THESIS APPROVAL

GRADUATE SCHOOL, KASETSART UNIVERSITY

Master of Engineering (Chemical Engineering)

DEGREE

Chemical Engineering	Chemical Engineering
FIELD	**DEPARTMENT**

TITLE: Design of Human Machine Interface for Chemical Process Safety of Continuous Biodiesel Production

NAME: Mr. Nakkarin Sainyamsatit

THIS THESIS HAS BEEN ACCEPTED BY

THESIS ADVISOR

(Associate Professor Thongchai Srinophakun, Ph.D.)

DEPARTMENT HEAD

(Associate Professor Paisan Kongkachuichay, Ph.D.)

APPROVED BY THE GRADUATE SCHOOL ON _____

DEAN

(Associate Professor Gunjana Theeragool, D.Agr.)

THESIS

DESIGN OF HUMAN MACHINE INTERFACE FOR CHEMICAL PROCESS SAFETY OF CONTINUOUS BIODIESEL PRODUCTION

NAKKARIN SAINYAMSATIT

A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
Master of Engineering (Chemical Engineering)
Graduate School, Kasetsart University
2008

Nakkarin Sainyamsatit 2008: Design of Human Machine Interface for Chemical Process Safety of Continuous Biodiesel Production. Master of Engineering (Chemical Engineering), Major Field: Chemical Engineering, Department of Chemical Engineering. Thesis Advisor: Associate Professor Thongchai Srinophakun, Ph.D. 135 pages.

Integration of human machine interface with a Hazard and Operability (HAZOP) analysis was proposed in this work. This concept potentially leads to the identification of some unexpected deviations and radically decreases the time necessary for the hazard identification process.

Continuous biodiesel production was simulated by ASPEN PLUS version 2006.5. It can be divided into six cases covering three conventional and three reactive distillation cases. In each case, soy bean oil compositions (trioleic, trilinoleic and tripalmatic oils) were varied in order to convert 1000 kg/hr feed to 99 wt % purity of biodiesel. Human machine interface (HMI) was designed to improve these processes by applying the automatic HAZOP analysis. With this approach, users can have sufficient information from simulation to analyze the optimum operation and safety. Severity level has also provided to classify the action in the process. Severity level 1 and 2 concerned to optimum conditions which are 58-64 °C, 50-200 KPa. If the analysis shows severity level 3, the safety instrument system (SIS) will automatically manage the operation in order to reduce/restrain the quantity of damage in this level. This proposed system could minimize the damage and also improve the overall quality of the process.

_____ _____ ___ / ___ / ___

Student's signature Thesis Advisor's signature

ACKNOWLEDGMENTS

I would like to express my sincere gratitude to my advisor, Assoc. Prof. Dr. Thongchai Srinophakun for his encouragement and valuable suggestions to this work. I would like to acknowledge Dr. Veerayut Lertbumrungsuk for helping, suggestions. I would like to pay our gratitude to Department of Chemical Engineering, Faculty of Engineering, Kasetsart University. This thesis was supported by National Center of Excellence for Petroleum, Petrochemicals and Advanced Materials.

Furthermore, I am also grateful to my committees for helpful comments and suggestions. Finally, I would like to express gratitude to my parents, brother, sisters, and my friends for giving me a chance and recommendation with love.

Nakkarin Sainyamsatit

October 2008

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF ABBREVIATIONS

B	=	Biodiesel
$C_{i, k, in}$	=	Average inlet concentration of contaminant k to operation i in ppm.
$C_{i, k, out}$	=	Outlet concentration of contaminant k water leaving operation i in ppm
$C_{i, out}$	=	Outlet concentration of water leaving operation i in ppm
C_o	=	Outlet concentration from regeneration in ppm
D	=	Distillate
DEG	=	Di-ethylene glycol
EO	=	Ethylene oxide
EG	=	Ethylene glycol
EQ	=	Equilibrium
F	=	feed stream, mol s^{-1}
FAME	=	fatty acid methyl ester
H	=	molar enthalpy, J mol^{-1}
K	=	vapor-liquid equilibrium constant, dimensionless
L	=	Liquid flow rate, mol s^{-1}
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
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}

LIST OF ABBREVIATIONS (Continued)

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

Subscripts

i	=	Component index
j	=	Stages index
m	=	reaction index

Superscripts

F	=	feed stream
L	=	liquid-phase
V	=	Vapor-phase

DESIGN OF HUMAN MACHINE INTERFACE FOR CHEMICAL PROCESS SAFETY OF CONTINUOUS BIODIESEL PRODUCTION

INTRODUCTION

There were many kinds of equipment in chemical process plants, and they were usually of complex structures. In the operation of those processes, there also existed many hazardous chemical, and very often the operational conditions go to high pressure and high temperature. Therefore, in many chemical process plants, ensuring plant safety was a important tasks.

Activities for the plant safety, hazard and operability study (HAZOP), had been performed by human experts using various hazard analysis techniques (Center for Chemical Process Safety (CCPS), 1992). However, whatever method was used, there had been no guarantee that all the causes and consequences of possible accidents in process plants might have been found and considered. Even worse, these techniques were well known to be labor- and time-intensive.

Safety assessment was a dimension which needs to be added to the life cycle of safety-critical software. Although safety assessment had been accepted as an important part of the software life cycle, little help was given to engineers about when and how to do it. Safety assessment involved two different activities: hazard identification and hazard analysis. The aim of the former was to identify the potential hazards that may arise from the use of a particular safety-critical system, and their possible causes. The aim of the latter was to quantify the risks that were associated with the identified hazards and to assess whether the risks were acceptable.

The biodiesel process was used to operate with HAZOP analysis. HAZOP analysis was a difficult, labor- and knowledge-intensive technique that could benefit from automation in several ways. An automated HAZOP analysis system would

reduce the time and effort involved in a HAZOP review, make the review more thorough and detailed, minimize or eliminate human errors, facilitate documentation for regulatory compliance and make the study results available on-line. In this work, we attempted to modify conventional HAZOP with automation. The application of the methodology complements the design of a programmable system, not only assesses safety but improves the overall quality of the system.

OBJECTIVES

1. To simulate the results of the conventional and reactive distillation of biodiesel process.

2. To find the effect of parameter to biodiesel process.

3. To construct the convenience module with automatic safety.

Scopes of Work

1. Use ASPEN PLUS version 2006.5 for the conventional and reactive distillation of biodiesel process simulation.

2. Use Genesis 32 version 9 for constructing a user interface.

3. Visual Basic version 6.5 is used to connect the Genesis 32 to ASPEN PLUS 2006.5.

4. Use Safety analysis (HAZOP) to develop the conventional and reactive distillation of biodiesel process.

LITERATURE REVIEW

In the following section, Biodiesel process, Soy bean oil, Transesterification, Reactive distillation, and Safety analysis will be reviewed by divided into 5 parts.

1. Biodiesel production

Biodiesel, an alternative energy, is usually made by a chemical reaction of alcohol and vegetable, animal or waste cooking oils. Biodiesel can be used as a pure fuel or blended with petroleum. Much of the world uses a system known as the "B" factor to state the amount of biodiesel in any fuel mix. The mixing of 20 percent by volume biodiesel with 80 percent by volume petroleum diesel is called B20 and pure biodiesel is referred to as B100. Using biodiesel in a conventional diesel engine reduced unburned hydrocarbons, carbon monoxide, and particulate matter compared to emissions from diesel fuel. This is because burning ancient fossil fuel adds carbon to the atmosphere upsetting the carbon balance, while growing part of our fuel consumes carbon in the growing process and then releases it in combustion.

There are variety of oils can be used to produced biodiesel such as vegetable oil, waste cooking oil and animal fat. Focusing on the vegetable oil, rapeseed and soybean are most commonly used and others are corn, peanut, rapeseed, soybean, sunflower and jatropha. Basically, all vegetable oils and animal fats consist of triglyceride (TG) molecules as shown in Figure 1.

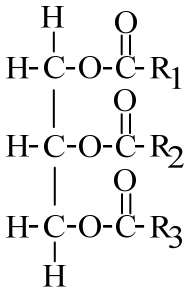


Figure 1 Molecular structure of Triglyceride

R1, R2 and R3 represent the hydrocarbon chain of the fatty acyl groups of the triglyceride. The properties of biodiesel depend on the amount of fatty acid. Fatty acid is designated by two numbers. First is the total number of carbon atom in the fatty acid chain and second is the number of double bounds in the chain. For example, 16:0 has a 16 atom of carbon and zero double bounds in molecule. The fatty acid of vegetable oils is summarized in the Table 1. Natural vegetable oils and animal fats are extracted or pressed to obtain crude oil or fat. These usually contain free fatty acids, phospholipids, sterols, water and other impurities. The free fatty acid and water contents have the significant effect on transesterification reaction of triglycerides with alcohols using alkaline or acid catalysts.

Table 1 Chemical properties of 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

Table 1 (Continued)

	Fatty acid composition, % by weight								
Vegetable Oil	16:0	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3
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	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

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

Source: Demirbas (2002)

The using direct vegetable oil or blending with the oil is not satisfied. The high viscosity, acid composition, free fatty acid content, gum formation due to oxidation and polymerization during storage and combustion, carbon deposits and lubricating may cause some problem (Harwood, 1984). To solve this problem, there are many techniques for converting the vegetable oil to biodiesel such as transesterification, pyrolysis, enzyme lipase, super critical fluid extraction.

In addition, there are common international standard for biodiesel (i.e. EN 14214, ASTM D 6751). The standards of the fuel production should be: (1) complete reaction (2) removal of glycerin (3) removal of catalyst (4) removal alcohol (5) absence of free fatty acid (6) low sulfur content. Table 2 shows the biodiesel specification of EN 14214 and ASTM D 6751.

Table 2 The biodiesel specification between 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	-	-

Table 2 (Continued)

Properties	EN 14214		ASTM D 6751	
	Unit	Limits	Unit	Limits
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/m)	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

Source: Demirbas (2002)

2. Soy bean oil

Biodiesel consists of mono alkyl esters produced from vegetable oils, animal or old cooking fats. Soy biodiesel is fuel alternative produced from soybean oil. Biodiesel contains no petroleum diesel, but it can be blended with petroleum diesel. Since the oil embargo of 1973 by the OPEC a lot of research was done on biodiesel in various universities and government agencies in the USA. Soy biodiesel can be used in diesel engines with little or no modifications. Soy biodiesel is made through a chemical process called transesterification whereby the glycerin is separated from the soybean oil. The process gives two products: methyl esters (the chemical name for biodiesel) and glycerin (used to make soap). Biodiesel is mainly produced and used in

the USA. In 1999 about 0.5 million gallons was produced and this value increased to about 25 million gallons in 2003.

Soy biodiesel is better for the environment because it is made from renewable resources and has lower emissions compared to petroleum diesel. The use of biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide, and soot. The use of biodiesel does not increase the CO_2 level in the atmosphere, since growing soybeans consumes also CO_2. Biodiesel is also more biodegradable than conventional diesel. Studies at the University of Idaho have illustrated biodiesel degraded for 95 percent after 28 days compared to 40 percent for diesel fuel. The composition of Soy bean oil is illustrated in the Table 3. The oleic, linoleic and palmitic acid are the major composition.

Table 3 Fatty acid composition of Soy bean oil

Fatty acid	% Composition
Saturated	
C12 (lauric acid)	Trace
C14 (myristic acid)	Trace
C16 (palmitic acid)	11.0
C18 (stearic acid)	4.1
C20 (arachidic acid)	Trace
Unsaturated	
16:1 (palmitioleic acid)	Trace
18:1 (oleic acid)	22.0
18:2 (linoleic acid)	54.0
18:3 (linolenic acid)	7.5

Sources: Demirbas (2002)

3. Transesterification

The transesterification is the reaction between triglyceride and alcohol to form biodiesel and glycerol by using catalyst. The reaction is shown in the Figure 2.

