

# Co-Production of Biodiesel and Activated Carbon from Rubber Seed

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## Abstract

A co-production process of biodiesel and activated carbon from rubber seed was proposed. Biodiesel was synthesized by in-situ transesterification of the oil extracted from rubber seed in n-hexane. Although the rubber seed contained a large amount of free fatty acids (FFA), the fatty acid methyl ester (FAME) yield reached 98 % after 15 min-reaction due to the low extraction of FFA from the rubber seed in n-hexane. Co-carbonization of the rubber seed residue after the in-situ transesterification and the crude glycerin containing KOH improved the pore properties of activated carbon product, such as BET surface area and pore volume. As a result, the resulting activated carbon indicated methylene blue adsorption ability.

Key words: Biodiesel, Rubber seed, Activated carbon, Transesterification, Carbonization

## 1. Introduction

Biodiesel (fatty acid methyl esters, FAME) has been increasingly used as an alternative fuel for diesel engines without any modification. Most biodiesel is made from vegetable oil by transesterification of the triglyceride contained in the oil with methanol and a base catalyst. However, the large consumption of edible oils such as rapeseed oil, soybean oil and palm oil for biodiesel production could bring a rise in food prices. In Malaysia, there are around 1.2 million hectares of rubber plantations. About 300 kilograms of rubber seed are produced per hectare of rubber plantation every year. The oil content in the rubber seed is roughly estimated to be 40 wt% [1]. However, rubber seed is normally regarded as waste because it is inedible. The estimated annual production of rubber seed oil is about 144,000 tons. Rubber seed oil is suitable for the feedstock of biodiesel.

The synthesis process of biodiesel from oilseed crops involves isolation of oil from seed, refining and transesterification. The separation processes in oil refining such as degumming, neutralization, bleaching and deodorization consume a large amount of energy, water and chemicals. Recently, the preparation of biodiesel using in-situ transesterification has been successfully carried out with various oilseed crops [2-4]. In-situ transesterification is a biodiesel production method that integrates the solvent extraction and transesterification reaction of triglyceride from a pulverized oilseed crop in a single step. This method might reduce the cost of biodiesel production. However, effective utilization of waste rubber seed residue derived from an in-situ transesterification has to be considered.

The main byproduct of biodiesel production by base-catalyzed transesterification is crude glycerin, which comprises about 10 w/v% of oils. Conversion of crude glycerin to valuable product is a key issue for the commercial production of biodiesel. Various forms of biomass were used to prepare activated carbon using potassium hydroxide (KOH) and potassium carbonate ( $K_2CO_3$ ) as activating agents [5, 6]. Co-carbonization of the waste rubber seed residue and the crude glycerin including KOH seems to be very promising for the low-cost production of activated carbon.

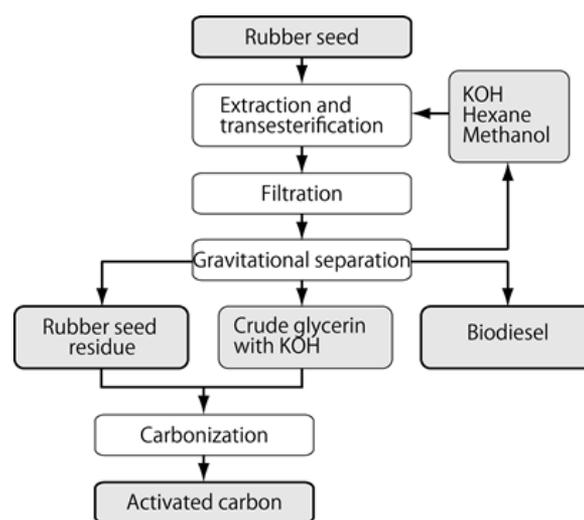


Fig. 1. Zero-emission biodiesel production.

Fig. 1 outlines the process of zero emission biodiesel production. In this study, we investigated the in-situ transesterification

where triglyceride was extracted from rubber seed by hexane and simultaneously FAME was produced by transesterification with methanol and KOH. The rubber seed residue after extraction and the crude glycerin were mixed and carbonized in nitrogen atmosphere to produce activated carbon.

