

Rapid Formation and Facile Separation of Biofuel 5-EMF over Integration of Sustainable Catalyst with Oxygen Environment under an Ultrasonic-Assisted Ethanolysis System

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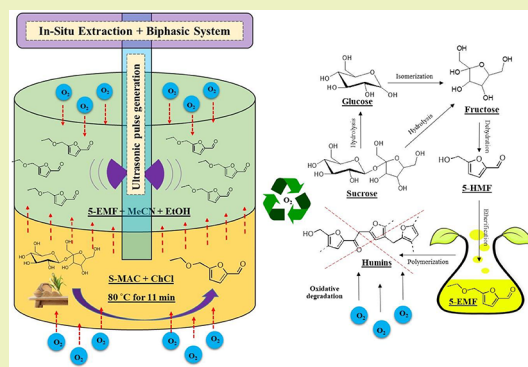
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ABSTRACT: In this work, ultrasonic-assisted ethanolysis of raw sugar (RS) into 5-ethoxymethylfurfural (5-EMF) product was performed under a biphasic system under mild conditions. The sulfonic-magnetic activated carbon (S-MAC) was prepared via pyrolysis and sulfonation processes and further applied for catalytic production of 5-EMF. The catalytic behaviors for facile formation/rapid production of 5-EMF were described through several factors such as type of catalyst, S-MAC and choline chloride (ChCl) adding amounts, reaction temperature, reaction time, and ultrasonic power generation. The integrating roles of various catalysts with the introduction of oxygen were described using turnover rate investigation, and the result found to be a great effect for improving the 5-EMF yield via major reactions such as hydrolysis, isomerization, dehydration, and etherification while side reactions for formation of polymeric intermediates were remarkably suppressed. Herein, a maximum yield of 5-EMF (actual yield = $93.2 \pm 0.6\%$) was obtained at a low temperature of 80 °C and short reaction time for 11 min under an optimization process via linear-quadratic designs. Finally, the reusable systems under O₂ and N₂ addition were compared up to 10 cycles, and the result found that very few changing in 5-EMF yield could be obtained while hard carbon/humins deposited on S-MAC structure was significantly obstructed and reduced in each cycle via special oxidative degradation. In addition, lower energy consumption was required for regeneration of spent catalyst derived from reaction under an oxygen environment. This work was notably expected for further application in practical procedure under a reusable system.

KEYWORDS: Raw sugar, 5-Ethoxymethylfurfural, Ethanolysis, Sulfonic-magnetic activated carbon, Reusable system



INTRODUCTION

Nowadays, with increasing demand for renewable energy, the investigation and development of new biorefinery technologies for biomass conversion to high-value added bio-oils and chemicals are currently enforced.^{1,2} Biomass-based raw sugar (RS) can be considered as a promising feedstock since it possesses low production cost, large abundance, and availability.^{3,4} To date, the specific productions of some value chemicals such as levulinic acid (LA), 5-hydroxymethylfurfuraldehyde (5-HMF), 5-ethoxymethylfurfural (5-EMF), ethyl levulinate (EL), and others were widely studied under green technologies.^{5–8} Among them, 5-EMF can be identified as 12 platform chemicals (according to the United States Department of Energy (DOE) in 2004).^{9,10} It can be applied as building-block compounds/multipurpose intermediates, and possibly used as biofuel additive in diesel engine as well for improving several properties such as lubricity and flashpoint stabilities under mild conditions.^{11,12} To date, sugars have been popularly utilized as a feedstock for 5-EMF

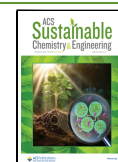
production via dehydration and ethanolysis reactions using strong acid catalysts.^{13–16} However, the further unwanted reaction for conversion of 5-EMF into form levulinic and fomic acids and humins may possibly occur, leading to the reduction of product yield.

Many studies have been tried to use heterogeneous catalysts in green systems, since they can overcome such above-mentioned problems.¹⁷ Dowaki et al.¹⁸ found that lignin-derived biochar with acidic functional groups (–COOH, –SO₃H, and –OH) could catalyze well for selective conversion of fructose to 5-EMF (62% yield) at 115 °C for 6 h. Morales et al.¹⁹ achieved to synthesize several sulfonic

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acid-functionalized heterogeneous catalysts for selective production of 5-EMF (63.4% yield) from fructose conversion at 116 °C for 4 h. Kumari et al.²⁰ successfully synthesized 5-EMF with a high yield (68%) under fructose dehydration at 120 °C for 8 h using heteropoly tungstate with tantalum ions. He et al.²¹ reported that glucose transformation to 5-EMF could be well achieved over sulfated complex metal oxides catalyst with the existence of dual Brønsted-Lewis acidic properties. Unlikely, long operation time and high operation cost were still highly required under complex separation procedures.^{22,23} Recently, Hafizi et al.²⁴ studied the method for preparation of hybrid magnetic dendritic fibrous silica core-shell catalyst consisting of Brønsted/Lewis acid sites, and applied for the ethanolsis of sugar into 5-EMF under notably catalytic efficiency and reusability. They found that spent catalyst could be easily separated after complete ethanolsis procedure, while EMF yields of 62.2% and 21.4% were obtained from the catalytic conversion of fructose and sucrose, respectively. Yuan et al.²⁵ prepared propyl magnetic Fe₃O₄@C-SO₃H via covalent hydrothermal techniques, leading to facile/fast separation by a magnet after complete reactions for 5-EMF production. They also discussed that Fe₃O₄@C-SO₃H not only gave a yield of 5-EMF (34%) from sucrose conversion at 140 °C for 24 h but also presented good recyclability of catalyst up to six cycles. To date, the new challenge of this research field is technological application for faster/cleaner production of high-value chemicals.^{26,27}

In this novel work, we studied and developed the green technology for 5-EMF production at short ethanolsis times and low ethanolsis temperatures. Here, 5-EMF was easily produced from the fast ethanolsis of RS under a reusable process over sulfonic-magnetic activated carbon (S-MAC). Interestingly, ultrasonic generation was also applied for improving the catalytic efficiency of sugar conversion. Also, to support the efficiency for catalytic recycling system, the environmental behaviors for 5-EMF production with humins suppression was studied via the introduction of O₂ and/or N₂. The S-MAC and other catalysts were specifically characterized to describe in detail their physicochemical properties. The optimization process for 5-EMF production under reusable process was investigated via regression models using a 2^k factorial and Box-Behnken designs. The possible mechanisms for 5-EMF formation assisted by ultrasound in this system were discussed via significant parameters. Turnover rate of as-prepared S-MAC for selective transformation of RS to 5-EMF was tested with various commercial catalysts. Finally, the reusability of the S-MAC catalyst was performed for 10 cycles under optimum conditions. This research is expected to further apply for facile production of 5-EMF in a practical process.

EXPERIMENTAL SECTION

Materials and Reagents. The details of chemical names, CAS registry numbers, sources, and purities of each chemical used in this study are listed in Table S1 in the Supporting Information. All chemicals and reagents were of analytical grade and utilized without further purification.

Catalyst Preparation. The catalyst preparation procedures were as follows.

