CHAPTER 1
INTRODUCTION

1.1 Rational/Problem Statement

In Thailand, the demand of fossil diesel fuel continuously increases due to the economic expansion of the country. At the same time, Thailand meets the energy crisis which is similar to other import diesel fuel countries because of the increasing price of petroleum in the global market. Hence, many researchers in Thailand look through the renewable energy for solving this problem. Since Thailand has a high potential in energy crops; consequently, biodiesel is one of the possible alternative fuels for being to replace petroleum-based diesel (petro-diesel) without any engine modifications. In fact, its properties are so similar to conventional diesel that it can be blended in any proportion with petro-diesel. Moreover, biodiesel (methyl and ethyl esters of natural vegetable oils and fats) obtained from energy crops produces beneficial effects on the environment. These include the reduction in acid rain and, indirectly, in the greenhouse effect of carbon dioxide caused by combustion. Not surprisingly, biodiesel is receiving increased attention as an alternative, non-toxic, biodegradable and renewable diesel fuel and biodiesels derived from a wide variety of sources can be used as a direct substitute for petro-diesel fuels.

In order to promote the utilization of biodiesel in Thiland, in 2005, biodiesel strategy was issued by Thai government. It aims to produce and to use 10% biodiesel instead of fossil diesel demands within 2012 (8.5 million litres per day). Moreover, oil palm strategy which plans to increase the oil palm plantation area to 4 million acres (10 million rai) for supporting the increasing of biodiesel consumption in the future was also issued. To give a respond to the Thai government policy, un-de-gummed mixed crude palm oil (MCPO), which is a mixture of palm fiber oil and palm kernel oil, having high free fatty acid (FFA) more than 8 wt.% of oil will be used as a raw material in this work.

Previously, prior to acquire the suitable method for producing biodiesel from high free fatty MCPO, transesterification was the fist method offered to observe the characteristic of reaction. The results indicated that low or without yield of methyl

ester (ME) was obtained. The reason is that while biodiesel is produced from MCPO with transesterification, FFA in MCPO is reacting with metallic alkoxide to produce soap (saponification). Therefore, it is necessary to reduce FFA in oil before starting the process for producing biodiesel. There are four feasibility methods that can solve this problem: enzymatic-catalyzed transesterification, acid-catalyzed transesterification, supercritical carbon dioxide technique and two-stage process. However, the two-stage process is chosen for producing biodiesel because this process requires lower reaction time, lower temperature and lower pressure more than other processes.

The two-stage process for producing biodiesel from crude oil consists of two methods: saponification followed by transesterification, and esterification followed by transesterification. Nevertheless, the latter two-stage process (esterification followed by transesterification) is offered in this investigation to produce biodiesel from oil containing high FFA in un-degummed state, because it requires shorter time and lower production loss than that from the process of saponification followed by transesterification. In this procedure, acid catalyst esterification (the first stage) was employed to reduce FFA by converting it into biodiesel. Then, alkali catalyst transesterification was subsequently used to convert glycerides (triglyceride (TG), diglyceride (DG) and monoglyceride (MG)) into biodiesel.

Biodiesel has been traditionally produced using batch reactor technology. However, for obtaining a large amount of product in batch process, large reactor size, high energy consumption and high labor cost were required. In addition, the quality of the product in each batch was difficult to control. In order to reduce the batch process problem; therefore, the continuous process was investigated. The continuous reactor can be classified into 3 types: continuous stirred tank reactors (CSTR), plug-flow tubular reactor (PFR), and packed bed reactor (PBR). A CSTR was chosen for producing biodiesel from high free fatty acid MCPO via the two-stage process in this investigation because of low investment cost, suitability for liquid-liquid reaction and simply design.

1.2 Literature Reviews

1.2.1 The Two-Stage Batch Process

The biodiesel production from natural vegetable oil or animal fat containing high FFA and high moisture can be solving the soap problem in alkali-catalyzed transesterification by the two-stage process (Issariyakul, 2006). The two-stage processes can be categorized into two types: 1) saponification followed by tranesterification (SFT) (Tongurai *et al.*, 2001) and 2) esterification followed by transesterification (the two-stage process: TSP) (Veljković *et al.*, 2006; Prateepchaikul *et al.*, 2007). Both types aim to reduce the high FFA content to less than 1 wt.% in the first step and additionally, to convert the first step product into an ester by alkali-catalyzed transesterification (Ma and Hanna, 1998; Tongurai *et al.*, 2001; Veljković *et al.*, 2006; Prateepchaikul *et al.*, 2007). Since, TSP was quicker, cheaper and produced a higher yield, it was considered more suitable for producing biodiesel from high FFA mixed crude palm oil (Jansri, 2010 and Jansri, 2011). FFA in oils was converted into biodiesel (methyl ester; ME) with acid-catalyzed esterification (the first process). Then alkali-catalyzed transesterification was used to generate glycerides (TG, DG and MG) that contained in de-acidified oil into ME (Jansri, 2007).

