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THESIS

SIMULATION OF BIODIESEL PRODUCTION FROM PALM OIL BY THE CONVENTIONAL AND THE REACTIVE DISTILLATION METHODS

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A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
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This thesis proposes the simulation, design and control of a biodiesel process by using ASPEN PLUS, ASPEN ICARUS and ASPEN DYNAMICS, respectively. Palm oil as a reactant contains three main fatty acids: palmitic, oleic and linoleic acids. The first step was to add molecular structure from GaussViewW and GAUSSIAN 03W into ASPEN PLUS for estimation of all missing parameters. The biodiesel production was simulated under the conventional and the reactive distillation processes. The purity from conventional process by sodium hydroxide (homogeneous) and strontium oxide (heterogeneous) were 99.45 and 95.21 %. On the other hand, the purity from reactive distillation with strontium oxide (99.87 %) was higher than sodium hydroxide (99.52 %). Then the steady state result was exported to ASPEN DYNAMICS for process control design and to ASPEN ICARUS for equipment design. The control systems design followed the concept of plant-wide control. The flow rate of oil and methanol reactants were varied ± 5 % to check the control performance and resulted in a good response. Total operating costs of the conventional process with two different catalysts (NaOH and SrO) were 1.30 and 0.89 M$/yr while the reactive distillation processes cost 0.90 and 0.88 M$/yr. In conclusion, the operating cost of biodiesel from sodium hydroxide was more expensive than from strontium oxide.

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Student’s signature Thesis Advisor’s signature

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Kantarod Chakton
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TABLE OF CONTENTS

Page

LIST OF TABLES

Appendix Table

LIST OF TABLES (Continued)

Appendix Table **Page**

LIST OF FIGURES

Figure **Page**

LIST OF FIGURES **(Continued)**

Figure **Page**

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

Figure **Page**

Appendix figure

LIST OF FIGURES (Continued)

Appendix figure **Page**

LIST OF ABBREVIATIONS

a = Maximum amplitude of PV signal

C_V = Valve size coefficient

°C = Degree Celsius

D = Diameter of equipment

EQ = Equilibrium

F = Flowrate

F(x) = Fraction of valve opening

F = feed stream, mol s^{-1}

FAME = fatty acid methyl ester

H = molar enthalpy, J mol^{-1}

H = Hour

h = Height of relay

K = vapor-liquid equilibrium constant, dimensionless

K_c = Controller gain

K_u = Ultimate gain

kg = Kilogram

L = Liquid flow rate, mol s^{-1}

L = Length of equipment

L_C = Length of distillation column in case of actual trays

L_{c*} = Length of distillation column in case of theoretical trays

L_W = Length of weir

MPC = Model predictive control

N_T = Number of actual trays

N_{T*} = Number of theoretical trays

OP = Output parameter (controller)

P = Proportional controller

PI = Proportional-integral controller

PID = Proportional-integral-derivative controller

PV = Process variable

P_u = Ultimate period

LIST OF ABBREVIATIONS (Continued)

ΔP_V = Valve pressure drop

ΔP_{tray} = Pressure drop of each tray

Q = heat duty, J s^{-1}

r = number of reaction

R = Liquid reflux

R = reaction rate, mol m^{-3} s^{-1}

R1, R2, R3 = hydrocarbon chain of the fatty groups of the triglyceride

RGA = Relative gain array

s = transformed stripping ratio, dimensionless

ss = steady state solution

u = input variables

U = molar hold-up, mol

u1 = subset of the elements of u

v = stoichometric coefficient, dimensionless

V = Vapor flow rate, mol s^{-1}

T_i = Integral or reset time constant

T_d = Derivative time constant

V = Volume of equipment

v_{max} = Maximum vapor velocity

wt % = Percents by weight

ρ_v = Vapor density

x = state variables

x = mole fraction in the liquid-phase, dimensionless

y = mole fraction in the vapor-phase, dimensionless

y = output variables

z = mole fraction in either vapor or liquid-phase, dimensionless

ε = reaction volume, m^3

LIST OF ABBREVIATIONS (Continued)

Subscripts

i = Component index

j = Stages index

m = reaction index

Superscripts

F = feed stream

L = liquid-phase

V = Vapor-phase

SIMULATION OF BIODIESEL PRODUCTION FROM PALM OIL BY THE CONVENTIONAL AND THE REACTIVE DISTILLATION METHODS

INTRODUCTION

Biodiesel is an alternative diesel fuel that is produced from vegetable oils and animal fats. There are many methods to produce biodiesel such as esterification, transesterification, pyrolysis, supercritical reaction and lipase-catalyzed for biodiesel production which transesterification methods give biodiesel grade near diesel.

Transesterification is the reaction between vegetable oils or animal fats with alcohol to produce ester and glycerol by using catalyst such as base catalyst, acid catalyst, lipase and heterogeneous catalyst. The advantages of homogeneous catalysts are the rapid reaction, high conversion. However, the disadvantages of homogeneous catalysts are saponification reaction, difficult separation between biodiesel and catalyst. Therefore the heterogeneous catalyst is studied to reduce the problem in biodiesel production because the biodiesel using heterogeneous catalyst is easy to separate between catalyst and glycerin.

Biodiesel process industry has rapidly changed because of the demand of new products, high quality, safety, clean and friendly environment. The operation at low cost and time is play an important role on successful companies. The success of the production depends on a great deal on the smooth operation of all units to achieve the target of the production. In the past, the typical approach is the design of control system for each individual unit. However, as the results of strict environmental regulation and economic consideration, today chemical plants tend to be highly integrated and interconnected. Nevertheless, the steady-state and dynamic behaviors of these interconnected units differ significantly from the individual units. Therefore, the problem of plantwide control becomes the operation and control of these interconnected process units. The examples of interconnected process units are the recycle systems or the process with material recycles. From a dynamic viewpoint, recycles provide positive feedback that alter the overall time constant of the process. From a steady-state viewpoint, recycles introduce the possibility of the snowball effect, where a small change in throughput or feed composition can produce a large change in the recycle flowrate. Conventional strategy to handle plants with recycle streams is to install large surge tanks between process units. The surge tanks can reduce the dynamic interaction from material recycles. However, these are an increasing of capital and operating costs. Therefore, modern chemical processes have to face the problem of steady-state and dynamic interaction. Design engineers have to eliminate many surge tanks, increase recycle streams and introduce heat integration for both existing and new plants. Hence, the interest in the study of dynamics in chemical plants with recycles and plantwide control design has increased significantly in the last four decades.

OBJECTIVES

1. To design and simulate the conventional and the reactive distillation of biodiesel production
2. To design the controllers for the heterogeneous conventional and the heterogeneous reactive distillation of the biodiesel production
3. To design the equipments the conventional and the reactive distillation of biodiesel production

Scope of work

1. To simulate the transesterification with using homogeneous (NaOH) and heterogeneous (SrO) catalysts for biodiesel production.
2. Comparison between the homogeneous and heterogeneous simulation of conventional and reactive distillation simulation.
3. To design the controllers for the conventional and the reactive distillation of the biodiesel production by using plantwide control of Luyben law.
4. To perform the steady state and dynamic by ASPEN PLUS and ASPEN DYNAMIC 2006.5; respectively.
5. To design the equipments by ASPEN ICARUS.

LITERATURE REVIEW

1. Biodiesel

Biodiesel is an alternative fuel for diesel engines that is produced by chemically reacting a vegetable oil or animal fat with an alcohol in the presence of a catalyst. The product is a mixture of methyl ester which is known as biodiesel, and glycerol. Biodiesel can be produced by four primary ways, direct use and blending, microemulsions, thermal cracking (pyrolysis) and transesterification. The most commonly used method is transesterification of vegetable oils and animal fats. The transesterification reaction is shown in Figure 1.

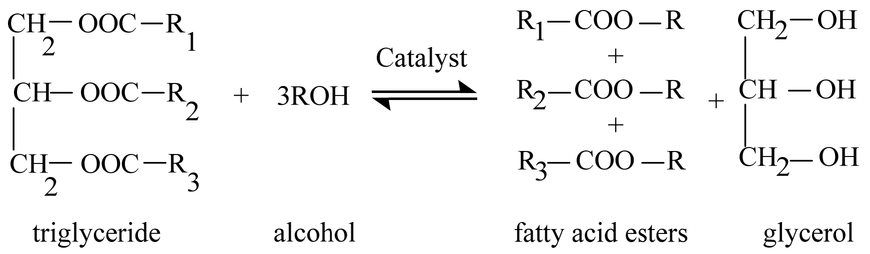


Figure 1 Transesterification reaction

Biodiesel production by transesterification contains three important substances, trigyceride of vegetable oil or animal fat, alcohol and catalyst. Trigyceride is the component in the vegetable oil or animal fat as shown in Figure 2. The properties of biodiesel depends on the hydrocarbon chain of reacting triglyceride such as total number of carbon atom and number of double bounds in the hydrocarbon chain. There are variety vegetable oils which compound many fatty acids as shown in Table 1.

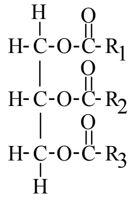


Figure 2 R1, R2 and R3 are hydrocarbon chain of fatty acyl groups of triglyceride

Table 1 Chemical properties of each vegetable oil

Vegetable Oil	Fatty acid composition, % by weight								
	16:0	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3
Corn	11.67	1.85	0.24	0.00	0.00	25.16	0.00	60.6	0.48
Cottonseed	28.33	0.89	0.00	0.00	0.00	13.27	0.00	57.51	0.00
Crambe	2.07	0.7	2.09	0.8	1.12	18.86	58.51	9	6.85
Peanut	11.38	2.39	1.32	2.52	1.23	48.28	0.00	31.95	0.93
Rapeseed	3.49	0.85	0.00	0.00	0.00	64.4	0.00	22.3	8.23
Soybean	11.75	3.15	0.00	0.00	0.00	23.26	0.00	55.53	6.31
Sunflower	6.08	3.26	0.00	0.00	0.00	16.93	0.00	73.73	0.00
Poppyseed	12.6	4	0.00	0.00	0.00	22.3	0.00	60.2	0.5
Safflower	7.3	1.9	0.00	0.00	0.00	13.6	0.00	77.2	0.00
Seameseed	13.1	3.9	0.00	0.00	0.00	52.8	0.00	30.2	0.00
Linseed	5.1	2.5	0.00	0.00	0.00	18.9	0.00	18.1	55.1
Wheat grain*	20.6	1.1	0.00	0.00	0.00	16.6	0.00	56	2.9
Palm	42.6	4.4	0.00	0.00	0.00	40.5	0.00	10.1	0.2
Tallow	23.3	19.3	0.00	0.00	0.00	42.4	0.00	2.9	0.9
Hazeelnot kernel	4.9	2.6	0.00	0.00	0.00	83.6	0.00	8.5	0.2
Walnut kernel	7.2	1.9	0.00	0.00	0.00	18.5	0.00	56	16.2
Almond kernel	6.5	1.4	0.00	0.00	0.00	70.7	0.00	20	0.00
Olive kernel	5	1.6	0.00	0.00	0.00	74.7	0.00	17.6	0.00

*Wheat grain oil contains 11.4% of 8:0 and 0.4% of 14:0 fatty acids.

Source: Demirbas (2002)

Table 2 The biodiesel specification of EN 14214 and ASTM D 6751

Properties	EN 14214		ASTM D 6751	
	Unit	Limits	Unit	Limits
Ester content	% (m/m)	96.5	-	-
Density at 15 °C	kg/m^3	860-900	-	-
Viscosity at 40 °C	mm^2/s	3.5-5.0	mm^2/sec	1.9-6.0
Flash point	°C	120 min	°C	130 min
Sulfur content	mg/kg	10 max	% mass	0.05 max
Carbon residue	% (m/m)	0.3 max	% mass	0.05 max
Cetane number		51 min		47 min
Sulfated ash	% (m/m)	0.02 max	% mass	0.02 max
Water content	mg/kg	500 max	% volume	0.05 max
Total contamination	mg/kg	24 max	-	-
Copper strip corrosion	rating	class 1		No. 3 max
Cloud Point	-	-	°C	Report
Oxidation stability	hours	6 min	-	-
Acid Value	Mg KOH/g	0.5 max	Mg KOH/g	0.8 max
Iodine value	g/100g	120 max	-	-
Linoolenic acid ME	% (m/m)	12 max	-	-
Polyunsat ME	% (m/m0	1 max	-	-
Methanol content	% (m/m)	0.2 max	-	-
Monoglyceride	% (m/m)	0.8 max	-	-
Diglyceride	% (m/m)	0.2 max	-	-
Triglyceride	% (m/m)	0.2 max	-	-
Free glycerol	% (m/m)	0.02 max	% (m/m)	0.02
Total glycerol	% (m/m)	0.25 max	% (m/m)	0.24
Alkali metals (Na+K)	mg/kg	5 max	-	-
Phosphorus content	mg/kg	10 max	% mass	0.001 max
Distillation temp.	-	-	°C	360 max

When the reaction complete and give biodiesel, it must check standard for biodiesel. There are two international standards which are EN 14212 and ASTM D 6751 as shown in Table 2

2. Palm oil

Palm oil and palm kernel oil are forms of edible vegetable oils obtained from the fruit of the oil palm tree. Palm oil and palm kernel oil are composed of fatty acids, esterified with glycerol just like any ordinary fat. Both are high in saturated fatty acids, about 50% and 80%, respectively. The palm oil and palm kernel oil fatty acids composition are shown in Table 3

Table 3 Fatty acid compositions of palm oil and palm kernel oil

palm oil		palm kernel oil	
Fatty acid	%	Fatty acid	%
Palmitic acid (16:0)	44.3	Lauric (12:0)	48.2
Myristic (14:0)	1.0	Myristic (14:0)	16.2
Stearic acid (18:0)	4.6	Palmitic (16:0)	8.4
Oleic acid (18:1)	38.7	Capric (10:0)	3.4
Linoleic acid (18:2)	10.5	Caprylic (8:0)	3.3
Other/unknow	0.9	Stearic (18:0)	2.5
Total saturated fatty acids	50	Oleic (18:1)	2.3
Total unsaturated acids	50	Other/unknow	0.9
		Total saturated fatty acids	80
		Total unsaturated acids	20

3. Transesterification

Transesterification is chemical reaction between triglyceride, alcohol with catalyst to produce biodiesel and glycerol. The catalyst is used in this method that can be classified as two groups. One is homogeneous catalyst and the other is heterogeneous catalyst. The both type catalyst, there are several kinds; alkali catalyst, acid catalyst, lipases (biocatalyst). These two catalysts are advantage and disadvantage. Producing biodiesel via homogeneous is fast reaction and give high conversion biodiesel but cannot recovery catalyst for next times. If choosing production biodiesel via heterogeneous catalyst, it can be solve problem of homogeneous catalyst and suitable for manufacturing industry.

Transesterification consists of 3 steps in series with 2 intermediates namely diglycerides (DG) and monoglycerides (MG). The steps are shown in Figure 3. The alcohol used in transesterification is a short type such as methanol, ethanol, propanol and butanol. However, methanol is the favorite choice since its low cost and physical and chemical advantages (polar and shortest chain alcohol). For the stoichiometry of transesterification, the ratio of alcohol to oil is 3:1 but an excess of alcohol is usually used in order to shift the reaction for more production of biodiesel.

$$\text{Triglyceride (TG)} + \text{ROH} \xrightleftharpoons{\text{Catalyst}} \text{Diglyceride (DG)} + \text{RCOOR}_1$$

$$\text{Diglyceride (DG)} + \text{ROH} \xrightleftharpoons{\text{Catalyst}} \text{Monoglyceride (MG)} + \text{RCOOR}_2$$

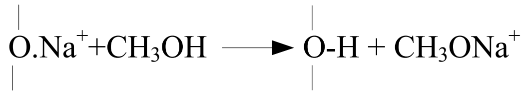
$$\text{Monoglyceride (MG)} + \text{ROH} \xrightleftharpoons{\text{Catalyst}} \text{Glycerol (GL)} + \text{RCOOR}_3$$

Figure 3 Three steps of transesterification

Transesterification can be either homogeneous or heterogeneous methods. However, each method has different advantages. Marchetti *et. al.* (2007) studied the possible methods for biodiesel production. For the homogeneous method, there are several kinds of catalyst such as alkali-catalyzed and acid-catalyzed. The advantages of alkali-catalyzed method are the fast reaction, high conversion and less corrosive than acid-catalyzed. However, the disadvantage of alkali-catalyzed method is the side-reaction that is saponification. The OH^- can react with free fatty acid to form soap. The soap formation is an undesirable side-reaction, because it consumes the catalyst, decreases the yield of biodiesel and complicates the separation and purification. The problem of the soap formation is solved by using acid-catalyzed method since it does not have OH^-. However the acid-catalyzed is not a favorite method because slow reaction, corrosive catalyst and high condition (e.g. pressure and temperature). For the heterogeneous method, there are several kinds of catalysts proposed. Lipase is one of heterogeneous catalysts. The advantages are the easy separation between catalyst and glycerin. Nevertheless, the disadvantages of lipase catalyst are slow reaction and expensive cost. Other catalysts in heterogeneous process are $Na/NaOH/g\text{-}Al_2O_3$, $ZrO_2\text{-}SiO_2$, $KOH/ZrO_2\text{-}SiO_2$, $Co_2O_3\text{-}SiO_2$, $Mo_2O_2\text{-}SiO_2$, $Na_2O\text{-}SiO_2$, La_2O_3-MCM-41 and MgO.

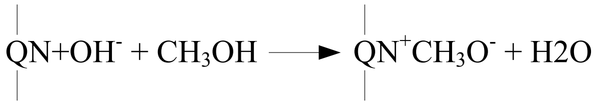
Reaction Mechanisms: A General Overview. Heterogeneous acid and basic catalysts could be classified as Bronsted or Lewis catalysts, though in many cases both types of sites could be present and it is not easy to evaluate the relative importance of the two types of sites in the reaction. A detailed description of some reaction mechanisms can be found in the paper of Lotero *et al* (2006) here for brevity's sake, they will report only a general overview on reaction mechanisms of the different catalyst types

A mechanism is operative in the case of a heterogeneous basic Bronsted catalyst such as basic zeolite Also in this case, the formed catalytic specie is a homogeneous alkoxide.



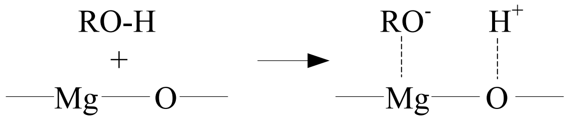
$$O.Na^{+} + CH_3OH \longrightarrow O\text{-}H + CH_3ONa^{+} \qquad (1)$$

In the case of heterogeneous basic Bronsted catalyst such as resin with quaternary ammonium functionality (QN+OH-), the positive counterions (organic ammonium groups), being bonded directly to the support surface, electronically retain the catalytic anions on the solid surface: The reaction occurs between methanol adsorbed on the cation and ester from the liquid (Eley–Rideal mechanism).



$$QN{+}OH^- + CH_3OH \longrightarrow QN^+CH_3O^- + H2O \quad (2)$$

The formation of alkoxide groups is also a fundamental step for heterogeneous basic Lewis catalyst. For example, in the case of ethylacetate transesterification, catalyzed by MgO, the reaction occurs between the methanol molecules adsorbed on amagnesium oxide free basic sites and the ethyl acetate molecules.



$$RO{-}H + {-}Mg{-}O{-} \longrightarrow {-}\overset{RO^-}{Mg}{-}\overset{H^+}{O}{-} \quad (3)$$

The kinetic model of biodiesel formation was proposed by many researches (Freedman *et al.*, 1986; Noureddini and Zhu, 1997; Darnoko and Cheryan, 2000; Foon *et al.*, 2004; Karmee *et al.*, 2004; Vicente *et al.*, 2005; Vicente *et al.*, 2006). The general form of governing differential equations involving three steps is following:

$$\frac{d[TG]}{dt} = -k_1[TG][A] + k_2[DG][E]$$

$$\frac{d[DG]}{dt} = k_1[TG][A] - k_2[DG][E] - k_3[DG][A] + k_4[MG][E]$$

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

$$\frac{d[GL]}{dt} = k_5[MG][A] - k_6[GL][E]$$

$$\frac{d[E]}{dt} = k_1[TG][A] - k_2[DG][E] + k_3[DG][A] - k_4[MG][E] + k_5[MG][A] - k_6[GL][E]$$

$$\frac{d[A]}{dt} = -\frac{d[E]}{dt}$$

where A and E are the alcohol and ester concentrations, respectively.

In addition, the activation energy and reaction rate shown in the Table 4 were estimated by the Arrhenius equation.

$$k(T) = AT^{n}e^{-E/RT}$$

Table 4 The energy of activation and reaction rate constant at 50 °C using NaOH

Reaction	Energy of Activation (cal/mol)	Reaction rate constants
TG → DG	13145	4.80E+07
DG → TG	9932	5.81E+05
DG → MG	19860	2.70E+11
MG → DG	14639	9.98E+09
MG → GL	6421	5.38E+07
GL → MG	9588	2.17E+04

Source: Noureddini and Zhu (1997)

Table 5 The energy of activation and reaction rate constant at 65 °C using SrO

Reaction	Energy of Activation (cal/mol)	Reaction rate constants
TG → DG	16.8	2.46E+10
DG → MG	7.97	1.79E+05
MG → GL	59.79	1.13E+34

Source: Petchtabtim (2008)

4. Reactive distillation

The reactive distillation is an operation which reactions and separations taking place in the same unit. This technique is especially useful for equilibrium-limited reactions such as esterification and ester hydrolysis reactions. Conversion can be increased far beyond the equilibrium due to the continuous removal of products from the reactive zone. This approach can potentially reduce capital investment and operation costs.

The integration of unit is an interesting**:** (1) simplification or elimination of separation system can lead to capital savings, (2) conversion can be increased by removing production continuously, (3) the azeotropes mixture can prevent by using reactive distillation instead of reactor and distillation. (4) removing one of the products from the reaction mixture can lead to reduction the rates of side reactions and by product formation, (5) if the reaction is exothermic, the heat of reaction can be used to provide the heat of vaporization that reduce the reboiler duty.

As previous mentioned, using the reactive distillation can reduce capital investment such as the production of methyl acetate. The acid catalyst reaction (methanol react with acetic acid to produce methyl acetate and water) was traditionally carried out by using the processing scheme as seen in the Figure 4(a). In this figure, there consists of one reactor and nine distillation. Figure 4(b) shows the reactive distillation implementation, only one column is required. The capital and operation costs are reduced (Siirola, 1995).

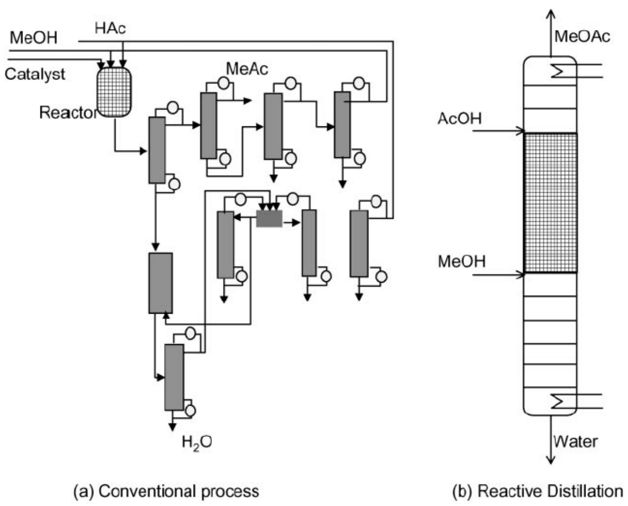


Figure 4 The Processing scheme for the esterification (a) conventional processing consists of one reactor and nine distillations. (b) The reactive distillation configuration.

Source: Siirola (1995)

4.1 Equilibrium (EQ) stage models

The development and application of the EQ stage model for reactive distillation has been described in several researches (Taylor *et al.*, 1999; John and Lee, 2002; Chen *et al.,* 2003; Pyhalahti, 2005; Alfradique and Castier, 2005; Cheng and Yu, 2005; Katora *et al.*, 2005; Dalaouti and Seferlis, 2006). The equilibrium stage models (Taylor *et al.*, 1999) are demonstrated for the calculation of the material balances, vapor-liquid equilibrium equations, mole fraction summations and enthalpy balances (MESH).

A schematic diagram of an equilibrium stage is shown in Figure 5(a). Vapor from the stage below and liquid from the stage above are brought to contact on the stage together with any fresh or recycle feeds. The vapor and liquid streams leaving the stage are assumed to be in equilibrium with each other. A complete separation process is modeled as a sequence of s of these equilibrium stages (Figure 5(b)).

