Synthesis of Biodiesel Catalyzed by Phosphotungstic Acid Supported on Silica

Hongxiong Yang¹, Junshu Chen²*

¹School of Management, Tianjin University of Technology, Tianjin, China
²School of Management, Tianjin University of Technology, Tianjin, China

Abstract: Using tetraethyl orthosilicate as silicon source, silica supported phosphotungstic acid catalyst was prepared by sol-gel method, and then biodiesel was synthesized from vegetable oil and methanol with self-made solid acid as catalyst. Through the temperature, time, dosage, use times and other factors. The optimal conditions for conversion were found to be 40% phosphotungstic acid loading, 6:1 ratio of alcohol to oil, the catalyst dosage is 10% of the rapeseed oil mass, and the reaction temperature was set at 68°C and the reaction time was 2.5h. Under these conditions, the conversion rate of biodiesel can reach 96.0%.

1. Introduction
Due to the global depletion of traditional mineral energy sources such as petroleum and the deterioration of the environment caused by burning mineral fuels, people are forced to develop alternative petrochemical diesel fuels. Biodiesel is a high-quality petrochemical diesel substitute that can be biodegraded, non-toxic and not harmful to the environment [1]. At present, the production methods of biodiesel mainly include chemical methods, biological enzyme methods, supercritical methanol methods, etc. [2]. Phosphotungstic acid is a type of oxygen-containing polyacid composed of oxygen atom coordination bridges, but pure phosphotungstic acid the specific surface area is small, and it is easily soluble in polar solvents, so its application in catalytic applications is limited. In this paper, silica is used as a carrier to fix the phosphotungstic acid load, and the silica-supported phosphotungstic acid catalyst is used for the catalytic synthesis of biodiesel.

2. Experimental materials and methods

2.1. Main materials
Edible rapeseed oil (Yihai Kerry Group), methanol (Beilian Fine Chemical Co., Ltd.), phosphotungstic acid (H₃PW₁₂O₄₀) and ethyl orthosilicate (TEOS), ethanol, hydrochloric acid, methyl oleate, linole Methyl acid ester, chromatographically pure. The other reagents are of analytical grade. NewClassic electronic balance, RE-52 rotary evaporator, DF-101S constant temperature magnetic stirrer, DZF-6020 vacuum drying oven, GC-2010 gas chromatograph, GCsolution chromatographic workstation, FID detector and RTX WAX capillary column.

2.2. Experimental method

2.2.1. Preparation of silica-supported phosphotungstic acid catalyst
Accurately weigh 2.0 g of phosphotungstic acid, dissolve it in a 100 mL beaker containing 5 mL of distilled water, add a certain amount of ethyl orthosilicate, and add 10 mL of ethanol, slowly drop 5 mL of 1 mol/L hydrochloric acid for acidification, and then leave it to soak adsorption for 5h to form a transparent sol. Place the sol in an oven and dry at 120 ° C for 10 hours. Grind the sample to obtain a light yellow or white powder, which is a solid-supported phosphotungstic acid catalyst, marked as HPW / SiO₂, to be used [3].

2.2.2. Synthesis of biodiesel
Put a certain proportion of methanol and rapeseed oil in a 100mL three-necked flask with a thermometer and a condenser tube. After preheating to the required reaction temperature, add the prepared catalyst and heat in a constant temperature oil bath. Remove the reflux condenser, install a distillation device, and pour the filtrate into a separatory funnel. Rinse the inner wall of the flask with a small amount of deionized water. The washing liquid is incorporated into the separatory funnel, shaken and washed, and stand to be separated. The water layer is separated. After repeated washing, the lower layer of waste liquid is discharged, and the upper layer is distilled under reduced pressure to obtain a biodiesel product [4].

2.2.3. Product analysis
Determine the content of fatty acid methyl esters in biodiesel products by gas chromatograph, and calculate conversion rate of biodiesel [5]. The conversion rate is shown in formula (1).

\[
\text{Conversion rates} = \frac{\sum CV}{M \times 100} \times 100\%
\]  

3. Results and discussion

3.1. Single factor experiment
Rapeseed oil 20mL, under the conditions of catalyst dosage 10% (based on rapeseed oil mass), alcohol-oil molar ratio 6: 1, reaction temperature 65 °C, reaction time 2h, load phosphotungstic acid and alcohol oil molar, the amount of catalyst, time, temperature as single factor variables, to investigate its impact on the conversion rate l.

