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Novel synthesized microporous ionic polymer applications in transesterification of *Jatropha curcas* seed oil with short Chain alcohol

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ABSTRACT

Keywords: Microporous ionic polymer (PIP) Free fatty acids Jatropha curcas seed oil Kinetics (Trans)esterification Catalyst reusability New suites of sulfonic acid-functionalized microporous ionic polymers (PIPs) catalysts were synthesized with polymer, alkyl bromides, and 1, 3-propane sultone via a two-step procedure. The synthesized microporous PIP catalysts were characterized using FT-IR, SEM-Mapping, XPS, N2 adsorption-desorption isotherms, solid NMR spectroscopy, and element analysis. Esterification of several fatty acids with ethanol, which was used as a model reaction in the stabilization of Jatropha curcas seed oil, was checked over functionalized PIP. We tested the catalytic performance of PIP-C₈ on the synthesis of fatty acid esters via the transesterification of J. curcas seed oil with a mixture of short-chain alcohols such as ethanol, ethanol-to-diethyl carbonate (1;1 molar ratio), and ethanol-to-dimethyl carbonate (1:1 molar ratio) with 170 mg of PIP-C₈ at reflux temperature with agitation. The PIP-C8 catalyst was particularly effective, having achieved yields of 85%, 94%, and 70% for J. curcas seed oil with ethanol, J. curcas seed oil with ethanol-to-DEC, and J. curcas seed oil with ethanol-to-DMC, respectively, under the optimized reaction conditions. The catalyst could be recycled more than five times without significant deactivation. Kinetic studies performed at different temperatures revealed that the conversion of oleic acid to an ethyl ester follows a first-order reaction. The best catalysts with microporous structure (average pore diameter: 1.7–1.9 nm, pore volume: 0.23-0.33 cm³ g⁻¹) and $-SO_3H$ density (0.70–0.84 mmol/g_{cat}) were obtained by 1, 3propane sultone of the chemically activated. The results indicate that the site activity of functionalized microporous ionic polymer materials shows promising approach for the development of environmentally friendly technology.

1. Introduction

The issues of environmental degradation and energy security are fundamental challenges of the 21st century. Dependence on conventional fossil fuels is leading to global warming and possible major disruptions in the social structure [1]. Therefore, diversification of the energy portfolio with an emphasis on renewable fuels is an imperative policy tool [2]. Biofuels such as biodiesel and bioalcohols (bioethanol/biobutanol) have the potential to be employed as a renewable, clean-burning substitute for petroleum diesel, and high biodegradability with low combustion pollution emissions [3,4]. Methanol and ethanol are more desirable than other alcohols as alternative fuels because the resulting emissions are much lower, and impact on the environment [5, 6]. To reduce the production cost, chief raw material such as *J. curcas* seed oil have been identified as an attractive oil feedstock, thus improving the economic feasibility of biodiesel production [7]. Recent studies have focused on an efficient and economical way to transform non-edible *J. curcas* seed oil. It is generally agreed that *J. curcas* biodiesel has little impact on food supply and the environment; its seeds contain approximately 25–30 wt% of non-edible oil with high FFA content of up to 15 wt% [8,9]. The fatty acid C16 and C18 profile present in the *J. curcas* seed oil, such as polyunsaturated fatty acids (PUFA), monounsaturated fatty acids (MUFA), and saturated fatty acids (SFA), as well as the presence of impurities, such as free fatty acids (AGL), influence the properties of biodiesel [10,11]. However, some feedstocks contain a significant amount of fatty acids other than C16 and C18 acids, palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2), and linolenic acid (C18:3) are the fatty acids commonly found in oils [12,13].

Currently, homogeneous alkaline catalysts, such as KOH, NaOH and NaOCH₃ are generally being utilized in the transesterification [14]. Difficult catalyst separation and consequently high cost for product

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Received 22 May 2021; Received in revised form 9 August 2021; Accepted 21 August 2021 Available online 30 August 2021 0926-860X/© 2021 Elsevier B.V. All rights reserved. purification are the major drawbacks of homogeneous alkaline catalysis systems [15], homogeneous acid catalysts are difficult to recycle and operate at high temperatures, and also give rise to serious environmental and corrosion problems [16]. In recent years, the emerging concept of green chemistry using eco-friendly materials and microporous advanced catalysts for chemical transformations has gained immense attention and its physicochemical properties that may lead to improved reaction activity for reactants with large molecular size and surface areas, thermal, and chemical stability [3,17,18]. The microporous PIP-C₈ catalyst have attracted much attention owing to their excellent properties such as good thermal stability, high surface area, and unique large pore structure. Here, we report for the first time the design and synthesis of a functionalized microporous PIP-C₈ catalyst for the (trans)esterification process. For biomass conversions, some Ls catalysts have been reported for the biodiesel synthesis with catalytic activities [19].

In the present study, [PIP-C_n] acidic catalysts containing an *N*, *N*-dimethylethylenediamine and sulfonic acid groups were prepared and subsequently characterized by various analysis techniques. Various reaction conditions that might influence the yield of ethyl esters, including the reaction temperature, and micoporous PIP-C₈ catalyst concentration, were explored in this study. This study aims to utilize the product of the processing of crude *J. curcas* seed oil as a raw material with microporous PIP-C₈ for biodiesel production, and qualities with yield as well as the economic viability of the processes were evaluated. The kinetic model for the conversion process, and the Arrhenius plot method was used to analyze the dependence of the rate constant on temperature.

2. Experimental

2.1. PIPs synthesis

PIPs synthesis is in under argon, in a three-necked flask, 1, 4-bis(bromomethyl)benzene ($C_8H_8Br_2$ -Mackline) (8 mmol, 2.112 g) and ferric chloride (2.42 g, 15 mmol) (FeCl₃-Mackline) were dissolved in 20 ml dichloroethane (DCE-Mackline) at 35 °C with stirring. Then, *N*, *N*dimethyl ethylenediamine (Mackline) (0.22 ml, 2 mmol) was added into the flask. The mixtures were stirred for 24 h at 80 °C, with the release of HBr gas. After the reaction, the solution was cooled to room temperature and the mixture was filtered through a funnel. The obtained solid product was washed with methanol until the filtrate was colorless. The brown porous ionic polymer (PIP) was dried at 60 °C under vacuum.

