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# Effect of Extraction Time on Unreacted Oil Removal in Biodiesel Purification Using Deep Eutectic Solvent

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**Abstract**

*Rice bran oil (RBO) based biodiesel contains unreacted oil such as monoglyceride (MG), diglyceride (DG) and triglyceride (TG) to be purified. The liquid-liquid extraction (LLE) method was used for purification using Deep Eutectic Solvent (DES). The objective of this work was to study the effect of extraction time on unreacted oil removal. RBO containing 16.49% oil with free fatty acids (FFA) content of 44.75%. Acid catalyzed methanolysis was used for biodiesel production under operating conditions: T = 60°C, t = 8 hours, molar ratio of oil/methanol was 1/10, $H_2SO_4$ 1% w/w of RBO. Crude biodiesel containing 89.05% fatty acid methyl ester (FAME), 0.05% FFA, TG 4.03%, DG 4.01% and MG 0.30%. DES was made from choline chloride and ethylene glycol with 1/2 molar ratio, while molar ratio of biodiesel/DES was 1/2. The extraction time was varied from 15 to 240 minutes at 30°C. The highest TG, DG and MG removal were obtained at 240 minutes, they were 3.01%, 0.22% and 0.03%, respectively. FAME and FFA content were 96.55% and 0.03%.*

**Keywords:** *biodiesel; DES; extraction; unreacted oil; purification*

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## INTRODUCTION

The utilization of biodiesel as an energy source get massive attention from the researchers and the policy makers in recent days. This is due to biodiesel is a main alternative of petrodiesel's substitute and also can be produced from various materials (Lu *et al.*, 2007; Chopade *et al.*, 2012). Biodiesel has some advantages compared to petrodiesel those are naturally biodegradable and produces low level of emission reviewed from $CO_2$, CO, particulate matters, hydrocarbon, and unburnt sulfur as well (Reinders, 2006; Qiu *et al.*, 2011). Beside that, biodiesel has high flash point, low sulfur concentration, lubricating efficiency, and better cetane number (Helwani *et al.*, 2009).

After production process, crude biodiesel must be purified for fulfilling biodiesel standard quality as stated at EN 14214, ASTM D6751, or SNI 7182:2012. The presence of impurities in biodiesel will give issues and damage in machine (Demirbas, 2009). When methanol presences in biodiesel, it can decrease the viscosity, density and flash point of biodiesel. The

presence of water decreases the heating value, hydrolyzes methyl esters, filter plugging, forming ice crystals which damages the fuel tube, and injector pump. Catalyst residue may harm the injector and it can be a suspect of corrosion issue, machine plugging, and weaken the engine. Glycerol caused the deposit in the bottom of the fuel tank, fouling in injector, higher emission release, and engine durability issue. Wet washing and dry washing methods are the most common purification methods. Currently, the newest method is already developed and tested such as membrane technology and ionic liquid assisted for distilling biodiesel (Stojkovic *et al.*, 2014).

Wet washing is a purification method to remove the impurities in biodiesel product by using water and solvent. Purification process using this method requires 60-80% of total production cost hence this method is not suitable for large scale biodiesel production (Atadashi *et al.*, 2011). Purification by using dry washing is a method in removing contaminants from crude biodiesel by adsorption or by allowing the biodiesel to pass through ion exchange resin (Stojkovic *et al.*, 2014; Faccini *et al.*, 2011) with magnesol, silica, Amberlite BD10 DRY® and Purolite PD® as adsorbents. The use of magnesol or silica shows better results than resin does. Ion exchange resin is not recommended to be regenerated, the main weakness of ion exchange utilization is the generated solid waste issues (Stojkovic *et al.*, 2014).

