Appendices

Appendix A Calculation of Molar Ratio

In chemistry, the measuring of substance is the mole basis.

- Molar Ratio of Methanol-to-oil

Methanol 64 ml equals 50.56 g (64 ml x 0.79 g/ml =50.56), equals 1.58 mole (50.56/32 = 1.58). Palm oil 36 ml equals 31.32 g (36 ml x 0.87 g/ml = 31.32 g), equals 0.0368 mole. Therefore, the molar ratio of methanol-to-oil is 42.9:1 (1.58/0.0368=42.9) or 43:1.

- Molar Ratio of Ethanol-to-oil

Ethanol 18 ml equals 14.2 g (18 ml x 0.79 g/ml = 14.2 g), equals 0.31 mole (14.2/46 = 0.309). Palm oil 50 ml equals 43.5 g (50 ml x 0.87 g/ml = 43.5 g), equals 0.05 mole (43.5/851.3 = 0.051). Therefore, the molar ratio of ethanol-to-oil is 6.06:1 (0.309/0.051 = 6.06), or 6:1.

Appendix B Calculation of the Fraction of Methyl Esters

The fraction of the methyl esters (x) is calculated from the summation of the four major methyl esters that are the main constituents of palm oil. They are methyl palmitate, methyl oleate, methyl linoleate and methyl stearate. Each methyl ester faction was quantiflied by GC-MS and its amount based on peak area via percent area normalization method.

$$x = (\%MTP + \%MTO + \%MTL + \%MTS)/100$$

where

%MTP is percent peak area of methyl palmitate,

%MTO is percent peak area of methyl oleate,

% MTL is percent peak area of methyl linoleate,

%MTS is percent peak area of methyl stearate.

It is assumed that the rate of increasing of methyl esters concentration is proportion of the rate of increasing of x as following equation,

$$\frac{dC_{ME}}{dt} = k_p \frac{dx}{dt}$$

where k_p is a proportionality constant.

To find the x, we have to look at the GC analysis data of kinetics experiments (Table B1). For example, the first sample collected from Test 1, ejected at 23 min. The sample had two phases (upper phase and lower phase) after standing for couple hours. Each phase was analyzed separately by GC-MS. The results showed that the upper phase has total percent peak area of four major methyl esters = 10.9, (4.4 + 5.2 + 1.2 + 0.0 = 10.9). And the lower phase had that = 28.7, (11.2+13.3+2.6+1.6=28.7). It was observed that mass ratio between upper phase and lower phase was around 0.95 : 0.05. Therefore, total percentage of the methyl esters in this product was 11.79, (0.95x10.9 + 0.05x28.7= 11.79). Therefore, x = 11.79/100 = 0.1179. The results of calculation of x were presented in Table B3.

Table B1 GC analysis data of kinetics experiment (Test 1)

Test 1	Colck time	Bottle	GC code	Time (min)	methanol (%peak area)	%methyl ester (based on peak area)			
						methyl palmitate	methyl oleate	methyl linoleate	methyl stearate
upper phase	11.10	101	B1	23	68.5	4.4	5.2	1.2	N.D.
	11.11	102	B2	24	91.1	3.2	3.7	0.8	0.4
	11.12	103	B3	25	90.7	2.9	3.2	0.7	0.3
	11.13	104	B4	26	89.6	3.2	3.5	0.8	0.4
	11.14	105	B5	27	88.3	3.8	4.2	1.0	0.4
	11.16	106	B6	29	84.0	5.6	6.0	1.3	0.6
	11.18	107	B7	31	80.6	7.5	8.0	2.0	0.8
	11.20	108	B8	33	72.2	10.8	11.8	2.8	1.1
	11.22	109	B9	35	60.9	15.0	16.2	4.1	1.6
	11.24	1010	B10	37	46.2	20.6	23.1	5.9	2.3
	11.26	1011	C1	39	24.8	26.1	30.2	7.9	3.0
	11.30	1012	C2	43	17.3	30.1	38.0	9.5	3.9
lower phase	11.10	101	BO1	23	70.3	11.2	13.3	2.6	1.6
	11.11	102	BO2	24	86.4	3.9	4.7	1.1	0.5
	11.12	103	BO3	25	27.8	26.5	28.7	5.4	4.2
	11.13	104	BO4	26	33.2	26.6	28.7	5.3	4.3
	11.14	105	BO5	27	44.1	20.2	21.6	4.0	2.9
	11.16	106	BO6	29	3.6	3.6	3.7	0.6	N.D.
	11.18	107	BO7	31	20.4	31.6	32.4	6.4	4.5
	11.20	108	BO8	33	13.6	35.0	35.3	7.1	4.8
	11.22	109	BO9	35	18.1	32.4	33.2	6.6	4.4
	11.24	1010	BO10	37	9.2	36.9	38.7	8.1	5.3
	11.26	1011	CO1	39	5.7	37.6	40.9	8.9	5.4
	11.30	1012	CO2	43	5.0	36.3	41.1	9.6	4.9

N.D. = Not detected (its value is below the limit of detection)

Table B2 GC analysis data of kinetics experiment (Test 2)

Test 2	Clock time	Bottle	GC code	Time (min)	methanol (%peak area)	%methyl ester (based on peak area)			
						methyl palmitate	methyl oleate	methyl linoleate	methyl stearate
upper phase	13.36	1014	A6	23	83.4	7.0	7.1	1.5	0.6
	13.37	1015	A7	24	89.1	4.3	4.5	1.0	0.5
	13.39	1016	A8	26	88.9	4.5	5.1	1.1	0.4
	13.41	1017	A9	28	86.3	5.6	6.2	1.3	0.6
	13.43	1018	A10	30	81.6	7.6	8.2	1.8	0.7
	13.45	1019	C3	32	73.2	11.1	11.6	2.6	1.1
	13.47	1020	C4	34	62.4	15.6	16.3	3.7	1.5
	13.49	1021	C5	36	53.6	19.1	20.1	4.6	1.9
	13.51	1022	C6	38	35.3	25.9	28.4	6.7	2.7
	13.53	1023	C7	40	21.1	31.1	34.8	8.5	3.4
lower phase	13.36	1014	A06	23	16.6	17.1	19.0	3.5	29.4
	13.37	1015	A07	24	43.2	18.3	20.9	4.3	6.8
	13.39	1016	A08	26	1.6	1.6	1.6	0.3	51.8
	13.41	1017	A09	28	N.D.	35.0	37.6	7.4	10.8
	13.43	1018	A010	30	4.8	35.2	37.0	7.3	8.7
	13.45	1019	C03	32	27.7	26.7	27.7	5.5	6.6
	13.47	1020	C04	34	20.1	31.4	32.5	6.4	6.0
	13.49	1021	C05	36	12.0	35.5	36.7	7.4	6.1
	13.51	1022	C06	38	4.6	38.7	41.4	8.6	6.1
	13.53	1023	C07	40	3.8	38.2	42.1	9.2	5.8

N.D. = Not detected (its value is below the limit of detection)

Table B3 Results of the Fraction of Methyl Exters (x)

	time (min)	% methyl esters in upper phase (%ME$_U$)	0.95(%ME$_U$)	% methyl ester in lower phase (%ME$_L$)	0.05(%ME$_L$)	% methyl ester (%TME= 0.95%ME$_U$+ 0.05%ME$_L$)	fraction of methyl esters (x= %TME/100)
Test 1	23	10.9	10.3	28.7	1.4	11.7	0.117
	24	8.1	7.7	10.2	0.5	8.2	0.082
	25	7.1	6.7	64.7	3.2	10.0	0.100
	26	7.9	7.5	64.9	3.2	10.7	0.107
	27	9.4	8.9	48.7	2.4	11.4	0.114
	29	13.6	12.9	8.0	0.4	13.3	0.133
	31	18.2	17.3	74.9	3.7	21.1	0.211
	33	26.5	25.2	82.1	4.1	29.3	0.293
	35	36.9	35.1	76.6	3.8	38.9	0.389
	37	52.0	49.4	88.9	4.4	53.8	0.538
	39	67.1	63.7	92.8	4.6	68.4	0.684
	43	81.5	77.5	91.9	4.6	82.0	0.820
Test 2	23	16.1	15.3	69.0	3.5	18.7	0.187
	24	10.3	9.8	50.2	2.5	12.3	0.123
	26	11.0	10.5	55.4	2.8	13.2	0.132
	28	13.6	12.9	90.8	4.5	17.5	0.175
	30	18.3	17.4	88.2	4.4	21.8	0.218
	32	26.3	25.0	66.5	3.3	28.3	0.283
	34	37.0	35.1	76.4	3.8	38.9	0.389
	36	45.7	43.4	85.7	4.3	47.7	0.477
	38	63.7	60.6	94.7	4.7	65.3	0.653
	40	77.7	73.8	95.3	4.8	78.6	0.786

Appendix C Calculation of the Activation Energy

- Using Dasari data

The activation energy was estimated at 136.2 kJ/mol using data found in a literature of Dasari et al. (2003). Calculation details were described step by step as follows:

