Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 93–95 (2004) 315–320

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst

Hak-Joo Kim [a], Bo-Seung Kang [a], Min-Ju Kim [a], Young Moo Park [a],
Deog-Keun Kim [b], Jin-Suk Lee [b], Kwan-Young Lee [a,*]

[a] *Department of Chemical and Biological Engineering, Korea University, 5-1, Anam-dong, Sungbuk-ku, Seoul 136-701, Republic of Korea*
[b] *Biomass Research Team, Korea Institute of Energy Research, 71-2, Jang-dong, Yuseong-ku, Daejon 305-343, Republic of Korea*

Abstract

Biodiesel produced by the transesterification of vegetable oils (VOs) is a promising alternative fuel to diesel regarding the limited resources of fossil fuel and the environmental concerns. In this work, an environmentally benign process for the production of biodiesel from VOs using heterogeneous catalyst was developed. Na/NaOH/γ-Al_2O_3 heterogeneous base catalyst was firstly adopted for the production of biodiesel. A study for optimizing the reaction conditions such as the reaction time, the stirring speed, the use of co-solvent, the oil to methanol ratio, and the amount of catalyst, was performed. The Na/NaOH/γ-Al_2O_3 heterogeneous base catalyst showed almost the same activity under the optimized reaction conditions compared to conventional homogeneous NaOH catalyst. The basic strength of Na/NaOH/γ-Al_2O_3 catalyst was estimated and the correlation with the activity towards transesterification was proposed.

Keywords: Transesterification; Vegetable oil; Methyl ester; Biodiesel; Heterogeneous base catalyst

1. Introduction

Air pollution is one of the most serious environmental problems all over the world. Since diesel engines of buses and trucks exhaust a huge amount of NO_x and particulates, a clean alternative fuel is highly demanded. For the recent few decades, many efforts to develop a clean fuel have been under way in many countries. Among many possible sources, biodiesel fuel derived from vegetable oil (VOs) attracts attention as a promising one to be substituted for conventional diesel fuels [1,2]. Continuously increasing use of petroleum will intensify local air pollution and accelerate the global warming problems caused by CO_2. If pure or blend biodiesel is used as fuel, the net production of CO_2 can be highly suppressed. Sharmer et al. have estimated that in the case of using 1 kg of pure biodiesel instead of the fossil fuel, 3.2 kg of CO_2 production could be reduced [3].

Biodiesel can be blended at any level with petroleum diesel to create a biodiesel blend. It can be used in compression-ignition (diesel) engines with little or no modifications. Biodiesel not only has proper viscosity, boiling point, and high cetane number [4], but also is simple to use, biodegradable, nontoxic, and essentially free of sulfur and aromatics [5].

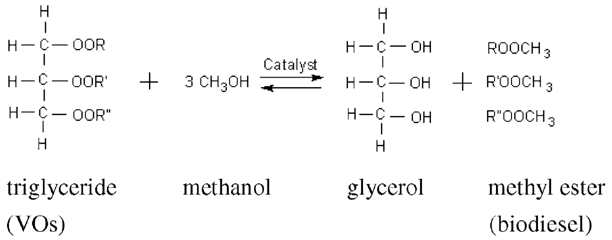
One hundred years ago, Rudolf Diesel tested VOs as fuel for his engine. With the advent of cheap petroleum, appropriate crude oil fractions were refined to be used as fuel, and diesel fuels and diesel engines were evolved together. In the 1930s and 1940s, VOs were used as diesel fuels from time to time, but usually only in emergency situations. Recently, because of rise in crude oil prices, limited resources of fossil oil, and environmental concerns, there has been a renewed focus on VOs to make biodiesel fuels.

Biodiesel has been produced by transesterification of triglyceride (VOs) to methyl esters with methanol using sodium or potassium hydroxide dissolved in methanol as catalyst, as represented by the following equation.

---

[*] Corresponding author. Tel.: +82 2 3290 3299; fax: +82 2 926 6102.
E-mail address: kylee@korea.ac.kr (K.-Y. Lee).

