ORIGINAL ARTICLE

# Esterification of cooking oil for biodiesel production using composites $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ionic liquids catalysts

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**Abstract** Here, two ionic liquids 1-methyl-3-propane sulfonic-imidazolium (PSMIM) and 1-methyl-3-propane sulfonic-imidazolium hydrosulfate (PSMIMHSO$_4$) are synthesized, and these ionic liquids mixed with different of heteropolyacid $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ have been used as catalysts for esterification of cooking oil for preparation of biodiesel. Then those catalysts are characterized by Infrared spectrometer, X-ray diffractometer, nuclear magnetic resonance, elemental analyses and high-performance liquid chromatography. PSMIM and PSMIMHSO$_4$ mixed with $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ at the mass ratio of 1:1 are able to effectively catalyze esterification, using cooking oil as starting material at ratio of 1:20 (catalyst/cooking oil) and cooking oil to methanol at mass ratio of 1:6 for preparation of biodiesel with 3.5 h at 343 K. The result showed that 97.1 % yield of biodiesel could be obtained at optimized operation using PSMIMHSO$_4$ mixed with $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ at the mass ratio of 1:1 as catalyst.

**Keywords** $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ · Ionic liquid · Biodiesel · Acidic catalyst

## Introduction

In the past decades, the global energy shortage and environment deterioration continue to grow rapidly. The quality of life today is dependent upon access to a bountiful supply of affordable and low-cost energy. For a sustainable development, the energy should be derived from non-fossil sources, which are ideally reliable and safe, affordable, and limitless. Therefore, development of clean alternative fuels and renewable energy has become an important subject for world-wide researchers. Because of its environmentally friendliness, renewability and other advantages, biodiesel is expected to replace traditional diesel fuel to meet the needs of sustainable development of society [1, 2]. At present, biodiesel production mainly uses a variety of oils and lower alcohol as raw materials, and acid and alkalinity can be used as catalyst [3] such as homogeneous acid or base, lipase, or heterogeneous acid or base catalysts. Conventionally, this reaction is carried out using homogeneous acid or base catalysts, such as sulfonic acid, potassium hydroxide, sodium hydroxide, or their alkoxides [4–8]. However, these catalysts are corrosive and are not easily recovered, leading to the release of environmentally unfriendly effluents, which inevitably leads to a series of environmental problems. Because of the detrimental effects of these catalysts, great efforts directed toward the development of environmentally friendly catalysts have been made. The use of lipases as biocatalysts for biodiesel production has been of great interest due to its environmental friendliness [9–12]. However, some alcohols such as methanol deactivate the lipase to some extent and the enzyme stability was poor. Moreover, glycerol, which is a byproduct, easily adsorbs on the surface of the lipase and inhibits the enzyme activity. Although heterogeneous acid or base catalysts are environmentally friendly, they also have drawbacks, such as low catalytic activity and deactivation [3, 13–15]. Due to the disadvantages of equipment corrosion and separation difficulty, concentrated sulfuric acid is much maligned in the esterification stage [16–20].

Keggin heteropoly acids (HPAs) have been reported to have the potential for biodiesel synthesis [14, 21–27]. Solid

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super acid $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is not only BrÖnsted acid, but also Lewis acid, which has good catalytic activity, selectivity, and corrosion resistance [28, 29]. The activity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ relative to the other catalysts became higher than conventional acids such as $H_2SO_4$, $Al_2O_3$–$SiO_2$, zeolites and acidic resins [15, 30–32]. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is a widely applicable water-tolerant solid acid. As an important green solvent, acidic ionic liquids (ILs) can dissolve a variety of solute and favor the dispersion of catalyst in catalytic phase transfer reaction. Ionic liquids have attracted much interest as relatively clean and promising catalysts and alternative solvents that possess important attributes, such as wide liquid range, negligible vapor pressure, high catalytic activity, excellent chemical and thermal stability, potential recoverability, design possibilities, and ease of separation of the products from reactants [33–37]. Meanwhile acidic ionic liquid could also improve the acid catalytic performance [38]. Due to the booming demand of biodiesel and the limitations of traditional method, a novel method for the synthesis of biodiesel has been highly desirable. The method of mixing phosphotungstic salt with ionic liquid presents the remarkable advantage over the high yield of esterification.

