APPLICATION OF LOW COST IONIC LIQUIDS FOR THE SEPARATION OF GLYCERINE FROM PALM OIL-BASED BIODIESEL

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ABSTRACT

One of the most serious obstacles in using biodiesel as an alternative fuel is the intricate and costly purification processes involved in its production. The difficulties in the separation of glycerine and other reaction mixtures necessitate the development of new competent low cost separation processes. In the present work, a low cost quaternary ammonium salt-glycerine-based ionic liquid is used as a solvent for extracting glycerine from the transesterification biodiesel product. The separation technique was tested on palm oil-based biodiesel. The laboratory-scale purification experiments established the viability of the technique as the purified biodiesel fulfilled the EN 14214 and ASTM D6751 standard specifications for biodiesel fuel in terms of glycerine content.

Keywords: ionic liquids; biodiesel; glycerine; liquid-liquid extraction

INTRODUCTION

Biodiesel is a clean burning diesel fuel produced from vegetable oils, animal fats, or grease. Its chemical structure is that of fatty acid alkyl esters. Biodiesel refers to the pure fuel before blending. Commercially, it is produced by transesterification of triglycerides in the presence of an alcohol and a catalyst with glycerine as a major by-product (Ma & Hanna, 1999; Dubé et al., 2007). After the reaction, the glycerine is separated by settling or centrifuging and the layer obtained is purified prior to using it for its traditional applications, such as for pharmaceuticals, cosmetics and food industries, or for the recently developed applications, such as for animal feed, carbon feedstock in fermentations, polymers, surfactants, intermediates and lubricants (Vicente et al., 2007).

Being renewable and having better quality of exhaust gas emissions, biodiesel is becoming very popular in the European Union which has set an objective for motor biofuels a market share of 20% of the total motor fuel consumption by 2020. On the other hand, by 2010, the United States is expected to become the world's largest single biodiesel market, accounting for approximately 18% of the world biodiesel consumption. At the same time, new and large single markets for biodiesel are expected to emerge in China, India and Brazil (Körbitz, 1999; Bozbas, 2005; Demirbas, 2007).

One of the most serious obstacles in the utilization of biodiesel is the intricate and costly purification processes involved in its production. Biodiesel must be purified to fulfill the EN 14214 and ASTM D6751 standard specifications for fuel, as listed in Table 1, otherwise the methyl esters formed cannot be classified as biodiesel. Removing glycerine from biodiesel is important since the glycerine content is one of the most significant precursors for the biodiesel quality. The glycerine can be in the form of free glycerine or bound glycerine, and the two forms together are referred to as total glycerine. A high content of free and total

glycerine can lead to severe consequences such as buildup in fuel tanks, clogged fuel systems, injector fouling and valve deposits.

The standard methods for glycerine removal is gravity separation and centrifugation but both are not completely efficient and therefore a final purification stage is necessary to meet the requirements of EN 14214 and ASTM D 6751 Standards. In addition to glycerine, the other impurities in the untreated biodiesel are soap, metals, methanol, free fatty acids, catalyst, water, and glycerides (Berrios & Skelton, 2008).

In general, there are two acceptable methods to purify fatty acid methyl esters. from other components, and these are wet washing and dry washing. Wet washing is widely used to remove excess contaminants and the left-over chemicals from biodiesel. Since both glycerine and methanol are highly soluble in water, water washing is very effective in removing both contaminants and until recently was the most common method of purification. It also has the advantage of removing any residual sodium salts and soaps. However, the inclusion of additional water to the process offers many disadvantages (Canakci & Van Gerpen, 2001). Dry washing replaces water with an ion exchange resin or a magnesium silicate powder to neutralize impurities, and both these methods are being used in industrial plants. Membrane reactors, addition of lime and phosphoric acid have also been employed in the purification of biodiesel but, in general, there are numerous problems associated with costs and complications of operating biodiesel synthesis on an industrial scale (Ma & Hanna, 1999).