Biodiesel purification process also can be performed by using membrane. He *et al.* (2006) purified biodiesel using hollowfiber polysulfone and polyacrylonitrile which is combined with conventional extraction. Alves *et al.* (2013) purified biodiesel derived from soybean oil using microfiltration and ultrafiltration. Purification process using membrane is profitable in economic aspect and preventing the waste generation to the environmental (Saleh *et al.*, 2010). The weaknesses of this technology are the final production cost increase and the possibilities of contamination (Leung *et al.*, 2010).

Ionic liquids are now attracting the attention in biodiesel production, which can act as a catalyst, co solvent or solvent extraction (Zhao and Baker, 2013). Chemically, ionic liquid is an organic salt with a melting point around or below the ambient temperature, which consists of organic cations and organic or inorganic anions. However, due to the complexity of ionic liquid synthesis and the high cost of chemicals, ionic liquids can be replaced with DES (Stojkovic *et al.*, 2014). DES is a new generation solvent formed from a mixture of quaternary ammonium salts with hydrogen bond donor (HBD). DES compared to conventional organic solvents, has advantages because it is not volatile and is not flammable, hence the storage is easier. DES has a lower melting point than each of its constituent components. DES is polar so that it can be used to separate biodiesel from impurities such as glycerol, water, FFA, MG, DG and TG which are polar. DES can dissolve water, but cannot dissolve biodiesel (Zhang *et al.*, 2012).

Some raw materials for biodiesel production have relatively expensive prices because their availability for biodiesel's feedstocks competes with food needs. The cost of raw materials reaches 60-75% of the total cost of biodiesel production. To reduce the cost of biodiesel production, many researchers are interested in using non-food raw materials such as rice bran (Boulifi *et al.*, 2013; Zullaikah *et al.*, 2005). The oil content of rice bran is 15-20%, with FFA levels of 44.56% (Ju and Siti, 2013; Nasir *et al.*, 2009). Crude biodiesel from rice bran containing side products called biodiesel residues consists of FFA, MG, DG, TG and antioxidant compounds such as oryzanol, tocopherols, tocotrienols phytosterol, polyphenols and squalene (Ju and Vali, 2005; Kasim *et al.*, 2007). The residue must be isolated from biodiesel to reduce the production costs of biodiesel (Ju and Siti, 2013). Most of the previous studies regarding the purification of biodiesel were aimed at separating glycerol, soap, FFA and residual TG from raw materials which have high TG content and low FFA. Meanwhile, purification of crude biodiesel from rice bran is more difficult than other vegetable oils because of its high free fatty acid content, dark color and differences in the composition of its minor compounds (Van Hoed *et al.*, 2006).

Several studies on the purification of crude biodiesel from rice bran have been carried out using the wet washing method. Lin *et al.* (2009) purified crude biodiesel from rice bran processed by the transesterification method using a KOH as catalyst. Boulifi *et al.* (2013) processed biodiesel from rice bran oil through the transesterification method, then biodiesel was purified by the wet washing method to remove residual catalyst, glycerol and soap. In addition, studies using dry washing methods such as Ozgul-Yücel and Selma (2003) used rice husk ash and commercial silica gel to purify methyl esters from rice bran by adsorption of free fatty acids in atmospheric conditions.

The purification of biodiesel in this study used the method of liquid-liquid extraction with DES as a solvent. The liquid-liquid extraction method was chosen because the components that will be separated from crude biodiesel are unreacted oil which has long chain carbon atoms. The longer carbon atoms components are harder to be distilled. Fatty acids with a number of carbon atoms chain more than 12 are difficult to be distilled. Whereas if the extraction of FFA, MG, DG and TG using water or other organic solvents will be difficult because the solubility of FFA, MG, DG and TG in water or organic solvents will decrease with the length of the carbon atom chain (Hoffman, 1989). Based on Shahbaz *et al.* (2011) that DES can reduce MG and DG levels from crude biodiesel made from palm oil, this is because DES forms hydrogen bonds with MG and DG. Hydrogen bonds occur between DES and hydroxyl groups in MG and DG. In addition to MG and DG, there are also other impurities such as FFA and bioactive compound in RBO based biodiesel such as oryzanol. It has benefits if it can be isolated from crude biodiesel. These

compounds have hydroxyl groups that can form hydrogen bonds with DES. Methyl ester as the main constituent compound of biodiesel is insoluble in DES, because methyl esters do not have hydroxyl groups.

