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Development of a Laboratory Scale Reactor with Controlled High Pressure Sampling for Subcritical Methanolysis of Biodiesel

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Abstract: The objective of this work was to develop a laboratory scale reactor for biodiesel production from subcritical methanol transesterification. The design was based on utilizing a high pressure system from diesel engine to regulate near critical condition and sample the converted product. The reactor consisted of a 400 ml autoclave, a 2-kW electrical heating furnace, and a product sampling system. The pressure system was adapted from a diesel fuel injector. High pressure and temperature inside the reactor was built up by means of external heat source. Rapid heat transfer was provided to the reactor, accompanied with simultaneous rise in pressure so that near critical conditions (temperatures between 180-200 °C and pressure around 140-190 atm) were attained for methanol. Synthesis product can be collected real time via injection. Limited product samples from preliminary tests with palm oil and methanol at molar ratio of 46:1 were collected and analyzed by gas chromatography – mass spectrometry. Analysis results showed high percentage conversion of vegetable oil to methyl esters. Yields of over 93% biodiesel were obtained. The reactor proved to be successful for producing biodiesel.

Key words: Biodiesel, Critical fluids, Methyl esters, Palm oil, Renewable energy

INTRODUCTION

Today, biodiesel plays an important role as alternative fuel for diesel engines. Various biodiesel production methods have been reported in the literature ranging from catalytic method (Tippayawong *et al*., 2005; Marchetti *et al.*, 2007; Chongkhong *et al.,* 2009) to non-catalytic method (Diasakou *et al.*, 1998; Saka and Kusdiana, 2001; Dasari *et al.*, 2003; Kusdiana and Saka, 2004; Madras *et al.*, 2004; Bunyakiat *et al.*, 2005; Han *et al.*, 2005; He *et al.*, 2006; Mahesh *et al.*, 2007; Yin *et al.*, 2008; Balat *et al.*, 2008; Petchmala *et al.*,2008; Lim *et al.*, 2010). One of the non-catalytic methods is the use of alcohols in supercritical state, i.e. at temperature and pressure above theirs critical point. Biodiesel production from supercritical alcoholysis is considered to be relatively new. Advantage of this method is that the process is simple, short time consuming and has no wastewater involved (Saka and Kusdiana, 2001). However, this method is expensive due to high cost of the apparatus involved, and requires high energy consumption due to high temperature and high pressure conditions for the process.

Most studies on biodiesel production from alcoholysis at sub- and super-critical states were carried out in laboratory scale reactors. From literature survey shown in Table 1, two types of reactor were used; batch and continuous. Capacity of theses reactors were between 0.2 to 250 ml. They can sustain pressure and temperature around 200 atm and 300°C, respectively. While most studies did not report the reactor heating rate, two works gave a similar heating rate of 20 ^{o}C/min. The reactors used in the literature showed various designs. The simplest one was the 0.2 ml sealed glass capillary tubes (Dasari *et al*., 2003). The sophisticated one adopted the 250 ml stainless steel autoclave with magnetic stirrer, internal cooling system and valves for adding co-solvent and releasing samples (Han *et al*., 2005). All reactors utilized direct heat from external sources to create critical

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conditions. Details were shown in Table 2. Typical heat sources were derived from electric heater or furnace. Other heat sources included the electrically heated salt bath (Bunyakiat *et al*., 2005) and the hot tin bath (Saka and Kusdiana, 2001). Short times taken to reach the critical condition were reported to be around 11 to 15 min. (Han *et al*., 2005; Saka and Kusdiana, 2001). To quench the reaction, most studies used either cold water baths or condenser.

