



Research article

Green heterogeneous catalyst based on cross-linked carrageenans for direct conversion of fructose to ethyl levulinate

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ABSTRACT

Ethyl levulinate (EL) is a biomass-derived compound, capable of being converted to an array of costly compounds and therefore is attracted by many researchers. In the present study, κ and ι -carrageenan grafted methylenebisacrylamide (MBA) catalysts (κ C-g-MBA and ι C-g-MBA) were prepared and applied to convert fructose to EL. FT-IR spectroscopy, XRD of both low-angle and wide-angle, N_2 adsorption-and-desorption, FESEM, and TGA were used to identify the catalysts. From the catalysts, κ C-g-MBA and ι C-g-MBA revealed the desirable results for EL with 80 and 82 % yields, respectively. The various parameters like reaction temperature, time, catalyst quantity, and the original fructose quantity were studied. Furthermore, experimental design was employed to create the ideal conditions for the reaction temperature 180 °C for the reaction, 5 h for the duration of the reaction, and 50 mg of catalyst for EL chosen. In addition, the catalyst's capability for reuse was explored and the catalyst was used repeatedly without a significant change in the catalyst activity.

1. Introduction

The fact that fossil fuels are rapidly being depleted and the environmental challenging issues of the resources have made researchers look for sustainable green alternatives. Biomass, thermochemically converted, is looked upon as a valuable ally in the production of biofuels, chemical derivatives, and widely-used materials, which due to their abundance, renewability, and fixed-carbon source have been broadly known to help develop a sustainable economy. A versatile product, widely used in industry, with promising molecules, is alkyl levulinate, derived from a process of biomass esterification, a catalytic thermochemical conversion. Moreover, sugar monomers are further recycled into alkyl levulinates using a variety of homogeneous and heterogeneous catalysts [1–3].

Alkyl levulinates with two functional groups (i.e., carboxyl and hydroxyl groups) are widely used for their flavor and perfume, in the water industry, food, medical, brewing, and cosmetic fields and as an additive to biodiesel fuel [4–6], deicer constituents [7], oxygenators, and lubricators are additives to petrodiesel [8]. Among them, ethyl levulinate is known as a readily-produced product from the alcoholysis of carbohydrates (e.g., fructose, glucose, or cellulose) in ethanol [9–12]. This, however, lacks the solubility of carbohydrates in ethanol, yielding a low quantity of EL and forming intractable humins [13,14]. Consequently, 5-hydroxymethyl furfural (HMF) is a potentially good alternative for EL production on a business scale. The conversion of HMF to EL with adequate production has been confirmed by acid catalysis. With ethanol used as the medium for reaction, the acid catalysts causing hydrogenation of HMF and conversion to EL, are considered an attractive alternative for an in-situ source of hydrogen.

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Homogeneous mineral acids and metal acids, traditionally used as catalysts, yield levulinate esters [15–17]. This method has led to high yields; yet, there is the challenge of recycling, slowed-up separation, machinery corrosion, and the difficulty of managing mineral acids are inevitable. To benefit from a green sustainable development as well as replacement and repeated reuse, heterogeneous catalysts such as metal oxides, heteropoly acids, and carbon materials were developed for esterification. They are adjustable for acidity, readily recyclable, economical, and potentially compatible with the environment [18,19].

Employing polysaccharides taken from the natural resources of various industrial uses over the past decades has been steadily on the rise. Recently, sea algae have been identified as the most abundant, and largely unused, natural resources, essential polysaccharides, including alginates, agar, and carrageenans, a linear copolymer, a repetitive sulfate, and non-sulfate, D-galactose-4-sulfate and 3, 6-anhydro-D-galactose, derived from the red algae of Rhodophyceae [20].

Commercially, due to such important physical and chemical properties as stabilizing, condensing, and gelatin agents, carrageenan is widely used in food technology [21]. It is also employed in such non-food products as pharmaceuticals, cosmetics, hygienic, printing, and textile formulas [22–25]. All the carrageenan fractions are solved in water but not solved in organic solvents, oils, or fat. However, the fact that they are solved in water depends on the sulfate-category surfaces (highly water-friendly) and their related cations. In their gelatin state, carrageenans have wide open structures, but their distribution depends on the solvents and can hardly be preserved in the dry state. Drying leads to the structural disintegration of the gelatinous state and will not allow maintained access to the agent groups [26].