In this study, 1-methyl-3-propane sulfonic-imidazolium (PSMIM), 1-methyl-3-propane sulfonic-imidazolium hydrosulfate (PSMIMHSO$_4$) and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ were prepared. Performances of two ionic liquids mixed with $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ were, respectively, evaluated as catalysts in the esterification. Catalysts were characterized by nuclear magnetic resonance (NMR), infrared (IR) spectroscopy, elemental analyses, X-ray diffractometer (XRD) and high-performance liquid chromatography (HPLC). The effects of varying reaction conditions on the production of biodiesel were extensively studied and compared to different catalysts.

## Experimental

### Preparation of PSMIM

1,3-propyl sulfonic acid (40.0 g) was completely dissolved in 300 mL toluene. N-methyl imidazole (27.0 g) was slowly added while being stirred under an ice bath. Then the temperature was slowly raised to 298 K and maintained for 2 h. The product was then filtered from the mixture liquid and washed with diethyl ether and ether acetate for three times, respectively. The solid was obtained after heating at 343 K for 5 h [38].

### Preparation of PSMIMHSO$_4$

PSMIM (23.3 g) was dissolved in 100 mL deionized water. Then sulfuric acid (10.9 g) was slowly added while being stirred at room temperature. After that, the temperature was raised to

363 K and then maintained for 2 h. The deionized water was removed from the product using a rotary evaporator [38].

### Preparation of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$

An aqueous solution of $Cs_2CO_3$ (0.3528 g) was added drop-wise to an $H_3PW_{12}O_{40}\cdot19H_2O$ (2.8000 g) solution under vigorous stirring. The fine suspension was held at room temperature overnight and subsequently to dryness at 323 K. The ratio polyacid–cesium carbonate was regulated in such a way that the final stoichiometry corresponded to $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ [39].

### Preparation of mixture catalysts

PSMIM was mixed with $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ with deionized water as catalyst at room temperature and dried at 353 K, while mixing at the mass ratio of 1:1 named PSC. Meanwhile, PSMIMHSO$_4$ was mixed with $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ with the same method, while mixing at the mass ratio of 1:1 named PSSC.

### Preparation of biodiesel

Cooking oil (10 g), methanol and the catalyst [40, 41] were taken into a flask with stirring and refluxing. Then the catalyst was separated from flask by centrifuge. Subsequently, methanol (5.0 g) and potassium hydroxide (0.25 g) were also added into the flask with stirring and reflux for 0.5 h. The methanol was removed from the product using a rotary evaporator at 313 K, followed by cooling to room temperature. After that, the supernatant was separated from product by centrifuge and quickly subjected for HPLC analysis,

### Characterization and evaluation of the catalyst

Infrared spectrometer (AVATAR 370 from Thermo Nicolet) was used to analyze the ionic liquid and heteropoly acid and its salt at 500–4,000 cm$^{-1}$.

X-ray Diffractometer (Deutschland RUKER D2 PHASER) was scanned with CuKα in the range of 10°–80° at a rate of 0.02°s$^{-1}$.

Nuclear magnetic resonance (NMR) was used to characterize the ionic liquid.

PSMIM $^1$HNMR (400 MHz, D$_2$O): $\delta2.138$ (m, 2H, $J = 7.2$ Hz), 2.822 (t, 2H, $J = 7.2$ Hz), 3.806 (s, 3H), 4.270 (t, 2H, $J = 7.2$ Hz), 7.365 (s, 1H), 7.437(s, 1H), 8.655 (s, 1H). $^{13}$CNMR (400 MHz, D$_2$O): $\delta25.11$, 35.73, 47.24, 47.72, 122.16, 123.76, 136.17.

