Preparation of Biodiesel Based on Alkaline Ionic Liquid [Bmim]OH Catalyzed Castor Oil

Aihua Zhang¹³, Qin Wang¹², Yidan He¹³, Pengying Lai¹³, Yifu Miu¹ and Zhihong Xiao*¹

¹ Hunan Academy of Forestry, Changsha, Hunan, 410004, China
² Changsha University of Science and Technology, Changsha, Hunan, 410114, China
³ Central South University of Forestry and Technology, Changsha, Hunan, 410004, China

*Corresponding author’s e-mail: xzhh1015@163.com

Abstract. In this experiment, a new basic ionic liquid [Bmim]OH was synthesized from 1-methylimidazole and sodium hydroxide, which was used to catalyze the preparation of biodiesel from castor oil. The catalyst of [Bmim]OH was compared with KOH and tetrabutylammonium hydroxide during the study. The experimental results showed that the latter two were better than the latter two. The orthogonal experimental design scheme was used to optimize the process conditions. The optimized catalytic conditions of alkaline ionic liquid [Bmim]OH were as follows: the catalyst dosage was 1%, the molar ratio of alcohol to oil was 6:1, the reaction temperature was 40 °C, and the reaction time was 60min. Under the optimized conditions, the crude methyl ester mixture yield is higher than 97%, the castor oil is more than 95% converted to the product methyl ester, and the catalyst of [Bmim]OH is used for six times without significant consumption, and the catalytic performance is stable.

1. Introduction

Castor oil is one of the oils with a high single fatty acid content, mainly hydroxy oils. The main component of fatty acids is ricinoleic acid, which accounts for more than 85% of the total acid. There are also a small amount of palmitic acid, oleic acid, linoleic acid, linolenic acid and stearic acid. The unsaponifiable matter is mainly sterols [1]. Castor oil contains a large amount of hydroxyl groups, and its solubility is very different from other oils. It has poor solubility in hydroxy solvents, but castor oil can be mixed with anhydrous ethanol at any room temperature, and 1 volume of castor oil can be dissolved in 5 volumes of 95% ethanol. Castor oil has unique properties. It does not solidify at -18℃ and deteriorate at 500℃-600℃, and does not burn. The preparation of biodiesel from modified castor oil has great potential in China.

At present, the main production methods of biodiesel are direct mixing, microemulsification, pyrolysis and transesterification[2]. Compared with other methods, transesterification has the advantages of mature technology, low cost and stable product properties, and has become the main method of biodiesel production. According to the type of catalyst used or whether catalyst is used, transesterification can be divided into chemical transesterification, enzymatic transesterification and supercritical fluid method [3]. Supercritical fluid method requires high molar ratio of alcohol to oil and reaction temperature as high as 350℃. The reaction conditions are relatively harsh, and it is difficult to achieve large-scale industrial applications [4]. Biodiesel prepared by enzymatic has the advantages
of mild reaction conditions, low alcohol consumption, easy collection of products and low environmental pollution. However, it is still in the stage of technological exploration. There is no report on the production practice of biodiesel prepared by enzymatic method. Moreover, the cost of lipase is too high and it is easy to deactivate. The by-product glycerol produced during the reaction is easy to adhere to the lipase surface, which makes the reaction difficult. The development of enzymatic transesterification of biodiesel was limited [5]. Chemical transesterification is the main method of biodiesel production because of its mature technology and low cost. However, both homogeneous and heterogeneous catalysts have their shortcomings, such as the catalyst can’t be recycled or the post-treatment method is more complex during in the chemical transesterification.

Ionic liquid catalysts have a series of excellent properties, such as low vapor pressure, wide liquid temperature range, good compatibility with reactants, easy operation and treatment, recyclable use, designable molecules, acid-base catalysis and phase transfer catalysis. In many catalytic reactions, ionic liquids have shown high activity and selectivity. In the field of catalysis and organic synthesis, acidic ionic liquid catalysis has been playing a very important role [6-9].

Inspired by literature [10-13], this study attempted to prepare biodiesel from castor oil catalyzed by basic ionic liquid of [Bmim]OH, studied and optimized the catalytic process conditions and catalyst stability, which laid a foundation for industrial application of the catalytic system.

