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Topic: Design of Two-Stage Continuous Reactor for Producing Methyl Ester from High Free Fatty Acid Mixed Crude Palm Oil

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ABSTRACT

Generally, high quality of biodiesel in high productivity is required under the low cost investment. Therefore, the continuous stirred tank reactors (CSTR) are preferred in the investment because it is easy to fabricate and to control the product quality from liquid-liquid reaction under the low cost investment. The principle of kinetics, unit operation of chemical engineering and heat transfer are used to design CSTR for producing biodiesel from mixed crude palm oil (MCPO) via the two-stage process (esterification followed by transesterification). After finishing the design, the designed system was verified by simulating with The ASPEN PLUS Simulation Engine (chemical commercial program). Finally, the system was fabricated and operated. The results indicated that the efficiency of the two-stage continuous process in full system was lower than the design around 10 %. FFA could be reduced from 16-18 wt% to less than 1 wt% under the optimization of 23.04 v% of methanol, 2.07 v% of sulfuric acid, 2.22 min of retention time, and 793 rpm of stirrer speed (40 L/hr of oily solution yield and 15 L/hr of waste solution yield). The concentration of biodiesel at 95.70 wt% having yield around 43 L/hr and of glycerin around 12 L/hr was obtained under the test operated condition of 24 v% of methanol and 1 %wt/v of potassium hydroxide under 4 min of retention time of and 793 rpm of stirrer speed. After purification, it was found that 75.06% of biodiesel based on initial MCPO (84.44% of biodiesel based on acidified MCPO) was obtained.

Keywords: Biodiesel, Continuous reactor, CPO, Methyl ester, Mixed crude palm oil, The two-stage process

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NOMENCLATURES

A	The initial regent
A_d	The surface area of decanter (m^2)
A_i	Area of inner surface of reactor (m)
A_o	Area of outer surface of reactor (m)
A_m	Logarithmic mean area (m^2)
A_s	Surface area (m^2)
ASTM	American standard test method
[A]	The molar concentration of reagent A
[AL]	The concentration of alcohol (mol/L)
a	The coefficient of reagent A, The reaction order of reagent A and FFA
a_1	The experiment determined constant
B	The initial reagent
[B]	The molar concentration of reagent B
b	The coefficient of reagent B, The reaction order of reagent B and alcohol
C	The product
C_A, C_{A0}	The concentration of reagent A (mol/L)
C_{AL}	The concentration of alcohol (mol/L)
C_B, C_{B0}	The concentration of reagent B (mol/L)
C_C, C_{C0}	The concentration of product C (mol/L)
C_D, C_{D0}	The concentration of product D (mol/L)
C_{DG}	The concentration of diglyceride (mol/L)
C_E	The concentration of ester (mol/L)
C_{FFA}	The concentration of free fatty acid (mol/L)
C_{GL}	The concentration of glycerol (mol/L)
C_{MG}	The concentration of monoglyceride (mol/L)
C_p	Specific heat at constant pressure, KJ/kg· °C or KJ/kg·K
C_{TG}	The concentration of triglyceride (mol/L)
C_{WT}	The concentration of water (mol/L)
CSTR, CSTRs	Continuous stirred tank reactors
[C]	The molar concentration of product C

NOMENCLATURES (Cont')

c	The coefficient of product C, The reaction order of product C and ester
D	The product
D_a	Diameter of turbine impeller (cm)
D_{am}	The diameter of impeller (m)
D_d	Diameter of turbine impeller disc (cm)
D_h	Diameter of hole on separate plate (cm)
D_i	The inside diameter of reactor (m)
D_o	The outside diameter of reactor (m)
D_r	Diameter of reactor or tube (m)
D_s	Diameter of separate tank plate (cm)
D_t, D_{tm}	The diameter of reactor or tank (cm, m)
DG	Diglyceride
[D]	The molar concentration of product D
[DG]	The concentration of diglyceride (mol/L)
d	The coefficient of product D, The reaction order of product D and water
E_s	Space between turbine and bottom tank (cm)
EN	European test method
[E]	The concentration of ester (mol/L)
e	The thickness of turbine (cm)
F_A, F_B, F_C, F_D	The molar flow rate
F_{A0}, F_{B0}, F_{C0}, F_{D0}	The initial molar flow rate
F_{A1}	The molar flow rate (mol/min)
FFA	Free fatty acid
[FFA]	The concentration of free fatty acid (mol/L)
f	The thickness of axle (cm)
G	Space between baffle and wall (cm)
GL	Glycerol
[GL]	The concentration of glycerol (mol/L)
g	The thickness of axle ring (cm)
H_n	Reactor height (m)

NOMENCLATURES (Cont')

H_t, H_{tm}	The height of reactor or tank (cm, m)
HOR', HOR"	Alcohol
H_2O	Water
H_2SO_4	Sulfuric acid
$h_{horizontal,\ n\ tube}$	The average heat transfer coefficient for vertical tier of *N* horizontal tube (W/m·°C)
$h_{horizontal,\ 1\ tube}$	The average heat transfer coefficient for vertical tier of 1 horizontal tube (W/m·°C)
h_i, h_2	The convection heat transfer coefficients inside ($W/m^2\cdot{}^\circ C$)
h_o, h_1	The convection heat transfer coefficients outside ($W/m^2\cdot{}^\circ C$)
J	Baffle width (cm)
KOH	Potassium hydroxide
k	Thermal conductivity, W/m· °C
k_a, k_1	The rate coefficient of the forward reaction
k_{-a}, k_2	The rate coefficient of the reverse reaction
k_m	Thermal conductivity of reactor material or tube wall ($W/m^2\cdot{}^\circ C$)
k_y	The amount of independent variables
L	Blade length (cm)
L_d	The length of decanter (m)
L_j	The length of jacket (m)
L_t	The thickness of reactor wall (m)
MCPO	Mixed crude palm oil
ME	Methyl ester or biodiesel
MeOH	Methanol
MG	Monoglyceride
[MG]	The concentration of monoglyceride (mol/L)
$\dot{m}$	Mass flow rate (kg/s)
N, N_s	The speed of stirrer (rpm, rps)
N	The number of horizontal tube vertical tier (tube)
N_{min}	The minimum number of distillatory plate

NOMENCLATURES (Cont')

N_{RE}	Reynolds number
NaOH	Sodium hydroxide
Nu	Nusselt number
n	The number of fin
P'_A	Vapor pressure of components A (N/m^2)
P'_B	Vapor pressure of components B (N/m^2)
PBR	Packed bed reactor
PFR	Plug-flow tubular reactor
Pr	Prandtl number
Q	The mixing flow rate (m^3/hr)
$\dot{Q}$	Rate of heat transfer of inner solution (KJ/s)
R, R', R", R'''	Alkyl group
R'COOH	Organic acid
RCOOR', R'COOR"	Ester
Re	Reynolds number
r_A	The reaction rate of regent A
r_{AL}	The reaction rate of alcohol ($mol \cdot L^{-1} \cdot min^{-1}$)
r_{A1}	The reaction rate of the first reactor
r_{A2}	The reaction rate of the second reactor
r_{DG}	The reaction rate of diglyceride ($mol \cdot L^{-1} \cdot min^{-1}$)
r_E	The reaction rate of ester ($mol \cdot L^{-1} \cdot min^{-1}$)
r_{FFA}	The reaction rate of free fatty acid ($mol \cdot L^{-1} \cdot min^{-1}$)
r_{GL}	The reaction rate of glycerol ($mol \cdot L^{-1} \cdot min^{-1}$)
r_i	Inner radius (m)
r_{MG}	The reaction rate of monoglyceride ($mol \cdot L^{-1} \cdot min^{-1}$)
r_o	Outer radius (m)
r_{TG}	The reaction rate of triglyceride ($mol \cdot L^{-1} \cdot min^{-1}$)
r_{WT}	The reaction rate of water ($mol \cdot L^{-1} \cdot min^{-1}$)
S	The optimum fin spacing (m)
SFT	Saponification followed by transesterification
T_1	Temperature at outside reactor wall (°C)

NOMENCLATURES (Cont')

$T_{1\infty}$	Temperature of paraffin oil (°C)
T_2	Temperature of inside reactor wall (°C)
$T_{2\infty}$	Temperature of solution in reactor (°C)
TG	Triglyceride
TLC/FID	Thin Layer Chromatography/ Flame Ionization Detector
TSP	The two-stage process
[TG]	The concentration of triglyceride (mol/L)
t	The fin thickness (m)
t_s	The separation time (hr)
t_T	The mixing time (s)
U	The force convection relations ($W/m^2 \cdot °C$)
U_o	The outer surface reactor overall heat transfer coefficient ($W/m^2 \cdot °C$)
V	The volume of reactor (L)
V_A	The volume of axle (cm^3)
V_{AR}	The volume of axle ring (cm^3)
V_B	The volume of four cylindrical baffles (cm^3)
VBL	The volume of six-blade (cm^3)
VD	The volume of disc (cm^3)
V_R	The volume of reactor (cm^3)
V_1	The volume of the first reactor (L)
V_2	The volume of the second reactor (L)
W	Blade width (cm)
Ws	The width surface of reactor (m)
WT	Water
[WT]	The concentration of water
X	Conversion
X_1	The conversion of the first reactor
X_2	The conversion of the second reactor
x_B	Mole fraction in bottom product
x_D	Mole fraction in overhead product
x_i, x_j	Independent variables

NOMENCLATURES (Cont')

x_w	Thickness of tube (m)
y	Response
Z_{A1}	The heavy phase depth (a half of the liquid depth) and the height of feed mixture entrance
Z_{A2}	The height of the heavy liquid overflow
Z_T	The liquid depth (90 % of the full separated tank) and the height of the light liquid overflow
β_0, β_i, β_{ij}, β_{ii}	Coefficient
ΔT	Temperature difference of solution (°C)
ΔT_{lm}	The logarithm mean temperature difference solution
ΔT_p	Temperature difference of paraffin oil (°C)
α	The center point
α_{AB}	Relative volatility of component A to component B
ρ	The density of liquid (kg/m^3)
ρ_A	The density of liquid of solution A (kg/m^3)
ρ_B	The density of liquid of solution B (kg/m^3)
τ	The retention time (min)
μ	The viscosity of liquid (Pa.s)
μ_t	The total viscosity (cP)
ν	The volumetric flow (L/min)
ν_k	Kinematics viscosity, m^2/s
ν_m	The mean velocity of liquid (m/s)
ν_0	The volumetric flow (L/min)
(1)	Triglyceride
(2)	Alcohol
(3)	Ester
(4)	Glycerol

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).

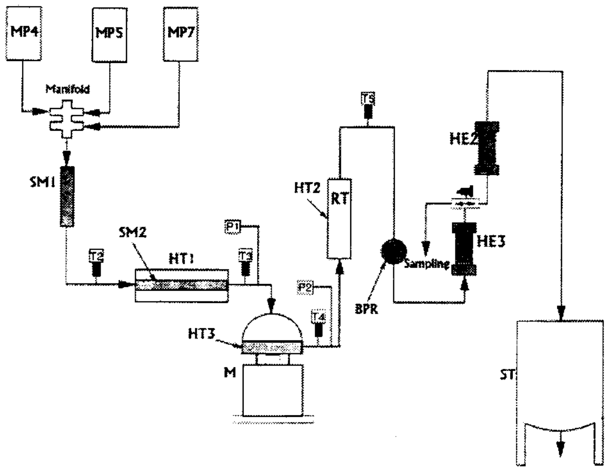
The oily phase containing FFA to less than 2 wt.% was used as a raw material in transesterification. In transesterification, the de-acidified MCPO was preheated and fed into a transesterification reactor. After that the methoxide solution was fed into the reactor. it was found that over 90 wt.% of methyl 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).



-Metering pumps: MPn,
-Motionless mixers: SMn,
-Heater: HTn,
-High shear mixer: M,
-Pressure transducers: Pn,
-Thermocouples: Tn,
-Residence tube: RT,
-Back Pressure regulator: BPR,
-Heat exchangers: Hen,
-Separator tank: ST

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.

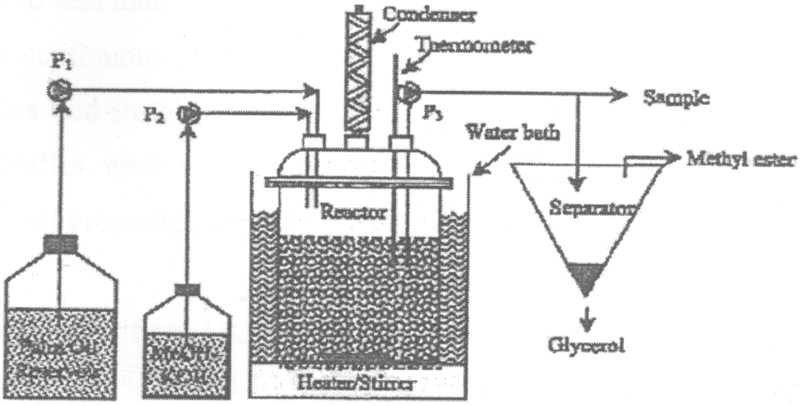
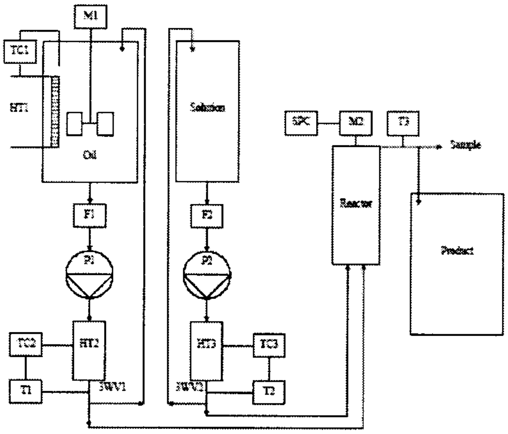


Figure 1.2 The continuous transesterification reactor (Darnoko, *et al.*, 2000)

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.

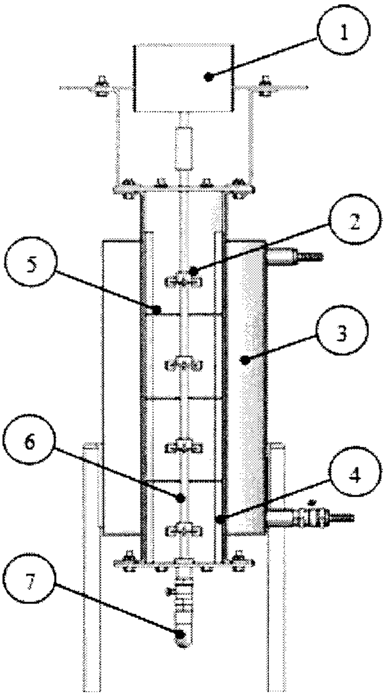


-In line flow mwter; F
-Heater; H
-Motor; M
-Peristaltic pump; P
-Speed control unit; SPC
-Temperature control unit; TC
-Temperature probe; T
-3-way valve; 3WV

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.

CHAPTER 2

THEORIES

2.1 History of Biodiesel

One hundred years ago, ground-nut oil was tested as fuel for the internal combustion diesel engine by Rudolf C. Diesel in 1885. However, vegetable oil was out of favour as a fuel in diesel engine because petroleum at that time was cheap. Until 1930s, alternative diesel fuels were investigated because it is the first time that the world met an oil crisis. Presently, the demand for fossil diesel fuel in this world is more than its supply and the price of petroleum has increased. In addition, petro-diesel is a main source of air pollution (green house gases: carbon dioxide and acid rain: sulfur dioxide). Therefore, vegetable oils and animal fats have returned to be used as an alternative diesel fuels.

Previously, if non-modified vegetable oils were used directly in diesel engines, they caused carbon deposits in the engine, decreased the durability of the engine, and caused lubricating oil contamination. In addition, animal fats could not be directly used as fuel because they were forming solid at ambient temperatures. Consequently, modified vegetable oils and animal fats were proposed as alternative fuels for diesel engines because their properties were similar to petro-diesel such as cetane number, density, and viscosity.

Microemulsion, pyrolysis, and transesterification are processes used to modify vegetable oils and animal fats to alternative diesel fuels now. However, transesterification is the basic method preferable used to generate biodiesel from vegetable oils and animal fats, because it is easier to produce biodiesel and to find suitable raw materials.

2.2 Biodiesel Production

In biodiesel production, biodiesel quality may not be reached the standard requirement. There is a possibility that the low quality of raw materials is used to produce biodiesel by transesterification. In addition, the reaction and other parameters such as mixing intensity, temperature and reaction time are not suitable for produce biodiesel from some materials. In order to obtain the standard biodiesel quality of Thailand, main parameters such as quality of raw materials, reactions and other parameter effects should be investigated.

2.2.1 Raw Materials

2.2.1.1 Fats and Oils

Oils and fats, water-insoluble substance, consisted of mono-, di- and tri-glycerides, which are the combination of one-three molecules of fatty acids and one molecule of glycerol, respectively. Chains of fatty acids in mono-, di- and tri-glyceride structure are specified by two numbers with a colon. The first numeral is a number of atoms of carbon in the chain that comprise carboxylic carbon at the end of fatty acid (the carbon atom has a double bond with the oxygen atom). The second numeral is the number of the double bonded atom (carbon atom to carbon atom) in fatty acid chain as shown in Table 2.1. In Table 2.2, vegetable oil and animal fats have variable saturation, chain length, and steric hindrance, which cause different rate coefficients to occur in the transesterification reaction.

Table 2.1 Fatty acid structure (Srivastava, *et al.*, 2000)

Fatty acid	Systematic name	Structure	Formula
Lauric	Dodecanoic	12:0	$C_{12}H_{24}O_2$
Myristic	Tetradacanoic	14:0	$C_{14}H_{28}O_2$
Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$
Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$
Oleic	*cis*-9-Octadecanoic	18:1	$C_{18}H_{34}O_2$
Linoleic	*cis*-9,*cis*-12-Octadecadienoic	18:2	$C_{18}H_{32}O_2$
Linolenic	*cis*-9,*cis*-12,*cis*-15-Octadecatrienoic	18:3	$C_{18}H_{30}O_2$
Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$
Behenic	Docosanoic	22:0	$C_{22}H_{44}O_2$
Erucic	*cis*-13-Docosenoic	22:1	$C_{22}H_{42}O_2$
Lignoceric	Tetracosanoic	24:0	$C_{24}H_{48}O_2$

To meet the requirement of Thai government strategy, MCPO, having high FFA and un-degumming, a mixture of palm fibre oil and palm kernel oil, will offer to be used as a raw material in this work. Palm oil, like other edible oils, is an organic compound which is called a glyceryl ester because each molecule is comprised of a glycerol

Table 2.2 The percentage of common fatty acids in oils and fats

Oils and fats	Type of fatty acid composition (%wt/wt)											References
	12:0	**14:0**	**16:0**	**18:0**	**18:1**	**18:2**	**18:3**	**20:0**	**22:0**	**22:1**	**24:0**	
Cottonseed oil	-	-	28.33	0.89	13.27	57.51	0.00	0.00	0.00	0.00	0.00	Ma, *et al.*, 1998
Mahua oil	-	-	16.00-28.20	20.00-25.10	41.00-51.00	8.90-13.70.	-	0.00-3.30	0.00	0.00	0.00	Srivastava, *et al.*, 2000
Peanut oil	-	-	11.38	2.39	48.28	31.95	0.93	1.32	2.52	0.00	1.23	Ma, *et al.*, 1998
Crude palm oil	0.00	0.30	46.70	3.10	42.60	9.50	0.20	0.40	-	-	-	Crabbe, *et al.*, 2001
Rapeseed oil	-	-	3.49	0.85	64.40	22.30	8.23	0.00	0.00	0.00	0.00	Ma, *et al.*, 1998
Crude rice bran oil	0.10-0.30	0.70-0.90	12.40-23.00	2.05-2.35	39.88-41.37	35.04-36.16	1.58-2.10	0.10-0.30	0.20-0.40	-	0.34-0.86	Zullaikah, et al.,2005
Soy bean oil	-	0.00-0.10	10.00-10.70	3.80-4.30	23.40-26.70	49.70-53.90	6.80-8.50	0.30-0.50	0.30-0.40	-	-	Liberty Vegetable Oil Company, 2000
Lard	0.10	1.40	23.60	14.20	44.20	10.70	0.40	-	-	-	-	Ma, *et al.*, 1998
Beef tallow	-	2.00-8.00	24.00-37.00	40.00-50.00	-	1.00-5.00	-	-	-	-	-	Ma, *et al.*, 1998

molecule bonded to a maximum of three fatty acid (carboxylic acid) residues. Each of the three fatty acid groups in palm oil is long chains comprising several carbon atoms (normally 14-20 atoms in length) but palmitic acid, oleic acid, stearic acid and linoleic acid are mainly fatty acids, which are found in MCPO.

2.2.1.2 Alcohols

Many several primary and secondary monohydric aliphatic alcohols having one to eight carbon atoms such as methanol, ethanol, buthanol, and amyl alcohol are suitable for being used in transesterification process. There are two main types of alcohol (methanol and ethanol), which are more preferred to be used as a reagent in biodiesel production. In fact, although the reaction that used methanol as a reagent is controlled by mass transfer, methanol is more commercially used as a raw material in biodiesel production than ethanol because it is cheap, easy to recover, easy to recycle, and denature. Moreover, glycerides can react quickly with methanol, catalyst can be simply dissolved in it and it does not promote strong emulsion form after finishing the reaction. Presently, although single alcohol is used in the biodiesel production, the mixture of two or more alcohols is offered because the obtained product can be used as fuel in diesel engine at low temperature. Most of all, the low moisture content in a raw material is required in process; therefore, the purity of alcohol at least 98 wt% must be used.

2.2.1.3 Catalysts

There are many several types of acid, base, and enzyme such as sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), and lipase which can be used as a catalyst in the transesterification. Alkali catalyst is the most frequently used to catalyze the reaction because it gives faster rate than acid and enzyme catalysis. However, if the oil containing high FFA and/or high moisture is used to produce biodiesel, saponification will be formed. That causes reduction in the biodiesel yield.

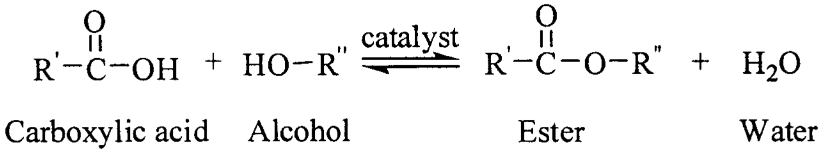
For solving saponification problem, acid catalyst is preferred to be used as a catalyst to produce biodiesel from the oil having high FFA and/or high moisture by transesterification reaction. In addition, acid catalyst is not only used as a catalyst in esterification but also as a main reagent for de-gumming or reducing phosphatide compound instead of phosphoric acid when the un-degummed crude oil (having high FFA) is used as a raw material in biodiesel production,. Therefore, the reaction time for preparing crude oil will be reduced.

As for the enzyme, it can effectively convert all of glycerides to biodiesel, but the product cost of enzyme catalytic is much expensive than other catalysts and the reaction time is much longer. Therefore, the process for producing biodiesel has not been popular with enzyme catalyst.

2.2.2 Relative Reactions

2.2.2.1 Esterification

In Equation 2.1, carboxylic acids react with alcohol to produce esters, which identify the reaction of esterification. Esters are compounds in which the hydroxyl group of carboxylic acid is substituted by an R"O group of alcohol. When ester is treated with acid or base in aqueous solution, the molecule of the ester divides into alcohol and an acid compound by hydrolysis. As for biodiesel production by a two-stage process, esterification is used to convert high FFA in oil to biodiesel by reacting it with alcohol using acid catalyst as shown in Equation 2.1.

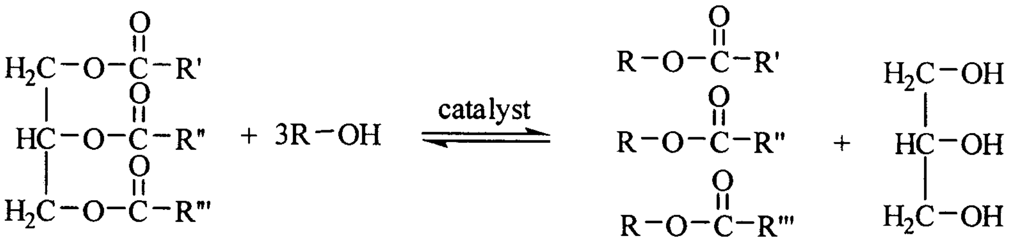


$$\underset{\text{Carboxylic acid}}{R'-\overset{\overset{O}{\parallel}}{C}-OH} + \underset{\text{Alcohol}}{HO-R''} \xrightleftharpoons{\text{catalyst}} \underset{\text{Ester}}{R'-\overset{\overset{O}{\parallel}}{C}-O-R''} + \underset{\text{Water}}{H_2O} \qquad (2.1)$$

2.2.2.2 Transesterification

Transesterification is a chemical process used to replace alcohol in ester with new one to generate new ester as shown in Equation 2.2. In the biodiesel production, 1, 2, 3-propanetriol (glycerol) of triglycerides is replaced with methanol or ethanol using catalyst for generating new ester (biodiesel) via transesterification as shown in Equation 2.3.

$$\begin{array}{ccccccc} RCOOR' & + & R''OH & \underset{}{\overset{\text{catalyst}}{\rightleftharpoons}} & RCOOR'' & + & R'OH \\ \text{Ester}_1 & & \text{Alcohol}_1 & & \text{Ester}_2 & & \text{Alcohol}_2 \end{array} \qquad (2.2)$$

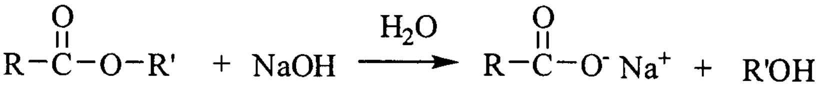


$$\begin{array}{l} H_2C-O-\overset{O}{\overset{\|}{C}}-R' \\ \;| \\ HC-O-\overset{O}{\overset{\|}{C}}-R'' \\ \;| \\ H_2C-O-\overset{O}{\overset{\|}{C}}-R''' \end{array} + 3R-OH \overset{\text{catalyst}}{\rightleftharpoons} \begin{array}{l} R-O-\overset{O}{\overset{\|}{C}}-R' \\ R-O-\overset{O}{\overset{\|}{C}}-R'' \\ R-O-\overset{O}{\overset{\|}{C}}-R''' \end{array} + \begin{array}{l} H_2C-OH \\ \;| \\ HC-OH \\ \;| \\ H_2C-OH \end{array}$$

Triglyceride Alcohol Ester Glycerol (2.3)

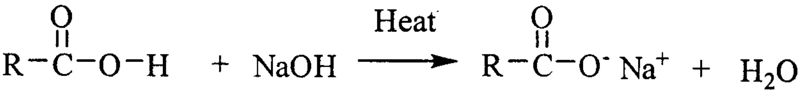
2.2.2.3 Saponification

Saponification is the hydrolysis reaction of an ester with strong base (NaOH and KOH). The ester is transferred into sodium salt of a long-chain carboxylic acid (soap) and alcohol as shown in Equation 2.4. In addition, the strong base transfers the FFA to soap and water as shown in Equation 2.5 during the reaction and emulsifies the mixture of glycerol and ester. It is difficult to recover ester from gel and to separate ester from the emulsion. Therefore, saponification is a significant cause of ester yield reduction in the biodiesel reaction.



$$R-\overset{O}{\overset{\|}{C}}-O-R' + NaOH \xrightarrow{H_2O} R-\overset{O}{\overset{\|}{C}}-O^-Na^+ + R'OH$$

Ester Sodium Hydroxide Sodium Salt Alcohol (2.4)



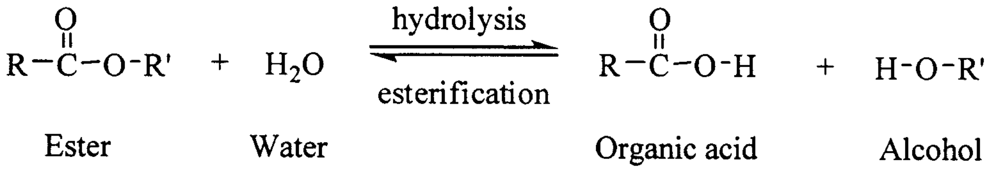
$$R-\overset{O}{\overset{\|}{C}}-O-H + NaOH \xrightarrow{\text{Heat}} R-\overset{O}{\overset{\|}{C}}-O^-Na^+ + H_2O$$

FFA Sodium Hydroxide Sodium Salt Water (2.5)

2.2.2.4 Hydrolysis

Hydrolysis (reversible reaction of esterification) is the reaction between ester and water catalyzed by sulfuric acid to produce organic acid and alcohol as shown in

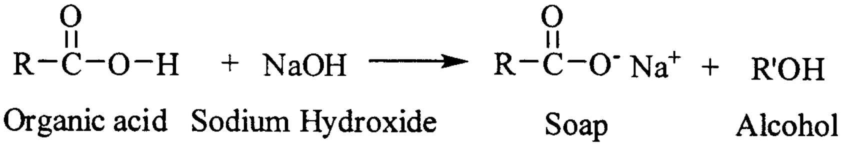
Equation 2.6. Therefore, this reaction depends on the amount of water, if the raw material has a lot of water; a lot of organic acid and alcohol are obtained.



$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}O{-}R'} + \mathrm{H_2O} \underset{\text{esterification}}{\overset{\text{hydrolysis}}{\rightleftharpoons}} \mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}O{-}H} + \mathrm{H{-}O{-}R'}$$

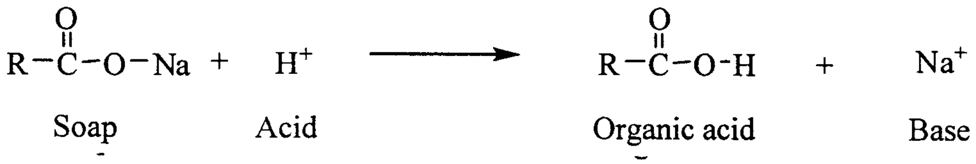
(2.6)

In addition, if alkali catalyst (sodium hydroxide and/or potassium hydroxide) is used as catalyst in hydrolysis reaction instead of acid catalyst, organic acid and alcohol are also occurred. After that, organic acid is reacted with alkali catalyst to produce soap and alcohol, which can be separated from solution as shown in Equation 2.7. This soap can be converted to organic acid again when it reacts with acid such as sulfuric acid and hydrochloric acid as shown in Equation 2.8. As for alcohol, it can be recovered by distillation during the hydrolysis reaction.



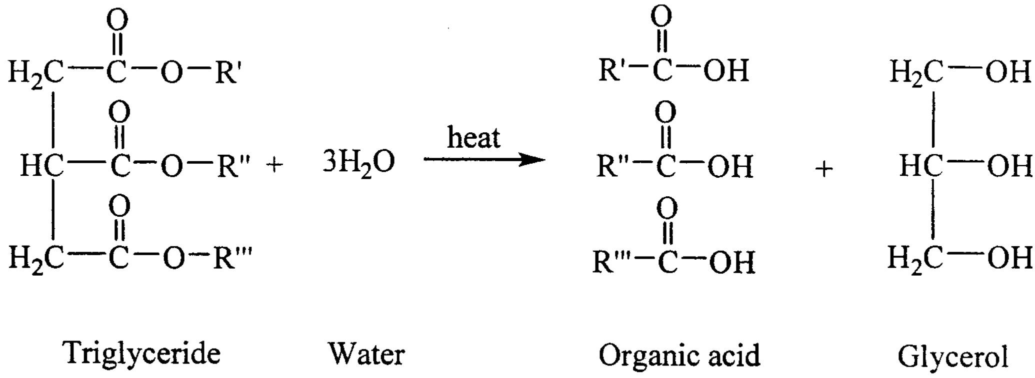
$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}O{-}H} + \mathrm{NaOH} \longrightarrow \mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}O^{-}Na^{+}} + \mathrm{R'OH}$$

(2.7)



$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}O{-}Na} + \mathrm{H^{+}} \longrightarrow \mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}O{-}H} + \mathrm{Na^{+}}$$

(2.8)



(2.9)

In biodiesel procedure, hydrolysis converts the structure of glycerides or of esters into FFA, and glycerol or alcohol as shown in Equation 2.9. Therefore, this reaction can be protected by using the raw material, which contain low moisture, and by draining water formed during esterification reaction.

Moreover, hydrolysis reaction is used to separate FFA, methanol and glycerol out of crude glycerol and to separate FFA out of soap. Separated free fatty acid can be used as a raw material in esterification or blended with oil to use as a raw material in the two-stage process. As for methanol and glycerol, they are purified by distillation.

2.2.3 Effect of Parameters in Biodiesel Production

2.2.3.1 Methanol Ratio

According to theory of biodiesel production, the stoichiometric molar ratio of alcohol to oil is three molecules of alcohol to one molecule of triglyceride in transesterification and is one molecule of alcohol to one molecule of free fatty acid in esterification. Practically, using the stoichiometric molar ratio of alcohol, the requirement of ester conversion can not be achieved. Therefore, to drive the forward reaction for getting the highest yield of the product according to Le Châtelier's Principle, higher molar ratio is required in the reaction. In addition, reaction temperature nearly methanol boiling point atmospheric pressure is used; therefore, methanol can continuously evaporate during the reaction.

Generally, it was found that the molar ratio of alcohol to oil at 6:1 or more is frequent used in biodiesel procedure by transesterification. In addition, the molar ratio of alcohol to oil in excess of 15:1 or more is required to get the highest conversion in biodiesel production in esterification. For two-stage process, FFA in oil was treated under a (2.5-20):1 molar ratio of alcohol to oil and TG could be converted to biodiesel under a (3-9):1 molar ratio of alcohol to oil. However, although a high methanol ratio is required to generate biodiesel, the glycerol separation is interfered with alcohol because of increasing solubility. Moreover, remained glycerol in biodiesel can promote the reversible reaction. That is one cause of lower ester yields. Consequently, to reduce the problem, the suitable molar ratio of methanol to oil, which is required in each reaction, should be investigated.

2.2.3.2 The Amount of Catalyst

Even though the catalyst was not added in biodiesel production, the reaction between oil and methanol is still continuing. The reason was that methanol has high polarity. However, the reaction time for driving the reaction to reach the highest yield is too long. For reducing reaction time (increasing the initial reaction rate); therefore, it is necessary to add the catalyst in the process.

In transesterification, sodium hydroxide is frequently used as a catalyst because it is cheaper and biodiesel can be generated under the small amount of it. In principle, if the amount of alkali catalyst is increased, the high percentages of biodiesel purification are also obtained. However, it causes to reduce biodiesel yield by gravity separation. In the same way, sulfuric acid is also usually used as a catalyst in esterification more than other acid. Due to a strong acid and toxicity, the reaction can be reached under the small. From literature reviews, it was showed that the amount of sodium hydroxide at 0.4-2.0 wt% of oil and of sulfuric acid at 2-3 wt% of oil was used as a catalyst in biodiesel production by transesterification and by esterification, respectively.

2.2.3.3 Mixing Intensity

In the first period of reaction, mixing is important for driving the reaction into forward side because it reduces diffusion and mass transfer reactions that control the overall rate of the reaction. Since oils and methanol are immiscible reagent, the reaction for producing biodiesel requires the suitable mixing intensity for promoting the homogeneous solutions. The mixing intensity, generally, around 150-600 rpm is suitable for producing biodiesel, however, all this is due to the physical and types of reactor.

2.2.3.4 Reaction Temperature

The reaction temperature strongly influences the rate of the biodiesel production because the reaction is typically endothermic reaction. When the temperature increases, the final conversion also increases. Therefore, to drive the reaction reached in the short period of reaction time, the reaction should be reacted under the suitable reaction temperature though the reaction will proceed to near completion even at the room temperature.

Although, the reaction is carried out nearly the boiling point of methanol (64.8°C) at the atmospheric pressure, from literature reviews, Ma, *et al.* (1998) indicated that the reaction temperature at 60°C is suitable for producing biodiesel by transesterification. However, the effect on the reaction temperature is not only the boiling point of alcohol but also the type of catalyst; for example, a high temperature is used to produce biodiesel by using acid catalyst and no-catalyst. As the two-stage process, both reactions are carried out at 60°C.

2.2.3.5 Moisture and FFA content

Raw materials (oil, alcohol, and catalyst) in transesterification must be anhydrous and had low FFA (< 1 wt%) content. Moisture and high FFA will cause gel to form by saponification, which results in lower yields and washing problems.

Therefore, before producing biodiesel, generally, the water content and FFA should be checked by titration technique. After that the oil is prepared by heating up to120 °C in order to de-moisture and then the FFA in oil is de-acidified by saponification. In addition, problems of high moisture and high FFA content of vegetable oils and animal fats can be solved by using the acid-catalyzed transesterification, the enzyme-catalyzed transesterification, supercritical CO_2 techniques or a two-stage process.

2.2.4 Specifications and Properties of Biodiesel

Biodiesel is produced from various vegetable oils and animal fats by different methods; therefore, the standardization of biodiesel quality is introduced to guarantee biodiesel for using in diesel engines without any problems. Some countries such as Germany, Italy, France, The Czech Republic, Australia, United States and Thailand have defined and approved standards for guideline biodiesel properties.

Table 2.3 The requirement of commercial biodiesel qualities and quantities in Thailand (Department of Energy Business, 2009)

Parameters	Corresponding Value	Method[1]
Methyl Ester (%wt)	≥ 96.5	EN14103
Density at 15°C (kg/m^3)	≥ 860 and ≤ 900	ASTM D 1298
Viscosity at 40°C (cSt)	≥ 3.5 and ≤ 5	ASTM D 445
Flash point (°C)	≥ 120	ASTM D 93
Sulphur (%wt)	≤ 0.0010	ASTM D 2622
Carbon Residue, on 10 % distillation residue (%wt)	≤ 0.30	ASTM D 4530
Cetane Number	≥ 51	ASTM D 613
Sulfated Ash (%wt)	≤ 0.02	ASTM D 874
Water (%wt)	≤ 0.050	EN ISO 12937
Total Contaminate (%wt)	≤ 0.0024	EN 12662
Copper Strip Corrosion	$\leq$ Number 1	ASTM D 130
Oxidation Stability at 110°C (hours)	≥ 10	EN 14112
Acid Value (mg KOH/g)	≤ 0.50	ASTM D 664
Iodine Value (g iodine /100g)	≤ 120	EN 14111
Linolenic Acid Methyl Ester (%wt)	≤ 12.0	EN 14103
Methanol (%wt)	≤ 0.20	EN 14110
Monoglyceride (%wt)	≤ 0.80	EN 14105
Diglyceride (%wt)	≤ 0.20	EN 14105
Triglyceride (%wt)	≤ 0.20	EN 14105
Free Glycerin (%wt)	≤ 0.02	EN 14105
Total Glycerin (%wt)	≤ 0.25	EN 14105
Group I metals (Na+K) mg/kg	≤ 5.0	EN 14108 and EN 14109
Group II metals (Ca+Mg) mg/kg	≤ 5.0	prEN 14538
Phosphorus (%wt)	≤ 0.0010	ASTM D 4951

Note: 1.The biodiesel quality can be verified with another method, but these methods used to obviate the argument.

ASTM test methods and some EN test methods are used to measure performance parameters of biodiesel production in Thailand. These methods are enacted in the Royal Gazette for controlling standards of production. The standard of biodiesel production in Thailand can be categorized in two groups which is the standard for commercial biodiesel production and for agriculture engine as shown in Table 2.3 and 2.4.

Table 2.4 The requirement of biodiesel qualities and quantities for agricultural engines in Thailand (Department of Energy Business, 2006)

Parameter	Corresponding Value	Method [1]
Density at 15°C (kg/m^3)	≥ 860 and ≤ 900	ASTM D 1298
Viscosity at 40°C (cSt)	≥ 1.9 and ≤ 8	ASTM D 445
Flash point (°C)	≥ 120	ASTM D 93
Sulphur (%wt)	≤ 0.0015	ASTM D 2622
Cetane Number	≥ 47	ASTM D 613
Sulfated Ash (%wt)	≤ 0.02	ASTM D 874
Water and Sediment (%vol)	≤ 0.2	ASTM D 2079
Copper Strip Corrosion	≤ Number 3	ASTM D 130
Acid Value (mg KOH/g)	≤ 0.80	ASTM D 664
Free Glycerin (%wt)	≤ 0.02	ASTM D 6584
Total Glycerin (%wt)	≤ 1.50	ASTM D 6584
Colour	Purple[2]	Eyesight
Additive	According to Department of Energy Business	

Note: 1.The biodiesel quality can be verified with another method, but these methods used to obviate the argument.

