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RESEARCH ARTICLE

Development of solid base catalyst X/Y/MgO/γ-Al_2O_3 for optimization of preparation of biodiesel from *Jatropha curcas* L. seed oil

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Abstract The preparation and regeneration conditions of the identified catalyst X/Y/MgO/γ-Al_2O_3 with high catalytic activity were studied and optimized. The biodiesel was prepared by transesterification of *Jatropha curcas* seed oil produced in Guizhou with methanol at its reflux temoerature in the presence of X/Y/MgO/γ-Al_2O_3 . The pilot plant tests were carried out in a 100 L reaction vessel. Both average yield and fatty acid methyl esters (FAME) content reached more than 96.50% under the optimum reaction conditions of the pilot plant tests designed with an oil/methanol molar ratio of 1 : 10, catalyst concentration of 1.00%, and reaction time of 3 h at reflux temperature. In addition, analysis shows that the quality of biodiesel meets the standard EN 14214.

Keywords Solid base catalyst, *Jatropha curcas* oil, Transesterification reaction, Pilot plant test

1 Introduction

Biodiesel is defined as fatty acid methyl or ethyl esters from renewable lipid feedstock, such as vegetable oil or animal fat [1–3]. In recent years, biodiesel has received considerable attention as a potential eco-friendly substitute for conventional diesel fuels due to its low emissions, biodegradability, non-toxicity, high flashpoint, superior cetane number, excellent lubricity and ability to be produced from renewable sources with high energetic efficiency [4–6].

In the conventional process of biodiesel production, the alkali or acid such as NaOH, KOH and H_2SO_4 [7,8] was usually employed as the homogeneous catalyst. However, removal of these homogeneous catalysts after the reaction imposes a technical difficulty, and massive wastewater is produced during the separation and cleaning of products. The use of heterogeneous catalysts, which can be separated relatively easily, can eliminate these disadvantages. As the alkali-catalyzed transesterification process is approximately 4000 times faster than the acid-catalyzed process [9], many researchers have studied heterogeneous alkali-catalyzed process and solid base catalysts to replace the conventional process. The supported catalysts have attracted much attention in the preparation of solid base catalysts because of their high specific surface area, stronger base strength and high catalytic activity [10–12]. A series of supported catalysts were studied and applied in this field. Kim et al. [10] reported a process for the production of biodiesel from vegetable oils using a Na/NaOH/γ-Al_2O_3 heterogeneous catalyst. Under optimized reaction conditions, Na/NaOH/γ-Al_2O_3 shows almost the same activity as that of a conventional homogeneous NaOH catalyst. Xie et al. [13] developed a type of Al_2O_3-loaded KNO_3 for the transesterification of soybean oil. The catalytic activity was ascribed to the presence of K_2O and K-O-Al groups derived from KNO_3 or other potassium compounds during high-temperature calcination.

The objective of this study is to develop an efficient catalytic process using a solid base catalyst with high activity for the production of biodiesel from *Jatropha curcas* L. seed oil. In the present study, X/Y/MgO/γ-Al_2O_3 exhibited high basicity, the best catalytic activity and mechanical strength for catalyzing the transesterification of *Jatropha curcas* L. seed oil. The optimum reaction conditions were obtained by an orthogonal experiment. At the same time, catalyst recycling and regeneration were also investigated. Furthermore, the pilot plant tests were carried out in a 100 L reaction vessel. The pilot product

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was tested by the laboratories of Daimler-Chrysler, Volkswagen, Royal Dutch Shell and Robert Bosch. The performances and indices meet the standard EN14214. The samples were also tested by Guangdong (Huizhou) Quality Supervision & Testing Center for Petroleum Products, National Lab of Auto Performance and Emission Test, Beijing Institute of Technology; State quality Supervision and Inspection Center for Heavy-trucks. Besides the power of biodiesel being close to $0^{\#}$ petroleum diesel, it is superior to other indices of domestic $0^{\#}$ diesel. In particular, smoke intensity and particulate emission are especially significantly lower.

2 Experimental

2.1 Materials and methods

Jatropha curcas oil was prepared by squeezing *Jatropha curcas* seeds collected from Luodian County, Guizhou Province, southwest China. The crude oil obtained was then purified by filtering out solid impurities and refined to reduce the water content. The fatty acid composition of *Jatropha curcas* oil was determined by gas chromatography (GC) and is shown in Table 1. The acid value of the oil was approximately 2.63 mg KOH/g, and an average molecular weight of 880 g/mol, which was calculated from the saponification value ($Sv = 194$ mg KOH/g). Methanol and other chemicals were obtained from a commercial source and were of analytical grade.

