Biodiesel production from ethanolysis of palm oil using deep eutectic solvent (DES) as co-solvent

R Manurung¹, A Winarta¹, Taslim¹, and L Indra¹
¹Department of Chemical Engineering, Engineering Faculty, University of Sumatera Utara, Medan, Indonesia
E-mail: renitachem@yahoo.com

Abstract. Biodiesel produced from ethanolysis is more renewable and have better properties (higher oxidation stability, lower cloud and pour point) compared to methanolation, but it has a disadvantage such as complicated purification. To improve ethanolysis process, deep eutectic solvent (DES) can be prepared from choline chloride and glycerol and used as co-solvent in ethanolysis. The deep eutectic solvent is formed from a quaternary ammonium salt (choline chloride) and a hydrogen bond donor (Glycerol), it is a non-toxic, biodegradable solvent compared to a conventional volatile organic solvent such as hexane. The deep eutectic solvent is prepared by mixing choline chloride and glycerol with molar ratio 1:2 at temperature 80 °C, stirring speed 300 rpm for 1 hour. The DES is characterized by its density and viscosity. The ethanolysis is performed at a reaction temperature of 70 °C, ethanol to oil molar ratio of 9:1, potassium hydroxide as catalyst concentration of 1.2 % wt. DES as co-solvent with concentration 0.5 to 3 % wt. stirring speed 400 rpm, and a reaction time 1 hour. The obtained biodiesel is then characterized by its density, viscosity, and ester content. The oil - ethanol phase condition is observed in the reaction tube. The oil - ethanol phase with DES tends to form meniscus compared to without DES, showed that oil and ethanol become more slightly miscible, which favors the reaction. Using DES as co-solvent in ethanolysis showed increasing in yield and easier purification. The esters properties meet the international standards ASTM D6751, with the highest yield achieved 83.67 % with 99.77 % conversion at DES concentration 2 %. Increasing DES concentration above 2 % in ethanolysis decrease the conversion and yield, because of the excessive glycerol in the systems makes the reaction equilibrium moves to the reactant side.

1. Introduction
Biodiesel is generally produced by the methanolysis of vegetable oil, waste oils, non-edible oils and animal fats. Its production from other alcohols, such as ethanol, is also possible. Methanol is generally selected because it costs less than ethanol, and the properties of the FAMEs (fatty acid methyl esters) obtained after transesterification are similar to the properties of diesel. However, biodiesel produced using methanol is not entirely renewable because methanol is predominately derived from fossil sources, including natural gas, petroleum and coal [1]. When ethanol is used in transesterification, the process can be called ethanolysis and the product is FAEEs (Fatty Acid Ethyl Esters).

Although ethanol is currently more expensive than methanol, it has the advantage of being more miscible in vegetable oils and has lower toxicity. Compared to methyl esters, ethyl esters have higher oxidation stability, lower iodine value, and improved lubricity properties. Additionally, ethyl esters have lower cloud point and pour point, which improves the engine starting at low temperatures, and the extra carbon atom provided by the ethanol molecule slightly increases the heat of combustion and...
the cetane number. The evaluation of exhaust emissions (NOx, CO2, soot) shows that the ethyl esters have a less negative effect on the environment, compared with that caused by the methyl esters [2].

However, the utilization of ethanol also presents inconveniences. Effectively, as it is indicated in the literature, the base-catalyzed formation of ethyl ester is difficult compared to the formation of methyl esters. Specifically, the formation of the stable emulsion during ethanolysis is a problem. Methanol and ethanol are not miscible with triglycerides at room temperature, and the reaction mixture is usually mechanically stirred to enhance mass transfer. During the course of the reaction, emulsions are usually formed. In the case of methanolysis, these emulsions break down quickly and easily to form a lower glycerol-rich layer and upper methyl ester rich layer. In ethanolysis, these emulsions are more stable and severely complicate the separation and purification of esters [3]. For an alkali-catalyzed transesterification, the glycerides and alcohol also must be substantially anhydrous because water makes the reaction partially change to saponification, which produces soap. The soap lowers the yield of esters and renders the separation of ester and glycerol and the water washing difficult. Low free fatty acids (FFAs) content in vegetable oil is required for alkali-catalyzed transesterification [4].