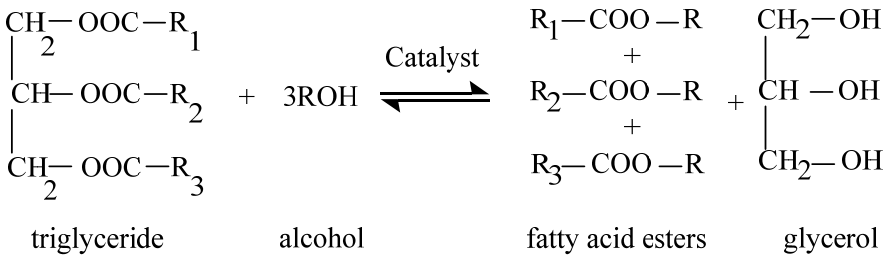


Figure 2 The transesterification reaction

The overall reaction consists of 3 stepwises with intermediate formation of diglycerides (DG) and monoglycerides (MG). The 3 step reactions are shown in the Figure 3. The alcohols that can be used in the tranesterification reaction are methanol, ethanol, propanol and butanol. Methanol is usually used because of low cost and its physical and chemical advantages (polar and shortest chain alcohol).The stecheometric between alcohol and the oil is 3:1. However, an excess of alcohol is usually more in order to shift the reaction to the right hand side.

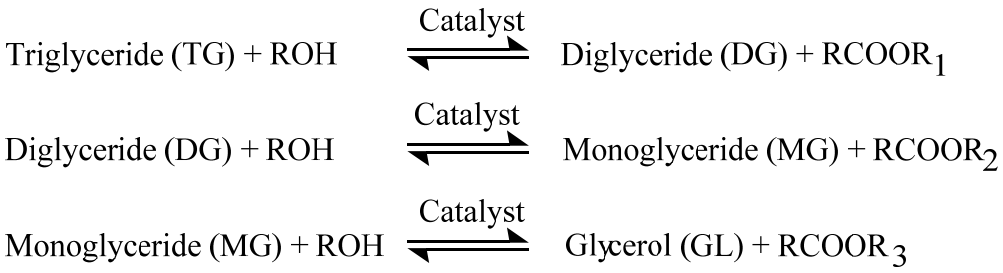


Figure 3 Three step of transesterification reaction

The mechanism of alkali catalyst transesterification with vegetable oil (Schuchardt *et al.*, 1997) is shown in the Figure 4. There are consists of three steps. The first step is an attack on the carbonyl carbon atom by the methoxide ion ($CH3O^-$) to form a tetrahedral intermediate. In the second step, the tetrahedral intermediate reacts with an alcohol (methanol) to regenerate the anion of the alcohol. In the last step, rearrangement of the tetrahedral intermediate results in the formation of a fatty acid ester and a diglyceride. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol.

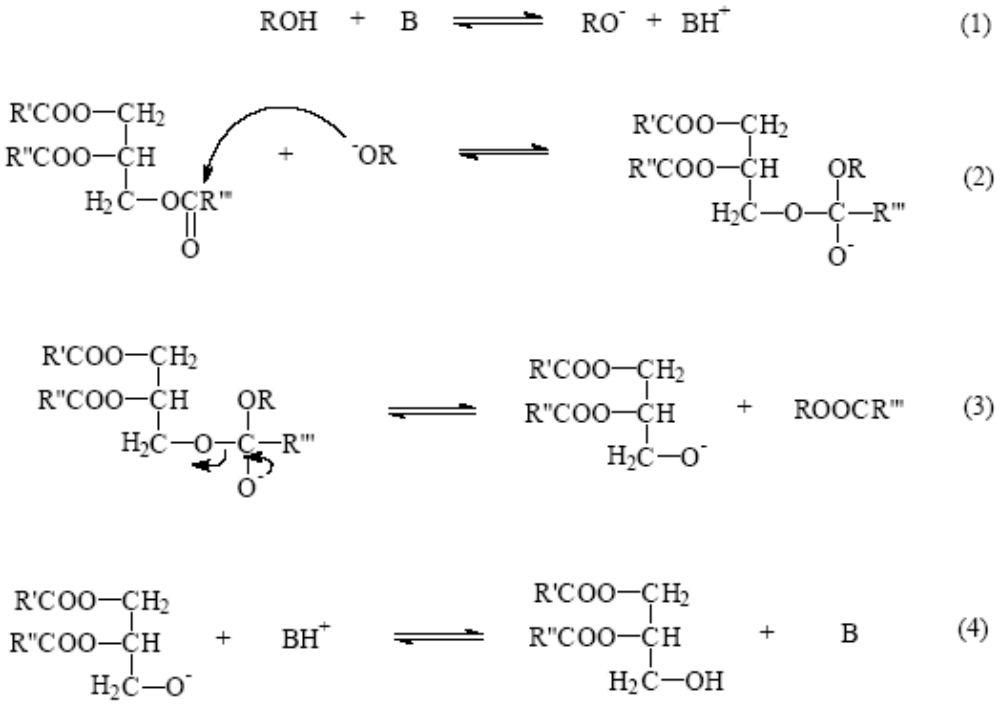


Figure 4 The mechanism of alkali catalyst transesterification

The transesterification reaction can be catalyzed by both homogeneous and heterogeneous catalyst. The advantages and disadvantages of each catalyst are described below.

Firstly, the common homogeneous are acid and alkali catalyst. Using alkali catalysts, the reaction is fast, high conversion and less corrosive than acid compound. However, hydroxide ion (OH^-) of alkali catalyst can react with the free fatty acid to produce soap. The soap formation is an undesirable side-reaction, because it partially

consumes the catalyst, decreases the biodiesel yield and complicates the separation and purification steps (Vicent *et al.*, 2003). The removal of these catalysts is technically difficult and brings extra cost to the final product. In addition, the difficulty for recycling and the generation of large waste amounts make the traditional catalysts less favorable. The soap formation can be suppressed by using acid catalyst because there is no hydroxide ion. The acid reacts with free fatty acid to produce fatty acid esters, increasing the biodiesel yield. Nevertheless, the reaction of acid catalyst is lower than the acid and also needs more extreme temperature and pressure conditions.

Although chemical transesterification using alkali catalyst process gives high conversion in small time. But it is difficult to removed glycerin and requires the waste water treatment. Therefore, using lipase as catalyst can overcome these problems. In addition, there are many advantages such as (1) possibility of regeneration and reuse (2) lower temperature of reaction (3) higher biodiesel. However, production cost of lipase catalyst is expensively than alkaline one.

Furthermore, other technique to produce biodiesel is transesterification using supercritical fluids. Saka and Kusdiana (2001) studied biodiesel production in super critical methanol. They demonstrated that preheating to 350 °C and treatment for 240 s during the reaction. The biodiesel has a higher than conventional method using base catalyst. However, the supercritical methanol method requires a high temperature of 350 °C and a pressure of 45 MPa, and in addition, large amount of methanol is necessary. The comparison of the advantages and disadvantages of each technique are summarized in the Table 4.

Table 4 Comparison of each technology to produce biodiesel

Variable	Alkali catalysis	Lipase catalysis	Supercritical alcohol	Acid catalysis
Reaction temperature(°C)	60 - 70	30 - 40	239 - 385	55 - 80
Free fatty acid in raw material	Saponification productions	Methyl esters	Esters	Esters
Water in raw material	Interference with reaction	No influence		Interference with reaction
Yield of methyl esters	Normal	Higher	Good	Normal
Recovery of glycerol	Difficult	Easy		Difficult
Purification of methyl esters	Repeated washing	None		Repeated washing
Production cost of catalyst	Cheap	Relatively expensive	Medium	Cheap

Source: Marchetti (2007)

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 5 were estimated by the Arrhenius equation.

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

Table 5 The energy of activation and reaction rate constant at 60 °C

Reaction	Energy of Activation (cal/mol)	Reaction rate constants (mol*sec)
TG → DG	13145	0.05
DG → TG	9932	0.11
DG → MG	19860	0.215
MG → DG	14639	1.228
MG → GL	6421	0.242
GL → MG	9588	0.007

Source: Noureddini and Zhu (1997)

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 5(a). In this figure, there consists of one reactor and nine distillation. Figure 5(b) shows the reactive distillation implementation, only one column is required. The capital and operation costs are reduced (Siirola, 1995).

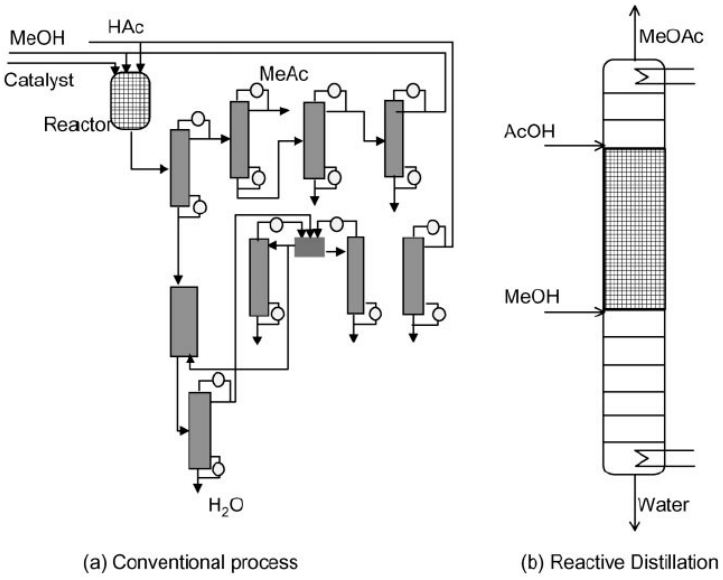


Figure 5 The Processing scheme for the esterification (a) conventional processing consists of one reactor and nine distillations (b) The reactive distillation configuration

Source: Siirola (1995)

For the acid catalyst reaction between iso-bytene and methanol to form methyl tert-butyl ether, the traditional reactor followed by distillation concept has inherently a complexity because the mixture leaving the reactor forms three boiling azeotropes. The reactive distillation implementation requires only one column as illustrated in the Figure 6. The butanes (consists of a mixture of n-butene as non-reactive, and iso-butene as reactive components) and methanol are fed near the bottom of the reactive section. The reactive distillation is capable achiving close to 100% conversion, and suppression of undesired product dimethyl ether (Sundmacher *et al.*, 1995). In addition, some of the azeotrope in the mixture is prohibited (Doherty and Buzad, 1992).

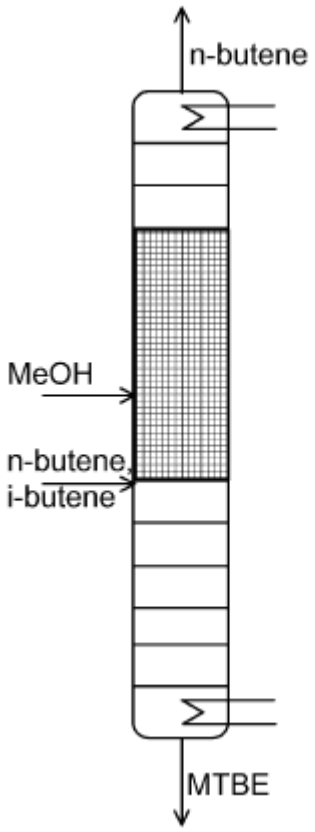


Figure 6 The reactive distillation concept for synthesis of methyl tert-butyl ether
Source: Sundmacher *et al.* (1995)

For the hydration of ethylene oxide to mono-ethylene glycerol: EO + H_2O EG, the reactive distillation in Figure 7 is used for two advantages (Ciric and Gu, 1994). Firstly, the side reaction EO + EG DEG is suppressed because the concentration of EG is removed continuously. Secondly, the high heat of reaction is utilized to vaporize the liquid phase mixture on the trays. To achieve the same conversion, the conventional plug flow reactor needs at least 60 % excess water (Ciric and Gu, 1994).

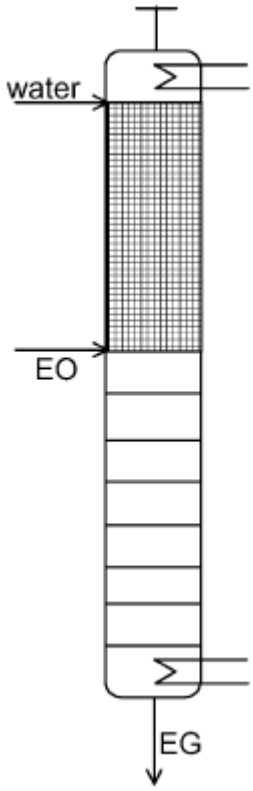


Figure 7 The reactive distillation concept for the hydration of ethylene oxide to ethylene glycerol

Source: Sundmacher *et al.* (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; Jhon & Lee, 2002; Cheng *et al.,* 2003; Pyhalahti, 2005; Alfradique and Castier, 2005; Cheng and Yu, 2005; Katora *et al*.,2005; Dalaouti and Seferlis, 2006; Venkateswarlu and Kumar, 2006;). The equilibrium stage models (Taylor *et al.*, 1999) are demonstrated for calculates 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 8(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, that is shown in Figure 8(b).