0920-5861/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2004.06.007



In this conventional method, a large amount of waste water was produced to separate and clean the catalyst and the products. Therefore, for the development of an environmentally benign process and the reduction of the production cost, a new process using heterogeneous catalyst should be introduced.

In this work, Na/NaOH/γ-Al_2O_3 heterogeneous base catalyst was firstly adopted for the production of biodiesel. Na/NaOH/γ-Al_2O_3 catalyst was prepared by the successive treatment of γ-Al_2O_3 with sodium hydroxide and sodium at 320 °C under nitrogen following the method proposed by Suzukamo et al. [6]. In their reports, Na/NaOH/γ-Al_2O_3 catalyst had basic sites stronger than $H_- = 37$ and exhibited high activity on olefin isomerization. The formation of the basic sites was studied with XRD, XPS and TPD analysis. And then, a correlation between the basic strength and the activity towards transesterification was proposed.

2. Experimental

2.1. Preparation of the catalyst

To eliminate chemical species adsorbed on the surface, γ-Al_2O_3 was pretreated at 550 °C for 12 h. The pretreated γ-Al_2O_3 was introduced into a stainless steel vessel equipped with a continuous stirring system, a nitrogen flow line, and two small solid reagent holders cooled to ambient temperature with cold circulating water flow. The vessel was heated up to 320 °C, into which predetermined amount of sodium hydroxide had kept in the reagent holder was added (0–30 wt.%). The stirring was continued for 3 h at the same temperature to give white solid. Then, metal sodium which had kept in the other reagent holder was added thereto (0–30 wt.%). The reaction mixture was stirred for another hour at the same temperature. The fresh catalyst was kept in a desiccator until the reaction. The apparatus used for the preparation of the catalyst is described in Fig. 1.

2.2. Characterization of the catalyst

The BET surface area and pore volume of the prepared catalysts were measured with ASAP 2010. The XPS spectra were recorded on ARIESARSC 10MCD 150 (VSW) spectrometer equipped with a monochromatized Mg Kα X-ray source of 1253.6 eV with a resolution of 0.7 eV and a hemispherical analyzer. Binding energies were referenced by setting the CH_x peak maximum in the resolved C 1s spectra to 284.8 eV. All samples were introduced into the preparation chamber of the spectrometer in UHV.

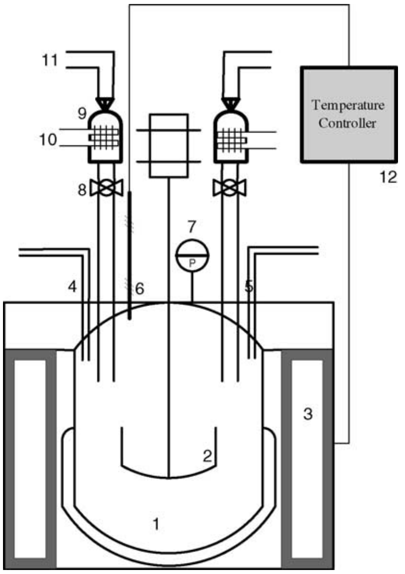


Fig. 1. Scheme of catalyst preparation apparatus. (1) Vessel, (2) stirrer, (3) furnace, (4) N_2 flow inlet, (5) N_2 flow outlet, (6) thermocouple, (7) pressure gauge, (8) ball valve, (9) reagent holder, (10) cooling jacket, (11) N_2 flow in (12) temperature controller.

The XRD analysis was performed with MAC Science X-ray diffraction system (MXP3A-HF) with a Cu Kα X-ray source.

The CO_2 temperature programmed desorption (TPD) analysis was performed with a stainless steel 3/8 in. reactor equipped by a on-line gas chromatography (Younglin M600). The catalyst was pretreated at 120 °C for 2 h under He flow and cooled at room temperature, then heated to 600 °C at 1 °C/min. The signals from thermal conductivity detector (TCD) were collected by a Pentium IBM compatible personal computer.

