

Facile In Situ 5-EMF Synthesis and Extraction Processes from Catalytic Conversion of Sugar under Sustainable Long-Life Cycle

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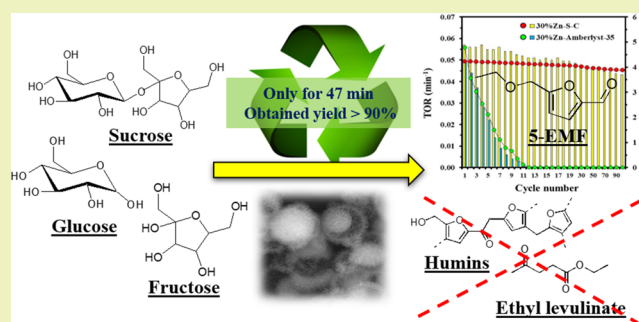
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Supporting Information

ABSTRACT: The catalytic behavior for 5-ethoxymethylfurfural (5-EMF) formation was systematically studied via facile conversion of sucrose under a sustainable ultrasonic-biphasic system using an active ZnO nanofiber-deposited-SO₃H-carbon catalyst (Zn-S-C). Interestingly, 5-EMF with a high yield could be easily obtained and separated from ethanol/tetrahydrofuran (THF) via green synthesis-extraction procedures in the presence of NaCl. Meanwhile, an actual 5-EMF yield of 93.5 ± 0.8% was successfully achieved at 98 °C for 47 min using a THF amount (0.25 mol) and catalyst adding amount (77.8 wt %) over the combination of 2^k factorial and Box–Behnken designs. The product selectivity and yield from sucrose conversion were systematically controlled by adjusting type/amount of catalyst, co-solvents or inorganic salts, and ultrasonic system. The activation energy (38.17 kJ/mol) obtained from ultrasound-assisted conversion of sucrose into 5-EMF was lower than that from the conventional system. Strikingly, a nonsignificant decrease in the turnover rate (TOR, min⁻¹) for conversion of sucrose into 5-EMF appeared when the catalyst was reused up to 100 cycles, indicating long-life cycle stability of the as-prepared catalyst.

KEYWORDS: sucrose, 5-EMF, reusable biphasic system, one-pot conversion, in situ extraction process



INTRODUCTION

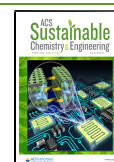
The biofuel or value chemical production from biomass feedstocks is highly needed at present due to the current increasing energy crisis with the highly decreasing fossil fuels.^{1,2} In biorefinery process, several kinds of sugars can be converted into some liquid biofuels such as 5-hydroxymethylfurfural (5-HMF), 2,5-dimethylfuran (2,5-DMF), and/or 5-ethoxymethylfurfural (5-EMF). The 5-EMF chemical, as one of the potential biofuels, can be easily produced from 5-HMF etherification.³ Interestingly, a high energy density of 30.3 MJ/L is found in this chemical, which is higher than that of ethanol (23.5 MJ/L) and also close to that of diesel (33.6 MJ/L).⁴ To date, several methods for converting 5-HMF into 5-EMF have been tested with etherification reaction over acidic catalysts.⁵ Anywise, due to the expensive cost of the 5-HMF substrate, its further application in practical processes might be inappropriate. Many works have been tried to solve such a problem using sugars as a feedstock for one-step synthesis of 5-EMF.^{6–8} Usually, good catalytic activity for 5-EMF production with high yield is found using some homogeneous catalysts.⁹ Unluckily, the recycle of the homogeneous catalyst is indeed one problem and might be related to safety concerns. In addition, the facile formation of humins via polymerization easily occurs when a strongly acidic catalyst is applied.

As mentioned above, the improvement of heterogeneous catalyst properties for selective production of 5-EMF should be considered.¹⁰ Bing et al.¹¹ found that the direct conversion of fructose into 5-EMF over the [MIMBS]₃PW₁₂O₄₀ catalyst was achieved at 90 °C for 24 h with a maximum yield of 90.3%. Yang et al.¹² found that the heteropoly acid H₃PW₁₂O₄₀ catalyst had selectivity for sucrose conversion using tetrahydrofuran (THF) as a solvent. A highest 5-EMF yield of 33% was derived within 30 min at a reaction temperature of 130 °C. Yuan et al.¹³ found that the Fe₃O₄@C-SO₃H catalyst exhibited good performance toward the one-step conversion of carbohydrate-based sucrose into 5-EMF (33.2% yield) at 140 °C for 24 h. Li et al.¹⁴ studied the acid–base bifunctional hybrid nanospheres for 5-EMF production using ethanol/dimethyl sulfoxide (DMSO) as the solvents. They found that a maximum 5-EMF yield of 36.5% was obtained from sucrose conversion at 120 °C for 15 h. Unluckily, a 5-EMF yield of <40% was always obtained, probably due to the occurrence of

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side reactions. Also, the catalyst reusability is not so good while rapid deactivation of the catalyst is found, indicating unsuitable application for real biorefinery processes.¹⁵

To overcome these problems, an active ZnO nanofiber-deposited-SO₃H-carbon catalyst (Zn-S-C) was applied, which could be easily synthesized using an in situ hydrothermal sulfonation-carbonization procedure. The characteristic properties of the catalyst were studied. The 5-EMF chemical was synthesized from catalytic conversion of sucrose using a sustainable ultrasonic-biphasic system. The as-synthesized chemicals could be easily separated and recycled via a green in situ extraction process. Yan et al.¹⁶ found that a facile separation of the chemical product was supported with the assistance of NaCl under a biphasic system while some side reaction could be efficiently suppressed. The statistical optimizations were systematically applied to search the important factors and optimal conditions. The catalytic behavior for 5-EMF formation from sucrose was studied via main factors such as types of catalyst, solvent and inorganic salt, and ultrasonic system. The activity and long-term stability of the developed catalyst were also compared with those of a commercial one, and their recycling abilities were also studied for 100 cycles. To our best knowledge, this research provided a new direction and idea for 5-EMF production with a high yield from sugar conversion, which might be further applied in practical biorefinery processes.

