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Green Synthesis of Methyl Palmitate as Biodiesel Main Target Compound by Organic Alkalis Based Deep Eutectic Solvents

Y.J. LEE, Y.R. LEE and K.H. ROW*

Department of Chemistry and Chemical Engineering, Inha University, Incheon 402-751, Republic of Korea

*Corresponding author: Fax: +82 32 8720959; Tel: +82 32 8607470; E-mail: rowkho@inha.ac.kr

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The green synthesis of methyl palmitate as a biodiesel main target compound was developed by the esterification of palmitic acid over organic alkali-based deep eutectic solvents. Three organic alkali-based deep eutectic solvents were assessed as catalysts for the synthesis in this study. The optimal deep eutectic solvent was prepared from choline chloride and glycerol (1:5) and the methanol to deep eutectic solvent ratio was 20 % (v:v). The reaction was optimized at a methanol/palmitic acid ratio of 10:1 (methanol 10 mL, palmitic acid 1 mg) at 30 °C for 60 min. Under optimized conditions, good calibration curves were obtained at phenolic acid concentrations, ranging from 10 to 500 µg/mL. The method recovery ranged from 99.2 to 99.8 % and the inter-day and intra-day relative standard deviations were less than 5 %. Under deep eutectic solvent catalysis, the methyl palmitate yield was 92.5 %. Overall, organic alkali-based deep eutectic solvents are expected to find applications in the preparation of biodiesel.

Keywords: Deep eutectic solvents, Biodiesel, Organic alkalis, Methyl palmitate, Palmitic acid.

INTRODUCTION

Recently, biodiesel has become increasingly attractive because of its environmental benefits and that it is made from renewable resources [1]. Owing to the increases in crude oil prices, limited feedstock of fossil oil and environmental concerns, there has been renewed focus on vegetable oils, such as corn [2], soybean and palm oil [3,4] and animal fats to produce biodiesel fuels [5]. Fats and oils are commonly water-insoluble, hydrophobic substances in the plants and animals that are made up of one mole of glycerol and three moles of fatty acids and are generally referred to as triglycerides [6]. Fatty acids differ according to the carbon chain length and the number of double bonds. Biodiesel is a renewable energy, alternative diesel fuel of a domestic origin derived from a variety of fats and oils from a transesterification reaction; accordingly, it is composed of the alkyl esters, normally methyl esters of the fatty acids of the parent oil or fat [7].

Generally, the catalysts for fatty acid esterification include alkalis and acids. This study assessed organic alkali-based deep eutectic solvents (DESs) as catalysts. Deep eutectic solvents are non-toxic, low reactivity with water and are prepared easily at low cost. Most important, deep eutectic solvents are bio-degradable [8,9]. Deep eutectic solvents are formed by mixing two or more components, such as a variety of quaternary ammonium salts and carboxylic acids. Therefore, they have a low melting point compared to their component compounds. The physical properties of deep eutectic solvents are affected considerably by the structure of the carboxylic acid. On the other hand, the phase behaviour of the mixtures can be modeled simply by considering the mole fraction of the carboxylic acid in the mixture [10]. In addition, deep eutectic solvents are generated from organic halide salts with organic compounds, which are hydrogen bond donors (HBDs). Charge delocalization is achieved through hydrogen bond donor between the halide anion and the amide moiety. A eutectic mixture of choline chloride (ChCl) with urea produced a liquid with a low melting point. This liquid was found to have interesting solvent properties similar to ambient temperature ionic liquids, which are called "green" solvents, Moreover, a wide variety of solutes were found to exhibit high solubility [11]. Based on this characteristic, the potential of deep eutectic solvent as synthesis catalysts for biodiesel preparation *via* deep eutectic solvent-based extraction from natural products has been reported [12-15].

To examine the preparation of methyl palmitate, which is synthesized from fatty acids, the individual fatty acid methyl ester itself was evaluated for its stability against exposure to methanol under a variety of exposure conditions. A range of organic alkali-based deep eutectic solvents with different mixing ratios were used to optimize the preparation of methyl palmitate. Other factors, such as temperature, time and deep

eutectic solvents/methanol ratio, were also examined systematically and the level of methyl palmitate production was determined by gas chromatography.