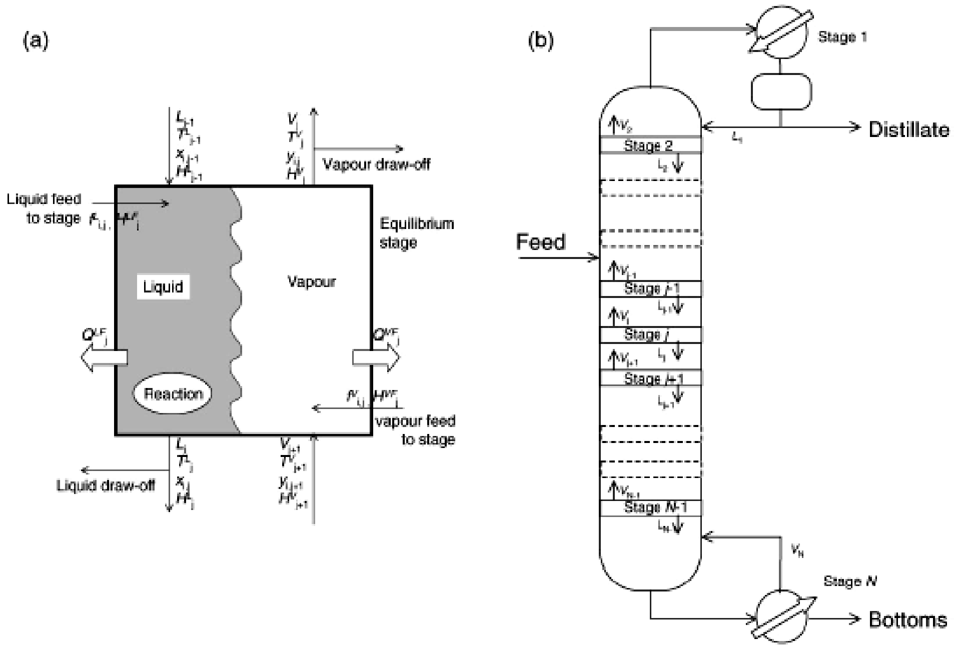


Figure 5 (a) The equilibrium stage (b) Multi-stage distillation column.
Source: Taylor and Krishna (2000)

4.1.1 The material balance equation (M) is

$$\frac{dU_j}{dt} = V_{j+1} + L_{j-1} + F_j - (1 + r_j^V)V_j - (1 + r_j^L)L_j + \sum_{m=1}^{r}\sum_{i=1}^{c} v_{i,m}R_{m,j}\varepsilon_j \qquad (4)$$

where *Uj* is the hold-up on stage *j*. With very few exceptions, *Uj* is considered to be the hold-up only of the liquid phase. It is more important to include the hold-up of the vapor phase at higher pressures. The component material balance (neglecting the vapor hold-up) is

$$\begin{aligned}\frac{dU_j x_{i,j}}{dt} &= V_{j+1}y_{i,j+1} + L_{j-1}x_{i,j-1} + F_j z_{i,j} \\ &\quad - (1 + r_j^V)V_j y_{i,j} - (1 + r_j^L)L_j x_{i,j} + \sum_{m=1}^{r} v_{i,m}R_{m,j}\varepsilon_j \qquad (5)\end{aligned}$$

In the material balance equations given above r_j is the ratio of side stream flow to inter stage flow:

$$r_j^V = \frac{s_j^v}{V_j}, \qquad r_j^L = \frac{s_j^L}{L_j} \tag{6}$$

$v_{i,m}$ represents the stoichiometric coefficient of component i in reaction m and ε_j represents the reaction volume.

4.1.2 The phase equilibrium equation (E) is

$$y_{i,j} = K_{i,j} x_{i,j} \tag{7}$$

Chemical reaction equilibrium is not considered in many of the early papers because it is more difficult to model.

4.1.3 The summation equation (S)

$$\sum_{i=1}^{c} x_{i,j} = 1, \quad \sum_{i=1}^{c} y_{i,j} = 1 \tag{8}$$

4.1.4 The heat balance equation (H)

$$\begin{aligned}\frac{dU_j H_j}{dt} &= V_{j+1} H_{j+1}^V + L_{j-1} H_{j-1}^L + F_j H_j^F \\ &\quad - (1 + r_j^V) V_j H_j^V - (1 + r_j^L) L_j H_j^L - Q_j\end{aligned} \tag{9}$$

The enthalpies of the appropriate phase are H^V, H^L and H^F. The enthalpy in the time derivative on the left-hand side represents the total enthalpy of the stage but, for the reasons given above; this will normally be the liquid-phase enthalpy. Some authors include an additional term in the energy balance for the heat of reaction. However, if the enthalpies are referred to their elemental state then the heat of reaction is accounted for automatically and no separate term is needed.

Under steady-state conditions all of the time derivatives in the above equations are equal to zero.

4.2 Feed location

The optimal feed location was studied by many researches. Luo and Xiao (2001) studied a reactive distillation process for a cascade and azetropic reaction system. They mentioned that the feed locations of the raw materials should have enough contact time for the reactions. The lower boiling point reactant is usually fed in the bottom section of column while the higher boiling point component should be fed in the top. But this general rule is not suitable for the azeotropes system. Cheng and Yu (2005) studied the optimal feed locations of reactive distillation and presented 3 heuristic. Firstly, the heavy reactant should not be fed below the feed tray of light reactant. Secondly, when the relative volatility between the reactant is small, the light and heavy reactant’s feed should be placed close to each other. Similarly, the feed location should be moved away from each other when the relative volatility of the reactant is large. Thirdly, when the relative volatility between the light reactant and the light product is large, the feed location should be in upper part of the reaction zone. On the other hand, if the relative volatility between the heavy reactant and the product is large, the feed location should be below the reaction zone. In addition, Bhatia *et al*. (2006) studied the production of isopropy palmitate in a catalytic distillation. The heuristics of feed location from Cheng and Yu (2005) were used to study on the conversion and energy saving. The results were good agreement with the heuristic.

4.3 Column pressure

Basically, the operation pressure in the distillation is carried out at the atmospheric pressure. However, there are some cases that operate at low or high pressure (Doherty and Malone, 2001). Low pressure distillation (typically in the range 0.039 – 0.395 atm) is frequently practiced for polymerize or react at normal boiling condition such as acetic anhydride-acetic acid, diketene-acetic acid. High-pressure distillation (typically 3 to 20 atm) is usually occurred when the normal boiling point of distillate is lower than the temperature of cooling water. In this case, it is cheaper to pressurize the column in order to raise the boiling point of the distillate that to install a refrigeration system to condense the substance.

However, in the reactive distillation, the operating pressure has affected on the reaction rate and the reaction equilibrium. In case of kinetically controlled and endothermic reaction such as esterification of palmitic acid with isopropanol, operation at the maximum possible pressure is beneficial from the chemical equilibrium and rate of reaction considerations (Subawalla and Fair, 1999). The effect of column pressure was studied by Muhammad (2001) and Bhatia *et al.* (2006). The olefin production was studied by Muhammad (2001). The number of trays, the operating pressure, the holdup per tray and the reflux ratio are studied. The conversion drops after reaching an optimum pressure when the only a small number of tray are used. This is due to the impact of pressure on relative volatilities. In addition, Bhatia *et al.* (2006) simulated the isopropyl palmitate production in a catalytic distillation column. The effects of pressure on the conversion of palmitic acid (PA), the purity of isopropyl palmitate (IPP) and reboiler duty were studied. The increasing of operating pressure raises the reaction rate. When the pressure of column is increased from 1 bar to 3 bar, the PA conversion increases about 3 %. While the IPP purity increases nearly 2 % with the increases of reboiler duty about 34%. However, increasing column pressure makes the higher cost of column.

4.4 Reflux ratio

The reflux ratio is ratio between the amount of reflux that goes back down the distillation column and the amount of product in distillate stream. If no distillate is collected, it is called total reflux ratio. Normally, reflux ratio is a variable controlling the composition in the over head. The desired separation can be achieved by using a large number of trays but it is a large capital costs. An increasing the reflux ratio, the over head composition can be met the specification by using a fewer number of trays. However, higher energy costs are increased due to increasing utilization of condenser. Figure 6 presents the reflux ratio schematic.

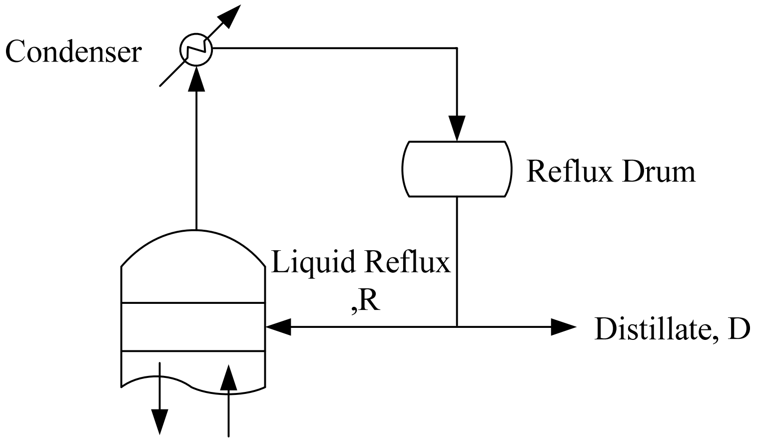


Figure 6 Reflux ratio schematic

In a reactive distillation column, reflux not only enhances the separation but also the reaction by recycling the unconverted reactants to the reaction zone. However, excessive reflux ratio leads to the operating problem and insufficient residence time (Agreda *et al.*, 1990; Chopade and Shubham 1997; Luo and Xiao 2001; Bhatia *et al.*, 2006). Therefore, the reactive distillation should be operated at an optimal reflux ratio to ensure the good performance and sufficient residence time in the column.

5. Packed bed Reactive distillation

The reactive distillation is a unit operation that integrated the reaction and the separation process in the same unit simultaneously. This is an interesting technique which technique is very useful for equilibrium reaction such as esterification and ester hydrolysis reaction. The equilibrium is shifted to increase the conversion by continuous removing of products from the reaction zone. The advantages of the reactive distillation are saving capital cost by reducing the number of unit, increasing conversion by shifting the equilibrium, preventing azeotropes mixture by using reactive distillation and decreasing rate of the side-reaction by removing one of the products. If reaction is the exothermic, the heat of reaction can be used to provide the heat of vaporization that reduces the reboiler duty. The calculations of Equilibrium stage are available in ASPEN PLUS simulation.

Anton *et al.* (2007) studied biodiesel production by catalytic reactive distillation in esterification using metal oxide solid acids catalyst. The reactive distillation used rigorous fractional which this technology is a feasible and advantageous for biodiesel production.

Cheng and Yu (2005) study the effects of the feed locations to the design of reactive distillation. Process parameters such as relative volatilities between reactants, relative volatilities between products, column pressure, activation energies and pre-exponential factors are varied to seek possible generalization. For all systems studied, the percentage of energy is saved ranges from 6% to 47% and this is obtained by simply rearranging the feed locations. Finally, the idea of optimal feed trays is extended to the operation/control of reactive distillation systems. First, steady state analysis is carried out to find the optimal feed trays as measurable load variable varies. Then a control structure is proposed to rearrange the feeds as the disturbance comes into the system. The results indicate that that, again, substantial energy can be saved by feed rearrangement via the coordinate control structure.

Sundmacher *et al.* (1995) Studying fuel ethers are produced very efficiently from alcohols in reactive distillation columns which are packed with acid ion exchange rings. In the present contribution first a detailed three phase nonequilibrium model for such a packed catalytic distillation column will be presented. Then it will be demonstrated how this model to use for the prediction of suitable operating conditions and optimal arrangement of feed steam and packing.

6. Dynamic Simulation of Process and Control (Luyben, 2002)

The simulation can be divided into two phases which are the steady-state and the dynamic simulations. The simulation of steady-state must be completed first and then exported to the dynamic simulation. The steady-state simulation affects significantly the result of the dynamic simulation. Before moving from steady-state to dynamic simulation in ASPEN PLUS, there are several tasks that must be completed in steady-state simulation. The list of the tasks is shown as follow:

1. Flowsheet topology (e.g. types and positioning of units).
2. Reactor types, sizes and conditions (e.g. temperature, pressure, catalyst amounts, heat-transfer area, cooling or heating medium).
3. Reaction kinetic data.
4. Physical property data.
5. Phase equilibrium data.
6. Number of stages in all staged-operations (e.g. distillation column, absorber, liquid extraction columns)
7. Heat-transfer rate, minimum approach temperatures, overall heat-transfer coefficient, flowrates of cooling or heating medium and areas in all heat exchanger.
8. Flowrates, temperatures, pressures and compositions of all process streams.

Some information such as column diameters, sizes of all surge vessels, and sizes of control valves does not require for running the steady-state simulation but it is very important for running the dynamic simulation. The dynamic response of the process depends on the sizes of the equipments, so all equipments must be size before performing the dynamic simulation. The other necessary information is the plumbing that includes the stalling pumps, compressors and control valves for realistic operation of the process. The control valves should be placed in the proper positions in order to control the process.

The ASPEN PLUS simulator can use either approximate physical property relationships or rigorous methods in the steady-state simulation for performing the dynamic simulation. Although the approximate physical property relationships can reduce the simulation times, it may introduce some errors occurring in the dynamic simulation.

6.1 Sizing Equipment

Before going to the dynamic simulation, all equipments must be approximately sized. It is not necessary to include the mechanical design. How to estimate the equipments is shown as follow:

6.1.1 Distillation Columns

The volume of a distillation column depends on its diameter and length. Both are easily calculated.

For the Length of a distillation column, if the column has N_T trays, the height of the tray section is $2N_T$. However, the column requires some additional height for reservation, particularly if thermosiphon reboilers are used. Hence the length of the column is normally increased about 20 %.

$$L_C\ (\text{ft}) = 2.4N_T \quad \text{for actual trays} \quad (10)$$

$$L_{C*}\ (\text{ft}) = 2.4(N_T)_{\text{Theoretical}}/\text{Efficiency} \quad \text{for theoretical trays} \quad (11)$$

Where L_C = the length of distillation column in case of actual trays

L_{C*} = the length of distillation column in case of theoretical trays

N_T = number of trays

Efficiency = tray efficiency

For the diameter of a distillation column, it depends on the maximum vapor velocity. The maximum vapor velocity can be found in the steady-state simulation or calculated by using the F-Factor parameter.

$$\text{F - Factor} = V_{\max}\sqrt{\rho_V} \tag{12}$$

$$\text{Area} = \frac{\text{Vapor volumetric flowrate}}{V_{\max}} = \frac{\pi \text{D}^2}{4} \tag{13}$$

Where F-Factor = 1 in English Engineering units or 1.22 in SI units

$V_{\max}$ = the maximum vapor velocity

ρ_V = vapor density

Area = the cross-sectional area of the column

Vapor volumetric flowrate = vapor volumetric flowrate in the column

D = the diameter of distillation column

6.1.2 Separators (Flash Tanks)

Separators are tanks used for separation of vapor and liquid in tanks. Since the separators have both vapor and liquid streams leaving from tanks, the sizing of the separators must be considered both of two phases. The vapor velocity must be kept low enough and liquid entrainment is small. The minimum diameter of the tanks can be calculated by using F-factor. The method to calculate the required diameter based on the vapor velocity is shown as follow:

$$\text{F - Factor} = V_{\max}\sqrt{\rho_V} \tag{14}$$

$$\text{Area} = \frac{\text{Vapor volumetric flowrate}}{V_{\max}} = \frac{\pi \text{D}^2}{4} \tag{15}$$

Where F-Factor = 0.5 in English Engineering units

Area = the cross-sectional area of the tank

D = the diameter of the tank

Vapor volumetric flowrate = vapor volumetric flowrate in the tank

However, the liquid hold up must be check that the normal heuristic is to provide at least five minutes of holdup. This means the volume of the liquid in the tank should be five times of the volumetric flowrate of the liquid leaving the tank with the tank half full. Therefore the volume and diameter of the tank should be calculated.

$$\begin{aligned}\text{Volume of the tank} &= 2 \times 5 \times \text{Liquid volumetric flowrate} \\ &= \frac{\pi}{4} D^2 L\end{aligned} \qquad (16)$$

Where L = Length or height of the tank

6.1.3 Surge Volumes

Tanks and surge volumes are required when the liquid is pumped. The examples of the surge volumes are the reflux drum and the base (or reboiler) of a distillation column. It is different that the steady-state simulation tries to minimize the capital cost by reducing the sizes of vessels as much as possible but the dynamic simulation needs lots of surge capacity to keep the liquid level of vessels from the disturbances in flowrates. The normal heuristic for surge vessel sizing is to provide at least five minutes of liquid holdup with the level half full. This is based on the total flowrate of liquid into the vessel.

$$\begin{aligned}\text{Volume of the tank} &= 2 \times 5 \times \text{Liquid volumetric flowrate} \\ &= \frac{\pi}{4} D^2 L\end{aligned} \qquad (17)$$

Where D = Diameter of the tank
L = Liquid volumetric flowrate into the tank

6.1.4 Heat Exchangers

The parameter of heat exchangers affecting to the dynamics is the volumes of both sides of the heat exchanger. For a tube-in-shell heat exchanger, the volumes can be estimated from total heat transfer area. The total heat transfer area is found in the steady-state simulation from the specified heat duty, overall heat transfer coefficient and temperature differential driving force. The calculation is shown as follow:

The circumferential heat transfer area of each tube is

$$A_{\text{tubes}} = \pi DL \tag{18}$$

The number of tubes required is

$$N_{\text{tubes}} = \frac{A_{\text{total}}}{A_{\text{tubes}}} = \frac{A_{\text{total}}}{\pi DL} \tag{19}$$

The total volume inside all the tubes is

$$V_{\text{tubes}} = N_{\text{tubes}}\left(\frac{\pi D^2}{4}\right)L = \left(\frac{A_{\text{total}}}{\pi DL}\right)\left(\frac{\pi D^2}{4}\right)L = \left(\frac{D}{4}\right)A_{\text{total}} \tag{20}$$

$$V_{\text{tubes}} = \left(\frac{D}{4}\right)A_{\text{total}} \tag{21}$$

Now the volume of the tubes is calculated. For the volume of the shell, it depends on the layout and spacing of the tubes but at the conceptual design stage, it does not need to go into all the nitty-gritty details. A simplifying approximation can be made that works pretty well for most tube-in-shell designs that the shell volume is equal to the tube volume.

$$V_{\text{shells}} \cong V_{\text{tubes}} \tag{22}$$

6.1.5 Furnaces

For the sizing of furnaces, the estimation of volume of the process material inside the tubes of a fired furnace is needed in dynamic simulation. The required heat transfer duty in the furnace resulting from the steady-state simulation is used to find the furnace size. The following rough estimates of the volumes of the process and combustion sides of a fired furnace can be used that are as follow:

$$\text{Process inside tube volume} = 14\ \text{ft}^3 / 10^6\ \text{Btu/hr} \tag{23}$$

$$\text{Total furnace volume} = 66\ \text{ft}^3 / 10^6\ \text{Btu/hr} \tag{24}$$

6.2 Plumbing

Normally the piping do not need in the dynamic simulation of a chemical process since the piping dynamic is fast compared to equipment dynamic. However, the piping must be considered when the process has a long pipe. It will create the deadtime affecting to the dynamic of the process. Moreover the liquid and gas cannot go to uphill so pumps, compressors and valves must be positioned and sized to provide the required variations in the process flowrates. Tanks and liquid surge volumes must be also installed to provide NPSH (net positive suction head) requirements for all pumps and to encounter flowrate disturbances. The pumping can be divided into two systems.

6.2.1 Liquid Pumping System

For the liquid pumping system, it needs a tank, pump and valve. A liquid is pumped up to a higher pressure using centrifugal pump. When a liquid flows pass though a unit operation such as heat exchanger or reactor, there is pressure drop through the unit. Not only pressure drop occurring in a unit operation, but also occurring in the control valve. Therefore the pressure drop through a unit and control valve must be specified. There are some laws for the locating of control valve. The first and second laws of plumbing are “Locate valves in liquid lines downstream of centrifugal pumps” and “Use only one valve in a liquid-filled line”. Figure 7 shows a typical liquid flow system with the required tank, pump and valve.

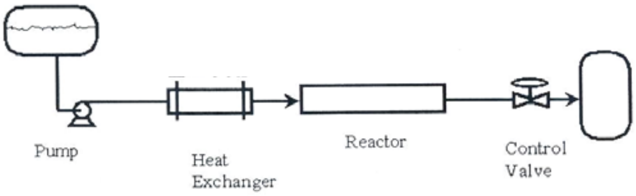


Figure 7 Typical liquid plumbing
Source: Luyben (2002)

Note that the control valve must be located after the pump. It cannot be located before the pump since it does not work for the pump NPSH requirements. Furthermore, the control valve is used one valve in each one line. For the use of positive displacement pumps, it does not required valves to regulate flow since the speed of the pump or its length is used to set the flow rate of liquid. Figure 8 shows some good plumbing and some forbidden plumbing arrangements.

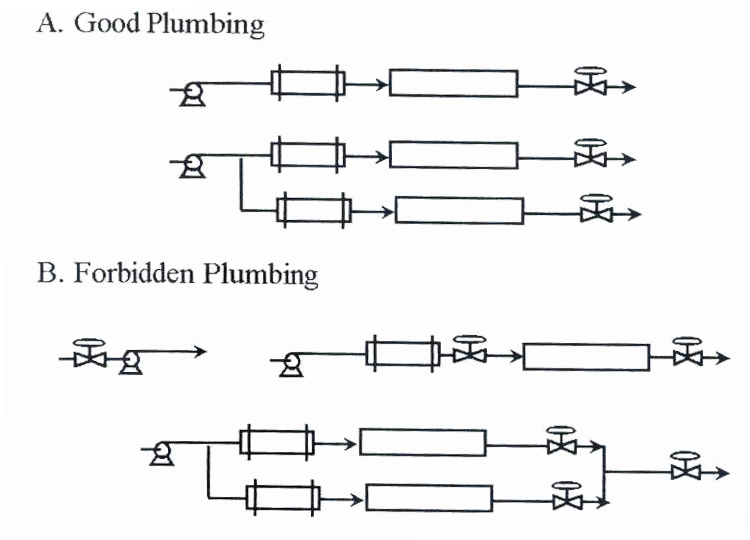
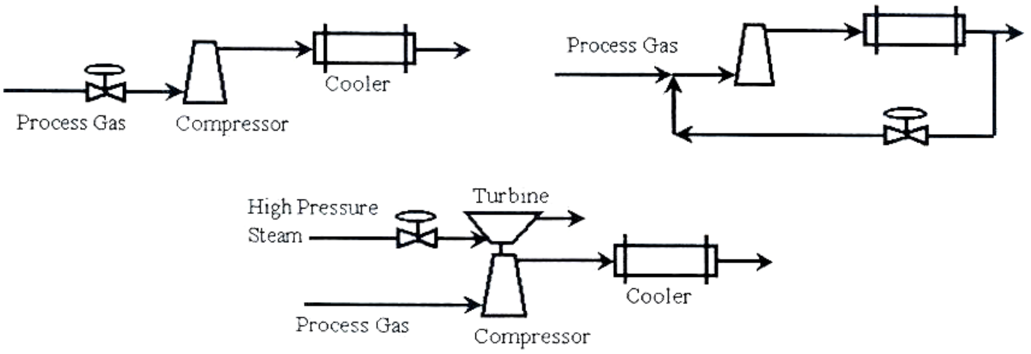


Figure 8 Liquid pumping systems
Source: Luyben (2002)

6.2.2 Gas Compression System

For a gas system, a compressor is needed to provide the pressure of gas required for flow through unit operation and valve. Since the compressor is volumetric device, it pumps a constant volume per time at suction conditions if operated at constant speed. If a valve is located at the discharge piping of a compressor, it does not change the amount of material flowing through the compressor. It just increases the compression ratio and the work. So the third law of plumbing is "Do not throttle the discharge of a compressor". Figure 9 shows how to control the flow through a compressor. Throttling the suction of a compressor does affect the amount of flow through the compressor.