PSMIMHSO$_4^1$HNMR (400 MHz, D$_2$O): $\delta2.135$(t, 2H, $J = 7.2$ Hz), 2.745 (s, 2H), 3.717 (s, 3H), 4.181 (t, 2H, $J = 7.2$ Hz), 7.271 (s, 1H), 7.339 (s, 1H), 8.560 (s, 1H). $^{13}$CNMR(400 MHz, D$_2$O): $\delta24.99$, 35.65, 47.15, 47.65, 122.10, 123.71, 136.06.

Elemental analyses (EA) were performed on a Perkin-Elmer 2,400 elemental analyzer for C, H, N and S. Anal. calc. for PSMIM: C, 41.18 %; H, 5.88 %; N, 13.73 %; S, 15.69 %; found: 41.24 %; H, 5.83 %; N, 13.74 %, S, 15.65 %. Anal. calc. for PSMIMHSO$_4$: C, 27.81 %; H, 4.64 %; N, 9.27 %; S, 21.19 %. found: C,27.83 %; H, 4.60 %; N, 9.33 %; S, 21.14 %.

The purity of the ionic liquid was analyzed by HPLC (Agilent1100). The conditions of HPLC: separation column is the ODS C18. Water and methanol were used as a mobile phase, the ratio of water and methanol was 1:9 and the speed was 1.0 mL/min. The detectable wavelength of UV was 215 nm at room temperature.

Analysis

The yield was analyzed by HPLC (Agilent1100). The conditions of HPLC: separation column is the ODS C18. Acetonitrile was used as a mobile phase at a flow rate of 1.0 mL/min. The volume of each sample was 15 μL. The detectable wavelength of UV was 205 nm at room temperature.

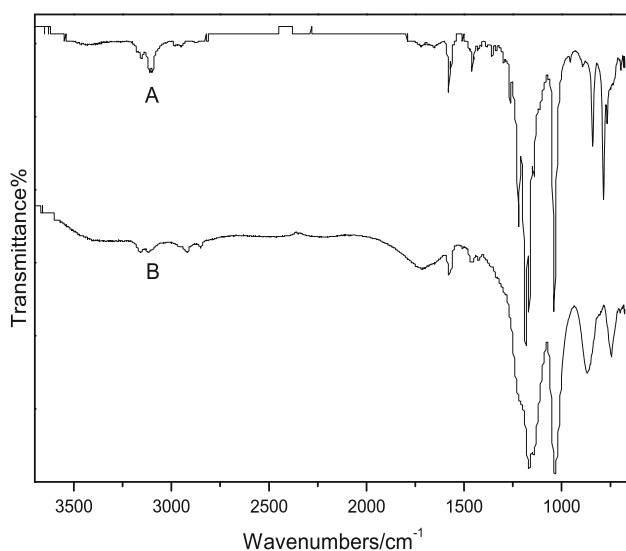The calculation formula is:

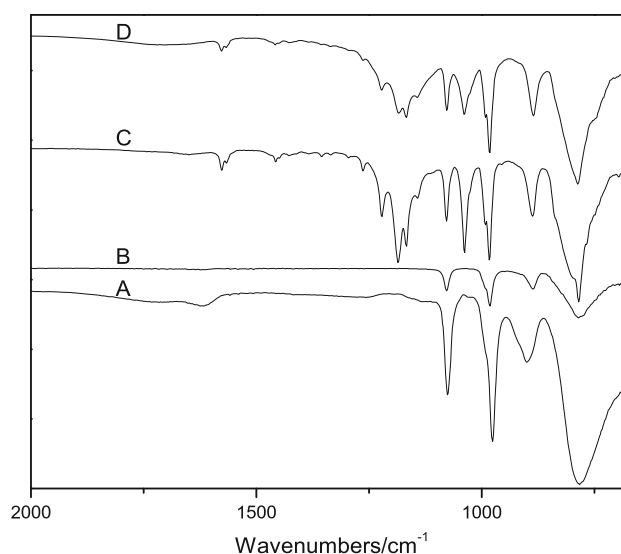Yield of biodiesel = (Conversion of cooking oil) × (Selectivity of cooking oil to biodiesel formation)