Magnetically Activated Carbon (MAC). For the synthesis of magnetically activated carbon (MAC), 10 g of biomass powder was impregnated with 1000 mL of FeCl₃ at a concentration of 0.01 mol/L, and stirred at ambient temperature for 2 h. Thereafter, a mixture was dried at 105 °C. To produce MAC, the dried sample was further pyrolyzed at 550 °C for 1 h under a N₂ atmosphere.²⁴

Sulfonic Magnetically Activated Carbon (S-MAC). For preparation of sulfonic-magnetically activated carbon (S-MAC), a certain amount of MAC (1 g) with chlorosulfonic acid (6 mL) was mixed with 40 mL of ethanol under setup equipment. It should be noted that chlorosulfonic acid was easily prepared from mixing together between 1,4-butane sultone with KCl solution.²⁵ Then, a mixture was stirred at room temperature for 6 h under N₂ atmosphere. Thereafter, the S-MAC catalyst was easily separated by external magnetic field, and washed with acetone or distilled water. Finally, it was dried at 105 °C and kept in a desiccator before further application in the catalytic process. For comparison, commercial catalysts such as sulfonic-commercial activated carbon (S-CAC), sulfonic-alumina (S-alumina), sulfonic-ZSM-5 (S-ZSM-5) were functionalized using the same method such S-MAC preparation. Herein, sulfonic-activated carbon (S-AC), MAC, S-MAC, S-CAC, S-Alumina, S-ZSM-5, SiO₂-Tosic acid and Amberlyst-35 were also tested for catalytic production of 5-EMF via the turnover rate (TOR, min⁻¹) method. All steps for facile preparation of S-MAC catalyst are summarized and shown in Figure S1 in the Supporting Information. The procedures for characterization of as-prepared catalysts including their physicochemical results and discussion, were clearly provided in the Supporting Information (SI) (Figures S2–S5).

Catalytic Production of 5-EMF under Reusable System.

Catalytic conversion of RS into 5-EMF over DES + S-MAC catalyst was carried out using 100 mL of a glass tube reactor equipped with ultrasonic probe and a thermocouple thermometer (Figure S6 in the Supporting Information). In a typical synthesis, 1 g of RS and 3.5 g of choline chloride (ChCl) were mixed with a certain volume ratio of acetonitrile (MeCN) to ethanol (10:1). Then, 0.82 g of S-MAC catalyst was added in mixture solution. The glass tube reactor containing of as-prepared mixture solution was steeped in oil bath and heated at 80 °C for 11 min including a stirring speed of 550 rpm, an ultrasonic frequency at 2500 Hz and ultrasonic pulse of 5 s on/5 s off. During reaction procedure, oxygen gas was added to the inside of the reactor at a flow rate of 20 mL/min. After finishing the process, the S-MAC catalyst was immediately separated from the mixture solution using an external magnetic field. Thereafter, ChCl in liquid phase was newly recrystallized and plummeted into the bottom layer. It should be noted that produced 5-EMF was in the upper layer/organic MeCN layer. Herein, obtained 5-EMF in MeCN solvent was corrected in the refrigerator for further analysis. The spent catalyst and ChCl crystal after reaction were washed with butanone and followed by washing with MeCN several times to remove some organic products adsorbed on their surfaces, dried at 105 °C, and kept in a desiccator for further reusability tests.

Experimental Design for 5-EMF Production. Several advantages from experimental designs were displayed, for instance, (I) it could decrease some error in determining the influence of each determinant and their interactions, (II) the production cost of 5-EMF could be significantly reduced since lower number of batch experiments were carried out, and (III) optimal conditions and maximal yield could be obtained.²⁷ The effects of independent input parameters such as X₁ (the amount of ChCl added (g)), X₂ (the amount of S-MAC added (g)), X₃ (the reaction temperature (°C)), and X₄ (the reaction time (min)) on response of 5-EMF yield were investigated to find the significant levels using 2^k factorial design at the 95% confidence level. The ranges of factorial design consisting of 16 experiments with their low (−1) and high (1) levels are shown in Table 1. The regression model for determining the effect of each parameter was provided as follows in eq 1:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i < j} \sum \beta_{ij} X_i X_j \quad (1)$$

where Y is the percentage of 5-EMF yield, β_0 is the intercept/constant coefficient, β_i is the linear coefficients, β_{ij} is the interaction coefficient of each parameter, and X_i and X_j are the codes of independent input parameters.

The optimization for synthesis of 5-EMF with their responses under ultrasonic-assisted ethanolsis was designed by using three

Table 1. Experimental Investigation for Ultrasound-Assisted Formation of 5-EMF Derived from 2⁴ Factorial Design^a

run	X ₁ (g)	X ₂ (W)	X ₃ (min)	X ₄ (°C)	5-EMF yield (%)
1	0.4 (-1)	60 (-1)	5 (-1)	80 (-1)	46.7 ± 0.1
2	1.2 (1)	60 (-1)	5 (-1)	80 (-1)	52.8 ± 0.3
3	0.4 (-1)	100 (1)	5 (-1)	80 (-1)	46.3 ± 0.1
4	1.2 (1)	100 (1)	5 (-1)	80 (-1)	62.6 ± 0.5
5	0.4 (-1)	60 (-1)	15 (1)	80 (-1)	50.8 ± 0.4
6	1.2 (1)	60 (-1)	15 (1)	80 (-1)	60.5 ± 0.2
7	0.4 (-1)	100 (1)	15 (1)	80 (-1)	53.1 ± 0.2
8	1.2 (1)	100 (1)	15 (1)	80 (-1)	77.3 ± 0.3
9	0.4 (-1)	60 (-1)	5 (-1)	120 (1)	49.4 ± 0.6
10	1.2 (1)	60 (-1)	5 (-1)	120 (1)	52.3 ± 0.2
11	0.4 (-1)	100 (1)	5 (-1)	120 (1)	52.1 ± 0.5
12	1.2 (1)	100 (1)	5 (-1)	120 (1)	63.3 ± 0.7
13	0.4 (-1)	60 (-1)	15 (1)	120 (1)	50.3 ± 0.1
14	1.2 (1)	60 (-1)	15 (1)	120 (1)	60.1 ± 0.3
15	0.4 (-1)	100 (1)	15 (1)	120 (1)	58.8 ± 0.3
16	1.2 (1)	100 (1)	15 (1)	120 (1)	81.5 ± 0.4

^aThe factors are coded as follows: X₁ = amount of S-MAC (g), X₂ = ultrasonic power (W), X₃ = reaction time (min), and X₄ = reaction temperature (°C).

levels of Box-Behnken model based on quadratic/response surface methodology.²⁸ The ranges of this design consisting of 15 experiments with their low (-1), medium (0), and high (1) levels

