

REVIEW

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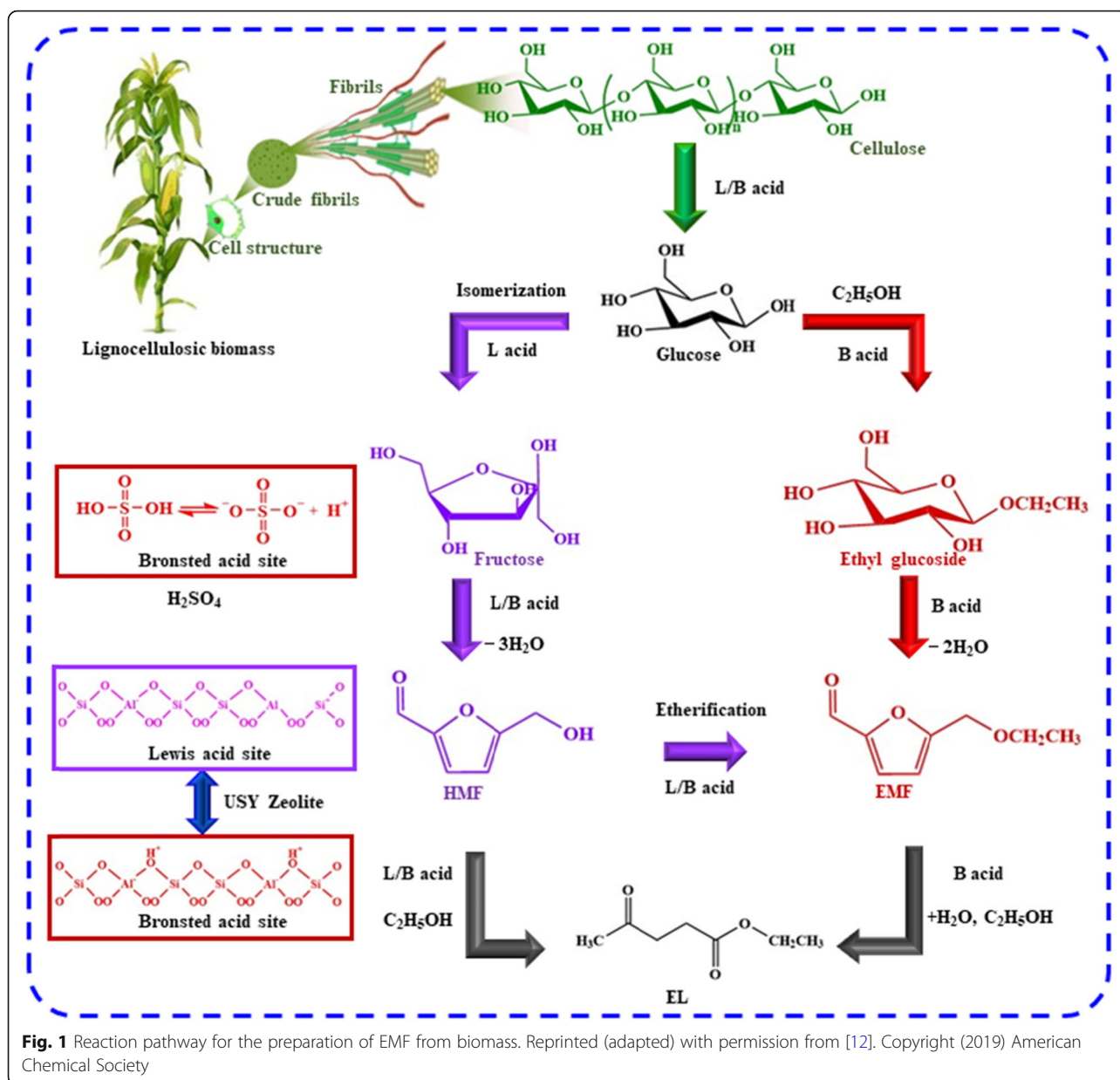
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called “one-pot” reaction. Given the above advantages, direct ethanolysis of biomass to prepare EMF is considered as a potential approach for biomass development and utilization.

