CHLORELLA BIODIESEL PREPARATION CATALYZED BY HETEROPOLYANION-BASED IONIC LIQUID

Lu Lin, Rui Wang*

*School of Environmental Science and Engineering, Shandong University, No. 27 Shanda South Road, Jinan 250100, P.R.China.*Email: ree_wong@hotmail.com*

Abstract

The reaction conditions of transesterification during *Chlorella* biodiesel preparation using three heteropolyanion-based ionic liquid $[Hmim]_4PMo_{11}VO_{40}$, $[Hmim]_5PMo_{10}V_2O_{40}$ and $[Hmim]_6PMo_9V_3O_{40}$ as catalysts were studied. The result showed that the best conditions of transesterification were as follows: the molar ratio of methanol to the microalgae oil was 9:1, the reaction time was 7h, the reaction temperature was 70°C and the dosage of the catalyst accounted for 7% of the mass of the microalgae lipid. Under this condition, the yield of biodiesel reached 69.4%, 72.2% and 75.0%, respectively. Among three catalysts, the ranking of catalytic efficiency was $[Hmim]_4PMo_{11}VO_{40} <$ $[Hmim]_5PMo_{10}V_2O_{40} < [Hmim]_6PMo_9V_3O_{40}$.

Key words: biodiesel; transesterification; algae.

1. Introduction

Biodiesel is the monoalkyl ester produced by transesterification reaction between long-chain fatty acids and alcohols with small molecular weight such as methanol and ethanol. Biodiesel can be used as a substitution of traditional petroleum. In addition, utilization of biodiesel can obviously improve air quality by reducing emission of CO_2 and SO_2.

At present, the transesterification methods can be divided into two categories -homogeneous and heterogeneous methods [1, 2]. Homogeneous method is more mature with its' high reaction efficiency, high yield and industrial application. However, strong acid and base catalysts have great corrosivity on equipment and hard to be separated from product. Heterogeneous catalytic method is very potential and promising due to many advantages compared to homogeneous catalytic method such as easy to be recovered, reusable and mild reaction condition [3]. However, heterogeneous method need more stirring to fulfill the sufficient contact between catalyst and stocks which may spend more energy and increase total cost.

Ionic liquid acid as a new kind of environmental friendly solvent and catalyst has both the high contact rate of homogeneous catalyst and the nonvolatility of heterogeneous catalyst. Products can be easily separated from reactants. Its structure and acid sites can be adjusted by adding or removing some acid structure. For these reasons, ionic liquid acid has the potential to substitute traditional catalysts and has drawn great attention of researchers [4, 5]. Wu [6] prepared five kinds of Brφnsted ionic liquid acid and used them into the production of cottonseed biodiesel. The results shows that under 170°C and reacted 5 hours, the conversion rate could reach 90.0%. Li [7] used $[Hmim]HSO_4$ as catalyst to prepare rapeseed biodiesel. Under 150°C and reacted 5 hours, he got the yield of 95%. These results demonstrate that ionic liquid acid can substitute the position of traditional acid catalyst. This article mainly analyze effects of different reaction conditions using hetero-polyanion-based ionic liquid to catalyze transesterification of algal biodiesel and hope to find more effective catalyst under moderate reaction conditions.

2. Materials and Methods

2.1 Materials

Chlorella powder with about 13% of lipid bought from Shandong Wuli Lvqi Biological Engineering Company; N-methyl imidazole (purity ≥ 98%) and concentrated sulfuric acid (AR) from Beijing Chemical Plant; Disodium phosphate, sodium methoxide, vanadium

pentoxide, petroleum ether (AR, boiling range: 60-90°C), methyl ether (AR) and n-hexane (AR) from Tianjin Fuyu Chemical co., Ltd; Absolute methanol bought from Tianjin Dengke Chemical Reagent co., Ltd; Methyl heptadecanoate internal standard and fatty acid methyl ester profiling mix bought from J&K Chemical.

2.2.Methods

2.2.1 Preparation of ionic liquid

Added 8.2g N-methyl imidazole (719 mL, 011 mmol) into a 250ml three-necked bottle with mechanical stirring. And then put this three-necked bottle into cold water to cool to 0~5°C. Added mixture of 10.2g 98% concentrated sulfuric acid and 10ml water within 30 minutes and kept stirring 2 hours under room temperature. Removed water by reduce pressure distillation under 75°C and got colorless and transparent ionic liquid [Hmim]HSO$_4$ 17.5g. The yield was 98.2% [9].