Table 2. Experimental Investigation for Ultrasound-Assisted Formation of 5-EMF Derived from Box–Behnken Design^a

run	X ₁ (g)	X ₂ (W)	X ₃ (min)	5-EMF yield (%)	
				observed	predicted
1	0.4 (-1)	60 (-1)	10 (0)	58.8 ± 0.4	58.7
2	1.2 (1)	60 (-1)	10 (0)	68.0 ± 0.3	65.2
3	0.4 (-1)	100 (1)	10 (0)	61.7 ± 0.5	64.5
4	1.2 (1)	100 (1)	10 (0)	74.4 ± 0.1	74.5
5	0.4 (-1)	80 (0)	5 (-1)	67.0 ± 0.2	63.6
6	1.2 (1)	80 (0)	5 (-1)	76.1 ± 0.4	75.4
7	0.4 (-1)	80 (0)	15 (1)	72.1 ± 0.3	72.7
8	1.2 (1)	80 (0)	15 (1)	74.0 ± 0.5	77.4
9	0.8 (0)	60 (-1)	5 (-1)	65.5 ± 0.1	69.0
10	0.8 (0)	60 (-1)	5 (-1)	74.1 ± 0.2	74.7
11	0.8 (0)	100 (1)	15 (1)	73.2 ± 0.2	72.6
12	0.8 (0)	100 (1)	15 (1)	85.6 ± 0.6	82.1
13	0.8 (0)	80 (0)	10 (0)	91.9 ± 0.5	91.9
14	0.8 (0)	80 (0)	10 (0)	92.2 ± 0.8	91.9
15	0.8 (0)	80 (0)	10 (0)	91.6 ± 0.4	91.9

^aThe factors are coded as follows: X₁ = amount of S-MAC (g), X₂ = ultrasonic power (W), and X₃ = reaction time (min).

are shown in Table 2. The quadratic model for maximizing the 5-HMF yield is provided as follows in eq 2:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad (2)$$

where Y is the percentage of 5-EMF yield, β_0 is the intercept/constant coefficient, β_1 , β_2 , and β_3 are the linear coefficients, β_{11} , β_{22} , and β_{33} are the quadratic coefficients, β_{12} , β_{13} , and β_{23} are the interaction coefficient of each parameter, and X₁, X₂, and X₃ are the codes of independent input parameters.

5-EMF Analysis. The product analysis of 5-EMF solution was detected by high-performance liquid chromatography (HPLC, Agilent 1200) using UV detector (284 nm), column temperature (30 °C), and mobile phase (H₂O:MeOH volume ratio of 0.8:0.2). The conversion percentage of RS into 5-EMF was analyzed by an Aminex HPLC-87H column using a refractive index detector, column temperature (65 °C) and mobile phase (0.05 M H₂SO₄). The 5-EMF yield were quantified using an exterior standard method.²⁹

RESULTS AND DISCUSSION

Ultrasound-Assisted Ethanolysis of RS into 5-EMF.

Table 1 shows the results of 5-EMF production (16 experiments) from ultrasound-assisted conversion of RS over S-MAC under oxygen environment via 2⁴ factorial design using a linear regression model. As obtained results, the yield of 5-EMF derived from ultrasound-assisted conversion of RS over S-MAC was in the range of 46%–82%. To screen the significant factors, as shown in Figure 1, normal probability

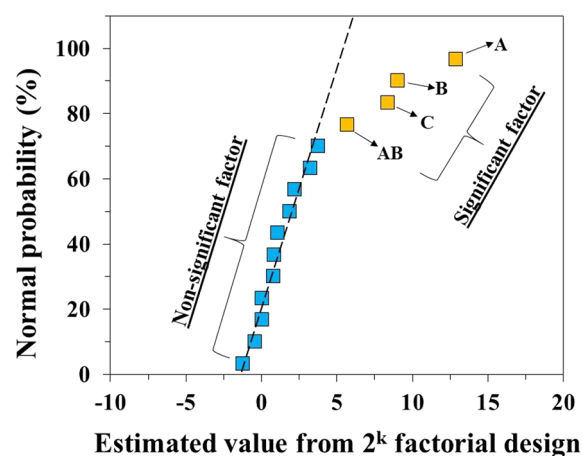


Figure 1. Normal probability plot for ultrasound-assisted formation of 5-EMF from RS conversion over S-MAC under an oxygen environment.

plots were primarily studied. One can see that three significant factors such as amount of S-MAC (X₁), ultrasonic power (X₂), and reaction time (X₃) including X₁X₂ interaction between S-MAC amount and ultrasonic power were clearly found. The order of three factors influenced for ultrasound-assisted formation of 5-EMF from RS conversion was amount S-MAC > ultrasonic power > reaction time. It should be mentioned here that the range of reaction temperature (80–120 °C) had a nonsignificant effect for improving the specific production of 5-EMF. In general, higher temperature was required for supporting the RS ethanolysis under conventional system. Meanwhile, 5-EMF could be further converted into unwanted products such as LA and humins via side reactions such as rehydration, condensation, and polymerization when too long of a reaction time was applied.³⁰ This indicated that the DES integration in the presence of ChCl + MeCN + S-MAC was well-achieved for ultrasound-assisted production of 5-EMF from RS conversion at a short reaction time. Also, the in situ generation of cavitation bubbles with hot spots promoted faster reaction rate for 5-EMF formation. Therefore, the lowest reaction temperature of 80 °C was certainly fixed for all experiments after this section. Table 3 presents the analysis of variance (ANOVA) for ultrasound-assisted production of 5-EMF from RS conversion over S-MAC with an oxygen environment using a confidence level of 95% with F_{0.05}.

Table 3. Analysis of Variance (ANOVA) Determined from 2⁴ Factorial Design for Ultrasound-Assisted Formation of 5-EMF from RS Conversion over S-MAC^a

source of variation	sum of square	degree of freedom	mean square	F _{value}	F _{critical}
X ₁	662.55	1	662.55	45.83	
X ₂	326.13	1	326.13	22.56	
X ₃	280.23	1	280.23	19.39	
X ₄	19.54	1	19.54	1.35	5.32
X ₁ X ₂	130.76	1	130.76	9.05	
X ₁ X ₃	56.61	1	56.61	3.92	
error	130.10	9	14.46		
total	1549.30	15			

^aThe factors are coded as follows: X₁ = amount of S-MAC (g), X₂ = ultrasonic power (W), X₃ = reaction time (min), and X₄ = reaction temperature (°C).

Herein, the observed factors had a significant effect when their *F*-values were more than the 5.32 value. The maximum and minimum *F*-values derived from the S-MAC amount and reaction time were 662.55 and 280.23, respectively. This should be noted that catalyst amount added in the system and ultrasonic power application had limitations since their interactions were presented. Thus, optimization via the quadratic regression model should be applied as well. The result of ANOVA agreed well with the estimated effect of normal probability, as shown in Figure 1. Based on the above results, the predicted 5-EMF yield was calculated via linear regression model consisting of low and high levels, as follows in eq 3:

$$Y = 57.36 + 6.435X_1 + 4.515X_2 + 4.185X_3 + 2.859X_1X_2 \quad (3)$$

where *Y* is the 5-EMF yield (%), X₁ is the amount of S-MAC (g), X₂ is the ultrasonic power (W), and X₃ is the reaction time (min).

The normal probability plot of the residual value and distribution plot of residual are shown in Figure 2. Here, the applied linear regression model had high dependability and precision, based on a good linearity with *R*² > 0.95 (variability of 98.45% for polynomial investigation). Also, the distribution of residue value was in the range of ±5.0%, indicating that a few errors from the linear equation were achieved without an anomaly pattern. From the results of 2⁴ factorial design, a lowest temperature at 80 °C was selected for further study on optimization of 5-EMF production from ultrasound-assisted conversion of RS over S-MAC with an oxygen environment via Box–Behnken design/quadratic regression model.

