Fuel 166 (2016) 560–566

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Synthesis of high oleic palm oil-based trimethylolpropane esters in a vacuum operated pulsed loop reactor

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HIGHLIGHTS

- Trimethylolpropane ester was produced via vacuum assisted pulsed loop reactor.
- High yield of trimethylolpropane triesters was obtained at low catalyst loading and lower mixing intensity.
- Loop reactor had minimized the issue of soap formation.
- Lubricating properties of high oleic palm oil-based TMP ester were excellent.

ARTICLE INFO

Article history:
Received 4 August 2015
Received in revised form 18 October 2015
Accepted 8 November 2015
Available online 18 November 2015

Keywords:
Biolubricant
Trimethylolpropane ester
Pulsed loop reactor
Methyl ester

ABSTRACT

The experimental studies have shown that a pulsed loop reactor can be used to successfully reduce the reaction time for the transesterification of oils and fats. In the present study, the transesterification of palm methyl ester (PME) and trimethylolpropane (TMP) to produce palm oil based TMP ester was conducted using the vacuum operated pulsed loop reactor. The reaction was catalyzed with sodium methoxide solution in methanol. The influences of five operating variables such as vacuum pressure, catalyst loading, molar ratio of high oleic PME to TMP, reaction temperature and oscillatory speed on the yield of TMP esters and unwanted fatty soap formation were examined. The optimum conditions for the reaction were found at 120 °C, 20 mbar, 3.9:1 M ratio of PME:TMP, 1.0 wt% catalyst solution and 180 rpm oscillatory speed. The product containing 95 wt% TMP triester was successfully synthesized in 1 h with 167 mg/g of fatty soap. The physicochemical properties of the TMP esters obtained using pulse reactor were comparable to characteristics of high oleic TMP esters.

1. Introduction

The research and development in the synthesis of biolubricants has escalated due to the overwhelming awareness of the environmental issues, constantly increasing mineral oil price and the strict legislations by several countries. Biodegradable synthetic ester lubricants are mostly derived from branched polyhydric alcohols polyol esters [1,2]. Among the polyols, TMP was commonly selected to produce trimethylolpropane triesters (TMPTE) due to its moderate price level and high performance [3–9].

Conventional batch reflux reactors in a laboratory scale are often used in numerous researches for the synthesis of TMPTE due to its simplicity [4,7,10–13]. Previous studies have focused on the homogeneous basic catalyst, namely sodium methoxide and the heterogeneous basic catalyst, which was calcium methoxide [12,14,15]. The studies have revealed that the mass transfer during the transesterification reaction between PME and TMP in the presence of sodium methoxide was better compared to the reaction carried out in the presence of calcium methoxide. Nonetheless, the drawback of the use of sodium methoxide catalyst was the fatty soaps formation by irreversible free fatty acids neutralization or saponification. Free fatty acids are formed as a result of the irreversible methyl esters hydrolysis. These unwanted side reactions complicate the separation and purification steps. A pulsed loop reactor or an oscillatory flow reactor offers better efficiency in mass and heat transfer with less energy requirement and high yield of product [16–19]. The hypothesis is that the reactor would be able to shorten the reaction time needed when the

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http://dx.doi.org/10.1016/j.fuel.2015.11.022
0016-2361/

reaction is carried out under low catalyst concentration. High catalyst concentration is one of the main contributors to the soap formation in the transesterification using a homogenous catalyst [12]. On the other hand, running under low catalyst concentration usually require longer time for completion. Thus due to its efficient mass and heat transfer system, it is envisaged that the pulse reactor running under vacuum would be able to speed up the reaction.

An imposed oscillatory flow of the reacting fluid is generated by a piston moving back and forth or by reciprocating pump at one end. The baffle cells basically act as a number of stirred tanks in series. A close approximation of plug flow (or a turbulent flow) can be achieved when there is enough series of baffles in the tubes of pulsed loop reactor [20,21].

The main purpose of this study was to synthesize high oleic palm oil-based TMP esters via transesterification in a pulsed loop reactor. The pulse reactor that has been designed and fabricated in-house complete with a vacuum system that removes methanol continuously from the reaction and thus accelerates the reaction further. The scope of this study covers the effects of vacuum pressure, catalyst loading, molar ratio of high oleic PME to TMP, reaction temperature and oscillatory speed on the transesterification of TMP with high oleic PME using sodium methoxide solution as catalyst. The TMP esters yields and soap contents were examined to determine the optimum operating conditions. Some properties of purified high oleic TMP esters were also analyzed and compared to the characteristics of high oleic TMP esters base stock from prior work.