EXPERIMENTAL SECTION

Preparation of the Catalyst. In a typical procedure, certain amounts of glucose and 2-hydroxyethylsulfonic acid were mixed in 50 mL of deionized water and then stirred at ambient temperature until a homogeneous solution was obtained.¹⁷ Based on our preliminary study, a mixture of glucose to 2-hydroxyethylsulfonic acid at a weight ratio of 1 to 3 was chosen to obtain a catalyst with the highest acidity. Here, the mixture solution was put into a hydrothermal autoclave, and heating treatment was applied at 180 °C for 9 h under stirring. After the complete procedure, a black powder or SO₃H-carbon sphere catalyst (S-C) was collected by centrifugation. The S-C was washed with deionized water several times until neutral pH was obtained and finally dried in an oven overnight.

For the deposition process of zinc nanofiber on the S-C catalyst (Zn-S-C) via template-free solvothermal treatment, 1 g of S-C was mixed with various zinc acetate solutions (Zn loading amounts of 10, 20, 30, and 40 wt %). Here, the mixture solution was put into a hydrothermal autoclave, and heating treatment was applied at 130 °C for 6 h under stirring. After the complete procedure, the Zn-S-C powder was collected by filtration. The Zn-S-C was washed with deionized water several times and then dried in an oven overnight. The methods and results of catalyst characterization are given in the Supporting Information (Figures S1–S8 and Table S1).^{18–32}

Catalytic Performance Testing for 5-EMF Production. In a typical run, a mixture solution consisting of sucrose (1 g), NaCl (1.25 g), THF (0.25 mol), EtOH (0.25 mol), and deionized water (10 mL) was initially prepared. The prepared solution and catalyst were added into a round-bottom flask, and then, the reaction conditions were performed under a stirring speed at 650 rpm with an ultrasonic frequency at 2500 Hz. It should be noted that the heating and stirring systems were controlled by a hot plate magnetic stirrer (C-MAG-HS7, IKA, GERMAN) while the ultrasonic application system was controlled by an ultrasonic probe sonicator (Athena Technology). The experimental designs were investigated to know catalytic behaviors via several factors such as catalyst loading amount (40–90 wt % sucrose), reaction time (10–60 min), reaction temperature (60–120 °C), and THF amount (0.25–0.50 mmol). The details on statistical optimization are given in the Supporting Information (Tables S2 and S3). Moreover, the influences of Zn loading, co-solvent, inorganic salt addition, and ultrasonic power/duty cycle for

direct conversion of sucrose into 5-EMF formation were systematically investigated.

After the complete procedure, the reaction was stopped by sousing in an ice bath. The spent catalyst was collected by centrifugation, washed with ethanol + deionized water several times, and then dried in an oven overnight before the reusability study. In the case of solution, it could be divided into two layers as follows: the above layer of which should be a mixture of 5-EMF/THF phase (Figure S9). For the underside layer consisting of NaCl/EtOH/water, it might be reused for the next cycle. It should be noted that spent THF with EtOH could be generally separated by the distillation method.

Analysis of Chemical Products. The quantitative analyses of chemical products such as 5-EMF or 5-HMF were performed using an Agilent 1200 HPLC chromatograph equipped with a UV detector. The column was maintained at a temperature of 30 °C, and the mobile phase was water/methanol = 0.8:0.2 (v/v). The amount of sugar was analyzed using an Aminex HPX-87H column and refractive index (RI) detector. Here, the column was entered at a temperature of 65 °C using 0.05 M H₂SO₄ solution as a mobile phase with a flow rate at 0.55 mL/min. The concentrations (mol %) of products were calculated based on the external standard method. The amount of zinc ion in the liquid sample, which leached from the Zn-S-C catalyst during the reaction, was also detected by ICP-AES.

RESULTS AND DISCUSSION

Experimental Analysis for Conversion of Sucrose into 5-EMF. The 5-EMF yield derived from 2⁴ factorial design with 16 experiments is shown in Table S2. It is found that the range of 5-EMF yields about 18 to 74% was obtained from direct conversion of sucrose using a sustainable ultrasonic-biphasic system over the 30%Zn-S-C catalyst. To screen the significant factors, the normal probability plot was primarily studied as shown in Figure 1. It should be noted that the normal

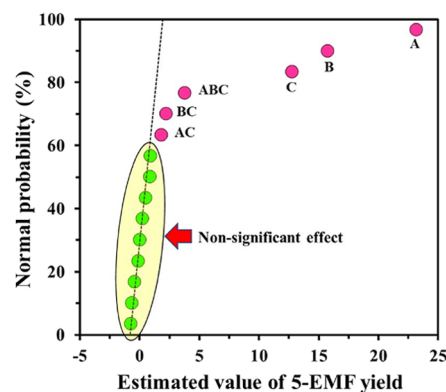


Figure 1. Normal probability plot obtained from direct conversion of sucrose into 5-EMF using a sustainable ultrasonic-biphasic system over the 30%Zn-S-C catalyst.

probability plot, as a graphical technique, was applied to identify substantive departures from normality. This could be also utilized to define if small sets of data come from a normal distribution.