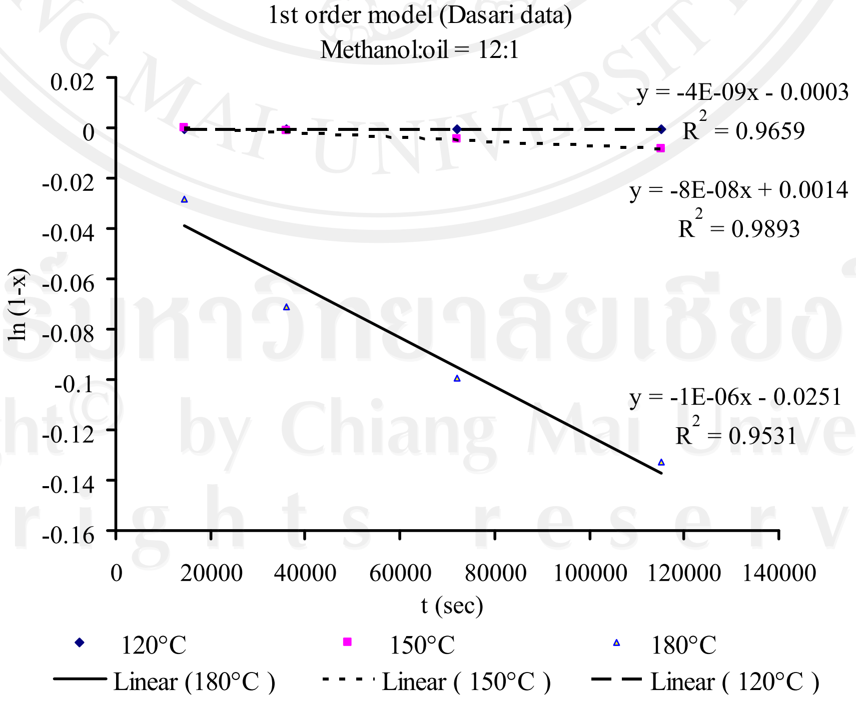
1) From the experimental data which carried out by Dasari et al.and employing soybean oil in methanol in combination 0.2 ml glass capillary tubes. Yield of methyl ester (% weight) was reported at various conditions as shown below.

Temperature (Molar ratio)	Time (h)	yield of methyl ester (%weight)
120°C (Methanol:oil=12:1)	4	0.03
	10	0.04
	20	0.06
	32	0.07
150°C (Methanol:oil=12:1)	4	0.02
	10	0.12
	20	0.44
	32	0.85
180°C (Methanol:oil=12:1)	4	2.82
	10	6.87
	20	9.47
	32	12.41

2) Switch the time unit from hour into min. and the yield of methyl ester from percent weight into x, where x is fraction of the methyl ester. Assumed the reaction rate to be a first order and then find numerical value of ln (1-x) as shown in Table below.

Temperature (Molar ratio)	t (sec)	x	ln (1-x)
120°C (Methanol:oil=12:1)	14400	0.0003	-0.0003
	36000	0.0004	-0.0004
	72000	0.0006	-0.0006
	115200	0.0007	-0.0007
150°C (Methanol:oil=12:1)	14400	0.0002	-0.0002
	36000	0.0012	-0.0012
	72000	0.0044	-0.00441
	115200	0.0085	-0.00854
180°C (Methanol:oil=12:1)	14400	0.0282	-0.02861
	36000	0.0687	-0.07117
	72000	0.0947	-0.09949
	115200	0.1241	-0.1325

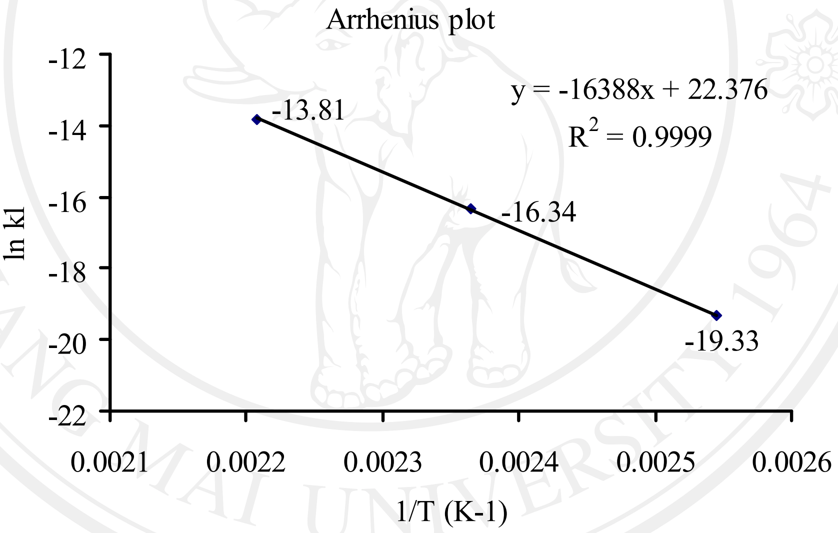
3) Draw a graph of ln (1-x) against t for each temperature, three lines were made. Gradient of each line was estimated using a function in the excel program called "add trendline".



4) Make a table of ln k1 and 1/T, where k1 is the gradient of each line from the above graph at the corresponding temperatures.

k1 (sec^{-1})	Temperature (°C)	ln k1	1/T (K^{-1})
4.0E-09	120	-19.33	0.002545
8.0E-08	150	-16.34	0.002364
1.0E-06	180	-13.81	0.002208

5) Make an Arrhenius plot of ln k1 and 1/T, where T is absolute temperature (Kelvin).



6) From the Arrhenius plot, the activation energy (Ea) was estimated at 136.2 kJ/mol (16388x8.314 J/mol =136249.83 J/mol= 136.2 kJ/mol)

7) Pre-exponential factor (k_0) = exp 22.376 = 5.22×10^9.

Details of the calculation using data from other literature are shown in Table C1.

Table C1 Details of the calculation using data from other literature

Ref.	T, °C	T,K	1/T, (K-1)	k1	ln k1	Ea/R	ln k1= -(Ea/R)(1/T) + ln k0	Ea, kJ/mol	ln k0	k0
He et.al.(2007):Soybean oil 240-280°C	280	553	0.0018	8.8E-04	-7.0	6724.5	y = -6724.5x + 5.1405	55.9	5.1405	1.7E+02
	270	543	0.0018	7.8E-04	-7.2					
	260	533	0.0019	5.3E-04	-7.6					
	250	523	0.0019	4.2E-04	-7.8					
	240	513	0.0019	3.7E-04	-7.9					
He et.al.(2007):Soybeen 210-230°C	230	503	0.0020	1.3E-04	-8.9	1349.9	y = -1349.9x - 6.2441	11.2	6.2441	5.1E+02
	220	493	0.0020	1.3E-04	-9.0					
	210	483	0.0021	1.2E-04	-9.0					
Kusdiana and Saka (2004):Rapeseed oil 200-270°C	200	473	0.0021	2.0E-04	-8.5	4628.3	y = -4628.3x + 1.2055	38.5	1.2055	3.3E+00
	230	503	0.0020	3.0E-04	-8.1					
	270	543	0.0018	7.0E-04	-7.3					
Kusdiana and Saka (2004):Rapeseed oil 300-487°C	300	573	0.0017	7.1E-03	-4.9	5664.3	y = -5664.3x + 4.9807	47.1	4.9807	1.5E+02
	350	623	0.0016	1.8E-02	-4.0					
	385	658	0.0015	2.5E-02	-3.7					
	431	704	0.0014	5.0E-02	-3.0					
	487	760	0.0013	8.0E-02	-2.5					
Cheng et.al.(2008):Penut oil 250-310°C	250	523	0.0019	2.3E-04	-8.4	3439.7	y = -3439.7x + 2.4677	28.6	2.4677	1.2E+01
	265	538	0.0019	3.9E-04	-7.8					
	280	553	0.0018	4.3E-04	-7.7					
	310	583	0.0017	4.9E-04	-7.6					
Joelianingsih et.al.(2008): Palm oil 250-290°C	250	523	0.0019	3.4E-03	-5.7	3699.7	y = -3699.7x + 1.4371	30.8	1.4371	4.2E+00
	270	543	0.0018	5.1E-03	-5.3					
	290	563	0.0018	5.6E-03	-5.2					
Dasair et.al (2003):Soybean oil,120-180°C, MeOH:Oil=3:1	120	393	0.0025	6.7E-09	-18.8	14814	y = -14814x + 18.646	123.2	18.646	1.3E+08
	150	423	0.0024	6.7E-08	-16.5					
	180	453	0.0022	1.0E-06	-13.8					
Dasair et.al (2003):Soybean oil,120-180°C, MeOH:Oil=6:1	120	393	0.0025	1.3E-08	-18.1	12615	y = -12615x + 17.63	104.9	17.63	4.5E+07
	150	423	0.0024	3.3E-08	-17.2					
	180	453	0.0022	1.0E-06	-13.8					
Dasair et.al (2003):Soybean oil,120-180°C, MeOH:Oil=12:1	120	393	0.0025	3.3E-09	-19.5	16387	y = -16388x + 22.375	136.2	22.376	5.2E+09
	150	423	0.0024	8.3E-08	-16.3					
	180	453	0.0022	1.0E-06	-13.8					

Appendix D Photograph of the Equipment

The Experimental Set up

The High Pressure Vessel Placed Inside the Oven

The High Pressure Vessel

Appendix E Photograph of the Biodiesel Product

Biodiesel Product from the Temperature Survey Test, From Left:
1)150°C,55min; 2)300°C, 10min; 3) 300°C,35min; 4) 350°C,35min; 5) 400°C,35min.