2. Materials and methods

2.1. Materials

High oleic PME was obtained from Carotino Sdn. Bhd. (Malaysia). Its composition is shown in Table 1. Trimethylolpropane (>98% pure grade) and sodium methoxide solution (30% w/w in methanol) were purchased from Sigma Aldrich Sdn Bhd. (Malaysia). For gas chromatography analysis, ethyl acetate (GC grade) was purchased from Fisher Scientific Sdn. Bhd. (Malaysia), while N, O-bis (trimethylsilyl)-trifluoroacetamide (BSTFA) (98%) was acquired from Acros Organic (Belgium).

Experiments were conducted using a vacuum operated pulsed loop reactor system (ID, 0.0732 m and H, 1.3 m) as shown in Fig. 1. The pulsed loop reactor consists of a gear motor, multiple-orifice baffles plate, oscillating piston, heating jacket and reaction chamber. The reaction chamber is made of two stainless steel cylindrical columns, which is interconnected via a U-shape configuration. An overhead expansion header with integrated condenser is located between the reaction chamber and vacuum pump, which has an in-line side viewing glass. The integrated condenser consists of coil and cooling jacket for cool water to flow in and out. The motor rotational speed is between 20 rpm and 540 rpm. The crankshafts are driven by the motor and the oscillating amplitude (peak to peak) is 40 mm. The vacuum is provided by a rotary vane vacuum pump during the synthesis. The product analysis was done by using a gas chromatography (GC) system (Agilent 7820A GC, USA) equipped with a flame ionization detector (FID).

Table 1
Composition of high oleic PME.

Methyl ester	Composition (wt%)
Methyl myristate ($C_{14:0}$)	0.4
Methyl palmitate ($C_{16:0}$)	3.7
Methyl stearate ($C_{18:0}$)	3.6
Methyl oleate ($C_{18:1}$)	74.9
Methyl linoleate ($C_{18:2}$)	17.4

2.2. Experimental procedure

Five process parameters were varied to evaluate their effects on the transesterification of high oleic PME and TMP; vacuum pressure, catalyst loading, PME to TMP molar ratio, reaction temperature and oscillatory speed. A total amount of reactants and sodium methoxide catalyst was calculated based on the total volume at 2.8 L for the reaction chamber, with 1.4 L for each reaction column. This was to make sure that the vapor space is kept at 50% of the reaction columns to pressure and liquid mixture build up. A calculated amount of high oleic PME was introduced into the pulsed loop reactor. The operating temperature was set at 100 °C and at the same time, the heater was turned on. The reactor was run at oscillatory speed of 60 rpm. When the operating temperature reached at 60 °C, a determined amount of TMP was fed through upper ports of the reactor, while the speed controller was turned off. The reactor was run again at 60 rpm, with vacuum level under 20 mbar at 100 °C for 15 min to ensure the homogeneity of the reaction mixture and moisture elimination. The desired reaction temperature was set and the oscillatory speed was maintained at 60 rpm. When the liquid mixture was at the desired temperature, the speed controller was switched off. The ball valve near to the safety relief valve was kept half-open. A required amount of sodium methoxide solution was charged in immediately through the catalyst ports. The speed controller was set at the required oscillatory speed. The safety relief valve was slowly regulated at the desired vacuum level while observing the sight viewing glass to ensure that the liquid mixture did not pass half of the sight viewing glass. The reaction was carried out under the required process conditions for 1 h.

Upon completion of the reaction, the speed of the oscillating crank was reduced to 10 rpm. The vacuum pump was turned off and the ball valve near to the safety valve was fully opened. The heater was stopped by pressing the heater button. The liquid product was discharged from the loop reactor. After that, the speed controller was stopped, and water supply valve was closed. When the product temperature was less than 50 °C, the unwanted fatty soap was separated from the liquid product through a filtration by using Whitman® qualitative filter papers of 20 cm diameter and 2.5 μm pore size.

2.3. Product purification

Prior to the physicochemical properties testing, the vacuum distillation was set up according to Yunus et al. [14]. The experiments were performed in a 1 L flat bottom three-necked flask made of borosilicate glass, equipped with a PTFE coated magnetic stirrer bar, a mercury thermometer, a reflux condenser, an air leakage valve and a sampling port. The condenser was attached to a vacuum line, which included an accumulator, a vacuum trap and a rotary vane vacuum pump. The three-necked flask was immersed into the silicone oil bath, which was placed on an electrical heater for heat reservoir supply. The removal of the unreacted (excess) high oleic PME was carried out under less than 1 mbar at 170–200 °C at the mixing speed of 1000 rpm for 3–4 h. When the vacuum distillation was completed, the three-necked flask was removed from the heating oil bath for cooling down. The process should result in the clear light yellowish product, which has high content of TMPTE.

2.4. Analytical methods

Samples of reaction products were analyzed to determine the yield of TMPTE by a gas chromatography-flame ionization detector (GC-FID) through a method described in an earlier report [22]. The sample was prepared by diluting 0.01 ± 0.005 g of a sample with