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Biodiesel production by non-catalytic supercritical methyl acetate: Thermal stability study

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ABSTRACT

Biodiesel production by non-catalytic supercritical methyl acetate (SCMA) reaction has been developed and optimized in previous study using *Jatropha* oil as oil feedstock. The reaction produces fatty methyl acid esters (FAME) as well as triacetin as the co-product. Due to the requirement of high reaction temperatures in SCMA treatment, thus the thermal stability of methyl oleate and methyl linoleate which are the major FAME in SCMA was investigated at temperature ranging from 330 °C to 420 °C. In addition, thermal stability of triacetin which was utilized as fuel additive in biodiesel was also investigated. The results revealed that the thermal stability of poly-unsaturated methyl linoleate decreases dramatically as temperature is increased from 330 °C to 420 °C while degradation of methyl oleate was only significant at 390 °C and above. Similar behaviour was also observed for triacetin which was found to degrade at high temperatures, resulting in low yield of biodiesel fuel even at optimum conditions.

1. Introduction

Biodiesel or also known as fatty acid methyl esters (FAME) is derived from edible and non-edible sources such as vegetable oils, animal fats or waste oils. It has recently attracted considerable attention due to its renewable, biodegradable and non-toxic fuel properties [1–3]. Currently, biodiesel can be produced conventionally by base- or acid-catalyzed method. However the problem with base-catalyzed method is that it could lead to saponification as it is very sensitive to the presence of water and free fatty acids [4]. Hence, this increases the complexity of this method and becomes costly since purification is needed to remove catalyst and saponified products. Meanwhile, acid-catalyzed reaction needs longer reaction period and necessitate higher reaction temperature [4].

Therefore, non-catalytic supercritical technology has been proposed to overcome the problems in conventional catalytic transesterification method. This method is simple as separation of products is easier and has high reaction rates. Although many researchers have shown the feasibility of supercritical methanol technology [6–9], the over-production of glycerol as the by-product could not be avoided which lead to uneconomical biodiesel processing.

As a result, a new process for glycerol-free production of biodiesel using non-catalytic supercritical methyl acetate has previously been developed to resolve the problem of over-produced glycerol [10]. As shown in Eq. (1), the reaction of triglyceride and methyl acetate produce FAME and triacetin (both compounds are collectively known as biodiesel fuel, BDF). Triacetin has no adverse effects on the main fuel characteristics and the addition of triacetin improve the cold flow properties and the pour point of biodiesel [5]. However, the results from previous study which was optimized by Response Surface Methodology (RSM) showed an optimum temperature of 400 °C was needed to achieve optimum biodiesel yield of 71.9% [10]. Due to the requirement of this high reaction temperature and low yield of biodiesel obtained, thus the thermal stability of FAME as well as triacetin was investigated in this study. To the best of our knowledge, there is still no study on thermal stability of FAME in SCMA treatment which is a major concern in order to produce good quality biodiesel.

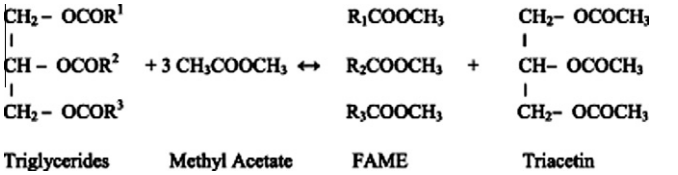

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Table 1
Fatty acids components of *Jatropha* oil.

Fatty acids	Compositions (%)
Palmitic (16:0)	13.3
Stearic (18:0)	4.9
Oleic (18:1)	32.0
Linoleic (18:2)	45.0
Linolenic (18:3)	0.2
Others	4.6

Table 1 shows the fatty acid components of *Jatropha* oil [11]. The major fatty acids components of *Jatropha* mainly consists of palmitic (16:0), oleic (18:1) and linoleic acids (18:2), in which the first number in the bracket is the number of carbons in the alkyl chain, while the second is the number of double bonds. *Jatropha* oil contained more unsaturated fatty acids indicated by high percentages of oleic and linoleic acids (78.94%) compared to saturated fatty acids (21.05%) [12]. Therefore, in this study, the thermal stability of mono-unsaturated (methyl oleate) and poly-unsaturated (methyl linoleate) were chosen to be investigated in supercritical methyl acetate.

2. Material and methods

2.1. Raw materials and chemicals

The raw feedstock which is *Jatropha curcas* L. oil was purchased from Bionas Sdn. Bhd., Malaysia. Methyl acetate (99%) and triacetin (99%) was purchased from Merck. For FAME analysis, methyl heptadecanoate was selected as internal standard and pure methyl esters such as methyl oleate and methyl linoleate were purchased from Fluka Chemie, Germany.