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

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	[MIMBS] ₃ 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	C/SBA(45)	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 ₃ N][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 ^b	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(100)	EtOH/THF (5:4)	130	15	67.7	[27]
32	Inulin	MIL-101-SO ₃ H(100)	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]

^aEtOH is ethanol; ^b THF is tetrahydrofuran; ^c The yield is EG yield; ^d The yield is mass yield

selectivity in various reaction processes [13–18]. Kumari et al. [13] conducted HMF etherification over Ta exchanged tungstophosphoric acid with SnO₂ support as the catalyst, the EMF yield was 90.2%. A 91% of EMF yield was reached from HMF used Cs₂STA 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

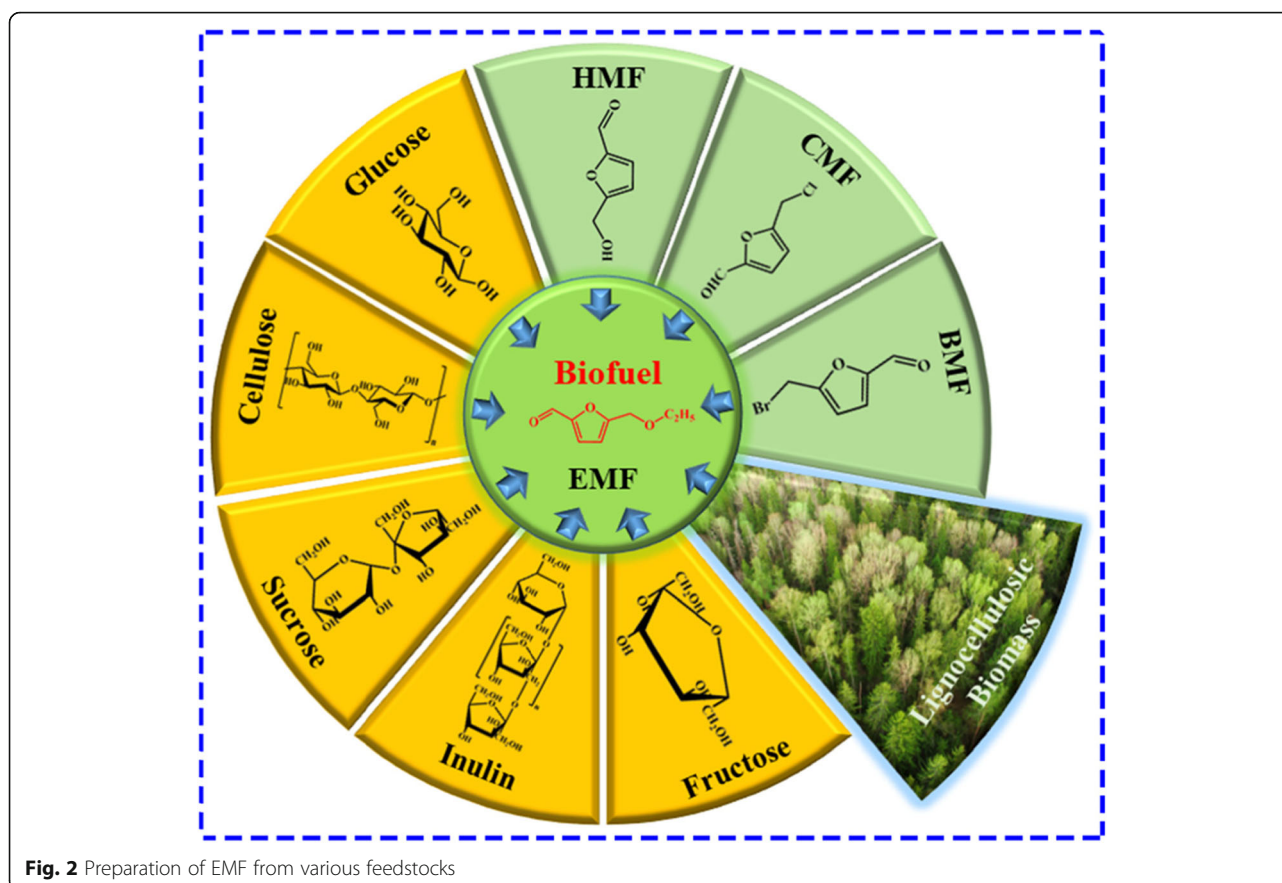


Fig. 2 Preparation of EMF from various feedstocks

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 $\text{Zr(O)Cl}_2/\text{CrCl}_3$ 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