2.2. PIP-Cn synthesis

Dried PIP (0.5 g), 1-bromoalkane (1.25 mmol) (99.99% purity-Mackline) and sodium hydroxide (72 mg, 1.8 mmol) (NaOH-Mackline) were dispersed in ethanol (C_2H_5OH -Energy chemical, 99.99%) in a glass flask. The resulting solution was magnetically stirred for 48 h at reflux. After reaction, the solution was cooled to room temperature and the mixture was separated by centrifugation. The alkylated PIP was washed with ethanol until no bromide ions were detected and dried overnight at 60 °C in an oven under vacuum. In a 25 ml round bottom flask, the second-step products were dispersed in ethanol and 1, 3-propane sultone (5 mmol, 0.44 ml) (99.99%-Mackline) was added to the flask; the mixture was further heated at reflux for 48 h. After the reaction, the mixture was cooled to room temperature and separated by centrifugation. The PIP-Cn was washed with ethanol several times and dried overnight at 60 °C in an oven under vacuum. The general synthesis of PIP is shown (Scheme 1).

2.3. Catalytic activity and transesterification of prepared PIP- C_8 catalyst

Oleic acid (99.9% purified-Mackline) esterification reactions were performed in a 150 ml three-necked flask equipped with a magnetic stirrer and a digital thermometer in an oil bath. Reactions were performed using oleic acid (C18:1), which is the most commonly used FFA to evaluate the catalytic performance [20], and 95 mg of catalyst loading at ethanol reflux temperature with different alcohol to acid molar ratios. The acid value of the ethyl oleate phase was determined by titration after the removal of excess ethanol with a standard potassium hydroxide (0.01 mol L⁻¹) potassium hydroxide (KOH, energy chemical, 99.0%) solution [21].

The acid value (AV) was determined using Eq. (1).

Acid value
$$(AV)\left(\frac{mgKOH}{g}\right) = \frac{V_{KOH}(X C_{KOH}) MW_{KOH}}{m(biodiesel)}$$
 (1)

where V_{KOH} is the volume of the titrant (ml), C_{KOH} is the concentration of the titrant (M), MW_{KOH} is the molar weight of the titrant (g/mol) and m (biodiesel) is the mass of biodiesel (g). The conversion was calculated by comparing the acid value of the initial oleic acid to that of the ethyl



Scheme 1. Synthesis of sulfonic acid functionalized porous ionic polymers.

oleate samples (Eq. (2).

$$X(\%) = \frac{AV_{oleic\ acid} - AV_{ethyl\ oleate}}{AV_{oleic\ acid}} [\times]100$$
(2)

Where $AV_{oleic \ acid}$ is the acid value of the oleic acid and $AV_{ethyloleate}$ is the acid value of the biodiesel sample given in mg KOH/g of sample.

The transesterification reaction was carried out in a 250 ml glass three-necked flask equipped with a water-cooled condenser and a magnetic stirrer. First, the *J. curcas* seed oil and catalyst were charged into the flask and heated to the required temperature by an oil bath. In addition, transesterification was conducted with ethanol–to–DEC (diethyl carbonate ($C_5H_{10}O_3$), 99.9% purified Mackline) and ethanol–to–DMC (dimethyl carbonate ($C_3H_6O_3$), 99.9% purified Mackline). After the reaction, excess solvent was distilled off under vacuum and the mixture was centrifuged to separate the solid catalyst. The ester contents in the upper layer were quantified using gas chromatography-mass spectroscopy (GC-MS). The yield of fatty acid esters was calculated as follows:

$$Yield \quad (\%) = m_{esters}/m_{oil} \times wt \quad \% \tag{3}$$

Where m_{ester} is the mass of the ester in the product and m_{oil} is the initial mass of the *J. curcas* seed oil.

2.4. Analysis of esters

The conversion of triglycerides to esters was monitored by TLC using silica gel as the stationary phase $(10 - 40 \,\mu\text{m}, \,\text{Q/YJY-001-2005},$ ISO9001). A small volume (20 µl) of biodiesel phase was taken and mixed with 50 µl n-hexane (C₆H₁₄-energy chemical, 99.9%). Following, 5 µl of the mixture was applied to a TLC. As a developing solvent, nhexane/ethyl acetate (C4H10O -energy chemical, 99.9%) /acetic acid (CH₃COOH-energy chemical, 99.9%) (90:10:1) was utilized, and ethanol/sulfuric acid (1:0.5) was used as a color reagent. After spraying the color reagent over the silica gel plate development, the plate was heated at a high temperature and analyzed [22]. The analysis of ester compositions was performed using a GC-MS system (Thermo Scientific Nicolet IS10) [23]. FT-IR analysis was performed at room temperature in the region of 4000–500 $\rm cm^{-1},$ with 45 scans and at 4 $\rm cm^{-1}$ resolution using the total attenuated reflectance technique [24]. TGA was performed using a TGA Q50 V20.13 Build 39. The samples (12 mg) were placed in aluminum pans and heated at a rate of 10 K min⁻¹ to 900 °C under nitrogen gas at a flow rate of 20 ml min $^{-1}$.