2. Materials and methods

2.1. Experimental materials

Methanol (AR, Tianjin Kemiou Chemical Reagent Co., Ltd.); NaOH(AR, Tianjin Fengchuan Chemical Reagent Co., Ltd.); KOH(AR, Tianjin Fengchuan Chemical Reagent Co., Ltd.); NaCl(AR, Tianjin Kemiou Chemical Reagent Co., Ltd.); 1-Methylimidazole (AR, Sinopharm Chemical Reagent Co., Ltd.); Acetonitrile (AR, Tianjin Fengchuan Chemical Reagent Co., Ltd.); Ethyl acetate (AR, Sinopharm Chemical Reagent Co., Ltd); Castor oil (CP, made by Hunan Academy of Forestry); n-butyl bromide (AR, Sinopharm Chemical Reagent Co., Ltd)

2.2. Experimental Methods

2.2.1. Synthesis of [Bmim] OH. 1-Methylimidazole 16.2g was added to a 250mL flask with thermometer and magnet. The flask was slowly filled with nitrogen, heated to 70℃, slowly added 27.4g of equal molar n-butyl bromide, and the pale yellow bromide [Bmim]Br was obtained after 4h of dropping reaction. [Bmim]Br 0.05mol was dissolved in 50mL dry acetonitrile, placed in 250mL round bottom flask, heated to 25℃, added KOH 0.06mol, reacted for 12h, stopped stirring, filtered the reaction materials, removed KBr, rotated evaporation to remove the solvent in the filtrate, and obtained crude ionic liquid [Bmim]OH. The crude ionic liquids were washed three times with ethyl acetate, and then dried in vacuum for 24 hours and obtained a yellowish transparent viscous liquid [Bmim]OH. The chemical reaction formulas are as follows:

Figure 1. Catalyst synthesis Roadmap

2.2.2. Transesterification reaction. Take a certain amount of castor oil and dry it for 2 hours in a rotary evaporator at 140 ℃ and 0.095mpa. Accurately weigh 200g of dried castor oil, put it into a 500ml three port flask, preheat to a certain temperature, and add alkaline ionic liquid and methanol into the three port flask together. After the reaction for a period of time, it is transferred to the
separation funnel for standing and layering. The catalyst phase at the lowest layer is recycled and the glycerine phase is separated. The methyl ester at the upper layer is first distilled under normal pressure, and the excess methanol is recovered, and then washed twice with 10% brine to remove the soap salt. The refined biodiesel was obtained by vacuum distillation at 198°C and 5pa.

3. Results and analysis

3.1. Physical and chemical constants of castor oil.

Table 1 lists the physical and chemical parameters of castor oil. It can be seen that castor oil is an excellent raw material for preparing biodiesel.

| Analysis item | Acid value / (mg·g⁻¹) | Viscosity (40°C)/(mm²·s⁻¹) | Saponification value / (mg·g⁻¹) | Iodine value / g/100g | Refractive index (n²₀) |
|---------------|------------------------|----------------------------|---------------------------------|-----------------------|-----------------------|
| Index         | 1                      | ≥14                        | 176~180                         | 82~86                 | 1.477~1.481          |

| Analysis item | Ricinol acid /%(w) | Oleic acid /%(w) | Molar mass / g/mol | Relative density / (g/cm³) | Ignition point / °C |
|---------------|--------------------|------------------|-------------------|-----------------------------|---------------------|
| Index         | 82~88              | 4~7              | 961.7             | 0.956                       | 322                 |

3.2. Catalyst selection.

The catalytic performance of different kinds of catalysts for the preparation of biodiesel was investigated. The experimental conditions were as follows: the amount of catalyst was 1% of castor oil mass, the alcohol oil ratio was 6:1, the reaction temperature was 40 °C, and the reaction time was 50 minutes.

Table 2. Comparison of catalysis with different catalyzers

| Type of catalyst | Productivity % |
|------------------|---------------|
| KOH              | 92.8          |
| TBAH             | 78.1          |
| [Bmim]OH         | 94.4          |

TBAH can be seen from table 2 that the catalytic performance is poor, and the post-treatment of the product is complex; KOH has good catalytic performance, but it can not be reused after the reaction, and a large number of waste alkali liquor is produced, causing serious environmental pollution. The catalytic performance of [bmim] Oh is good, almost no consumption in the reaction, and the catalytic performance is stable.

3.3. Optimization of synthesis conditions.

In the preparation of biodiesel from castor oil catalyzed by [Bmim]OH, four factors and three levels of orthogonal test were used to optimize the molar ratio of alcohol to oil, the amount of catalyst, the reaction temperature and the reaction time. The level of selected factors is shown in Table 3, and the results of orthogonal test are shown in Table 4.

