

Transesterification of soybean oil using combusted oyster shell waste as a catalyst

Nobutake Nakatani ^{a,b,*}, Hitoshi Takamori ^a, Kazuhiko Takeda ^a, Hiroshi Sakugawa ^a

^a *Graduate School of Biosphere Science, Hiroshima University, 1-7-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8521, Japan*

^b *Graduate School for International Development and Cooperation, Hiroshima University, 1-5-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8529, Japan*

* Corresponding author. Tel.: +81 82 424 6504; fax: +81 82 424 6504.

E-mail address: nnakatan@hiroshima-u.ac.jp (N. Nakatani)

Abstract

Transesterification of soybean oil catalyzed by combusted oyster shell, which is waste material from shellfish farms, was examined. Powdered oyster shell combusted at a temperature above 700°C, at which point the calcium carbonate of oyster shell transformed to calcium oxide, acted as a catalyst in the transesterification of soybean oil. On the basis of factorial design, the reaction conditions of catalyst concentration and reaction time were optimized in terms of the fatty acid methyl ester concentration expressed as biodiesel purity. Under the optimized reaction conditions of a catalyst concentration and reaction time of 25% wt. and 5 h, respectively, the biodiesel yield, expressed relative to the amount of soybean oil poured into the reaction vial, was more than 70% with high biodiesel purity. These results indicate oyster shell waste combusted at high temperature can be reused in biodiesel production as a catalyst.

Keywords: Biodiesel; Factorial design; Fatty acid methyl ester; Oyster shell; Soybean oil;

Transesterification

1. Introduction

Biodiesel is an alternative fuel for diesel engines that is gaining attention in terms of the depleting fossil fuel resources of the world and the mitigating of greenhouse effects due to carbon dioxide. The primary advantages of using a biodiesel are that it is one of the most renewable fuels available and it is also non-toxic and biodegradable (Van Gerpen et al., 2004). In addition, this fuel can be used directly or mixed with conventional fuel for most diesel engines without requiring extensive engine modifications (Van Gerpen, 2005).

Fatty acid methyl esters (FAMES) are major components of biodiesel produced by chemically reacting vegetable oils or animal fats with an alcohol such as methanol and ethanol in a process called transesterification or alcoholysis. The transesterification of oils and fats with methanol can be conducted using homogenous and heterogeneous catalysts (Meher et al., 2006). Alkali-hydroxides such as sodium and potassium hydroxides are more effective homogenous catalysts, while an acid catalyst is suitable for the transesterification of oil and fat containing high concentrations of free fatty acid and water (Ma and Hanna, 1999). However, a large amount of wastewater is discharged in removing alkali-hydroxide dissolved in transesterified product and there is loss of the product due to soap formation (Kouzu et al., 2006). On the other hand, the use of heterogeneous catalyst simplifies greatly the technological process by facilitating the separation of the post-reaction mixture (Gryglewicz, 1999; Suppes et al., 2004), although transesterification proceeds at a relatively slow

rate (Peterson and Scarrah, 1984). Alkaline-earth metal oxides, especially calcium oxide, were used as heterogeneous catalysts in the transesterification of rapeseed (Peterson and Scarrah, 1984; Gryglewicz, 1999) and soybean (Kouzu et al., 2006) oil in the production of FAME. Since the process of transesterification using both homogenous and heterogeneous catalysts is affected by various factors depending on the reaction conditions, the optimization of the operating conditions in producing biodiesel has been examined by the statistical analysis of the factorial design of experiments and response surface methodology (Vicente et al., 1998, 2007; Ooi et al., 2004; Chang et al., 2005; Albuquerque et al., 2008).

In Japan, oyster farming is one of the major marine aquacultures. The annual production of cultured oyster was over two hundred thousand tons (including oyster shell weight) in 2006, more than half of which was cultured in Hiroshima prefecture (Ministry of Agriculture, Forestry and Fisheries of Japan, 2007), resulting in the production of much oyster shell waste. The disposal of oyster shell waste from shellfish farms is a serious problem. In most cases, the waste has often been left untreated for a long time in the field, giving a nasty smell. To reduce the amount of oyster shell waste, researchers have investigated its use as a construction material (Yoon et al., 2003), a stabilizer of acid sulfate soil (Yamada et al., 2005) and an adsorbent for phosphate (Namasivayam et al., 2005). The dominant component of oyster shell (more than 95%) is calcium carbonate, which is called calcite (Yoon et al., 2003), and it is easy to transform calcium carbonate to calcium oxide by

combustion at high temperature in air. Therefore, from a chemical point of view, it is possible to use combusted oyster shell as a catalyst for the production of biodiesel.