Picture explanation

1) Two phases were clearly shown after standing still for five min. The upper phase was cloudy brownish thick liquid and the lower phase was clear thinner liquid.
2) Mixture of yellowish thick liquid with many tiny white solid waxes was shown.
3) Two phases shown after standing for four days. The upper phase was clear yellowish thin liquid and the lower one was brownish thicker liquid
4) Homogeneous, dark brownish thin liquid was obtained.
5) Homogeneous, very dark brownish (almost back) thin liquid was obtained.

Appendix F List of Publication

1. Permsuwan, A., N. Tippayawong, T. Kiatsiriroat, C. Thararux and S. Wangkarn, 2011. Development of a Laboratory Scale Reactor with Controlled High Pressure Sampling for Subcritical Methanolysis of Biodiesel, *Australian Journal of Basic and Applied Sciences*, 5 (5): 214-220

2. Permsuwan, A.,C. Thararux and T. Kiatsiriroat, Experimental study on non-catalytic biodiesel production from palm oil methanolysis under high pressure, Pure and Applied Chemistry International Conference, Sustainable Development in Chemistry Based on Indigeneous Knowledge (PACCON2009), 14-16 Jan 2009, Naresuan University, Phitsanulok, Thailand

3. Permsuwan, A.,C. Thararux and T. Kiatsiriroat, Experimental study on non-catalytic biodiesel production from palm oil and ethanol under pressurized carbon dioxide, Commemorative International Conference of the Occasion of the 4th Cycle Anniversary of KMUTT, Sustainable Development to Save the Earth: Technologies and Strategies Vision 2050: (SDSE2008), 11-13 December 2008, Bangkok, Thailand

CURRICULUM VITAE

Name Mr. Anusan Permsuwan
Date of Birth 28 September 1968

Academic Background

- Primary school certificate from Norrabut Sugksa School, Tapanhin, Pichit, 1980.
- High school certificate from Bunyawat Wittayalai School, Lampang, 1986.
- B.Eng. (Mechanical) degree holder from Chiang Mai University, 1990.
- M.Phil.(The use of Vegetable Oils as Internal Combustion Engine Lubricants) degree holder from De Montfort University, Leicester, UK, 1997.

Australian Journal of Basic and Applied Sciences, 5(5): 214-220, 2011
ISSN 1991-8178

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

[1]Anusan Permsuwan, [1]Nakorn Tippayawong, [1]Tanongkiat Kiatsiriroat,
[2]Churat Thararux and [3]Sunanta Wangkarn

[1]Department of Mechanical Engineering, Faculty of Engineering, Chiang Mai University, Chiang Mai, 50200, Thailand
[2]Department of Mechanical Engineering, Faculty of Engineering, Rajamangkala University of Technology Lanna, Chiang Mai, 50300, Thailand
[3]Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, 50200, Thailand

---

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 ºC/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

---

Corresponding Author: Anusan Permsuwan, Department of Mechanical Engineering, Faculty of Engineering, Chiang Mai University, Chiang Mai, 50200, Thailand
Tel.: +66 5394 4144 ext 953, fax: +66 5394 4145,
E-mail: enmei017@chiangmai.ac.th

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 ºC. Heat was transferred to the reactor where the reactor temperature was increased from room temperature (28 ºC) at a constant heating rate of about 6 ºC/min, reaching 200ºC 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

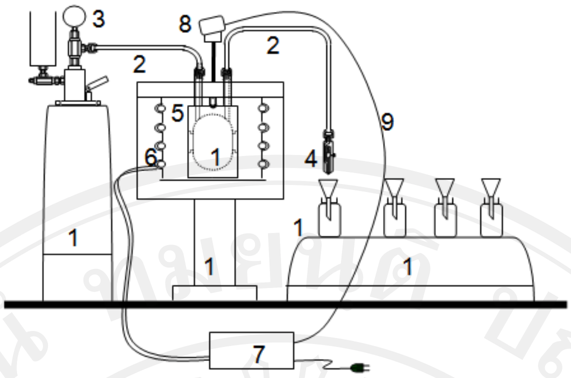


Fig. 1: Experimental setup; (1) reactor, (2) pipes, (3) pressure gauge, (4) high pressure injector, (5) oven chamber, (6) electrical heater, (7) temperature controller, (8) thermocouple, (9) signal cable, (10) containers, (11) stand.

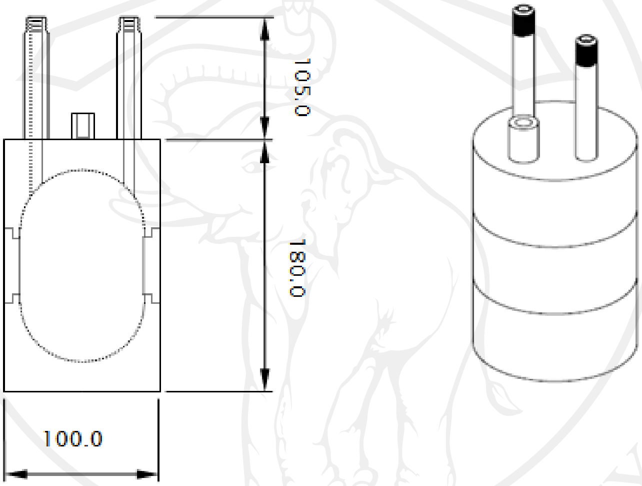


Fig. 2: Batch reactor.

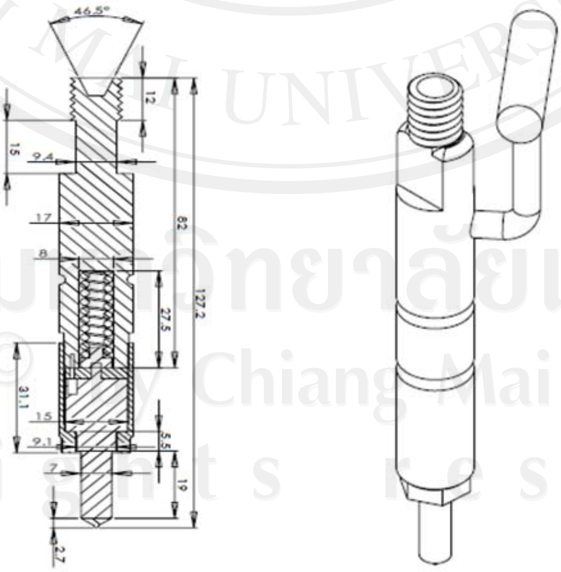


Fig. 3: High pressure fuel injector.

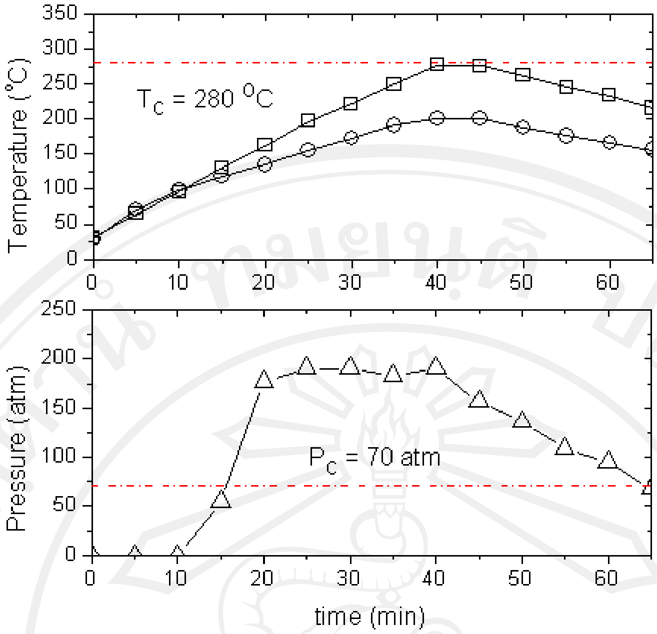


Fig. 4: Evolution of temperature and pressure during typical experimental runs; ☐ = oven temperature, ○ = reactor temperature, Δ = reactor pressure, red lines = critical values.