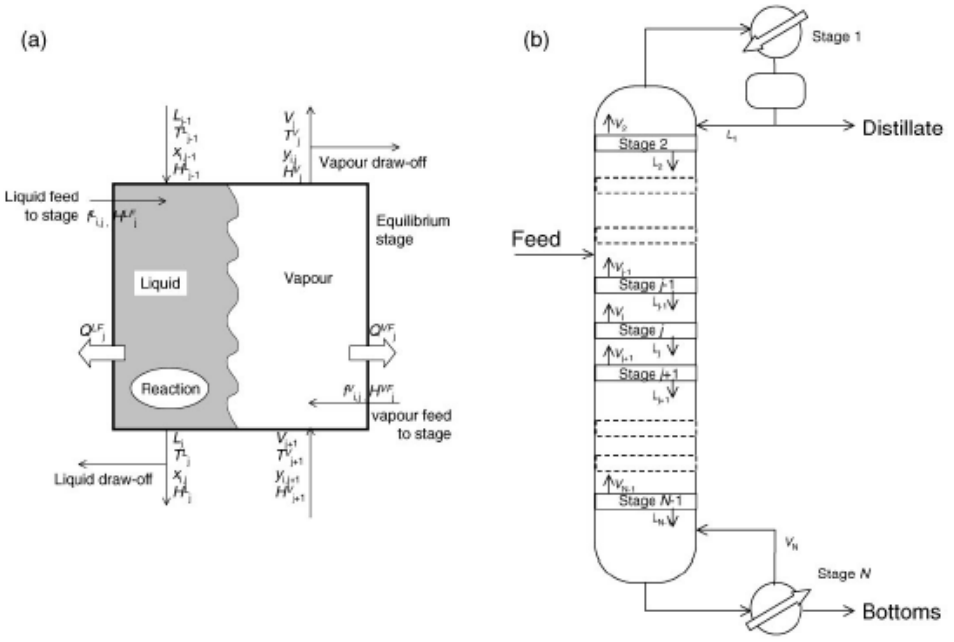


Figure 8 Models of separation process (a) The equilibrium stage (b) Multi-stage distillation column

Source: Taylor and Krishna (2000)

4.1.1 The material balance equation (M) is

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

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

$$\frac{dU_j x_{i,j}}{dt} = V_{j+1} y_{i,j+1} + L_{j-1} x_{i,j-1} + F_j z_{i,j}$$
$$-(1+r_j^V) V_j y_{i,j} - (1+r_j^L) L_j x_{i,j} + \sum_{m=1}^{r} v_{i,m} R_{m,j} \varepsilon_j \qquad (2)$$

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

$$r_j^V = \frac{s_j^v}{V_j}, \qquad r_j^L = \frac{s_j^L}{L_j} \qquad (3)$$

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

4.1.2 The phase equilibrium equation (E) is

$$y_{i,j} = K_{i,j} x_{i,j} \qquad (4)$$

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)

$$\sum_{i=1}^{c} x_{i,j} = 1, \quad \sum_{i=1}^{c} y_{i,j} = 1 \tag{5}$$

4.1.4 The heat balance equation (H)

$$\frac{dU_j H_j}{dt} = V_{j+1} H_{j+1}^{V} + L_{j-1} H_{j-1}^{L} + F_j H_j^{F} - (1 + r_j^{V}) V_j H_j^{V} - (1 + r_j^{L}) L_j H_j^{L} - Q_j \tag{6}$$

The superscripted *H*'s are the enthalpies of the appropriate phase. 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 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 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 hold up 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 9 presents the reflux ratio schematic.

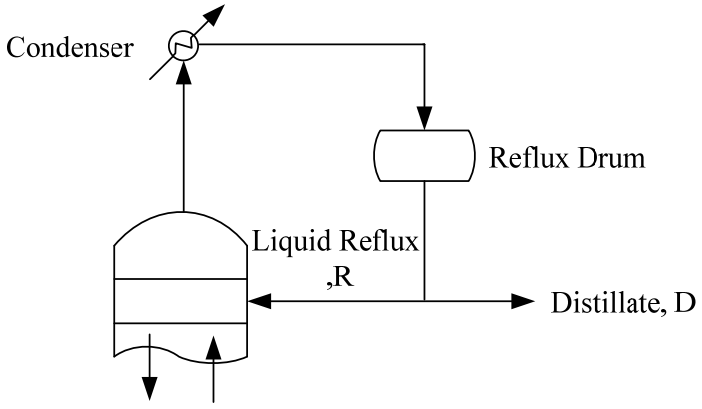


Figure 9 Reflux ratio schematic

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. In this work, we use reactive distillation for biodiesel process.

5. Safety analysis

In the past thirty years, the growth of industrial activities has resulted in many new problems which are concerned with environmental protection, energy consumption, resource conservation and safety. However, industry has been continually developing its design methods and operation techniques in order to overcome these problems (Pitblado and Turney, 1996). Nevertheless, the improvement of these problems is the important obstacle for increasing the benefit of industrial companies.

Especially for safety, most industries have to be considered in this problem. The process industries, which operate chemical plants, handle a wide range of flammable and toxic materials, which are potentially hazardous. Therefore, safety consideration is the first critical issue in the process operation. In addition, the successful safety program requires several ingredients as follow.

- Safety knowledge
- Safety experience
- Technical competence
- Safety management support
- Commitment

Safety knowledge is the knowledge of safety gained through classroom or Independent study. This includes knowledge of the fundamental laws of nature, the dangerous properties of chemicals and how these knowledge can be applied in the real world. About safety experience, the safety participants must have experience with the process and safety procedures, which is used to prevent the hazardous events. The technical competence includes the ability to make proper safety decisions based on a technical evaluation. In addition, safety management support has to be required to monitoring losses and near misses and to make the safety plans for future losses prevention. Finally, safety commitment is necessary for improving or practicing of safety in a company.

In addition, recent advances in chemical plant safety emphasize the use of appropriate technological tools to provide information for making safety decisions with respect to plant design and operation (Crowl *et al*., 1990). Although, safety is a meaningful terminology for many fields but its definition and relevant terminology for the chemical field can be demonstrated as follows.

- Safety or loss prevention is the prevention of accidents by the use of appropriate technologies to identify the hazards of a chemical plant and to eliminate them before an accident occurs.
- A hazard is anything with the potential for producing an accident.
- Risk is the probability of a hazard resulting in an accident.
- Accident is an unplanned event which has a probability of causing personal injury or property damage (Magid, 1979).

5.1 Causes of accidents

One of the aims in safety is reducing accidents, which may cause invisible injury or damage, property damage, minor injury or serious injury. It is axiom of accident prevention that all accidents have causes. Therefore, study in causes of accidents can be introduced to reduce the possibility of accidents. The causes of accidents can be classified as shown in Figure 10.

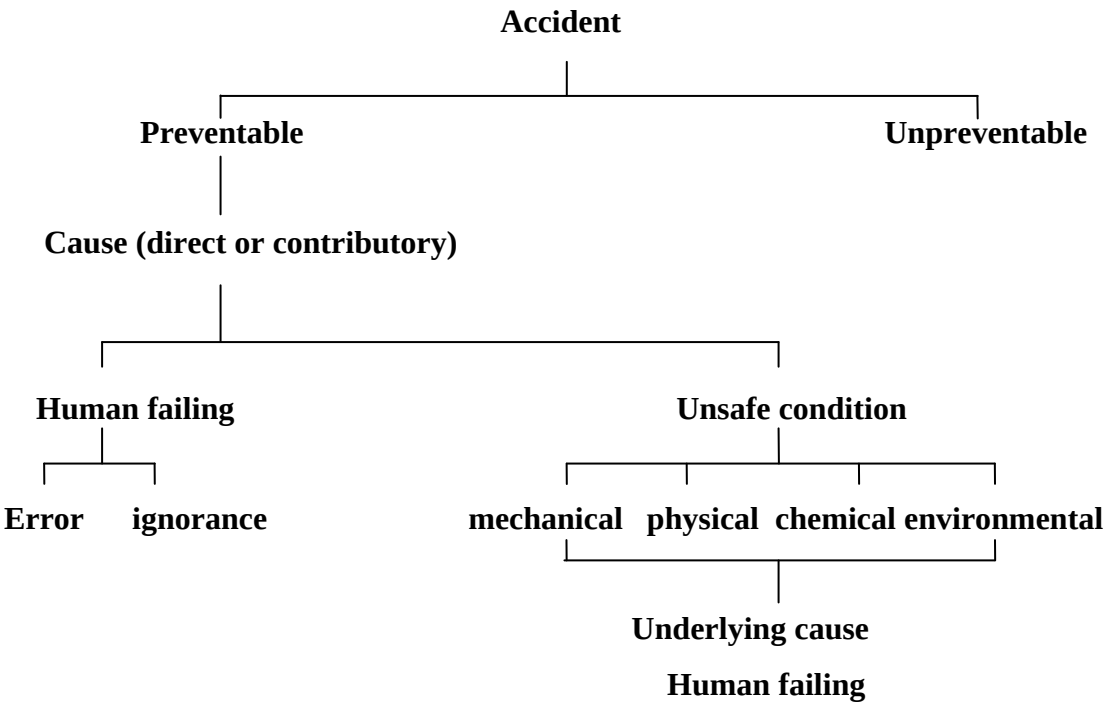


Figure 10 Causes of accident classification
Source: Magid (1979)

The causes of accident can be divided into two main types, which are preventable and unpreventable cause. Most causes are preventable such as human or condition factor. Therefore, improvement of safety has to be concerned with the techniques, which can identify or eliminate these causes.

In addition, the causes of accidents generally retain latent for some time before an accident occurs. These latent or potential causes are hazards, which have to be identified.

5.2 Hazard recognition

Hazard is a condition with the potential of causing injury or damage. It can be referred to almost synonymously with accident causes. However, hazard and

accident cause is different. Hazard can exist without an accident while an accident cause without an accident is impossible.

In this moment, hazard is an important factor for improving safety because identifying hazards can prevent the process from accidents. Therefore, hazard recognition is essential to any successful safety program and it is shown in Figure 11.

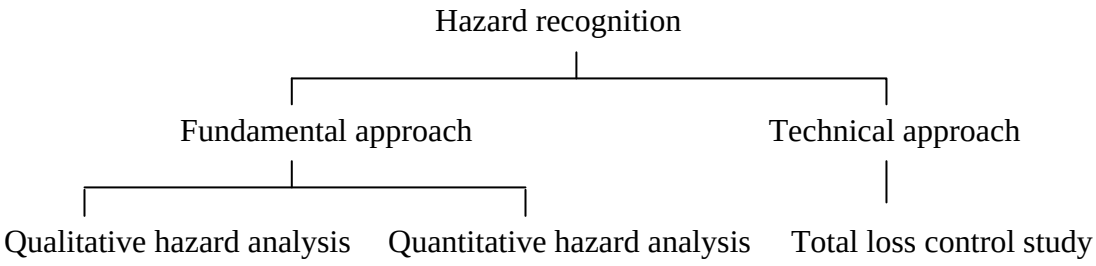


Figure 11 Hazard recognition
Source: Magid (1979)

The fundamental approach is a study of all possible hazards that could exist. It consists of two sections, which are qualitative and quantitative hazard analysis. Qualitative analysis is about identifying or classifying hazards whereas quantitative analysis is about calculating the probability of hazards occurrence. For technical approach or loss control, it relates with the recording and studying of many accidents to find the ways of hazard elimination. Although, both approaches are not similar but they are very useful for safety improvement.

5.3 Hazard and Operability (HAZOP) Analysis

The improvement of safety and reliability of the complex processing plant has to be concerned with the procedures, which can minimize or eliminate the potential problems in the system. The HAZOP analysis is one of those procedures that are generally applied in the complex process. HAZOP analysis is a systematic procedure for determining the abnormal causes of process deviations from normal behavior and their adverse consequences in chemical plant (Srinivansan and

Venkatasubramanian, 1998). However, it is usually carried out by a team who has experience both in the HAZOP technique and the system under investigation. Therefore, it is a difficult, time-consuming and labor-intensive activity.

HAZOP analysis is one of many techniques of hazard identification, which has long been an integral part of design and operational practice. It is aimed at two particular outcomes. First, there is the identification of serious incidents, which may result directly in danger to operators, public and financial loss. These are commonly known as the top events. Second, the fundamental procedures can be applied to identify the possible causes, which can lead to the top events (Pitblado and Turney, 1996).