To overcome the disadvantages of existing biodiesel production processes, novel technologies are emerging. The use of ionic liquids (ILs) as a catalyst, a co-solvent or an extracting solvent have recently attracted attention in the biodiesel production. A new generation of ILs, called deep eutectic ILs or deep eutectic solvents (DESs), became a target of interest for many researchers studying biodiesel production due to their advantages and environmentally-friendly nature. DESs might reduce the side reactions (such as saponification), and make separation and purification processes easier. Some DESs are also efficient in removing glycerol and remaining alkaline catalyst from crude biodiesel. [5]

Recent studies had demonstrated the use of DES as co-solvent and catalyst in methanolysis can increase yield, and make the purification easier. Few studies reported the use of ChCl based DES with palm oil examples are the removal of an alkaline transesterification catalyst such as potassium hydroxide (KOH) and the separation of glycerol from biodiesel [6,7]. Recently, Hayyan et al (2011) used a novel phosphonium based deep eutectic solvent (P-DES) to produce biodiesel from industrial low-grade crude palm oil. Allyltriphenylphosphonium bromide or N,Ndiethylenethanol ammonium chloride were used as salts to prepare DES [8]. Recently, Gu, et al (2015) proposed a greener biodiesel synthesis by using ChCl : glycerol (1:2) as the co-solvent in the NaOH-catalyzed transesterification via methanolysis of rapeseed oil. Under the Optimum conditions determined by RSM based on BBD, the ester yield is higher in the presence of the DES [9]. However, The use of DES as co-solvent in ethanolysis is not yet reported.

In this work, DES was produced from choline chloride and glycerol (molar ratio 1 : 2) and used in ethanolysis of palm oil, it is expected to remove the disadvantages of ethanolysis such as low mass transfer and formation of stable emulsion which complicate the purification step by reducing its interfacial tension and side reaction (saponification).

2. Materials and Method

2.1 Materials
Choline Chloride and glycerol (98 %) were acquired from Sigma - Aldrich, Potassium hydroxide, ethanol (96 %), and phosphoric acid was acquired from Merck. Crude palm oil was collected from palm oil mill PTPN IV.

2.2 Deep Eutectic Solvent Synthesis
Choline chloride and glycerol with molar ratio 1 : 2 was mixed and the mixture was stirred at 80 °C, stirring speed 300 rpm for 1 hour until homogeneous and transparent liquid is formed.
2.3 Ethanolysis of Palm Oil
The crude palm oil was degummed using phosphoric acid to remove the gum, before used as raw material. The ethanolysis reaction was carried out in 0.5 L flask with magnetic stirring at 400 rpm, atmospheric pressure, under reflux condition. 20 g oil was preheated until reaction temperature of 70 °C and then 9.6 g ethanol, 0.24 g potassium hydroxide, and DES were added. After 1 hour, the reaction mixture was settled to separate ethyl ester and glycerol. The ester phase was analyzed using GCMS. After separating esters from glycerol, the esters is then washed with wet washing method, and the final biodiesel product is analyzed for its density, viscosity, flash point and ester content. The experiment was done in a duplex.

2.4 Product Analysis
The free fatty acid content of oil was analyzed using AOCS Official Method Ca 5a-4. The viscosity, density, flash point, and ester content of biodiesel was analyzed using standard ASTM test method.

3. Results and Discussion

3.1 Degumming Process of Crude Palm oil
Before used in ethanolysis, the crude palm oil was degummed with phosphoric acid (acid degumming). The degummed palm oil was then analyzed for its FFA content and moisture content, Figure 1 show the result of FFA and moisture content analysis.

![Figure 1. FFA content of CPO and DPO](image)

Based on Figure 1, we can see that the FFA content of the oil increased from 4.71 to 4.84 %. The small rise of FFA content due to acidity of the phosphoric acid used. Phospholipid was suggested as the source of catalyst destruction, phospholipids did not carry over into methyl esters, while cause the biodiesel yield decrease, also added the difficulty separating the glycerol from the esters [10]. Although the degumming process increases the FFA and moisture content of the crude palm oil, the degumming process was needed to remove the gum, which can complicate the separation process and decrease the biodiesel yield.

3.2 Effect of DES on biodiesel yield
DES (choline-chloride and glycerol 1:2 M) was used in ethanolysis of palm oil at various dose. The reaction was carried out at 70 °C, 1.2 % KOH, ethanol to oil ratio 9:1, and stirred at 400 rpm at atmospheric pressure. Figure 2 shows the effect of DES on biodiesel yield.