3. Results and discussion

3.1. Microporous PIPs characterization

To identify the structure of the microporous PIPs by Fourier transform infrared (FT-IR) spectroscopy (using KBr pellets on a Nicolet Impact 410, FT-IR spectrophotometer) spectra confirmed the effective functionalization of the materials through the presence of vibration bands ascribed to different functional groups. The FT-IR spectra of PIP-C4, PIP-C8, PIP-C12, and PIP-C16 are presented in Fig. 1. The peak at 3426 cm⁻¹ corresponds to strong OH absorption, which is the Bronsted acid. The absorption peaks at 1636 cm⁻¹ and 1589 cm⁻¹ were attributed to the stretching vibrations of the C-C and C-H bonds, respectively, from the phenyl unit. Strong absorption peaks at 1210 cm⁻¹ and 1050 cm⁻¹ were attributed to the S=O asymmetric and symmetric stretching vibrations of the -SO₃H group, and a peak at 860 cm⁻¹ assigned to the S=O stretching vibration was observed in the PIP-C₈ spectrum, which illustrate the successful formation of the sulfonic acid group [25]. The loaded acidic species can provide more easily accessible of catalytic sites to the feedstocks, and therefore the catalytic activity was enhanced thanks to the increased acidic sites of the synthesized catalyst. The FT-IR spectra imply the successful synthesis of PIP. These results reveal that



Fig. 1. FT-IR spectra of PIP-C₄, PIP-C₈, PIP-C₁₂, and PIP-C₁₆ catalysts.

various, 1, 3-propane sultone concentrations in a synthetic method for PIP production induce varying degrees of chemical interaction in PIP. These results confirm the successful reaction of polymer and sulfonic acids as well as the formation of zwitterions ($-SO_3...N^+$) [26]. The band at 1350 cm⁻¹ is assigned to sulfonic acid groups [27], which facilitates the reaction rate of the transesterification, and this reaction can be improved in the presence of strong acidic sites [28,29].

Elemental analysis of PIP-C8 was conducted on a CHNS elemental analyzer (using a Perkin-Elmer analyzer, 2400 series II). The elemental analysis results are summarized in Table 1. The acid strength plays a crucial role in the catalytic performance of the catalysts. The acid strength of the microporous PIP-C8 catalyst was studied using solid nuclear magnetic resonance (solid-NMR) spetroscopy, a reliable technique for the evaluation of the acidity of various types of solid acid catalysts [30,31]. Fig. 2 shows the solid NMR spectra of PIP-C₈. PIP-C₈ displayed resonances at approximately 10-20 ppm and 60-70 ppm associated with the weak acid sites; the signals of the weak acid sites were largely decreased. The resonances at approximately 30-40 ppm and 120-150 ppm associated with strong acid sites, while the signals of strong acid sites were largely improved [32]. These results can be attributed to the increased acidic site of PIP-C8. The strong acid strength was helpful for improving their catalytic activities in (trans)esterification. These results can be attributed to the increased content of the -SO₃H group site of PIP-C₈. The strong acid strength helped improve the catalytic activities in (trans)esterification.

The crystal morphology of the PIP-C₈ catalyst was investigated by scanning electron microscopy (SEM)-Mapping (using the SUPRA 55 VP (Carl Zeiss) after platinum sputtering at 10 mA for 100 s). SEM images clearly show that the morphology of the PIP-C₈ derived microporous materials was directly affected by the preparation method and exhibited many porous structures with surfaces that were formed by the flake structures, which was favorable for mass transfer and the enhancement of its catalytic activity. This effect was observed in the SEM images obtained from the different biomass sources showing varying sizes and shapes of particles. As shown in the representative SEM images (Fig. 3a), consisting of flake-like particles with 1.00 μ m diameter (Fig. 3b), the primary particles appear to be aggregated into larger clusters. PIP-C₈ consisted of uniformly and separated particles with 5.00 μ m (Fig. 3c).

Table 1CHNS analysis of PIPs.

5				
PIP	Ν	С	Н	S
PIP-C ₄	7.13	60.28	7.71	1.42
PIP-C ₈	6.32	60.53	7.48	1.80
PIP-C ₁₂	6.07	60.73	7.55	2.24
PIP-C ₁₆	5.79	60.35	7.21	3.32



Fig. 2. Solid NMR spectra of PIP-C8 catalyst.



Fig. 3. SEM images (a) SEM images, (b)1.0 µm diameter, (c) 5.0 µm diameter, and (d) 500 nm of PIP-C8 catalyst.

The morphology were very similar to that of the microporous ionic liquid, PIP-C₈ consisted of nanoparticles with 500 nm size (Fig. 3d). It was confirmed that the materials possessed uniform pore structures.

To confirm the validity of PIP-C₈ results, X-ray photoelectron spectroscopy (XPS) analysis (performed using a K-alpha XPS spectrometer (Thermo) with a monochromatic Al K α X-ray source) was carried out (Fig. 4a-e). Fig. (4a) shows the O1s spectra of PIP-C₈ microporous catalyst. The XPS spectrum of PIP-C₈ exhibits only one O1s peak at 532.2 eV, which was attributed to the C–O bond. Fig. (4b) shows the C1s spectrum of PIP-C₈, divided into two single peaks at binding energies of 285 eV, which belong to the C–C bond. From the XPS analysis, the functional groups containing oxygen, such as R-OH, were found on the

surface, and the intensity of the higher-binding energy regions of the carbon element levels is much stronger than that of the original surfaces. Fig. (4c) shows the spectrum of PIP-C₈, divided into multiple N1s peak at 399–404eV, which was due to the N bonds. Fig. (d) shows the S2p spectrum of PIP-C₈ at 168.2 eV which belongs to sulfur element of sulfonic acid group. The catalytic effects of sulfonated materials has been credited to $-SO_3H$ groups, thus its density has a distinct effect on catalyst activity [33]. Generally, the S2p photoelectron peak is of particular significance in the sulfonated materials and has been used to confirm the presence of $-SO_3H$ groups [34]. Fig. (4e) shows the Br2d spectrum of PIP-C₈, divided into three peaks at binding energies of 70.6, 71.4, and 71.7 eV, which, respectively, belong to the Br–C and Br anion. XPS



Fig. 4. XPS spectra of the PIP-C₈ catalyst.

results shows that the saturated solution peak is larger than that of the known concentration. The O1s signal at 1.50 eV was used to calibrate the spectral frequency whenever minor charging effects were observed [35].

