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Biodiesel Preparation from *Styrax confusus Hemsl.* Oil Catalyzed by Magnetic Catalyst $S_2O_8^{2-}$-ZrO_2/Fe_3O_4

Zhenxing LIU[1,a], Xiaoan NIE[1,2,b], Yigang WANG[1]

[1]Institute of Chemical Industry of Forest Products, National Engineering Lab. for Biomass Chemical Utilization, Key and Open Lab. on Forest Chemical Engineering, Key Lab. of Biomass Energy and Material, Jiangsu Province, Nanjing 210042, China

[2]Institute of New Technology of Forestry, CAF, Beijing 100091, China

[a]nan.gong.ci@163.com, [b]niexiaoan@126.com

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Abstract: Styrax confusus Hemsl., a promising energy plant, was used as raw material for biodiesel preparation in this paper. The transesterification was catalyzed by magnetic catalyst $S_2O_8^{2-}$-ZrO_2/Fe_3O_4, prepared by chemical co-precipitation method. TEM images indicate that the average particle diameter of magnetic core Fe_3O_4 and catalyst carrier ZrO_2/Fe_3O_4 are 5-20 nm and 30-50 nm respectively. Because of its unique porous structure the BET surface area could up to 140.75 m^2/g. The results show that a best catalytic activity is obtained when the solid catalyst impregnated in 2.5 $mol \cdot L^{-1}$ $(NH_4)_2S_2O_8$, calcined at 400 ºC for 3 h, and a high methyl ester yield could be obtained under the optimal reaction conditions of catalyst amount 4.5 % (wt/wt oil), molar ratio of methanol/oil 6:1, reaction temperature 65 ºC and time 2.0 h.

Introduction

With the aggravation of traditional fossil resources depletion and the increasing pollution of environment, biodiesel, namely fatty acid methyl esters (FAMEs) [1], has received lots of attentions in recent years as a kind of promising fossil energy substitute [2].

However, most of the common oils and fats used as raw materials are too expensive to be applied in large-scale production of biodiesel [3]. As a promising energy plant, *Styrax confusus Hemsl.*, a kind of arbor of styrax genera, possesses a high oil content and is widely distributed in southwest China. While there were few studies associated with it because most of the energy plants including *Styrax confusus Hemsl.* are still in the wild state. Thus, in order to research the application value of *Styrax confusus Hemsl.* as biomass energy, its seed-oil was selected as the material oil in the paper.

Catalyst is another important effect factor in biodiesel preparation. Traditionally, the preparation process was carried with homogeneous base catalysts like KOH and NaOH. Nevertheless, the separation and purification of products are time-consuming and expensive accompanied with lots of waste water [4,5]. To circumvent these challenges, magnetic catalyst may be a better choice because the magnetic solid could be separated from the products easily by an added magnetic field.

In this paper, a magnetic catalyst $S_2O_8^{2-}$-ZrO_2/Fe_3O_4 was prepared and its catalytic activity was evaluated in biodiesel preparation of *Styrax confusus Hemsl.* seed-oil. The effect of various influence factors on the methyl ester yield was also investigated.

Experimental

Materials

Styrax confusus Hemsl. seed, obtained from Wuchao mountain, Zhejiang province, China. $ZrOCl_2 \cdot 8H_2O$, $(NH_4)_2S_2O_8$, $FeCl_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$, C_2H_5OH, CH_3OH and $NH_3 \cdot H_2O$ were supplied by Nanjing Ningshi Chemical Reagent Co., Ltd. All the reagents used in the experiments were analytical grade.

Catalyst preparation

The Fe_3O_4 were prepared by chemical co-precipitation method. 2.0 g of $FeCl_2 \cdot 4H_2O$ and 4.7 g of $FeCl_3 \cdot 6H_2O$ were dissolved in 10 mL deionized water. Then $NH_3 \cdot H_2O$ was added dropwise tardily at 65 ºC with N_2 passing over the solution. Stirring the aqueous solution until the final pH value reached to 13.0. Then 20 mL C_2H_5OH was added and the mixture was aged for 30 min at 80 ºC. The particles was separated by a NdFeB magnet and washed by dissolved water until the pH of filtrate reduced to 7.0. After dried in a vacuum oven at 80 ºC for 8 h, the magnetic cores were pulverized.