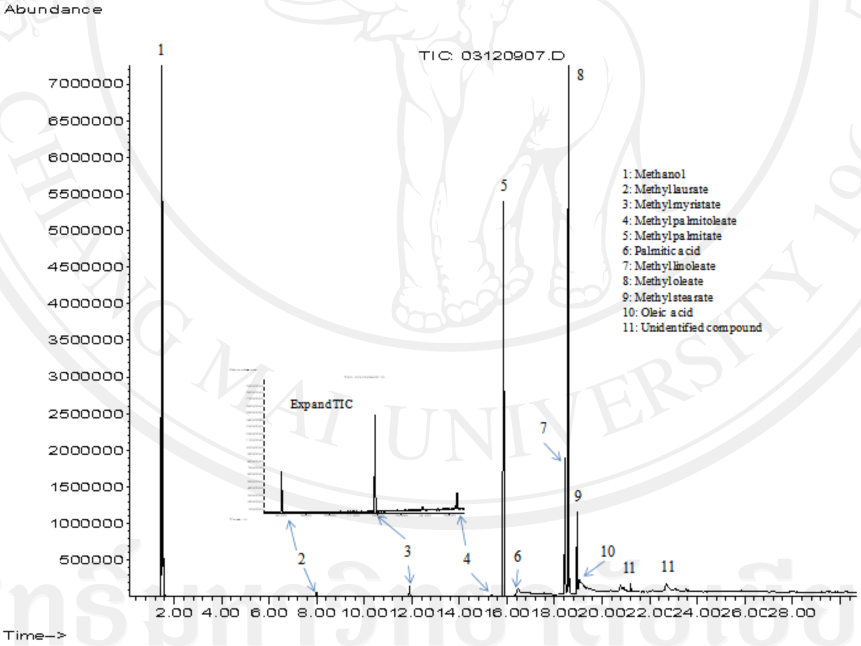


Fig. 5: Chromatogram of the representative product samples.

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.

ACKNOWLEDGEMENT

Financial support from the Faculty of Engineering, Chiang Mai University, is highly appreciated. The authors also wish to thank Mr. Danupon Jippman and Mr. Anupong Khothathum for technical assistance.

REFERENCES

Balat, M., 2008. Biodiesel Fuel Production from Vegetable Oils via Supercritical Ethanol Transesterification. Energy Sources Part A, 30: 429-440.

Bunyakiat, K., S. Makmee, R. Sawangkeaw and S. Ngamprasertsith, 2006. Continuous Production of Biodiesel via Transesterification from Vegetable Oils in Supercritical Methanol. Energy & Fuels, 20: 812-817.

Chongkhong, S., C. Tongurai and P. Chetpattananondh, 2009. Continuous Esterification for Biodiesel Production from Palm Fatty Acid Distillate using Economical Process. Renewable Energy, 34: 1059-1063.

Dasari, M.A., M. J. Goff and G. J. Suppes, 2003. Noncatalytic Alcoholysis Kinetics of Soybean Oil. Journal of the American Oil Chemists' Society, 80: 189-192.

Diasakou, M., A. Louloudi and N. Papayannakos, 1998. Kinetics of the Non-catalytic Transesterification of Soybean Oil. *Fuel*, 77: 1297-1302.

Han, H., W. Cao and J. Zhang, 2005. Preparation of Biodiesel from Soybean Oil using Supercritical Methanol and CO_2 as Co-solvent. Process Biochemistry, 40: 3148-3151.

He, H., T. Wang and S. Zhu, 2007. Continuous Production of Biodiesel Fuel from Vegetable Oil using Supercritical Methanol Process. Fuel, 86: 442-447.

Kusdiana, D. and S. Saka, 2004. Effects of Water on Biodiesel Fuel Production by Supercritical Methanol Treatment. Bioresource Technology, 91: 289-295.

Madras, G., C. Kolluru and R. Kumar, 2004. Synthesis of Biodiesel in Supercritical Fluids. Fuel, 83: 2029-2033.

Marchetti, J.M., V.U. Miguel and A.F. Errazu, 2007. Heterogeneous Esterification of Oil with High Amount of Free Fatty Acids. Fuel, 86: 906-910.

Petchmala, A., D. Yujaroen, A. Shotipruk, M. Goto and M. Sasaki, 2008. Production of Methyl Esters from Palm Fatty Acids in Supercritical Methanol. Chiang Mai Journal of Science, 35: 23-28.

Saka, S. and D. Kusdiana, 2001. Biodiesel Fuel from Rapeseed Oil as Prepared in Supercritical Methanol. Fuel, 80: 225-231.

Tippayawong, N., E. Kongjareon and W. Jompakdee, 2005. Ethanolysis of Soybean Oil into Biodiesel: Process Optimization via Central Composite Design. Journal of Mechanical Science & Technology, 19: 1902-1909.

Varma, M. N. and G. Madras, 2007. Synthesis of Biodiesel from Castor Oil and Linseed Oil in Supercritical Fluids. Industrial & Engineering Chemistry Research, 46: 1-6.

Yin, J.Z., M. Xiao and J.B. Song, 2008. Biodiesel from Soybean Oil in Supercritical Methanol with Co-solvent. Energy Conversion & Management, 49: 908-912.

Experimental study on non-catalytic biodiesel production from palm oil methanolysis under high pressure

Anusan Permsuwan [1*], Churat Thararux [2], Tanongkiat Kiatsiriroat[1]

[1] Department of Mechanical Engineering, Faculty of Engineering Chiangmai University, Thailand
[2] Department of Mechanical Engineering, Faculty of Engineering, Rajamangkala University of Technology Lanna, Chiangmai, Thailand

[*] Corresponding Author E-Mail Address : enmei017@chiangmai.ac.th

Abstract: The aim of this study is to investigate whether palm oil methanolysis can be carried out using a non-catalytic method. Refined palm oil and methanol were used as input materials. Two methanol-to-oil molar ratios, 12:1 and 24:1, were tested in a 400 ml batch-type high pressure reactor installed in an electrical oven. The oven was programmed to heat the reactor from room temperature up to 300 °C in 15 minutes, then dwelled in this temperature for another 15 minutes, and cooled down to room temperature naturally. Samples were periodically released from the reactor when the reactor pressure reached the set point (200 bar). It was found that, each sample was yellow-brown emulsion. Two phases were shown after standing for a couple hours. The lower phase, about 5% in volume, was a clear dark brown thick liquid and the upper one was a clear pale yellow thin liquid. Thin-layer chromatography (TLC) analysis results showed that the upper phase liquid contained some biodiesel.

Introduction

Biodiesel is defined as mono alkyl ester of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat [1]. Biodiesel can be produced either by catalytic or non-catalytic method. In the catalytic method, small amount of a catalyst is included causing the reaction to perform at a milder condition, such as at the atmospheric pressure with a low temperature. Although this method is easy to perform, some problems still presenting, such as difficulty of catalyst removal from final product and reaction obstructed by free fatty acid in the feedstock [2]. The non-catalytic method eliminates the mentioned problems. However, it needs a severe operating condition; temperature and pressure must be above the critical point. At such condition, alcohol becomes supercritical fluid. Saka and Kusdiana [3] succeeded in making biodiesel (methyl esters) from rapeseed oil in 4 minutes using non-catalytic method at the temperature of 350°C and pressure of 190 bar, with molar ratio of methanol-to-oil at 42:1. Bunyakiat and et al. [4] reported theirs experiment on palm kernel oil with the same condition as Saka and Kusdiana. They found that palm kernel oil was converted to methyl esters in 7 minutes using a continuous reactor system. Another experiment, carried out by Han [5], employed carbon dioxide (CO_2) as a co-solvent in non-catalytic biodiesel production from . Han believed that the co-solvent can lower the supercritical point of alcohol and methanolysis can develop at a milder condition. Although Han idea is interesting, sophisticated equipment is required.

In this paper, experimental study on non-catalytic biodiesel production from palm oil methanolysis under pressure of 200 bar without co-solvent was carried out. The results were presented in terms of: 1) pressure variation during the process, 2) product analysis

Materials and Methods

The palm oil used in this work was refined palm olein. It was cooking oil contained 0.0075% butylated hydroxytoluene (BHT) as an antioxidant, supplied by Morakot Industry Co.Ltd. The methanol was 99.8% purified industrial grade which supplied by O.V. Chemical & Supply Co.Ltd. The methanolysis reaction was performed in a batch-type high pressure reactor, with 400 ml vessel capacity and 400 bar maximum working pressure as shown in Fig.1.

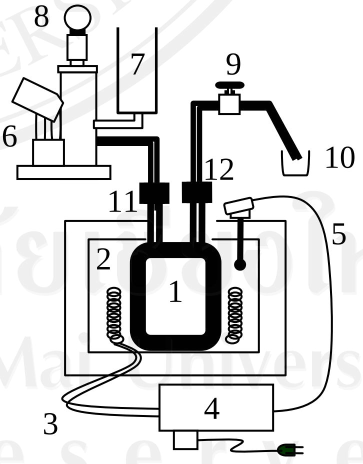


Figure 1. Schematic diagram of the batch-type high pressure reactor. 1.Vessel, 2.oven, 3.electrical heater, 4.heater-controller, 5.thermocouple, 6.pump, 7.feedstock container, 8.pressure gauge, 9.outlet valve, 10.sample container, 11.inlet connector, 12.outlet connector.