It was clearly seen that most experimental setups to investigate biodiesel production from supercritical methanol were based on hot bath and expensive high pressure equipment which may not be widely accessible. Furthermore, due to highly severe conditions required, supercritical technology is limited to practical applications. Investigation and development of milder method will be of great interest and offer new trend in biodiesel production. In this work, attempt was made to demonstrate that subcritical methanol condition may be created using a simple autoclave with high pressure facilities available cheaply from diesel engines. High pressure sampling can be regulated simply by setting controlled pressure at the injector. The aim of this work is to develop a reactor for biodiesel production from subcritical methanol synthesis which is simple to control the reaction and collect the product in real time.

MATERIALS AND METHODS

Raw Materials:

Refined palm olein (palm oil) was supplied by the Morakot Industry Co. Ltd, Thailand. It was a cooking oil grade containing 0.0075% butylated hydroxytoluene as an antioxidant. It can be found in a supermarket. Methanol used was 99.8% purified industrial grade supplied by the O. V. Chemical & Supply Co. Ltd, Thailand.

Experimental Setup:

An experimental setup for supercritical reaction test is shown in Fig. 1. The setup consists of (1) a supercritical reactor connected with (2) two seamless steel pipes of 6.25 mm in diameter, 0.45 m long with female connector ends with metal-seal fitting, (3) a hydraulic high pressure gauge, up to 700 ±5 atm pressure range, bottom mount, equipped with 70547H-51102 N981 Yanma diesel fuel injector tester as tube adaptor, and (4) a high pressure injector. The reactor is heated in (5) a fire-resistant cylindrical concrete casting furnace of 180 mm inside diameter, 55 mm wall thickness, 300 mm high, with (6) a 2-kW spiral wire coil electrical heater built in the furnace wall. The oven chamber temperature is controlled by (7) a heater controller, equipped with JCS 33A Shinka microcontroller, and (8) a type-K thermocouple (measurement range between 0-1000°C with accuracy ± 1°C). The high pressure injector will release the product into (10) 10-ml plastic containers when the pressure is over the set point of 190 atm. The pipes, the pressure gauge and the high pressure injector are modified from exiting diesel fuel injector systems.

Reactor:

The reactor is a high pressure vessel that enables near critical condition to develop inside. It must be able to withstand sustained pressure over 300 atm and temperature over 300°C. Diesel fuel injector system is a system used for feeding fuel at high pressure into the diesel engine combustion chamber. This system is available from local part suppliers at relatively low costs. From these advantages, the diesel injector system was adopted in our design. The reaction product can be collected by simply setting overpressure of the injector so that the product inside the reactor can be released, in which reaction can be quenched when the product is exposed to room environment.

The reactor was a batch reactor made of St35 seamless steel pipe, with volume capacity of 400 ml. It had two necks, shown in Fig. 2. The outside diameter and the total height were 100 and 285 mm, respectively. The inside body was a capsule-shape with 7 mm minimum wall thickness. The neck was 105 mm high, and had 13 mm outside diameter, and 4 mm wall thickness. The male connectors were made from diesel fuel injector connectors. The thermocouple holder had 10 mm internal diameter and 4 mm wall thickness, mounted on top of the reactor body. The specification of the St35 is given in Table 3. The wall thickness of the middle part was 7 mm, corresponding to the average designed working pressure of 300 atm.

High Pressure Injector:

High pressure injection is served as a means for product collection during the reaction process. As the reaction is ongoing, change of the product composition helps us to understand the reaction kinetics. In this design, the injector will release the product when the pressure inside the supercritical reactor exceeds the pre-set value.

The high pressure injector shown in Fig. 3 was modified from a diesel fuel injector (Isuzu fuel injector model 4JA1). It had a plunger which pushed against the main gate by a specific spring. When the reactor pressure is greater than the spring pressure, the needle will be lifted and the product sample is released. Because the injector was obtained from a diesel fuel injector, the return pipe was normally used as a path way for excess fuel to be returned back to the source. Pre- determined injection pressure can be set by the spring pressure. In this work, the pre-set pressure was designated at 190 atm.