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. Flannelly 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. Sulfuric 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 ^a	[41]
7	Fructose	H_2SO_4 (0.1 wt.%)	EtOH/n-hexane	120	3	66	[42]
8	Fructose	$CuCl_2 \cdot 2H_2O$	EtOH	100	12	12	[43]
9	Fructose	$NiCl_2 \cdot 6H_2O$	EtOH	100	12	5	[43]
10	Fructose	$SnCl_4 \cdot 5H_2O$	EtOH	100	12	23	[43]
11	Fructose	$FeCl_3$	EtOH	100	12	28	[43]
12	Fructose	$CrCl_3 \cdot 6H_2O$	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	$AlCl_3 \cdot 6H_2O / BF_3 \cdot (Et)_2O$	EtOH	110	3	55	[47]
21	Fructose	$AlCl_3 \cdot 6H_2O / B(OH)_3$	EtOH	110	3	22	[47]
22	Fructose	$AlCl_3 \cdot 6H_2O / NaF$	EtOH	110	3	25.1	[47]
23	Fructose	$AlCl_3 \cdot 6H_2O / NaCl$	EtOH	110	3	28.9	[47]
24	Fructose	$AlCl_3 \cdot 6H_2O / NaBr$	EtOH	110	3	26.3	[47]
25	Sucrose	$AlCl_3 \cdot 6H_2O / BF_3 \cdot (Et)_2O$	EtOH	110	3	23.9	[47]
26	Inulin	$AlCl_3 \cdot 6H_2O / BF_3 \cdot (Et)_2O$	EtOH	110	3	45.4	[47]

^aMass yield

[43]. They found that LiCl, NaCl, and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ had no catalytic activity for fructose and the amount of EMF was almost not detected. However, 23, 28 and 33% yield of EMF could be detected from $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, FeCl_3 , and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, respectively. Zhou et al. [44] also found that FeCl_3 acted as the catalyst could reach acceptable EMF yield. In another case, AlCl_3 was introduced into EMF production from glucose in an ethanol-water mixture, it was beneficial to prepare furan products (included HMF and EMF) with 57% yield in short reaction time (15 min). Unfortunately, only 33% EMF yield was detected, indicating its selectivity for EMF production was not satisfactory [45]. Inspired by this, Liu et al. [46] further studied the conversion of glucose-to-EMF over AlCl_3 as a homogeneous catalyst in ethanol medium, and the reactions were conducted at 100 °C for 11 h. However, the improvement of the EMF amount was not significant by this modification and EMF yield only increased to 38.4%. It was worth noticing that AlCl_3 had excellent catalytic activity and the yield of HMF etherification to EMF was 92.9%. At the same time, AlCl_3 also showed great catalytic activity for other carbohydrates, 71.2, 58.2 and 27.2% EMF yields could be reached from fructose, inulin, and starch, respectively. The combinations of AlCl_3 and $\text{BF}_3 \cdot (\text{Et})_2\text{O}$, $\text{B}(\text{OH})_3$ or halide salts (i.e. NaF, NaCl, and NaBr) were explored for the production of EMF from fructose by Jia et al. [47]. $\text{AlCl}_3 \cdot 6\text{H}_2\text{O} / \text{BF}_3 \cdot (\text{Et})_2\text{O}$ was the most advantageous combination for continuous dehydration and etherification of fructose, and it also had a good promoting effect on sucrose and inulin. Generally, the nature of metal chloride acted as Lewis acid is responsible for the good performance in the isomerization of glucose or glucose-based polymers. Unfortunately, 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 limit 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] successively supported $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (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 m^2/g) and uniform mesoporous structure, and the introduction of Al^{3+} 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 Brønsted 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 Brønsted 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 $\text{Ag}_1\text{H}_2\text{PW}$ catalyst via an Ag^+ exchange between HPW and AgNO_3 . 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 SO_3H 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- SO_3H) was designed by Zhang's group [56], which could efficiently transform HMF, fructose, inulin, and sucrose utilized as feedstocks

