CHAPTER 1

INTRODUCTION

1.1. Background and Problem Statement

The crisis of petroleum shortage is an inevitable problem for mankind, although it is difficult to predict when they will be permanently used up, strategies for confronting this crisis have been prepared. Development of alternative fuels from renewable sources such as biomass, biogas and biodiesel is one of the strategies that all countries give priority. In Thailand, diesel fuel consumption of the transportation accounts for more than 50% of the total fuel consumption of the transportation. Therefore, the government has a strategy to reduce the diesel fuel consumption by promoting the use of biodiesel (Siriwardhana et al.,2009). Statistical data reveal that this strategy is successful. The consumption of B5-diesel (a mixture of 95% perto-diesel and 5% biodiesel by volume) increased from 4 ktoe in 2005 to 3258 ktoe in 2008 as shown in Table 1.1.

Table 1.1. Thailand national consumptions of B5-diesel during 2005-2008

2005	2006	2007	2008
4 ktoe	37 ktoe	540 ktoe	3258 ktoe

ktoe = kilo ton crude oil equivalent,
source: Department of alternative energy development and efficiency. Ministry of energy, Thailand~~.~~

Biodiesel is defined as mono alkyl esters of fatty acids derived from lipid feedstock, such as vegetable oils or animal fats (Marchetti et al.,2007). Currently, the production of biodiesel uses the conventional methods which involve with alkaline catalysts (potassium hydroxide or sodium hydroxide). These methods have many limitations such as: (1) High water and time consumptions during the product purification process, (2) Unsuitable for low grade feedstock which contains high level of free fatty acids and water as they block the reaction and reduce the production yield. Therefore, there is a need to have better method that can produce biodiesel from low grade feedstock, because this feedstock has a lower price.

Recently, a novel method of non-catalyst which involves with sub- and supercritical conditions has been introduced. Laboratory investigations (Lim et al.,2010; Marchetti et al., 2007; Kusdiana and Saka, 2004) revealed that this method was compatible with such low grade feedstock that contained high level of free fatty acids and water. The process was very simple because it dose not need the purification process. Therefore, the process was completed in a short time. However, little information has been found in the existing literature, particularly for palm oil which is an important vegetable oil of Thailand.

Palm oil methyl ester (POME) has been proved as a good biodiesel because it gives low engine emissions (except for the NOx which is rather high) and high oxidation stability (Jayed et al., 2009) of which a long storage without properties changing could be obtained. Additionally, palm oil is a common feedstock for biodiesel production in Thailand because of its highest oil yield per land used (Siriwardhana et al.,2009). A hectare (6.25 rai) of palm oil trees cultivation yields biodiesel about 3,527 liters per year which is ten times of soybean, as shown in Fig.1.1. Palm oil is the cheapest oil in Southeast Asia because of the climate and labor cost conditions. Therefore, biodiesel from palm oil holds the most promise to be a major source of biodiesel in the future, particularly in Southeast Asia.