32.0 g of $ZrOCl_2 \cdot 8H_2O$ was dissolved in 20 mL deionized water. Then 2.0 g of Fe_3O_4 were added to the soulution. $NH_3 \cdot H_2O$ was added dropwise tardily at 65 ºC until the final pH value reached 12.0. Then aged the mixture for 3 h with vigorous stirring. The solid was separated and washed by distilled water until there was no Cl^- in the filtrate. Then the solid was dried in a vacuum oven at 90 ºC for 8 h.

The active group $S_2O_8^{2-}$ was loaded by impregnation method. 5.0 g of ZrO_2/Fe_3O_4 was completely dipped in aqueous solution of $(NH_4)_2S_2O_8$ and subsequently dried at 90 ºC for 8 h. Finally, the dried material was calcined at temperature range from 300 to 600 ºC for 3 h in a muffle furnace.

Transesterification

30.0 g of *Styrax confusus Hemsl.* seed-oil, different amount of methanol and catalyst were added to a 250 mL 3-necked flask, and reacted at 65 °C with vigorous stirring. After reaction, the catalyst was separated by a NdFeB magnet. The excess methanol was recovered under vaccum at 60 °C, and the mixture was left to separate into two layers, which were biodiesel (uper) and glycerol (lower).

Analysis and Characterization

The catalyst was characterized with X-ray diffractions (XRD) , transmission electron microscope (TEM) and BET surface area analyzer. The fatty acid composition of product was determined by GC-AG Shimadzu Japan series gas chromatography fitted with FID detector and Shimadzu CRIG microcomputer treatment system.

Results and Discussion

Catalyst Characterizations

XRD pattern of magnetic catalyst $S_2O_8^{2-}$-ZrO_2/Fe_3O_4 calcined at 400 ºC was showed in Fig. 1. It is obvious that there are peaks existing at 2θ=30º, 35º, 50º and 60º in the pattern, which demonstrate that tetragonal ZrO_2 (t) is the main crystal phase of the catalyst carrier. Calcination is the key process for activate the catalyst, whose crystal phase would change from amorphous form to tetragonal form.

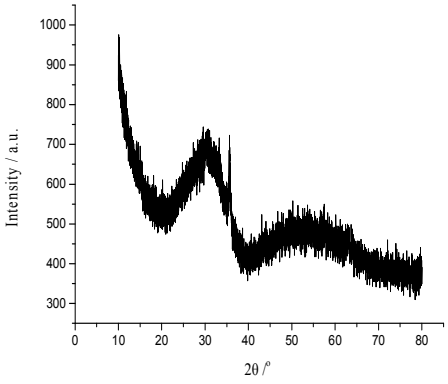


Fig. 1. XRD pattern of calcined catalyst

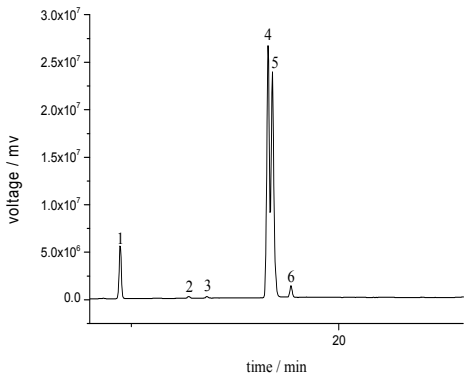


Fig. 3. Total ion chromatogram (TIC) of biodiesel from *Styrax confusus Hemsl.*

TEM images of nano-particles Fe_3O_4 and catalyst carrier ZrO_2/Fe_3O_4 were depicted in Fig. 2. As showed in Fig. 2A, the average particle diameter of Fe_3O_4 is about 5-20 nm, while that of ZrO_2/Fe_3O_4 reaches to 30-50 nm as showed in Fig. 2B. Although the diameter of magnetic core would increase after coated ZrO_2 to the surface of Fe_3O_4, the agglomeration of nano-particles would be reduced and a unique porous structure could be formed by this way. BET surface area analysis showed that the catalyst possessed a unique microstructures with a BET surface area of 140.75 m^2/g. The nano-particles are superparamagnetic, that could be recovered easily by applied magnetic field.