The objective of this paper is to demonstrate that the combusted oyster shell can be used as a catalyst in the production of biodiesel from soybean oil. A factorial design was applied to optimize the reaction condition of the catalyst concentration and reaction time in terms of the FAME concentration expressed as biodiesel purity. Finally, the biodiesel yield from soybean oil was determined under the optimized reaction condition.

2. Methods

2.1. Materials

Oyster shell waste (5 kg) was obtained from the commercial oyster farm in Akitsu-cho, Higashi-Hiroshima city, western Japan. All reagents were of reagent grade and used as received. Soybean oil, hydrochloric acid, anhydrous sodium sulfate, hexane and acetone were purchased from Sigma-Aldrich Japan KK (Tokyo, Japan). Methanol (>99.8%) was purchased from Riedel-de Haën (Seelze, Germany). Calcium oxide (CaO) and acetic acid were purchased from Katayama Chemical Industries (Osaka, Japan).

2.2. Preparation and characterization of combusted oyster shell

To remove sands and seaweeds deposited on the shell surface, the oyster shells were washed with tap water and dried naturally. The shells were roughly crushed using a hammer and grounded using a pestle and mortar to a powder to pass through a 0.8 mm sieve. The powdered shell was then dried at 110°C for 2 h and stored in a desiccator.

The weight-loss of the powdered shell was measured after combustion with air in an electric furnace at a given temperature (100, 500, 700, 800, 900 and 1000°C) for 3 h and then the combusted shell was stored in a desiccator. X-ray powder diffraction (XRD) patterns for each combusted oyster shell and calcium oxide were analyzed (Rotaflex RU-200, RIGAKU). Data were collected over a 2θ range of 10-90°, with a step size of 0.1° at a scanning speed of 3° min⁻¹.

2.3. *Equipment*

Transesterification was carried out in a screw-capped vial (capacity ca. 50 cm³) with a Teflon/silicon rubber septum that retained any vaporized mixture. The reaction vial was immersed in a thermostatic water bath to maintain the reaction temperature between 65 and 70°C, slightly below the boiling point of methanol (Gryglewicz et al., 2003). The bath was placed on the plate of a magnetic stirrer. During the reaction, the mixture of oil, catalyst and methanol was completely stirred by a cross-headed stirrer bar.

2.4. Experimental procedure

The reaction vial filled with 18.5 g soybean oil was immersed in the constant-temperature water bath placed on the plate of the magnetic stirrer. After heating to 65°C, a given amount of the combusted oyster shell as a catalyst in the range from 5.86 to 34.14% wt. (Table 1) and 5 mL methanol (methanol/oil molar ratio of 6:1) were added to the vial. After the vial was tightly-sealed with its cap, the reaction was carried out for a given reaction time in the range from 1.17 to 6.83 h (Table 1) in the thermostatic water bath. After the reaction, the vial was cooled to ambient temperature and the reaction product was centrifugated at 3,000 rpm for 20 min. A supernatant was filtrated through a syringe filter with 0.45 µm pores (Millex-LH, Millipore Co.). To remove the methanol and residual base, the filtrated product was washed with acidic solution (acetic or hydrochloric acid) so that it was neutral and then with distilled water. After adding a small amount of anhydrous sodium sulfate to remove residual water and filtrating with a syringe filter with 0.45 µm pores (Millex-LH, Millipore Co.), the biodiesel yield was calculated from the weight of the product relative to the amount of soybean oil poured into the reaction vial. A portion of the product was stored in a freezer at -20°C until determination of the FAME concentration.

2.5. Gas chromatography

The FAME concentration expressed as the biodiesel purity of the product was determined using a

gas chromatograph (GC-14B, Shimadzu Co.) equipped with a flame ionization detector and a capillary column (SP-2380, Supelco Inc., 30 m in length with 0.25 mm i.d. and 0.20 μm film thickness). The programmed column oven temperature increased by $4^{\circ}\text{C min}^{-1}$ from 100 to 200°C and $10^{\circ}\text{C min}^{-1}$ to 250°C with 10 min holding time. The carrier gas was helium at a flow rate of 1.0 mL min^{-1} . Both the inlet and detector temperatures were maintained at 250°C . The diluted solution (1 μL) with hexane added as an internal FAME standard (GLC-90, Supelco Ltd.) was injected in the split mode (1:50). A standard FAME mixture (RM-1, Supelco Ltd.) was used as an external standard for quantitative analysis of the FAME concentration.