## Result and discussion

FT-IR of ionic liquids

Figure 1 shows FT-IR of sulfonic acid ionic liquids. The peaks at 3156, 3116 and 1575 cm$^{-1}$ represent –N–H, –C–H and –C=N– stretching vibration of the imidazole ring,

**Fig. 1** FT-IR of ionic liquids *A* PSMIM, *B* PSMIMHSO$_4$

**Fig. 2** FT-IR of phosphotungstic acid, its salt and compound *A* H$_3$PW$_{12}$O$_{40}$·19H$_2$O, *B* Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$, *C* PSC *D* PSSC

respectively. The peaks from 2,965 to 2,992 cm$^{-1}$ are ascribed to the C–H stretching vibration of –CH$_2$ and N–CH$_2$, and the peaks at 1,487 and 1,398 cm$^{-1}$ are formation vibration of CH$_2$ and CH$_3$. The peak at 749 cm$^{-1}$ is the bending vibration of the imidazole ring. Meanwhile, a strong peak appears at 1,171 cm$^{-1}$, which is the S=O stretching vibration of HSO$_4$- and -SO$_3$ [38].
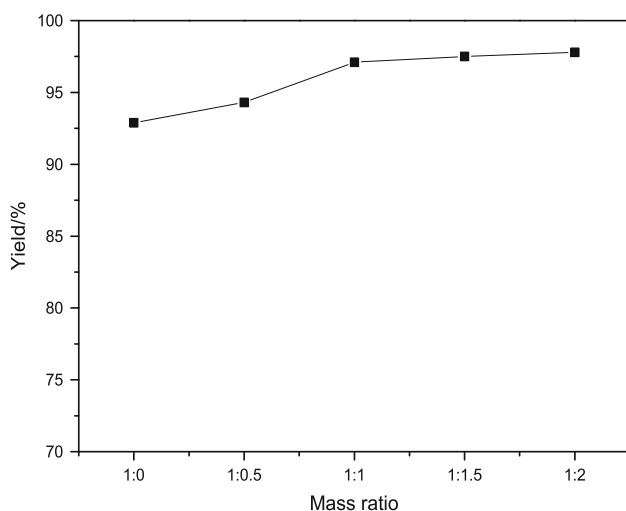
FT-IR of phosphotungstic acid and its salt

Figure 2 shows FT-IR of phosphotungstic acid and its salt. The peaks at 1,075, 976, 904 and 787 cm$^{-1}$ represent H$_3$PW$_{12}$O$_{40}$·19H$_2$O. The peaks at 1078, 983, 889 and 785 cm$^{-1}$ represent Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$. It can be seen that H$_3$PW$_{12}$O$_{40}$·19H$_2$O and Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ keep the Keggin structure of phosphotungstic acid from FT-IR. The peak at 1,078 cm$^{-1}$ belongs to P-O$_a$ (Oa-oxygen atoms bound to three W atoms and to P) stretching vibration of the center of tetrahedron. The peak at 983 cm$^{-1}$ is W-O$_b$ (O$_b$-terminal oxygen atom) vibration. The peak at 889 cm$^{-1}$ is W-O$_c$-W (O$_c$-corner sharing bridging oxygen atom) vibration. The peak at 785 cm$^{-1}$ is W-O$_e$-W (O$_e$-edge sharing bridging oxygen atom) vibration [39, 42]. When Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ mixed with ionic liquids, compounds also keep the Keggin structure of phosphotungstic acid and the structure of ionic liquids.