Transesterification

Constituents analysis The total ion chromatogram (TIC) and constituents of biodiesel were shown in

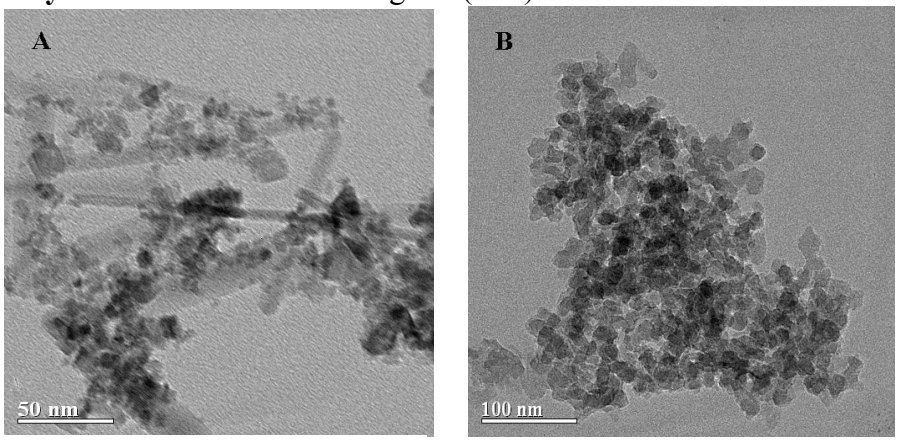


Fig. 2. TEM images of magnetic core Fe_3O_4 (A), catalyst carrier ZrO_2/Fe_3O_4 (B)

Fig. 3 and Tab. 1 respectively. As listed on Tab. 1, linoleic acid and oleic acid are the predominant fatty acid in the biodiesel from *Styrax confusus Hemsl.*, whose percentage compositions were 45.20 % and 43.07 % respectively. Unsaturated fatty acids occupy a high level in the product by a percentage of 88.58 %. High content of unsaturated fatty acids would improve the cold flow properties of biodiesel and make it suitable in temperate areas.

Table 1 Fatty acid composition (wt%) of biodiesel from *Styrax confusus Hemsl.*

No.	Retention time (min)	Components	Content (wt%)
1	17.368	Palmitic acid	8.42
2	18.194	Heptadecenoic acid	0.31
3	18.414	15-methyl hexadecanoic acid	0.31
4	19.151	Linoleic acid	45.20
5	19.201	Oleic acid	43.07
6	19.427	Stearic acid	2.05

Effect of calcination temperature Fig. 4 showed the effect of various calcination temperatures. The activity of $S_2O_8^{2-}$-ZrO_2/Fe_3O_4 rose greatly with the increase of calcination temperature when the temperature was lower than 400 ºC. The yield reduced sharply when the temperature was higher than 400 ºC because of the damage of solid acid structure and the loss of active group $S_2O_8^{2-}$-ZrO_2. What more, the magnetic properties of catalyst would be weaken with the calcination temperature rises. Therefore, 400 ºC would be the optimal calcination temperature of catalyst.

Effect of $S_2O_8^{2-}$ concentration Appropriate $S_2O_8^{2-}$ concentration is an important factor for the activity of catalyst. As shown in Fig. 5, when the concentration was lower than 2.5 mol·L^{-1}, the $S_2O_8^{2-}$ loaded on the catalyst was not enough for the reaction. While when the concentration was over 2.5 mol·L^{-1}, the yield would decrease because of the uneven distribution of active group. The optimal $S_2O_8^{2-}$ concentration would be 2.5 mol·L^{-1}.

Effect of reaction conditions Different reaction conditions such as catalyst amount, molar ratio of methyl/oil, reaction time and recycling times of catalyst were also researched. The results were shown in Fig.6. From Fig. 6, the optimal reaction conditions are, catalyst amount 4.5 % (wt/wt, oil), methanol/oil molar ratio 6:1, reaction time 2.0 h. Fig. 6D showed that the activity of catalyst $S_2O_8^{2-}$-ZrO_2/Fe_3O_4 declined gradually with the recycling times increased. Agglomeration of catalyst particles in the recycling process, loss of active group and damage of solid acid structure aggravate the activity declining in recovery.

