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SODIUM PHOSPHATE AS A SOLID CATALYST FOR BIODIESEL PREPARATION

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Abstract - Sodium phosphate (Na_3PO_4) was chosen as catalyst for biodiesel preparation from rapeseed oil. The effects of mass ratio of catalyst to oil, molar ratio of methanol to oil, reaction temperature and rotation speed on biodiesel yield were investigated. For a mass ratio of catalyst to oil of 3%, molar ratio of methanol to oil of 9:1, reaction temperature of 343K and rotation speed of 600rpm, the transesterification was nearly completed within 20 minutes. Na_3PO_4 has a similar activity to homogeneous catalysts. Na_3PO_4 could be used repeatedly for 8 runs without any activation treatment and no obvious activity loss was observed. The concentrations of catalyst in biodiesel ranged from 0.6 to 0.7 mg/g. Compared to Na_3PO_4, $Na_3PO_4.10H_2O$ was cheaper, but the final yield was 71.3%, much lower than that of Na_3PO_4 at 99.7%.
Keywords: Sodium phosphate; Biodiesel; Solid base; Activity loss; Concentration of catalyst.

INTRODUCTION

Biodiesel derived from biological resources is a renewable fuel, which has drawn more and more attention recently (Kondili and Kaldellis 2007). A fatty acid methyl ester (FAME) is the chemical composition of biodiesel. Transesterification is widely used for the transformation of triglyceride into FAME (Nelson and Schrock 2006). Catalysts for transesterification can be classified into two kinds: homogeneous and heterogeneous (Meher et al. 2006). The drawbacks of homogeneous catalysts such as sodium and potassium hydroxide are apparatus corrosion and catalyst separation (Helwani et al. 2009). A heterogeneous catalyst is insoluble and can be easily separated, thus simplifying the production and purification processes (Kawashima et al. 2008). In order to overcome the limitations of homogeneous catalysts, many efforts have focused on the development of heterogeneous catalyst (Zabeti et al. 2009). Solid acid and solid base are the main heterogeneous catalysts for biodiesel preparation.

Compared to solid acid, solid base provides a faster rate to transesterification under mild condition. Many solid bases have been reported to transesterify triglyceride, such as alkaline earth oxides (Corma et al. 2006, Kouzu et al. 2008, Liu et al. 2007, Liu et al. 2008), anion exchange resin (Shibasaki-Kitakawa et al. 2007), organic solid base (Faria et al. 2008, de Rezende et al. 2008), supported solid base (Samart et al. , Verziu et al. 2009). Recently, many types of alkali metal compounds have been employed for biodiesel preparation: biodiesel was produced from soybean oil over sodium aluminate; the solid base showed high catalytic activity for methanolysis, reaching a 93.6% yield under optimal reaction conditions, and the reaction contained homogeneous and heterogeneous contributions at the same time (Tao Wan et al. 2009); Arzamendi et al. (2008) reported that sodium, potassium carbonate and sodium phosphate all catalyzed transesterification; potassium carbonate had the highest activity, while sodium carbonate and sodium phosphate exhibited almost the same activity which was much lower than potassium carbonate. After 5 hours of reaction, 55% of the potassium carbonate dissolved, but the losses of sodium carbonate and sodium phosphate were 20% and 15%, respectively. A 97% biodiesel yield

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was obtained using sodium phosphate as the catalyst and the experimental data were interpreted by using a kinetic model (Filippis et al. 2005). Sodium phosphate seems to be a promising solid catalyst for biodiesel preparation with more chemical stability than sodium aluminate and less solubility in FAME than sodium and potassium carbonate, but more information must be acquired about the catalytic behavior and catalyst stability of sodium phosphate under different reaction conditions.

In this study, effects of mass ratio of catalyst to oil, molar ratio of methanol to oil, reaction temperature and rotation speed on biodiesel yield were investigated and sodium phosphate was used repeatedly without any activation treatment. We also determined the catalyst leaching under reaction conditions.

MATERIALS AND METHODS

Material and Chemicals

Refined rapeseed oil branded "Fengda" was from Anhui Fengda Ltd. Co.; the rapeseed oil properties and free fatty acid composition are listed in Table 1 and Table 2. Methanol of analytical grade (AR) was purchased from Shanghai Zhongshi Chemical Company. n-Hexane and methyl heptadecanoate were obtained from Sigma Chemical Company. Both hydrated and anhydrous sodium phosphates were from Sinopharm Reagent Chemical Co., Ltd. and used as catalysts without further processing. All other chemicals were analytical grade and from Sinopharm Reagent Chemical Co. Ltd.

