

Review Article

Catalytic Synthesis of the Biofuel 5-Ethoxymethylfurfural (EMF) from Biomass Sugars

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A new generation of bioplateform molecule 5-ethoxymethylfurfural (EMF) has excellent energy density and combustion performance, which makes it a potential fuel additive. This article reviews the factors that affect the production of EMF from different feedstocks, including platform compounds, monosaccharides, polysaccharides, and raw lignocellulosic biomass. Focus is placed on discussing the catalytic efficiency with pros and cons of different acid catalysts, including homogeneous catalysts (i.e., liquid acids and metal salts), heterogeneous catalysts (i.e., zeolites, heteropolyacid-based hybrids, and SO₃H-based catalysts), ionic liquids, mixed acid catalysts, and deep eutectic solvents (DESs). Except for the commonly used ethanol solvent, this review also summarizes the influence of the cosolvent system (e.g., ethanol/dimethylsulfoxide (DMSO), ethanol/tetrahydrofuran (THF), and ethanol/ γ -valerolactone (GVL)) on the EMF yield.

1. Introduction

The current production of fuels and chemicals is mainly based on nonrenewable fossil resources, such as coal and petroleum. With the increasing depletion of nonrenewable energy and the growing demand for energy by human beings, it is an urgent priority task to develop and utilize green and renewable energy [1, 2]. Biomass is a new kind of sustainable resource on the earth that can replace fossil resources to obtain fuel and chemicals [3–6]. Meanwhile, it is widespread, abundant, diverse, and inexpensive [7]. To propose the development of a biorefinery plant, 12 platform chemicals derived from biomass substrates have been delimited by the US Department of Energy [8], such as hexoses, pentoses [9], 5-hydroxymethylfurfural (HMF) [10], EMF [11], levulinic acid (LA) [12], and ethyl levulinate (EL)

[13]. In order to obtain biofuels from carbohydrates, researchers have developed many methods, such as thermochemical treatment, enzymatic catalysis, and chemical catalysis [14–16].

Among these biofuels, EMF shows excellent physical and chemical properties and is considered as a prospective fuel additive and transportation fuel [17]. The high boiling point of EMF (235°C) is comparable to that of petrol (30–220°C), and its energy density (30.3 MJ/L) is significantly higher than that of ethanol (23.5 MJ/L) and proximate to that of diesel fuel (33.6 MJ/L) and regular petrol (31.3 MJ/L) [18, 19]. EMF has a high cetane number and superior oxidation stability, because of which it can significantly reduce the emission of harmful particles and sulfides such as NO_x, SO₂, CO₂, and CH₄ [20]. 17wt% EMF was added to commercial gasoline. This mixed diesel was used to test engine performance and

showed good results with a 16% reduction in soot [21]. In addition, EMF can also be used as a reaction substrate for the synthesis of other industrially significant chemicals. EMF can synthesise 5-ethoxymethylfurfuryl alcohol, dimethyltetrahydrofuran, and 2,5-diethoxymethylfuran through a one-step or multistep hydrogenation reaction [22, 23]. EMF can also be converted into cyclopentenone in a stereoselective way via the Piancatelli rearrangement reaction [24]. In the process of EMF synthesis reaction, the ring is usually further opened to generate the high value-added chemical EL [25]. Meanwhile, EMF can also be used as an additive for beer flavor and aroma [26].

Currently, the mainstream synthesis path of EMF is the use of an acid catalyst to promote biomass sugars (e.g., fructose, glucose, and inulin) being converted via cascade reactions such as hydrolysis, dehydration, and etherification under the ethanol system. Although the feedstocks are different, the most classic method is the utilization of fructose as the raw material to synthesise EMF. The involved reaction mechanism is shown in Scheme 1. It is worth noting that EMF can also be obtained directly by etherification of HMF. Meanwhile, changing the solvent system to obtain a high yield of EMF has also been explored in the past few years. This paper reviewed recent research on the use of biomass sugar conversion to synthesise EMF and focused on the effects of different feedstocks, catalysts, and solvent systems on the yield of EMF.

2. The Synthesis of EMF

In the process of synthesising EMF, catalysts, raw materials, and solvents are the key components in the reaction system. Acids are important and regular catalysts to catalyze biomass conversion into platform chemicals and advanced biofuels. Therefore, EMF can be produced by the etherification of HMF in an ethanol medium with an acid catalyst as motivation. Scheme 2 shows the reaction pathways of EMF synthesis from ethanolysis of carbohydrates (e.g., fructose, glucose, sucrose, and cellulose).

With a “one-pot” method, direct assembly of EMF from disaccharides, polysaccharides, and biomass sugars shows obvious advantages in the economy and less energy intensity. This method can reduce the cost and steps of intermediate separation and purification [27–29]. But, it always has a relatively lower yield of EMF from these complex carbohydrates, compared with fructose, HMF, 5-chloromethylfurfural (CMF), and 5-bromomethylfurfural (BMF) [29–33]. Also, EMF can be prepared by nucleophilic substitution of BMF and CMF [34, 35] or etherification of HMF in ethanol [36, 37]. Among the three chemical platform molecules, HMF is the most commonly used one for the preparation of EMF. Transformation of disaccharides, polysaccharides, and biomass sugars into platform compounds (e.g., HMF, CMF, and BMF) typically undergoes hydrolysis, isomerization, esterification, chlorination, and etherification. The lengthy chemical reaction process will increase energy consumption and result in more byproducts, which is the cause of the low yield of EMF. For example, cellulose as a feedstock undergoes at

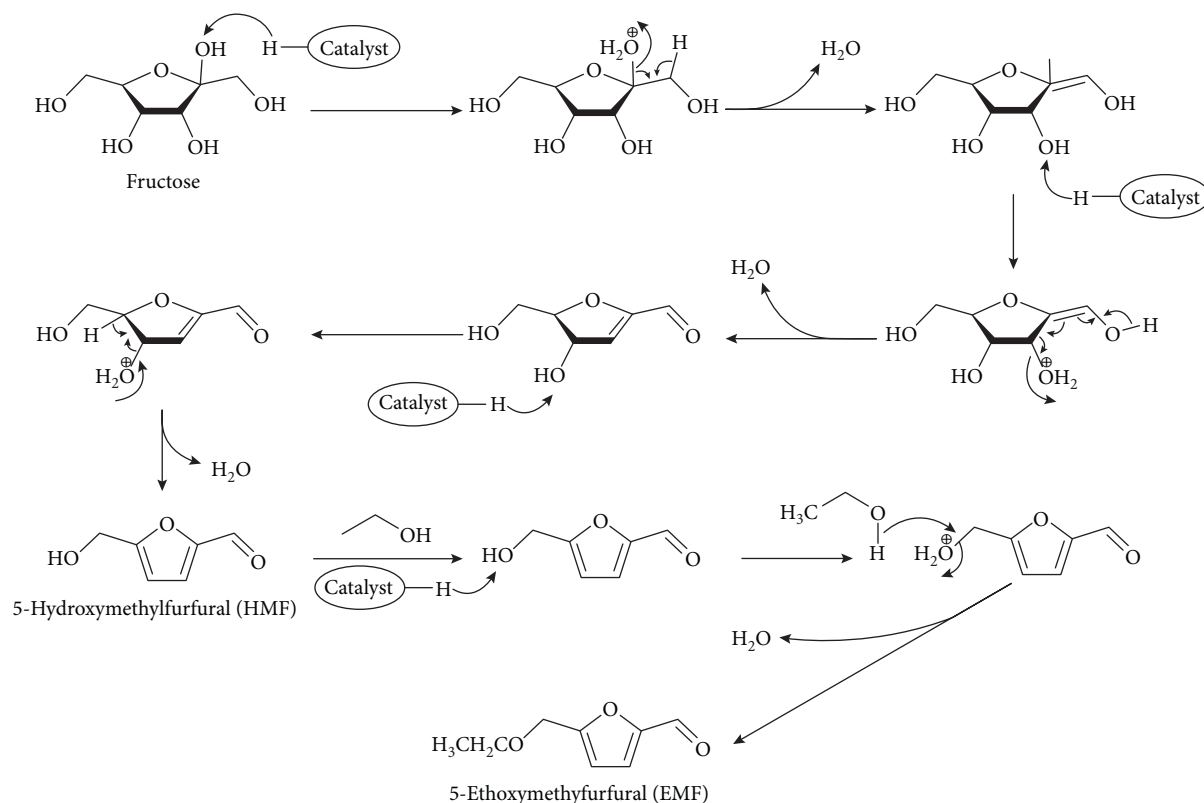
least four steps to synthesise EMF. First, cellulose is hydrolyzed to glucose, and then, fructose comes from glucose isomerization, followed by dehydration of three H₂O molecules to give HMF. Finally, EMF is synthesised by etherification of HMF [38, 39]. Because of the multiple steps required for the synthesis of EMF, side reactions are more likely to occur, which convert intermediate products into other byproducts or humins.

