

## Waste-Cooking-Oil Free Fatty Acid Reduction Using Deep Eutectic Solvent as Raw Material of Biodiesel

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### Abstract

The purpose of this study was to extract the free fatty acid (FFA) of waste-cooking-oil through liquid-to-liquid extraction using choline chloride as a raw material for Deep Eutectic Solvent (DES) as a waste-cooking-oil purifier. Waste-cooking-oil is obtained from the waste of a fast food factory located in Sukarame, South Sumatera. Making a Deep Eutectic Solvent (DES) using compounds of *ethylene glycol* as Hydrogen Bond Donor mixed with a *choline chloride* Hydrogen Bond Acceptor with five molar ratios, a reaction temperature of 60 °C and a stirring speed of 150 rpm and 200 rpm for 90 minutes. The extraction molar ratio of waste-cooking-oil and DES with four ratios of molar ratios, extraction time of 2 hours at 60 °C and retention time of separation between DES and used cooking oil was 24 hours. The decrease in FFA of waste-cooking-oil was the highest at 83.87% in the DES 2. It proves that DES is able to purify waste-cooking-oil by extraction methods to reduce FFA and adsorb other materials.

**Keywords:** *Deep Eutectic Solvent, Free Fatty Acid, Hydrogen Bond Acceptor, Hydrogen Bond Donor, Purification, Waste Cooking Oil.*

### Abstrak (Indonesian)

Tujuan penelitian ini adalah melakukan ekstraksi untuk menurunkan free fatty acid (FFA) minyak jelantah yang dihasilkan melalui ekstraksi cair-cair yang menggunakan choline chloride bahan baku deep eutectic solvent (DES) sebagai pemurni minyak jelantah. Minyak jelantah diperoleh dari limbah pabrik makanan cepat saji yang berlokasi di Sukarame, Sumatera Selatan. Pembuatan deep eutectic solvent (DES) menggunakan hydrogen bond donor ethylene glycol yang dicampur dengan hydrogen bond acceptor choline chloride dengan lima perbandingan rasio molar, temperatur reaksi 60 C serta kecepatan pengadukan 150 rpm dan 200 rpm selama 90 menit. Rasio molaritas ekstraksi minyak jelantah dan DES dengan empat perbandingan rasio molar, waktu ekstraksi selama 2 jam pada temperatur 60 C dan waktu retensi pemisahan antara DES dan minyak jelantah 24 jam. Penurunan FFA minyak jelantah paling tinggi pada 83.87% pada rasio DES 2. Hal ini membuktikan bahwa DES mampu memurnikan minyak jelantah dengan metode ekstraksi untuk menurunkan FFA dan mengadsorpsi material lainnya.

**Kata Kunci:** *Deep Eutectic Solvent, Free Fatty Acid, Hydrogen Bond Acceptor, Hydrogen Bond Donor, Minyak Jelantah, Purifikasi*

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### INTRODUCTION

Cooking oil is the primary food consumption from human activities. Cooking oil that has been used, is usually still used for frying again. In fact, oil that is used repeatedly can endanger health. Cooking oil undergoes a heating process which will cause various chemical reactions, including hydrolysis, oxidation,

isomerization, polymerization; and will produce substances that affect health issues [1]. Heating oil at high temperatures repeatedly can produce trans fatty acid isomers that are associated with many health problems, such as an increase in C-LDL (cholesterol low density lipoprotein) and a decrease in C-HDL (cholesterol high density lipoprotein), fat deposition in

blood vessels, disorders of the metabolism of omega-3 fatty acids which play a role in the brain and vision, trigger breast cancer, and also affect fetal development [2]. Oil damage will affect the quality and nutritional value of fried foods.

The main damage to the oil is the appearance of a rancid smell and taste, while other damage includes an increase in free fatty acids (FFA), peroxide value (PV), and a darker oil discoloration [3]. To reduce health risks due to the use of used cooking oil, it is necessary to make efforts to process (regenerate) used cooking oil in terms of saving but not endangering health and easy to do. Oil regeneration aims to improve the quality of used cooking oil, which can be done through several methods, one of which is by means of adsorption [4]. Adsorption was chosen because it is easy to implement and economical [5]. Selection of adsorbents can use chemicals such as bentonite, zeolite, sulfuric acid, solvent extraction and agricultural waste in the form of rice husks, coconut shells, bagasse, rice straw, corn cobs, etc [6]. On the other hands, FFAs reduction could be used reaction temperature and using sodium methoxide solution during transesterification process [7]. Amount of methanol can be determined to reduces the acid value of the biodiesel product from waste cooking oil produced [8]. Another result of research, amount of methanol also makes more of the conversion of triglycerides into biodiesel so the free fatty acids contained in the oil are reduced [9].

