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Biodiesel Synthesis from Rapeseed Oil Catalysed by Different Ionic Liquids

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The synthesis of biodieselfrom renewable sources has become mmore important today for both environmental reasons and also the increasing shortage of fossil fuels. The main method for the production of biodiesel is the transesterification of vegetable oils catalysed by acid, basic or enzymatic catalysts in homogeneous or heterogeneous phases. This paper presents a new method of biodiesel production from rapeseed oil by using ionic liquids, which are completely ionic compounds with melting points equal to or less than 100°C, as catalysts. The SO_3H-functional acidic ionic liquids have been successfully synthesised and were promising catalysts for the transesterification of rapeseed oil with alcohols to produce biodiesel. 1-(4-sulfobutyl)-pyridinium hydrogen sulfate hada higher rate enhancement compared tothe other ionic liquids synthesised in this work. Theacidic or lipophilic characteristics of theionic liquids were found to be key factors in obtaining good reaction rates. In this work, ethanol and propan-1-ol were more reactive than methanol due to theirgood solubility in the oils. The ionic liquids could be recycled and the esters of the fatty acids were separated *via* simple settling.

Key words: Biodiesel, ionic liquid, transesterification, catalyst, rapeseed oil, triglyceride

INTRODUCTION

Today, thanks to the depletion of fossil energy resources and environmental pollution concerns, bio carburant biocarburant (French) – biofuel has become an interesting alternative for sustainable development as it is a renewable resource and produces less gas thus reducing thegreenhouse effect. The main materials used inbiofuel production include vegetable oils, animal fats (known as biodiesel) (Aransiola *et al*., 2014), andplants such as sugar cane, sugar beet, maize andwheat (known as bioalcohols). The use of bioalcohols require modification of engines while biodiesel does not need this change (Sharma & Singh, 2009).

Biodiesel, which contain alkyl esters of fatty acids, is produced mainly from the catalytictransesterification of triglycerides (the main component of vegetable oil) with mono alcohols (Figure 1). Thus is a reversible reaction, that requires a higherratio of reagents than the stoichiometric ratio in order to move the equilibrium towards the formation of the products. Traditionally, homogeneous acidic or basiccatalysts have been widely used for this reaction (Avhad & Marchetti, 2016). These homogeneous catalysts often provide a high conversion rate at mild temperatures, but are corrosive and require further steps for product treatment like neutralisation and purification. In addition, basic catalysts are not favorable for materials that contain more that 3% free acids, due tospontaneous saponification. Heterogeneous catalysts such as metal oxides and zeolites have alsobeen studied for this reaction. They also have good activity but they need to be operated at severe temperatures with a higher quantity of reagents compared to reactions using homogeneous catalysts. The advantages of heterogeneous catalysts are the relatively simple separation of the products and the possibility of recycling the catalysts. However, the second advantage is still under study asthe stability of the solid catalysts in the reaction has not been fully elucidated.

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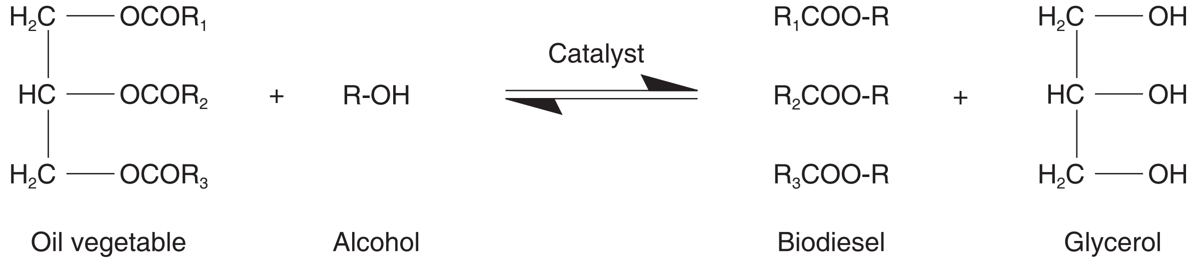