In order to identify the hazardous events, which may occur in the considered process, the guide words are introduced for generating the process variables. When the guide words are applied to the process variables of each unit, the process variable deviations are considered.

5.4 Guide words and their definitions

The group of guide words usually used in HAZOP analysis and their definitions are as follows

NONE: No flow, reverse flow, i.e., no forward flow when there should be.

MORE OF: More of flow, temperature, pressure, viscosity, etc., i.e., higher flow, higher temperature, or whatever, than there should be.

LESS OF: Lower flow, temperature, pressure, viscosity, etc., than there should be.

PART OF: Change in composition of the stream, e.g., ratio of components different from it should be.

MORE THAN: Impurities present, e.g., ingress of air, water, acids. Extra phase present, e.g., vapor, solids.

OTHER: What else apart from normal operations can happen, e.g., start up, shutdown, maintenance, catalyst change, and failure of plant services (Venkatasubramanian and Vaidhyanathan, 1998).

However, the guide words and process variables should be combined in a meaningful way. For example, if the process variable is temperature, there are only two guide words, MORE OF and LESS OF, could be used meaningfully in this consideration. Therefore, all guide words cannot be applied to all process variables.

5.5 HAZOP analysis procedures

After the definition of guide words are described, the sequence of HAZOP analysis is shown Figure 12. The steps for performing HAZOP analysis can be classified as follows.

5.5.1 Select the line or section of the process unit before carrying out HAZOP analysis.

5.5.2 Create the deviations in a selected section by applying the guide wards.

5.5.3 Identify the abnormal causes of each deviation following the conditions of a selected section.

5.5.4 Identify the consequences of each deviation following the abnormal causes.

5.5.5 Create the action plan for protect the considered process unit from that deviation.

5.5.6 If the other meaningful deviations in the considered process are presented, the identification of the possible causes, consequences and action plan have to be carried out again.

5.5.7 If all deviations are determined, the other lines or sections in considered process unit have to be carried out.

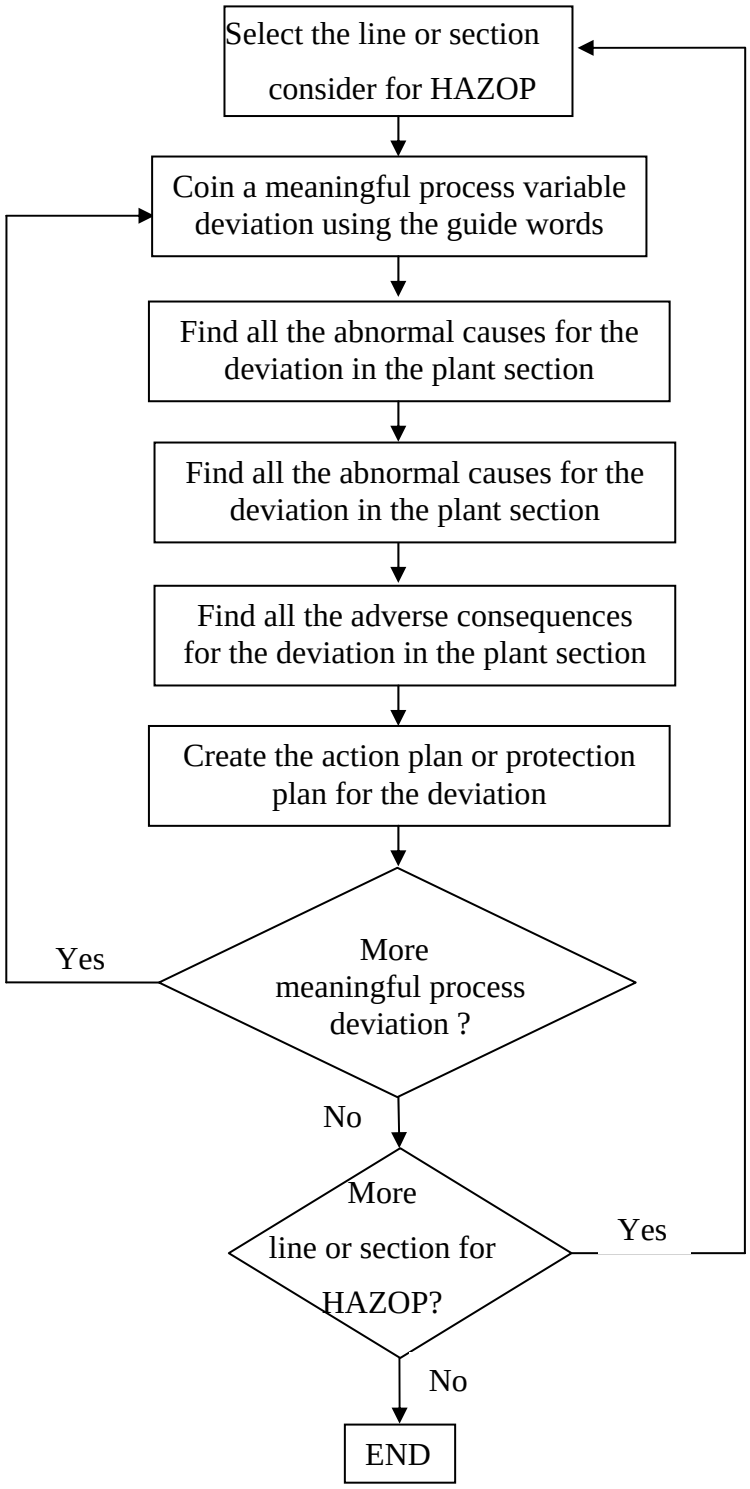


Figure 12 HAZOP analysis procedure

Source: Venkatasubramanian and Vaidhyanathan (1998)

5.6 Degree of hazard Evaluation

5.6.1 Introduction to degree of hazard evaluation

Accident initiation is concerned with the causes of an undesirable event but the severity of an accident depends on the level of hazard in surrounding conditions Degree of hazard evaluation is a concept applied for determining the conditions which cause an abnormal events. Therefore, it can be used to imply the degree of hazard in those abnormal events.

There are many theories that relate with degree of hazard evaluation such as Firenze's theory and Fine's theory. Firenze's theory is the concept of risk ranking. It simply defines the level of seriousness following the severity of the hazardous event, which affects the humans and assets. However, it just demonstrates the probability of hazardous event. It does not combine the probability in order to report the degree of hazard. For example, this theory cannot compare the risk between these two events, a high seriousness event with low probability of occurrence and a low seriousness event with high probability of occurrence. For Fine's theory, it is the systematic procedure to evaluate the risk ranking. It combines the level of seriousness and the probability together in order to calculate the risk score. Then, the degree of hazard could be evaluated following the criterions of this theory.

However, Fine's theory has some disadvantages. It was created for about three decades ago and it is not concerned with the materials used in a process. Therefore, the accuracy of risk analysis is not satisfied for the modem technology processes, which require high accuracy. At this moment, there are many adapted methods for evaluating degree of hazard and the widely well-known one is the approach to assessing chemical plant risks developed by Dow Chemical Company.

Dow Chemical Company is a big chemical organization in United State of America. They have many chemical industries in many countries around the world. They developed the method for determining the risks in chemical

plants and this method has been adopted by the Dutch Regulatory Authority and by other organizations. This method is pragmatic, but is based on an immense amount of experience. It does not only concern about the chemical plant risk .but it also includes the cost of business interruption. In order to determine the costs, which are caused by the hazardous events, the information about financial status and the cost of damages and protections are required. Therefore, this project concerns mainly with the chemical plant risks.

5.6.2 Risk Assessment

In this period, rapid developments are taking place in other fields of new technology, such as the use of atomic energy for power generation. Little relevant experience for assessing the safety aspects of new designs is available from the past and this led to the development of predictive quantitative risk assessment (QRA) techniques as an aid to decision making in the areas of reliability and safety. In HAZOP analysis, the hazardous events are identified in terms of qualitative results. However, if the consequences are not acceptable and their magnitude cannot be reduced, it is necessary to prevent the occurrence of these events. Also, when the consequences are very serious, the quantitative estimation of event probability and risk has to be made.

Risk assessment is applied in the considered process in order to evaluate the probability of risk in the abnormal causes and consequence. Risk assessment is integrally linked with reliability engineering, wherein failure frequency analysis of instruments or equipment data is vital relevance. The procedure for the application of risk assessment is shown in Figure 13.

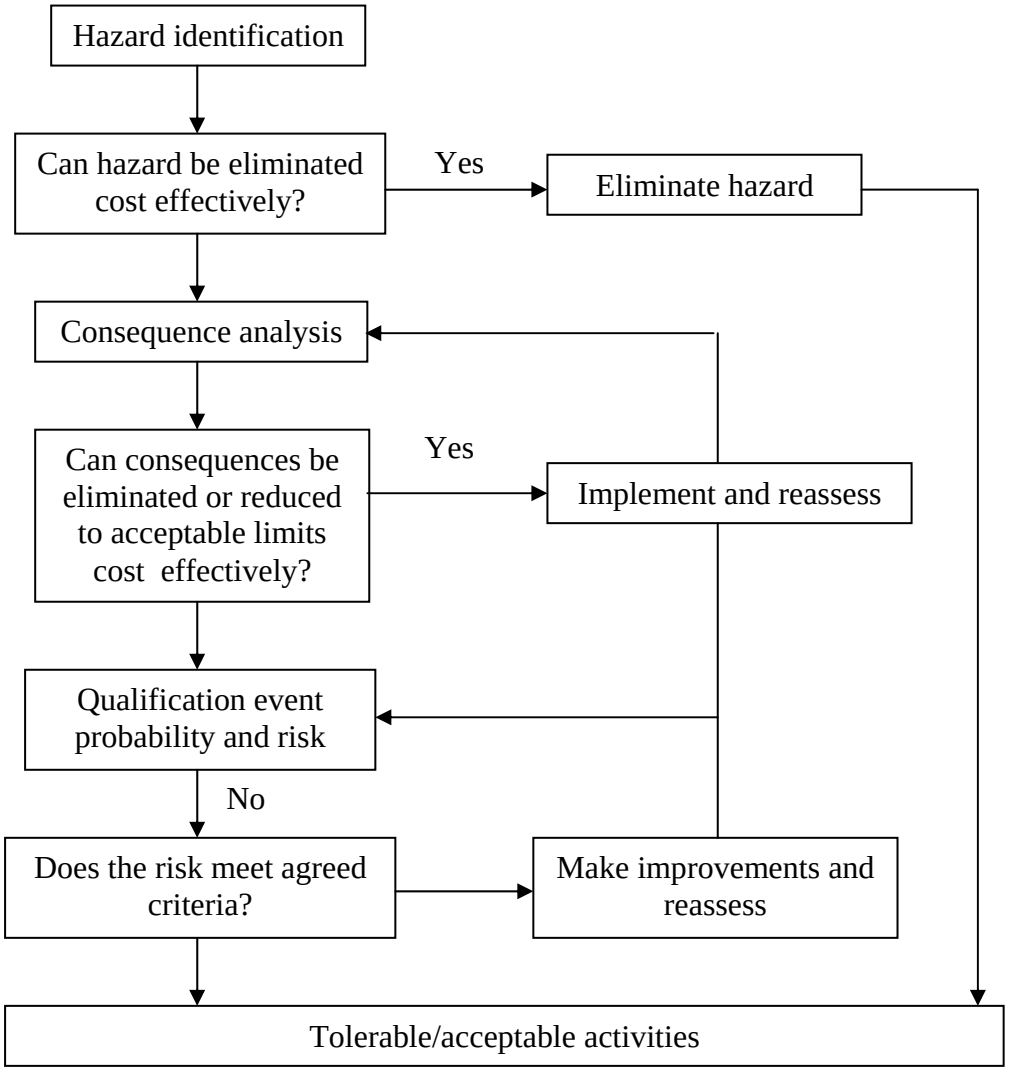


Figure 13 Procedure for application of risk assessment

Source: Pitblado and Turney (1996)

5.6.3 Instrument failure

Most chemical processes have many complex equipment or instruments in order to operate effectively. Therefore, the efficiency of processing seriously depends on the efficiency of these equipments on instruments, which are defined as the failure rate. In addition, these instruments can be classified into two main types, which are measuring instruments and control elements. The objective for operating or the application of each type can be shown in Table 6.