EXPERIMENTAL

Choline chloride (ChCl) (> 98.0 %) and ethylene glycol (> 99.5 %) were purchased from Tokyo Chemical Industry Co. Methanol (> 99.9 %) was acquired from Duksan Pure Chemicals Co., Ltd. (Ansan, Korea). Glycerol (> 99.0 %) was supplied by Duksan Pure Chemicals Co., Ltd. (Ansan, Korea). Urea (> 98.0 %) was obtained from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). Methyl palmitate (> 97.0 %) was acquired from Tokyo Chemical Industry Co.

Preparation of deep eutectic solvents: Three deep eutectic solvents were prepared by heating choline chloride and an organic alkali as a hydrogen bond donor, such as urea, ethylene glycol and glycerol, at a setting ratio to 60 °C for 60 min with constant stirring until a homogeneous liquid formed. Table-1 lists the compositions of the synthesized deep eutectic solvents.

TABLE-1
COMPOSITIONS OF THE SYNTHESIZED DEEP EUTECTIC SOLVENTS

Abbreviation	Salt	Hydrogen bond donor	Salt/hydrogen bond donor ratio
DES-1	Choline chloride	Urea	1:1
DES-2	Choline chloride	Ethylene glycol	1:1
DES-3	Choline chloride	Glycerol	1:1
DES-4	Choline chloride	Glycerol	1:2
DES-5	Choline chloride	Glycerol	1:5

Synthesis of methyl palmitate: To prepare the sample solution, palmitic acid (5 mg) and methanol (1 mL) and deep eutectic solvents were placed into a flask. The mixture was then stirred at 60 °C for 1 h for different times and the temperature and reaction ratio was varied. After the reaction, the mixture was analyzed by gas chromatography.

Gas chromatography analysis: To obtain the standard curves, a solution with an accurate concentration of methyl palmitate (0.25, 0.5, 1.0 and 2.0 mg/mL) in methanol was prepared. 2 μL of each of the five standard solutions was injected into the gas chromatography. The results were used to produce linear regression equations for methyl palmitate. Gas chromatography analysis was conducted on a Yong Lin Instrument (Korea) GC-6100 equipped with a DB-1701 capillary column (30 m × 0.320 mm × 1.00 μm) (Agilent Technologies) and detected using a flame ionization detector. The carrier gas used was nitrogen with a flow rate of 1.8 mL/min. The gas chromatography injection temperature was 280 °C and the detector temperature was 300 °C. The temperature program of the oven was set from 60 to 140 °C at a rate of 5 °C/min and afterward increased to 220 °C at a rate of 10 °C/min. Finally, the temperature was increased to 280 °C in 4 min.

RESULTS AND DISCUSSION

Effect of deep eutectic solvents: The deep eutectic solvents have specific chemical properties such as melting point, solubility, viscosity and density that properties are similar with ionic liquids (ILs). Deep eutectic solvents have high polarity that used separation of biodiesel [16]. Three organic alkali-based deep eutectic solvents were selected to catalyze the synthesis of methyl palmitate. Fig. 1 shows the effects of the different alkali-based deep eutectic solvents on the synthesis of methyl palmitate. When ChCl-urea or ChCl-glycerol was used a catalyst, the yield of methyl palmitate was only 42.6 and 36.6 %, respectively. On the other hand, ChCl-ethylene glycol was better for synthesis and the related yield of methyl palmitate was 56.8 %. The results showed that ChCl-ethylene glycol was suitable for the catalysis of methyl palmitate synthesis.