2. 1.4-dialkylamino anthraquinone and alkyl derivatives of azobenzene-4-azo-2-naphthol are used as the analytical regents.

2.3 Types of reactor

In batch process, the large reactor, high capital investment, high energy consumption and product quality control difficulty are unavoidable; therefore, the continuous reactor was investigated. The investigation found that continuous reactor, present, can be classified into 3 types: continuous stirred tank reactors (CSTRs), plug flow reactor (PFR) and packed bed reactor (PBR) as shown the detail of each type as followed:

2.3.1 Continuous Stirred Tank Reactors (CSTRs)

CSTRs connected in series (Figure 2.1 and 2.2) consist of one or more tanks (dependent on the kinetics of reaction) and an impeller in each tank. The process of CSTRs is similar to the process of batch reactor but for the CSTRs, the reagents are feeding into the reactor and product is transferred out of the reactor all the time. When the reagents pass through each tank of reactor, the reagents are homogeneous mixing under the similar reaction temperature and the retention time.

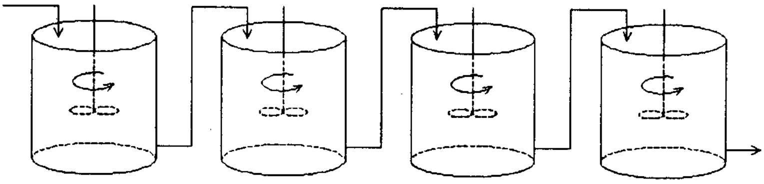


Figure 2.1 Continuous stirred tank reactors in series (Fogler, 2006)

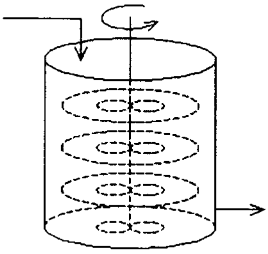


Figure 2.2 Continuous stirred tank reactors in vertical series (Fogler, 2006)

2.3.2 Plug Flow Reactor (PFR)

The characteristic of plug flow reactor (Figure 2.3) is a blank column in straight line whose length depended on the reaction rate. When un-reacted reagents are fed into PFR flowing through cross-sectional area, it is found that the concentration of reagent in perpendicular and in horizontal must be equal. Conversely, reagents in parallel flow are not equivalent in concentration when the reacted reagents are fed in to PFR. This reactor is frequent used in gas phase reaction.

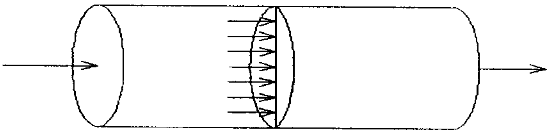


Figure 2.3 Plug flow reactor (Fogler, 2006)

2.3.3 Packed Bed Reactor (PBR)

Although the characteristic of PBR is similar to plug flow reactor, inside of reactor is packed with solid catalyst for promoting the reaction as shown in Figure 2.4. The reagents can be reacted inside column by counter-flow feeding. The advantage of reactor is high efficiency, low investment cost but the reactor must be fabricated in the large size.

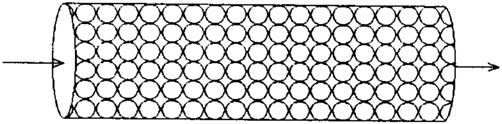


Figure 2.4 Pack bed reactor (Fogler, 2006)

CHAPTER 3
CONTINUOUS REACTOR DESIGN

To obtain the suitable method for producing biodiesel from high free fatty MCPO, transesterification was the fist method offered to observe the characteristic of reaction. It was found that FFA in MCPO is reacting with metallic alkoxide to produce soap (saponification). Then obtained soap induces other compositions in oil to convert into soap that caused low or without yield of methyl ester (ME). Therefore, it is necessary to reduce FFA in oil before starting the process for producing biodiesel. Although many methods could be solved the problem as above-mentioned, the two-stage was selected for producing biodiesel from this oil. Actually, the two-stage process 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 of short time and low production loss. 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 size reactor, 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. Owing to requirement of low investment cost, suitability for liquid-liquid reaction and simply design in this investigation, a CSTR was selected for producing biodiesel from high free fatty acid MCPO via the two-stage process.

In design, the reaction rate of the two-stage process (batch reactor) in the previous work and the principle of chemical reactor design (unit operation and chemical kinetics) were necessary for the two-stage process continuous reactor.

3.1 n Tank Reactor in Series

Although continuous reactor can be classified into 3 types: continuous stirred tank reactors (CSTRs), plug flow reactor (PFR) and packed bed reactor (PBR), CSTRs are offered to produce biodiesel from high free fatty acid MCPO via the two-stage process in this investigation because it is low investment cost, suitable for liquid-liquid reaction and easy to design.

From the literature reviews, the number of researchers showed the amount and size of tank, but they did not show the technique for estimating tanks of CSTR. For example Darnoko, *et al.* (2000) produced biodiesel from palm oil by using a 1 litre CSTR tank and a 2 litres CSTR tank was used to produce biodiesel from soybean oil in Noureddini's experiment (Noureddini, *et al.*, 1998).

However, few researchers tried to estimate the amount and size of tank. For example, Leevijit, *et al.* (2004) investigated the design of 10 L/hr continuous reactor for palm oil transesterification. After studying the kinetics of tranesterification, the estimation of the amount of tank was investigated. The least-squares regression technique and solver tool in Microsoft Excel 2000 program was used in calculation. In addition, the efficiency of n CSTR tank was investigated the conversion at a various resident times in PFR by computing with MALAB (commercial program). Study showed that 6 ideal CSTR tank in series (2.272 litres in total) was suitable to be used in biodiesel production. Prateepchaikul, *et al.* (2009) investigated the design of esterification continuous reactor. The first procedure of his work was to estimate the amount of tank with kinetics of esterification for reducing FFA in MCPO (Jansri, 2007 and Jansri, *et al.*, 2011) and with the principle of the n tank reactor in series estimation (Fogler, 2006). After that, the suitable tank was determined by using retention time. the results indicated that 4 CSTR tanks in series (2.5 litres in total and feeding MCPO flow rate at 10 L/hr) was suitable for reducing high FFA containing in MCPO to less than 1 % wt/wt (0.035 mol/L).

Although, there were the number of researchers proposed the technique to design continuous reactor for reducing FFA and for producing biodiesel, this investigation would like to thoroughly present other technique for estimating the amount of CSTR tanks in series.

3.1.1 Rate Law

The general equation for reversible reaction as shown in Equation 3.1 is indicated the reaction between reactant A and reactant B to form product C and product D. The reversible specific reaction rate coefficients (k_a and k_{-a}) are defined with respect to reactant A

$$aA + bB \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} cC + dD \tag{3.1}$$

The rate of forward reaction indicates the disappearance of the reactant A, which defines the forward rate coefficient (k_a) with respect to reactant A as followed

$$r_{A.forward} = -k_a [A]^a [B]^b \tag{3.2}$$

The rate of reverse reaction indicates the appearance of the reactant A and the reverse rate coefficient (k_{-a}), which is defined with respect to reactant A as followed

$$r_{A.reverse} = k_{-a} [C]^c [D]^d \tag{3.3}$$

A mole balance for a constant volume reactor shows that the net rate of the reversible reaction is the sum of the reaction rate of the forward and the reverse reaction of reactant A as show in Equation 3.6.

$$r_A = k_{-a} [C]^c [D]^d - k_a [A]^a [B]^b \tag{3.4}$$

$$r_A = \frac{d[A]}{dt} \tag{3.5}$$

$$\frac{d[A]}{dt} = k_{-a}[C]^c[D]^d - k_a[A]^a[B]^b \tag{3.6}$$

3.1.1.1 Esterification

Esterification is the reaction for producing ester by converting the organic acid with alcohol as shown in Equation 3.7. This reaction can be reversed when it is treated with acid or base in aqueous solution (hydrolysis reaction).

$$\text{R'COOH} + \text{HOR''} \overset{\text{catalyst}}{\rightleftharpoons} \text{R'COOR''} + H_2O \tag{3.7}$$

In the two-stage process, esterification is used for converting FFA in the oil to biodiesel thus enabling the subsequent conversion of the triglyceride to biodiesel by transesterification. The FFA containing in the oil is converted into ester by reacting it with alcohol in the presence of sulfuric acid as catalyst as shown in Equation 3.8. However, it should be noted that this reaction is reversible:

$$\text{FFA} + \text{HOR'} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{RCOOR'} + H_2O \tag{3.8}$$

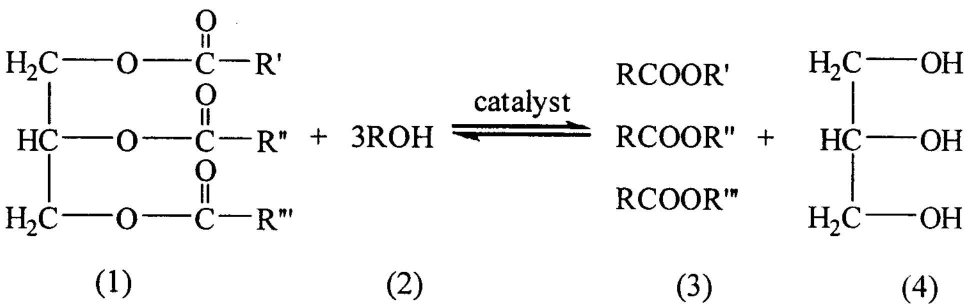
As a consequence, the rate of appearance of free fatty acid (FFA) can be presented as Equation 3.9. The rate of appearance of water is similarly presented as Equation 3.10.

$$\frac{d[FFA]}{dt} = -k_1[FFA]^a[AL]^b + k_2[E]^c[WT]^d \tag{3.9}$$

$$\frac{d[WT]}{dt} = k_1[FFA]^a[AL]^b - k_2[E]^c[WT]^d \tag{3.10}$$

3.1.1.2 Transesterification

Transesterification is a chemical process in which an acyl group in an ester is exchanged with a hydroxyl group in an alcohol thus generating a new alcohol and a new ester. In the production of biodiesel, the various acyl groups in the esters of the tri-hydric alcohol, 1, 2, 3-propanetriol (glycerol), are replaced with the hydroxyl groups of an alcohol such as methanol (CH_3OH) or ethanol (C_2H_5OH). This reversible reaction is facilitated by a catalyst and produces a new ester (biodiesel) and the tri-hydric alcohol (glycerol) as shown in Equation 3.11. The most common acyl groups in MCPO are the palmityl and stearyl group derived, respectively, from palmitic and stearic acids. However similar derivatives of other fatty acids may also be present.



(3.11)

The overall transesterification reaction (Equation 3.11) takes place in three successive stages. The corresponding rate equations for the appearance of triglyceride (TG), diglyceride (DG), monoglyceride (MG), alcohol (AL), ester (E) and glycerol (GL) are given in Equation 3.12. All of reactions are reversible and are of pseudo-secondary order overall.

$$\frac{d[TG]}{dt} = -k_3[TG][AL] + k_4[DG][E]$$

$$\frac{d[DG]}{dt} = k_3[TG][AL] - k_4[DG][E] - k_5[DG][AL] + k_6[MG][E]$$

$$\frac{d[MG]}{dt} = k_5[DG][AL] - k_6[MG][E] - k_7[MG][AL] + k_8[GL][E]$$

$$\frac{d[GL]}{dt} = k_7[MG][AL] - k_8[GL][E]$$

$$\frac{d[E]}{dt} = k_3[TG][AL] - k_4[DG][E] + k_5[DG][AL] - k_6[MG][E] + k_7[MG][AL] - k_8[GL][E]$$

$$\frac{d[AL]}{dt} = -\frac{d[E]}{dt} \qquad (3.12)$$

3.1.2 Rate Coefficients

Previous work, the biodiesel production from high FFA mixed crude palm oil (> 0.8 wt% of oil) by using the two-stage process (esterification followed by transesterification) was investigated in batch process based on parameters such as the speed of stirrer, the catalyst concentration, the amount of methanol, and reaction temperature. It was found that the suitable condition for reducing high FFA in MCPO (8-12 wt% oil) by using esterification was a 10:1 molar ratio of methanol to FFA and 10 wt% H_2SO_4 of FFA. As for ME production from the first solution by transesterification, it was found that the suitable condition was a 6:1 molar ratio of methanol of TG (triglyceride) in MCPO and 0.6 wt% sodium hydroxide of TG in MCPO. Both of reactions were carried out for 20 minutes under a 300 rpm speed of stirrer at 60°C. The samples were analyzed the concentration of TG, DG (diglyceride), MG (monoglyceride), FFA, and ME (methyl ester) by TLC/FID, the concentration of water by Karl Fischer, and the concentration of FFA, GL (glycerol) and NaOH (for neutralizing acid value in the first stage solution) by titration technique. The analyzed data were used to calculate the rate coefficients and the reaction orders of two-stage process by using curve-fitting tool of MATLAB as show the results in Equation 3.13-3.20.

$$r_{FFA} = -1.340C_{FFA}^{0.5}C_{AL}^{0.5} + 0.682C_{E}^{0.5}C_{WT}^{0.5} \qquad (3.13)$$

$$r_{WT} = 1.340C_{FFA}^{0.5}C_{AL}^{0.5} - 0.682C_{E}^{0.5}C_{WT}^{0.5} \qquad (3.14)$$

$$r_{TG} = -2.600C_{TG}C_{AL} + 0.248C_{DG}C_{E} \qquad (3.15)$$

$$r_{DG} = 2.600C_{TG}C_{AL} - 0.248C_{DG}C_{E} - 1.186C_{DG}C_{AL} + 0.227C_{MG}C_{E} \qquad (3.16)$$

$$r_{MG} = 1.186C_{DG}C_{AL} - 0.227C_{MG}C_{E} - 2.303C_{MG}C_{AL} + 0.022C_{GL}C_{E} \qquad (3.17)$$

$$r_{GL} = 2.303C_{MG}C_{AL} - 0.022C_{GL}C_{E} \qquad (3.18)$$

$$r_E = 2.600C_{TG}C_{AL} - 0.248C_{DG}C_E + 1.186C_{DG}C_{AL} - 0.227C_{MG}C_E + 2.303C_{MG}C_{AL} - 0.022C_{GL}C_E \quad (3.19)$$

$$r_{AL} = -r_E \quad (3.20)$$

3.1.3 The Rate Determining Step

Generally, the chemical reactions occur from the mechanism more than one elementary step, which is controlled by its rate coefficient and activation energy. Often one of the steps is slower than the others; therefore, the overall reaction rate can not exceed the rate of the slowest elementary step of its mechanism. So that the rate-determining step is controlled by the slowest step because it is the overall reaction limitation.

Table 3.1 The initial concentration of components in MCPO and de-acidified MCPO

Esterification			
Initial components	**Initial concentration (mol/L)**	**Product components**	**Product concentration (mol/L)**
FFA	0.359	FFA	0.018
AL	2.813	AL	2.541
ME	0.051	ME	0.322
WT	0.050	WT	0.255
Transesterification			
Initial components	**Initial concentration (mol/L)**	**Product components**	**Product concentration (mol/L)**
TG	0.806	TG	0.020
DG	0.096	DG	0.010
MG	0.016	MG	0.007
ME	0.269	ME	2.502
AL	6.119	AL	3.886
GL	0.000	GL	1.818

Equation 3.13-3.20 are used to determine the rate determining step of esterification and transesterification (feeding MCPO flow rate at 50 L/hr) using the initial concentration of main components in MCPO and de-acidified MCPO, respectively, which are analyzed by TLC/FID and titration technique as shown the values in Table 3.1.

It was found that Equation 3.13 was the rate determining step of esterification because it was the slowest elementary of its mechanism as shown the reaction rate in Table 3.2. Although reaction rate of alcohol disappearance was the slowest reaction rate in transesterification as shown the reaction rate in Table 3.2, its rate law was not considered because the excess of alcohol was used as a main reagent in the reaction. Therefore, the rate law of TG disappearance (Equation 3.15) was used to determine the reaction step because it was the second slower reaction rate in transesterification.

Table 3.2 Reaction rate of esterification and transesterification

Rate of esterification	**Reaction rate** ($mol \cdot L^{-1} \cdot min^{-1}$)
r_{FFA}	-1.312
r_{WT}	0.091
Rate of transesterification	**Reaction rate** ($mol \cdot L^{-1} \cdot min^{-1}$)
r_{TG}	-12.816
r_{DG}	-0.501
r_{MG}	-0.183
r_{GL}	0.054
r_{E}	0.201
r_{AL}	-13.738

3.1.4 Rate Law of Esterification and Transesterification in Flow System

Fogler (2006) explained that, in the flow system, the concentration of reagent A determines from the molar flow rate and the volumetric flow rate of it as shown in Equation 3.21.

$$C_A = \frac{F_{A1}}{v} = \frac{\text{moles}}{\text{litre}} \tag{3.21}$$

The concentration of reagent A and B and Product C and D in Equation 3.1 can be written in term of their respective entering molar flow rates, the conversion and the volumetric flow rate as shown in Equation 3.22.

$$\begin{aligned} C_A &= \frac{F_A}{v} = \frac{F_{A0}}{v}(1-X) \\ C_B &= \frac{F_B}{v} = \frac{F_{B0}-(b/a)F_{A0}X}{v} \\ C_C &= \frac{F_C}{v} = \frac{F_{C0}-(c/a)F_{A0}X}{v} \\ C_D &= \frac{F_D}{v} = \frac{F_{D0}-(d/a)F_{A0}X}{v} \end{aligned} \tag{3.22}$$

For the flow system of liquid phase concentrations, the volume change in each reaction is negligible. Consequently, the concentration of reagent B and product C and D can be determined on the initial concentration A and the conversion as shown in Equation 3.23. Finally, the equations of the liquid phase flow system give the rate law in term of conversion.

$$C_A = C_{A0}(1-X)$$

$$C_B = C_{B0} - (\frac{b}{a})C_{A0}X$$

$$C_C = C_{C0} - (\frac{c}{a})C_{A0}X$$

$$C_D = C_{D0} - (\frac{d}{a})C_{A0}X \qquad (3.23)$$

The rate determining step of esterification and transesterification in biodiesel production two-stage process (Equation 3.13-3.20) could be shown in the term of conversion by using the principle of the flow system of liquid phase concentrations (Equation 3.23) and the initial components concentration (Table 3.1) as shown in Equation 3.24 and 3.25, respectively.

$$-r_{FFA} = 0.223X - 1.585X^{0.5} + 1.274 \qquad (3.24)$$

$$-r_{TG} = 1.529X^2 - 14.451X + 13.961 \qquad (3.25)$$

3.1.5 Estimation of n Tanks Reactor in Series for Continuous Stirred Tank Reactors

Reactors in this investigation are connected in series in order that the exit stream of one reactor is the initial mixture of another reactor as shown in Figure 3.1. In a combination of CSTRs, X_1 at point *i*=1 is the achievement conversion in the first CSTR but X_2 at point *i*=2 is the total achievement conversion by all two reactors. Hence, to estimate the n tanks reactor, experimental data of batch system that give the reaction rate at difference conversions is used.

Conversion, reactor size or the amount of tanks of the first and second reactors as shown in Figure 3.1 can be calculated by combining a mole balance on each reactor and the molar flow rate at each point and rearranging as shown in Equation 3.26 and 3.27.

This principle of the continuous flow system in series is used to estimate the amount of tanks in series of esterification and transesterification of this study by calculating until it reaches the required conversion.

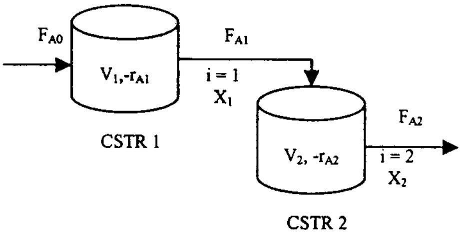


Figure 3.1 Two tanks reactor in series for continuous stirred tank reactors

Reactor 1: $$V_1 = F_{A0}\left(\frac{1}{-r_{A1}}\right)X_1 \qquad (3.26)$$

Reactor 2: $$V_2 = F_{A0}\left(\frac{1}{-r_{A2}}\right)(X_2 - X_1) \qquad (3.27)$$

3.1.5.1 Esterification

The esterification continuous process was required to reduce 8-12 wt% in MCPO to less than 1 wt%. That was the requirement conversion of FFA in MCPO was 0.92 (Jansri, 2007). To achieve the requirement, the volume of each tank was fixed at 0.5, 1.0 and 2.0 litre, rate law of esterification in flow system (Equation 3.24) and the principle of the continuous flow system in series were used to estimate the amount of tanks in series.

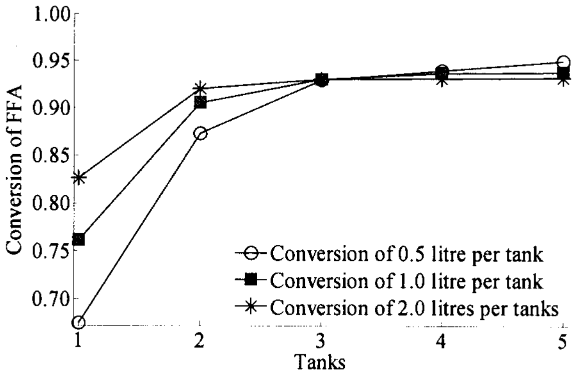


Figure 3.2 The relation between the amount of tank and FFA conversion in esterification

The results in Figure 3.2 indicated that at the volume of 0.5 and 1.0 litre per tank, the requirement conversion (0.92) was reached for 3 tanks in series (1.5 and 3 liters of the total volume, respectively). In addition, 2 tanks in series could reach the conversion of esterification, when the 2.0 litre per tank (4 L in the total volume) was used to calculation.

3.1.5.2 Transesterification

The conversion at 0.99 was the requirement for converting TG, DG and MG in de-acidified MCPO into biodiesel (Jansri, 2007). Similar to the estimation of the number of tank of esterification, the predetermined fixed volume of each tank, the rate law of transesterification in flow system (Equation 3.25) and the principle of the continuous flow system in series were used. Figure 3.3 showed that the fixed volume at 1.0 litre per tank was satisfied the requirement of ME conversion by using 3 tanks of CSTR (3.0 L in total volume). In addition, when the fixed volume at 2.0 L per tank was used for calculation, 2 tanks of CSTRs (4.0 L in total volume) were reached the conversion. On the other hand, when the fixed volume at 0.5 litre per tank was used to calculation, the conversion was not reached the requirement.

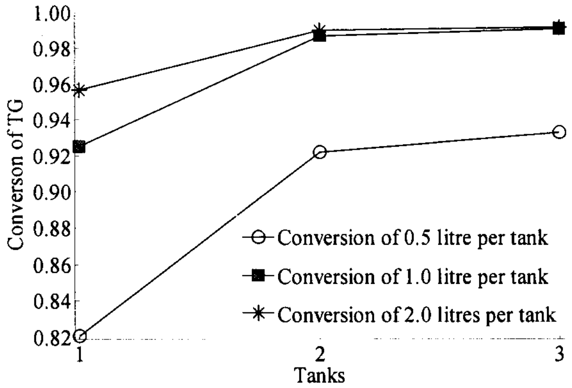


Figure 3.3 The relation between the amount of tank and ME conversion in transesterification

3.1.6 Retention Time for Determining the Amount and Volume of Tank in the Two-Stage Process Continuous Flow System

Although the number of tanks could be estimated by calculating with the rate law of the two-stage process and the principle of the continuous flow system in series, the definite number and volume of tank could not be determined. In addition, due to MeOH having high vapor pressure, the remaining MeOH in de-acidified MCPO (production of esterification) can evaporate continuously. Therefore, to minimize methanol evaporation, retention time for feeding solution to the second-stage process was adopted to determine the required capacity of reactor.

$$\tau = \frac{V}{v_0} \tag{3.28}$$

The results in Table 3.3 estimating retention time with Equation 3.28 indicated that the combination between esterification reactor total volume of 1.5 L separated into 3 tanks and 3 L reactor separated into 3 tanks of transesterification reactor could reach the requirement because of the small of theirs retention time lag.

Additionally, the required conversion of this process could also reach when 3 tanks (3.0 L of total volume) of both reactors were combined. However, it was found that the retention of transesterification reactor in Table 3.3 was smaller than esterification reactor. This caused, for a long time, esterification reactor could be not promptly supplied de-acidified MCPO to feed as a raw material in transesterification. Moreover, although the same conversion can be achieved with smaller size of tanks, larger size is required, hence, larger amount of reagents and longer retention time. Therefore, the first combination of reactor was selected to confirm in the next step.

Table 3.3 Retention time of each CSTR using in esterification and transesterification

Esterification

Tank	Total volume (L)	Conversion	Retention time (min)
1	2.00	0.827	2.14
2	4.00	0.921	4.27
3	6.00	0.931	6.41

Tank	Total volume (L)	Conversion	Retention time (min)
1	1.00	0.762	1.07
2	2.00	0.906	2.14
3	3.00	0.931	3.20

Tank	Total volume (L)	Conversion	Retention time (min)
1	0.50	0.675	0.53
2	1.00	0.874	1.07
3	1.50	0.930	1.60

Transesterification

Tank	Total volume (L)	Conversion	Retention time (min)
1	2.00	0.957	1.95
2	4.00	0.990	3.90
3	6.00	0.992	5.85

Tank	Total volume (L)	Conversion	Retention time (min)
1	1.00	0.925	0.98
2	2.00	0.987	1.95
3	3.00	0.991	2.93

Tank	Total volume (L)	Conversion	Retention time (min)
1	0.50	0.821	0.49
2	1.00	0.922	0.98
3	1.50	0.933	1.46

3.1.7 Verification of the Amount of CSTR Tank

Make certain that the adjudged number of tanks (Table 3.3) could be used for producing de-acidified MCPO and biodiesel. Therefore, the number of tanks for reducing FFA and for producing biodiesel from MCPO was confirmed under the selected reactor capacity by the Damköhler number and analyzing with the ASPEN PLUS Simulation Engine shown in Figure 3.4-3.7. Each reactor was separated into 1, 2 and 3 tanks, respectively, by fixing the total volume at 1.5 and 3 L for esterification and for transesterification, respectively. Then the tank number was verified by Damköhler number.

In numerical analysis, the initial conditions (Table 3.1), reaction temperature, the rate law, and the number and size of CSTR tank were installed in the program for verifying the number of CSTR tank. The results in each step were printed in term of mass flow rate and then they were converted into term of conversion. Obtained esterification and transesterification conversion from three different methods were then compare and the conversion that closely matched among the 3 methods was selected

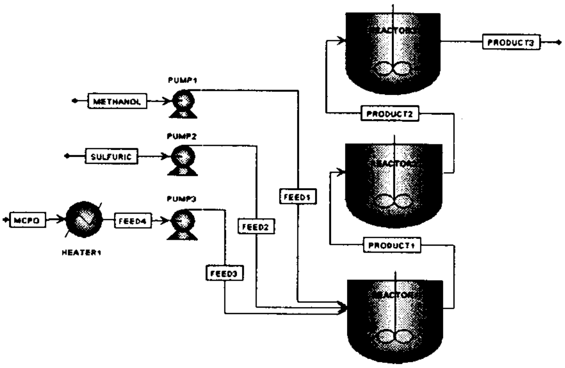


Figure 3.4 ASPEN PLUS Simulation Engine model for analysis the number of esterification CSTR tank

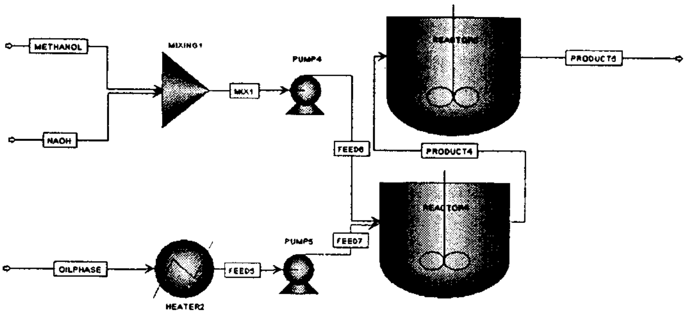


Figure 3.5 ASPEN PLUS Simulation Engine model for analysis the number of transesterification CSTR tank

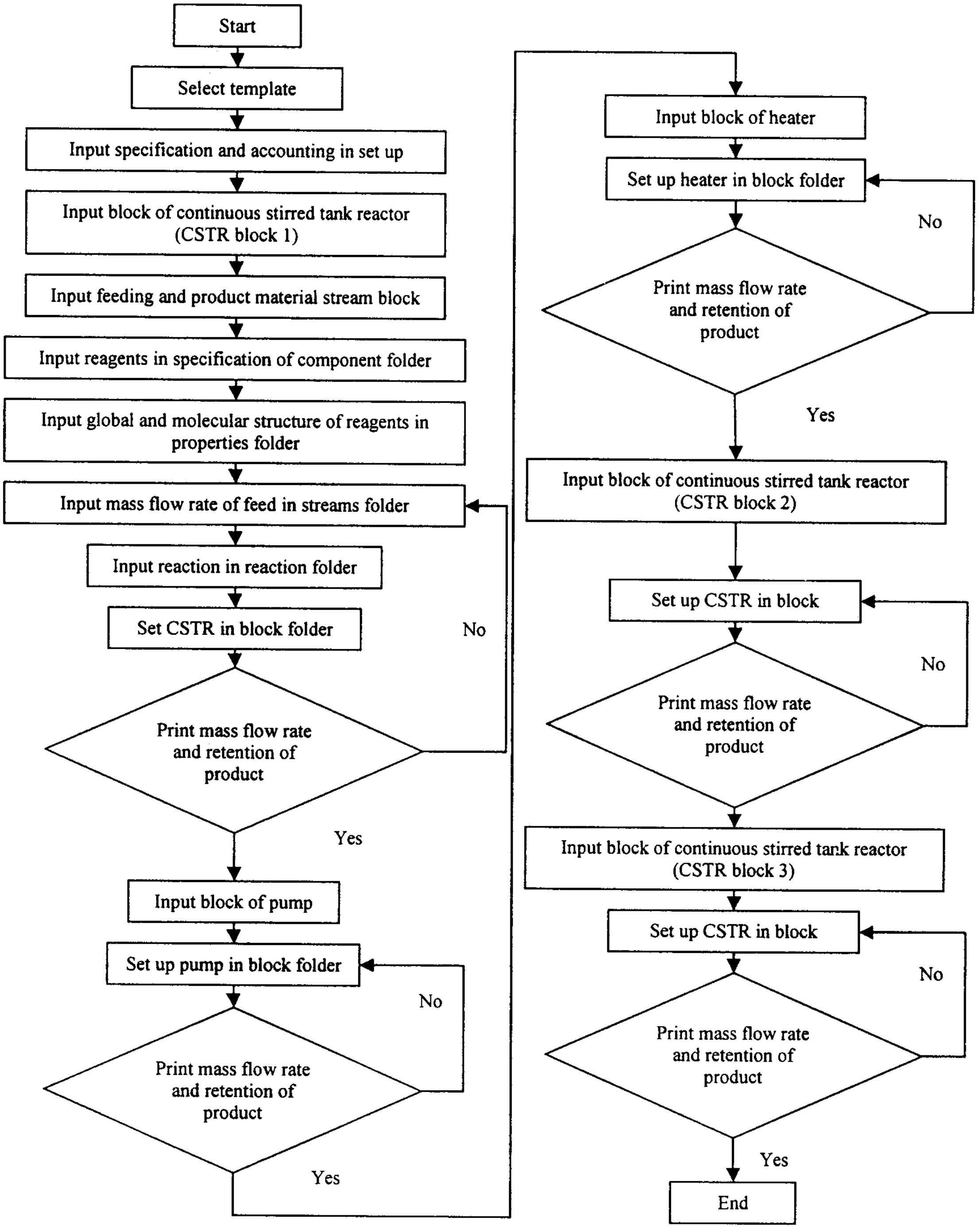


Figure 3.6 Diagram for analysis the number of esterification CSTR tank

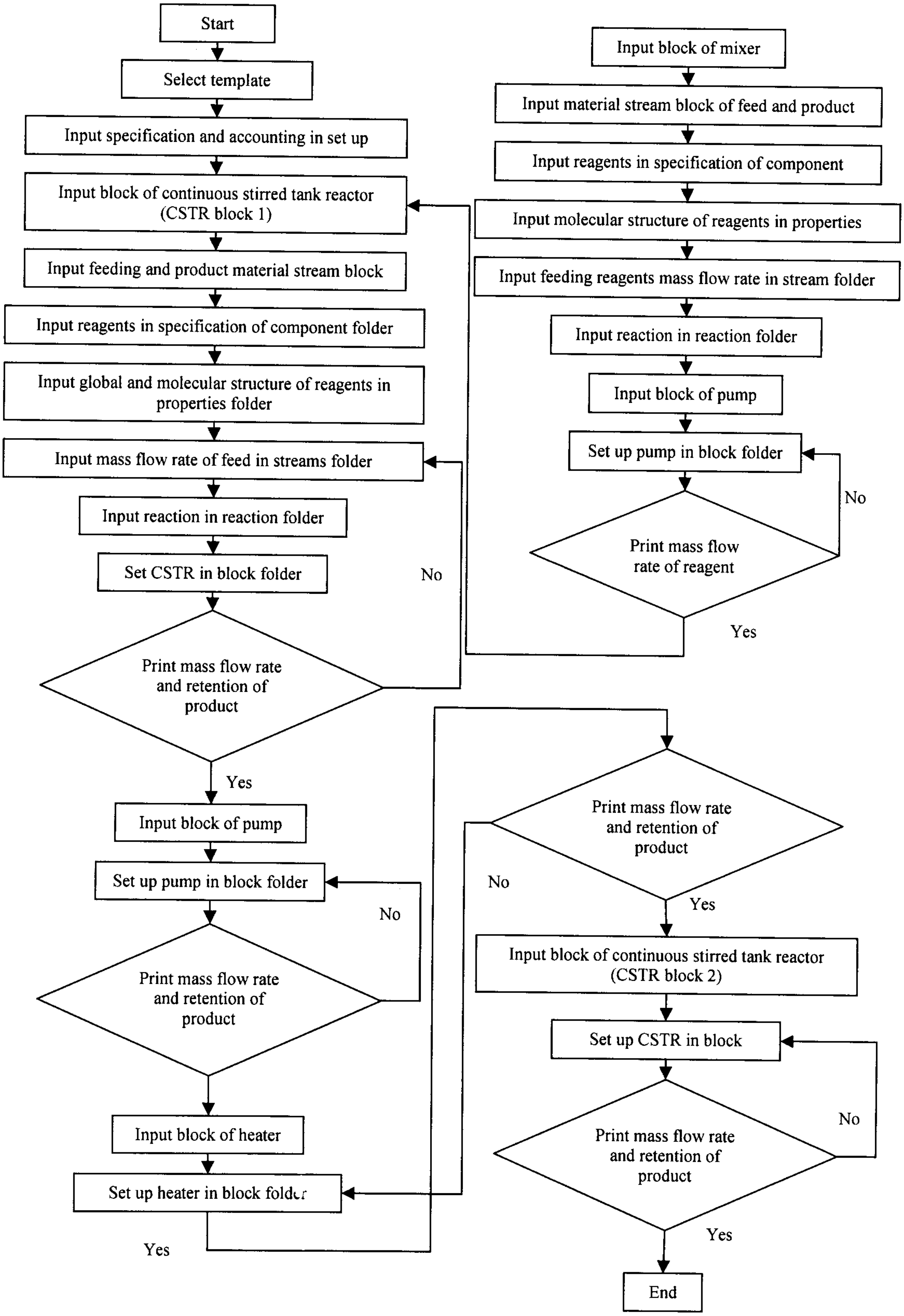


Figure 3.7 Diagram for analysis the number of transesterification CSTR tank

The perspective on the conversion and retention time of all estimation technique in each tank as shown in Table 3.4 was rather similar except for the retention time of FFA conversion. The reason for high error of reaction time for reducing FFA that was obtained from simulation was not exactly known. Likewise, the simulation data of transesterification in Table 3.4 showed that the conversion of ME could not reach the requirement of 99%. In presumption, both errors might have occurred in the boundary of retention time proceeding to steady state that set in this commercial program. However, this investigated focused on prediction about the number of tanks before fabrication. The results in Table 3.4 showed that 3 and 2 tanks were the most suitable number of tank for reducing FFA and producing biodiesel, respectively because they achieved the requirement for reaction conversion.

Table 3.4 Verification the suitable amount of tank by fixing the reactor volume

Total volume (L)	**Separated tanks**	**FFA conversion** (0.92)			**Retention time** (min)	
		Design	**Simulation**	**Damköhler number**	**Design**	**Simulation**
1.5	1	0.800	0.989 (23.62%)*	0.854 (6.75%)*	1.60	0.90 (43.75%)*
	2	0.895	0.990 (10.61%)*	0.979 (9.38%)*		
	3	0.930	0.990 (6.45%)*	0.997 (7.20%)*		
Total volume (L)	**Separated tanks**	**ME conversion** (0.99)			**Retention time** (min)	
		Design	**Simulation**	**Damköhler number**	**Design**	**Simulation**
3	1	0.968	0.904 (6.61%)*	0.979 (1.14%)*	2.93	2.68 (8.53%)*
	2	0.991	0.905 (8.68%)*	0.999 (0.81%)*		
	3	0.991	0.905 (8.68%)*	0.999 (0.81%)*		

*error

3.1.8 The Limited of FFA and TG Content in MCPO

Even though the simulation data indicated that 3 and 2 tanks CSTR could be reduced FFA and produced ME reached the requirement under the suitable batch condition, the reactor was not demonstrated its performance. Therefore, the highest amount of FFA and of TG content that could be used in each reactor was investigated by simulation again.

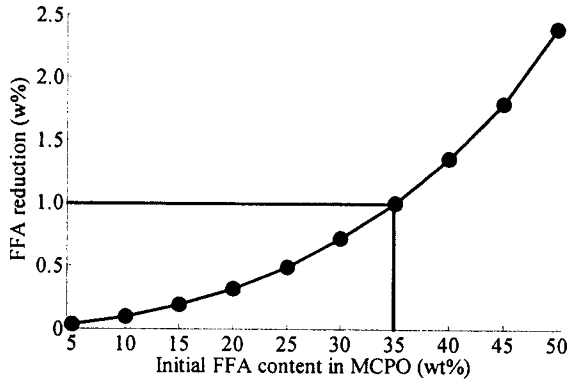


Figure 3.8 The limited concentration of initial FFA concentration using in esterification CSTR by simulation with ASPEN PLUS Simulation Engine

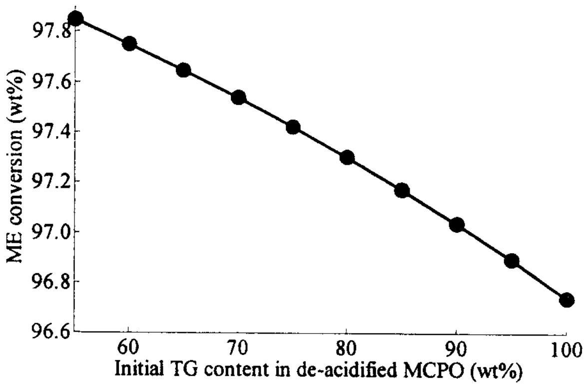


Figure 3.9 The limited concentration of initial TG concentration using in transesterification CSTR by simulation with ASPEN PLUS Simulation Engine

However, the concentration of FFA, TG, DG, MG, ME and WT were adjusted to a contrast between the mass fraction of MCPO composition (getting from the batch condition) and the assumption of an increase of FFA and TG content in MCPO. The results indicated that 35 wt% of FFA in MCPO (Figure 3.8) and 100 wt% of TG in de-acidified MCPO (Figure 3.9) were the highest concentration of FFA and TG could be used in the CSTR.

3.1.9 Conclusions

This investigation indicated that although larger size could be achieved the predetermined conversion, larger amount of reagents and longer time of reaction were required. Therefore, smaller size that matched retention time was selected to produce biodiesel via the two-stage process. The suitable tank number for reducing FFA in MCPO to less than 1 wt% (conversion more than 0.92) and for producing biodiesel from de-acidified MCPO to more than 97 wt% (conversion more than 0.99) were 3 tanks (1.5 L in total volume) and 2 tanks (3 L in total volume), respectively. Moreover, 35 wt% of FFA in MCPO and 100 wt% of TG in de-acidified MCPO were the highest FFA and TG concentration could be used in the CSTRs that were designed in this work.