Two tests were carried out; Test 1 and Test 2. Each test used different composition of raw materials. They were 1:1 and 1:2 methanol-to-oil volume ratios. These volume ratios, after converted to molar ratios, became 24:1 and 12:1, respectively, as shown in Table 1. Properties using in the conversions are in Table 2. Volume, mass and mole equivalent of each material are in Table 3.

Table 1. Tests Details

	Test 1	Test 2
	methanol:oil	methanol:oil
volume ratio	1:1	1:2
molar ratio	24:1	12:1

Table 2. Properties using in conversions

	Methanol	Palm Oil
Density (g/ml)	0.8	0.9
Molecular Mass (g/mole)	32.0	851.3 [6]

Table 3 Volume, mass and mole equivalent

	Test 1	Test 2
	methanol:oil	methanol:oil
volume	200ml:200ml	133ml: 267ml
mass	160g : 180g	106g : 240.3g
mole	5mole:0.21mole	3.3mole:0.28mole

To run a test, the inlet and outlet connectors (11,12) were disconnected. The vessel (1) was removed from the oven and cleaned with an appropriate solvent, the methanol. After cleaning, the vessel then filled with the raw materials (palm oil and methanol). The amount of each material was determined by the volume basis as stated in Table 3. For example, Test 1 used 200 ml methanol and 200 ml palm oil. The vessel then was placed into the oven and the two connectors (11, 12) were connected firmly. The inlet connector (11) allowed the pressure gauge (8) to be part of the system for monitoring the vessel pressure during the operation. The pump (6) was a spare one which operates, manually, in case that the vessel pressure could not reach the required point after the oven met the set temperature. Initially, the vessel pressure was set at the atmosphere pressure. Extra raw materials will be added into the container (7) ready for pump operating. The outlet valve (9) was shunted tightly. The electrical heater (3) was switched on. The oven temperature then increased which was controlled by a temperature control unit. The unit composed of a heater (3), a controller (4) and a thermocouple (5). The oven temperature was varied as following; 1) warming up from room temperature up to 300 °C in 15 minutes, 2) dwelling at 300 °C for another 15 minutes, and 3) cooling down from 300 °C to the room temperature in several hours. During the warming up and the dwelling steps, the vessel pressure was strictly observed so that the vessel would not burst because of over pressure. Once the pressure reached to 200 bar, the outlet valve (9) must be opened. The sample then released into the sample contained (10). When the pressure reduced to about 140 bar, the outlet valve (9) was closed tightly. After the first sample was collected, the pressure then increased from 140 bar 200 bar again. Then the second sample was released into the second container. In each test, three samples were collected by this manner. The vessel pressure and the oven temperature were recorded, during the process, as shown in Figure 2.

Thin-layer chromatography (TLC) was used to analyze the sample. A sample, after eliminating of excessive methanol, was spotted onto the 3x7 cm^2 TLC plate by a capillary tube. The position of the spot was near the bottom edge of the plate as shown in Figure 2. The TLC plate details were given in Table 4.

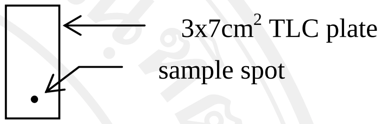


Figure 2. The sample spotted on the TLC plate

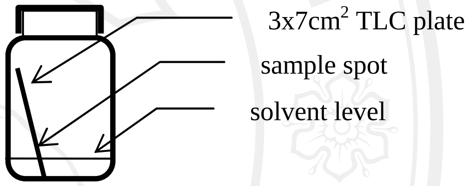


Figure 3. The TLC plate placed in the solvent

Table 4 The TLC plate details

Plate Material:	Aluminum sheet
Adsorbent Material:	Silica gel (SiO_2) : Partical size range : 60-200 micron (70-230 mesh ASTM)
Commercial available at :	Merck Company, Germany Product Name: TLC alumimum sheets Siliga gel 60 F_{254} plate size: 20 cm x 20 cm

Table 5. The solvent

Agent	Fraction
n-heptane	90
ethyl acetate	10
acetic acid	1

After spotting, the plate then was placed in a solvent bottle, in the position that the spot was slightly above the solvent level as shown in Figure 3. The solvent was a mixture of three agents as listed in Table 5. Once the plate was dipped into the solvent, the solvent then slowly spread up on the plate from the bottom to the upper. As it spread passed the spot, the ingredients in the spot were moved along with the solvent. Each ingredient had its own moving characteristic. The biodiesel moved fastest among the ingredients. The plate was left in the bottle until the solvent boundary was nearly touching the upper edge, then the plate was taken out to dry for few minutes. After drying, the TLC chromatogram revealed. However, it could not be seen with bare eyes. To see the chromatogram, there are two methods. Firstly, see it under the UV light.

Secondly, put the plate into contact with iodine vapor for few minutes and the chromatogram revealed as brown colors. In this work, the second method was applied. The TLC chromatogram results then were photographed.

Results and Discussion

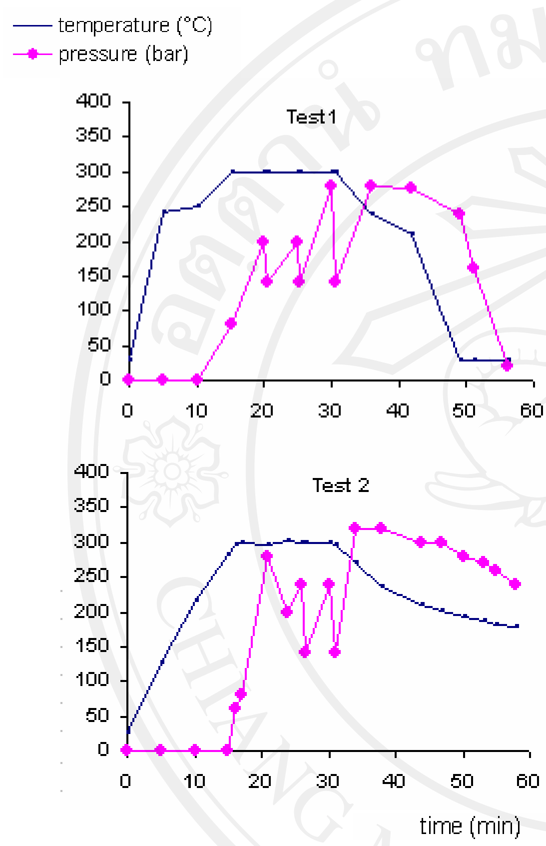


Figure 4. Vessel pressure and oven temperature during the process

When considering the vessel pressure of Test 1 in Figure 4, it was found that the pressure remained constant at 0 bar during the first 10 minute, then increased to 200 bar at the 20th minute, dropped to 140 bar after the 1st sample collecting. And back to 200 bar in 5 minutes. After the 2nd sample was collected, the pressure then reduced to 140 bar, and then back to 270 bar, before 3rd sample collecting. After the 3rd sample collecting, at the 30th minute, the pressure reduced to 140 bar. Then, the heater was switched off and the oven temperature reduces. However, the pressure still increased to 270 bar at the 35th minutes, before reduced to 25 bar at the 66th minute. It was clearly seen that the vessel pressure was increased and decreased by the effect of the oven temperature and the sample collecting, respectively. When considering the pressure curve of Test 2, it was quite different from that of Test 1.

Sample Analysis

The samples that collected during the experiment had some common characteristics. For example, immediately after leaving the vessel, they were thin yellow-brown emulsions looked like milk coffee. Two phases were shown after standing for a couple hours. The lower phases has little amount, only 5% in volume. They were clear dark brown thick liquids. The upper ones were clear pale yellow thin liquids. The upper phases of all samples, after eliminating of excessive methanol, were analyzed using the thin-layer chromatography (TLC). Results were presented as shown in Figures 5 and 6, in terms of TLC chromatograms and the product compositions were identified.