2.2.1 Preparation of heteropoly acids containing different amount of V and Mo

Preparation of H$_4$PMo$_{11}$VO$_{40}$

Dissolved 3.58g Na$_2$HPO$_4$·12H$_2$O into 50mL distilled water and 26.65g Na$_2$MoO$_4$·2H$_2$O into 60mL distilled water. Mixed these two solution and heated to boil to react for 30 minutes. Dissolved 0.91g V$_2$O$_5$ into 10mL Na$_2$CO$_3$ solution with the concentration of 1.0 mol/L, and put this solution into the former mixed solution under stirring to react 30 minutes under 90°C. Then stopped heating, added 1:1 H$_2$SO$_4$ into the solution till pH=2.0 and kept stirring to room temperature. Put 50mL diethyl ether into mixed solution and stirred. After that, added 1:1 H$_2$SO$_4$ and kept stirring to make this solution divided by 3 layers after completely static. The middle scarlet oily layer is heteropoly etherate. Took this layer and remove diethyl ether reduced pressure distillation. Added some distilled water and put it into vacuum drier to crystal completely appear. Then got product H$_4$PMo$_{11}$VO$_{40}$ by recrystallization.

Preparation of H$_5$PMo$_{10}$V$_2$O$_{40}$ and H$_6$PMo$_9$V$_3$O$_{40}$

The processing was like the preparation of H$_4$PMo$_{11}$VO$_{40}$ with the only difference of the amount of material. H$_5$PMo$_{10}$V$_2$O$_{40}$: 3.58g Na$_2$HPO$_4$·12H$_2$O, 24.20g Na$_2$MoO$_4$·2H$_2$O, 2.28g V$_2$O$_5$, which was that n$_p$: n$_{Mo}$: n$_v$=1:10:2.5; H$_6$PMo$_9$V$_3$O$_{40}$: 3.58g Na$_2$HPO$_4$·12H$_2$O, 21.80g Na$_2$MoO$_4$·2H$_2$O, 3.20g V$_2$O$_5$, which was that n$_p$: n$_{Mo}$: n$_v$=1:9:3.5. The bottom amaranth oily layer was heteropoly etherate. Took this layer and remove diethyl ether reduced pressure distillation. Added some distilled water and put it into vacuum drier to crystal completely appear. Then got products by recrystallization.

2.2.2 Preparation of heteropolyanion-based ionic liquid

Took some sample of the prepared ionic liquid and added three kinds of heteropoly acids respectively as the molar ratio of ionic liquid to heteropoly acid 4:1, 5:1 and 6:1. Using ethanol as solvent reacted for 20 hours under 70°C. When the product was completely static, two layers could be got. Took the bottom layer and dried in vacuum drier to get the final products.

2.2.3 Extraction of Chlorella lipid

Put 5g dry *Chlorella* powder into a conical flask containing a certain extraction agent and extracted lipid under ultrasonic condition. After extraction, centrifugalized for 10 minutes under condition of 3500r/min. Collected supernatant and separated by reduced pressure distillation. Dried to constant weight under 50°C

2.2.4 Preparation of biodiesel

Took 10g of *Chlorella* lipid into a 250ml round-bottom flask, added a certain amount of methanol and catalyst and reflux reacted under hydrothermal condition. Stopped heating and stirring after reaction several hours. Put mixture into a separating funnel and stratified statically. The bottom layer was ionic liquid layer and ionic liquid could be reused after separation; the upper layer was product layer and biodiesel could be separated after removing methanol, water and glycerinum by reduced pressure distillation. Biodiesel product was analyzed chromatographically then.

2.2.5 Analysis of product

Analyzed products using SP6800A gas chromatography by internal standard method [8]. Injected 1μL of biodiesel product into a 1ml volumetric flask, weighed the mass of the injected product and recorded it. Then diluted with n-hexane after adding 1mg internal standard. Sampled this solution 1μL with micro-syringe and analyzed with chromatography. Calculated conversion rate using the following formula:

$$Yield = \frac{Total\ peak\ area\ of\ FAME}{Peak\ area\ of\ internal\ standard} \times \frac{Mass\ of\ internal\ standard}{Mass\ of\ biodiesel\ product\ sample}$$

3. Results and discussion

3.1 Effect of molar ratio of methanol to lipid on biodiesel yield

This experiment studied the effect of molar ratio of methanol to lipid on biodiesel yield at the conditions of reaction time 7h, reaction temperature 70°C, and catalyst dosage 7%. The result shows that the biodiesel yield of three catalyst share the same trend that it rises as the ratio increases when this ratio is under 9:1. But after 9:1, the yield has a little decrease. (Fig 1.)