3. Feedstocks

Currently, the feedstocks for the formation of EMF are mainly divided into four types based on the difference in reaction pathways. (i) EMF is prepared by directly etherifying platform compounds, such as HMF, BMF, and CMF [29–32]. (ii) Monosaccharides such as fructose and glucose are dehydrated to HMF followed by etherification to synthesise EMF under acidic conditions [40, 41]. (iii) Disaccharides and polysaccharides such as starch, sucrose, cellobiose, inulin, and cellulose are used to produce EMF via the steps of hydrolysis, isomerism, dehydration, and etherification [29, 41–44]. (iv) Lignocellulosic biomass such as corn stover, cassava, and sugarcane bagasse is directly converted to EMF through a “one-pot” method [45, 46]. The results of different feedstocks used to produce EMF are summarized in Table 1.

3.1. Platform Molecules. The platform molecules such as HMF, BMF, and CMF all have a furan ring and an aldehyde group, which can be used to transform and prepare a variety of biofuels and fine chemicals. HMF can usually be directly etherified in an ethanol medium in the presence of an acid catalyst to obtain EMF. Also, HMF is composed of a furan ring, an aldehyde group, and a hydroxymethyl group, which makes its chemical properties active. Due to the excellent characteristics of HMF, many studies have proved that a high EMF yield (ca. 90%) can be obtained from it. Yang et al. [11] explored a niobium-molybdate solid acid that was recyclable and had a multilayer structure. The authors utilized this catalyst to promote HMF being transformed into EMF at 100°C for 12 h. Surprisingly, the highest yield of EMF was over 99%. Another high yield of EMF was 92.9% from HMF at 100°C for 5 h with AlCl₃ in ethanol [47]. However, the high cost of HMF limits the feasibility of its industrial application.

3.2. Monosaccharides. Fructose and glucose are the main monosaccharide raw materials for the formation of EMF. Generally, the yield of EMF is higher when fructose is used as raw material. Karnjanakom et al. [27] used Zn-S-C to transform fructose into EMF (95.5% yield) in an ethanol solvent with tetrahydrofuran (THF) as a cosolvent under the optimal conditions (98°C, 47 min). However, glucose as a substrate always leads to a low yield of EMF (10%–40%) [44, 47–49] due to the effect of the speed limit of glucose being isomerized into fructose. Xin et al. [48] used a composite catalyst consisting of PTSA-POM and AlCl₃·6H₂O to catalyze glucose into EMF, and the yield was only 30.6%.



SCHEME 1: The reaction mechanism involved in the conversion of fructose to EMF.

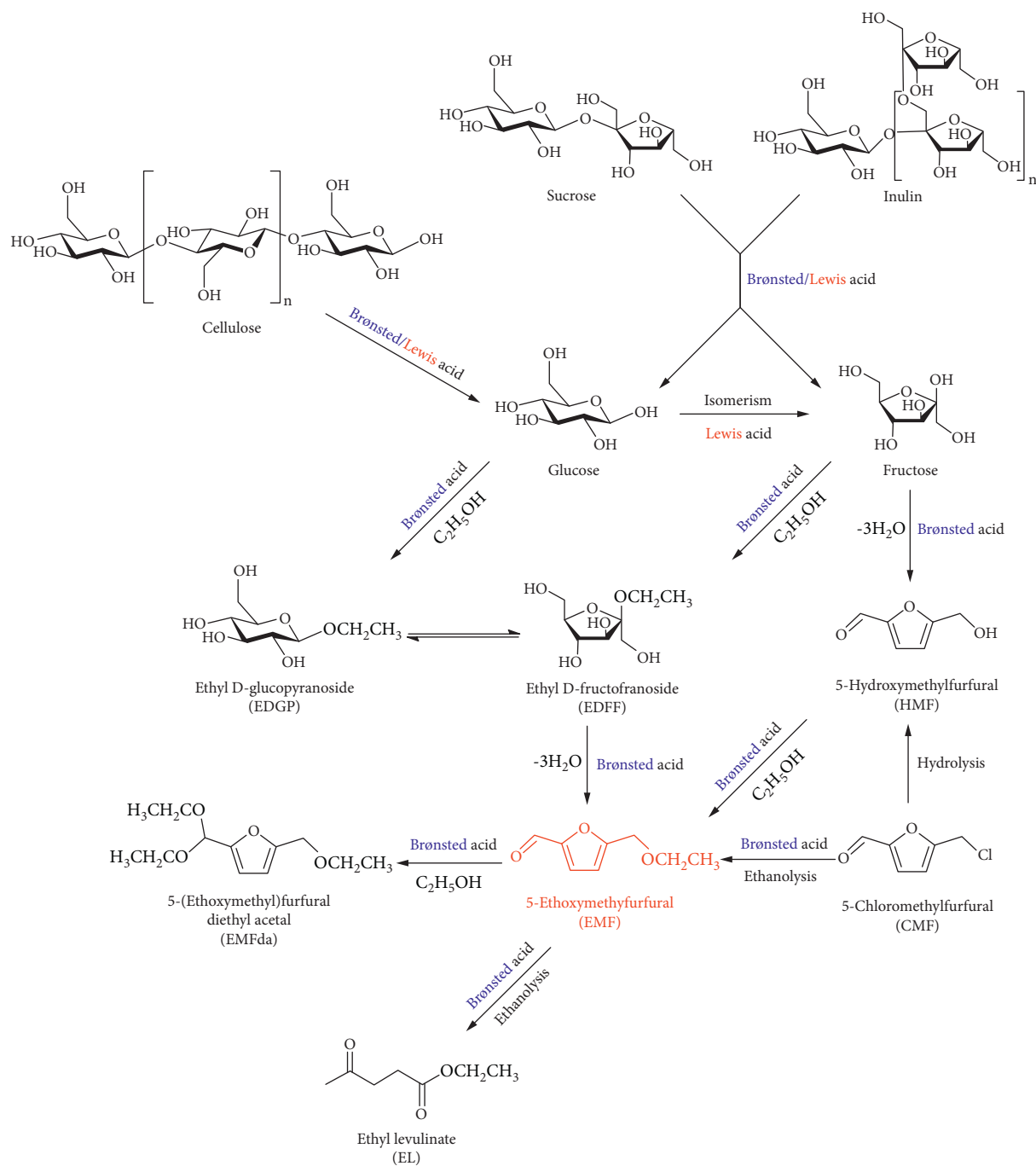
3.3. Di- and Polysaccharides. When using biomass sugars such as sucrose, inulin, and starch as feedstocks to produce EMF, a higher content of fructose molecules in the internal biomass sugars is positively correlated with the yield of EMF. One molecule of inulin is composed of one unit of glucose and 1–59 units of fructose, and the obtained yield of EMF is between 55% and 80% [49–52]. Furthermore, one molecule of sucrose comprises one unit of glucose and one unit of fructose, with a fructose content of 50% that is lower than inulin, and its yield of EMF is between 10% and 45% [53–56]. The hydrolysate of starch [28, 50], cellobiose [50, 51, 56], and cellulose [51, 52] is glucose, so the EMF yield of these substrates is generally low. From Scheme 2, we can know that glucose-based carbohydrates (starch, cellobiose, and cellulose) have two ways to convert glucose into EMF. These carbohydrates are initially hydrolyzed into glucose. Then, two possible ways may be involved: (i) fructose prepared by isomerizing glucose is dehydrated to EMF and (ii) glucose is esterified to ethyl-D-glucopyranoside (EDGP) in an ethanol medium in the presence of Brønsted acid followed by isomerization to ethyl-D-fructofuranoside (EDFF) and final dehydration to produce EMF.

3.4. Lignocellulosic Biomass. Lignocellulosic biomass has widespread, abundant, and inexpensive advantages. It is, therefore, regarded as an appealing and promising alternative to produce EMF [16]. At present, the raw materials used to directly prepare EMF from waste biomass are mainly sugarcane bagasse, corn stover, and cassava. Dutta et al. [53] used $\text{Zr}(\text{O})\text{Cl}_2\text{-CrCl}_3$ metal chloride catalysts to produce EMF (21.6% yield) from

sugarcane bagasse in ethanol-[BMIM]Cl at 120°C for 15 h. A relatively satisfactory EMF yield (23.9%) was detected from corn stover at 210°C for 125 min by using a mixed acid catalyst (0.1% H_2SO_4 and zeolite USY) [45]. In addition, Tan et al. [46] selected some sulfates such as $\text{Al}_2(\text{SO}_4)_3$, $\text{Fe}_2(\text{SO}_4)_3$, NaHSO_4 , MgSO_4 , ZnSO_4 , and NiSO_4 to catalyze the synthesis of EMF from cassava, and the obtained yield of EMF was 0.36%, 3.01%, 4.43%, 0.09%, 3.25%, and 11.04%, respectively. In general, when using lignocellulosic biomass as the feedstock, the yield of EMF is very low, possibly attributed to the complex structure of lignocellulosic biomass, which reduces the catalyst accessibility. Therefore, researchers should focus on the recycling of lignocellulosic biomass and explore more effective catalysts.