One can see that three significant factors such as catalyst loading amount/A (wt %), reaction time/B (min), and reaction temperature/C (°C) including their interactions were found since they did not exist within the linear line, except THF adding amount/D (mol). Here, factor A (catalyst loading amount) had the most significant influence based on the longest distance from the linear line. The order of the three factors for 5-EMF production was catalyst loading amount > reaction time > reaction temperature. It should be mentioned

here that the range of THF adding amounts (0.25 to 0.50 mol) had a nonsignificant effect for enhancing the selective formation of 5-EMF. According to Le Chatelier's theory, in order to promote the equilibrium forward to the wanted product, the excess amount of solvent was extremely desired. Here, the presence of THF solvent was very important for acidic reaction conditions, especially for dehydration-etherification, while the side reactions could be well suppressed.¹² However, it should be considered the problem of phase separation when an over amount of THF was used. Meanwhile, a large amount of THF molecules could cover the surface of the catalyst, leading to rapid deactivation during the reaction process. Therefore, the lowest THF adding amount of 0.25 mol was certainly fixed for all experiment after this. Table S4 presents the analysis of variance (ANOVA) at a confidence level of 95% with $F_{0.05}$. Here, the observed factors had a significant effect when their F -values were more than 5.32. The maximum and minimum F -values derived from the catalyst loading amount and reaction temperature were 1414.17 and 429.34, respectively. The result of ANOVA was in good agreement with the estimated effect of normal probability as shown in Figure 1. Based on the above results, the predicted 5-EMF yield (Y) was calculated via the linear regression model consisting of low and high levels as follows in eq 1

$$Y = 43.97 + 11.581A + 7.869B + 6.381C + 0.919AC + 1.106BC + 1.894ABC \quad (1)$$

The normal probability plot of residual value and distribution plot of residual is shown in Figure 2. Here, the applied linear regression model had high dependability and

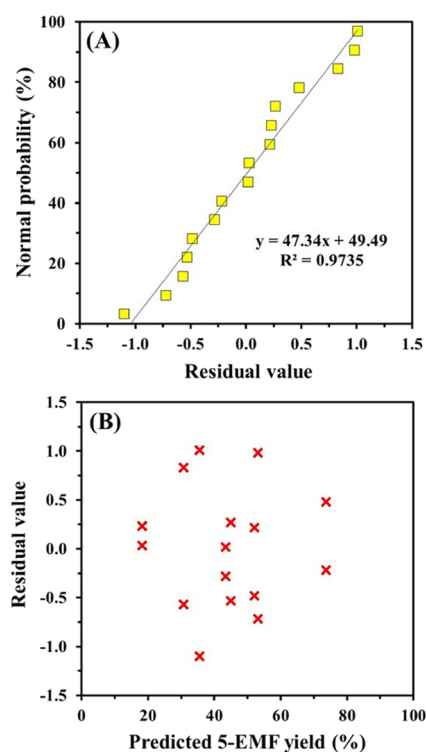


Figure 2. (A) Normal probability plot of 5-EMF residual and (B) distribution plot of 5-EMF residual versus predicted 5-EMF yield derived from 2^4 factorial design for direct conversion of sucrose into 5-EMF using a sustainable ultrasonic-biphasic system over the 30% Zn-S-C catalyst.

precision based on good linearity with $R^2 > 0.9$, while the distribution of residue values was in the range of $\pm 1.2\%$. From results of 2^4 factorial design, the lowest THF amount was selected for further study on optimization of 5-EMF production via Box–Behnken design.

The 5-EMF yield derived from Box–Behnken design with 15 experiments is shown in Table S3. The predicted 5-EMF yield was calculated via the quadratic regression model consisting of low, medium, and high levels as follows in eq 2

$$Y = 87.933 + 12.338X_1 + 9.3X_2 + 7.813X_3 - 16.492X_1^2 - 15.017X_2^2 - 20.292X_3^2 + 6.975X_1X_2 + 4.25X_1X_3 + 3.275X_2X_3 \quad (2)$$

It should be noted that this regression model was mainly used to check the accuracy of Box–Behnken design and maximization of 5-EMF yield. The predicted yield of 5-EMF was determined from eq 2, and their results are presented in Table S3. As shown in Figure S10, $R^2 > 0.95$ with a variability of 98.69% for polynomial investigation was obtained from the plot of predicted 5-EMF yield versus observed 5-EMF yield, suggesting that the predicted yield of 5-EMF was well close to the observed yield based on the term of high accuracy. To know more details on the interaction of each independent input factor, the optimization using response surfaces is presented in Figure 3. The interaction of the catalyst amount with reaction time for direct conversion of sucrose into 5-EMF using a sustainable ultrasonic-biphasic system over the 30% Zn-S-C catalyst at a constant reaction temperature of 90 °C (medium level) is shown in Figure 3A. Increasing the catalyst loading amount from 40 to 70 wt % promoted the formation of 5-EMF, whereas percent yield increased from 41.7 to 64.0%. This phenomenon should be ascribed to available active sites and collision rate between sucrose and catalyst, leading to a facile reaction process. However, when a catalyst loading amount of >70 wt % was utilized, the formation rate based on 5-EMF yield was reduced to some extent, probably due to the resistance effect in mass transfer that occurred from very high viscous slurries and poor mixing in mixture solution. Moreover, large catalyst dosages may accelerate more side reactions such as ring-opening and polymerization reactions of 5-EMF into ethyl levulinate (EL) and humins, respectively.³³

