Preparation of Biodiesel through Transesterification of Animal Oil and Alcohol Under the Catalysis of $\text{SO}_4^{2-} / \text{TiO}_2$

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Abstract: Biodiesel was obtained through transesterification of animal oil and ethanol under the catalysis of $\text{SO}_4^{2-} / \text{TiO}_2$. We have inspected the activation of $\text{SO}_4^{2-} / \text{TiO}_2$ prepared under different dipping vitriol concentration, baking activation temperature. The optimum conditions to prepare $\text{SO}_4^{2-} / \text{TiO}_2$ are; dipping vitriol concentration of TiCl_4 hydrolysis product is 1.5 mol / L, baking activation temperature for this catalyst takes 500°C. It can guarantee the catalyst has a smaller size and a higher load of vitriol. With animal oil as raw materials, ethanol as transesterifying agent and $\text{SO}_4^{2-} / \text{TiO}_2$ as catalyst, the influence of reaction time, mass ratio of ethanol to oil and the dosage of catalyst were investigated. Optimum condition to obtain biodiesel was studied through orthogonal experiment, and it is listed as follow: mass ratio of ethanol to oil is 1.5:1.0, dosage of catalyst is 30 g $\text{SO}_4^{2-} / \text{TiO}_2$ versus per 100 g animal oil, and reaction time is 8.0 h when reaction temperature is controlled as 80°C. The yield of biodiesel is 0.796 g/g under the above condition. $\text{SO}_4^{2-} / \text{TiO}_2$ can be used as an effective catalyst during transesterification of animal oil and ethanol, and it can be reused.

Keywords: Solid acid catalyst $\text{SO}_4^{2-} / \text{TiO}_2$, Biodiesel, Animal oil, Transesterification

Introduction

Fossil diesel is a kind of non-reproducible energy resources and it will be exhausted some day¹. Thus, looking for a substitute for diesel (biodiesel) is a compulsory task for human. Biodiesel is derived from the oils and fats of plants and animals, is becoming popular.

The main advantages to utilize biodiesel are its renewability, better quality of exhaust gas emissions, its biodegradability, given all organic carbon is photosynthetic in origin, it does not contribute to a net rise in the level of carbon dioxide in the atmosphere, and to the greenhouse effect.

The most common way to produce biodiesel is transesterification of waste oil with alcohol². The reaction can be alkali catalyzed, acid catalyzed or enzyme catalyzed and chemically catalyzed processes have proved to be more practical because of the short reaction times and low cost compared with enzyme catalyzed³. An alkali catalyzed process can achieve high purity and yield of biodiesel product in a short time⁴⁻⁶. However, it is very sensitive to the purity of the reactants. Only well refined vegetable oil with less than 0.5 wt% free fatty acid and can be used as the reactant in this process. The high cost of raw material is the major obstacle to its commercialization. When waste oil with higher content of fat acid is used, an acid catalyzed process is preferred⁷⁻⁹. But it requires high cost stainless steel equipment when the reaction is catalysed with homogeneous vitriol, and the catalyst can not be recycled.

TiO₂ is widely used as catalyst, but when it is modified by vitriol, the product of SO₄²⁻/TiO₂ often possesses super acidity. It has been used as solid acid catalyst in the preparation of linoleic acid¹⁰, cycloketals¹¹ and ester reaction¹² for its excellent characteristics such as high activities, easy separability and renewability and recycles.

In this paper, SO₄²⁻/TiO₂ is prepared through two phase precipitation, physical dipping, activation under higher temperature, and the reaction condition is optimized. With animal oil as raw materials, ethanol as transesterifying agent and SO₄²⁻/TiO₂ as catalyst, biodiesel is prepared through transesterification, and the optimum condition is studied.

Experimental

Instruments and reagents

Y-4Q XRD diffractometer (Dandong, China) and EDS (Thermo NORAN Vantage DIS. Titanium(IV) chloride, H₂SO₄ (96%), ethanol, ammonia (25%-28%) are all analytical reagents. Animal oil is fat melts of pig.

