

Application of deep eutectic solvents as catalysts for the esterification of oleic acid with glycerol



Scott T. Williamson^a, Kaveh Shahbaz^{b,*}, Farouq S. Mjalli^c, Inas M. AlNashef^d,
Mohammed M. Farid^{b,**}

^a Chemical Engineering Department, Faculty of Engineering, Loughborough University, Loughborough, England, UK

^b Department of Chemical and Materials Engineering, University of Auckland, Private Bag 92019, Auckland, New Zealand

^c Petroleum and Chemical Engineering Department, Sultan Qaboos University, Muscat 123, Oman

^d Department of Chemical Engineering, Khalifa University of Science and Technology, Masdar Institute, Abu Dhabi, United Arab Emirates

ARTICLE INFO

Article history:

Received 13 November 2016

Received in revised form

20 June 2017

Accepted 10 July 2017

Available online 14 July 2017

Keywords:

Biodiesel

Deep eutectic solvent

Esterification

Free fatty acids

Glycerol

Catalyst

ABSTRACT

Free fatty acids (FFA) in low grade oil could be reduced by using an esterification reaction with glycerol, which itself is a waste product of biodiesel synthesis to give mono- and di-glycerides. This study investigated, for the first time, the reaction between oleic acid as a FFA with glycerol, using a phosphonium-based deep eutectic solvent (DES) as a catalyst. The effects of temperature (120 °C, 150 °C and 180 °C) and the DES catalyst concentration (1, 3 and 5 wt%) on the esterification efficiency of fatty acid conversion were observed. The glycerol to fatty acid molar ratio (6:1) and agitation speed (600 rpm) were kept constant. The results revealed that the lowest activation energy of 54.64 kJ/mol was attained using 5 wt% of DES catalyst. Accordingly, optimum reaction conditions were found at a temperature of 150 °C with a 5 wt% DES catalyst, which produced 95% FFA conversion after 30 min of reaction time. In addition, 85% of combined mono- and di-glycerides was observed at the optimum condition, which will be easier to transesterify using alcohol. The process was repeated without adding any fresh catalyst and results showed that catalyst activity sustained very well, suggesting that it can be reused a number of times.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Increased environmental awareness concerning global warming and carbon emissions have encouraged the search for renewable energy sources and technologies. The world currently relies on non-renewable energy sources such as petroleum, natural gas and coal in day to day life activities. However, these resources are limited and depleting and hence interests have shifted towards finding alternative energy sources. One such energy source is bio-fuels [1]. These fuels are obtained from biological sources such as sugar, animal fats and vegetable oils [2]. Bioethanol, biodiesel, and biogas are commonly found examples of biofuels [3]. Much research has already been conducted on the manufacturing and application of these fuels [4,5]. However, few processes have

reached full commercialization with the main limiting factor being the relatively high cost of the raw materials. Indeed, production, transportation, storage and refining of vegetable oils are responsible for more than 85% of the total cost of producing biodiesel [6,7].

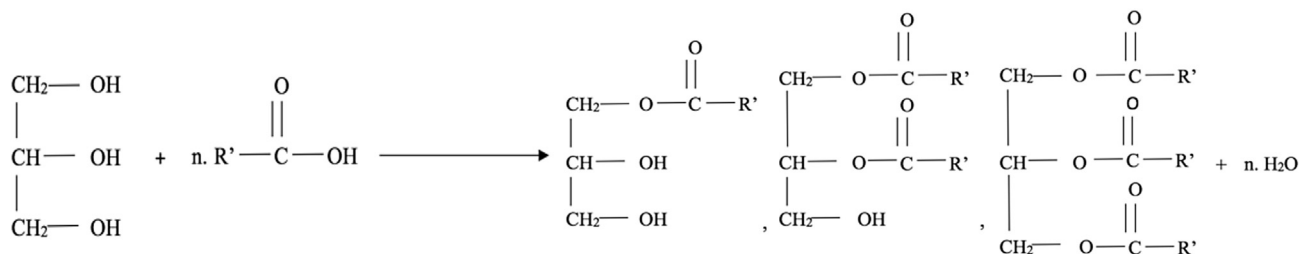
One possible way of lowering the cost of raw materials for biodiesel production, is through the esterification of free fatty acids (FFA) available in low cost feedstock with glycerol [8]. This esterification is known as “glycerolysis” and used to produce mono-, di- and tri-glycerides which can be used as a feedstock for biodiesel production. A general reaction scheme for glycerolysis is given in Scheme 1. A major benefit of this process is that glycerol itself is a by-product of the synthesis of biodiesel, which produce 1.0 kg of glycerol with every 10 kg of biodiesel produced [8]. This means that a waste product of the primary process can be recycled to form part of the feedstock for the next process, which, will create a much more efficient and cost effective process.