From Figure 2, it can be observed that the biodiesel yield was increased from 75.12 % to 83.67 %, with the increase of DES from 0.5% to 2 %, then the decreased with DES dose more than 2 %. Gu et al., (2015) proposed a reaction process for transesterification using DES as co-solvent, the reaction can maintain as two phases with the aid of DES. Since ester is not soluble in the DES/methanol mixture, the direct contact between ester and base is significantly reduced and the ester becomes one single phase; as a result, the saponification side-reaction is effectively minimized and the separation
and purification process is simplified. On the contrary, when no DES is added, both FAME and base are soluble (at least slightly for base) in methanol which induces saponification, decreases the ester yield and complicates the separation and purification procedure. On the contrary, when no DES is added, both ester and base are soluble (at least slightly for base) in methanol which induces saponification, decreases the ester yield and complicates the separation and purification procedure [9].

![Figure 2](image_url)

**Figure 2.** The effect of DES on biodiesel yield

Besides, the addition of DES increases the dissolution of base in DES/methanol mixture due to the ionic nature of DES, producing a higher concentration of methoxide needed for the transesterification. In addition, DES can capture the byproduct glycerol from reactant mixture during the reaction, which shifts the reaction equilibrium to the product side and increases the ester yield. An over-dosed concentration of DES reduced the ester yield because excess glycerol molecules in DES tend to bind with methanol molecules which results in few free methanol molecules for the reaction and thus inhibits the reaction. Moreover, the hydroxyl group in concentrated DES might also compete with methanol to react with the catalyst, which lowers the methoxide concentration and ester yield.

Figure 3 shows the effect of DES on ester content of biodiesel, DES addition from 0.5 % to 2 % didn’t show many changes, however, with excess DES addition (2.5 to 3 %), biodiesel contains the trace of monoglyceride, diglyceride, and even triglyceride, indicating the ethanolysis reaction was not complete. In ethanolysis, saponification occurs because of the hydrolysis of the oil (triglyceride), free fatty acid, and ester in base condition. This reaction decreases the amount of triglyceride available for ethanolysis, decreasing ester yield and complicate the purification.

![Figure 3](image_url)

**Figure 3.** The effect of DES on ester content

DES mixture has a high affinity for hydroxyl group and water, which can decrease their effectiveness in hydrolysis, and prevent saponification reaction. With excess DES addition, DES not only prevent saponification, but also attract C\textsubscript{2}H\textsubscript{5}O, thus decreasing C\textsubscript{2}H\textsubscript{5}O available for ethanolysis reaction.

ethyl ester production from crude palm oil also done by Suppalakpanya, et al., (2010) in a two step transesterification using microwave system, with highest ester yield 80 % with ester content 97.4 %. The biodiesel production from crude oil usually done in two step reaction, a pretreatment process
(esterification) to decrease FFA and the transesterification process. The high FFA content in oil can lead to a formation of soap and post-reaction problem. From this experiment, DES can decrease the saponification reaction, make the one-step transesterification of crude oil or high FFA oil available without pretreatment [11]. It can be concluded that DES can increase the ester yield by decreasing saponification reaction and capturing byproduct glycerol.

3.3 Effect of DES on biodiesel purification

The effect of DES on biodiesel purification (separation and washing process) was evaluated. Figure 4. shows the effect of DES on biodiesel separation process.

![Figure 4. Ester and glycerol separation step (a) without and (b) with DES](image)

It can be observed that the ester and glycerol separation step without DES form stable emulsion, which complicates the separation process. The ester and glycerol separation step with DES did not form stable emulsion. The higher mutual miscibility between the glycerol and the esters in the presence of ethanol, severely complicate the phase separation operation after the reaction. Depending upon the ethanol/oil volume fraction loaded to the reactor, the phase separation may not occur, being necessary to add glycerin or to evaporate the ethanol in order to induce phase separation. Another problem is the intensive soap formation that occurs in this system and leads to the formation of stable emulsions that also complicates the separation of phases. Therefore, the washing procedure requires large volumes of water being necessary to improve this part of the process [12].