A. Good Plumbing



B. Forbidden Plumbing

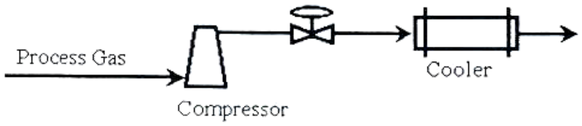


Figure 9 Gas compression systems
Source: Luyben (2002)

6.3 Control Valve Sizing

After the control valve is located in the proper place, the size of the control valve must be specified. This boils down to setting their percent opening and their pressure drop under design conditions. Although the design pressure drop can be low or high, it affects to the steady-state economics and dynamic control. Since the cost of energy of pump or compressor is depends on the design pressure drop of control valve, the design pressure drop should be low. However the low pressure drop leads to low ability to change the flowrate from the nominal steady-state value. The high design pressure drop causes the good dynamic control since large changes in the flowrate of manipulated variables can reject disturbances more quickly. A simple equation for calculating the flow through a control value is shown as follow.

$$F = f_{(x)} C_V \sqrt{\Delta P_V} \tag{25}$$

Where F = flowrate through the valve
$f_{(x)}$ = fraction of the valve opening
C_V = valve size coefficient
ΔP_V = valve pressure drop

6.4 Tuning Controllers

There are many controllers used in the plant. All of the controllers must be specified algorithms such as P, PI, PID, MPC and nonlinear. The parameters of each algorithm must be tuned such as gain, integral time and derivative time. Several methods are proposed to tune parameters of algorithm. However a standard method is illuminated in this work. The conventional linear PI controllers in a decentralized environment (single-input-single-output) are preferred since they are widespread in industries. Although model predictive control (MPC) is used in many industrial applications, it must be applied on top of a basic regulatory PI controller structure. Therefore the important objective of an industry is to improve a basic regulatory PI controller. PID controllers do not mention in this work even if they can improve the effectiveness of PI controller. In theory, control performance can be improved by the use of derivative action but it may not true in practice. In practice, the use of derivative has some of disadvantage: (1) three tuning constants must be specified, (2) signal noise is amplified, (3) several types of PID control algorithms are used, so you must be careful that the right algorithm is used with its matching tuning method. However this work roughly performs plantwide dynamic control using PI controllers. The high-performance PI control in simulation does not guarantee high-performance control in the real plant. On the other hand, the low-performance PI control in simulation may be work as well in the real plant and it is flexible to improve the performance by PID or MPC.

6.4.1 Tuning Flow Loops

For tuning flow controller, it is simple to tune flow controllers. Usually the characteristic of flow controller loops consists of an orifice-plate sensor, a differential-pressure transmitter, a PI controller and a control valve. The dynamics of flow measurement are fast. Normally the time constant of control valve is small unless a very large valve is used. Hence a flow controller is tuned with small integral or reset time constant (τ_I). The value of $\tau_I = 0.3$ minutes often works in most flow controllers. For the controller gain (K_C), it should modest since the flow signals are sometime noisy due to the turbulent flow through the orifice plate. The value of $K_C = 0.5$ is often used. Derivative function should not be involved. The noise in the dynamic simulation is not the problem.

6.4.2 Tuning Level Loops

For the tuning of level controllers, the type of level controller usually is proportional action with a gain of 1 to 2. Since the proportional action is only used, the steady-state offset will be occurred. However, the stead-state offset is not the problem in controlling of level because the liquid capacity of a vessel is designed to solve this problem as surge volume. Therefore the value of $K_C = 2$ is used. There are several exceptions that the value of $K_C = 2$ cannot be used:

1. Reactor level control because level impacts reaction rates. However, proportional-only level control can still be applied in reactors if a higher value of gain is used gain ($K_C = 10$).
2. Column bases when level-sensitive thermosiphom reboilers are used.
3. Distillation column reflux drums where level is held by reflux and distillate flow is manipulated to control a temperature or composition. In this setup, the level control should be tight since the level loop is nested inside the temperature loop.
4. Distillation colunm base where level is held by reboiler heat input and bottoms flow is manipulated to control a temperature or composition (for the same reason as in Item 3).

6.4.3 Tuning Pressure Loops

For the tuning of pressure controllers, it is rather easily to tune. The process time constant can be estimated by dividing the gas volume of the system by the volumetric flow rate of gas that flow through the system. The integral time should be set to 2 to 4 times the process time constant. For the controller gain, it depends on the span of the pressure transmitter and the contentment of the pressure control. The tuning constants for columns and tanks are $K_C = 2$ and $\tau_I = 10$ minutes. If a very fast loop such as compressor controls is considered, the integral times should be much smaller.

Wu and Yu (1996) investigate the steady-state and dynamic behavior of the reactor/separator system. The results can be concluded that the snowball effect come from the recycle system. Limited throughput handling capability was observed when the control structure was no appropriately chosen. Balance scheme was proposed to overcome the snowball effect. The simulation results showed that the balanced control structure is effective in handling large load changes while maintaining good closed-loop performance

Dimian *et al*. (1997) presented the integration of process design and plantwide controllability analysis of a large plant, where recycle effects are significant. It was demonstrated how connectivity between units and interactions between recycles may be exploited to create flowsheet alternatives with feasible plantwide control structures which are impossible to achieve with stand-alone units. The steady-state and dynamic simulations were combined with controllability analysis, both in steady-state and in dynamic modes. A methodology has been developed to study the interactions of recycles and their impact on plantwide control structures. The results of a case study, VCM process, showed that the recycle structure has a stabilizing effect on the control of the main distillation column. Closed loop simulation showed a significant advantage in time response for the flowsheet alternative with a shorter recycle path. The interactions effects between recycles may stimulate or damp the rejection of some disturbances. Both shorter recycle path and favorable effects of interactions on resiliency properties enable to justify the choice of the best plantwide control structure.

Now, the publications about the controlling of the reactive distillation column are continuously reported. Quantitative comparison of dynamic controllability between a reactive distillation column and a conventional multi-unit process was studied by Kaymak *et al*. (2007). An exothermic reversible reaction $A+B \leftrightarrow C+D$ occurred in both flowsheets, which consist of a conventional multi-unit reactor/separator/column/recycle structure and a reactive distillation column. Results showed that the reactive distillation process is significantly less expensive than the conventional process for a wide range of the chemical equilibrium constant, when there is no mismatch between the temperature favorable for reaction and the temperature favorable for vapor-liquid separation. The reactive distillation column has a fewer control degrees of freedom than the conventional multi-unit system. So, the conventional multi-unit process provided significantly better control. The operability region of the conventional process is much larger. There is less variability in product quality and the dynamic responses are faster than those of the reactive column.

6.5 Plantwide Process Control Design Procedures

Luyben *et al*. (1999) proposed nine steps of plantwide process control procedure. The steps of the procedure were shown as follows:

1. Establish control objectives
2. Determine control degrees of freedom
3. Establish energy management system
4. Set production rate
5. Control product quality and handle safety, Environmental, and operational constraints
6. Fix a flow in every recycle loop and control inventories
7. Check component balances
8. Control individual unit operation
9. Optimize economics and improve dynamic controllability

Steps 1 and 2 establish the objectives of the control system and the available degrees of freedom. Step 3 ensures that any production of heat within the process is properly dissipated and that the propagation of thermal disturbances is prevented. In steps 4 and 5, the key business objectives concerning production rate, product quality and safety was considered. Step 6 involes total mass balance control. While step 7 ensures that nonconserved chemical components are accounted for. In step 8, the control systems for individual unit operations are completed. Step 9 uses the remaining degrees of freedom for optimization and improved dynamic controllability. This heristic procedure will generate a workable plantwide control strategy which is not necessarily the best solution. Because the design problem is open-ended, the procedure will not produce a unique solution.

6.6 The relative gain array

The relative gain array (RGA) approach by Bristol (1996) for the analysis of multivariable process control problems. The concept of relative gain array considers a process with controlled variables and manipulated variables. The relative gain between a controlled variable and manipulated variable is defined to be the dimensionless ratio of two steady-state gains:

$$\lambda_{ij} = \frac{(\partial y_i / \partial u_j)_u}{(\partial y_i / \partial u_j)_y} = \frac{\text{open-loop gain}}{\text{closed-loop gain}} \tag{26}$$

The symbol $(\partial y_i / \partial u_j)_u$ denotes a partial derivative that is evaluated with all of the manipulated variables except u_j held constant. Thus, this term is open-loop gain between y_i and u_j, corresponds to the gain matrix element K_{ij}. Similarly, $(\partial y_i / \partial u_j)_y$ is evaluated with all of the controlled variables except y_i held constant. $(\partial y_i / \partial u_j)_y$ can be interpreted as a closed-loop gain that indicates the effect of u_j or y_i when all of the other controlled variables ($y_i \neq y_j$) are held constant.

It is convenient to arrange the relative gains in a relative gain array (RGA), denoted by Λ:

$$\Lambda = \begin{array}{c} \\ \mathrm{y}_1 \\ \mathrm{y}_2 \\ \cdots \\ \mathrm{y}_\mathrm{n} \end{array} \begin{array}{c} \begin{array}{cccc} u_1 & u_2 & \cdots & u_n \end{array} \\ \begin{bmatrix} \lambda_{11} & \lambda_{12} & \cdots & \lambda_{1\mathrm{n}} \\ \lambda_{21} & \lambda_{22} & \cdots & \lambda_{2\mathrm{n}} \\ \cdots & \cdots & \cdots & \cdots \\ \lambda_{\mathrm{n}1} & \lambda_{\mathrm{n}2} & \cdots & \lambda_{\mathrm{nm}} \end{bmatrix} \end{array} \tag{27}$$

The each λ can be considered:

1. $\lambda\ = 1$ the open-loop and closed-loop gains between y_1 and u_1 are identical. In this ideal situation, opening and closing loop 2 has no effect on loop 1.
2. $\lambda\ = 0$ indicates that the open-loop gain between y_1 and u_1 is zero, and u_1 has no direct effect on y_1. Consequently, u_1 should be paired with y_2 rather than y_1

3. $0 < \lambda < 1$, the closed-loop gain between y_1 and u_1 is larger than the open-loop gain. The interaction between the two loops is largest when $\lambda = 0.5$, which indicates that the second term is equal to -1.
4. $\lambda > 1$, for this situation, closing the second loop reduces the gain between y_1 and u_1. The interaction increase and becomes most several as $\lambda \rightarrow \infty$. When λ is very large, it is possible to control both outputs independently.
5. $\lambda < 1$, when λ are a negative, the open-loop and closed-loop gains between y_1 and u_1 have different signs. Thus, opening or closing loop 2 has an adverse effect on the behavior of loop 1 such as oscillation. It follows that y_1 should not be paired with u_1. For $\lambda < 0$ the control loops interact by trying to "fight each other", and the closed-loop system may become unstable.

The RGA measure enables the experienced user to point out easily all important interactions induced by inputs on outputs. The RGA-matrix is calculated utilizing the following matrix operation.

$$\mathrm{RGA}(\mathrm{G(s)}) = \Lambda(\mathrm{G(s)}) = \mathrm{G(s)} \otimes (G(s)^{-1})^T \qquad (28)$$

RGA-elements close to one on the diagonal of the matrix indicate an almost non-interacting system. Negative or high values show that the system is interacting highly, which is not at all desired.

METERIALS AND METHODS

Materials

Materials used in this process are shown as follows:

1. Personal Computer (PC)
    a. CPU (Intel(R) Pentium(R) D CPU 3.40 GHz (2CPUs))
    b. 2.00 GB of RAM
    c. 240 GB of hard disk
2. Operating System: Microsoft Window XP Professional 2002 service pack 2
3. Softwares
    - ASPEN PLUS version 2006.5
    - ASPEN DYNAMICS version 2006.5
    - ASPEN ICARUS version 2006.5

Methods

The biodiesel production from palm oil consists of three parts as steady state simulation, the control process and the design equipment. This biodiesel is produced by using the transesterification method which is the process of exchanging the alcohol group between ester compound and another alcohol. This reaction is often catalyzed by adding acids or base catalysts. The type of catalyst can be divided into two main types; homogeneous and heterogeneous. In a heterogeneous reaction, the catalyst is in a different phase from reactants where as the catalyst is in the same phase as reactants in a homogeneous reaction. Therefore, these works simulated the biodiesel production from two different types of catalyst (NaOH and SrO), are studied the conventional distillation and the reactive distillation processes.

1. Steady-state simulation

In this work, the biodiesel was carried out by the transesterification including NaOH (homogeneous) and SrO (Heterogeneous) as catalysts under the conventional and the reactive distillation. The simulation procedures involves defining chemical components, selecting a thermodynamics property, determining plant capacity, choosing proper operating units and setting up input conditions (flowrate, temperature, pressure and other conditions). Many components such as methanol, sodium hydroxide and glycerol are available from the library of ASPEN PLUS. The tripalmitic trioleic and trilinoleic acid are major components of Palm oil while methyl palmitate methyl oleate and methyl linoleate are biodiesel. These structures cannot constructing data from ASPEN PLUS library. Therefore, all of the unavailable components such as mono, di, tri and methyl ester of palmitic oleic and linoleic acid were defined by GaussViewW. The GAUSSIAN 03W was used for optimizing the proposed structures in order to the most stable structure. Then these structures were imported to ASPEN PLUS in the mol format to fulfill the simulation data. Due to the highly polar of methanol and glycerol were the non-random two liquid (NRTL) thermodynamic/activity models was recommend to predict the activity coefficients of the components in the liquid phase.

For the homogeneous transesterification process used the reaction rate of which they were studied the reaction rate constants of soy bean oil. Therefore the biodiesel from soy bean was simulated by ASPEN PLUS with the rate constants of Noureddini and Zhu (1997) before applying with palm oil. The result of biodiesel purity was 98.7. Another process used the reaction rate of Petchtabtim (2008). The biodiesel purity was about 95 %.

2. Dynamic simulation

2.1 Plantwide control

For performing dynamic simulation, the nine-step procedure of Luyben was followed. The details of each step were described as follow:

Step 1: Establish control objective

This step included the establishment of steady-state design and dynamic control objectives for the process. Furthermore on-demand product or on-supply reactant must be defined because it effects to the control configuration of the process. The biodiesel business was considered to define the type.

Step 2: Determine control degree of freedom

This step aims to determine the available control valves. This is explained as the number of degree of freedom that can be controlled such as the number of variables controlled to set point. But, all valves must be installed properly. The placement of these control valves can sometimes be made to improve dynamic performance. In this step, each stream and unit operation was considered, either to be manipulated variables or not.

Step 3: Establish energy management

Thirdly, this step is the management of the energy consuming in the process in order to make sure that energy disturbances must not propagate throughout the process by transferring the variability to the plant utilities system. The reactor must also be considered the heat releasing or consuming.

Step 4: Set production rate

The variables that dominate the productivity of the reactor were established and the most appropriate manipulator to control the production rate was determined in this step. The chosen variables should provide smooth and stable production rate transitions and effectively reject disturbance. The consideration of this step involved the proposed objectives in the first step, which leaded to the configuration of the control system.

Step 5: Control product quality and handle safety, operational and environmental.

In the fifth step, the suitable valves were selected to control each of the product quality, safety and environmental variable. The tight control of these important quantities for economic and operational reasons is needed. Hence, the manipulated variables which abruptly effect to controlled product quality were chosen. The dynamic relationships between the controlled variables and manipulated feature are small time constants, dead times and large steady-state gains. The safety was considered by checking the possibility of the uncontrolled variable that leaded to the unsafe evens such as temperature and pressure of reactors.

Step 6: Fix a flow in every recycle loop and control inventories (Pressure and Liquid Level)

Every recycle loop was firstly fixed for the prevention of the snowball effect. Then the unit operations required for controlling of level or pressure were explored, including controlled and adjusted these variables.

Step 7: Check component balances

This step aims to identify how chemical components enter, leave and are generated or consumed in the process. Some components would be balanced. In the present of recycles, the inert components must be considered for eliminating out of process.

Step 8: Control individual unit operations

The control loops operate each of the individual unit operations were established in this step. All changing pressure units and pumping system must be installed in steady-state simulation. On the other hand the sizing equipments are necessary in the dynamic simulation. The equations for sizing equipments are mentioned in Literature review. After the sizing of equipments is completed, the configuration of the control system was performed. This depended on the experience of the process control engineers. Then the controller was tuned. The PI algorithm is used in this work. The methods for tuning parameters of PI controller are already described in Literature review. However, those methods are roughly tuning. The trial and error tuning should be involved for improving control efficiency.

Step 9: Optimize economics or improve dynamic controllability

After satisfying all of the basic regulatory requirements, some degrees of freedom, which have not been used in the control system, can be adjusted. In this step, the remaining degrees of freedom were found and utilized either to optimize steady-state economic process performance or to improve dynamic response.

2.2 The relative gain array

The results of ASPEN PLUS were used to calculate the relative gain. Before going to calculate gain the first step should be defined manipulated variable and controlled variable. Then calculations follow equation 26 and 28 in Literature review.

3. Design equipment

This work used ASPEN ICARUS for designing equipment and calculating cost. Before imported the result from steady-state to ASPEN ICARUS, the first step must added variables follow:

Mass vapor fraction for mixture (MASSVFRA)
Mass solid fraction for mixture (MASSSFRA)
Mass flow rate for mixture (MASSFLMX)
Volumetric flow rate for mixture (VOLFLMX)
Mass flow rate for component mixture (MASSFLOW)
Temperature of mixture (TEMP)
Pressure for mixture (PRES)
Molecular weight for mixture (MWMX)

The second step imports the steady-state to ASPEN ICARUS. After that the ASPEN ICARUS would calculate sizing of each units and production cost.

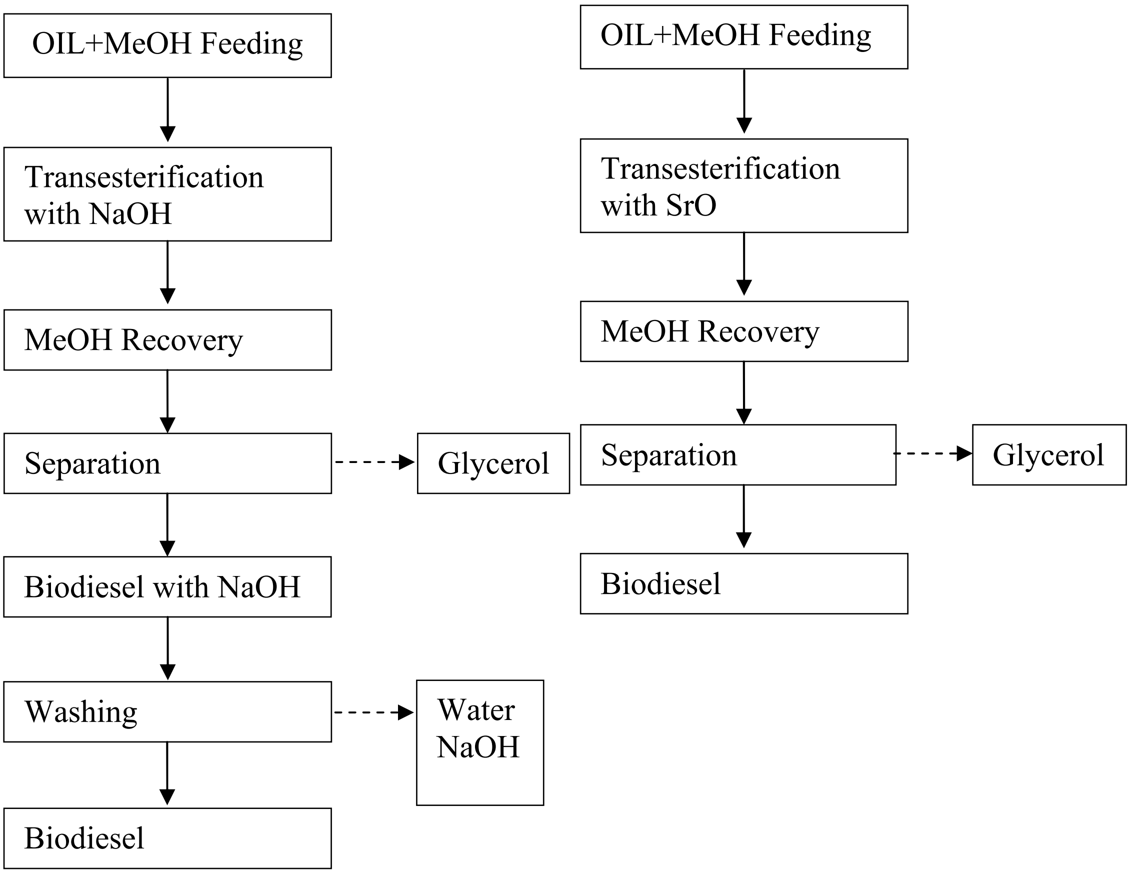
RESULT AND DISCUSSION

Biodiesel production in this research, consist of two process simulations namely; the conventional distillation process and the reactive distillation process. The biodiesel can be produced by several methods such as esterification, transesterification and supercritical fluid. However, this work focused on biodiesel production by transesterification with heterogeneous catalyst and homogeneous catalyst because the product cost of catalyst is cheap and gives high conversion. The biodiesel process can be divided into transesterification reaction, methanol recovery and separation in addition washing would be required if a homogeneous catalyst was used in the process. The biodiesel simulation used palm oil contained palmitic acids (44.3%), oleic acids (38.7%), linoleic acids (10.5%) and other fatty acids (7.5%) as reactant. Therefore, both processes are subdivided into three cases, case I fed only tripalmitate of palm oil (mass fraction is 1), case II fed tripalmitate and trilinolein (mass fraction is 0.5337 and 0.4663) and case III is fed tripalmitate, trilinolein and triolein (mass fraction is 0.4512, 0.4323 and 0.1165). However, the molecular structure of some components are unavailable in ASPEN PLUS so the molecular structure of tripalmitate, diplamitate, monoplamitate, methyl palmitate, trilinolein, dilinolein, monolinolein and methyl linolein were created and imported as mole files. All missing parameter were estimated by ASPEN PLUS except the surface tension of tripalmitate, trilinolein and triolein were added in pure component. Chumpitaz *et al* (1999) were determined the surface tension of tripalmitate, trilinolein and triolein are 28.20, 26.51 and 29.60 (dynes·cm^{-1}) subsequently. This simulation used NRTL model (non-random two-liquid) for the thermodynamic property method.

1. Steady-state simulation

1.1 Steady-state simulation of the conventional distillation

There are six steady-state simulations; three cases steady state simulations are conventional distillation with homogeneous catalyst and the others are the conventional distillation with heterogeneous catalyst. The conventional distillation simulations used different types of catalyst to produce biodiesel. The conventional distillation with homogeneous catalyst used sodium hydroxide (NaOH) as a catalyst. These processes contain four parts which are the transesterification reaction, the methanol recovery, the separation between glycerol and biodiesel and the washing part. If these processes used heterogeneous catalyst as strontium oxide, the washing part would be eliminated and the catalyst would be reduced. This is the advantages between homogeneous catalyst and heterogeneous catalyst. Figure 10 shows the comparison between the conventional distillation with homogeneous catalyst and the conventional distillation with heterogeneous catalyst.



a) The conventional with homogeneous catalyst

b) the conventional with heterogeneous catalyst

Figure 10 The comparison between the conventional distillation with homogeneous catalyst and the conventional distillation with heterogeneous catalyst

1.1.1 The conventional distillation with homogeneous catalyst

In conventional distillation with homogeneous catalyst by using palm oil, the flow rate of oil, fresh methanol, sodium hydroxyl and water were 1000, 120, 12 and 900 kg/h, respectively. The temperature of these feeds was room temperature (25°C) excepting for fresh water (50°C). The flow rate of oils, methanol and sodium hydroxyl are pre-heated to 60°C by heat exchanger before sending to the reaction unit. The rigorous continuous stirred tank reactor model (RCSTR) was used as a reaction unit in this simulation. The reaction occurred isothermally in the reactor at 1 bar and 60°C within liquid phase. All of these steps in the transesterification reaction and their kinetic parameters were described in the Literature review (Noureddini and Zhu, 1997). The effluent from the reactor was sent to the rigorous fractionation model (RadFrac) in order to recover the excess methanol. Next, the bottom product flowed to separation units consisted of two decanter models. Glycerol was first removed in the first decanter. Then the effluent from first decanter was sent to washing part. The sodium hydroxide is contaminated in biodiesel can be remove by pure water before sending to the second decanter. The first and the second decanter were operated at 50 and 90°C, respectively.

The operated simulation result of the conventional distillation with homogeneous catalyst of each case is shown in Table 6. In the fractionation unit, the configuration results show that the number of stages was 10 and the feed stage was 3. A furthermore, these fractionation units can recover 28.61 kg/hr of methanol. The process flow diagram of the conventional distillation is shown in Figure 11. The percentage of oil conversions in three cases are 98.65, 99.63 and 99.62. Biodiesel purities are 98.38, 99.49 and 99.45 respectively.