Table 2 shows the results of 5-EMF production (15 experiments) from ultrasound-assisted conversion of RS over S-MAC with oxygen environment via Box–Behnken design using a quadratic regression model. The predicted 5-EMF yield was calculated via the quadratic regression model consisting of low, medium, and high levels as follows in eq 4:

$$Y = 91.9 + 4.108X_1 + 3.796X_2 + 2.761X_3 - 14.246X_1^2 - 11.934X_2^2 - 5.364X_3^2 + 0.88X_1X_2 - 1.805X_1X_3 + 0.953X_2X_3 \quad (4)$$

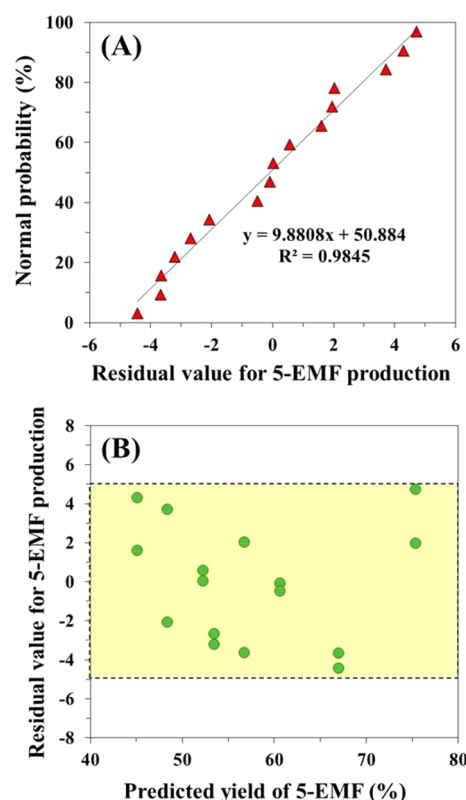


Figure 2. (A) Normal probability plot of residual value and (B) distribution plot of residual versus predicted 5-EMF yield determined from 2⁴ factorial design for ultrasound-assisted formation of 5-EMF from RS conversion over S-MAC under an oxygen environment.

where *Y* is the 5-EMF yield (%), X₁ is the amount of S-MAC (g), X₂ is the ultrasonic power (W), and X₃ is the reaction time (min).

The predicted yield of 5-EMF was calculated from eq 4, and the result is shown in Table 2. As presented in Figure 3, *R*² > 0.95 with variability of 96.02% for polynomial investigation was obtained from the plot of observed yield versus predicted yield of 5-EMF, suggesting that the predicted yield of 5-EMF was very close to the observed yield, based on high accuracy. To access more details via interaction of each factor, the optimization using response surfaces and contour plots is presented in Figure 4. The interaction between the S-MAC amount and ultrasonic power generation for ultrasound-assisted formation of 5-EMF from RS conversion under an oxygen environment at a constant value of reaction time = 10 min (medium level) is shown in Figures 4A and 4B. The increase in the amount of S-MAC, from 0.40 g to 0.88 g, over an ultrasonic power generation of 84 W significantly promoted the specific formation of 5-EMF, where the percent yield increased from 73.7% to 92.5%. This phenomenon should be ascribed in accreting of available active sites and collision rate between RS and S-MAC + ChCl catalysts consisting of hydrogen bond acceptor and donors, leading to a facile reaction process.³¹ However, when an S-MAC amount of >0.88 g 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 too high viscous slurries and poor mixing in mixture solution. Remarkably, with the increment of ultrasonic power from 60 W to 84 W, a dramatic increase of 5-EMF yield could be evidently obtained,

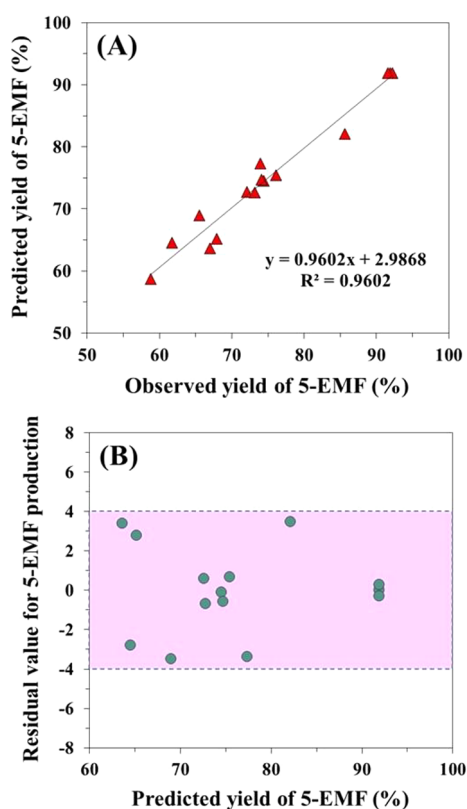


Figure 3. (A) Plot of observed versus predicted values of 5-EMF yields and (B) distribution plot of residual value versus predicted 5-EMF yield determined from Box-Behnken design for ultrasound-assisted formation of 5-EMF from RS conversion over S-MAC under an oxygen environment.

demonstrating that higher procreation of ultrasonic power supplemented the selective transformation RS into 5-EMF, because of a facile protonation on carbonyl-hydroxyl groups of RS structure via interaction role at active sites of S-MAC structure. Also, the levels of cavitation bubbles/hot spots that occurred under the reaction medium system were associated with expanding of ultrasonic power, improving the RS ethanolysis into 5-EMF. However, too high of a level of ultrasonic power, such as >84 W, promoted further decomposition of 5-EMF into other products, especially for humins via polymerization reaction, which was confirmed by the color changing from brown to black. In other words, the reaction media may vary, which would be direct variation with a change of the selectivity to 5-EMF product. When traditional method without ultrasonic generation was applied, only an 5-EMF yield of 17.6% was found at 140 °C for 4 h, demonstrating that much higher reaction temperature and much longer reaction were higher required to approach the formation level of 5-EMF product. Herein, for comparison, with verification on physical-chemical characteristic, instability of spent catalyst and liquid product were clearly observed in conventional reaction method which was totally opposite, comparing with ultrasonic reaction system. This displays that the ultrasound application was not only regained for reaction level but also obstructed the further transformation of polymeric humins, leading to preservation in catalyst durability.