Table 1 shows the ester and total glycerol content on ester phase after one minute of settling time, it can be observed that the reaction with DES, the ester phase did not contain bonded glycerol, this can be concluded that DES can capture the byproduct glycerol, and shortening the settling time.

| Reaction     | After one minute settling time |
|--------------|--------------------------------|
|              | FAEE % | Glycerol % |
| without DES  |         |            |
| with DES     | Ester phase | 94.60 % | 0.40 % |
|              | 98.41%  | -          |

Figure 5 shows the washing process of biodiesel produced without and with DES, it can be observed that biodiesel produced without DES form an emulsion in washing, which decrease the biodiesel yield. The biodiesel produced with DES form less emulsion when washed, because of the less soap formed.
Figure 5. The washing process (a) without and (b) with DES

Figure 6. Volume of water needed for wet washing biodiesel

Figure 6 shows the volume of water needed for wet washing biodiesel, it can be observed that without DES, the volume of water required for wet washing is greater than with DES. Wet washing method was successful in removing residual sodium compounds and soap resulting from raw materials having free fatty acids. The saponification reaction is undesirable because it not only consumes the catalyst but also causes problems in phase separation due to the formation of a stable emulsion during water washing. The amount of soap formed during ethanolysis is three or four times higher than that formed during methanolsysis under similar reaction conditions. Therefore, the washing method will require a large amount of water [13]. Wet washing biodiesel produced with DES did not form a stable emulsion, because of the less soap formed, and the amount of water needed can be reduced, then decreasing cost in biodiesel purification. It can be concluded that DES can improve the purification process (separation and washing) of biodiesel by decreasing the soap formation and capturing byproduct glycerol.

3.4 Effect of DES on Ethanol – Oil phase
The effect of DES on ethanol – oil phase was observed in a reaction tube, shown in Figure 7.
It can be observed that with addition of DES on ethanol–oil, the DES form a meniscus between the ethanol and oil (interfacial). Capillary forces can be considered in a general way in which one fluid phase forms a meniscus in another fluid phase capillary forces can also be caused by capillary bridges of one liquid in another immiscible liquid. The capillary force can attract the adjacent particle.

With addition of DES, the interfacial tension between ethanol and oil was decreased, increasing the mass transfer, so the reaction proceeds better and faster. DES form a new attractive force between ethanol–DES, and DES–oil, also can be a media for reaction, reducing soap formation and capturing the byproduct glycerol. However, without the addition of DES, the attractive force between ethanol–oil is very weak, thus the interfacial tension is strong and decreases the mass transfer.

3.5 Characteristic of Biodiesel produced with DES

Characteristic of biodiesel produced with DES can be seen on Table 3. The main criterion of biodiesel quality is the inclusion of its physical and chemical properties into the requirements of the adequate standard. Quality standards for biodiesel are continuously updated, due to the evolution of compression ignition engines, ever stricter emission standards, reevaluation of the eligibility of feedstocks used for the production of biodiesel, etc. The current standards for regulating the quality of biodiesel on the market are based on a variety of factors which vary from region to region, including characteristics of the existing diesel fuel standards, the predominance of the types of diesel engines most common in the region, the emissions regulations governing those engines, the development stage and the climatic properties of the region/country where it is produced and/or used, and not least, the purpose and motivation for the use of biodiesel [14].

| Parameter                  | Unit     | Value     | ASTM D6751 Standard | SNI Standard |
|----------------------------|----------|-----------|----------------------|--------------|
| Ester Content              | % (m/m)  | 99.728    | -                    | > 96.5       |
| Density at 40 °C           | kg/m³    | 861.7     | -                    | 850-900      |
| Kinematic viscosity at 40 °C| mm/s²    | 3.7032    | 3.5-5                | 2.3 - 6      |
| Flash Point                | °C       | 180       | > 130                | >100         |
| Free Glycerine             | % (m/m)  | 0         | < 0.02               | <0.02        |
| Total Glycerine            | % (m/m)  | 0         | < 0.24               | <0.24        |
| Monoglyceride content      | % (m/m)  | 0.0271    | < 0.80               | -            |
| Diglyceride content        | % (m/m)  | 0         | < 0.20               | -            |
| Triglyceride content       | % (m/m)  | 0         | < 0.20               | -            |

It can be concluded that the biodiesel produced with DES had met the standard both ASTM and SNI, indicating that the use of DES as co-solvent in ethanolysis to produce biodiesel is a new method to solve the disadvantage in using ethanol to produce biodiesel, as it can reduce the soap formation, and make the purification easier.

4. Conclusion

The use of DES as co-solvent in ethanolysis of palm oil to produce biodiesel indicating the interfacial tension between ethanol and oil was decreased, increasing the mass transfer, so the reaction proceeds better and faster, thus the yield increased, Also can reduce soap formation and capturing byproduct glycerol, simplifying the purification. It was found the highest yield was 83.67 % with ester content 99.7 %. This study exemplifies that the use of DES as co-solvent in ethanolysis to produce biodiesel is a new method to solve the disadvantages in using ethanol to produce biodiesel.
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