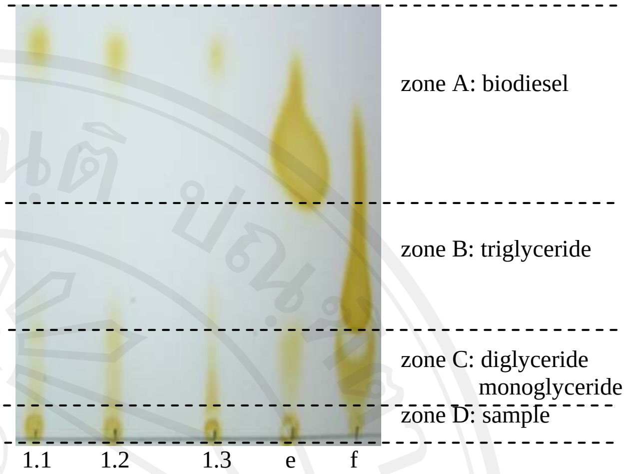


Figure 5. TLC chromatograms of samples collected from Test 1, e. biodiesel standard, f. palm oil

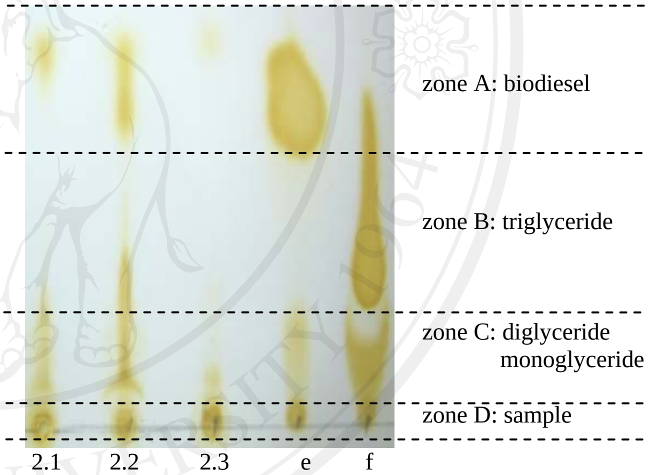


Figure 6. TLC chromatograms of samples collected from Test 2, e. biodiesel standard, f. palm oil

Four main compositions laid in four zones: A, B, C and D. A is methyl esters of fatty acids (biodiesel), B is triglyceride, C is diglyceride and monoglyceride, and D is the sample spot. When looking at the biodiesel standard (e), in Figure 6, there was a big brown circular area presented in the zone A, the bigger the area the higher content of fatty acids methyl esters (biodiesel). The biodiesel standard (e) in Figure 3 also showed a big brown area, although the area shape was slightly different with that in Figure 5, however, both chromatograms were developed from the same sample. When looking at the palm oil chromatograms (f), both in Figures 5 and 6, their patterns were quite similar. The upper part is longer than the lower one. The upper part had a head started in the zone B and its tail went upward into zone A. Although some part of the tail went into zone A, this did not mean there was biodiesel in the palm oil. It was triglycerides that have moving speed as fast as the biodiesel. When considering the chromatograms of the samples collected from the Test 1 (1.1, 1.2 and 1.3) in Figure 5, there were small brown circular areas laid in zone A. These showed that there were biodiesel contained in all three samples. All these samples also had di- and monoglycirde as long patterns in zone D. The three collected samples from Test 2 (2.1, 2.2 and 2.3) in Figure 6 had biodiesel in all samples. The 2.2 chromatogram was remarkable of two long parts with a big gap in between; the lower part was longer than the upper one. Color of the lower part was quite strong indicated tri-, di- and monoglyceride in significant concentration. The slim shape of the upper part presented in the zone A probably was not biodiesel because it was not a circular shape. One possible reason was the interference of the reversed reactions. Test 2 employed only 12:1 methanol-to-oil molar ratio, nearly four times lower than that of Saka [3] and Kunchana [4] recommended which was at 42:1.

Conclusions

Experimental study of palm oil methanolysis under pressure 200 bar without catalyst was investigated. The 24:1 and 12:1 molar ratios of methanol-to-oil were good trials. The pressure variations were increased and decreased according to the oven temperature variation and the sample collecting, respectively. The thin-layer chromatography is a good tool for detecting the methyl esters (biodiesel) and intermediate products in the samples. Therefore, methanolysis of palm oil without catalyst is another potential method for producing biodiesel. Further experiment is to increse the test duration and also the molar-ratio of methanol-to-oil..

Acknowledgments

The authors would like to thank Dr.Dammrong Santiarworn, Associate Professor of the Faculty of Pharmacy, Chiangmai University, for his encouragement and training of the thin-layer chromatography technique. Additionally, we would like to thank Associate Professor Aurawan Titwan, Dean of Faculty of Pharmacy, for providing this project with facilities and staff.

References

[1] Marchetti, J.M.,V. Miguel, Errazu A., Heterogeneous esterification of oil with high amount of free fatty acid, *Fuel*, **86**, (2007), pp. 906-910

[2] Pinto A.C.Lilian L.N.G, Rezende M.J.C., Biodiesel: an overview, *J.Braz.Chem.Soc*., **16**, 6B, (2005), pp. 1313-1330

[3] Saka, S. and Kusdiana, D., Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol, *Fuel*, **80**, (2001), pp. 225-231

[4] Kunchana Bunyakiat, Sukunya Makmee, Ruengwit Sawangkeaw, and Somkiat Ngamprasertsith, Continuous Production of Biodiesel via Transesterification from Vegetable Oils in Supercritical Methanol, *Energy Fuels*, **20** (2), (2006), pp. 812 -817

[5] Han Hengwen, Weiliang Cao and Jingchang Zhang, Preparation of biodiesel from soybean oil Using supercritical methanol and CO_2 as co-solvent, *Process Biochemistry*, **40** (9) , (2005), pp. 3148-3151

[6] Porntippa Angkanurukpun, Methanolysis of triglycerides by lipase from carica papaya latex for biodiesel fuel synthesis (Ph.D. Thesis), 2006, Chiang Mai University, [cite 2008 Oct 31].Available from: http://library.cmu.ac.th/digital_collection/etheses

Commemorative International Conference of the Occasion of the 4th Cycle Anniversary of KMUTT
Sustainable Development to Save the Earth: Technologies and Strategies Vision 2050: (SDSE2008)
11-13 December 2008, Bangkok, Thailand

Experimental Study on Non-catalytic Biodiesel Production from Palm oil and Ethanol under Pressurized Carbon dioxide

Anusan Permsuwan [1*], Churat Thararux [2], Tanongkiat Kiatsiriroat[1]

[1]Department of Mechanical Engineering, Faculty of Engineering Chiangmai University, Thailand
[2] Department of Mechanical Engineering, Faculty of Engineering, Rajamongkala University of Technology Lanna, Chiangmai, Thailand, Tel: (6653) 944144 ext 953, Fax: (6653) 944145
[*]Corresponding author: enmei017@chiangmai.ac.th

Abstract: The experimental study on non-catalytic biodiesel production from palm oil and ethanol under pressurized carbon dioxide were presented. Four molar ratios of ethanol-to-oil, 6:1, 12:1, 18:1 and 24:1, were studied. The reactions were carried out in a stirred reactor with pressurized carbon dioxide at 60 bar, initially. Temperatures were varied from the room temperature to 250 °C in 3 hours and then cooled to room temperature again in several hours. Product was analyzed using the Thin-Layer Chromatography (TLC) technique. It was found that at the 24 molar ratio of ethanol-to-oil, with the pressurized carbon dioxide, biodiesel was found in the significant fraction. Therefore, the pressurized carbon dioxide can be a method for biodiesel production.

Keywords: biodiesel production, non-catalyst, palm oil, ethanol, carbon dioxide

1. INTRODUCTION

Biodiesel is defined as mono alkyl ester of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat [1]. To produce biodiesel, transesterification reaction of triglycerides is involved. The reaction can be performed either by catalytic or non-catalytic method. In the catalytic method, small amount of a catalyst is included causing the reaction to perform at a milder condition, such as at the atmospheric pressure with a low temperature. Although this method is easy to perform but some problem still presenting, such as difficult catalyst removing from the product, high water consumed, and free fatty acid in the feedstock interfere the reaction [2]. The non-catalytic method eliminates the mentioned problems. However, it needs a severe condition, for example high operating pressure and temperature which are above 80.9 bar and 239.6 degree C which is the critical point of methanol, to perform the reaction. At such condition, the methanol becomes the supercritical state. Saka and Kusdiana [3] succeeded in making methyl esters from rapeseed oil in 4 minutes using non-catalytic method at the temperature of 350 C and pressure of 190 bar, with molar ratio of methanol-to-oil at 42:1. Bunyakiat and et al. [4] reported theirs experiment on palm kernel oil with the same condition as Saka and Kusdiana. The palm kernel oil was converted to methyl esters in 7 minutes. Han [5] proposed an idea of adding carbon dioxide in the non-catalytic method. Han believed that carbon dioxide is an appropriate co-solvent that can lower the critical point of methanol, and allow the transesterification reaction to be carried out under milder conditions. Han demonstrated that at the temperature of 280 C and pressure of 143 bar, methanol to soybean oil ratio of 24:1, carbon dioxide to methanol ratio of 0.1:1, a 98 % yield of methyl esters was observed in 10 minutes In this paper, the results of experimental study on non-catalytic biodiesel production from palm oil and ethanol under pressurized carbon dioxide were presented. The results divided into 3 aspects; 1) pressure variation during the process, 2) product analysis, and 3) product's volume evaluation.

2. METHODOLOGY

2.1 Materials and equipment

The palm oil used in this work was refined palm olein. It was a cooking oil contained 0.0075% butylated hydroxytoluene (BHT) as an antioxidant, supplied by Morakot Industry Co.Ltd. The ethanol was 99.8% purified industrial grade which supplied by Liquor Distillery Organization Excise Department. The CO_2 was an industrial grade, stored in a cylindrical tank, supplied by Lanna Gas Industry Co.Ltd. A batch-type high pressure reactor, with 450 ml vessel capacity and 400 bar maximum working pressure, was used. Fig.1 shows the reactor details.