Ionic liquids (ILs) which are sometimes referred to as "green solvents" have the potential of replacing hazardous and polluting organic solvents because of their favourable characteristics. ILs can dissolve many different organic, inorganic, and organometallic materials. They are immiscible with many organic solvents; moreover, the solvation properties of ILs can be tuned for a specific application by varying the anion-cation combinations. In addition, ILs have very low vapour pressure making them less flammable and safe for industrial applications. However, the environmental fate and any potential toxicity issue for most ILs are still largely unknown, and up to the present only a few preliminary reports on the toxicological properties are available.

The development of low cost ILs termed "deep eutectic solvents" or DES has recently received intense interest due to their potential as environmentally benign solvents and their unusual solvation properties. A DES is a mixture of two or more compounds which has a melting point lower than that of either of its components. They are liquids at temperatures of 100 °C or below and exhibit similar solvent properties to the conventional ILs. They comprise mixtures of organic halide salts, such as choline chloride (ChCl) with an organic compound which is a hydrogen bond donor (HBD) capable of forming a hydrogen bond with the halide ion, such as amides, amines, alcohols, carboxylic acids and many more (Liu et al., 2008).
The liquid state of DES is produced through freezing point depression, whereby hydrogen-bonding interactions between an anion and an HBD are more energetically favoured relative to the lattice energies of the pure constituents (Nkuku & LeSuer, 2007). DES have several advantages over conventional ILs in that they are easy to prepare in a pure state. They are nonreactive with water. Furthermore, toxicological properties of the components used for DES have been determined and are available, with some DES being biodegradable (Abbott et al., 2004). Recently, Abbott et al. (2007) have shown that DES can be a suitable extraction media for glycerine from biodiesel derived from soy bean oil.

Table 1: Biodiesel specifications according to EN 14214 and ASTM D6751 standards, (Monteiro et al., 2008).

Property	EN 14214		ASTM D 6751	
	Test Method	Limits	Test Method	Limits
Ester content	EN 14103	96.5 % (mol mol^{-1}) min	-	-
Linolenic acid content	EN 14103	12.0 % (mol mol^{-1}) max	-	-
Content of FAME[a] with ≥ 4 double bonds	-	1.0 % (mol mol^{-1}) max	-	-
MAG[b] content	EN 14105	0.80 % (mol mol^{-1}) max	-	-
DAG[c] content	EN 14105	0.20 % (mol mol^{-1}) max	-	-
TAG[d] content	EN 14105	0.20 % (mol mol^{-1}) max	-	-
Free glycerine	EN 14105	0.02 % (mol mol^{-1}) max	ASTM D 6584	0.020 % (w/w) max
Total glycerine	EN 14105	0.25 % (mol mol^{-1}) max	ASTM D 6584	0.240 % (w/w) max
Water and sediment or water content	EN ISO 12937	500 mg kg^{-1} max	ASTM D 2709	0.050 % (v/v) max
Methanol content	EN 14110	0.20 % (mol mol^{-1}) max	-	-
(Na +K) content	EN 14108	5.0 mg kg^{-1}max	UOP 391	5.0 mg kg^{-1}max
(Ca +Mg) content	prEN 14538	5.0 mg kg^{-1} max	-	-
P content	EN 14107	10.0 mg kg^{-1} max	ASTM D 4951	0.001 % (w/w) max
Oxidative stability (110 °C)	EN 14112	6 h min	-	-
Density (15 °C)	EN ISO 3675	860–900 kgm^{-3}	-	-
Kinematic viscosity or viscosity (40 °C)	EN ISO 3104	3.5–5.0 mm^2 s^{-1}	ASTM D 445	1.9–6.0 mm^2 s^{-1}
Flash point	EN ISO 3679	120 °C min	ASTM D 93	130 °C min
Cloud point	-	-	ASTM D 2500	Not specified
Sulphur content	EN ISO 20864	10.0 mg kg^{-1} max	ASTM D 5453	0.05 % (w/w) max
Carbon residue	EN ISO 10370	0.30 % (mol mol^{-1}) max	ASTM D 4530	0.050 % (w/w) max
Cetane number	EN ISO 5165	51 min	ASTM D 613	47 min
Sulphated ash	ISO 3987	0.02 % (mol mol^{-1}) max	ASTM D 874	0.020% (w/w) max
Total contamination	EN 12662	24 mg kg^{-1} max	-	-
Copper strip corrosion (3 h, 50 °C)	EN ISO 2160	1 (degree of corrosion	ASTM D 130	No. 3 max
Acid number or acid value	EN 14104	0.50 mg KOH g^{-1} max	ASTM D 664	0.50 mg KOH g^{-1}max
Iodine value	EN 14111	120 g I2·100 g^{-1} max	-	-
Distillation temperature (90% recovered)	-	-	ASTM D 1160	360 °C max