The catalytic reaction pathways for formation of the 5-EMF chemical and others from sucrose conversion are previously reported.³⁴ The first step is the hydrolysis process of a sucrose molecule to glucose and fructose intermediates on the sulfonic group Brønsted acid sites. Here, the glucose molecule could be further converted into fructose molecules via the isomerization process on the zinc Lewis acid sites. Then, fructose was converted into 5-HMF via dehydration catalyzed by Brønsted acid sites. Meanwhile, fructose molecules might be attacked by ethanol to form ethyl fructoside through ethanolysis and dehydration before further 5-EMF creation. Lastly, the etherification process of 5-HMF occurs to produce the 5-EMF product. For this novel Zn-S-C catalyst, the zinc element could act as the Lewis acid site for improving the glucose isomerization. On the other hand, the zinc atom in the Zn-S-C catalyst was enveloped by water complex ions, which may be then hydrolyzed to generate H^+ , resulting in high H^+ mobility. This generated H^+ was highly beneficial for 5-EMF via catalyzing hydrolysis, dehydration, and etherification. In addition, ultrasonic application could well facilitate an

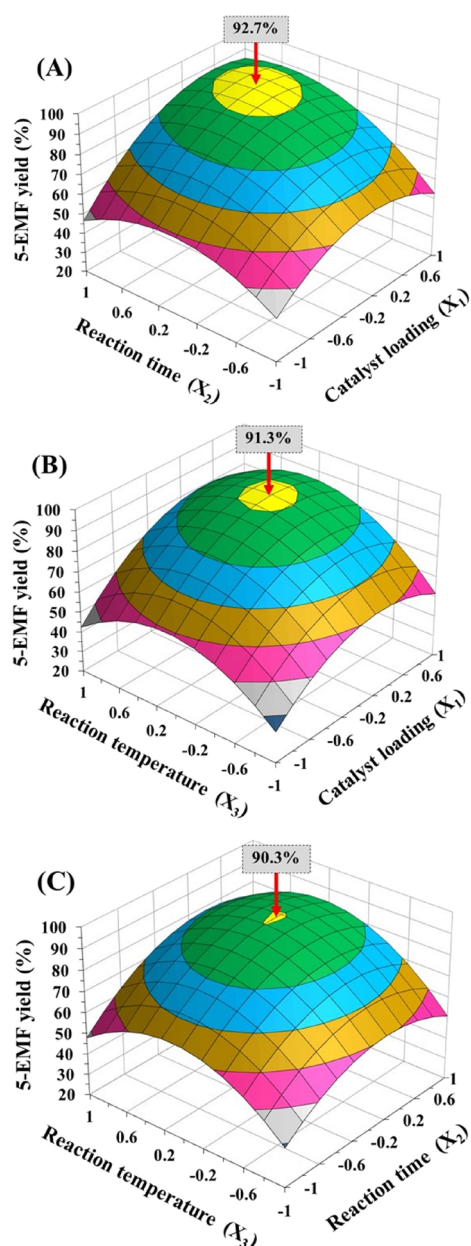


Figure 3. Response surface 3D plots defined from 5-EMF yield: (A) interaction effect of catalyst loading with reaction time, (B) interaction effect of catalyst loading with reaction temperature, and (C) interaction effect of reaction time with reaction temperature.

interfacial area and mass transfer through cavitation bubble magnitudes and energy hotspots, leading to sucrose toward a rapid reaction kinetic rate.³⁵ Meanwhile, the side products such as EL or humins may be easily formed via ring-opening and polymerization reactions when inappropriate conditions were applied. For possible recycling in practical large-scale processes, a biphasic reaction system and in situ extraction technology were applied in this study. Here, NaCl was mixed to escalate the immiscibility between EtOH/water with THF and phases, resulting in creation of two layers finally (Figure S9).³⁶

As shown in Figure 3B, the highest 5-EMF yield about ~91% was derived from interaction of a catalyst loading amount of 75 wt % with a reaction temperature of 96 °C at a constant reaction time of 35 min (medium level). For Figure 3C, considering the effects of reaction time and temperature, the highest 5-EMF yield was found at 96 °C for 45 min at a constant catalyst loading amount of 65 wt %. The yield of 5-EMF was decreased to some extent when reaction time (>50 min) and reaction temperature (>100 °C) were applied, suggesting that the 5-EMF product was further converted into side products such as EL or humins.³⁷ This phenomenon should be distinguished by product color by changing from brown to black. As observed in Figure 3B,C, the reaction temperature about 100 °C was enough for 5-EMF production while high reaction temperature (>100) resulted in significant reduction of 5-EMF yield. This should be due to the contribution of ultrasonic energy. It is also probable that at very high reaction temperature, THF and ethanol solvents might be converted from liquid phase to vapor phase, resulting in less solvent available in the reaction media.

From response surface analysis, the optimization in equilibrium conditions could be systematically predicted through Box–Behnken design with the quadratic regression model. Here, the optimal conditions are a catalyst amount of 77.8 wt %, reaction time of 47 min, reaction temperature of 98 °C, a THF amount of 0.25 mol, ultrasonic power of 90 W, and duty cycle of 6 s ON/4 s OFF, obtaining a highest predicted 5-EMF yield of 94.3%. To identify the exactitude for this design, veritable experiments were performed through obtained optimum conditions for three duplicates. It is found that an average yield of 5-EMF ($93.5 \pm 0.8\%$) was practically achieved. Based on these results, such optimal conditions were chosen for further studies. For comparison, the efficiency for catalytic conversion of sucrose into 5-EMF derived in this study was compared with those in previous works (Table 1).^{12–14,38,39}

