Korean J. of Chem. Eng., 13(3), 242-245 (1996)

PRODUCTION OF BIO-DIESEL FUELS BY TRANSESTERIFICATION OF RICE BRAN OIL

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(Received 7 July 1995 • accepted 2 March 1996)

Abstract – Transesterification of rice bran oil was investigated to produce the bio-diesel oil. Experimental conditions included molar ratio of rice bran oil to alcohol (1 : 3, 1 : 5 and 1 : 7), concentration of catalyst used (0.5, 1.0 and 1.5 wt%), types of catalysts (sodium methoxide, NaOH and KOH), reaction temperatures (30, 45 and 60°C) and types of alcohols (methanol, ethanol and butanol). The conversion of rice bran oil increased with the alcohol mixing ratio and with the reaction temperature. Sodium methoxide was the most effective among the catalysts. The conversion was increased with the concentration of catalyst, but slightly increased over 1.0 wt%. The best conversion was obtained using methanol with sodium methoxide. In that case, 98% conversion was achieved within 1 hr. The physical properties of rice bran oil for diesel fuel can be significantly improved by transesterification reaction.

Key words: Transesterification, Alcoholysis, Rice Bran Oil, Bio-Diesel, Bio-Fuel

INTRODUCTION

Alternative fuel of diesel engine that is derived from the oils and fats of plants was used for the first time at the 1900 paris exhibition by running a diesel engine with peanut oil, but it didn't meet with public approval because of economical problem. The oil crisis after the two consecutive OPEC oil embargo necessitated developing alternative sources of energy from renewable resources. Also, the pollution problem of exhaust gas from the diesel engine is all the more at issue today, because in case of gasoline engine, the pollutant such as CO, HC, and NO_x can be reduced more than 90% by using a ternary catalyst. Of the total emissions exhausted from the cars in Korea in 1990, significant portions of pollution substances were found to come from diesel engine, i.e., 33% of CO, 37% of HC, 83% of NO_x, 92% of SO_2 and 90% particulate [Kim 1992]. Especially, particulates were considered a very serious harmful matter because they contain carcinogenic substance like polynuclear aromatic compounds.

Bio-diesel fuel as a renewable energy is an alternative liquid fuel that can help reduce energy dependence on petroleum and that contributes little net pollution substances to the atmosphere. Oils and fats have heat contents approximately 90% of that of NO.2 diesel fuel, but their viscosities are nearly 10 times or more than that of NO.2 diesel fuel. This high viscosity causes durability problem in the engine, such as poor atomization of the fuel, incomplete combustion, coking of the fuel injectors, accumulation of fuel in the lubricating oil and so forth. In order to solve these problems, dilution, microemulsification, pyrolysis, and transesterification have been devised. Among these techniques, chemical conversion of the oil through transesterification with short-chain alcohols, such as methanol and ethanol, to its corresponding fatty ester appears to be the most promising solution.

The overall objective of this study was to investigate the important parameters of the transesterification process using rice bran oil and alcohol. The rice bran oil is producing from rice flour, which is the most readily available vegetable oil source in Korea.

EXPERIMENTAL

1. Materials and Reaction

The vegetable oil used in this study was rice bran oil. Its general properties and the fatty acid composition are listed in Table 1. As shown in the Table 1, the major components of the rice bran oil were about 71% of oleic acid, 18% of palmitic acid and 11% linoleic acid.

A 1000 ml 3-necked flask equipped with mechanical stirrer and thermometer was heated by heating mantle. Alcohols used in this study were methanol, ethanol and butanol, and the molar ratios of rice bran oil to alcohol were 1 : 3, 1 : 5 and 1 : 7. Sodium methoxide (S.M.), sodium hydroxide (NaOH) and potassium hydroxide (KOH) as the catalyst were used in the concentrations of 0.5, 1.0 and 1.5 wt% based on the weight of rice