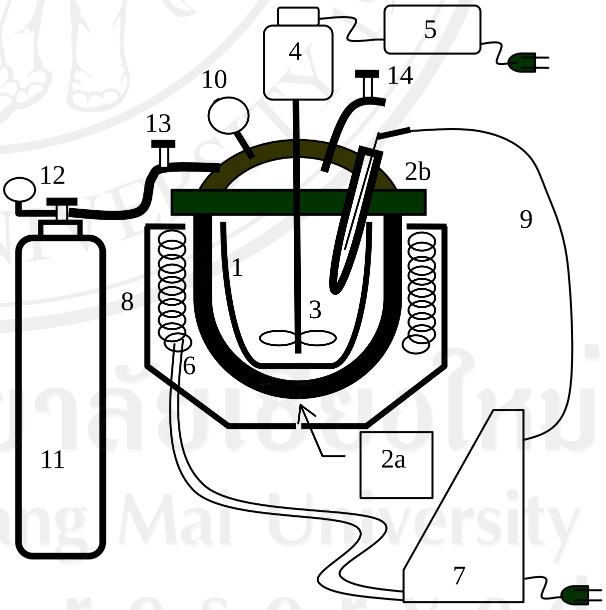


Fig.1 Schematic diagram of the high pressure reactor. 1.Vessel, 2a.Reactor body, 2b.Reactor lid, 3.Stirrer, 4.Motor, 5. Motor speed controller, 6.Electrical Heater, 7.Heater Controller, 8.Insulator, 9. Thermocouple, 10.Pressure gauge, 11.CO_2 tank, 12.CO_2 regulator, 13.Reactor inlet value, 14.Reactor outlet value

2.2 Experimental program

The experimental program in this work composted of 8 tests as listed in Table 1. The first four tests, test 1- 4, carried out with pressurized CO_2, at various molar ratio ethanol-to-oil (6:1, 12:1, 18:1 and 24:1). The last four tests, tests 5-8, were of without pressurized CO_2, at the same molar ratios, as references.

Table 1 Experimental Program

	test	molar ratio of ethanol-to-oil
with pressurized CO_2	1	6 : 1
	2	12 : 1
	3	18 : 1
	4	24 : 1
without pressurized CO_2	5	6 : 1
	6	12 : 1
	7	18 : 1
	8	24 : 1

2.3 Testing Procedure (tests 1-4): with pressurized CO_2

The high pressure reactor as showed in Fig.1 was used. Raw materials (ethanol and palm oil) were loaded into the vessel (1). The volume of each material used for each test was according to the molar ratio as in Table 2. After tightening the reactor lid, the motor (4) then was switched on and the stirrer (3) was rotated at a constant speed for providing the turbulence movement. The reactor was flushed with the CO_2 for couple seconds by regulating the inlet and outlet values (13,14) and the CO_2 regulator (12) so that no air be presented in the reactor. Then, the outlet value (14) was closed. The inlet value (13) and the CO_2 regulator (12) then were opened wilder, so the CO_2 in the tank was more released into the reactor, the reactor pressure then increased until equal to the CO_2 tank which was about 60 bars at room temperature. Then, the inlet value and the CO_2 regulator were closed, so that the CO_2 could not be transferred between the tank and the reactor during the experiment. The heater controller (7) and the electrical heater (6) then were switched on. The reactor temperature, then, increased from the room temperature to 250 °C within 3 hours. During this period, the temperature and the pressure were recorded every 10 minutes and the data was presented in Fig.2. The heater and the stirrer then were switched off. The reactor was left for several hours so that its temperature was reduced to the room temperature. The reactor lid then was opened and the product was removed for further analysis.

Table 2 Raw material volume converted to molar ratio*

test	ethanol volume (ml)	palm oil volume (ml)	molar ratio of ethanol-to-oil
1	18	50	6 : 1
2	36	50	12 : 1
3	54	50	18 : 1
4	72	50	24 : 1
5	18	50	6 : 1
6	36	50	12 : 1
7	54	50	18 : 1
8	72	50	24 : 1

2.4 Testing Procedure (tests 5-8): without pressurized CO_2

The testing without pressurized CO_2 quite similar with that with pressurized CO_2. Except that the pressure in the reactor was at 0 bar, initially. The reactor was flushed with the CO_2 as well. After flushing, both inlet and outlet values were closed so that nothing could be released from the reactor. The reactor temperature was started from the room temperature and reached to 250 °C within 3 hours as well. The pressure and temperature also were recorded as shown in Fig.2.

2.5 Product analysis

Thin-layer chromatography (TLC) was used to analyze the biodiesel presented in the products. A product sample was spotted onto the 3x7 cm^2 TLC plate by a capillary tube. The position of the spot was near the bottom edge of the plate as shown in Fig. 2a. The plate details were given in Table 3.

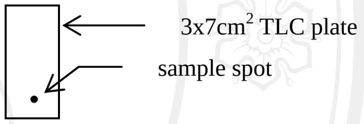


Fig.2a The sample spotted on the TLC plate

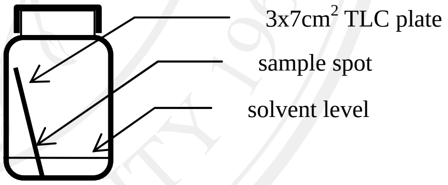


Fig.2b The TLC plate placed in the solvent

Table 3 The TLC plate details

Plate Material:	Aluminum sheet
Adsorbent Material:	Silica gel (SiO_2) : Partical size range : 60-200 micron (70-230 mesh ASTM)
Commercial available at :	Merck Company, Germany Product Name: TLC alumimum sheets Siliga gel 60 F_{254} plate size: 20 cm x 20 cm

After spotting, the plate then was placed in a bottle that contained the solvent, in the position that the spot was slightly above the solvent level as shown in Fig.2b. The solvent was a mixture of three agents as listed in Table 4. Once the plate was dipped into the solvent, the solvent then slowly spread up on the plate from the bottom to the upper. As it spread passed the spot, the ingredients in the spot were moved along with the

Table 4 The solvent

Agent	Fraction
n-heptane	90
ethyl acetate	10
acetic acid	1

---

* The conversion example between volume and the molar ratio of ethanol-to-oil is explained here. For test 1, the 18 ml ethanol volume equals 14.2 g (18ml x 0.79 g/ml = 14.2g), equals 0.31 mole (14.2/46 = 0.31). The 50 ml palm oil volume equals 43.5 g (50ml x 0.87g/ml=43.5), equals 0.05 mole (43.5/800 = 0.05). Therefore, the molar ration of ethanol-to-oil is 6.2:1 (0.31/0.05 = 6.2), and simplified to 6:1 as in Table 2.

solvent. Each ingredient has its own moving characteristic. The biodiesel moved fastest among the ingredients. The plate was left in the bottle until the solvent boundary was nearly touching the upper edge, then the plate was taken out to dry for few minutes. After drying, the TLC chromatogram revealed. However, it cannot be seen with bare eyes. To see the chromatogram, there are two methods. Firstly, see it under the UV light. Secondly, put the plate into contact with iodine vapor for few minutes and the chromatogram revealed as brown colors. In this work, the second method was applied. The TLC chromatogram results then were photographed as shown in Figs. 4-5.

3. RESULTS AND DISCUSSION

3.1 Pressure variation during the process

When considering tests 1-4 in Fig.3 all tests started with same initial pressure, about 60 bar, then, the pressure increased with time, however, in the different patterns. For tests 1-3, the pressure rose up to certain points and then dropped. Only test 4, the pressure just rose up without dropping. It quit hard explaining why the pressure displayed as they were. A possible reason was the effect of the molar ration of ethanol-to-oil. However, the relationship between the pressure variation and the molar ratio needs more studying.

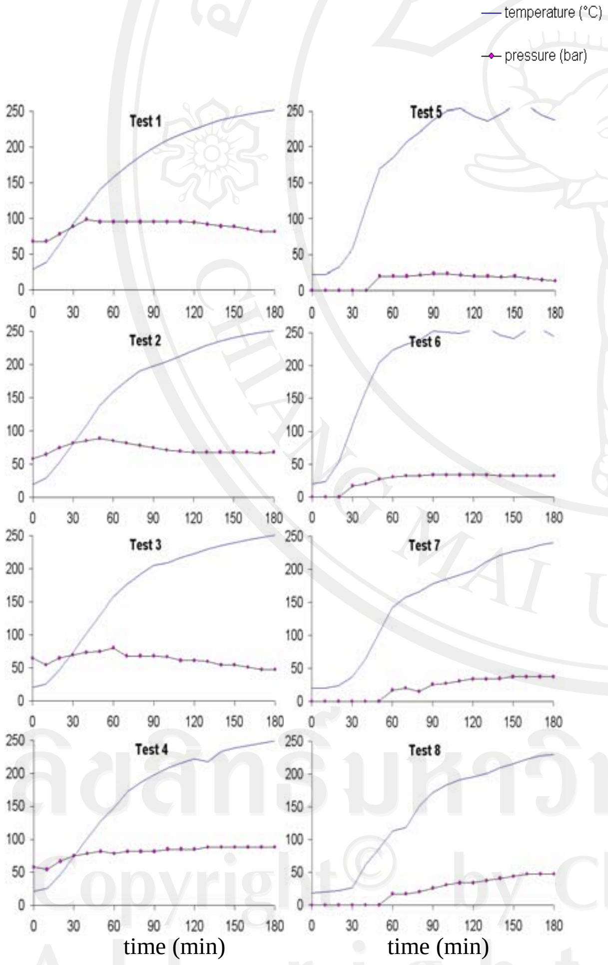


Fig.3 Pressure variation during the heating period

3.2 Product analysis

The TLC chromatograms, in Figs..4-5, revealed the products' compositions. The chromatograms were divided into 4 zones: A, B, C and D. A is biodiesel, B is triglyceride, C is diglyceride and monoglyceride, and D is the sample spot. When looking at the biodiesel standard (e), in Fig.5, there was a big brown circular area presented in the zone A which was biodiesel, the bigger the area the higher yield the biodiesel. The biodiesel standard (e) in Fig.4 also showed the big brown area, although the area shape was different with that in Fig.5, however, both came from the same sample. When looking at the palm oil chromatogram (f), both in Fig.4 and Fig.5 which were the same sample, they were like slim sticks that broken into two parts with a small gap between them. The upper stick, the longer one, had a head started in the zone B and its tail gone upward into zone A. Although its tail went into zone A, this did not mean there was biodiesel presented in the palm oil. It, however, probably was triglycerides that have moving speed as fast as the biodiesel