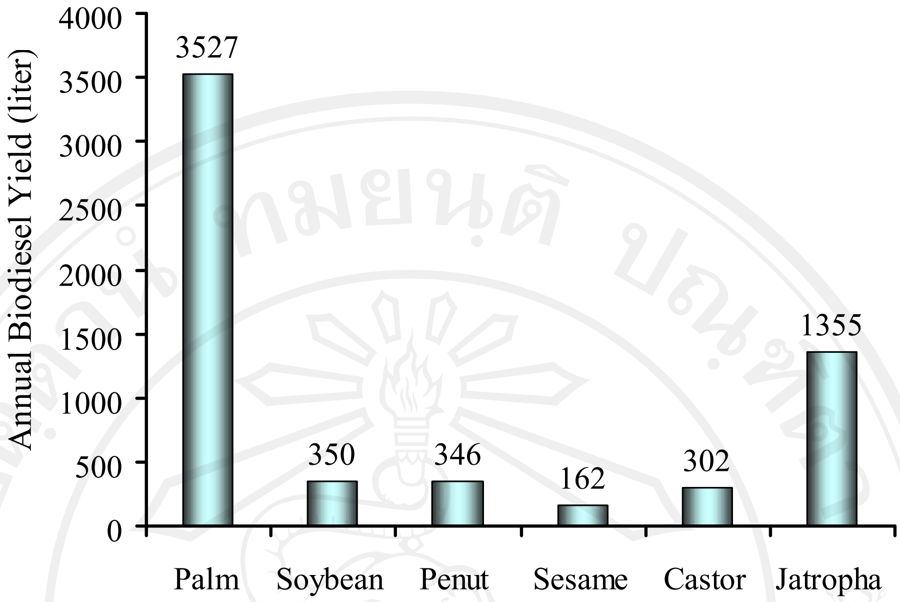

Fig.1.1 Annual biodiesel yield of selected vegetable oils per one hectare (6.25 rai) of oil crops cultivation,
source: (Martchamadol,2007)~~.~~

To produce palm oil biodiesel by the non-catalyst method of sub- or supercritical alcohol, a number of technical issues must be overcome. For example, the best operating condition, rate of the reaction and other kinetics data. These are essential parameters for engineers to have efficient biodiesel production.

Therefore, problem statement is:

What is the most suitable condition and how fast the process of palm oil biodiesel production in the non-catalyst technique can be under sub- and supercritical methanol?

The thesis statement is:

This thesis is about empirical investigations of palm oil biodiesel production in the non-catalyst technique under sub- and supercritical methanol to disclose kinetics data and effects of operating variables on the biodiesel production yield.

1.2. Literature Reviews

1.2.1. Biodiesel History

Duffy and Patrick (1853) introduced a method of separation of glycerin from vegetable oils using alcoholysis reaction. A product that floated above the glycerin layer was generated. It was biodiesel, however, unrecognized as biodiesel at that time. This was because of unavailability of diesel engine. Duffy and Patrick were the pioneers in the alcoholysis reaction. Chavanne (1937) from Belgium succeeded in producing methyl esters and ethyl esters of rapeseed oil and used them run a diesel engine. Chavanne registered this invention under the Belgian patent (in Frence language); "Procédé de Transformation d'Huiles Végétales en Vue de Leur Utilisation comme Carburants" means "Procedure for the transformation of vegetable oils for their uses as fuels". This was the first application of biodiesel. The methods that Chavanne, Duffy and Practrick used were recognized today as the homogeneous alkaline catalytic methods of biodiesel production.

1.2.2. Biodiesel Production

Various methods of biodiesel production from alcoholysis reaction have been developed. These include catalytic and non-catalytic methods.

a) Catalytic Method

In catalytic methods, small amount of catalysts are employed. They help the alcoholysis reaction to process at a milder condition such as at the atmospheric pressure and a relatively low temperature (below alcohol boiling point). The catalysts could have same phase (homogeneous) or different phase (heterogeneous) with the reactants. The homogeneous catalysts could be acids such as sulfuric acid or alkaline such as sodium hydroxide and potassium hydroxide. The heterogeneous catalysts could be enzyme, resins, zeolites or metal oxides.

i) Alkaline Catalyst

Alkaline catalyst like sodium hydroxide or potassium hydroxide is the most common method has been used. This is because of theirs high efficiency in speeding up the reaction rate with the low prices. The catalyst is dissolved in the alcohol before mixing with the fixed oil. Biodiesel is produced in a short period. However, the product is contaminated with the catalyst and soap then a cleaning up process is needed. The cleaning up process uses a lot of water which needs a proper treatment. Soap is a product of the sponification reaction of the catalyst and free fatty acids in the oil. Alcohol used in the production process must be an anhydrous grade and the fixed oils must free from moisture and free fatty acids. These types of fixed oils are considered as high quality oils and theirs costs are relatively high.