Table 6 The operating unit of each unit in the conventional distillation process with homogeneous catalyst

	case I	case II	case III
Transesterification	one component transesterification	two components transesterification	three components transesterification
Reactor type	CSTR	CSTR	CSTR
Temperature (°C)	60	60	60
Pressure (bar)	1	1	1
Methanol recovery			
Column type	Radfac	Radfac	Radfac
Reflux ratio	1	1	1
Biolup ratio	0.5	0.5	0.45
Top/bottom pressure (bar)	1	1	1
Glycerol separation			
Equipment	decanter	decanter	decanter
Temperature (°C)	50	50	50
Biodiesel separation			
Equipment	decanter	decanter	decanter
Temperature (°C)	90	90	90

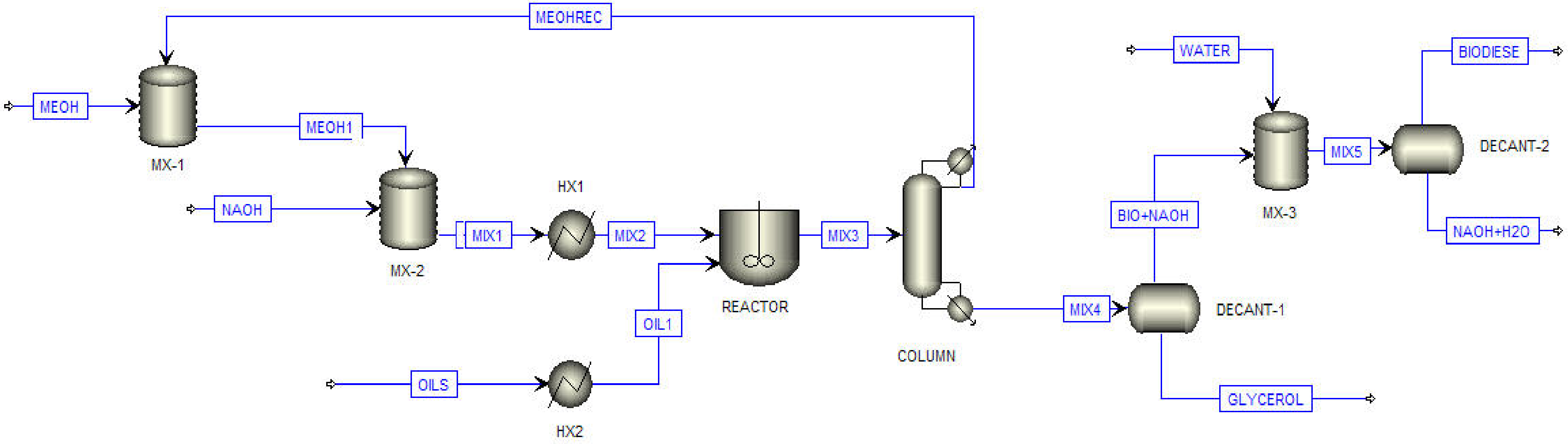


Figure 11 Process flow diagram of the conventional distillation with homogeneous catalyst process

1.1.2 The conventional distillation with heterogeneous catalyst

In conventional distillation with heterogeneous catalyst by using palm oil, the flow rate of oil and fresh methanol were 1000 and120 kg/h. The temperature of these feeds was room temperature (25°C).The flow rate of oils and methanol are heated up to 65°C by heat exchanger before sending to the reaction unit in this simulation. The rigorous plug flow reactor model (PFR) was used as a reaction unit. The strontium oxide was presented in it. The reaction occurred isothermally in the reactor at 1 bar and 65°C. All of these steps in the transesterification reaction and their kinetic parameters were described in the Literature review (Pechtabthim, 2008). The effluent from the reactor was sent to the rigorous fractionation model (RadFrac) in order to recover the excess methanol. Next, the bottom product flowed to separation unit consisted of one decanter model separated glycerol and biodiesel. The decanter was operated at 35°C.

The operated simulation result of the conventional distillation with heterogeneous catalyst of each case is shown in Table 7. The sensitivity analysis was used as a tool for finding the new operating condition. The sensitivity analysis of the conventional process was done in Appendix A. In the fractionation unit, the configuration results show that the number of stages was 10; and the feed stage was 3. A furthermore, these fractionation units can recover 10, 12 and 18 kg/hr of methanol respectively. The process flow diagram of the conventional distillation is shown in Figure 12. The percentage of oil conversions in three cases are 95.01, 95.88 and 95.90. Biodiesel purities are 94.61, 95.21 and 95.21 respectively.

Table 7 The operating unit of each unit in conventional distillation process with heterogeneous catalyst

	case I	case II	case III
Transesterification	one component transesterification	two components transesterification	three components transesterification
Reactor type	Rplug	Rplug	Rplug
Temperature (°C)	65	65	60
Pressure (bar)	1	1	1
Bed void	0.65	0.65	0.65
Methanol recovery			
Column type	Radfac	Radfac	Radfac
Reflux ratio	1	1	1
Distillation rate	10	12	18
Top/buttom pressure (bar)	1	1	1
Glycerol separation			
Equipment	decanter	decanter	decanter
Temperature (°C)	35	35	35

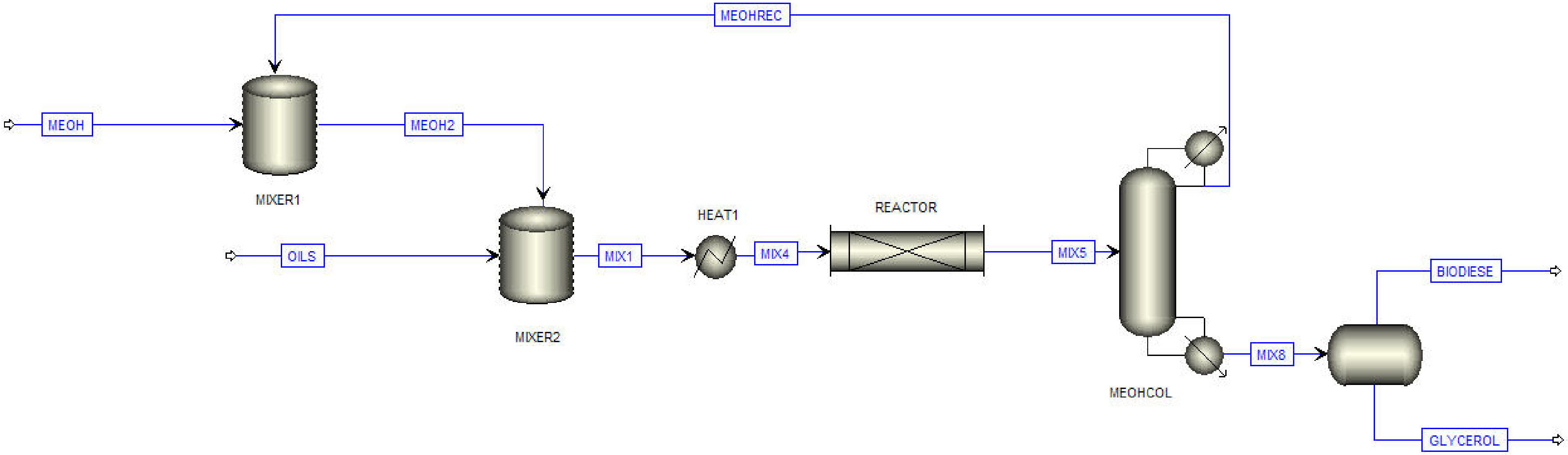


Figure 12 Process flow diagram of the conventional distillation with heterogeneous catalyst process

1.2 Steady-state the simulation of reactive distillation process

The reactive distillation integrated reaction and distillation is introduced in order to increase the efficiency of biodiesel production. The simulation of biodiesel production used the reactive distillation was done in ASPEN PLUS. The rigorous fractionation column (RadFrac) was used in this simulation. The fractionation column can be separate in three sections which are rectifying section, reaction section, and stripping section. The reactions which are homogeneous transesterification and heterogeneous transesterification occurred in from the fourth tray to the eighth tray of column. The homogeneous kinetic reaction was studied by Noureddini and Zhu (1997) and The heterogeneous kinetic reaction was studied by Pechtubtim (2008). Oil and methanol are fed at the fourth tray and the eighth tray respectively.

1.2.1 The reactive distillation with homogeneous catalyst

The NRTL-RK property model was used in this simulation 1,000 kg/hr of oil and 120 kg/hr of methanol are fed at the eight tray and at the fourth tray respectively. In addition, the composition of oil fed was separated into three cases; case I contained 1 mass fraction of tripalmitate, case II contained 0.5337 mass fraction of tripalmitate and 0.4663 mass fraction of triolein and case III contained 0.4512 mass fraction of tripalmitate, 0.4323 of triolein and 0.1165 of triolein. The reactive distillation has ten stages, the reflux ratio is 1, the boil up ratio is 0.6 and the pressure column is 1 bar for all cases. The results from simulating homogeneous reactive distillation were shown in Table 8.

Table 8 The results from simulating homogeneous reactive distillation

	case I	case II	case III
effluents from the bottom reactive distillation			
Methyl ester (kg/hr)	1004.81	1004.66	1003.82
Methanol (kg/hr)	40.96	15.85	13.28
Glycerol (kg/hr)	114.05	109.36	108.45
Sodium hydroxide (kg/hr)	12	12	12
Decanter			
Glycerol (kg/hr)	106.79	104.75	106.79
Biodiesel's purity	99.79.	99.87	99.52

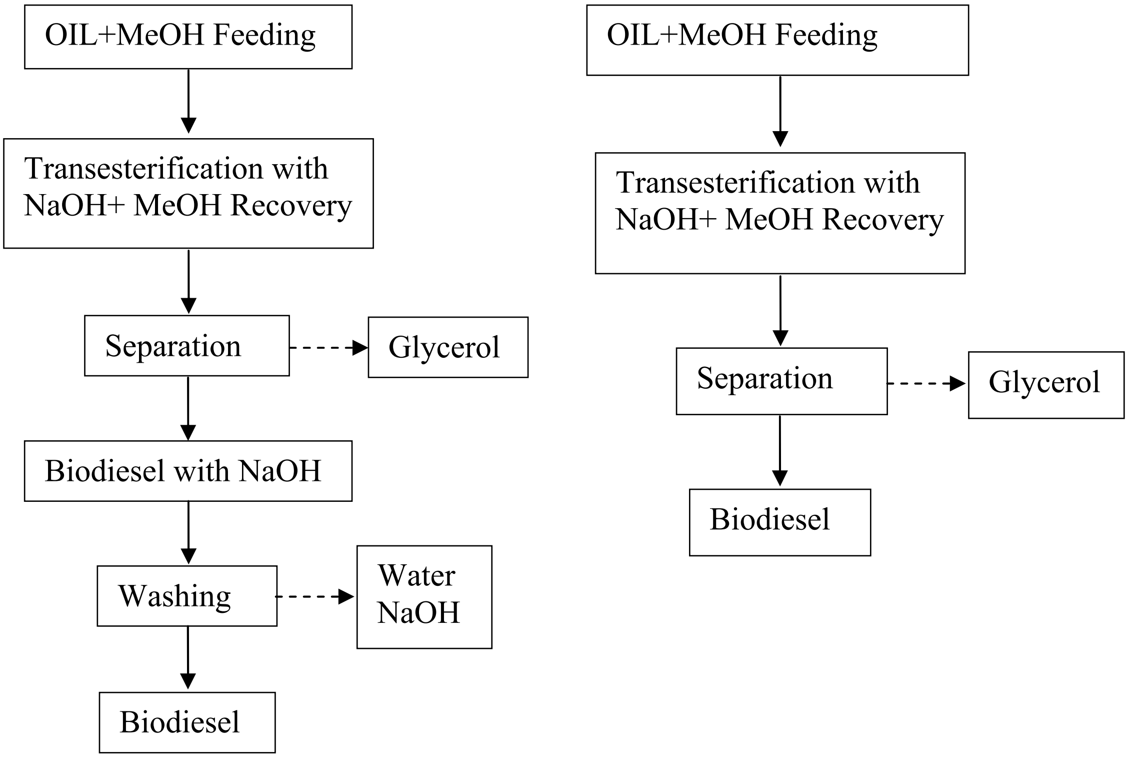
1.2.2 The reactive distillation with heterogeneous catalyst

The reactive distillation with heterogeneous was separated into three cases similar the reactive distillation of homogeneous catalyst. But the reactive distillation with heterogeneous was packed strontium oxide at from the fourth stage to the eighth stage. The reactive distillation has 10 stages, the feeding oil at the fourth stage and methanol at the eighth stage for all case. The results from simulating heterogeneous reactive distillation were shown in Table 9.

The comparison between homogeneous and heterogeneous of the reactive distillation process shows that the heterogeneous reactive distillation could regenerate catalysts easier than the homogeneous reactive distillation because the homogeneous reactive distillation must use a lot of water to wash alkaline catalyst. Both flow sheets are shown in Figure 13. The temperature profile of homogeneous reaction slightly increased and methyl ester generated are shown in Figure 14. Figure 15 shows the temperature profile of heterogeneous reaction increased from the first stage to the third stage then after the 3rd stage the temperature profile is decreased.

Table 9 The results from simulating heterogeneous reactive distillation

	case I	case II	case III
Reflux ratio	1.5	1.2	1
Distillation rate (kg/hr)	20	18	21
Effluents from the bottom reactive distillation			
Methyl ester (kg/hr)	1003.25	1003.60	1003.57
Methanol (kg/hr)	1.14	2.04	2.08
Glycerol (kg/hr)	113.77	110.31	108.43
Decanter			
Glycerol (kg/hr)	113.66	109.66	106.79
Biodiesel's purity	99.74.	99.61	99.52



a) RD with homogeneous catalyst b) RD with heterogeneous catalyst

Figure 13 Comparison of reactive distillation with homogeneous catalyst and reactive distillation with heterogeneous catalyst

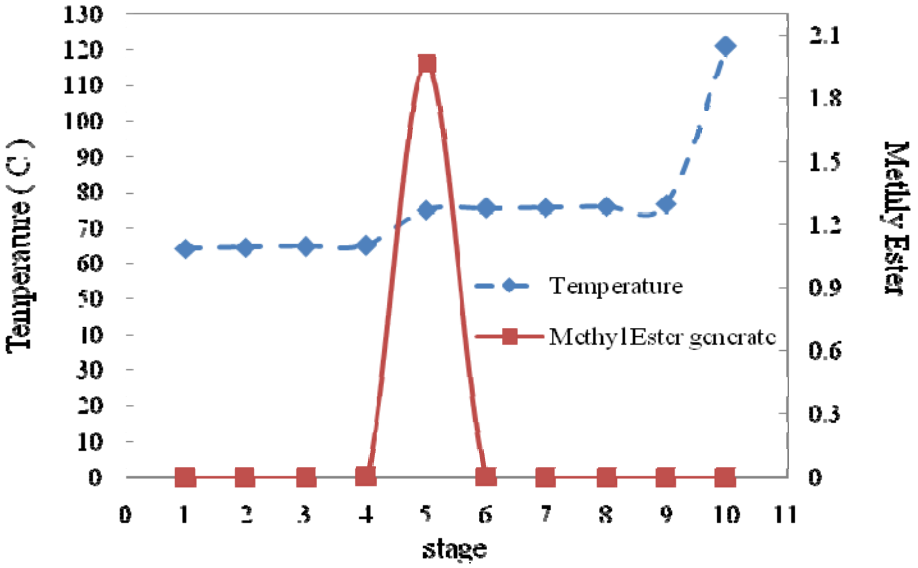


Figure 14 Temperature profile and methyl ester generated during the homogeneous reaction

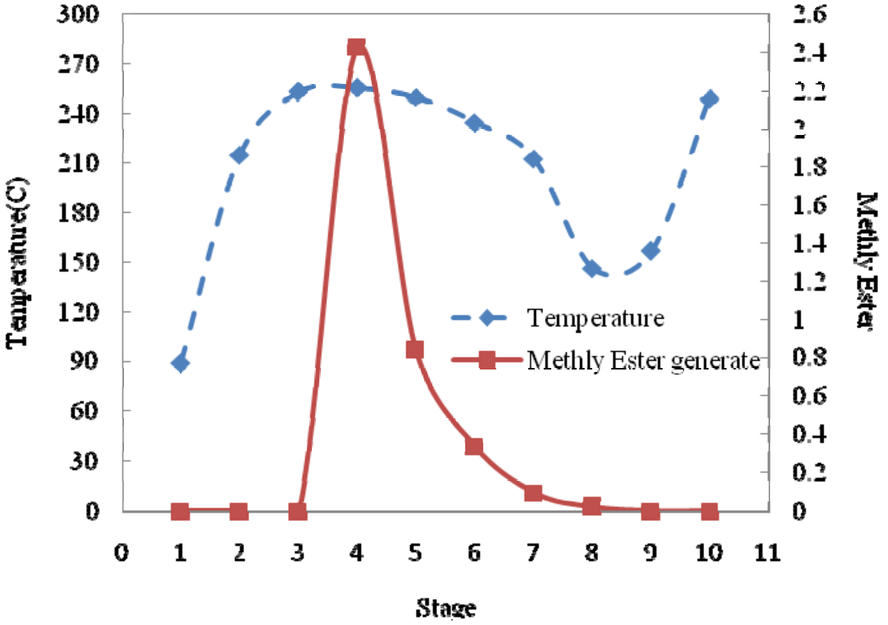


Figure 15 Temperature profile and methyl ester generated during heterogeneous reaction

2. Dynamic Simulation

2.1 Plantwide application of Luyben

The results of the nine steps plantwide procedures of Luyben (1999) are shown as follows:

Step 1: Establish control objectives

This step is probably the most important of this problem because the different control objectives lead to different control structures. In this work, the control objectives related to product quality and on-supply reactant. The acceptable purity of biodiesel product is 96.5 wt % which is the limitation of EN 14214.

The on-supply reactant or on-demand product is important to be set as one of control objectives because it affects the configuration of control system. Due to the highly requirement of biodiesel, the on-demand of biodiesel was also set as one of the control objectives which can be changed later.

Step 2: Determine control degrees of freedom

The objective of this step is to count an amount of control valves which is available to be adjusted in the process. In this work, there are 14 manipulated variables for conventional distillation process, shown as follow:

- 2 feed valves
- 2 valves at outlet of decanter
- 2 steam valves at two heaters
- 1 steam valve at reactor
- 1 steam valve at reboiler
- 1 steam valve at condenser
- 1 valve at distillate product of column (recycle stream)

- 1 valve at reflux stream
- 1 valve at bottom product of column
- 1 valve at reactor effluent
- 1 valve at inlet of the decanter

For the reactive distillation process, there are 11 manipulated variables which are available for adjusting in the process. The list of them was shown as follow:

- 2 feed valves
- 2 valves at outlet of decanter
- 2 steam valves at two heaters
- 1 steam valve at reboiler
- 1 steam valve at condenser
- 1 valve at distillate product of column (recycle stream)
- 1 valve at reflux stream
- 1 valve at bottom product of column

Step 3: Establish energy management

The transesterification occurred in the reactor is an endothermic reaction. Therefore, the energy disturbance during reaction does not propagate throughout the process. To handle the endothermic transesterification reaction, the duty of the reactor is adjusted to meet the designed temperature at 65 °C. For the function of energy integration, both conventional and reactive distillation processes do not have any energy integration.

Step 4: Set production rate

The aim of this step is to establish the variables that dominate the productivity of the reactor and determine the most appropriate manipulator for controlling production rate. In this work, there are some parameters which affect the conversion or productivity of the process such as the temperature of reactor (in conventional distillation process), the temperature of reactive distillation column (in reactive distillation process) and the rate of methanol inlet of reactor. However, the dominated variable which affect directly to the oil conversion is temperature of reactor in case of conventional distillation process and temperature of reactive distillation column in case of reactive distillation process because the kinetic of transesterification depends on reaction temperature.

To control temperature of reactor, the specific heat duty of reactor was selected. For reactive distillation process, the reaction was occurred in the reactive distillation column. Therefore, the heat duty of reboiler was chosen to control the temperature of the reactive distillation column.

However, there is a constraint of productivity that the flow rate of the product is fixed by on-supply reactant from the first step. For this constraint, the flow rate of reactants in this process was controlled by controllers.

Step 5: Control product quality and handle safety, operational and environmental

The product quality and safety were concerned in this step. For the product quality, the effect of the distillation column is more important than the decanters because it is independent from temperature and pressure. Therefore, the product quality was controlled by controlling temperature of the distillation column. In addition the temperature of distillation column is highly depended on the heat duty of reboiler and the temperature on the temperature-controlled tray.

One way to locate the temperature-controlled tray is to identify where the temperature is changing significantly from tray to tray. Figures 16 and 17 showed the temperature profile of conventional and reactive distillation column, respectively. From these two figures, the temperature of the reboiler should be controlled at setpoint maintain the product quality.

For safety viewpoint, the pressure of condenser should be controlled whereas the pressure of other equipments is not necessary because this process is the liquid system. Therefore, the manipulated variable of this pressure control was the heat duty of condenser. For the temperature of this process, the temperature of the reactor is not critical because the reaction occurred in the reactor is endothermic reaction.

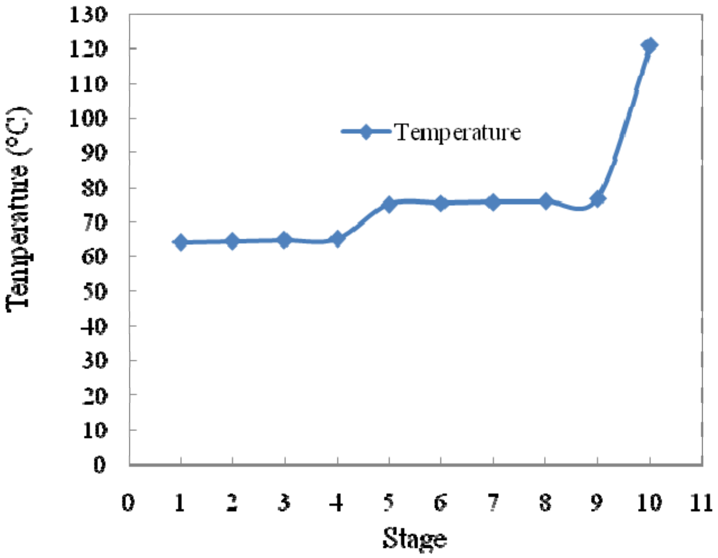


Figure 16 Temperature profile of conventional distillation

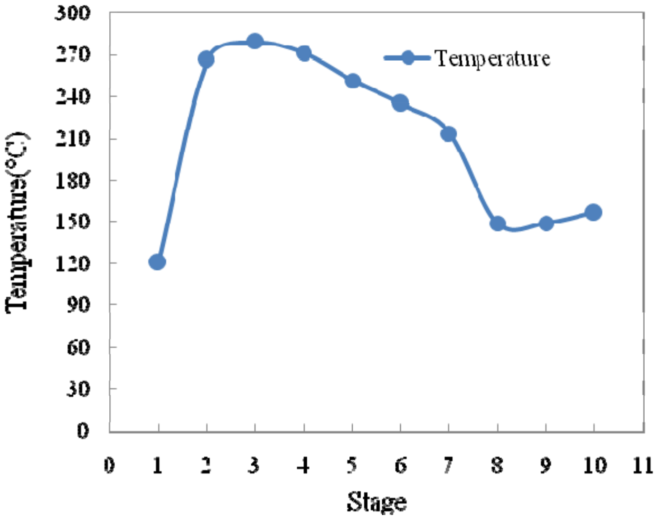


Figure 17 Temperature profile of reactive distillation

Step 6: Fix a flow in every recycle loop and control inventories (Pressures and Levels)

For this step, every recycle stream must be controlled that is the main objective of this step. This is to prevent the snowball effect. This work has a recycle stream of methanol from distillation column so a controller is installed to control the recycle flowrate. For the control of inventories, there are four liquid levels to be controlled for conventional distillation process, consisting of reactor level, sump level, and two liquid levels of decanter. For the reactive distillation process, there are six liquid levels which the reactor is not presented in the process. To control the reactor level in conventional distillation process, the effluent flow rate of reactor was selected to be adjusted. In column of both conventional and reactive distillation processes, the level of reflux drum was controlled by selecting reflux flow rate as manipulated variable. The sump (reboiler) level was controlled by adjusting flow rate of bottom product. For the decanters, there are two phases of liquid which are required to be controlled. The effluent from each phase was chosen to control the level of that phase.

Step 7: Check component balances

This step is necessary if inert components exist in the process. However, the biodiesel process that is simulated in ASPEN PLUS program does not have any inert component. Therefore, this step is not concerned in this work.