4. Catalysts

A catalyst is an indispensable and significant component in the catalytic system. The preparation of EMF with carbohydrates as raw materials usually needs to be carried out under the action of acid catalysts. Acid catalysts can stimulate some necessary reactions such as hydrolysis of disaccharides and polysaccharides to fructose and glucose, glucose isomerization, fructose dehydration, and HMF etherification. Furthermore, it is indicated that the ratio of Lewis acid and Brønsted acid can influence the selectivity of EMF, and Brønsted acid plays a very imperative part in catalyzing the reaction of carbohydrates and HMF to prepare EMF [28, 48, 57, 58]. Nowadays, both homogeneous catalysts and heterogeneous catalysts have been developed to be widely used in this reaction.



SCHEME 2: The reaction paths of synthesising EMF from carbohydrates.

4.1. Homogeneous Catalysts. Homogeneous acid catalysts have excellent catalytic performance in etherification, dehydration, and other reactions and are superior choices for catalytic synthesis of EMF. The synthesis of EMF by homogeneous catalysts from different carbohydrates is summarized in Table 2, including liquid acids and metal salts.

4.1.1. Liquid Acid Catalysts. Liquid acids such as H₂SO₄, HCl, and H₃PO₄ are the typical homogeneous catalysts. Their excellent catalytic performance is due to their uniform

distribution in the solvent, which can increase the accessibility of the catalyst and substrate. H₂SO₄ is most frequently used in the process of biomass alcoholysis. Balakrishnan et al. [21] used a low concentration of H₂SO₄ (10 mol%) to obtain EMF from fructose with an acceptable yield (70%). When replacing fructose with HMF, they obtained a higher EMF yield (81%) by H₂SO₄ (5 mol%) in ethanol. Another high yield of EMF was also observed at 79.8% for 5 mol% H₂SO₄ with 100% conversion of HMF [59]. Although a higher EMF yield can be obtained when H₂SO₄ is used as a catalyst, there are some obstructions: (i) High

TABLE 1: Catalytic preparation of EMF from various feedstocks.

Entry	Feedstock	Catalyst	Solvent	Reaction condition	Yield (%)	Ref.
1	Fructose	$H_{1.15}Nb_{1.15}Mo_{0.85}O_6$	Ethanol	100°C, 1 h	67	[11]
2	HMF	$H_{1.15}Nb_{1.15}Mo_{0.85}O_6$	Ethanol	100°C, 1 h	>99	[11]
3	HMF	$AlCl_3$	Ethanol	100°C, 5 h	92.9	[47]
4	Glucose	$AlCl_3$	Ethanol	100°C, 11 h	38.4	[47]
5	Fructose	$AlCl_3$	Ethanol	100°C, 11 h	71.2	[47]
6	Fructose	Zn-S-C	Ethanol/THF	98°C, 42 min	95.5	[27]
7	Sucrose	Zn-S-C	Ethanol/THF	98°C, 42 min	93.5	[27]
8	Glucose	Zn-S-C	Ethanol/THF	98°C, 42 min	80.9	[27]
9	Inulin	Zn-S-C	Ethanol/THF	98°C, 42 min	64.8	[27]
10	Inulin	GO	Ethanol/DMSO	130°C, 24 h	71	[44]
11	Fructose	GO	Ethanol/DMSO	130°C, 24 h	3	[44]
12	Sucrose	GO	Ethanol/DMSO	130°C, 24 h	66	[44]
13	Glucose	GO	Ethanol/DMSO	130°C, 24 h	34	[44]
14	Glucose	PTSA-POM/ $AlCl_3 \cdot 6H_2O$	Ethanol/ H_2O	150°C, 30 min	30.6	[48]
15	Glucose	PU-Cat	Ethanol/1, 4-dioxane	140°C, 4 h	9.2	[49]
16	Sucrose	PU-Cat	Ethanol/1, 4-dioxane	140°C, 4 h	31.3	[49]
17	Inulin	PU-Cat	Ethanol/1, 4-dioxane	140°C, 4 h	58.1	[49]
18	Starch	$Al_2(SO_4)_3/H_3PO_4$	Ethanol/DMSO	170°C, 10 h	34.3	[28]
19	Starch	BFC-3	Ethanol/THF	100°C, 12 h	28.8	[50]
20	Cellobiose	BFC-3	Ethanol/THF	100°C, 10 h	37.1	[50]
21	Cellobiose	PSDVB- SO_3H	Ethanol	120°C, 2 h	Trace	[51]
22	Cellulose	H_2SO_4	Ethanol	200°C, 1.5 h	3.05	[52]
23	Corn stover	$H_2SO_4(0.1 \text{ wt } \%) / USY$	Ethanol	210°C, 2 h	23.9	[45]
24	Cassava	$NiSO_4$	Ethanol	200°C, 6 h	11.04	[46]
25	Cassava	$NaHSO_4$	Ethanol	200°C, 6 h	4.43	[46]
26	Bagasse	$Zr(O)Cl_2/CrCl_3$	Ethanol/[BMIM]Cl	120°C, 15 h	21.6	[53]

TABLE 2: Various homogeneous catalysts used for EMF synthesis.

Entry	Catalyst	Feedstock	Solvent	Reaction condition	Yield (%)	Ref.
1	5 mol% H_2SO_4	HMF	Ethanol	75°C, 24 h	81	[21]
2	10 mol% H_2SO_4	Fructose	Ethanol	100°C, 24 h	70	[21]
3	H_2SO_4	HMF	Ethanol	70°C, 18 h	79.8	[59]
4	$FeCl_3$	Fructose	Ethanol/[Bmim]Cl	120°C, 10 h	39.9	[60]
5	$AlCl_3 \cdot 6H_2O$	HMF	Ethanol/ H_2O	160°C, 15 min	70	[61]
6	$AlCl_3 \cdot 6H_2O$	Fructose	Ethanol/ H_2O	160°C, 15 min	46	[61]
7	$AlCl_3 \cdot 6H_2O$	Glucose	Ethanol/ H_2O	160°C, 15 min	33	[61]
8	$AlCl_3 \cdot 6H_2O$	Ethyl glucoside	Ethanol/ H_2O	160°C, 15 min	27	[61]
9	$CuCl_2 \cdot 2H_2O$	Fructose	Ethanol	100°C, 12 h	12	[62]
10	$NiCl_2 \cdot 6H_2O$	Fructose	Ethanol	100°C, 12 h	5	[62]
11	$SnCl_4 \cdot 5H_2O$	Fructose	Ethanol	100°C, 12 h	23	[62]
12	$FeCl_3$	Fructose	Ethanol	100°C, 12 h	28	[62]
13	$CrCl_3 \cdot 6H_2O$	Fructose	Ethanol	100°C, 12 h	33	[62]
14	$AlCl_3$	Fructose	Ethanol	140°C, 10 h	45	[63]
15	$CuCl_2$	Fructose	Ethanol	140°C, 10 h	34.7	[63]
16	$FeCl_3$	Fructose	Ethanol	140°C, 10 h	24.7	[63]
17	$CrCl_3$	Fructose	Ethanol	140°C, 10 h	36.9	[63]
18	$Al_2(SO_4)_3$	Fructose	Ethanol	140°C, 10 h	20.8	[63]
19	$CuSO_4$	Fructose	Ethanol	140°C, 10 h	14.7	[63]
20	$Fe_2(SO_4)_3$	Fructose	Ethanol	140°C, 10 h	18.2	[63]
21	$Cr_2(SO_4)_3$	Fructose	Ethanol	140°C, 10 h	0.5	[63]
22	$AlCl_3 \cdot 6H_2O$	Fructose	Ethanol	110°C, 5 h	25.8	[64]
23	$AlCl_3 \cdot 6H_2O / BF_3 \cdot (Et)_2O$	Fructose	Ethanol	110°C, 3 h	55	[64]
24	$AlCl_3 \cdot 6H_2O / B(OH)_3$	Fructose	Ethanol	110°C, 3 h	22	[64]
25	$AlCl_3 \cdot 6H_2O / NaF$	Fructose	Ethanol	110°C, 3 h	25.1	[64]
26	$AlCl_3 \cdot 6H_2O / NaCl$	Fructose	Ethanol	110°C, 3 h	28.9	[64]
27	$AlCl_3 \cdot 6H_2O / NaBr$	Fructose	Ethanol	110°C, 3 h	26.3	[64]

concentrations of liquid acids will corrode the equipment. (ii) A low concentration of liquid acids requires harsh reaction conditions such as higher pressure and higher temperature. (iii) The product separation is a significant issue. (iv) Liquid acids will cause environmental pollution.