Figure 1. General ransesterification reactionof triglycerides

There has been muchesearch on new methods or new catalysts for the production of biodiesel that are more sympathetic to the environment. One of the methods reported is asupercritical method that does not use a catalyst. This method is very rapid reacti(2 to 4 minutes), has a high conversion rate and therecovery of products is by simple depressurisation. However, the reaction requiresvery severe temperature and pressure (350 - 400°C, 20-25 MPa) conditions, with large quantities of alcohol compared to reactions using acatalyst (Saka & Kusdiana, 2001, Demirbas, 2002). Enzymatic catalysts such as lipozyme and novozyme have been used for the production of biodiesel. Their advantages include the ability to accelerate both esterification and transesterification at low temperatures (40-60°C), and the ease of recovery of glycerol. Furthermore, immobilised enzymes can also be recycled several times. However, the reaction times are quite long (24-48h 24 to 48 hours) and enzymatic catalysts are expensive and tend tobecomeinactive because of impurities(Rodrigues *et al.*, 2008, Antczak *et al.*, 2009).

In recent decades, ionic liquids have attracted the attention of researchers. Ionic liquids are completely ionic compounds with melting points equal to or less than 100°C. With specific properties like negligible vapor pressure, high thermal stability, high ionic conductivity and the ability to dissolve organic, or inorganic polymers, ionic liquids can be alternative 'green' solvents to replace volatile organic solvents in hydrogenation and coupling reactions, for example (Chiappe & Pieraccini, 2005, Olivier-Bourbigou & Magna, 2002). According to the structure of the anion and cation, ionic liquids can haveacidic or basic properties, enabling them to act as catalysts (Majid & Heshmatollah, 2016). For the transesterification of vegetable oil, ionic liquids functionalised by an alkane sulfonic acid group have been used as an acid catalyst (Wu *et al.*, 2006). They have been reported asgood catalysts and were able to be recycled several times.

EXPERIMENTAL SECTION

Synthesis of ionic liquids

The SO_3H functionalised acidic ionic liquids were prepared using aprocedure similar to that reportedpreviously with some modifications (Gui *et al.*, 2004, Cole *et al.*, 2002).1-methyl-imidazole (Fluka, 99%), 1,4-butane sultone (Fluka, 99%), pyridine (RPE, 99.6%), sulphuric acid (Fluka, 95-97%), Bis(trifluoromethane)sulphonimide (Fluka, >95%) and other chemicals (AR) were commercially available and were used without further purification.

The synthesis of 1-(4-sulphobutyl)-3-metyl-imidazolium hydrogen sulphate (LI_1) was prepared as follows. First, equimolar amounts of 2-methylimidazole and 1, 4 butane sultone were mixed and stirred, solvent free for 18 hours at 40°C. The solid whitezwitteriononis 1-(4-sulphonatebutyl)-3-methyl-imidazoliumproduced waswashed several times with diethyl ether to remove any unreacted material and then dried in vacuo for 2 hours at 40°C. Subsequently, a stoichiometric amount of concentrated sulphuric acid (95-98%) was added drop wise to the zwitterionic product, and the mixture was stirred at 90°C for 6 hours, resulting in the formation of the ionic liquid. The ionic liquid was washed several times with diethyl ether to remove any unreacted material and then dried in vacuo for 2 hours at 130°C. Other LIs 1-(4-sulphobutyl)-pyridinium hydrogen sulfate (LI_2), and 1-(4-sulphobutyl)-3-methyl-imidazolium bis(trifluoromethanesulphonyl)imide (LI_4) were synthesised *via*the same process, using pyridine, and 2-methylimidazole respectively. In this study, a commercial ionic liquid sulphobutyl-triethylammonium hydrogen sulphate LI_9 [SBTEA]HSO_4 was also used to evaluate the influence of different cations/anions on the catalytic avtivity.