Table 1. Catalytic Comparison of Zn-C-S and Representative Catalysts for the Conversion of Carbohydrates into 5-EMF

entry	catalyst	substrate	solvent	reaction conditions	5-EMF yield (%)	ref
1	H ₃ PW ₁₂ O ₄₀	sucrose	ethanol/THF	microwave system: 130 °C for 30 min	33.0	12
2	Fe ₃ O ₄ @C-SO ₃ H	sucrose	ethanol	solvothermal system: 140 °C for 24 h	33.2	13
3	Lys/PW	sucrose	ethanol/DMSO	ace pressure system: 120 °C for 15 h	36.5	14
4	PSDVB-SO ₃ H	sucrose	ethanol	glass vessel reactor: 120 °C for 2 h	31.1	38
5	S-PANI-FeVO ₄	sucrose	Ethanol	solvothermal system: 90 °C for 24 h	57.2	39
6	Zn-S-C	sucrose	ethanol/THF	ultrasonic system: 98 °C for 47 min	93.5	this work
7	Zn-S-C	cellobiose	ethanol/THF	ultrasonic system: 98 °C for 47 min	74.6	this work
8	Zn-S-C	glucose	ethanol/THF	ultrasonic system: 98 °C for 47 min	80.9	this work
9	Zn-S-C	fructose	ethanol/THF	ultrasonic system: 98 °C for 47 min	95.5	this work
10	Zn-S-C	sorbose	ethanol/THF	ultrasonic system: 98 °C for 47 min	82.4	this work
11	Zn-S-C	inulin	ethanol/THF	ultrasonic system: 98 °C for 47 min	64.8	this work
12	Zn-S-C	sucrose	ethanol/THF	reflux system: 98 °C for 12 h	90.8	this work

One can see that Zn-S-C exhibited better catalytic activity than $H_3PW_{12}O_{40}$, $Fe_3O_4@C-SO_3H$, and Lys/PW (Table 1, entries 1–5 vs 6). The reason should be suggested that the surface area/pore size was much larger than those of representative catalysts. The Zn-S-C stability with its abundant acidity should be a reason for promoting the facile reaction. Here, a biphasic system including co-solvent and inorganic salt was also applied, which might also be one reason for improving the 5-EMF yield. When a conventional reflux system (entry 12) was applied, complete reaction was done in 12 h in order to achieve a 5-EMF yield of 90.8%. This indicates that ultrasonic application could effectively reduce the reaction time for 5-EMF production. To get more details, six carbohydrates such as fructose, glucose, sorbose, sucrose, cellobiose, and inulin were utilized as the feedstocks for 5-EMF synthesis (Table 1, entries 6–11). It was found that a sustainable catalytic system in this work had high potential for converting each carbohydrate into a 5-EMF product, especially for mono-disaccharide groups. A minimal yield of 5-EMF (64.8%) was derived from conversion of inulin, probably due to the strong linkage of the glycosidic bond in the polysaccharide structure. Thus, the specific reaction conditions should be needed for application of inulin feedstock.

Effect of the Zinc Loading Amount on the S-C Catalyst. The influences of zinc loading with different amounts on S-C were studied, and their results are shown in Figure 4. It is found that the yield of 5-EMF was clearly

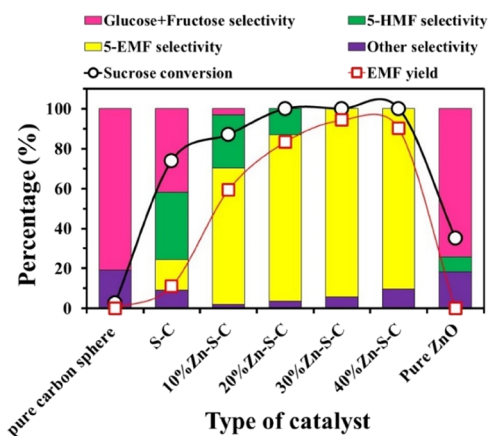


Figure 4. Effect of the catalyst type on direct conversion of sucrose into 5-EMF using a sustainable ultrasonic-biphasic system.

increased over 10%Zn-S-C when compared with S-C without zinc loading and then dramatically escalated over 20%Zn-S-C and 30%Zn-S-C. It suggests that specific reactions such as hydrolysis, isomerization, dehydration, and etherification could be well supported with a proper amount of Zn loading. However, it should be considered in the facile formation of humins via polymerization reaction based on acidity of the catalyst. Here, the yield of 5-EMF was slightly reduced when the zinc loading amount exceeded 30 wt % while another product selectivity such as EL was escalated via etherification reaction. Meanwhile, a very large amount of zinc could easily cover the Brønsted acid site via the accumulation process, leading to the reduction of catalytic performance. For the sole carbon sphere with zinc oxide, they did not promote formation of 5-EMF because of very low acidity.

Effect of Co-Solvent. To study the role of each solvent for direct synthesis of 5-EMF from sucrose, various co-solvents such as THF/EtOH, methylisobutylketone (MIBK)/EtOH, dimethyl sulfoxide (DMSO)/EtOH, acetonitrile (ACN)/EtOH, dimethylacetamide (DMA)/EtOH, and *N*-methylpyrrolidone (NMP)/EtOH were investigated while the molar ratios of each one were fixed at 1:1 (Figure 5). As obtained, 5-

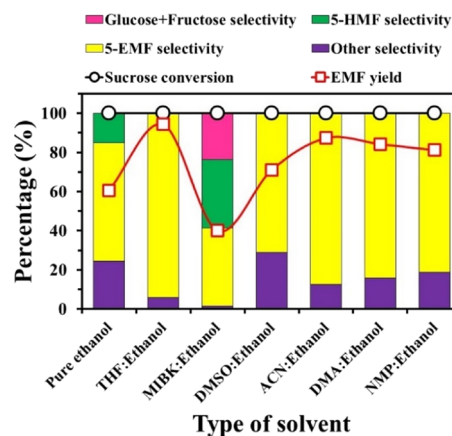


Figure 5. Effect of co-solvent on direct conversion of sucrose into 5-EMF using a sustainable ultrasonic-biphasic system over the 30%Zn-S-C catalyst.