2.3. Reaction

A 100 ml stainless steel batch reactor (Autoclave Engineers) equipped with a stirrer and a cooling jacket surrounded by a heating mantle controlled by a proportional integral derivative (PID) temperature controller was used for the transesterification of VO (soy bean oil) to biodiesel. Fifty milliliters of soy bean oil, 18.3 ml of methanol (molar ratio of methanol to soy bean oil 9:1) and 10 ml of *n*-hexane were added with 1 g of catalyst into the reactor, and then the temperature was raised to 60 °C under stirring at 300 rpm. The transesterification was carried out for 2 h. Samples were taken out from the reaction mixture and biodiesel portions were separated by means of centrifuge. The concentrations of biodiesel were analyzed by gas chromatography (GC). The soy bean oil was of commercial edible grade. Compositions of fatty acids in triglycerides were adopted from the literature shown in Table 1 [7].

Table 1
Fatty acid compositions of soy bean oil

Acidity index	Composition (wt.%)
Palmitic (C16:0)[a]	11
Stearic (C18:0)	4
Oleic (C18:1)	23
Linoleic (C18:2)	54
Linoleic (C18:3)	8

[a] Numbers in parenthesis signify the number of carbon atoms and the unsaturated centers (double bonds).

Reference materials and samples were analyzed by a gas chromatography (DONAM DS6200), equipped with a capillary column (Agilent INNOWAX, 30 m × 0.53 mm × 1 μm) and a flame ionization detector (FID). Helium was used as the carrier gas. The injection was performed in split mode with a split ratio of 100:1. The analysis of biodiesel for each sample was carried out by dissolving 1 ml of biodiesel sample into 5 ml of *n*-hexane and injecting 0.5 μl of this solution in GC, in the same condition described as above. The conversion of oil to biodiesel was calculated from the content of methyl esters analyzed by GC with the following equation:

$$\text{Conversion (\%)} = \frac{(\text{weight of biodiesel produced}/\text{MW of biodiesel}) \times \text{biodiesel conc.}}{(\text{weight of oil}/\text{MW of oil}) \times 3} \times 100$$

Molecular weights of biodiesel and oil were calculated according to the compositions of fatty acids in Table 1. The factor 3 in the formula was taken for the fact that each triglyceride molecule yields three methyl ester molecules.

3. Results and discussion

3.1. Catalyst characterizations

The measured BET surface area, pore volume, and pore diameter are shown in Table 2. The BET surface areas as well as the pore volumes decreased with loading sodium and sodium hydroxide, and this tendency was more outstanding in the case of sodium. As shown in the XRD analysis presented in Fig. 2, sodium aluminate was formed by the introduction of the sodium hydroxide. The crystal structure of sodium aluminate seems to be formed by the reaction with γ-Al_2O_3 according to the following equation:

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$$

Table 2
BET surface areas, pore volumes and pore diameters of the prepared catalysts

Catalyst	BET area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)
γ-Al_2O_3	143.1	0.481	134.3
NaOH/γ-Al_2O_3	120.7	0.416	137.8
Na/γ-Al_2O_3	97.7	0.362	148.2
Na/NaOH/γ-Al_2O_3	83.2	0.322	155.0

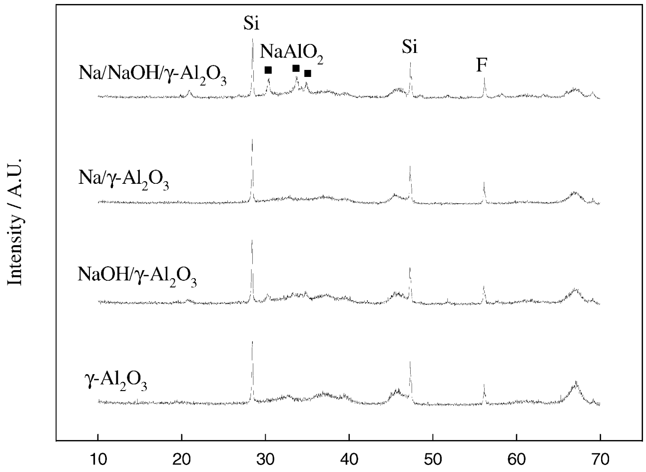


Fig. 2. XRD patterns of the prepared catalysts.