With the changes in polysaccharides, is it possible to compete with the acidic catalysts? Carrageenans can be perceived as a valid cost and green chemistry standard. Because of their structures, carrageenans are potential candidates for catalysts, meeting most of the property standards required for catalysts or absorbents: good biocompatibility, non-toxicity, proper thermal stability, PH, solvents, and electric fields. For instance, Jing Gu et al. heterogenized HDS using strong Brønsted acidity, efficient solid acids, to produce EL from fructose, measuring it over a 75.3 % yield in 3.5 h at 423 K [27]. Similarly, Mita Halder et al. confirmed the synthesis of SBZ@POP, by using only Friedel-Crafts alkylation of benzene and dimethoxymethane before the process of aromatic rings sulfonation, to produce 88 % EL yield, achieved at 90 °C for 10 h [28]. Karnjanakom et al. produced 72.1 % EL yield in the vicinity of Zn-SC as the catalyst at a reaction temperature of 100 °C for 1h reaction time [29]. Besides, Quereshi and colleagues confirmed that over 90 % of LA conversion occurs at 110 °C in 30 min in the proximity of ESZN-4, in a solution of levulinic acid and ethanol to synthesize EL [30]. Su et al. demonstrated that the reaction of fructose ethanolysis was capable of being converted to EL with [C₃N] [SO₃CF₃]-HCSs, as catalyst, to attain a high proportion of 90 % at 110 °C [31]. Babaei et al. achieved 58 % EL yield with fructose using alumina-coated mesoporous silica, SBA-15, as acid catalyst [32]. Hu Li et al. used acid-base bifunctional ZrFeO_x nanocatalysts (ZrFeO(1:3)-300) in ethanol to convert EL for giving γ -valerolactone (GVL), 87.2 % at 230 °C in 3 h [33].

The goal of this study is to synthesize EL directly from fructose by developing two heterogeneous acidic catalysts. For this reason, κ C and ι C as the acidic biopolymers need to be improved to qualify for use as catalysts. In this work, MBA was grafted on κ C and ι C to simultaneously pave the way for the formation of the polymer network, ι C -g-MBA and κ C -g-MBA.

2. Experimental section

2.1. Materials

κ -Carrageenan (κ C), ι -Carrageenan (ι C), methylenabisacrylamide (MBA, 99 %), potassium peroxydisulfate (KPS 99 %), fructose ethanol was procured by Merck Chemical Co. Ethyl levulinate (EL, 99 % purity as standard in GC analysis) and biphenyl (99.5 % as internal standard) were obtained from Sigma-Aldrich.

2.2. Catalyst characterization

The synthesized catalysts were all identified with the help of the tools and techniques used for this purpose. The X-ray diffraction patterns for the synthesized catalysts were recorded with a diffractometer of the type Asenware DXM-300, Ni-filtered Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), with a 2θ scanning range of 10–80°. The infrared spectra of catalysts were scanned at room temperature and within a distance of 400–4000 cm⁻¹ with KBr disks using a Jasco-680 FT-IR (Japan) spectrometer. The surface catalyst morphologies were studied with the aid of FESEM (Zeiss EVO 50) and FEI-Quanta-FEG450 equipment, a scanning electron microscope. Using the static volumetric Brunauer-Emmett-Teller (BET), the surface area was computed using N₂ adsorption–desorption isotherms of 77 K: Belsorp Mini. The overall pore volume was calculated using the amount adsorbed at a relative pressure of around 0.99. Barrett-Joyner-Halenda (BJH) method was used to determine pore diameter. Furthermore, the thermogravimetry analyzer, TGA Setaram Labsys TG (STA), was calibrated at 25–800 °C, 10 °C/min in the N₂ atmosphere.

2.3. Catalyst preparation

To synthesize the κ C-g-MBA and ι C-g-MBA, 0.1 g of either κ C or ι C was poured over 15 mL of degassed and distilled water in a 50-mL reactor equipped with a mechanically-stirred device. Then, the reactor was placed in a thermostatic water bath and the reaction temperature was set at 80 °C. When κ C or ι C was fully dissolved, the KPS initiator (0.5 g, dissolved in 5 mL of water) was added to it. Next, in 5 min, MBA (0.5 g, dissolved in 5 mL of water) was emptied into the reactor. The mixture from the reaction was stirred continuously (200 rpm) for 3h at 80 °C. Then, the composite was rinsed with distilled water several times, and emptied over ethanol (300 mL), and left there for 48 h to dehydrate. After that, the product was shredded, washed repeatedly with ethanol, filtered, and

dried in an oven heated for hours to 50 °C [34,35]. After that, it was pulverized and stashed in a place protected from humidity.

2.4. Fructose to EL conversion using catalysts

Fructose was converted to EL by being dehydrated in a 65 mL cylindrical stainless-steel reactor. 5 mL of ethanol as solvent, 50 mg of fructose along with different amount of catalysts were emptied into the reactor. Then, using an external source of heat, the reactor was heated to the intended temperature and agitated at 6000 rpm. The reaction starting time was noted once the oil bath temperature got to its optimum. Once the reaction was complete; the reactor was relocated to the ice-cool bath for completion of the reaction. Now, the mixture resulting from the reaction was filtered by centrifuging to separate the solid catalyst. Finally, liquid products were filtered for gas chromatography (GC) analysis. The products were separated using GC (Agilent6890) having a flame ionization detector (FID) with a capillary HP5 column (with a film thickness of 30.0 m*0.25 mm*0.25 μm). Helium was employed as carrier gas at 1.0 mL/min, the temperature of the oven, initially 160 °C, was maintained for 20 min and then increased to 200 °C and so maintained for 10 min. The injector and detector temperature were set to 220 and then 260 °C, respectively. The EL peak was confirmed by analyzing the pure components (reference standard), used too to prepare the calibration curves to an internal standard (biphenyl) for quantitative analysis using GC.