Table 3 Preparation of EMF from biomass by heterogeneous catalysts

Entry	Feedstock	Catalyst	Solvent	Temp./°C	Time/h	Yield/%	Ref.
1	HMF	20%HSiW/M-Ns	EtOH	90	2	82.7	[40]
2	HMF	40%HSiW/M-Ns	EtOH	90	2	85.8	[40]
3	HMF	40%HSiW/M-Ns	EtOH	90	4	84.1	[40]
4	HMF	60%HSiW/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	EtOH/DMSO(7:3)	200	15	76.6	[53]
12	Inulin	Lys/PW	EtOH/DMSO(7:3)	200	15	58.5	[53]
13	Sorbose	Lys/PW	EtOH/DMSO(7:3)	200	15	42.4	[53]
14	Sucrose	Lys/PW	EtOH/DMSO(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 ₁ H ₂ PW	EtOH	100	10	88.7	[55]
18	Fructose	Ag ₁ H ₂ PW	EtOH	100	10	69.5	[55]
19	HMF	Silica-SO ₃ H	EtOH	100	10	83.8	[56]
20	Fructose	Silica-SO ₃ H	EtOH	100	10	63.1	[56]
21	Inulin	Silica-SO ₃ H	EtOH	100	10	60.7	[56]
22	HMF	Fe ₃ O ₄ @SiO ₂ -SO ₃ H	EtOH	100	10	89.3	[57]
23	Fructose	Fe ₃ O ₄ @SiO ₂ -SO ₃ H	EtOH	100	10	72.5	[57]
24	Inulin	Fe ₃ O ₄ @SiO ₂ -SO ₃ H	EtOH	100	10	63.3	[57]
25	HMF	Fe ₃ O ₄ @SiO ₂ -SH-Im-HSO ₄	EtOH	100	12	89.6	[58]
26	Fructose	Fe ₃ O ₄ @SiO ₂ -SH-Im-HSO ₄	EtOH	120	24	60.4	[58]
27	Sucrose	Fe ₃ O ₄ @SiO ₂ -SH-Im-HSO ₄	EtOH	120	24	34.4	[58]
28	Inulin	Fe ₃ O ₄ @SiO ₂ -SH-Im-HSO ₄	EtOH	120	24	56.1	[58]
29	HMF	Cellulose sulfuric acid	EtOH	100	10	84.4	[59]
30	HMF	Cellulose sulfuric acid	EtOH	100	10	72.5	[59]
31	Fructose	Cellulose sulfuric acid	DMSO	100	0.75	93.6 ^a	[59]
32	Fructose	Ar-CMSs-SO ₃ H	EtOH	100	12	68	[60]
33	HMF	C-SO ₃ H	EtOH	100	6	71	[61]
34	HMF	C-SO ₃ H	EtOH	140	8	81 ^b	[61]
35	HMF	30% Glu-Fe ₃ O ₄ -SO ₃ H	EtOH	80	2	92	[62]
36	Fructose	50% Glu-Fe ₃ O ₄ -SO ₃ H	EtOH	80	24	81	[62]
37	Glucose	50% Glu-Fe ₃ O ₄ -SO ₃ H	EtOH/DMSO	140	48	27	[62]
38	Inulin	50% Glu-Fe ₃ O ₄ -SO ₃ H	EtOH/DMSO	100	24	85	[62]
39	Fructose	Fe ₃ O ₄ @C-SO ₃ H	EtOH/DMSO	100	10	64	[63]
40	Fructose	OMC-SO ₃ H	EtOH	140	24	55.7	[64]
41	Inulin	OMC-SO ₃ H	EtOH	140	24	53.6	[64]
42	Sucrose	OMC-SO ₃ H	EtOH	140	24	26.8	[64]
43	HMF	LS-SO ₃ H	EtOH	80	11	85.5	[65]
44	Fructose	LS-SO ₃ H	EtOH	110	11	57.3	[65]
45	Glucose	LS-SO ₃ H	EtOH	110	15	77 ^c	[65]
46	Inulin	LS-SO ₃ H	EtOH	110	15	46.8	[65]

^aThe yield is HMF yield; ^b The yield is ethyl levulinate (EL) yield; ^c The yield is EG yield

into EMF while the yield of EMF was extremely low for glucose. The results showed that Silica-SO₃H had little activity for the isomerization of glucose to fructose, but the catalyst was much conducive to the reaction of dehydration and etherification. Subsequently, the sulfonic acid functionalized catalyst was further improved by silica-encapsulated Fe₃O₄ nanoparticles supported sulfonic acid catalyst (Fe₃O₄@SiO₂-SO₃H) [57]. In addition, magnetic material-supported polyionic liquid acid catalyst (Fe₃O₄@SiO₂-SH-Im-HSO₄) 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 sulfonation 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 sulfonation of cellulose with chlorosulfonic acid in organic solvents, 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 functionalized aromatic carbon microspheres (Ar-CMSs-SO₃H) catalyst through waste camellia oleifera shells as carbon group. Due to Ar-CMSs-SO₃H catalyst with abundant -SO₃H groups and numerous spherical microstructure, it had an excellent activity for EMF preparation from HMF. Metal-Organic Frameworks (MOFs) were also applied as carbon groups for preparing the sulfonic acid functionalized catalyst, which exhibited highly considerable catalytic for etherification 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, respectively. 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 effectively 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%), sucrose (34%) and inulin (66%) in the ethanol-DMSO solvent 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 glucose, 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 AlCl₃ 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 proposed 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 Brønsted acid sites is a promising one for the ethanolysis of glucose-based substrates to EMF. The study on the synergistic 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 solvent systems used in the catalytic preparation of EMF were summarized 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