Step 8: Control individual unit operations

After finished those of seven steps, the control system of the process was already created as shown in Figure 18 and Figure 19 for conventional distillation process and reactive distillation process. In this step, all of controllers which were installed in the ASPEN DYNAMIC were tuned. The tuning parameters were performed by using Tyreus-Luyben method shown in Appendix C. The results of tuning parameter are shown in Table 10 for conventional distillation and Table 11 for reactive distillation process. Furthermore, the IAE tool boxes were created on these processes to measure the error between input and a set point value. The IAE results from Tables 10 and 11 indicated the control efficiency. If comparison between two control systems. The IAE of control system is lower than others shown the control efficiency is better than the others. The Appendix D displayed the IAE calculation.

Table 10 Results of tuning parameter from conventional distillation process

Controller	Type of controller	Tuned parameter		IAE
		K_C	τ_i	
Flow controller at oil feed (FC1)	PI	0.5	0.3	0.6188
Flow controller at methanol feed (FC2)	PI	0.5	0.3	0.4125
Flow controller at recycle stream (FC3)	PI	0.50	0.30	2.2095
Temperature controller at reactor (TC)	PI	5	6	0.7826
Temperature controller at reboiler (TC1)	PI	68.98	1	1.2136
Pressure controller at condenser (PC)	PI	3	10	0.0031
Level controller at reactor (LC1)	P-only	10	100,000	0.0088
Level controller at reboiler (LC2)	P-only	44.89	100,000	0.0079
Level controller at decanter (L1_LC)	P-only	2	100,000	0.0109
Level controller at decanter (L2_LC)	P-only	4	100,000	0.0101

Table 11 Results of tuning parameter from reactive distillation process

Controller	Type of controller	Tuned parameter		IAE
		K_C	τ_i	
Flow controller at oil feed (FC1)	PI	0.5	0.3	0.6236
Flow controller at methanol feed (FC2)	PI	0.5	0.3	0.3235
Flow controller at recycle stream (FC3)	PI	0.50	0.30	0.3412
Temperature controller at reboiler (TC1)	PI	66.46	4.5	0.3474
Pressure controller at condenser (PC1)	PI	20	12	0.0018
Level controller at reboiler (LC1)	P-only	2	100,000	0.0026
Level controller at decanter (L1_LC)	P-only	2	100,000	0.0059
Level controller at decanter (L2_LC)	P-only	2	100,000	0.0054

Step 9**:** Optimize economics or improve dynamic controllability

From the original 14 degrees of freedom in conventional distillation process and 11 degrees of freedom in the reactive distillation process, some of them were used for controlling methanol feed, oil feed, recycle stream, reactor temperature, reboiler temperature, reactor level, reboiler level, 1st phase level of decanter, 2nd phase level of decanter and condenser pressure control. For the improvement of controllability, the controllability was checked by disturb feeding oil and methanol increasing and decreasing in the next part. If the results in the next part are not good, this section will be talked again.

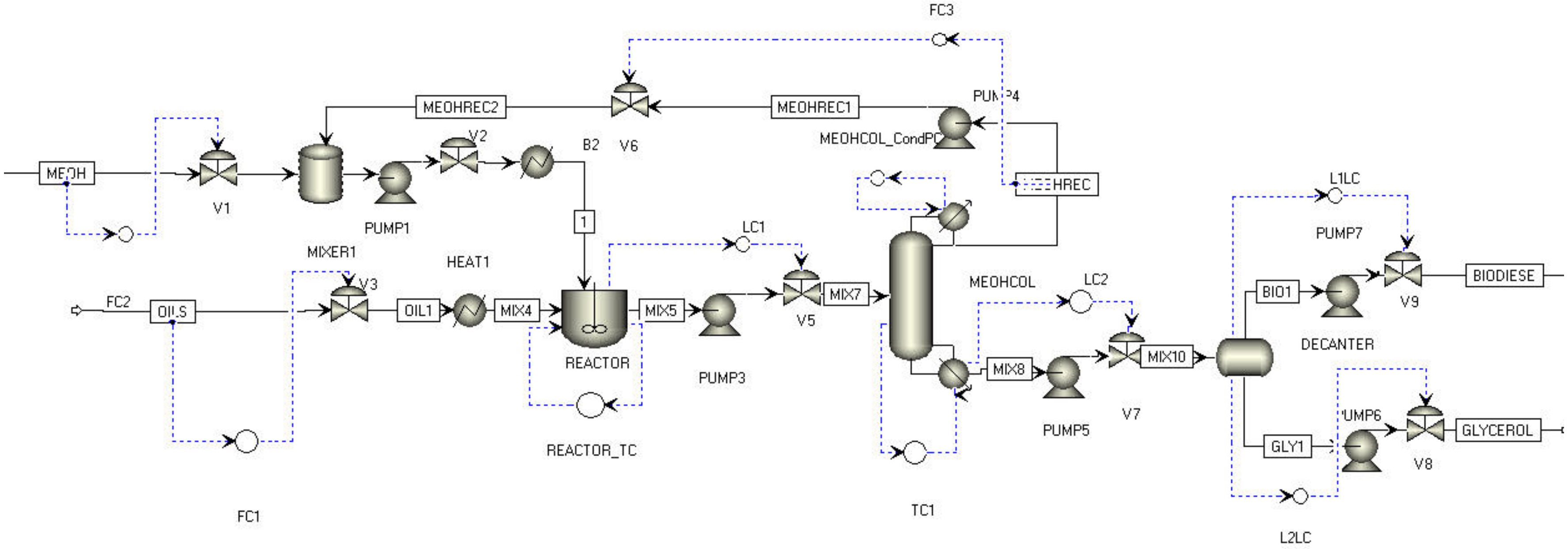


Figure 18 The conventional distillation process with control system

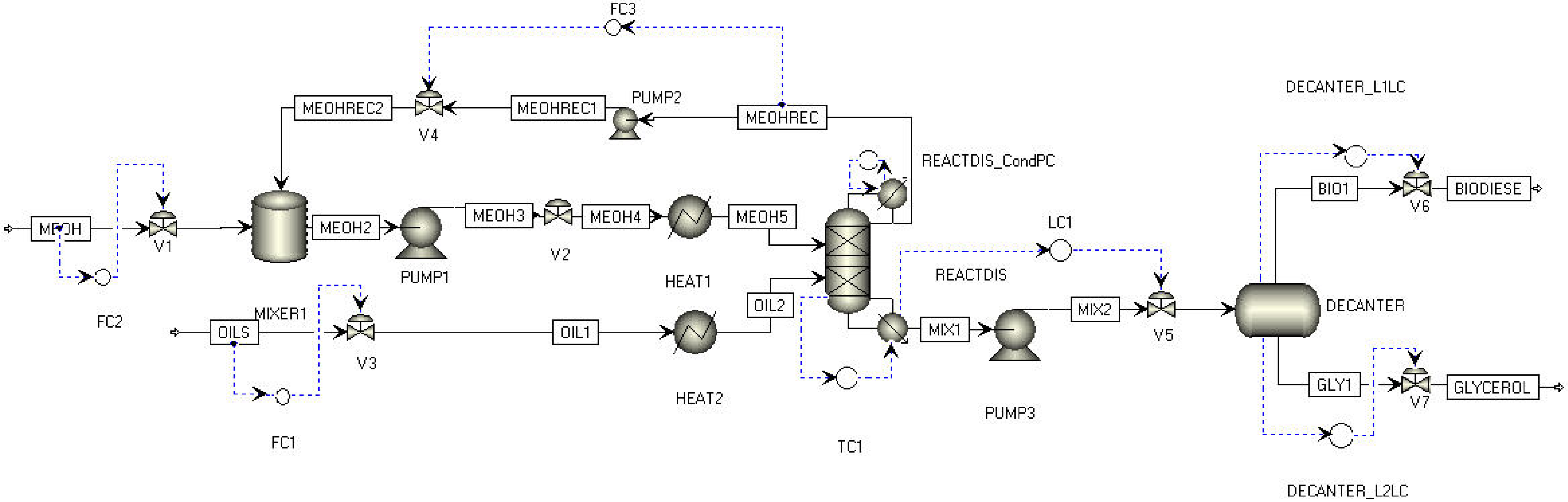


Figure 19 The reactive distillation process with control system

2.2 Test of System Controllability

The concept of plantwide was illustrated to design the configuration of control system. Then, the controllability of the designed system was tested by changing the feed flow rate in order to observe the dynamic responses of the process. The process variables should reach the designed set point or new steady-state after changing the feed flow rate. The purity of the process must not lower than the limitation of 96.5 wt%.

To test the controllability of the control system, the feed flow rate of oil and methanol was changed to ± 5 % of original steady-state designed value. For 5 % increasing, the flow rate of oil and methanol were changed to 1,050 and 126 kg/h respectively. For the 5 % decreasing, the flow rate of oil and methanol was changed to 950 and 114 kg/h respectively. Furthermore, the controllability of the control system was tested by changing ±10, ±15, ±20 and ±25 %. The results of the test were shown in Table 12.

Table 12 The biodiesel purity and the mass flow rate of biodiesel.

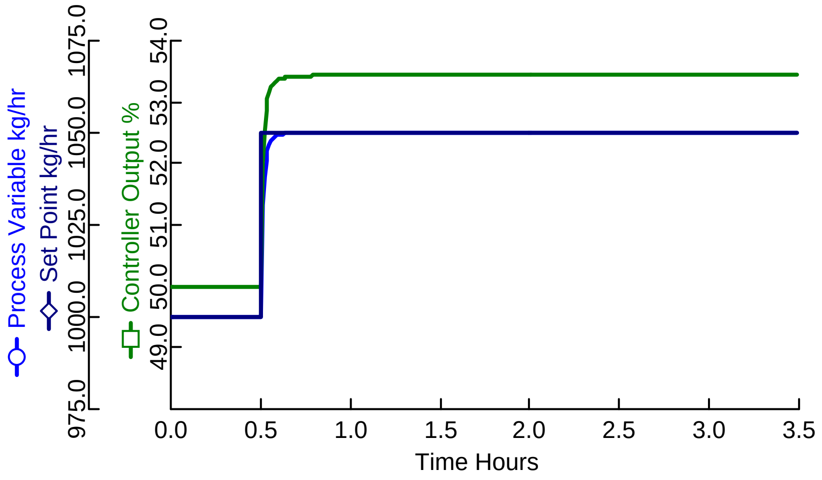
	Conventional distillation		Reactive distillation	
	Flowrate (kg/hr)	Purity	Flowrate (kg/hr)	Purity
Increase 10	1125.42	99.78	1111.66	99.46
Increase 15	1162.31	99.78	1158.91	99.46
Increase 20	1225.68	99.77	1212.31	99.45
Decrease 10	910.08	99.80	902.54	99.48
Decrease 15	862.47	99.81	852.40	99.49
Decrease 20	811.52	99.82	802.11	99.50

The result from Table 10 found that when the reactant was decreased, the biodiesel purity was increased. Because in the dynamic mode at the same time observed at the decanter cloud separated between biodiesel and glycerol to depend on the flowrate of reactant. If the flowrate of reactant was decreased

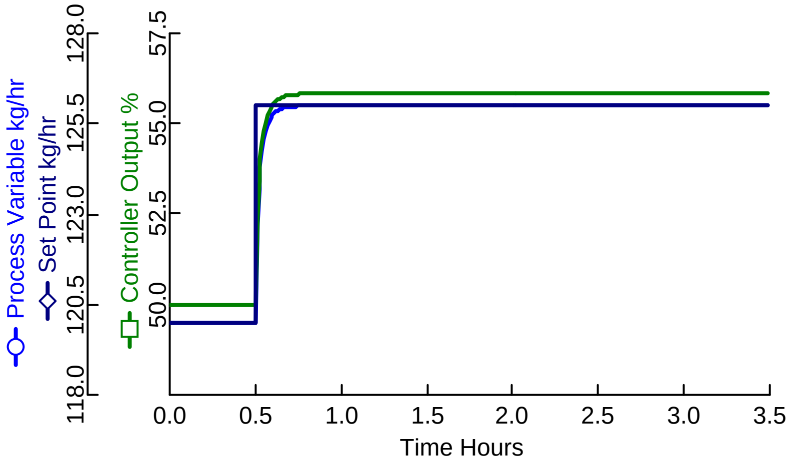
2.2.1 Test of the controllability for reactive distillation process

2.2.1.1 Increasing 5 % of Reactant Feed

In this task, the testing controllability of reactive distillation process, the flow rate of the feed oil and methanol were changed 5 % higher than the value of the steady-state condition at 0.5 hour of the simulation time. Figure 20 shows that. The previous steady-state value of feed oil and methanol flow rate were 1,000 and 120 kg/h respectively. At the new steady state, the values of each flow rate were 1,050 and 126 kg/h.



(a)



(b)

Figure 20 Responses of FC1, FC2 controller for increasing 5 % of feed flow rate of reactive distillation process (a) FC1 (b) FC2

In this process, temperature of reboiler was selected to control the temperature of the column. The set point of reboiler temperature is 157 °C. The reboiler temperature was controlled by changing the reboiler duty. The responses of TC1 controller shows in Figure 21 illustrated that TC1 worked well to for returning the reboiler temperature back to set point. The more feed flow rate of the process the energy was required to maintain the temperature of reboiler..

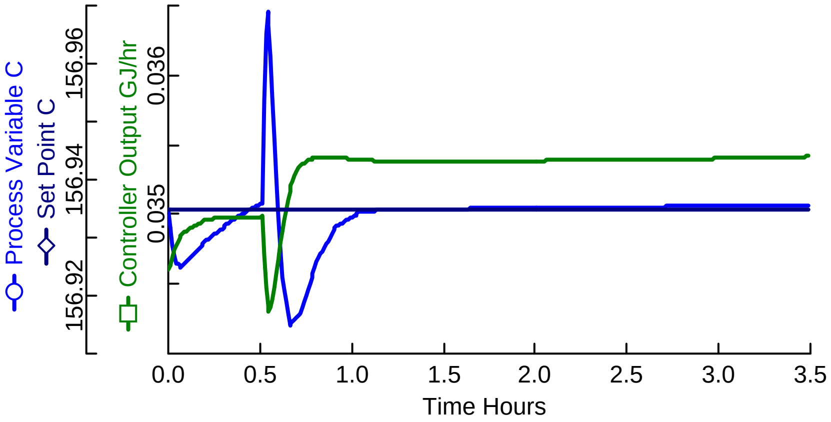


Figure 21 Responses of TC1 controller for increasing 10 % of feed flow rate of reactive distillation process

For the pressure control of reactive distillation column, condenser duty was observed to reach the designed pressure of condenser. Figure 22 shows that the PC controller works well for controlling pressure of condenser.

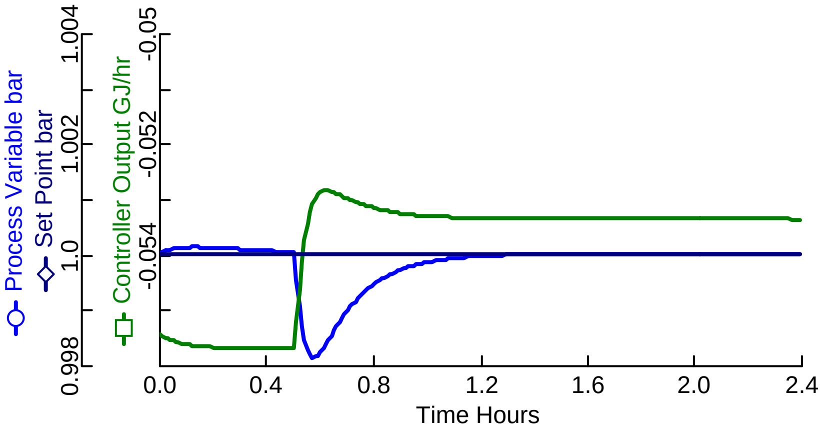


Figure 22 Responses of PC controller for increasing 5 % of feed flow rate of reactive distillation process

In the decanter, there are two controllers installed (L1LC, L2LC) to control the level of biodiesel phase and glycerol phase. The results of LC3 and LC4 are plotted in Figure 23 and 24, respectively. From Figure 23 and 24, the levels of the two phases reach the new steady-state levels.

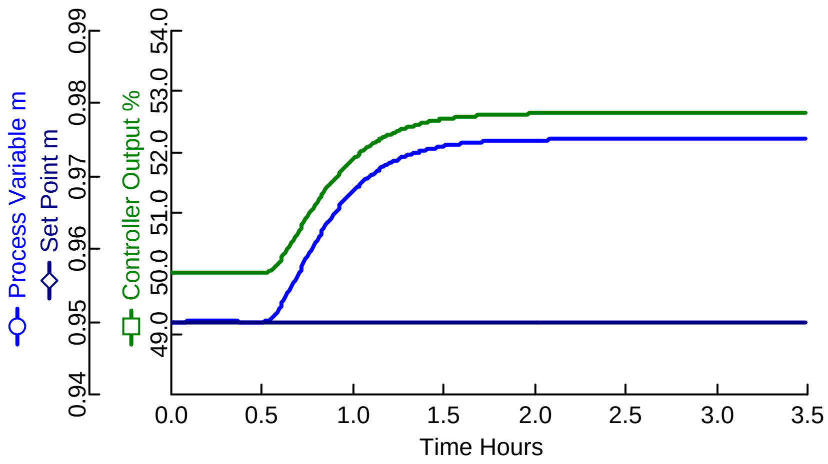


Figure 23 Responses of L1LC controller for increasing 5 % of feed flow rate of reactive distillation process

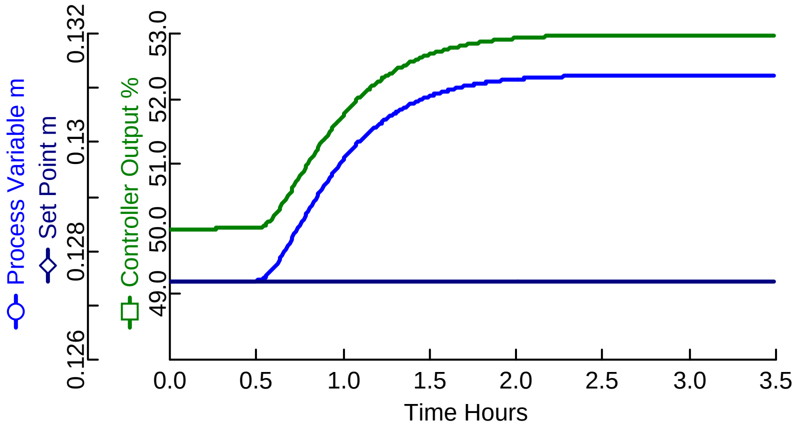


Figure 24 Responses of L2LC controller for increasing 5 % of feed flow rate of reactive distillation process

For the biodiesel productivity of the process and biodiesel purity, the results were observed and plotted in Figure 25 and 26, respectively. The flow rate of biodiesel product was increased from 1003.85 kg/h to 1053.26 kg/h when the reactant flow rate was increased 5 % of the original flow rate. For the purity of biodiesel product, the control system can handle all of variables in the process especially the temperature of the column that leads to the good control of biodiesel purity. Therefore, the biodiesel purity of the process is 99.47 wt% while the purity of the original process is 99.58 wt%.

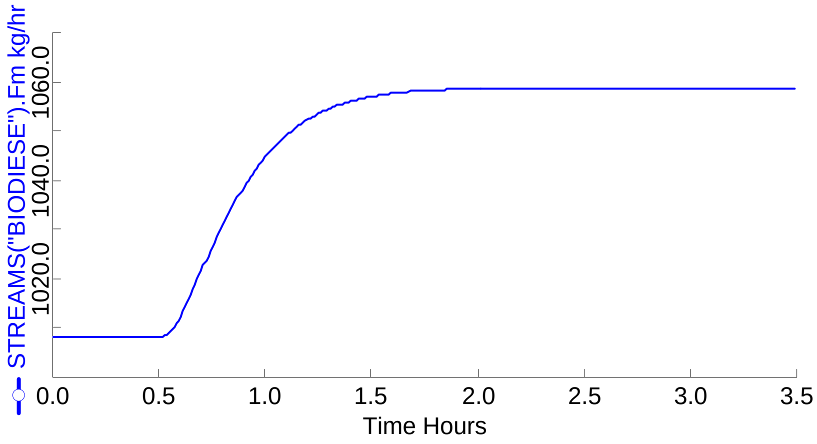


Figure 25 Responses of biodiesel flow rate for increasing 5 % of feed flow rate of reactive distillation process

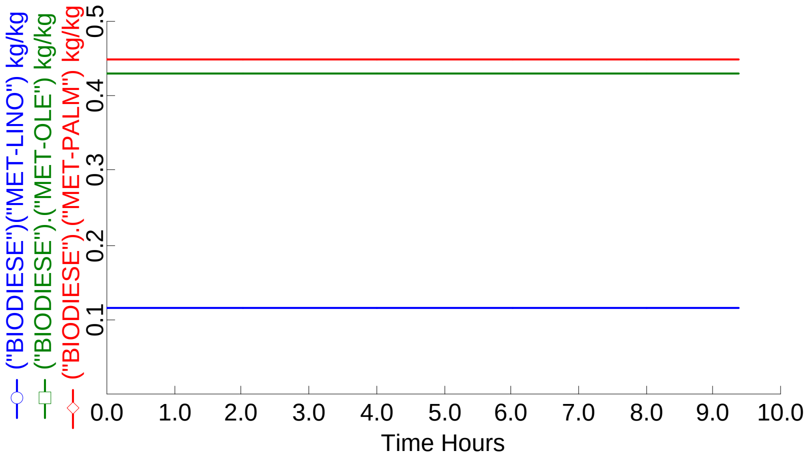
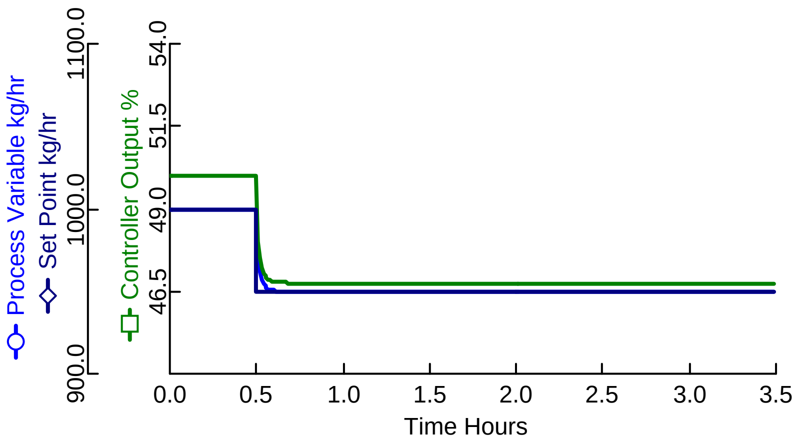


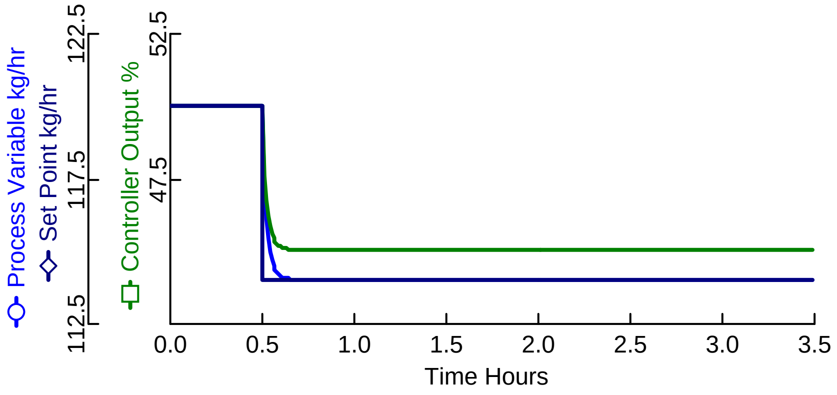
Figure 26 Responses of biodiesel mass fraction for increasing 5 % of feed flow rate of reactive distillation process

2.2.1.2 Decreasing 5 % of reactant feed

The controllability of the reactive distillation process is also tested by decreasing 5 % of reactant flow rate. Figure 27 exhibits the changing of flow rate at 0.5 hour of simulation time from 120 kg/h of methanol, and 1000 kg/h of oil to 114 kg/h of methanol and 950 kg/h of oil.



(a)



(b)

Figure 27 Responses of FC1, FC2 controller for decreasing 5 % of feed flow rate of reactive distillation process (a) FC1 (b) FC2

The temperature of the reboiler was also increased when the reactant flow rate was decreased. Because the original heat duty was high maintaining the temperature of reboiler at 157°C. However, TC1 controller can control the temperature by adjusting the specific heat duty of reboiler. The responses of TC1 are shown in Figure 28.