Low molar ratio of methanol to lipid may result in incomplete reaction and the equilibrium coefficient inclines left which leads to a corresponding low yield. But when it comes to 9:1 or higher ratio, no more contribution on the positive reaction will be found. At the same time, because too much methanol will dilute the concentration of catalyst, the yield of biodiesel declines instead [9].
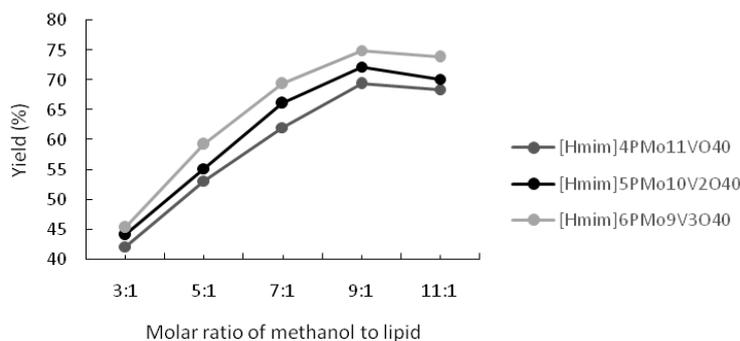

Fig 1. Effect of molar ratio on biodiesel yield

3.2. Effect of reaction time on biodiesel yield

This experiment studied the effect of reaction time on biodiesel yield under the condition of reaction temperature 70°C, catalyst dosage 7% and molar ratio of methanol to oil 9:1. Fig. 2 shows that biodiesel yield rises with the increase of reaction time and the speed gradually deceases after 6 hours. $[Hmim]_6PMo_9V_3O_{40}$ has the highest efficiency of 75% at 7 hours. At the beginning of reaction, there is little product in the system. Consequently, this reversible reaction inclines right till reaction equilibrium as more biodiesel is produced. But when it comes to reaction equilibrium, the increase of reaction time does no help to the right shift of this reaction. Therefore, the increasing rate gradually declines. Many side reactions and equipment cost will also be considered in this scenario.
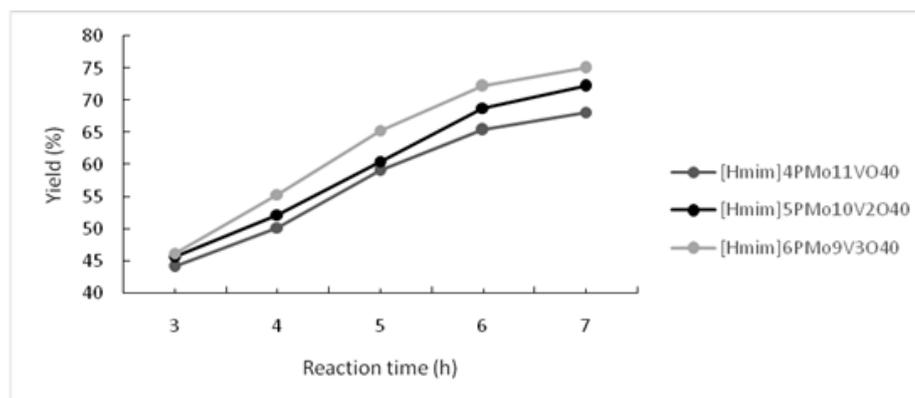

Fig 2. Effect of reaction time on biodiesel yield

3.3. Effect of reaction temperature on biodiesel yield

This experiment studied the effect of reaction temperature on biodiesel yield under the condition of reaction time 7h, catalyst dosage 7% and molar ratio of methanol to oil 9:1. Fig 3. demonstrates that the yield increases with the increase of reaction temperature and it reaches the highest 74.8% ($[Hmim]_6PMo_9V_3O_{40}$) at 70°C. However, higher temperature dose not contribute to the yield. Because the boiling point of methanol is just 64.7^{o}C, too high temperature will decrease the content of methanol in solution which means that there is too much gas phase methanol will not react will the lipid. This situation seems like low molar ratio of methanol to lipid which has been discussed before that will lead to a low efficiency.
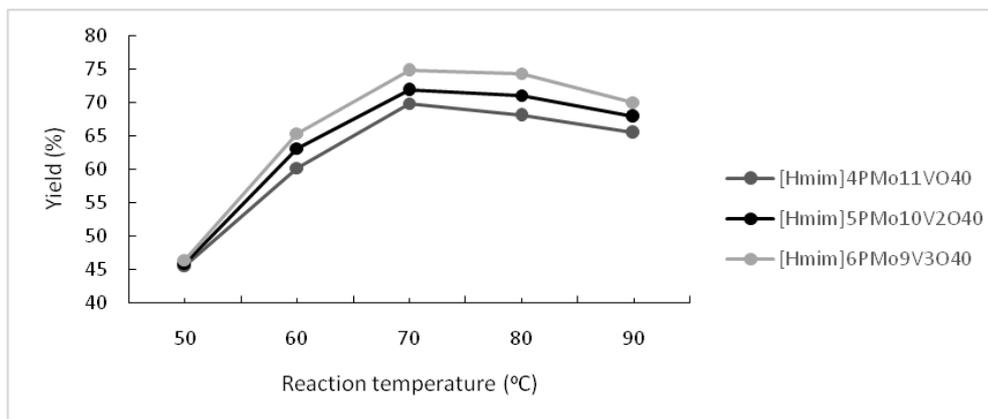