Table 3. Factors and levels of orthogonal experiment

| Level | Factor | Catalyst dosage /% | Alcohol oil ratio | Reaction temperature / °C | Reaction time /min |
|-------|--------|--------------------|-------------------|---------------------------|------------------|
| A     |        |                    |                   |                           |                  |
| 1     | 0.9    | 5:1                | 30                | 40                        |
| 2     | 1.0    | 6:1                | 40                | 50                        |
| 3     | 1.1    | 7:1                | 50                | 60                        |

Table 4. The results of orthogonal test

| Type of catalyst | Productivity % |
|------------------|---------------|
| KOH              | 92.8          |
| TBAH             | 78.1          |
| [Bmim]OH         | 94.4          |
Table 4. Results of orthogonal experiment

| Number | 1   | 2   | 3   | 4   | Conversion rate % |
|-------|-----|-----|-----|-----|------------------|
| 1     | 1   | 1   | 1   | 1   | 77.51            |
| 2     | 1   | 2   | 2   | 2   | 87.72            |
| 3     | 1   | 3   | 3   | 3   | 85.67            |
| 4     | 2   | 1   | 2   | 3   | 91.06            |
| 5     | 2   | 2   | 3   | 1   | 96.42            |
| 6     | 2   | 3   | 1   | 2   | 92.37            |
| 7     | 3   | 1   | 3   | 2   | 81.03            |
| 8     | 3   | 2   | 1   | 3   | 94.09            |
| 9     | 3   | 3   | 2   | 1   | 86.10            |

\[
\begin{align*}
K_1 & = 250.9 \quad 249.6 \quad 263.97 \quad 260.03 \quad \text{Sum}=791.97 \\
K_2 & = 279.85 \quad 278.23 \quad 264.88 \quad 261.12 \\
K_3 & = 261.22 \quad 264.14 \quad 263.12 \quad 270.82 \quad \text{Average}=88.0 \\
R & = 28.95 \quad 28.63 \quad 1.76 \quad 10.79
\end{align*}
\]

At the level of orthogonal test, the transesterification can be carried out well, and the static mixture has obvious stratification. Theoretically, the mass of methyl ester and glycerin from 200 g castor oil is about 200.9 g and 20.7 g respectively. The highest conversion of the product was 96.42%, which indicated that the transesterification reaction was basically complete under suitable reaction conditions.

According to table 4, the conversion rate of A2 Level transesterification is the highest, and the amount of catalyst is 1.0% of the oil weight. It is found in the experiment that excessive amount of catalyst will aggravate product saponification and make post-treatment difficult. The conversion rate of B2 level transesterification is the highest. From the trend of 1-3 level, it can be seen that the optimal amount of alcohol oil mole ratio is 6:1. The conversion rate of C2 level transesterification is C factor. The highest, but from the 1-3 level trend, there is little difference.

There is an optimal reaction temperature for transesterification. Low temperature will slow down the reaction and reduce the conversion rate. Too high temperature will accelerate the volatilization of methanol and reduce the volume concentration of methanol in the liquid phase, which will also reduce the conversion rate. Therefore, in the actual operation process, the lower reaction temperature can be selected, which will not affect the reaction speed too much, but also effectively avoid the reduction of conversion rate caused by methanol volatilization and reduce energy consumption; among the D factors, the conversion rate of D3 level transesterification reaction is the highest, but the difference is slightly larger than that of C factor from the perspective of 1-3 level trend. It can be seen that in a certain period of time, with the reverse reaction, the With the increase of reaction time, the conversion of biodiesel increased obviously. This is because in the initial stage of the reaction, the reaction has not reached equilibrium. Increasing the reaction time can make the reaction reach equilibrium, thus increasing the conversion of biodiesel.

The range is \(R_A > R_B > R_D > R_C\). From the data in Table 4, it can be concluded that the values of \(R_C\) and \(R_D\) are far less than \(R_A\) and \(R_B\), indicating that the amount of catalyst and molar ratio of alcohol to oil have a significant impact on the conversion rate. Therefore, \(A_2B_2C_2D_3\) is the best experimental condition for the preparation of biodiesel by catalytic castor oil, that is, the amount of catalyst is 1%, the molar ratio of alcohol to oil is 6:1, the reaction temperature is 40℃, and the reaction time is 60 minutes.

3.4. Stability of [Bmim]OH.

Ionic liquid is a new type of catalyst. The separation of product and ionic liquid can be realized by simple phase separation. The separated ionic liquid can be reused after simple treatment. The stability of ionic liquid catalyst was investigated under the optimized conditions. The results are shown in
Fig.2.

![Conversion rate vs Frequency of use](image)

**Figure 2. Stability of the ionic liquid**

It can be seen from Figure 2 that [Bmim]OH can be stably recycled for more than six times. In the figure, after the second reaction, the product is stratified. The lower [Bmim]OH is directly used for the third reaction without any treatment, and the other several reaction catalysts are recycled for the next experiment. It can be seen that, except for the third cycle, the conversion rate of the product biodiesel slightly decreased, the catalyst activity of the other cycles basically did not change, indicating that [bmim] Oh catalyst has good stability.