The plausible mechanism and recycling system for ultrasound-assisted transformation of RS into the 5-EMF product

over DES-biphasic integration in the presence of ChCl + MeCN + S-MAC are shown in Figure 5. During hot condition, RS molecule was interacted with ChCl (nucleophile site) via an electrostatic mechanism, resulting in further transformation into intermediate chemicals over the S-MAC catalyst. During the reactions, ChCl could mainly serve as the H-bond acceptor for stabilizing the H-bond donor from $-\text{SO}_3\text{H}$, $-\text{COOH}$, and/or phenolic groups on S-MAC, resulting in well enhancement of 5-EMF product selectivity with suppression of humins formation.^{32,33} Interestingly, the existence of ChCl with a suitable amount (3.5 g, based on our preliminary study) could suppress the side reactions as well as avoid its further degradation during the reaction process. Anyway, if too large of an amount of ChCl was used, the 5-EMF molecule might be possibly adsorbed on ChCl recrystallized after finishing the reaction process, resulting in the reduction of 5-EMF yield. It should be noted that ChCl crystal did not destroy even a large amount of S-MAC (heterogeneous acid catalyst) was added. This was totally different when compared by using a homogeneous acid catalyst. The ChCl molecule could be easily destroyed when too large of an amount of homogeneous acid catalyst was used, leading to improbability for recrystallization and recycling processes of spent ChCl. Meanwhile, MeCN could be also protonated by proton transfer from Brønsted acid sites of $-\text{SO}_3\text{H}$ and $-\text{COOH}$ on the S-MAC catalyst.^{34,35} In addition, in this work, a certain volume ratio of acetonitrile (MeCN) to ethanol (10:1) was fixed due to preservation of the ChCl crystal. It should be remarked that ChCl recrystallization did not occur when an unsuitable amount of ethanol was applied. In this way, the hydroxyl group or glycosidic bond of the anomeric center of the RS structure would interact at the electrophilic position of protonated MeCN, leading to the generation of a covalent bond at O and S atoms. Due to the stable interactions between DES (ChCl + MeCN + S-MAC) with RS molecules, higher reactivity for RS hydrolysis into glucose and fructose should easily occur. Furthermore, the existence of hydrogen bonding with electrostatic interaction on C–H and/or C–O bonds of intermediates could promote further dehydration of fructose into 5-HMF product, followed by facile etherification of 5-HMF into 5-EMF. Here, the glucose molecule was isomerized into fructose via Lewis-acid sites in the S-MAC catalyst (L/B ratio = 0.24). It is well-recognized that ultrasonic pulse application could possibly split the $-\text{OH}$ created in situ from water structure to generate oxidizing species such as hydrogen radicals ($\bullet\text{H}$) and hydroxyl radicals ($\bullet\text{OH}$).²⁶ Here, the presence of substantial oxidizing species might interact with the RS structure, leading to facile formation of the desired value product. In an economical way, the possibility to be applied in practical processes for reusable systems could be truly focused under the presence of DES (ChCl + MeCN + S-MAC) via an in situ extraction procedure. For instance, (I) S-MAC could be conveniently separated using external magnetic field and well reused without significant reduction of catalytic activity, (II) spent ChCl could be facily recrystallized and recovered several times, and (III) the mixture between 5-EMF and solvent could be easily separated via distillation procedure based on different principles in their boiling points.

As shown in Figures 4C and 4D, the highest 5-EMF yield of 92.4% was derived from interaction between an S-MAC amount of 0.88 g with a reaction time of 11 min at a constant value of ultrasonic power = 80 W (medium level). For Figures 4E and 4F, considering the interaction effect between

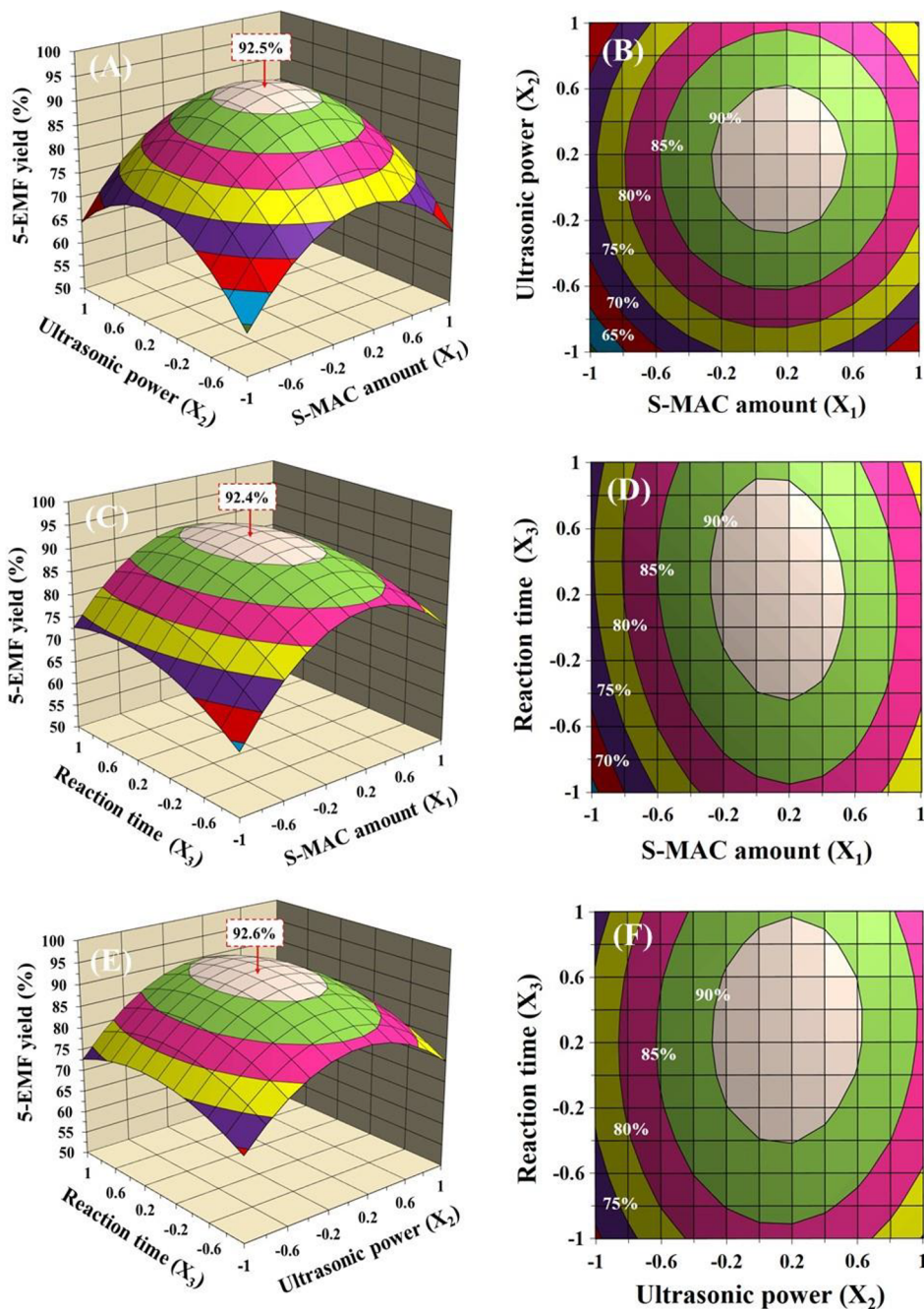


Figure 4. Response surfaces and contour plots determined from 5-EMF yield: (A, B) interaction effect of ChCl and S-MAC adding amount, (C, D) interaction effect of ChCl adding amount and reaction temperature, and (E, F) interaction effect of S-MAC adding amount and reaction temperature.