Test Procedure:

To start an experimental test run, the reactor was loaded with methanol and palm oil at a given molar ratio. The reactor was then placed in the oven chamber which was initially at room temperature. The pressure gauge and the high pressure injector were installed. All connectors were fastened and the oven lid was closed. The 2 kW electrical heater was subsequently switched on. The oven and the reactor were heated from room temperature (about 25 °C) to about 300 °C. Evolution of the reactor pressure and temperature were recorded periodically with a data acquisition system. Once the pressure raised to the pre-set value, the products were sampled intermittently. Samples were collected at intervals in separated containers, and stored at ambient condition for further analysis.

Analysis:

A Hewlet Packard gas chromatograph-mass spectrometer, (GC-MS) model 5973 EI, equipped with Alltech column model AT-1MS (30 m x 0.25 mm x 0.25 μm film thickness) was used as an analyzer. Helium was used as a carrier gas at a flow rate of 1.0 ml/min. The GC-MS injector temperature was set at 250 °C. Samples were diluted in n-hexane prior to analysis. The oven temperature program started with initial temperature of 130 °C. The temperature was held at this point for 2 min, then increased to 200 °C at a heating rate of 5 °C/min, and to 250 °C at 10 °C/min. It was kept at 250 °C for further 10 min. The temperature of MS Quadrupole and MS Source were 150 and 230 °C, respectively. The total time consumed for a single analysis was about 30 min.

RESULTS AND DISCUSSION

Operating Characteristics:

For preliminary test runs of more than 70 hours in accumulated operating time, the reactor appeared to work satisfactorily well. The reactor had been operated with palm oil and methanol at various conditions for over 70 tests. All connectors were functioned properly even though they were connected and disconnected for many times. The near critical condition was achieved. For a typical run, the oven was heated for 40 min, before the oven power supply was switched off. The oven temperature was observed to reach 280 ^{o}C. Heat was transferred to the reactor where the reactor temperature was increased from room temperature (28 ^{o}C) at a constant heating rate of about 6 ^{o}C/min, reaching 200^{o}C in approximately 30 min. Fig. 4 shows evolution of temperature and pressure near critical condition. The oven and reactor temperatures were slowly dropped due to natural convection. This way, reaction temperature can be maintained at high level for a period of time. Since the autoclave was a closed system, the reactor pressure was also found to increase dramatically to 190 atm with the heating. The pressure can be maintained at the level between 175-190 atm by intermittent injection. From the observation, the subcritical methanol condition was found to be established in about 30 min. The critical values of the mixture of methanol and palm oil were calculated according to the Lorentz-Berthelot mixing rules. For a molar ratio of methanol to palm oil of 46, critical pressure (P_c) and temperature (T_c) of the mixture system were 70 atm and 280°C, respectively. It can be seen that near critical condition was available for a time window of about 15 min during which products can be collected in real time. Each ejection was observed to provide about 1.5 g of product sample. The duration between each sampling was about 1-2 min.

There were a few minor problems encountered during the operation which can be easily taken care of. The injector plunger was jammed on several occasions, leading to product loss. The injector had to be disassembled and cleaned regularly. Leakages were also detected at the welding joints between the necks and the male's connector of the reactor. These leakages were the results of the poor welding, and can be easily repaired.

Product Composition and Biodiesel Yields:

The collected samples were analyzed by GC-MS. A representative chromatogram of the analysis result is shown in Fig. 5. It was revealed that there were high concentrations of methyl esters (biodiesel) in the sample. Ten components were identified from the peaks shown in which seven of them were biodiesel (peak number 2-5 and 7-9). High peak represented high concentration of the component. Some peaks were very small, like peak

number 2, 3 and 4 shown clearly in the inset. The concentration of each component was estimated by means of the area method. The result is shown in Table 4. Methyl palmitate and methyl oleate were the two main ingredients, totaling over 77% of palm oil methyl esters. The biodiesel yield, defined as the mass ratio of the methyl esters in the product and the theoretically calculated methyl esters from the starting material, of over 93 % was obtained from non-catalytic, subcritical methanol transesterification.