This study aims to determine the composition (ratio) of the solvent that are effective in reducing free fatty acids, peroxides, and the dark color of used cooking oil. This purification process uses chemical extractor DES (Deep Eutectic Solvents) is a solvent consisting of two components (quaternary ammonium salt with hydrogen bond donor) mixed together in the right ratio so that the eutectic point can be reached. Currently DES can replace the Ionic Liquids (ILs) method because it has physic-chemical properties, DES has several advantages over traditional ILs, including: the synthesis process is simpler because the ingredients can be mixed easily, can be used without the need for further purification which shows that each component has high purity [10]. In addition, DES is non-toxic, has no reactivity with water, and most importantly is biodegradable [11].

Fossil energy has a limitation, its need diversification of energy resources in order to guarantee the availability of renewable energy [12]. Biodiesel is one of the options for the energy needs of the future. This purification process can also affect the purity of biodiesel to become biofuel which will determine the quality of performance in diesel engines,

because in other chemical processes such as in the lathering process, esterification can be involved and poison diesel engines which are commonly referred to as impurities [1]. Impurities in the biodiesel content will reduce the performance of biodiesel in the engine which will affect engine efficiency, reduce combustion heat, hydrolyze methyl esters, clog filters, form ice crystals that damage the fuel tube and injector pump [13].

#### **Waste-Cooking-Oil**

The content of free fatty acids (FFA) in used cooking oil is higher than the FFA in fresh oil. Usually the FFA content is greater than 1% by weight. The content of FFA in oil greatly affects the transesterification reaction process of oil when using an alkaline catalyst. Because FFAs in oil and alcohol in the presence of bases will form soap (solid) [3]. This mixture of soap, oil and alcohol forms an emulsion that can inhibit the speed of the transesterification reaction and cause problems in the separation process of biodiesel and glycerol (reaction product) [14].

#### **Deep Eutectic Solvent**

A deep eutectic solvent is formed between a ammonium salt which is a hydrogen bond acceptor and a hydrogen bond donor. The hydrogen bonds between the ions of ammonium salt compound and the hydrogen donors form large and asymmetrical ions which result in a decrease in the melting point of the mixture compared to the melting point of each component [15]. The de-localization of charge that occurs via hydrogen bonding is a major factor in reducing the melting point of the mixture. This liquid is called DES to distinguish it from ionic liquid, DES can be defined as a liquid that is close to the eutectic composition of a mixture, the eutectic composition is the condition when the molar ratio of the components provides the lowest melting point [16]. In addition, compared to traditional ILs, DES has many advantages, such as:

1. Low cost.
2. Chemically inert with water (makes it easier for storage) [17].
3. It is easy to prepare because DES is obtained only by mixing two components so that it does not require the purification and waste disposal problems commonly encountered with ILS [18].
4. Most of DES is biodegradable, biocompatible and non-toxic. For this reason, DES derived from ChCl is also known as a biocompatible bio-renewable ionic liquid in several studies [19].

## MATERIALS AND METHODS

### Materials

Waste-cooking-oil was donated by PT. Indofood CBP Sukses Makmur, Palembang, Indonesia. Choline Chloride (ChCl) (98%) bought from Geojaya, (Bogor, Indonesia), Ethylene Glycol (99%) bought from Bratachem, (Palembang, Indonesia). All other chemicals used were obtained from Energy Engineering Laboratory, State Polytechnic of Sriwijaya.

### Synthesis of Deep Eutectic Solvent

This study used a DES-based ChCl as Hydrogen Bond Acceptor (HBA) and ethylene glycol as Hydrogen Bond Donor (HBD). The synthesis of deep eutectic solvents (DES) was performed with a variable of 150 rpm and 200 rpm stirring rate with a reaction temperature of 60 °C for 1 hours. The molar ratio of ChCl: ethylene glycol is DES 1 (1: 1), DES 2 (1: 2) and DES 3 (1: 4), DES 4 (1: 6) and DES 5 (1: 8).