Previously, crude tobacco seed oil, fryer grease, jatropha seed oil, mahua oil, mixed crude palm oil, rubber seed oil, and used cooking oil, having free fatty acid around 5 to 40 wt.%, had been investigated in biodiesel production by the latter two-stage process (Cannakci and Gerpan, 2001; Crabbe et al., 2001; Kac, 2001; Ramadhas et al., 2004; Ghadge and Raheman, 2005; Marchetti et al., 2005; Veljković et al., 2006; Prateepchaikul et al., 2007; Tiwari et al., 2007;).

The oil was preheated and fed into an esterification reactor. Then the reagents (alcohol and catalyst) were fed into the reactor. FFA containing in oil was reduced from 5 to 40 wt.% to less than 1-2 wt.% by converting into ME in 20 minutes to 5 hours. The suitable condition for converting FFA into biodiesel was a (2.5-20):1 molar ratio of methanol to oil and 0.8-3 wt.% of H_2SO_4 at 60°C. After reaching the first stage process, the solution was transferred to separation tank for separating the

impurities such as H_2SO_4, water and gum out of the oily solution. If this H_2SO_4 from the first stage solution still remained in the solution, more alkali catalyst would have to be used in the neutralization process (Thaweesinsopha, 2006). That caused methyl ester to promote the solubility in glycerol phase (Noureddini, *et al.*, 1998). In addition, if high water was not removed from the solution, saponification (Hanna, 2003) and hydrolysis (Prateepchaikul, et al., 2008) in transesterification process would occur. Final reason, if the first stage solution still contained high gum (phosphatide compound), phosphorous would be promoted to content in biodiesel that caused for decreasing in the lubricant of engine (www.blackcatbiodiesel.com, 2007).

The oily phase containing FFA to less than 2 wt.% was used as a raw material in transesterification. In transesterification, the de-acidified MCPO was preheated and fed into a transesterification reactor. After that the methoxide solution was fed into the reactor. it was found that over 90 wt.% of methyl ester was obtained in 20 minutes to 2 hours under molar ratio of methanol to oil around (3-9):1, the amount of alkali catalyst (NaOH or KOH) around 0.5-1 wt.%, plus the amount of alkali for neutralization (using titration technique applying from Taweesinsopha (2006)) at 60 °C.

Finally, crude biodiesel in which glycerol was already separated was generally purified by wet washing or dry washing process to remove glycerol, catalyst, excess methanol and impurities. Suwanmanee (2006) investigated spray and air bubble technique in wet washing process. Water around 200 vol.% of crude biodiesel in 14 hours was used and then cleaned biodiesel was heated at 70 °C around 30 minutes. Not only heating was used to remove the remained moisture in biodiesel, centrifuge and salt adsorption could also be used (Teall, *et al.*, 2003; Zullaikah, *et al.*, 2005). For saving water consumption and reducing time for de-moisture content, dry washing was preferred to purify crude biodiesel by ion exchanging with resin, amberlite and purolite, or absorbing with silicates, magnesol (magnesium silicates) and trisyl (Schroeder Biofuels, 1946).

1.2.2 The Two-Stage Continuous Process

Due to, in batch process, requirement of large size of reactor, high energy consumption, high labor cost and difficult to control the production quality (Darnoko, *et al.*, 1999; Frogler, 2006), the continuous process was investigated. Although many type of reactor can be used to produce biodiesel, the CSTR was chosen for producing biodiesel in this investigated due to low investment cost, suitability for liquid-liquid reaction and simply design. In the process, the CSTR was fed with a preheated mixture of oil, alcohol and catalyst continuously. At the same time, product was continuously removed from the reactor at the same feeding flow rate to a separation tank.

From the literature reviews, many of researchers studied the producing of biodiesel with the CSTR. For example, first, a 2 L high shear mixer tank combined with a 1 liter motionless mixer as shown in Figure 1.1 were used for producing biodiesel from soybean oil in Noureddini's experiment (1998).