3. Results and discussion

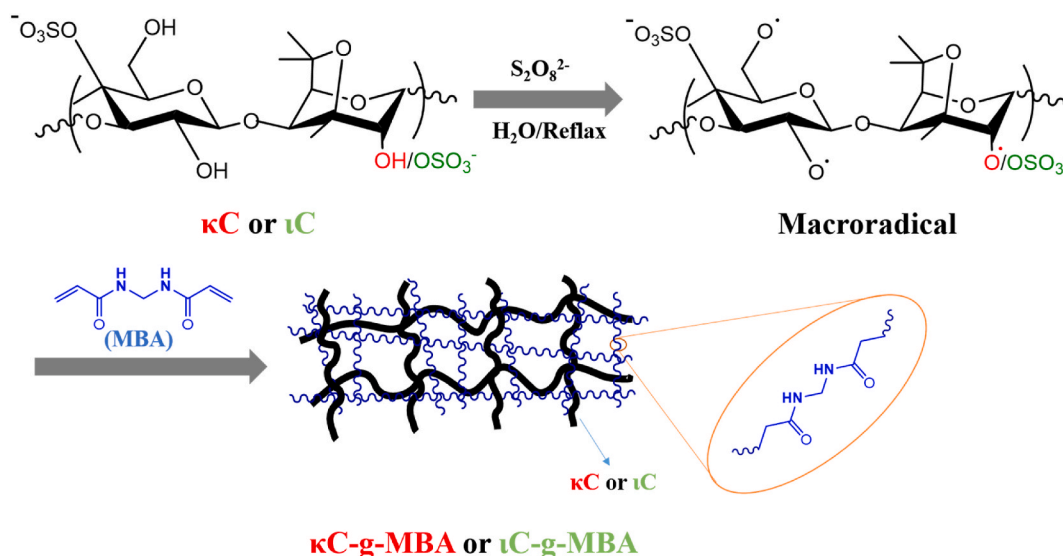
Initially, using KPS, the Carrageenan gel was produced. Then, MBA was used as a crosslinker to synthesize the heterogeneous catalyst and the ester sulfonic acid group (Scheme 1) [34,35]. As the catalyst performance depends on the properties, BET, XRD, SEM, TGA, and FTIR were employed to confirm the presence of the solid catalyst. Moreover, it was revealed that it was possible to crosslink κC and ιC with MBA. To attain good EL efficacy, fructose was dehydrated in the presence of κC-g-MBA and ιC-g-MBA used as acid catalysts under varied conditions.

3.1. Nitrogen adsorption-desorption analysis

Fig. 1 presents the N₂ adsorption-desorption isotherms of the resulting composites. The samples were degassed in a vacuum at 200 °C before conducting the conventional nitrogen (N₂) adsorption and desorption at -196 °C. The Brunauer-Emmette-Teller (BET) method was employed to compute the overall area, while Barrette-Joyner-Halenda (BJH) was utilized to measure the pore diameter of materials. The κC-g-MBA and ιC-g-MBA isothermals were compared with that of the parent samples. Furthermore, the textural and structural properties of the solid catalysts are indicated in Table 1. The cross-linked samples had a larger area than those of their parents. From Fig. 1, at a high-pressure region ($P/P_0 > 0.75$), the observed hysteresis confirmed the presence of generous quantities of interparticle void structures. Additionally, the parent carrageenan materials (κC and ιC), too, possessed a lower area, pore size, and volume than did the κC-g-MBA and ιC-g-MBA; hence, it is reasonable to crosslink with MBA through in-situ polymerization.

3.2. TGA study

The TGA thermogram presented in Fig. 2, illustrates three steps in weight loss. The first occurs at <200 °C, resulting in



Scheme 1. Schematic for catalyst preparation.

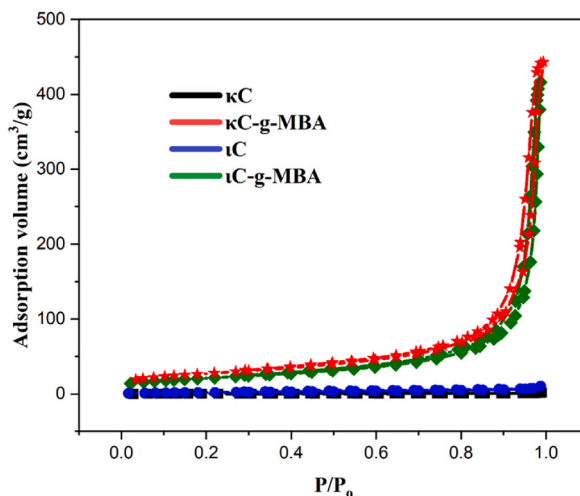


Fig. 1. N_2 adsorption-desorption diagram of κC , ιC , κC -g-MBA and ιC -g-MBA samples.

Table 1

Porosity details of ιC , κC , κC -g-MBA and ιC -g-MBA.