### Waste-Cooking-Oil Purification Process

Waste-cooking-oil was purified by liquid-liquid extraction method using DES as a solvent. Waste-cooking-oil and DES was added to Erlenmeyer. Molar ratio of waste-cooking-oil to DES were varied 1: 1, 1: 3, 1: 4 and 1: 6. The mixture was varied settling time for 1 hour and 2 hours with constant temperature 60 °C and under stirring 200 rpm, then 2 layers were formed. The mixture was separated from DES using separator funnel. The upper layer was purified waste-cooking-oil and the bottom layer was DES. For purified waste-cooking-oil was analysis by titration method to measure FFA content after liquid-liquid extraction.

## RESULTS AND DISCUSSION

### Characteristic of Deep Eutectic Solvent

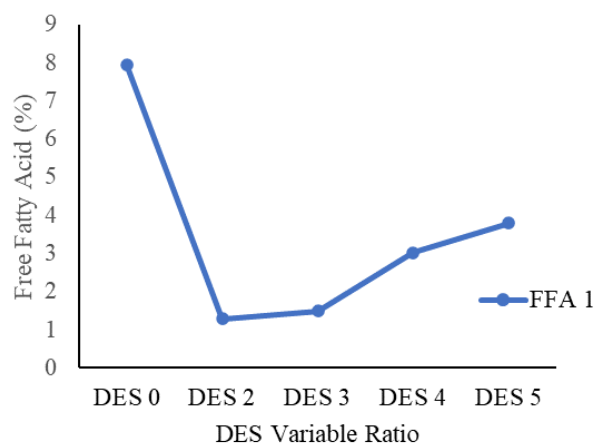
The results of DES synthesis with ChCl/ethylene glycol at molar ratio of DES 2, DES 3, DES 4 and DES 5 produces a colorless liquid form at room temperature so it can be used as a solvent in the next process. And other phenomenon for DES 1 crystallization so it could not be to the next process. It is means DES 1 supercooled phenomenon, having a single chemical composition which freezes at a lower temperature at 28 °C after a mixing or reaction process at 60 °C. If waste-cooking-oil using DES solution which crystallizes to purification, it would make coagulate or solidification the product.



**Figure 1.** DES 1 Crystallization

### Effect of Extraction Time for Free Fatty Acid Reduction

Analysis of effect extraction time in the purification of waste-cooking-oil on the free fatty acid finished by applying different molar ratio. After did analysis process, free fatty acid comparing with the result analysis from extraction time for 1 hour and extraction time for 2 hours. Free fatty acid without using DES in 7.94%. Free fatty acid of waste-cooking-oil can be seen in Fig. 2 and Fig. 3 below:



**Figure 2.** Effect of Extraction Time to Free Fatty Acid Reduction operation temperature = 60 °C; extraction time = 1 hour; molar ratio WCO to DES = 1: 6

Base on the Figure 2 above can be seen that the resulting graph fluctuated for percentages free fatty acid on the DES variable ratio. From Figure 2, it can be seen that DES 0 has highest FFA content because the sample was a blank sample only. And for others DES 2, DES 3, DES 4, DES 5, was purify using DES. The graphic above, showed FFA for DES 2 (WCO/DES 1:6 and DES (ChCl/Ethylene Glycol 1:2)) lower than DES 5 (WCO/DES 1:6 and DES (ChCl/Ethylene Glycol 1:8)) because of the contained

of material which making DES have more hydrogen bond acceptor than hydrogen bond donors. Hydrogen bond acceptor is acts important role to adsorption the hydrogen contained which makes FFA increases [19]. For conversion to biodiesel, we need waste-cooking-oil that has a FFA content lower under 2% of FFA to avoid saponification during conversion process to biodiesel [20].

### Effect of Molar Ratio of Waste-Cooking-Oil to DES for Free Fatty Acid Reduction

Analysis of effect extraction time in the purification of waste-cooking-oil on the free fatty acid finished by applying four different molar ratios for both of waste-cooking-oil and DES. After did analysis process, free fatty acid comparing with the result analysis from effect of DES 2 and DES 3. Free fatty acid without using DES in 7.94%. Free Fatty Acid of waste-cooking-oil can be seen in Table 1 below:

**Table 1.** Effect of molar ratio on the content of FFA before and after liquid-to-liquid extraction

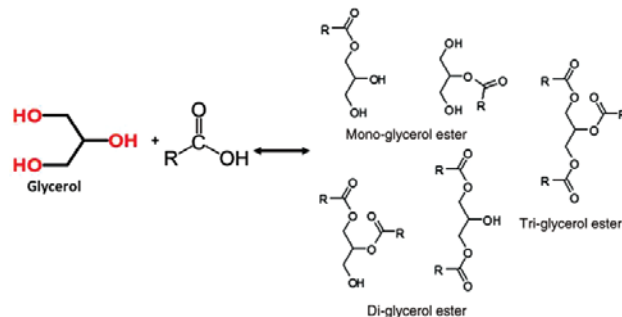
| Composition |          | FFA <sub>0</sub> | FFA <sub>1</sub> | Eff.  |
|-------------|----------|------------------|------------------|-------|
| DES         | WCO: DES | (%)              | (%)              | (%)   |
| DES 2       | 1 : 0    | 7.94             | 7.94             | 0.00  |
|             | 1 : 1    | 7.94             | 4.45             | 43.87 |
|             | 1 : 3    | 7.94             | 2.56             | 67.74 |
|             | 1 : 4    | 7.94             | 1.54             | 80.65 |
|             | 1 : 6    | 7.94             | 1.28             | 83.87 |
| DES 3       | 1 : 0    | 7.94             | 7.94             | 0.00  |
|             | 1 : 1    | 7.94             | 6.20             | 21.94 |
|             | 1 : 3    | 7.94             | 3.07             | 61.29 |
|             | 1 : 4    | 7.94             | 1.69             | 78.71 |
|             | 1 : 6    | 7.94             | 1.48             | 81.29 |

Based on the Table 1 above, the lower FFA content was obtained from DES 2 purification with molar ratio between waste-cooking-oil and DES 1: 6. And also for DES 3 FFA lower was obtained from 1: 6 molar ratio for waste-cooking-oil and DES. In this work, waste-cooking-oil to DES of DES 2 was found the most effectiveness for extracting FFA from the waste-cooking-oil.

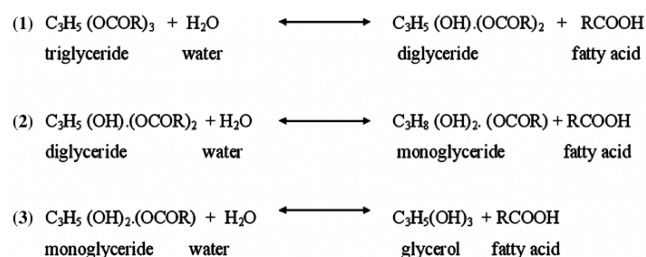
For DES 2 and DES 3, ChCl content was greater than DES 4 and DES 5 which contained more ethylene glycol. The following of the molar ratio of DES solution to ChCl/ethylene glycol in DES, DES 2 (1:2), DES 3 (1: 4), DES 4 (1: 6) and DES 5 (1: 8). Therefore, the compound that acts an important role in the extraction process for the reduction of free fatty acids is ChCl as a hydrogen bond acceptor. According to research [21], if there is higher the ethylene glycol

content will increases the amount of glycerol of the oil. ChCl will adsorb hydrogen<sup>b</sup> and also glycerol<sup>a</sup> that would be reaction to oxygen then being a water content. Water content could have a reaction with triglyceride<sup>c</sup> in oil that produce free fatty acid then it would be increasing. Following the explanation below:

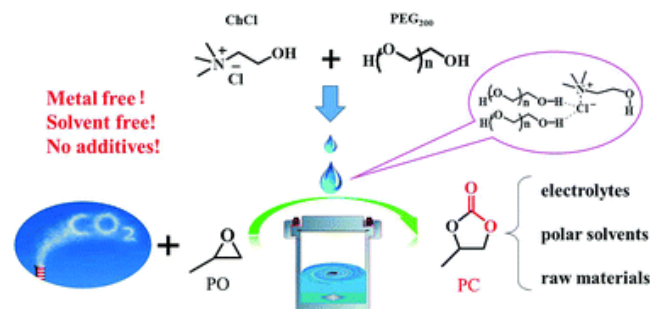
a) Reaction between DES and glycerol [22]



b) Reaction between DES and water [23]



c) Reaction between water and triglyceride [24]



## CONCLUSION

The research that has been done is liquid-to-liquid extraction using Deep Eutectic Solvent as raw material to reduce FFA levels in used cooking oil as a raw material for making biodiesel. 2. The best reduction free fatty acid absorption ability of DES can reduce FFA by 83.87%. The decrease in FFA in the initial used cooking oil was 7.94% and after extraction it became 1.28% in the mixture of WCO: DES 1: 6 and DES 2 ratios. But on the other side, DES is more chemically used for purification, so it needs to be further studied. DES is more effectiveness used to reduction free fatty acid from waste-cooking-oil for raw material of biodiesel.

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