Fig 3. Effect of reaction temperature on biodiesel yield

3.4. Effect of catalyst dosage on biodiesel yield

This experiment studied the effect of catalyst dosage on biodiesel yield under the condition of reaction time 7h, reaction temperature 70°C and molar ratio of methanol to oil 9:1. Result shows that at first biodiesel yield rises as catalyst dosage increasing and then it has a little decrease when the dosage is bigger than 7%. Low content of catalyst means insufficient catalyst in reaction system. And with the increase of catalyst dosage, the need of catalyst will gradually be satisfied till 7%. After this threshold, more catalyst not only dose no help to the biodiesel yield, but also will bring more problems such as the product separation, cost and side effects. Therefore, based on the result of this experiment, the best catalyst dosage should be 7%.
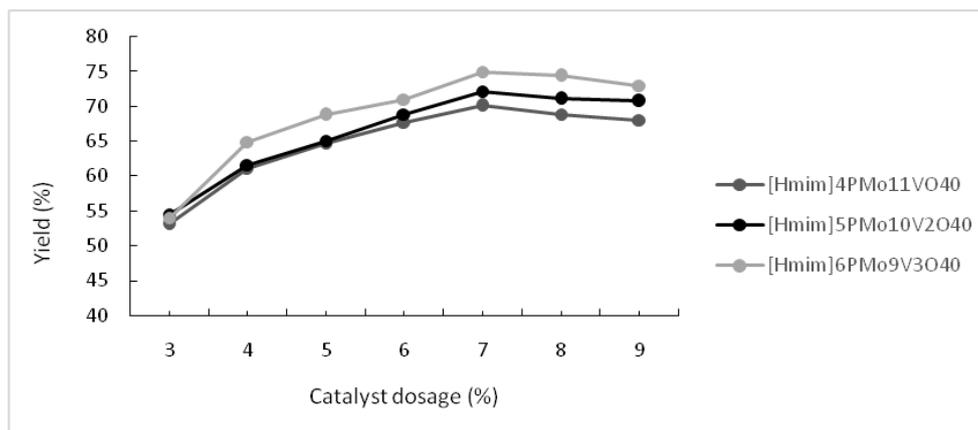

Fig 4. Effect of catalyst dosage on biodiesel yield

3.5. Comparison of three heteropolyanion-based ionic liquid

There is a common phenomenon that among three catalysts, $[Hmim]_6PMo_9V_3O_{40}$ has the highest catalytic efficiency at same reaction conditions compared to $[Hmim]_4PMo_{11}VO_{40}$ and $[Hmim]_5PMo_{10}V_2O_{40}$. This results may because the acidity of these three heteropoly anions is increasing as the molar number of vanadium increases. Therefore the catalytic efficiency of these three heteropolyanion-based ionic liquids increases as the molar number of vanadium increases. The other explanation is that because the molecule with higher molar mass will have a bigger size. Bigger size means the heteropolyanion-based anions

can provide more inner space for reactant which will lead to a higher contact rate of reactant. Therefore, higher efficiency will be observed of $[Hmim]_4PMo_{11}VO_{40.}$

Table 1. Comparison of three heteropolyanion-based ionic liquid

Catalyst	Yield
$[Hmim]_4PMo_{11}VO_{40}$	69.4%
$[Hmim]_5PMo_{10}V_2O_{40}$	72.2%
$[Hmim]_6PMo_9V_3O_{40}$	75.0%

4. Conclusions

In this research, three heteropolyanion-based ionic liquid were successfully prepared and used as catalysts to produce algal biodiesel. The suitable reaction conditions by transesterification reaction using $[Hmim]_4PMo_{11}VO_{40}$, $[Hmim]_5PMo_{10}V_2O_{40}$ and $[Hmim]_6PMo_9V_3O_{40}$ as catalyst were as follows: molar ratio of methanol to oil 9:1; reaction time 7h; reaction temperature 70°C; catalyst dosage 7%. Under these conditions, the biodiesel conversion rates were 69.4% 72.2% and 75.0%, respectively. These results were acceptable under low reaction temperature. Due to low content of lipid in the chosen *Chlorella* in this research, in the future, more research about improving lipid content of *Chlorella* should be done like transgenic technology or cultural condition optimization to increase conversion rate and lower cost.

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