Previous research has been carried out by Niawanti and Zullaikah (2017) using DES for removal of bioactive compounds ɣ-oryzanol from crude biodiesel. The lowest content of ɣ-oryzanol (1.18%) was obtained at 240 minutes extraction time at 30 ° C and molar ratio of crude biodiesel to DES was 1:4. The study showed that DES has the potential to purify biodiesel and reduce the content of unsaponifiable matter (γ-oryzanol). The DES used in this study is the same as the one used in the previous study, ChCl-based DES as quaternary ammonium salt and ethylene glycol as HBD. This work studied the effect of extraction time on removal of unreacted oil (MG, DG and TG) in biodiesel products.

## RESEARCH METHODS

### Materials

The raw material used in this study was IR 64 rice bran from Banyuwangi, before being used rice bran was sifted first to separate the impurities that are included in rice bran. Other materials used were Choline chloride (≥ 98%) from Sigma Aldrich (China), Ethylene Glycol (99%) from SAP Chemical (Indonesia), N-hexane, methanol and sulfuric acid (98%) were purchased from ANHUI FULLTIME (Anhui, China). Other chemicals are analytical grades and are obtained from commercial sources.

### Rice Bran Oil Extraction

Fifty g of rice bran was wrapped using filter paper and filled into soxhlet. 300 mL of N-hexane as a solvent was put into a 500 mL round bottom flask equipped with a mantle heater and connected to a reflux condenser. The N-hexane was then heated to 70°C and the extraction time was 8 h until the RBO was completely obtained. N-hexane and RBO were then separated using a rotary vacuum evaporator. RBO contains wax and gum which were separated from RBO by crystallization at low temperatures using acetone. RBO (5 g) was dissolved in 30 mL acetone in a 50 mL-stopper glass vessel. The vessel was maintained at 60°C for an hour then cooled at room temperature. The vessel was then cooled at ± 5°C for 24 hours to crystallize the wax. The solid phase was separated by filtration while the solvent in the filtrate (acetone) was separated using a rotary evaporator. The RBO was then weighed to determine the yield produced and analyze the levels of FFA, MG, DG and TG in RBO.

### Biodiesel Production

The process of biodiesel production used the acid catalyzed methanolysis method that has been carried out by Zullaikah et al. (2005). Based on this study, 10 g of rice bran oil was reacted with methanol at atmospheric pressure at 60°C, the molar ratio of rice to methanol was 1:10 and sulfuric acid catalyst was 1 wt-% of RBO. Biodiesel was washed with 300 mL N-hexane to remove sulfuric acid. The produced Crude biodiesel contains 89.05% FAME and 0.05% FFA. The contents of FFA, FAME, MG, DG and TG in biodiesel were analyzed using High Temperature Gas Chromatography (HTGC) Shimadzu GC-2010 Plus (Kyoto, Japan).

### Preparation of Deep Eutectic Solvent

DES was made with a molar ratio between ChCl as a hydrogen bond acceptor (HBA) and ethylene glycol as a hydrogen bond donor (HBD) of 1:2. The mixture was heated at 60$^{o}$C with constant stirring at 300 rpm until a transparent homogeneous liquid was obtained.

