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Purification of Biodiesel by Choline Chloride Based Deep Eutectic Solvent

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Abstract. Purification is a crucial step in biodiesel production to meet the biodiesel standard. This study purified biodiesel using choline chloride based deep eutectic solvent (DES). DES was used to reduce unreacted oil and unsaponifiable matter in rice bran oil based biodiesel. The objective of this work was to study the effect of extraction time using DES on the content and yield of fatty acid methyl ester (FAME). Rice bran used in this work contains 16.49 % of oil with initial free fatty acids (FFA) of 44.75 %. Acid catalyzed methanolysis was employed to convert rice bran oil (RBO) into biodiesel under following operation conditions: T = 60 ^{o}C, t = 8 h, molar ratio of oil to methanol = 1/10, H_2SO_4 = 1% w/w of oil. Rice bran oil based biodiesel obtained contain 89.05 % of FAME with very low FFA content (0.05 %). DES was made from a mixture of choline chloride and ethylene glycol with molar ratio of 1/2. Molar ratio of crude biodiesel to DES were 1/2 and 1/4. Extraction time was varied from 15 minutes to 240 minutes at 30 ^{o}C. The highest FAME content was obtained after purification for 240 min. at molar ratio crude biodiesel to DES 1/4 was 96.60 %. This work shows that DES has potential to purify biodiesel from non-edible raw material, such as RBO.

KEYWORDS: Biodiesel; Deep Eutectic Solvent; FAME; Purification; Rice bran oil

INTRODUCTION

Biodiesel as an energy resources has gained attention from researchers and policy-makers because it is the main alternative for petrodiesel and made from various raw materials[5,14]. It has several advantages compared to petrodiesel that are biodegradable, lower emissions, in terms of CO_2, CO, particulate matter, hydrocarbons and sulfur [17,18]. After production process, crude biodiesel must be purified to meet international standards such as EN 14214 or ASTM D6751. The presence of impurities in biodiesel will cause problems to the machine through a number of negative effects[6].

Wet washing and dry washing methods are the most commonly method for biodiesel purification. Wet washing was purification method of biodiesel using water or acid such as phosporic acid, sulfuric acid and hydrochloric acid. Wet washing method required 60 – 80 % of total production costs; it was not suitable for the production of biodiesel in large quantities[2]. Dry washing method removed impurities from crude biodiesel by adsorption or ion exchanger [21]. Magnesol powder or silica gel used as an adsorbent in adsorption of impurities from crude biodiesel[7]. Novel method had been developed and tested for refining crude biodiesel, such as using membrane separation technology, ionic liquids and deep eutectic solvent[21].

Deep Eutectic Solvent (DES) was a new generation solvent formed from a mixture of quaternary ammonium salts with hydrogen bond donor (HBD). DES compared to traditional organic solvents, had advantage of being non-volatile and non-flammable, making storage easier. DES had a high polarity so it can be used to separate biodiesel from its impurities, such as glycerol, water, FFA, triglycerides (TG), monoglycerides (MG) and diglycerides (DG). DES is soluble in water and insoluble in biodiesel[22]. Previous research used DES to purified biodiesel from soybean oil and rapeseed oil[1]. DES which is a mixture of quaternary ammonium salts with HBD molecules, namely glycerol

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was used in that study with molar ratio of 1: 1 and 1: 2 for HBD: salt. DES had strong affinity between two components and formed strong hydrogen bonding interactions. The high affinity of salt in mixture resulting glycerol was able extracted glycerol from biodiesel. The high affinity of ionic liquids for alcohol also lead to excess ethanol was extracted from biodiesel. DES also used to remove free glycerol and total glycerol from palm oil based biodiesel by liquid-liquid extraction[19]. The optimum molar ratio of DES to biodiesel was 1: 1. DES type which was used to removed glycerol was a combination of choline chloride (CHCl) with ethylene glycol as HBD and also 2,2,2, - trifluracetamide as HBD. Shahbaz et al also reported the removal of free glycerol and total glycerol from palm oil based biodiesel using methyl triphenyl phosphunium bromide as salt and glycerol, ethylene glycol and triethylene glycol as HBD[20]. This research reported that glycerol as HBD was not effective to reduced TG, DG and MG in biodiesel. While ethylene glycol and triethylene glycol succeeded in decreasing the content of DG and MG. Total glycerol successfully reduced to meet ASTM standards. The best molar ratio to reduce total glycerol was at a ratio of 3: 1 (DES/biodiesel).