Table 4 Preparation of EMF from various solvents system

Entry	Feedstock	Catalyst	Solvent	Temp/ °C	Time/h	Yield/ %	Ref.
1	Fructose	H ₃ PW ₁₂ O ₄₀	EtOH/DMSO(7:3)	140	130 min	64	[82]
2	Sucrose	H ₃ PW ₁₂ O ₄₀	EtOH/DMSO(7:3)	140	130 min	28	[82]
3	Inulin	H ₃ PW ₁₂ O ₄₀	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-SO ₃ H	EtOH/GVL(2:3)	120	24	67.4	[84]
6	Glucose	MHGC-SO ₃ H	EtOH/GVL(2:3)	120	24	3	[84]
7	Sucrose	MHGC-SO ₃ H	EtOH/GVL(2:3)	120	24	33.1	[84]
8	Inulin	MHGC-SO ₃ H	EtOH/GVL(2:3)	120	24	52.4	[84]
9	Glucose	Zn-SO ₃ H-GR-carbon	ethanol/water/THF (20 mL:5 mL:250 mmol)	106	1.2	86.3	[85]
10	Fructose	[MIMBS] ₃ PW ₁₂ O ₄₀	EtOH	90	24	90.5	[14]
11	HMF	[MIMBS] ₃ PW ₁₂ O ₄₀	EtOH	70	24	90.7	[14]
12	HMF	[DMA] ⁺ [CH ₃ SO ₃] ⁻	EtOH	120	15	82.8	[86]
13	Fructose	[DMA] ⁺ [CH ₃ SO ₃] ⁻	EtOH	120	16	57.6	[86]
14	Cellobiose fibers	[DMA] ⁺ [CH ₃ SO ₃] ⁻	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	[C ₄ mim][HSO ₄]	EtOH	130	20	83	[88]
18	Fructose	[C ₁ mim][HSO ₄]	EtOH	130	15	77	[88]
19	Fructose	[C ₂ mim][HSO ₄]	EtOH	130	30	81	[88]
20	Inulin	[BMIM][HSO ₄]	EtOH/water	130	30	77	[89]
21	Inulin	[EMIM][HSO ₄]	EtOH/water	130	30	51	[89]
22	Inulin	[HMIM][HSO ₄]	EtOH/water	130	30	63	[89]
23	Inulin	Amberlyst-15/ [BMIM][Cl]	EtOH	130	30	49	[89]
24	Sucrose	[BMIM][HSO ₄]	EtOH/water	130	30	43	[89]
25	Fructose	[BMIM][HSO ₄]	EtOH/water	130	20	79	[89]
26	Glucose	[BMIM][HSO ₄]	EtOH/water	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]₃PW₁₂O₄₀ 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]⁺[CH₃SO₃]⁻ 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, dimethylphosphate ILs and chloride ILs) were investigated by Qi and co-authors [88], and the results showed that [C₄mim][HSO₄] was more conducive 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][HSO₄], [EMIM][HSO₄] and [HMIM][HSO₄]) 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 [HSO₄]⁻ 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 large specific surface area, proper pore size and adjustable acid sites of Brønsted and Lewis acid are conducive to EMF preparation from glucose-based biomass by a series of reactions of isomerization, dehydration and etherification. Thus, the multifunctional solid acid catalysts with specific porosity, magnetic components, non-precious metals and adjustable acidity are desirable for EMF synthesis.

(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.

(4) The thorough exploration of mechanism. Up to now, the reaction mechanism is still not clear. The reaction mechanism is the foundation of catalyst optimization and solvent design, and it could provide theoretical evidence for it. Based on this, the reaction mechanism might make a breakthrough by computational simulations and theoretical calculations (i.e. molecular dynamics, quantum mechanics and density functional theory).

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

BMF: 5-Bromomethylfurfural; CMF: 5-Chloromethylfurfural; DESs: Deep eutectic solvents; DMSO: Dimethyl sulfoxide; EG: Ethyl glucoside; 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; HPW: $H_3PW_{12}O_{40}$; ILs: Ionic liquids; MeCN: Methyl cyanide; MOFs: Metal-Organic Frameworks; THF: Tetrahydrofuran

Acknowledgements

We would like to acknowledge Dr. Jonathan Sperry from the Centre for Green Chemical Science, University of Auckland, New Zealand for his English refinery on this work.

Availability of data and materials

Not applicable.

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.

Funding

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (Nos. 21978248, 21676223), the special fund for Fujian Ocean High-Tech Industry Development (No. FJHJF-L-2018-1), China, the Natural Science Foundation of Fujian Province of China (No.2019J06005), and the Energy development Foundation of the College of Energy, Xiamen University (No. 2017NYFZ02).

Competing interests

The authors declare that they have no competing interests.

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Received: 8 October 2019 Accepted: 27 February 2020

Published online: 11 March 2020

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