Preparation of SO₄²⁻/TiO₂

30.0 mL TiCl₄ was dropped slowly into a 600 mL distilled water with stirring and then 14% NH₃·H₂O was dropped slowly with stirring. pH of this mixed system was adjusted to 8.0 and precipitates was formed. After aging for 24 h, filtration and washings was done with distilled water until no Cl⁻ detected (tested with AgNO₃ water solution), the precipitates were dried at less than 110°C for 24 h. The obtained powders were rubbed and filtered with sieve No 100 and then a definite mass were mixed with vitriol responding to a definite concentration. After 24 h, the solids re filtrated and dried at less than 110°C for 24 h, then incubated at an optimum temperature for 5 h and SO₄²⁻/TiO₂ solid acid catalyst obtained.

Characteristic of SO₄²⁻/TiO₂ catalysts

XRD and EDS are used to determine powder crystal phase, size and sulfur content held by SO₄²⁻/TiO₂ catalysts.

Transesterification of animal oil and ethanol

With a definite mass ratio, animal oil, catalyst and ethanol were added into a reactor appending stirrer and water segregator. The reaction lasted a certain time under the catalysis of $\text{SO}_4^{2-}/\text{TiO}_2$. After filtration of catalyst and recycle of excess ethanol in filtrate through distillation, the remained solution was separated through centrifuge and biodiesel was obtained from the upper layer.

Yield of biodiesel is calculated according to the following equation:

$$Y = W_b / W$$

W_b - mass of the biodiesel g, W - mass of the origin animal oil g, Y - yield of biodiesel.

In transesterification, the influences of catalyst amount, ratio of alcohol to oil, reaction time and dosage of catalyst were studied through multi-factor $L_9(3^4)$ orthogonal experiment. Value of these factors is listed in the Table 1 and reaction temperature takes boiling point at 78°C of ethanol.

Table 1. Value of influence factors in $L_9(3^4)$ orthogonal experiment

Factors level	Ethanol oil g/g	Catalyst oil g/g	Reaction time /h
1	1.0:1.0	0.1:1.0	8.0
2	1.5:1.0	0.2:1.0	12.0
3	2.0:1.0	0.3:1.0	16.0

Results and Discussion

Analyse of $\text{SO}_4^{2-}/\text{TiO}_2$:- XRD of $\text{SO}_4^{2-}/\text{TiO}_2$

To illustrate crystalline structure and existing form of the prepared catalyst, XRD analysis was carried out for $\text{SO}_4^{2-}/\text{TiO}_2$ and TiO_2 material respectively. As shown in Figure 1, $\text{SO}_4^{2-}/\text{TiO}_2$ has the same crystal phase of anatase as TiO_2 , the sulfating of TiCl_4 hydrolysate can not change the structure. But it can make surface free energy or diffusivity decrease, then prevent burning together and growth up of crystal¹³, so smaller size powders are obtained. The crystal size is 14.6 nm calculated according to Sherrer equation¹⁴.

At the same time, powder size of $\text{SO}_4^{2-}/\text{TiO}_2$ activated at 500, 550 and 600°C is detected and calculated according to Sherrer equation. As shown in Figure 2, it increases along with the increase of activating temperature. This may be caused by powder's burning together and reunite under high temperature.

EDS of $\text{SO}_4^{2-}/\text{TiO}_2$

With the same dipping vitriol concentration of 1.5 mol/L, the influence of activation temperature on S relative content held by $\text{SO}_4^{2-}/\text{TiO}_2$ is detected with EDS. Figure 3 shows that the mass ratio of S/Ti increases with the increase of temperature. At 550°C, the maximum S/Ti is obtained. Then it decreases with the increase of temperature.

Influence of dipping vitriol concentration on activation of $\text{SO}_4^{2-}/\text{TiO}_2$

The hydrolysate of TiCl_4 is treated with vitriol possessing different concentration of 0.5 ~ 3.0 mol/L and then activated at 550°C. Catalysis activation on transesterification of animal oil and ethanol is studied. As showed in Figure 4, catalysis activation increases with the increase of vitriol concentration. But when it larger than 1.5 mol/L, the yield of TiCl_4 hydrolysate decrease obviously for the reason of dissolving. So 1.5 mol/L vitriol is used.