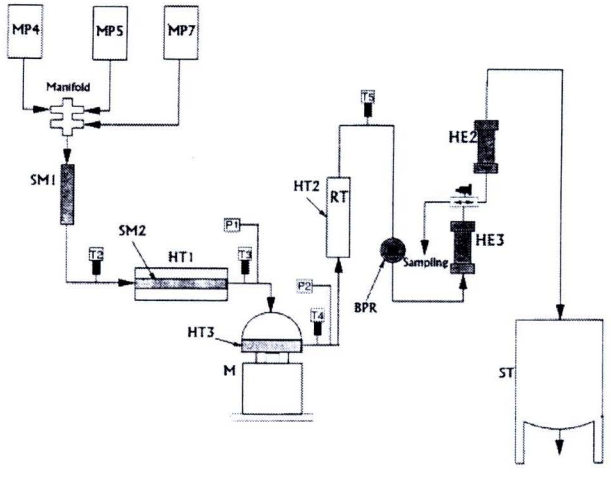


Figure 1.1 The pilot biodiesel plant in continuous process (Noureddini, *et al.*, 1998)

The methanol ratios at 6:1 and 8:1, and the amount of NaOH at 0.1-1.0 wt.% reacted with soybean. The speed of stirrer at 0-3600 rpm and the feeding flow rate at 0.25-0.35 L/min at 80 °C were used under the pressure of 172.37 kPa. The investigation indicated that it was not significant difference in the concentration of methyl ester

when the motionless mixer or high shear mixing at 1800 rpm was only used under the condition of a 6:1 molar ratio of methanol to oil and a 0.40 wt.% of NaOH. However, when the motionless mixer and high shear mixing were both used, it was found that 98% of methyl ester conversion was achieved. High conversion of methyl ester was obtained when large amount of methanol was used. Moreover, high catalyst concentration is also increased the conversion of biodiesel; however, it promoted the solubility of methyl ester in the glycerol layer.

Second, Darnoko, *et al.* (2000) found that methyl ester at 97.3 wt.% was obtained from the one litre continuous reactor (Figure 1.2) under the condition of a 6:1 molar ratio of methanol to oil by using potassium hydroxide as a catalyst and reaction time at 60 °C. The reaction was reached the reaction time at 60 minutes.

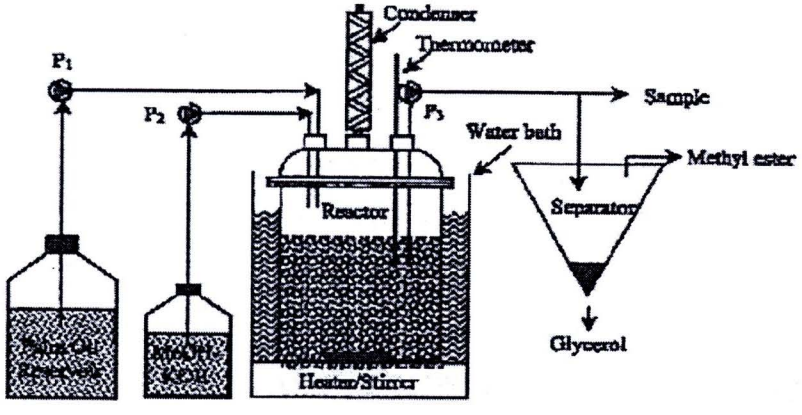


Figure 1.2 The continuous transesterification reactor (Darnoko, *et al.*, 2000)

Third, Leevijit et al. [7] investigated the design of continuous reactor for producing biodiesel from refined palm oil by transesterification under feeding flow rate at 10 L/hr of initial oil (Figure 1.3). After the kinetics of transesterification was investigated, the number of CSTR tank was estimated using the least-squares regression technique and solver tool in Microsoft Excel 2000 program. In addition, n CSTR tank was estimated at various resident times by computing the ME conversion according to the theory of PFR with MALAB (a commercial program). Those researchers showed that 6 ideal CSTR tank in series (2.27 L in total) was suitable for producing biodiesel in continuous system.

