]. Not only do magnetically sulfonic acid functionalized catalysts have a great catalytic effect, but also they have excellent paramagnetism, resulting in the catalyst could be easily separated from the reaction mixture by magnetic separation.

Sulfonic acid functionalized catalysts supported carbon materials have attracted increasing attention, and they were prepared by incomplete carbonization of biomass and sul-
fonation treatment. Not only do catalysts have a similar catalytic effect with sulfuric acid, but also they have the advantages of good thermal stability and easy recycling and reuse. Cellulose sulfuric acid was prepared by direct sulfon-
ation of cellulose with chlorosulfonic acid in organic sol-
vents, and most of the S existed in the form of sulfonic groups with the content of 0.56 mmol/g. The catalyst had an excellent catalytic activity for the synthesis of EMF in the ethanol system, it also could efficiently convert fructose to HMF (93.6%) in the DMSO medium [59]. Zhao et al. [60] successfully fabricated sulfonic acid groups functiona-
ized aromatic carbon microspheres (Ar-CMSs-SO$_3$H) catal-
yst through waste camellia oleifera shells as carbon group. Due to Ar-CMSs-SO$_3$H catalytic activity for EMF preparation from HMF. Metal-
Organic Frameworks (MOFs) were also applied as carbon groups for preparing the sulfonic acid functionalized cata-
lyst, which exhibited highly considerable catalytic for etheri-
fication of HMF to EMF (71%) or esterification of HMF to ethyl levulinate (81%) in ethanol medium [61]. In addition, glucose [62], wheat straw [63], carbon nanomaterial [64], lignosulfonate [65] used as carbon groups were studied, re-
spectively. The specific structures and chemical properties of carbonyl sulfonated solid acids were similar while the preparation methods and starting materials acted as carbon groups were different, which lead to a relatively high catalytic for the conversion of fructose-based carbohydrates to EMF. However, the catalysts generally could not effect-
ively isomerize glucose to fructose.

Other catalysts
In addition, there were other heterogeneous catalysts for the preparation of EMF. Gupta and Saha [72] found a dual acidic titania carbocatalyst (Glu-TSOH-Ti) interplayed synergistically for EMF preparation by one-pot, 91 and 64% EMF yield could be reached from HMF and fructose, respectively. Graphene oxide (GO) was discovered as a highly-efficient and stable catalyst through fructose-based carbohydrates to transform EMF [73]. GO performed great catalytic activity in the conversion of EMF for HMF etherification (92%) in ethanol, and for fructose (71%), suc-
crose (34%) and inulin (66%) in the ethanol-DMSO solv-
ent system. Niobium molybdate, as a multilayer-like polyoxometalate with the varied metal components, was successfully designed by Yang et al. [74]. The record of EMF yield from HMF was broken with over 99% due to the accurate regulation of the interlayer space of the Nb-
Mo oxides layer and the acid amount by the components of varied metal.

Although heterogeneous catalysts are convenient for separation and recovery and have relatively high catalytic efficiency for HMF and fructose-based carbohydrates, the efficiency is low. Meanwhile, some of them need to be calcined at a high temperature for regeneration, which is troublesome.

Mixed-acid catalytic system
In view of the unsatisfactory catalytic effect of a single acid, the mixed-acid catalytic system has been receiving the spotlight for the production of EMF from glucose or glucose-based polymers [75–77]. For example, a mixed-
acid system was explored via a combination of Amberlyst-
131 and zeolite Sn-BEA for EMF preparation from glu-
cose, 31% EMF yield was obtained in ethanol for 24 h [25]. Xin et al. [78] have measured a moderate EMF yield of 30.6% from glucose catalyzed by the AlCl$_3$ and PTSA-
POM at 150°C for 30 min. In addition, the one-pot two-
step method was utilized to product EMF from glucose, which was carried out by adding H-USY for 5 h and followed by Amberlyst-15 for 6 h [36]. Taking a clue from the above-mentioned design of catalyst, Peng’s group pro-
posed a mixed-acid system consisting of Al (OTf)$_3$ and Amberlyst-15, an optimized EMF yield could be obtained in the ethanol-DMSO solvent system [79]. Presently, the mixed-acid catalytic system with both Lewis acid sites and Bronsted acid sites is a promising one for the ethanalysis of glucose-based substrates to EMF. The study on the syn-
ergistic effect between them will provide some valuable guidance for the design of catalysts in the future.