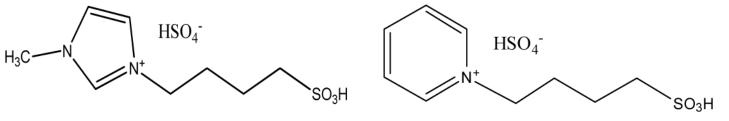
The purity of the ionic liquids produced was more than 95% as characterised by NMR spectroscopy, and the data is displayed below:

LI$_1$ 1-(4-sulphobutyl)-3-methyl-imidazolium hydrogensulfate ^{1}H RMN (400MHz, D_2O) : δ = 8,65 (br s, 1H), 7,41 (dd, 1H, $^3J_{H\text{-}H}$ = 1,8, $^4J_{H\text{-}H}$ = 1,7), 7,35 (dd, 1H, $^3J_{H\text{-}H}$ = 1,8, $^4J_{H\text{-}H}$ = 1,7), 4,16 (t, 2H, $^3J_{H\text{-}H}$ = 7,1), 3,81 (s, 3H), 2,86 (dd, 2H, $^3J_{H\text{-}H}$ = 7,7, $^3J_{H\text{-}H}$ = 5,9), 1,94 (dq, 2H, $^3J_{H\text{-}H}$ = 7,7, $^3J_{H\text{-}H}$ = 6,7), 1,66 (m, 2H).^{13}C RMN (100MHz, D_2O) : δ 135,9 , 123,6 , 122,1 , 49,9 , 48,8 , 35,6 , 28,0 , 20,8 .

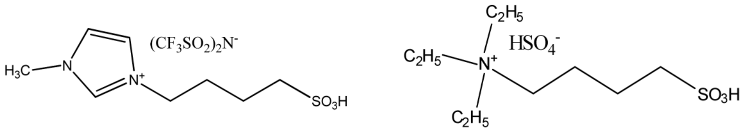
LI$_2$ 1-(4-sulphobutyl)-pyridinium hydrogensulphate ^{1}H RMN (400MHz, D_2O) : δ = 8,74 (dd, 2H, $^3J_{H\text{-}H}$ = 6,5, $^4J_{H\text{-}H}$ = 5,5), 8,43 (tt, 1H, $^3J_{H\text{-}H}$ = 7,8, $^4J_{H\text{-}H}$ = 1,2), 7,95 (dd, 2H, $^3J_{H\text{-}H}$ = 7,5, $^3J_{H\text{-}H}$ = 6,7), 4,19 (t, 2H, $^3J_{H\text{-}H}$ = 7,0), 2,84 (dd, 2H, $^3J_{H\text{-}H}$ = 7,7, $^3J_{H\text{-}H}$ = 7,6), 2,05 (dq, 2H, $^3J_{H\text{-}H}$ = 7,7, $^3J_{H\text{-}H}$ = 7,6), 1,68 (dq, 2H, $^3J_{H\text{-}H}$ = 7,8, $^3J_{H\text{-}H}$ = 7,6). ^{13}C RMN (100MHz, D_2O) : δ = 145,5 , 144,1 , 128,2 , 61,1 , 49,8 , 29,2 , 20,7 .

LI$_4$ 1-(4-sulphobutyl)-3-méthyl-imidazolium bis(trifluoromethanesulphonyl)imide: ^{1}H RMN (400MHz, D_2O) : δ = 8,68 (br s, 1H), 7,44 (dd, 1H, $^3J_{H\text{-}H}$ = 1,8, $^4J_{H\text{-}H}$ = 1,7), 7,38 (dd, 1H, $^3J_{H\text{-}H}$ = 1,8, $^4J_{H\text{-}H}$ = 1,7), 4,20 (t, 2H, $^3J_{H\text{-}H}$ = 7,0), 3,81 (s, 3H), 2,89 (dd, 2H, $^3J_{H\text{-}H}$ = 7,7, $^3J_{H\text{-}H}$ = 6,0), 1,97 (dq, 2H, $^3J_{H\text{-}H}$ = 7,9, $^3J_{H\text{-}H}$ = 6,9), 1,68 (m, 2H). ^{13}C RMN (100MHz, D_2O) : δ = 135,9 , 123,5 , 122,1 , 50,0 , 48,8 , 35,5 , 28,0 , 20,8 .

