



Continuous production of palm biofuel under supercritical ethyl acetate



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ARTICLE INFO

Article history:

Received 9 December 2014

Accepted 14 January 2015

Available online 2 February 2015

Keywords:

Biofuel

Continuous system

Palm oil

Supercritical ethyl acetate

Water addition

ABSTRACT

The transesterification of palm oil in supercritical ethyl acetate (ETA) to produce fatty acid ethyl ester (FAEEs) or biofuel was conducted in a continuous tubular reactor. The density of the mixtures in the system was estimated using the Peng–Robinson equation of state process simulator, and the residence time was calculated. The effects of the reaction conditions, including the molar ratios of palm oil to ethyl acetate, the temperature, and the pressure, were investigated under various mass flow rates of the mixtures and optimized. The results showed that reaction temperatures above 653 K and long residence times affected the content of FAEEs and triacetin, a valuable by-product. The addition of water to the mixture in a 1:30:10 M ratio of palm oil to ethyl acetate to water at 653 K, 16 MPa, and a mixture mass flow rate of 1.5 g/min increased the total production of FAEEs and triacetin from 90.9 to 101.5 wt% in 42.4 min. The main finding of the present study is that triglyceride associated with ETA hydrolysis used to form acetic acid protected the products from decomposition at high temperatures and long residence times. The results will aid the selection of an efficient and economical process for alternative biofuel production from palm oil in supercritical ETA.

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1. Introduction

Excessive dependence on petroleum fuel for daily activities has raised a concern due to the unpredictability of oil prices and issues surrounding energy security. Moreover, the incomplete combustion of petro-diesel in engines continuously increases greenhouse gases, which adversely affects ecosystems worldwide and causes climate change [1,2]. Thus, the potential of bioenergy, with alternative biofuels produced from biomass [3] or fatty acid ethyl ester (FAEEs), as a partial substitute for petroleum diesel fuel has attracted increased [4]. Conventional biofuel is produced via a transesterification reaction of vegetable oil and short-chain alcohol in the presence of either a basic [5] or an acidic [6] catalyst. After the completion of the reaction, the catalyst and glycerol by-products have to be removed from the resultant FAEEs and pre-treated before utilization [7–9]. This step limits biofuel production that uses the catalytic transesterification processes. Thus, many researchers are exploring and developing noncatalytic procedures for biofuel production [10].

Noncatalytic transesterification of vegetable oil and alcohol in supercritical conditions has been widely investigated [11] with studies suggesting that it may be an alternative method for clean biofuel production [12]. As the reaction operates under high-temperature and high-pressure conditions, it enhances the phase solubility, mitigates mass transfer limitations, provides higher reaction rates, and facilitates the separation and purification steps of the products [13]. Moreover, research has shown that the supercritical method is more resistant to contamination by water and free fatty acids than the conventional alkali-catalyzed technique. However, the catalyst-free production of biofuel in supercritical alcohol does not prevent the formation of glycerol by-products, which have to be removed [14], and the glycerol has to be purified.

The purified glycerol can be used as a raw material in many industries [15], such as pharmaceuticals, personal care, food, cosmetics, and fuel additive, via chemical reaction processes [16]. Interest in the potential of triacetin, a fuel additive, has increased due to its complete solubility in biofuel and improved cold flow properties, including its cloud point and pour point, compared to neat biofuel [17]. Triacetin can be synthesized without a catalyst in a stirring reactor at 433 K and 1.07 MPa via the reaction of glycerol with excess acetic acid [18]. The esterification of glycerol with acetic acid utilizes dodeca molybdophosphoric acid ($H_3PMO_{12}O_{40}$) encaged in a USY zeolite catalyst [19]. The transesterification of

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ethyl acetate (ETA) utilizes glycerol in the presence of an acid catalyst [20]. The latter reaction is depicted in Fig. 1.

However, supercritical transesterification of triglyceride (TG) with alcohols does not avoid glycerol production and requires a post-reaction to remove the glycerol. Recent prospective studies have described the use of dimethyl carbonate [21] and methyl- or ethyl acetate [22] as supercritical reactants to transform TG into biofuel through an transesterification reaction without glycerol formation. The transesterification reaction yields valuable by-products of glycerol carbonate [21] and triacetin [22]. An attractive advantage of these reactants compared to alcohols is that they synthesize biofuel and biofuel additives simultaneously.