Table 6 The application of the measuring instrument and control element

Instrument	System application
Measuring instrument	Display system (measurement, status and alarm) Control loop, Trip system and Computer model
Control element	Control loop and Trip system

Source: Pitblado and Turney (1996)

In addition, measuring instruments are included digital and analogue inputs where as control elements are included power cylinder, motor and etc. However, the failure rate of instruments is difficult to define because of the accuracy of instruments. For example, the accuracy of flow meter may be sufficient for flow control, but it may not be good enough for an input to a mass balance model on a computer. Therefore, the various kinds of failure have to be considered. The failure rate and reliability of instruments should be depended on their application or failure definition and factors affecting failure.

5.6.4 Factors affecting failure Some factors, which affect instrument failure, can be described as follows (Lees, 1986)**.**

5.6.4.1 System context: For example, application (display, control and etc.), specification (accuracy, response and etc.) and definition of failure.

5.6.4.2 Installation practices.

5.6.4.3 Environmental factors (process materials): For example, degree of contact, material phase (gas, liquid and solid), cleanliness, temperature, pressure, corrosion and erosion.

5.6.4.4 Environmental factors (ambient and plant conditions): For example, temperature, humidity, dust, frost exposure, vibration and impact exposure.

5.6.4.5 Operating factors; for example, movement and cycling.

5.6.4.6 Maintenance practices.

In this work, SCADA program (GENESIS32) is used to construct the safety module. Biodiesel process is simulated by ASPEN Plus to find the optimal condition. This module can connect to the ASPEN Plus. Results of biodiesel process from ASPEN Plus are shown in the module. The module includes safety methodologies. HAZOP is used to develop the biodiesel process with safety concerning.

METERIALS AND METHODS

Materials

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. Software

   - GENESIS 32 Version 9.
   - Microsoft Visual Basic Version 6.5
   - ASPEN PLUS version 2006.5

Methods

Theoretically, the conventional and the reactive distillation process of biodiesel require the experiment data for design and construction. In order to reduce tedious work and time, the simulation can be served this design information. In this research, the simulations were carried out by the industrial simulation package named ASPEN PLUS 2006.5. Moreover, GENESIS 32 and Microsoft Visual Basic are used to construct the module and to communicate ASPEN PLUS.

The objective is to develop the biodiesel processes. In this work, automated HAZOP analysis is proposed to develop the operation conditions and safety.

1. Process description

The production of biodiesel by alkali catalyst transesterification was simulated by Zhang *et al*. (2003). There are 6 processes as shown in the Figure 14.

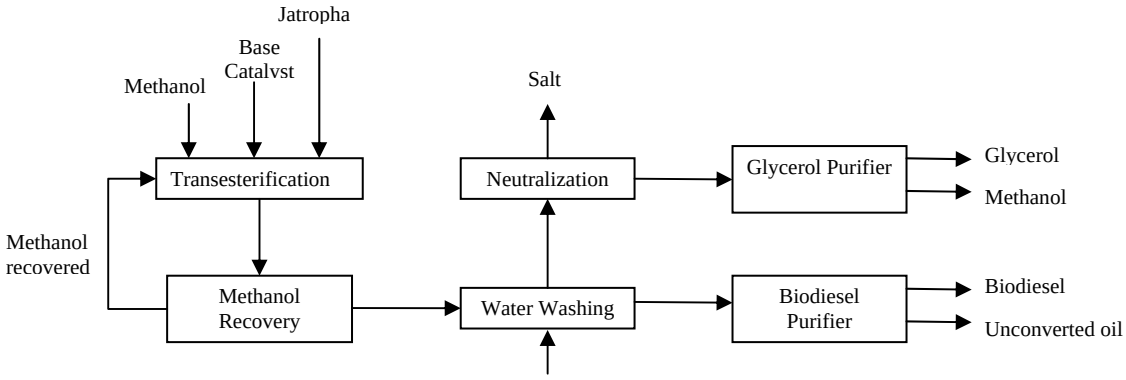


Figure 14 Process of biodiesel process

The details of each process are described below.

1. Transesterification section: Jatropha oil reacts with methanol and akali catalyst.
2. Methanol recovery section: the excess of methanol are separated and recycled.
3. Water washing section: NaOH is diluted by water.
4. Biodiesel purifier section: the unconverted oil is separated.
5. Alkali removal section: NaOH is neutralized.
6. Glycerol purification section: the glycerol is refined as good grade (more than 80% or 93%).

However, the biodiesel and glycerol are not soluble (Zhou *et al*., 2006). The solubility of multi components that consists of FAME, methanol, oil and glycerol were illustrated by phase diagram. As a result, FAME and glycerol can slightly dissolve. After the transesterification reaction is completed, two layers; FAME and glycerol, can be formed. Therefore, the recovery methanol section is needed to separate the FAME and glycerol. Then, the biodiesel process can be seen in the Figure 15.

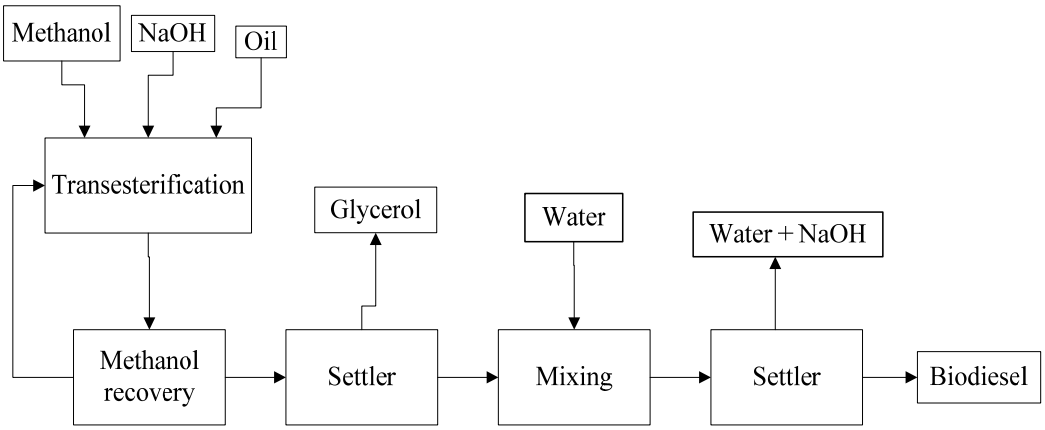


Figure 15 The biodiesel process

Source: Zhang *et al*. (2003)

1.1 Conventional process of biodiesel

According to Zhang's work (Zhang *et al*., 2003), there were four simulations of biodiesel production. Two of them were alkali-catalyzed process, one using virgin oil and other using waste cooking oil. The remaining two were acid-catalyzed processes using waste cooking oil as the raw material. Because this research focuses on the alkali catalyst, the alkali catalyst process of Zhang will be used for applying the reactive distillation. Figure 15 shows the alkali catalyst process to produce biodiesel from virgin oil. This work consists of 7 processes which are transesterification, methanol recovery, water washing, biodiesel purification, alkali removal, glycerin purification and waste treatment. Normally, after complete reaction, there are two layers between biodiesel and glycerol. The water washing unit was used to separate the biodiesel and glycerol but it is easy to separate by gravity unit introduced by (Krawcyk, 1996). Therefore, the water washing unit of Zhang (2003) was replaced by using the gravitational unit. Figure 16 displays the modification alkali catalyst process from Zhang (2003). As seen in this, there are 4 sections which are transesterification, methanol recovery, glycerol and alkali removing. The sequence of biodiesel production is changed after the methanol recovery. The gravity unit was used to remove glycerol and catalyst. The biodiesel quantity between Zhang's work

(Zhang *et al.*, 2003) and this work are 997 kg/h and 998 kg/h, respectively. Obviously, the equipment can be reduced from five to two. The detail of each process was described as follow.

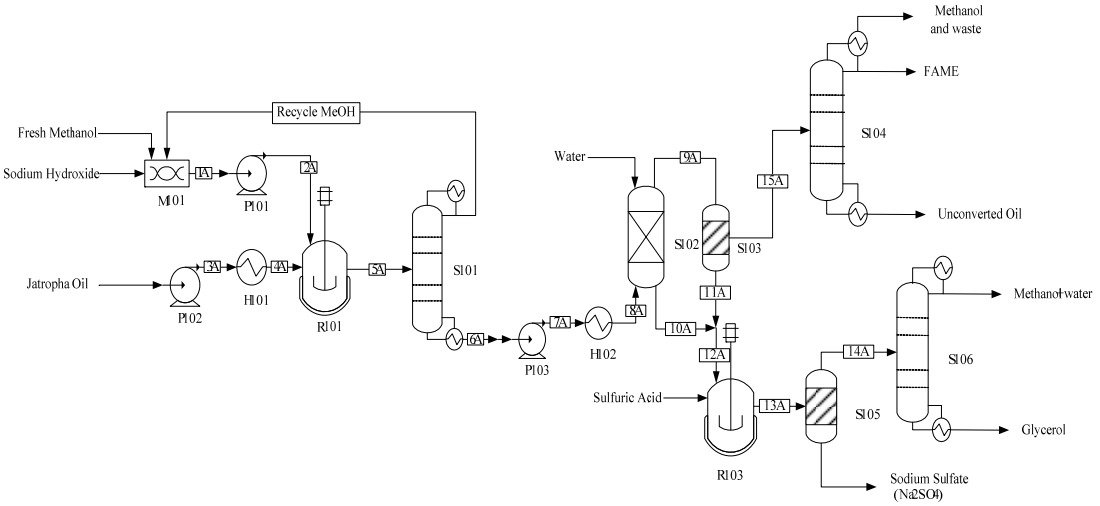


Figure 16 The alkali catalyst process to produce biodiesel from virgin oil
Source: Zhang *et al.* (2003)

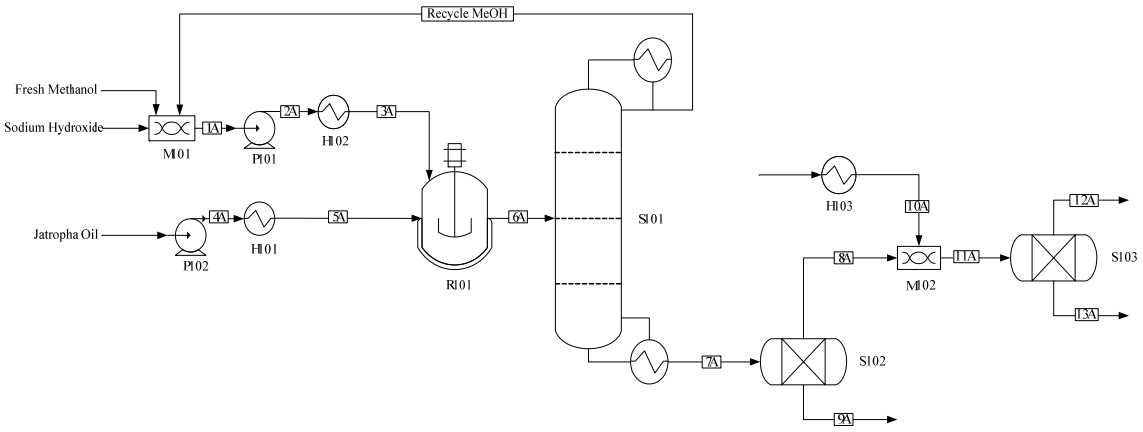


Figure 17 The biodiesel production of this work

1.1.1 Transesterification

The detail of the transesterification is shown in the Figure 18. The process started with the 1000 kg/hr of soy bean oil was heated to 60°C before sent into the reactor. At the same time, the sodium hydroxide, was mixed with methanol of 1:5 mass ratio or 6:1 molar ratio alcohol to oil in static mixer M101 to produce 0.5% sodium methoxide which used as a catalyst. The fresh methanol was mixed with recycle methanol before mixing sodium hydroxide to form sodium methoxide. After that, sodium methoxide was sent to the reactor which transesterification was occurred. Due to the detail information on the kinetic is not available, a simple conversion of biodiesel is assumed to be 95%. But there are a lot of kinetic models of transesterification reaction available. Because of the same catalyst selected and similar component of oil, the kinetic model of Noureddini and Zhu (1997) is selected to describe the transesterification reaction of soy bean oil. The excess of methanol is sent to the recovery section in order to recycle the methanol.