NMR spectra were obtained from a Bruker Av-400 (400 MHz) Fourier-transform spectrometer with reference D_2O. The structures of the ionic liquids are illustrated in Figure 2.



LI$_1$ [SBMI] HSO$_4$ LI$_2$ [SBPy] HSO$_4$



LI$_4$ [SBMI]N(CF$_3$SO$_2$)$_2$ LI$_9$[SBTEA] HSO$_4$

Figure 2. Structures of the synthesised ionic liquids

Transesterification reaction and analysis

Rapeseed oil which was purchased in the Carrefour commercial center, was of foodgrade andwas used directly without further treatment. Methanol (Aldrich, 99%), Absolute Ethanol (Prolabo), 1-Propanol (HPLC, Aldrich) were dried using molecular sieve 3A before use. The transesterification reaction was carried out in a 300 mL cylindrical stainless steel reactor, equipped with a thermostat, a mechanical stirrer, agas inlet, a sampling outlet and an event. The procedure, a sequence of operations, was performed over 4-6h. Initially, 40g oil colza was introduced in the reactor to be heated. Secondly, the ionic liquid was dissolved separately in the alcohol with a molar ratio of 12:0.05 for alcohol:ionic liquid. This solution was added into the reactor when the temperature reached the boiling point of alcohol. The molar ratio of alcohol:oil was 12:1. As the temperature reached the desired value, the agitator was set to a speed of 550 tours per minute andthe reaction was timed. Samples (1ml) were removed from the reaction mixture during the progress of the reaction, and analysed by HPLC, using a refraction index detector with a C18 Eclipse XDB column (5mm, 4,6x150mm) heated at 30°C. The mobile phase was a methanol/isopropanol mixture (60/40 v/v) with a flow rate of0.4 mL/min for the first 16 minutes, then 2 mL/min until 33 minutes.

The percentage yield of alkyl ester (biodiesel yield) was calculated using the following formula:

$$\text{Yield ester} = \frac{n_{esterT}}{3n_{TGo}} \times 100$$

with n_{TGo} : number of moles of oil (or triglycerides) at the beginning of the reaction
n_{esterT} : number of moles of methyl ester obtained at time T of the reaction

RESULTS AND DISCUSSION

Catalyst characterisation

As shown in Figure 3, for the ionic liquid with the methylimidazole ring (LI_1 [SBMI]HSO_4, LI_4 [SBMI]$N(SO_2CF_3)_2$), the stretching vibrations of N-H, C-H, and C=N in the imidazole ring were observed at 3155, 3115, and 1575 cm^{-1}. For the ionic liquid with a pyridine ring (LI_2 [SBPy]HSO_4), the stretching vibrations of C-H, C=N, and C=C were foundat 3070, 1636, and 1490 cm^{-1}. The vibrations between 1170 and 1030 cm^{-1} were characteristicof the sulphonic group (S=O liason). The (CH_2) group of allfour ionic liquids were observedat 2960 cm^{-1}. For the fluoro ionic liquid LI_4 [SBMI] $N(SO_2CF_3)_2$, the C-F vibrations were observed at around 1250 and 1350 cm^{-1}.