N2 adsorption-desorption isotherm (using nitrogen N2 adsorption at liquid nitrogen temperatures on a Carlo Erba Sorptomatic 1990 instrument) curves of the acid-activated PIPs show that these materials have microporous structures (Fig. 5) and surface area values that are higher than those of PIP-C₄, PIP-C₁₂, and PIP-C₁₆ (Table 3). This results from acid leaching, and consequently, the presence of micropore in the sample, with PIP-C_8 presenting the largest surface area (480 $m^2/g^{-1}).$ The measured particle size values showed that PIP-C₈ was more effective than other PIPs. These results are coherent with the surface area values of each PIP. The specific surface areas, total pore volume, and average pore volume are presented in Table 2. The catalyst possessed a surface area of 660 m 2 g $^{-1},$ 480 m 2 g $^{-1},$ 564 m 2 g $^{-1},$ and 448 m 2 g $^{-1},$ for PIP-C4, $PIP\text{-}C_8, PIP\text{-}C_{12}, and PIP\text{-}C_{16}, respectively. The total pore volumes were 0.2739 cm³ g⁻¹, 0.2332 cm³ g⁻¹, 0.2378 cm³ g⁻¹, and 0.2342 cm³ g⁻¹,$ for PIP-C₄, PIP-C₈, PIP-C₁₂, and PIP-C₁₆, respectively. An average pore diameter of 1.7 nm, 1.9 nm, 1.7 nm, and 1.9 nm was obtained for PIP-C₄, PIP-C₈, PIP-C₁₂, and PIP-C₁₆, respectively. PIP-C₈ exhibits a high surface area and total pore volume that enhance the efficiency of mass transfer and prevents the release of acid sites. The large surface area and pore volume, and small pore diameters, are favorable for enhanced



Fig. 5. Nitrogen adsorption-desorption isotherm and pore size distribution of the PIP-C₄, PIP-C₈, PIP-C₁₂, and PIP-C₁₆ catalysts.

catalytic activity [36]. Mostly, the small size of the porous support results in a highly share of the catalytically active sites located on the support surface, which can obtain more contact opportunities between the active sites and substrates and thus greatly improve the catalytic

Table 2

The BET analysis results of PIP catalyst.

PIPs	$S_{BET}^{a} (m^2 g^{-1})$	V_{p}^{b} (cm ³ g ⁻¹)	D _{ave} ^c (nm)
PIP-C ₀	715	0.3238	1.7
PIP-C ₄	660	0.2739	1.7
PIP-C ₈	480	0.2332	1.9
PIP-C ₁₂	564	0.2378	1.7
PIP-C ₁₆	448	0.2342	1.9

^a BET surface area,

^b Total pore volume

^c Average pore size

(trans)esterification efficiency. The BET surface of PIP-C₈ is 480 m²/g⁻¹. The PIP material exhibited several disordered nanopores with uniform pore sizes ranging from 1.7 to 1.9 nm, in accordance with the BET surface analysis [37], high surface area, which was favorable for the catalytic (trans)esterification reaction. Thus, although various research groups have proved the existence of microporous PILs, the micropores PILs active sites remains a great challenge despite an enormous development in the catalyst synthesis. Also the generation of microporosity is a promising strategy for endowing with a specific functionality. Such PIL catalysts catalytically active sites in micropores within the walls of mesopores would be ideal catalysts, because organic molecules are first freely diffused through the main channels and then strongly interact with the active sites located in the micropores for better reactivity [38].

3.2. Selection of a high-activity PIP catalyst

In this study, four PIP catalysts were prepared by adding respective acids, i.e., sulfonic acid, 1-bromobutane (C₄H₉Br-energy chemical 99.9%), 1-bromooctane (C8H17Br-energy chemical 99.9%), 1-bromohexadecane (C16H33Br-energy chemical 99.9%), 1-bromododecane (C12H25Br-energy chemical 99.9%), and 1, 3-propane sultone (C₃H₆O₃S-energy chemical 99.9%). During the reaction, it was observed that the PIP-C₈ catalyst could be used to prepare the desired products. Each experiment was conducted under the same conditions: a catalyst concentration of 95 mg based on the lipid molar, oleic acid (4.23 g, 15 mmol), and ethanol (3.78 m, 90 mmol), at 65 °C, for 3 h with agitation. Under these conditions, the catalytic activities of PIP-C₄, PIP- $C_{8,}$ PIP- $C_{12,}$ and PIP- C_{16} were compared; the obtained oleic acid conversion results using these four ionic PIPs are presented in Table 3. The catalyst acidity is the primary factor impacting catalyst efficiency during the esterification reaction, namely, the PIP-C₈ catalyst, which has the highest acidity as well as the largest number of strong acid sites among all the PIP catalysts. The ethyl oleate yield (61.5%) was much higher when catalyzed by the PIP-C₄, PIP-C₁₂, and PIP-C₁₆ catalysts. Under the same reaction conditions, an ethyl oleate yield above 44.2% was obtained in the presence of the PIP-C12 catalyst. The yield of 39.4% and 27.1% were obtained with PIP-C₁₆ and PIP-C₄ catalysts, respectively. The PIP-C₈ acidity and structure had significant effects on oleic acid conversion into ethyl oleate. It is already understood that the nature of the anion affect the catalytic activity of -SO₃H functionalized PILs [39]. Therefore, the sulfonic acid-functionalized PIP-C₈ was selected for further studies.

Table 3
Effect of porous ionic polymers on esterification of oleic acid and ethanol.

Entry	PIP- catalyst	Conversion (%)
1	PIP-C ₄	27.1
2	PIP-C ₈	61.5
3	PIP-C ₁₂	44.2
4	PIP-C ₁₆	39.4

Reaction conditions: catalyst (95 mg), oleic acid (4.23 g, 15 mmol), ethanol (3.78 m, 90 mmol), 80 $^\circ$ C, 3 h.

3.3. Esterification over PIP- C_8

The catalytic activity of the sulfonic acid-functionalized PIP-C8 catalyst was tested for the esterification reaction of oleic acid with ethanol into ethyl oleate. First, the catalytic behavior of the microporous PIP-C₈ as a function of the reaction was studied using the following experimental conditions. The experimental results showed that the yield increased with increasing catalyst concentration and reached 88.7% when the PIP-C₈ concentration was 170 mg (Fig. 6a). As shown in Fig. 6b, the yield increased with increasing molar ratio of oleic acid to ethanol up to 1:6. This is due to the inductive effect of the increased carbon chain of alcohol. Fig. 6c shows the reaction time of yield change. The yield increased with reaction time, reaching a maximum of 93.6% after 7.5 h. A high conversion was achieved using PIP-C₈ in a short time; this is because of its high acidity and number of strong acid sites. The yield increased with increasing reaction temperature, and reaching 79.9% at 85 °C (Fig. 6d). This is probably due to the better solubility and miscibility of oleic acid with ethanol at higher temperatures, which facilitates the protonation of the carbonyl group of oleic acid and lowers the mass transfer limit, resulting in the increased yield of the product. Roman et al. [40] evaluated a novel 1-methylimidazolium hydrogen sulfate, [HMIM]HSO₄, ionic liquid was successfully applied as a catalyst in the biodiesel production through the esterification reaction of oleic acid with methanol. The yield of 90% was achieved for product after 8 h.