Several studies have reported that the esterification of FFA with glycerol encountered major drawbacks including the need of high reaction temperatures, long reaction times and low yields [8–10].

* Corresponding author.

** Corresponding author.

E-mail addresses: k.shahbaz@auckland.ac.nz (K. Shahbaz), m.farid@auckland.ac.nz (M.M. Farid).



Scheme 1. General reaction scheme for the esterification of free fatty acids with glycerol.

Previous work done by our research group investigated the effects of temperature (180 °C–240 °C), molar ratio of FFA to glycerol (1:1 to 1:10) and agitation rate (200 rpm–800 rpm) on an esterification reaction between FFA and glycerol without the use of catalysts. The optimum operation conditions were found at 220 °C, 600 rpm and 1:6 M ratio (FFA: glycerol) using 99% pure glycerol and oleic acid, achieving 99.7% conversion of oleic acid after 300 min [8].

In order to overcome the above-mentioned problems, various catalysts have been employed for glycerolysis reaction. Guner et al. [11] explored the esterification of oleic acid with glycerol in the presence of a metal oxide catalyst namely sulphated iron oxide. The effect of temperature (180 °C–220 °C) with a 5.1 wt% catalyst loading and 200 min reaction time was investigated, resulting in an activation energy of 68.16 kJ/mol. Pouilloux et al. [12] examined the use of solid based catalysts (i.e. magnesium oxide, zinc oxide and sodium carbonate) and achieved a conversion of 67.5%, 36.5% and 43.9%, respectively for the esterification of glycerol with octadecanoic acid at 160 °C with a catalyst loading of 0.7 wt% after 24 h. Diaz et al. [9] also studied the effect of *p*-toluenesulfonic acid (PTSA) as the catalyst for the glycerolysis of oleic acid. A 100% conversion of FFA was achieved at 120 °C, molar ratio of 1:1 (FFA: oil) and 0.5% w/w PTSA. However, the reaction time was 6 h [9]. Macierzanka and Szelag [13] reported the effect of temperature (130 °C–160 °C) and catalyst loading (0.006–0.05 mol) using a zinc carboxylate as a catalyst and attained a 90.1% conversion of free fatty acid after 6 h reaction time. Wibowo et al. [14] observed a 71% conversion of lauric acid in an esterification reaction with glycerol over organomontmorillonite catalysts (i.e. tetra butyl ammonium bromide and cetyl trimethyl ammonium bromide). This conversion occurred over 8 h at 130 °C, a catalyst loading of 5 wt% and at molar ratio of 6:1 (glycerol: lauric acid) [14]. Mostafa et al. [15] explored the production of mono-, di- and tri-glycerides from waste fatty acids using a metal halide catalyst in the form of zinc chloride. They studied the effect of temperature (180 °C–260 °C), catalyst concentration (0.1 wt% to 0.3 wt%), glycerol: FFA molar ratio (1:1, 1:2, 1:3 and 3:1) and agitation speed (200 rpm, 500 rpm and 1000 rpm). Oleic acid conversion of 99% was achieved after 100 min at 195 °C, 0.3% catalyst concentration, 500 rpm and at 1:1 M ratio of glycerol to oleic acid [15]. Singh et al. [10] also reported the effects of catalyst loading (0.25%, 0.5% and 1%), temperature (140 °C–160 °C) and glycerol to FFA molar ratio (2:1, 4:1, 6:1) using a zinc oxide catalyst on the conversion of FFA to mono-, di- and tri-glycerides. An optimum condition was found after 350 min at 0.5 wt% catalyst loading, 4:1 M ratio of glycerol to FFA and at 140 °C [10].

