ISSN : 0974 - 7435 Volume 8 Issue 4

BioTechnology

An Indian Journal

FULL PAPER

BTAIJ, 8(4), 2013 [512-517]

Preparation and its properties of biodiesel by CaO/NaY supported catalys

Wang Xiaoguang*, YangYueyun

College of Chemistry and Chemical Engineering, Zhoukou Normal University, Zhoukou Henan 466001 (CHINA)

E-mail : wangqinghua201@163.com

ABSTRACT

Under the microwave irradiation, CaO could be dispersed on the NaY zeolite to form strong basic sites on the host. After activatiol, some CaO/NaY composites were found to exhibit an extraordinaryly high base strength. Therefore they were expected to be novel superbasic catalytic materials. The transesterification of rapeseed oil was carried out by using treated CaO/NaY as catalyst, the conversion rate and yield of biodiesel were studied. The result shows that under the small test optimized reaction conditions, i.e. crude rapeseed oil 100g, ethanol-oil mole ratio 6:1, mass fraction of catalyst 2%, reaction time 2h, and reaction temperature 55!, the conversion rate and yield of biodiesel reach more than 97%. The amplification experiments result shows that crude rapeseed oil input was 13.37 kg in 20-L reactor, and based on the small test conditions, the conversion rate of raw oil, yield of biodiesel and glycerol reach more than 95%. The fluidity of the biodiesel fuel at low temperature was much better than that of No.0 diesel fuel and the flash point was as high as170!. The biodiesel fuel could be blended with No.0 diesel fuel at any ratio.

KEYWORDS

Supported catalys;
Calcium oxide;
Rapeseed oil;
Biodiesel fuel.

INTRODUCTION

Biodiesel can be used as a substitute for fossil fuels, with renewable, easy to biodegradation, non-toxic, which is low in sulfur and waste gas emissions of harmful substance in the advantages of small, is a environment friendly fuel. The transesterification of vegetable oil, animal oil, waste cooking oil as raw materials and alcohol (methanol, ethanol) was carried out[1,2], the product is biodiesel (fatty acid ester), by-product is glycerin. The traditional ester exchange reaction using homogeneous catalyst[3,4], such as NaOH, KOH, sodium methylate dosage, about 1% (oil weight) or so, reaction temperature is generally the boiling point of methanol, reaction speed, high conversion rate, but at the same time also has the obvious shortcomings, the product should be neutral washed and bring a large amount of industrial waste water, cause environmental pollution, post-processing complex. Using supercritical non catalytic method for the transesterification reaction[5-8], short reaction time, conversion rate can reach 95%, the product does not need washing, post-processing is simple, but the alcohol oil mole ratio is high, the reaction temperature and pressure more than methanol critical temperature and critical pressure, the production process of equipment requirement is high. Lipase for ester exchange reaction, product separation and post-processing is convenient, no waste water generation, reaction temperature as room temperature, reaction time, but for several days, lipase immobilization, activity and price is the key[9]. Solid base catalyst used for ester exchange reaction[10-12], simple production technology, product post-processing is convenient, no wastewater produced. Firstly, microwave legal system was used for load type catalyst CaO/NaY to catalytic the transesterification reaction of rapeseed oil, and then the main properties of biodiesel was investigated.

EXPERIMENTS

NaY zeolite was bought from wenzhou catalyst factory, its chemical composition for $Na_{52}[(ALO)_{52}SiO_{140}]\cdot 268H_2O$, specific surface area is 766 m^2 / g. CaO is Shanghai chemical reagent company product. CaO powder and NaY zeolite according to certain quality ratio mix evenly, placed in the microwave oven (working frequency for 2450 MHZ), radiation twenty minutes, get CaO/NaY sample[13].

Experiment of transesterification reaction: According to the alcohol-oil molar ratio, join dryed oil and methanol in 250mL four flask, stirred, heated to reaction temperature, join CaO/NaY catalyst, keep return reaction for several hours, distillation out redundant methanol, reaction liquid filtered, while hot, the catalyst separated, then the filtrate into separatory funnel, stewing, overnight stratification. Upper products was biological diesel oil, and the lower layer was glycerol respectively, weigh, analysis. The content of fatty acid methyl ester in biological diesel oil products was detected by using 1102 type gas chromatograph. Chromatographic parameters: hydrogen flame ionization detector,2m×3mm stainless steel packed column, OV-17stationary phase, furnace temperature 250°C, detector temperature 320°X, sampler temperature 300°C, sample for 0.1ul, internal standard method (internal standard content: eleven acid methyl ester) calculating the content of fatty acid methyl ester[14]. All experimental drugs were analytically pure.