ultrasonic power and reaction time, the highest 5-EMF yield (92.6%) was found at 80 °C for 11 min. As clearly observed in Figure 4, the reaction time applied in this study did not exceed 11 min; even, in general, a longer reaction time was required as a positive effect since the ethanolysis process for 5-EMF synthesis was an endothermic reaction. It is possible that further polymerization of 5-EMF into polymeric humins was significantly preferred, which could be observed from the color changing in the mixture from light brown to dark brown. Also, at times exceeding the reaction time, some protonated MeCN solvent might be decomposed from the liquid phase into the vapor phase since ultrasonic treatment could generate hot spots in situ, leading to less solvent being available in the

reaction system. Therefore, the optimization using Box-Behnken design with the quadratic regression model was significantly important for the catalytic production of 5-EMF from ultrasound-assisted conversion of RS over DES-biphasic system. Based on the above analysis, a highest predicted 5-EMF yield of 92.9% was evidently achieved via quadratic regression model under the optimal conditions, such as an S-MAC amount of 0.82 g, a reaction time of 11 min, a reaction temperature of 80 °C, and an ultrasonic pulse of 83 W. To verify the exactitude for this prediction, a veritable experiment was investigated by obtaining optimum conditions for three duplicates, and the result found that an average/actual yield of 5-EMF (93.2% ± 0.6%) was obtained in a good way. Herein,

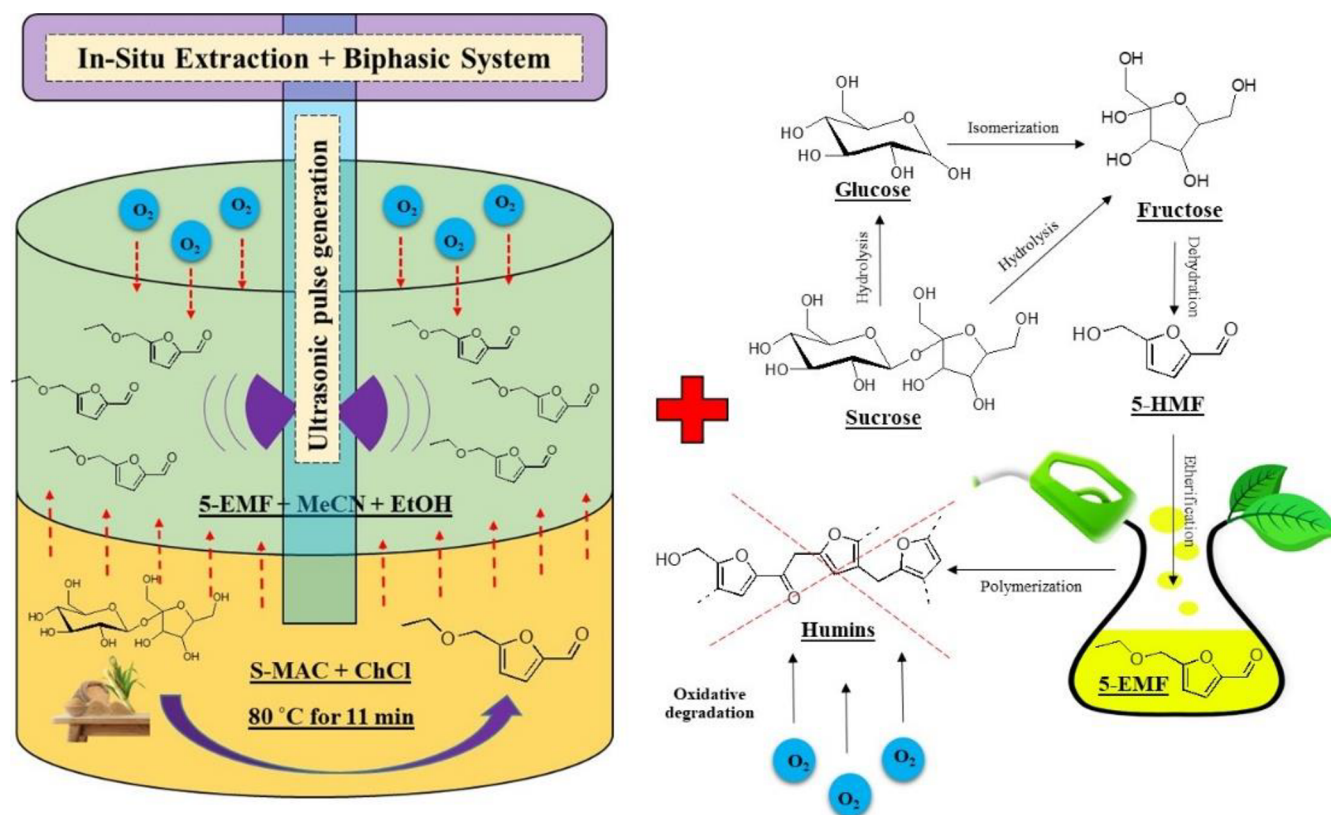


Figure 5. Plausible mechanism of ultrasound-assisted formation of 5-EMF from RS conversion over the DES-biphasic system with the introduction of oxygen.

pre-exponential and activation energies for 5-EMF formation that occurred from ultrasonic pulse generation were $1.88 \times 10^2 \text{ min}^{-1}$ and 24.85 kJ/mol , respectively, which was significantly lower, in comparison with traditional systems ($3.38 \times 10^2 \text{ min}^{-1}$ and 45.09 kJ/mol). This demonstrates that 5-EMF production via the rapid ethanolysis of RS could be achieved in our developed system.

Catalytic Comparison. To update the results from this work, the comparison in each system for catalytic production of 5-EMF from RS substrate is shown in Table 4.^{13–15,21,24,25,36} As expected, S-MAC + ChCl clearly presented better performance than previously other catalysts while lower energy consumption could be found via DES integration in the presence of ChCl + MeCN + S-MAC. In addition, one can see that DMSO solvent was quite popular for 5-EMF production, since it exhibited high polar characteristics.³⁷ In this case, even DMSO solvent was good for hydrolysis and dehydration reactions, but it was not suitable for the ChCl recrystallization process. For separation/distillation/recycling procedures, they were quite difficult since the boiling point of DMSO (189 °C) was very high, when compared with MeCN (82 °C) and 5-EMF (270 °C). This indicates that the application of reusable-biphasic DES system not only promotes the selective formation of 5-EMF, but also could obstruct the polymerization for humins formation. More remarkably, a much lower reaction temperature with shorter reaction time required for RS ethanolysis into 5-EMF was obviously applied over ultrasonic pulse generation, compared with high thermal + pressure reactors (see entries 1–7 vs 8 in Table 4). These verify that our developed system had perfect effectiveness for the sustainable synthesis of 5-EMF biofuel.