Table 1: Literature survey on sub- and super-critical biodiesel reactor design

Reference	Type	Volume	Pressure	Temperature	Heating rate	Reactor design
Cheng *et al.* (2008)	Batch	100 ml	100-160 atm	250-310 ºC	-	Autoclave, 500 rpm stirrer
Yin *et al.* (2008)	Batch	250 ml	320 atm	260-350 ºC	-	Stainless steel autoclave, 300 rpm stirrer with internal cooling
Petchmala *et al.* (2008)	Batch	9 ml	-	250-300 ºC	-	Stainless steel autoclave, no stirrer
Mahesh *et al.* (2007)	Batch	11 ml	200 atm	200-350 ºC	-	Stainless steel autoclave
He *et al.* (2007)	Continuous	75 ml	100-400 atm	240-340 ºC	-	Tubular reactor with preheater and high pressure pump feeding
He *et al.* (2007)	Continuous	200 ml	87-360 atm	210-280 ºC	-	Continuous stirred tank reactor
Bunyakiat *et al.* (2005)	Continuous	90 ml	100-190 atm	270- 350 ºC	-	Tubular reactor with preheater and high pressure pump feeding
Han *et al.* (2005)	Batch	250 ml	30-230 atm	240-330 ºC	20 ºC/min	Stainless steel autoclave, magnetic stirrer, internal cooling
Madras *et al.* (2004)	Batch	8 ml	200 atm	200-400 ºC	-	Stainless steel autoclave
Dasari *et al.* (2003)	Batch	0.2 ml	-	120-180 ºC	-	Sealed glass capillary tubes
Demirbas *et al.* (2002)	Batch	100 ml	-	177-250 ºC	-	Stainless steel autoclave
Saka and Kusdiana (2001)	Batch	5 ml	450-650 atm	350-400 ºC	20 ºC/min	Inconel-625 vessel

Table 2: Literature survey on heating and quenching for sub- and super-critical biodiesel production

Reference	Heating method	Quenching method
Cheng *et al.* (2008)	Direct heat from unknown heat source	Immersed the reactor in cold water bath
Yin *et al.* (2008)	Direct heat from external heater	Immersed the reactor in ice water bath
Petchmala *et al.* (2008)	Direct heat from external heater	Immersed the reactor in cold water bath
Mahesh *et al.* (2007)	Direct heat from furnace	Immersed the reactor in cold water bath
He *et al.* (2007)	Preheat separately in hot oil bath, then stirred blender into reactor	Passed the product through condenser
He *et al.* (2007)	Preheat separately in heating coils, then fed into reactor	Passed the product through condenser coil
Bunyakiat *et al.* (2005)	Electrical heated salt bath with high pressure pump	Passed the product through condenser coil
Han *et al.* (2005)	Direct heat from external heater, reaching critical condition in 13-15 min	Immersed the reactor in ice water bath
Madras *et al.* (2004)	Direct heat from furnace	-
Dasari *et al.* (2003)	Direct heat from furnace	Left the reactor to cool at room condition
Demirbas *et al.* (2002)	Direct heat from external heater	Passed the product through condenser
Saka and Kusdiana (2001)	Heat in 400°C tin bath, reaching critical condition in 11 min	Immersed the reactor in cold water bath

Table 3: Specification of St 35 seamless steel pipe used for constructing the reactor

% carbon:	0.18
Ultimate strength:	340-440 MPa
Tensile strength:	235 MPa
Equivalent material:	ASTM A53-S

Table 4: The percent peak area of each ingredient corresponding with the peak size