4.1.2. Metal Salt Catalysts. Metal salts exhibit excellent catalytic performance and low toxicity in catalytic chemical reactions. As Lewis acid catalysts, they have been widely used to catalyze the conversion of carbohydrates to EMF in recent years. A series of metal salts, mainly including metal chlorides and sulfates, have been investigated, such as AlCl_3 , CuCl_2 , FeCl_3 , CrCl_3 , SnCl_4 , NiCl_2 , $\text{Al}_2(\text{SO}_4)_3$, CuSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, and $\text{Cr}_2(\text{SO}_4)_3$. A normal metal chloride (FeCl_3) was used to discuss the effects of different reaction temperatures and time on the yield of EMF in a cosolvent system (ethanol and ionic liquid [Bmim]Cl) by Zhou et al. [60]. When the temperature was raised from 80°C to 120°C , the yield of EMF increased from 6.4% to 39.9%, but there was still a problem of low yield. Yang et al. [61] utilized $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ as an efficient catalyst to obtain EMF from various carbohydrates (i.e., glucose, ethyl glucoside, fructose, and HMF) in an ethanol-water mixture at 160°C for 15 min. Glucose, ethyl glucoside, and fructose gave a moderate EMF yield of 33%, 27%, and 46%, respectively. However, a relatively high EMF yield (70%) was detected from HMF. Another study showed a satisfactory EMF yield (92.9%) from HMF by using AlCl_3 . Various metal chlorides (i.e., $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, FeCl_3 , and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) were also investigated as catalysts to synthesise EMF, but all with low EMF yields [62]. According to the research of Yu et al. [63], except metal chlorides, metal sulfates were also used to synthesise EMF from fructose in an ethanol medium, but with a disappointing yield (0.5%–20.8%) that is even lower than that of metal chlorides. It can be found that AlCl_3 obtained the highest yield of EMF (45%), while $\text{Fe}_2(\text{SO}_4)_3$ produced the highest EL yield (56.8%). These research studies indicate that AlCl_3 can be a better option for metal salt catalysts in the synthesis of EMF from different carbohydrates. In an effort to improve the catalytic activity of AlCl_3 , a cocatalyst system was explored by Jia et al. [64] which consists of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and a cocatalyst (i.e., $\text{BF}_3 \cdot (\text{Et})_2\text{O}$, $\text{B}(\text{OH})_3$, NaF , NaCl , and NaBr), and the molar ratio of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ /cocatalyst was 1:1. When $\text{B}(\text{OH})_3$ and NaF were used as cocatalysts, the yield of EMF had a slight reduction to 22% and 25.1%, respectively. On the other hand, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (25.8%) with $\text{BF}_3 \cdot (\text{Et})_2\text{O}$, NaCl , and NaBr as cocatalysts could all improve the EMF yield; especially, $\text{BF}_3 \cdot (\text{Et})_2\text{O}$ had the highest EMF yield (55%).

Currently, the use of homogeneous catalysts to prepare EMF has a relatively mature system and higher yields. However, due to a large number of byproducts from homogeneous acid catalysts, the corrosion of the equipment and the high requirements for reaction conditions have restricted their use in industry. Therefore, green, economical, and recyclable heterogeneous catalytic systems have great potential in this field [27, 55, 65–68].

4.2. Heterogeneous Catalysts. Heterogeneous catalysts have been the focus of research in recent years, which have the advantages of being easily separated from the reaction system, not corroding equipment, superior recyclability, and excellent thermal stability [69]. In addition, heterogeneous catalysts can be modified in the process of preparation to obtain more excellent catalytic performance, such as adjustable Lewis acid sites and Brønsted acid sites or specific surface areas [67]. In the process of biomass ethanolysis to produce EMF, the main heterogeneous catalysts include zeolites, heteropolyacids-based hybrids, and sulfonic acid-functionalized catalysts, which are summarized in Table 3.

4.2.1. Zeolite Catalysts. Zeolite is also known as a molecular sieve catalyst, which is either a natural or synthetic chemical substance with a network structure. With the development of ZSM-5 molecular sieves as a catalyst, such catalysts (e.g., MCM-41, SBA-15, and USY) have received widespread attention. In recent years, researchers have applied these catalysts for the synthesis of EMF [80].

Zeolites are solely used to catalyze a reaction, typically with poor catalytic performance. Therefore, zeolites can be modified to obtain high-efficiency catalysts with different specific surface areas, different acidity, and alkalinity. For instance, Liu et al. [70] successfully loaded different concentrations of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW) onto MCM-41. They found that the yield of EMF by MCM-41 was only at a very weak concentration (0.2%). However, when the MCM-41 was loaded with 40 wt% of $\text{H}_3\text{PW}_{12}\text{O}_{40}$, the achieved EMF yield was 83.4%. The high yield of EMF achieved by MCM-41-HPW loaded with 40 wt% $\text{H}_3\text{PW}_{12}\text{O}_{40}$ could be attributed to its strong acidity, with an E_i value of 667 mV. In addition, Che et al. [71] used MCM-41 nanospheres (M-Ns) and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (HSiW) to synthesise a mesoporous nanosphere catalyst (HSiW/M-Ns). They measured the acid strength of various acids, and the order was $\text{HSiW} \approx \text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW) > H_2SO_4 > PTSA > H_3PO_4 . Then, they used 20 wt% ~ 60 wt% HSiW/M-Ns and these acids to transform HMF into EMF. The results show that the highest conversion of HMF (92%) and selectivity of EMF (84.1%) could be obtained by using 40 wt% HSiW/M-Ns. The conversion rate lower than that of HSiW/M-Ns by other acids indicated that tungstosilicate anion and acid strength could promote HMF conversion and increase EMF selectivity. Lanzafame et al. [81] synthesised a sequence of Al-MCM-41 zeolites which had a mesoporous structure and different Si/Al ratios, and ZrO_2 introduced into the SBA-15, named Z-SBA-15, could both obtain higher EMF yields from HMF. This is because these catalysts had remarkable Lewis acid sites and Al^{3+} sites were isolated outside the framework. Through the sulfonation modification of SBA-15, the catalyst Ar- SO_3H -SBA-15 was prepared by Morales et al. [66]. A maximum EMF yield (63.4%) was obtained from fructose over Ar- SO_3H -SBA-15 at 116°C for 4 h in a cosolvent system with ethanol and DMSO. The excellent catalytic capability of Ar- SO_3H -SBA-15 was due to the combination of outstanding structural properties and the surface concentration of acid sites and strength. Zeolite USY was also used for EMF

TABLE 3: Various heterogeneous catalysts used for EMF synthesis.

Entry	Catalyst	Feedstock	Solvent	Reaction condition	Yield (%)	Ref.
1	MCM-41	HMF	Ethanol	100°C, 12 h	0.2	[70]
2	10 wt.% MCM-41-HPW	HMF	Ethanol	100°C, 12 h	25.8	[70]
3	20 wt.% MCM-41-HPW	HMF	Ethanol	100°C, 12 h	49.3	[70]
4	40 wt.% MCM-41-HPW	HMF	Ethanol	100°C, 12 h	83.4	[70]
5	20% HSiW/M-Ns	HMF	Ethanol	90°C, 2 h	70.1	[71]
6	40% HSiW/M-Ns	HMF	Ethanol	90°C, 4 h	77.4	[71]
7	60% HSiW/M-Ns	HMF	Ethanol	90°C, 2 h	65.6	[71]
8	Ar-SO ₃ H-SBA-15	Fructose	Ethanol/DMSO	116°C, 4 h	63.4	[66]
9	USY	Fructose	Ethanol	120°C, 25 min	73.8	[72]
10	USY	Corn stover	Ethanol/THF	168°C, 175 min	21.8	[38]
11	H ₃ PW ₁₂ O ₄₀	Fructose	Ethanol/THF	130°C, 30 min	76	[55]
12	H ₃ PW ₁₂ O ₄₀	Sucrose	Ethanol/THF	130°C, 30 min	33	[55]
13	H ₃ PW ₁₂ O ₄₀	Inulin	Ethanol/THF	130°C, 30 min	62	[55]
14	Fe ₃ O ₄ @SiO ₂ -HPW	HMF	Ethanol	150°C, 11 h	83.6	[73]
15	Fe ₃ O ₄ @SiO ₂ -HPW	Fructose	Ethanol	100°C, 24 h	54.8	[73]
16	30 wt.% K-10 clay-HPW	HMF	Ethanol	100°C, 10 h	91.5	[31]
17	30 wt.% K-10 clay-HPW	Fructose	Ethanol	100°C, 10 h	61.5	[31]
18	PY-PW-1	HMF	Ethanol	80°C, 24 h	90	[74]
19	PY-PW-2	HMF	Ethanol	80°C, 24 h	70	[74]
20	TEA-PW-1	HMF	Ethanol	80°C, 24 h	59	[74]
21	TEA-PW-2	HMF	Ethanol	80°C, 24 h	43	[74]
22	Silica-SO ₃ H	HMF	Ethanol	100°C, 24 h	83.8	[56]
23	Silica-SO ₃ H	Fructose	Ethanol	100°C, 24 h	63.1	[56]
24	Silica-SO ₃ H	Sucrose	Ethanol	100°C, 24 h	34.9	[56]
25	Silica-SO ₃ H	Inulin	Ethanol	100°C, 24 h	60.7	[56]
26	OMC-SO ₃ H	Fructose	Ethanol	140°C, 24 h	55.7	[75]
27	OMC-SO ₃ H	Sucrose	Ethanol	140°C, 24 h	26.8	[75]
28	OMC-SO ₃ H	Inulin	Ethanol	140°C, 24 h	53.6	[75]
29	T-CeMOF	Fructose	Ethanol/DMSO	130°C, 16 h	69.6	[76]
30	FW-SO ₃ H	Fructan-rich food	Ethanol	140°C, 4 h	49.4	[77]
31	FW-SO ₃ H	Fructan-rich food	Ethanol/DMSO	140°C, 4 h	52.1	[77]
32	FW-SO ₃ H	Fructan-rich food	Ethanol/THF	140°C, 4 h	35.7	[77]
33	FW-SO ₃ H	Fructan-rich food	Ethanol/H ₂ O	140°C, 4 h	48.7	[77]
34	FW-SO ₃ H	Fructan-rich food	Ethanol/DMSO/H ₂ O	140°C, 4 h	30.4	[77]
35	D-SPC	Fructose	Ethanol/THF	140°C, 18 h	68.8	[67]
36	PDVTA-SO ₃ H	HMF	Ethanol	110°C, 30 min	87.7	[78]
37	MCC-SO ₃ H	Fructose	Ethanol	120°C, 16 h	63.2	[79]
38	MCC-SO ₃ H	Sucrose	Ethanol	120°C, 16 h	32.5	[79]
39	MCC-SO ₃ H	Inulin	Ethanol	120°C, 16 h	51.3	[79]