Reaction Procedure

Initially, about 400g of rapeseed oil was poured into a 2 L stainless reactor and then the amount of catalyst and methanol were added. The transesterification was carried out at the required temperature and rotation speed for 2h. The reaction parameters were chosen as follows: temperature ranged from 333 to 353K, molar ratio of methanol to oil from 6:1 to 12:1, mass ratio of catalyst to oil from 1% to 3% and rotation speed from 200 to 600rpm. In order to measure FAME content, a transesterification sample was analyzed at every 20 min. Finally, catalyst was separated from the mixture by centrifugation. After methanol was removed by distillation, the remaining liquid was allowed to settle and separated into two layers; the biodiesel was collected from the upper layer.

GC Analysis

Biodiesel samples were analyzed with a SHIMADZU 2010 gas chromatography equipped with a flame ionization detector (FID) and a DB-WAX capillary column (30m×0.25mm×0.25μm), 0.1g biodiesel was dissolved in 7mL of n-hexane containing 100μg of internal standard (heptadecanoic acid methyl ester) for GC analysis. Sample (1μl) was injected at a FID temperature of 533K, and an injector temperature of 523K. The initial oven temperature was 473K; after an isothermal time of 1 min, the oven was heated at a rate of 3K/min to 503K and kept for 6 min. Helium was employed as carrier gas at a flow rate of 30mL/min; the split ratio was 10:1.

Biodiesel yield was calculated by Eq.1:

$$\text{yield} = \frac{m_i A_b}{A_i m_b} \tag{1}$$

where m_i is the mass of internal standard added to the sample, A_i is the peak area of internal standard, m_b is the mass of the biodiesel sample, A_b is the peak area of the biodiesel sample. All samples were measured in triplicate with an uncertainty within 5%.

Table: 1 Rapeseed oil properties

Acid value (mg KOH/g oil)	Saponification value (mg KOH/g oil)	Iodine value (g idine/100 g oil)	Free fatty acid content (%)	Water content (%)
0.5	75	143	1.1%	0.3

Table 2: The free fatty acid composition of the rapeseed oil

Free fatty acid	Content (%)
Palmitic acid	3.850
Stearic acid	1.966
Oleic acid	46.564
Linoleic acid	14.693
Linolenic acid	7.550
Arachidonic	7.529
Erucic acid	16.674

Catalyst Reusability

In order to investigate the catalyst reusability, 2.73g of catalyst, 9.1g of rapeseed oil and 5 mL of methanol were added to a 250 mL round bottom flask. With magnetic stirring, the transesterification was carried out at 343K for 2 hours. After transesterification, catalyst was carefully filtered and reused directly under the above condition.

Catalyst Solubility

Catalyst was separated from samples drawn from the reactor after each reaction by centrifugation, methanol was evaporated under vacuum and glycerol was removed. In order to determine the Na_3PO_4 content by Atomic Absorption Spectrophotometry (AAS Perkin), the above remaining fraction was combined and diluted with methanol (chromatographic grade). Catalyst solubility was calculated from Eq. 2:

$$\text{catalyst solubility(mg/g biodiesel)} = \frac{C \times V}{M} \qquad (2)$$

where C is the Na_3PO_4 content in the methanol solution (mg/mL), V is the volume of the methanol solution (mL) and M is the mass of biodiesel (g). All samples were analyzed in duplicate and the uncertainties were controlled within 5%.

RESULTS AND DISCUSSION

Effects on Biodiesel Yield

Mass Ratio of Catalyst to Oil

Figure 1 illustrates the effect of mass ratio of catalyst to oil from 2% to 4% on biodiesel yield. It can be seen that the whole reaction can be divided into three stages: in the first stage, biodiesel yield increased greatly within 20min; in the second stage, biodiesel yield increased slowly over the next 60 minutes; in the third stage, the transesterification almost achieved equilibrium and the biodiesel yield changed little after 80 min.

In the first two stages, biodiesel yield increased with the increase of mass ratio of catalyst to oil at each given time, while in the third stage biodiesel yields were approximately 96% at different mass ratio of catalyst to oil. When the mass ratio of catalyst to oil was improved from 2% to 4%, the active sites of Na_3PO_4 increased; thus, the transesterification reaction was accelerated and biodiesel yield increased in the first two stages. In the third stage, the transesterification almost achieved equilibrium and biodiesel yields were not affected by the mass ratio of catalyst to oil.