[a] FAME = fatty acid methyl esters.   [b] MAG = monoacylglycerines   [c] DAG = diacylglycerines   [d] TAG = triacylglycerine

The main objective of the present work is to investigate the viability of quaternary ammonium salt-glycerine based DES in the removal of total glycerine from biodiesel derived from palm oil.

EXPERIMENTAL METHODOLOGY

Biodiesel production

Palm oil was selected as the feedstock for biodiesel production based on the fact that this commodity is readily available in Malaysia. The transesterification reaction product was purified from the glycerine by-product using liquid-liquid extraction with DES as a solvent. KOH and methanol were chosen to synthesize the biodiesel due to their ability to convert the triglycerides to fatty acid methyl esters. The following materials were used: Refined palm oil (FFM Sdn Bhd), methanol (Merck 99%), potassium hydroxide as a catalyst (HMGM Chemicals >98%). Methanol and potassium hydroxide were pre-mixed to form potassium methoxide, and then added to the palm oil in a reactor with a mixing speed of 400 rpm for 2 hr at 50 °C. The molar ratio of palm oil to methanol was 1:10 (Cheng et al., 2004). The mixture was left overnight, thus forming two layers, namely: biodiesel phase (upper layer) and the glycerine-rich phase (lower layer). Following the biodiesel synthesis, free glycerine was separated from crude biodiesel by gravity settling. Analysis using HPLC showed that 0.28 wt% total glycerine was present in the refined biodiesel. This value is higher than that acceptable by international standards, EN 14214 and ASTM D 6751.

Extraction of glycerine

The preparation of DES involved choline chloride, ChCl (Merck 99%) which was dried under vacuum, and this was then mixed with glycerine (Merck 99.5%) using different mole ratios (1:1, 1:1.25, 1:1.5, 1:2, 1:3). The mixture was stirred at 300 rpm under 50 °C for a period of 2 hr until a homogenous transparent liquid was formed. The DES was then added to the synthesized biodiesel in different quantities according to the biodiesel:DES molar ratios of 1:1, 1:1.5, 1:2. Each mixture was agitated at 170 rpm for 1 hr and left to settle for 2 hr, after which samples of 0.5 g were collected from the upper layer. Each sample was then filtered using a vacuum filter and then stirred with 5 ml of tetrahydrofuran solvent. Analysis were performed using an HPLC (Waters 600E) equipped with an auto sampler and differential refractive index detector. Table 2 provides the HPLC specifications and the analytical conditions. The refractive index detector was purged for at least 1 hr prior to use and monitored for a steady baseline, and this was followed by a system suitability test.

Table 2: HPLC specifications and analytical conditions.

Analytical Instruments		Analytical Conditions	
HPLC System	Waters HPLC pump	Mobile phase	THF, HPLC grade
	Waters 600E system controller	Flow rate	1 mL/min, isocratic
	Waters model 401 differential RID	Column temperature	25°C
		Detector temperature	35 °C
	Waters 717 plus auto sampler	Sparge gas	Helium
		Sparge rate	30 mL/min
	Waters millennium software	Detector sensitivity	32
		Injection volume	10 μL
Column	Size: 300 x 7.8 mm Description: phenogel 5U 50A		
Guard column	50 x 7.8 mm		