Deep eutectic solvents (DESs) are defined as mixtures of hydrogen bond donor (HBD) with hydrogen bond acceptor (HBA) materials. These mixtures have lower melting points than their constituting compounds [16] and are being used both in research and industry because of their potential as green solvents. This means that they can be formulated as environmentally benign solvents with advantages such as low vapour pressure, non-toxicity, non-reactivity with water and biodegradability [17]. DESs

can be prepared easily at low cost and high purity as long as the respective components are of high quality [16]. DESs offer a wide range of applications such as organic synthesis, catalysis, electrochemistry, nanotechnology and other applications [18–22].

Recently, Hayyan et al. [23–25] comprehensively investigated the use of DESs as catalyst in esterification of crude palm oil with methanol in order to reduce the FFA content in crude palm oil. The FFA content in crude palm oil is reacted with excess methanol in order to form fatty acid methyl esters (FAME). They have introduced three DES catalysts based on *p*-toluenesulfonic acid monohydrate and using three different salts namely; (allyl triphenylphosphonium bromide [23], NN-diethylenethanol ammonium chloride [24]; and finally choline chloride [25]. Through the use of the ammonium-based DESs, the FFA content of the acidic crude palm oil (ACPO) was decreased from 9% to less than 1% using a 0.75 mass ratio of the catalyst to ACPO within a 30 min reaction time [24,25]. Moreover, 1 wt% of phosphonium-based DES reduced the FFA content of the low grade crude palm oil (LGCPPO) from 9.5% to less than 2% within a 30 min reaction time [23]. It should be also pointed out that the phosphonium-based DES showed its reusability through the four times recycling runs [23].

In this paper, the feasibility of using the phosphonium based-DES as a catalyst in the direct esterification reaction of glycerol with oleic acid is investigated for the first time to the best of our knowledge. Moreover, the reusability of the catalyst for the glycerolysis reaction is examined. The effect of changing catalyst concentration (1, 3 and 5 wt%) and temperature (120 °C, 150 °C and 180 °C) is also studied to find the optimum conditions. It should be noted that in this study, 6:1 M ratio of glycerol to fatty acids and 600 rpm agitation speed were used and kept constant in the glycerolysis reaction. These conditions were found to be optimum for the esterification of oleic acid and glycerol in the absence of catalyst in a previous work [8].

2. Experimental

2.1. Materials

Glycerol (C₃H₈O₃, 99%), oleic acid (C₁₈H₃₄O₂, 90%), allyl triphenylphosphonium bromide (C₂₁H₂₀BrP, 99%) and *p*-toluenesulfonic acid monohydrate (PTSAM) (C₇H₁₀O₄S, 98%) were obtained from Sigma-Aldrich (St. Louis, USA). All purchased chemicals were used as received without additional purifications.

2.2. Catalyst preparation and characterization

A glass Schott bottle along with a magnetic stirrer were used to prepare the phosphonium-based DES catalyst by mixing allyl triphenylphosphonium bromide as HBA and PTSAM as HBD at 700 rpm, molar ratio of 1:3 (HBA to HBD) and at 80 °C until a transparent, yellow, homogeneous mixture was formed. The final mixture of the catalyst was in a jelly viscous form at room

Download English Version:

<https://daneshyari.com/en/article/4926167>

Download Persian Version:

<https://daneshyari.com/article/4926167>

[Daneshyari.com](https://daneshyari.com)