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Short Communication

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

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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 25wt.%. 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.

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),

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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 $3^\circ\ \mathrm{min}^{-1}$.

2.3. Equipment

Transesterification was carried out in a screw-capped vial (capacity ca. 50 cm^3) 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 34.14wt.%. (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 centrifuged 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.

Table 1
Levels of factors for the central composite design

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

$+\alpha$, high star point level; +1, high fractional point level; 0, central point level; −1, low fractional point level; $-\alpha$, low star point level.

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 $4\ ^\circ\mathrm{C\ min}^{-1}$ from 100 to 200 °C and $10\ ^\circ\mathrm{C\ min}^{-1}$ to 250 °C with 10 min holding time. The carrier gas was helium at a flow rate of $1.0\ \mathrm{mL\ min}^{-1}$. 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