Samples	BET		BJH	
	Area ($m^2 g^{-1}$)		V_p (cm^3/g)	D_p (nm)
ι -Carrageenan (ιC)	7.3		1.6	8.0
ιC -g-MBA	72.7		16.7	33.2
κ -Carrageenan (κC)	0.16		14.1	0.72
κC -g-MBA	26.7		21.4	93.3

approximately 10, and 15 % decreases in the weights of κC and ιC , respectively, caused by the removal of the water on the surface and that locked up in the polymer structure. The second began at 200 °C, and continued on a sharp upward trend to 400 °C. κC and ιC revealed 47 and 38 % of the weight loss, respectively, ascribed to a break in the organic functional groups (-SOOH, OH) linked to the κC and ιC rings. The third occurs at 210–430 °C, resulting in a decrease of about 23 and 24 % weight of κC -g-MBA and ιC -g-MBA, respectively, an indication of maintained thermal consistency on cross-linking.

3.3. XRD analysis

The XRD patterns for κC , ιC , κC -g-MBA, and ιC -g-MBA, are presented in Fig. 3. 2θ values, that is, 18, 20, and 28° were measured for

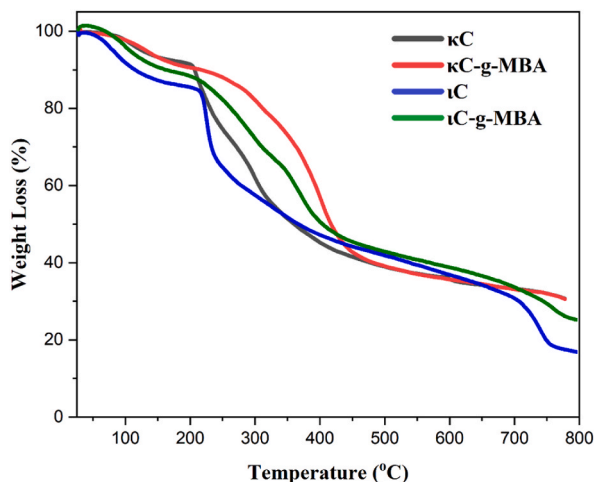


Fig. 2. TGA thermograms of κC , ιC , κC -g-MBA, and ιC -g-MBA samples.

the κ C structure [36]. However, at 20, 28, 32, 38, and other 2θ values, the presence of peaks, show the ι C structure [37]. In contrast, in the synthesized catalysts, the peaks of diffraction were not significantly vivid, reaffirming the uniform and homogeneous crosslink over the κ C and ι C support. Yet, at 2θ values, different from that of ι C, one or two peaks were visible in the ι C-g-MBA, but not in κ C-g-MBA and ι C-g-MBA, showing some uncrystallized substance which, because of carrageenan chains crosslink, was destructive to the original structure.

3.4. FTIR spectroscopy

Fig. 4 illustrates the FTIR spectra of the ι C and κ C biopolymers and corresponding heterogeneous catalysts. The distinctive C-O-SO₃ peaks stretching in (1-3)-D-galactose, C-O-C in 3,6 anhydro-galactose, C-O, O=S=O asymmetry and O-H, can be seen at 845, 930, 1070, 1260, and 3500 cm⁻¹, in κ C and ι C structures, respectively [38,39]. At 1541 cm⁻¹, 3307 cm⁻¹, and 1657 cm⁻¹ (Fig. 4B), the absorption bands were ascribable to the vibrations of the N-H bend, N-H stretch and the C=O stretch in the amide groups in MBA, respectively, while employing the additive *N, N*-methylene bisacrylamide as the crosslink agent in the procedure, provided new bands measured at 1228 cm⁻¹, 860 cm⁻¹, 1657 cm⁻¹, 1525 cm⁻¹ and 2916 cm⁻¹, are the peaks characteristic of the κ C-g-MBA and ι C-g-MBA. The identical peaks prepared for two heterogeneous catalysts; lending added support to the fact that the original carrageenan unit structure of the catalysts crosslinked with MBA.

3.5. FESEM analysis

By comparing the morphology of the ι C and κ C surfaces with those of ι C-g-MBA and κ C-g-MBA (Fig. 5: a-h), it can be understood that the surfaces of the parent samples were too wavy and irregular before crosslinking, whereas in the e-h images, the changes in surface morphology of κ C-g-MBA and ι C-g-MBA are seen due to the chemical bond between κ C and ι C with MBA as linker. κ C-g-MBA surface looks steadier and softer after crosslinking. Moreover, the ι C-g-MBA surface has been filled with elliptical clods.

4. Catalytic conversion of fructose to EL

The general procedure for dehydration and conversion of fructose to EL is to add 5 ml ethanol, 0.20 g fructose, and 0.02 g of catalyst to a 50 ml autoclave, and put it in an oven heated to 180 °C for 4 h. When the reactions were complete, the autoclave temperature was changed to the ambient temperature, and then, the mixture from the reactions was separated from the catalyst using a centrifuge. Gas chromatography and calibration plotting were used for analysis and identification.