Table 1. The properties of rice bran oil sample

Acid value		0.157
Saponification value		202.7
Iodine value		134
Density (17°C)		0.929 g/cm^3
Viscosity (17°C)		93cP
Refractive index (17°C)		1.4775
Fatty acid composition wt%	palmitic	17.99
	stearic	0.668
	oleic	70.667
	linoleic	10.65
	linolenic	0.005

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bran oil. The reaction temperature was in the range of 30, 45 and 60°C. To carry out a reaction, the rice bran oil (200 g) was mixed with the selected alcohol and catalyst, and then heated to the desired reaction temperature. At the end of the reaction, the reaction mixture was cooled to the room temperature and taken into a separatory funnel where the ester and glycerol layers separated. Excess methanol in the ester layer was removed by distillation at atmospheric pressure. The ester was purified further by dissolving in petroleum ether (operating temperature 35-60°C), washing with water, adjusting pH to 7 with glacial acetic acid or phosphoric acid, washing 3 times with water, drying the petroleum ether solution over magnesium sulfate, filtering and distilling at atmospheric pressure. The amount of glycerol produced was measured and the conversion was calculated. The rotary VT-30 Viscometer and the 106 Refractometer were used to measure viscosities and refractive indexs, respectively.

2. Analytical Methods

The glycerol in products was determined by ASTM 1615-60 method and the conversion of rice bran oil was calculated by the following formula.

$$\text{Conversion}(\%) = \frac{\text{Amount of glycerol produced actually}}{\text{Amount of glycerol produced stoichiometrically}} \times 100$$

Acid value, saponification value and iodine value of the rice bran oil were determined by KS H2101 method. Average molecular weight (M) of the oil was related to the saponification value as follows.

$$M = \frac{3 \times 56100}{\text{Saponification value}}$$

Fatty acid composition of rice bran oil was determined by Waters 201 HPLC with R.I. detector, after converting the rice bran oil to the corresponding fatty acids. μ-Bondapax C18 column and mixing solvent ($MeOH : H_2O : CHCl_3 = 70 : 19 : 10$) was used.

RESULTS AND DISCUSSION

1. Effect of Alcohol Mixing Ratio on Conversion

One of the most important variables affecting the transesterification is the molar ratio of vegetable oil to alcohol. The oil conversion with time was investigated at various molar ratios of rice bran oil to alcohol at 0.5 wt% catalyst concentration.

Fig. 1 shows the conversion of rice bran oil to ester with 0.5 wt% S.M. In the 60 min reaction time, 56, 71 and 98% of oil conversions were observed at the molar ratio of 1 : 3, 1 : 5 and 1 : 7, respectively. The highest conversion was achieved in 1 : 7 molar ratio. 81, 89 and 98% of conversions were obtained at the reaction times of 8, 30 and 60 min, respectively. The oil conversion increased with the increase in the excess amount of alcohol, and the increase of reaction time. When NaOH and KOH were used as the catalyst, the results obtained from the methanolysis of rice bran oil were similar to that obtained from S.M..

Bradshow [1942] and Bradshow and Meuly [1944] stated that 1 : 4.8 molar ratio of vegetable oil to methanol led to 98%

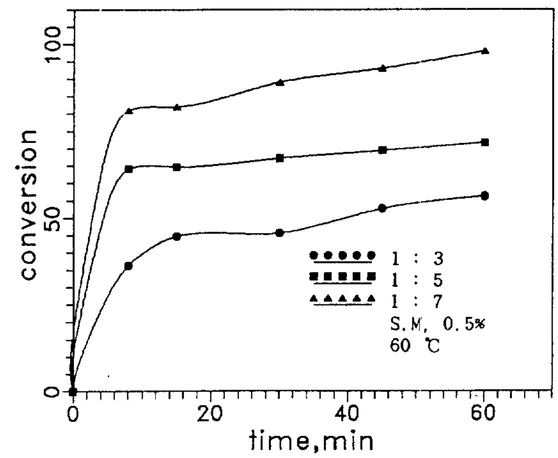

Fig. 1. The effect of methanol mixing ratio on conversion.

conversion. They noted that ratio greater than 1 : 5.25 interfered gravity separation of the glycerol. But Lehman and Gauglitz [1963] obtained more high oil conversions with 1 : 6 molar ratio of vegetable oil to methanol than with 1 : 3 molar ratio.