XRD of phosphotungstic acid and its salt

XRD patterns of t phosphotungstic acid and its salt are shown in Fig. 3. XRD patterns of H$_3$PW$_{12}$O$_{40}$·19H$_2$O at 8.5°, 10.6°, 20.4° and 27.9° are the characteristic peaks. XRD patterns of Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ at 10.4°, 18.3°,
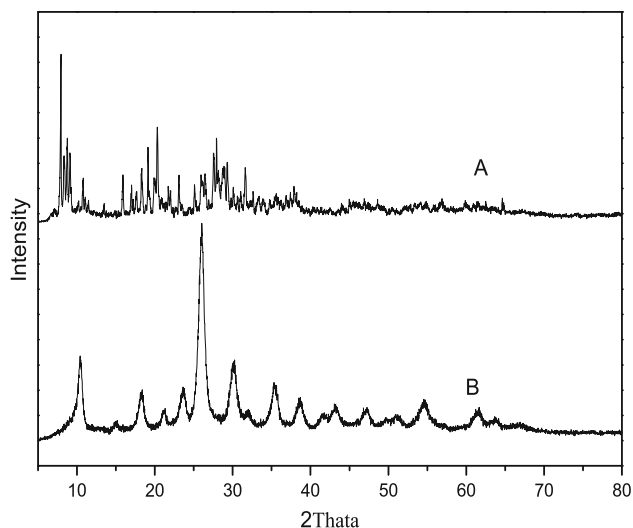
**Fig. 3** XRD of phosphotungstic acid and its salt *A* $H_3PW_{12}O_{40}\cdot19H_2O$, *B* $Cs_{2.5}H_{0.5}PW_{12}O_{40}$



**Fig. 5** Effect of reaction temperature on PSSC-catalyzed esterification

## Effect of reaction temperature

The experiment of esterification was tested while using PSSC (0.5 g) as catalyst from 313 to 363 K for 3.5 h, cooking oil was 10 g and methanol was 60 g. By adjusting the temperature of water bath kettle to what it is needed.

Figure 5 shows that the yield of biodiesel significantly increases with the rising of the temperature. From Fig. 5, it is observed that the higher activity is favored at high temperature, which is likely related to that the more $H^+$ released from the ionic liquid at higher temperature, thus leading to the stronger acidity, and the higher yield [38]. Meanwhile, the acidic activity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ also is increasing while rising the temperature. After 343 K, the yield of biodiesel is nearly full and yield incremental very slow. Thus, 343 K is the temperature to obtain the satisfactory esterification yield.

## Effect of reaction time

The experiment of esterification was tested while using PSSC (0.5 g) as catalyst at 343 K by adjusting the time.