EMF yield (60.6%) was found when pure ethanol was used, suggesting that the use of solely ethanol without any co-solvent was not effective enough for the equilibrium shift to the sucrose conversion into 5-EMF. Meanwhile, the side reactions could be also promoted. Interestingly, the 5-EMF yields were enhanced to 93.5, 71.1, 87.4, 84.3, and 81.2% using co-solvents of ethanol with THF, DMSO, ACN, DMA, and NMP, respectively. This suggests that polar aprotic solvents could improve the main reactions for 5-EMF synthesis.^{40–42} In contrast, when DMSO co-solvent was applied, the insoluble black was found in the chemical product while high selectivity of EL or humins was obtained, suggesting that the highest polarity of DMSO co-solvent could well promote side reactions such as condensation, ring-opening, and polymerization reactions. Here, MIBK presented a poor catalytic activity, which should be attributed to the lower solubility of the substrate. It should be noted that considering environmental hazardous implications based on the CHEM21 solvent selection guide, THF solvent was classified as problematic.^{43,44} However, in practical processes, THF could be easily separated since it has much lower boiling point than 5-EMF and might be reused several times. Therefore, THF/ethanol was chosen as an optimum co-solvent for 5-EMF synthesis in this work.

Effect of Inorganic Salt Addition. The role of the ions presented in the inorganic salt solution for in situ 5-EMF synthesis and extraction processes from sucrose conversion is presented in Figure 6. Here, the effect of the addition of different monovalent and divalent ions was evaluated in the biphasic THF/ethanol system. As shown in Figure 6A, in the case of without salt addition, only a 5-EMF yield of 17.4% was obtained, indicating that the existence of inorganic salt was very important for 5-EMF formation. The sucrose conversion and 5-EMF yield were significantly increased in the presence of inorganic salts, probably owing to the fact that it has a salting-out phenomenon in the solution and could efficiently support the reaction rate, therefore improving the in situ extraction rate

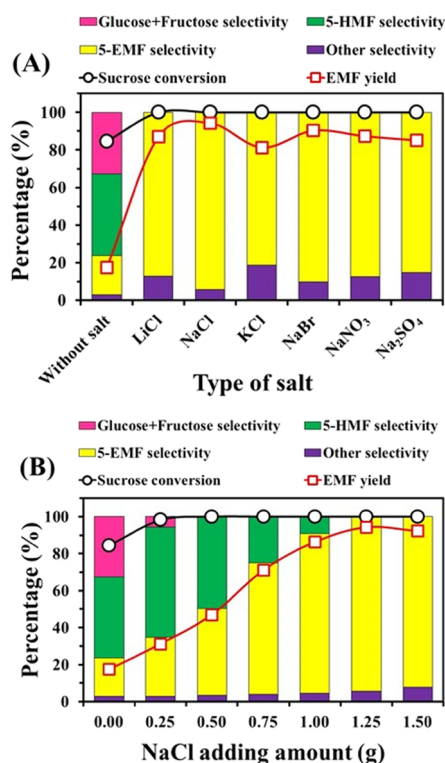


Figure 6. Effects of (A) the type of inorganic salt and (B) NaCl adding amount on direct conversion of sucrose into 5-EMF using a sustainable ultrasonic-biphasic system over the 30%Zn-S-C catalyst.

of 5-EMF. Interestingly, in the presence of chloride anions, the selectivity for 5-EMF production was in the order of $\text{Na}^+ > \text{Li}^+ > \text{K}^+$. On altering the anion nature and Na^+ counter ion, the selectivity for 5-EMF production was in the order of $\text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{SO}_4^{2-}$. The role of these anions in the conversion of sucrose into 5-EMF was described by the offering of electron density to the C atoms of sucrose, obstructing the polymerization for humin production.⁴⁵ Sulfate ions exhibited lowest selectivity for 5-EMF production, suggesting association of their H bonds with H_2O molecules and OH groups of sucrose, leading to the formation of reaction intermediates.⁴⁶ Moreover, the 5-EMF yields in the biphasic system were also studied with the increase in the NaCl adding amount (Figure 6B). According to these results, when a higher NaCl amount was employed, a higher 5-HMF yield was achieved, being a maximum 5-EMF yield with 1.25 g of NaCl amount at saturated point. However, the catalytic result was slightly decreased when the NaCl adding amount was over the saturation value (1.5 g of NaCl). Here, the saturated NaCl solution effectively improved the interaction between molecular bonds in the components and the immiscibility of organic/aqueous phases, thereby supplementing the distribution rate of 5-EMF in organic phases.^{42,47} In other words, saturated NaCl solution was the optimal point for sucrose conversion into 5-EMF.

Effect of Ultrasonic Power and Ultrasonic Duty Cycle.

The effect of ultrasonic power for synthesis of 5-EMF from sucrose is presented in Figure 7A. As expected, since the ultrasonic power was generated from 50 to 90 W, the 5-EMF yield was significantly enhanced, resulting from association of niche collapse. It should be resulted from energy transfer in the reaction conditions. At the same time, the power energy from ultrasonic application promoted the reaction rate for facile

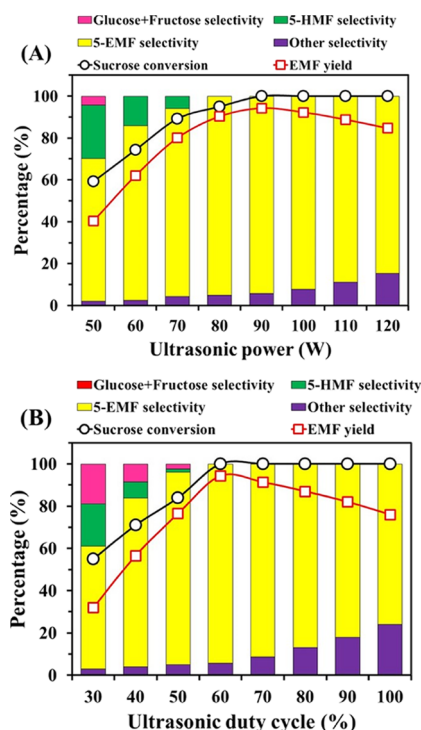


Figure 7. Effects of (A) ultrasonic power and (B) duty cycle on direct conversion of sucrose into 5-EMF using a sustainable ultrasonic-biphasic system over the 30%Zn-S-C catalyst.