3.4. Catalytic performance of PIP- C_8 on various fatty acids with shortchain alcohol yields

The PIP-C₈ catalyst was evaluated for the esterification of various fatty acids such as lauric acid, myristic acid, palmitic acid, stearic acid, linoleic acid, and oleic acid with ethanol and methanol to produce esters. Optimum reaction conditions were explored by examining the impact of a PIP-C₈ catalyst loading of 145 mg, fatty acids (15 mmol), alcohols (90 mmol), and a reaction time of 7.5 h at the reflux temperature with agitation. The PIP-C₈ catalyst is highly active in the esterification reaction. Thus, the esterification yields of lauric acid, myristic acid, palmitic acid, stearic acid, and linoleic acid under optimized reaction conditions with ethanol were 90.7%, 93.1%, 91.5%, 92.9%, and 91.7%, respectively (Table 4, entry nos. 1-5). The esterification yields of oleic acid, lauric acid, myristic acid, palmitic acid, stearic acid, and linoleic acid under optimized reaction conditions with methanol were 92.3%, 92.0%, 93.5%, 92.2%, 92.5%, and 92.4%, respectively and are presented in Table 4 (entry nos. 6-11). PIP-C₈ exhibited outstanding catalytic performance with a high yield under mild conditions, which was comparable to that of ethanol and methanol. The catalytic performance of PIP-C₈ could be ascribed to its remarkable properties, such as strong acidity and a larger number of acid sites. The esterification of palmitic acid with methanol was studied over microporous sulfated zirconia solid acid catalyst; the catalyst showed 88-90% yield of methyl palmitate after 5–7 h [36]. It is important to mention that the loading of functional groups (-SO3H) on the surface of PIP-C8 may lead to improved hydrophilicity and increase the accessibility of raw material (FFAs, ethanol, and methanol) to the -SO₃H groups in the esterification.

3.5. Recycling experiments for PIP-C8

As the cost of biodiesel production is a major concern nowadays, the recyclability of PIL catalysts used in the biodiesel process should be taken into account. Recycling of PILs reduces the cost of biodiesel production. In the recycling process, we were able to easily separate the PIP- C_8 catalyst from the resultant mixture products owing to the insolubility of the PIP- C_8 catalyst. The PIP- C_8 catalyst with sufficient functionality and high oxidation stability exhibited a high conversion yield with high recyclability. The PIP- C_8 catalyst has a large surface area and a large number of acidic sites, which help in separating the polar compounds effectively from the acidic sites and preventing the acidic sites from



Fig. 6. (a). The effect of PIP-C₈ concentration on the ethyl oleate yield. Reaction conditions: oleic acid (4.23 g, 15 mmol), ethanol (3.78 ml, 90 mmol), 85 °C for 7.5 h, and various catalyst Concentrations of 45–170 mg (b) The effect of oleic acid: ethanol molar ratio on the ethyl oleate yield. Reaction conditions: catalyst PIP-C₈ (95 mg), oleic acid (4.23 g, 15 mmol), 85 °C for 7.5 h, and various molar ratio of oleic acid and ethanol of 1:2–1:10. (c) The effect of reaction time on the ethyl oleate yield. Reaction conditions: catalyst PIP-C₈ (95 mg), oleic acid (4.23 g, 15 mmol), 85 °C, and various reaction time of 1.5–7.5 h. (d) The effect of reaction temperature on the ethyl oleate yield. catalyst PIP-C₈ (95 mg), oleic acid (4.23 g, 15 mmol), ethanol (3.78 ml, 90 mmol), 7.5 h, various reaction temperature of 50–85 °C.

Table 4

Catalytic performance of ${\rm PIP}\text{-}{\rm C}_8$ on esterification of fatty acids and short-chain alcohols.

Entry	Fatty acids	Alcohols	Conversion (%)
1	Lauric acid	Ethanol	90.7
2	Myristic acid	Ethanol	93.1
3	Palmitic acid	Ethanol	91.5
4	Stearic acid	Ethanol	92.9
5	Linoleic acid	Ethanol	91.7
6	Oleic acid	Methanol	92.3
7	Lauric acid	Methanol	92
8	Myristic acid	Methanol	93.5
9	Palmitic acid	Methanol	92.2
10	Stearic acid	Methanol	92.5
11	Linoleic acid	Methanol	92.4

Reaction conditions: catalyst PIP-C8 (145 mg), fatty acids (15 mmol), alcohols (90 mmol), reflux temperature at 7.5 h.

being released. PIP-C₈ could be recycled at least five times without any significant decrease in the catalytic activity, as shown in Fig. 7. For the novel PIP-C₈ catalyst, the yields were 92.3% (first run), 92.1% (second run), 91.8% (third run), 91.2% (fourth run) and 88.9% in the fifth run, mostly due to the unavoidable leaching of the catalyst during the reaction, blockage of acid sites by adsorbed organic species [41]. The PIP-C₈ was more active; the spent catalyst showed no structural changes and, hence, could be efficiently recycled with almost no loss in performance. This work suggests that *J. curcas* seed oil with PIP-C₈ catalyst is a promising process that can sustain biodiesel growth.