Fig. 1 shows the freezing points and the viscosities of the mixture as a function of glycerine mole fraction (Abbott et al., 2007) whereby the minimum eutectic temperature and viscosity are achieved at 0.67 glycerine mole fraction. The DES molar ratios of 1:1 to 1:3, corresponding to 0.5 - 0.75 glycerine molar fractions in Fig.1, attained the lowest viscosity and freezing point ranges (i.e. 293.8-316.7 cP and 281.8-240.5 K, respectively). Lower solvent viscosity enhances the mixing efficiency and consequently the mutual transfer rate of glycerine between the two phases.
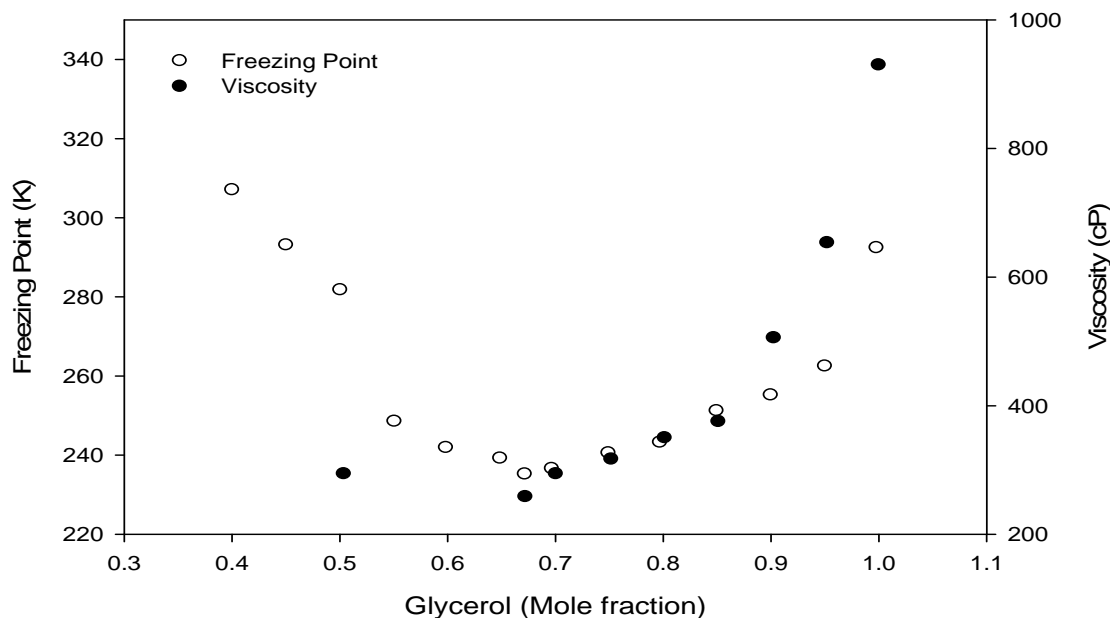

Fig.1: Freezing points and viscosities at different glycerine mole fractions, (Abbott et al., 2007).

RESULTS AND ANALYSIS

Extraction efficiency of DES

The synthesized DES was used to extract the glycerine from biodiesel. Three molar ratios of biodiesel to DES were investigated, namely, 1:1, 1:1.5, and 1:2. Two distinct layers of the two phases were observed after settling. The analysis revealed that the DES was completely separable and there was no emulsion formation. The amount of glycerine extracted as a function of DES composition is depicted in Fig. 2. In general, all ratios can reduce the total glycerine content in biodiesel to a certain extent. It is clear that the percentage of extracted glycerine is inversely proportional to the biodisel:DES molar ratio.

Another factor that govened the extraction process was the DES composition molar ratio , i.e.ChCl:glycerine. This was dictated by the synthesis specification of the DES. As the DES composition ratio changes from 1:1 to 1:3 (i.e. 0.5 to 0.75 glycerine molar fraction in Fig.2), its ability to remove glycerine from the extraction mixture is reduced. This can be explained by the fact that lower glycerine content DES has a greater tendency to attract more glycerine molecules, forming a higher ratio DES. However, this capability is reduced as the glycerine content in DES increases. This is indicated by the little change in the total glycerine profile at the higher DES ratios (1:1.5 to 1:3). Moreover, Fig. 2 indicates the existence of an optimum DES composition for each extraction feed ratio. The optimum DES composition is 1:1 (0.5 glycerine molar