ii) Acid Catalyst

Acid catalyst like sulfuric acid is used when the fixed oils contain high level free fatty acids such as waste oils and unrefined oils. The advantage of acid catalyst is that both transesterifiaction and esterification reactions are simultaneously performed (Pinnarat and Savage, 2008). The free fatty acids are converted to alkyl esters by the esterification reaction. The drawbacks of acid catalyst are that: 1) It is very water sensitive. 2) It requires a high molar ratio of alcohol to oil, around 30:1. And 3) the reaction time is very long (3-20 h) (Pinnarat and Savage, 2008).

iii) Heterogeneous Catalyst

Enzyme, resin, zeolite and metal oxide are examples of the heterogeneous catalyst. The catalysts are in the solid phases and theirs particle sizes are so big that could be easily removed from the product by filtration or centrifugation. The product is not contaminated by the catalysts or soap. However, the cost of heterogeneous catalyst is quite high when comparing with that of homogeneous catalyst. Examples of the catalytic method are in Table 1.2.

b) Non-catalytic Method

The non-catalytic method involves with a high solubility of the fixed oils in alcohol when they are under the sub- or the supercritical condition. In this condition the oil and the alcohol are miscible. This phenomenon allows the alcoholysis reaction to develop and yield biodiesel. The product has no contaminant. Vairous studies were found in the liturature as shown in Table 1.3.

Diasakou (1998) produced biodiesel from soybeen oil under subcritical methanol in a Series 4560 Bench Top Mini Reactor. After 600 minute, at 235 °C, over 85%

Table 1.2~~.~~ Catalytic Method

Author	Year	Catalytic type			Process Condition			
		Alkaline homogeneous	Acid homogeneous	Heterogeneous	Temp(°C)	Pressure (atm)	Reaction time (min)	M
Chongkhong	2009	x	x[1]		75-80	1+	80	8.8
Chongkhong	2007	x[2]	x[1]		70-100	1+	15-240	5-8
Angkanurukpun	2006			x[3]	25-65	1	2-48 h	1-5
Marchetti	2007			x[4]	30-55	1	180	6
Shibasaki	2007			x[4]	50	1	60	10
Sukhawanit	2004	x[2 and 5]			30-65	1	30-240	3-20
Petchtong	-		x[6]	x[7]	60-80	1	150	20
Satoshi	2004		x[8]	x[9]	200-300	1	20-200 h	40
Suppes	2004			x[10]	60-150	1+	0-500	6

M = Molar ratio of alcohol-to-oil, [1]sulfuric acid (H_2SO_4),,[2]NaOH, [3] Carica papaya lypese enzyme, [4]resin , [5]KOH and sodium methoxide ($NaOCH_3$), [6]HPW/Al_2O_3, HsiW/ Al_2O_3, and H_2SO_4/Al_2O_3 , [7]alumina oxide, [8]WO_3/ZrO_2(tungstated zirconia), SO_4/ZrO_2(sulfated zirconia), and SO_4/SnO_2(sulfated tin oxide), [9]solid superacid, [10] zeolite and metal catalysts~~.~~

biodiesel conversion was reported. Saka (2001) used supercritical methanol in a 5 ml Inconel-625 vessel (batch-type) to produce biodiesel from 3.36 g methanol and 2.0 g rapeseed oil, 42:1 molar ratio methanol-to-oil , at 350 C and 40-65 MPa, 1.98 g biodiesel produced in 4 min. The 1.98 g biodiesel considered as 98% of the theoretical value (the theoretical value is 2.01 g). Dermirbus (2002) used supercritical methanol in a 100 ml 316 stainless steel autoclave (bath-type) to produce biodiesel from six vegetable oils; cottonseed, hazelnut kernel, poppyseed, rapeseed, saffowerseed and sunflowerseed, at various conditions. Dermirbus reported that 20-30 g hazelnut kernel