3.6. Testing of PIP- C_8 on J. curcas seed oil with different alcohol yields

Fatty acids are *J. curcas* seed oil compounds that vary in chain length, degree of unsaturation, and structure. Fatty acids were determined by GC-MS using AOAC (969.33), and compared with the available GC standards. *J. curcas* seed oil was distinguished from the plant lipids with straight-chain carbon compounds like C14-C18 and C20 saturated and unsaturated fatty acids. Long-chains polyunsaturated fatty acids (LC-



Fig. 7. PIP-C₈ catalyst recyclability for esterification of oleic acid with ethanol. Reaction conditions: reaction temperature at 85 $^\circ$ C for 7.5 h.

PUFA) such as C18:1 and C18:2 with greater double bonds are also found in *J. curcas* seed oil. The different fatty acids identified in this study are listed in Table 5. *J. curcas* seed oil contents myristic acid (14:0; 0.1%), palmitic acid (16:0; 14.2%), palmitoleic acid (16:1; 0.7%), margaric acid (17:0;0.1%), steric acid (18:0;7.0%), oleic acid (18:1; 44.7%), linoleic acid (18:2; 32.8%), linolenic acid (18:3; 0.2%), arachidic acid (20:0; 0.2%), total saturated fatty acids (21.6%), total mono-unsaturated fatty acids (45.4%), and total polyunsaturated fatty acids (33.0%). The non-edible characteristics of oil play a vital role for their utilization as ideal feedstocks in biodiesel production [42]. *J. curcas* seed oil has a better perspective due to its high mono-unsaturated content (45.4%) and its abundant availability in China.

The catalytic activity of the porous ionic polymer (PIP) solid catalyst was evaluated in the transesterification of *J. curcas* seed oil. As expected, the transesterification could not occur under the employed reaction conditions. When the prepared PIP-C₈ was used as a catalyst for the transesterification, the conversion to esters could be obtained. The catalytic activity of the PIP-C₈ catalyst was tested for the transesterification reaction of *J. curcas* seed oil into biodiesel using short-chain alcohol (ethanol, DEC, DMC). The catalytic activity of PIP-C₈ on the transesterification of *J. curcas* seed oil with ethanol, ethanol–to–DEC (1:1 molar ratio), and ethanol–to–DMC (1:1 molar ratio) were also studied. The catalyst was particularly effective, achieving a high biodiesel yield from *J. curcas* seed oil. Parameter condition was same in all experiments.

 Table 5

 Fatty acids composition of Jatropha curcas seed oil used in this study

A PIP-C₈ catalyst loading of 170 mg (based on the molar concentration of lipids) and a J. curcas oil: alcohol molar ratio of 1:6, with a constant agitation speed of 500 rpm after 5 h of reaction at reflux temperature. The results showed that the acid-functionalized PIP-C8 catalyst could efficiently trigger biodiesel production. Thus, the transesterification yields for J. curcas seed oil with ethanol, ethanol-to-DEC, and ethanol-to-DMC under optimized reaction conditions were 85%, 94%, and 70%, respectively. In addition to biodiesel production, the prepared active PIP-C₈ catalyst is applicable to a wide range of solvents. The PIP-C8 catalyst with a high surface area improves the catalytic activity because the accessibility of reactant molecules to active sites is relatively high on microporous PIP-C8 catalyst. Being a stronger organic acid, sulfonic acid could ionize a proton quickly because of the negative induction effect of the atoms between the CH₃ and -SO₃H groups. The proton, then, combines with the triglyceride carbonyl group to form a carbocation intermediate, which reacts through a nucleophilic substitution reaction with alcohol. It has been reported that the dimensions of triglyceride, methyl ester, and glycerin are approximately 5.8, 2.5 and 0.6 nm, respectively [43]. It was understood that the glycerin molecules can easily infiltrate the pores of the catalyst and most of the active sites will be utilized during the transesterification reaction [44,45]. ILs functionalized with sulfonic acid groups are one of the most useful types of functional ILs because they are highly effective in many acid-catalyzed reactions [46,47]. The results indicate that the PIP-C8 catalyst is a good choice for different alcohol; the catalyst could efficiently catalyze raw oil.

3.7. Analysis of biodiesel

We tested the transesterification of J. curcas seed oil with a mixture of short-chain alcohols such as ethanol, ethanol-to-DEC, and ethanol-to-DMC with 170 mg of PIP-C₈ at reflux temperature with agitation. GC-MS was used for the characterization of synthesized biodiesel and J. curcas seed oil. The most important factor relevant to catalytic activity is the total ester content (%), which indicates how much J. curcas seed oil is converted to biodiesel. Overall, when the reaction temperature matches the reflux temperature, catalyst show improved catalytic properties due to enhanced activation energy and mass transfer resistance. The PIP-C₈ catalyst exhibited a significant increase in the ester conversion due to acidity, whereas the PIP-C8 catalyst with ethanol-to-DEC (1:1 mol/mol) showed high catalytic activation with a high ester concentration (94%); whereas PIP-C₈ with ethanol exhibited low catalytic activation with a low esters concentration (85%), especially the PIP-C₈ catalyst with ethanol-to-DMC which was not exhibited the activation with a high esters concentration (70%). In Fig. 8, PIP-C₈ with a large surface area of $480 \text{ m}^2/\text{g}^{-1}$, and ethanol-to-DEC achieved the highest ester conversion, probably resulted from the strong acidity of these solvents. These results indicate that PIP-C₈ has synergetic effects on ester conversion efficiency in the transesterification process. Zhu et al. [48], reported the ethanol-to-DEC was investigated by an efficient

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Fatty acids	Structure ^a	Formula	Oil (wt%)	Saturated (wt%)	Mono-unsaturated (wt%)	Poly-unsaturated (wt%)
Myristic	14:0	C14H28O2	0.1	0.1	-	-
Plamitic	16:0	$C_{16}H_{32}O_2$	14.2	14.2	_	_
Palmitoliec	16:1	$C_{16}H_{30}O_2$	0.7	-	0.7	_
Margaric	17:0	C17H34O2	0.1	0.1	_	_
Steric	18:0	$C_{18}H_{36}O_2$	7	7	_	_
Oleic	18:1	$C_{18}H_{34}O_2$	44.7	-	44.7	_
Linoleic	18:2	C18H34O2	32.8	-	_	32.8
Linolenic	18:3	C18H30O2	0.2	-	_	0.2
Arachidic	20:0	$C_{20}H_{40}O_2$	0.2	0.2	_	_
Total			100	21.6	45.4	33

^a The former number represents the number of the carbons in the hydrocarbon chain while the latter represents the number of the double bond in the respective fatty acid.