Physical and chemical of crude rapeseed oil analysis

The measurement method of the acid value reference GB/T5530-2005, moisture and volatile matter determination method of reference GB/T5528-1995. The measurement method of the erucic acid reference GB/T22507-2008. relative molecular mass of oil average can be calculated by saponification valueplant, the measurement method of the saponification value of reference GB/T5534-1995.

Determination of conversion rate:Because of glycerol production rate is equal to the conversion of vegetable oil, through the saponification-periodic acid oxidation method was used for determination of the content of product glycerin, and conversion for vegetable oil conversion.

Measurement of glycerol production

In biological diesel pilot production, glycerin content determination using international standards ISO2879-1975 "industrial glycerol content determination-titration method".

RESULTS AND DISCUSSION[15]

Physical and chemical indicators of crude rapeseed oil:TABLE 1 shows crude rapeseed oil acid value is 0.25mg·g-1, moisture and volatile matter mass fraction was 2.47%. Erucic acid mass fraction was 14.6%, far higher than the national standard of pollution-free rapeseed oil industry (NY5118-2002) erucic acid mass fraction not more than 5% of the requirements, not suitable for normal food, but can be used as raw oil biodiesel production.

TABLE 1 : Physical and chemical indicators of crude rapeseed oil

Acid value /(mg ·g-1)	Matter mass fraction of moisture and volatile /%	Mass fraction of erucic acid /%	Saponification value /(mg ·g-1)	Relative molecular mass
0.25	2.47	14.6	173.89	969.22

Test results of crude rapeseed oil

Influence of the ester exchange reaction of raw material oil inventory: On the conditions of catalyst mass fraction 2.5%, reaction temperature 55°C, reaction time120 min, three kinds (7:1, 6:1, 5:1) of alcohol oil ratio (mole ratio) raw oil inventory to the influence of the ester exchange reaction was investigated. The results shown as shown in Figure 1-2.