synthesis. Xu et al. [72] and Chen et al. [38] used USY to obtain 73.8% and 21.8% of EMF from fructose in the ethanol system and corn stover in the ethanol/THF system, respectively.

4.2.2. Heteropolyacid-Based Hybrid Catalysts.

Heteropolyacids (HPAs) are a type of oxygen-containing polyacids composed of heteroatoms (e.g., P, Si, Fe, and Co) and polyatoms (e.g., Mo, W, V, Nb, and Ta) by oxygen atom bridging connections in a certain structure [82]. HPAs have the following advantages when they are used as catalysts. Under mild conditions, they exhibit fast and reversible multielectron redox conversion and provide a strong Brønsted acidity [83]. Due to these excellent properties, HPAs are widely used in the preparation of EMF.

Yang et al. [55] used fructose, sucrose, and inulin as substrates to synthesise EMF under the conditions of microwave heating at 130°C within 30 min with H₃PW₁₂O₄₀ as

a catalyst. After continuous improvement of the tested plan, the solvent was changed from ethanol to a cosolvent system with THF, and the EMF yield increased from 65% to 76% using fructose as the substrate. However, most HPAs are soluble acids, so they are difficult to separate, inconvenient for recycling, and easily corrode equipment. To overcome this trouble, many researchers loaded HPAs onto solid supports to form load-type HPAs. A load-type HPA (H₄SiW₁₂O₄₀/MCM-41) was obtained by loading H₄SiW₁₂O₄₀ on nano-MCM-41, and a satisfactory EMF yield (92% HMF conversion and 84.1% EMF selectivity) was obtained [71]. Furthermore, to better recover the catalyst, the catalyst can be magnetized by adding Fe₃O₄ into it. Wang et al. [73] first embedded Fe₃O₄ in silica to form silica-coated Fe₃O₄ nanoparticles, and then, HPW was loaded on it to synthesise Fe₃O₄@SiO₂-HPW with both catalytic activity and magnetic properties. They employed Fe₃O₄@SiO₂-HPW to catalyze HMF into EMF with a high yield (83.6%) and observed a moderate EMF yield (54.8%) from fructose. The

K-10 clay-HPW catalyst was prepared by fixing HPW on K-10 clay as a carrier and used in the reaction process for the conversion of fructose and HMF to EMF by Liu et al. [31]. The EMF yield was 91.5% after 10 h for 100°C from HMF, and another was 61.5% after 24 h for 100°C from fructose through a one-pot method. Organic-heteropolyacid (organic-HPA) hybrids can be prepared by simple self-assembly of electrostatic interactions [84]. Wang et al. [74] used HPW and pyridine (PY) or triethylamine (TEA) through the self-assembly method to prepare a string of organic-inorganic acidic hybrids (PY-HPW-x and TEA-HPW-x). PY-HPW-1 had higher acidity and a tiny particle size and exhibited great catalytic performance for HMF to EMF (90%) under 80°C after 24 h. Carbonaceous materials as supporters to accept HPAs were reported by García-Bosch et al. [85]. They loaded 15 wt% phosphotungstic acid (TPA) or tungstosilicic acid (STA) onto activated carbon (AC) and graphite (HSAG) to prepare the catalysts TPA-AC/HSAG and STA-AC/HSAG. They exploited STA-HSAG to get nearly a 50% yield of EMF + EMFDA from fructose in ethanol. Here is a noteworthy research, which obtained the highest EMF yield (over 99%) and 100% HMF conversion, by Yang et al. [11]. They accurately adjusted the content of niobium and molybdenum to prepare a series of layered-niobium-molybdate solid acids, which could control the amount of Brønsted acid and mezzanine space coupled with clear Lewis acid sites.

4.2.3. SO₃H-Based Catalysts. Brønsted acid has a significant catalytic performance that can etherify HMF into EMF and the alcoholysis of fructose and other carbohydrates to form EMF. Sulfuric acid is a typical Brønsted acid; therefore, the introduction of sulfonic acid groups into the supporters to obtain solid-SO₃H-based catalysts is an effective program, especially for the preparation of EMF [86]. A proton acid solid catalyst with high acidity can be produced by loading sulfonic acid groups onto supporters, which is defined as a -SO₃H-based catalyst. These typical catalysts have many advantages such as high catalytic capability, easy separation and recycling, no-corrode equipment, and environmental friendliness. Furthermore, their catalyst activity can be adjusted by the amount of supported acid [87].

Initially, Liu et al. [56] prepared a silica-SO₃H catalyst, which was obtained by immobilizing sulfonic acid to silica. The catalyst could promote the transformation of HMF, fructose, glucose, sucrose, cellobiose, and inulin into EMF in the presence of a silica-SO₃H catalyst in ethanol. Also, the EMF yields from HMF, fructose, sucrose, and inulin were 83.8%, 63.1%, 34.9%, and 60.7%, respectively. However, glucose and cellobiose as feedstocks detected no EMF. It is indicated that the silica-SO₃H catalyst which had Brønsted acid sites could carry out hydrolysis and etherification reactions but could not isomerize glucose. Morales et al. [66] successfully fabricated a sulfonic acid-functionalized catalyst (Ar-SO₃H-SBA-15) by loading arene sulfonic acid on modified SBA-15 mesostructured silica. They used response surface methodology to optimize the catalyst loading, temperature, and cosolvent concentration (DMSO) of reaction by Ar-SO₃H-SBA-15. The optimal reaction

conditions (116°C, 13.5 mol% catalyst loading, and 8.3 vol% of DMSO for 4 h) could obtain a 63.4% yield of EMF in the medium of ethanol from fructose.

Carbon-based catalysts to hold the sulfonic acid group have been developed by researchers in recent years. Ordered mesoporous carbon (OMC) was used to support chlorosulfonic acid, and a sulfonic acid-functionalized OMC catalyst (OMC-SO₃H) was synthesised by Wang et al. [75]. Fructose, sucrose, and inulin were successfully transformed into EMF by using OMC-SO₃H, and yields of 55.7%, 26.8%, and 53.6% were obtained, respectively, at more severe conditions (140°C, 24 h) in ethanol. Another carbon-SO₃H-based catalyst was prepared by Antunes et al. [88]. They used the reduction of graphene oxide as the carbon-based catalyst and sulfuric acid as the sulfonating agent to prepare the catalyst S-RGO and found that S-RGO had more remarkable catalytic performance than other carbon-SO₃H-based catalysts and the commercial acid resin Amberlyst-15. The high efficiency of the catalyst is due to its different acid sites (-SO₃H, -COOH, and -OH) with the 2D structure of graphene that could enhance the accessibility of the active sites.

A metal-organic framework- (MOF-) derived carbon-SO₃H-based catalyst was prepared by Wang et al. [89]. They utilized Cu-benzene-1,3,5-tricarboxylate (Cu-BTC) as a predecessor to direct pyrolysis and then used sulfuric acid to treat the sample to obtain the C-SO₃H catalyst. A normal yield of 71% for HMF conversion into EMF was detected over C-SO₃H at 100°C for 6 h with ethanol as a solvent. A novel Ce-MOF doped with taurine (T-CeMOF) was fabricated by bonding Ce to 1,3,5-benzenetricarboxylic acid (BTC) also accompanied by the taurine in this system, which transformed fructose into 69.6% EMF at 130°C after 16 h in the ethanol/DMSO medium [76]. Catalyst characterization indicated that the surface of T-CeMOF existed with massive swinging of -COOH, and the -SO₃H of taurine was successfully introduced into T-CeMOF. These were beneficial to the catalytic activity of T-CeMOF in the conversion of HMF to EMF.