Several raw materials of biodiesel are expensive due to food versus energy. Raw materials cost about 60-75 % of total production cost of biodiesel. Many researchers were interested in using non-food raw materials such as rice bran in order to decrease the total production cost [4,24]. Rice is a staple food in Indonesia. Rice bran is the main byproduct of rice milling process and contains 10-26 % of oil[11]. RBO contain of FFA up to 44.56 % [15]. Crude biodiesel from rice bran contain byproducts called biodiesel residue consists of FFA, MG, DG, TG and bioactive compounds such as oryzanol, tocopherols, tocotrienols, phystosterol, polyphenols and squalene [10,13]. It was need to be isolated from biodiesel to reduce the production cost of biodiesel [11]. Purification of crude biodiesel from rice bran is more difficult than other vegetable oils because FFA content was high as well as the unsaponifiable matters and its color was dark. Purification of crude biodiesel from rice bran oil is rarely reported. Some research about purification of crude biodiesel from rice bran that has been reported using wet washing method. However, some also used other method such as dry washing. Yücel Ozgul & Selma used rice husk ash and silica gel to purified commercial methyl ester of rice bran with the adsorption of FFA under atmospheric conditions[16]. Purification of biodiesel from rice bran oil using DES has not been reported. This study was purified rice bran oil based biodiesel using DES by liquid-liquid extraction. This research studied the effect of extraction time on the purity and recovery of biodiesel.

METHODS

Materials

Rice bran (IR 64) was donated by a rice mill located in Banyuwangi, Indonesia. Choline chloride (CHCl) (≥ 98%) was obtained from Sigma Aldrich (China), Ethylene Glycol (99%) was obtained from SAP Chemical (Indonesia), n-hexane, Methanol (ACS grade) and sulfuric acid (ACS grade, 98%) were obtained from ANHUI FULLTIME (Anhui, China). All other chemicals used were obtained from commercial sources.

Extraction of Rice Bran Oil (RBO)

Crude RBO was extracted from rice bran using soxhlet extraction for 8 hours. 50 g of rice bran was covered by filter paper was put in a soxhlet extractor and 300 mL of n-hexane was used as a solvent to extracted RBO from rice bran. Temperature of extraction was carried out at 70 ^{o}C. Solvent was separated from RBO using rotary vacuum evaporator (Yamato Model RE-46, USA). FFA content was measured using AOCS official method Ca 5a-40. The average molecular weight of RBO was calculated using saponification value (SV), SV for RBO obtained was 193.8039 mg KOH/g ± 1.53. The molecular weight of RBO was 868.40 g/mol. RBO content of IR 64 after the extraction process obtained was 16.49 % ± 0.00. Rice bran oil used in this study contains high level of FFA (44.75 %).

Acid Catalyzed Methanolysis of RBO

Biodiesel in this work was produced according to our previous work[23]. Acid-catalyzed methanolysis reactions were carried out with 10 g of RBO at 60 ^{o}C and atmospheric pressure under stirring at 300 rpm. Molar ratio of RBO to methanol was 1:10. Afterwards, sulfuric acid (1 wt %) dissolved in methanol was injected into the reaction vessel through a septum after the RBO was heated to the required temperature (60 ^{o}C) under stirring. Biodiesel was washed

using 300 mL of n-hexane to remove sulfuric acid. Crude biodiesel obtained contain 89.05 % of FAME and less than 0.05 % of FFA. FFA, FAME, MG, DG and TG content in biodiesel was analyzed using Shimadzu GC-2010 Plus (Kyoto, Japan) gas chromatograph equipped with a flame ionization detector. Separations were carried out on a ZB-5HT (5%-phenyl)-methylpolysiloxane non-polar column (15 m × 0.32 mm i.d., 0.1 mm film thickness; Agilent Tech. Palo Alto, California). The temperatures of injector and detector were both set at 370 ºC. Temperature of the column was started at 80 ºC, increased to 365 ºC at 15 C/min, and maintained at 365 ºC for 8 min. The split ratio was 1:50 and the carrier gas was nitrogen. Twenty milligrams sample was dissolved in 1.5 mL ethyl acetate, heated until clear solution was observed and 1.5 µL samples was injected into the high temperature gas chromatography (HTGC).

Synthesis of Deep Eutectic Solvent

In this study DES was formed by combination of CHCl and ethylene glycol (EG) as hydrogen bond donor. 10 g of CHCl and 8.89 g of ethylene glycol (molar ratio of CHCl/EG = 1:2) was added into a stopper glass. The mixture was stirred at 300 rpm and the temperature was maintained at 60 ºC until homogenous transparent liquid formed. Density of DES was 1.0217 g/mL, measured by picnometer (IWAKI Pyrex).