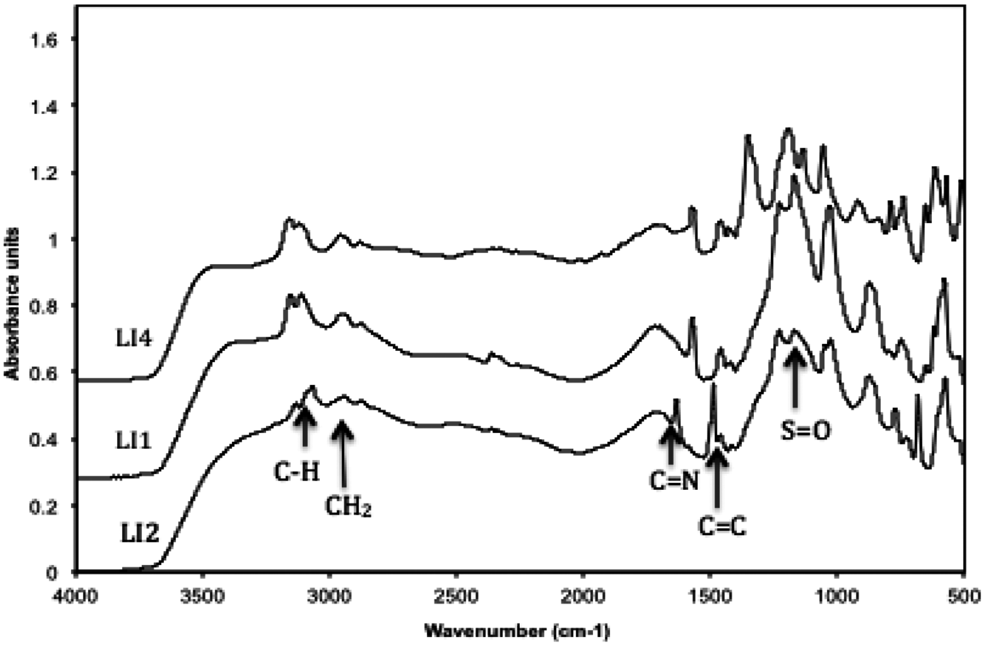


Figure 3. FT-IR spec tra of the synthesised ionic liquids

Catalytic activities of the ionic liquids

The experiments were performed with four different ionic liquids at 107°C for 6 hours. These results obtained showed that the methyl ester yield was93% (the lowest value) with LI_4 and 98% (the highest value) with LI_2 (Figure 3). This indicated that the catalytic activity of the ionic liquids were relatively the same after a certain time at high temperatures. It was also observed that the ionic liquid LI_2 (pyridine) advanced the reaction more quickly than the other ionic liquids. LI_2 was found to be the best catalyst for the transesterification reaction, probably due to itsstable structure with a six-membered ringand the electronic attraction ofpyridine, which makesprotons more labile, thus resulting in a stronger acidity of LI_2.

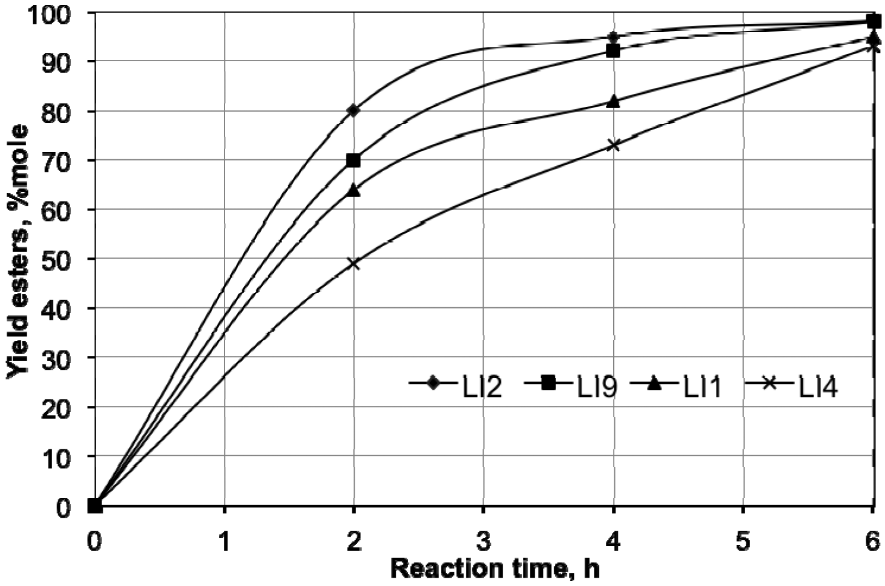


Figure 4. Effect of different ionic liquids on the transesterification reaction. *Reaction conditions: molar ratio of methanol:oil:LI = 1:1:0.05 at 107°C*

The ionic liquid 9 (LI_9) was more effective than ionic liquid 1 (LI_1) which could be explained by the presence of the ethyl group in theionic liquid which was able topromote the solubility of the ionic liquids in the oil phase andimprove the solubility of methanol and oil. Thus the mass transfer was improved thereby increasing the speed of reaction.