The effect of reaction time on the yield is presented (Fig. 6). It can be seen from Fig. 6 that the PSSC is very efficient for biodiesel. The high yield 97.1 % is achieved after 3.5 h, which is very high for biodiesel synthesis from cooking oil [43, 44]. It is generally known that the biodiesel reaction is carried out through three steps. The triglycerides are transformed to diglycerides, monoglycerides and glycerol. The byproduct content would cause the hydrolysis of the ester compounds. The diglycerides and monoglycerides have both the hydrophobic long carbon chain and the hydrophilic hydroxyl, which can bring the
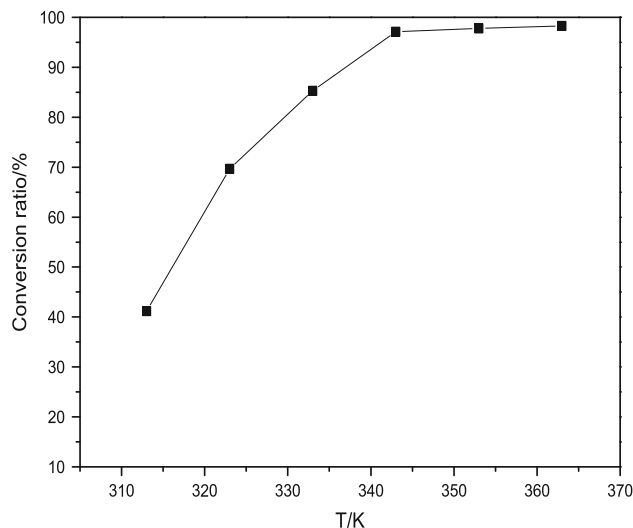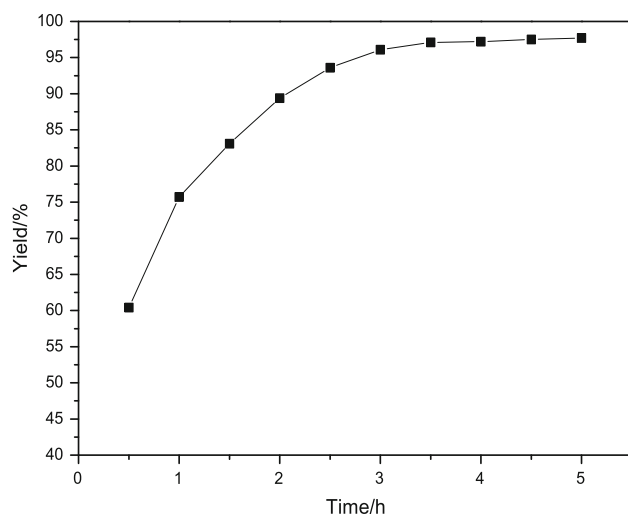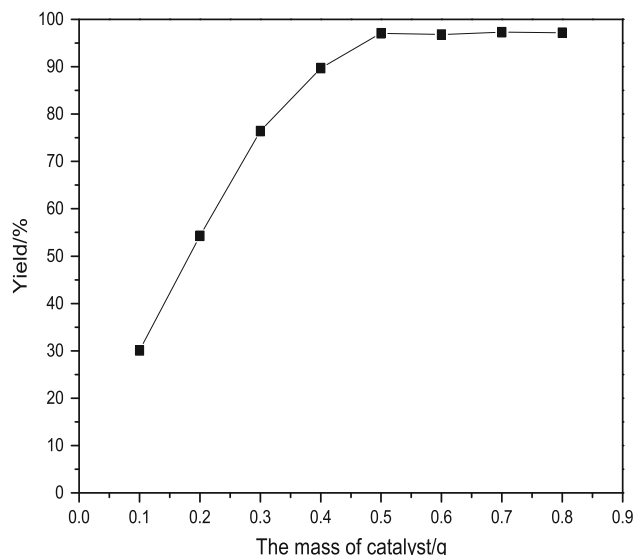


**Fig. 4** Yield of biodiesel at different mass ratio at 343 K (The weigh of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ precedes over PSMIMHSO$_4$ in the mass ratio)

26.0°, 30.1° and 35.4° are the characteristic peaks [39, 42]. As $H_3PW_{12}O_{40}\cdot19H_2O$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ remain the same, characteristic peaks of XRD patterns, it is concluded that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ keep the Keggin structure.

## Effect of mass ratio of mixed catalytic system

$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was mixed with PSMIMHSO$_4$ at different mass ratio to catalyze the reaction at 343 K for 3.5 h.

Figure 4 shows that the yield of biodiesel rises, as the ratio of PSMIMHSO$_4$ is increasing. After the mass ratio of 1:1, the yield of biodiesel rises slowly. Thus, the optimized mass ratio is 1:1 in the reaction.

Fig. 6 Effect of reaction time



Fig. 8 Effect of the amount of methanol

### Effect of the methanol amount

The experiment of esterification was tested while using PSSC as catalyst at different mass at 343 K for 3.5 h.

The mass ratio of the cooking oil and methanol is investigated (Fig. 8). The methanol amount is vital for the reaction. Since the reaction involved in biodiesel is reversible, one would expect that increasing the amount of methanol would shift the reaction equilibrium toward the products [45]. The biodiesel would produce water and the byproduct water would cause the hydrolysis of the ester, which reduced the yield. More methanol promotes the reaction equilibrium forward to obtain the high yield. On the other hand, too much methanol may cause the dilute effect and decrease yield [38]. When 60 g methanol is added, the maximum yield is reached. Therefore, the mass of methanol is optimized as 60 g.