### 3.5. Analysis of physical and chemical constants of biodiesel

| Item                          | Analysis method | Product sample | ASTM 6751-03 | 0# diesel standard |
|-------------------------------|-----------------|----------------|--------------|--------------------|
| Acid value /(mg.g⁻¹)          | GB/T 5530-2005  | 0.4052         | ≤0.8         | -                  |
| Closed flash point /°C        | GB 267-88       | 179            | ≥130         | ≥55                |
| Density (20°C)/ (g.cm⁻³)      | GB/T 2540-1981  | 0.938          | 0.875~0.90   | 0.820~0.860        |
| Kinematic viscosity (40°C)/(mm².s⁻¹) | GB/T 265-1988 | 15.1           | 1.9~6.0      | 2.0~4.5(20°C)      |
| Calorific value /(KJ/g)       | GB/T 384-1981   | 40.1           | -            | -                  |
| Water content /%(w)           | GB/T 260-1977   | Trace          | ≤0.05        | Trace              |
| Ash content /%(w)             | GB/T 508-1965   | 0.005          | ≤0.02        | -                  |
| Freezing point /°C            | GB/T 510-83     | -19.2          | -            | 0                  |
| Pour point /°C                | GB/T 3535-83    | -23.1          | -            | -2                 |
| Cloud point /°C               | GB/T 6986-86    | -14.6          | -            | 7                  |

It can be seen from table 5 that this experimental product basically meets the American ASTM 6751-03a biodiesel standard, some of which meet the 0# diesel quality index of China, but the kinematic viscosity of castor oil methyl ester exceeds the standard, which may be caused by the following two aspects: first, the average carbon chain length of the biodiesel molecule is longer than that of the mineral diesel molecule; second, the castor oil methyl ester contains hydroxyl group, which can produce molecules The hydrogen bond between. Therefore, diluents, such as ethanol and petrochemical diesel oil, need to be added in use.

### 4. Conclusion and discussion

In this study, castor oil is used as raw material and [bmim] Oh is used as catalyst to prepare biodiesel. The optimum process conditions are as follows: the amount of catalyst is 1% of the quality of raw oil, the molar ratio of alcohol to oil is 6:1, the reaction temperature is 40°C, the reaction time is 50min, and the conversion rate is over 95%.
Acknowledgments
The author is grateful to the Hunan Provincial Natural Science Foundation (2018JJ2218), the introduction of foreign intellectual special projects in Hunan Province (2019YZ3026), the Changsha, Zhuzhou and Xiangtan National Independent Innovation Demonstration Project (2018XK2005) and the Hunan Provincial Key Laboratory (2018TP1029).

References
[1] Xuebing Xu. Oil chemistry [M]. Bei Jing: China Commercial Publishing House, 1993: 326–327.
[2] Yiping Wang, Yi Zhai, Jinli Zhang, et al. Research Progress of Biodiesel Preparation [J]. Chemical industry and engineering progress, 2003, 22(8–12).
[3] Helin Wang, Wudi Zhang, Shiqing Liu, et al. Study on production of biodiesel from castor oil [J]. Energy engineering, 2007, 3 (24–26).
[4] Freedman B, Butterfield R O, Pryde E H. Transesterification Kinetics of Soybean Oil. J Am Oil Chem Soc, 1986, 63(10): 1375–1380.
[5] Boocock D G B, Konar S K, Mao V, et al. Fast One Phase Oil Rich Processes for the Preparation of Vegetable Oil Methyl Esters. Bioresour Technol, 1996, 11(1): 43–50.
[6] Ruxiong Li, Jianji Wang. Synthesis and application of ionic liquid. Chemical reagents, 2001, 23(4): 211–215.
[7] Zhao H. Current Studies on Some Physical Properties of Ionic Liquids. Physics and Chemistry of Liquids, 2003, 41(6): 545–557.
[8] Cloe A C, Jensen J L, et al. Novel Brønsted Acidic Ionic Liquids and Their Use as Dual Solvent-Catalysts. J Am Chem Soc, 2002, 124(21): 5962–5963.
[9] Yoshizawa M, Hirao M, Ito-Akita K, et al. Ion Conduction in Zwitterionic-Type Molten Salts and Their Polymers. J Mater Chem, 2001, 11(4): 1057–1062.
[10] Branco L C, Rosa J N, Moura Ramos J J, et al. Preparation and Characterization of New Room Temperature Ionic Liquids. Chem Eur J, 2002, 8(16): 3671–3677.
[11] Zhu Huaping, Yang Fan, He Mingyuan. Brønsted Acidic Ionic Liquid 1-Methylimidazolium Tetrafluoroborate: A Green Catalyst and Recyclable Medium for Esterification. Green Chem, 2003, 5(1): 38–39.
[12] Pernak J, Czepukowicz A. New Ionic Liquid and Their Antielectrostatic Properties. Ind Eng Chem Res, 2001, 40(11): 2379–2383.
[13] Atef A, Jean P B. Efficient Combination of Recycle Task Specific Ionic and Microwave Dielectric Heating for the Synthesis of Lipophilic Esters. Org Process Res Dev, 2005, 9(4): 743–748.