## 2. Methods

### 2.1 In-situ transesterification

Potassium hydroxide, hexane, acetone, diethyl ether, dehydrated methanol and corn oil were purchased from Wako Chemicals (Japan). The rubber seeds were supplied by a rubber plantation in Malaysia. The peeled rubber seeds were ground to a fine powder with a laboratory pulverizer. The oil content of the seeds was determined through Soxhlet extraction using hexane as a solvent for 6 h. The acid value of the extracted oil was determined by titration method (EN1405). Water content in the oil was determined using a Karl-Fischer moisture titrator (MKC-610, Kyoto Electronic Manufacturing Co. Ltd.). The viscosity was determined with a torsion-balanced, oscillation-type viscometer (VM-1G, CBC Materials Co., Ltd.). The density was determined using a picnometer.

The preliminary extraction test of oil from rubber seed was carried out using n-hexane, acetone, diethyl ether or methanol at room temperature. In order to investigate the influence of the extracting solvent on the biodiesel production, transesterification of corn oil (5 mL), which was used as a model reactant, was carried out in the mixture of a methanol solution of KOH (2 wt%, 5 mL) combined with extraction solvent (1.5 mL; n-hexane, acetone or diethyl ether) at room temperature. In these experiments, acetone and diethyl ether were partially miscible with methanol, resulting in the dilution of KOH. n-Hexane was almost immiscible with methanol. At the initial stage of transesterification, a liquid-liquid two phase system still formed in any solvents.

In-situ transesterification was carried out in a flask which was equipped with a magnetic stirrer at a room temperature of 60 °C. About 5 g of pulverized rubber seeds were loaded and then 10 mL of a methanol solution of KOH (2 wt%) and 10 mL of n-hexane were added into the flask. The suspension was stirred for 15, 30 and 60 min.

A sample was collected and then acetic acid solution was added for the termination of the reaction. The sample was then centrifuged at 4000 rpm for 900 s. The collected upper FAME layer was washed several times with deionized water to remove residual inorganic components.

The concentrations of unreacted triglyceride and FAME in the sample were analyzed using a high-performance liquid

chromatograph (HPLC, Tosoh Corp.) equipped with a silica-gel column (Shimpack CLC-SIL, Shimadzu Corp.) and a refractive index detector. The concentrations of FAMES after complete transesterification of rubber seed oil were determined with a gas chromatograph (Shimadzu GC-8A) equipped with a glass column (Shimpack CLC-SIL, Shimadzu Corp.) and a flame ionized detector.

The FAME yield in the product was calculated as follows:

$$\text{FAME yield} = (C_{\text{FAME}}/3C_{\text{oil}}) \times 100 \quad (1)$$

where  $C_{\text{oil}}$  and  $C_{\text{FAME}}$  are the concentrations of triglyceride in the feed and FAME in the product, respectively.

### 2.2 Co-carbonization of rubber seed residue and crude glycerin

Glycerol was purchased from Wako Chemicals (Japan). Also, crude glycerin produced from waste cooking oil in a biodiesel production factory was used. Density of the crude glycerin was 1140 kg.m<sup>-3</sup> at 298 K. Hydroxide ion concentration in the crude glycerin was measured by a back-titration technique. Filtered rubber seed residue after the in-situ transesterification was washed with water and dried at 353 K overnight. The raw material for co-carbonization was prepared by mixing with 0.6 g of the rubber seed residue and 6 mL of the crude glycerin. Thermogravimetry (TG) was carried out to study the pyrolysis of pure glycerol, crude glycerin, and the mixed matter of rubber seed and crude glycerin. The thermogravimetric data were collected from room temperature to 1073 K at heating rates of 10 K.min<sup>-1</sup> in dry nitrogen atmosphere by using TG-DTA8120 (Rigaku, Japan). Carbonizations of the rubber seed residue, crude glycerin and their mixture were carried out in a horizontal tube furnace in dry nitrogen atmosphere at 773 K for 1 hour. The BET surface area of the carbonization product was determined with a BET surface area and pore size distribution analyzer (Trister II 3020, Shimadzu, Japan). The yield of carbonization was determined from the following equation:

$$\text{Carbonization yield} = (m/m_0) \times 100 \quad (2)$$

where  $m$  is the weight of the carbonization products and  $m_0$  is the weight of the initial dry carbonaceous matter.