### Compared with traditional acid catalysts

By comparing the yield of PSMIM and its functionalized PSMIMHSO$_4$ from Table 1, it is found that the yield of PSMIMHSO$_4$ improves more than PSMIM. It is explained that the presence of the anionic group HSO$_4^-$ enhanced the acidity of BrÖnsted acid, which improve the activity of ionic liquid and have the positive of acid catalyst in the process of esterification. But the acidity of two ionic liquid is lower than H$_2$SO$_4$, so their yields are lower than H$_2$SO$_4$ [38]. However, the high byproduct content causes the serious hydrolysis of ester products to decrease the yield of reaction. The traditional homogeneous catalyst H$_2$SO$_4$ has relatively low activities for the production of biodiesel. Although H$_2$SO$_4$ has a strong acidity, materials and
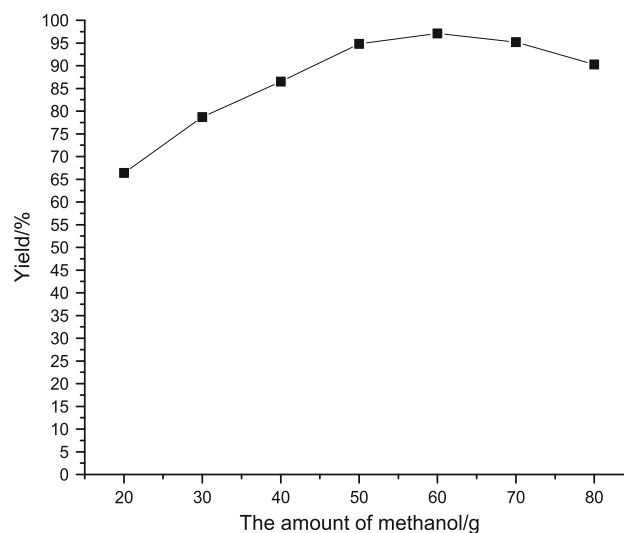


Fig. 7 Effect of the mass of catalyst

water to the acid sites. The yield varies little after 3.5 h, which remained nearly constant, indicating a nearly equilibrium yield. Therefore, the appropriate reaction time is 3.5 h.

### Effect of the mass of catalyst

The experiment of esterification was tested while using PSSC as catalyst at different mass at 343 K for 3.5 h.

In Fig. 7, the influence of the mass of catalyst is presented. The optimum mass of catalyst was found to be 0.5 g in this reaction. The excessive of the catalyst did not lead to an obvious further increase in yield, indicating a nearly equilibrium yield was achieved.

**Table 1** Yield of biodiesel in different catalytic (0.5 g) at 343 K for 3.5 h

| The sample number | Component | Yield (%) |
|---|---|---|
| 1 | PSMIM | 70.2 |
| 2 | PSMIMHSO$_4$ | 73.1 |
| 3 | H$_2$SO$_4$ | 88.9 |
| 4 | H$_3$PW$_{12}$O$_{40}$·19H$_2$O | 89.1 |
| 5 | Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ | 92.9 |
| 6 | PSC | 94.3 |
| 7 | PSSC | 97.1 |
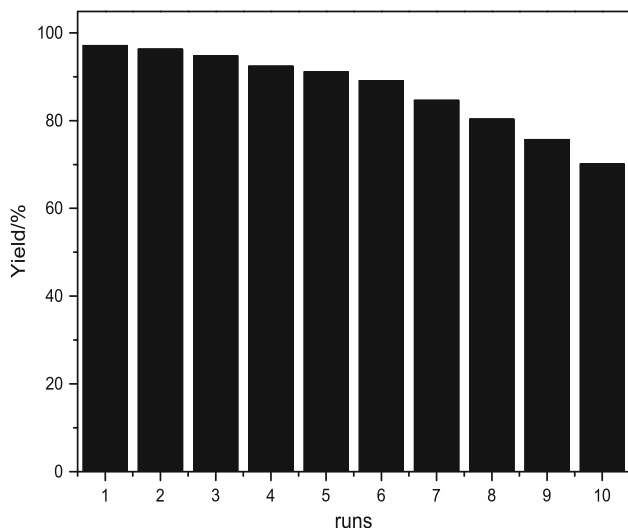


**Fig. 9** Catalyst reusability at 343 K for 3.5 h

products are carbonized partly during the process, which reduced the biodiesel quality.