As the acidity of sulphuric acid (pKa = 1.99) and acid bis (trifluoromethanesulphonyl) imide (pKa = 1.95) is similar, thus the activity of LI_1 and LI_4 were also similar. As the structure of bis(trifluoromethanesulphonyl)imide (NTf_2) anion is larger than HSO_4, this weakens the mobility of proton H in LI_4 compared to LI_1, so in the first step of the transesterification mechanism, acid attack was more difficult (Lotero *et al*., 2006). In addition, LI_1 hadbetter immiscibility withthe ester as compared to LI_4, which facilitated the reaction equilibrium shifting to the product side (Xing *et al*., 2007, Xie *et al*., 2008)

The experimental results also showed that the activity of ionic liquid depended on the temperature. The rate of reaction (vi) at the different temperatures is shown inTable 1. Clearly, the higher the temperature, the fasterwas the rate of reaction.

Table 1. Reaction rates at different temperatures.

Ionic liquid	LI_1 [SBMI]HSO_4	LI_2 [SBPy]HSO_4	LI_4 [SBMI]$N(SO_2CF_3)_2$	LI_9 [SBTEA]HSO_4
T °C	$v_i * 10^4$ $mol.L^{-1}.s^{-1}$			
67	0,09	0,12	0,09	--
95	0,56	1,18	0,39	0,75
107	1,90	2,42	1,44	2,08

Reaction conditions: molar ratio methanol:oil:LI = 12:1:0.05

Comparing the activities of different alcohols

A series of experiments was conducted using the ionic liquids with different alcohols: methanol, ethanol and 1-propanol. Figure 5 shows the effect of alcohol on the transesterification reaction. It was observed that ethanol and 1-propanol were more active compared to methanol in this case. This result was similar to that reported by of Rathore and Morin *et al*., (Rathore, & Madras, 2007, Morin *et al*., 2007) explained by the better solubility of the alcohols with longer chain in the oil. Another explanation given by Asakuma (Asakuma *et al*. 2009) showed that, the activation energy for the formation of esters was lower with longer chain alcohols. In another study on biodiesel synthesis by the alcoholysis of vegetable oils catalysed by three commercial lipases such as Novozym 435, Lipozyme TLIM and

Lipozyme RM-IM, (Rodrigues *et al.*, 2008), the highest conversion yields were obtained with the higher molecular weight alcohols (butanol, propanol). This was indicative that these enzymes were easily deactivated by substrates with low molecular weight alcohols (methanol).