Table 1 Fatty acid composition of *Jatropha curcas* oil used in present study

fatty acids	palmitic acid	palmitoleic acid	stearic acid	oleic acid	linoleic acid
wt.%	12.47	0.23	6.42	32.04	42.47

2.2 Catalyst preparation

A series of alkali or alkaline earth metal salts and their oxides, artificial zeolite, spinel, Al_2O_3 and so on, were used as precursor of active site and supports, respectively. Catalysts were prepared by impregnation or grinding method. The solution was mixed with the support and the resulting pastes were dried in an oven at 383 K for 12 h. The mixture was then calcined at 573–1223 K for 2–6 h, if required.

2.3 Transesterification reaction

All same-scale reactions were performed in a 250 mL three-necked glass flask equipped with a water-cooled condenser, thermometer and magnetic stirrer. The transesterification reaction was carried out with 110.0 g (125 mmol, calculated from the average molecular weight) of *Jatropha curcas* oil, different volumes of methanol and various amounts of catalyst. The mixture was vigorously stirred and refluxed for the required reaction time. After reaction, the mixture was filtered and excess methanol was recovered by rotary evaporation. The liquid phase was transferred into a separating funnel and allowed to settle and the upper layer was analyzed by GC.

3 Results and discussion

3.1 Initial screening of catalyst

Initial screening tests were carried out to evaluate the catalytic activity of more than 200 solid base catalysts under the same reaction conditions as described above, and the preliminary results are presented in Table 2.

As is shown in Table 2, $X/Y/MgO/\gamma\text{-}Al_2O_3$ shows the highest catalytic activity under the same reaction conditions. The content of fatty acid methyl esters (FAME) of biodiesel product reached up to 96.50 wt.% (entry 6), so this catalyst was selected for optimization of the investigation.

Table 2 Catalytic results of partial heterogeneous catalysts*

entry	catalysts	calcination temperature/K	calcination time/h	FAME/ wt.%
1	MgO	773	3	55.64
2	$\gamma\text{-}Al_2O_3$	773	3	38.57
3	artificial zeolite	773	3	34.16
4	ZrO_2	773	3	21.48
5	CaO/NaY	773	3	64.35
6	$X/Y/MgO/\gamma\text{-}Al_2O_3$	773	3	96.50
7	$X/Y/\gamma\text{-}Al_2O_3$	773	3	87.15
8	$X/MgO/\gamma\text{-}Al_2O_3$	773	3	82.23
9	$X/Mg(OAc)_2/\gamma\text{-}Al_2O_3$	773	3	80.47
10	$X/CaO/\gamma\text{-}Al_2O_3$	773	3	77.61

*Reaction conditions: methanol/oil molar ratio 10: 1, catalyst amount 5 wt.% of *Jatropha curcas* oil, reflux temperature, reaction time 3 h.

3.2 Optimization of the preparation conditions of catalyst $X/Y/MgO/\gamma\text{-}Al_2O_3$

3.2.1 Effect of preparation method

In order to determine the optimum preparation method, the catalyst $X/Y/MgO/\gamma\text{-}Al_2O_3$ was separately prepared by impregnation and grinding method respestively under the same conditions of reactants ratio, calcination temperature and calcination time. From Table 3, it can be seen that the grinding method shows higher catalytic activity.

3.2.2 Optimization of preparation of $X/Y/MgO/\gamma\text{-}Al_2O_3$ and transesterification reaction conditions

For obtaining the optimum preparation conditions of $X/Y/MgO/\gamma\text{-}Al_2O_3$, an orthogonal experiment was carried out. The effects of various factors on the catalytic activity

Table 3 Effect of different preparation methods on catalytic activity

preparation method	*ratio	calcination temperature/K	calcination time/h	FAME/wt.%
Impregnation	5 : 1 : 1 : 3	773	3	88.70
Grinding	5 : 1 : 1 : 3	773	3	96.50

*The ratio of X, Y, MgO and γ-Al_2O_3.

were also studied in the transesterification reaction as described above. The orthogonal scheme chosen and the data obtained are shown in Table 4.