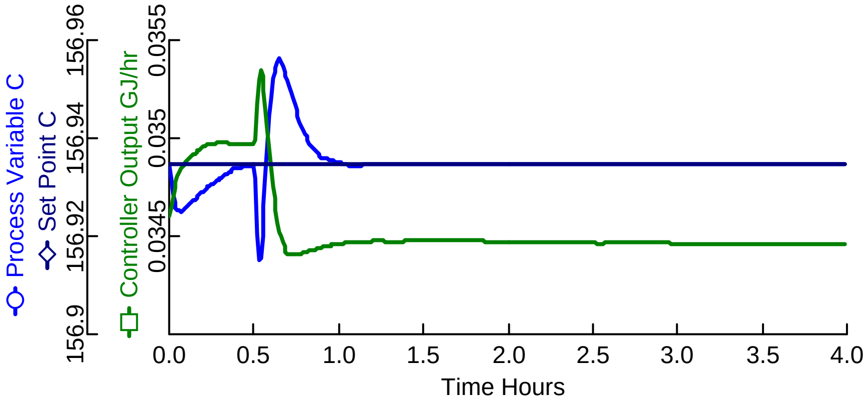


Figure 28 Responses of TC1 controller for decreasing 5 % of feed flow rate of reactive distillation process

PC controller was installed to control the pressure of the column by manipulating the temperature of condenser. Figure 29 shows that the controller works well for controlling the pressure of condenser.

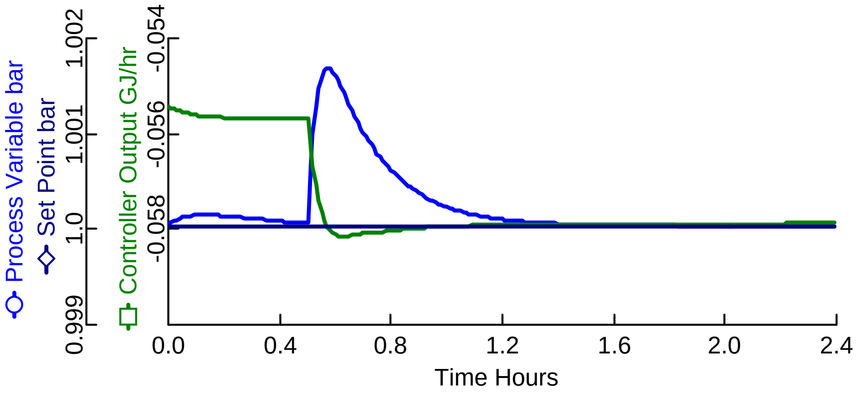


Figure 29 Responses of PC controller for decreasing 10 % of feed flow rate of reactive distillation process

L1LC and L2LC controllers are used to maintain the level of the biodiesel phase and the glycerol phase of the decanter. Figure 30 and 31 exhibits the responses of these two controllers. The levels of the decanter were decreased when the reactant flow rate was deceased. However, the levels reached the new steady-state values.

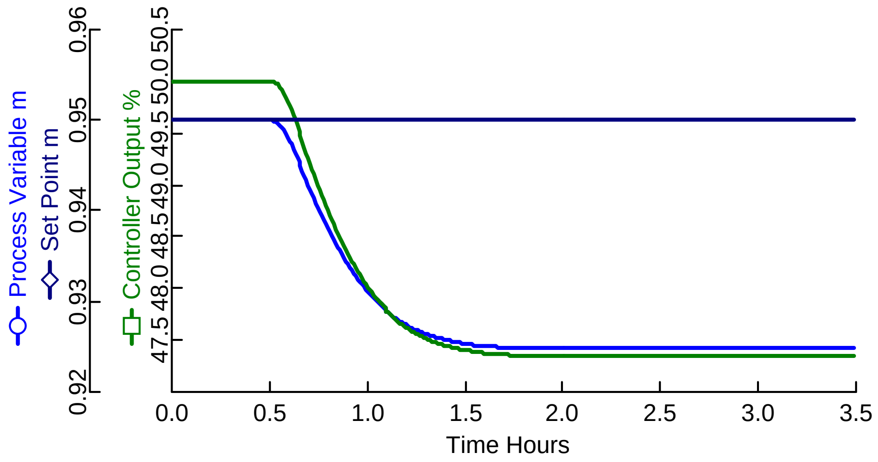


Figure 30 Responses of L1LC controller for decreasing 5 % of feed flow rate of reactive distillation process

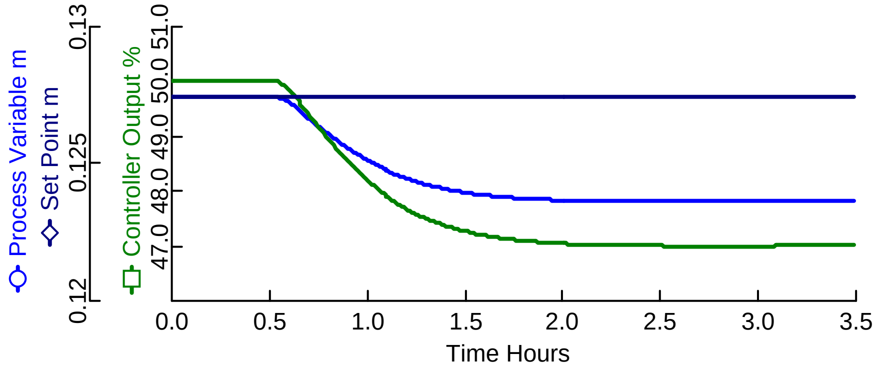


Figure 31 Responses of L2LC controller for decreasing 5 % of feed flow rate of reactive distillation process

For the responses of the flow rate of biodiesel product and its purity, they are shown in Figure 32 and 33, respectively. The biodiesel productivity is decreased from 1003.85 kg/h to 952.678 kg/h when the reactant flow rate is decreased about 5 % of original flow rate. For the purity of biodiesel product, the control system worked well for controlling the purity of biodiesel product when the reactant flow rate was decreased. As the reactant flow rate was decreased, the purity of biodiesel product was about 99.48 wt%.

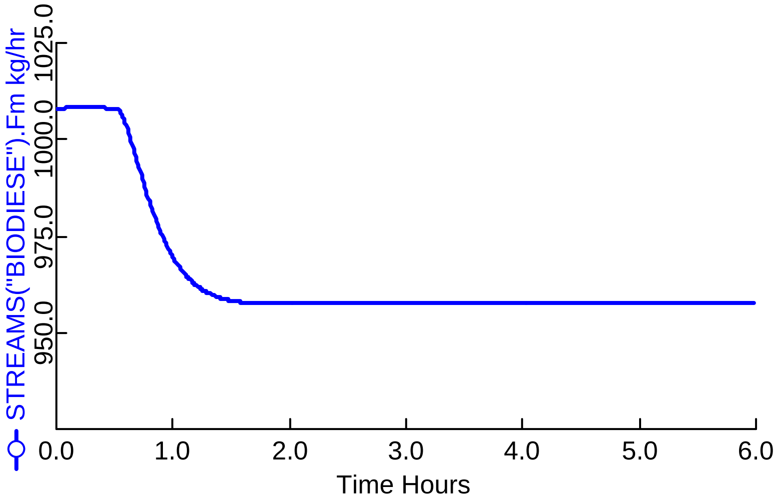


Figure 32 Responses of biodiesel flow rate for decreasing 5 % of feed flow rate of reactive distillation process

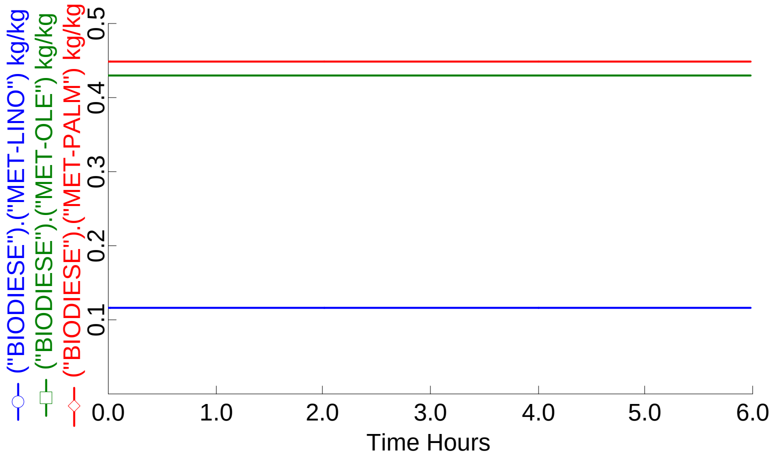
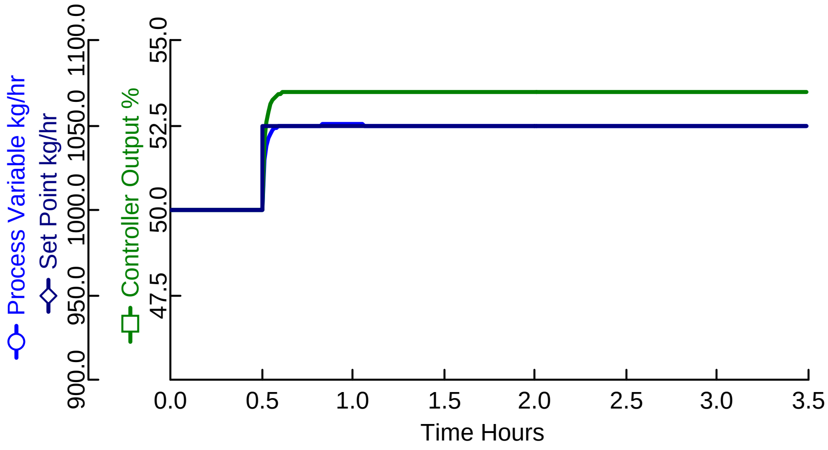


Figure 33 Responses biodiesel mass fraction for decreasing 5 % of feed flow rate of reactive distillation process

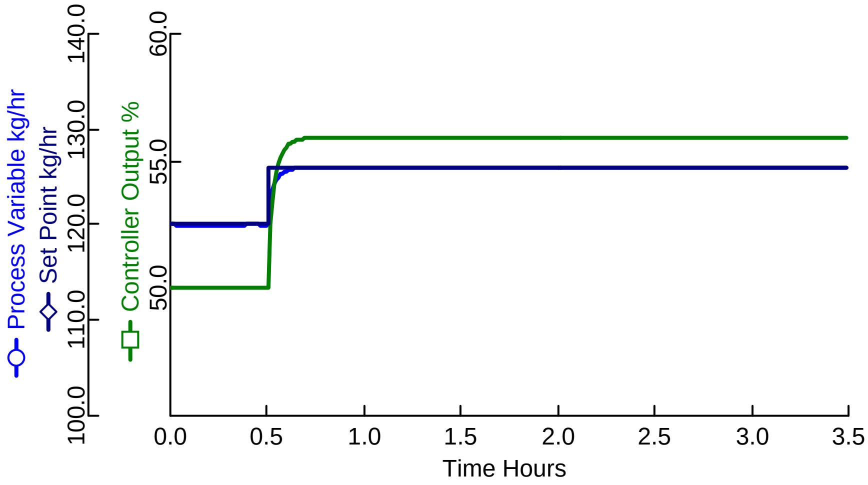
2.2.2 Test of Controllability for Conventional Distillation Process

2.2.2.1 Increasing 5 % of Reactant Feed

In this task, the testing controllability of conventional distillation process, the flow rate of the feed oil and methanol were changed 5 % higher than the value of the steady-state condition at 0.5 hour of the simulation time Figure 34shows that. The previous steady-state value of feed oil and methanol flow rate were 1,000 and 120 kg/h respectively. At the new steady state, the values of each flow rate were 1,050 and 126 kg/h.



(a)



(b)

Figure 34 Responses of FC1 and FC2 controller for increasing 5 % of feed flow rate of conventional distillation process (a) FC1 (b) FC2

For the reactor, the responses of the Reactor_TC and LC1 were shown in Figure 35 and Figure 36, respectively. The control of reactor temperature is an important for biodiesel production because it affects to the conversion of oil. From the results shown in the Figure 35, the temperature of the reactor was decreased when the flow rate of reactant feeds were increased. However, the Reactor_TC controller was used to adjust the heat duty of the reactor to 65 °C of which is the set point. LC1 which is used to control the level of the reactor and its responses in the Figure 36 shows an increasing of reactor level from the original set point at 4.72 m to the new set point at 4.74 m. The slow response of level control is not a problem because it does not affect to product purity or productivity.

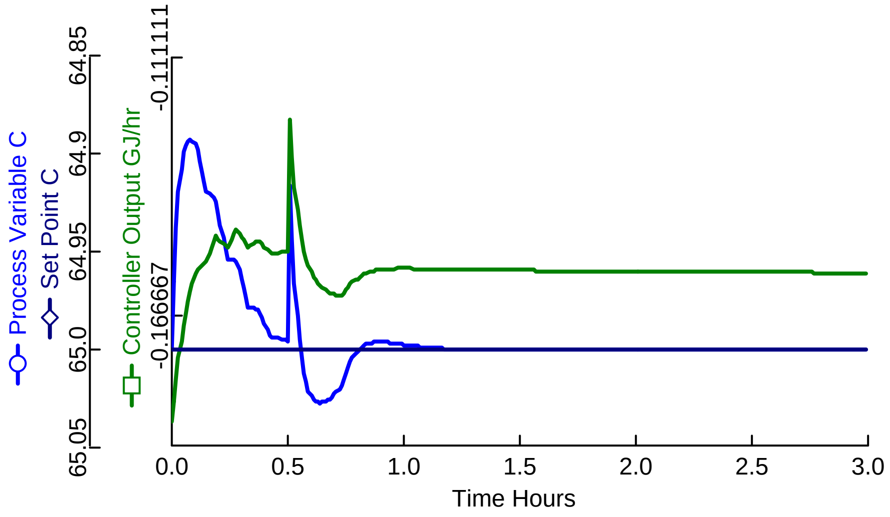


Figure 35 Responses of REACTER_TC controller for increasing 5 % of feed flow rate of conventional distillation process

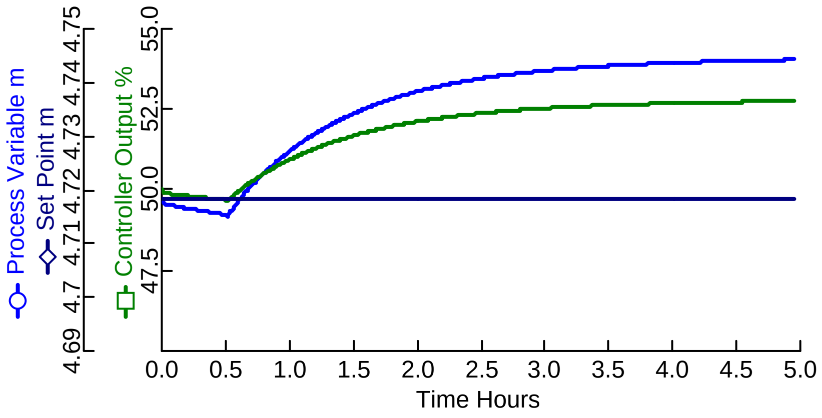


Figure 36 Responses of LC1 controller for increasing 5 % of feed flow rate of conventional distillation process

For the temperature control of conventional distillation column, the temperature of the reboiler was selected to control by manipulating reboiler duty. Figure 37 shows the responses of TC1 controller which worked well for controlling reboiler temperature. The reboiler temperature can be controlled at 125 °C

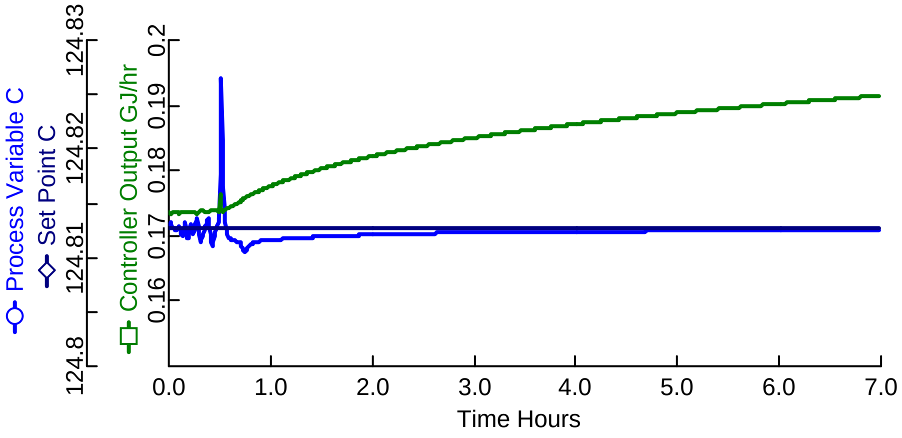


Figure 37 Responses of TC1 controller for increasing 5 % of feed flow rate of conventional distillation process

Pressure of the distillation column is important for safety consideration. PC controller at the top of conventional distillation column is installed to control the pressure of condenser by manipulating condenser duty. The responses in Figure 38 showed the dynamic of pressure when the feed flow rate was changed to 5 % of steady-state value. The Condenser pressure was good controlled at nearly 1 bar.

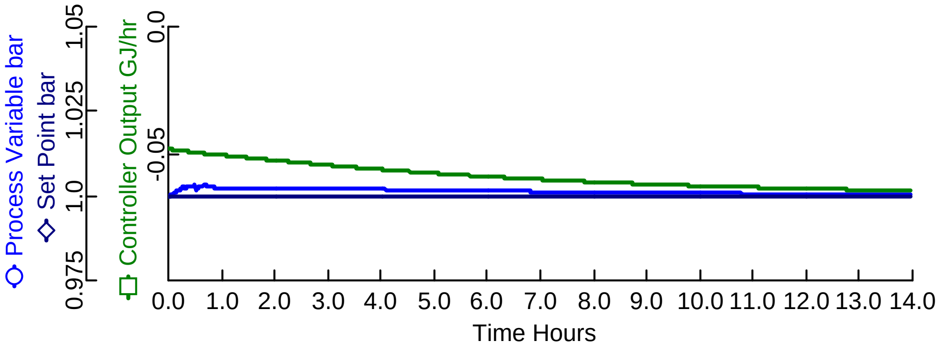


Figure 38 Responses of PC controller for increasing 5 % of feed flow rate of conventional distillation process

For the level control of the decanter, there were two controllers which were installed into the process. L1LC and L2LC controllers were used to control level of biodiesel phase and separated glycerol phase, respectively. Figure 39 and 40 shows the responses of L1LC and L2LC controller to control the level of each phase. The levels of the decanter reached the steady-state value. The slow responses are not a problem because this is not a critical parameter. The levels are increased because of the increasing of products.

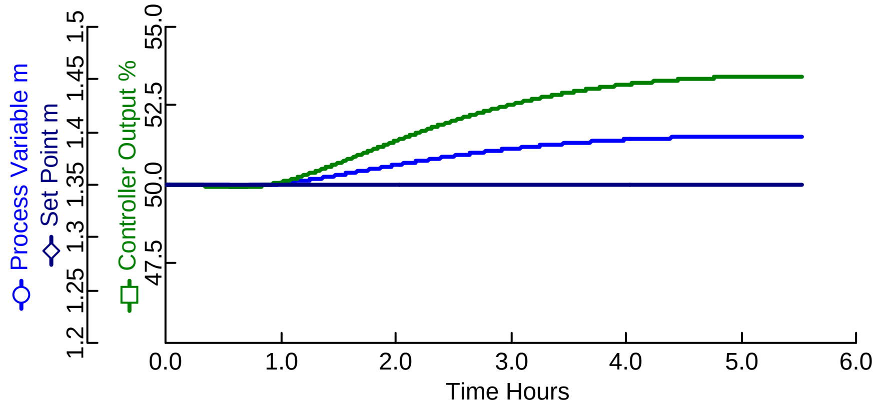


Figure 39 Responses of L1LC controller for increasing 5 % of feed flow rate of conventional distillation process

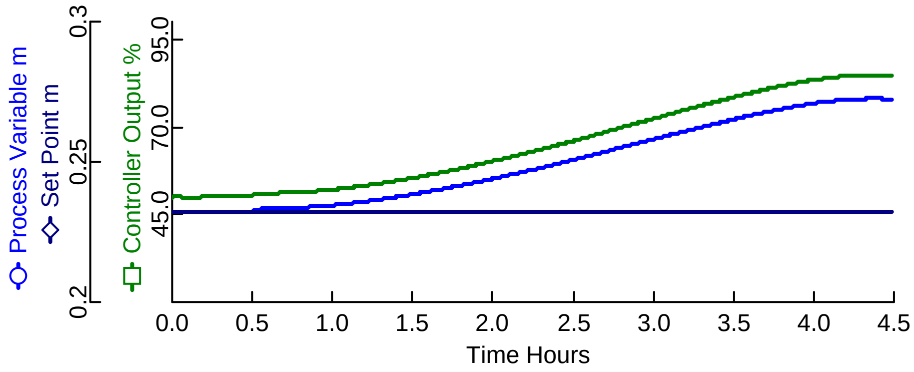


Figure 40 Responses of L2LC controller for increasing 5 % of feed flow rate of conventional distillation process

After changing the reactant flow rate, the productivity of the process and purity of biodiesel product were investigated. The productivity of this biodiesel process was increased from 1001.71 kg/h to 1099.76 kg/h, shown in Figure 41.