Biomass-SO₃H-based catalysts were prepared by Zhao et al. [68] and Wen et al. [90], and they both directly used waste *Camellia oleifera* shells to fabricate biobased sulfonic acid-functionalized catalysts by a hydrothermal sulfonation. These two biomass-SO₃H-based catalysts had spherical microstructures and abundant surface-SO₃H, showing excellent catalytic performance. Simultaneously, the EMF yield was significantly affected by the sulfonation conditions of the biomass-SO₃H-based catalysts preparation process. In addition, lignosulfonate [91], glucose-derived magnetic solid acid [92], food waste-derived solid acid [77], and cellulose sulfuric acid [93] were used as biomass sulfonic acid-functionalized catalysts to obtain EMF.

Organic polymer-based catalysts to support -SO₃H can be used to synthesise a novel solid organic polymer catalyst which includes the sulfonic acid group. Dai et al. [67] reported a sulfonated organic polymer catalyst (D-SPC) which had a special double hydrogen-bonded structure. Also, it was prepared by copolymerization of aniline (AN) and 2,2'-benzidinedisulfonic acid (BDSA) to form SPC and then treated with 1,3-dihydroxypropan-2-one (DHA) to form

D-SPC. They found that DHA bonded with SPC through carbonyl and sulfonic acid groups, forming a hydrogen bond between the two (Scheme 3). Also, adjusting the dosage of DHA, AN, and BDSA could control the acid strength and density of D-SPC that could pick the yield of EMF (68.8%). Xiang et al. [78] also assembled a sulfonic acid-based porous organic polymer (PDVTA-SO₃H); they first synthesised PDVTA by mixing divinylbenzene (DVB) and triallylamine (TAA) by a solvothermal copolymerization method, and then, PDVTA-SO₃H was prepared by the sulfonation process of PDVTA. They used the Box-Behnken response surface method to adjust the reaction conditions and observed a 99.8% HMF conversion and 87.5% EMF yield at 110°C within 30 min.

Magnetic-SO₃H-based catalysts can be simply extracted from the reaction system using a permanent magnet, improving catalyst recovery rate and showing high stability in the cycling experiment. In recent years, the synthesis of magnetic sulfonic acid catalysts by adding magnetic nanoparticles has become the focus. Originally, inspired by the Fe₃O₄@SiO₂-HPW developed by Wang et al. [73], Fe₃O₄@SiO₂-SO₃H NPs were prepared by Zhang et al. [29]. Fe₃O₄@SiO₂-SO₃H was used to convert HMF, fructose, and inulin into EMF, and the yields were 89.3%, 72.5%, and 63.3%, respectively. After this, Yuan et al. [94], Thombal et al. [92], and Bai et al. [95] changed SiO₂ to glucose, and they all successfully synthesised a carbon-based magnetic sulfonic acid-functionalized catalyst to produce EMF. Furthermore, Chen et al. [79] utilized different biomass-based compounds such as glucose, sucrose, starch, and cellulose to synthesise carbon-based sulfonic acid-functionalized catalysts, namely, GC-SO₃H, SuC-SO₃H, StC-SO₃H, and CC-SO₃H, respectively. Also, CC-SO₃H was magnetized to generate MCC-SO₃H, which had -COOH, -SO₃H, and phenolic -OH groups. It could catalyze fructose, sucrose, and inulin to produce 63.2%, 32.5%, and 51.3% EMF, respectively, at 120°C for 16 h in an ethanol medium. In summary, magnetic -SO₃H-based materials can be used as efficient, highly stable, and recyclable catalysts for the transformation of carbohydrates into EMF.

4.3. Ionic Liquid Catalysts. Mixing of organic cations and inorganic anions can yield typical ionic liquids (ILs), which have outstanding physical and chemical attributes, such as great thermochemical stability, low melting point, and great solubility [102]. ILs are widely used in a range of biomass conversions as a solvent and catalyst, showing great catalytic potential in etherification reactions [103, 104]. Table 4 shows the preparation of EMF from different ILs.

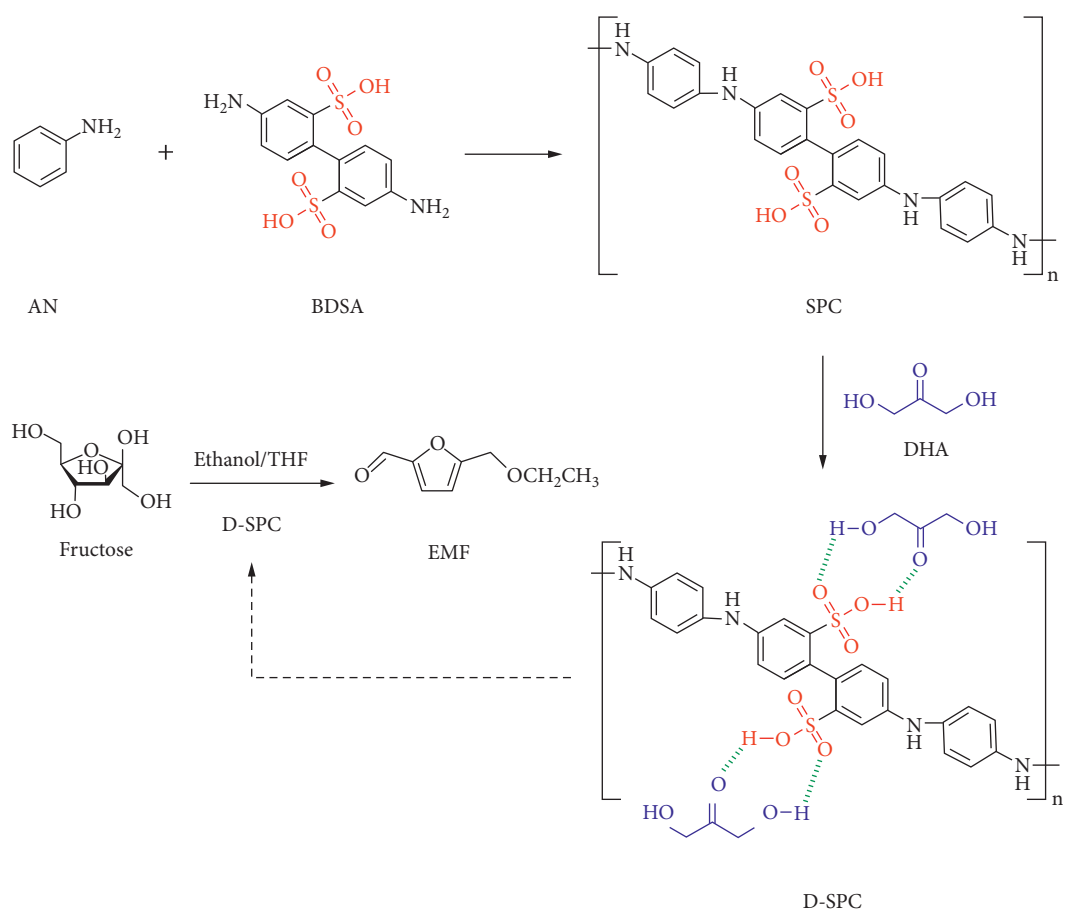
Yin et al. [54] successfully immobilized polyionic liquid on a magnetic Fe₃O₄@SiO₂ material to prepare an acid recyclable catalyst (Fe₃O₄@SiO₂-SH-Im-HSO₄). It was applied to obtain EMF, with yields of 89.6% from HMF, 60.4% from fructose, 56.1% from inulin, and 34.4% from sucrose. In addition to being a catalyst, ionic liquids can also be used as cosolvents for the synthesis of EMF. In 2016, Guo et al. [40] investigated whether under milder conditions, using an IL which had a hydrogen sulfate, both as a cosolvent and a

catalyst, could directly catalyze the fructose being converted to EMF in the ethanol system. They found that the yield of fructose being converted to EMF reached 83% in the [C₄mim][HSO₄]-ethanol system at 130°C for 20 min, due to the acidity of anion and the stable hydrogen bond formed between the ionic liquid and HMF (Scheme 4). On this basis, in 2017, they synthesised another ionic liquid ([BMIM][HSO₄]) [43] to analyze the conversion efficiency of inulin and sucrose to EMF. 77% and 43% of EMF were detected from inulin and sucrose, respectively, at 130°C within 30 min in the [BMIM][HSO₄]-ethanol system. It was deemed that the hydrogen sulfate group of [BMIM][HSO₄] could promote the breakage of glycosidic bonds, dehydration, and etherification of fructose and glucose isomerization to fructose. But, the rate of detected EMF was only 8% when changing glucose as the substrate. So, after this, to increase the efficiency of glucose conversion, AlCl₃ was added to the [BMIM][HSO₄]-ethanol system to form the AlCl₃-[BMIM][HSO₄]-ethanol system [96]. AlCl₃ could enhance the isomerization of glucose by the Lewis acid site present in AlCl₃, and the EMF yield was 37% from glucose via a one-pot reaction. Nonfood biomass (mushroom) as feedstuff could be converted into EMF (33%) using IL as a catalyst at 120°C after 20 h [97]. The IL was compounded by N, N-dimethylacetamide (DMA) as a cation and methanesulfonic acid as an anion named [DMA][CH₃SO₃].