Molar Ratio of Methanol to Oil

Figure 2 demonstrates the effect of molar ratio of methanol to oil, ranging from 6:1 to 12:1, on biodiesel yield. Similar to Figure 1, the reaction was also composed of three stages. In the first stage, the reaction developed rapidly within 20min and the biodiesel yields varied from 69.8% to 78.6%, depending on the different molar ratios of methanol to oil at the end of this stage; over the next 40 minutes, biodiesel accumulated slowly in the second stage. In the last stage, the transesterification reached a state of equilibrium, but the final yield of biodiesel was different, increasing from 94.9% for 6:1 to 99.3% for 12:1. The stoichiometry of transesterification requires 3 mol of methanol per mol of rapeseed oil; an excess of methanol can shift the equilibrium to the product side and biodiesel yield was improved.

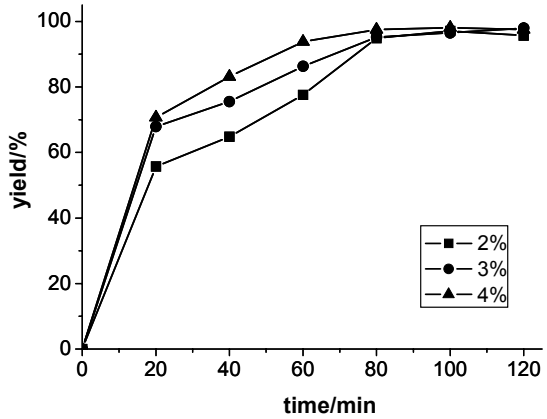

Figure 1: Effect of mass ratio of catalyst to oil on biodiesel yield. Temperature 333K; Molar ratio of methanol to oil 6:1; Rotation speed 400 rpm.

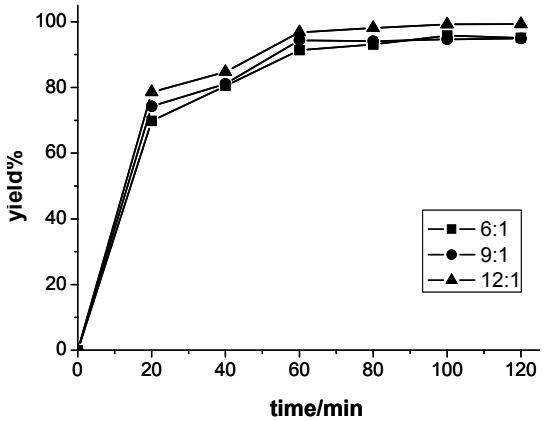

Figure 2: Effect of molar ratio of methanol to oil on biodiesel yield. Temperature 333K; mass ratio of catalyst to oil 3%; Rotation speed 400 rpm.

Reaction Temperature

Figure 3 illustrates the relationship between biodiesel yield and time at temperatures of 333, 343 and 353K. It can be seen that the biodiesel yields increased with the increase of temperature. After 60 minutes, the transesterification reached equilibrium and the equilibrium yields were 97.9%, 97.1% and 93.4% at 353, 343 and 333K, respectively. Other research (Liu et al. 2007) reported that biodiesel yield at 333K was higher than that at 343K, which is consistent with theory; because biodiesel transesterification is a mild exothermic reaction, the equilibrium yields should decrease with increasing temperature. The discrepancy in the two reports may arise from the different reactors that were used. The reactor employed in this research can maintain the pressure that is caused by the vaporization of methanol at 343 and 353K. It is probably the pressure that increases the equilibrium yields at higher temperatures. However, the precise reason for the discrepancy was not found and deserves further study to improve the biodiesel yield. The reaction rates at the 3 different temperatures were calculated from the data using a pseudo second-order model; reaction rate constants for triglyceride methanolysis, k_{TG}, were 0.00186, 0.00237 and 0.00392 min^{-1} at 333, 343 and 353K, respectively. The data indicate that the reaction rate accelerates with the increase in temperature. k_{TG} for palm oil, using KOH as catalyst, was 0.048 min^{-1} at 338 K (Darnoko and Cheryan 2000), one order of magnitude larger than in this work.