3.2 Continuous Stirred Tank Reactors Agitations

This work focuses on changing of physical property oil and increasing the reaction rate of liquid-liquid mixing. Therefore, the agitations were designed for mixing immiscible reagent in esterification and in transesterification under ambient pressure at 60 °C will be investigation.

Before estimating the dimension of reactor agitations, three main composition of reactor agitation: tank, buffer and impeller were appreciated the physical properties of their type as followed.

3.2.1 Tank

Frequently, vertical cylindrical reactor having a cover is used as an agitated vessel for liquid-liquid mixing. The preferred bottom of the vessel is in 3 shapes such as round, flat and cone. Nevertheless, the reactor should not in cubic configuration because the reactor has shape corners and area, which fluid currents would not penetrate.

3.2.2 Baffle

Baffles are installed vertical strips perpendicular to the wall of the tank for controlling the fluid flow pattern. For the liquid having viscosity less than 20000 cP and for mixing in turbulence, baffles can be protected the circulatory and swirling flow pattern as shown in Figure 3.10.

However, the liquid in tank with installing baffles can not penetrate any tank area as show in Figure 3.11. Therefore, when baffles are installed in reactor, it should be spaced out reactor wall as shown in Figure 3.12.

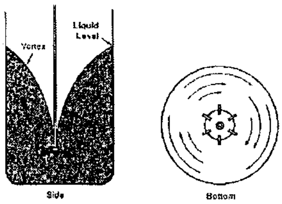


Figure 3.10 Swirling flow pattern with a radial-flow turbine in un-baffled reactor (McCabe, *et al.*, 2001)

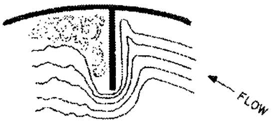


Figure 3.11 Non-penetration area (Holland, *et al.*, 1966)

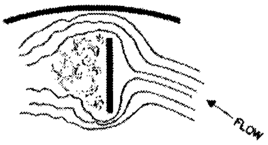
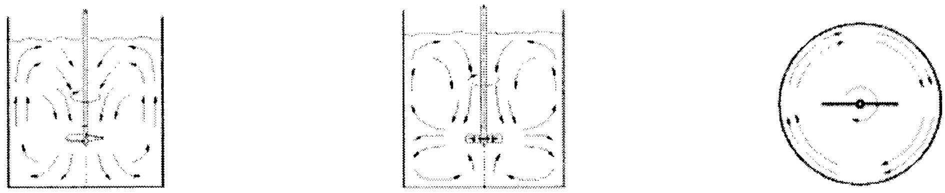


Figure 3.12 Leaving a space for protecting non-penetration area (Holland, *et al.*, 1966)

3.2.3 Impeller

Impeller is used to mix the heterogeneous liquids. Impeller can be categorized into 2 groups, which are axial-flow impellers (an axis of the impeller shaft) and radial-flow impellers (a radial and a tangential direction) as shown in Figure 3.13. In addition, the viscosity of liquids is indicated to determine the suitable impeller type for mixing the liquid as shown in Figure 3.14.



Axial flow Radial flow Tangential flow

Figure 3.13 Fluid-flow patterns (McCabe, *et al.*, 2001)

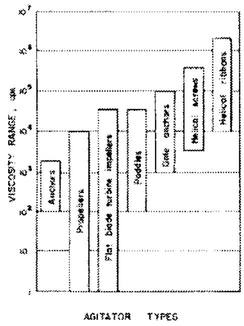
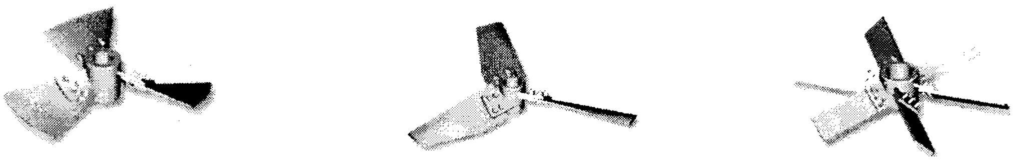


Figure 3.14 The relation between viscosity range and impeller types (Holland, *et al.*, 1966)

3.2.3.1 Axial flow impellers

Axial flow impellers generate currents parallel with the axis of the impeller shape such as marine propeller, hydrofoil and pitched blade turbine as shown in Figure 3.15. They are enhanced the pumping capacity, in addition to be suitable mixed the soluble liquids and between solid and liquid.

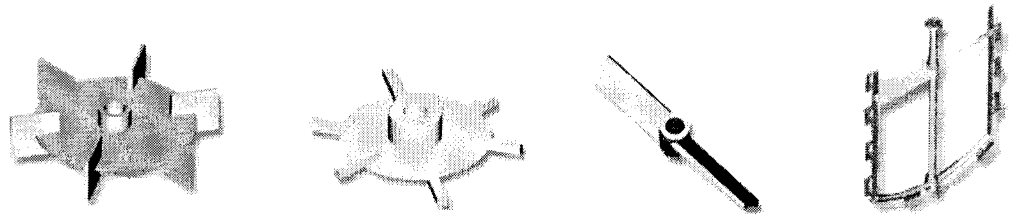


Marine propeller Hydrofoil Pitched blade turbine

Figure 3.15 Types of axial-flow impellers (Wellman, 2007a)

3.2.3.2 Radial flow impellers

Radial flow impellers can be categorized in two groups, which are flow in radial direction (six-blade disc turbine and bar disc) and tangential direction (paddle and anchor impeller) as shown in Figure 3.16. For radial direction, the liquids are pushed in outward to the vessel wall and then flow both upward and downward. The impellers can create the high shear zone for mixing immiscible liquids that mean the impellers used for decreasing the particle size of liquids which both liquids can be reacted or mixed easily. For tangential direction, the impeller provides good agitation near the wall and the floor of the tank. It promotes good heat transfer to or form vessel wall and uses to remove the liquids from the tank wall.



Six-blade disc turbine Bar disc Paddle impeller Anchor impeller

Figure 3.16 Types of radial-flow impellers (Wellman, 2007b and Wellman, 2007c)

3.2.4 Dimension of Continuous Stirred Tank Reactors Agitations

Above description, the vertical cylindrical tank having bottom in flat pattern installed four baffles is selected because it is in general agreement. Furthermore, six-blade disc turbine is also selected to install in this reactor because it promotes the mixing of immiscible liquid by creating zone of high shear rate.

The portions of vessel agitations as shown in Table 3.5 can be rearrangement as followed.

The vertical cylindrical tank was chosen as a reactor configuration of this work so the volume of reactor is calculated by using Equation 3.29.

$$V_R = \frac{\pi D_t^2 H_t}{4} \tag{3.29}$$

Table 3.5 indicates that the diameter of reactor is equal to the reactor height. Therefore the new formula of the reactor volume is shown in Equation 3.30 as followed

$$V_R = 0.785 H_t^3 \tag{3.30}$$

Table 3.5 The portions of vessel agitations

Aparatus	**Size of CSTR Agitations (cm)**	**References**
Diameter of tank (D_t)	$D_t = H_t$	(McCabe, *et al.*, 2001) (Geonkoplis, 1993)
Height of tank (H_t)	H_t	(McCabe, *et al.*, 2001) (Geonkoplis, 1993)
Baffle width (J)	$J = \frac{H_t}{12}$	(Geonkoplis, 1993)
Diameter of turbine impeller (D_a)	$D_a = \frac{H_t}{2}$	(Geonkoplis, 1993)
Diameter of turbine impeller disc (D_d)	$D_d = \frac{H_t}{3}$	(Geonkoplis, 1993)
Blade width (W)	$W = \frac{H_t}{15}$	(Geonkoplis, 1993)
Blade length (L)	$L = \frac{H_t}{12}$	(Geonkoplis, 1993)
Space between baffle and wall (G)	$G = \frac{0.15H_t}{12}$	(Geonkoplis, 1993)
Diameter of separate tank plate (D_s)	$D_s = H_t$	(Geonkoplis, 1993)
Diameter of hole on separate plate (D_h)	$D_h = \frac{H_t}{3}$	(Geonkoplis, 1993)
Space between turbine and bottom tank (E_s)	$Es = \frac{H_t}{3}$	(McCabe, *et al.*, 2001) (Geonkoplis, 1993)

Due to installation four cylindrical baffles and six-blade disc turbine in the reactor so that the volume of their must be used to calculate for finding the real size of reactor.

The formula for finding four cylindrical baffles volume and six-blade disc turbine are shown in Equation 3.31 and 3.32, which are in term of the reactor height.

The volume of four cylindrical baffles:

$$V_B = \frac{4\pi(H_t/12)^2 H_t}{4} \tag{3.31}$$

$$V_B = 0.022H_t^3 \tag{3.32}$$

The volume of six-blade disc turbine consists of volume of disk, six-blade, axle and axle ring:

$$V_T = V_D + V_{BL} + V_A + V_{AR} \tag{3.33}$$

$$V_T = [6e \times \frac{H_t}{12} \times \frac{H_t}{15}] + [\frac{\pi e}{4} \times \left(\frac{H_t}{3}\right)^2] + [\frac{f^2}{4} \times \pi H_t] + [\frac{\pi}{2} \times \frac{H_t}{15} \times \frac{(f)^2 - (g)^2}{4}] \tag{3.34}$$

$$V_T = 0.120(e)H_t^2 + (0.785f^2 + (0.026(f^2 - g^2)))H_t \tag{3.35}$$

Equation 3.30, 3.32 and 3.35 are combined.

$$V_R = 0.763H_t^3 - 0.120(e)H_t^2 - (0.785f^2 + (0.026(f^2 - g^2)))H_t \tag{3.36}$$

The final equation (Equation 3.36) is obtained in cubic polynomial with the variable of the height of tank, the thickness of turbine, the dimension of axle and the thickness of axle ring. It will be used to estimated the portions of vessel agitations

3.2.5 Conclusions

Equation 3.36 was used to calculation the vessel agitation of CSTR for esterification and of transesterification by setting the thickness of turbine, the dimension of axle and the thickness of axle ring as 0.2, 0.8 and 0.2, respectively. After obtaining the height of tank value, their standard portions of reactor was substitute with the height of tank value as shown the results in Table 3.6.

Actually, a small calculation cylindrical tube according theory could not be found (esterification). Moreover, a metal rolling machine could not roll the stainless steel plate into the requirement size (transesterification). In order that, the cylindrical tube size of each reactor was increased causing other agitations that were the inside element of reactor were also increased as shown the results in Table 3.6.

Table 3.6 Size of CSTRs agitations for esterification and transesterification

	CSTR agitations for Esterification (cm)		**CSTR agitations for Transesterification (cm)**	
	Estimation	**Actual work**	**Estimation**	**Actual work**
D_t	8.72	9.70	12.55	14.00
H_t	8.72	9.70	12.55	14.00
Tanks height in series	26.16	29.10	25.10	28.00
Height total	28.78*	32.01*	28.70*	32.20*
J	0.73	0.81	1.05	1.17
D_a	4.36	4.85	6.28	7.00
D_d	2.91	3.23	4.18	4.67
W	0.87	0.97	1.26	1.40
L	1.09	1.21	1.57	1.75
G	0.11	0.12	0.16	0.18
D_s	8.71	9.69	12.54	13.99
D_h	2.91	3.23	4.18	4.67
Es	2.91	3.23	4.18	4.67

*Include 30% of reactor head (Somnuk, 2008)

3.3 Mixing Intensity

3.3.1 Mixing

Initial reagents of biodiesel production such as MCPO, methanol, sulfuric acid, and methoxide solution are the immiscible liquids. Therefore, the mixing of initial reagents is required until it reaches the homogeneous phase. In the first time, the mixing intensity (speed of stirrer) affect on the reaction because the dispersion of initial reagents was not enough. However, when initial reagents is stirred for a moment, ester is occur, which promotes the homogeneous reaction. Consequently, for reducing the mixing time of immiscible liquids, the mixing intensity, which can be estimated by Reynolds number, will be investigated. In addition, the mixing intensity is necessary to design the reactor and scale it up.

3.3.2 Reynolds Number

From previous work, the FFA reduction and the methyl ester production could be reached in 30 sec. and 5 min., respectively, when Reynolds number around ≥1,680 was used. Therefore, previous Reynolds number was used to estimate the mixing intensity or speed of stirrer by using Equation 3.37 and the other parameters in Table 3.7 and the calculated results in Topic 3.2.4.

$$N_{RE} = \frac{ND_{am}^{2}\rho}{\mu} \tag{3.37}$$

Table 3.7 Initial parameters for estimating the speed of stirrer

	Esterification	**Transesterification**
Total viscosity (Pa.s)	0.02530	0.00896
Total density (kg/m^3)	884.44	864.00
Reynolds number (N_{RE})	1,680	1,680

3.3.3 Mixing Time

Equation 3.38 is used to estimate the retention time for mixing the solution in the reactor. This equation indicates that 5 times of the retention time is required to well mix in the six-blade disc turbine reactor. However, the retention time depended on the size of reactor, of turbine, and the speed of stirrer.

$$t_T = \frac{5}{4} \times \frac{\pi D_{tm}^{2} H_{tm}}{0.92 N_s D_{am}^{2} D_{tm}} \tag{3.38}$$

3.3.4 Conclusions

For the estimation of mixing intensity, it was found that the lower initial speed of stirrer at 1,225 and 213 rpm were used to reduce FFA in 0.836 sec and produce ME in 4.810 sec, respectively. The highly speed of stirrer was used in esterification because the main reagent (MCPO) had high viscosity more than the main reagent (de-acidified MCPO containing some methanol) in transesterification as shown in Table 4.1. To be according to previous work, although, the speed of stirrer in the actual work should not to less than 1,225 and 213 rpm in esterification and transesterification; it was depended on the motor efficiency.

3.4 Design of Double-Pipe Heat Exchanger in Parallel Flow (Jacket)

3.4.1 Heating Solution in a Parallel Flow Heat Exchanger

Both solutions in esterification and transesterification process will be heated in a parallel flow double-pipe heat exchanger by paraffin oil as shown in Figure 3.15. The length of the heat exchangers (jacket) will be determined. This investigation is assumed that operating conditions and fluid properties (Table 3.8) are constant, and the heat exchanger is well insulated so that heat loss to environment is negligible. In addition, the kinetics and potential energies of fluid streams were also negligible and there was no fouling.

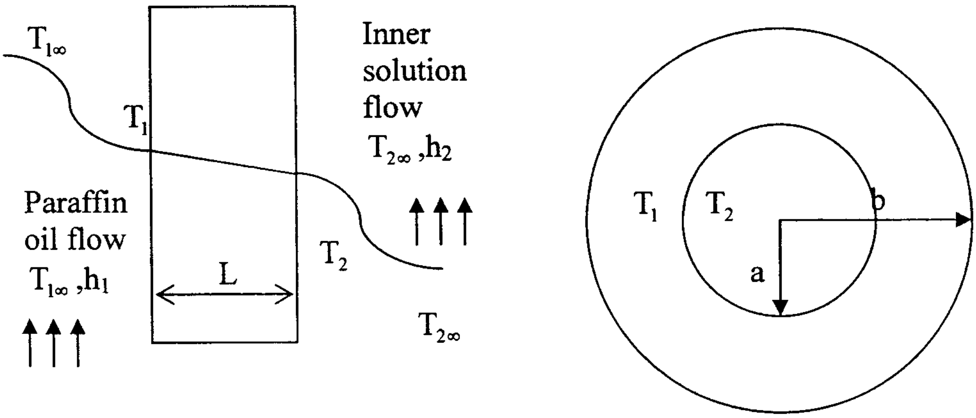


Figure 3.17 Thermal resistance for heat flow through a reactor wall with convection at both surfaces

In Figure 3.17, the heat flow is by convection from hot paraffin oil in jacket to the surface of the outside reactor wall. Then the heat flow is by conduction the reactor wall and by convection from the inside reactor wall to the solution in reactor. The rate of heat transfer in the heat exchange can be determined by using Equation 3.39 and the temperature of paraffin oil in jacket is determined by Equation 3.40.

$$\dot{Q} = \dot{m} C_p \Delta T \tag{3.39}$$

$$\dot{Q} = A_m h_1 (T_{1\infty} - T_1) = A_m k_m \left(\frac{T_1 - T_2}{L_t} \right) = A_m h_2 (T_2 - T_{2\infty}) \tag{3.40}$$

The convection heat transfer coefficients inside and outside the tube can be determined using the force convection relations. The hydraulic diameter for a circular tube is the diameter of each reactor, which is used to determine the mean of solution in reactor velocity and the Reynolds number as shown in Equation 3.41 and 3.42, respectively.

$$v_m = \frac{\dot{m}}{\rho(\frac{1}{4}\pi D_r^2)} \tag{3.41}$$

$$\mathrm{Re} = \frac{v_m D_r}{v} \tag{3.42}$$

The Nusselt number can be determined with Equation 3.43 by assuming that the flow to be fully developed. This equation can be investigated from Table 7-1, which is indicted by Çengel (2004).

$$\mathrm{Nu} = a_1 \cdot \mathrm{Re}^x \cdot \mathrm{Pr}^{0.4} \tag{3.43}$$

Then, Equation 3.44 is used to determine the convection heat transfer coefficients inside.

$$h = \frac{k \cdot \mathrm{Nu}}{D} \tag{3.44}$$

After that, the hydraulic diameter for the annular space is settle for step by step calculation of the convection heat transfer coefficients outside, which is similar to determine the convection heat transfer coefficients inside. Finally, both the convection heat transfer coefficients inside and outside are used to determine the temperature of paraffin oil. This investigate will be design the reactor in cylinder shape. Therefore, the logarithmic mean area is used Equation 3.45 and Figure 3.17, which is shown the calculation step in Equation 3.45-3.47.

$$A_m = \frac{A_o - A_i}{\ln(A_o / A_i)} \tag{3.45}$$

$$A_o = 2\pi r_o H_n \tag{3.46}$$

$$A_i = 2\pi r_i H_n \tag{3.47}$$

Table 3.8 Solution properties for solving the size of jacket

Properties	1st solution*	2nd solution*	Paraffin oil	References (paraffin oil)
Density, kg/m^3	884.440	864.000	825.000	(http://www.cartage.org.lb, 2008) and (Wikipedia, 2008a)
Viscosity, $Pa \cdot s$	2.530×10^{-2}	8.960×10^{-3}	1.900	(http://www.cartage.org.lb, 2008)
Kinematics viscosity, m^2/s	2.860×10^{-4}	1.037×10^{-5}	2.315×10^{-3}	-
Specific heat at constant pressure, KJ/kg· °C	1.996	2.050	2.130	(http://www2.ucdsb.on.ca, 2008)
Thermal conductivity, W/m· °C	0.174	0.176	0.250	(The Engineering ToolBox, 2008)
Mass flow rate, kg/s	1.230×10^{-2}	9.960×10^{-2}	0.220	-

*Appendix B and C

After that the flow rate of paraffin oil, the surface area and the length of heat exchanger is determined by Equation 3.39, 3.48 and 3.49, respectively.

$$\dot{Q} = UA_s\Delta T_p \tag{3.48}$$

$$A_s = \pi D_r L_j \tag{3.49}$$

Özişik (2000) indicated that, the overall heat transfer coefficient base on the outer reactor surface is usually used in the heat exchanger applications. The overall heat transfer coefficient can be expressed as the thermal resistance base on the outside surface of the reactor. Therefore, the overall heat transfer coefficient can be determined by using Equation 3.51.

$$U_o = \frac{1}{A_0 R} \tag{3.50}$$

$$U_o = \frac{1}{(D_o / D_i)(1/h_2) + (1/2k)D_o \ln(D_o / D_i) + 1/h_1} \tag{3.51}$$

If the length of jacket is higher than reactor length, fins should be used for increasing the surface area of reactor, which can reduce the length of jacket. The number of fins can be determined by Equation 3.52.

$$n = \frac{Ws}{S + t} \tag{3.52}$$

3.4.2 Conclusions

The length at 25.00 cm. and the diameter at 25.00 cm. (including the diameter of reactor) were established in estimation of esterification jacket size. The dimension of transesterification jacket at 25.00 cm in length and at 27.60 cm in diameter (including the diameter of reactor) was also obtained. Paraffin oil at 60.12 and 68.89 °C was used for heating solution in esterification and transesterification, respectively.

3.5 Design of Continuous Gravity Decanter Separation

Several methods can be used to separate immiscible liquids such as continuous gravity decanter, centrifugal decanter and hydro-cyclone. This investigation is purposed to separate the two liquids (de-acidified MCPO: the first stage waste, and crude biodiesel: crude glycerin) which are the large different density as shown in Appendix A, so that the continuous gravity decanter separation is considered to separate the immiscible liquids in reasonable time.

3.5.1 Principle of Continuous Gravity Decanter Separation Calculation

Continuous gravity decanter in horizontal cylinder is used to separate the different density two liquids. The slowly flow of feed mixture enters at the one end of the separator and then the mixture separates into two layers. After that, the two liquids discharge through overflow lines at the other end of the vessel.

3.5.1.1 Requirement Time

First of all, the required time for separating the immiscible liquids should be recognized the establishment of the size of decanter. The separation time depends on the difference between the densities of two liquids and on the viscosity of the continuous phase as shown in Equation 3.53.

$$t_s = \frac{100\mu_t}{\rho_A - \rho_B} \tag{3.53}$$

3.5.1.2 Size of Decanter

After that, the length and diameter of decanter is estimated by using the relationship between the separated time, the mixing flow rate and the cross section area of decanter as shown in Equation 3.54. In addition, the length of the decanter should be about 5 times of diameter and the existent volume of the separate tank is 95 % of the full vessel. After establishing the full size of the continuous gravity separated decanter, the height of liquid overflow will be calculation by using Equation 3.55.

$$L_d = \frac{Q \times t_s}{A_d} \tag{3.54}$$

$$Z_{A2} = Z_{A1} + (Z_T - Z_{A1}(\frac{\rho_B}{\rho_A})) \tag{3.55}$$

3.5.2 Conclusion of Continuous Gravity Decanter Separation Design

The principle design of continuous gravity separated decanter, the total viscosity and total densities of two liquids (Table 3.7) were used to calculation the size of decanter and the height of the liquid over flow as shown in Table 3.8.

Table 3.9 Size of continuous gravity decanter separation for esterification and transesterification

	Esterification	Transesterification
Separation time (hr.)	3.67	0.91
Length of decanter (cm.)	187.25	121.36
Diameter of decanter (cm.)	38.41	24.92
Decanter value (L)	206.15	56.19
Full decanter value (L)	217.00	59.15
Liquid depth, Z_t (cm.)	34.57	22.42
Heavy phase depth, Z_{A1} (cm.)	17.28	11.21
Light phase depth, Z_B(cm.)	17.28	11.21
Feed hold, Z_{A1}(cm.)	17.28	11.21
Light liquid overflow, Z_t (cm.)	34.57	22.42
Heavy liquid overflow, Z_{A2} (cm.)	31.82	21.07

3.6 Design of Methanol Distillatory

Normally, the production cost of biodiesel is higher than diesel due to the cost of vegetable oil and excess methanol, which are used in the process. To control the production cost of biodiesel, raw material cost (vegetable oil and methanol) have to be reduced. It is found that the price of vegetable oil can not be reduced because it is depended on marketing mechanisms. The simply method to control the price of pure biodiesel is to reduce the utilization of methanol by recovering excess methanol containing in crude biodiesel and waste.

3.6.1 Estimation of Minimum Number of Plates in Methanol Distillatory

McCabe-Thiele Method is generally used to estimate the number of plate in methanol distillatory. In experiment, methanol is recovered from the solution of methanol-water, of methanol-crude biodiesel and of methanol-glycerol. It is found that McCabe-Thiele Method can not used to estimate the plate number in methanol distillatory because it does not have equilibrium curve of methanol-crude biodiesel and of methanol-glycerol. Therefore, a simple method based on the relative volatility (the ratio of the vapor pressure) of the two components is used to calculate the minimum number of plate from the terminal concentration of mass fraction or mole fraction in bottom and in overhead product, which is defined in term of the equilibrium concentrations.

3.6.1.1 The Minimum of Plates

The equilibrium concentrations of two components is defined by an ideal mixture follows Raoult's law and the relative volatility (McCrabe, 2001), which is the ratio of the vapor pressure as shown in Equation 5.36

$$\alpha_{AB} = \frac{P'_A}{P'_B} \qquad (3.56)$$

The minimum number of plate can be solved by using Table 3.10, and Equation 3.56 and 3.57 (McCrabe, 2001). In addition, the mass fractions in bottom and in overhead product are fixed at 0.01 and 0.99, respectively.

$$N_{min} = \frac{\ln[x_D(1-x_B)/x_B(1-x_D)]}{\ln \alpha_{AB}} \qquad (3.57)$$

Table 3.10 Vapor pressure of components

Components	Temperature (°C)	Vapor pressure (kPa)	Reference
Glycerol	60.00	8.933×10^{-4}	Jungermann, 1991
	70.00	2.266×10^{-3}	
Methyl ester	59.50	5.000×10^{-4}	Genderen, 2002
	61.25	8.000×10^{-4}	
Water	60	19.947	Çengel, et al., 2008
	65	25.043	
Methanol	64.8	101.124	Department of Chemical and Materials Engineering, University of Alberta, 2009

3.6.1.2 Conclusions

In the estimation, the minimum stages for distilling methanol from the solution of methanol-water, of methanol-biodiesel and of methanol-glycerol was shown in Table

3.11. The results indicated that the distillatory tower of methanol-water solution has a large number of plates more than other solution because the water could be evaporated at the boiling point of methanol more than other solution as could be seen the vapor pressure in Table 3.10. However, in simulation process (Chapter 4), it was found that two plates of methanol-biodiesel distillatory and of methanol-glycerol distillatory were the minimum plate number that could be input in the block of distillation. Therefore, the plate number of plate in simulation process was used for fabricating the distillatory in this work.

Table 3.11 The minimum number of plate in methanol distillatory

Solution	**Number of stage**		
	Design	Design include 40% of equipment efficiency	Simulation
Methanol-water	4.7097	~7	7
Methanol-biodiesel	0.1350	~1	2
Methanol-glycerol	0.0265	~1	2

3.6.2 Design of Sieve-Plate Columns

After estimating the plate number of methanol distillatory, the complete design will be investigated. The investigation (McCabe, 2001) of distillation tower design indicates that tower diameter and plate spacing (plate n to plate n-1) of distillatory should not be less than 30 and 15 centimeter, respectively as shown in Figure 3.18. In addition, each downcomer usually occupies 15 % of the column cross section, and for bubbling or contacting, each downcomer should be living 80 % of the column length. The plate hole should not be less than 0.5 centimeter. Moreover, to permit some degassing of the liquid before it passes over the weir, one or two rows of holes may omit near the overflow weir.

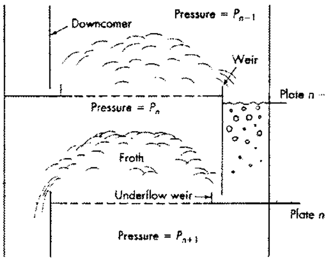


Figure 3.18 Normal operation of sieve plate in methanol distillation tower

(McCrabe, 2001)

3.6.3 Design of Condenser

3.6.3.1 Condenser

Methanol in vapor phase flowing in the jacket is condensed with ambient temperature water flowing in the inner pipe of a double pipe heat exchanger as shown in Figure 3.19.

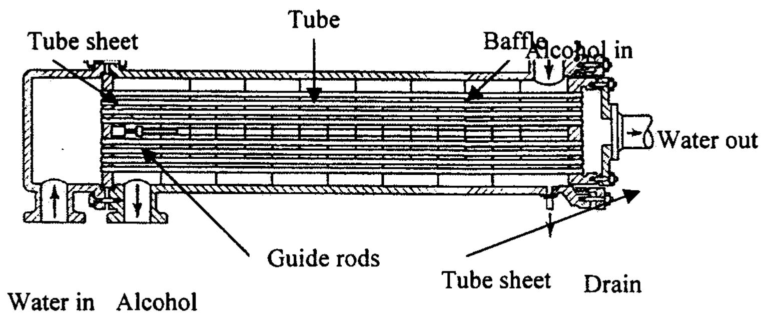


Figure 3.19 Methyl alcohol condenser (McCrabe, 2001)

The rate of heat transfer in the heat exchange can be determined by using Equation 3.41 (Çengel, 2004). After that the surface area and the length of cooler is determined by Equation 3.58 and 3.59, respectively (Çengel, 2004).

$$\dot{Q} = UA_s\Delta T_{lm} \tag{3.58}$$

$$A_s = \pi D_r L_j \tag{3.59}$$

The overall heat transfer coefficient can be determined by using Equation 3.60 (McCabe, 2001).

$$\frac{1}{U} = \frac{1}{\frac{1}{h_i} + \frac{x_w}{k_m} + \frac{1}{h_o}} \tag{3.60}$$

Table 3.12 The properties of water at 25 °C (Çengel, 2004)

Properties	Water
Density, kg/m^3	997.000
Viscosity, Pa.s	0.891×10^{-3}
Kinematics viscosity, m^2/s	8.937×10^{-7}
Specific heat at constant pressure, KJ/kg· K	4.108
Thermal conductivity, W/m·°C	0.697

The convection heat transfer coefficient inside the tube (water) is determined similar to the step of jacket estimation (Topic 3.4) by using the properties of water at Table 3.12. The mean velocity of the solution in inner tube is fixed at least 0.9 m/s and the inner tube is made from 5/8 in. (15.9 mm.) BWG no. 18 tube data indicating by McCabe (2001). Moreover, the convection heat transfer coefficient outside the tube (methanol alcohol) is fixed at 1,000 $\mathrm{W/m\cdot{}^{\circ}C}$ giving from the least of condensing organic vapor in Table 11.2 of McCabe (2001) handbook. The result indicated that length of cooling tube is around 90 centimeters.

3.6.3.2 Condensation of Methanol vapor on Horizontal Tube Banks

After getting the length of tube, it is cut into 9 horizontal tubes of 10 centimeters per tube and arranged the horizontal tube in a square (3×3 tubes). Therefore, the average heat transfer coefficient for vertical tier of 3 horizontal tubes, which is related to the one for a single horizontal tube getting in Topic 3.6.3.1, is determined by Çengel (2004) in the topic of horizontal tube banks as shown in Equation 3.61.

$$\mathrm{h}_{\text{horizontal,n tube}} = \frac{1}{N^{\frac{1}{4}}}\mathrm{h}_{\text{horizontal,1 tube}} \qquad (3.61)$$

Subsequently, the heat transfer coefficient for vertical tier of 3 horizontal tubes is used to recalculate the rate of heat transfer. The result of calculation indicated that 9 horizontal tubes of 10 centimeters per tube, which was arranged in a square (3×3 tubes) has enough rate of heat transfer for cooling the methanol vapor from distillation.

3.6.4 Purification System

After draining glycerol which occurred in transesterification batch process, crude biodiesel was washed four times under ambient temperature. In the first two times, the ambient-temperatured water was sprayed over the surface of the solution until the water volume was equal to the biodiesel volume. After 15 minutes, the washing water was drained. Subsequently, in the third time, the ambient-temperatured water at equal volume to the biodiesel was sprayed over the surface of solution again and then the solution was washed with a bubble technique for 15 minutes. Next, the solution was left for 15 minutes and the washed water was again drained. In the forth and final time, the method was similar to the third time; however, the bubble technique was extended to around 8-12 hours. Finally, after draining, the cleansed solution was heated until it was clear (Suwanmanee, 2006). Not only was heating 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 offered to purify crude biodiesel by ion exchanging with resin, amberlite and purolite, or absorbing with silicates, magnesol (magnesium silicates) and trisyl (Schroeder Biofuels, 1946).

Resin (Lewtit® GF 202: a macroporous cation exchange) was used as adsorbent in dry washing continuous system of this work. Due to resin having high price, Bayer Thai Co., Ltd. (Ion Exchange Resins Group) was assisting this work with giving 0.7 L of resin. Although the obtained resin was not enough to use in full scale of biodiesel production, it was adequate for using in LAB scale. Therefore, the column of biodiesel purification was fabricated according to the guide for laboratory tests with Lewitt Ion Exchanges that Bayer Thai Co., Ltd. (Ion Exchange Resins Group) provided for this work as shown parameters in Table 3.13.

Table 3.13 The portions of resin column

Column	Dimensions
Resin volume (L)	0.6
Diameter (cm)	5
Bed Depth (cm)	30
Column height (cm)	50

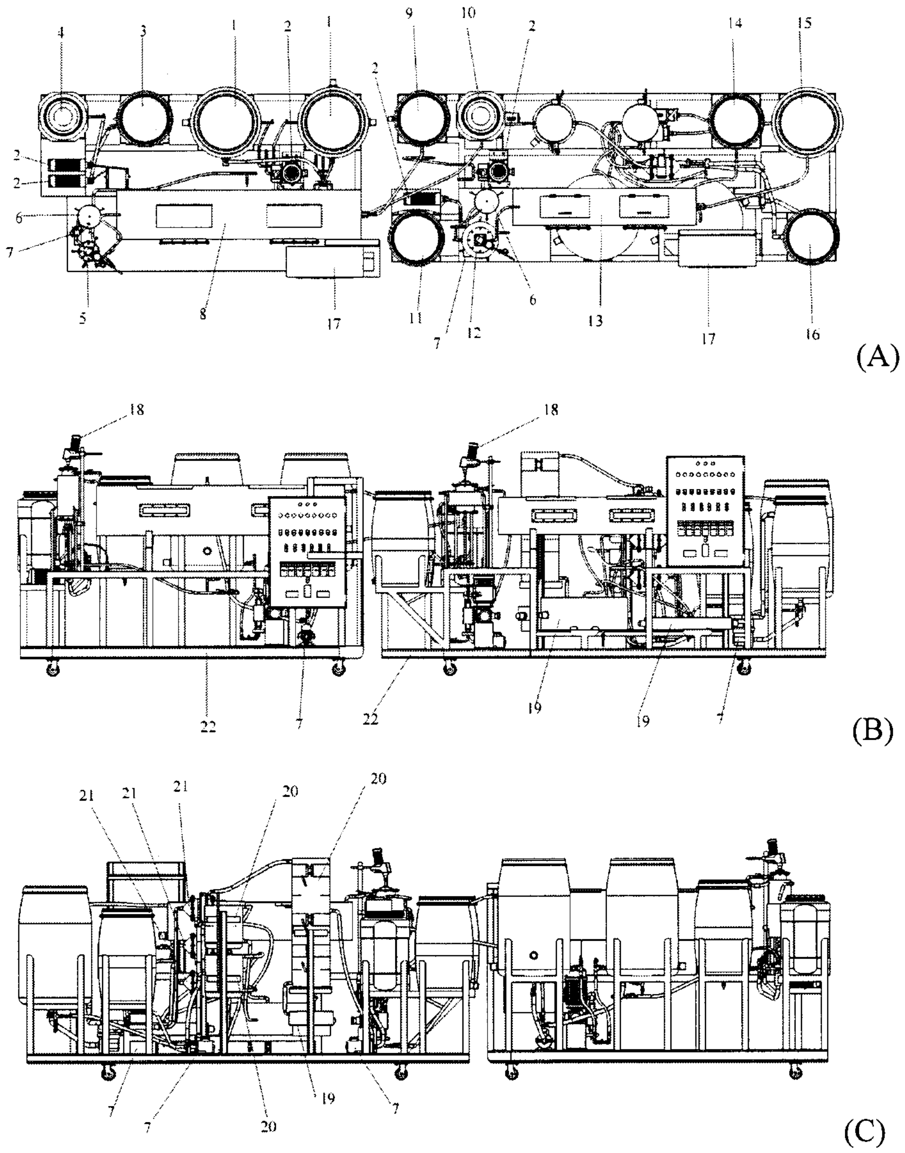
3.7 Conclusions

- The design of the two-stage process continuous stirred tank reactor as shown in Figure 3.20 and Appendix D indicated the reactor (the six-blade disc turbine reactor installed with 4 baffles) capacity of 1.5 L (esterification) and 3 L (transesterification) separating into 3 and 2 tank for reducing FFA in MCPO to less than 1 wt% by esterification and producing ME to more than 97 wt% by esterification, respectively. The highest concentration of FFA and TG could be used in the CSTR of this work were 35 wt% and 100 wt%, respectively.

- The size of reactor depended on the reaction rate of each reaction and the flow rate of feeding solution. The six-blade disc turbine reactor installed with 4 baffles was used in this process, which was found that the vessel agitation size was related to the height and the diameter of vessel.

- After establishing the reactor and vessel agitation size, the speed of stirrer, which depended on the viscosity of solution, was determined. The lower initial speed of stirrer at 1,225 and 213 rpm were used to reduce FFA in 0.836 sec and produce ME in 4.810 sec, respectively.

- Double-pipe heat exchanger in parallel flow was estimated for heating the solution in the reactor to reach the required temperature (60 °C). It was found that paraffin oil around 60 - 69 °C was used when the length of jacket was 25.00 and 25.00 cm. and the diameter of jackets was 17.00 and 27.60 cm. (including the diameter of reactor) for esterification and transesterification, respectively.



1. MCPO storage tank
2. Metering pump
3. Methanol storage tank
4. Sulfuric acid storage tank
5. CSTR of esterification
6. Hot paraffin oil tank
7. Pump
8. Separate tank of esterification
9. De-acidified MCPO storage tank
10. 1st-stage waste solution storage tank
11. Potassium methoxide solution storage tank
12. CSTR of transesterification
13. Separate tank of transesterification
14. Crude glycerol storage tank
15. Crude biodiesel storage tank
16. Water tank
17. Controller
18. Stirrer motor
19. Re-boiler
22. Distillation tower
25. Condenser
26. Base

Figure 3.20 Top view (A), front view (B) and back view (C) of the two-stage continuous process

- At the end of the process, the solution was separated by horizontal cylinder continuous gravity decanter, which sized 217 L for esterification and 59.15 L for transesterification. The results indicated that both the densities of two liquids and the viscosities of the continuous phase were affected on the separated time and separated agitation size.

- The minimum plates for distilling methanol from the solution of methanol-water, of methanol-crude biodiesel and of methanol-glycerol were 7, 2 and 2, respectively. The number of distillation methanol plates was depended on the vapor pressure of each compound in solution.

- The condenser for cooling the vapor phase of methanol was consisted of 9 horizontal tubes sizing of 10 centimeters per tube and it was arranged into horizontal tube in a square (3×3 tubes).

- Due to high price of resin, the purification of biodiesel in LAB scale was investigated. Therefore, drawing of it was not shown in the Figure 3.20 and Appendix D. The total volume of column was 981.75 cm^3 that contained resin of 0.6 L in bed depth at 30 cm.

CHAPTER 4

SIMULATION FOR VERIFICATION THE DESIGN OF TWO-STAGE CONTINUOUS SYSTEM

Normally, simulation is used (prior to start the chemical laboratory) to study the competence of system and the tendency of final product (such as retention time, product components and flow rate) for verifying the settle of experiments, which can reduce the experimental failure, and help to cut down the laboratory experiments and the operating of pilot plant (Fogler, 2002). In addition, the comparison between experimental data and simulation data is required for increasing the high quality of published paper. The ASPEN PLUS Simulation Engine, a commercial program, is used for estimating the biodiesel production from MCPO having high FFA by using the two-stage continuous process because it is suitable for using to simulate the chemical reaction and easy to input, and verify the information.

4.1 Physical Properties of ASPEN PLUS Simulation Engine

4.1.1 ASPEN PLUS Main Window

In the main window, title bar, menu bar, toolbar, process flow sheet window, selection bottom of the steam type, and model library are showed. The process flow sheet window is used to create, and to display simulation flow sheets and drawings. The model library at the bottom of the main window employs in selecting unit operation models and icons by placing on the flow sheet.

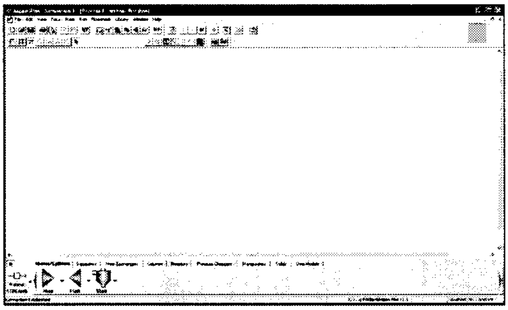


Figure 4.1 ASPEN PLUS Main Window

4.1.2 Setup

The required input specifications are entered in order of setting up the global simulation and of accounting options for running the flow sheet as shown in Figure 4.2 and 4.3.