As for the sodium, there was no evidence of existence of sodium metal on the surface of γ-Al_2O_3 and other crystal structure formed with γ-Al_2O_3. As shown in the XPS results (Fig. 3), the binding energies of O 1s orbital of NaOH/γ-Al_2O_3 and Na/γ-Al_2O_3 catalysts shifted to lower binding energy compared to that of γ-Al_2O_3, which means the increase of the electron pair donating ability of the surface oxygen atom. This increased electron pair donating ability was supposed to originate the formation of basic sites. Furthermore, in the case of Na/NaOH/γ-Al_2O_3, the chemical shift of the binding energy of O 1s orbital was intensified, which indicates a formation of stronger basic sites. Similarly with the XRD analysis, no information of the state of sodium was obtained from the XPS analysis. For the case of alkali doped MgO catalysts reported in many literatures, superbasic sites were generated from the electron donated by the alkali metal to the oxide lattice [8]. This was generally believed to reside in a defect site

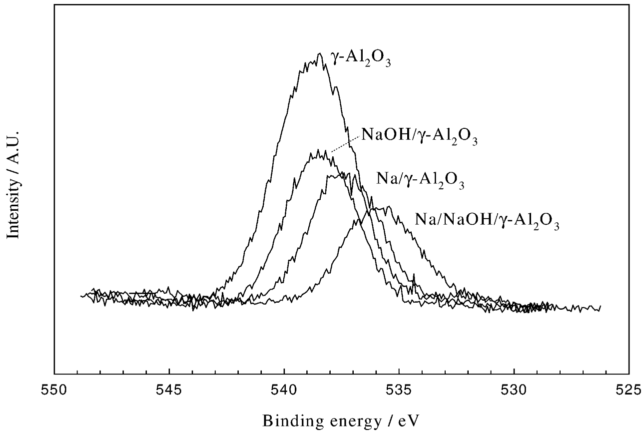


Fig. 3. XPS analysis of O 1s orbital of the prepared catalysts.

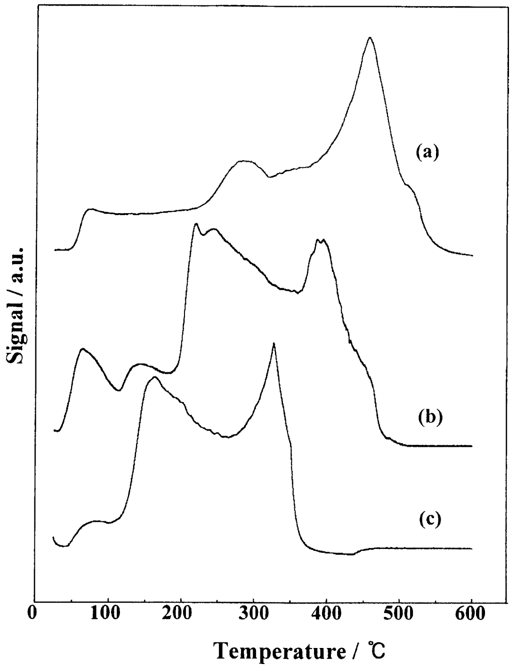


Fig. 4. TPD analysis of CO_2 for the prepared catalysts: (a) Na/NaOH/γ-Al_2O_3, (b) Na/γ-Al_2O_3, (c) NaOH/γ-Al_2O_3.

such as an oxygen vacancy [9]. Similarly, it was supposed that the loaded sodium was completely ionized and dispersed into the defect sites of γ-Al_2O_3 structure formed during the thermal pretreatment, which caused to increase the electron pair donating ability of the surface oxygen atom.

From the temperature programmed desorption (TPD) analysis of CO_2 shown in Fig. 4, Na/NaOH/γ-Al_2O_3 catalyst had stronger base sites than Na/γ-Al_2O_3 and NaOH/γ-Al_2O_3 catalyst, which explained well the XPS and XRD analysis results. On the other hand, three catalysts have nearly same area of CO_2 desorption peak. It means that the basic concentration is not so much different from each other.