3.1.1. Effect of Loading Amount on Conversion
The mass ratio of alcohol oil is also one of the important numbers that affect the transesterification reaction, and the mass ratio of alcohol oil is also one of the important parameters affecting the transesterification reaction.

Known from Figure 1: when the loading of phosphotungstic acid is 10% to 20%, conversion rate of biodiesel is low; while the loading of phosphotungstic acid is 20% to 40%, the conversion rate increases significantly. Loading of phosphotungstic acid is 40%, the conversion rate is the highest. On the basis of 40%, the loading of phosphotungstic acid continues to increase, but rate decreases. Therefore, be sure that the loading of phosphotungstic acid is 40%.
3.1.2. Effect of molar ratio on conversion

In the preparation of supported catalysts, the dispersion effect of the active component on the support is the first factor to be considered.

![Figure 2: Effect of molar ratio on conversion](image)

Known from Figure 2: the ratio of alcohol to oil is 3: 1 to 7: 1, conversion rate of biodiesel is increasing. When it is increased to 8: 1, rate is mainly reduced due to the dilution effect of methanol, and as the ratio increases, conversion rate gradually decreases. When ratio is 7: 1, the conversion rate reaches 95.3%, at 6: 1, the conversion rate is 94.09%. Considering the subsequent recovery load of methanol, energy consumption and economic cost, choose a molar ratio is 6: 1.

3.1.3. Effect of Catalyst Amount on Conversion

The more times a catalyst is reused, the lower the industrial cost. Ashless filter paper was used for the recovery of catalyst. When the methanol was dried, the catalyst was directly put into repeated use. The catalytic effect of transesterification was investigated and compared with the blank test without catalyst. The effect of catalyst amount on the reaction,

![Figure 3: Effect of Catalyst Amount on Conversion](image)

From Figure 3: when the amount of catalyst is small, the reaction cannot proceed sufficiently, and the conversion rate of biodiesel is low. As the amount of use increases, the probability of contact between the catalyst and the substrate increases. When the amount of catalyst exceeds 10%, the conversion rate tends to be gentle. Comprehensive consideration, the catalyst dosage of 10% is the best.

3.1.4. Effect of reaction time on conversion

Effect of reaction time on conversion of biodiesel in different Effects of Time on Biodiesel Conversion by Observation Reaction.
3.1.5. Effect of temperature on conversion
The effect of different calcination temperature on the yield of the catalyst was investigated.

In Figure 5: between 40 °C and 65 °C, the conversion rate quickly increases conversion reached 95.64% at 65 °C. The temperature increase will lead to methanol volatilization and product color changes, affecting conversion efficiency [6]. Transesterification can avoid the yield reduction and energy consumption due to alcohol volatilization. Combined with the experimental results to determine the reaction temperature is 65 °C, the best conversion effect.

3.2. Compare with each other
To optimize the biodiesel synthesis conditions, select the biodiesel conversion rate index, the fixed phosphotungstic acid loading is 40%, mole ratio (W), amount of catalyst (X), reaction temperature (Y) and reaction time (Z) were used as the indexes, and orthogonal experiments were carried out. please see table 1.

| Experiment number | W | X/% | Y/°C | Z/h | Conversion rates /% |
|-------------------|---|-----|------|-----|---------------------|
| 1                 | 5 : 1 | 9  | 62   | 1.5 | 75.5                |
| 2                 | 5 : 1 | 10 | 65   | 2.0 | 83.2                |
| 3                 | 5 : 1 | 11 | 68   | 2.5 | 88.5                |
| 4                 | 6 : 1 | 9  | 65   | 2.5 | 93.0                |
| 5                 | 6 : 1 | 10 | 68   | 1.5 | 94.7                |
| 6                 | 6 : 1 | 11 | 62   | 2.0 | 87.3                |
| 7                 | 7 : 1 | 9  | 68   | 2.0 | 91.4                |
| 8                 | 7 : 1 | 10 | 62   | 2.5 | 85.0                |
| K1                |     |    |      |     | 82.4 86.6 82.6 83.9 |
From Table 1: the amount of catalyst had the least effect on the conversion rate, followed by the reaction temperature and time. Under the optimal process conditions, 5 verification experiments were conducted, and the conversion rates of biodiesel were 95.7%, 96.6%, 96.5%, 95.1% and 96.3%, the average conversion rate is 96.0%. The results of many experiments show that the process conditions of W2 X2 Y3 Z3 are high, and the conversion rate is maintained at 96%.