Per equal catalyst weight, H$_3$PW$_{12}$O$_{40}$·19H$_2$O is almost as effective as H$_2$SO$_4$ [46] and the yield of H$_3$PW$_{12}$O$_{40}$·19H$_2$O is almost the same as H$_2$SO$_4$. H$_3$PW$_{12}$O$_{40}$·19H$_2$O is more active than H$_2$SO$_4$ in the reaction and exhibits the great advantage of these H$_3$PW$_{12}$O$_{40}$·19H$_2$O as catalyst compared to the traditional catalyst in view of corrosivity. However, H$_3$PW$_{12}$O$_{40}$·19H$_2$O is soluble in methanol and difficult to separate from water or methanol. Therefore, salts of alkaline cation Cs$^+$ for H$_3$PW$_{12}$O$_{40}$·19H$_2$O are introduced in the study. The salts with large monovalent ions exhibited an impressive performance that they revealed similar activities compared to the parent acid in acid-catalyzed reactions [47]. On the other hand, Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$, which are both BrÖnsted acid and Lewis acid, exhibits larger surface area and higher activity than H$_3$PW$_{12}$O$_{40}$·19H$_2$O [46], and the acid activity of Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ is about 15 times higher than H$_2$SO$_4$ [28]. That is, the yield of Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ is higher than H$_3$PW$_{12}$O$_{40}$·19H$_2$O and H$_2$SO$_4$.

Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ and ionic liquid are mixed to form new catalytic system to improve the yield. As a result, the yield has been obviously improved. Because ionic liquid has a high viscosity, it could disperse Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ uniformly so as to increase the contact area of Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$. In addition, the ionic liquid could dissolve the carbon deposition, which could probably cover the acid site of Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$. So it could be used as a phase transfer catalyst. Thus, the yield of mixed catalytic system is improved.

Catalyst reusability

Catalytic stability of Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$/PSMIMHSO$_4$, which is presented in Fig. 9, is evaluated by performing consecutive batch runs with the same catalyst sample, at same conditions. It is found that the yield of biodiesel kept unchanged, even slightly decreased with runs at the first five runs. This may be because the more acids of catalyst are formed under mechanical agitation, which increases the surface area of catalyst to enhance the catalytic property. However, the yield of biodiesel obviously decreased after the sixth run mainly due to the loss of acids in the process of taking sample or separating product. Nevertheless, about 70.1 % yield can still be obtained even when esterification reaction of the 10th run is finished. Therefore, the advantage of esterification using Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$/PSMIMHSO$_4$ as phase transfer catalyst is obvious.

**Conclusions**

In the present investigation, PSMIM, PSMIMHSO$_4$ and Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ were successfully prepared. Then two ionic liquids mixed with Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ were used as the phase transfer catalysts for biodiesel production. And those were characterization by NMR, IR, EA, XRD and HPLC. PSSC was used as a catalyst to test the optimum conditions, which was the mass ratio of 1:1(PSMIMHSO$_4$/Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$). The best reaction temperature was determined at 343 K, the best reaction time was 3.5 h, the optimum mass of catalyst was 0.5 g and the optimum amount of methanol was 60 g. Meanwhile, through the comparison for the catalytic activity of PSMIM, PSMIMHSO$_4$, H$_2$SO$_4$, H$_3$PW$_{12}$O$_{40}$·19H$_2$O and Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$, the acid activity of Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ was higher than others under the same conditions. After mixing, the yield was improved, so the acid activity of the mixed catalytic system was higher than any others. In addition, because of the presence of anionic group HSO$_4^-$, the acid activity of Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ mixed with PSMIMHSO$_4$ was higher than the acid activity of Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ mixed with PSMIM.

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