### Purification Process

Crude RBO was purified using the LLE method and using DES as solvent. DES was added to biodiesel with a molar ratio of biodiesel to DES was 1:2. Extraction times were varied of 15, 30, 45, 60, 120 and 240 minutes with extraction temperature at 30$^{o}$C. After the extraction time was complete, the sample was settled for 2 h until the upper layer and bottom layer are formed, then the upper layer (biodiesel) was separated from the bottom layer (DES) using a funnel separator like presented in Figure 1. Biodiesel was analyzed using HTGC to determine the contents of FAME, FFA, TG, DG and MG

Figure 1. Mixture of DES and Crude Biodiesel at Settling Time

### HTGC Analysis Method

Characterization of raw materials and analysis of MG, DG and TG content in samples after the purification process were carried out using the Gas Chromatography method. The HTGC Shimadzu GC-2010 Plus (Kyoto, Japan) tool with a flame ionization type detector was equipped with a ZB-5HT (5%-phenyl)-methylpolysiloxane column non-polar column (15 m × 0.32 mm id, 0.1 mm film thickness; Agilent Tech. Palo Alto, California). 20 mg of rice bran oil or biodiesel samples were dissolved by adding 1.5 mL of ethyl acetate. The solution was then taken as much as 1.5 µL to be injected into HTGC. The temperature of the injector and detector of HTGC were both operated

at a temperature of 370°C. The column temperature was maintained at an initial temperature of 80°C to 365°C at temperature ramp of 15°C/min after 8 minutes and the carrier gas was nitrogen with a split ratio of 1:50.

## RESULTS AND DISCUSSION

### RBO and Crude Biodiesel Characteristics

RBO contains FFA, but also contains bioactive compounds such as ɣ-oryzanol and triacylglycerol which consist of TG, DG and MG, like presented in Table 1. While crude biodiesel contains methyl ester as the main constituent component, unreacted oil consisting of TG, DG and MG and unsaponifiable matter. The following is the chemical composition found in the RBO and crude biodiesel in this study.

Table 1. Chemical composition in RBO and CBD

| Components | RBO | CBD |
|---|---|---|
| FAME (% wt) | N.D* | 89.05 |
| FFA (% wt) | 44.75 | 0.05 |
| Triglyceride (% wt) | 25.22 | 4.03 |
| Diglyceride (% wt) | 17.85 | 4.01 |
| Monoglyceride (% wt) | 9.27 | 0.30 |
| *Others* (% wt) | 2.91 | 2.55 |

*N.D (*not detected*)

Decrease in FFA value indicates that FFA is converted to methyl ester. The content of TG, DG and MG is still quite large after the esterification process, this is because the conversion of TG, DG and MG in the process of biodiesel production with the esterification method is not optimal. This value is not in accordance with the SNI 7182: 2012 standard for biodiesel, where a minimum of FAME is 96.5%. Biodiesel from RBO is prepared by several types of methyl esters. The composition of methyl esters as a result of GC analysis: Chomatograph of biodiesel like presented in Figure 2. Type of methyl ester in biodiesel from RBO like presented in Table 2. Oleic acid methyl ester was dominated in biodiesel about 73.99%.

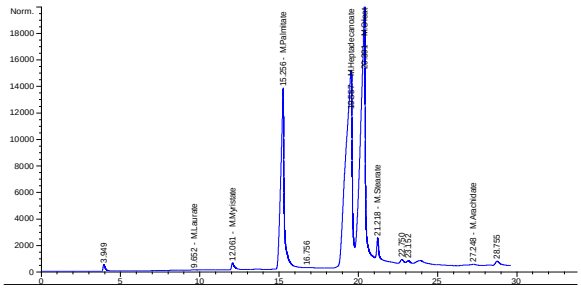


Figure 2. Chemical composition of crude biodiesel

Extraction time is one of the factors that influence the extraction process. The longer extraction time provides longer contact time between DES solvents and crude biodiesel. Hence, more solutes are separated from biodiesel. The results of this study show that as time increases, the content of MG, DG, TG in biodiesel decrease significantly, like presented in Figure 3. The purity of produced biodiesel increases as well. It can be seen from the increased levels of FAME and the decreased FFA levels after the extraction process.

