CHAPTER 1
INTRODUCTION

1.1 Background and Rationale

Energy is one of the important drivers of the economic growth contributing to the development of Thailand. Fossil fuels promote the majority of Thailand energy for driving industrial, agriculture, and transportation sectors. That is the reason to continuously increase the import of fossil diesel fuel for supporting high petroleum consumption in Thailand. In addition, the fossil diesel fuel causes significant pollution problems such as increasing of green house gases and sulfur dioxide. Therefore, alternative diesel fuels are being investigated to substitute the import of petroleum and to reduce pollution problems in Thailand. Moreover, alternative fuels make a balance growth on the demand side.

Biodiesel made from vegetable oils and animal fats, is one of the possible alternative fuels for diesel engines in Thailand because it is biodegradable, non-toxic, and produces low emissions of polluting gases. Furthermore, it also makes the balance between agriculture, economic, and environment needs. Accordingly, the biodiesel strategy of Thailand, which was established by the Thailand government in 2004, aims to produce and to use 10% biodiesel instead of fossil diesel demands in 2012 (8.5 million litres per day). There are seven oil vegetables in Thailand, which can be considered for producing biodiesel, such as oil palm, coconut, soybean, ground nut, jatropha, sesame, and sunflower seed. However, oil palm has regarded for utilization as the main material in the biodiesel production due to the highest potentiality of oil vegetables in Thailand. Hence this study is aimed at producing biodiesel by using palm oil as a raw material.

Generally, biodiesel (methyl ester) is the product of a chemical process: transesterification, which is the reaction of triglyceride with alcohol by using alkali catalyst. Raw materials in this process must be anhydrous and have low content of free fatty acid (FFA). Moisture and high FFA (more than 1 %wt) will cause the saponification reaction, which results in lower yields and washing difficulties. Thus, the acid-catalyzed transesterification, the enzyme-catalyzed transesterification, supercritical CO_2 techniques

and the two-stage process can be used to solve the problem arising from a high moisture and a high FFA content in vegetable oils and animal fats.

Mixed crude palm oil (MCPO), which was un-degummed, un-deacidified and a mixture between palm fibre oil and palm kernel oil having a high FFA (8-14 %wt) content, was used as a feedstock for the biodiesel production in this study because it is much cheaper than refined palm oil (RPO). At present, there are four methods that can be used to produce biodiesel from MCPO, which contains high FFA: the acid-catalyzed transesterification, the enzyme-catalyzed transesterification, supercritical techniques, and the two-stage process. However, the two-stage process was preferred to produce biodiesel from MCPO in this work because of the need to generate biodiesel in a short time, at a low temperature, and a low pressure. The two-stage process reduced the high FFA content to less than 1 %wt with an acid-catalyzed esterification in the first step. After that, the alkali-catalyzed transesterification converted the first step product into ester.

Currently, it is difficult to predict the capacity of a reactor required to produce biodiesel from MCPO at the end of the two-stage process reaction when the ratio of methanol to oil and the reaction temperature were changed. Consequently, the aim of this thesis is to create a biodiesel reaction model of the two-stage process on MATLAB7 by using mathematical techniques and chemical equations for predicting biodiesel production. In addition, the molar ratio of methanol to oil and the reaction temperature, which have an effect on the two-stage of biodiesel reaction, are investigated.

1.2 Literature Review

Foon, *et al.*, (2004) studied the kinetics of the base-catalyzed transesterification of palm oil based on the molar ratio of methanol to oil, the amount of catalyst, and the reaction temperature to optimize the conversion rate. Their findings showed that both sodium hydroxide and sodium methoxide had high kinetics indicating the fast formation of palm oil methyl esters with conversions above 99 %. Fast formation of palm oil methyl esters with a rate constant of 0.163 litre mole min^{-1} were obtained when reaction was carried out at 60 degree Celsius, using a 1:10 molar ratio of oil to methanol, and catalyzed by 0.125 mole kg^{-1} oil NaOH.