Table 4 Results of orthogonal experiment $L_9(3^4)$ for catalyst X/Y/MgO/γ-Al_2O_3 preparation conditions and range analysis

No.	factors and levels			results
	A	B	C	FAME/wt.%
1	1	1	1	76.3
2	1	2	2	97.6
3	1	3	3	81.1
4	2	1	3	86.3
5	2	2	1	80.9
6	2	3	2	95.7
7	3	1	2	80.9
8	3	2	3	86.5
9	3	3	1	88.1
I	255.0	241.6	258.6	
II	262.8	264.9	270.6	
III	255.6	264.9	243.3	
R	2.6	7.2	9.7	

*Factors and levels are as follows: A. calcination time (h): 1 (2), 2 (3), 3 (4); B. calcination temperature (K): 1 (673), 2 (773), 3 (873); C. ratio of X, Y, MgO and γ-Al_2O_3: 1 (3 : 1 : 1 : 5), 2 (5 : 1 : 1 : 3), 3 (7 : 1 : 1 :1)

As shown in Table 4, the extent to which the transesterification of *Jatropha curcas* oil was affected in terms of the range (R) value was $C > B > A$, i.e., ratio of X, Y, MgO and γ-Al_2O_3 (C) in the lead, followed by calcination temperature (B) and then, calcination time (A). Taking the content of FAME into account, the optimum catalyst preparation conditions were established as $A_2B_2C_2$; i.e., ratio of X, Y, MgO and γ-Al_2O_3, 5: 1: 1: 3; calcination temperature, 773 K; and calcination time, 3 h. An average FAME content of 96.90% ($n = 3$) was obtained in transesterification under the optimum preparation conditions.

The optimum transesterification conditions of X/Y/MgO/γ-Al_2O_3 were studied by orthogonal experiment again. The factor level and results are listed in Table 5. Obviously, the amount of catalyst is the most important factor that affects the transesterification reaction. The orthogonal experiment revealed $A_2B_2C_2$ as the optimal reaction conditions i.e., the catalyst amount of 1 wt.%, with a 10 : 1 molar ratio of methanol to *Jatropha curcas* oil, reaction time of 2 h at reflux temperature 2 h.

The verification experiments were carried out according to the optimum transesterification conditions, an average FAME content of 97.18 % ($n = 3$) was obtained.

3.3 Catalyst regeneration and reusage

The regeneration and reusage of heterogeneous catalysts are key parameters for transesterification reaction in practical applications. The activity of reclaimed catalyst X/Y/MgO/γ-Al_2O_3 after transesterification of *Jatropha curcas* oil was also studied. The catalyst was carefully separated by filtration after reaction. When the catalyst was recovered and then reused to catalyze transesterification after a direct calcination, a FAME content of 21.30% was obtained (entry 1), which was much lower than the catalytic activity over the original catalyst. The catalysts were washed thoroughly using various organic solvents and calcined at 500 K for 3 h. The observed effect is listed in Table 6. It indicated that X/Y/MgO/γ-Al_2O_3 catalyst was deactivated sharply and could not be directly reused after simple washing and calcination. The reason could probably be attributed to the neutralization of the catalyst with free fatty acid, leading to the loss of active sites and

Table 5 Results of orthogonal experiment $L_9(3^4)$ for transesterification conditions and range analysis*

No.	factors and levels			results
	A	B	C	FAME/wt.%
1	1	1	1	82.9
2	1	2	2	90.6
3	1	3	3	89.6
4	2	1	3	94.2
5	2	2	1	98.1
6	2	3	2	97.8
7	3	1	2	93.7
8	3	2	3	96.9
9	3	3	1	96.5
I	263.1	270.9	277.5	
II	290.1	285.6	281.4	
III	287.1	283.8	281.4	
R	2.6	7.2	9.7	

*Factors and levels are as follows: A. catalyst amount: 1 (0.5 wt.%), 2 (1.0 wt.%), 3 (1.5 wt.%); B. oil/methanol molar ratio: 1 (1: 6), 2 (1: 8), 3 (1: 10); C. reflux time: 1 (1 h), 2 (2 h), 3 (3 h)

Table 6 Catalytic activity of a series of reclaimed catalyst

entry	organic solvent	calcination temperature/K	FAME/wt.%
1	–	723	21.30
2	methanol	723	29.72
3	tetrahydrofuran (THF)	723	24.50
4	aqueous ammonia	723	28.40
5	cyclohexane	723	28.88

Table 7 Effect of regeneration conditions on activity of reclaimed catalysts

organic solvent	supplement of X/%$^{a)}$	immersion time/h	calcination temperature/K	FAME/wt.%
Methanol	5	12	723	89.87
Methanol	10	12	723	97.58
Methanol	15	12	723	84.35

$^{a)}$The recruitment of X is based on the weight of catalyst

surface of catalyst being covered by lipid and products during the course of reaction.