fraction in DES) for the case of 1:1 biodiesel:DES ratio and 1:1.25 (0.555 glycerine molar fraction in DES) for the 1:1.5 and 1:2 biodiesel:DES ratios.
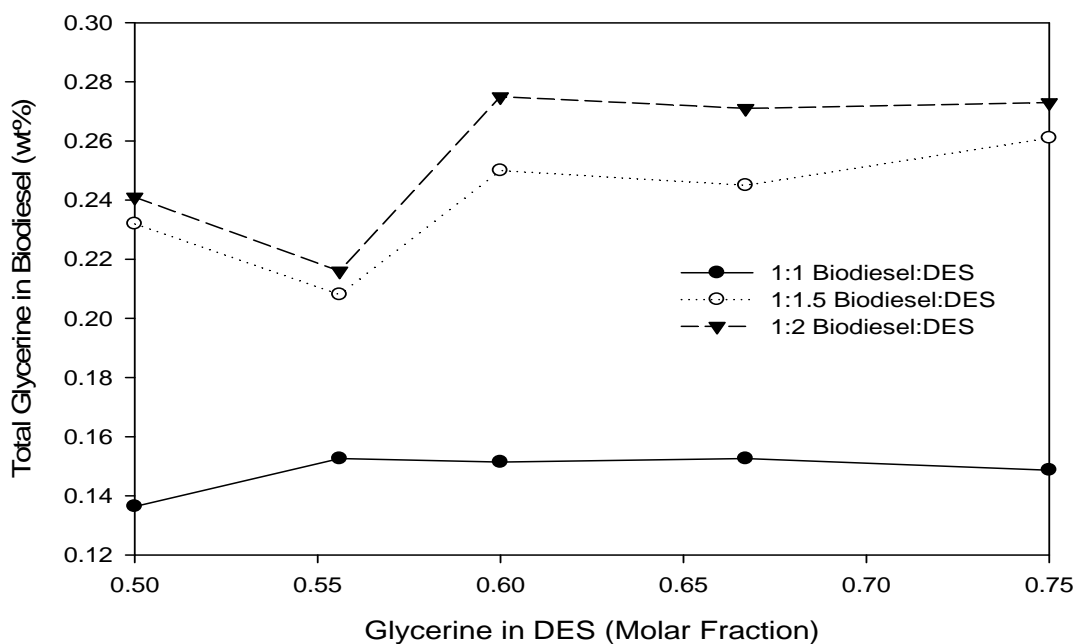

Fig.2: Total glycerine extracted from biodiesel.