2.6. Data analysis

The reaction condition for the transesterification of soybean oil using a combusted oyster shell as a catalyst was optimized with the biodiesel purity as the response, following factorial design and response surface methodology. The experimental design applied in the present study was a full 2^2 factorial design, where the catalyst concentration and reaction time were selected as factors each at two levels, together with four central points. The central points make it possible to evaluate the curvature effects defined as the difference between the average of the center point responses and the average of the factorial point responses. The levels of the selected factors and the central points are given in Table 1; star points from additional experiments are included to form a central composite

design. The distance of the star points encoded as $+\alpha$ and $-\alpha$ from the center point was $\alpha = 2^{n/4}$, where n is the number of factors ($\alpha = 1.414$).

3. Results and discussion

3.1. Effect of the combustion temperature of oyster shell on the biodiesel purity

The weight-loss of powdered oyster shell dramatically increased with the combustion temperature rising from 700 to 900°C to reach ca. 45%, while the weight-loss from 100 to 700°C slightly increased and that at 700°C was less than 10%. Above 900°C, the weight-loss remained constant. There was no difference in the powder XRD patterns for oyster shell combusted between 100 and 500°C. Peaks corresponding to CaO ($2\theta = 32.2^\circ$, 37.4° and 53.8°) appeared in the XRD pattern of oyster shell combusted at 700°C. Furthermore, the patterns for the oyster shells combusted at 800°C and above were identical to that of CaO, while peaks corresponding to CaCO₃ ($2\theta = 29.4^\circ$, 47.5° and 48.5°) disappeared. These results indicate calcium carbonate transformed to calcium oxide by combustion at or above 700°C.

Using the combusted oyster shells as catalysts, the transesterification of soybean oil was performed. For this experiment, the reaction conditions of catalyst concentration and reaction time were set as 25% wt. and 5 h, respectively. FAME concentrations expressed as biodiesel purity in the product produced using oyster shell combusted at 100 and 500°C were 0 and 0.7% wt., respectively.

However, using shells combusted at 700°C and higher, the biodiesel purity was over 95%.

From these results, it can be concluded oyster shell combusted above 700°C could be used as a catalyst in the transesterification of soybean oil to form FAME. Because the weight-loss was constant above 900°C, the oyster shell combusted at 1000°C was selected as a catalyst in this study.

3.2. Optimization of the catalyst concentration and reaction time for biodiesel purity

The experimental matrix and results for this study are shown in Table 2. The first eight rows (run numbers 1-8) correspond to the 2² design and the center point, while the last four rows (run numbers 9-12) correspond to the star points. The order in which the experimental runs were performed was random to minimize systematic errors.

Using the experimental results for the 2² factorial design, where the catalyst concentration and reaction time were set as variables, the two main effects and the interaction effect of the variables on biodiesel purity were tested. The results of statistical analysis are shown in Table 3. Since both the main effects and their interaction values were higher than the confidence interval (± 3.211), the variables and their interaction significantly affected biodiesel purity with a 95% significance level.

Experimental results were fitted to a first order model, and the following equation was obtained.

$$P = 76.90 + 17.93X_C + 21.83X_R - 17.18X_{CR} \quad (r^2 = 0.894) \quad (1)$$

where P is the percentage of biodiesel purity and X_C , X_R and X_{CR} are the coded variables of catalyst

concentration (C), reaction time (R) and their interaction (CR). However, the curvature effect defined as the difference between the average of the center point responses and the average of the factorial point responses was -25.47%, while the confidence interval for the curvature was ± 4.541 with a 95% significance level. Therefore, the first order model was insufficient to present the experimental field considered in this study and it is necessary to apply the second order model to fit the data obtained.

The four runs called star points and coded $\pm\alpha$ were added to the 2^2 factorial design and the center points to form a central composite design. The experimental matrix and results corresponding to the central composite design are also shown in Table 2. The second order model was determined using multiple regression analysis. By considering both the coded and real factor levels, the equations for the statistical and industrial model were given by the following equations.

Statistical model:

$$P = 97.27 + 19.00X_C + 26.49X_R - 12.37X_C^2 - 17.18X_{CR} - 21.56 X_R^2 \quad (r^2 = 0.936) \quad (2)$$

Industrial model:

$$P = -192.37 + 9.71C + 73.10R - 0.11C^2 - 0.86CR - 5.41R^2 \quad (r^2 = 0.931) \quad (3)$$

The response surface corresponding to the industrial model is shown Fig. 1. From the statistical analysis of the experimental result, the reaction time was the most important factor in the biodiesel purity response followed by the catalyst concentration. Both factors have a positive effect on the biodiesel purity. In other words, the biodiesel purity increased with catalyst concentration and

reaction time. However, their interaction was a negative effect on the biodiesel purity. For a short reaction time, the biodiesel purity rapidly increased with increasing catalyst concentration while the purity for a long reaction time remained nearly constant with high values. These results indicate the long reaction time achieves desirable biodiesel purity over a wide range of catalyst concentrations.