Table 2. Composition list of fatty acid methyl esters

| Senyawa | Komposisi (%) |
|---|---|
| Lauric acid methyl ester | 0.07 |
| Myristic acid methyl ester | 1.25 |
| Palmitic acid methyl ester | 14.72 |
| Heptadecanoic acid methyl ester | 6.96 |
| Oleic acid methyl ester | 73.99 |
| Stearic acid methyl ester | 2.26 |
| Arachidic methyl ester | 0.76 |

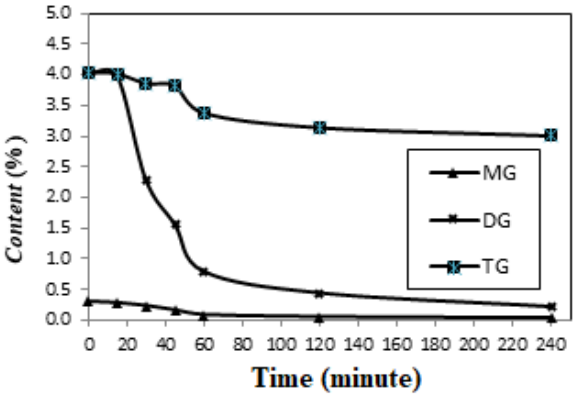


Figure 3. The effect of extraction time on the level of MD, DG dan TG after purification (T = 30ºC; *crude* biodiesel/DES = 1/2; CHCL/EG = 1/2).

Unreacted oil consisting of TG, DG and MG is not desired to be found in biodiesel products. TG, DG and MG are bound glycerol, commonly called triacylglycerol. TG, DG and MG can be hydrolyzed to glycerol and FFA with the presence water in biodiesel. Triacylglycerol is difficult to be separated from biodiesel using a conventional distillation method because of its low vapor pressure. Although it can occur, it will cause the decomposition of triacylglycerol into glycerol and FFA (Hoffman, 1989). This research shows that DES can separate DG and MG from crude biodiesel properly.

Extraction time affects the content of TG, DG and MG in biodiesel. The longer of extraction time, MG and DG decreased significantly where the lowest content was obtained at the extraction time of 240 minutes with MG levels of 0.03%, while the DG content was 0.22%. The longer of extraction time provides longer interaction time between DES with MG and DG in the formation of hydrogen bonds, so that more MG and DG are dissolved in DES.

The DES effect in separating DG from crude biodiesel at the extraction time of 240 min was more significant than with MG. Removal efficiency from DG is 94.56%, while for MG is 91.08%. This is in accordance with previous research conducted by Shahbaz *et al.* (2011) that DES has a tendency to be more effective in removing DG than MG from

biodiesel made from palm oil. Whereas TG reduction is not significant, removal efficiency of TG is only 25.28%. The TG content after purification process at 240 min is 3.01%. This is could be due to the absence of hydroxyl groups in TG molecule. Therefore, DES unable to separate TG from crude biodiesel through hydrogen formation bonding completely. The total glycerol in this study was calculated using an equation based on the ASTM D6584-07 as shown in equation (1).

Total glycerol = Glycerol + 0.255MG + 0.146DG + 0.103TG (1)

The total glycerol in biodiesel products in the best condition is 0.34%, this value is still higher than the maximum standard for total glycerol content in SNI or ASTM D6751, which is 0.24%. This is might be due to the TG content level is still quite high in biodiesel products.

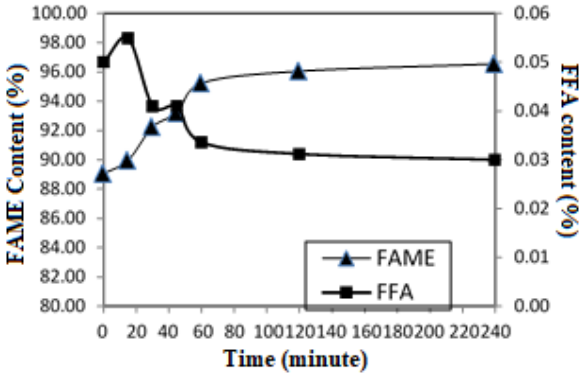


Figure 4. The effect of extraction time on the FAME and FFA content level after purification (T = 30°C; *crude* biodiesel/DES = 1:2; CHCl/EG = 1:2).