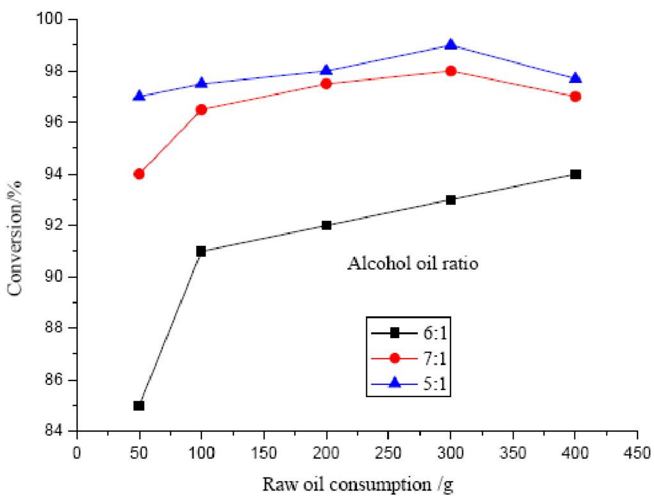

Figure 1 : Influences of sample mass on conversion rate

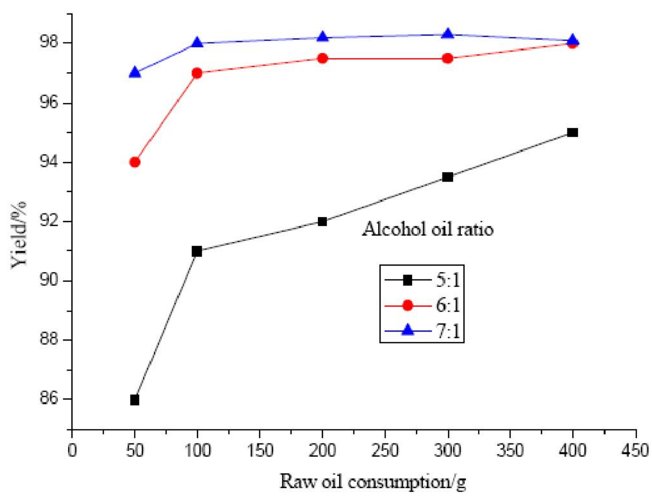

Figure 2 : Influences of sample mass on yield

Figure 1-2 show that the most obvious effect of the inventory of low alcohol-oil ratio. Alcohol-oil ratio 5:1, raw oil 50g, conversion and yield were below 90%, the reason might be that raw oil 50g, relative alcohol-oil ratio 5:1, mass fraction of methanol was relatively small, too much alcohol to gas in the form of reaction vessel, and in the reaction liquid and raw oil reaction of methanol production had greatly reduced, go against reaction the positive direction, glycerin in the solubility of methanol is bigger, too much alcohol made generated from the reaction system was difficult to leave. when alcohol-oil ratio 6:1or 7:1, raw oil more than 100g the conversion and yield basically unchanged. So the underbrush with 100g inventory was advisable.

Influence of alcohol oil ratio and catalyst dosage on the transesterification: According to the ester exchange reaction equation, it was known that moderate excess methanol to response to positive direction, reference reports in the literature[16], alcohol oil ratio 6:1, reaction temperature 55°C, reaction time 120 min, the effects of the dosage of catalyst on the transesterification was investigated. The results shown as shown in Figure 3-4.

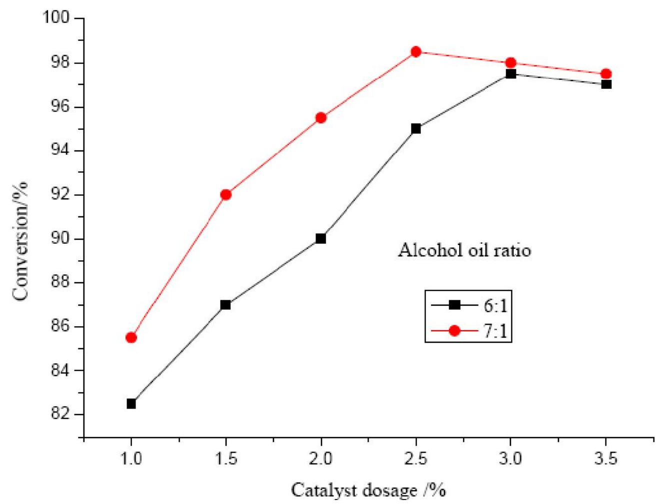

Figure 3 : Influences of catalyst amount on conversion rate

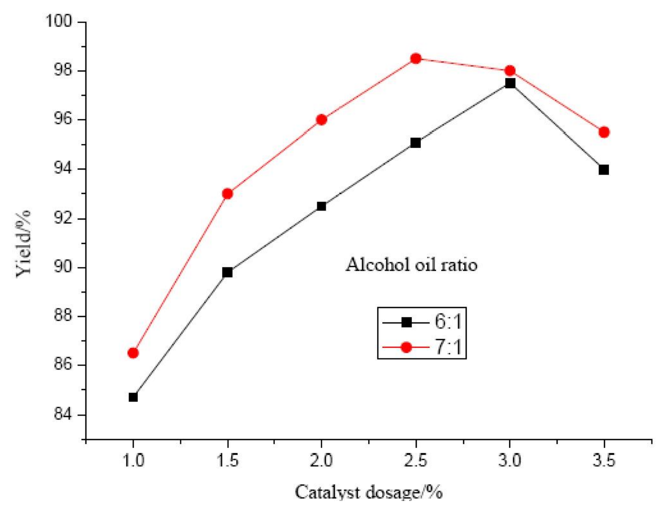

Figure 4 : Influences of catalyst amount on yield

Figure 3-4 show that alcohol-oil ratio 6:1, the conversion and yield were higher than that of 7:1 corresponding values, catalyst dosage in 1% to 2.5% range, the conversion rate and yield were increased, whihle 2.5%, reached to 97.15% and 97.18% respectively. Catalyst dosage continue to increase, the conversion rate did not change, but yield declined slightly, and catalyst dosage too much would affect the reaction mass transfer rate, to a certain extent, prolong reaction equilibrium time.