The simulation results, the fresh and recycle methanol which were 130 kg/h and 38.4 kg/h respectively was mixed with the sodium hydroxide (12 kg/hr) in the static mixer M101. The mixture called sodium methoxide at rate 180 kg/h was pumped to the heat exchanger in order to increase the temperature to 60°C. The 1,000 kg/h of fresh Soy bean oil which was assumed to trioleic, trilinoleic and tripalmatic as a major composition were pumped and preheated with heat exchanger H101 to reach 60 °C before sent to reactor. In the reactor R101, temperature was controlled at 60 ^{o}C, 1 atm pressure and 1 hour operated. The final product is approximately 1,180 kg/h that contain biodiesel (methyl oleic, methyl linoleic and methyl palmatic), glycerol, unreacted methanol, catalyst and some of intermediate substance.

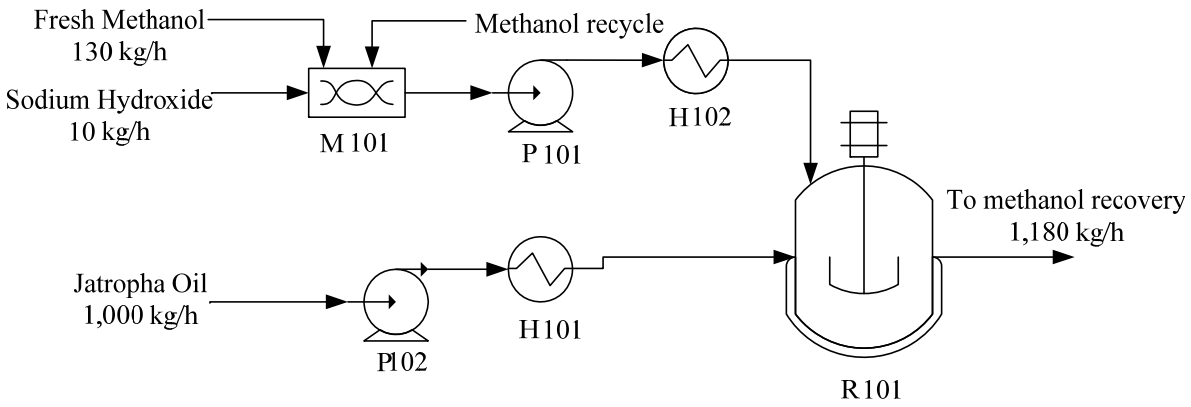


Figure 18 Transesterification section

1.1.2 Methanol recovery

From transesterification section, the product and unreacted reactant are sent to distillation to remove and recycle unreacted methanol in order to reduce fresh feed of methanol. Figure 19 shows the methanol recovery section which methanol and other components are separated by the distillate and bottom stream respectively. The pressure column should be operated between 1 – 1.5 atm and keep the bottom temperature below 150 ^{o}C because of declining of biodiesel. The designs of distillation are 10 stages, reflux ratio of 1 and boiler ratio of 0.6 to separate methanol from other component.

The 1,180 kg/h from reactor R101 are sent to distillation. The top and bottom pressures of distillation are fixed at 1 atm and the bottom temperature is lower than 150 ^{o}C. Therefore, the operation at the atmospheric pressure is better because higher capital cost come up with high operating pressure. In the recycle stream, 38.4 kg/h of methanol is recycled and mixed with fresh methanol, then charged back into reactor. The 1,142 kg/h of bottom stream is sent to glycerin removing. The quality of methanol in this stream should not higher than 0.2 % wt. If there is excess methanol, the separation unit should be installed in the down stream.

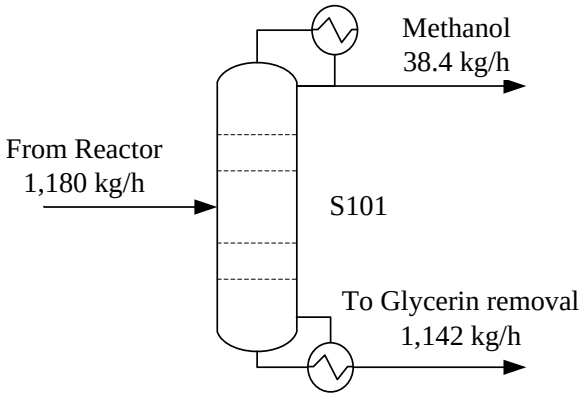


Figure 19 Methanol recovery section

1.1.3 Glycerin removal

Due to the mass fraction of glycerol in biodiesel should not be over 0.24 %, the removal glycerin unit is significantly. After the methanol recovering section, the water washing column was used to separate the biodiesel from the glycerin. But it is easy to remove glycerin from other component instead of using water because glycerin does not dissolve in the biodiesel. There are two layers between biodiesel and glycerin. The residue curve is applied to study the dissolves of biodiesel and glycerin. Figure 20 shows the residue curve for glycerin, biodiesel and methanol. Glycerin is hardly soluble in biodiesel and the mixtures are two phase. Therefore, the gravity unit is enough to be used for this separation.

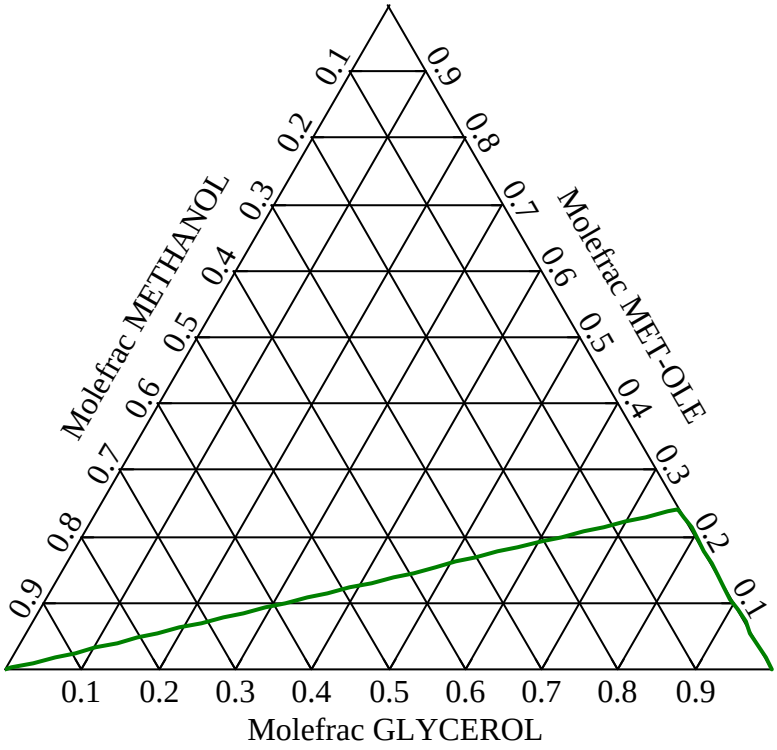


Figure 20 Residue curve for glycerol, biodiesel and methanol

Figure 21 shows the glycerin removal unit (decanter). The bottom stream from distillation was sent to the decanter unit to separate first and second liquid. Glycerin identified as a key component of second liquid was removed in the second liquid stream. The first liquid stream consisting 96.9 % biodiesel was sent to the alkali removal unit. Glycerin containing which is lower than 0.1 % was acceptable with the standard. In the second liquid stream, there were 80.4 % glycerin and only 7 % biodiesel. Therefore, glycerin can be sold as a low grade because of its quality.

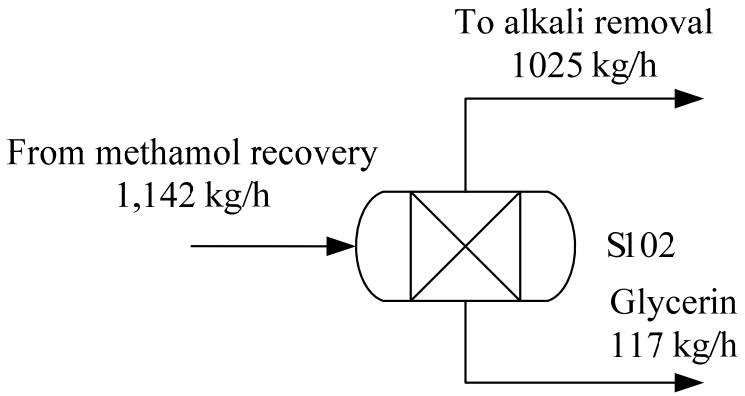


Figure 21 Glycerin removal section

1.1.4 Alkali removal

The amount of sodium hydroxide should not be higher than 0.8 % (EN 14214). Therefore, the alkali removal section shown in the Figure 22 is used in order to decrease the amount of sodium hydroxide in biodiesel product. First of all, 900 kg/h of hot water (50 ^{o}C) is mixed with the first liquid stream coming from the glycerol removal in the static mixer. Secondly, the mixing component is sent to decant which operates at 50 ^{o}C and 1 atm. The water; as a key component, is removed in the second liquid stream. The efficiency of decant is 100 % because biodiesel and water are not dissolve together. These results can observe in the Figure 23 which shows the residue curve for biodiesel, water and methanol.

As seen in the Figure 22, the biodiesel leaving from glycerin removal is sent to the alkali removal. The 900 kg/h of water which is a minimum requirement is used to dissolve sodium hydroxide in the product. In the static mixer, the alkali catalyst is then dissolved into water. The mixtures are sent to decanter used for removing between biodiesel and water. The biodiesel 97.7 % at rate 982 kg/h is obtained. The quality of biodiesel meets the standard (EN 12142).

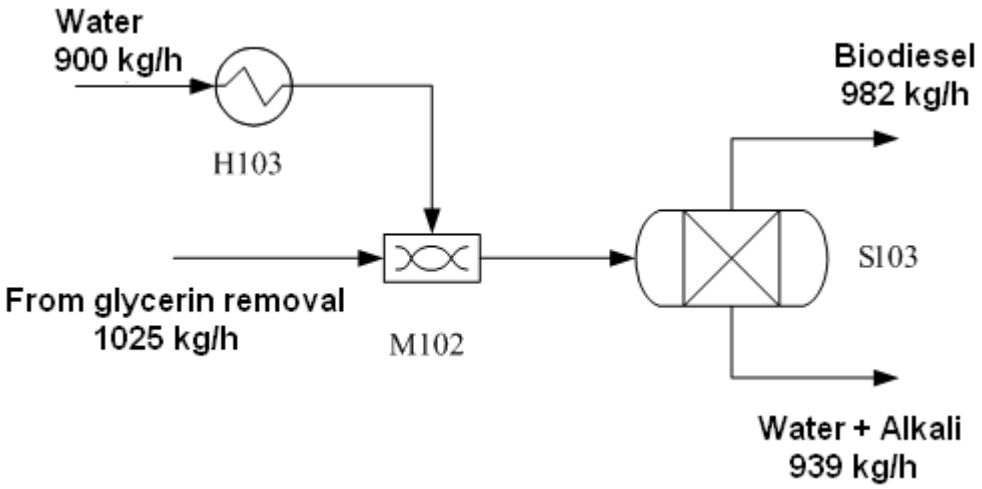


Figure 22 Alkali removal section

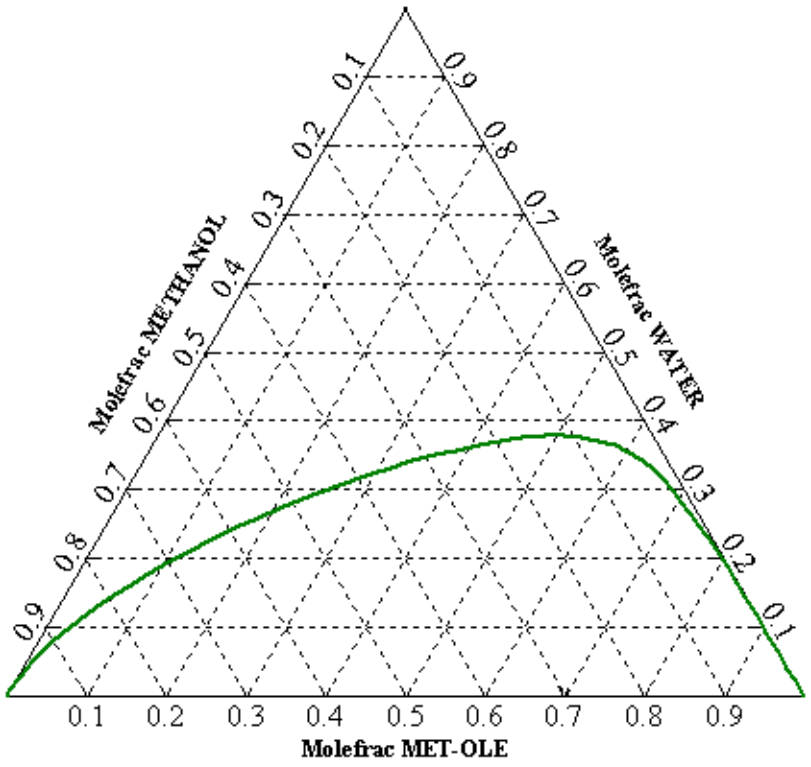


Figure 23 Residue curve for biodiesel, water and methanol

1.2 The Biodiesel production by reactive distillation

In the conventional biodiesel productivity, it consists of reactor and distillation. Transesterification is a reversible reaction which conversion is limited by the equilibrium. Using reactive distillation can be obtained higher conversion due to removing product continuously. In addition, combining unit may reduce capital and operating cost. That is using reactive distillation integrating two units is a challenging task. The process is based on the conventional process (above process). The reactor and distillation column are replaced by single reactive distillation. In addition, most detail of process is similar to the conventional one. Figure 24 shows the biodiesel process using reactive distillation. There are three steps process which are reactive distillation, glycerin and alkali removal.