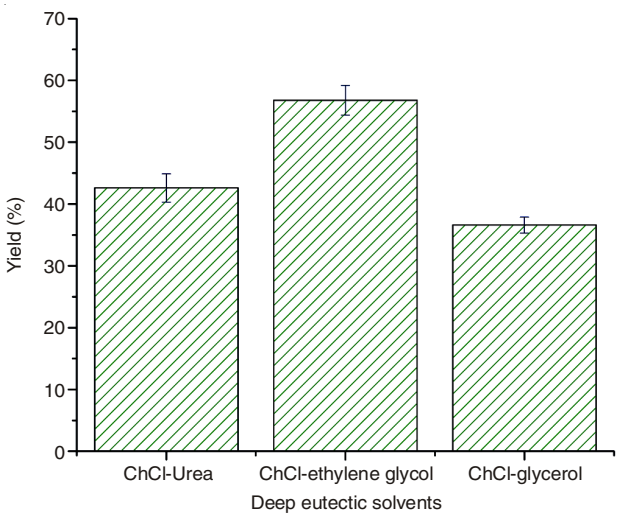

Fig. 1. Effect of three alkalis deep eutectic solvents (DESs) on the synthesis of methyl palmitate

The deep eutectic solvent composition molar ratio (ChCl: ethylene glycol) is also an important factor for the catalysis effect and ChCl-ethylene glycol deep eutectic solvents were synthesized with three composition ratios (ChCl:ethylene glycol molar fraction) of 1:1, 1:2 and 1:5 (DES-3~DES-5). The yield of methyl palmitate increased with increasing ChCl:ethylene glycol ratio (Fig. 2). The yield of the three deep eutectic solvent was DES-3 56.8 %, DES-4 68.3 % and DES-5 83.2 %. Therefore, the optimal condition of deep eutectic solvent was ChCl/ethylene glycol (1:5).

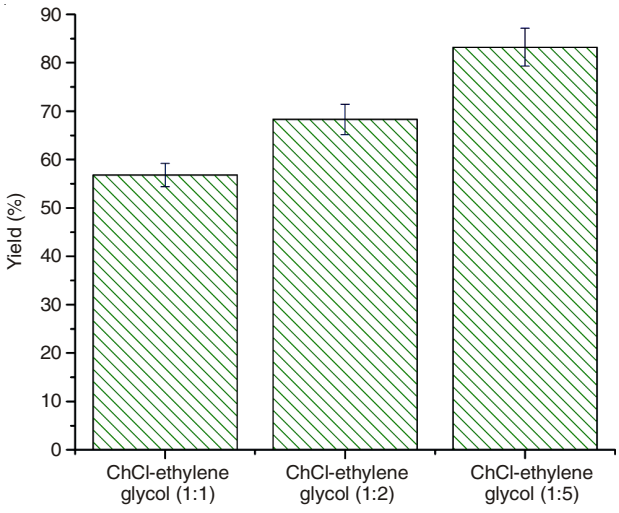

Fig. 2. Effect of the salt to hydrogen bond donor ratio in ChCl-ethylene glycol on the synthesis of methyl palmitate

Effect of deep eutectic solvent to methanol ratio: Deep eutectic solvents have a lower reaction effect owing to their high viscosity. Therefore, the addition of a reaction solvent to ChCl-ethylene glycol to reduce the viscosity can be a considerable advantage. Fig. 3 shows the effects of the ChCl-ethylene glycol to methanol ratio. In this experiment, the amount of methanol was fixed to 1 mL and the amount of ChCl-ethylene glycol was varied; 1, 5, 10 and 20 % (v:v) in methanol. The yield increased with increasing amount of ChCl-ethylene glycol. The highest yield was observed when 20 % (v:v) of ChCl-ethylene glycol in methanol was added. Consequently, the optimal deep eutectic solvents/methanol ratio was 20 % (v:v).

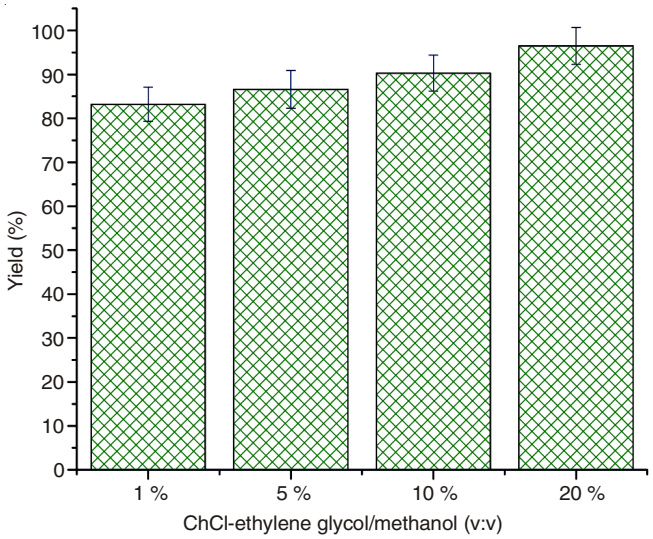

Fig. 3. Effect of deep eutectic solvent to methanol ratio on the synthesis of methyl palmitate