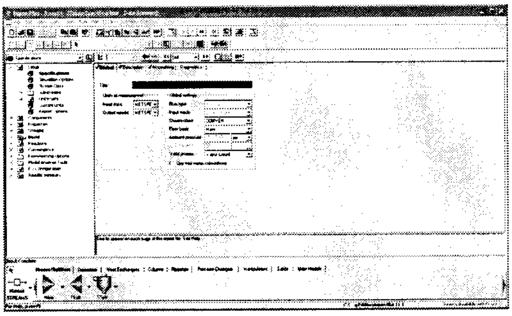


Figure 4.2 Global simulation options

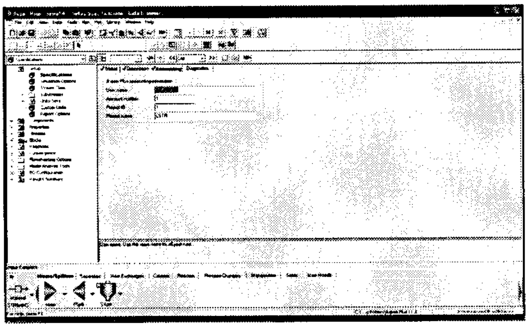


Figure 4.3 Accounting options

4.1.3 Component

After entering the required input specification in setup, the conventional chemical components of each reaction, which is used in simulation, are adding from databank list by normally searching with component name or formula. In addition, molecular weight, boiling point, and component identification are also used to search the component from databank list as shown in Figure 4.4.

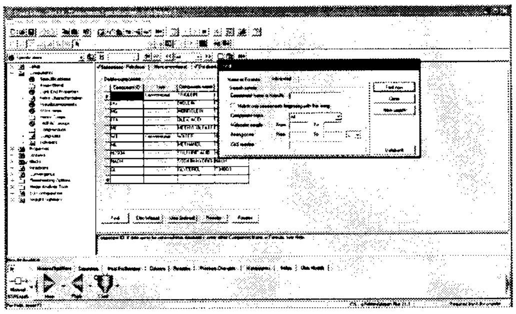


Figure4.4 Component folder

4.1.4 Properties

The required specifications of property methods and models options in properties are input into property specification folder as shown in Figure 4.5. Then the molecular structures, which are written by ChemDraw, are imported to the conventional chemical components as shown Figure 4.6. After that, the molecular structure bond is calculated as shown in Figure 4.7.

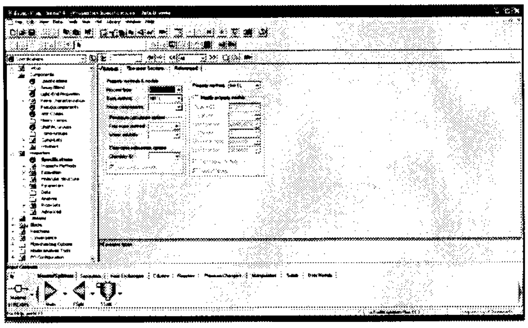


Figure 4.5 Property methods and models options

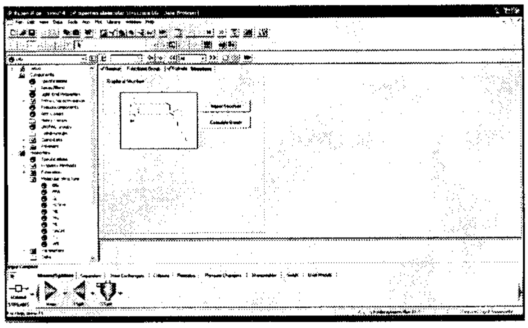


Figure 4.6 Graphical structure

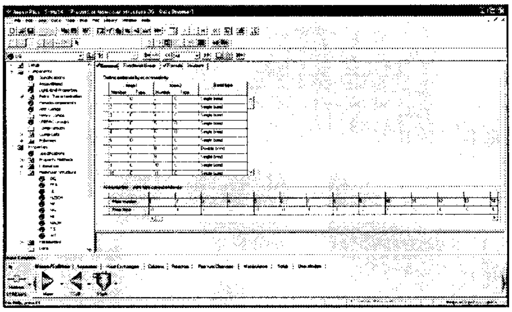


Figure 4.7 Molecule definitions by its connectivity

4.1.5 Streams

The required input specifications and flash options of composition, flows and thermodynamic condition are entered for initial material process feed streams as shown in Figure 4.8.

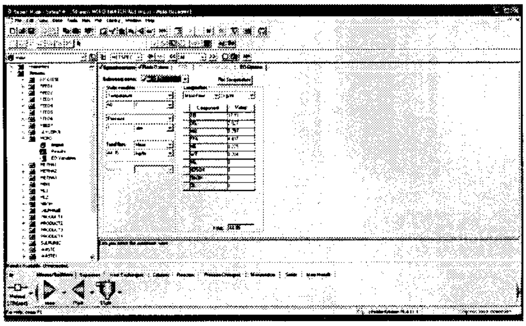


Figure 4.8 Steam properties and phase conditions determination

4.1.6 Blocks

The unit operation models are used to represent actual pieces of equipment, which are found in processing biodiesel plants. A flow sheet simulation is run under the specification at least one unit operation model.

4.1.6.1 Heater

The block of heater is installed in ASPEN PLUS main window, and then the material stream block is connected to feed line and production line of heater as shown in Figure 4.9. The specification options of its block (temperature and pressure) are required before running the program (Figure 4.10).

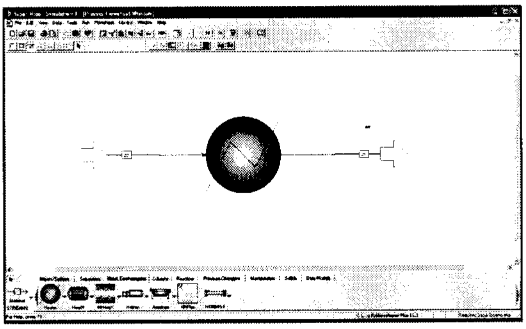


Figure 4.9 The block of heater in ASPEN PLUS main window

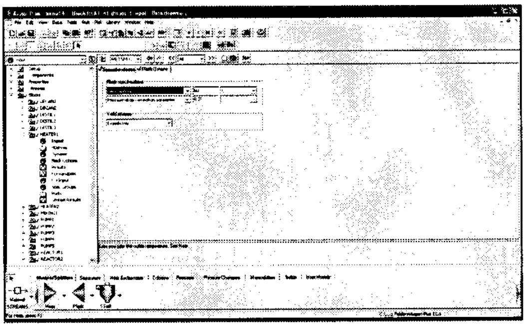


Figure 4.10 The specification options of heater block

4.1.6.2 Pump

The block of pump (connecting feed line and production line with material stream block) is installed in ASPEN PLUS main window as shown in Figure 4.11. The condition of its block (pressure and pump efficiency) are input in specification options as shown in Figure 4.12.

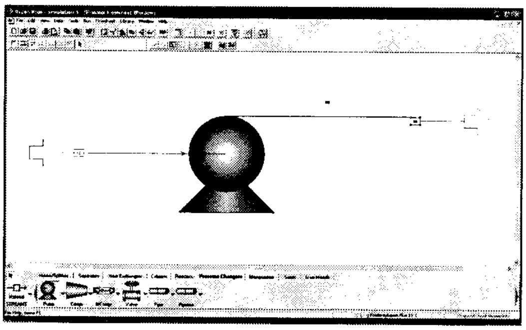


Figure 4.11 The block of pump in ASPEN PLUS main window

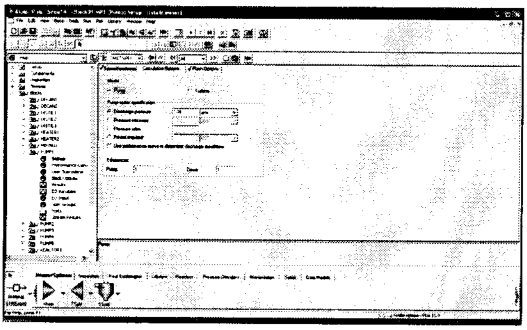


Figure 4.12 The specification options of pump block

4.1.6.3 Mixer

In ASPEN PLUS main window as shown in Figure 4.13, Mixer block is installed and then connected with two feed lines and one production line of material stream block. After that, in Figure 4.14, the requirements of flash options (pressure and temperature) are input.

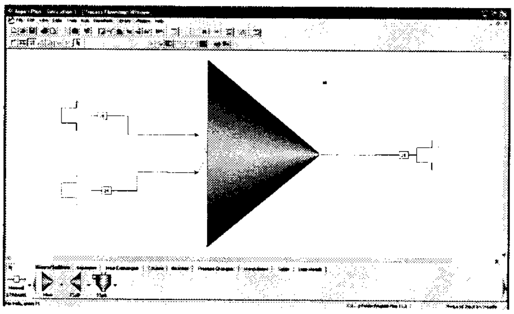


Figure 4.13 The block of mixer in ASPEN PLUS main window

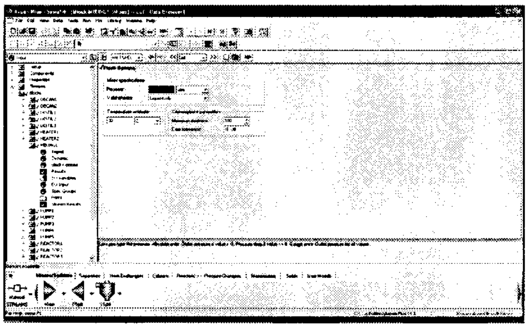


Figure 4.14 The flash options of mixer block

4.1.6.4 Reactor

Two blocks of CSTR are selected from reactor unit operation models and connected with three feed lines and a line of each production as shown in Figure 4.15. After that, the requirements (temperature, pressure and volume of reactor) of CSTR block are input in specification options as shown in Figure 4.16. After that, the reaction is added into reaction options (Figure 4.17) before simulating the model.

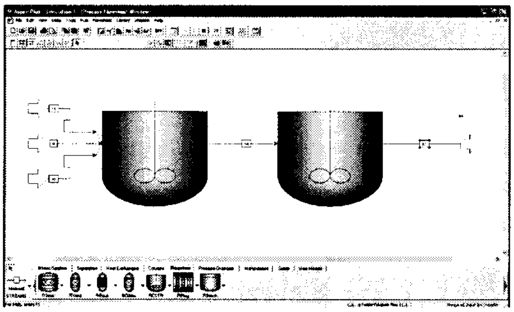


Figure 4.15 The block of reactor in ASPEN PLUS main window

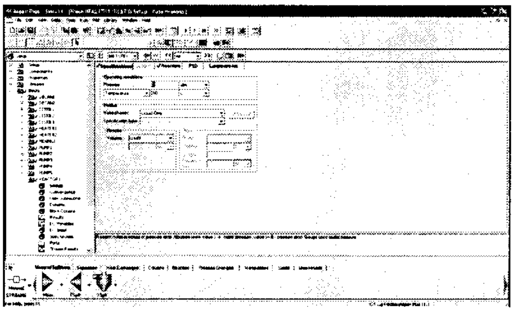


Figure 4.16 The specification options of CSTR block

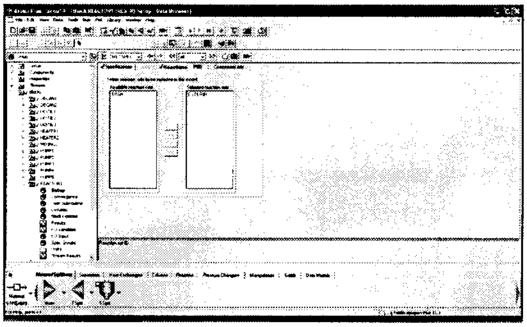


Figure 4.17 The reaction option of CSTR block

4.1.6.5 Decanter

In ASPEN PLUS main window, decanter is installed and connected with one feed line and two production lines of material stream block as shown in Figure 4.18.

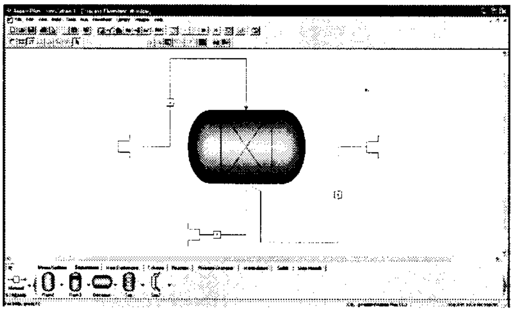


Figure 4.18 The block of decanter in ASPEN PLUS main window

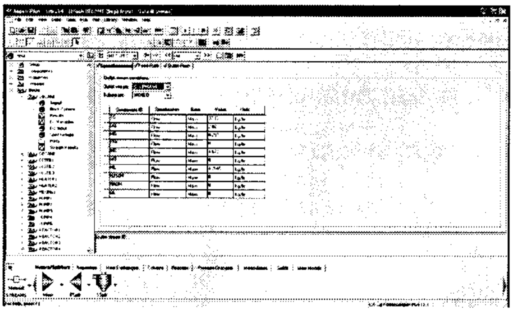


Figure 4.19 The specification options of decanter block

Then the outlet steam conditions in specification options are set are shown in Figure 4.19. Finally, both of temperature and pressure in feed flash options and outlet options are set as shown in Figure 4.20 and 4.21.

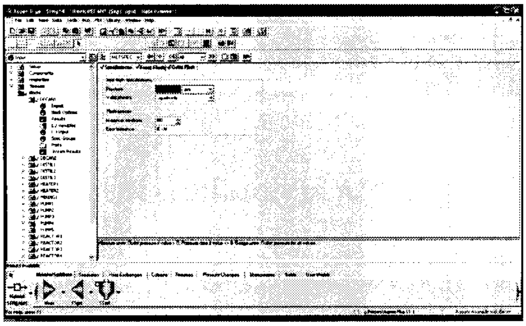


Figure 4.20 The feed flash options of decanter block

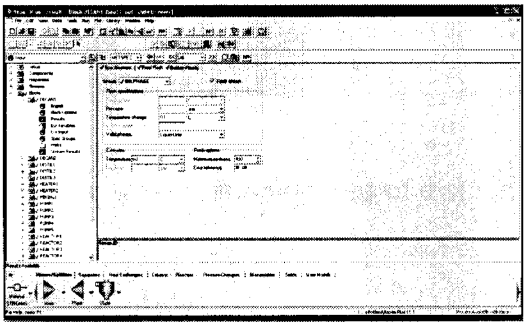


Figure 4.21 The outlet flash options of decanter block

4.1.6.6 Distillatory

The distillatory in Figure 4.22, which is installed in main window of ASPEN PLUS, is connected with a feed line, over phase production line and bottom phase production line. The number of stages, pressure, and component recovery of light phase and heavy phase are set in specification options of distillation as shown in Figure 4.23.

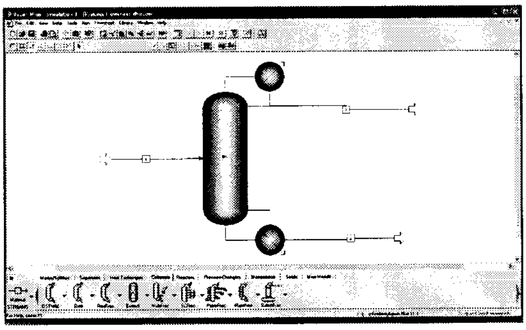


Figure 4.22 The block of distillatory in ASPEN PLUS main window

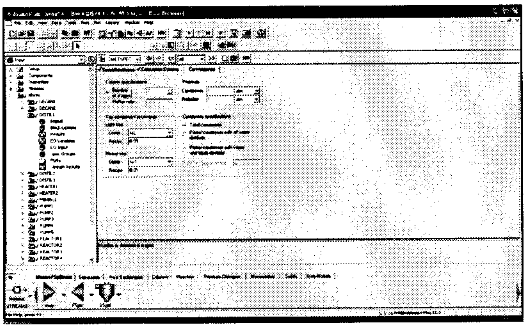


Figure 4.23 The specification options of distillatory block

4.1.7 Reactions

First, rate lows of reactions (Equation 3.13-3.20) are added into stoichiometry options as shown in Figure 4.24. Then rate coefficient and exponent of reactants and products are also added in stoichiometry options as shown in Figure 4.25. Finally, the required kinetics of each reaction as shown in Equation 3.13-3.20 is input in kinetic options as shown in Figure 4.26.

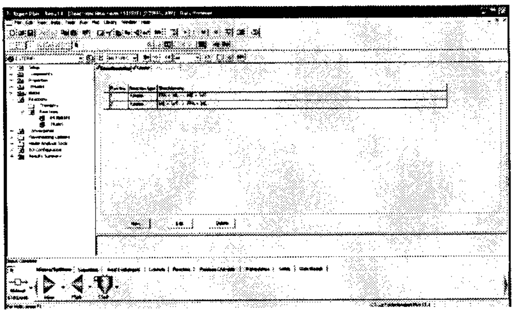


Figure 4.24 The stoichiometry options of reactions

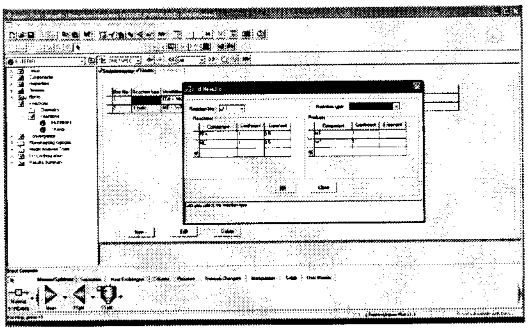


Figure 4.25 Addition of rate coefficient and exponent of reactants and products

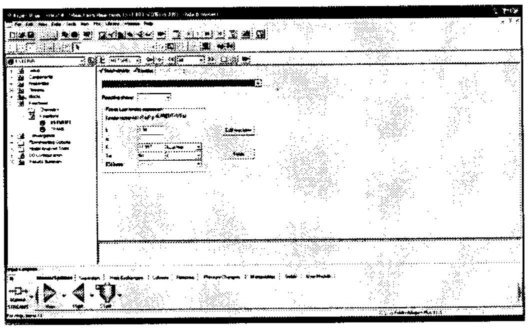


Figure 4.26 The kinetic options of reactions

4.1.8 Steam Result

After achieving simulation, the results in stream result are shown according to the requirement, which is set in Topic 4.1.2 as shown in Figure 4.27.

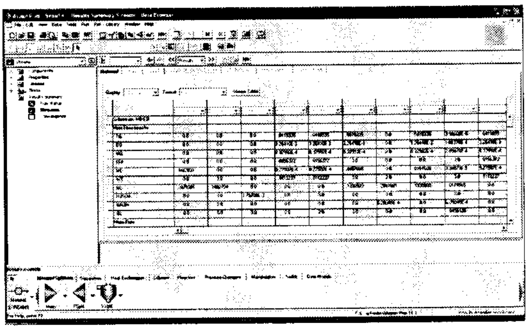


Figure 4.27 Steam result

4.2 Methodology

The continuous of FFA reduction containing in MCPO and of biodiesel production from MCPO under the suitable condition by the continuous stirred tank reactor (CSTR) in series were investigated. The amount of tank with kinetics of esterification and transesterification, horizontal separation decanter, and methanol distillatory were estimated by the principle of process design as shown in Chapter 3 and by condition as followed:

First, MCPO, which consisted of 9.966 wt% of FFA, 0.618 wt% of ME, 83.718 wt% of TG, 4.566 wt% of DG, 0.676 wt% of MG and 0.458 wt% of WT, was heated until it reached 60 °C. After that, the suitable flow rate of MCPO, methanol and sulfuric acid at 44.35, 4.751, and 0.368 kg/hr, respectively, was fed into reactor which will be heated by hot oil and stirred all the time. At least 2 wt% of FFA must be resulted the periodically monitoring. After that, the waste solution was separated by decanter and then the acid value in oily solution was monitoring. The suitable flow rate of oily solution and sodium methoxide solution at 43.25 and 9.182 kg/hr were fed into reactor heating at 60 °C by hot oil and stirred all the time. The result of the periodically monitoring must be indicated biodiesel at least 96.5 wt%. Finally, before cleaning biodiesel, methanol in the final production and waste solution were distilled and verified its purity.

The ASPEN PLUS Simulation Engine was used to verify the design in Chapter 3 and to investigate a tendency of biodiesel production before stating the experiment. The methodology (Figure 4.28, 4.29 and 4.30) could be simulated as followed:

1. Specific chemical with metric units' template was selected in this study.

2. The global simulation and accounting options in setup were set.

3. The first block of CSTR and material steam block of feed (MCPO, Methanol and H_2SO_4) and product was installed in the ASPEN PLUS main window.

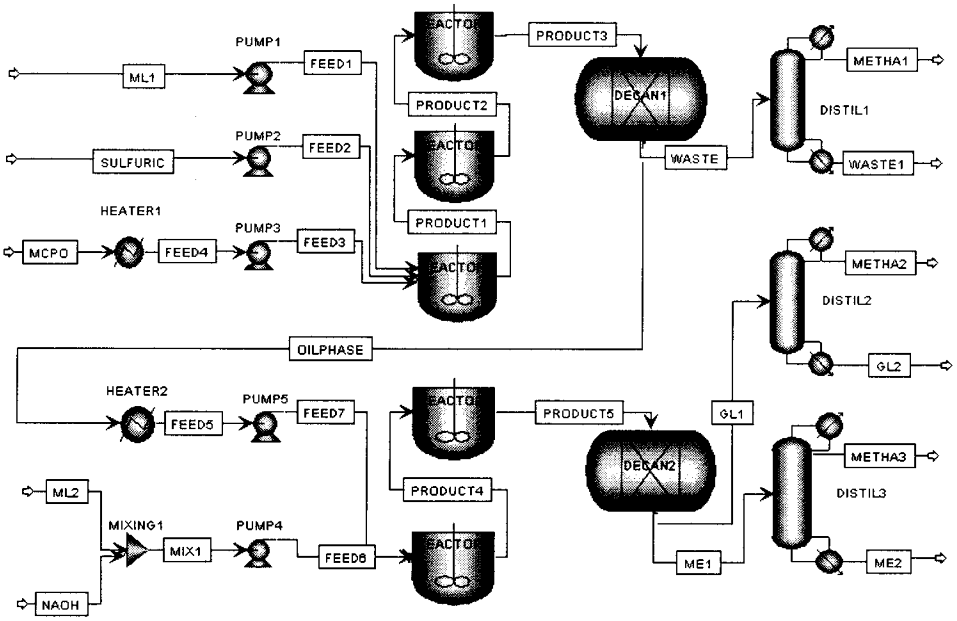


Figure 4.28 ASPEN PLUS Simulation Engine model for analysis full system of biodiesel production from MCPO

4. The chemical structures of MCPO, Methanol and H_2SO_4 in esterification reaction, which was used in simulation, were adding from databank list in components.

5. The methods option and the structures of MCPO, Methanol and H_2SO_4 were set in properties.

6. Mass flow rates of MCPO, Methanol and H_2SO_4 in term of kg/hr were input in steams according to condition of design.

7. Esterification reaction and reaction kinetics in Equation 3.8, 3.15 and 3.16 were set in reactions. Then CSTR in blocks was set.

8. The simulation was run. If it failed, the initial conditions of mass flow rate, reaction and block of CSTR were verified again until the simulation succeeded.

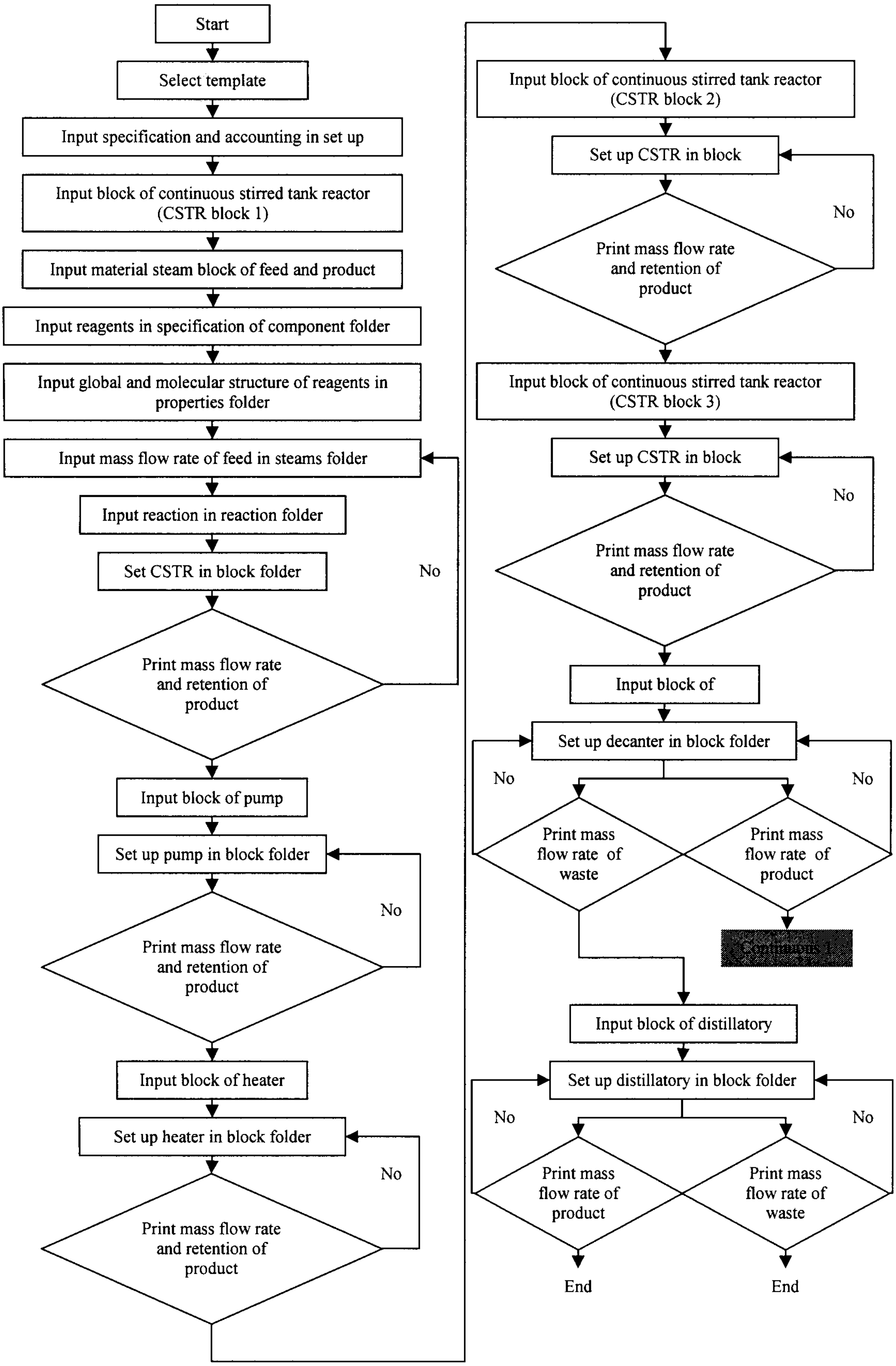


Figure 4.29 Diagram for simulation the process of biodiesel production from MCPO with ASPEN PLUS Simulation Engine

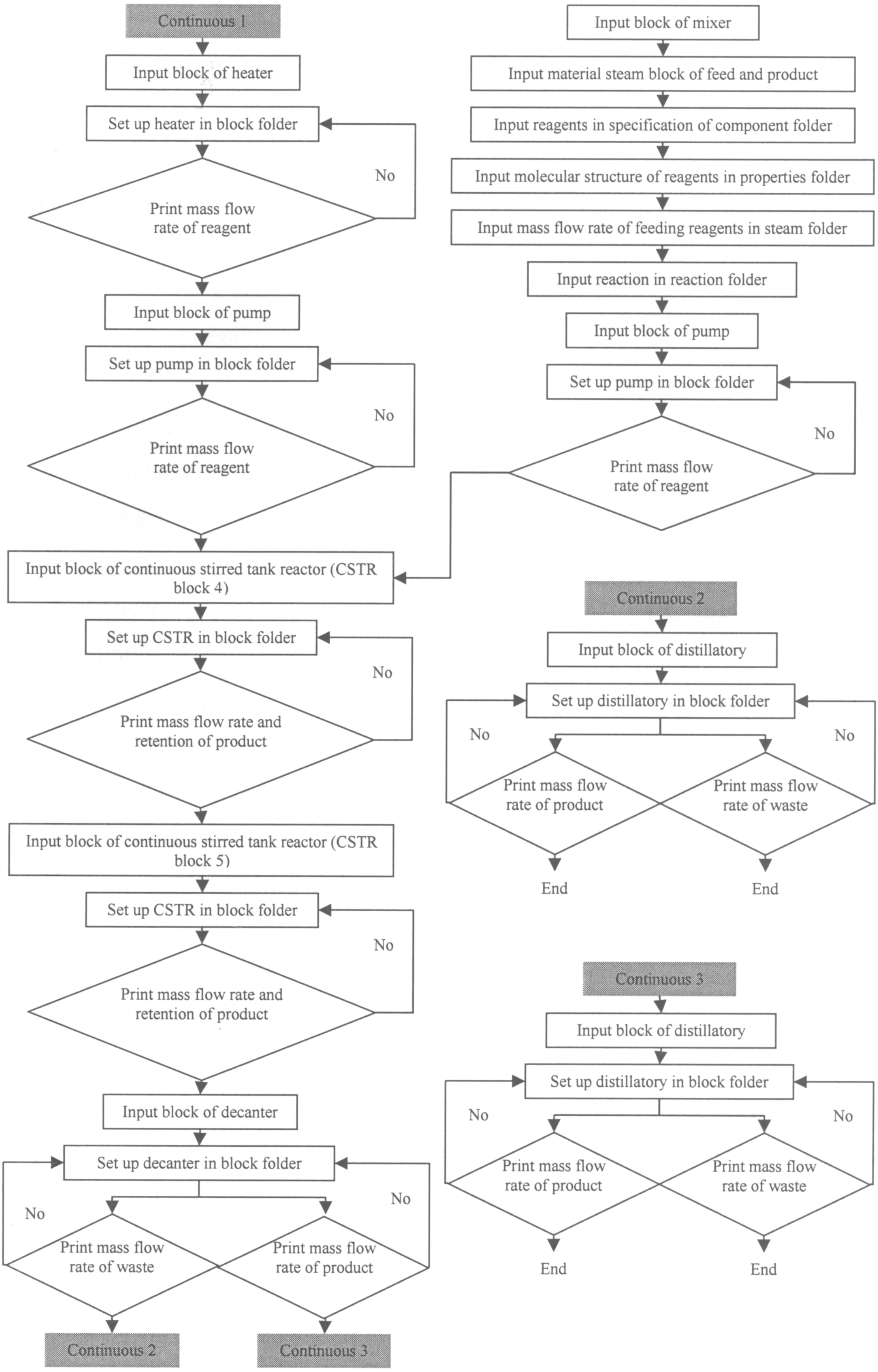


Figure 4.30 Diagram for simulation the process of biodiesel production from MCPO with ASPEN PLUS Simulation Engine (Cont')

9. The blocks of MCPO, methanol and sulfuric acid pump were installed and reconnected destination. After that the conditions of pumps were set and the simulation was run. If it could not print the results, the conditions of pump were verified until the simulation was achieved.

10. The block of heater was installed and reconnected destination to the block of pump. After installing and setting the heater for heating MCPO in main window, the simulations was run again until it succeeded.

11. The second block of CSTR was installed and reconnected destination, respectively. The conditions of each block such as initial conditions of reactor and the reaction were set. Subsequently, the simulation was run until it was successful.

12. After succeeding simulation the second block of CSTR, the third one was similarly simulated in the step for the second block of CSTR.

13. The block of decanter was installed and reconnected destination. The solution was separated into 2 phases: oily solution and waste by setting in the decanter condition. If the results could not print, the conditions of decanter were verified until the simulation was achieved.

14. Process line of oily solution was added the block of heater and pump, respectively. Both conditions were set and simulation until the simulation was reached.

15. During setting the block of heater and pump, the sodium methoxide solution was started to install the block of mixer and material steam block of methanol, sodium hydroxide and production.

16. The chemical structure of sodium hydroxide, which was used in the simulation of transesterification reaction, was adding from databank list in components.

17. The methods option and the structures of sodium hydroxide were set in properties.

18. According to condition of design, mass flow rates of methanol and sodium hydroxide in term of kg/hr were input in steams.

19. Transesterification reaction and reaction kinetics in Equation 3.13 and 3.17-3.20 were set in reactions. Then CSTR in blocks for transesterification process was connected to the line of sodium methodixe solution.

20. After setting the conditions in CSTR, the simulation was run. If it failed, the initial conditions of mass flow rate, reaction and block of CSTR were verified again until the simulation achieved.

21. After succeeding simulation the first block of CSTR for transesterification, the second one was similarly simulated in the step for the first block of CSTR.

21. The block of decanter was installed and reconnected destination to the end line of second CSTR block. Before printing the results, the condition of decanter was set for separating final product into crude biodiesel and glycerin. If the results could not print, the conditions of decanter were verified until the simulation was achieved.

22. The final product of each end line was connected to the distillatory block for studying the conditions of methanol recovery. The conditions of distillatory were verified until the simulation was succeeded.

4.3 Results and Discussion

After finishing the simulation, the results of final product was printed for verifying the design. The results were shown in term of mass flow rate, retention time, the concentration of product and some conditions, which was usefully for future work.

4.3.1. Esterification

After already setting the conditions of esterification reaction according to the reactor design, the simulation was run. It was found that the total retention time of each tank CSTR in series was around 18 seconds. The concentration of FFA at 9.96 wt% (the ratio between FFA mass flow rate and total flow rate) could be reduced to less than 1 wt% from the first tank as shown the results in Table 4.1. On the other hand, it was found that the retention time for reducing the concentration of FFA to less than 1 wt% of each tank in process design (around 32 seconds) was more than the time in simulation. The reason was that only oleic acid might be used in simulation but three fatty acids (palmitic acid, oleic acid and linoleic acid) were used to calculate in process design. After achieving the simulation of esterification, the production was fed into decanter for separating the solution into oily solution and the first process waste. Oily solution consisted of TG, DG, MG, ME, and ML. For the first process waste, it consisted of FFA, ML, WT, and H_2SO_4 as shown in Table 4.2.

Table 4.1 The simulation conditions and results of esterification

Results	MCPO	MeOH	H_2SO_4	Reactor 1	Reactor 2	Reactor 3
Volume (L)	-	-	-	0.5	0.5	0.5
Retention time (sec)	-	-	-	18	18	18
Mass fraction						
TG	0.8372	0.0000	0.0000	0.7506	0.7506	0.7506
DG	0.0457	0.0000	0.0000	0.0410	0.0410	0.0410
MG	0.0067	0.0000	0.0000	0.0060	0.0060	0.0060
FFA	0.0996	0.0000	0.0000	0.0010	0.0009	0.0009
ME	0.0062	0.0000	0.0000	0.0983	0.0983	0.0983
WT	0.0046	0.0000	0.0000	0.0097	0.0098	0.0098
ML	0.0000	1.0000	0.0000	0.0860	0.0860	0.0860
H_2SO_4	0.0000	0.0000	1.0000	0.0074	0.0074	0.0074
Total Mass flow rate (kg/hr)	44.3500	4.7510	0.3680	49.4690	49.4690	49.4690

Table 4.2 The simulation results of the first decanter

Results	Reactor 3	Oily Solution	The 1st waste
Volume (L)	0.5	-	-
Retention time (sec)	18	-	-
Mass fraction			
TG	0.7506	0.7703	0.0000
DG	0.0410	0.0421	0.0000
MG	0.0060	0.0062	0.0000
FFA	0.0009	0.0000	0.0347
ME	0.0983	0.1009	0.0000
WT	0.0098	0.0000	0.3809
ML	0.0860	0.0805	0.2942
H_2SO_4	0.0074	0.0000	0.2902
Total Mass flow rate (kg/hr)	49.4690	48.2010	1.2680

Because, in experiment, FFA in oil was neutralized, the remained concentration of FFA in this step of simulation was eradicated from the esterification solution. In addition, the oily solution and the first stage waste were verification the remained methanol as shown in Appendix E. Therefore, theirs values were used to estimated the remained methanol values in both solution that was leaving the decanter.

4.3.2 Transesterification

The oily solution, methanol and sodium hydroxide (a raw material of transesterification) were fed into reactor in which the required condition was already set. After that the simulation was run until it reached the retention time. It was found that the concentration of TG, DG and MG were reduced to less than 1 wt%. Besides, the concentration of ME and GL were increased from 10.97 and 0.00 wt% to 90.24 and 8.41 wt%, respectively as shown in Table 4.3. In addition, the results indicated that the retention time for produce biodiesel of simulation was less than the retention time of process design, which the reason was similarly to Topic 4.3.1.

After that the production was fed into the second decanter. The product was separate into crude biodiesel phase and glycerol phase as shown in Table 4.4. The reason for grouping TG, DG, MG and ME in biodiesel phase because their concentrations were detected when biodiesel was analyzed with TLC/FID in previous work.

Table 4.3 The simulation conditions and results of transesterification

Results	**Oily solution**	**MeOH**	**NaOH**	**Reactor 4**	**Reactor 5**
Volume (L)	-	-	-	1.5	1.5
Retention time (min)	-	-	-	1.34	1.34
Mass fraction					
TG	0.7703	0.0000	0.0000	0.0008	0.0000
DG	0.0421	0.0000	0.0000	0.0036	0.0019
MG	0.0062	0.0000	0.0000	0.0098	0.0094
ME	0.1009	0.0000	0.0000	0.7612	0.7639
GL	0.0000	0.0000	0.0000	0.0708	0.0712
ML	0.0805	1.0000	0.0000	0.1534	0.1532
NaOH	0.0000	0.0000	1.0000	0.0004	0.0004
Total Mass flow rate (kg/hr)	48.2010	9.1060	0.0250	57.3320	57.3320

44.32082 43.7902 44.4438 4.082 48.5258

Due to the molecule of methanol consisted of polar function (hydroxyl group) and non-polar function (alkyl group); therefore, methanol (could be dissolved in both phases) are shown the analyzed results in Appendix E. Although, small amount of methanol in crude biodiesel was detected, because of no analyzing of methanol in vapor phase, it was assumed that a lot of methanol was remained in crude biodiesel. After separating glycerol out of the final product, the concentration of TG, DG, MG and ME at 0.00, 0.22, 0.68 and 99.09 wt% was obtained, respectively.

Table 4.4 The simulation results of the second decanter

Results	**Reactor 5**	**Crude biodiesel**	**Glycerol**
Volume (L)	1.5	-	-
Retention time (min)	1.34	-	-
Mass fraction			
TG	0.0001	0.0000	0.0000
DG	0.0019	0.0021	0.0010
MG	0.0094	0.0064	0.0229
ME	0.7638	0.9352	0.0000
GL	0.0712	0.0000	0.3887
ML	0.1532	0.0563	0.5850
NaOH	0.0004	0.0000	0.0024
Total Mass flow rate (kg/hr)	57.3320	46.826	10.5000

4.3.3 Distillation

Methanol in the 1st stage waste, crude biodiesel and glycerol were recovered by distillation. Due to absence of the equilibrium curve of a pair of solution (methanol-water, methanol-crude biodiesel and of methanol-glycerol), only the number of plates in methanol distillatory tower was estimation. Therefore, reflux ratio, feed stage, and temperature was simulated by ASPEN PLUS Simulation Engine which results are shown in Table 4.5. The simulation of methanol distillatory of methanol-crude biodiesel and of methanol-glycerol had some errors because the number of plate in the design work was lower than the limit of plate number, which could added in the simulation. However, the simulation results were the guideline for fabricating the distillatory in actual work.

In experiment, excess methanol was used to produce biodiesel so the un-reacted methanol in each solution should be recovered for using to reduce the concentration of FFA in esterification. From the simulation results shown in Table 4.5, it was found that 63.65 % of excess methanol could be recovered from all final products.