Peak number	Component	Biodiesel	Percentage of peak area
1	Methanol	No	5.01
2	Methyl laurate	Yes	0.33
3	Methyl myristate	Yes	0.79
4	Methyl palmitooleate	Yes	0.16
5	Methyl palmitate	Yes	36.27
6	Palmitic acid	No	1.17
7	Methyl linoleate	Yes	9.63
8	Methyl oleate	Yes	41.12
9	Methyl stearate	Yes	4.84
10	Oleic acid	No	0.65
	Total peak area of biodiesel		93.14

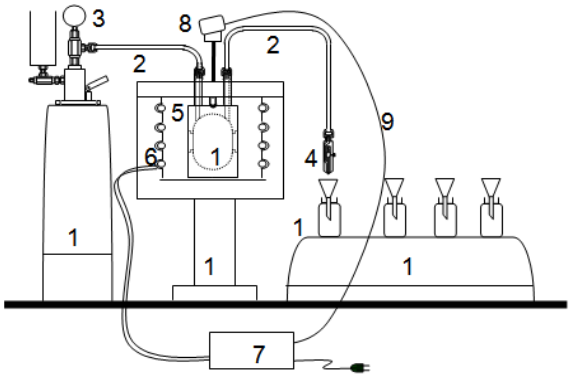

Fig. 1: Experimental setup; (1) reactor, (2) pipes, (3) pressure gauge, (4) high pressure injector, (5) oven chamber, (6) electrical heater, (7) temperature controller, (8) thermocouple, (9) signal cable, (10) containers, (11) stand.

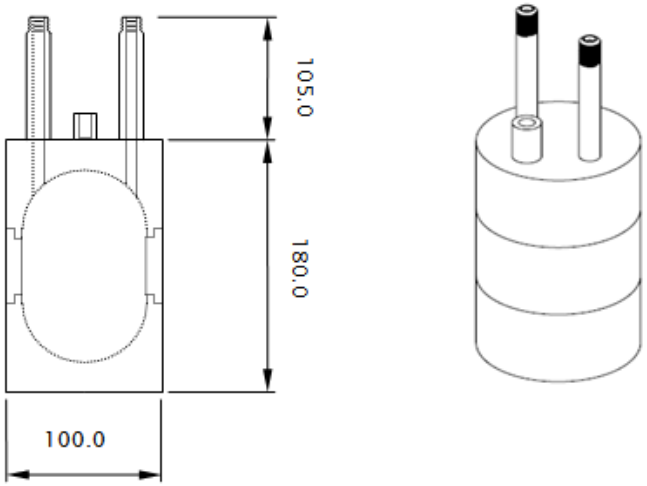

Fig. 2: Batch reactor.

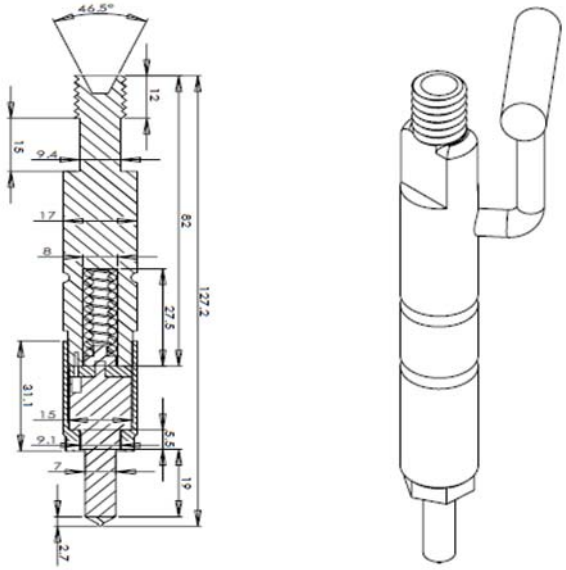

Fig. 3: High pressure fuel injector.