3.3. Effect of Catalyst Times on Conversion

After the catalyst is separated by suction filtration without any treatment, the next synthesis reaction is directly carried out[7]. Under the optimal process conditions, to observe the effect of the number of catalyst used on the conversion rate.

Known from Figure 6: the catalyst activity has decreased, but the overall stability is better and still has a higher activity. After 5 repeated uses, the conversion rate of biodiesel is still above 85%. As catalyst cycles increases, Conversion can go down. The possible main reason is that the catalyst has some parts at any time in multiple experiments. In addition, glycerol is produced during the entire reaction process, and the adsorption of glycerol is relatively strong, limiting the substrate and contact of the active center of the catalyst causes the conversion rate to gradually decrease.

4. Conclusion

Using phosphotungstic acid and ethyl orthosilicate as raw materials, a silica-supported phosphotungstic acid catalyst was prepared, and the prepared solid acid was used as a catalyst, and vegetable oil and methanol as feedstocks to prepare biodiesel. Loading of phosphotungstic acid was 40%. The catalyst dosage is 10% by mass of vegetable oil, the molar ratio is 6: 1, time is 2.5h, and temperature is 68 °C. Conversion rate of biodiesel can reach 96.0%. The catalyst can be used repeatedly after 5 times. The conversion rate is still above 85%, and it has good reuse performance. After being loaded with phosphotungstic acid, it not only has many advantages inherent in the original catalyst, but also improves the specific surface area and catalytic performance, overcomes the problems of corrosion and pollution of the homogeneous acid catalytic reaction, and is easy to recover and continuous production, to improving the product Quality and lower production costs.

References

[1] Nabel A. Negm, Mohamed A. Betiha, Mosaed S. Alhumaimess, Hassan M.A. Hassan, Abdelrahman M. Rabie. (2019) Clean transesterification process for biodiesel production using heterogeneous polymer-heteropoly acid nanocatalyst. Journal of Cleaner Production.,238:1642-1658.

[2] Dolores M. Morales, Romina A. Frenzel, Gustavo P. Romanelli, Luis R. Pizzio. (2020) Synthesis and characterization of nanoparticulate silica with organized multimodal porous structure impregnated with 12-phosphotungstic acid for its use in heterogeneous catalysis. Molecular
Catalysis., 481: 1862-1871.

[3] Shi Gaofeng, Miao Changlin, Xia Jun, etc. (2010) Microwave irradiation of ethyl orthosilicate supported phosphotungstic acid catalyzed synthesis of tributyl citrate. Engineering Plastics Application., 38: 15-17.

[4] Miao Changlin, Fan Pei, Lu Pengmei, etc. (2018) Sulfonic ionic liquid synthesis and catalytic preparation of biodiesel technology. Journal of Solar Energy., 39: 1861-1867.

[5] Yousra S. Kareem, Saad H. Ammar, Ruaa A. Darwash. (2020) Microwave-induced catalytic oxidative desulfurization of gasoil fraction over phosphotungstic acid-based magnetic silica (Ni@SiO 2 \ PWA) nanocatalyst. Catalysis Communications., 136: 483-488.

[6] S. Yuzbashi, M. H. Mousazadeh, N. Ramezani, H. Sid Kalal, B. Sabour. (2020) Mesoporous zirconium–silica nanocomposite modified with heteropoly tungstophosphoric acid catalyst for ultra deep oxidative desulfurization. Applied Organometallic Chemistry., 34: 4090-4095.

[7] Nanotechnology - Nanocatalysts. (2020) Researchers from Al Nahrain University Report on Findings in Nanocatalysts. Technology News Focus., 202: 3824-3836.