Freedman et al. [1984] studied the methanolysis of sunflower oil at various molar ratio of sunflower oil to methanol from 1 : 1 to 1 : 6, and the conversion of 82% and 98% were obtained at 1 : 3 and 1 : 6 molar ratios, respectively. Also, they investigated the methanolysis of 4 refined vegetable oils (soybean, sunflower, peanut and cotton seed oils) at 1 : 6 molar ratio and 0.5 wt% S.M. as the catalyst. After 1 min of reaction time, about 80% conversion was observed for soybean and sunflower oils, while about 53% conversion for peanut and cotton seed oils. But, after 1 hr, the conversions of methyl ester were reached to 92-98% for all 4 oils, meaning that the types of oil do not affect much on oil conversion after sufficient reaction time.

In this study, though lower than 1 : 5.25 molar ratio of vegetable oil to methanol was used, the glycerol and the ester was sucessfully separated gravitationally.

2. Effect of Catalyst Type and Concentration on Conversion

The catalysts for transesterification reaction can be divided into alkali catalyst and acid catalyst. In this study, alkali catalysts (S.M., NaOH and KOH) were used and the concentrations of catalysts were 0.5, 1.0 and 1.5 wt% based on the weight of rice bran oil. The molar ratio of rice bran oil to methanol was fixed to 1 : 5 for S.M. and NaOH, but 1 : 3 for KOH. The different molar ratio was used because of difficulty in product separation into ester and glycerol layers when the concentrations of S.M. and NaOH was 1.0 wt%. The reaction temperature was set at 60°C.

The effect of the catalyst concentration on the conversion was shown in the Fig. 2. As the concentrations of catalysts were changed to 0.5, 1.0 and 1.5 wt%, the conversions were increased 64-92, 80-90 and 86-94%, respectively. Similar results were obtained when using NaOH and KOH.

Freedman et al. [1984] studied the transesterification of soybean oil with acid catalyst (1.0 wt% H_2SO_4) and alkali catalyst (0.5 wt% S.M.). The conversion with alkali catalyst was 98% within 1 hr in the condition of methanol mixing ratio 1 : 6. But, for acid catalyst (1 wt% H_2SO_4), conversions were unsatisfac-

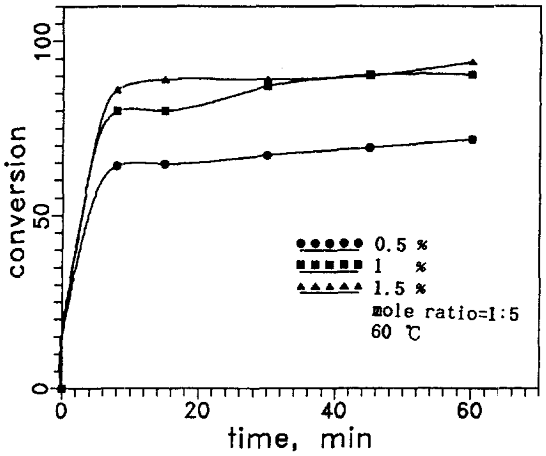

Fig. 2. The effect of concentration of sodium methoxide on conversion.

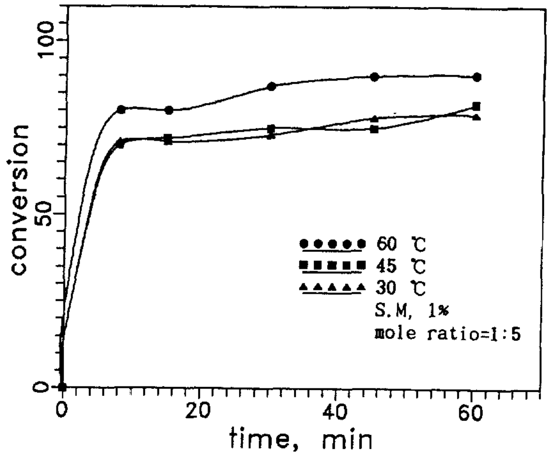

Fig. 4. The effect of reaction temperature on conversion.