Darnoko, *et al.*, (2000) studied the kinetics of methyl ester produced from palm oil, which was produced by the transesterification of palm oil with methanol using KOH. The rate of transesterification in a batch reactor with temperatures up to 60 degree Celsius did not reduce the time to reach the maximal conversion. The conversion of TG, DG, and MG appeared to be second order up to 30 min of reaction time. Reaction rate constants for TG, DG, and MG hydrolysis reactions were 0.018-0.191 %wt mol min^{-1} and were higher at higher temperatures and higher MG reaction than for the TG hydrolysis. Activation energies for TG, DG, and MG hydrolysis reactions were 14.7, 14.2, and 6.4 kcal/mol, respectively. The optimal catalyst concentration was 1 % KOH.

Noureddini, *et al.*, (1997) studied the transesterification of soybean oil. Three stepwises and reversible reactions are believed to occur. The effect of variations in the mixing intensity (Agitator Reynolds number = 3,100 to 12,400) and temperatures (30 to 70 degree Celsius) on the rate of reaction were studied while the molar ratio of alcohol to triglyceride [6:1] and the concentration of catalyst [0.20 %wt] were held constant. Variations in the mixing intensity appeared to affect the reaction in a similar way to the variation in temperature. A reaction mechanism was proposed consisting of an initial mass transfer-controlled region followed by a kinetically controlled region. Experimental data for the latter region appeared to be in good agreement with a second-order kinetic mechanism. Reaction rate constants and activation energies were determined for all forward and reverse reactions.

Jansri, *et al.*, (2007) studied the acid-catalyzed esterification for reducing high free fatty acid (FFA), which occurs in mixed crude palm oil (MCPO), using a constant-temperature hot water bath based on parameters such as the speed of stirrer, the catalyst concentration (H_2SO_4), the molar ratio of methanol to oil and the reaction temperature. Samples were analyzed by Thin Layer Chromatography for determining the decreasing FFA concentration in MCPO. High FFA initially found in MCPO was rapidly reduced to less than 1 %wt in the first 30 seconds under reaction conditions of a 3:1 molar ratio of methanol to oil and 0.8 %wt H_2SO_4 at 60 degree Celsius.

Thaweesinsopha, (2006) and Thaweesinsopha, *et al.*, (2005) studied the two-stage process for producing methyl ester from mixed crude palm oil (MCPO), which was degummed with phosphoric acid, in a batch reactor. In the first step (esterification), H_2SO_4 was used as catalyst at concentrations of 1, 3, and 5 %wt. The second step (transesterification) used alkali catalyst (NaOH) at the concentration of 2 %wt. This study varied the molar ratio of methanol to oil in both steps at 24, 30, and 36 %v. The composition of the biodiesel production was analyzed with Thin Layer Chromatograph. Results showed yields of methyl ester as high as 99 % under the molar ratio of methanol to oil at 30 %v and the concentration of H_2SO_4 and NaOH at 3 and 2 %wt, respectively.

Veljković, *et al.*, (2006) studied the production of fatty acid methyl esters (FAME) from crude tobacco seed oil (TSO) having high FFA content. Due to its high FFA content, TSO was processed in two steps: the acid-catalyzed esterification (ACE) followed by the base-catalyzed methanolysis (BCM). The first step reduced the FFA level to less than 2% in 25 min for a molar ratio of 18:1. The second step converted the product of the first step into FAME and glycerol. The maximum yield of FAME was approximately 90 % in about 30 min.

Ghadge, *et al.*, (2005) developed a technique to produce biodiesel from mahua oil (Madhuca) having high FFA (19 % FFA). The high FFA level of mahua oil was reduced to less than 1 % by a two-step pretreatment process. Each step was carried out with 0.30-0.35 %v methanol to oil ratio in the presence of an acid catalyst (H_2SO_4) at 1 %v in 1 hour reaction at 60 degree Celsius. After the reaction, the mixture was allowed to settle for an hour and the methanol-water mixture that separated at the top was removed. The second step, the product of the bottom fraction was transesterified using methanol 0.25 %v and alkaline catalyst (KOH) 0.7 % wt/v to produce biodiesel.

Zullaikah, *et al.*, (2005) studied a two-step acid-catalyzed methanolysis process for the efficient conversion of rice bran oil into methyl ester. The first step was carried out at 60 degree Celsius. Depending on the initial FFA content of oil, 55-90 % methyl ester content in the reaction product was obtained. More than 98 % FFA and less than 35 % of TG were reacted in 2 hours. The organic phase of the first reaction product was used as the substrate for a second acid-catalyzed methanolysis at 100 degree Celsius.