Solvent system
In addition to the catalysts, the reaction solvents also played an essential role in the process of EMF preparation [80, 81]. A good reaction solvent system could increase the amount of substrates and the yield of EMF to a certain extent. To study the effects of different solvents, the solv-
ent systems used in the catalytic preparation of EMF were summarizined in four categories: 1) single-phase solvent
system, 2) biphasic solvent system, 3) ionic liquids system (ILs) and 4) deep eutectic solvents (DESs) system, which were listed in Table 4.

Single-phase solvent system
Ethanol was a common solvent for the production of EMF, but humins and other by-products were easily produced during the ethanolysis of carbohydrates [90]. When organic solvents such as n-hexane [42], DMSO [82], THF [83] and γ-valerolactone (GVL) [84] were used as co-solvents, the production of by-products could be effectively reduced and the EMF yield could be remarkably increased. Wang et al. [82] used “one-pot” method for EMF conversion from fructose, it was found that adding DMSO to ethanol system could increase the selectivity of the target product (EMF). With the increase of DMSO content in co-solvent, the yield of EMF increased from 28% to 64%, which might be that DMSO could effectively inhibit the production of humins and the occurrence of side reaction (i.e. HMF rehydration). Meanwhile, they found that the yield of EMF began to decrease when the content of DMSO continued to increase, indicating that the etherification of HMF might be affected by the decrease of ethanol concentration in the reaction solvent system, and the reversible reaction was promoted at the same time. The author’s group [83] studied the effect of THF on the conversion of corn stover and the reaction was optimized via response surface methodology. It was found that the introduction of THF could significantly increase the yield of EMF (21.8%) in the ethanol/THF (1:1) medium after 2.9

| Entry | Feedstock         | Catalyst | Solvent             | Temp./°C | Time/h  | Yield/% |
|-------|-------------------|----------|---------------------|----------|---------|---------|
| 1     | Fructose          | H₃PW₁₂O₄₀ | EtOH/DMSO(7:3)      | 140      | 130 min | 64 [82] |
| 2     | Sucrose           | H₃PW₁₂O₄₀ | EtOH/DMSO(7:3)      | 140      | 130 min | 28 [82] |
| 3     | Inulin            | H₃PW₁₂O₄₀ | EtOH/DMSO(7:3)      | 140      | 130 min | 54 [82] |
| 4     | Corn stover       | USY      | EtOH/THF(1:1)       | 168      | 2.9     | 21.8 [83]|
| 5     | Fructose          | MHGC–SO₃H | EtOH/GVL(2.3)       | 120      | 24      | 67.4 [84]|
| 6     | Glucose           | MHGC–SO₃H | EtOH/GVL(2.3)       | 120      | 24      | 3 [84]  |
| 7     | Sucrose           | MHGC–SO₃H | EtOH/GVL(2.3)       | 120      | 24      | 33.1 [84]|
| 8     | Inulin            | MHGC–SO₃H | EtOH/GVL(2.3)       | 120      | 24      | 52.4 [84]|
| 9     | Glucose           | Zn-SO₃H-GR-carbon | ethanol/water/THF (20 mL:5 mL:250 mmol) | 106 | 1.2 | 86.3 [85]|
| 10    | Fructose          | [MIMBS]₅PW₁₂O₄₀ | EtOH | 90 | 24 | 90.5 [14]|
| 11    | HMF               | [MIMBS]₅PW₁₂O₄₀ | EtOH | 70 | 24 | 90.7 [14]|
| 12    | HMF               | [DMAJ⁺][CH₃SO₃]⁻ | EtOH | 120 | 15 | 82.8 [86]|
| 13    | Fructose          | [DMAJ⁺][CH₃SO₃]⁻ | EtOH | 120 | 16 | 57.6 [86]|
| 14    | Cellobiose fibers | [DMAJ⁺][CH₃SO₃]⁻ | EtOH | 120 | 20 | 19.8 [86]|
| 15    | Fructose          | 1-Butyl-3-(3-sulfopropyl)-imidazolium chloride | EtOH/Hexanes | 100 | 80 min | 55 [87]|
| 16    | Fructose          | 1-Methyl-3-(3-sulfopropyl)-imidazolium chloride | EtOH/Hexanes | 100 | 80 min | 54 [87]|
| 17    | Fructose          | [C₄mim][HSO₄] | EtOH | 130 | 20 | 83 [88]|
| 18    | Fructose          | [C₅mim][HSO₄] | EtOH | 130 | 15 | 77 [88]|
| 19    | Fructose          | [C₆mim][HSO₄] | EtOH | 130 | 30 | 81 [88]|
| 20    | Inulin            | [BMIM][HSO₄] | EtOH/Hexanes | 130 | 30 | 77 [89]|
| 21    | Inulin            | [EMIM][HSO₄] | EtOH/Hexanes | 130 | 30 | 77 [89]|
| 22    | Inulin            | [HMIM][HSO₄] | EtOH/Hexanes | 130 | 30 | 63 [89]|
| 23    | Inulin            | Amberlyst-15/ [BMIM][Cl] | EtOH | 130 | 30 | 49 [89]|
| 24    | Sucrose           | [BMIM][HSO₄] | EtOH/Hexanes | 130 | 30 | 43 [89]|
| 25    | Fructose          | [BMIM][HSO₄] | EtOH/Hexanes | 130 | 20 | 79 [89]|
| 26    | Glucose           | [BMIM][HSO₄] | EtOH/Hexanes | 130 | 20 | 8 [89]|
h. THF could provide a better hydrophobic environment and inhibit the formation of humins than ethanol. Although organic co-solvents can inhibit the formation of EMF degradation products to some extent, their solubility for carbohydrates is generally low, which limits the application of co-solvents in large-scale production of EMF. On the other hand, organic co-solvents usually have a higher boiling point, which brings great barriers to the separation and purification of EMF.