Effect of methanol to palmitic acid ratio: The methanol and palmitic acid ratio is one of the main conditions for the reaction. Fig. 4 shows the effects of the methanol/palmitic acid ratio. In this experiment, the reaction temperature and time were fixed to 90 °C and 60 min, respectively. The methanol: deep eutectic solvents ratio was fixed to 20 % (v:v). The methanol to palmitic acid ratio varied; 100:1, 50:1, 10:1, 5:1 and 2:1. In Fig. 4, the methyl palmitate yields were relatively constant at ratios of 100:1, 50:1 and 10:1, but the yields were lower at ratios of 5:1 and 2:1. Therefore, the optimal methanol and palmitic acid ratio was 10:1 (methanol 10 mL, palmitic acid 1 mg).

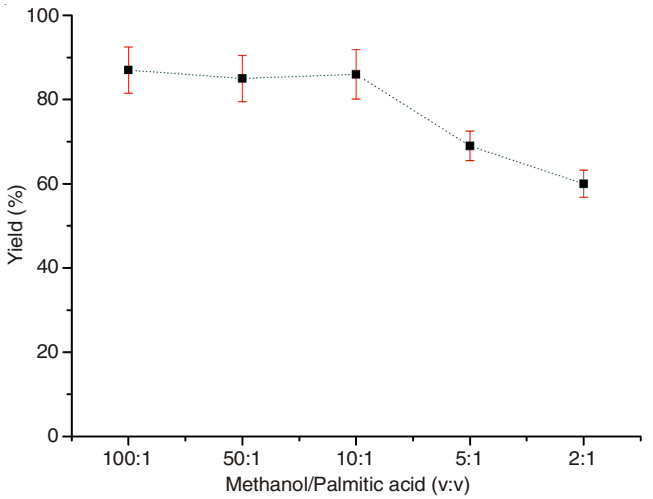

Fig. 4. Effect of methanol to palmitic acid ratio on the synthesis of methyl palmitate

Effect of temperature: Normally, temperature is one of the key factors to an effective catalyst in the reaction. Although the reaction rates increased with increasing temperature, a high temperature might have a reverse effect because of the vapourization of methanol in the esterification reaction. In this study, the methanol to palmitic acid ratio was fixed to 10:1. Fig. 5 shows that temperature affects the methyl palmitate yield in the esterification reaction. The reaction temperature was in the range, 30-100 °C and the yield showed a fixed value from 30 to 90 °C. On the other hand, the yield decreased at 100 °C. Temperature was not the driving force for the reaction under the catalyst effect and the high temperature was deleterious for the yield because methanol is vapourized rapidly. Therefore, the temperature of the esterification was not a significant factor in the synthesis of methyl palmitate using the ChCl-ethylene glycol catalyst.