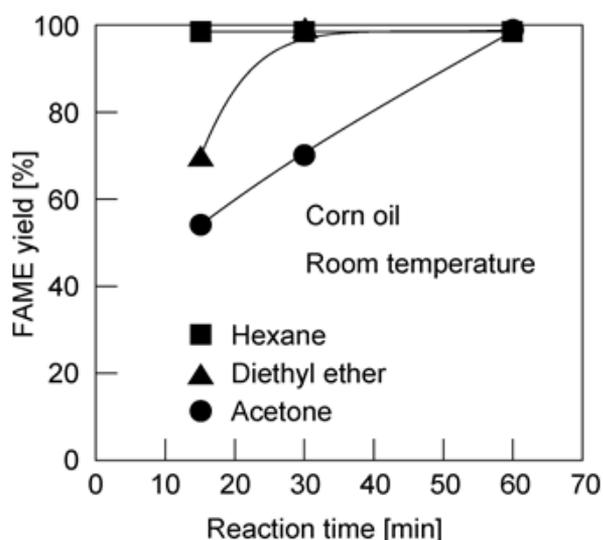
Adsorption activity of the carbonization product was examined using methylene blue dye. The carbonization product (0.03 g) was immersed into  $2.5 \times 10^{-1}$  mol.m<sup>-3</sup> methylene blue solution (30 mL) for 3 hours. Methylene blue concentration in the supernatant solution was determined with UV-Vis spectrometry.

### 3. Results and discussion

#### 3.1 In-situ transesterification

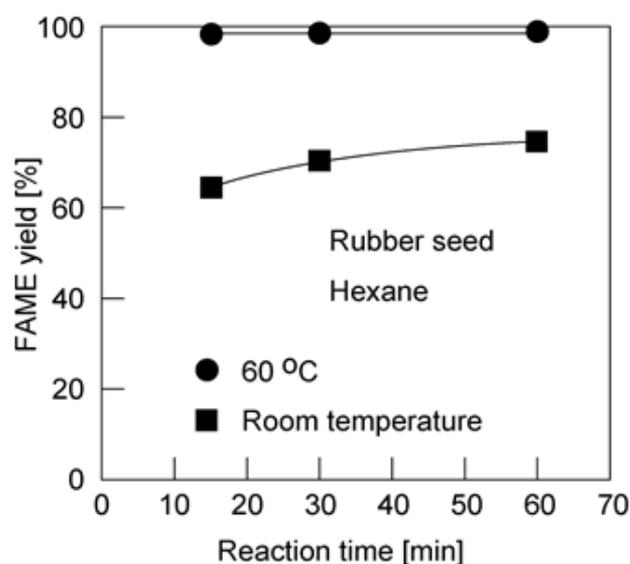
Acetone (boiling point (b.p.) = 56.5 °C), diethyl ether (b.p. = 34.6 °C), n-hexane (b.p. = 68-69 °C), and methanol (b.p. = 64.7 °C) were chosen as extraction solvents for rubber seeds considering the simultaneous recovery of unreacted methanol and extraction solvent by vaporization after in-situ transesterification. From the results of preliminary extraction experiments, about 0.4 g of oil component was extracted from 1.0 g of rubber seeds in the solvent of acetone, diethyl ether or n-hexane. When methanol as a less compatible solvent was used, 0.1 g of oil component per 1 g of rubber seed was extracted. The fatty acid composition of rubber seed oil used in this study was palmitic (9.9%), stearic (9.3%), oleic (23.8%), linoleic (39.2%) and linolenic (17.9%). The extracted oil was rich in oleic and linoleic acids and this composition agreed with the results reported by other research [7, 8]. Density and viscosity of the rubber seed oil at 298 K were 0.881 kg.m<sup>-3</sup> and 40.9 mPa.s, respectively. Acid value of the rubber seed oil was 34.0 mg-KOH.g<sup>-1</sup>.

Fig. 2 indicates FAME yields in transesterification of corn oil at room temperature regarding the mixed solution of methanol containing 2 wt% KOH and extraction solvent. The highest FAME yield was obtained in the mixture of n-hexane and the methanol solution after 15min reaction. Hence n-hexane was used as a solvent of in-situ transesterification.



**Fig. 2.** Effect of organic solvents on FAME yield in transesterification of corn oil at room temperature. ■, n-hexane; ▲, diethyl ether; ●, acetone.