To study the extraction efficiency of the proposed DES solvent, the distribution coefficient of glycerine was calculated for different DES compositions and biodiesel:DES ratios. The distribution coefficient was calculated as the ratio of the molar concentration of glycerine in the DES phase to that in the biodiesel phase under equilibrium conditions. The results are illustrated in Fig.3 as a function of glycerine molar fraction in the used DES. There is an inverse relationship between the effect of varying the biodiesel:DES molar ratio and the extraction efficiency. As the DES content in biodiesel:DES ratio increases, the glycerine distribution between the two extraction phases shifts more to the biodiesel phase resulting in a corresponding decrease in the extraction efficiency. Fig.3 also reveals the high capacity of the 1:1 (for the case of 1:1 extractive feed ratio) and the 1:1.25 (for the case of 1:1.5 and 1:2 extractive feed ratios) biodiesel:DES mixtures for selectively dissolving more glycerine from the biodiesel phase. Additionally, the distribution coefficient profile for the higher DES composition molar ratios of 1:1.5 to 1:3 (0.6-0.75 glycerine molar fraction in DES) are flat which indicates the minor effect of increasing glycerol content of the DES above the optimum composition values of 1:1 or 1:1.25.
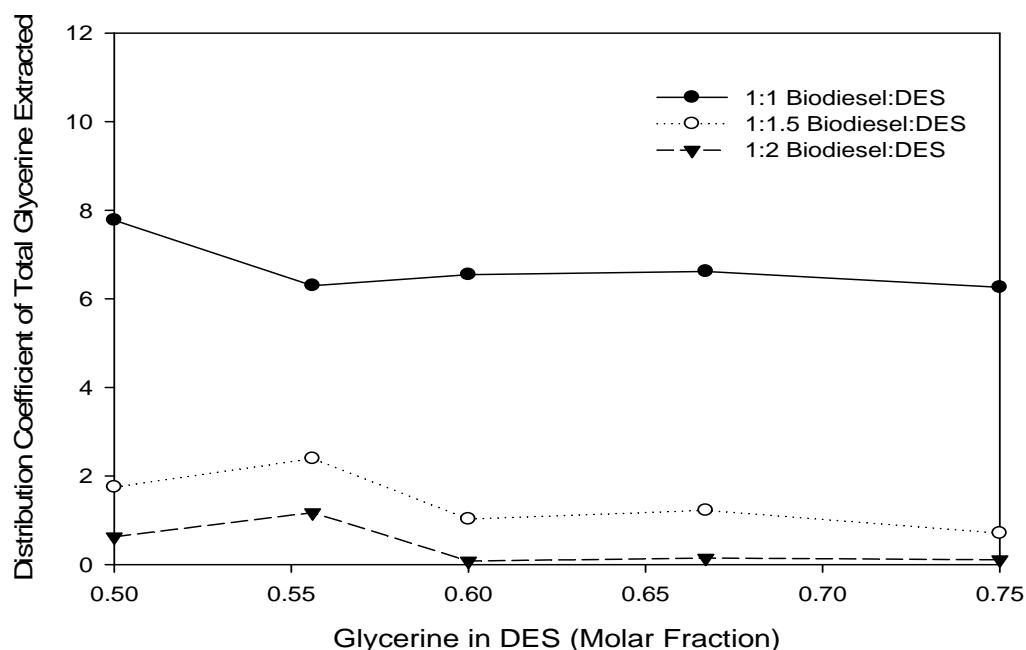
Fig.3: Distribution coefficient of total glycerine extracted from biodiesel

Table 3 provides the relative percentage of extracted glycerine for the three tested DES ratios. It is clear from the results that the biodiesel:DES ratio is more effective than the DES composition ratio in improving the extraction efficiency. Changing the biodiesel:DES ratio from 1:2 and 1:1.5 to 1:1 generally increases the percentage of extracted glycerine by more than double.

Table 3: Percentage extracted glycerine for the tested DES.

DES ratio	Biodiesel: DES Ratio		
(ChCl:glycerine)	1:1	1:1.5	1:2
1:1	51.25%	17.14%	13.92%
1:1.25	45.45%	25.71%	22.86%
1:1.5	45.89%	10.71%	1.78%
1:2	45.46%	12.50%	3.21%
1:3	46.85%	6.78%	2.50%

Solvent recovery

To justify the use of DES as a solvent for glycerine from biodiesel, several recovery methods for ChCl from the used DES were considered. One possible separation technique is to re-crystallise the ChCl, either by cooling or by the addition of an anti-solvent. In the present work, 1-butanol was employed as an anti-solvent, and mixed with the extract phase, in two compositions, i.e 8 wt% and 15 wt% of 1-butanol. The mixture was subcooled to -20 °C, after which ChCl crystals were formed and these were separated by vacuum filtration. The separated quantities of the solid ChCl were in agreement with that reported by Abbott et al., (2007). Crystallization, a relatively low-cost alternative separation technique, can therefore be used for the salt recovery. The recovered salt can be mixed with the purified glycerine to reproduce the DES which can then be utilized in the extraction process.

CONCLUSION

Laboratory-scale batchwise experiments were carried out to separate glycerine from transesterification biodiesel product. It was found that a ratio of 1:1 of biodiesel: DES gave the best extraction yield. Moreover, biodiesel to DES ratio was found to be more significant than the DES composition ratio in affecting the extraction efficiency. By carefully selecting this ratio, a favourable distribution of solute in the extraction system is obtainable. The purified biodiesel fulfils the international standards of EN 14214 and ASTM D6751 in terms of glycerine content. The used solvent can be recovered through crystallizing the ammonium salt.

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