Fig. 8. GC-MS spectra of synthesized esters, synthesis conditions (a) *J. curcas* seed oil, (b) *J. curcas* seed oil: ethanol molar ratio of 1:6, (c) *J. curcas* seed oil: ethanol-to-DEC (1:1) molar ratio of 1:6, (d) *J. curcas* seed oil: ethanol-to-DMC (1:1) molar ratio of 1:6, PIP-C₈ catalyst loading of 170 mg, with a constant agitation speed of 500 rpm after 5 h of reaction at reflux temperature.

solvent system comprising of other solvent system. We further investigated the changes in the composition of the main products, such as ethyl myristate (14:0), ethyl palmitate (16:0), ethyl palmitate (16:1), ethyl margariate (17:0), ethyl stearate (18:0), ethyl oleate (18:1), ethyl linoleiate (18:2), ethyl linolenicate (18:3), and ethyl arachidicate (20:0) with respect to PIP-C₈ and ethanol-to-DEC. The overall ester compositions are similar to the expected ratio. However, there are some changes in each composition depending on the PIP-C₈ and a mixture of solvents, which may indicate a high catalytic activity. The conversion levels were found to be higher; this could be due to their inherent FFA composition of mono-unsaturation, leading to a higher reactivity with novel PIP-C₈. This clearly shows that the transesterification reaction rate in the presence of PIP-C₈ is the highest for the triglycerides of mono-unsaturated and poly-unsaturated fatty acids, followed by that of saturated acids. The ester compositions of the saturated fatty acids (16:0 and 18:0) decreased and the shorter chains converted to the longer chain esters. However, it was found that the ester contents of ethanol, ethanol-to-DEC and ethanol-to-DMC consisted primarily of ethyl oleate (C18:1) and ethyl stearate (C18:0). In particular, the esters containing double bonds, such as C18:1, C18:2, and C18:3, are easily converted to

ethyl esters. Generally, this is because the double bonds have an electron-donating group, which can facilitate the reaction rate of the transesterification, and this reaction can be improved in the presence of strong acidic sites. Therefore, we believe that the strong acidity with sufficient acidic sites can facilitate the formation of esters, which determines the total amount and quality of ester through synergetic effect of PIP-C₈. Interestingly, DEC and DMC-based esters is reported to have better lubricating properties and oxidation stability vis-a-vis conventional esters due to miscibility of formed synthesized intermediate, glycerol carbonate, glycerol dicarbonate by product in the DEC and DMC-esters phase [49].

FT-IR spectroscopy was used for the synthesized esters and *J. curcas* seed oil characterization, and spectra are shown in Fig. 9. The peaks at 2920.30 cm⁻¹ and 2851.91 cm⁻¹ are assigned to the stretching vibrations of symmetric and asymmetric aliphatic C–H in the CH₂ and the terminal CH₃ groups, respectively. At 1743.10 cm⁻¹, there is a strong absorption peak, which is attributed to the carbonyl group (C=O) stretching vibration of triglycerides. The peaks in 1200–1400 cm⁻¹ are mostly assigned to CH₂ and CH₃ aliphatic group bending vibrations, such as symmetric H-C-H bending at 1377.25 cm⁻¹ and CH₂ scissoring at



Fig. 9. FT-IR spectra of synthesized esters, compared with (b) *J. curcas* seed oil with (c) *J. curcas* seed oil: ethanol molar ratio of 1:6, (d) *J. curcas* seed oil: ethanol-to-DEC (1:1) molar ratio of 1:6, and (e) *J. curcas* seed oil: ethanol-to-DMC (1:1) molar ratio of 1:6, PIP-C8 catalyst loading of 170 mg, with a constant agitation speed of 500 rpm after 5 h of reaction at reflux temperature.

1463.79 cm⁻¹. The peaks in the region 1096–1116 cm⁻¹ are assigned to the C-O ester group stretching vibration and CH₂ wagging. However, there are very few differences between the FT-IR spectrum of *J. curcas* seed oil and three esters (used ethanol, ethanol–to–DEC, and

ethanol-to-DMC). The observed peaks of the J. curcas seed oil and ethanol-to-DEC appeared at 1743.10 cm⁻¹, 1377.26 cm⁻¹, 1157.19 cm⁻¹, 1031.96 cm⁻¹, 871.18 cm⁻¹ are transesterification into 1743.95 cm⁻¹, 1361.91 cm⁻¹, 1170.91 cm⁻¹, 1016.31 cm⁻¹,



Fig. 10. Thermal stability of synthesized esters, (a) *J. curcas* seed oil: ethanol molar ratio of 1:6, (b) *J. curcas* seed oil: ethanol-to-DEC (1:1) molar ratio of 1:6, (c) *J. curcas* seed oil: ethanol-to-DMC (1:1) molar ratio of 1:6, PIP-C₈ catalyst loading of 170 mg, with a constant agitation speed of 500 rpm after 5 h of reaction at reflux temperature.

880.38 cm⁻¹ in the esters, respectively. So, the disappearance of the peak at 1463.79 cm⁻¹, 1096.86 cm⁻¹, and 965.93 cm⁻¹ from the *J. curcas* seed oil spectrum and in the biodiesel sample and the obtained of the novel peaks at 1436.14 cm⁻¹, and 1196.25 cm⁻¹ clearly show the transesterification of *J. curcas* seed oil into biodiesel. It is noted that the peaks of the *J. curcas* seed oil and ethanol that presented at 1648.10 cm⁻¹, 1272.22 cm⁻¹, 1067.13 cm⁻¹, 1000.12 cm⁻¹, and 852.22 cm⁻¹ are transesterification to 1678.95 cm⁻¹, 1287.91 cm⁻¹, 1070.91 cm⁻¹, 1010.35 cm⁻¹, and 860.34 cm⁻¹ in the esters, respectively.