For the biodiesel purity, the responses of mass fractions of methyl-palmitate ,methyl-olein and methyl-linolein were shown in Figure 42. The mass fraction of biodiesel product is the sum of methyl-palmitate ,methyl-olein and methyl-linolein. The total mass fraction of biodiesel is not changed when the flow rate of reactant feeds was changed. The biodiesel purity is 99.80 wt% that slightly decreased from the original steady-state value (99.82 %wt). From the results in Figure 42, the designed control system of this process by using plantwide concept of Luyben works well for productivity of the process and purity of biodiesel product

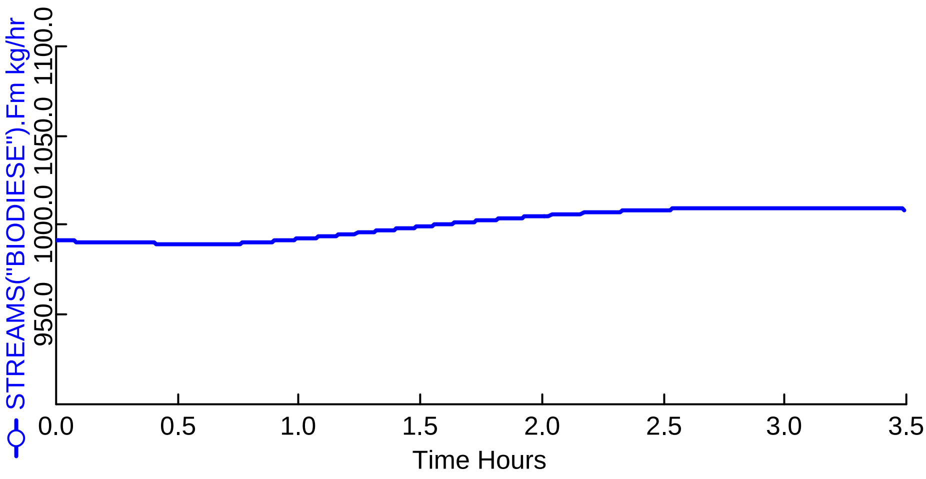


Figure 41 Responses of biodiesel flow rate for increasing 5 % of feed flow rate of conventional distillation process

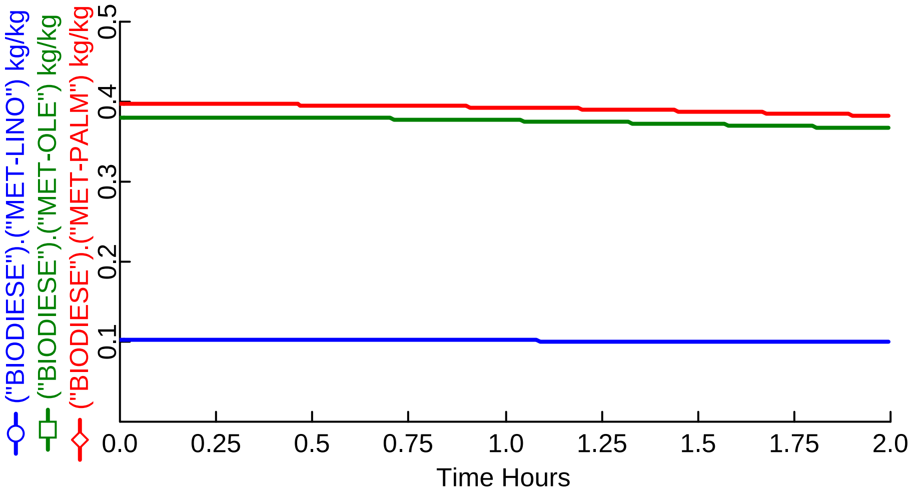
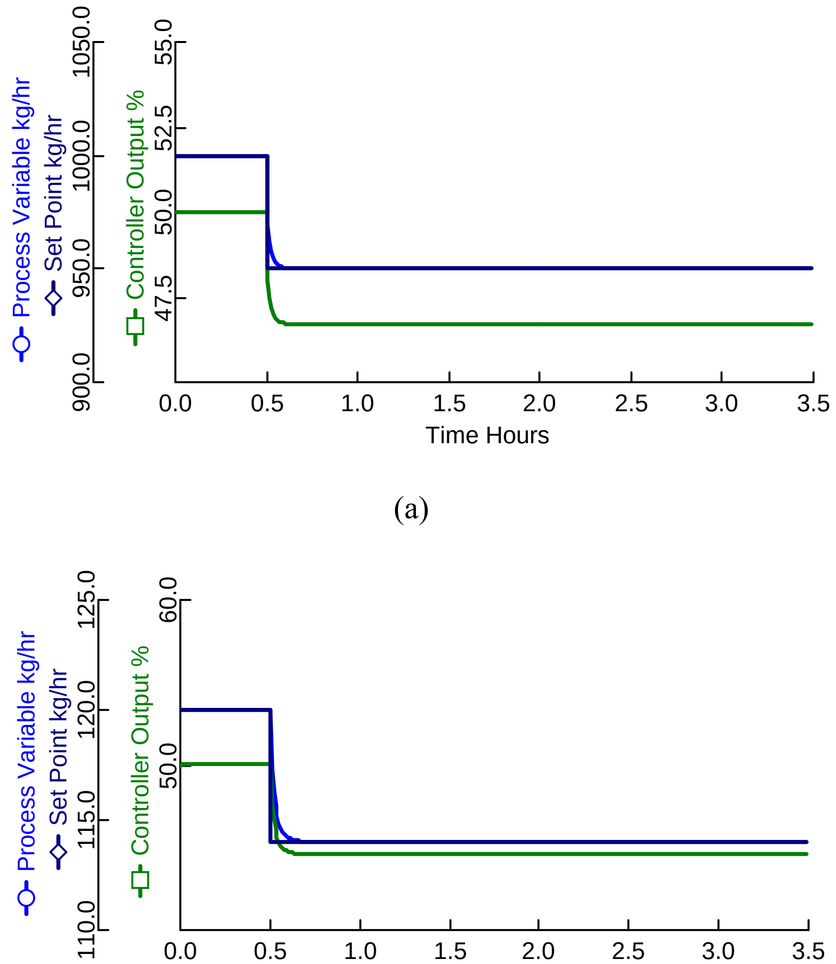


Figure 42 Responses of biodiesel mass fraction for increasing 5 % of feed flow rate of conventional distillation process

2.2.2.2 Decreasing 5 % of reactant feed

The controllability of the conventional distillation process is also tested by decreasing reactant flow rate about 5 % of the original flow rate. Figure 43 exhibits the changing of flow rate at 0.5 hour of simulation time from 120 kg/h of methanol, and 1000 kg/h of oil to 114 kg/h of methanol and 950 kg/h of oil.



(a)

(b)

Figure 43 Responses of FC1, FC2 controller for decreasing 5 % of feed flow rate of conventional distillation process (a) FC1 (b) FC2

The reactor temperature, the TC1 controller adjusted the heat duty of the reactor to the higher value to reach the 65 °C of temperature setpoint. The temperature controller worked well for this process show in Figure 44. For the LC1 which is used to control the level of the reactor, the responses in the Figure 45 showed the increasing of reactor level from the original setpoint at 3.86 m to be the new setpoint at 3.92 m. The slow response of level control is not a problem because it does not affect to product purity or productivity.

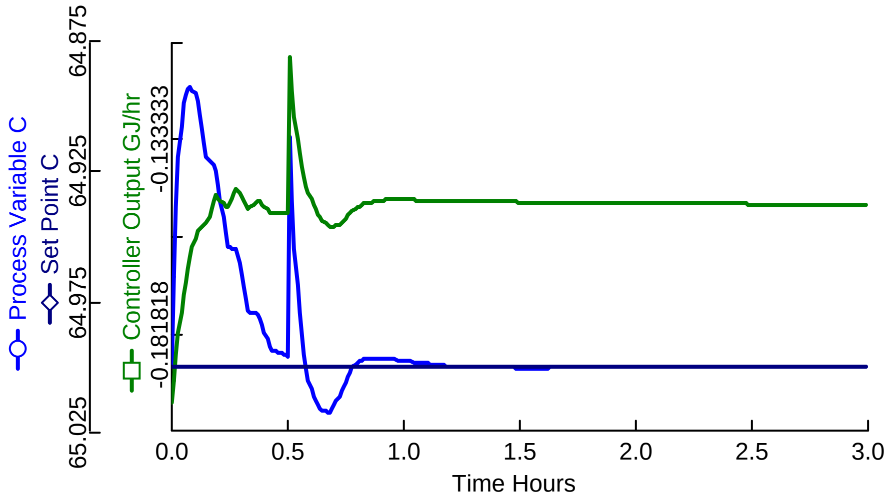


Figure 44 Response of ReactorTC controller for decreasing 5 % of feed flow rate of conventional distillation process

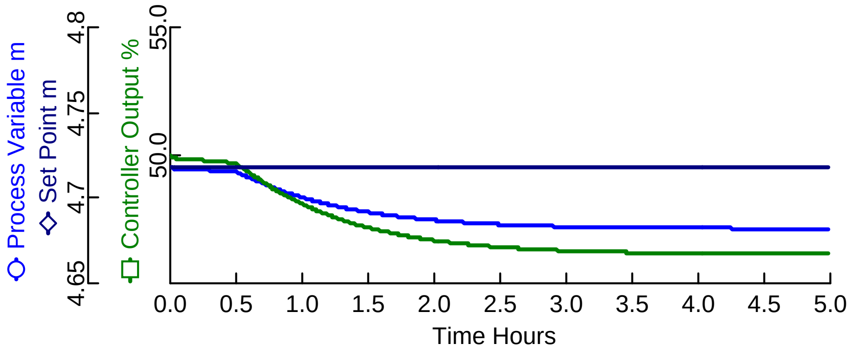


Figure 45 Response of LC1 controller for decreasing 5 % of feed flow rate of conventional distillation process

The temperature of the reboiler is also increased when the reactant flow rate is decreased. This because the original heat duty is too much for maintaining the temperature of reboiler at125°C. However, TC1 controller can be used to control the temperature by adjusting the specific heat duty of reboiler. The responses of TC1 are shown in Figure 46.

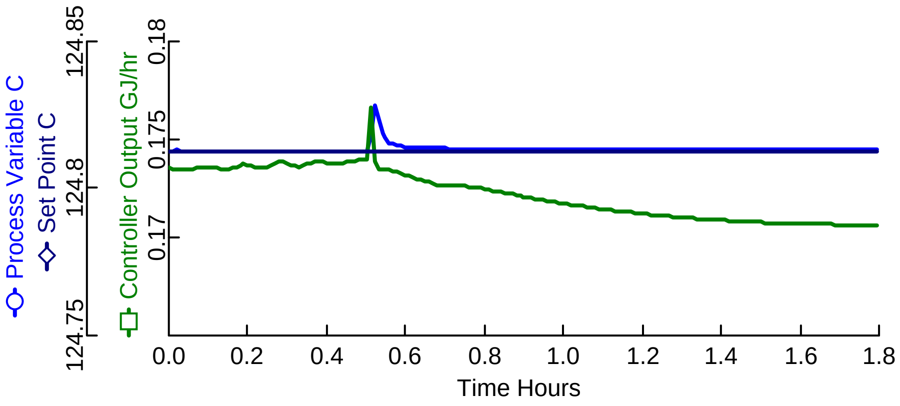


Figure 46 Responses of TC1 controller for decreasing 10 % of feed flow rate of reactive distillation process

PC controller was installed to control the pressure of the column by control the temperature of condenser. Condenser duty was the manipulated variable for controlling the pressure of condenser. The responses are shown in Figure 47. This controller is work well for this job.

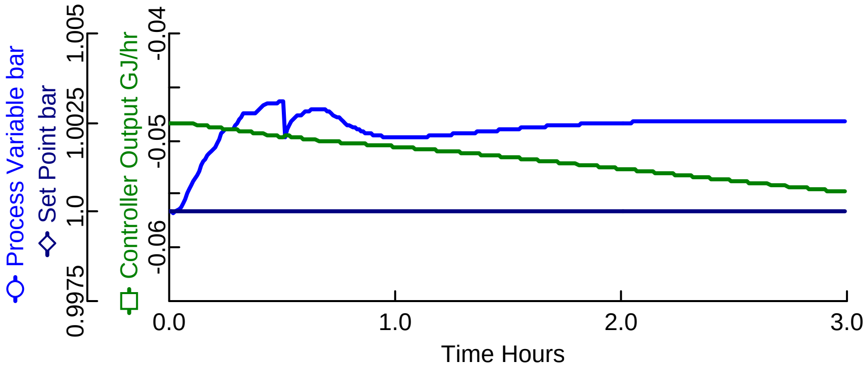


Figure 47 Responses of PC controller for decreasing 5 % of feed flow rate of conventional distillation process

L1LC and L2LC controllers are used to controller the level of the biodiesel phase and the glycerol phase of the decanter. Figure 48 and 49 exhibits the responses of these two controllers. The levels of the decanter are decreased when the reactant flow rate is deceased. However, the levels can reach the new steady-state values.

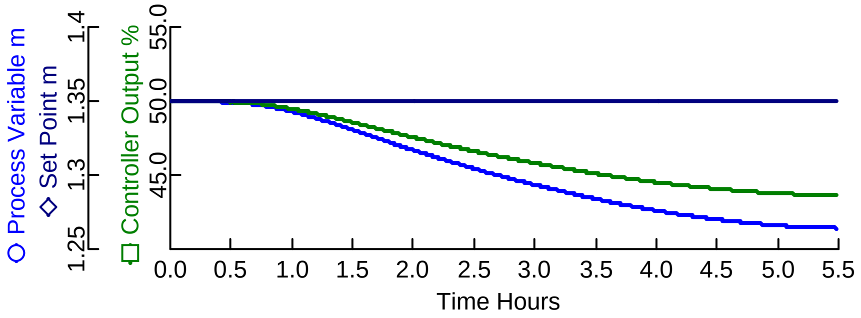


Figure 48 Responses of L1LC controller for decreasing 5 % of feed flow rate of conventional distillation process

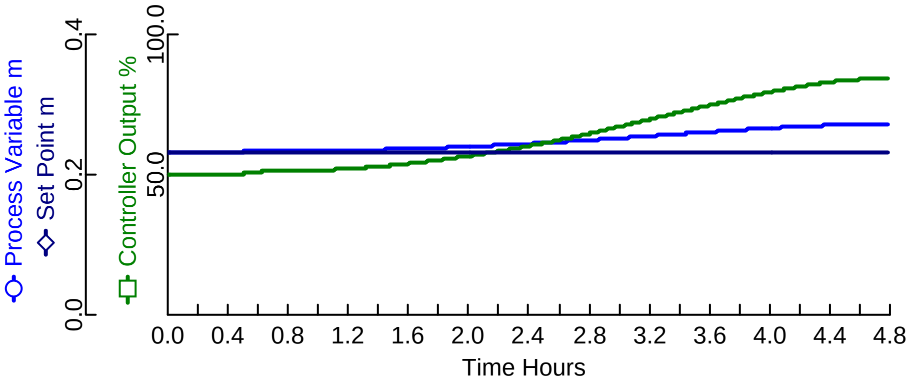


Figure 49 Responses of L2LC controller for decreasing 5 % of feed flow rate of conventional distillation process

For the responses of the flow rate of biodiesel product and its purity, they are shown in Figures 50 and 51, respectively. The biodiesel productivity is decreased to 953.352 kg/h from 999.886 kg/h when the reactant flow rate is decreased about 5 % of original flow rate. For the purity of biodiesel product, it was found that the control system worked well for controlling the purity of biodiesel product when the reactant flow rate was decreased. As the reactant flow rate was decreased, the purity of biodiesel product is about 99.53 wt%.

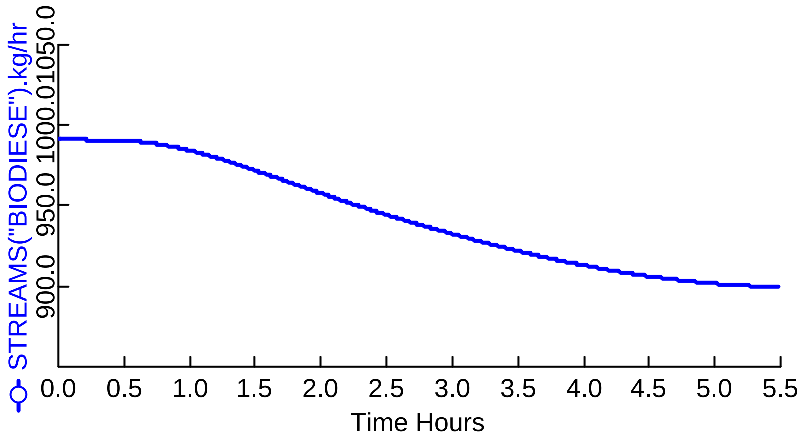


Figure 50 Responses of biodiesel flow rate for decreasing 5 % of feed flow rate of conventional distillation process

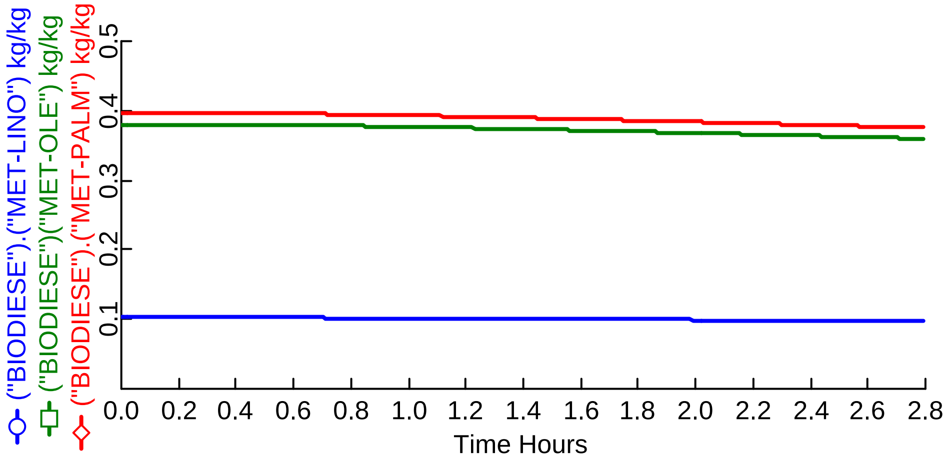


Figure 51 Responses of biodiesel mass fraction for increasing 5 % of feed flow rate of conventional distillation process

As the previous topic, the controllability of reactive distillation process was tested and the results showed the good controllability in both of increasing and decreasing of reactant flow rate. However, if the plantwide concept is not used to design the control system, the control of individual unit will be considered.

The configuration of the control system which is designed by individual unit design will lead to uncontrollable of the process because this process has a recycle stream. Generally, the distillate stream of the distillation column is selected to be the manipulated variable for controlling level of condenser. However, the distillate stream in this work is a recycle stream. This is possible to be a snowball effect if the individual unit design is considered. Therefore, the plantwide concept is necessary for this work.

2.3. The relative gain array

In this work, the first step considers the controlled variable and the manipulated variable of the reactive distillation process. The reactive distillation was focus to find calculate gain values. The relative gain array was shown in Table 13. From Table 13 considering the relative gain array of each loop controllers were suitable for the manipulated variables and the controlled variable. Moreover the reactive distillation process was no decoupling between each loop controller.

Table 13 The relative gain array of the reactive distillation.

	FC2	FC1	TC1	L2LC	PC1	LC1	L1LC
FC2	**0.5283**	0.0323	-0.0028	-0.0001	0.4431	-0.0007	-0.0002
FC1	0.0518	**1.7514**	0.0041	0.0001	-0.8099	0.0022	0.0002
TC1	-0.0875	0.1457	**1.1112**	-0.0001	-0.168	-0.0011	-0.0002
L2LC	0.0049	-0.0206	-0.0008	**0.8895**	0.0202	0.1068	0.0000
PC1	0.497	-0.8879	-0.1078	0.0107	**1.5061**	-0.0238	0.0056
LC1	0.0042	-0.0104	-0.0036	0.088	0.0025	**0.8216**	0.0977
L1LC	0.0013	-0.0105	-0.0003	0.0118	0.0059	0.0951	**0.8967**

3. Design simulation by ASPEN ICARUS

This research studies the biodiesel production in two processes these are the conventional distillation and the reactive distillation. These processes use transesterification method to produce biodiesel, which the transesterification reaction need catalyst to reduce active energy. This study has transesterification with two type catalysts; there are two kind of catalysts which are homogeneous catalyst (NaOH) and heterogeneous catalyst (SrO). So the biodiesel production, there are four case studies. These are conventional distillation with homogeneous and heterogeneous catalyst and reactive distillation with homogeneous and heterogeneous catalyst. The four case studies used ASPEN ICARUS to design equipment for biodiesel production plant. Design equipments shown in Appendix B and Table 14 shown the production cost of each process.

Table 14 Production cost of each process

	conventional homogeneous	conventional heterogeneous	reactive homogeneous	reactive heterogeneous
Total Project Capital Cost(USD)	3,791,478.57	2,711,535.99	2,848,273.15	2,467,157.28
Total Operating Cost (USD/Year)	1,269,728.18	898,916.86	902,039.70	884,398.77
Total Utilities Cost (USD/Year)	91,024.24	54,110.43	54,991.95	39,272.75
Desired Rate of Return (Percent/Year)	20	20	20	20

CONCLUSION

In this work, the simulation and design of biodiesel production was studied in two scenarios: the conventional distillation and the reactive distillation. This biodiesel processing was based on transesterification reaction. Basically, the transesterification reaction needs such a catalyst to reduce activation energy. In this study we needed two types of catalyst: sodium hydroxide for homogeneous reaction and strontium oxide for heterogeneous reaction. The reaction rate is important for the simulation.

The steady state simulation started by adding the component of triglyceride. GaussViewW optimized the structure of tri-di-mono palmitate, tri-di mono olein, and tri-di-mono linooleate. The molecular structure was created and imported in mole file in order to estimate the missing parameters by Aspen Plus except the surface tensions of tripalmitate, trilinolein and triolein added in databank for heterogeneous transesterification reaction. The thermodynamic property used NRTL (non-random two-liquid). The purity of biodiesel from conventional distillation with sodium hydroxide was 99.45. The purity of biodiesel from conventional distillation with strontium oxide was 95.21. The result of conventional distillation with sodium hydroxide was better than with strontium oxide, although the NaOH needed more water for washing. The purity of biodiesel from reactive distillation with strontium oxide was 99.52. The purity of biodiesel from reactive distillation with sodium hydroxide was 99.87. The reactive distillation was better than conventional distillation. Then the steady state was exported to Aspen Dynamic to control the process and sent to ASPEN ICARUS to design the equipment.

The control systems for biodiesel processes were designed by using the concept of plant-wide control. The designed control systems by using the plant-wide concept were installed in dynamic part. The feed flow rate of oil and feed flow rate of methanol reactants were changed ± 5 % to check the performance of the control system. The controller could handle the process. The designed equipment from ASPEN ICARUSwas acceptable. Total operating costs of the conventional process with two different catalysts (NaOH and SrO) were 1,269,728.18 and 898,916.86

USD/year. Total operating costs of reactive distillation process with two different catalysts (NaOH and SrO) were 902,039.70 and 884,398.77 USD/year. The operating cost of biodiesel production with sodium hydroxide was more expensive than biodiesel produced with strontium oxide.

RECOMMENDATIONS

1. In addition, the effects of reactive distillation processing on environmental should be investigated. The Life Cycle Assessment (LCA) is introduced to indicate the correlation of environmental impact and to have a suitable management process in order to reduce the hazardous effect to humans and the environment.

2. The heat integration of process can be determined by computing the minimum usage of heating and cooling utilities. Moreover, the number of heat exchanges can be reduced by breaking the heat loops. These calculations can be performed by ASPEN PINCH.

3. In this research, only controllability of feed disturbances was considered. The plantwide process control should also investigate to provide an economic advantage by enabling closer operation to optimization constraints, decreasing the number of shut-downs and by reducing the amount of off-specification products.

4. This work used the general plantwide concept of Luyben. The result from Luyben concept should be compared to other plantwide concepts such as the text book of Erickson (1999).

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APPENDICES

APPENDIX A

Sensitivity Analysis

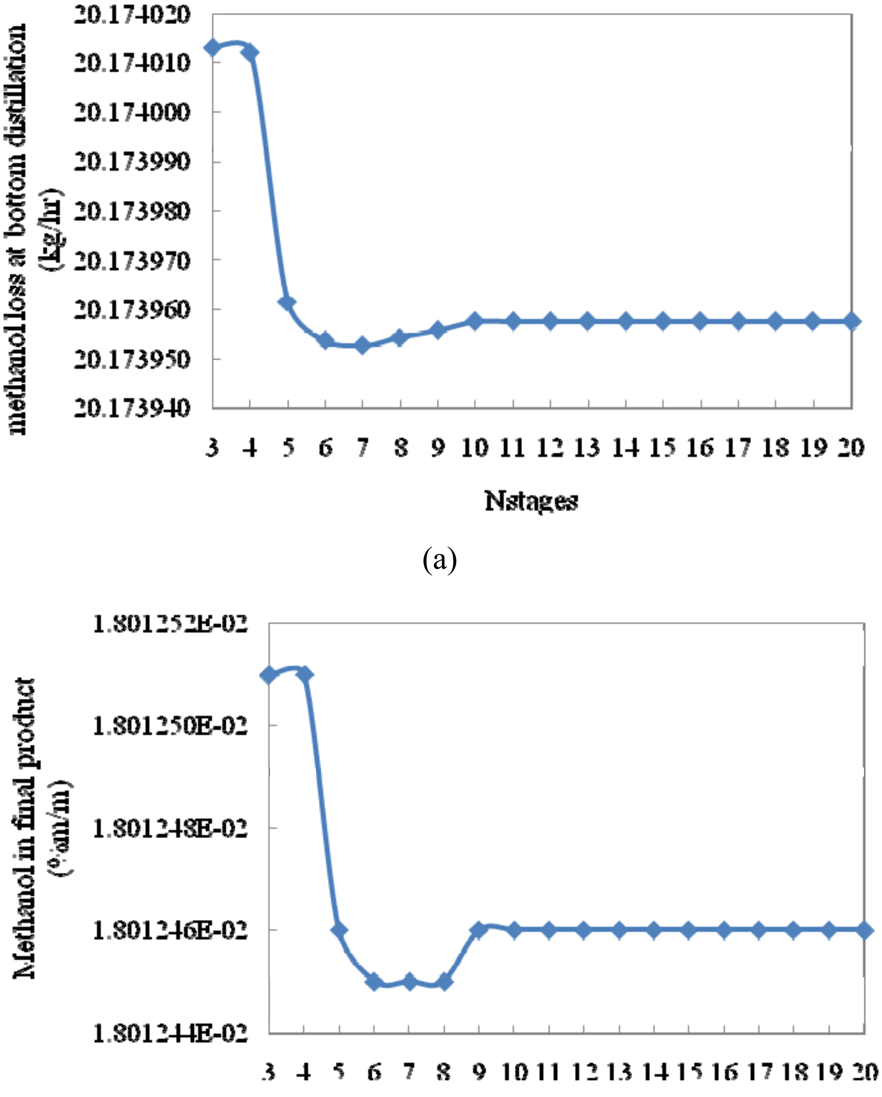
APPENDIX A SENSITIVITY ANALYSIS

A. Sensitivity Analysis of Conventional Configuration

The new steady-state simulation of the conventional distillation process with heterogeneous catalyst was performed in this task. All of the doubtful points were solved and the new operating condition was found. The new representative oil namely Palmitic acid and Linoleic acid were added, the recycle stream was tear and the initial data of the recycle stream was input Because of adding new reactant, the operating condition may be changed. So, the sensitivity analysis is necessary to use as a tool for finding the new operating condition.