Fig. 3 shows the FAME yield obtained from in-situ transesterification of rubber seed. FAME yield at room temperature increased slightly with reaction time and reached 74% after a lapse of 60 min. Increasing the reaction temperature from room temperature to 60 °C, FAME yield reached 98 % after a lapse of 15 min. n-Hexane is an efficient solvent for oil extraction from rubber seed and its non-polarity can also inhibit the dissolution of free fatty acid and water from the seed [9]. Kartika et al. [4] investigated in-situ transesterification of *Jatropha* seeds at 50 °C for 5 h using a mixture of methanol solution of 0.075 mol/L KOH and n-hexane. The highest FAME yield obtained was 87 %



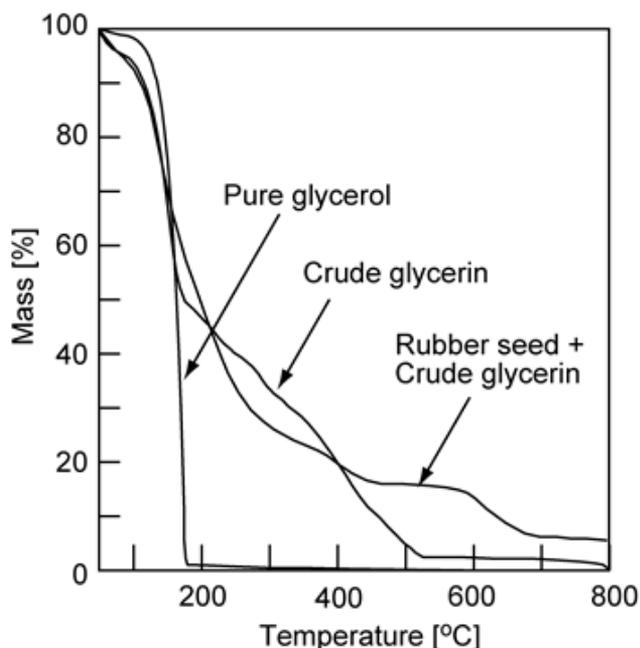
**Fig. 3.** Effect of reaction temperature on FAME yield in in situ transesterification by using n-hexane. ●, 60 °C; ■, room temperature.

#### 3.2 Co-carbonization of rubber seed residue and crude glycerin

Fig. 4 shows the TG mass loss curves of pure glycerol, the crude glycerin, and the mixture of the rubber seed residue and the crude glycerin. Hydroxide ion concentration in the crude glycerin was as high as 76 mol.m<sup>-3</sup>. The mass loss temperature of pure glycerol started at approximately 100 °C and finished at 176 °C. The boiling point of pure glycerol is 290 °C and reduces when glycerol is diluted with water. The boiling point of 95 wt% glycerol became 167 °C. In addition, thermal decomposition of glycerol has been observed at low temperature [10]. Stein et al. [11] investigated the pyrolysis of glycerol in steam. The initial decomposition products of glycerol were CO, acetaldehyde and acrolein. Therefore, the mass loss might be caused by vaporization and decomposition of glycerol at temperature lower than 167 °C. When crude glycerin was heated, the initial

mass loss temperature of the crude glycerin was lower than that of pure glycerol due to the low temperatures volatiles such as residual methanol. The mass loss value during the first stage was about 50 %. The further mass loss occurred during the second stage from 167 °C to 520 °C where the mass loss value was 47 %. This second stage would have consisted of the thermal degradation of the impurities originated from the waste cooking oil as a feedstock and the residual fatty acid methyl esters. When 0.6g of the rubber seed residue was added in 6 mL of crude glycerin, co-carbonization continued to 687 °C and carbonization yield at 800 °C was 5.5 % by combining the rubber seed residue with the organic components in crude glycerin.

When carbonization was carried out in a horizontal electric furnace, the carbonization yields of the rubber seed residue and the crude glycerin were 21.3 % and 7.5 %, respectively. When 0.6 g of the rubber seed residue and 6 mL (6.84 g) of the crude glycerin were mixed and carbonized, the carbonization yield became 10.0 % and was higher than the value (8.6 %) calculated from each carbonization yield and fraction.



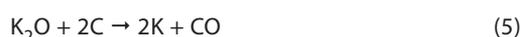
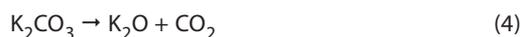
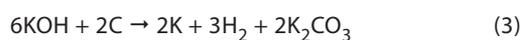
**Fig. 4.** TG mass loss curves of pure glycerol, the crude glycerin and the mixture of the rubber seed residue and the crude glycerin.