The TGA curves of the three esters and *J. curcas* seed oil are presented in Fig. 10a. The thermal stability curve shows that esters (*J. curcas* seed oil with ethanol–to–DEC) are less thermally stable than *J. curcas* seed oil. The onset temperature of *J. curcas* seed oil is 385 °C whereas that of the ester is 191 °C, and the ester is completely volatilized at 250 °C. Fig. 10b, the thermal stability curve shows that esters (*J. curcas* seed oil with ethanol) are less thermally stable than *J. curcas* seed oil; the ester is 187 °C and is completely volatilized at 242 °C (Fig. 10c). The thermal stability curve shows that the esters (*J. curcas* seed oil with ethanol–to–DMC) are less thermally stable than *J. curcas* seed oil with ethanol–to–DMC) are less thermally stable than *J. curcas* seed oil with ethanol–to–DMC) are less thermally stable than *J. curcas* seed oil with ethanol–to–DMC) are less thermally stable than *J. curcas* seed oil with ethanol–to–DMC) are less thermally stable than *J. curcas* seed oil with ethanol–to–DMC) are less thermally stable than *J. curcas* seed oil with ethanol–to–DMC) are less thermally stable than *J. curcas* seed oil with ethanol–to–DMC) are less thermally stable than *J. curcas* seed oil with ethanol–to–DEC and the ester is completely volatilized at 234 °C. Therefore, the synthesized esters from *J. curcas* seed oil with ethanol–to–DEC as an alternative fuel [50,51].

4. Kinetic model

Kinetic models have been used to describe the ethyl oleate production from oleic acid esterification with ethanol using the PIP-C₈ catalytic system. The kinetics of the conversion process was simulated as a function of temperature ranging from 50° to 80°C (Fig. 11). According to our previous research, the process of ethyl oleate production was proven to be a first-order reaction, and the exponential equation was fitted using Eq. (4) for the experimental data to represent the kinetic behavior throughout the reaction duration. The rate of the esterification reaction was independent of the ethanol concentration and was assumed to follow first-order kinetics as represented in the following equation.

$$-In \quad (1 - X_{oleic} \quad acid) = kt \tag{4}$$

where, $X_{oleic \ acid}$ esterification is at time 't' and k is the rate constant.

As shown in Fig. 11, the correlation coefficient ($R^2 = 0.98$) of ANOVA statistics demonstrates that the model is well fitted for the experimental data. The results of constant values at different temperatures indicate that the conversion process is significantly and positively affected by the increasing temperature, and a high conversion yield



Fig. 11. Kinetics of the conversion process at different temperature: 50 °C, 60 °C, 70 °C and 80 °C.



Fig. 12. Arrhenius plot of the conversion process catalyzed by the prepared microporous PIP-C₈ at 50 $^{\circ}$ C, 60 $^{\circ}$ C, 70 $^{\circ}$ C, and 80 $^{\circ}$ C.

Table 6
Rate constants and the activation energy of the reaction process.

Temperature (°C)	Rate constant (min ⁻¹)	Activation energy (kJ mol ⁻¹)
50	0.09527	36.5
60	0.14364	32.8
70	0.20075	30.3
80	0.29315	22.3

(approximately 90%) for ethyl oleate production can be theoretically achieved at 80 °C. Because of the significant effect of temperature on the conversion process, their correlation was represented and analyzed using the Arrhenius plot, which correlates the rate constant ln(k) with temperature (1/T). Moreover, the activation energy (Ea) of the reaction was calculated using the Arrhenius Eq. (5).

$$In(k) = -\frac{E_a}{RT} + In(A)$$
(5)

Where, R is the ideal gas constant and A is the pre-exponential factor.

Fig. 12, shows the Arrhenius plot of the conversion process catalyzed by the prepared microporous PIP-C₈ at 50–80 °C. It was confirmed that ln(k) changes linearly with 1/T in the studied temperature range, as expected for a single rate-limited thermally activated process ($R^2 =$ 0.99). In this study, the activation energy value (22.3 kJ mol⁻¹) is consistent with the reported range of 17.9–51.9 kJ mol⁻¹ [52]. The activation energy is relatively low in comparison with previous report [53]. As evident from Table 6, the results of rate constants under different temperatures prove that temperature is closely related to the efficiency of the conversion process.

5. Conclusion

Microoporous PIP-C₈ catalyst with a high specific surface area of 480 m² g⁻¹, and an acidic nature enables the catalysis of the (trans) esterification reaction. The best property of this new catalyst is its stability during (trans)esterification in at 250 °C. The chosen catalyst, PIP-C₈ displayed better catalytic activity in the esterification of several FFAs into esters; its recyclability was successfully proven in five consecutive runs. Therefore, it is suitable and promising catalyst in the context of ester production, primarily for the treatment of oleic acid, lauric acid, myristic acid, palmitic acid, stearic acid, and linoleic acid. PIP-C₈ has also been used for the transesterification of *J. curcas* seed oil with ethanol, ethanol–to–DEC, and ethanol–to–DMC. The factors affecting the conversion of FFAs were determined to be the reaction time, temperature, molar ratio of FFA-to–alcohol, and catalyst loading; GC-MS, FT-IR, and TGA analyses showed that the triglycerides of the *J. curcas*

seed oil were completely converted into esters under optimal conditions. It is envisaged that the synthesized microporous PIP-C₈ catalyst exhibits potential for use in the catalytic production of esters and fine chemicals through green and promising for the further industrial applications. For the novel PIP-C₈ catalytic cycle, the yields were 92.3% (first cycle), yield in the fifth cycle decreased to 88.9% from 92.3%, loss of activity caused by the alcohol and stirring force. This represents the most critical aspect in the reaction and it has to be improved in future.

CRediT authorship contribution statement

Balaji Panchal: Data curation, Formal analysis, Writing – original draft. Tao Chang: Data curation, Formal analysis, Methodology, Writing – review & editing. Shenjun Qin: Methodology, Supervision, Writing – review & editing. Cunling Zhao: Software, Visualization. Yongjing Hao: Software, Visualization. Wang Jinxi: Software, Visualization. Qiaojing Zhao: Formal analysis, Software. Bian Kai: Software, Visualization. Yuzhuang Sun: Project administration, Resources.

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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