2.2. Thermal stability of FAME and triacetin

The thermal stability of FAME was done by exposing 160 mg of each pure methyl esters (methyl oleate and methyl linoleate) in 8 mL methyl acetate using batch-type reactor system which consists of a 12 mL tube reactor made from stainless steel 316. This tube reactor was attached with a temperature controller, a pressure gauge and furnace to heat up the reaction at the desired reaction temperature and a chilled-water bath used to stop the reaction immediately. Experiments were conducted at reaction temperature ranging from 330 °C to 420 °C and 20–60 min of reaction time for thermal stability of FAME. The reaction pressure was consistently operated above the critical pressure of methyl acetate which is 4.7 MPa. Initially, fatty acid methyl esters and methyl acetate were charged into the tube reactor. The tube reactor was inserted into a furnace and was heated to pre-determined temperature. After the desired reaction period was reached, the reaction was transferred automatically into a chilled water bath to quench the reaction immediately. The sample was then analyzed using gas chromatography.

For thermal stability of triacetin, 1.5 g of triacetin was exposed to supercritical methyl acetate using the same batch reactor system. The exposure was made within 60 min reaction time using the optimum temperature as obtained in SCMA reaction which is 400 °C. Thermal stability of triacetin over reaction temperature ranging from 330 °C to 420 °C was also investigated at fixed reaction time of 32 min. At the end of reaction, excess methyl acetate was evaporated and subsequently the obtained sample was analyzed using gas chromatography.

2.3. Analytical procedure

Analytical procedures were conducted using gas chromatography (PerkinElmer, Clarus 500) with Nukol™ capillary column (15 m × 0.53 mm; 0.5 μm film) and flamed ionized detector (FID). The solvent used was *n*-Hexane while helium was used as the carrier gas operated at oven temperature of 110 °C and then increased to 220 °C at a rate of 10 °C/min. Methyl heptadecanoate as well as other pure methyl esters have been injected prior to sample analysis to determine their standard area and retention time. Temperatures of detector and injector were set at 250 °C and 220 °C, respectively. After all samples have been diluted with internal standard, 1 μL of each sample was injected into the gas chromatography column.

2.4. Calculation of biodiesel yield

In the SCMA reaction, both FAME and triacetin can be utilized as biodiesel fuel (BDF). Hence, the total weight of BDF generated per unit of oil in the sample was used to define the yield of FAME and triacetin. According to the reaction stoichiometry, 1 mol of triglyceride reacted with 3 mol of methyl acetate will produce 3 mol of FAME and 1 mol of triacetin. Equivalently, the mass ratio of FAME to triacetin was found to be 4:1 in weight percent bases. Consequently, the maximum theoretical weight of BDF (FAME and triacetin) in a single phase is 125% (Eq. (2)). Considering the actual yield of triacetin peaks from GC, the actual yield of BDF can be calculated using Eq. (3). Meanwhile, Eq. (4) is used to calculate the yield of triacetin in the thermal stability study if triacetin in SCMA reaction.

$$\text{Theoretical yield of BDF} = \frac{\sum \text{Weight of fatty acid methyl esters (g)}}{\text{Weight of } \textit{Jatropha} \text{ oil used (g)}} \times 100 \times 1.25 \quad (2)$$

$$\text{Actual yield of BDF} = \frac{\sum \text{Weight of fatty acid methyl esters} + \text{Triacetin (g)}}{\text{Weight of } \textit{Jatropha} \text{ oil used (g)}} \times 100 \quad (3)$$

$$\text{Yield of triacetin} = \frac{\sum \text{Weight triacetin determined from GC (g)}}{\text{Weight of triacetin initially used (g)}} \times 100 \quad (4)$$

3. Results and discussion

3.1. Thermal stability of FAME in supercritical methyl acetate

Due to the severe optimum conditions proposed in previous study [10] especially on the high reaction temperature of the SCMA reaction, thermal stability of fatty acid methyl ester was studied in supercritical methyl acetate over a range of its condition between 330 °C and 420 °C. The task was done by taking the main component of fatty acid methyl esters in *Jatropha* biodiesel which are methyl oleate and methyl linoleate to be exposed in SCMA within the designated reaction temperature and time.

Fig. 1 shows the recovery of methyl oleate after exposure to supercritical methyl acetate at temperature of 330–420 °C. It can be seen from the figure that this mono-unsaturated fatty acid methyl ester is relatively stable at temperature ranging from 330 °C to 360 °C. Prolonging the exposure time does not cause severe decomposition at these temperatures and the losses is insignificant since the recovery of methyl oleate within 60 min is still high which are 83% and 77%, respectively. On the other hand, degradation of methyl oleate was obvious at 390 °C and when the exposure time was prolonged, only a recovery of less than 80% was obtained. Decomposition becomes significant with further rise