Rotation Speed

Figure 4 illustrates the relationship between biodiesel yield and time at different rotation speeds. Rotation speeds from 200 to 600 rpm were chosen in the experiment. The biodiesel yield increased and reached an equilibrium yield of 95% at about 120, 60 and 20 min with rotation speeds of 200, 400 and 600 rpm, respectively. Increase of the rotation speed could tremendously shorten the reaction time. There are probably two reasons that rotation speed can intensify the transesterification catalyzed by Na_3PO_4:

1) rotation promotes the mixing of rapeseed oil and methanol; methanol lies on the top of rapeseed oil without stirring. The methanol and oil layers break up and the reactants form droplets once stirring starts. The droplets of the reactants depend on rotation speed if the reactor is fixed and can be expressed as:

$$d_o = \frac{k}{n^2} \tag{3}$$

where d_0 is the diameter of the reactant droplet, k is the constant and n is the rotation speed (Ma et al. 1999, Stamenkovic et al. 2007). From Equation 3, it can be seen that an increase of rotation speed leads to a decrease in the diameter of the reactant droplets. Smaller droplets mean better dispersion of the reactants, which guarantees faster reaction.

2) Na_3PO_4 is insoluble in the reaction mixture and stirring is needed to help the mixing of catalyst with the reactants. Acceleration of the rotation speed could make the mixing more efficient and increase the reaction rate. The improvement of the reaction rate by increasing the rotation rate was also observed by other researchers when a different solid base was used (Ma et al. 2008).

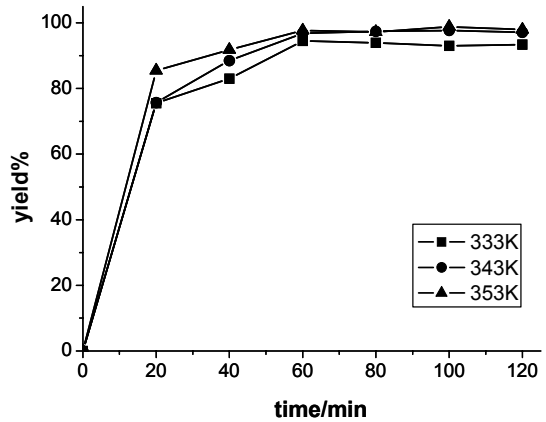

Figure 3: Effect of temperature on biodiesel yield. Mass ratio of catalyst to oil 3%; Molar ratio of methanol to oil 9:1; Rotation speed 400 rpm.

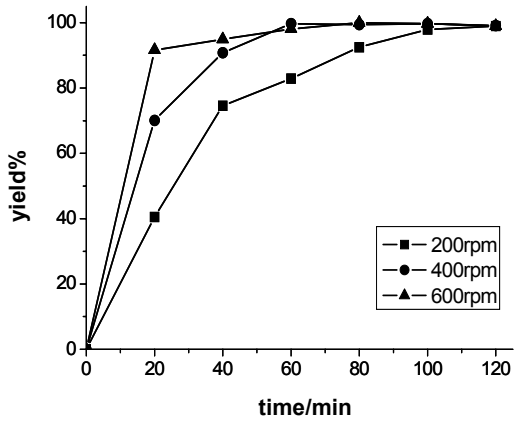

Figure 4: Effect of rotation speed on biodiesel yield. Temperature 343K; Molar ratio of methanol to oil 9:1; Mass ratio of catalyst to oil 3%.

Hydrated and Anhydrous Sodium Phosphates

Both hydrated and anhydrous sodium phosphate can catalyze transesterification (Filippis et al. 2005). In this research, the effect of different sodium phosphates on biodiesel yield was investigated. The result is illustrated in Figure 5, the transesterification reaches equilibrium with Na_3PO_4 or $Na_3PO_4.10H_2O$ as catalyst within 2 hours, but the final yields differ greatly, being 99.7% for Na_3PO_4 and 71.3%.for $Na_3PO_4.10H_2O$. The difference may be caused by saponification with $Na_3PO_4.10H_2O$.

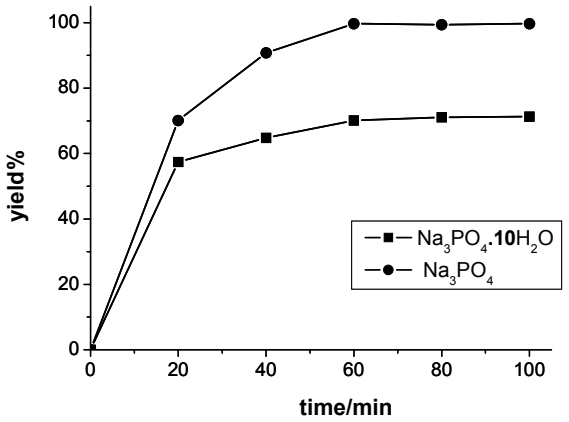

Figure 5: Effect of different catalysts on biodiesel yield. Reaction proceeded for 2 hours under the conditions as follows: temperature 343K; mass ratio of catalyst to oil 3%; molar ratio of methanol to oil 9:1; rotation speed 400rpm.