Taking all the information obtained from the catalyst characterization into account, we can finally conclude that both the sodium aluminate formed by loading sodium hydroxide on γ-Al_2O_3, and the ionization of sodium, originated the stronger basic sites of the catalysts.

3.2. Reaction

The activities of the catalysts having different basic strength toward transesterification were measured. From the results presented in Fig. 5, the activities of the catalysts could be correlated to their basic strength which was estimated by the shift of XPS. The most active catalyst was found to be Na/NaOH/γ-Al_2O_3 which had the highest basic strength as mentioned above. Among the Na/NaOH/γ-Al_2O_3, a catalyst containing 20 wt.% of Na and 20 wt.% of NaOH showed the highest activity.

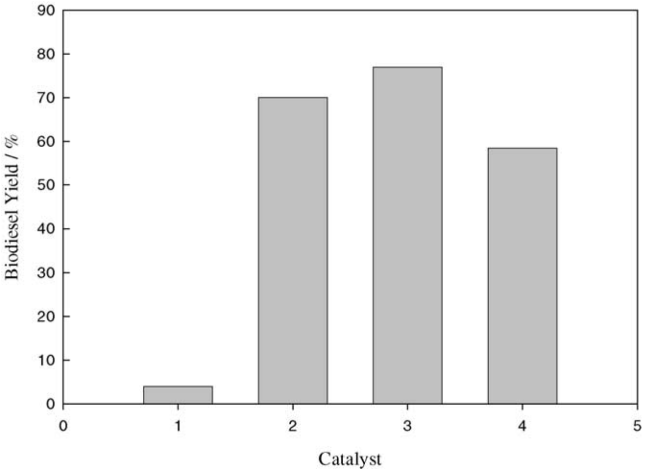


Fig. 5. Effect of basic strength on the biodiesel production yield. (1) γ-Al_2O_3, (2) Na/γ-Al_2O_3, (3) Na/NaOH/γ-Al_2O_3, (4) NaOH/γ-Al_2O_3. Methanol/VO molar ratio 6:1, reaction temperature 60 °C, stirring speed 300 rpm, without co-solvent.

As shown in Fig. 6, the maximum biodiesel production yield was reached within 1 h both for the case of homogeneous and heterogeneous catalyst system. For the homogeneous catalyst system, the maximum biodiesel production yield was higher by 20% than that of the heterogeneous catalyst system. However, since the reaction conditions adopted were what were optimized for the homogeneous catalyst system, the optimum reaction conditions for heterogeneous catalyst system to maximize the biodiesel production yield were surveyed.

First, the effect of mixing was investigated. Basically, methanol and VOs were immiscible [10]. In the homogeneous system, the catalyst of NaOH acted as a solvent that made the reactants be miscible. When the NaOH catalyst was loaded to the reactor with methanol, small bubbles were formed and the transesterification took place on the

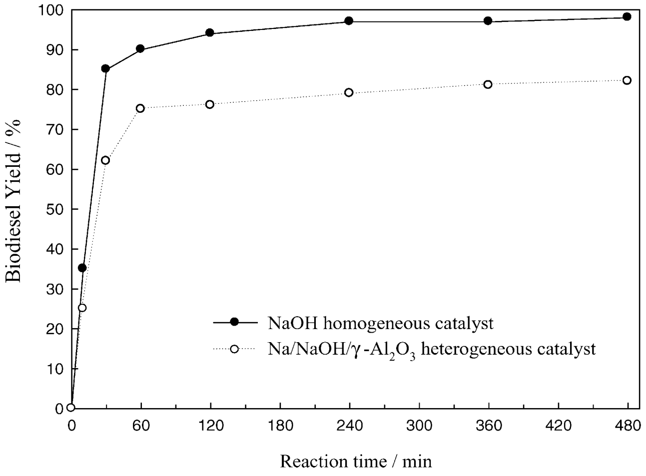


Fig. 6. Effect of reaction time on the biodiesel production yield. Methanol/VO molar ratio 6:1, reaction temperature 60 °C, stirring speed 300 rpm, without co-solvent.