Table 1.3~~.~~ Non-catalytic Method

Author	Year	Non-catalytic method						Process Condition			
		I	II	III	IV	V	VI	T (ºC)	P (atm)	t (min)	M
Diasakou	1998	I						220-235	55-62	600	6-27
Saka	2001			III				350	190	4	42
Demirbas	2002			III				177-250	-	3.3	1-41
Dasari	2003	I	II ^{1}			V		120-180	-	240-1920	3-12
Dasari	2003		II ^{2}					120-180	-	4-32	6
Kusdiana	2004			III				350	430	4	42
Madras	2004						VI	200-400	200	0-40	40
Bunyakiat	2006			III				270-350	100-190	7	6-42
Han	2005				IV ^{3}			240-330^{4}	30-230 ^{5}	10	6-42^{6}
He	2007			III				240-340	100-400	12-50	5-80
Varma	2007			III			VI	200-350	200	40	10-70
Yin	2008				IV ^{3}			300	-	30	42
Yin	2008				IV ^{1}			300	-	-	-
Yin	2008			III				260-350	-	10-60	24-55
Balat	2008					V		177-251	-	0.8-5	1-40
Petchmala	2008			III				250-300	-	10-80	1-12

I = subcritical methanol, II = subcritical methanol with co-solvent, III = supercritical methanol, IV = supercritical methanol with co-solvent, V = subcritical ethanol, VI = supercritical ethanol, M = Molar ratio alcohol-to-oil, ^{1}hexane, ^{2}methyl esters 0.5-1 mole/mol of oil, ^{3}CO_2, ^{4}optimum at 280, ^{5}optimum at 143, ^{6}optimum at 24~~.~~

oil with 30-50 g methanol (molar ratio of methanol-to-oil was 42), at 177-250 °C, a 90% biodiesel conversion was found after 3.3 min.

1.2.3. Types of Input Material

Fixed oils and alcohols are the main input materials. The fixed oils refer to vegetable oils or animal fats. Fixed oils have many classes including refined oils, crude oils and used oils. The used oils sometimes called waste oils. Any alcohols are useable, but only two alcohols were frequently used; methanol and ethanol. Methanol has a lower cost than ethanol. But ethanol is less toxic. Table 1.4 shows different input materials of some research studies.

Table 1.4 Input Material

Reference	Year	Oil Name				Oil Class					Alcohol	
		Soybean	Palm	Palm Kernel	Other	Refined	Crude	waste	FAD	ND	Methanol	Ethanol
Saka	2001				x(R)	x					x	
Bunyakiat	2006			x	x(C)					x	x	
Han	2005	x				x					x	
Marchetti	2007				x(S)	x						x
He	2007	x								x		x
Sukhawanit	2006				x(S)		x				x	
Petchtong	-		x				x				x	
Chongkhong	2007		x						x		x	
Satoshi	2004	x									x	

R = Rapeseed, S = Sunflower, C = Coconut, FAD = Fatty Acid Distillate, ND = No Data~~.~~

1.2.4. Control Variables in Reaction Process

Four variables involved in the non-catalytic methods; temperature, pressure, time of reaction and molar ratio of alcohol-to-oil. These variables control the reaction process and the product quality. High quality product contains high fraction of alkly esters.

High temperature, high pressure and high molar ratio of alcohol-to-oil speed up the reaction rate, however, they must be at suitable ranges. The temperature should not be over 350 °C for avoiding the product deterioration (Saka and Kusdianna , 2001). The increasing of molar ratio of methanol-to-oil to more than 42:1 dose not significantly increases the production yield. It is only added to the production cost in the methanol separation process. Time of reaction should be controlled to the point that the optimum yield is met. Too long reaction time results in the product loss due to the thermal decomposition and the dehydrogenation reactions (He et al.,2007).

1.2.5. Products Analysis

To determine the composition of product, analytical equipments are needed which include thin layer chromatography (TLC), gas chromatography (GC), high performance liquid chromatography (HPLC), near-infrared spectroscopy (NIR), Fourier-transformed infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR). Gas chromatography is the most frequent used as shown in Table 1.5.