Influence of reaction time on the transesterification:Alcohol oil molar ratio 6:1, reaction temperature 55°C, catalyst dosage 2.5%, influence of reaction time on the transesterification was investigated, the results shown as shown in Figure 5.

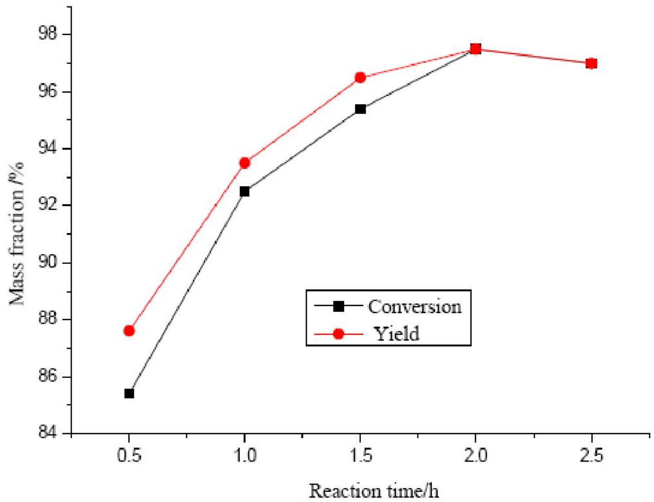

Figure 5 : Influences of reaction time on conversion rate and yield (small scale)

The Figure 5 shows that the reaction time from 0.5h to 2h gradually extends, conversion rate and yield basically ascendant trend. The influence of reaction time on the conversion is more obvious than that of biodiesel production rate, and the reaction time 2h, the conversion and yield were above 97%.

Determined the best conditions of the transesterification: Using orthogonal test method to determine the best ester exchange reaction process conditions, preliminary experiments and literature[10,12] show that the influence factors of the ester exchange reaction for: reaction temperature, catalyst dosage (A), molar reactant ratio (B) and reaction time (C), etc. Influence of temperature on the transesterification was very big, At low temperature, conversion rate was low, the reaction time was long, temperature 55°X was appropriate. The other three factors selected three level respectively: 1.5% (A_1), 2% (A_2) and 2.5% (A_3); 5:1 (B_1), then (B_2) and then (B_3); 1.5 h (C_1), 2 h (C_2) and 2.5 h (C_3). The results as shown TABLE 2.

From range value R in TABLE 2, it was known that the influence factors of fatty acid methyl ester content was as follows: catalyst dosage > alcohol oil mole ratio > reaction time. According to the content of methyl ester in biological diesel oil products, the optimal conditions was A3B2C3. But the reaction time from level a°C to level b°C increase to improve the content of fatty acid methyl ester hade little effect, therefore, the reaction time chooseda°C level; When catalyst dosage 2.5%, although the highest content of methyl in product, saponification phenomenon appeared in the process of reaction, gel disc precipitation from product, the product of biodiesel and byproduct glycerol separation also difficult, from visual analysis table can also know, catalyst dosage from level a°C to level °C increased, the increase in fatty acid methyl ester hade slowed, comprehensive consideration level a°C was more appropriate. Rapeseed oil and methanol transesterification reaction was reversible reaction, alcohol-oil mole ratio increased help reaction to life was direction, when alcohol-oil mole ratio 6:1, the highest content of methyl alcohol in product, and mole ratio 7:1, the content of methyl instead of down, this was because the amount of alcohol increased, the reactant concentration of oil became low and made the reaction rate drop, in reaction time ester exchange reaction had not became balance. Methanol too much would make the separation of glycerol difficult, and methanol recovery cost and the loss of methanol increase. So the best alcohol-oil mole ratio was 6:1.