Given the results of gas-mass chromatography [40], the following mechanism has been proposed for the reaction of fructose dehydration and conversion to EL using the acidic catalysts of κ C-g-MBA or ι C-g-MBA (Scheme 2).

4.1. Effect of reaction temperature on fructose to EL conversion

To assess dehydration reaction temperature, 0.20 g of fructose was used with 0.02 g heterogeneous catalysts (κ C-g-MBA or ι C-g-MBA), at the differing temperatures of 150, 160, 170, 180, 190, and 200 °C for 4 h, and then the results of the experiments were summarized in Fig. 6. As seen from Fig. 6, with a rise in temperature from 150 to 180 °C, the EL yield in the vicinity of κ C-g-MBA increased from 10 to 72.1 %. With more elevation in temperature up to 200 °C, EL yield fell by 62.4 %. With an elevation in reaction temperature from 150 to 180 °C, the EL yield rose from 11 % to 76.5 % in the proximity of ι C-g-MBA. With an upward trend in

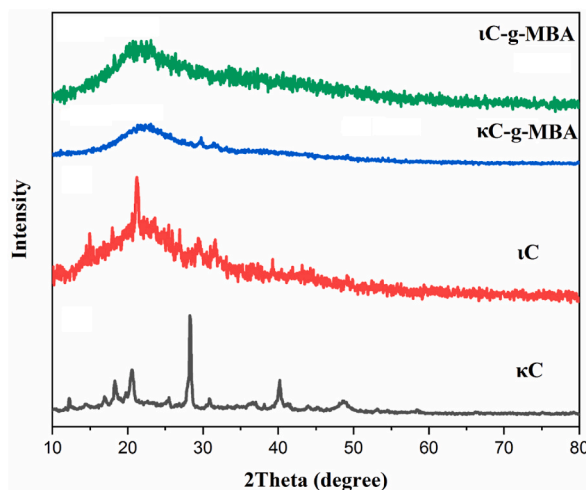


Fig. 3. XRD patterns of κ C, ι C, κ C-g-MBA, and ι C-g-MBA.

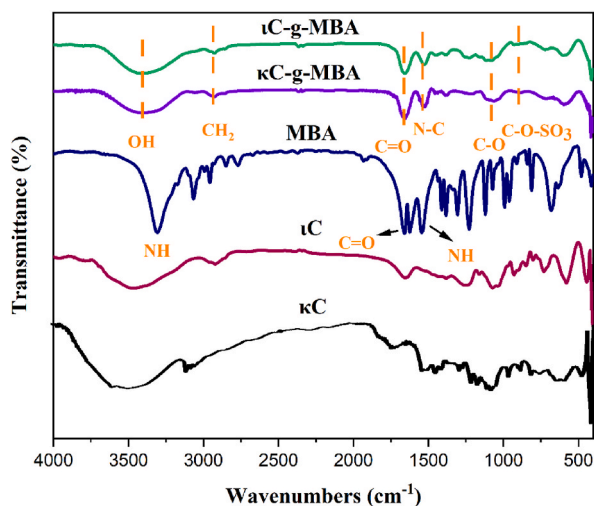


Fig. 4. FT-IR spectra of κ C, ι C, MBA, κ C-g-MBA, and ι C-g-MBA samples.

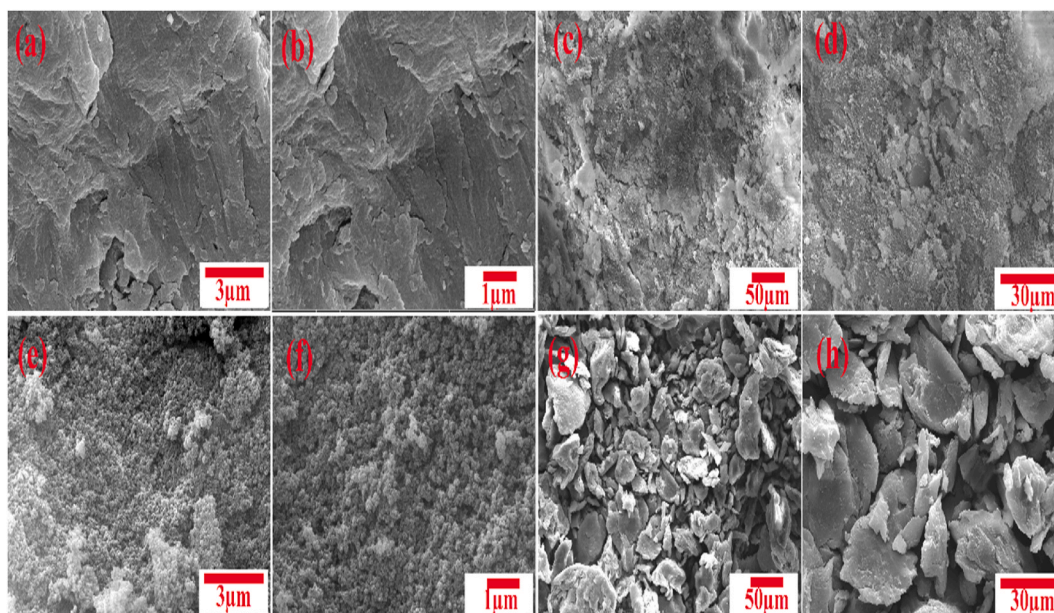


Fig. 5. FESEM of κ C (a,b), ι C (c,d), κ C-g-MBA (e,f), and ι C-g-MBA (g,h) samples.

temperature from 190 °C, side reactions occurred forming humin and polymers, covering the acidic sites. Furthermore, at temperatures above 180 °C, EL might have undergone degradation.