Catalyst Solubility

Biodiesel catalyzed under different conditions was subjected to AAS analysis to determine the catalyst content. The analytical results are listed in Table 3. In all experiments, catalyst contents slightly increased with the increase of the variable parameter when the fixed parameters were the same, but ranged from 0.6 to 0.7 mg/g biodiesel. The data indicated that 15% of the Na_3PO_4 dissolved after the completion of the transesterification. The catalyst concentration was very low, equivalent to just 0.2%NaOH (Arzamendi et al. 2008), but in our experiments only about 3-3.5% of the calculated Na_3PO_4 was lost when the mass ratio of catalyst to oil was 2%. Most of the catalyst was preserved after reaction and easily separated by centrifugation. Biodiesel yields after 80 minutes of reaction are also listed in the table. There seemed to be an interrelation between the biodiesel yield and the catalyst content. An increase in the biodiesel caused an increase in the catalyst content. Thus the dissolution of Na_3PO_4 could by partly, if not completely, attributed to the existence of fatty acid methyl esters.

Catalyst Reusability

Reusability is one of the most important properties of a solid catalyst. In this experiment, the reactants and catalyst were introduced into the round bottom flask for transesterification, catalyst was collected after the reaction and fresh reactants added without any treatment, Biodiesel yield, determined after each catalyst collection, was employed to evaluate the reusability. The operating conditions, i.e., a temperature of 343K, mass ratio of catalyst to oil of 3%, molar ratio of methanol to oil of 9:1, rotation speed of 400rpm and reaction time of 2h were determined by the operational parameters employed in the reactor. Under those conditions, a high biodiesel yield was obtained. The result is illustrated in Figure 6. Biodiesel yields exhibited no apparent decrease and surmounted 93% in every run for 8 runs. The reusabilities of different solid bases for biodiesel preparation varied greatly: SrO maintained sustained activity even after being used for 10 cycles and the biodiesel yield was only slightly decreased (Liu et al. 2007); for alkaline metal supported catalyst, such as $K/\gamma\text{-}Al_2O_3$, a large catalyst activity loss could be observed even when recycled twice, potassium leaching being confirmed by instrumental methods (Alonso et al. 2007). Na_3PO_4 showed similar reusability with SrO. Unlike $K/\gamma\text{-}Al_2O_3$, which lost activity severely during reaction, Na_3PO_4 kept 85% of its initial amount up to the 8th run, as calculated from Table 3. Small loss of the catalyst is an important factor for good catalyst reusability.

Comparison of Different Heterogeneous and Homogeneous Catalysts with Na_3PO_4

Table 4 lists different heterogeneous and homogeneous catalysts and their highest biodiesel yields under the optimum operating conditions. Both animal fats and vegetable oils were employed. Compared to homogeneous catalysts, a large majority of the heterogeneous catalysts required a longer reaction time and sometimes a larger catalyst amount (5.52 wt% for KF/ZnO and 25wt.% for calcined oyster shell) to finish the reaction. The biodiesel yields for heterogeneous catalysts were also lower than those for homogenous catalysts. Na_3PO_4 had a better catalytic performance than most of the heterogeneous catalysts listed except for SrO, for which it took only 20 min to obtain a 94.9% biodiesel yield. The reaction time for Na_3PO_4 could compete with homogeneous catalysis, though the final biodiesel yield was a little lower. To complete the reaction, a higher methanol to oil molar ratio than in homogeneous catalysis was required in the

transesterification with Na_3PO_4. Homogeneous catalysts achieved the best biodiesel yields in the temperature range from 303K to 338K. The temperature in this work was 343K, close to the upper limit of homogeneous catalysis. The optimum catalyst to oil ratio was 3%, which was 2-3 fold higher than its homogeneous counterpart. Considering the reusability, Na_3PO_4 has an advantage over homogeneous catalyst in this respect. Overall, Na_3PO_4 is a prominent solid catalyst for biodiesel preparation and its activity can match that of a homogeneous catalyst.