Table 4.5 The simulation results of distillation

Results	**Distillatory 1**			**Distillatory 2**			**Distillatory 3**		
Reflux ratio	1.22			0.74			0.27		
Number of stages	7			2			2		
Feed stage	4.70			1.81			1.82		
Distillate temperature (°C)	64.9			64.6			69.2		
Bottom temperature (°C)	103.2			160.3			160.0		
Mass fraction	**The 1st waste**	**Methanol**	**The final waste**	**Glycerol 1**	**Methanol**	**Glycerol 2**	**Crude biodiesel**	**Methanol**	**Biodiesel**
TG	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DG	0.0000	0.0000	0.0000	0.0010	0.0000	0.0024	0.0021	0.0000	0.0025
MG	0.0000	0.0000	0.0000	0.0229	0.0000	0.0548	0.0064	0.0008	0.0074
FFA	0.0347	0.0000	0.0492	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ME	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	0.9352	0.6482	0.9836
WT	0.3809	0.0134	0.5347	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
GL	0.0000	0.0000	0.0000	0.3887	0.0067	0.9228	0.0000	0.0000	0.0000
ML	0.2942	0.9866	0.0045	0.5850	0.9933	0.0140	0.0563	0.3510	0.0066
H_2SO_4	0.2902	0.0000	0.4116	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NaOH	0.0000	0.0000	0.0000	0.0024	0.0000	0.0057	0.0000	0.0000	0.0000
Total flow rate (kg/hr)	1.2680	0.3740	0.8940	10.5000	6.1200	4.3800	46.826	6.7561	40.0699

Its concentration that estimated by simulation was around 96.37 wt%. The tendency estimated concentration of methanol was lower the requirement of methanol concentration in actual work because high temperature was used to re-boiling solution. Therefore, some impurities such as water, triglyceride and methyl ester, was blended in methanol. Therefore, this concentration of methanol should be verified again by experiment.

4.4 Conclusions

The results of simulation (closing to the process design) were summarized as followed:

- The total retention time of 3 tanks CSTR in series within 1 minute could be reduced the concentration of FFA at 9.96 wt% to less than 0.50 wt%.

- The concentration of ME more than 96.5 wt% was detected when the reaction was performed in a tank of CSTR within 3 minutes.

- 63 % of excess methanol could be recovered from all final products, which 96 wt% concentration was detected.

CHAPTER 5
EXPERIMENT

Palm oil, like other edible oils, is an organic compound which is called a glyceryl ester because each molecule is comprised of a glycerol molecule bonded to a maximum of three fatty acid (carboxylic acid) residues. Each of the three fatty acid groups in palm oil is long chains comprising several carbon atoms (normally 11-19 atoms in length). In the production of palm-oil, there are two crude oil products extracted: one is crude oil from palm fruit fibre and the other is oil from palm fruit kernel. Free fatty acids from these two kinds of oil are normally controlled at 5 wt% but for small palm oil extracting industries, palm oil from the whole fruit is extracted (kernel and fibre). Because palm fruit in this process has to be toasted before extraction takes place, the FFA of the oil produced is usually quite high (typically greater than 10 wt%).

It is difficult to utilize MCPO for making biodiesel by the alkaline transesterification process because the FFA content is too high. In countries where there are large numbers of small oil palm plantations, especially where commercial fuel (petroleum products) is imported, it is essential that farmers should be able to produce their own energy from their own product. For economic reasons, they would prefer to extract palm oil for themselves using the processes generally used in small oil-producing industries. As a consequence, the oil produced by farmers always contains high levels of FFA. There are other potential sources of biodiesel that contain high concentrations of FFA which make them unsuitable for a one-stage transesterification process. These sources include badly stored vegetable oils and waste cooking oils. It follows that there is a need for a simple process for the production of biodiesel from high FFA mixed crude palm oil by a two- stage esterification-transesterification process.

Esterification (the first process) was selected to reduce FFA by converting it into biodiesel or methyl ester (ME). Then glycerides: triglyceride (TG), diglyceride (DG) and monoglyceride (MG) were also converted into ME by transesterification (the second process). For obtaining a large amount of biodiesel in batch process, large size reactor, 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 in form of CSTR was investigated because of low investment cost, suitability for liquid-liquid reaction and simply design.

In a brief procedure, estimation of the number and volume of tanks is the first procedure of the continuous reactor. Then the estimation was confirmed by numerical and analytical technique. After that other apparatuses such as decanters, methanol recovery system and washing system were designed. Prior to the fabrication of the system, it was simulated for verifying the competence of system and for investigating the tendency of final product (such as retention time, product components and flow rate). While the system was simulating, it was sketched followed by fabrication. Finally, after acquiring the continuous system for producing biodiesel from MCPO, the performance of this system was tested as followed:

5.1 Materials

Mixed crude palm oil (MCPO) (un-degummed and containing FFA around 16-18 wt%) is used as the feed stock for biodiesel production. It is obtained from a local palm oil mill in Had Yai, Songkhla, Thailand. Sulfuric acid, potassium hydroxide and methanol of 98% purity commercial grade are purchased from a local chemical store in Had Yai, Songkhla, Thailand. Moreover, commercial grades of potassium hydroxide (pelleted), HYDRANAL-coulomat AG No. 34836, and Lewtit® GF202 macroporous cation exchange resin were used.

5.2 Apparatus

The two-stage continuous technology of this study (Figure 5.1 and Appendix D) was used to producing biodiesel from high free fatty acid MCPO (feeding flow rate 50 L/hr). Like the work of Lastella (2005) and of Teall *et al.* (2005), production unit, separator unit, distillation unit were installed in the part of transesterification of this system as shown in Figure 5.2. However, this process proposed to produce biodiesel from high FFA oil though the part of esterification was an adjunct to the aid of generating biodiesel (Figure 5.3). In addition, this thesis focused on cleansing of biodiesel with dry process. Due to high investment cost, only laboratory scale at 0.6 L/hr of crude biodiesel feeding flow rate as shown in Figure 5.4 was used.

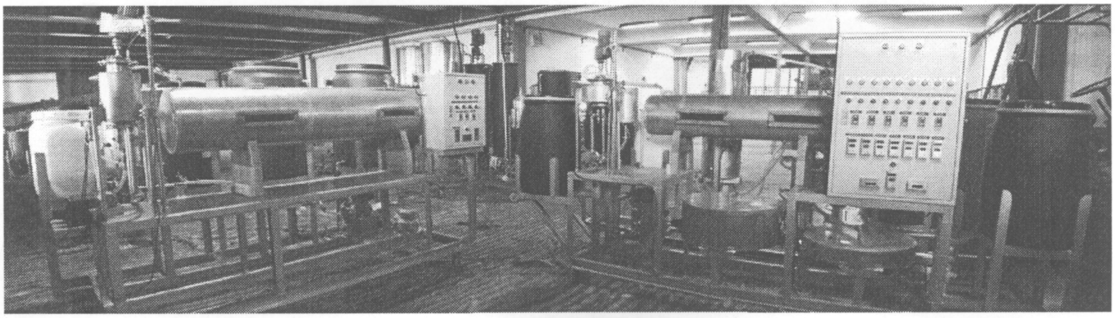
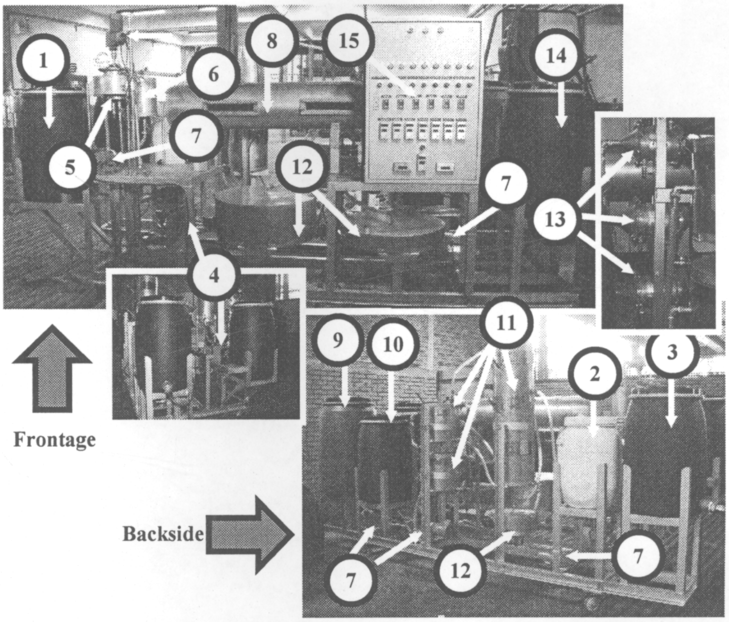
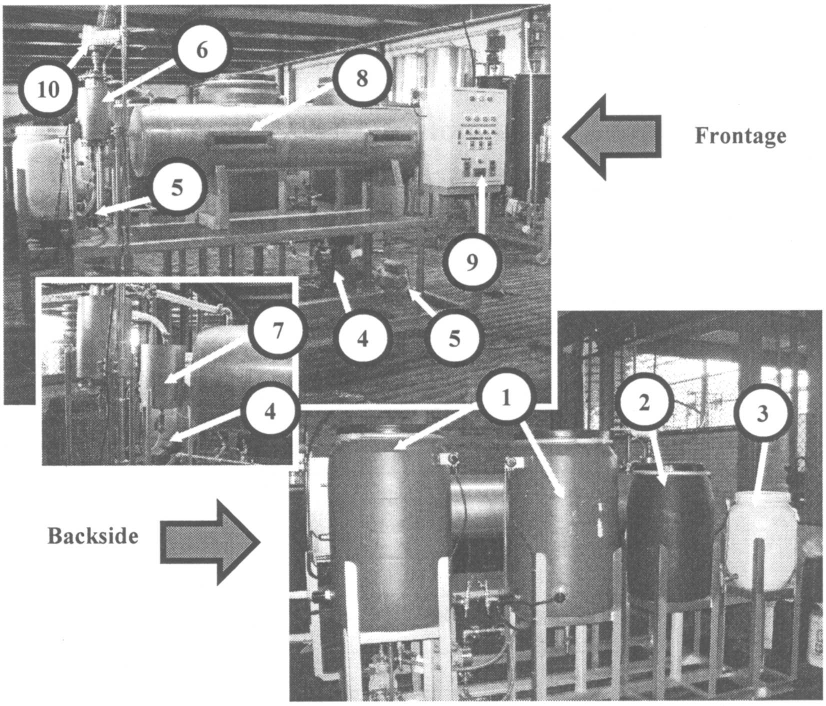


Figure 5.1 Continuous pilot plant for producing biodiesel from MCPO



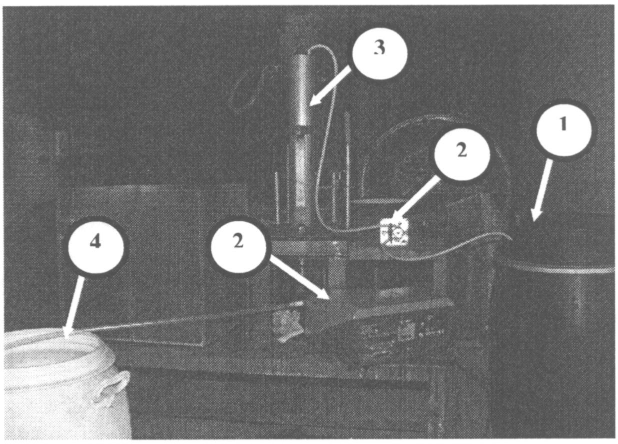
1. De-acidified MCPO storage tank
2. 1^{st}-stage waste solution storage tank
3. Potassium methoxide solution storage tank
4. Metering pump
5. CSTR
6. Hot paraffin oil tank
7. Pump
8. Separate tank
9. Crude biodiesel storage tank
10. Crude glycerol storage tank
11. Distillation tower
12. Re-boiler
13. Condenser
14. Water tank
15. Controller
16. Stirrer motor

Figure 5.2 Transesterification System



1. MCPO storage tank
2. Methanol storage tank
3. Sulfuric acid storage tank
4. Metering pump
5. Pump
6. CSTR
7. Hot paraffin oil tank
8. Separate tank
9. Controller
10. Stirrer motor

Figure 5.3 Esterification system



1. Crude biodiesel storage tank
2. Peristaltic pump
3. Resin column
4. Clean biodiesel storage tank

Figure 5.4 Biodiesel washing system

5.3 Methodology

According the diagram in Figure 5.5, before starting experiments, the oxidation reaction of MCPO was stopped by heating until it reached 60 °C and then adding 0.02 wt% of butylated hydroxytoluene (BHT) as an antioxidant (Food and Drug Administration, 1981).

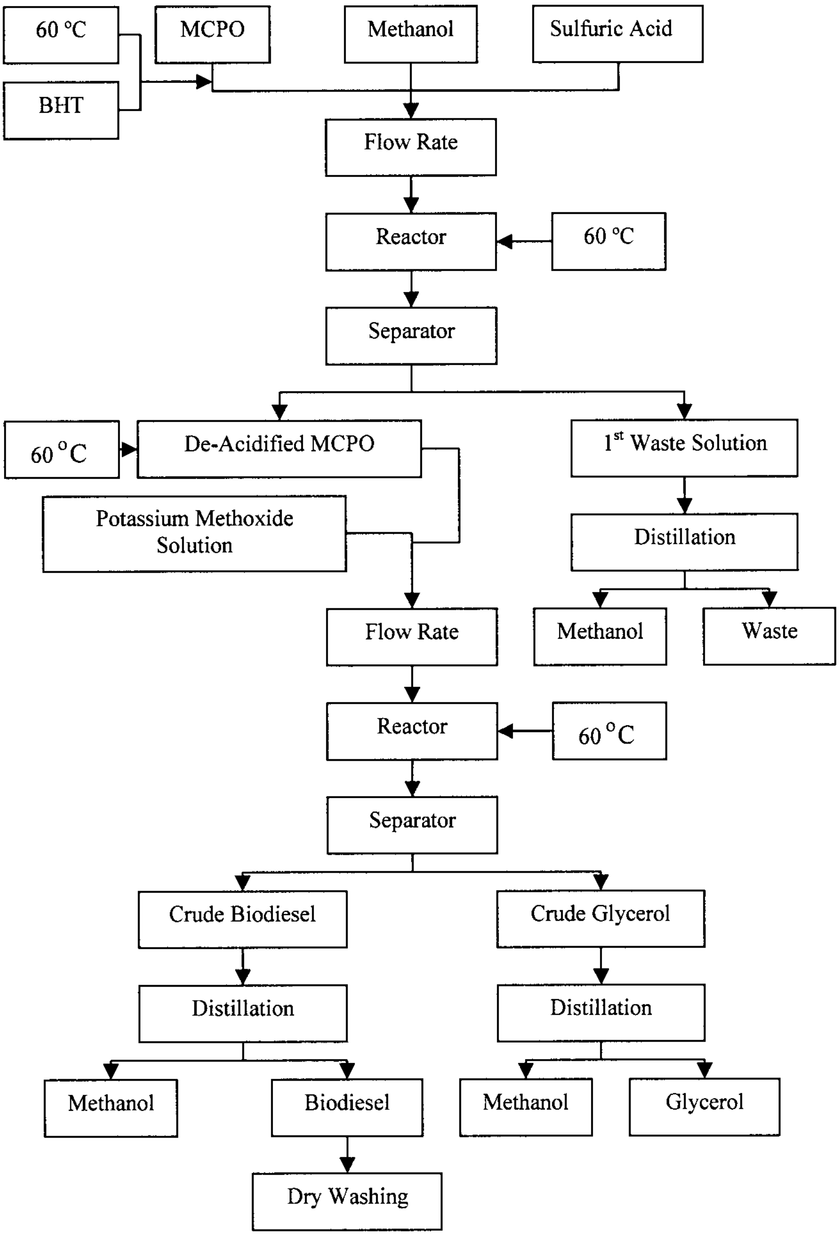


Figure 5.5 Methodology

After that, the flow rate of MCPO, methanol and sulfuric acid was checked and fed into the reactor, which was warmed up by hot paraffin oil (Somnuk, 2008 and Prateepchaikul, 2009). During mixing reactants in the esterification reactor, the temperature of reagent was controlled at 60 °C. After reaching the reaction time, the solution flew to the separated tank. The solution separated into 2 phases: oily phase (top phase) and black phase (bottom phase). Oily phase flew to a de-acidified MCPO storage tank and its temperature at 60 °C was controlled by immerse heater. Simultaneously, the waste solution (black phase) was kept for recovering methanol. Next, acid value content of de-acidified MCPO (oily phase) was checked and then the potassium methoxide solution was prepared. Afterward, the flow rate of de-acidified MCPO and the potassium methoxide solution was checked. Then both solutions were fed into the transesterification reactor which was warmed up and controlled the reaction temperature at 60 °C with hot paraffin oil. Then the solution was released in the separated tank for separating solution into crude biodiesel (top phase) and glycerol (bottom phase) and kept in their storage tank. Methanol in crude biodiesel, glycerol and the first waste solution was recovered. Finally, the recovered crude biodiesel in this process was purified with dry washing process.

5.4 Monitoring

Previous, the composition of the solution was monitoring periodically the two-stage process by Thin Layer Chromatography/ Flame Ionization Detector (TLC/FID), Karl Fischer titration technique, and titration technique. Now, since TLC/FID was broken, only titration techniques were used to progress the reaction. Make certain that the acid-base titration could be used instead of TLC/FID; therefore, the accuracy of them was compared. Figure 5.6 showed that there was no significant difference in FFA analysis. Therefore, only acid-base titration was used to analyze FFA in this investigated. Additionally, the analysis of ME concentration in biodiesel by TLC/FID was replaced with ^{1}H-NMR (in house method refer to WI-RES-NMR and REF-RES-NMR-023 of the Science Equipment Cetre, Prince of Songkla University, Had Yai, Thailand).

When the reaction time reached the requirement, the sample of 50 ml was withdrawn (Somnuk, 2008 and Prateepchaikul, 2009). The sample reaction was stopped immediately by chilling with 5 °C of cold water (Jansri, 2007) and then freezing in refrigerator. Un-purified samples of the first stage were analyzed the water content by Karl Fischer titration technique. After that, the impurities of samples was removed by washing with 250 ml of hot water (80 °C) in three times (Jansri, 2007) or cleaning until the wasted water reached pH = 7 for protecting the interference of the contaminations in solution during analysis. Finally, cleansed samples were analyzing the concentration of FFA with titration in esterification and the concentration of ME with ^{1}H-NMR in transesterification. The disadvantage of both analysis methods was that the concentration of DG, MG and TG of each sample was not shown. Therefore, the progression of reaction was difficult to monitor. It caused unknown something might have happened during the reaction.

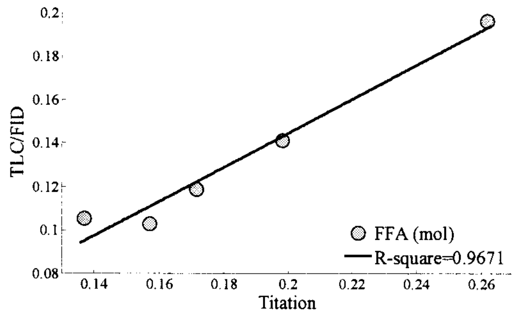


Figure 5.6 Accuracy of analytical method

5.5 Analytical Methods

5.5.1 Acid Value

The acid value of the initial oil and the final product of the first stage were determined by the acid-base titration technique. The sample of 5.6 ml was withdrawn from un-cleaned solution with pipette and then the sample was diluted with 15-20 ml. iso-propanol by using 5 % wt/v of phenolphthalein as an indicator. The solution was titrated with a 0.1 mol/L of KOH solution until the solution reached the end point. The acid value of the sample ratio in gram of potassium hydroxide to litre of oil was determined (applying from Link (1989)).

5.5.2 FFA Content

Although the process for preparing the titrand (analyst) and the titrant (titrator) of FFA analysis was similar to the analysis of acid value, the samples in this method must be weighed. After reaching the end point the mass ratio of FFA were calculated by Equation 5.1.

$$\%\mathrm{FFA} = \frac{\text{ml of KOH} \times \mathrm{N} \times 27.3}{\text{weight of sample}} \tag{5.1}$$

Where N is concentration of KOH solution (N)

5.5.2 Karl Fischer Titration Technique

Karl Fisher titration technique was used to analyze the water content in each sample. Analysis was performed via Metter Toledo DL39 Karl Fisher coulometer. The external solution was prepared by mixing the weighed sample with the weighed commercial methanol and then the solution was released for separating the solution into two phases: the top phase (the clear solution or the external solution) and the bottom phase (the oily phase). Commercial methanol and the external solution are also determined the water content by titrating with hydranal - coulomat AG No. 34836: Karl Fischer reagent. The mass ratio of water in commercial methanol and the external solution was determined. After that, the mass ratio of water in each sample was calculated with the water content value of both commercial methanol and the external solution.

5.5.3 Physical-Chemical Properties of Biodiesel Production from High Free Fatty Acid MCPO

The final biodiesel production from the suitable condition and some sample, in which physical and chemical properties were determined according to the standard procedures such as ASTM, and EN analyzing by the Science Equipment Cetre, Prince of Songkla University, Had Yai, Thailand.

5.6 Experimental Design

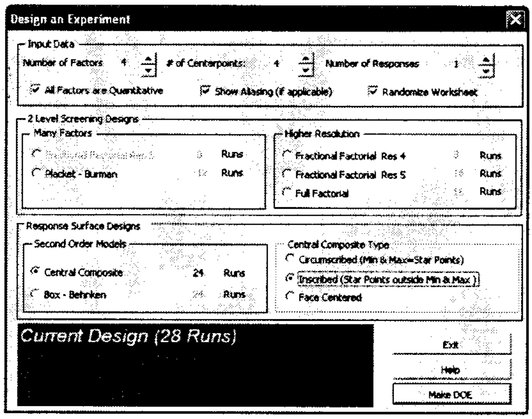
The suitable condition for reducing FFA that contained in MCPO was obtained by using response surface modeling (RSM) in term of central composite design (CCD). Generally, CCD in 2^k factorial term (Equation 5.2) was used for designing the experiment for finding an axle point or star point. For example, if 2 independent variables was used in this experiment, it was found that 2^k factorial factors in normal term consists of (-1, -1), (+1, -1), (-1, +1), (+1, +1) in contrast to in an axle point. 2^k factorial factors in an axle point consist of ($-\alpha$, 0), ($+\alpha$, 0), (0, $-\alpha$), (0, $+\alpha$) and replicate 4-6 runs in the centre point (Steppan, 1998).

$$\alpha = \sqrt[4]{2^{k_y}} \tag{5.2}$$

5.6.1 Experimental Design for Esterification

The main factors for reducing FFA to less than 1 wt% in esterification process was alcohol (M), catalyst (S), stirrer speed (P) and retention time (T). Therefore, they were used as factors for designing the experiment. CCD is used to design experiment under 4 independent variable 5 parameter levels (-2, -1, 0, 1, 2) and a response as shown the setting in Figure 5.7.

After setting the experiment, the ranks of independent variables in Table 5.1 are assigned by essential experimental design and essential regression as shown the method in Figure 5.8 and the results in Table 5.2 [4 independent variable 5 parameter levels (-2, -1, 0, 1, 2)]. The results indicated that there were 28 runs of each process were experimented as shown in Table 5.3.



Design an Experiment

Input Data

Number of Factors 4

# of Centerpoints: 4

Number of Responses 1

☑ All Factors are Quantitative ☑ Show Aliasing (if applicable) ☑ Randomize Worksheet

2 Level Screening Designs

Many Factors

○ Placket - Burman Runs

Higher Resolution

○ Fractional Factorial Res 4 Runs

○ Fractional Factorial Res 5 Runs

○ Full Factorial Runs

Response Surface Designs

Second Order Models

● Central Composite 24 Runs

○ Box - Behnken Runs

Central Composite Type

○ Circumscribed (Min & Max=Star Points)

● Inscribed (Star Points outside Min & Max)

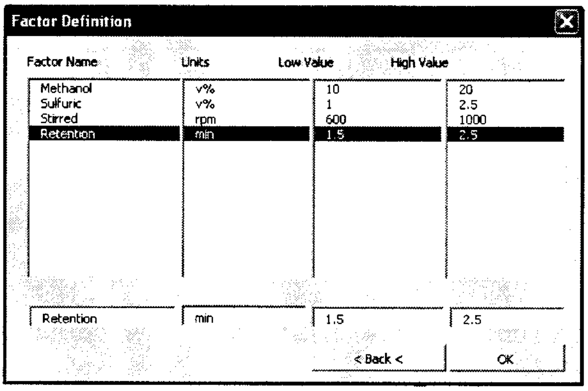
○ Face Centered

Current Design (28 Runs)

Figure 5.7 Experiment design

Table 5.1 Ranks of independent variables

Independent variables	Ranks of experimental parameters
Esterification	
Methanol (v%)	[10-20]
Sulfuric acid (v%)	[1.0-2.5]
Retention time (min)	[1.5-2.5]
Speed of Stirrer (rpm)	[600-1000]



Factor Definition

Factor Name	Units	Low Value	High Value
Methanol	v%	10	20
Sulfuric	v%	1	2.5
Stirred	rpm	600	1000
Retention	min	1.5	2.5

Retention min 1.5 2.5

Figure 5.8 Variable assignment

Table 5.2 Independent variables and parameter levels of esterification

Independent variables	Parameter levels				
	-2	-1	0	1	2
Methanol (M) (vol%)	10	15	20	25	30
Sulfuric acid (S) (vol%)	1.0	1.5	2.0	2.5	3.0
Retention time (T) (min)	1.75	2.00	2.25	2.50	2.75
Speed of Stirrer (P) (RPM)	400	600	800	1000	1200

Table 5.3 Esterification experimental design

Experiments	Methanol (vol %)	Sulfuric acid (vol %)	Retention time (min)	Speed of stirrer (RPM)
1	20 (0)	1.0 (-2)	2.25 (0)	800 (0)
2	20 (0)	2.0 (0)	1.75 (-2)	800 (0)
3	25 (1)	1.5 (-1)	2.00 (-1)	600 (-1)
4	15 (-1)	2.5 (1)	2.50 (1)	600 (-1)
5	25 (1)	2.5 (1)	2.50 (1)	600 (-1)
6	20 (0)	2.0 (0)	2.25 (0)	800 (0)
7	20 (0)	2.0 (0)	2.25 (0)	400 (-2)
8	30 (2)	2.0 (0)	2.25 (0)	800 (0)
9	20 (0)	2.0 (0)	2.75 (2)	800 (0)
10	25 (1)	1.5 (-1)	2.00 (0)	1000 (1)
11	15 (-1)	1.5 (-1)	2.00 (0)	600 (-1)
12	20 (0)	2.0 (0)	2.25 (0)	800 (0)
13	15 (-1)	1.5 (-1)	2.50 (1)	1000 (1)
14	25 (1)	1.5 (-1)	2.50 (1)	600 (-1)
15	15 (-1)	1.5 (-1)	2.50 (1)	600 (-1)
16	20 (0)	2.0 (0)	2.25 (0)	1200 (2)
17	25 (1)	2.5 (1)	2.50 (1)	1000 (1)
18	25 (1)	2.5 (1)	2.00 (-1)	600 (-1)
19	15 (-1)	2.5 (1)	2.00 (-1)	1000 (1)
20	25 (1)	2.5 (1)	2.00 (-1)	1000 (1)
21	15 (-1)	2.5 (1)	2.50 (1)	1000 (1)
22	15 (-1)	1.5 (-1)	2.00 (-1)	1000 (1)
23	10 (-2)	2.0 (0)	2.25 (0)	800 (0)
24	20 (0)	2.0 (0)	2.25 (0)	800 (0)
25	25 (1)	1.5 (-1)	2.50 (1)	1000 (1)
26	15 (-1)	2.5 (1)	2.00 (-1)	600 (-1)
27	20 (0)	2.0 (0)	2.25 (0)	800 (0)
28	20 (0)	3.0 (2)	2.25 (0)	800 (0)

5.7 Regression Model

Response surface modeling was proposed to identify the detailed dependence of different factors on a response. This study fairly convinced that all factors were important and the response regression model was indicated in the term of a full quadratic model which was computed by the multiple regression technique under 95 % of coefficient confidence intervals as shown in Equation 5.3 (Steppen, 1998).

$$y = \beta_0 + \sum_{i=1}^{k_y} \beta_i x_i + \sum_{i<j=1}^{k_y} \beta_{ij} x_i x_j + \sum_{i=1}^{k_y} \beta_{ii} x_i^2 \qquad (5.3)$$

After getting the regression model, P-value and F-test was be used for getting rid of no significant parameter. Finally, the complete regression model was used for plotting response surface graph and presenting the relation between response and independent variables by contour graph (Somnuk, 2008).

5.8 Results and Discussion

5.8.1 Testing the Distribution of Reaction Time within the Reactor

Somnuk (2008) and Ruangying (2002) suggested that before testing the performance of continuous reactor, the distribution of reaction time should be investigated. Hence, this experiment was investigated the reaction time distribution for confirming the results of Somnuk (2008), and Ruangying (2002). There were 6 conditions set by RSM [experiment number (condition number) 11 (1), 13 (4), 15 (3), 19 (6), 22 (2) and 26 (5)] were selected as a case study of the retention time distribution in esterification reactor as shown condition in Table 5.3.

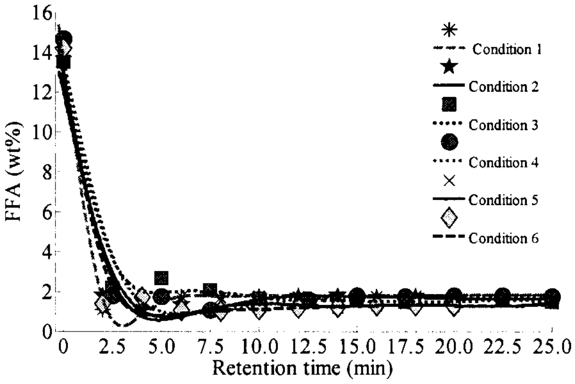


Figure 5.9 The distribution of reaction time within the esterification continuous reactor

The results as shown in Figure 5.9 indicated that FFA of all condition was reduced rapidly around 2.5-6.0 min. Due to effecting of mixing intensity, the concentration of FFA, then, decreased and formed steadily. All reactions had been a steady state about 10 min which were similar to the distribution of retention time of Somnuk (2008) and Ruangying (2002) experiment. Moreover, like FFA reduction, ME concentration was speedy increased in first 5 min and then go to equilibrium as shown in Figure 5.10.

Reactants should be allowed to react in process around 20 min for making sure that the reactants in transesterification r

eactor were mixed well. Therefore, the sample of FFA reduction and ME production should be start keeping around 12 and 24 min until the reaction reached the requirement time.

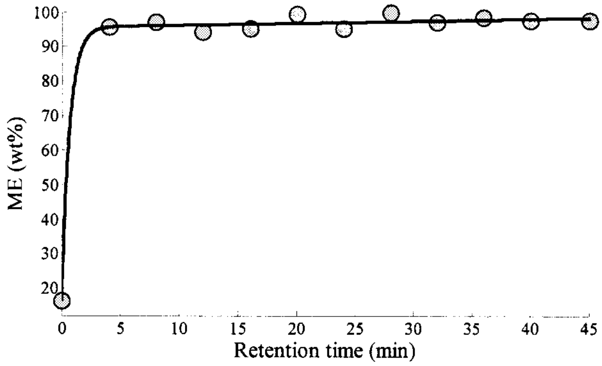


Figure 5.10 The distribution of reaction time within the transesterification continuous reactor

5.8.2 Multiple Regression Analysis Model of Esterification

The results (Table 5.4) were used for estimating the optimization of 50 L/hr continuous esterification reactor for reducing FFA in MCPO by multiple regression analysis model (Appendix F). After computation, the equation in term of full quadratic polynomial was obtained as shown in Equation 5.4 and Table 5.5 was shown theirs statistic. Under the coefficients confidence intervals at 95 %, statistic of Equation 5.4 indicated that $R^2 = 0.986$ and $R^2_{\text{adjusted}} = 0.971$. Although the value of R^2 was rather similar to R^2_{adjusted}, some factor had P-vale more than 0.05. Therefore, P-value was considered the significant factors again. According the statistic, the significant factors must be had P-value to less than 0.05, so some factor in Equation 5.4 was eliminated.

$$\text{FFA} = \beta_0 + \beta_1(\text{M}) + \beta_2(\text{S}) + \beta_3(\text{T}) + \beta_4(\text{P}) + \beta_5(\text{M}^2) + \beta_6(\text{S}^2) + \beta_7(\text{T}^2) + \beta_8(\text{P}^2) + \beta_9(\text{MS}) + \beta_{10}(\text{MT}) + \beta_{11}(\text{MP}) + \beta_{12}(\text{ST}) + \beta_{13}(\text{SP}) + \beta_{14}(\text{TP}) \qquad (5.4)$$

Table 5.4 Esterification results

Experiments	**Methanol** (%vol/vol)	**Sulfuric acid** (%vol/vol)	**Retention time** (min)	**Stirrer speed** (RPM)	**FFA** (%wt/wt)
1	20 (0)	1.0 (-2)	2.25 (0)	800 (0)	1.413
2	20 (0)	2.0 (0)	1.75 (-2)	800 (0)	1.074
3	25 (1)	1.5 (-1)	2.00 (-1)	600 (-1)	0.969
4	15 (-1)	2.5 (1)	2.50 (1)	600 (-1)	1.349
5	25 (1)	2.5 (1)	2.50 (1)	600 (-1)	1.032
6	20 (0)	2.0 (0)	2.25 (0)	800 (0)	0.870
7	20 (0)	2.0 (0)	2.25 (0)	400 (-2)	1.154
8	30 (2)	2.0 (0)	2.25 (0)	800 (0)	1.155
9	20 (0)	2.0 (0)	2.75 (2)	800 (0)	1.154
10	25 (1)	1.5 (-1)	2.00 (0)	1000 (1)	1.028
11	15 (-1)	1.5 (-1)	2.00 (0)	600 (-1)	1.761
12	20 (0)	2.0 (0)	2.25 (0)	800 (0)	0.870
13	15 (-1)	1.5 (-1)	2.50 (1)	1000 (1)	1.773
14	25 (1)	1.5 (-1)	2.50 (1)	600 (-1)	0.991
15	15 (-1)	1.5 (-1)	2.50 (1)	600 (-1)	1.507
16	20 (0)	2.0 (0)	2.25 (0)	1200 (2)	1.151
17	25 (1)	2.5 (1)	2.50 (1)	1000 (1)	1.066
18	25 (1)	2.5 (1)	2.00 (-1)	600 (-1)	1.058
19	15 (-1)	2.5 (1)	2.00 (-1)	1000 (1)	1.252
20	25 (1)	2.5 (1)	2.00 (-1)	1000 (1)	0.943
21	15 (-1)	2.5 (1)	2.50 (1)	1000 (1)	1.331
22	15 (-1)	1.5 (-1)	2.00 (-1)	1000 (1)	1.709
23	10 (-2)	2.0 (0)	2.25 (0)	800 (0)	2.159
24	20 (0)	2.0 (0)	2.25 (0)	800 (0)	0.870
25	25 (1)	1.5 (-1)	2.50 (1)	1000 (1)	0.952
26	15 (-1)	2.5 (1)	2.00 (-1)	600 (-1)	1.277
27	20 (0)	2.0 (0)	2.25 (0)	800 (0)	0.870
28	20 (0)	3.0 (2)	2.25 (0)	800 (0)	1.061

Table 5.5 Regression coefficients and statistics of Equation 5.4

Terms	**Regression coefficients**	**P-value**	**Std Error**
Intercept			
B_0	15.190	9.406×10^{-8}	1.437
Linear			
B_1	-0.436	1.071×10^{-8}	3.437×10^{-2}
B_2	-2.757	2.171×10^{-6}	0.344
B_3	-4.827	1.220×10^{-4}	0.894
B_4	-2.85×10^{-3}	5.540×10^{-3}	8.590×10^{-4}
Quadratic			
B_5	7.600×10^{-3}	3.081×10^{-10}	4.490×10^{-4}
B_6	0.340	4.093×10^{-6}	4.489×10^{-2}
B_7	0.867	3.290×10^{-4}	0.180
B_8	1.594×10^{-6}	7.513×10^{-5}	2.806×10^{-7}
Interaction			
B_9	4.250×10^{-2}	3.247×10^{-6}	5.500×10^{-3}
β_{10}	4.110×10^{-3}	0.714	1.100×10^{-2}
β_{11}	-1.452×10^{-5}	0.310	1.374×10^{-5}
β_{12}	0.246	4.333×10^{-2}	0.110
β_{13}	-2.240×10^{-4}	0.127	1.370×10^{-4}
β_{14}	4.710×10^{-4}	0.110	2.750×10^{-4}

$R^2 = 0.986$, $R^2_{\text{adjusted}} = 0.971$

After removal the insignificant factors, the new equation as shown in Equation 5.5 and shown it's statistic in Table 5.7 ($R^2 = 0.979$, $R^2_{\text{adjusted}} = 0.966$, P-value < 0.05 under the coefficients confidence intervals at 95 %).

$$\begin{aligned} \text{FFA} = {} & \beta_0 + \beta_1(\text{M}) + \beta_2(\text{S}) + \beta_3(\text{T}) + \beta_4(\text{P}) + \beta_5(\text{M}^2) + \beta_6(\text{S}^2) + \beta_7(\text{T}^2) + \beta_8(\text{P}^2) \\ & + \beta_9(\text{MS}) + \beta_{10}(\text{MT}) \end{aligned} \tag{5.5}$$

After that, Equation 5.5 was considered with F-test again. The results indicated that Equation 5.5 had F-value at 77.84 (Appendix F), which was greater than F-critical as shown in Appendix G. Hence, Equation 5.5 could be used for calculating the optimization of this reactor. Finally, equation 5.5 and independents variables (the amount of methanol and sulfuric acid, speed of stirrer and retention time) were used for creating contours as shown in Figure 5.11 -5.16. The investigation indicated that the amount of methanol and sulfuric acid, speed of stirrer and retention time were also impact on FFA reduction (considering for P-value in Table 5.6). The amount of methanol had strong influence on the FFA reduction because it had the lowest P-value.