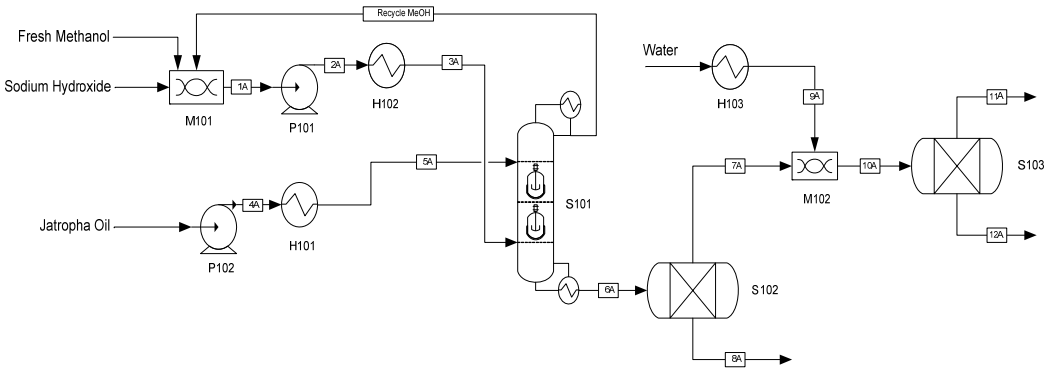


Figure 24 The biodiesel production by using reactive distillation

Where: M101 and M102 = mixers H101, H102, H103 = heaters
P101 and P102 = pumps S101 = reactive distillation
S102, S103 = decanters

1.2.1 Reactive distillation

Biodiesel production from reactive distillation is similar to the conventional process. The transesterification and methanol recovery section were replaced by reactive distillation as seen in the Figure 25. This column were used both reaction and separation. Methanol 130 kg/h was mixed with sodium hydroxide to produced sodium methoxide which is a catalyst. After that, catalyst was heated to

60 ^{o}C that is an optimal condition for producing biodiesel and was sent to the reactive distillation. Soy bean oil 1,000 kg/h was heated to 60 ^{o}C and was charged to reactive distillation. The methanol and oil were fed at tray three. The transesterification reaction occurred in reactive distillation which the operating conditions are 1 reflux ratio, 0.6 boiler, 1 atm and 10 stages. The reaction zones were set between tray four and seven. Methanol which was an overhead product in the distillate stream was recycled and combined with fresh methanol. Biodiesel and other components were removed in the bottom stream and sent to the purification section.

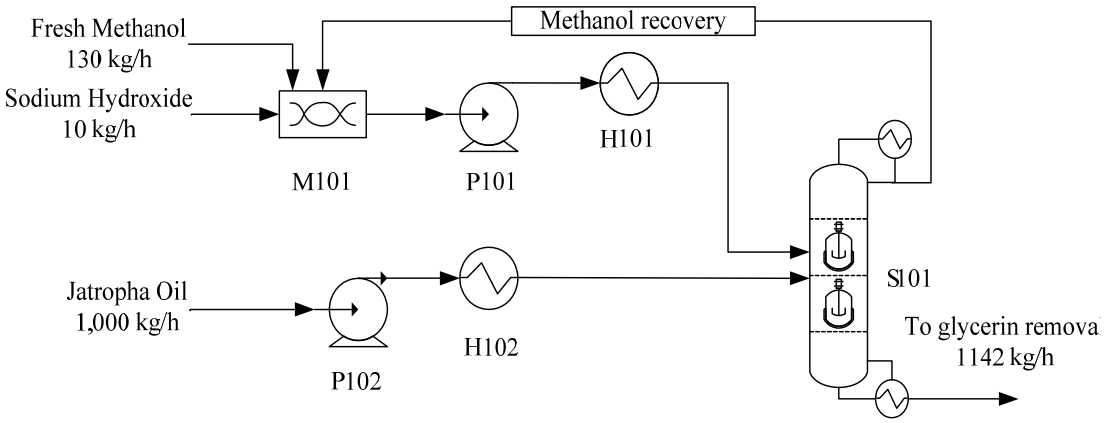


Figure 25 Reactive distillation section

1.2.2 Glycerin removal

The amount of glycerin always affects to the biodiesel quality. The gravity unit (decanter) shown in the Figure 26. The glycerin phase which is lower than biodiesel was set as a second liquid and removed by the second liquid stream. The condition in the decanter was set 25 ^{o}C and 1 atm. Biodiesel and other components were removed by first liquid stream and sent to the alkali removal. The amount of glycerin in the biodiesel is 0.001% that was in standard.

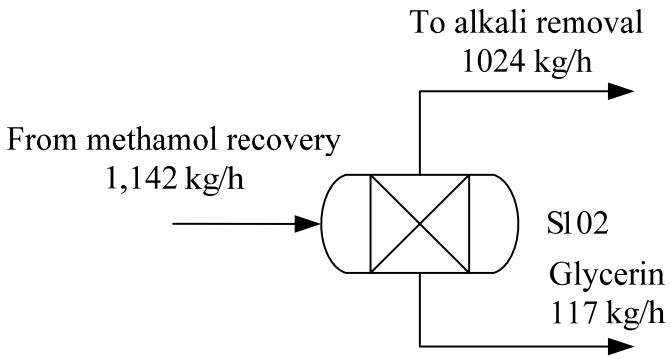


Figure 26 Glycerin removal section

1.2.3 Alkali removal

After removing glycerol, there is still a lot of base catalyst dissolving in biodiesel. Therefore, the catalyst was removed by using hot water. Catalyst was dissolved in to the water phase. There are two layers which are biodiesel and water layer. Figure 27 shows the decanter units used to separate biodiesel and water. Hot water 900 kg/h at 50 ^{o}C was used in order to dissolve catalyst. The alkali removal section, the amount of catalyst in the biodiesel was less than 0.0005 % which meets the standard.

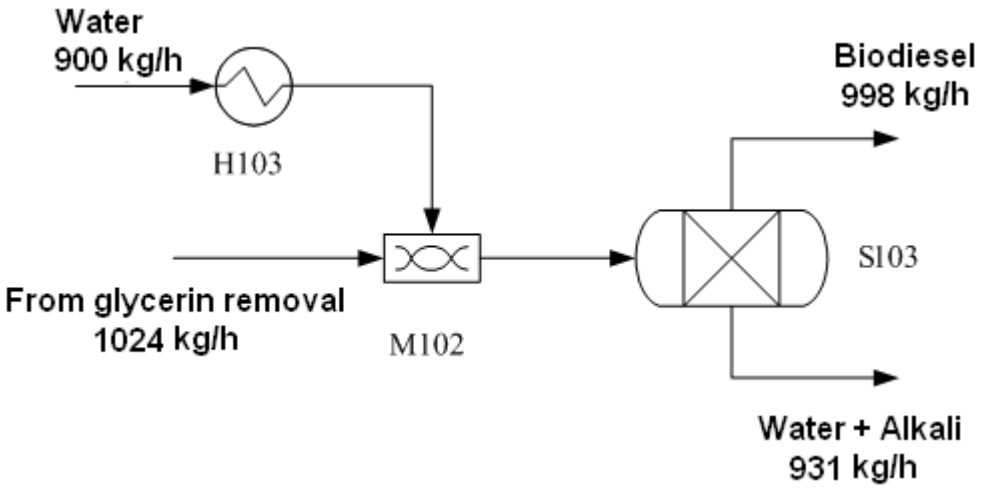


Figure 27 Alkali removal section

2. The process with Safety analysis

2.1 Methods for finding abnormal causes

The methods for finding abnormal causes have knowledge about process-general unit malfunctions which will cause a process variable deviation in a process unit. For example, in the *find-cause* method for pipe shown in Figure 28, 'leak in pipe causes low flow' is a process-general unit malfunction. The find-cause method of the pipe checks the values of the attributes flow, temperature and pressure of the pipe, and depending on the value of these attributes it searches the 'abnormal causes' knowledge base of pipe to find the abnormal causes which can cause the process variable deviations. Similarly, in the *find-cause* method for heat exchanger shown in Figure 29, 'tube leak causes low tube side outlet flow' and 'tube fouling causes high tube side outlet temperature' are process general abnormal causes.

The methods for finding abnormal causes also a search for any properties of the process materials present in the process unit which might cause the process variable deviation. The process variable deviation 'low flow,' the presence of any solid process material in the pipe is checked and the cause, 'partial blockage of pipe' is found. Thus, there is interaction between the process-general knowledge (methods

for finding abnormal causes) and the process-specific knowledge (process material properties). Similarly, in the find-cause method for heat exchanger, the abnormal cause for the process variable deviation, ‘low tube side outlet flow’ is found.

The abnormal causes for the process variable deviations which will be found by the find-cause methods of the pipe and the heat exchanger are given in Figures 28 and 29, respectively.

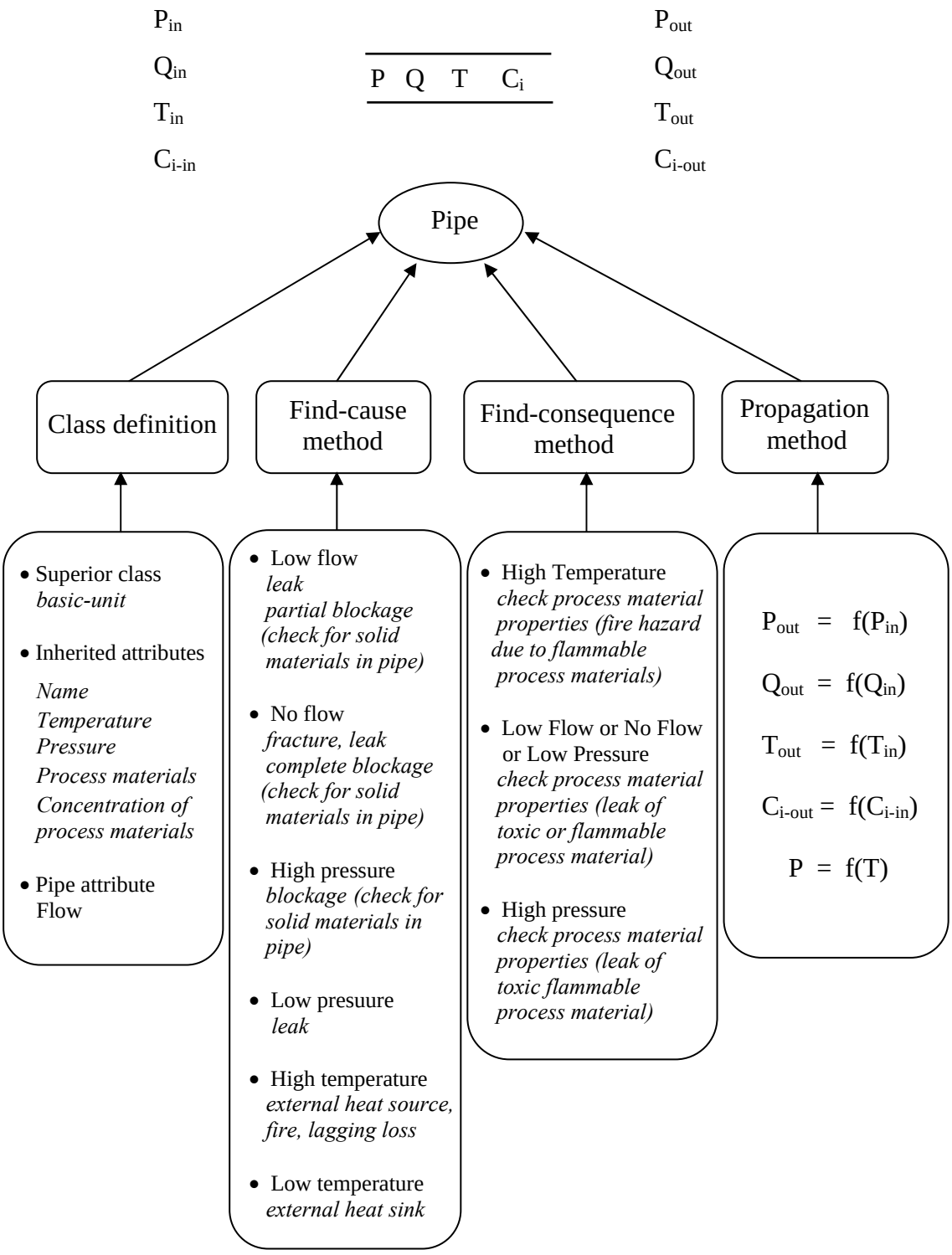


Figure 28 HAZOP model of a pipe.