There were some unit operations which the new operating condition must be investigated by sensitivity analysis. First is the configuration and operating condition of the distillation column. Generally, the optimal configuration and operating condition of distillation column can be found by considering economics. However, in this work, economics is not in the scope of work. Therefore, the optimal configuration and operating condition were considered the performance of the methanol removal and consumption of the reboiler duty. For selecting the configuration, the number of stages and feed stages was varied to investigate the performance of methanol recovery and methanol impurity in the final product. The results of sensitivity analysis show in Figure A.1. Increasing the number of stages lead to the decreasing of the methanol loss. So, methanol in the final product is also decreased. However, the investment cost will increase when the number of stages increases. Thus, the 10 stage configuration was chosen. Then the feed stage was studied and the results were shown in Figure A.2. The optimal feed stage that makes the highest methanol recovery is 3. For the operating condition of the distillation column, reflux ratio and distillation rate were selected to be performed sensitivity analysis. Heat duty of reboiler and mass fraction of the methanol impurity in the final product were considered. The sensitivity results of reflux ratio and distillation rate were shown in Figure A.3 and A.4, respectively. The chosen value was 1 for reflux ratio.

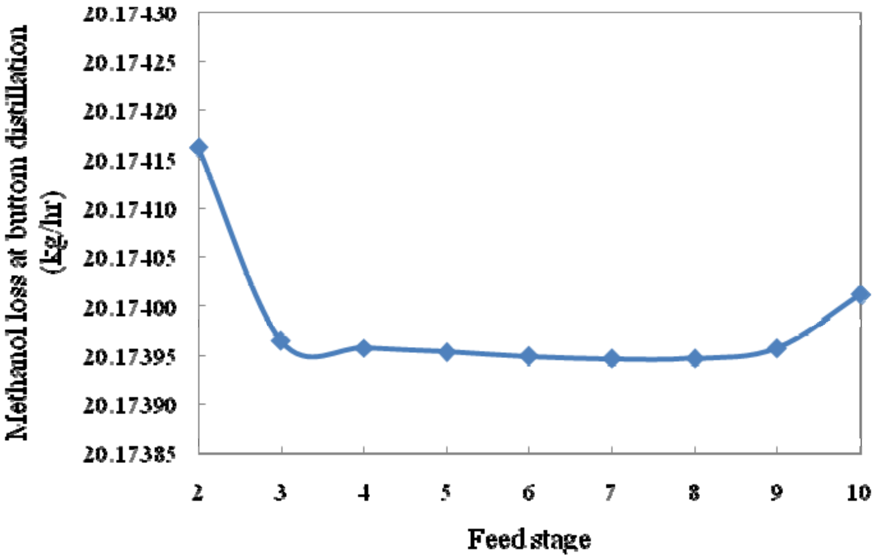
For the temperature which was used in the decanter, the sensitivity analysis was applied to investigate the effect of the temperature to the mass fraction of glycerol. From sensitivity analysis, shown in the Figure A.5, the temperature slightly affects to the mass fraction of the impurities. So, the temperature of the decanters was set to be 35 °C for saving investment and operating cost. The Figure A.6 shown the effect of bed void to produce biodiesel. The chosen value was 0.65.



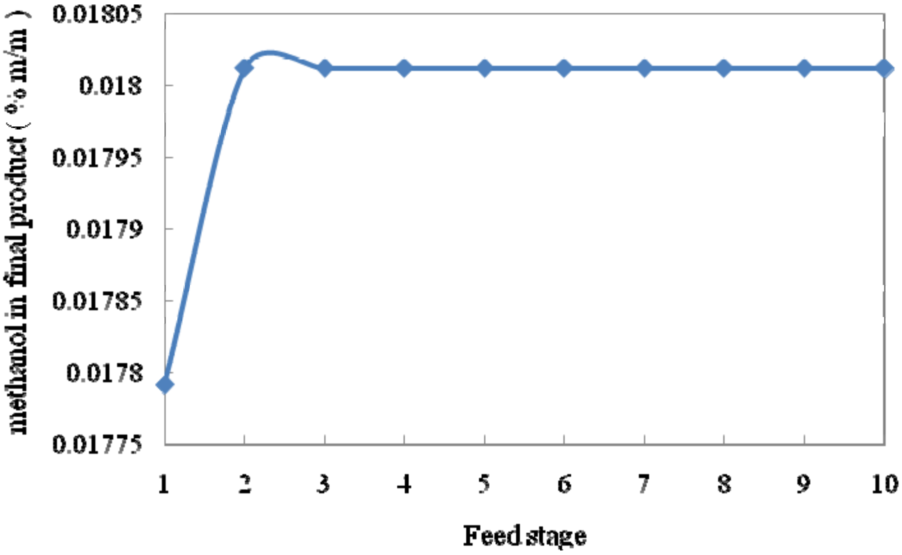
(a)

(b)

Appendix Figures A1 (a) Sensitivity analysis of number of stages to methanol loss in distillation column (b) Sensitivity analysis of number of stages to methanol in final product.

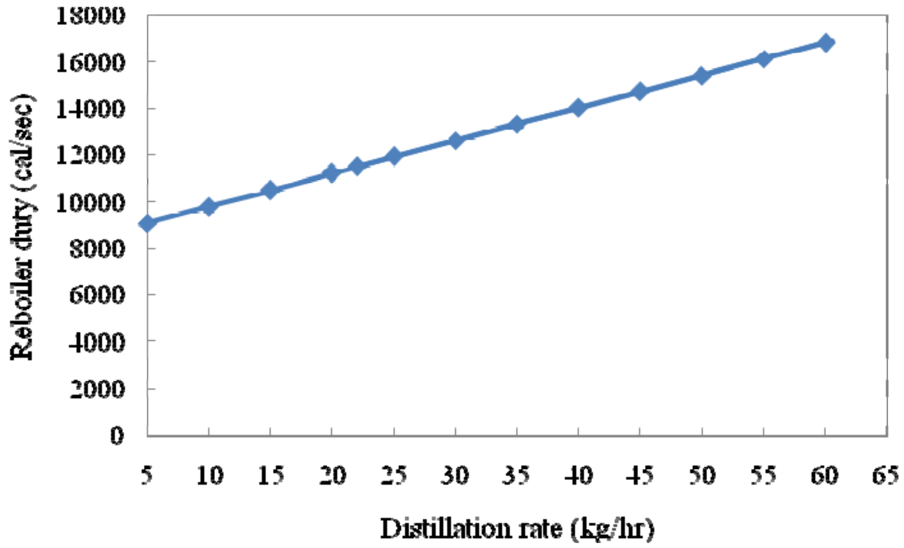


(a)

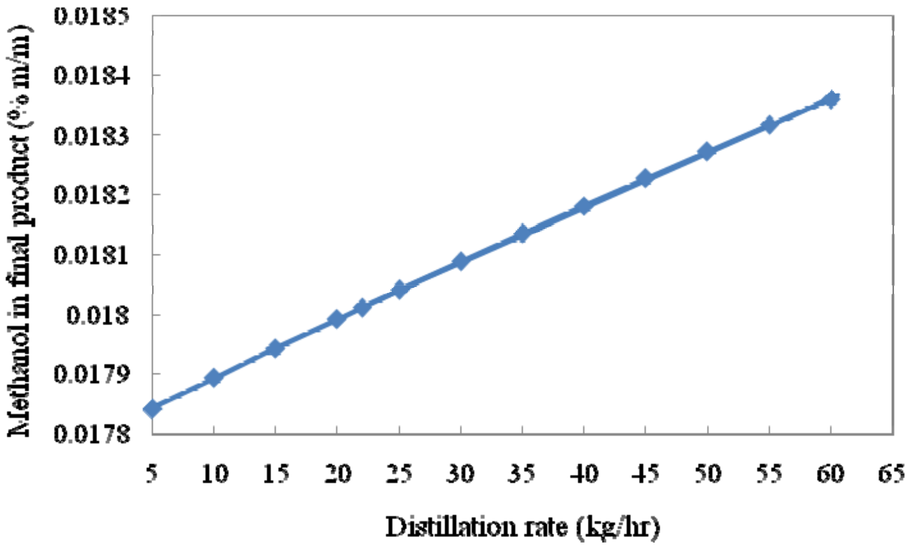


(b)

Appendix Figures A2 (a) Sensitivity analysis of feed stage to methanol loss in distillation column (b) Sensitivity analysis of feed stage to methanol in final product.

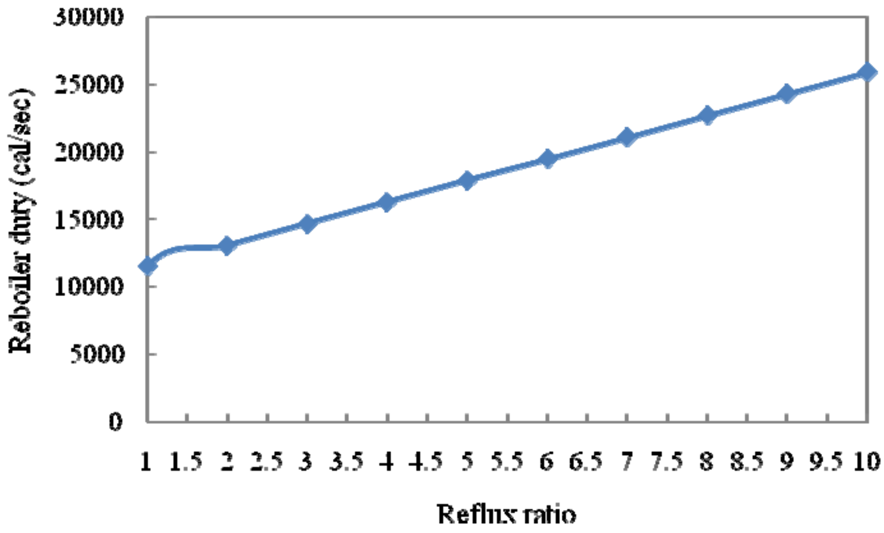


(a)

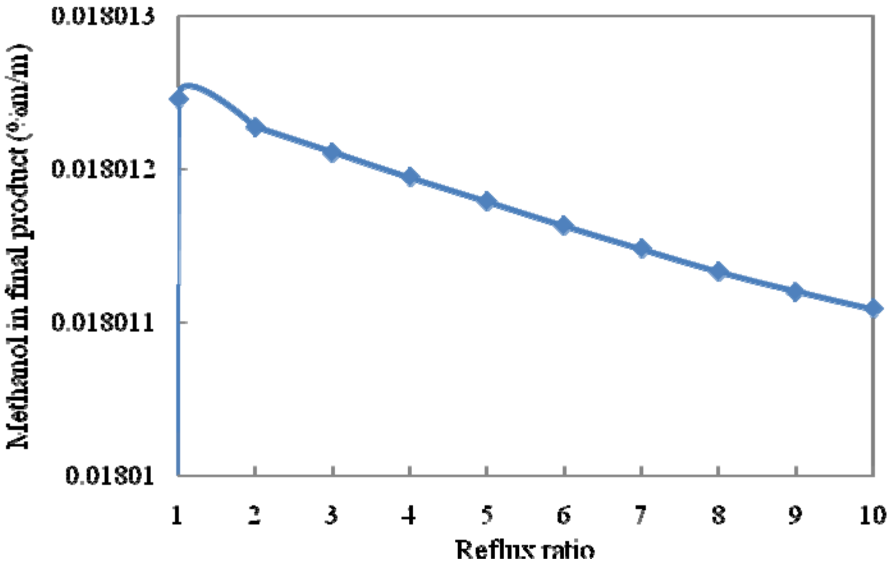


(b)

Appendix Figure A3 (a) Sensitivity analysis of distillation rate to reboiler duty of distillation column (b) Sensitivity analysis of distillation rate to methanol in final product.

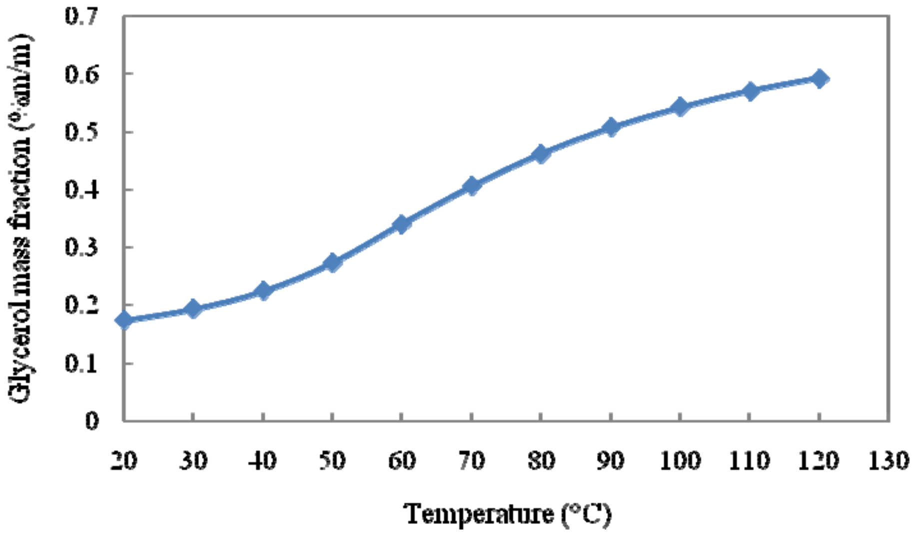


(a)

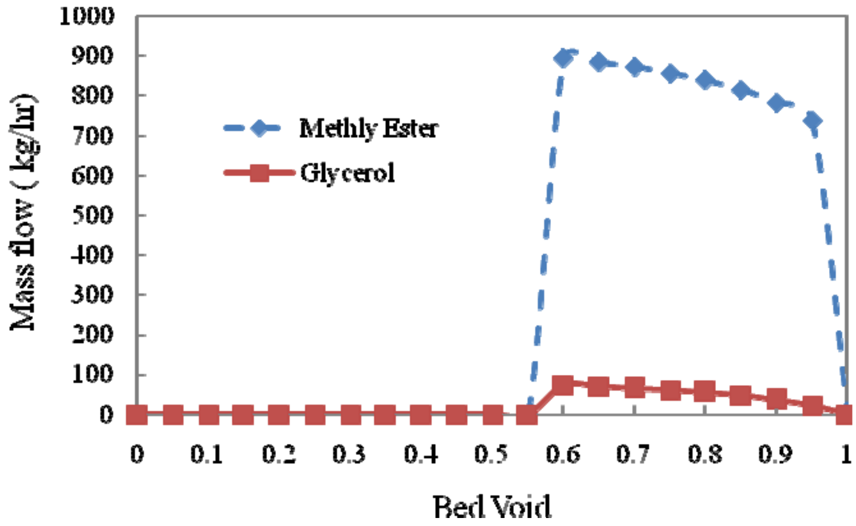


(b)

Appendix Figure A4 (a) Sensitivity analysis of reflux ratio to reboiler duty of distillation column (b) Sensitivity analysis of reflux ratio to methanol in final product.



Appendix Figure A5 Sensitivity analysis of the decanter



Appendix Figure A6 Sensitivity analysis of bed void to methyl ester of reactor.

APPENDIX B

Design Equipment

Appendix Table B1 Sizing of column condenser

Column condenser	Units	Conventional Homogeneous	Conventional Heterogeneous
Liquid volume	GALLONS	475.921	475.921
Vessel diameter	FEET	3.0000	3.0000
Vessel tangent to tangent length	FEET	9.0000	9.0000
Design temperature	DEG F	250.000	250.000
Design gauge pressure	PSIG	14.100	14.100
Vacuum design gauge pressure	PSIG	-14.6960	-14.6960
Base material thickness	INCHES	0.3125	0.3125
Total weight	LBS	2700	2700

Appendix Table B2 Sizing of column reboiler

Column reboiler	Units	Conventional Homogeneous	Conventional Heterogeneous
Heat transfer area	SF	11.000	34.657
Shell design gauge pressure	PSIG	68.637	68.637
Shell design temperature	DEG F	287.594	365.650
Shell diameter	INCHES	6.0000	9.0000
Shell length	FEET	13.000	13.000
Tube port diameter	INCHES	4.0000	6.0000
Tube design gauge pressure	PSIG	110.304	110.304
Tube design temperature	DEG F	377.800	377.800
Tube outside diameter	INCHES	1.0000	1.0000
Tube length extended	FEET	20.000	20.000
Total weight	LBS	640	1000

Appendix Table B3 Sizing of column reflux pump

Column reflux pump	Units	Conventional Homogeneous	Conventional Heterogeneous
Liquid flow rate	GPM	0.5908	0.1938
Fluid head	FEET	225.000	225.000
Design temperature	DEG F	250.000	250.000
Speed	RPM	3600.000	3600.000
Driver power	HP	0.1250	0.1250
Design gauge pressure	PSIG	14.100	14.100
Driver type	-	MOTOR	MOTOR
Total weight	LBS	200	200
Fluid viscosity	CPOISE	-	0.3418

Appendix Table B4 Sizing of column tray tower

Column tray tower	Units	Conventional Homogeneous	Conventional Heterogeneous
Tray type	SF	SIEVE	SIEVE
Number of trays	PSIG	12	12
Vessel diameter	DEG F	1.5000	1.5000
Vessel tangent to tangent height	INCHES	36.000	36.000
Design temperature	FEET	287.594	365.650
Design gauge pressure	INCHES	35.304	35.304
Tray spacing	PSIG	24.000	24.000
Tray thickness	DEG F	0.1875	0.1875
Base material thickness	INCHES	0.3750	0.3750
Total weight	FEET	4700	4700

Appendix Table B5 Sizing of decanter for four process

Decanter	Units	ALL
Liquid volume	GPM	634.561
Vessel diameter	FEET	3.0000
Vessel tangent to tangent length	DEG F	12.000
Total weight	LBS	2600

Appendix Table B6 Sizing of the reactive distillation condenser

reactive distillation condenser	Units	Reactive Homogeneous	Reactive Heterogeneous
Liquid volume	GALLONS	475.921	475.921
Vessel diameter	FEET	3.0000	3.0000
Vessel tangent to tangent length	FEET	9.0000	9.0000
Design temperature	DEG F	298.662	298.662
Design gauge pressure	PSIG	14.100	14.100
Vacuum design gauge pressure	PSIG	-14.6960	-14.6960
Base material thickness	INCHES	0.3125	0.3125
Total weight	LBS	2700	2700

Appendix Table B7 Sizing of reactive distillation pump

Column reflux pump	Units	Reactive Homogeneous	Reactive Heterogeneous
Liquid flow rate	GPM	0.4793	0.4793
Fluid head	FEET	225.000	225.000
Design temperature	DEG F	298.662	298.662
Speed	RPM	3600.000	3600.000
Driver power	HP	0.1250	0.1250
Design gauge pressure	PSIG	14.100	14.100
Driver type		MOTOR	MOTOR
Total weight	LBS	200	200
Fluid viscosity	CPOISE	-	8.7752

Appendix Table B8 Sizing of reactive distillation reboiler

reactive distillation reboiler	Units	Reactive Homogeneous	Reactive Heterogeneous
Heat transfer area	SF	21.000	7.000
Shell design gauge pressure	PSIG	68.637	68.637
Shell design temperature	DEG F	299.816	363.671
Shell diameter	INCHES	9.0000	4.0000
Shell length	FEET	13.000	13.000
Tube port diameter	INCHES	6.0000	3.0000
Tube design gauge pressure	PSIG	110.304	110.304
Tube design temperature	DEG F	377.800	377.800
Tube outside diameter	INCHES	1.0000	1.0000
Tube length extended	FEET	20.000	20.000
Total weight	LBS	920	390

Appendix Table B9 Sizing of reactive distillation tower

reactive distillation tower	Units	Reactive Homogeneous	Reactive Heterogeneous
Tray type		SIEVE	SIEVE
Number of trays		13	12
Vessel diameter	FEET	2.000	1.5000
Vessel tangent to tangent height	FEET	38.000	36.000
Design temperature	DEG F	299.816	584.796
Design gauge pressure	PSIG	35.304	35.304
Tray spacing	INCHES	24.000	24.000
Tray thickness	INCHES	0.1875	0.1875
Base material thickness	INCHES	0.3125	0.3750
Total weight	LBS	6600	4700

APPENDIX C

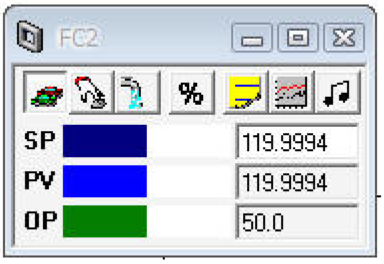
Tuning controller

APPENDIX C TUNING CONTROLLER

C. Tuning controller

In this work the product quality is important. Therefore the control system is set in biodiesel production. The control loops contained temperature, pressure, level and flow control loops. Furthermore the loop controllers must tune to smooth and keep the product quality. The controller tuning procedures are shown as follow;

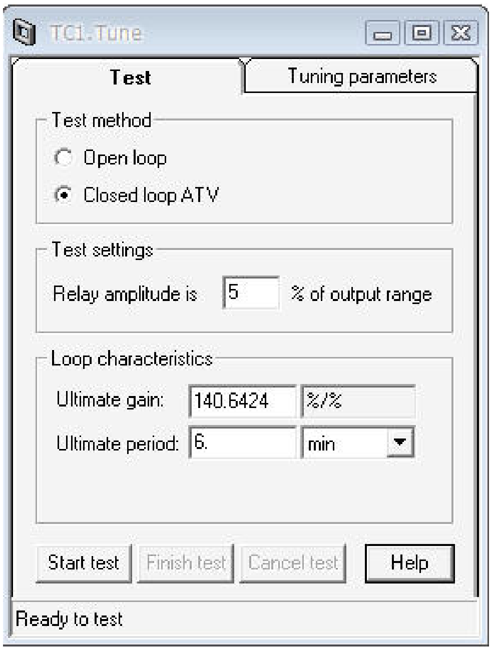
1. Click at PID controller, the PID form appeared in Figure C1.



SP 119.9994
PV 119.9994
OP 50.0

Appendix Figures C1 The PID form

2. Then click at seventh button, the tune box appeared in Figure C2. The tune box contained test and tuning parameter button. This work used the close loop to test controller. After that click at start test for a period and click finish button, the ultimate gain and ultimate period results are shown value.



Test method

○ Open loop

● Closed loop ATV

Test settings

Relay amplitude is 5 % of output range

Loop characteristics

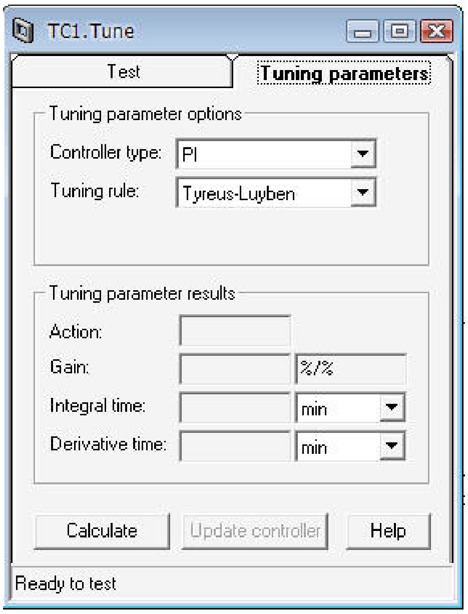
Ultimate gain: 140.6424 %/%

Ultimate period: 6. min

Ready to test

Appendix Figures C2 The tune box

3. Finally click tuning parameter and choose PI at controller type and Tyreus-Luyben at tuning rule. Then click calculate button. The gain and integral time is the result of controller shown in Figure C3.



Tuning parameter options

Controller type: PI

Tuning rule: Tyreus-Luyben

Tuning parameter results

Action:

Gain: %/%

Integral time: min

Derivative time: min

Ready to test

Appendix Figures C3 The tuning parameter box

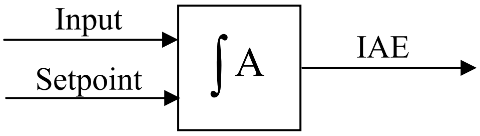
APPENDIX D

IAE

APPENDIX D IAE

D. IAE (Integral absolute error)

IAE calculates the integral of the absolute value of the error between input and a set point value shown as Figure D1. The IAE value shown the control efficiency. If comparison between two control systems. The IAE of control system is lower than others shown the control efficiency is better than the others.



Appendix Figures D1 IAE box

The equation used to calculate the integral of the absolute value of the error

$$\mathrm{IAE} = \int_{0}^{T} \left|\mathrm{e}(t)\right| \, dt$$

Where e = Deviation of the variable from the desired set point

t = Time

IAE = Integral absolute error value

T = Current time

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