Table 5.6 Regression coefficients and statistics of Equation 5.5

Terms	Regression coefficients	P-value	Std Error
Intercept			
B_0	14.740	2.775×10^{-9}	1.314
Linear			
B_1	-0.438	6.037×10^{-13}	2.288×10^{-2}
B_2	-2.936	2.048×10^{-7}	0.352
B_3	-4.368	1.600×10^{-4}	0.906
B_4	-2.530×10^{-3}	7.622×10^{-5}	4.890×10^{-4}
Quadratic			
B_5	7.600×10^{-3}	1.553×10^{-11}	4.850×10^{-4}
B_6	0.340	2.130×10^{-6}	4.851×10^{-2}
B_7	0.867	3.370×10^{-4}	0.194
B_8	1.594×10^{-6}	6.405×10^{-5}	3.032×10^{-7}
Interaction			
B_9	4.250×10^{-2}	1.615×10^{-6}	5.940×10^{-3}
B_{10}	0.246	5.385×10^{-2}	0.119

$R^2 = 0.979$, $R^2_{\text{adjusted}} = 0.966$, P-value < 0.05

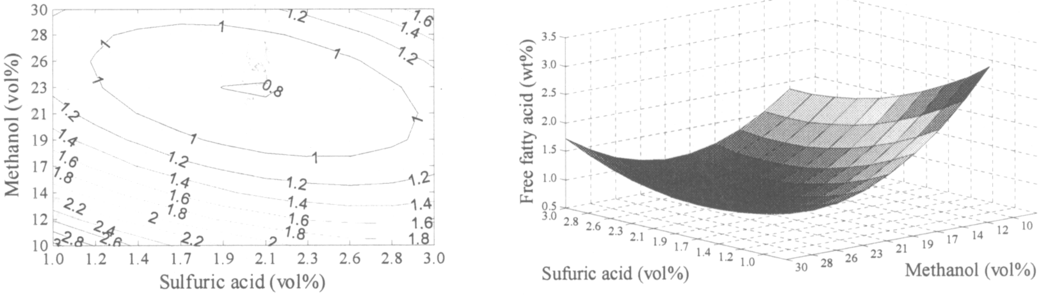


Figure 5.11 The FFA reduction contour and surface are of the relationship between the amount of methanol and the amount of sulfuric acid in unit of wt%

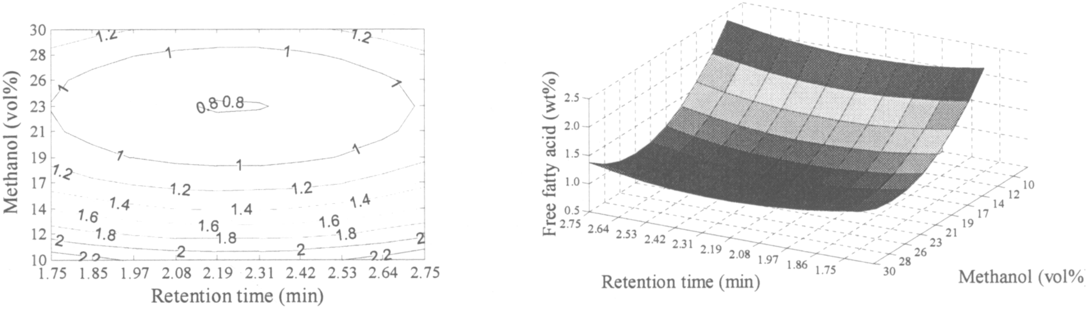


Figure 5.12 The FFA reduction contour and surface are of the relationship between the amount of methanol and retention time in unit of wt%

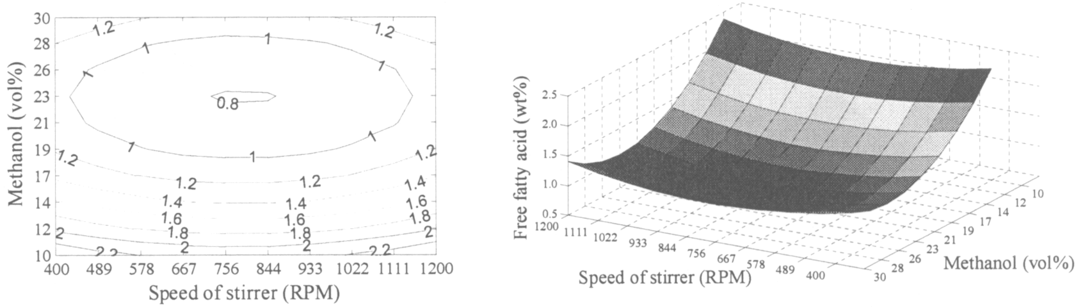


Figure 5.13 The FFA reduction contour and surface area of the relationship between the amount of methanol and speed of stirrer in unit of wt%

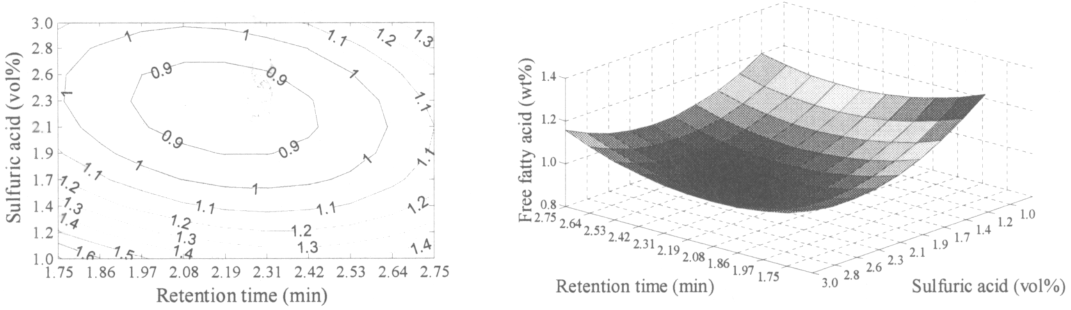


Figure 5.14 The FFA reduction contour and surface area of the relationship between the amount of sulfuric acid and retention time in unit of wt%

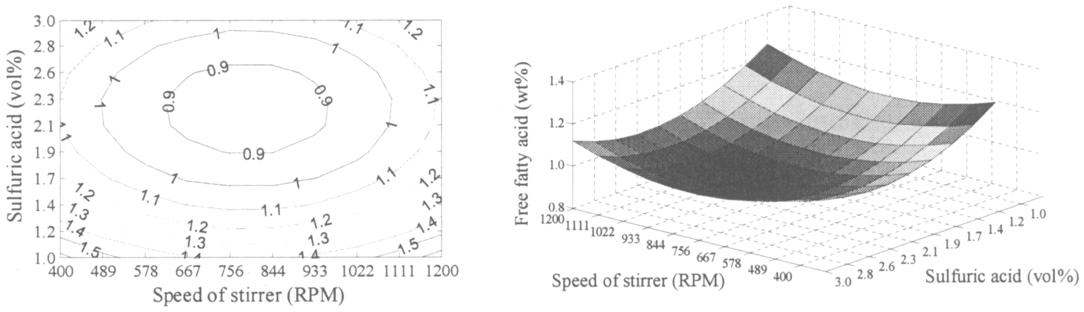


Figure 5.15 The FFA reduction contour and surface are of the relationship between the amount of sulfuric acid and speed of stirrer in unit of wt%

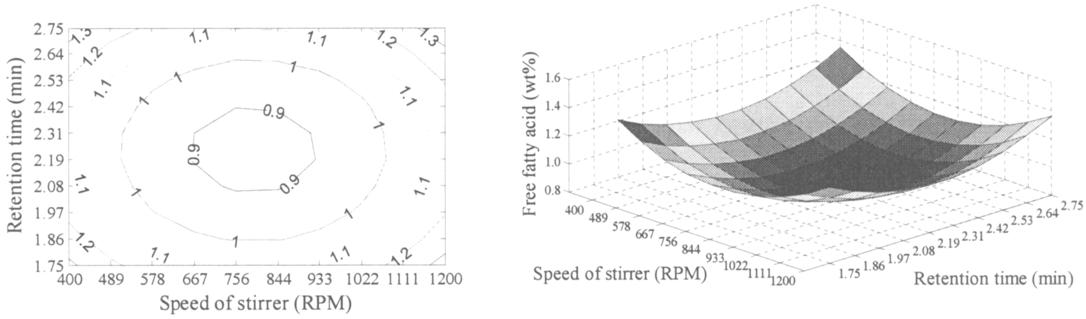


Figure 5.16 The FFA reduction contour and surface are of the relationship between retention time and speed of stirrer in unit of wt%

In addition, methanol was main reagent which was necessary for driving the forward reaction to obtain the highest yield of the product according to Le Châtelier's Principle (Brown et al., 2003). Moreover, P-value of retention time indicated that it had a little effect on the FFA treatment due to using high volume of methanol, volume of sulfuric and speed of stirrer which caused the reaction to go to equilibrium rapidly. On the other hand, if low speed of stirrer was used, retention time had strong influence on the reduction of FFA as could see the result in thesis of Somnuk (2008).

5.8.3 Optimization for Reducing FFA in MCPO with Esterification Continuous Reactor

The results, which was predicted from the Multiple Regression Analysis Model as shown the contour Figure 5.11-5.16, indicated that the continuous reactor of esterification could be reduced FFA from 16-18 wt% to 0.870 wt%. The optimum condition for reducing FFA to less than 1 wt% was used methanol of 23.04 v% and sulfuric acid of 2.07 v% under the retention time of 2.22 min and the speed of stirrer of 793 rpm. Actually, the efficiency of the reactor was lower than the design around 10 %. The reason was that MCPO of this work was contained FFA higher than the design about more than 30%. Moreover, the analytical method of two works was different. The results of FFA reduction from TLC/FID were used in design but from acid-base were used in RSM. That might cause to be predicted the optimal condition in error. However, it was found that a little bit error occurred when TLC/FID and titration analyzed results as shown in 5.6 were compared. Thus, the analytical method was not the main reason to make an error in design and actual work. In fact, the concentration of FFA in MCPO was the main problem in calculation. Therefore, the flow rate of MCPO at 45 L/hr was offered to use for operating the optimization of FFA reduction in full system.

5.8.4 Operation of the Two-Stage Process in Full System

Beginning, the esterification continuous system was verified under the optimal condition as shown in an above discussion. The results in Figure 5.17 indicated that FFA could be reduced from 18 wt% to less than 0.908 wt% and water was appeared around 1 wt% on average. That was the reduction of FFA reached the requirement which was assigned in the objective of thesis.

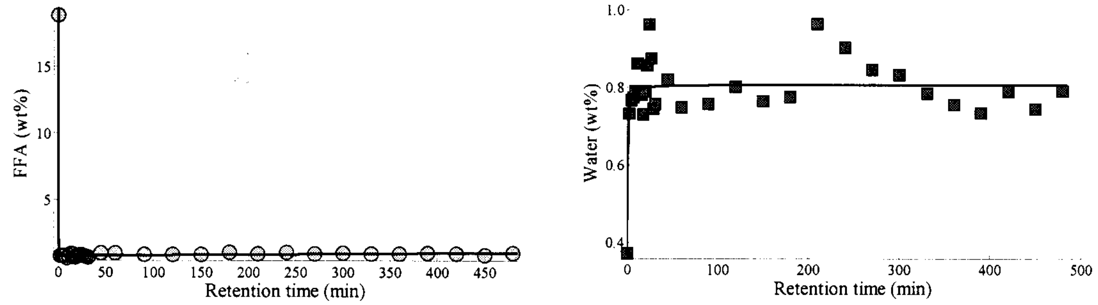


Figure 5.17 Verification the optimization for reducing FFA (Appendix H)

After reaching the reaction, its product was then continuous transferred to the decanter in order to separate waste from oily solution which caused to protect the high consumption of alkali catalyst and the soap formation in the next process. During transferring the product to the decanter, the sample was withdrawn for analyzing acid value and water content of it. The results in Figure 5.18 indicated that the acid value more than 20 g KOH/ L of oil was contained in the product owing to including the acid value of H_2SO_4. Moreover, approximately 1.482 wt% of water was obtained in sample. After the product was reached the separation by gravity, final product found that the acid value and water contained lower than the initial one around 88 and 75 % respectively. Moreover, 40 L/hr of oily solution yield and 15 L/hr of waste solution yield were obtained approximately.

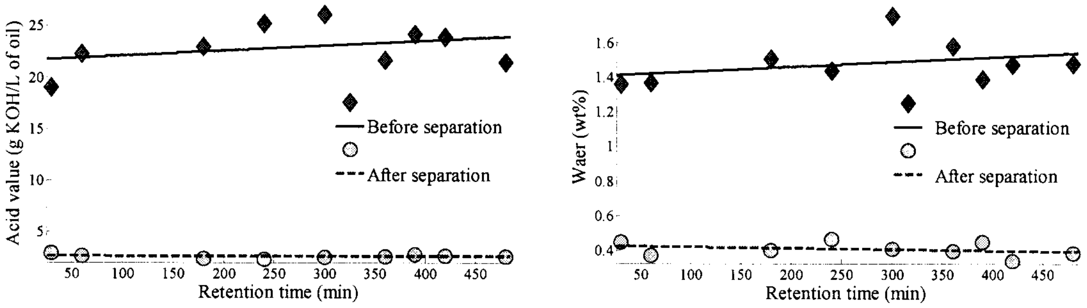


Figure 5.18 Acid value before and after separation by esterification decanter (Appendix H)

In addition, 4.17 hr was spent on the separation time of this work which was higher than the separation time in design around 10 wt% because of the change of the flow rate of MCPO.

After obtaining the treated oil from the first-stage, the continuous system of transesterification was starting to produce biodiesel. However, this work proposed to check on the system operation, so only one condition was offered. The oily solution (de-acidified MCPO) obtained from the esterification was analyzed acid value and then heated until it reached 60°C. While oil was warming up, potassium methoxide solution was prepared by using 12.60 g/L of oil of potassium hydroxide (acid value and catalyst (1.0 wt% of potassium hydroxide)) and 24 vol % of methanol. For reducing the space of the retention time of esterification system to combine with transesterification system, the flow rate of oily solution in transesterification should be equal to esterification. Therefore, oily solution at the feeding flow rate of 45 L/hr was used to operate the biodiesel production. In addition, 10.72 L/hr of potassium methoxide solution feeding flow rate was used under similar in the speed of stirrer to esterification condition.

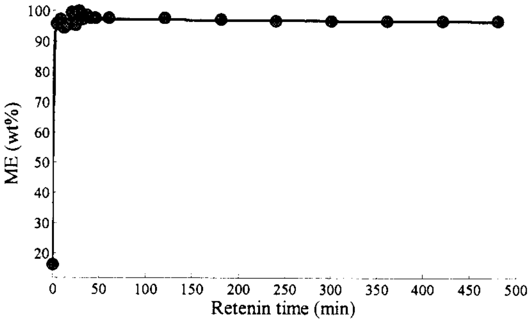


Figure 5.19 Methyl ester production under the condition of 45 L/hr of oily solution, 10.72 L/hr of potassium methoxide solution, 793 rpm of stirrer speed and 60 °C of reaction temperature

The results that were analyzed by ^{1}H-NMR as shown in Figure 5.19 indicated that the reactor can be produce biodiesel to more than 97.68 wt% on average. Make certain that the biodiesel production reached the requirement, final produce was verified according to the standard procedures of ASTM, and EN by the Science Equipment

Cetre, Prince of Songkla University, Had Yai, Thailand, again as show the results and discussion later.

Then the product was continuous transferred to transesterification decanter. It was found that the product was gravitational separation completed in 60 min. In addition, the yield of crude biodiesel around 43 L/hr and of glycerin around 12 L/hr was obtained. Afterward, the separated biodiesel was sent to the Science Equipment Cetre for analyzing ME and GL concentration. The results shown that 96.62 wt% of ME and 0.56 wt% of free glycerin was obtained in crude biodiesel. It meant that the decanter could be separated glycerin out of product quite achievement. Next, both products were transferred to their storage tanks.

The 1st-stage waste solution, crude biodiesel and crude glycerin which were kept in their storage tank were used as a feed stock in methanol recovery. Since full system was operated in only two times; therefore, the amount of product and by-product was not enough to operate all conditions that had been arranged by RSM. For that reason, only one condition was used to test for recovering methanol from them.

Before starting to recover methanol, the initial methanol that contained in each sample was analyzed. The results indicated that a large amount of methanol was contained in 1st-stage waste solution, crude glycerin and crude biodiesel, respectively. Beginning, the feeding flow rate of initial feed stocks was set on 1.20 L/hr of 1st- stage waste solution, 40 L/hr of crude biodiesel and 10 L/hr of crude glycerin. Next, 65°C, 70°C and 65°C were set according to simulation in distillation tower of 1st-stage waste solution, crude biodiesel and crude glycerol, respectively. Finally, the re-boiler of 1st-stage waste solution, crude biodiesel and crude glycerol was set on 105°C, 165°C and 165°C, respectively.

The results in Figure 5.20 indicated that small amount of methanol remained in crude biodiesel and crude glycerin when they were throughout the process around 3 hr. Due to large amount of methanol contained in 1st-stage waste solution that caused more time was spent to recover methanol. Recovery methanol system indicated that 4.5 L/hr of methanol in total (10 % of total methanol using in system) could be recovered under the purity of 85 %.

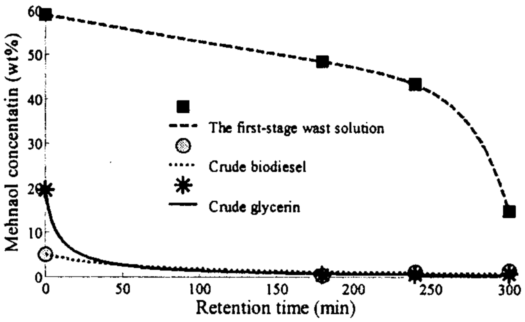


Figure 5.20 Methanol content during distillation

Finally, distilled crude biodiesel was cleansed with Lewtit resin under crude biodiesel feeding flow rate of 0.6 L/hr and analyzed its properties. The results in Table 5.7 were indicated that the properties of biodiesel were not succeeded in the requirement of both biodiesel standard that enacted in the Royal Gazette of Department of Energy Business (2006 and 2009). The reason was that the properties crude biodiesel (Table 5.7) before passing through the Lewtit GF202 column was not achieved in the requirement of Bayer Thai Co., Ltd. (Ion Exchange Resins Group) (GL < 0.15 wt%, soap < 0.05 wt%, water < 0.05 wt%, MeOH < 0.10 wt% and salt < 0.10 wt%).

Therefore, the purification of biodiesel under Suwanmanee technique (2006) was took the place of dry washing technique. The results showed that its properties reached only adequate qualities of biodiesel standard for agriculture engine. As a result of lower ME concentration, high water remainder, high acid number and high DG concentration containing in biodiesel, that caused the biodiesel was not succeeded in the requirement of commercial biodiesel standard. The reason was that the optimization of transesterification (the amount of reagent, the reaction time and the speed of stirrer) was not investigated casing could not be promoted the completed reaction. Therefore, the concentration of ME and of DG was not reached the biodiesel standard. For solving this problem, the optimization of transesterification should be study again.

Table 5.7 Properties of biodiesel production

Parameters	Corresponding Value					
	Commercial Biodiesel	**Biodiesel for Agricultural Engine**	**Crude Biodiesel**	**Cleaned Biodiesel (Resin)**	**Cleaned Biodiesel (Water)**
Methyl Ester (%wt)	≥ 96.5		92.08	91.18	95.70
Density at 15°C (kg/m^3)	≥ 860 and ≤ 900	≥ 860 and ≤ 900	879.8	878.7	877.2
Viscosity at 40°C (cSt)	≥ 3.5 and ≤ 5	≥ 1.9 and ≤ 8	4.92	4.78	4.59
Flash point (°C)	≥120	≥ 120	71	55	162
Sulphur (%wt)	≤ 0.0010	≤ 0.0015	-	-	-
Carbon Residue, on 10 % distillation residue (%wt)	≤ 0.30	-	0.27	0.15	0.047
Cetane Number	≥ 51	≥ 47	-	-	-
Sulfated Ash (%wt)	≤ 0.02	≤ 0.02	0.27	0.04	0.0093
Water (%wt)	≤ 0.050	-	0.146	0.135	0.118
Total Contaminate (%wt)	≤ 0.0024	-	0.0066	0.0005	0.0002
Water and Sediment (%vol)	-	≤ 0.2	-	-	-
Copper Strip Corrosion	≤ Number 1	≤ Number 3	Number 1	Number 1	Number 1
Oxidation S.ability at 110°C (hours)	≥ 10	-	4.47	1.08	10.28
Acid Value (mg KOH/g)	≤ 0.50	≤ 0.80	0.34	0.37	0.61
Iodine Value (g iodine /100g)	≤ 120	-	47.93	51.85	47.2
Linolenic Acid Methyl Ester (%wt)	≤ 12.0	-	0.33	0.32	0.1
Methanol (%wt)	≤ 0.20	-	0.41	0.11	< 0.20
Monoglyceride (%wt)	≤ 0.80	-	0.96	0.83	0.56
Diglyceride (%wt)	≤ 0.20	-	0.68	0.67	0.61
Triglyceride (%wt)	≤ 0.20	-	0.19	0.23	0.13
Free Glycerin (%wt)	≤ 0.02	≤ 0.02	0.46	0.02	0.00047
Total Glycerin (%wt)	≤ 0.25	≤ 1.50	0.86	0.35	0.24
Group I metals (Na+K) mg/kg	≤ 5.0	-	-	-	-
Group II metals (Ca+Mg) mg/kg	≤ 5.0	-	-	-	-
Phosphorus (%wt)	≤ 0.0010	-	-	-	-
Colour	-	Purple	-	-	-
Additive	-	According to Department of Energy Business	-	-	-

Moreover, large amount of KOH was used in this condition as a result of being in difficulty to eradicate alkali by cleaning according to the step of Suwanmanee purifiction. Thus, in the first step, acidic water was spray on the surface of crude biodiesel and then cleansing biodiesel following the second step of Suwanmanee technique. Although KOH was eliminated from biodiesel, some acid was still remained in it that meant 4 times of biodiesel washing were not enough to eliminate acid from biodiesel. For preventing the raising of acid number, the consumption of alkali catalyst in biodiesel production should be reduced and/or the step of purification should be increased.

Finally, after cleaning biodiesel, it was found that some water was suspended in it. Therefore, prior to consumption biodiesel, remained waster must be removed from biodiesel. Beginning, cleansed biodiesel was heated until the temperature of biodiesel was reached 80°C around 30 min in order to get rid of water contamination. Then, biodiesel was released overnight in un-cover vessel for cooling down until it reached the ambient temperature. After that water which was deposited at the bottom was drained. The analyzed result indicated that high water still remained in biodiesel. The reason was that during to be bottled biodiesel into container as an analyzed sample, some water may be mixed in the biodiesel.

The yield of biodiesel after washing with water was found that 75.06% of biodiesel based on initial MCPO (84.44% of biodiesel based on acidified MCPO) was obtained. Although during treatment FFA and producing ME, some oil was lost during separation, it was lost lower than during purification. The reason was that large amount of KOH was used in transesterification; therefore, some biodiesel could be promoted the emulsion. When the waste water was drained some biodiesel in the form of emulsion was also drained that may cause this process obtain lower yield of biodiesel.

5.8.5 Estimation the Biodiesel Production Cost

Cost of raw material, chemical reagents and public utility, except for fabricated cost and labor cost were used for estimating the biodiesel cost in this investigated. All of unit variable costs as shown in Table 5.8 were obtained from experiments. The result showed that the price of biodiesel depended on the price of MCPO and MeOH. At this time, the price of MCPO and petroleum was increased that caused its price was higher than petro-diesel. For reducing the price of biodiesel, producers should be extract palm oil for themselves using the processes generally used in small oil-producing industries. Moreover, for reducing the biodiesel investment cost, recovered methanol should be as an initial reagent in esterification.

Table 5.8 Unit variation cost and the estimation cost of biodiesel production based on initial MCPO

Variable cost	Unit cost (THB)	Amount	Cost/hr (THB)	Cost/yield (THB/L)
Raw material*				
- MCPO (L)	32	45.00	1440.00	42.67
Chemical reagents*				
- MeOH (L)	20.00	16.14***	322.80	9.56
- H_2SO_4 (L)	38.15	0.93	35.48	1.05
- KOH (kg)	99.30	0.013	1.29	0.04
Public utility**				
- Electricity (kwh)	3.107	38.40	119.31	3.53
- Water (L)	0.00163	75.00	0.12	0.01
Total (THB)			**1919.00**	**56.86**

Note:

* Price including VAT 7% and transportation cost

** The rate of household used of Thailand

*** Excluding recovered MeOH

5.9 Conclusions

- The optimum condition for reducing FFA (16-18 wt%) to less than 1 wt% was used methanol of 23.04 v% and sulfuric acid of 2.07 v% under the retention time of 2.22 min and the speed of stirrer of 793 rpm. After separating solution, the yield oily solution and waste solution were obtained approximately at 40 and 15 L/hr, respectively.

- The concentration of biodiesel at 97.68 wt% (analyzed by ^{1}H-NMR) having yield around 43 L/hr and of glycerin around 12 L/hr was obtained under the test operated condition of 45 L/hr of oily solution, 10.72 L/hr of potassium methoxide solution under the retention time of 4 min, 793 rpm of stirrer speed and 60 °C of reaction temperature.

- The yield of recovered methanol in the purity of 85% was obtained around 4.5 L/hr of methanol in total (10 % of total methanol using in system).

- Due to crude biodiesel having initial concentration such as MeOH, GL and water higher than the limitation of the requirement of Bayer Thai Co., Ltd. (Ion Exchange Resins Group), the cleansed biodiesel was not achieved in Thailand biodiesel standard. Therefore, washing biodiesel with Suwanmanee technique was used instead of resin ion-exchange technique.

- The final yield of biodiesel was found that 75.06% of biodiesel based on initial MCPO (84.44% of biodiesel based on acidified MCPO) was obtained when 45 L of MCPO, 16.14 L of MeOH, 0.93 L of H_2SO_4. 0.013 kg of KOH were used in an hour. In addition, 38.40 kwh of electricity and 75 L of water were also used.

- The price of biodiesel that generate by this step was higher than petro-diesel because its price was depended on the price of MCPO and petroleum. Therefore, producers should be extract palm oil for themselves and the methanol distillation system should be investigated again.

- The efficiency of the two-stage continuous process in full system was lower than the design around 10 %.

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APPENDIX A

DENSITIES AND VISCOSITIES

Table A.1 Density and viscosity of reagents

Reagent	**Temperature** (degree Celsius)	**Density** (kg/m^3)	**Viscosity** (cSt)
MCPO	60	887	19.15
De-acidified MCPO	60	865	8.315
1st-stage waste	60	1029	1.708
Crude biodiesel	60	847	2.535
Glycerol	60	964	5.323

APPENDIX B

PROPERTIES OF SOLUTION IN ESTERIFICATION AND TRANSESTERIFICATION

Mass fraction

Esterification

MCPO = 0.896

Methanol = 0.097

Sulfuric acid = 0.007

Transesterification (without NaOH)

De-acidified MCPO = 0.826

Methanol = 0.174

Transesterification (include)

De-acidified MCPO = 0.818

Methanol = 0.172

NaOH = 0.010

Density

Esterification

Average density = (887 × 0.896) + (791.8 × 0.097) + (1840 × 0.007)
= 884.44 kg/m^3

Transesterification

Average density = (865 × 0.818) + (791.8 × 0.172) + (2100 × 0.010)
= 864 kg/m^3

Viscosity

Esterification

$$\text{Average viscosity} = (0.0216 \times 0.896) + (0.0059 \times 0.097) + (0.0267 \times 0.007)$$
$$= 0.0253 \ \text{Pa} \cdot \text{s}$$

Transesterification

$$\text{Average viscosity} = (0.0096 \times 0.826) + (0.0059 \times 0.174)$$
$$= 0.00896 \ \text{Pa} \cdot \text{s}$$

Specific heat at constant pressure (Cp)

Esterification

$Cp_{\text{MCPO}} = 1.959 \ \text{KJ/kg} \cdot {}^\circ\text{C}$ (CHEMPRO, 2008)

$Cp_{\text{methanol}} = 2.480 \ \text{KJ/kg} \cdot {}^\circ\text{C}$ (Wikipedia, 2008b)

$Cp_{\text{sulfuric acid}} = 0.028 \ \text{KJ/kg} \cdot {}^\circ\text{C}$ (Stetina, 2008))

$$\text{Average } C_p = (1.959 \times 0.896) + (2.480 \times 0.097) + (0.028 \times 0.007)$$
$$= 1.996 \ \text{KJ/kg} \cdot {}^\circ\text{C}$$

Transesterification

$Cp_{\text{de-acidified MCPO}} = 1.959 \ \text{KJ/kg} \cdot {}^\circ\text{C}$

$Cp_{\text{methanol}} = 2.480 \ \text{KJ/kg} \cdot {}^\circ\text{C}$

$$\text{Average } C_p = (1.959 \times 0.826) + (2.480 \times 0.174)$$
$$= 2.050 \ \text{KJ/kg} \cdot {}^\circ\text{C}$$

Thermal conductivity (k)

Esterification

k_{MCPO} $= 0.1691\ \mathrm{W/m\cdot{}^{\circ}C}$ (CHEMPRO, 2008)

$k_{methanol}$ $= 0.2100\ \mathrm{W/m\cdot{}^{\circ}C}$ (Wikipedia, 2008c)

$k_{sulfuric\ acid}$ $= 0.2600\ \mathrm{W/m\cdot{}^{\circ}C}$ (Stetina, 2008))

$$\text{Average } k = (0.1691 \times 0.896) + (0.2100 \times 0.097) + (0.2600 \times 0.007)$$
$$= 0.174\ \mathrm{KJ/kg\cdot{}^{\circ}C}$$

Transesterification

k_{MCPO} $= 0.1691\ \mathrm{W/m\cdot{}^{\circ}C}$

$k_{methanol}$ $= 0.2100\ \mathrm{W/m\cdot{}^{\circ}C}$

$$\text{Average } k = (0.1691 \times 0.826) + (0.2100 \times 0.174)$$
$$= 0.176\ \mathrm{KJ/kg\cdot{}^{\circ}C}$$

Mass flow rate ($\dot{m}$)

Esterification

$\dot{m}_{MCPO}$ $= 0.0213$ kg/s

$\dot{m}_{methanol}$ $= 0.0013$ kg/s

$\dot{m}_{sulfuric\ acid}$ $= 0.0001$ kg/s

$$\text{Average } \dot{m} = (0.0213 \times 0.896) + (0.0013 \times 0.097) + (0.0001 \times 0.007)$$
$$= 0.0123\ \mathrm{kg/s}$$

Transesterification

$\dot{m}_{\text{de-acidified MCPO}} = 0.120 \text{ kg/s}$

$\dot{m}_{\text{methanol}} = 0.0025 \text{ kg/s}$

$$\begin{aligned}\text{Average } \dot{m} &= (0.120 \times 0.826) + (0.0025 \times 0.174) \\ &= 0.096 \text{ kg/s}\end{aligned}$$

APPENDIX C

VISCOSITY ESTIMATION OF BLENDS OF LIQUIDS (SAMPLE)

The viscosity blending number (V_{BN}) of Esterification could be calculated by using Equation C.1 (Wikipedia, 2008d)

$$V_{BN} = 14.534 \times \ln[\ln(\mu + 0.8)] + 10.9175 \tag{C.1}$$

Where

$\mu_{\text{de-acidified MCPO}} = 8.315 \text{ cSt} = 7.192 \text{ cP}$

$\mu_{\text{waste}} = 1.708 \text{ cSt} = 1.758 \text{ cP}$

The results indicated that V_{BN} of de-acidified MCPO ($V_{BN,\,A}$) and of the 1st-stage waste was 21.608 and 10.064 cP, respectively. After that, the average viscosity blending number could be calculated by using Equation C.2. In addition, the mass fraction of de-acidified MCPO (X_A) and of 1st-stage waste (X_B) at 0.9 and 0.1, respectively, were also used.

$$V_{BN,\,aver} = (V_{BN,\,A} \times X_A) + (V_{BN,\,B} \times X_B) \tag{C.2}$$

Finally, the average viscosity blending number at 4.136 cP was used to estimate the average viscosity with Equation C.3 (Wikipedia, 2008d). It was found that the average viscosity of blending was 6.019 cP.

$$\mu_{\text{aver}} = e^{e^{\frac{V_{BN,\,aver} - 10.975}{14.534}}} \tag{C.3}$$

APPENDIX D

ELEMENTS AND DRAWINGS OF CONTINUOUS REACTOR

Detail of the two-stage process continuous system components

The first stage process (Esterification)

1. MCPO storage tank

Two 200-liter plastic tanks consisted of heaters and temperature controllers were used as a container for storing and preparing MCPO before feeding it into system as shown in Figure D.1. Both tanks were connected to two pumps. First one was used to circulate MCPO during heating it up. Other one (metering pump) was used to feed warmed MCPO into esterification reactor.

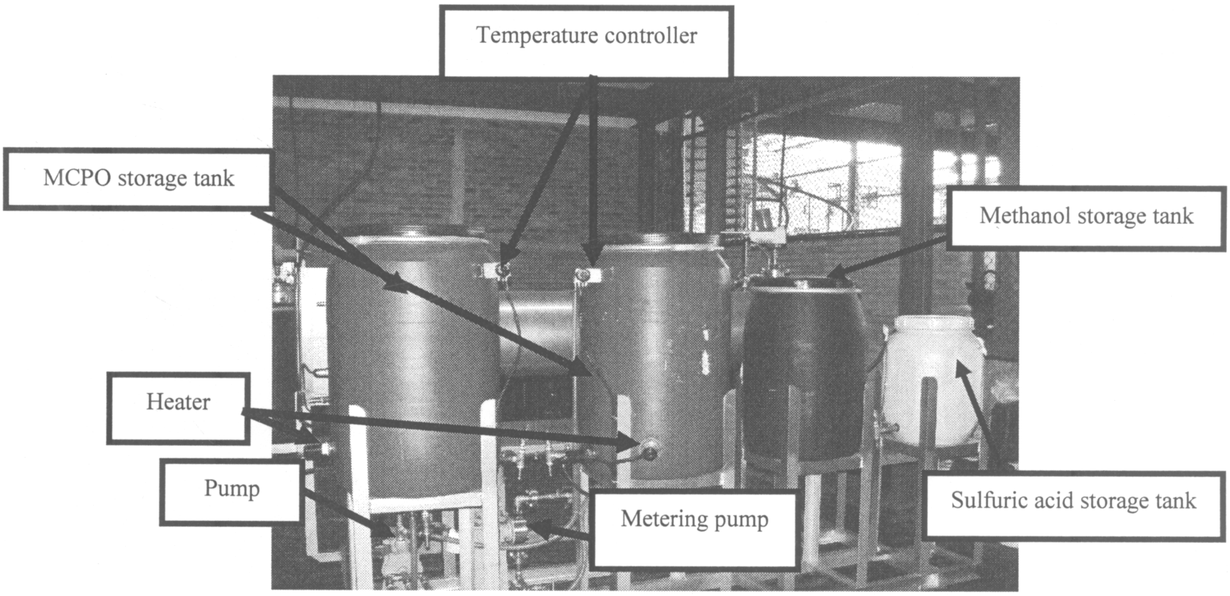

Figure D.1 Back side of the first stage system

2. Methanol storage tank

A 120-liter plastic tank was used as a container for storing methanol. It was connected to metering pump for feeding it into esterification reactor as shown in Figure D.1.

3. Sulfuric acid storage tank

Like methanol storage tank, a 50-liter plastic tank connected to metering pump was used to store sulfuric acid which was used as a catalyst in esterification process as shown in Figure D.1.

4. Esterification reactor

Esterification reactor as shown the detail in Figure D.2 was fabricated by using 1.5 mm thick stainless #304 for reactor body and 4 mm thick jacket # 304 stainless for flange sheets, cover sheet and bottom sheet.

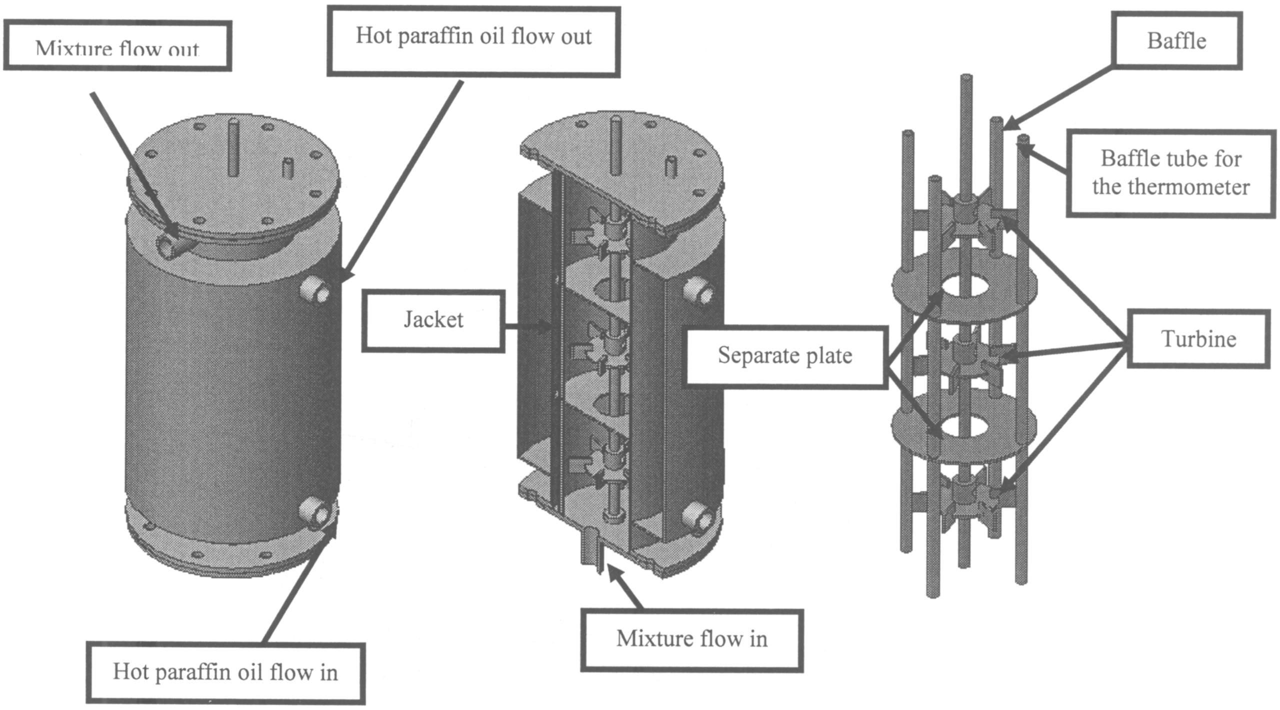

Figure D.2 Esterification reactor

5. Hot paraffin oil tank

A 1.5-liter hot paraffin oil tank installing with heater was fabricated from #304 stainless sizing 250 mm diameter and 300 mm high.

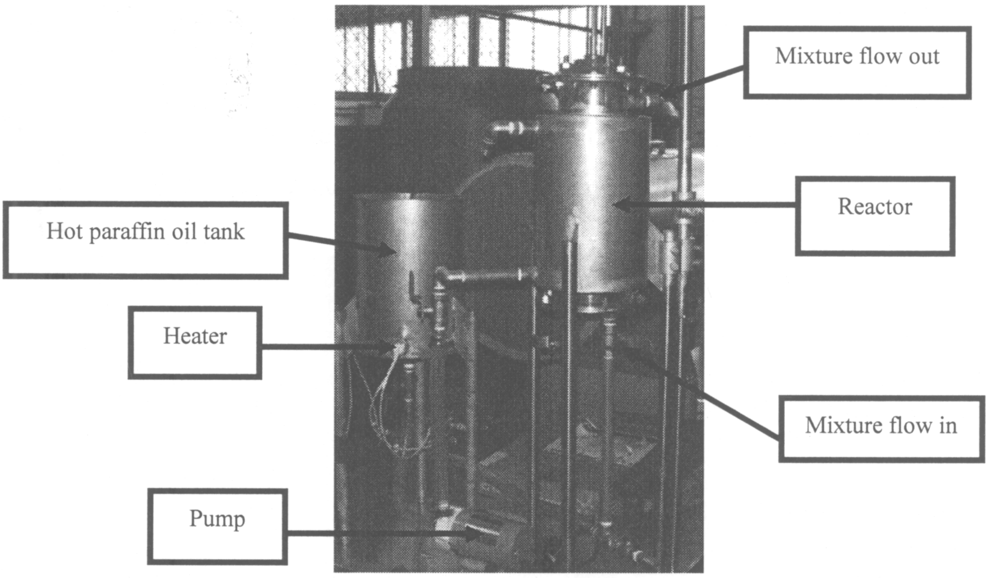

Figure D.3 Hot paraffin oil tank and reactor

6. Separate tank

A separate tank installing with heater was fabricated from #304 stainless sizing 300 mm diameter and 1,500 mm long.

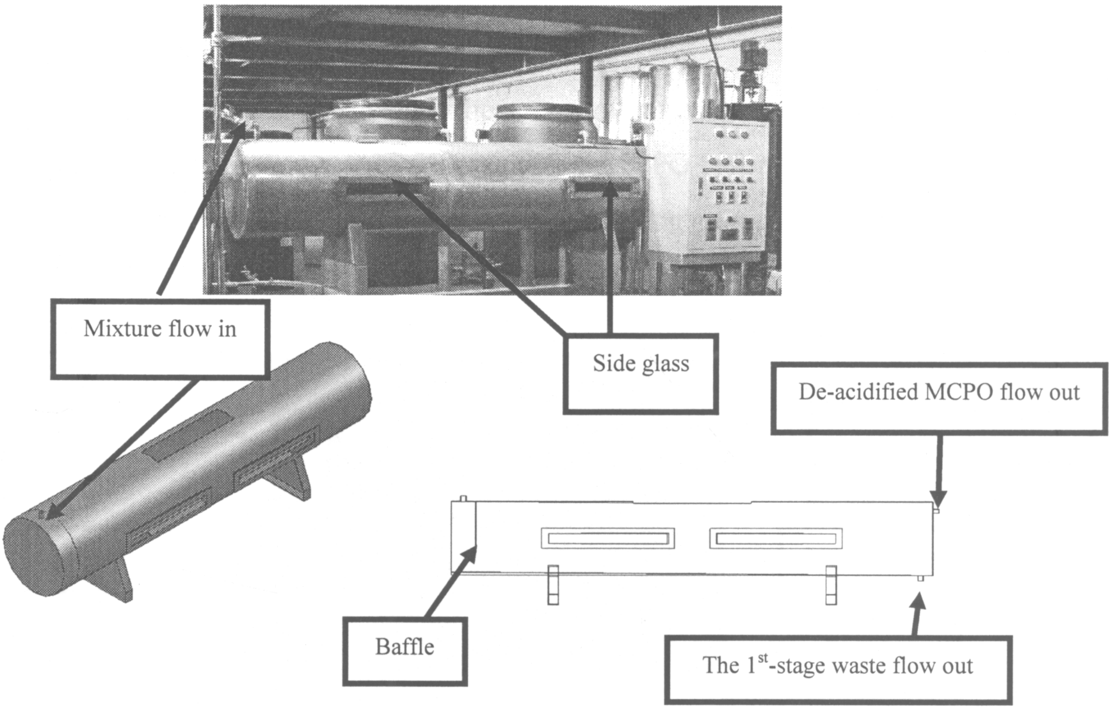

Figure D.4 The 1st-stage separate tank

7. Controller box of the 1st-stage process

Controller box of the 1st-stage process as shown in Figure D.5 consisted of heater lamp, heater switch, pump switch, temperature controller.