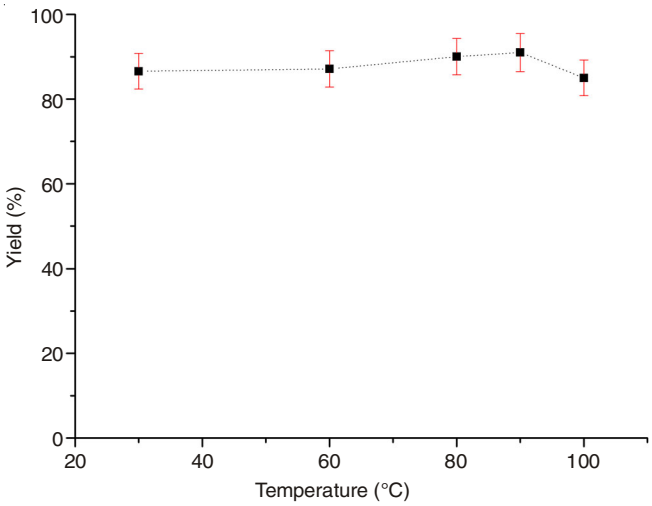

Fig. 5. Effect of temperature on the synthesis of methyl palmitate

Effect of time: Fig. 6 shows the effects of the reaction time. The reaction temperature was fixed to 30 °C and the methanol: deep eutectic solvent ratio was fixed to 20 % (v:v). The reaction time was between 30 and 150 min to optimize the synthesis. The yield increased from 30 to 60 min, but was relatively constant from 60 to 150 min. This shows that the optimal synthesis time was 60 min. Under the above conditions, the highest methyl palmitate yield was 92.5 %.

Analytical performance: A set of experiments were carried out to determine the linearity, precision, detection limits and other characteristics of the method under optimized conditions. Methyl palmitate showed good linearity from 0.25 to 2.00 mg/mL with a regression equation of Y = 175.05 + 1775.7x ($R^2 > 0.9975$). The limit of determination (LOD) was 0.15 µg/mL and the limit of quantitation (LOQ) was 0.28 µg/mL. The above mentioned data is unnecessary because the concentration of the real samples should between these concentrations when preparing the calibration curves; the lowest concentration was 10 µg/mL. The precision was determined by repeating the analysis six times and the method recovery

TABLE-2
INTRA-DAY AND INTER-DAY PRECISIONS, ACCURACIES AND RECOVERIES OF METHYL PALMITATE WITH THREE DIFFERENT CONCENTRATIONS

Concentration (μg mL^{-1})	Intra-day		Inter-day		Method recovery (%)
	Measured concentration (μg mL^{-1})	Precision RSD (%)	Measured concentration (μg mL^{-1})	Precision RSD (%)	
1	1.23 (± 0.25)	4.15 (± 3.85)	1.14 (± 2.11)	3.06 (± 1.98)	99.8
25	25.18 (± 1.22)	3.32 (± 2.18)	25.11 (± 0.38)	1.82 (± 0.14)	99.2
100	99.85 (± 0.48)	3.12 (± 3.12)	99.52 (± 1.34)	2.15 (± 2.15)	99.5

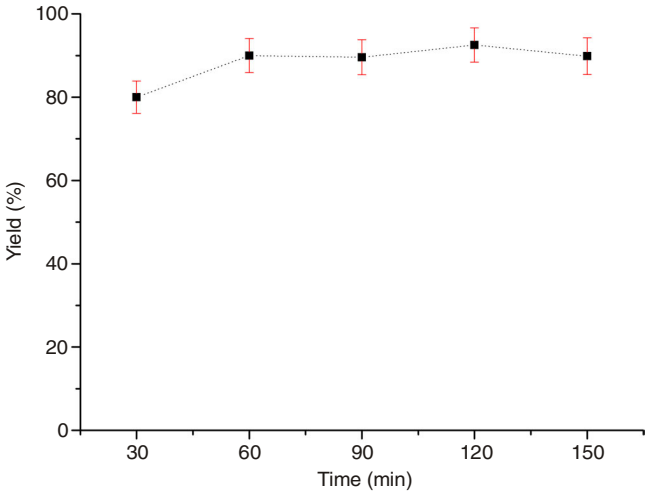

Fig. 6. Effect of time on the synthesis of methyl palmitate

ranged from 99.2 to 99.8 % (Table-2). These results show that the proposed method is stable with a wide range of potential applications.

Conclusion

The study was applied successfully to the pretreatment of biodiesel by the esterification of palmitic acid over alkali-based deep eutectic solvent. The synthesis conditions of the deep eutectic solvents, such as salts, hydrogen bond donors and ratio, were varied to determine the optimal conditions. The reaction conditions, such as methanol/palmitic acid ratio, time and temperature, were varied. The optimal conditions were confirmed using the numerical concentration ($R^2 > 0.9975$). Under optimal conditions, the yield was 92.5 %. Therefore, organic alkali-based deep eutectic solvents can be developed as a catalyst for the esterification of palmitic acid and have potential applicability to other biodiesel pretreatments.

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