From a response surface plot (Fig. 1), the optimum reaction conditions for the catalyst concentration and reaction time are selected as 25% wt. and 5 h, respectively. Under these conditions, the theoretical biodiesel purity obtained from a second order statistical model (Eq. 2) met the European Standard EN 14214 requiring the FAME content in biodiesel to be greater than or equal to 96.5% wt. (European Standard EN 14214, 2003). Therefore, in the following experiment for the biodiesel yield, the transesterification of soybean oil using combusted oyster shell was performed under these optimum conditions.

3.3. Yield of biodiesel production under the optimized reaction condition

At first, 5% diluted acetic acid solution was used to neutralize the base present in the transesterified oil produced using combusted oyster shell. However, a large amount of the acetic acid solution was required to neutralize the base and emulsion formed during washing with deionized water, resulting in a reduction in the biodiesel yield (around 40%). When concentrated hydrochloric acid (ca. 30%) was dropped into the transesterified soybean oil until neutralization, the amount of

emulsion formed during washing was reduced. In this case, the biodiesel yield using a combusted oyster shell as a catalyst under the optimum reaction conditions reached 73.8% with high biodiesel purity (98.4% wt.), which was comparable result to the yield with CaO (72.5%) under the same reaction conditions. This result indicates oyster shell waste combusted at high temperature can be reused in biodiesel production as a catalyst.

4. Conclusions

The following conclusions are drawn from the present study.

1. After combusting oyster shell at or above 700°C, at which point calcium carbonate transforms to calcium oxide, the shell was able to catalyze the transesterification of soybean oil with methanol.
2. Factorial experimental design and surface response methodology were applied to optimize the reaction conditions of catalyst concentration and reaction time for the transesterification of soybean oil with methanol using combusted oyster shell as a catalyst in terms of the FAME concentration expressed as biodiesel purity. From a second order model, the optimum reaction conditions of catalyst concentration and reaction time were 25% wt. and 5 h, respectively.
3. Under the optimum conditions obtained, the biodiesel yield, relative to the amount of soybean oil, was 73.8% with high biodiesel purity (98.4% wt.), indicating oyster shell can be used as a catalyst for the transesterification of soybean oil,

Acknowledgements

We thank Dr. S. Tanaka, Faculty of Integrated Arts and Sciences, Hiroshima University, for measuring the X-ray powder diffraction patterns. We also thank to EarthBand, Limited and Prof. K. Nakane, Hiroshima University, for supporting this study.

References

- Albuquerque, M.C.G., Jiménez-Urbistondo, I., Santamaría-González, J., Mérida-Robles, J.M., Moreno-Tost, R., Rodríguez-Castellón, E., Jiménez-López, A., Azevedo, D.C.S., Cavalcante Jr., C.L., Maireles-Torres, P., 2008. CaO supported on mesoporous silicas as basic catalysts for transesterification reactions. *Appl. Catal. A* 334, 35-43.
- Chang, H.-M., Liao, H.-F., Lee, C.-C., Shieh, C.-J., 2005. Optimized synthesis of lipase-catalyzed biodiesel by Novozym 435. *J. Chem. Technol. Biotechnol.* 80, 307-312.
- European standard N 14214, 2003. Automotive fuels – Fatty acid methyl esters (FAME) for diesel engine – Requirements and test methods. CEN – European Committee for Standardization, Brussels, Belgium.
- Gryglewicz, S., 1999. Rapeseed oil methyl esters preparation using heterogeneous catalysts. *Bioresour. Technol.* 70, 249-253.