There are no reports in the current literature on biofuel production from palm oil in supercritical ETA using continuous flow reactors. Therefore, in this research, the transesterification reaction of palm oil in supercritical ETA using a continuous tubular reactor under different conditions was experimentally investigated as a means of alternative biofuel production. The oil palm feedstock was mainly grown in southern Thailand, and the ETA used was a derivative of ethanol, produced from cane molasses fermentation [23]. These local raw materials are readily available and inexpensive, both of which are important for renewable energy and sustainability. The presence of water in the transesterification of palm oil in supercritical ETA was also investigated and optimized to evaluate whether including this impurity could improve the yields.

2. Materials and methods

2.1. Materials

The refined palm oil used in this experiment was from Morakot Industries Co., Ltd. The fatty acid compositions of the palm oil are given in Table 1 [24]. The ETA (99.97% purity) used for the reaction and the analysis was obtained from Fisher Scientific (UK), and FAEEs, triacetin, and diacetin were purchased from Sigma–Aldrich (Germany). The TG was triolein. The FAEEs, triolein, and triacetin were used to generate an external calibration curve.

2.2. Apparatus and experimental procedure

The experimental setup of the continuous biofuel production system is schematically shown in Fig. 2. Supercritical transesterification was conducted twice using a tubular reactor with a volume of 189 cm³ made of stainless steel tubing (550-cm long with an internal diameter of 0.635 cm). The reactor was placed in a fluidized sand bath, electrically heated, and controlled by a temperature controller (Sigma Model SF48, USA). The reactor was monitored by two K-type thermocouples directly connected at the inlet and outlet of the reactor inside the bath. The reactor also comprised a back-pressure regulator (Swagelok, UK) and external cooling water for cooling down the obtained product.

When the operating condition reached a steady state [25], the mixture of palm oil and ETA stored in a beaker was fed into the

Table 1
The fatty acid composition of palm oil.

Fatty acid	Composition (wt%) [24]
C12:0	0.4
C14:0	0.8
C16:0	37.4
C16:1	0.2
C18:0	3.6
C18:1	45.8
C18:2	11.1
C18:3	0.3
C20:0	0.3
C20:1	0.1

reaction system by a high-pressure liquid pump (Model P-50, Thar Technology, USA). The reactant mixture was heated and depressed under a desired condition. After the residence time (the expected time needed from entering at the input of the flow system to exiting at the output [26]) had passed for three times, approximately 50 cm³ of the liquid product was collected in a glass flask and placed at the reactor outlet. The product was weighed and put in a rotary evaporator to remove excess ETA. The FAEEs and by-products were then quantitatively analyzed by gas chromatography (GC). To investigate the effects of water and the addition of acetic acid on the production of FAEEs and triacetin products, a predetermined amount of water was initially measured and added to the reaction mixture. The resultant mixture was then examined for FAEEs and triacetin using GC using the aforementioned procedure.

2.3. Analysis of reaction products

Excess ETA in the sample product was first removed by a rotary evaporator (Heidolph, Germany). The product was then weighed, and 0.1 g was dissolved in n-heptane. Subsequently, 1 µl of the prepared sample was injected into a GC column. External calibration curves were generated using 0.02–0.1 g of standard ethyl palmitate, ethyl oleate, and ethyl stearate dissolved in n-heptane. Calibration curves were then generated by curve fitting as a straight line, with $R^2 \geq 0.999$.

The intermediate compounds (a mixture of monoacetin and diacetin) [22] and the by-product triacetin produced by supercritical transesterification of the palm oil and ETA were quantitatively analyzed. As the boiling point of diacetin (532 K) and triacetin (531 K) is very close, their separation is difficult [27]. Therefore, the known composition of commercial triacetin was used as a reference standard for the calibration of the combination of diacetin and triacetin (hereafter, referred to as TAs).

The qualitative and quantitative analyses of the biofuel components were performed using a gas chromatograph (Agilent Technology Model 7890A), equipped with a capillary column (MTX-65TG, 30 m long and an outside diameter of 0.25 mm) and a FID (flame ionization detector). The temperatures of the injector and detector were set to 603 K and 653 K, respectively. The column

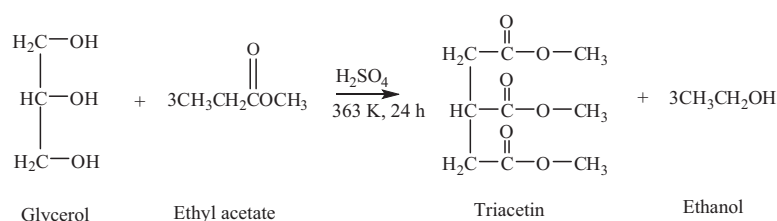


Fig. 1. Transesterification reaction of glycerol and ethyl acetate to produce triacetin and ethanol.

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