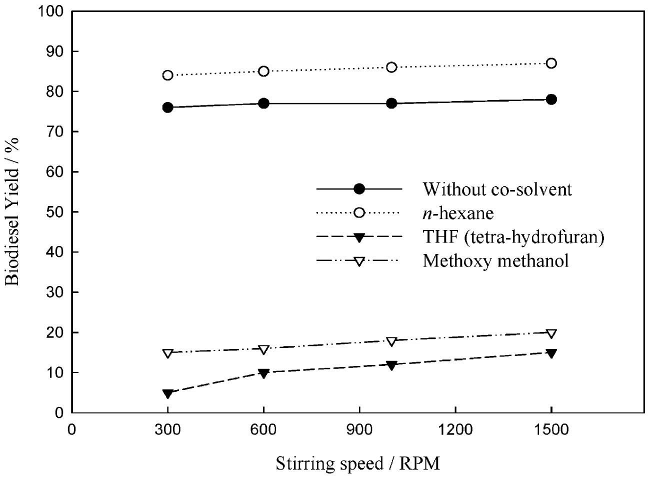


Fig. 7. Effect of mixing on the biodiesel production yield. Methanol/VO molar ratio 6:1, reaction temperature 60 °C, reaction time 2 h, stirring speed 300–1500 rpm, co-solvent, amount of catalyst 1 g.

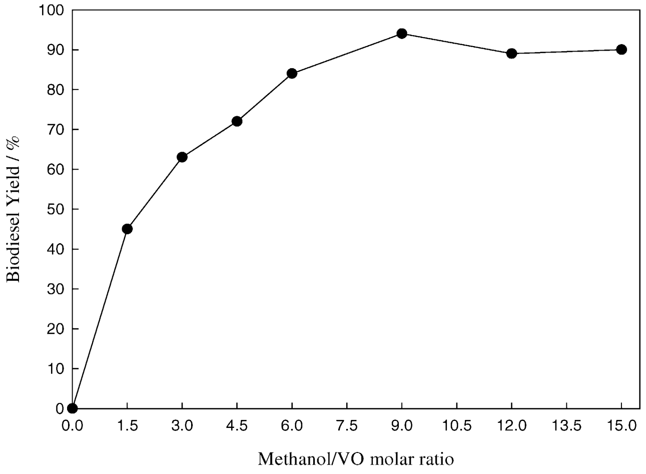


Fig. 8. Effect of methanol feed composition on the biodiesel production yield. Reaction temperature 60 °C, reaction time 2 h, stirring speed 300 rpm, co-solvent *n*-hexane 10 ml, amount of catalyst 1 g.

interface of the reactants. In the heterogeneous system, however, the reactants were separated in two phases by the lack of NaOH, which retarded the reaction rate. To overcome the mixing problems, an appropriate co-solvent had to be introduced. From the result shown in Fig. 7, *n*-hexane was the most effective co-solvent and the biodiesel production yield was increased by 10%. But, the stirring speed almost had no effect on the production yield. Optimum loading amount of *n*-hexane was found to be 5:1 VO to *n*-hexane molar ratio. When *n*-hexane was added, the immiscible two phase system was changed to the homogeneous emulsion state.

The stoichiometric molar ratio of methanol to VO was 3:1 as mentioned above. But when mass transfer was limited due to problems of mixing, the mass transfer rate seemed to be much slower than the reaction rate, so the production yield could be elevated by introducing excess amount of the reactant methanol to shift the equilibrium to the right-hand side. As represented in Fig. 8, by increasing the methanol loading amount, biodiesel production yield was increased considerably. The optimum molar ratio of methanol to VO was found to be 9:1, which was distinguished from the value for homogeneous catalyst system [11,12]. Beyond the molar ratio of 9:1, the excessively added methanol had no significant effect on the production yield. Therefore, we could conclude that to elevate the biodiesel production yield an excess methanol feed was effective to a certain extent.

When increasing the amount of loading catalyst, the slurry (mixture of catalyst and reactants) became too viscous giving rise to a problem of mixing and a demand of higher power consumption for adequate stirring. On the other hand, when the catalyst loading amount was not enough, maximum production yield could not be reached. To avoid this kind of problem, an optimum amount of catalyst loading had to be investigated. As shown in Fig. 9, the optimum catalyst loading amount was found to be 1 g in this system. The maximum biodiesel production yield reached to 94%, which was almost the same value compared to the conventional homogeneous NaOH catalyst system.