By this two-step methanolysis reaction, more than 98 % methyl ester in the product can be obtained in less than 8 hours. The distillation of the reaction product gave 99.8 % methyl ester with recovery of more than 96 %.

Ramadhas, *et al.*, (2004) developed a two-step transesterification process to convert high FFA oils to corresponding esters. In the first step, the acid-catalyzed esterification reduced the FFA content of the oil to less than 2 %. The second step, the alkaline-catalyzed transesterification process converts products of the first step to its ester and glycerol. Major factors affecting the conversion efficiency of the process such as alcohol molar ratios, the catalyst concentration, the reaction temperature, and the reaction time were analyzed. The two-step esterification procedure was used to convert rubber seed oil to its methyl ester.

Cradde, *et al.*, (2001) studied three principal variables: the molar ratio of methanol to oil, the amount of catalyst, and the reaction temperature, affecting the yield of the acid-catalyzed production of methyl ester (biodiesel) from crude palm oil. The optimized variables, a 40:1 molar ratio of methanol to oil with 5 % H_2SO_4 reacted at 95 degree Celsius for 9 hours, gave a maximum ester yield of 97 %.

Kac, (2001) produced methyl ester from used cooking oil with a two-stage process. Before producing the biodiesel, the water content must be reduced. The first step generated biodiesel with 8%v methanol and 0.1 %v H_2SO_4 as catalyst in 1 hour at 35 degree Celsius. Then the mixture was rested overnight. In the second step, the mixture was heated to 55 degree Celsius and the reaction carried out with sodium methoxide (the mixture of 12 % methanol and 0.3 %wt/v NaOH). The mixture was allowed to settle for 1 hour to separate glycerine from biodiesel.

Kac, (2000) studied the two-stage process, which was used to produce biodiesel from waste vegetable oil. Each step was carried out with a 0.75 of prepared methoxide (the mixture of 25 %v methanol to oil ratio and a base catalyst (NaOH) at 0.625 %wt/v) in 1 hour at 48-52 degree Celsius. After the reaction, the mixture was allowed to settle for 12 hours and glycerin that separated at the bottom was removed. In the second step, the product at the top was transesterified using remaining methoxide to

produce biodiesel in 1 hour at 48-52 degree Celsius. Kac allowed the mixture to rest for 12 hours to separate glycerine from ester.

Jansri, *et al.*, (2007) created a model for predicting the biodiesel production from soybean oil and palm oil at 50, 55, 60, and 65 degree Celsius. This model, which was extended from the Allen and Prateepchaikul's model, was created in MATLAB7 by using the Runge-Kutta method, and the rate law and rate constants of transesterification. There was no significant difference in results when methyl ester values of this model were compared with "The Modeling of The Biodiesel Reaction and Runge-Kutta method". Therefore, this model could be used to calculate methyl ester yields from soybean oil and palm oil.

Allen, *et al.*, (2003) created a model for reversible reactions to predict the production of palm oil methyl ester. In this case, a finite-difference technique was used based on simple worksheet functions. The resulting model was compared with results published in the literature as well as with results obtained in the Department of Mechanical Engineering of the Prince of Songkla University. Applying this model made possible several recommendations to enhance palm oil methyl ester production in a batch reactor of the form currently operated by the Energy Group of the Prince of Songkla University.

1.3 Objectives of this Present Work

1. To create a biodiesel reaction model of the two-stage process by using the kinetics of the two-stage process and suitable mathematical techniques.

2. To study the effect of the molar ratio of methanol to FFA in the first stage process, of the molar ratio of methanol to TG in the second stage process, and of the temperature on the two-stage process of biodiesel production.

1.4 Expected Result

The biodiesel reaction model of the two-stage process could be used to predict methyl ester yields from MCPO by using the acid-alkali catalyst in the two-stage process.

1.5 Scopes

1. To design the model for a two-stage reversible process using MATLAB7, which using the initial concentration of TG, FFA, DG, MG, ME, GL, and WT as boundary until the second conditions reaction was achieved by using the kinetics of the two-stage process

2. To study the effect of the molar ratio of methanol to FFA in the first stage process, of the molar ratio of methanol to TG in the second stage process, and of temperatures variation on esterification and transesterification.