An attempt to regenerate the activity of used catalyst samples by impregnating them in an aqueous solution of X was made in the study. When the reclaimed catalyst was supplied with an appropriate amount of X, dried and calcined as described in the experimental section, as shown in Table 7, the activity of the treated catalyst was approximately equal to that of the catalyst before reaction and the content of FAME reached up to 97.58%. However, excessive recruitment of X resulted in inactivation. The content of FAME was still above 95% when the catalyst was regenerated and repeatedly used for 5 times according to the method.

3.4 Pilot plant process

Transesterification reaction was gradually scaled up to 40 times under the optimal reaction conditions as described above. The amplification effect is shown in Fig. 1. It should be noted that no significant effect was observed with the amplification process. When the inventory rating of *J. curcas* oil reached 4400 g/pot, a yield of 97.27% and FAME content of 97.56% were obtained under the same conditions.

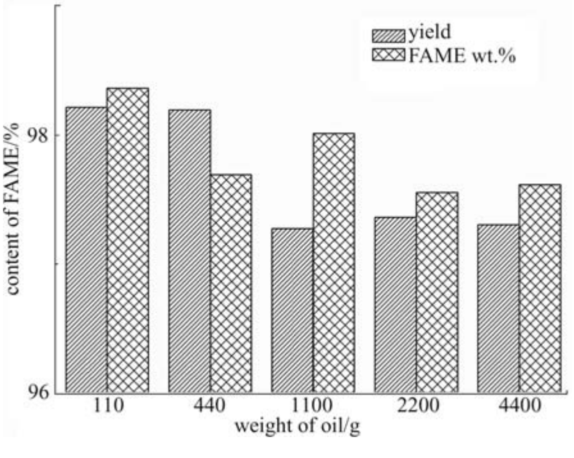

Fig. 1 Effect of amplification on content of FAME. Reaction conditions: catalyst amount of 1 wt.%, methanol/oil molar ratio 10: 1, reflux temperature

For obtaining the process parameters of a pilot plant test, experiments which were scaled up to 400 times were repeated for 15 times. Perhaps, because of the mass transfer, the reaction time is the most important parameter that affects the conversion to FAME in pilot plant test. Fig. 2 shows that the yield and fame content tended to be stable when reaction time was extended to 3 h, and the effect is equivalent to small tests conducted above. Therefore, the optimum reaction conditions of the pilot plant test were established with an oil/methanol molar ratio of 1: 10, catalyst concentration of 1 wt.% and a reaction time of 3 h at reflux temperature. The maximum content of FAME reached up to 96.85%.

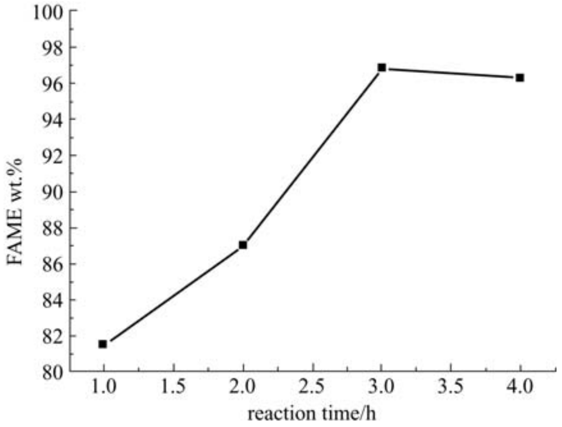

Fig. 2 Effect of reaction time on FAME content. Reaction conditions: catalyst amount of 1 wt.%, oil 44 kg, methanol 16 kg (methanol/oil molar ratio 10: 1), reflux temperature

4 Conclusions

The catalyst X/Y/MgO/γ-Al_2O_3 with high catalytic activity was screened out from a pool consisting of more than 200 catalysts. The identified catalyst is cheap and can be re-used for several runs without significant deactivation after regeneration. The utilization of catalyst X/Y/MgO/γ-Al_2O_3 could cope with most of the economical and environmental drawbacks of a homogeneous process. The optimum catalyst X/Y/MgO/γ-Al_2O_3 preparation conditions are achieved with X, Y, MgO and γ-Al_2O_3, ratio of 5: 1: 1: 3; calcination temperature of 773 K; and calcination time of 3 h. Both yield and FAME content were over 96.50% using a 1: 10 molar ratio of *Jatropha curcas* L. seed oil to methanol and a catalyst amount of 1 wt.% at reflux temperature for 3 h under pilot plant test. Analysis shows that the quality of pilot biodiesel product meets European standards EN 14214. The biodiesel obtained under the optimum conditions is a promising substitute for fossil fuels.

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