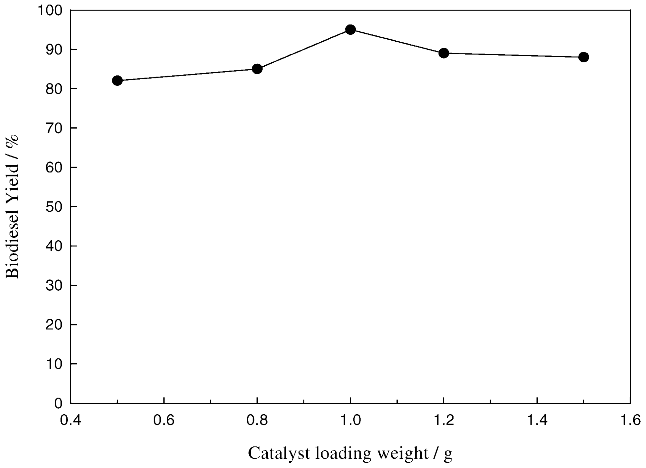


Fig. 9. Effect of the catalyst amount on the biodiesel production yield. Methanol/VO molar ratio 9:1, reaction temperature 60 °C, reaction time 2 h, stirring speed 300 rpm, co-solvent *n*-hexane 10 ml.

4. Conclusions

Na/NaOH/γ-Al_2O_3 heterogeneous base catalyst was firstly used for the production of biodiesel from the soybean oil. Both the sodium aluminate formed by loading sodium hydroxide on γ-Al_2O_3, and the ionization of sodium, originated the strong basic sites of the catalysts. The activities of the heterogeneous base catalysts correlated with their basic strengths. The reaction conditions for the system were optimized to maximize the biodiesel production yield. A utilization of a co-solvent was found to be inevitable for the transesterification of VOs to biodiesel. Among the co-solvent tested, *n*-hexane was the most effective with a loading amount of 5:1 VO to *n*-hexane molar ratio. The optimum methanol to oil loading ratio was found to be 9:1. The Na/NaOH/γ-Al_2O_3 heterogeneous base catalyst showed almost the same activity under optimized reaction conditions compared to the conventional homogeneous NaOH catalyst.

Acknowledgements

The authors appreciate the support by research grants from the Korea Science and Engineering Foundation (KOSEF) through the Applied Rheology Center (ARC) at Korea University.

References

[1] D. Laforgia, V. Ardito, Bioresource Technol. 51 (1995) 53.
[2] L.G. Schumacher, S.C. Borgelt, D. Fosseen, W. Goets, W.G. Hires, Bioresource Technol. 57 (1996) 31.
[3] K. Sharmer, Umweltaspekte bei Herstellung und Verwendung von RME, in: RME Hearing, Ministry for Agriculture, Vienna, Austria, 1993.
[4] T.W. Ryan, L.G. Dodge, T.J. Callahan, JAOCS 61 (1984) 1610.
[5] A. Srivastava, R. Prasad, Renew. Sustain. Energy Rev. 4 (2000) 111.
[6] G. Suzukamo, M. Fukao, M. Minobe, Chem. Lett. (1987) 585.
[7] F.D. Gunstone, Fatty Acid and Lipid Chemistry, Blackie Academic & Professional, Chapman & Hall, London, 1996, p. 61.
[8] A.M. Ferrari, G. Pacchioni, J. Phys. Chem. 99 (1995) 17010.
[9] H. Matsuhashi, M. Oikawa, K. Arata, Langmuir 16 (2000) 8201.
[10] D.G.B. Boocock, S.K. Konar, H. Sidi, JAOCS 73 (1996) 1247.
[11] B. Freedman, E.H. Pryde, T.L. Mounts, JAOCS 61 (1984) 1638.
[12] Y.C. Bak, J.H. Choi, S.B. Kim, D.W. Kang, Kor. J. Chem. Eng. 13 (1996) 242.