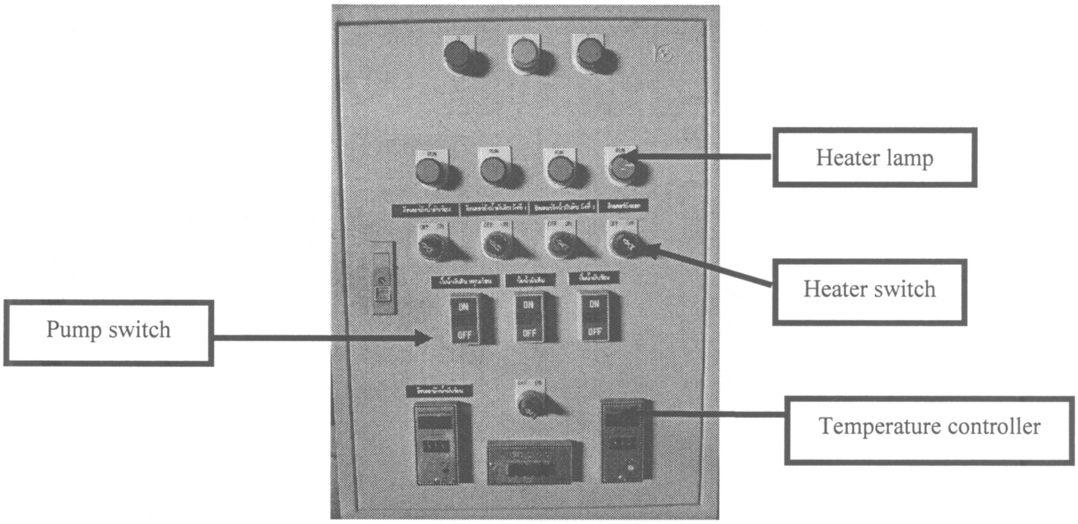

Figure D.5 Controller box of the 1st-stage process

The second process (Transesterification)

1. De-acidified MCPO storage tank

A 200-liter plastic tank consisted of heaters and temperature controllers was used as a container for storing and warming de-acidified MCPO before feeding it into system as shown in Figure D.6. It was connected to metering pump for feeding warmed de-acidified MCPO into transesterification reactor.

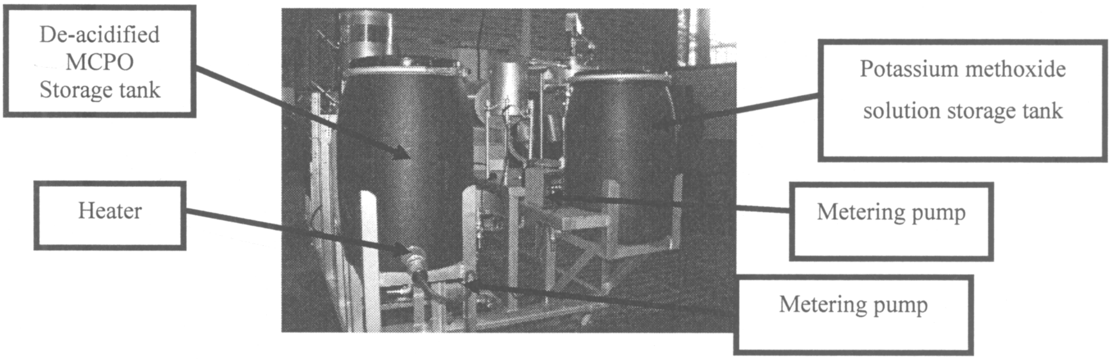

Figure D.6 Left side of the second stage

2. The first stage waste solution storage tank

A 120-liter plastic tank connected to pump for feeding waste solution into distillation tower was used as a container for storing the first stage waste solution as shown in Figure D.7.

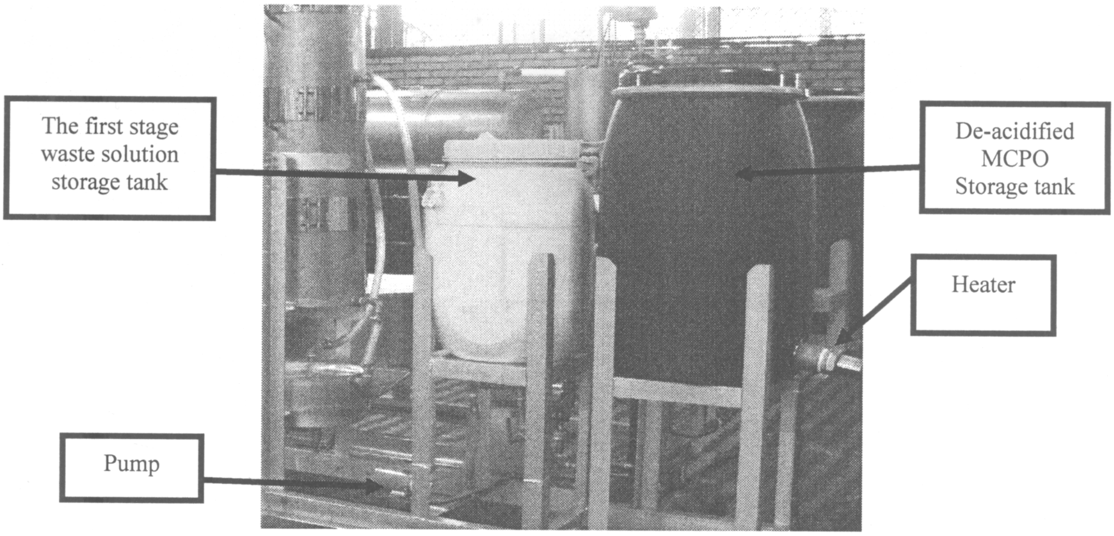

Figure D.7 The first stage waste solution storage tank

3. Potassium methoxide solution storage tank

A 120-liter plastic tank connected to metering pump for feeding potassium methoxide solution into reactor was used as a container for storing potassium methoxide solution as shown in Figure D.6.

4. Transesterification reactor

Similar to esterification reactor, transesterification reactor as shown the detail in Figure D.8 and D.9 was fabricated by using 1.5 mm thick #304 stainless for reactor body and 4 mm thick jacket # 304 stainless for flange sheets, cover sheet and bottom sheet.

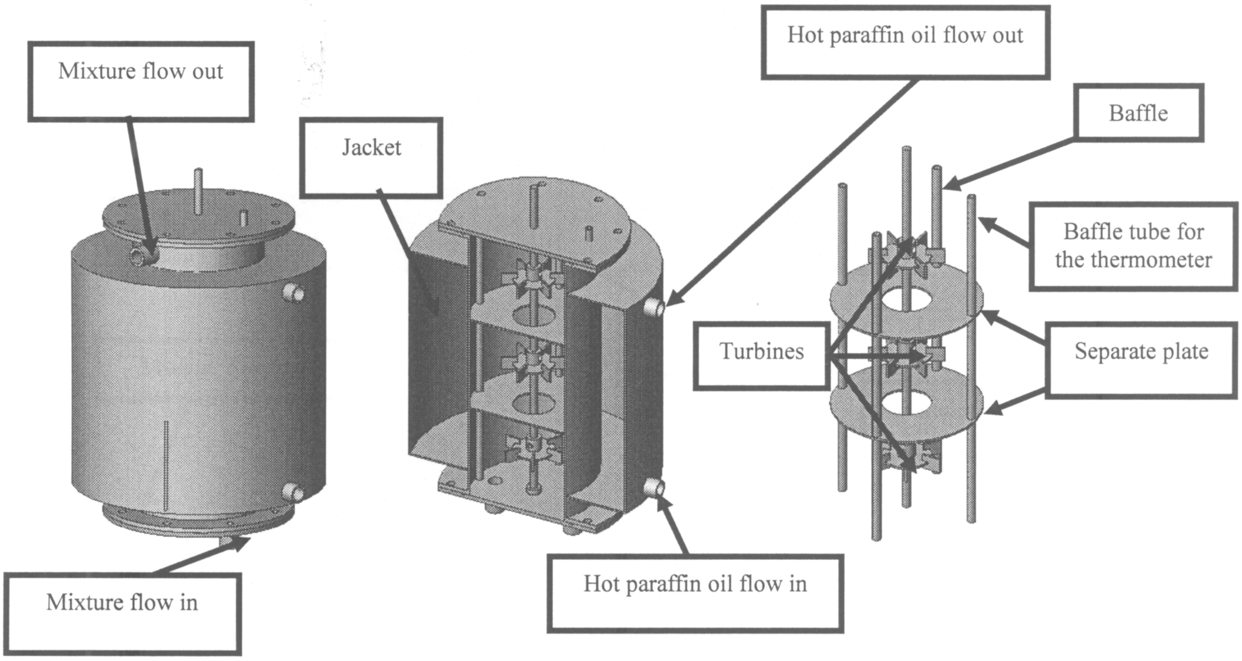

Figure D.8 Details of transesterification reactor

5. Hot paraffin oil tank

A 1.5-liter hot paraffin oil tank installing with heater was fabricated from stainless #304 sizing 250 mm diameter and 300 mm high which was similar to hot paraffin oil tank used for warming mixture in esterification reactor.

6. Separate tank

A separate tank installing with heater was fabricated from #304 stainless sizing 250 mm diameter and 300 mm long as shown in Figure 9.

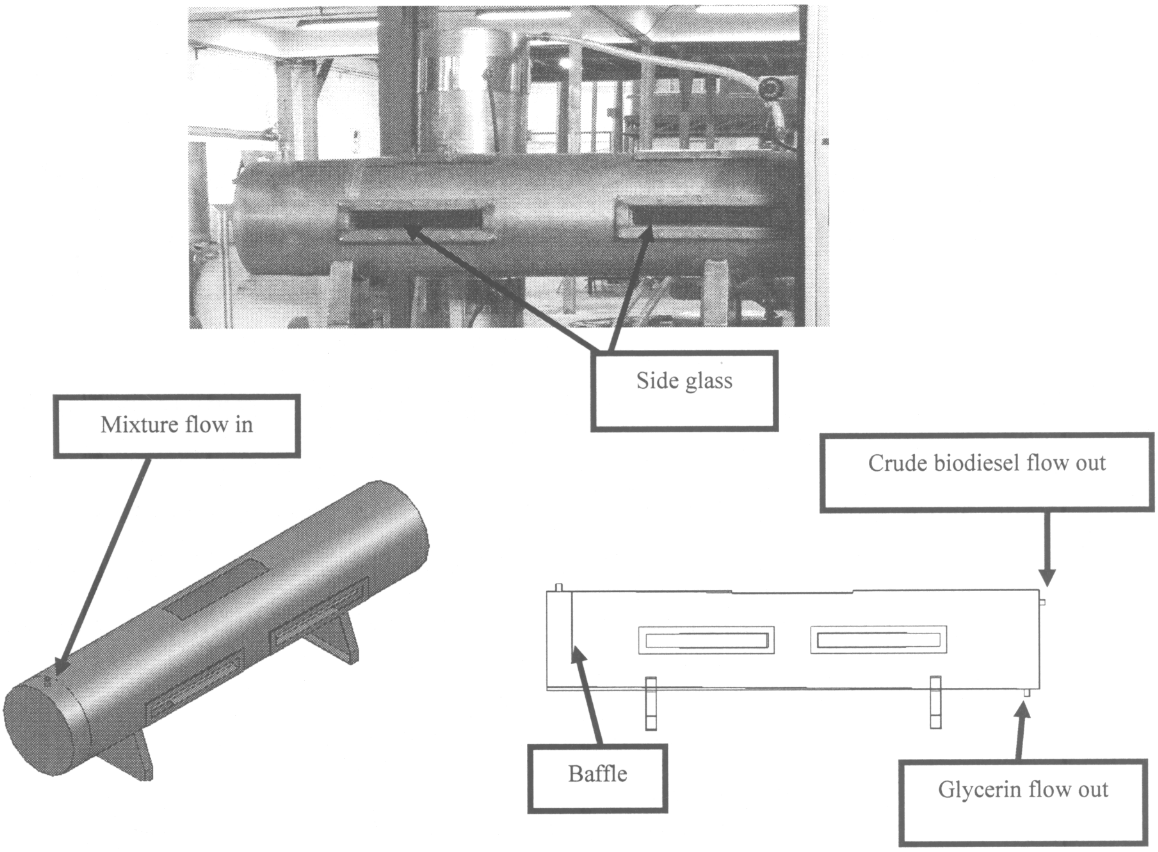

Figure D.9 The 2nd-stage separate tank

7. Crude biodiesel storage tank

A 200-liter plastic tank connected to pump for feeding crude biodiesel storage tank into distillation tower was used as a container for storing crude biodiesel storage tank as shown in Figure D.10.

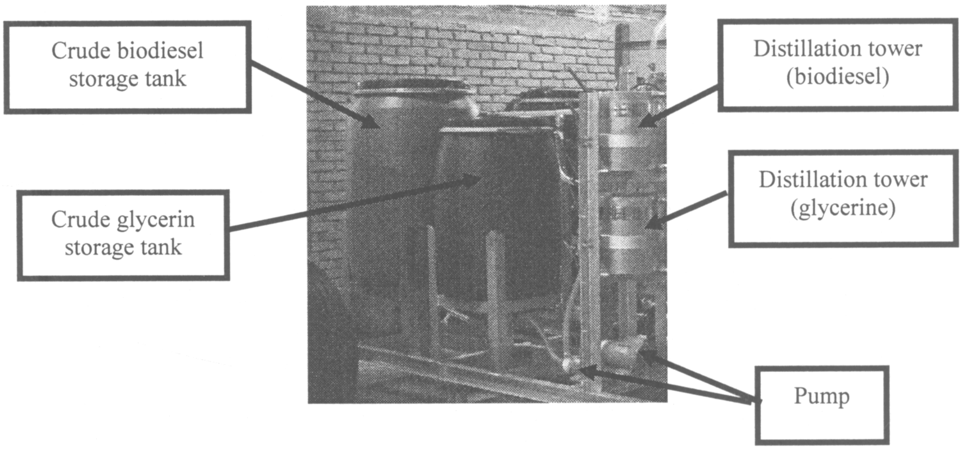

Figure D.10 Crude biodiesel and crude glycerin storage tank

8. Crude glycerin storage tank

A 160-liter plastic tank connected to pump for feeding crude biodiesel storage tank into distillation tower was used as a container for storing crude biodiesel storage tank as shown in Figure D.10.

9. Distillation tower

There were 3 distillation towers used to recovery methanol from crude biodiesel, crude glycerin and the 1st-stage waste solution. All of them were fabricated from #304 stainless and installed with band heater as shown in Figure D.11-13.

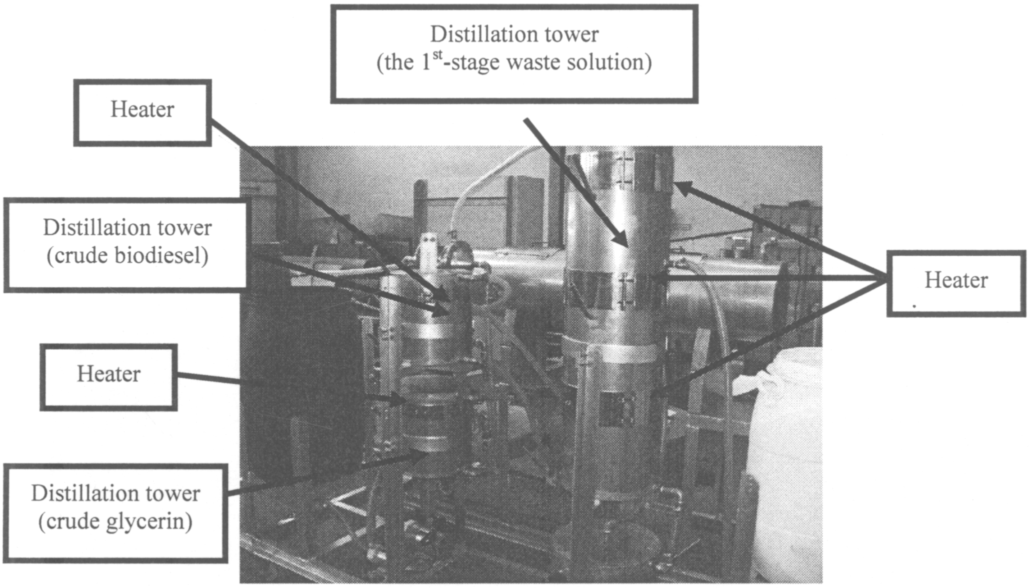

Figure D.11 Distillation tower

10. Re-boiler

There were 3 re-boilers used to evaporate remained methanol that contained in crude biodiesel, crude glycerin and the 1st-stage waste solution. Re-boilers were fabricated from #304 stainless and installed with heater as shown in Figure D.14.

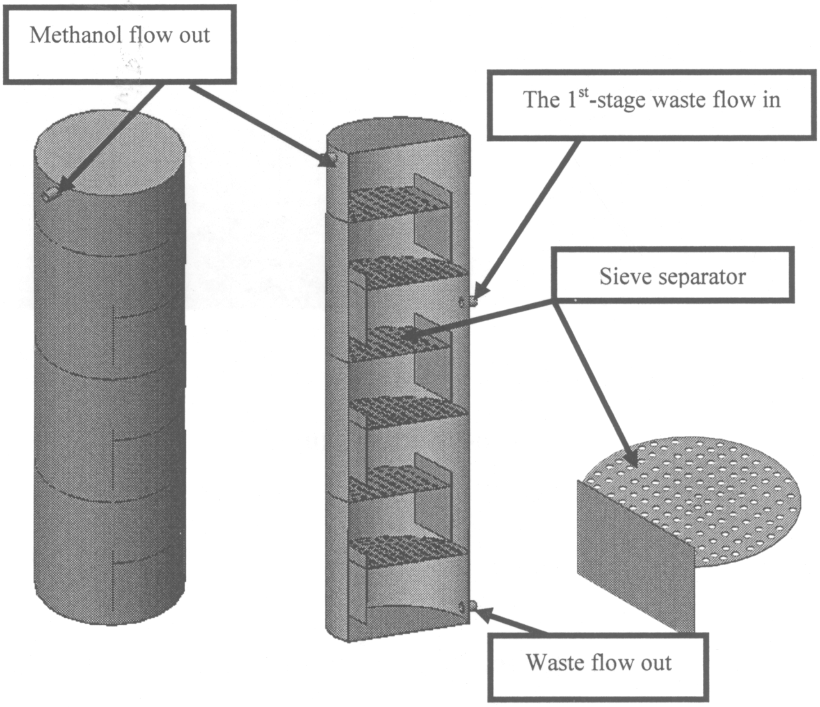

Figure D.12 Detail of the 1st-stage waste distillation tower

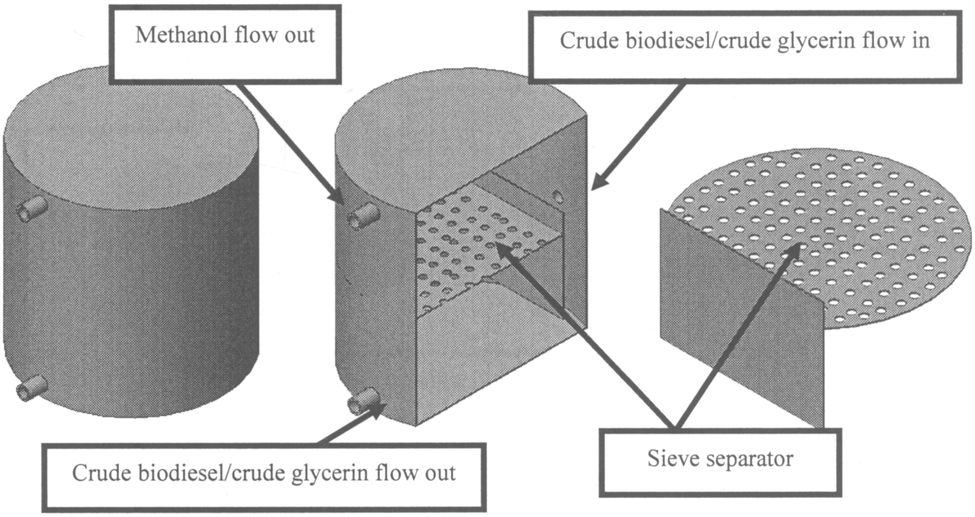

Figure D.13 Detail of crude biodiesel/crude glycerin distillation tower

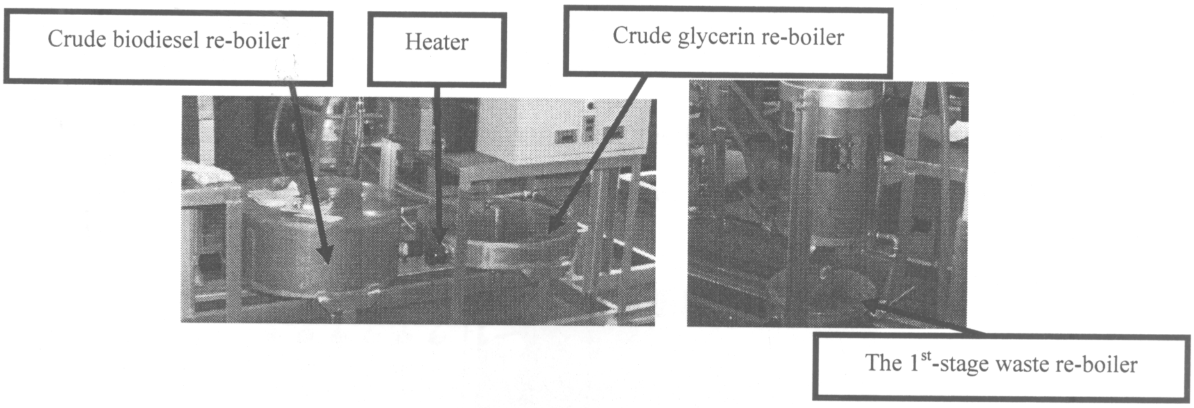

Figure D.14 Re-boilers

11. Condenser

Condenser as shown the detail in Figure D.15 was fabricated by using 1.5 mm thick #304 stainless for body of condenser and baffles, and 4 mm thick jacket # 304 stainless for flange sheets. Moreover, 10 mm long stainless tubes were used as cooling water tubes.

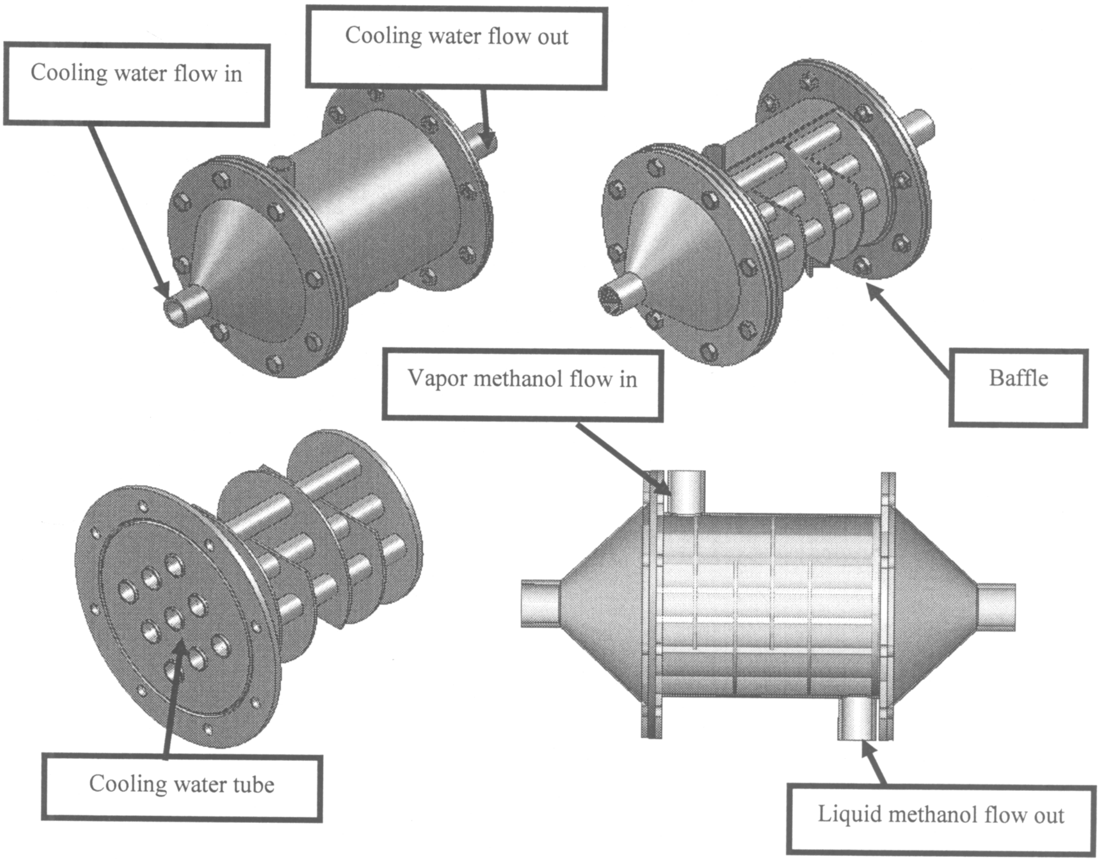

Figure D.15 Condenser

12. Cooling water tank

A 160-liter plastic tank connected to pump for feeding cooling water into condensers was used as a container for storing cooling water as shown in Figure D.16.

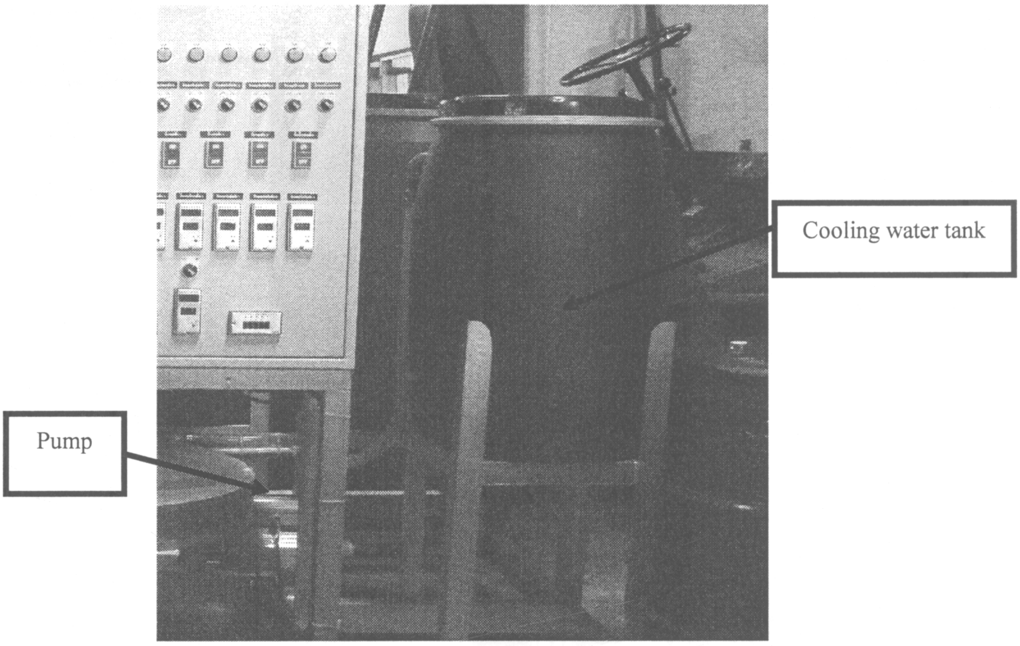

Figure D.16 Cooling water tank

13. Controller box of the 2nd-stage process

Similar to the 1st-stage process, controller box of the 2nd-stage process as shown in Figure D.17 consisted of heater lamp, heater switch, pump switch, temperature controller.

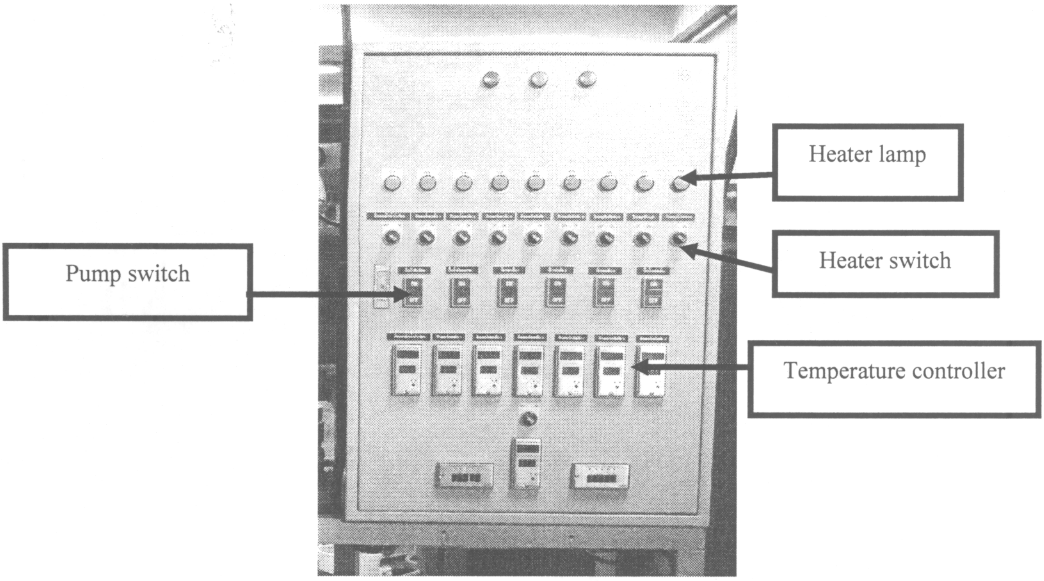

Figure D.17 Controller box of the 2^{nd}-stage process

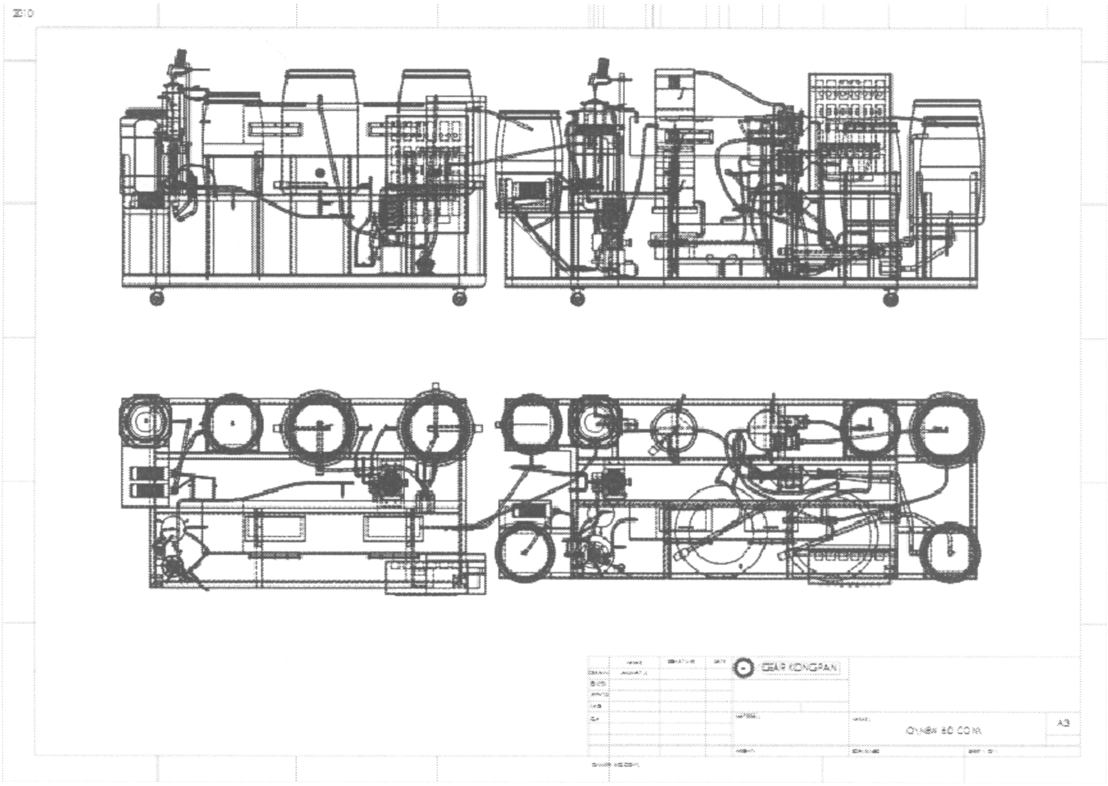

Figure D.18 Full view

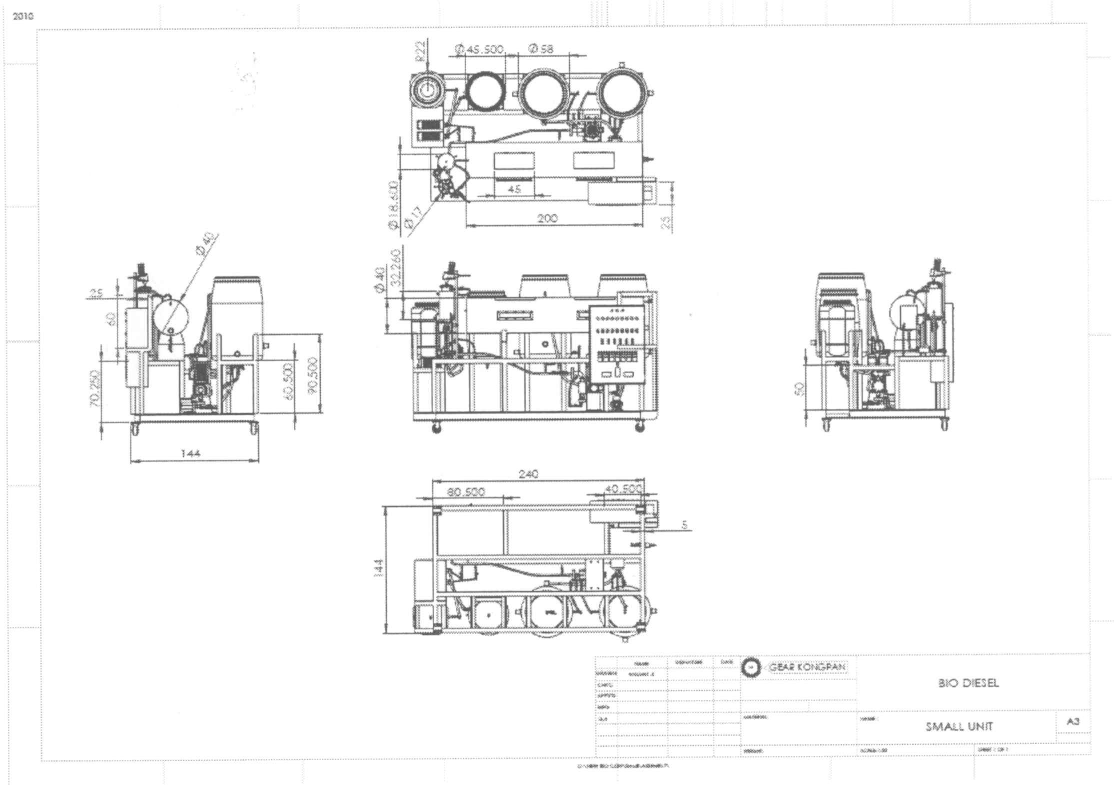

Figure D.19 Full view of esterification part

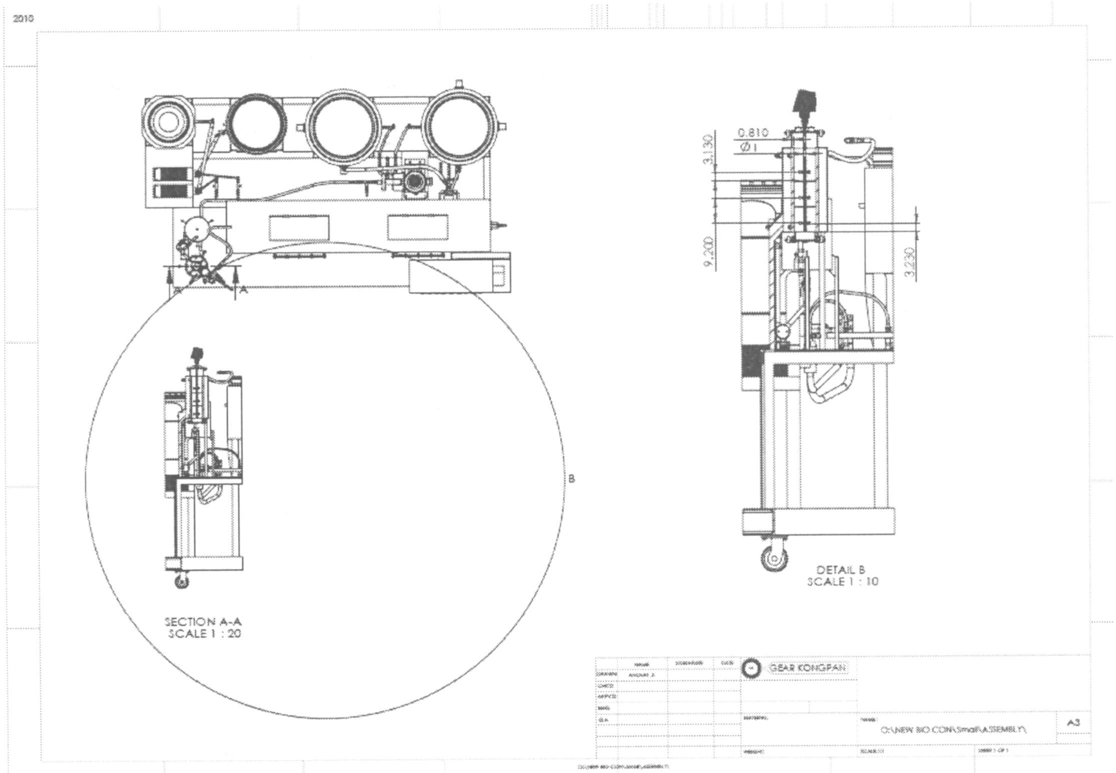

Figure D.20 Section view of reactor in esterification part

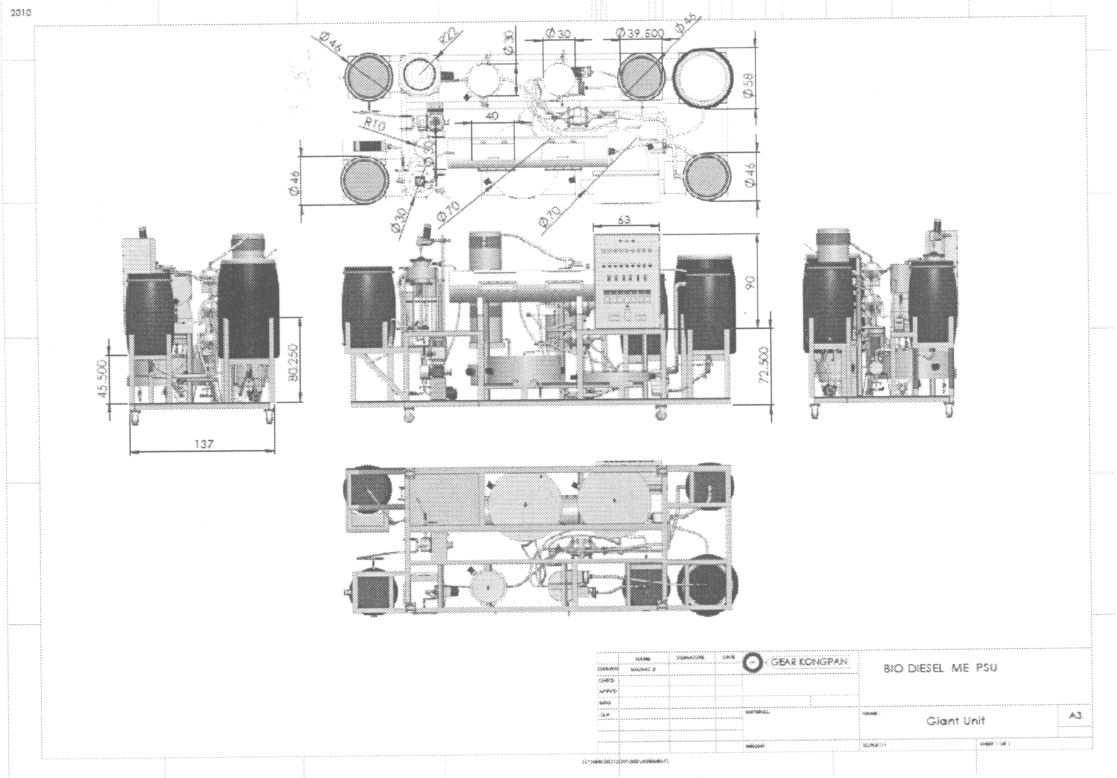

Figure D.21 Full view of transesterification part

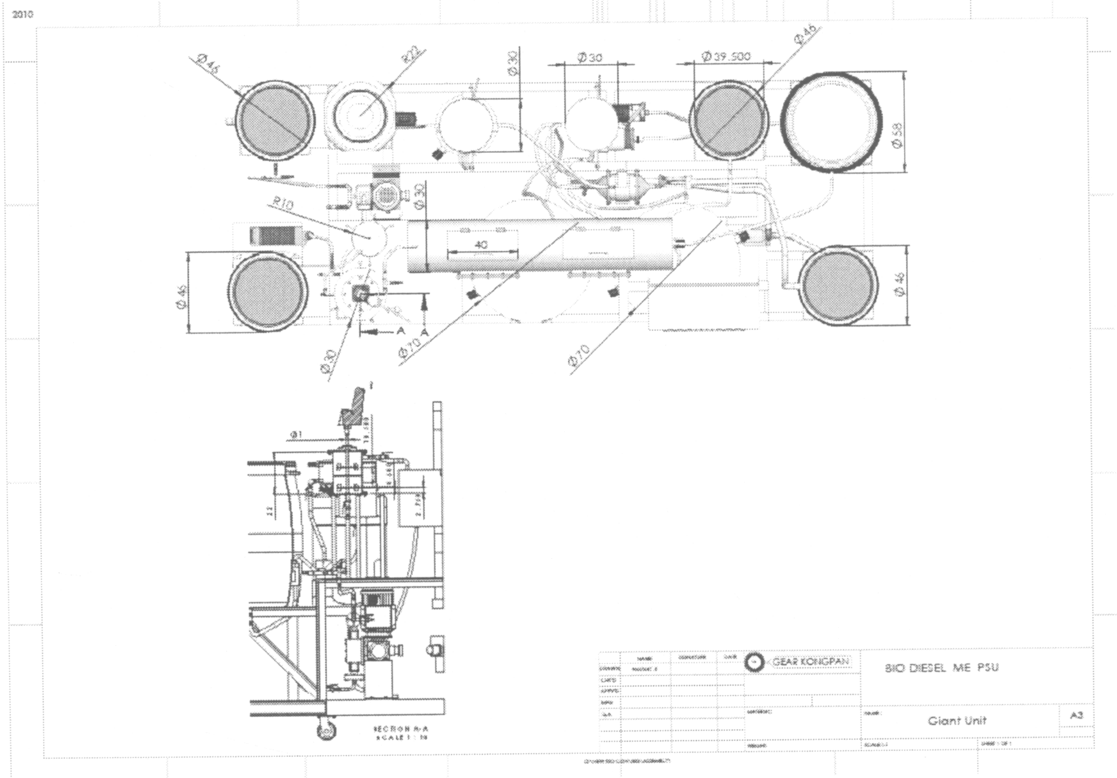

Figure D.22 Section view of reactor in transesterification part

E

METHANOL CONTENT

Table E.1 Methanol content (old condition)