4.2. Effect of reaction time on fructose to EL conversion

To assess the reaction time, fructose was converted with catalysts at 180 °C. The catalysts κ C-g-MBA or ι C-g-MBA were used for 3, 4, 5, and 6 h, and then the results were recorded in Fig. 7. With time protracted from 3 to 5 h, the EL yield rose from 45.2 to 75.3 % in the presence of κ C-g-MBA. However, with an increase in time up to 6 h, the EL yield decreased to 69.1 %, and the time up to 7 h, the yield decreased to 61.1 %. Therefore, 5 h was selected as the optimal time for reaction. The EL yield in the presence of ι C-g-MBA increased from 51.1 to 79.5 %. However, with an increase in time of up to 6 h, the EL yield decreased to 75.1 %, and with an increase in time of up to 7 h, the yield decreased to 68.3 %. The decrease in yield can be linked to several factors. The decomposition or transformation of EL to other derivatives can be attributed to 190 °C and the increase in time. The formation of the scope of intermediates in the esterification reactions occurs with prolonged time, and that the conversion of the intermediates to EL paves the ground for the determination of the reaction speed. In the reaction with a time exceeding 5 h may lead to polymerization in alcohol [41].

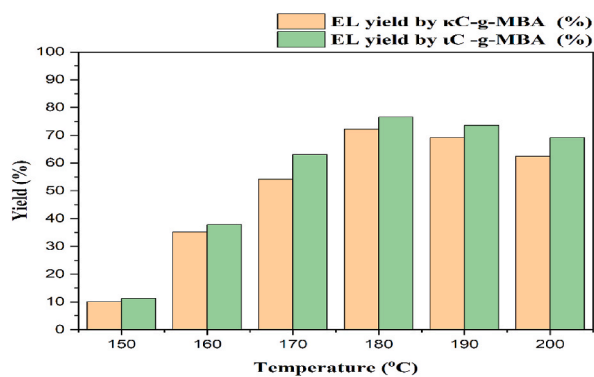
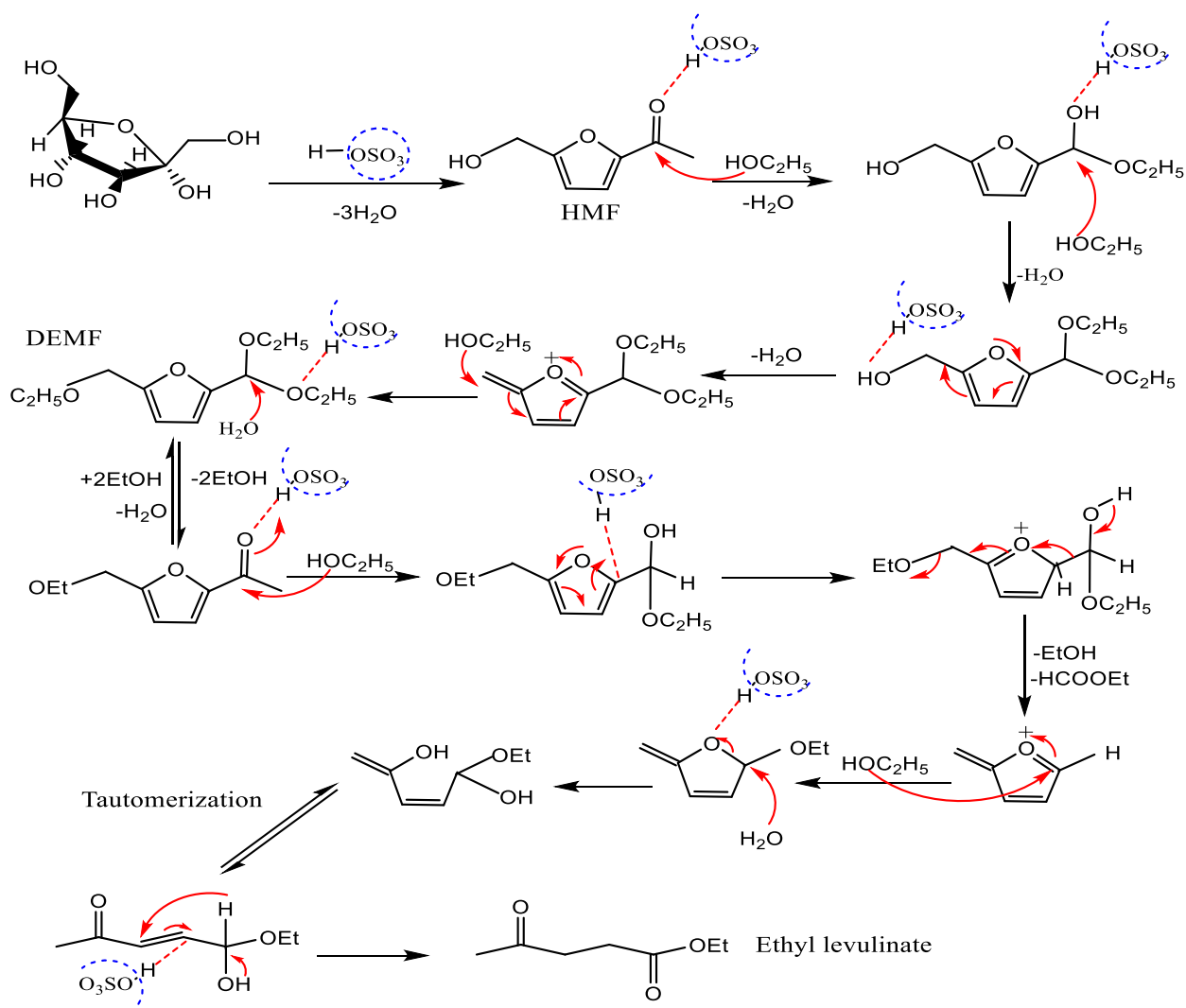