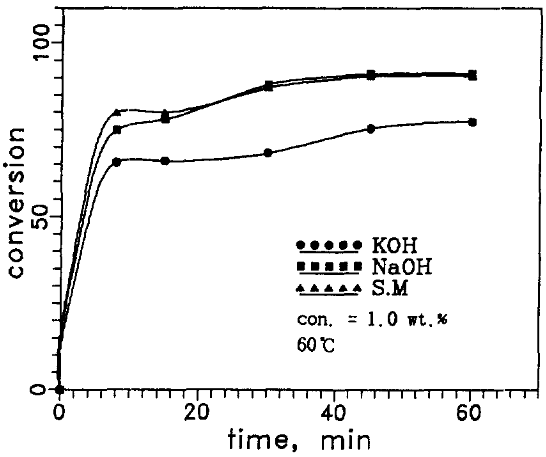

Fig. 3. The effect of catalyst type on conversion.

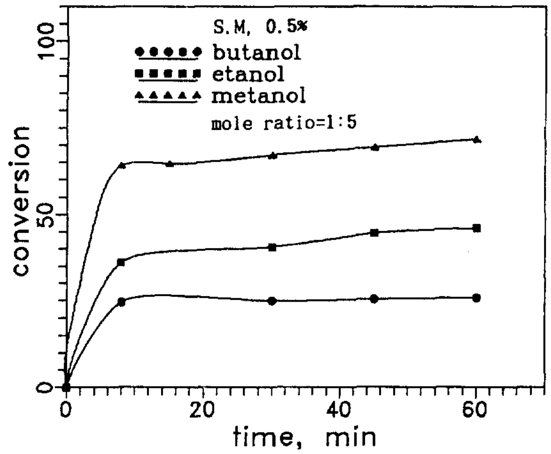

Fig. 5. The effect of alcohol type on conversion.

tory with 1 : 6 and 1 : 20 mixing ratios at the reaction time of 3 and 18 hr, and 95-98% conversion were obtained at the 1 : 30 molar ratio. Keim [1954] reported that alkali catalysis was faster than acid catalysis for the alcoholysis of oils. Freedman et al. [1984] compared 0.5 wt% S.M. with 1.0 wt% NaOH at 1 : 6 and 1 : 3 molar ratio. At the 1 : 6 molar ratio, conversions for both catalyst were very simlar. However, at the 1 : 3 molar ratio, 0.5 wt% S.M. was clearly superior to 1.0 wt% NaOH during the reaction time of 60 min.

As shown in the Fig. 3, the conversions with S.M. and with NaOH were similar, and higher than with KOH.

3. Effect of Reaction Temperature on Conversion

In order to find the effect of reaction temperature, the molar ratio (1 : 5) and the concentration of catalyst was fixed at 1.0 wt% for S.M. and NaOH, and 0.5 wt% for KOH. As shown in the Fig. 4, the conversions at 30°C, 45°C and 60°C using S.M. were 71-79, 70-82 and 86-94%, respectively. Although the results obtained using NaOH and KOH catalysts were similar to that obtained using S.M., the conversions at the 30°C using NaOH and KOH catalyst were much lower than that at 45°C.

Schwab et al. [1987] studied the effect of reaction temperature with sunflower oil. Reaction temperatures were set at 32°C, 45°C and 60°C in the condition of 1.0 wt% S.M. catalyst. After 6 min, conversions were 64, 87 and 94%, respectively. After 4 hr, conversion to ester was 98% at 32°C. Thus, if reaction time is enough, transesterification of vegetable oil can proceed satisfactorily even at ambient temperature. Shidaran and Mathai [1974] and Markely [1961] reported that the alkali-catalyzed reaction proceeds rapidly at ambient temperature, whereas acid-catalyzed reactions commonly require temperatures above 100°C.