4.4. Brønsted and Lewis Acid Bifunctional Catalysts. The single-acid catalysts as described in Sections 4.1, 4.2 and 4.13 can hardly convert glucose or glucose-based products to produce EMF, which only have Brønsted acid sites. Due to the lack of Lewis acid species, the isomerization of glucose hardly occurs, and it is more inclined to produce ethyl glucoside catalyzed by Brønsted acid. With the intent of raising the efficiency of glucose-based conversion to EMF, the researchers developed mixed-acid catalysts for this purpose, which are summarized in Table 4.

Mixed acids have been used to catalyze the synthesis of EMF. For example, Xin et al. [48] utilized paraformaldehyde (POM) and polymerizing p-toluenesulfonic acid (PTSA) in H₂SO₄ to synthesise a mixed-acid catalyst (PTSA-POM) which contained Brønsted acid sites. Compared with a single-acid catalyst, PTSA-POM combined with AlCl₃·6H₂O could obtain a satisfying EMF yield (30.6%) from glucose. An optimistic EMF yield was obtained from glucose-based saccharides, such as corn starch (36.9%), amylose (39.8%), and amylopectin (34.7%), by using a mixed-acid catalyst that contains H₃PO₄ and Al₂(SO₄)₃ in an ethanol/DMSO medium [28].

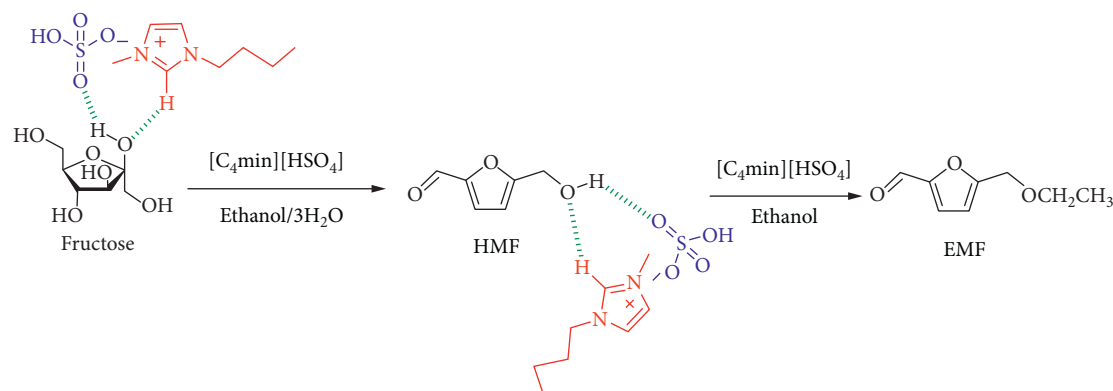
Different from a simple mixed state, grafting two acids into a whole seems to be a better way. Generally, zeolite molecular sieve catalysts contain Brønsted acid species Al-O(H)-Si (framework four-coordinate aluminum), and Lewis acid species Al- (framework three-coordinate aluminum) can be obtained after high-temperature dealumination [105]. These bifunctional acid catalysts have been used to synthesise EMF from glucose-based carbohydrates. USY and β zeolite (DeAl-H-β) that have been dealuminated at a high



SCHEME 3: The synthesis of D-SPC used for catalytic conversion of fructose to EMF.

TABLE 4: Ionic liquid, mixed-acid catalyst, and deep eutectic solvents used for EMF synthesis.

Entry	Catalyst	Feedstock	Solvent	Reaction condition	Yield (%)	Ref.
1	[C ₄ mim][HSO ₄]	HMF	Ethanol	130°C, 20 min	83	[40]
2	[BMIM][HSO ₄]	Inulin	Ethanol	130°C, 30 min	77	[43]
3	[BMIM][HSO ₄]	Sucrose	Ethanol	130°C, 30 min	43	[43]
4	[BMIM][HSO ₄]	Glucose	Ethanol	130°C, 30 min	8	[43]
5	[BMIM][HSO ₄]/AlCl ₃	Glucose	Ethanol	130°C, 30 min	37	[96]
6	[DMA][CH ₃ SO ₃]	Mushroom	Ethanol	120°C, 20 h	33	[97]
7	PTSA-POM/AlCl ₃ ·6H ₂ O	Glucose	Ethanol/H ₂ O	150°C, 30 min	30.6	[48]
8	DeAl-H-β	Glucose	Ethanol	125°C, 10 h	41	[80]
9	SnSTA	Glucose	Ethanol	140°C, 9 h	41	[98]
10	MFI-Sn/Al	Glucose	Ethanol	140°C, 9 h	44	[58]
11	BFC-3	Glucose	Ethanol/THF	100°C, 10 h	48.1	[50]
12	BFC-3	Cellobiose	Ethanol/THF	100°C, 10 h	37.1	[50]
13	Zn-S-C	Glucose	Ethanol/THF	98°C, 47 min	80.9	[27]
14	Zn-S-C	Cellobiose	Ethanol/THF	98°C, 47 min	74.6	[27]
15	Zn-SO ₃ H-GR-carbon	Glucose	Ethanol/THF	106°C, 72 min	86.3	[99]
16	ChCl-oxalic (DES)	Fructose	Ethanol	70°C, 3 h	74	[100]
17	DES/Amberlyst-15	Fructose	Ethanol	100°C, 12 h	77.3	[101]
18	DES/Amberlyst-15	Inulin	Ethanol	100°C, 12 h	65.2	[101]
19	DES/Amberlyst-15	Sucrose	Ethanol	100°C, 12 h	50.2	[101]
20	DES/Amberlyst-15	Glucose	Ethanol	100°C, 12 h	46.7	[101]



SCHEME 4: The conversion of fructose to EMF catalyzed by $[C_4mim][HSO_4]$.

temperature can obtain 21.8% EMF yield from corn stover and 41% EMF yield from glucose, respectively [38, 80]. In addition, the introduction of additional metal species in the zeolites can also be used as Lewis acid. For example, the Lewis acid species Sn- and Al- were coloaded onto zeolite to form a bifunctional acid catalyst named MFI-Sn/Al [58]. It can provide 44% EMF yield from glucose. It can also introduce Brønsted and Lewis acids into zeolite at the same time, like SnSTA, which was synthesised by loading $H_4[Si(W_3O_{10})_4]$ and $SnCl_4$ onto SBA-15, which generated 41% EMF yield from glucose [98]. A soft template HIPE was used to support the sulfonic acid group and Cr^{3+} to synthesise a BFC-3 catalyst (Scheme 5), and 48.1% (glucose) and 37.1% (cellobiose) EMF yield were detected by using it [50]. Furthermore, Brønsted and Lewis acids can also be grafted into carbon-based materials. An amazing EMF yield was observed by utilizing a Zn-S-C catalyst from glucose-based carbohydrates, such as cellobiose (74.6%) and glucose (80.9%) [27]. Zn-S-C was formed by coloaded ZnO and 2-hydroxyethylsulfonic acid onto carbon-based material. Also, ZnO provides Zn^{2+} (Lewis acid site), while 2-hydroxyethylsulfonic provides $-SO_3H$ (Brønsted acid site). Another higher EMF yield (86.3%) was obtained from glucose by using Zn- SO_3H -GR-carbon, which includes both Brønsted ($-SO_3H$) and Lewis (Zn -) acid species [99].

4.5. Deep Eutectic Solvents (DESs). DESs are new-generation solvents synthesised at the beginning of this century, which are a mixture of hydrogen bond acceptors (HBAs; e.g., the most typical is choline chloride) and hydrogen bond donors (HBDs; e.g., metal salts and their halides, polyols, and organic acids) [106]. They have the same excellent solvent characteristics as ILs, including low melting point, low viscosity, and high thermal stability [107]. Besides, DESs also have the advantages such as simple synthesis steps, low cost, being renewable, low toxicity, and biodegradable characteristics [108]. Table 4 summarizes some DESs used in EMF synthesis systems.