Fig. 6. Impact of reaction temperature on conversion of fructose to EL: 0.20 g fructose, 0.02 g of catalyst, 5 mL of solvent, 4 h.

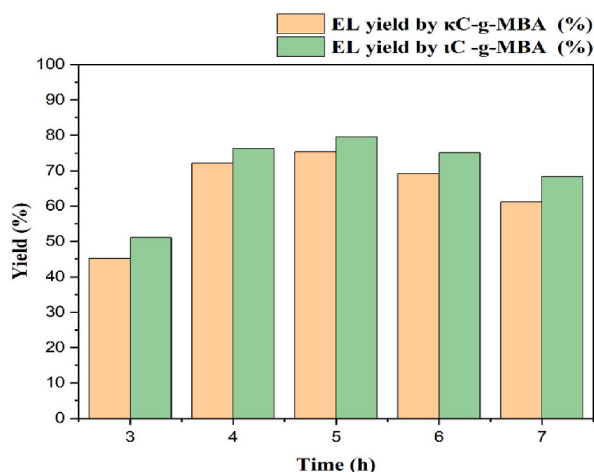


Fig. 7. Impact of reaction duration on fructose-to-EL conversion: 0.20 g of fructose, 0.02 g of catalysts, 5 mL of solvent at 180 °C.

4.3. Impact of reaction catalyst on conversion of fructose to EL

The quantity of the catalyst is vital to the conversion of fructose to EL. Therefore, the effect of the amount of the catalyst on fructose dehydration using different quantities of κ C-g-MBA and ι C-g-MBA, that is, 0.02–0.12, was assessed, and the results were presented in Fig. 8. The results revealed that an increase in κ C-g-MBA from 0.02 to 0.04 led to a rise in the EL yield from 75.1 % to 80 %. As for ι C-g-MBA, an increase from 0.02 to 0.04, the EL yield rose from 79.2 % to 82 %. With higher quantities of the catalysts, though, the EL yield went down. The relation between the increase in the catalysts and the fall in the EL yield can be ascribed to further side reactions taking place, the formation of humin, polymers, and the involvement of the active sites of catalysts [42].

4.4. Assessment of catalyst recoverability

The heterogeneous acidic κ C-g-MBA and ι C-g-MBA revealed good recoverability. This quality was assessed four times. There was no significant decrease observed in the EL (Table 2). When the reactions were complete, the catalysts were easily separated using a centrifuge, reused on being washed with water and acetone, and then dried. Compared to the fresh catalysts, the FT-IR spectra indicate that there are no changes in the structures after the fourth cycle (Fig. 9).

In order to comparison of our results with other studies, the results of the EL produced from fructose with a variety of catalysts are presented in Table 3. The EL yield was different because of the difference between the catalysts. The EL yield can optimally reach a

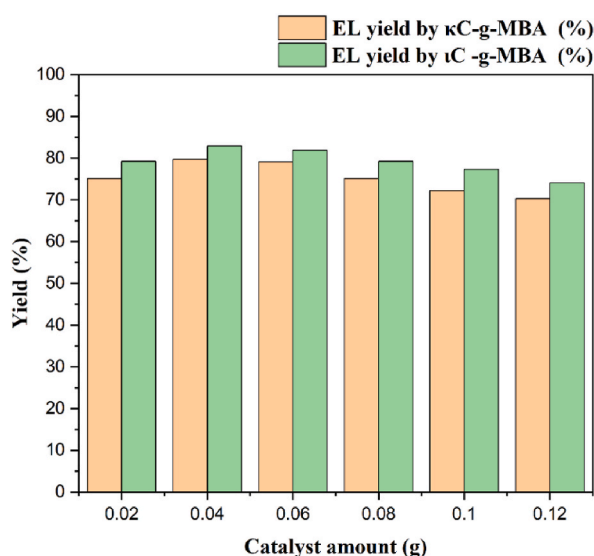


Fig. 8. Impact of quantity of catalyst on reaction of fructose for conversion to EL: 0.20 fructose, 5 mL solvent, temperature 180 °C, and 5 h for reaction.