Table 3: Catalyst content in biodiesel prepared under different conditions

Fixed parameter	Variable parameter	Catalyst content (mg/g biodiesel)	Biodiesel yields after 80 minutes of reaction
reaction temperature 60℃, rotation speed 400rpm, molar ratio of methanol to oil 6:1	2%	0.63	94.7
	3%	0.66	95.2
	4%	0.68	97.5
reaction temperature 60℃, rotation speed 400rpm, mass ratio of catalyst to oil 3%	6:1	0.60	93.1
	9:1	0.61	94.1
	12:1	0.66	98.1
molar ratio of methanol to oil 9:1, rotation speed 400rpm, mass ratio of catalyst to oil 3%	333K	0.63	93.9
	343K	0.67	97.2
	353K	0.71	97.4

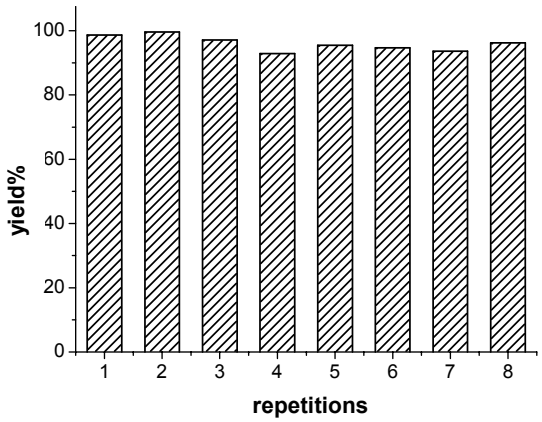

Figure 6: Effect of repeated use of catalyst on biodiesel yield. Experiments were carried out for 2 hours under the following conditions for 2 hours: temperature 343K; mass ratio of catalyst to oil 3%; molar ratio of methanol to oil 9:1; rotation speed 400rpm

Table 4: Comparison of different homogeneous and heterogeneous catalysts for biodiesel preparation

				The optimum operating condition				
Authors	Catalysts	Raw materials	Catalyst amount	Molar ratio of methanol to oil	Reaction temperature	Reaction time	Rotation speed	Biodiesel yield
			1.26%	7.5:1	338K	20 min	—	
Rashid et al. (2008)	sodium hydroxide	crude sunflower oil.	1.00%	6:1	333K	—	—	—
Yang et al. (2009)	potassium hydroxide	vestita fruit oil.	1.0%	6:1	303K	40min	—	Over 99%
Li et al. (2007)	Eu_2O_3/Al_2O_3	soybean oil	—	—	343K	8h	—	—
Nakatani et al. (2009)	calcined oyster shell	soybean oil	25wt.%	—	—	5h	—	70%
Kawashima et al.(2009)	CaO	plant oil.	0.1g	3.9g methanol15g rapeseed oil	333K	3h	—	90%
Zeng et al. (2008)	hydrotalcite	Rape oil	1.5%	6:1	338 K	4h	300 rpm	90.5%
Liu et al. (2007)	SrO	soybean oil	—	—	Below 343K	Within 30min	—	Over 95%
Hameed et al. (2009)	KF/ZnO	Palm oil	5.52wt%	11.43	333K	9.72 h	—	89.23%
This work	Na_3PO_4	Rape oil	3%	9:1	343K	20min	600 rpm	94.9%

— not given in the paper

CONCLUSIONS

The experimental results show that Na_3PO_4 had excellent activity and stability during transesterification. Of all the variables studied, rotation speed had more influence on the yield of the reaction. The dissolution of catalyst in the reaction was very small. During the transesterification of rapeseed oil to biodiesel, the yield attained 95% with a mass ratio of catalyst to oil of 3%, molar ratio of methanol to oil of 9:1, reaction temperature of 343K and rotation speed of 600rpm. At this speed, the reaction reached equilibrium after 20 min. Na_3PO_4 has an activity comparable to homogeneous catalysts. The catalyst was used for 8 runs and no apparent activity loss was observed. The catalyst content in the final product was 0.6-0.7mg/g biodiesel and dissolved Na_3PO_4 accounted for only a very small part of the catalyst which was used. As a solid catalyst, Na_3PO_4 can decrease the cost of biodiesel and the steps of purification. It has potential for industrial application in the transesterification of rapeseed oil to biodiesel.

NOMENCLATURE

A_b	peak area of biodiesel sample	(-)
A_i	peak area of internal standard	(-)
C	Na_3PO_4 content in the methanol solution	mg/mL
FAME	Fatty acid methyl ester	(-)
M	the mass of remaining fraction	g
V	the volume of the methanol solution	mL
m_b	the mass of the biodiesel sample	g
m_i	mass of internal standard	g

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