Samples	**Methanol Content (wt%)**
Methanol content in crude biodiesel	6.31
Methanol content in 1st-waste	8.76
Methanol content in glycerol	3.24

APPENDIX F

MULTIPLE REGRESSION ANALYSIS

Multiple regression model before considering the significance of each factor was shown in equation B.1 and in table as followed

$$FFA = \beta_0 + \beta_1(M) + \beta_2(S) + \beta_3(T) + \beta_4(P) + \beta_5(M^2) + \beta_6(S^2) + \beta_7(T^2) + \beta_8(P^2) + \beta_9(MS) + \beta_{10}(MT) + \beta_{11}(MP) + \beta_{12}(ST) + \beta_{13}(SP) + \beta_{14}(TP) \qquad \text{(B.1)}$$

Summary	
|R|	0.993
R^2	0.986
R^2 adjusted	0.971
Standard Error	5.498×10^{-2}
# Points	28
PRESS	0.23
R^2 for Prediction	0.919
Durbin-Watson d	2.027
First Order Autocorrelation	-0.032
Collinearity	0.000
Coefficient of Variation	4.554

ANOVA						
Source	*SS*	*SS%*	*MS*	*F*	*F Signif*	*df*
Regression	2.768	99	0.198	65.41	1.050×10^{-9}	14
Residual	3.929×10^{-2}	1	3.020×10^{-3}			13
Total	2.807	100				27

Terms	**Regression coefficients**	**P value**	**Std Error**	**-95%**	**95%**	**t Stat**	**VIF**
β_0	15.190	9.406×10^{-8}	1.437	12.080	18.290	10.570	-
β_1	-0.436	1.071×10^{-8}	3.437×10^{-2}	-0.510	-0.362	-12.690	234.50
β_2	-2.757	2.171×10^{-6}	0.344	-3.499	-2.014	-8.022	234.50
β_3	-4.827	1.220×10^{-4}	0.894	-6.759	-2.895	-5.397	397.00
β_4	-2.85×10^{-3}	5.540×10^{-3}	8.590×10^{-4}	-4.710×10^{-3}	-9.960×10^{-4}	-3.319	234.50
β_5	7.600×10^{-3}	3.081×10^{-10}	4.490×10^{-4}	6.630×10^{-3}	8.570×10^{-3}	16.930	65.14
β_6	0.340	4.093×10^{-6}	4.489×10^{-2}	0.243	0.437	7.566	65.14
β_7	0.867	3.290×10^{-4}	0.180	0.479	1.255	4.830	325.14
β_8	1.594×10^{-6}	7.513×10^{-5}	2.806×10^{-7}	9.881×10^{-7}	2.200×10^{-6}	5.682	65.14
β_9	4.250×10^{-2}	3.247×10^{-6}	5.500×10^{-3}	3.062×10^{-2}	5.438×10^{-2}	7.731	49.00
β_{10}	4.110×10^{-3}	0.714	1.100×10^{-2}	-1.964×10^{-2}	2.787×10^{-2}	0.374	146.50
β_{11}	-1.452×10^{-5}	0.310	1.374×10^{-5}	-4.421×10^{-5}	1.517×10^{-5}	-1.057	49.00
β_{12}	0.246	4.333×10^{-2}	0.110	8.580×10^{-3}	0.484	2.238	146.50
β_{13}	-2.240×10^{-4}	0.127	1.370×10^{-4}	-5.210×10^{-4}	7.308×10^{-5}	-1.629	49.00
β_{14}	4.710×10^{-4}	0.110	2.750×10^{-4}	-1.220×10^{-4}	1.070×10^{-3}	1.715	146.50

Multiple regression model after considering the significance of each factor was shown in equation B.2 and in table as followed

$$FFA = \beta_0 + \beta_1(M) + \beta_2(S) + \beta_3(T) + \beta_4(P) + \beta_5(M^2) + \beta_6(S^2) + \beta_7(T^2) + \beta_8(P^2) + \beta_9(MS) + \beta_{10}(MT) \qquad \text{(B.2)}$$

Summary	
|R|	0.989
R^2	0.979
R^2 adjusted	0.966
Standard Error	5.941×10^{-2}
# Points	28
PRESS	0.16
R^2 for Prediction	0.943
Durbin-Watson d	2.044
First Order Autocorrelation	-0.034
Collinearity	0.000
Coefficient of Variation	4.921

ANOVA

Source	*SS*	*SS%*	*MS*	*F*	*F Signif*	*df*
Regression	2.747	98	0.275	77.84	3.520×10^{-12}	10
Residual	0.060	2	3.530×10^{-3}			17
Total	2.807	100				27

Terms	**Regression coefficients**	**P value**	**Std Error**	**-95%**	**95%**	**t Stat**	**VIF**
β_0	14.740	2.775×10^{-9}	1.314	11.970	17.520	11.220	-
β_1	-0.438	6.037×10^{-13}	2.288×10^{-2}	-0.487	-0.390	-19.160	89.00
β_2	-2.936	2.048×10^{-7}	0.352	-3.678	-2.194	-8.344	210.50
β_3	-4.368	1.600×10^{-4}	0.906	-6.280	-2.456	-4.820	349.00
β_4	-2.530×10^{-3}	7.622×10^{-5}	4.890×10^{-4}	-3.560×10^{-3}	-1.50×10^{-3}	-5.174	65.00
β_5	7.600×10^{-3}	1.553×10^{-11}	4.850×10^{-4}	6.570×10^{-3}	8.62×10^{-3}	15.660	65.14
β_6	0.340	2.130×10^{-6}	4.851×10^{-2}	0.237	0.442	7.002	65.14
β_7	0.867	3.370×10^{-4}	0.194	0.458	1.277	4.470	325.14
β_8	1.594×10^{-6}	6.405×10^{-5}	3.032×10^{-7}	9.545×10^{-7}	2.234×10^{-6}	5.258	65.14
B_9	4.250×10^{-2}	1.615×10^{-6}	5.940×10^{-3}	2.997×10^{-2}	5.503×10^{-2}	7.154	49.00
β_{10}	0.246	5.385×10^{-2}	0.119	-4.560×10^{-3}	0.497	2.071	146.50

APPENDIX G

F-TEST

Table G.1 F-test (Kleinbaum, *et al.*, 1988)

	DEGREES OF FREEDOM FOR NUMERATOR																										
DEGREES OF FREEDOM FOR DENOMINATOR	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	25	30	40	50	100	150	200
1	161	200	216	225	230	234	237	239	241	242	243	244	245	245	246	246	247	247	248	248	249	250	251	252	253	253	254
2	18.5	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.5	19.5	19.5	19.5	19.5	19.5	19.5
3	10.1	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79	8.76	8.74	8.73	8.71	8.70	8.69	8.68	8.67	8.67	8.66	8.63	8.62	8.59	8.58	8.55	8.54	8.54
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.94	5.91	5.89	5.87	5.86	5.84	5.83	5.82	5.81	5.80	5.77	5.75	5.72	5.70	5.66	5.65	5.65
5	6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.70	4.68	4.66	4.64	4.62	4.60	4.59	4.58	4.57	4.56	4.52	4.50	4.46	4.44	4.41	4.39	4.39
6	5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	4.03	4.00	3.98	3.96	3.94	3.92	3.91	3.90	3.88	3.87	3.83	3.81	3.77	3.75	3.71	3.70	3.69
7	5.59	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.60	3.57	3.55	3.53	3.51	3.49	3.48	3.47	3.46	3.44	3.40	3.38	3.34	3.32	3.27	3.26	3.25
8	5.32	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.31	3.28	3.26	3.24	3.22	3.20	3.19	3.17	3.16	3.15	3.11	3.08	3.04	3.02	2.97	2.96	2.95
9	5.12	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.10	3.07	3.05	3.03	3.01	2.99	2.97	2.96	2.95	2.94	2.89	2.86	2.83	2.80	2.76	2.74	2.73
10	4.96	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.94	2.91	2.89	2.86	2.85	2.83	2.81	2.80	2.79	2.77	2.73	2.70	2.66	2.64	2.59	2.57	2.56
11	4.84	3.98	3.59	3.36	3.20	3.09	3.01	2.95	2.90	2.85	2.82	2.79	2.76	2.74	2.72	2.70	2.69	2.67	2.66	2.65	2.60	2.57	2.53	2.51	2.46	2.44	2.43
12	4.75	3.89	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.72	2.69	2.66	2.64	2.62	2.60	2.58	2.57	2.56	2.54	2.50	2.47	2.43	2.40	2.35	2.33	2.32
13	4.67	3.81	3.41	3.18	3.03	2.92	2.83	2.77	2.71	2.67	2.63	2.60	2.58	2.55	2.53	2.51	2.50	2.48	2.47	2.46	2.41	2.38	2.34	2.31	2.26	2.24	2.23
14	4.60	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60	2.57	2.53	2.51	2.48	2.46	2.44	2.43	2.41	2.40	2.39	2.34	2.31	2.27	2.24	2.19	2.17	2.16
15	4.54	3.68	3.29	3.05	2.90	2.79	2.71	2.64	2.59	2.54	2.51	2.48	2.45	2.42	2.40	2.38	2.37	2.35	2.34	2.33	2.28	2.25	2.20	2.18	2.12	2.10	2.10
16	4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.46	2.42	2.40	2.37	2.35	2.33	2.32	2.30	2.29	2.28	2.23	2.19	2.15	2.12	2.07	2.05	2.04
17	4.45	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49	2.45	2.41	2.38	2.35	2.33	2.31	2.29	2.27	2.26	2.24	2.23	2.18	2.15	2.10	2.08	2.02	2.00	1.99
18	4.41	3.55	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41	2.37	2.34	2.31	2.29	2.27	2.25	2.23	2.22	2.20	2.19	2.14	2.11	2.06	2.04	1.98	1.96	1.95
19	4.38	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42	2.38	2.34	2.31	2.28	2.26	2.23	2.21	2.20	2.18	2.17	2.16	2.11	2.07	2.03	2.00	1.94	1.92	1.91
20	4.35	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.31	2.28	2.25	2.22	2.20	2.18	2.17	2.15	2.14	2.12	2.07	2.04	1.99	1.97	1.91	1.89	1.88
21	4.32	3.47	3.07	2.84	2.68	2.57	2.49	2.42	2.37	2.32	2.28	2.25	2.22	2.20	2.18	2.16	2.14	2.12	2.11	2.10	2.05	2.01	1.96	1.94	1.88	1.86	1.84
22	4.30	3.44	3.05	2.82	2.66	2.55	2.46	2.40	2.34	2.30	2.26	2.23	2.20	2.17	2.15	2.13	2.11	2.10	2.08	2.07	2.02	1.98	1.94	1.91	1.86	1.83	1.82
23	4.28	3.42	3.03	2.80	2.64	2.53	2.44	2.37	2.32	2.27	2.24	2.20	2.18	2.15	2.13	2.11	2.09	2.08	2.06	2.05	2.00	1.96	1.91	1.88	1.82	1.80	1.79
24	4.26	3.40	3.01	2.78	2.62	2.51	2.42	2.36	2.30	2.25	2.22	2.18	2.15	2.13	2.11	2.09	2.07	2.06	2.04	2.03	1.97	1.94	1.89	1.86	1.80	1.78	1.77
25	4.24	3.39	2.99	2.75	2.60	2.49	2.40	2.34	2.28	2.24	2.20	2.16	2.14	2.11	2.09	2.07	2.06	2.04	2.02	2.01	1.96	1.92	1.87	1.84	1.78	1.76	1.75
26	4.23	3.37	2.98	2.74	2.59	2.47	2.39	2.32	2.27	2.22	2.18	2.16	2.12	2.09	2.07	2.05	2.03	2.02	2.00	1.99	1.94	1.90	1.85	1.82	1.76	1.74	1.73
27	4.21	3.35	2.96	2.73	2.57	2.46	2.37	2.31	2.25	2.20	2.17	2.13	2.10	2.08	2.06	2.04	2.02	2.00	1.99	1.97	1.92	1.88	1.84	1.81	1.74	1.72	1.71
28	4.20	3.34	2.95	2.71	2.56	2.45	2.36	2.29	2.24	2.19	2.15	2.12	2.09	2.06	2.04	2.02	2.00	1.99	1.97	1.96	1.91	1.87	1.82	1.79	1.73	1.70	1.69
29	4.18	3.33	2.93	2.70	2.55	2.43	2.35	2.28	2.22	2.18	2.14	2.10	2.08	2.05	2.03	2.01	1.99	1.97	1.96	1.94	1.89	1.85	1.81	1.77	1.71	1.69	1.67
30	4.17	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.13	2.09	2.06	2.04	2.01	1.99	1.98	1.96	1.95	1.93	1.88	1.84	1.79	1.76	1.70	1.67	1.66
32	4.15	3.29	2.90	2.67	2.51	2.40	2.31	2.24	2.19	2.14	2.10	2.07	2.04	2.01	1.99	1.97	1.96	1.94	1.92	1.91	1.85	1.82	1.77	1.74	1.67	1.64	1.63
34	4.13	3.28	2.88	2.65	2.49	2.38	2.29	2.23	2.17	2.12	2.08	2.05	2.02	1.99	1.97	1.95	1.93	1.92	1.90	1.89	1.83	1.80	1.75	1.71	1.65	1.62	1.61
36	4.11	3.26	2.87	2.63	2.48	2.36	2.28	2.21	2.15	2.11	2.07	2.03	2.00	1.98	1.95	1.93	1.92	1.90	1.88	1.87	1.81	1.78	1.73	1.69	1.62	1.60	1.59
38	4.10	3.24	2.85	2.62	2.46	2.35	2.26	2.19	2.14	2.09	2.05	2.02	1.99	1.96	1.94	1.92	1.90	1.88	1.87	1.85	1.80	1.76	1.71	1.68	1.61	1.58	1.57
40	4.08	3.23	2.84	2.61	2.45	2.34	2.25	2.18	2.12	2.08	2.04	2.00	1.97	1.95	1.92	1.90	1.89	1.87	1.85	1.84	1.78	1.74	1.69	1.66	1.59	1.56	1.55
42	4.07	3.22	2.83	2.59	2.44	2.32	2.24	2.17	2.11	2.06	2.03	1.99	1.96	1.94	1.91	1.89	1.87	1.86	1.84	1.83	1.77	1.73	1.68	1.65	1.57	1.55	1.53
44	4.06	3.21	2.82	2.58	2.43	2.31	2.23	2.16	2.10	2.05	2.01	1.98	1.95	1.92	1.90	1.88	1.86	1.84	1.83	1.81	1.76	1.72	1.67	1.63	1.56	1.53	1.52
46	4.05	3.20	2.81	2.57	2.42	2.30	2.22	2.15	2.09	2.04	2.00	1.97	1.94	1.91	1.89	1.87	1.85	1.83	1.82	1.80	1.75	1.71	1.65	1.62	1.55	1.52	1.51
48	4.04	3.19	2.80	2.57	2.41	2.29	2.21	2.14	2.08	2.03	1.99	1.96	1.93	1.90	1.88	1.86	1.84	1.82	1.81	1.79	1.74	1.70	1.64	1.61	1.54	1.51	1.49
50	4.03	3.18	2.79	2.56	2.40	2.29	2.20	2.13	2.07	2.03	1.99	1.96	1.92	1.89	1.87	1.85	1.83	1.81	1.80	1.78	1.73	1.69	1.63	1.60	1.52	1.50	1.48
60	4.00	3.15	2.76	2.53	2.37	2.25	2.17	2.10	2.04	1.99	1.95	1.92	1.89	1.86	1.84	1.82	1.80	1.78	1.76	1.75	1.69	1.65	1.59	1.56	1.48	1.45	1.44
70	3.98	3.13	2.74	2.50	2.35	2.23	2.14	2.07	2.02	1.97	1.93	1.89	1.86	1.84	1.81	1.79	1.77	1.75	1.74	1.72	1.66	1.62	1.57	1.53	1.45	1.42	1.40
80	3.96	3.11	2.72	2.49	2.33	2.21	2.13	2.06	2.00	1.95	1.91	1.88	1.84	1.82	1.79	1.77	1.75	1.73	1.72	1.70	1.64	1.60	1.54	1.51	1.43	1.39	1.38
90	3.95	3.10	2.71	2.47	2.32	2.20	2.11	2.04	1.99	1.94	1.90	1.86	1.83	1.80	1.78	1.76	1.74	1.72	1.70	1.69	1.63	1.59	1.53	1.49	1.41	1.38	1.36
100	3.94	3.09	2.70	2.45	2.31	2.19	2.10	2.03	1.97	1.93	1.89	1.85	1.82	1.79	1.77	1.75	1.73	1.71	1.69	1.68	1.62	1.57	1.52	1.48	1.39	1.36	1.34
125	3.92	3.07	2.68	2.44	2.29	2.17	2.08	2.01	1.96	1.91	1.87	1.83	1.80	1.77	1.75	1.73	1.71	1.69	1.67	1.66	1.59	1.55	1.49	1.45	1.36	1.33	1.31
150	3.90	3.06	2.66	2.43	2.27	2.16	2.07	2.00	1.94	1.89	1.85	1.82	1.79	1.76	1.73	1.71	1.69	1.67	1.66	1.64	1.58	1.54	1.48	1.44	1.34	1.31	1.29
200	3.89	3.04	2.65	2.42	2.26	2.14	2.06	1.98	1.93	1.88	1.84	1.80	1.77	1.74	1.72	1.69	1.67	1.66	1.64	1.62	1.56	1.52	1.46	1.41	1.32	1.28	1.26
300	3.87	3.03	2.63	2.40	2.24	2.13	2.04	1.97	1.91	1.86	1.82	1.78	1.75	1.72	1.70	1.68	1.66	1.64	1.62	1.61	1.54	1.50	1.43	1.39	1.30	1.26	1.23
500	3.86	3.01	2.62	2.39	2.23	2.12	2.03	1.96	1.90	1.85	1.81	1.77	1.74	1.71	1.69	1.66	1.64	1.62	1.61	1.59	1.53	1.48	1.42	1.38	1.28	1.23	1.21
1000	3.85	3.00	2.61	2.38	2.22	2.11	2.02	1.95	1.89	1.84	1.80	1.76	1.73	1.70	1.68	1.65	1.63	1.61	1.60	1.58	1.52	1.47	1.41	1.36	1.26	1.22	1.19

APPENDIX H
RAW DATA

Table H.1 Raw data of esterification under the condition of 20 v% of methanol, 1 v% of sulfuric acid, retention time of 2.25 min and stirrer speed at 800 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	14.892	0.367
2.25	1.122	1.447
4.50	1.113	1.430
6.75	1.249	1.257
9.00	1.042	1.440
11.25	1.038	1.237
13.50	1.231	1.297
15.75	1.669	1.173
18.00	1.320	1.253
20.25	1.613	1.227
22.50	1.235	1.193
Average (6 to 10 times of retention time)	1.413	1.229

Table H.2 Raw data under of esterification the condition of 20 v% of methanol, 2 v% of sulfuric acid, retention time of 1.75 min and stirrer speed at 800 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	14.425	0.435
1.75	0.967	1.470
3.50	0.998	1.490
5.25	1.026	1.330
7.00	1.172	1.257
8.75	1.046	1.467
10.50	1.091	1.427
12.25	1.070	1.157
14.00	1.021	1.310
15.75	1.094	1.293
17.50	1.096	1.447
Average (6 to 10 times of retention time)	1.074	1.327

Table H.3 Raw data of esterification under the condition of 25 v% of methanol, 1.5 v% of sulfuric acid, retention time of 2 min and stirrer speed at 600 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	14.529	0.511
2.00	0.923	1.500
4.00	0.825	1.457
6.00	1.071	1.360
8.00	1.080	1.377
10.00	0.988	1.390
12.00	1.091	1.437
14.00	0.998	1.370
16.00	0.849	1.530
18.00	1.017	1.410
20.00	0.890	1.333
Average (6 to 10 times of retention time)	0.969	1.416

Table H.4 Raw data of esterification under the condition of 15 v% of methanol, 2.5 v% of sulfuric acid, retention time of 2.5 min and stirrer speed at 600 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	13.871	0.326
2.50	1.623	0.723
5.00	1.234	1.037
7.50	1.405	0.863
10.00	1.306	0.877
12.50	1.079	1.097
15.00	1.447	0.817
17.50	1.310	0.920
20.00	1.315	1.170
22.50	1.263	1.017
25.00	1.409	0.823
Average (6 to 10 times of retention time)	1.349	0.949

Table H.5 Raw data of esterification under the condition of 25 v% of methanol, 2.5 v% of sulfuric acid, retention time of 2.5 min and stirrer speed at 600 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	14.057	0.592
2.50	1.725	2.160
5.00	1.193	1.990
7.50	1.532	1.863
10.00	1.427	1.463
12.50	1.082	1.547
15.00	1.004	1.373
17.50	1.022	1.667
20.00	1.041	1.390
22.50	1.052	1.383
25.00	1.044	1.543
Average (6 to 10 times of retention time)	1.032	1.471

Table H.6 Raw data of esterification under the condition of 20 v% of methanol, 2 v% of sulfuric acid, retention time of 2.25 min and stirrer speed at 800 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	13.663	0.510
2.25	1.083	1.083
4.50	0.976	1.133
6.75	1.086	1.240
9.00	1.443	1.163
11.25	0.935	1.157
13.50	0.894	1.100
15.75	0.877	1.220
18.00	0.865	1.343
20.25	0.854	1.997
22.50	0.861	1.167
Average (6 to 10 times of retention time)	0.870	1.365

Table H.7 Raw data of esterification under the condition of 20 v% of methanol, 2 v% of sulfuric acid, retention time of 2.25 min and stirrer speed at 400 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	14.842	0.524
2.25	1.161	1.227
4.50	1.385	1.297
6.75	1.151	1.330
9.00	1.047	1.513
11.25	1.318	1.410
13.50	1.047	1.347
15.75	1.126	1.317
18.00	1.270	1.550
20.25	1.294	1.340
22.50	1.031	1.577
Average (6 to 10 times of retention time)	1.154	1.426

Table H.8 Raw data of esterification under the condition of 30 v% of methanol, 2 v% of sulfuric acid, retention time of 2.25 min and stirrer speed at 800 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	14.017	0.244
2.25	0.792	1.227
4.50	1.269	1.233
6.75	0.847	1.233
9.00	0.986	1.457
11.25	0.906	1.210
13.50	1.140	1.123
15.75	1.147	1.063
18.00	1.147	1.107
20.25	1.187	1.057
22.50	1.154	1.163
Average (6 to 10 times of retention time)	1.155	1.103

Table H.9 Raw data of esterification under the condition of 20 v% of methanol, 2 v% of sulfuric acid, retention time of 2.75 min and stirrer speed at 800 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	14.308	0.533
2.75	0.799	1.147
5.50	0.817	1.573
8.25	0.983	1.270
11.00	1.310	1.503
13.75	1.232	1.297
16.50	1.194	1.283
19.25	1.123	1.357
22.00	1.123	1.387
24.75	1.142	1.607
27.50	1.186	1.350
Average (6 to 10 times of retention time)	1.154	1.397

Table H.10 Raw data of esterification under the condition of 25 v% of methanol, 1.5 v% of sulfuric acid, retention time of 2 min and stirrer speed at 1000 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	15.288	0.408
2.00	0.863	1.360
4.00	0.882	1.377
6.00	0.950	1.490
8.00	1.127	1.447
10.00	0.967	1.437
12.00	1.165	1.470
14.00	0.949	1.307
16.00	0.987	1.417
18.00	1.057	1.280
20.00	0.980	1.443
Average (6 to 10 times of retention time)	1.028	1.383

Table H.11 Raw data of esterification under the condition of 15 v% of methanol, 1.5 v% of sulfuric acid, retention time of 2 min and stirrer speed at 600 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	13.791	0.652
2.00	1.108	1.063
4.00	1.108	1.253
6.00	1.749	1.397
8.00	1.710	1.460
10.00	1.789	1.350
12.00	1.746	1.403
14.00	1.750	1.433
16.00	1.753	1.450
18.00	1.763	1.407
20.00	1.794	1.407
Average (6 to 10 times of retention time)	1.761	1.420

Table H.12 Raw data of esterification under the condition of 15 v% of methanol, 1.5 v% of sulfuric acid, retention time of 2.5 min and stirrer speed at 1000 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	14.673	0.624
2.50	1.774	1.397
5.00	1.755	1.437
7.50	1.064	1.407
10.00	1.391	1.363
12.50	1.591	1.377
15.00	1.772	1.407
17.50	1.747	1.617
20.00	1.795	1.443
22.50	1.797	1.430
25.00	1.755	1.480
Average (6 to 10 times of retention time)	1.773	1.475

Table H.13 Raw data under of esterification the condition of 25 v% of methanol, 1.5 v% of sulfuric acid, retention time of 2.5 min and stirrer speed at 600 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	14.538	0.677
2.50	0.894	1.720
5.00	0.829	1.397
7.50	0.909	1.563
10.00	0.681	1.400
12.50	0.608	1.377
15.00	0.992	1.637
17.50	1.003	1.440
20.00	0.941	1.513
22.50	0.921	1.597
25.00	1.096	1.527
Average (6 to 10 times of retention time)	0.991	1.543

Table H.14 Raw data under of esterification the condition of 15 v% of methanol, 1.5 v% of sulfuric acid, retention time of 2.5 min and stirrer speed at 600 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	13.485	0.868
2.50	2.194	1.633
5.00	2.670	1.507
7.50	2.055	1.510
10.00	1.634	1.527
12.50	1.538	1.613
15.00	1.565	1.680
17.50	1.457	1.730
20.00	1.473	1.633
22.50	1.563	1.667
25.00	1.477	1.657
Average (6 to 10 times of retention time)	1.507	1.673

Table H.15 Raw data of esterification under the condition of 20 v% of methanol, 2 v% of sulfuric acid, retention time of 2.25 min and stirrer speed at 1200 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	14.946	0.596
2.25	0.865	1.173
4.50	0.921	1.483
6.75	0.942	1.690
9.00	0.968	1.383
11.25	1.127	1.470
13.50	1.136	1.693
15.75	1.183	1.367
18.00	1.139	1.400
20.25	1.132	1.397
22.50	1.162	1.553
Average (6 to 10 times of retention time)	1.151	1.482

Table H.16 Raw data of esterification under the condition of 25 v% of methanol, 2.5 v% of sulfuric acid, retention time of 2.5 min and stirrer speed at 1000 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	14.805	0.474
2.50	1.026	1.583
5.00	0.891	1.507
7.50	1.198	1.337
10.00	1.198	1.313
12.50	1.046	1.457
15.00	1.057	1.363
17.50	1.076	1.300
20.00	1.088	1.317
22.50	1.065	1.357
25.00	1.044	1.507
Average (6 to 10 times of retention time)	1.066	1.369

Table H.17 Raw data of esterification under the condition of 25 v% of methanol, 2.5 v% of sulfuric acid, retention time of 2 min and stirrer speed at 600 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	14.948	0.385
2.00	1.052	1.733
4.00	1.234	2.043
6.00	1.194	1.570
8.00	1.013	1.773
10.00	1.417	1.647
12.00	1.028	1.377
14.00	1.047	1.213
16.00	1.108	1.313
18.00	1.075	1.270
20.00	1.031	1.417
Average (6 to 10 times of retention time)	1.058	1.318

Table H.18 Raw data of esterification under the condition of 15 v% of methanol, 2.5 v% of sulfuric acid, retention time of 2 min and stirrer speed at 1000 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	14.172	0.872
2.00	1.368	1.823
4.00	1.689	2.210
6.00	1.045	1.890
8.00	1.024	1.720
10.00	1.084	1.893
12.00	1.181	2.030
14.00	1.215	1.880
16.00	1.284	1.753
18.00	1.305	1.727
20.00	1.276	1.313
Average (6 to 10 times of retention time)	1.252	1.741

Table H.19 Raw data of esterification under the condition of 25 v% of methanol, 2.5 v% of sulfuric acid, retention time of 2 min and stirrer speed at 1000 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	13.562	0.468
2.00	1.208	1.553
4.00	0.971	1.767
6.00	0.629	1.300
8.00	0.909	1.233
10.00	0.970	1.290
12.00	0.889	1.343
14.00	0.968	1.290
16.00	0.923	1.060
18.00	0.998	1.317
20.00	0.935	1.387
Average (6 to 10 times of retention time)	0.943	1.279

Table H.20 Raw data of esterification under the condition of 15 v% of methanol, 2.5 v% of sulfuric acid, retention time of 2.5 min and stirrer speed at 1000 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	14.495	0.387
2.50	1.267	1.213
5.00	1.306	1.303
7.50	1.257	1.163
10.00	1.127	1.233
12.50	1.073	1.443
15.00	1.341	1.233
17.50	1.326	1.197
20.00	1.301	1.263
22.50	1.359	1.190
25.00	1.329	1.277
Average (6 to 10 times of retention time)	1.331	1.232

Table H.21 Raw data of esterification under the condition of 15 v% of methanol, 1.5 v% of sulfuric acid, retention time of 2 min and stirrer speed at 1000 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	14.079	0.536
2.00	1.764	1.123
4.00	1.046	1.177
6.00	1.284	1.280
8.00	1.145	0.980
10.00	1.692	1.013
12.00	1.734	1.163
14.00	1.797	1.430
16.00	1.650	1.503
18.00	1.721	1.347
20.00	1.641	1.227
Average (6 to 10 times of retention time)	1.709	1.334

Table H.22 Raw data of esterification under the condition of 10 v% of methanol, 2 v% of sulfuric acid, retention time of 2.25 min and stirrer speed at 800 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	14.652	0.869
2.25	1.915	1.207
4.50	1.796	1.400
6.75	1.487	1.127
9.00	1.805	2.280
11.25	1.837	2.417
13.50	2.114	1.573
15.75	2.201	1.440
18.00	2.054	2.220
20.25	2.319	1.477
22.50	2.106	1.677
Average (6 to 10 times of retention time)	2.159	1.677

Table H.23 Raw data of esterification under the condition of 25 v% of methanol, 1.5 v% of sulfuric acid, retention time of 2.5 min and stirrer speed at 1000 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	15.165	0.433
2.50	0.930	1.173
5.00	1.239	0.970
7.50	0.945	1.253
10.00	0.984	1.330
12.50	0.880	1.317
15.00	0.956	1.307
17.50	0.949	1.373
20.00	0.978	1.410
22.50	0.947	1.307
25.00	0.928	1.383
Average (6 to 10 times of retention time)	0.952	1.356

Table H.24 Raw data of esterification under the condition of 15 v% of methanol, 2.5 v% of sulfuric acid, retention time of 2 min and stirrer speed at 600 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	13.768	0.764
2.00	1.355	1.170
4.00	1.391	1.687
6.00	1.243	1.540
8.00	1.531	1.140
10.00	1.395	1.467
12.00	1.276	1.433
14.00	1.198	1.643
16.00	1.284	1.630
18.00	1.375	1.427
20.00	1.254	1.737
Average (6 to 10 times of retention time)	1.277	1.574

Table H.25 Raw data of esterification under the condition of 20 v% of methanol, 3 v% of sulfuric acid, retention time of 2.25 min and stirrer speed at 800 rpm

Retention time (min)	FFA (wt%)	WT (wt%)
0.00	14.467	0.748
2.25	1.053	1.360
4.50	0.958	1.533
6.75	0.828	1.407
9.00	0.837	1.573
11.25	1.231	1.403
13.50	1.092	1.407
15.75	1.094	1.650
18.00	1.029	1.453
20.25	1.047	1.853
22.50	1.044	1.640
Average (6 to 10 times of retention time)	1.061	1.601

Table H.26 Raw data of esterification under the optimization condition of 23.04 v% of methanol, 2.07 v% of sulfuric acid, retention time of 2.22 min and stirrer speed at 793 rpm

Sample	Retention Time (min)	1st experiment				2nd experiment			
		FFA (wt%)	FFA disappearance (mol)	WT (wt%)	WT appearance (mol)	FFA (wt%)	FFA disappearance (mol)	WT (wt%)	WT appearance (mol)
1	0.00	18.943	0.000	0.385	0.000	18.828	0.000	0.477	0.000
2	2.22	0.701	0.601	1.213	0.460	0.916	0.590	1.440	0.535
3	4.44	0.658	0.602	1.313	0.516	0.920	0.590	1.513	0.576
4	6.66	0.652	0.602	1.270	0.492	0.900	0.591	1.597	0.622
5	8.88	0.610	0.604	1.417	0.573	0.652	0.599	1.527	0.583
6	11.10	0.669	0.602	1.583	0.666	0.880	0.591	1.720	0.691
7	13.32	1.014	0.591	1.507	0.623	0.909	0.590	1.397	0.511
8	15.54	1.027	0.590	1.333	0.527	0.784	0.594	1.563	0.603
9	17.76	0.728	0.600	1.243	0.477	0.688	0.597	1.400	0.513
10	19.98	0.848	0.596	1.570	0.658	0.727	0.596	1.377	0.500
11	22.20	0.950	0.593	1.773	0.771	0.691	0.597	1.507	0.572
12	24.42	0.929	0.593	1.647	0.701	0.732	0.596	2.160	0.935
13	26.64	0.849	0.596	1.377	0.551	0.695	0.597	1.990	0.841
14	28.86	0.815	0.597	1.337	0.529	0.704	0.597	1.383	0.503
15	31.08	0.786	0.598	1.313	0.516	0.618	0.600	1.470	0.552
16	45	0.845	0.596	1.457	0.596	1.166	0.582	1.637	0.644
17	60	0.891	0.595	1.363	0.543	1.167	0.582	1.373	0.498
18	90	0.842	0.596	1.300	0.508	1.005	0.587	1.483	0.559
19	120	0.921	0.594	1.317	0.518	0.860	0.592	1.690	0.674
20	150	0.808	0.597	1.357	0.540	1.005	0.587	1.457	0.544
21	180	1.083	0.589	1.507	0.623	0.993	0.588	1.363	0.492
22	210	0.942	0.593	1.916	0.851	0.956	0.589	1.900	0.791
23	240	0.927	0.594	1.990	0.892	1.170	0.582	1.517	0.578
24	270	0.940	0.593	1.863	0.821	0.991	0.588	1.357	0.489
25	300	1.019	0.591	1.463	0.599	0.957	0.589	1.693	0.676
26	330	0.905	0.594	1.547	0.646	0.948	0.589	1.367	0.494
27	360	1.054	0.589	1.373	0.549	0.879	0.591	1.400	0.513
28	390	1.110	0.588	1.267	0.490	0.900	0.591	1.397	0.511
29	420	1.114	0.588	1.390	0.558	0.786	0.594	1.553	0.598
30	450	0.836	0.596	1.383	0.554	0.896	0.591	1.337	0.478
31	480	1.077	0.589	1.543	0.643	0.926	0.590	1.413	0.520
Average (6 to final times of retention time)		**0.931**	**0.593**	**1.485**	**0.611**	**0.886**	**0.591**	**1.535**	**0.588**

Table H.27 Raw data of decanter separation

Sample	Retention time (min)	1st experiment				2nd experiment			
		Before		After		Before		After	
		Acid value (g KOH/L of oil)	WT (%wt)	Acid value (g KOH/L of oil)	WT (%wt)	Acid value (g KOH/L of oil)	WT (%wt)	Acid value (g KOH/L of oil)	WT (%wt)
1	30	17.067	1.337	2.633	0.566	20.933	1.383	3.167	0.327
2	60	21.167	1.363	2.567	0.278	23.400	1.373	2.700	0.468
4	180	24.600	1.317	2.167	0.498	21.333	1.690	2.533	0.299
5	240	27.300	1.507	2.233	0.420	23.233	1.363	2.433	0.513
6	300	30.200	1.990	2.467	0.396	22.000	1.517	2.567	0.420
7	360	22.300	1.463	2.700	0.282	21.000	1.693	2.433	0.509
8	390	25.400	1.373	2.833	0.500	22.967	1.400	2.800	0.394
9	420	23.800	1.390	2.567	0.359	24.033	1.553	2.800	0.318
10	480	21.967	1.543	2.667	0.342	20.933	1.413	2.500	0.424
Average		**23.756**	**1.476**	**2.537**	**0.405**	**22.204**	**1.487**	**2.659**	**0.408**

Table H.28 Raw data of transesterification under the condition of 24 v% of methanol, 1 %wt/v of potassium hydroxide, retention time of 4.50 min and stirrer speed at 793 rpm

Sample	Time (min)	ME (wt%)	Sample	Time (min)	ME (wt%)
1	0	16.33	12	45	97.56
2	4	95.69	13	60	97.56
3	8	97.09	14	120	97.56
4	12	94.34	15	180	97.09
5	16	95.24	16	240	96.62
6	20	99.5	17	300	96.62
7	24	95.24	18	360	96.62
8	28	100	19	420	96.62
9	32	97.09	20	480	96.62
10	36	98.52	**Average (Sample 7-20)**		**97.23429**
11	40	97.56			

Table H.29 Raw data of methanol recovery

Sample	Retention time (min)	1st waste solution (wt%)	Crude biodiesel (wt%)	Crude glycerin (wt%)
1	0	59.00	5.08	19.68
2	180	48.50	0.47	0.57
3	240	43.40	1.21	0.71
4	300	15.00	1.47	0.85