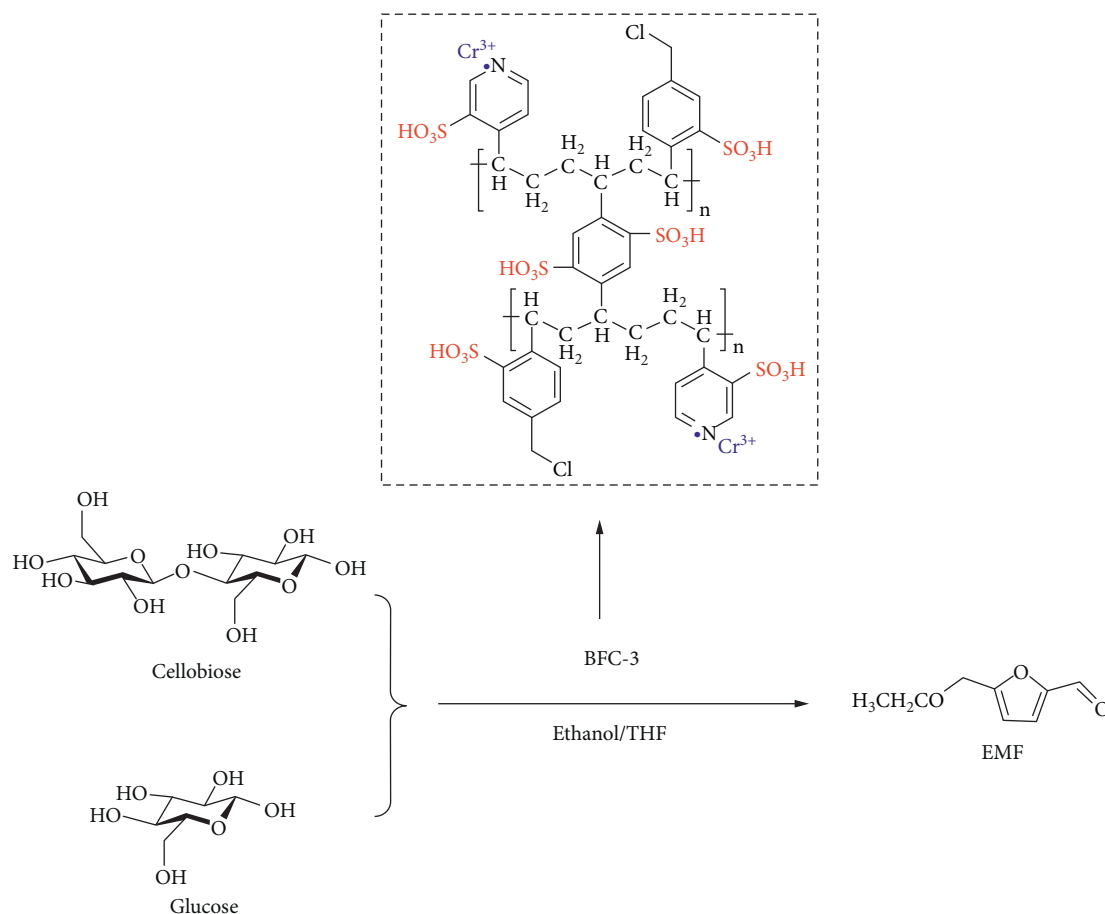
Currently, there are few studies on the use of DESs to prepare EMF from carbohydrates. Gawade et al. [100] used a variety of dicarboxylic acids (e.g., oxalic acid, malic acid, malonic acid, tartaric acid, itaconic acid, and succinic acid)

combined with choline chloride (ChCl) to form a variety of DESs. Then, they used these DESs for the one-pot transformation of fructose into EMF in an ethanol medium under microwave radiation. A series of polar intermediates are produced in these processes. It was found that these polar intermediates could be stabilized by DESs, which are polar; thereby, DESs could enhance EMF selectivity. Among these DESs, ChCl-oxalic showed the most excellent catalytic performance, obtaining 74% EMF yield at 70°C for 3 h. Some studies showed that the DESs system could prevent the further hydration of HMF to produce byproducts, so this system is conducive to the acquisition of high-yield HMF [109, 110]. According to this, Zuo et al. [101] developed a two-step method to convert carbohydrates into EMF. In the first step, the carbohydrates were dehydrated to form HMF in the DESs system. After that, the HMF was dissolved into methyl cyanide for the next esterification reaction to form EMF. The final EMF yield was 77.3% from fructose, 65.2% from inulin, 50.2% from sucrose, and 46.7% from glucose.

5. Solvent Systems

Except for feedstocks and catalysts, solvents also play a necessary role in the preparation of EMF. They can dissolve the feedstock, as well as bring the feedstock and the catalyst fully in contact to increase the mass transfer coefficient. In some way, a better solvent can raise the yield of EMF, and many solvents or cosolvents have been investigated for the manufacture of EMF, such as ethanol, DMSO, and THF. Table 5 summarizes the influence of various solvents on the EMF yield.

5.1. Ethanol System. Ethanol is the most common solvent used for the preparation of EMF. As a necessary reactant in the one-pot EMF process, it is widely sourced, cheap, nonpolluting, and easy to recycle. In the current research on the preparation of EMF, many researchers used ethanol as a solvent [92, 93], and the HMF etherification reaction was directly carried out, accompanied by ethanol under heating and acidic conditions, with the highest yield of 92.9% [47]. Another satisfactory EMF yield (85.5%) was obtained in the reaction of the ethanol system from HMF at 80°C for 11 h with the existence of an $LS-SO_3H$ catalyst [91].



SCHEME 5: The transformation of cellobiose and glucose to EMF catalyzed by BFC-3.

TABLE 5: Various solvents used for EMF synthesis.

Entry	Solvent	Feedstock	Catalyst	Reaction condition	Yield (%)	Ref.
1	Ethanol	HMF	$AlCl_3$	$100^\circ C$, 5 h	92.9	[47]
2	Ethanol	Fructose	$AlCl_3$	$100^\circ C$, 11 h	71.2	[47]
3	Ethanol	Glucose	$AlCl_3$	$100^\circ C$, 11 h	38.4	[47]
4	Ethanol	HMF	LS- SO_3H	$80^\circ C$, 11 h	85.8	[91]
5	Ethanol	Fructose	HCP-1	$105^\circ C$, 12 h	43.7	[111]
6	Ethanol/DMSO (8 : 2)	Fructose	HCP-1	$105^\circ C$, 8 h	78.9	[111]
7	Ethanol	Fructose	$H_3PW_{12}O_{40}$	$130^\circ C$, 30 min	65	[55]
8	Ethanol/THF (5 : 3)	Fructose	$H_3PW_{12}O_{40}$	$130^\circ C$, 30 min	76	[55]
9	Ethanol/GVL (1 : 1)	Fructose	MHGC- SO_3H	$120^\circ C$, 24 h	67.4	[95]

5.2. Cosolvent System. In an attempt to raise the EMF yield, adding a cosolvent is a common method. The addition of a suitable cosolvent under the same reaction conditions can significantly increase the EMF yield, and the commonly used cosolvents usually include DMSO, THF, and GVL. It was indicated that the additive of DMSO could promote the formation of EMF and reduce the formation of byproducts [66]. Zhang et al. [111] found that, under the same reaction system, the yield of EMF in the ethanol system was 43.7%, and when the solvent was changed to ethanol/DMSO (8 : 2), the yield of EMF was greatly improved to 78.9%. THF could

also effectively increase the yield of EMF and inhibit side reactions. Yang et al. [55] used fructose to prepare EMF by the one-pot method, and the yield in the ethanol system was 65%. After changing the solvent system to ethanol/THF (5 : 3), the yield of EMF was remarkably raised to 76%. Similarly, GVL could also significantly enhance the EMF yield. Bai et al. [95] found that compared with pure ethanol solvents, GVL could provide a hydrophobic environment for the reaction system and reduce the production of humus. Under the most appropriate reaction system, the EMF yield of the ethanol/GVL solvent system could reach 67.4%.

6. Conclusions

The conversion of various carbohydrates catalyzed by Brønsted acid and Lewis acid into a promising fuel additive EMF has made significant progress in the past few decades. Generally, HMF as a substrate can obtain a high EMF yield. However, the higher cost limits its industrial development. Furthermore, fructose-based saccharides (e.g., fructose, sucrose, and inulin) used as substrates produced EMF in higher yields than glucose-based ones (e.g., glucose, cellobiose, cellulose, and starch). This is because glucose-based saccharide is more difficult to be dehydrated, and glucose needs to be isomerized in the presence of Lewis acid before forming fructose. The use of solid catalysts can make the catalysts reusable, and magnetizing the solid catalysts can make the separation process simpler. Yet, most of the current catalysts generally have the disadvantages of the complex preparation process, such as high cost or low catalytic activity and selectivity, especially for glucose-based carbohydrates as the reaction substrates. The use of a cosolvent can effectively improve the selectivity and yield of EMF, but the existence of a cosolvent increases the difficulty of the separation and purification process, with potentially increased toxicity of the reaction system. Therefore, the development of efficient, economical, and recyclable solid catalysts containing both Brønsted and Lewis acid sites for the conversion of glucose-based carbohydrates is still the main future research direction

Conflicts of Interest

The authors declare no conflicts of interest.

Authors' Contributions

Dayong Yu and Xiaofang Liu contributed equally to this work.

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