Conclusion

A magnetic solid catalyst $S_2O_8^{2-}$-ZrO_2/Fe_3O_4 was prepared by chemical co-precipitation method and characterized by various techniques. TEM images indicate that the average particle diameter of magnetic core Fe_3O_4 and catalyst carrier ZrO_2/Fe_3O_4 were 5-20 nm and 30-50 nm respectively. The

catalyst possesses unique porous structure with a BET surface area of 140.75 m^2/g. The solid catalyst impregnated in 2.5 $mol \cdot L^{-1}$ $(NH_4)_2S_2O_8$, calcined at 400 ºC for 3 h, showed a best catalytic activity. *Styrax confusus Hemsl.* is a promising energy plant. In the process of biodiesel preparation, a high methyl ester yield could be obtained under the optimal reaction conditions of catalyst amount 4.5 % (wt/wt, oil), methanol/oil molar ratio 6:1, reaction time 2.0 h and temperature of 65 ºC. The magnetic solid catalyst used in the preparation of biodiesel showed a promising application prosect.

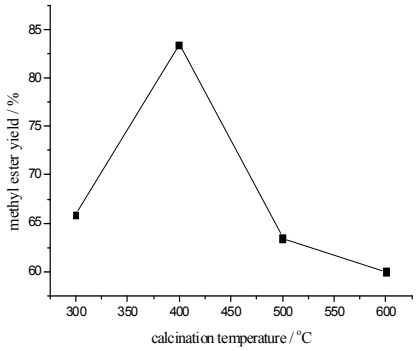


Fig. 4 Effect of calcination temperature

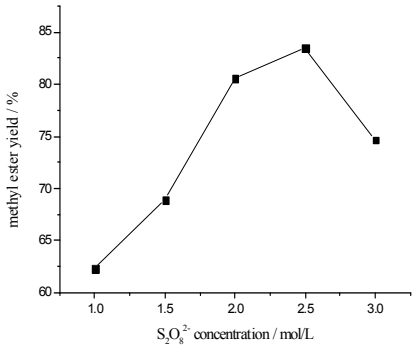
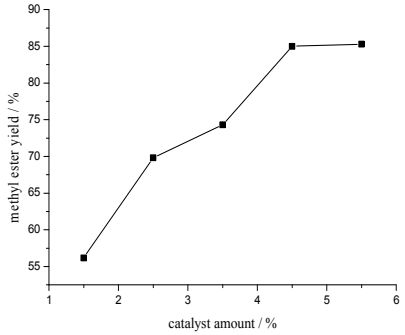
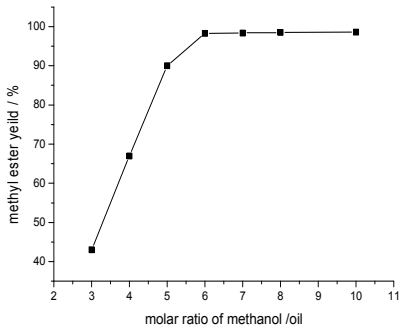


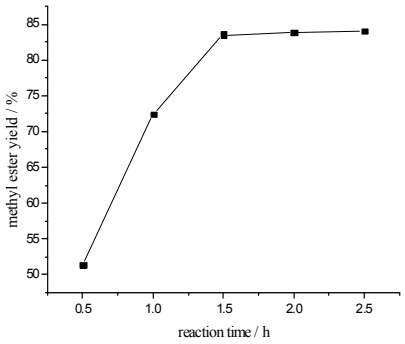
Fig. 5 Effect of $S_2O_8^{2-}$ concentration



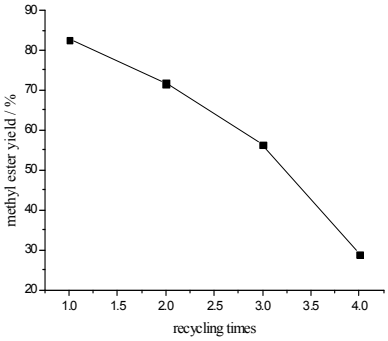
A



B



C



D

Fig. 6 Effects of the usage of catalyst (A), molar ratio of methanol/oil (B), Reaction time (C), recycling times of catalyst (D).

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