Purification Using Deep Eutectic Solvent

Crude biodiesel was purified by liquid-liquid extraction (LLE) method using DES as a solvent. Biodiesel and DES was added into a stopper glass with molar ratio of biodiesel to DES were 1:2 and 1:4. Extraction time was varied from 15 minutes to 240 minutes at constant temperature 30 ºC. The mixture of biodiesel and DES was heated under stirring at 300 rpm. The mixture was settling for 2 hours and 2 layers were formed. The upper layer was biodiesel and the bottom layer was DES and impurities. Purified biodiesel was separated from DES using separator funnel. The upper layer was analyzed by HTGC to measure FAME, FFA, MG, DG and TG content after purification.

RESULTS AND DISCUSSION

Effect of Extraction Time

Several factors that influence extraction process were extraction temperature, extraction time, size, shape and condition of the solid particles and the type of solvent. The longer of extraction time cause the longer of interacting time between crude biodiesel with DES. Based on the previous work, MG and DG can be extracted into DES from crude biodiesel due to hydrogen bonding between MG, DG and DES[20]. Hydrogen bonding interaction occurred when there was dipole-dipole between electronegative atoms with hydrogen atoms which was bonded to other electronegative atom. In addition to MG and DG, biodiesel from RBO contain other impurities such as FFA, water, residual methanol and bioactive compound such as γ-oryzanol. Those compounds have hydroxyl groups and formed hydrogen bonding with DES. While FAME compound as the main constituent of biodiesel does not have hydroxyl group, FAME is immiscible in DES. Compound which has hydroxyl groups can be extracted from biodiesel using DES through interaction with CHCl as hydrogen bond acceptor (HBA) and ethylene glycol as hydrogen bond donor (HBD). One parameter that gives an eeffect to the extraction process was extraction time. This work shows that the longer of extraction time, the purer biodiesel was produced; it can be seen from the increasing of FAME content in biodiesel after purification. In this work, DES forming hydrogen bonds due to the interaction between H in HBD with Cl^-, where Cl^- is the element in group VII A, which has a large electronegativity, it equal to 3.0. There was also a hydrogen bond between the methyl protons (CH) in choline with oxygen from the HBD. Effect of extraction time on RBO-based biodiesel composition after liquid-liquid extraction with DES was shown in fig. 1 and 2.

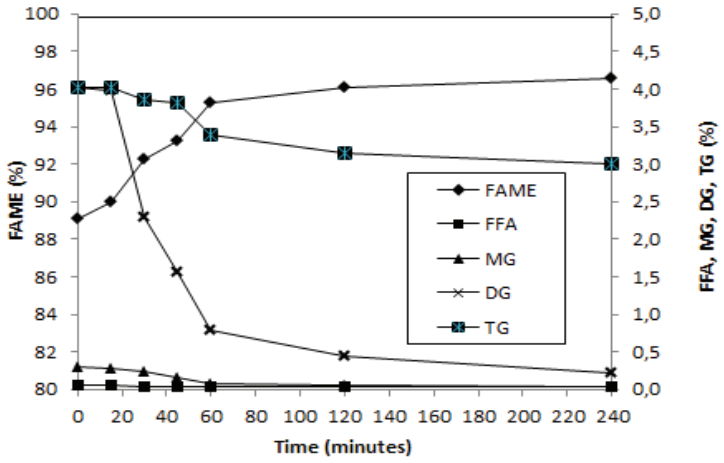

Fig. 1 Effect of extraction time on the content of FAME, FFA, MG, DG and TG in RBO-based biodiesel after LLE Operation condition: T = 30 °C; molar ratio of crude biodiesel: DES = 1: 2; molar ratio of CHCl: EG = 1: 2

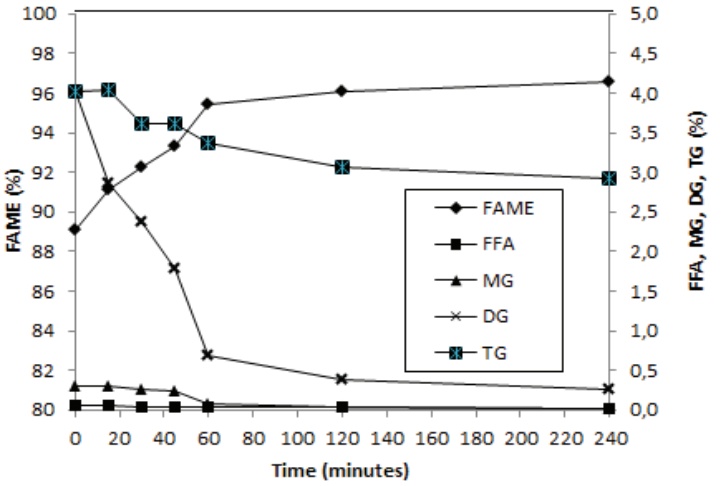

Fig. 2 Effect of extraction time on the content of FAME, FFA, MG, DG and TG in RBO-based biodiesel after LLE Operation condition: T = 30 °C; molar ratio of crude biodiesel: DES = 1: 4; molar ratio of CHCl: EG = 1: 2