**Biphasic solvent system**

In order to overcome the shortcomings of single-phase solvent systems, biphasic solvent systems consisting of water and various organic solvents (such as benzene, methyl isobutyl ketone, and THF) have received increasing attention. Up to now, there are few reports about the application of the biphasic solvent system in the field of EMF preparation. Karnjanakom and Maneechakr (2019) [85] studied a novelty catalytic transformation of glucose in the ultrasound-assisted biphasic solvent system (ethanol-water-THF). Up to 86.3% of EMF yield could be obtained at 106 °C after 72 min, resulting in the easy production of EMF via isomerization, dehydration, and etherification in an excellent biphasic-heterogeneous reaction system. It was noteworthy that the biphasic solvent reaction system could improve the conversion of biomass-based carbohydrates, the selectivity and yield of EMF. As an efficient solvent system for the conversion of carbohydrates to EMF, the biphasic solvent system might be the first choice for the industrialization of EMF.

**Ionic liquids system**

Ionic liquids with excellent physicochemical properties have been employed for EMF preparation in recent years. For example, N-methylimidazole, 1,4-butane sultone and HPA were used to synthesize HPA-based IL hybrid catalyst [MIMBS]$_3$PW$_{12}$O$_{40}$ through two-step method, the EMF yield was up to 90.5% from fructose at 90 °C after 24 h [14]. De et al. introduced [DMA]$^+$(CH$_3$SO$_3$)$^-$ as ILs to produce EMF [86], the yields were 82.8% from HMF, 57.6% from fructose and 19.8% from cellobiose fibers, respectively. Functional ionic liquids containing sulfonic acid groups were designed for conversion of fructose into EMF by Kraus and Guney [87]. The yield of EMF was 55 and 54% over 1-butyl-3(3-sulfopropyl)-imidazolium chloride and 1-methyl-3(3-sulfopropyl)-imidazolium chloride, respectively. To our happiness, the catalytic performance of tailored ILs did not decrease significantly after 5 recycles. A series of ionic liquids (hydrogen sulfate ILs, acetate ILs, diethylphosphate ILs, dimethylphosphinate ILs and chloride ILs) were investigated by Qi and co-authors [88], and the results showed that [C$_4$mim][HSO$_4$] was more conductive to EMF preparation in ethanol medium. The yield of EMF was up to 83% in a short time (20 min), which might be a result of the acidity of anion and a stabilizing hydrogen bond between HMF and ILs. Based on that, other types of hydrogen sulfate groups in the ionic liquids ([BMIM][HSO$_4$], [EMIM][HSO$_4$] and [HMIM][HSO$_4$]) were also further explored for transform carbohydrates into EMF by Qi and co-authors [89]. It was found that glycoside bond was easy to break and the reaction intermediates were stable when [HSO$_4$]$^-$ group of ionic liquid used as catalyst, and yields of EMF were 79, 77 and 49% from fructose, inulin and sucrose, respectively. The highly considerable EMF yield could be obtained in ILs solvent system while there are still some barriers, such as high boiling point, high price and difficulty to recycle. Consequently, it would be worthy in-depth to develop a low boiling point, cheap and recyclable ionic liquid.