formation of the 5-EMF product. Unfortunately, the application of ultrasonic power had some limitations; for example, ultrasonic power (>90 W) could lead to formation of side products. As shown in Figure 7B, the 5-EMF yield was increased with increasing duty cycle from 30 to 60% and then surprisingly reduced. Here, the use of ultrasonic technology exhibited several advantages, which are as follows: (I) the reaction may be conducted at a short time or low temperature when compared with the traditional method, and (II) the formation of humins or EL could be effectively obstructed.

Reaction Kinetics for 5-EMF Production. To determine the activation energies and pre-exponential factors for 5-EMF production via ultrasonic and conventional systems, we investigated the effects of reaction temperatures (70, 80, 90, and 100 °C) and reaction times (10, 20, 30, 40, and 50 min) on sucrose conversion into 5-EMF while other factors were kept constant (Figure 8). Here, a first-order reaction could be applied to find the reaction rate of sucrose conversion into 5-EMF ($r[\text{sucrose}]$), while the Arrhenius model was used to determine the activation energy with the pre-exponential factor in the catalytic system.^{48–51}

As shown in Figure 8A,B, the conversions of sucrose into 5-EMF obtained from both systems were clearly increased with the increase of temperature up to 100 °C for 50 min. Also, the linear kinetic relationship between $-\ln(1 - X)$ and reaction time was strongly accorded with the hypothesis of pseudo-first order ($R^2 > 0.99$) for one-pot conversions of sucrose into 5-EMF. The reaction rate constants were also increased to some extent when the reaction temperatures were increased from 70 to 100 °C for both systems, confirming again that the effect of reaction temperature well enhanced the 5-EMF formation. It should be noted that reaction rate constants for all temperatures derived from the ultrasonic system were much higher than those from the conventional system. The Arrhenius plots

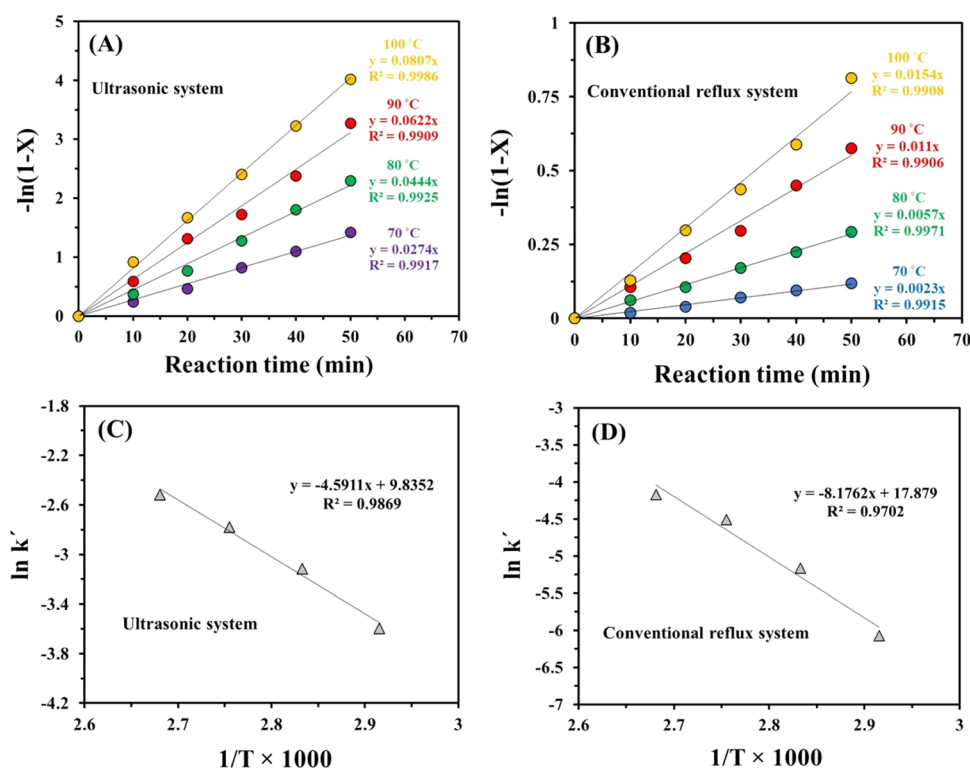


Figure 8. (A,B) Logarithms of sucrose conversion into 5-EMF as a function of reaction time at 70–100 °C and (C,D) Arrhenius plots with reaction rate constants as a function of reaction temperature.