4. Effect of Alcohol Type on Conversion

In order to find the effect of alcohol type on conversion, methanol, ethanol and butanol were used. Reaction temperature was near the boiling point of each alcohol at 0.5 wt% S.M.

The conversion with methanol was the highest among them, and then followed by ethanol and butanol, as shown in Fig. 5. Methanol having low molecular weight requires lower energy to break the hydrogen bond than that for ethanol and butanol, therefore conversion rate in the case of using methanol is the highest among three alcohols.

But some researcher produced different results from us. Schwab et al. [1987] studied the alcoholysis with methanol, ethanol and butanol near the boiling point of each alcohol. The conversions of each alcohol were 78% (MeOH), 75% (EtOH) and 88% (BuOH) after 1 min, and the conversions after 1 hr were almost same, 98%.

Freedman et al. [1984] studied the alcoholysis of sunflower oil with methanol, ethanol and butanol near the boiling point

Table 2. Viscosity of the rice bran oil esters at various temperatures

Tem. \ Cat.	Sodium methoxide	Sodium hydroxide	Potassium hydroxide
17°C	7.3cP	7.5cP	7.5cP
40°C	4.5cP	4.5cP	4.5cP
75°C	2.1cP	2.4cP	2.3cP

Table 3. Comparison of properties of ester fuel and NO.2 diesel fuel

Properties	Rice bran oil ester	Diesel No.2
Cetane index	55.0	45>
Flash point (°C)	-	74
Pour point (°C)	−30.0	−14
Viscosity (40°C) (cP)	4.5	2.4
Carbon (wt%)	77.8	86.6
Hydrogen (wt%)	11.9	13.1
Nitrogen (wt%)	18.4	-
Oxygen (wt%)*	10.29	-
Sulfur (wt%)	0.02	0.3
C/H ratio	6.54	6.61
Specific gravity (15.6°C)	0.853	0.850
95% distillate	80% at 340°C	Max at 360°C
Higher heating value (kcal/kg)	9,414	10,840

*oxygen by difference

of each alcohol by 0.5 wt% S.M.. At the 1 : 6 molar ratio, the conversions for all 3 alcohols were in the nearly same range of 96-98% within 1 hr, whereas, at the 1 : 3 molar ratio, conversions for butanol, methanol and ethanol were 88, 82 and 81%, respectively.

5. Viscosity

The viscosity of ester fuel obtained at each experimental condition was listed in Table 2. The viscosity of ester fuels obtained from methanolysis did not depend on the type of the catalyst, and the viscosity of ester fuels was somewhat higher than that of NO.2 diesel fuel (2.4 cP at 40°C).

Schwab et al. [1987] studied the methyl ester of soybean oil. The viscosities of raw soybean oil and soybean ester were 30.3 cP (37.8°C) and 3.61 cP (40°C), respectively. This was somewhat higher than 2.4 cP (40°C) of NO.2 diesel oil, but much lower than that of raw soybean oil.

As shown in the table, the viscosity of rice bran oil ester was much lower compared to 93 cP (at 17°C) of raw rice bran oil.

6. Comparison of Properties

Table 3 listed comparing the physical properties of ester oil with that of the No.2 diesel fuel. The viscosity and cetane index of bio-diesel fuel were somewhat higher than that of diesel fuel.

CONCLUSION

Transesterification was investigated using rice bran oil. As the excess amount of alcohol increased, the conversion was increased. Among the catalysts, sodium methoxide (S.M.), NaOH and KOH, the most effective one was S.M. at 1.0 wt%. The conversion of rice bran oil increased with the reaction temperature. The conversion of transesterification by methanol was the highest among methanol, ethanol and butanol. The bio-diesel fuel produced from the rice bran oil had significantly lower viscosity than that of the parent oil, and the cetane index of bio-diesel fuel was somewhat higher than that of No.2 diesel fuel. This results provided a significant insight into the potential use of the bio-diesel as diesel fuel alternative.

ACKNOWLEDGEMENT

This research was financially supported by Korea Science and Engineering Foundation in 1995.

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