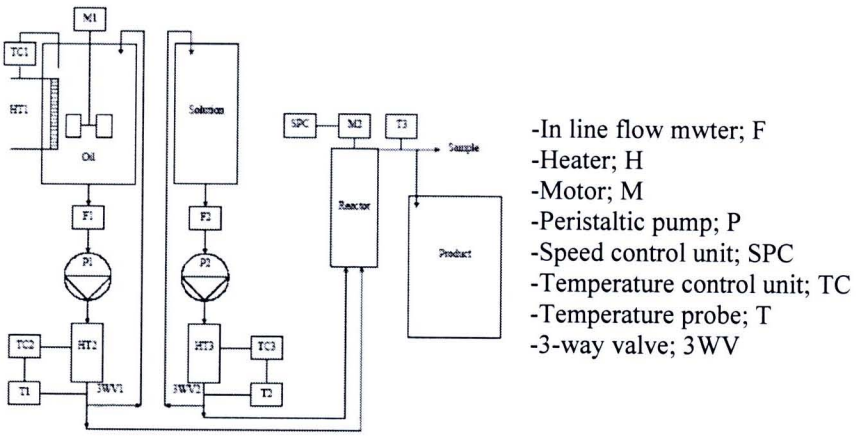
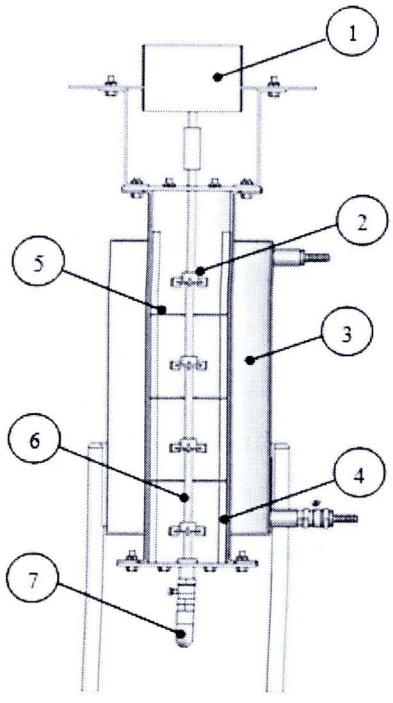


Figure 1.3 The continuous stirred tank reactor in 6 tanks series (Leevijit, 2006)

Fourth, the continuous stirred tank reactor (CSTR) was designed by Somnuk (2008). It was used to reduce high free fatty acid (FFA), which contained in mixed crude palm oil (MCPO), to less than 1 wt% of oil by the acid-catalyzed esterification continuous process. The continuous reactor was 4-CSTRs in series, which was separated by 3-separate plates and installed the six-blade disk turbine in each individual tank. In addition, 4-baffles were vertically installed on the walls of the tank for reducing swirling and still promoting good mixing as show in Figure 1.4.

As for methodology, first, MCPO, which consisted of FFA 9.966 wt.%, ME 0.621 wt.%, TG 83.718 wt.%, DG 4.566 wt.%, MG 0.676 wt.% and WT 0.458 wt.%, was heated until it reached 60 °C. After that, the suitable flow rate of MCPO, methanol and sulfuric at 7.603, 0.9201, and 0.260 L/hr, respectively was checked. Then they were fed into reactor which was heated by hot oil and stirred all the time. The periodically monitoring results indicated that 1 wt.% FFA could be reached when the operating time was throughout 5 times of retention time. The composition of de-acidified MCPO was FFA 0.472 wt.%, ME 13.622 wt.%, TG 76.626 wt.%, DG 6.381 wt.%, MG 1.073 wt.% and WT 1.826 wt.%



No.	Apparatus
1	Motor
2	6-blade disc turbine
3	Jacket
4	Baffle
5	Separate tank plate
6	Axle
7	Feeding hole

Figure 1.4 The continuous stirred tank reactor in 4 tanks series (Somnuk, 2008 and Prateepchaikul, *et al.*, 2009)

1.3 Objectives

1.3.1. To design and fabricate the two-stage continuous reactor having 50 L/hr MCPO feeding for producing methyl ester from high FFA mixed crude palm oil.

1.3.2. To design and fabricate separator, dry washing and methanol recovery system, which are suitable for this two-stage continuous system.

1.3.3. To investigate the performance of reactor and the suitable condition for the two-stage process continuous reactor, which can reduce high FFA (> 8 wt %) containing in MCPO to less than 1 wt.% of oil, by using esterification (the first stage) and produce methyl ester from MCPO that FFA was reduced by esterification in the first stage to more than 96.5 wt % of oil by transesterification (the second stage).

1.4 Scopes of Research Work

1.4.1. The two-stage continuous reactor for reducing high FFA (> 8 wt.%) in MCPO to less than 1 wt.% of oil, using esterification and producing methyl ester from MCPO that FFA was reduced by esterification to more than 96.5 wt.% of oil by transesterification will be designed and fabricated.

1.4.2. The two-stage continuous reactor having 50 L/hr MCPO feeding rate will be designed and fabricated for producing methyl ester from high free fatty acid MCPO.

1.4.3. The two-stage continuous reactor, separator, methanol recovery system and dry washing system will be installed and tested.