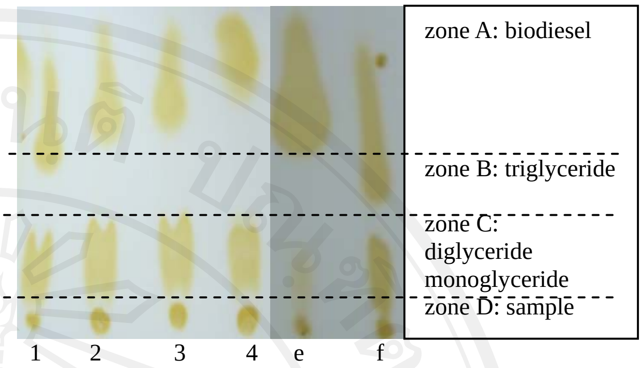


Fig.4 TLC chromatograms of products from tests 1-4
e. biodiesel standard, f. palm oil

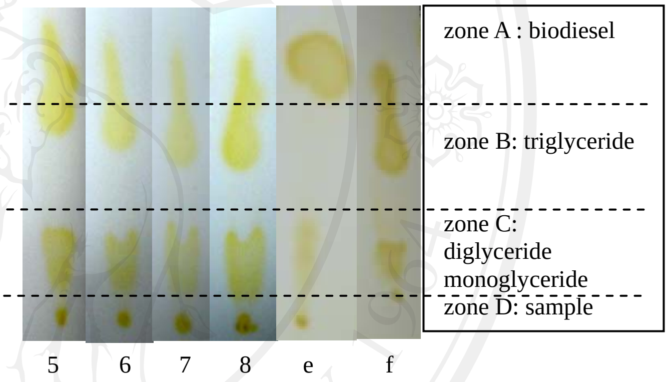


Fig.5 TLC chromatograms of products from tests 5-8
e. biodiesel standard, f. palm oil

When considering Fig.4, at the zone A of test 4, there was a big brown circular area presented. This showed that there was biodiesel in the test 4 product at a significant level, while as, no circular area was found in other tests at the zone A. However, when looking at the tests 1-3 at zone A, two things were observed. Firstly, the shape of the upper areas trended to change from the slim stick to circle, for example the upper stick of test 3 was shorter than that of test 2, while as, that of test 1 was longest. Secondly, the gap between the upper and the lower stick were increased. For example, the test 1 was smaller than that of test 2. These two observations proved that the biodiesel content were increased with the ethanol content. Increasing the ethanol content was increasing the contact area between ethanol and triglycerides; therefore, the reaction rate was speeded up. When looking at test 4 in Fig.4, no brown area in zone B, means no triglycrecide remained in the product. The triglyceride probably was totally converted to the di and monoglyceride. If the reaction time were longer, the di and monoglyceride would be totally converted to the biodiesel.

When considering the test 5 in Fig.5, less triglyceride than other products among tests 5-8. One possible reason was because the effect of temperature increasing rate which was very quick as shown in Fig.3. This was an error of the heater controller caused the test 5 temperature dramatically increased, from room temperature to 250 °C only in about 100 minutes. This error, however, produced a good outcome because it did help the reaction to develop faster. When looking at the zone °C of all products, they proved that the reactions of all tests were not complete yet. This implied that the tests conditions were not severe enough, so, the reaction rates were too slow. To fasten the reaction rate, the following factors must be adjusted to be higher: temperature, pressure, time and molar of ethanol.

3.3 Product's volume evaluation

When considering Fig.6, total raw material volume and total product volume were compared; it was found that the total product volume of all tests were less than the total raw material volume. The lost during the processes was probably because the reactor lid or the value connecting joints were not perfectly sealed. The turbulent movement via the stirrer rotating also promoted the leaking. To minimize the leaking, two things are recommended. Firstly, all joints and lid must be more tighten. This was not easy because over-tightening may damage the fastener. Second, the stirrer speed must be slower. In our studying, the stirrer speed was kept at a constant speed; however, this was probably so fast that caused the mixture inside the vessel splashed out. The volume of the splashed out for each test was reported in terms of the "outside vessel" as shown Fig.7.

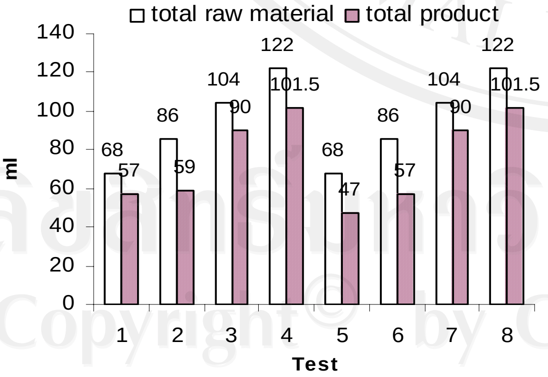


Fig.6 Comparison of the volume between total raw material and total product

When considering Fig.7, the inside vessel and the outside vessel products, the term "inside vessel" represented the volume of the product that remained inside the vessel. Therefore, when added the two volumes together, the inside and the outside, the total product arrived as stated in Fig.6. Both products had different characteristics. For example, the outside vessel product was less viscosity than the inside vessel product, data was not available here. This also needed more investigation.

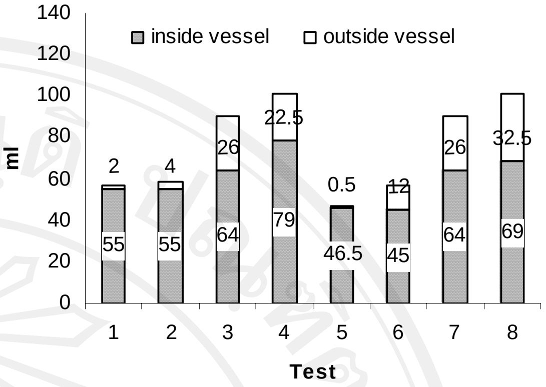


Fig.7 The inside vessel and the outside vessel products

4. CONCLUSION

Non-catalyst biodiesel production from refined palm oil and ethanol under pressurized carbon dioxide was studied, experimentally. It was found that 1) the pressure of the reactor was increased with the increasing of temperature, 2) at the 24 molar ratio of ethanol-to-oil, with the pressurized carbon dioxide, biodiesel was found in the significant fraction and 3) lost of materials during the process must be taken into account.

5. ACKNOWLEDGMENTS

The authors would like to thank Dr.Dammrong Santiarworn, Associate Professer of the Faculty of Pharmacy, Chiangmai University, for his encouragement and support until this project was complete. Additionally, we would like to thank Associate Professor Aurawan Titwan, Dean of Faculty of Pharmacy, for providing this project with facilities.

6. REFERENCES

[1] Marchetti, J.M.,V. Miguel, Errazu A. (2007), Heterogeneous esterification of oil with high amount of free fatty acid, *Fue,l* **86**, pp. 906-910

[2] Pinto A.C.Lilian L.N.G, Rezende M.J.C. (2005) Biodiesel: an overview, *J.Braz.Chem.Soc.*, **16**, (6B), pp. 1313-1330

[3] Saka, S. and Kusdiana, D. (2001) *Fuel*, (80), pp. 225-231

[4] Kunchana Bunyakiat, Sukunya Makmee, Ruengwit Sawangkeaw, and Somkiat Ngamprasertsith, (2006) Continuous Production of Biodiesel via Transesterification from Vegetable Oils in Supercritical Methanol, *Energy Fuels*, **20** (2), pp. 812 -817

[5] Han Hengwen, Weiliang Cao and Jingchang Zhang, (2005), Preparation of biodiesel from soybean oil Using supercritical methanol and CO_2 as co-solvent, *Process Biochemistry*, **40** (9) pp. 3148-3151