TABLE 2 : Orthogonal test result and analysis of transesterification of rapeseed oil

Test samples	Catalyst (on oil basis)/%	Methan ol : rape seedoil(molar ratio)	React ion time/h	Yields of fatty acid methyl ester/%
1	1.5(A_1)	5:1(B_1)	1.5(C_1)	83.1
2	1.5	6:1(B_2)	2(C_2)	93.8
3	1.5	7:1(B_3)	2.5(C_3)	91.1
4	2(A_2)	5:1	2	92.5
5	2	6:1	2.5	98.0
6	2	7:1	1.5	93.8
7	2.5(A_3)	5:1	2.5	95.5
8	2.5	6:1	1.5	99.0
9	2.5	7:1	2	97.3
optimum	2	6:1	2	97.7
I	264.0	267.1	271.9	
II	280.3	286.8	279.6	
III	287.8	278.2	280.6	
R	23.8	19.7	8.7	

Results of biodiesel amplification experimental:

Influence of reaction time on the transesterification: According to the test results of biodiesel made of crude rapeseed oil production, In 20-L reaction kettle, input raw oil 6.50 kg, alcohol-oil mole ratio 6:1, catalyst dosage 2%, reaction temperature 55°C (60°C is closer to the boiling point of methanol, considering the safety of industrial application, the lower reaction temperature), on this condition, for different reaction time, biodiesel conversion rate and yield was investigated. The results as shown Figure 6.

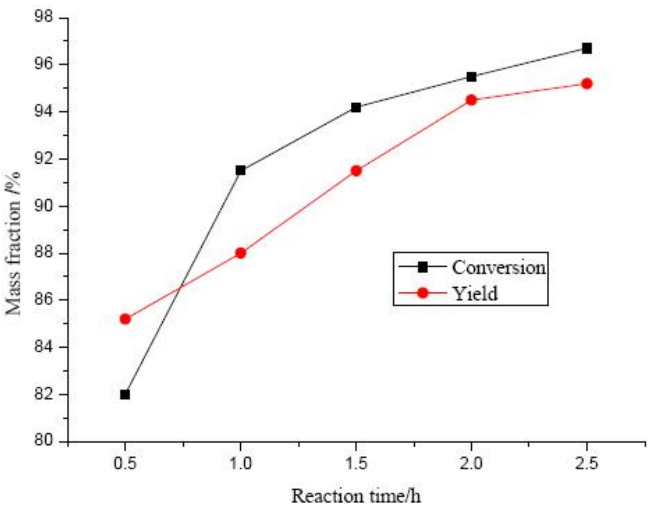

Figure 6 : Influences of reaction time on conversion rate and yield (amplification experiment)

The Figure 6 shows that the reaction time from 0.5h to 1h, the conversion and yield with the extension of time increased quickly, when the reaction time after 1.5h, conversion rate increased from 95.22% to 96.65%, change was relatively slow. The conversion and yield were above 90%, comprehensive consideration of the amplification experimental conditions: reaction time 2.5h, biodiesel conversion rate was 96.65%, the yield was 95.22%. It was reported[17] that the traditional catalyst get yield was 92%, indicating that CaO/NaY load type catalyst performance was good.

Biodiesel conversion rate and yield of amplification reaction were lower than that of test, the main reason was: (1) The biodiesel of water phase with no recovery; (2) The biological diesel in glycerin contains no recovery; (3) A small amount of loss in the process of transfer of products.

Biodiesel performance: Biodiesel cold filter point -11°C, solidifying point -16°C, greatly lower than that of 0 # diesel, flow properties beteer than that of 0 # diesel in the low temperature; flash point was as high as 170°C, storage, transportation and using more security; content of sulfur was extremely low, diesel engine exhaust emissions of SOx drops greatly; content of aromatic was 0, did not contain aromatic hydrocarbon composition, had no carcinogenicit; biodiesel had higher motion viscosity, in no effect of fuel atomization, more easily in the cylinder wall form a layer of oil film, so as to improve the moving parts lubricity, reduce wear and tear parts. in addition to the high iodine value, the other main performance indicators were in line with 0 # diesel standards (GB 252-94). The content of oxygen in biological diesel was 11%, higher than that of 0 # diesel, required amount of oxygen in the combustion processis less than that of 0 # diesel, combustion and ignition performance than that of 0 # diesel.