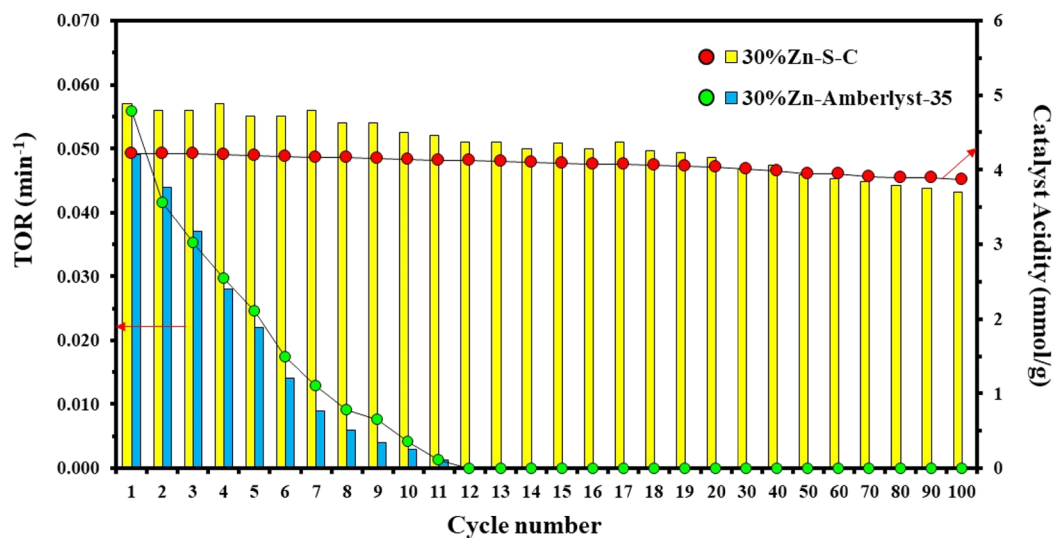


Figure 9. Reusability test of 30%Zn-S-C and 30%Zn-Amberlyst-35 catalysts for 5-EMF synthesis from direct conversion of sucrose using a sustainable ultrasonic-biphasic system.

with reaction rate constants are shown in Figure 8C,D. The activation energies and pre-exponential factors obtained from ultrasonic and conventional systems were determined to be 38.17 kJ/mol with $1.87 \times 10^4 \text{ min}^{-1}$ and 69.98 kJ/mol with $5.82 \times 10^7 \text{ min}^{-1}$, respectively. Interestingly, the value of activation energy obtained from the ultrasonic system was much lower than that from the conventional system. It suggests that the microemulsion generation from the ultrasound system promoted a faster reaction rate for sucrose conversion into 5-EMF, resulting in the obvious reduction of the activation energy value. Here, the evident activation energies determined in this study were followed to a kinetically controlled regimen,

as appraised by the Weisz–Prater criterion factor, indicating that no mass-transfer limitations interfered.⁵² For comparison, the value of activation energy reported in this study was lower than those in previous works.^{53–56} Here, the values of activation energy for 5-EMF formation in this study were lower than those of 5-EMF and 5-HMF, indicating that our catalytic system was beneficial to the conversion of sucrose into 5-EMF.

Recycling of the Catalyst. Long-term stability of 30%Zn-S-C was tested with synthesis of 5-EMF under optimum conditions over 100 cycles (Figure 9). Also, the recycling of 30%Zn-S-C was also compared with that of 30%Zn-Amberlyst-

35. Here, the turnover rate (TOR, min^{-1}) for sucrose conversion (50%) into 5-EMF was applied in this section. One can see that 30%Zn-Amberlyst-35 exhibited much lower recyclability than 30%Zn-S-C while only a slight reduction of 30%Zn-S-C activity through the TOR value was found for 100 cycles. This could be attributed to sulfonic leaching based on acidity results. The acidity of 30%Zn-Amberlyst-35 was exceedingly reduced from 1st to 10th cycles. This should be ascribed to water interaction since its characteristic properties exhibited robust hydrophilic nature, leading to rapid deactivation.⁵⁷ Another reason should be ascribed to the deposition of oligomeric/polymer products on the catalyst surface at active sites.^{58,59} It indicates that the commercial catalyst is not stable in our reaction system.

30%Zn-S-C showed excellent reusability, probably due to the synergistic influence of sulfonic, carboxylic, lactone, and phenolic acid sites on the S-C surface. Concurrently, the presence of hydrophobic groups on the carbon structure such as C-C polyaromatics promoted the practical mass transfer of the chemical, leading to a sustainable long-life cycle of the catalyst. The physicochemical properties of fresh and spent catalysts after the reusability test for 100 cycles are shown in Table S1. It is found that the adsorption of oligomeric products on the catalyst resulted in the reduction of surface area and pore size. Interestingly, the spent catalyst structure and sulfur/zinc distributions did not significantly vary, compared with the fresh one, as confirmed by SEM-EDX and XRD (Figure S8). This indicates that the as-prepared catalyst had long-term stability and long-life cycle in the reaction system. Based on the obtained results, the sustainable synthesis of 5-EMF with a high yield from sucrose conversion was well achieved, which might be further applied in practical biorefinery processes.

CONCLUSIONS

The sustainable synthesis of 5-EMF from direct conversion of sucrose using a sustainable ultrasonic-biphasic system was perfectly achieved. The use of Zn-S-C provided excellent selectivity for 5-EMF production. A maximum 5-EMF yield of $93.5 \pm 0.8\%$ was obtained at 98 °C for 47 min using a THF amount (0.25 mol), catalyst adding amount (77.8 wt.%), ultrasonic power (90 W), and ultrasonic duty cycle (6 s ON and 4 s OFF). The behavior for formation of 5-EMF and other side products such as EL or humins could be easily controlled by adjusting the catalyst loading, co-solvents, type/amount of inorganic salts, ultrasonic powers, and ultrasonic duty cycles. The activation energy obtained from the ultrasonic system was much lower than that from the conventional system. The Zn-S-C exhibited excellent recycling for 100 cycles with a few reductions in the TOF value, indicating a slow deactivation process.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.0c04517>.

Schematic representation of in situ 5-EMF synthesis and extraction processes; characterization results and discussion of fresh and spent catalysts by BET-BJH, XRD, Py-FTIR, ICP, NH_3 -TPD, SEM, and TEM; description on experimental designs; experimental conditions for 5-EMF production and their yields; analysis of variance

(ANOVA); analysis plot determined from Box–Behnken design (PDF)

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Notes

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