Fig. 1 and **Fig. 2** show that the content of FAME increased with extraction time. The longer of extraction time, the higher of FAME content was obtained. It was because the interaction between impurities in crude biodiesel was longer. Unreacted oil (FFA, MD, DG and TG) and unsaponifiable matters were removed from crude biodiesel, it cause increasing of FAME content. MG and DG significantly decreased with extraction time (>90 %). However, TG was difficult to remove from crude biodiesel. TG extracted into DES at molar ratio of DES to crude biodiesel of ½ and 1/4 was 25.32 % and 27.63 %, respectively. The highest FAME content (96.5 %) for molar ratio of DES to crude biodiesel of 1/2 and 1/4 was 96.55 % and 96.60 %, respectively, after 240 min of extraction time. FAME content in biodiesel after purification was fulfilling Indonesia standard specification (SNI 7182: 2012) and international standard specification (EN 14214) for biodiesel as fuel.

Effect of Molar Ratio of Crude Biodiesel to DES

Molar ratio of crude biodiesel to DES is one of parameter that influences liquid-liquid extraction (LLE). In this work molar ratio of crude biodiesel to DES was 1/2 and 1/4. The composition of upper layer (biodiesel rich phase) was shown in table 1 and 2.

Table 1 Effect of molar ratio on the content of FAME, FFA, MG, DG and TG in RBO-based biodiesel after LLE[a]

Extraction Time (min.)	FFA (%)	MG (%)	DG (%)	TG (%)	Others (%)	FAME (%)
0	0.05	0.30	4.01	4.03	2.55	89.05
15	0.05	0.28	3.99	4.01	1.70	89.96
30	0.04	0.23	2.28	3.86	1.34	92.24
45	0.04	0.16	1.56	3.82	1.21	93.21
60	0.03	0.08	0.79	3.38	0.48	95.23
120	0.03	0.05	0.44	3.14	0.28	96.05
240	0.03	0.03	0.22	3.01	0.17	96.55

[a]Operation condition: T = 30 ºC; molar ratio of crude biodiesel: DES = 1: 2; molar ratio of CHCl: EG = 1: 2

Table 2 Effect of molar ratio on the content of FAME, FFA, MG, DG and TG in RBO-based biodiesel after LLEa

Extraction Time (min.)	FFA (%)	MG (%)	DG (%)	TG (%)	Others (%)	FAME (%)
0	0.05	0.30	4.01	4.03	2.55	89.05
15	0.05	0.30	2.86	4.03	1.62	91.13
30	0.04	0.26	2.37	3.61	1.47	92.25
45	0.04	0.24	1.78	3.61	1.06	93.28
60	0.04	0.09	0.69	3.36	0.41	95.41
120	0.03	0.03	0.38	3.06	0.39	96.11
240	0.02	0.02	0.25	2.92	0.19	96.60

[a]Operation condition: T = 30 ºC; molar ratio of crude biodiesel: DES = 1: 4; molar ratio of CHCl: EG = 1: 2

Based on Table 1 and Table 2, the highest FAME content was obtained at molar ratio of crude biodiesel to DES was 1: 4. Since higher DES was added, more molecule of DES which made hydrogen bonding with polar component in crude biodiesel, such as MG, DG, FFA and bioactive compounds. Extraction of MG and DG from crude biodiesel is better than extraction of TG, since TG does not have hydroxyl group. In this work, molar ratio of crude biodiesel to DES of 1: 4 was found to be the most effective for extracting FFA, MG and DG from the biodiesel product.

CONCLUSION

The highest FAME content of 96.60 % was obtained after purification for 240 minutes at molar rasio of crude biodiesel to DES of 1: 4. FAME content after purification at both molar ratio of crude biodiesel to DES (1: 2 and 1: 4) was succesfully fulfill Indonesia standard specification (SNI 7182: 2012) and International standard (EN 14214). FFA, MG and DG content reduced with extraction time using DES. This work shows that DES has potential to purify biodiesel from non-edible raw material, such as RBO and extraction time influence the reduction of impurities in RBO-based biodiesel.

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