CONCLUSION

Combination of the reaction results, test conditions: alcohol-oil ratio 6:1, catalyst dosage 2%, reaction temperature 55°C, reaction time 2h, conversion rate and yield of biodiesel were above 98%; Amplification in 20-L reactor and based on the small test conditions, conversion rate and yield of biodiesel reach more than 95%; In addition to the high iodine value, the other main performance indicators were in line with 0 # diesel standards, indicating that CaO/NaY load type catalyst performance was good to crude rapeseed oil that contains a certain amount of free fatty acid had good catalytic effect, could be applied to large scale production application.

REFERENCES

[1] F.Ma, M.A.Hanna; Biodiesel production: A review. Bioresource Technology, **70**, 1-15 **(1999)**.

[2] A.Demirbas; Biodiesel fuels from vegetable oil svia catalytic and non-catalytic supercritical alcohol transest erifications and other methods: A survey. Energy Conversion and Management, **44**, 2093-2109 **(2003)**.

[3] G.Vicente, M.Martinez, J.Aracil; Integrated biodiesel production: a comparis on of different h om ogeneous catalysts systems. Bioresource Technology, **92**, 297-305 **(2004)**.

[4] Y.Zhang, M.A.Dube, D.D.McLean, M.Kates; Biodiesel production from waste cooking oil: (1). Process design and technological assessment. Bioresource Technology, **89**, 1-16 **(2003)**.

[5] S.Saka, D.Ku sdian a; Biodiesel fuel from rapeseed oil as prepared in supercritical methanol, Fuel, **80**, 225-231 **(2001)**.

[6] D.Kudiana, S.Saka; Kinetics of transest erificat ion in rapeseed oil to biodiesel fuel as treated in supercritical methanol. Fuel, **80**, 693 -698 **(2001)**.

[7] A.Demirbas; Biodiesel from vegetable oils viatrans esterication in supercritical methanol. Ener gy Conversion and Management, **43**, 2349-2356 **(2002)**.

[8] Y.Warabi, D.Ku sdiana, S.Saka; Reactivity of triglycerides and fatty acids of rapeseed oil in s upercritical alcohols.Bioresource Technology, **91**, 283-287 **(2004)**.

[9] Y.Watanabe, Y.Shimida, A.Sugihara, Y.Tominaga; Conversion of degummed soybean oil to biodiesel fuel with immobilized Candida antarctica lipase. Journal of Molecular Catalysis B: Enz ymatic, **17**, 151-155 **(2002)**.

[10] Lu Liang, Wu Guoqiang, Duan Xue, Li Feng, Du Yibo; Preparati on and charact erization of hydrot alcite and their application in ester interchange reaction. Special Petrochemicals, **1,** 9-12 **(2001)**.

[11] S Gryglewicz; Rapeseed oil methyl esters preparation using heterogen eous catalysts. Biore source Technology,**70**, 249 -253 **(1999)**.

[12] Kim H ak-Joo, Kang Bo-Seung, Kim Min-Ju, Park Young Moo, Kim Deog-Keun, Lee Jin-S uk, Lee Kwan Young; Trans esterification of vegetable oil to biodiesel using heterogeneous base catalyst. Catalysis Today, **93-95**, 315 -320 **(2004)**.

[13] ChunYuanÿ Zhu Jianhuan, XuQinhua; Chin Sci BuU, **41**, 1858 **(1996)**.

[14] Li Weimin, Zheng Xiaolin, Xu Chunming, Xu Ge, Wu Guoying; Preparation and its properties of biodieselby using solid base catalyst. Journal of Chemical Industry and Engineering, **56**, 711-716 **(2005)**.

[15] Li Guo-ping, Li Cong, Chen Bang, Wang Yan, Wang Yi-zhuo, Shen Ye-hua; Preparation of biodiesel from crude rapeseed oil and amplification experiments. Chemical Engineering, **40**,19-23 **(2012)**.

[16] S.P.Singh, D.Singh; Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: a review. Renewable and Sustainable Energy Reviews, **14**, 200-216 **(2010)**.

[17] Ishihara Atsushi, Wang Danhong, Dumeignil Franck; Oxidative desulfurization and denitrogenation of alight gas oil using an oxidation / adsorption continuous flowprocess. Applied Catalysis A: General, **279**, 279-287 **(2005)**.