Table 1 indicates the BET surface areas and the pore properties of the carbonization products obtained from the rubber seed residue, the crude glycerin and the mixed matter of both. The BET surface area of the carbonization product from the crude glycerin was higher than that of the rubber seed residue due to the development of pore structure by the influence of

KOH. As shown in Fig.4, about half the amount of the crude glycerin might be vaporized or decomposed with less contact of KOH. Therefore the contribution of KOH on the yield of carbonization was low for the crude glycerin. The rubber seed residue was mixed with the crude glycerin at the weight ratio of KOH/rubber seed residue = 0.04. As shown in Table 1, the BET surface area of the activated carbon from the mixed matter was dramatically increased to 217.6 m<sup>2</sup>.g<sup>-1</sup> by co-carbonization. In the presence of KOH, the following reactions occurred during carbonization [12].

**Table 1.** BET surface areas and the pore volume structures of the carbonization products after 1 h calcination at 500 °C

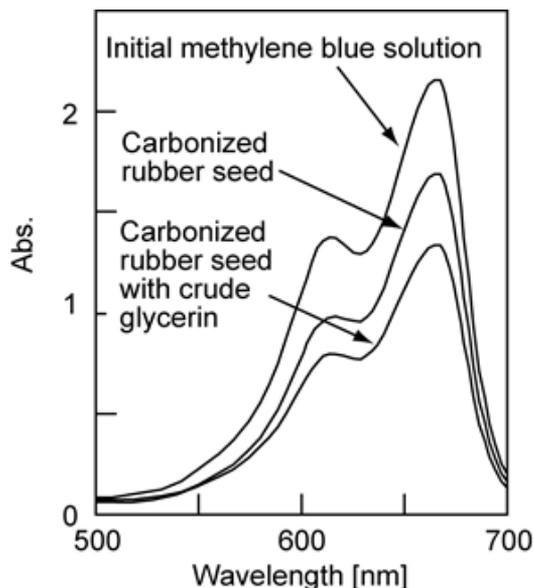
Sample	BET surface area [m <sup>2</sup> .g <sup>-1</sup> ]	Pore volume [cm <sup>3</sup> .g <sup>-1</sup> ]	Average pore diameter [nm]	Carbonization yield [%]
Rubber seed residue	3.0	0.004	5.0	21.3
Crude glycerin	10.2	0.009	3.4	7.5
Mixed matter of both	217.6	0.128	2.4	10.1



Decomposition of potassium carbonate formed in the internal structure of the rubber seed residue during the carbonization promotes pore formation in the activated carbon. It can also modify the surface of the pore and result in some functional groups. Hence, a high BET surface area can be obtained in the final product in the presence of KOH. Borhan and Kamil [13] prepared the activated carbon from rubber seed shell by KOH activation. Results show that the BET surface area was 1289 m<sup>2</sup>.g<sup>-1</sup> at the weight ratio of KOH/rubber seed shell = 1.

Fig. 5 shows vis absorption spectra of methylene blue solution after adsorption treatment by the activated carbons obtained from rubber seed with or without crude glycerin. The amount of methylene blue adsorbed by the activated carbon prepared from the mixed matter was 30.6 mg-methylene blue/g-activated carbon after a lapse of 3 hours. The adsorbed amount of methylene blue was lower than that for the commercial activated carbon (300-400 mg/g). Further research for optimization of the activation conditions such as

the carbonization temperature, the ratio of the rubber seed residue and the crude glycerin is required.



**Fig. 5.** Vis-absorption spectra of methylene blue solution before and after treatment with activated carbon formed by carbonization of rubber seed residue and co-carbonization of rubber seed residue and crude glycerin.

#### 4. Conclusion

This study showed a co-production process of biodiesel and activated carbon from the rubber seeds to build the zero-emission biodiesel production plant. FAME yield reached 98 % at 60 °C in the mixture of methanol solution of KOH, n-hexane and fine powder of rubber seed. This high yield was caused by the inhibition of free fatty acid extraction from the rubber seed by n-hexane. Co-carbonization of the rubber seed residue and the crude glycerin was examined to produce the activated carbon. The activated carbon produced at 500 °C indicated the BET surface area of 217.6 m<sup>2</sup>.g<sup>-1</sup> and its methylene blue adsorption ability.

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