1.2.6. Effect of Co-solvent

Co-solvent is a solvent added into the reaction to speed up the reaction rate by increasing the miscibility of methanol and oil. It could be propane, butane or carbon dioxide. Han took carbon dioxide in the methanolysis of soybean oil. The experiment was at temperature 280 C and pressure 143 atm, molar ratio of methanol-to-oil ratio at 24:1, molar ratio of carbon dioxide-to-methanol at 0.1:1. The maximum yield of methyl esters was observed at 98% in 10 min.

Table 1.5 Product Analysis and Fuel Properties

		Product analysis					Fuel properties ASTM D6751				
Author	Year	HPLC	GC	TLC	NIR	FTIR or NMR	Spcific gravity	Cetane No.	Flash point	Heating value	Viscosity
Saka	2001	x									
Bunyakiat	2006		x				x	x	x	x	x
Han	2005		x								
Marchetti	2007		x								
Saka	2001	x	x								
He	2007		x								
Sukhawanit	2006			x							
Petchtong	-			x							
Chongkhong	2007			x							
Knothe	2006	x	x	x	x	x^1	x	x	x	x	x
Knothe	2001				x						
Monteiro	2009					x^2					
Satoshi	2004		x								

^{1} = FTIR, ^{2} =NMR

1.2.7 Effect of Free Fatty Acids

In the homogeneous alkaline catalytic method, the content of free fatty acid in the fixed oil must be less than 0.5% to avoid excessive soap formation. Soap is a product of reaction between the free fatty acids and the alkaline. It is unwanted product in the biodiesel production and it increases the production cost due to: (1) extra process must be added for the soap removal, and (2) excessive alkaline is consumed and the yield of biodesel is reduced. However, under supercritical condition (no alkaline catalyst involved), the high content of free fatty acids in the fixed oil increases the biodiesel yield and also reduces the production time. This is because the esterification of free fatty acids and the transesterification of triglyceride can occur simultaneously. It has been demonstrated that under a supercritical condition (350 °C, 43 atm, 42:1 molar ratio of methanol-to-oil, 4 min. reaction time) a mixture of rapeseed oil with a high percentage of free fatty acid (30% of oleic acid) can yield biodesel at almost 100% (Kusdiana and Saka , 2004).

1.2.8. Summary

From the literature review, it was found that the non-catalytic biodiesel production method has many advantages such as; the process is much simpler because of it does not require purification process to remove catalyst or soap from the products the glycerol by-product also has a higher value because it contains less contamination. However, only few research works have been reported so far. Reaction kinetics and the optimum operating conditions of many vegetable oils are not yet revealed. Therefore, investigations in these areas are needed.

1.3. Objectives

- To set up a laboratory facility for producing biodiesel under sub- and supercritical conditions
- To determine the relationship between the operating variables and the biodiesel yield
- To purpose the reaction kinetics of the methanolysis of palm oil to biodiesel

1.4. Scope

- Experiments are carried out in a 400 ml laboratory bath reactor.
- The raw materials are refined palm oil and methanol.
- The operating variables are composed of 1) Molar ratio of methanol-to-oil between 8:1 to 43:1, 2) Reaction temperature between 25-400 °C, 3) Reaction pressure between 1-190 atm, and 4) Reaction time between 0-24 h.
- The analysis methods to determine the biodiesel yield are Thin-layer chromatography (TLC) and gas chromatography (GC).
- The reaction kinetics of the methanolysis of palm oil to biodiesel composed of 1) Activation energy, 2) Rate constant, and 3) Reaction rate

1.5. Benefits of the Study

As there are many advantages of the non-catalytic method for the biodiesel production such as low water waste, low cost of input materials and short time of process. Therefore, this method is considering an attractive method. The reaction kinetics are essential data for engineers to determine the type and size of reactors which suit the production requirements. Therefore, this study provides the data of the non-catalytic biodiesel production.