**Deep eutectic solvents (DESs) system**

DESs was known as a liquid mixture composed of the hydrogen-bonded donor (HBD, i.e. carboxylic acid, polyols) and hydrogen-bonded acceptor (HBA, i.e. choline salts), its solidification point was significantly lower than that of pure substances [91, 92]. Although the physical and chemical properties of DESs are similar to ionic liquids, they are regarded as a new green solvent due to its low toxicity, low-cost, environment-friendly and biodegradable [93, 94]. At present, there are few reports about the synthesis of EMF in the DESs system. The author's group [95] designed a novel DES system for the preparation of EMF by one-pot two-step method. Dehydration of carbohydrates to HMF was first conducted in the DESs system and then the generated HMF was extracted in situ into methyl cyanide (MeCN). Ethanol and Amberlyst-15 were added into the obtained HMF solvent and then followed directly by the etherification. The two-phase solvent system (DESs/MeCN) showed excellent and stable recycling performance. After extracting and separating HMF, CHCl could be directly used in the next recycling reaction. This method has highly industrial application value in preparing EMF from carbohydrates. Even though there are still limitations of the DESs system in converting biomass to EMF, it would be a trend to develop a highly active and easily recoverable catalyst for the preparation of EMF in the DESs system.

**Current challenges and future prospects**

The present review has outlined and discussed the latest achievements on the preparation of EMF from biomass in various solvents system over homogeneous, heterogeneous catalysts or mixed acid catalysts. Although many satisfactory results have been achieved, it should be noted that there are still many enormous challenges for the industrial production of EMF. In order to accelerate
this process, some potential points should be addressed in future studies:

1. The comprehensive utilization of lignocellulosic biomass raw. For the reaction system with a highly considerable yield of EMF, the feedstocks are mainly HMF or fructose with high cost, which is not conducive to the economic benefits of industrial production. Therefore, we should focus on developing the conversion of cheaper lignocellulosic biomass resources (i.e. forestry and agricultural wastes) into EMF, the pretreatment technology of raw materials should be applied as well.

2. The innovative investigation of catalysts. The isomerization of glucose is the main bottleneck for the preparation of EMF. Theoretically, solid acid catalysts containing ionic liquids and especially deep-eutectic solvents should be exploited with excellent properties such as biological degradability, low viscosity, low cost, strong solvency and so on. Presently, the published researches on the solvent system mainly focus on the single-phase solvent system, while the research publications on the two-phase solvent system, ionic liquid system, especially DESs system are not enough. Therefore, based on the available publications, the potential relationship between the catalyst system and the solvent system is unclear, which is still a challenge for a better design of the reaction system.

3. The strategic preparation of reaction mediums. It is well known that reaction mediums have an inestimable effect on improving the catalysts activity and reactants dissolution. Taking green chemistry, atomic economy and practical application into consideration, the ionic liquids and especially deep-eutectic solvents should be exploited with excellent properties such as biological degradability, low viscosity, low cost, strong solvency and so on. Presently, the published researches on the solvent system mainly focus on the single-phase solvent system, while the research publications on the two-phase solvent system, ionic liquid system, especially DESs system are not enough. Therefore, based on the available publications, the potential relationship between the catalyst system and the solvent system is unclear, which is still a challenge for a better design of the reaction system.

Conclusions

EMF is a promising transportation fuel and fuel additive. The biomass (especially low-cost and abundant agricultural and forestry wastes) is utilized for the preparation of EMF with very broad prospects. The innovative aspects of catalysts and solvents systems as well as mechanism should be invested twice as much effort according to current technologies and theories and then apply them in the preparation of EMF to clear up obstacles on the road of industrialized production, where amazing happens!

Abbreviations

- HMF: 5-Hydroxymethylfurfural; CMF: 5-Chloromethylfurfural; DESs: Deep eutectic solvents; DMSO: Dimethyl sulfoxide; EG: Ethyl glycolide; EL: Ethyl levulinate; EMF: 5-Ethoxymethylfurfural; EtOH: Ethanol; GO: Graphene oxide; GVL: γ-valerolactone; HBA: Hydrogen-bonded acceptor; HBD: Hydrogen-bonded donor; HMF: 5-Hydroxymethylfurfural; HPA: Heteropoly acids; HPN: H3PW12O40; ILs: Ionic liquids; MeCN: Methyl cyanide; MOFs: Metal-Organic Frameworks; THF: Tetrahydrofuran

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Authors’ contributions

XZ and BC conceived and designed this work; BC drafted the paper; XZ, GY and BC have revised the writing; All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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