Figure 4 shows that the longer the extraction time, the higher FAME content is obtained. This is due to the longer extraction time provide higher possibility of interaction between DES and impurities compounds that will be bound through hydrogen bonds. FFA and unreacted oil could be removed from crude oil using DES effectively at longer extraction time. The highest FAME content was obtained at 240 min extraction time with FAME content of 96.55%. The FAME content obtained has fulfilled the requirement standard based on SNI 7182: 2012 (the minimum methyl ester content was 96.5%). The longer extraction time also resulted in the higher removal efficiency of FFA from biodiesel. The lowest FFA value was obtained at the extraction time of 240 minutes with FFA content of 0.03%, if it was converted to acid value the value was 0.06 mg KOH/g. This value still meets SNI standards, where the maximum acid value for biodiesel is 0.06 mg KOH/g.

## CONCLUSIONS

The unreacted oil contents (MG, DG and TG) decreased as the function of extraction time. The best extraction time in this study was achieved at 240 min during extraction process. The removal efficiency of MG, DG and TG are 91.08, 94.56 and 25.28%, respectively. The FAME content in the mentioned conditions was obtained at 96.55% and FFA levels at 0.03%. The contents of FAME and FFA meet the biodiesel standard specifications based on SNI 7182: 2012 standard for commercial biodiesel. However, the total glycerol in biodiesel is out of the specification standard because TG is difficult to be purified using DES. This study shows that DES can be used to separate MG, DG and TG from crude biodiesel and extraction time significantly affects the purification products specification.

## REFERENCES

Alves, M.J., Suellen, M.N., Pereira, I.G., Martins, M.I., Cardoso, V.L., and Reis, M., (2013), Biodiesel Purification Using Micro and Ultrafiltration Membranes, *Renewable Energy*, 58, pp. 15-20.

Atadashi, I.M., Aroua, M.K., Abdul Aziz, A.R., and Sulaiman, N.M.N., (2011), Refining Technologies for the Purification of Crude Biodiesel, *Applied Energy*, 88, pp. 4239-4251.

Boulifi, N.E., Bouaid, A., Martinez, M., and Aracil, J., (2013), Optimization and Oxidative Stability of Biodiesel Production from Rice Bran Oil, *Renewable Energy*, 53, pp. 141-147.

Chopade, G.S, Kulkarni, K.S., Kulkarni, A.D., and Topare, N.S., (2012), Solid Heterogeneous Catalysts for Production of Biodiesel from Trans-Esterification of Tryglicerides with Metanol: A Review, *Acta Chemica & Pharmaceutica Indica*, 1, pp. 8-14.

Demirbas, A., (2009), Progress and Recent Trends in Biodiesel Fuels, *Energy Conversion Management*, 50, pp. 14-34.

Faccini, C.S., Michele, E.C., Maria Silvana, A.M., Laiza, C.K., Marcia, C.M., Maria, R.A.R., Edilson, V.B., and Elina, B.C., (2011), Dry Washing in Biodiesel Purification: A Comparative Study of Adsorbents, *Journal Brazilian Chemistry Society*, 22, pp. 558-563.

He, H.Y., Guo, and Zhu, S.L., (2006), Comparison of Membrane Extraction with Tradition Extraction Methods for Biodiesel Production, *Journal of the American Oil Chemists' Society*, 83, pp. 457-460.

Helwani, Z., Othman, M.R., Aziz, N., Kim J., and Fernando, W.J.N., (2009), Solid Heterogeneous Catalysts for Trans-Esterification of Triglycerides with Methanol, *Applied Catalysis A: General*, 363, pp. 1-10.