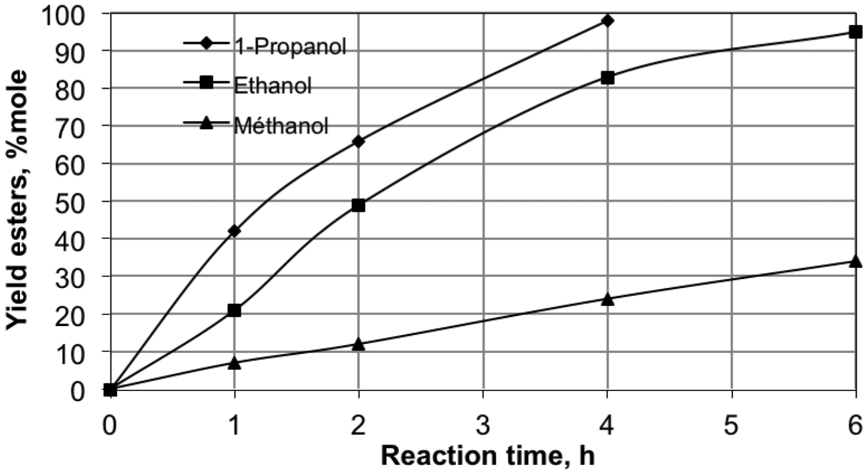


Figure 5. Effect of alcohol type on the transesterification reaction. *Reaction conditions: molar ratio Alcohol:oil:*LI_4 *= 12:1:0.05 at 96°C*

However, in most transesterification studies that usedbasic catalysts, methanol was the most active alcohol because of its smaller size and the higher polarity of the methoxy anion that ould attack the carbonyl group of the triglyceride molecule (Hoang *et al.,* 2009). Lotero *et al*. (Lotero *et al*., 2005) assumed that initial reagent phase miscibility was more critical in acid catalysis than in base catalysis.

Recycling of the ionic liquids

At the end of reaction and 2h of decantation, the mixture was dividedinto two phases: product phase and catalyst phase. The ionic liquid wass easily recovered from the catalyst phase (containing the glycerol and alcohol) by washing with diethyl ether, then drying in vacuo.

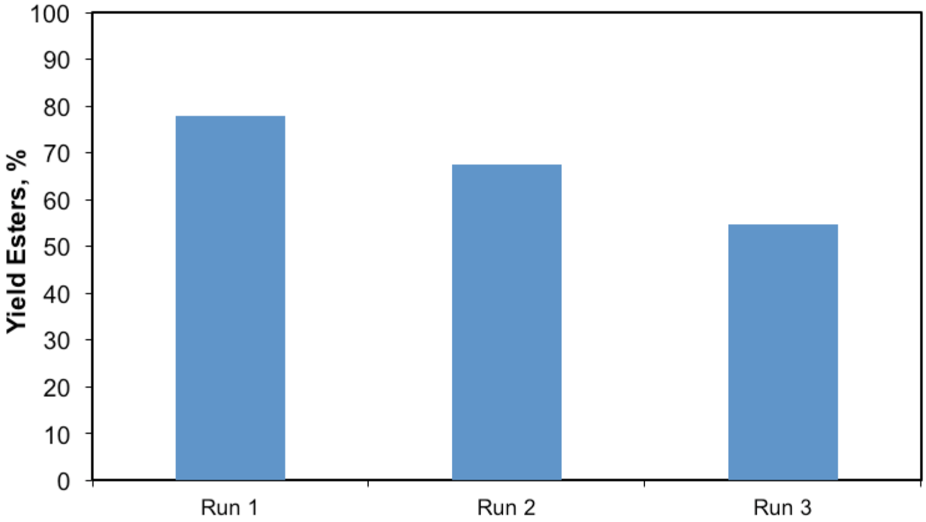


Figure 6. Recycling ability test of the ionic liquid. Reaction conditions: *molar ratio methanol:oil:* LI_2[SBPy]HSO_4*= 12:1:0.05 at 114°C*

The results show that LI_2[SBPy]HSO_4 was successfully recycled three times butits activity decreased after each recycle step. This could have been due to the slight loss of ionic liquid during the recovery; some glycerol existing in the reseused ionic liquid could have shifted the equilibrium according to Le Châtelier's principle, thereby decreasing the yield of the reaction.

CONCLUSIONS

These SO_3H-fuctional acidic ionic liquids have been synthesised successfully and could be used as catalysts for the transesterification of colza oil with alcohol to biodiesel.1-(4-sulfobutyl)-pyridinium hydrogen sulphate had a higher rate enhancement than the other ionic liquids and this was dependent on the structure. Both acidic or lipophilic characteristic of the ionic liquid are key factor in obtaining good reaction rates. From this study, it was alsoobserved that 1-propanol and ethanol were more active compared to methanol due to their better solubility in the oil.

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