- Gryglewicz, S., Piechocki, W., Gryglewicz, G., 2003. Preparation of polyol esters based on vegetable and animal fats. *Bioresour. Technol.* 87, 35-39.
- Kouzu, M., Umemoto, M., Kasuno, T., Tajika, M., Aihara, Y., Sugimoto, Y., Hidaka, J., 2006. Biodiesel production from soybean oil using calcium oxide as a heterogeneous catalyst. *J. Jpn. Inst. Energy* 85, 135-141 (in Japanese with English abstract).
- Ma, F., Hanna, M.A., 1999. Biodiesel production: a review. *Bioresour. Technol.*, 70, 1-15.
- Meher, L.C., Vidya Sagar D., Naik, S.N., 2006. Technical aspects of biodiesel production by transesterification – a review. *Renew. Sustain. Energy Rev.* 10, 248-268.
- Ministry of Agriculture, Forestry and Fisheries of Japan, 2007. Statistics of Agriculture, Forestry and Fisheries. Association of Agriculture and Forestry Statistics, Tokyo.
- Namasivayam, C., Sakoda, A., Suzuki, M., 2005. Removal of phosphate by adsorption onto oyster shell powder – kinetic studies. *J. Chem. Technol. Biotechnol.* 80, 356-358.
- Ooi, Y.-S., Zakaria, R., Mohamed, A.R., Bhatia, S., 2004. Catalytic conversion of palm oil-based fatty acid mixture to liquid fuel. *Biomass Bioenerg.* 27, 477-484.
- Peterson, G.R., Scarrah, W.P., 1984. Rapeseed oil transesterification by heterogeneous catalysis. *J. Am. Oil Chem. Soc.* 61, 1593-1597.
- Suppes, G.J., Dasari, M.A., Doskocil, E.J., Mankidy, P.J., Goff, M.J., 2004. Transesterification of soybean oil with zeolite and metal catalysts. *App. Catal. A* 257, 213-223.

Van Gerpen, J., Shanks, B., Pruszko, R., Clements, D., Knothe, G., 2004. Biodiesel Production Technology. NREL/SR-510-36244, Colorado.

Van Gerpen, J., 2005. Biodiesel processing and production. *Fuel Process. Technol.*, 86, 1097-1107.

Vicente, G., Coteron, A., Martinez, M., Aracil, J., 1998. Application of the factorial design of experiments and response surface methodology to optimize biodiesel production. *Ind. Crops Prod.* 8, 29-35.

Vicente, G., Martínez, M., Aracil, J., 2007. Optimisation of integrated biodiesel production. Part I. A study of the biodiesel purity and yield. *Bioresour. Technol.* 98, 1724-1733.

Yamada, M., Tatsuno, T., Sano, H., Tanabe, K., 2005. A study on stabilization effect of the acid sulfate soil by using crushed oyster shell. *J. Soc. Mat. Sci. Jpn.* 54 (11), 1117-1122 (in Japanese with English abstract).

Yoon, G.-L., Kim, B.-T., Kim, B.-O., Han, S.-H., 2003. Chemical-mechanical characteristics of crushed oyster-shell. *Waste Manage.* 23, 825-834.

Table 1

Levels of factors for the central composite design

Factor	Levels				
	+ α	+ 1	0	- 1	- α
Catalyst concentration (C) (% wt.)	34.14	30	20	10	5.86
Reaction time (R) (h)	6.83	6	4	2	1.17

Note : + α , high star point level; +1, high fractional point level; 0, central point level; -1, low fractional point level; - α , low star point level.

Table 2

Experimental matrix and experimental results for the central composite design

Run number	C (% wt.)	R (h)	X_C	X_R	P (% wt.)
1	10	2	- 1	- 1	14.87
2	10	6	- 1	+ 1	92.87
3	30	2	+ 1	- 1	85.08
4	30	6	+ 1	+ 1	94.38
5	20	4	0	0	96.01
6	20	4	0	0	95.20
7	20	4	0	0	99.56
8	20	4	0	0	98.32
9	34.14	4	+ α	0	92.45
10	20	6.83	0	+ α	89.76
11	20	1.17	0	- α	1.62
12	5.86	4	- α	0	35.69

Note : C , catalyst concentration; R , reaction time; X , coded value; P , biodiesel purity.

Table 3

Statistical analysis for the 2^2 factorial design

Response	Biodiesel purity (% wt.)
Number of experiments	4
Degrees of freedom	3
Main effects and interaction effect	$I_C = 35.86, I_R = 43.65, I_{CR} = -34.35$
Significance test	Student's t
Confidence level	95%
Average of factorial runs	71.80
Standard deviation	2.018
Student's t -value	3.182
Confidence interval	± 3.211
Significant effects	C, T, CR
<i>Significance of curvature</i>	
Average of center point responses	97.27
Curvature	-25.47
Confidence interval for the curvature	± 4.541
Significance	Yes

Note: C , catalyst concentration; R , reaction time; I , main effect or interaction.

Figure captions

Fig. 1. Response surface plot of the second-order model for biodiesel purity as a function of catalyst concentration and reaction time.