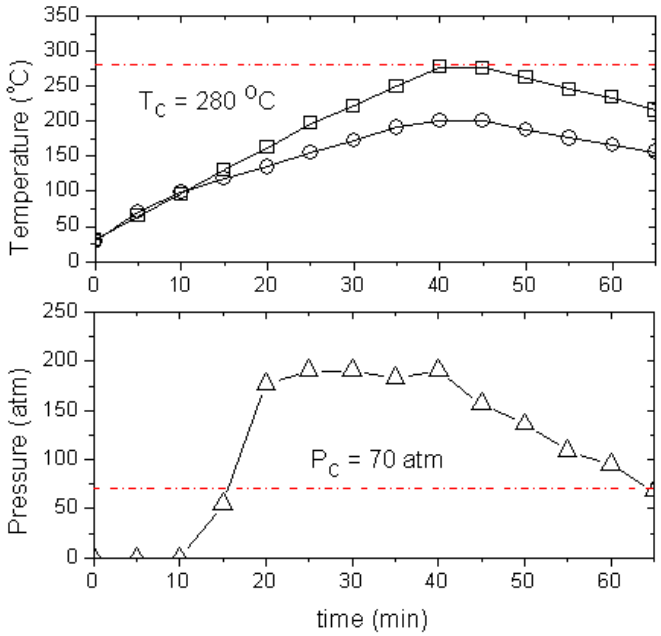

Fig. 4: Evolution of temperature and pressure during typical experimental runs; □ = oven temperature, ○ = reactor temperature, Δ = reactor pressure, red lines = critical values.

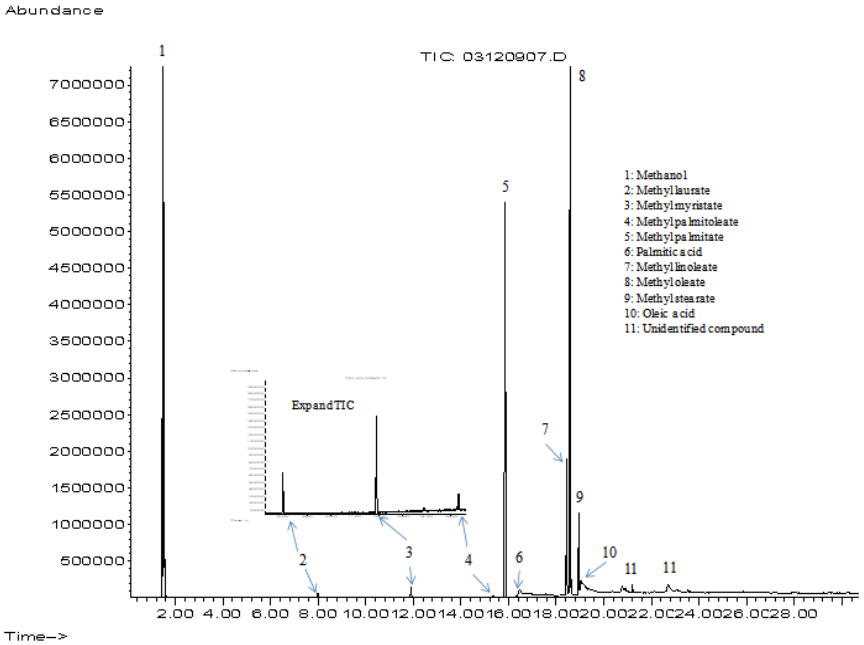

Fig. 5: Chromatogram of the representative product samples.

Conclusion:

In this work, a laboratory scale reactor for subcritical methanol condition has been developed. A diesel fuel injector was utilized as a product sampling system. Operating characteristics have been evaluated. Test runs for biodiesel production have been carried out. Evolutions of pressure and temperature were measured. The reactor was found to operate well with a few minor problems such as jamming of the injector plunger and leakage due to poor welding. Near critical methanol condition was found to be established in relatively short time. High conversion of palm oil to biodiesel was observed. Methyl esters found in the sample indicated that the present setup can be used successfully to produce biodiesel from subcritical methanol synthesis.

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