Table 4. Catalytic Comparison of Different Acid Catalysts for 5-EMF Production from RS/Sucrose Conversion

entry	catalyst	solvent	reactor system	reaction conditions	5-EMF yield (%)	ref
1	OMC-SO ₃ H	ethanol	autoclave	140 °C for 24 h	26.8	13
2	MIL-101-SO ₃ H	ethanol + THF	autoclave	130 °C for 15 h	34.0	14
3	[BMIM][HSO ₄]	ethanol + water	autoclave	130 °C for 30 min	43.0	15
4	Zr-Sn-Al-Fe-O-S	ethanol + DMSO	autoclave	160 °C for 12 h	20.1	21
5	Fe ₃ O ₄ @SiO ₂ @KCC-1	ethanol	ACE pressure tube	120 °C for 3 h	21.4	24
6	Fe ₃ O ₄ @C-SO ₃ H	ethanol	autoclave	140 °C for 24 h	33.0	25
7	Fe ₃ O ₄ @SiO ₂ -SH-Im-HSO ₄	ethanol	autoclave	120 °C for 24 h	34.4	36
8	S-MAC + ChCl	ethanol + MeCN	ultrasonic pulse	80 °C for 11 min	93.2	this work

Catalytic performances/behaviors of S-MAC, S-AC, and MAC were also compared with different commercial catalysts such as S-Alumina, S-ZSM-5, SiO₂-Tosic acid, and Amberlyst-35. Herein, S-AC, S-alumina, S-ZSM-5 was prepared under the same sulfonating method as S-MAC. Figure 6 shows the turnover rate (TOR, min^{-1}) of RS conversion to 5-EMF using active acid catalysts. It should be mentioned here that TOR value was determined by dividing the molar amount of RS that transformed to 5-EMF per the catalyst adding amount with

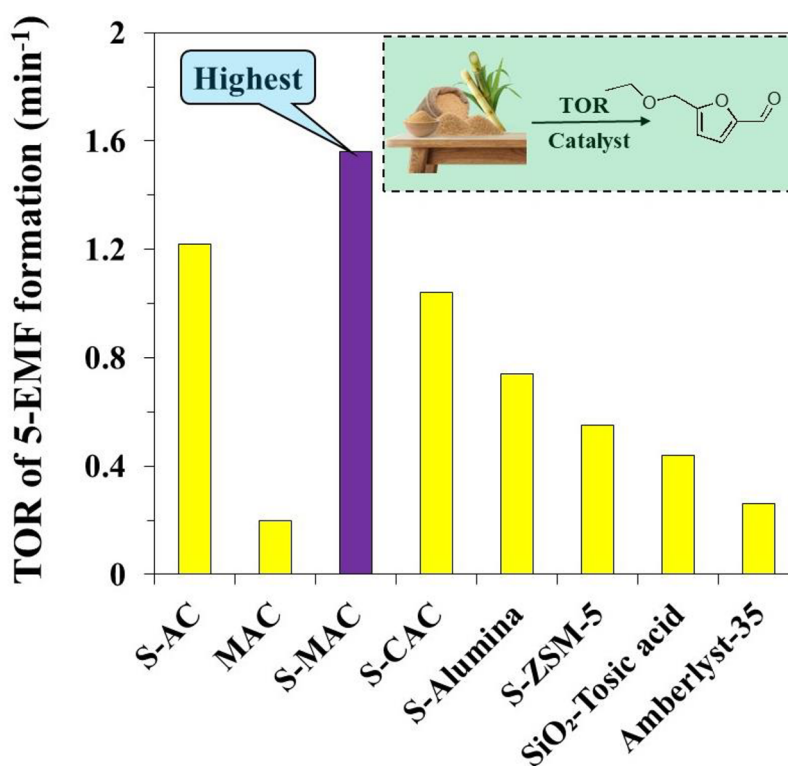


Figure 6. Turnover rate (TOR) for ultrasound-assisted formation of 5-EMF from RS conversion using different catalysts under an oxygen environment.

reaction time (mol/(g min)) by catalyst acidity (mol/g). In addition, selective production of 5-EMF was carefully specified at 50% of RS conversion for all catalytic testing in order to evade some puzzles from concentration amounts of reactants. The obtained results show that MAC presented the lowest catalytic performance based on TOR result, resulting from the only existence of Lewis acid site as a mainly active site on S-MAC. It is well-known that, for RS conversion into 5-EMF, a Lewis acid site was only suitable for glucose isomerization into fructose while RS hydrolysis, fructose dehydration, and 5-HMF etherification were required for Brønsted acid sites such as sulfonic, carboxylic, and/or phenolic groups. In the case of S-AC or S-CAC, even it had high TOR value for RS conversion into 5-EMF but some 5-EMF could not be produced since glucose isomerization did not promote via Lewis acid site, resulting in lower catalytic activity, when compared with S-MAC. Thus, the integration of Brønsted + Lewis sites on the catalyst was very important. In addition, the integrating effect of sulfonic, carboxylic, and phenolic groups on S-MAC could improve the catalytic dehydration and etherification via the generation of H-bonds.^{38,39} As expected, a better catalytic performance for 5-EMF production was observed for S-MAC with the presence of an L/B ratio of 0.24 (see Table S2 in the Supporting Information). For such an exorbitant acidity of Amberlyst-35 (5.20 mmol/g), side reactions such as rehydration and polymerization were preferred, resulting in the occurrence of low TOR value for 5-EMF production.⁴⁰ The difficult accessibility of chemical intermediates to active sites on catalyst structure resulted in the apparent reduction of TOR results; for instance, S-Alumina had a pore size that was too large (9.07 nm), while pore sizes that were too narrow (0.26 nm) were found for S-ZSM-5. From these results, S-

MAC could possibly be applied as an alternative catalyst for the sustainable production of 5-EMF in an industrial process.

Catalytic Reusability. Figure 7A shows the reusability result of the S-MAC catalyst for ultrasound-assisted formation of 5-EMF from RS conversion under an oxygen environment. Herein, to reduce the cost for 5-EMF production and to approach the reusable system in sustainable/practical process, the catalyst reusability was evaluated up to 10 cycles without regeneration process. As expected in Figure 7A, no significant decrease in catalytic system based on 5-EMF yield was observed for 10 successive cycles with a small decrease of 5-EMF yield (~12.6%), indicating that S-MAC had excellent stability and reusability for 5-EMF production from RS transformation. For Figure 7B, one can clearly see that catalytic ethanolysis under nitrogen introduction was considerably degenerated with a strong reduction of 5-EMF yield from first cycle (90.8%) to 10th cycle (43.4%), resulting from adsorption behavior of polymeric humins on the surface of catalyst, leading pore blocking and hard accessibility of chemical intermediates into active sites of catalyst structure.⁴¹ This could be obviously verified from the significant reduction of surface area (from 421 m²/g to 287 m²/g) and pore size (from 4.74 nm to 3.01 nm) of spent catalyst after the reusability test (10th cycle) under nitrogen introduction (see Table S2). It should be remarked that the phenomenon for sulfonic leaching was not the main reason for catalyst deactivation since S percentages for fresh and spent S-MAC were 5.22% and 5.19%, respectively.

In contrast, the presence of an oxygen environment in the reaction system could promote the long-term reusability and stability of S-MAC catalyst, and effectively suppress the formation of polymeric humins via an oxidative degradation process.⁴² It should be noted that the acidities of fresh and