Figure 1. XRD of $\text{SO}_4^{2-}/\text{TiO}_2$ and TiO_2

Figure 2. Influence of activation temperature on particle size

Figure 3. Influence of activation temperature on mass ratio of S/Ti

Figure 4. Influence of vitriol concentration on analysis activation

Transesterification of animal oil and ethanol

Optimizing of parameter

With $\text{SO}_4^{2-}/\text{TiO}_2$ as catalyst prepared under optimum condition, the optimum parameter of transesterification was studied. The influences of catalyst amount, mass ratio of ethanol to oil and reaction time on yield of biodiesel was studied through multi-factor $L_9(3^4)$ orthogonal experiment. Optimum condition is gained as: $m(\text{ethanol}): m(\text{oil})=1.5:1.0$, $m(\text{catalyst}): m(\text{oil})=0.3:1.0$, reaction time 8 h and temperature keeping at the boiling point. Yield of biodiesel reaches 79.6%.

Analyses of extremum difference testify that dosage of $\text{SO}_4^{2-}/\text{TiO}_2$ has the most important influence on yield of biodiesel and then followed by mass ratio of ethanol to oil and reaction time. The trendline between total yield and every factor is shown in Figure 5. Yield of product increases with the increase of catalyst's dosage, but the influence gets smaller. So the optimum values of analyst dosage, mass ratio of ethanol to oil and reaction time were determined as 0.3:1.0, 1.5:1.0 and 8 h, respectively.

Figure 5. Trendline between total yield and influence factor.

Influence of different catalyst on yield of biodiesel

With $\text{SO}_4^{2-}/\text{TiO}_2$, expandable graphite¹⁵, expandable graphite loaded vitriol¹⁶ as catalyst respectively, their catalysis activation in transesterification was investigated. Yields of biodiesel in different catalyzing reaction are listed in Table 2. Compared with the others, $\text{SO}_4^{2-}/\text{TiO}_2$ possesses the maximum activation.

Table 2. Catalysis activation of different catalysts

Catalyst	Expanded graphite (210 mL/g)	Expanded graphite (250 mL/g)	Expanded graphite loaded vitriol (270 mL/g)	$\text{SO}_4^{2-}/\text{TiO}_2$
Yield %	64.3	71.0	78.3	79.6

Length of life of $\text{SO}_4^{2-}/\text{TiO}_2$

To $\text{SO}_4^{2-}/\text{TiO}_2$ prepared under optimum condition, its service life in transesterification is investigated. Yields of biodiesel keep little change after $\text{SO}_4^{2-}/\text{TiO}_2$ is continuously used three times. It's only a decrease of 6.2% of yield. The re-activation of $\text{SO}_4^{2-}/\text{TiO}_2$ is necessary. Otherwise, yield will have an obvious decline.

Figure 6. Length-of-life of $\text{SO}_4^{2-}/\text{TiO}_2$

Conclusions

$\text{SO}_4^{2-}/\text{TiO}_2$ with high catalysis activation can be prepared according to following condition: dipping vitriol concentration of TiCl_4 hydrolysis product is controlled as 1.5 mol/L, baking activation temperature for the catalyst takes 500°C .

With $\text{SO}_4^{2-}/\text{TiO}_2$ as catalyst, the optimum condition to get biodiesel through transesterification of ethanol and animal oil is gained as: $m(\text{ethanol}): m(\text{oil})=1.5:1.0$, $m(\text{catalyst}) : m(\text{oil})=0.3:1.0$, reaction time 8.0 h and temperature keeping at the boiling point. Yield of biodiesel can reach 79.6%. $\text{SO}_4^{2-}/\text{TiO}_2$ possesses higher catalysis activation than other tested catalysts.

As a kind of polyphase catalyst, $\text{SO}_4^{2-}/\text{TiO}_2$ can be used in organic reaction which had proton transfer.

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