Table 2
Recoverability of the catalyst.

Entry	Cycle	Yield%	
		κ C-g-MBA	ι C-g-MBA
1	1st run	79	82
2	2nd run	78.8	81.9
3	3rd run	78.5	81.6
4	4th run	77.3	81.1

Conditions for reaction: 0.20 g of fructose, 0.02 g of catalysts, 5 mL solvent, t: 180 °C, and time:5h.

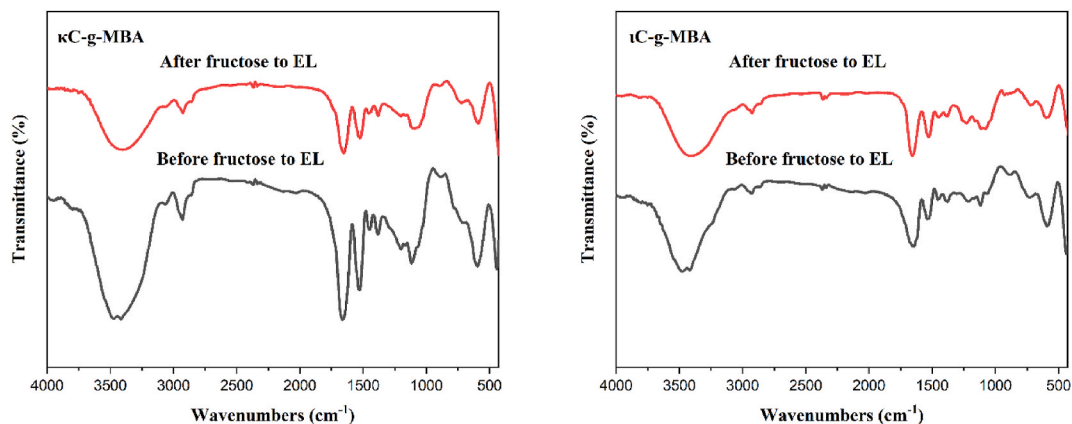


Fig. 9. The FT-IR test before and after four recycling of κ C-g-MBA and ι C-g-MBA.

Table 3
Comparison of conversion values with literature.

Catalysts	Conditions	EL (yield%)	Ref.
HDS-3.6	ethanol, 150 °C, 3.5 h,	70.3	[43]
[NEt ₃ B-SO ₃ H] [HSO ₄]	ethanol, 140 °C, 24 h,	74	[44]
<i>p</i> -Styrene sulfonic acid grafted on nanotubes (ethanol, 120 °C, 24 h,	84	[44]
Potassium Phosphotungstate	Ethanol & toluene, 150 °C, 2 h,	67.8	[45]
ZrOCl ₂ ·8H ₂ O	ethanol, 200 °C, 2 h,	4.6	[46]
PWA) H ₃ PW ₁₂ O ₄₀	ethanol, 100 °C, 24 h,	48	[47]
CMK-HPM-50	ethanol, 180 °C, 3 h,	72	[48]
κ C-g-MBA	ethanol, 180 °C, 5 h,	80	[49]
ι C-g-MBA	ethanol, 180 °C, 5 h,	82	This study

maximum of 80 % in this study, indicating that κ C-g-MBA and ι C-g-MBA perform as efficient catalysts in the production of EL from fructose.

5. Conclusion

The characterization of modified κ C and ι C shows that the catalysts have been successfully highly acidic, with the area of the catalyst providing excellent accessibility to the acid site for reaction. The ethanolsis of sugar yielded a high EL under selected conditions. The -SO₃H provides a combination of Brønsted acidity of κ C-g-MBA and ι C-g-MBA which enhance fructose ethanolsis and increase EL yield. Besides, an experiment, orthogonal in nature, was conducted, resulting in the most dramatic impacts of the three factors on the EL production, such that the duration of reaction, quantity of catalyst, and temperature of the reaction, respectively, left their greatest effect on the EL production. It was found that 5 h was needed to convert 0.2 g of fructose at 180 °C to obtain a good EL yield. The increased reaction was needed to convert fructose to EL with the aid of κ C-g-MBA and ι C-g-MBA in proportions of 80.0 % and 82.0 % respectively. κ C-g-MBA and ι C-g-MBA provide the Brønsted acidity site for the isomerization of fructose and further ethanolsis reaction. Direct biomass conversion by ethanolsis has proved to have the potential of κ C-g-MBA and ι C-g-MBA for EL production.

Data availability

Data will be made available on request.

CRedit authorship contribution statement

Mahsa Rezaie: Writing – original draft, Software, Investigation, Formal analysis, Data curation. **Mohammad Dinari:** Writing – review & editing, Visualization, Supervision, Funding acquisition, Conceptualization. **Alireza Najafi Chermahini:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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