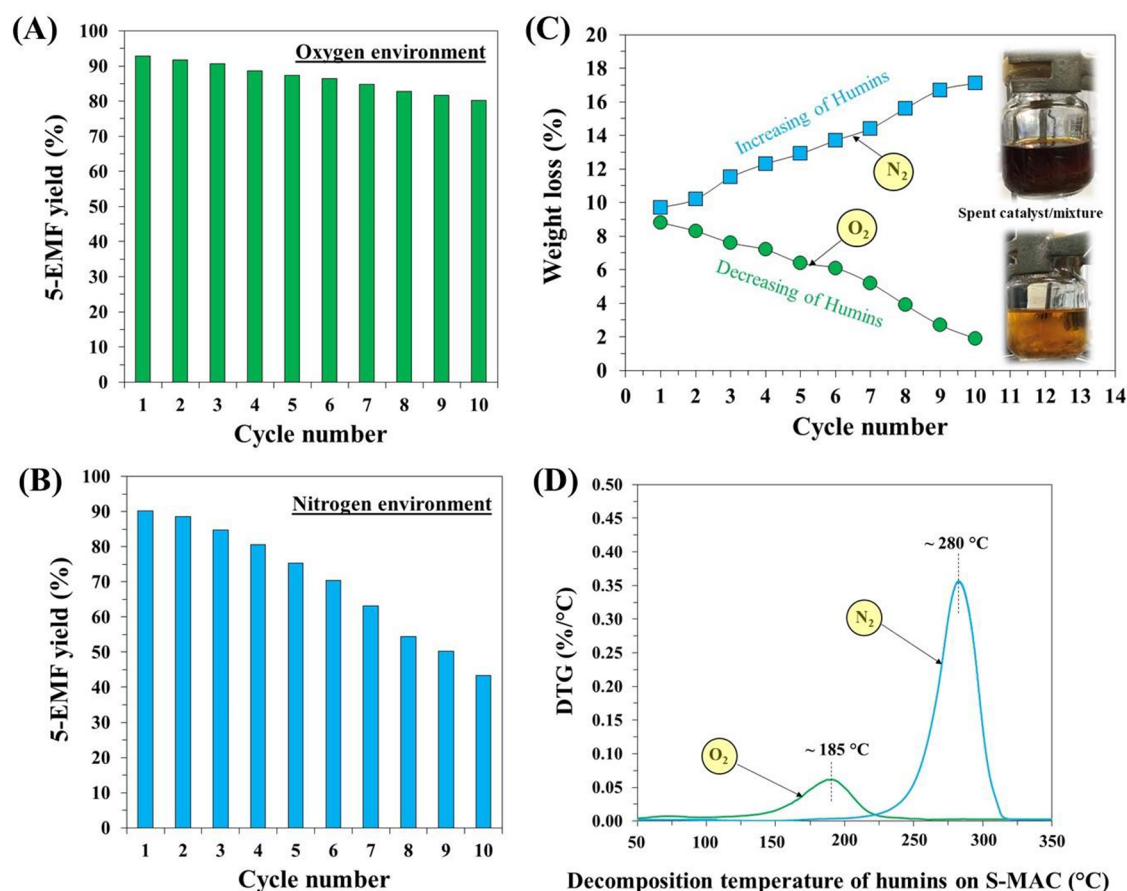


Figure 7. Catalytic reusability for ultrasound-assisted formation of 5-EMF from RS conversion using S-MAC catalyst via introduction of (A) oxygen and (B) nitrogen. (C) Influence of polymeric humins deposited on S-MAC versus recycling number. (D) DTG profiles of spent S-MAC after a reusability test for 10 cycles on ultrasound-assisted formation of 5-EMF from RS conversion under oxygen and nitrogen environments. Reaction conditions: RS amount, 1 g; amount of S-MAC, 0.82 g; reaction time, 11 min; reaction temperature, 80 °C; and ultrasonic power, 83 W.

spent catalyst in all systems had no significant change, suggesting that catalyst deactivation from sulfonic leaching did not occur under these reaction conditions. Interestingly, Figures 7C and 7D presents the role and behavior characteristics of humins formation on spent S-MAC versus recycling number derived from ultrasound-assisted production of 5-EMF under oxygen and nitrogen environments. Herein, the mass loss that occurred from humin decomposition on spent S-MAC was studied at a temperature range of 50–350 °C. As presented in Figure 7C, the amount of polymeric humins formed on spent S-MAC under oxygen introduction was lower than that under a nitrogen environment, while the color of liquid-mixture product was lighter orange. Moreover, the number of polymeric humins deposited on spent S-MAC consistently decreased as the recycling number increased from first cycle to 10th cycle under oxygen introduction. In general, the depositing number of polymeric humins should be increased to some extent as such nitrogen introduction. To advocate this information, we had tested on catalytic ethanolysis of RS at the first cycle under nitrogen introduction, and thereafter performed again without the addition of RS in the second cycle over an oxygen environment. As an achieved result, the amount of humins deposited on spent S-MAC was absolutely reduced and its catalytic activity in RS ethanolysis was perfectly recovered. This clearly demonstrates that RS ethanolysis under an oxygen environment could truly retain

the sustainable stability of S-MAC and well suppress humin formation in the reaction system.

Figure 7D presents DTG results of spent S-MAC after the reusability test on ultrasound-assisted ethanolysis of RS for 10 cycles. It is found that specific species of polymeric humins on S-MAC had significant differences based on thermal decomposition range observed in DTG profiles. The RS ethanolysis under nitrogen environment affected in expedient deposition of polymeric humins (hard species) on spent S-MAC structure, leading to higher decomposition range (280 °C) in DTG result when compared with under oxygen environment (185 °C). This verifies that polymeric humins (soft species) on spent S-MAC derived from RS ethanolysis under oxygen environment was easily removed and regenerated at lower temperature. In addition, to recover the catalytic performance after reusability test for 10 cycles, the spent S-MAC was regenerated by the heating process at a temperature of 200 °C for removal of polymeric humins deposited on catalyst surface. As our expectation, catalytic activity of regenerated S-MAC was absolutely recovered the same as the first cycle for RS ethanolysis. This exactly verifies that humin formation on S-MAC resulted in a deactivation problem without significant leaching of the active site on S-MAC. This assumption was supported via their physicochemical properties, and the results are provided in Table S2. Thus, it can be summarized that the as-developed sustainable system was likely preserved for long-term stability/reusability, which

was highly possible to be further applied in practical processes for 5-EMF production from RS conversion.

CONCLUSIONS

In summary, S-MAC catalyst was successfully prepared and applied for sustainable upgrading of CS into 5-EMF using ultrasonic pulse system with oxygen introduction. The as-prepared S-MAC catalyst presented outstanding properties such as high porosity/surface area, high stability in thermal reaction (>300 °C) and proper active sites (acidity = 2.84 mmol/g with L/B ratio = 0.24). The noticeable parameters such as catalyst adding amount/catalyst type, ultrasonic power generation, reaction temperature and time had an important role for sustainable production of 5-EMF from RS ethanolysis. An integrating role between S-MAC + ChCl with oxygen introduction was beneficial in promoting the 5-EMF formation as well as suppressing the polymeric formation in the catalytic system. The existence of magnetic Fe₃O₄ in the S-MAC catalyst not only was support for a facile separation process but also could well promote the isomerization during the reaction step. A highest actual yield of 5-EMF (93.2%) was well obtained via RS ethanolysis at low temperature and short reaction time under oxygen environment. The long-term reusability and excellent recrystallization of S-MAC + ChCl were successfully archived for 10 cycles with a slight decrease of 5-EMF yield from 93.2% (1st cycle) to 86.4% (10th cycle), which was without significant leaching of acidity in catalyst structure. This research is greatly expected that novel strategy for catalytic upgrading of RS into 5-EMF could be further applied in real practical processes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.3c03082>.

Details and information for characterization of as-prepared catalysts using BET, XRD, SEM-EDS, VSM, XPS, TGA, NH₃-TPD and Py-FTIR techniques; schematic diagram for preparation of S-MAC; experimental setup for 5-EMF production (PDF)

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Notes

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