Hoffman, G., (1989), *The Chemistry and Technology of Edible Oils and Fats and their High Fat Products*, Academic Press.

Ju, Y. and Vali, S., (2005), Rice Brain Oil as a Potential Resource for Biodiesel: A Review, *Journal of Scientific and Industrial Research*, 64, pp. 866-882.

Kasim, N.S., Chen, H., and Ju, Y-H., (2007), Recovery of ϒ-Oryzanol from Biodiesel Residue, *Chinese Institute of Chemical Engineering*, 38, pp. 229-234.

Leung, D.Y.C., Wu, X., Leung, M.K.H., (2010), A Review on Biodiesel Production Using Catalyzed Transesterification, *Applied Energy*, 87, pp. 1083–1095.

Lin, L., Ying, D., Chaitep, S., and Vittayapadung, S., (2009), Biodiesel Production from Crude Rice Bran Oil and Properties as Fuel, *Applied Energy*, 86, pp. 681–688.

Lu, G.Q., Diniz da Costa, J.C., Duke, M., Giessler, S., Socolowe, R., and Williams, R.H., (2007), Inorganic Membranes for Hydrogen Production and Purification: A Critical Review and Perspective, *Journal of Colloid and Interface Science*, 314, pp. 589-603.

Nasir, S., Fitriyanti, F., and Kamila, H., (2009), Extraction of Rice Bran into Crude Rice Bran Oil Using N-Hexane and Ethanol, *Journal of Chemical Engineering*, 2(16), pp. 1-10

Niawanti, H. and Zullaikah, S., (2017), Removal of Bioactive Compound (ϒ-Oryzanol) from Rice Bran Oil-Based Biodiesel Using Deep Eutectic Solvent, *Chemical Engineering Transaction*, 56, pp. 1513-1518.

Qiu, F., Li, Y., Yang, D., Li, X., and Sun, P., (2011), Biodiesel Production from Mixed Soybean Oil and Rapeseed Oil, *Applied Energy*, 88, pp. 2050-2055.

Saleh, J., Tremblay, A.Y., and Dubé, M.A., (2010), Glycerol Removal from Biodiesel Using Membrane Separation Technology, *Fuel*, 89, pp. 2260–2266.

Sevil, O-Y. and Türkay, S., (2003), Purification of FAME by Rice Hull Ash Adsorption, *Journal of the American Oil Chemists' Society*, 80,pp. 373-376.

Shahbaz, K., Mjalli, F.S., Hashim, M.A., and AlNashef, I.M., (2011), Using Deep Eutectic Solvents Based on Methyl Triphenyl Phosphunium Bromide for the Removal of Glycerol from Palm-Oil-Based Biodiesel, *Energy and Fuel*, 25, pp. 2671–2678.

Stojkovic, I.J., Oliviera, S.S., Dragan, S.P., and Vlada, B.V., (2014), Purification Technologies for Crude Biodiesel Obtained by Alkali-Catalyzed Transesterification, *Renewable and Suistanable Energy Reviews*, 32, pp. 1-15.

Van Hoed, V., Depaemelaere, G., Ayala, J.V., Santiwattana, P., Verhe, R., and De Greyt, W., (2006), Influence of Chemical Refining on The Major and Minor Components of Rice Bran Oil, *Journal of the American Oil Chemists' Society*, 83, pp. 315–321.

Zhang, Q., Vigier, K.D.O., Royer, S. and Jerome, F., (2012), Deep Eutectic Solvents: Syntheses, Properties and Applications, *Chemical Society Reviews*, 41, pp. 7108-7146

Zhao, H. and Baker, G.A., (2013), Ionic Liquids and Deep Eutectic Solvents for Biodiesel Synthesis: A Review, *Journal Chemical Technology Biotechnology*, 88, pp. 3–12.