Source: Venkatasubramania and Vaidhyanathan (1994)

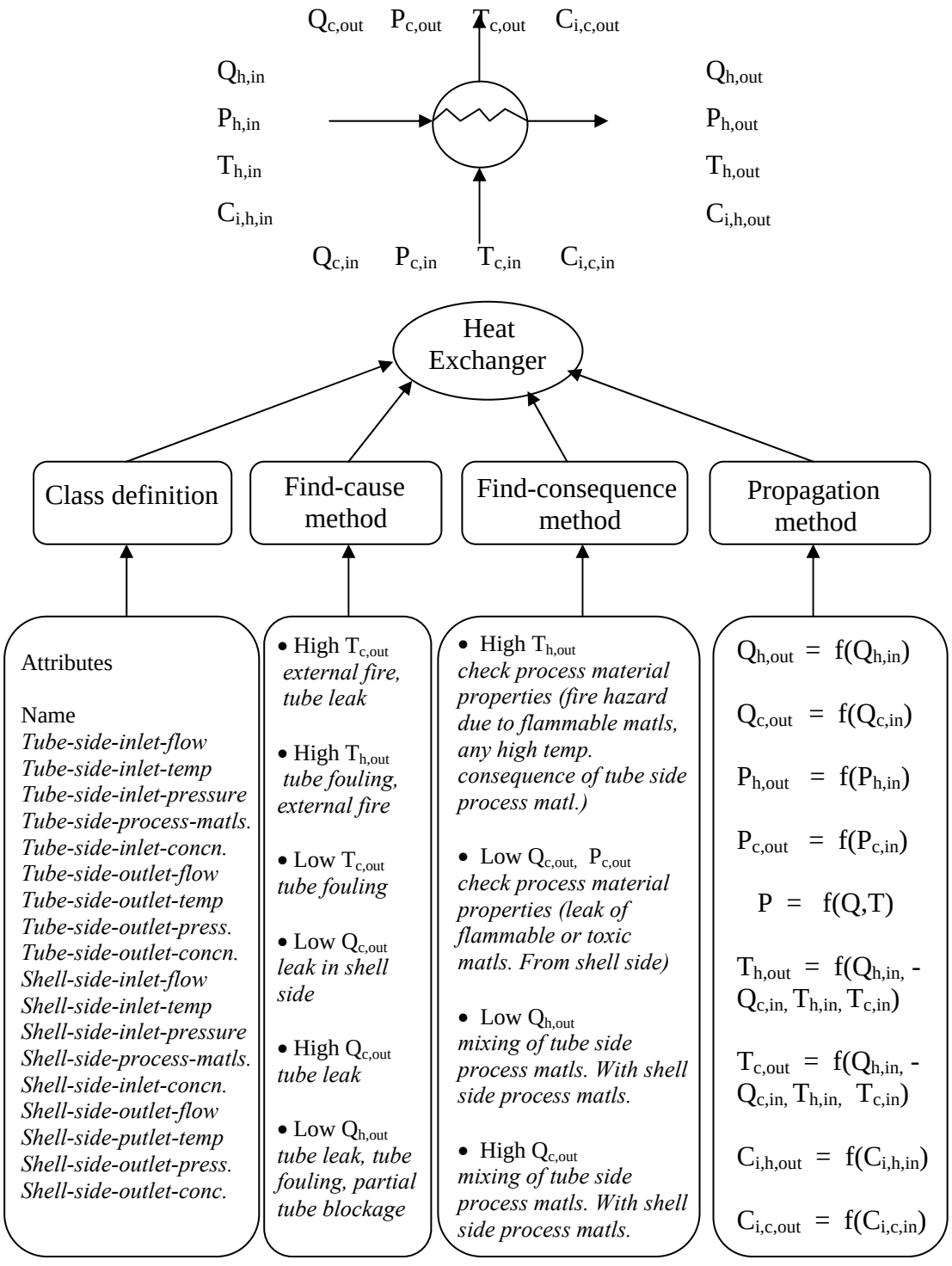


Figure 29 HAZOP model of a heat exchanger.

Source: Venkatasubramania and Vaidhyanathan (1994)

2.2 Methods for finding adverse consequences

The methods for finding adverse consequences have knowledge about process-general adverse consequences of process variable deviations which can occur in a process unit. For example, ‘no flow in centrifugal pump causes overheating of pump,’ is a process-general consequence in a centrifugal pump. The methods for finding adverse consequences also search for the properties of any process materials presented in the process unit which in the presence of the process variable deviation will cause adverse consequences. For example, in the find-consequence method for pipe shown in Figure 28, for the process variable deviation ‘high temperature,’ the properties of process materials in the pipe are checked to see if there is any flammable process material and the consequence ‘fire hazard due to flammable process material’ is found. Similarly, in the find-consequence method for the heat exchanger shown in Figure 29, the consequences for the process variable deviation ‘high tube side outlet temperature’ are found.

The methods for finding adverse consequences also search for any combination of the process material properties with the ‘process unit malfunction causing the process variable deviation’ which will lead to adverse consequences. For example, in the find-consequence method for pipe shown in Figure 28, for the process variable deviation ‘low flow,’ ‘no flow,’ or ‘low pressure,’ the properties of process materials are checked to see if there is any flammable or toxic process material present in the pipe and the consequence, ‘leak of flammable or toxic process material’ is found. In this case, the ‘leak in pipe’ is the malfunction of the pipe which causes the process variable deviation low flow, no flow, or low pressure in the pipe. Similarly, in the find-consequence method for the heat exchanger shown in Figure 29, the consequences for the process variable deviation ‘low shell side outlet flow’ which might cause by the malfunction ‘leak in shell side of the heat exchanger,’ as well as the consequences for the process variable deviations ‘low tube side outlet flow’ or ‘high shell side outlet flow’ which might be caused by the malfunction ‘leak from the tubes of heat exchanger’ are found. The adverse consequences for the process variable

deviations which will be found by the find-consequence methods of the pipe and the heat exchanger are given in Figures 28 and 29, respectively.

2.3 Methods for propagation

The methods for propagation are used for propagating the deviation of a process variable in a process unit in the following manner:

- To find the local causes for process variable deviations in the process unit and in the pipes connected at the inlet ports of the process unit; and
- To find the local consequences of process variable deviations in the process unit and in the pipes connected at the outlet ports of the process unit.

The methods for propagation use the causal models of process units, which consist of the causal relations between process variables. The causal models of process units are derived from the material and energy balances and confluence equations (qualitative differential equations) which represent the influence of one process variable on another process variable. The derivation of causal models from confluences and the propagation of process variable deviations using a quasi-steadystate approach is described in detail by DeKleer and Brown (1984). Additional literature on qualitative modeling of propagation of process variable deviations in chemical plants can be found in Umeda *et al*. (1980), Andow *et al*. (1980), Lees (1984), Oyeleye and Kramer (1988), and Grantham and Ungar (1990).

The causal relations between the process variables of a pipe in the form of qualitative functional relations that are used by the propagation method for pipe are shown in Figure 28. The causal relation Q_{out}, = f (Q_{in}) means, as Q_{in} (inlet flow) increases Q_{out}, (outlet flow) increases and vice versa. Similar causal relations exist for temperature, pressure, and composition of process materials in the pipe. These causal relations are derived from the steady-state material and energy balances and confluence equations of the pipe. The causal model that is used by the propagation method of the heat exchanger is shown in Figure 29. The causal relation Th_{out} = f(

Qh,in,- Qc,in, Th,in, Tc,in) means Th,out (tube side hot fluid outlet temperature) increases as Qh,in (tube side hot fluid inlet flow) increases, or Qc,in (shell side cold fluid inlet flow) decreases, or Th,in (tube side hot fluid inlet temperature) increases, or Tc,in (shell side cold fluid inlet temperature) increases, and vice versa. The causal relations between the process variables of the heat exchanger are derive from the steady-state material and energy balances and confluence equations of the heat exchanger.

The propagation methods propagate the effects of process variable deviations from one variable to another, eventually satisfying the steady-state process unit constraints. The propagation of process variable deviations enables the determination of all the abnormal causes and adverse consequences which could occur in the plant due to a process variable deviation in a process unit.

Using the qualitative values, ‘high’ and ‘low,’ for process variable deviations can lead to ambiguous values for some of the process variables. For example, consider the case of three inlets and three outlets. If one of the inlet flows has the qualitative value high and the other inlet flow has the qualitative value low, then it is not clear what the resulting liquid level would be. The level can increase, decrease, or remain constant. This is due to the fact that the result of adding qualitative high and qualitative low can be high, low or normal. Thus, the level of the tank can have the values high, low or normal as a result of this propagation. This kind of ambiguity that is inherent in qualitative reasoning can lead to such undecidable behaviors as well as spurious ones.

Several strategies for tackling this situation have been provided in the literature. DeKleer (1979) uses the quantitative and ‘design-purpose’ information, Raiman (1986) uses order of magnitude information, and Oyeleye and Kramer (1988) use redundant process constraints for reducing the spurious behaviors. It is important to note here that this problem of ambiguity is also encountered during conventional HAZOP analysis performed by human HAZOP experts, as the experts also use qualitative guide words. However, this problem is circumvented in conventional

HAZOP by recognizing that one is only interested in *worst* case situations in HAZOP analysis. Thus, we need to consider only the abnormal states (for example, tank level 'high' leading to an overflow or 'low' leading to the tank running dry), and we can neglect the other intermediate states during propagation of process variable deviations.

2.4 Inference mechanism and the flow of control

The top level goal of the knowledge-based system is to perform HAZOP analysis for a process variable deviation in a process unit or line. The flow of control in the HAZOP inference engine of system is outlined in Figure 30. All the abnormal causes in the process plant for a process variable deviation in a process unit are found by executing the propagation and the find-cause methods of that process unit and all the upstream process units. Similarly, all the adverse consequences in the process plant for a process variable deviation in a process unit are found by executing the propagation and the find-consequence methods of that process unit and all the downstream process units.

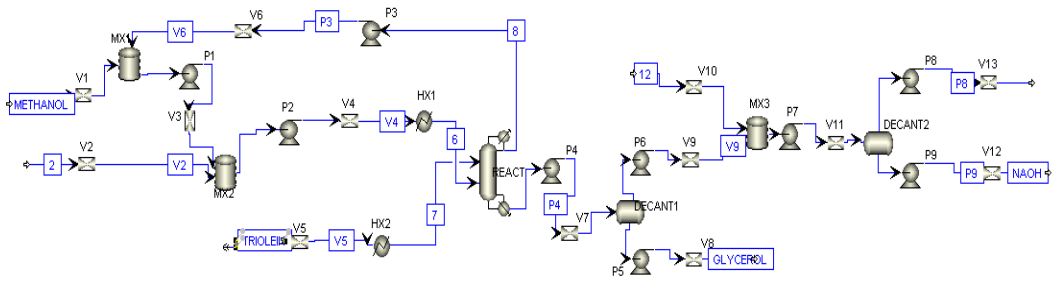


Figure 30 Feed section of biodiesel plant

The find-cause and the find-consequence methods of the process units interact with the process material models of the process materials are presented in the process unit to find the process-specific abnormal causes and adverse consequences. The HAZOP results from system is in the form of all the abnormal causes and adverse consequences in the plant for the process variable deviation in the process unit or line.

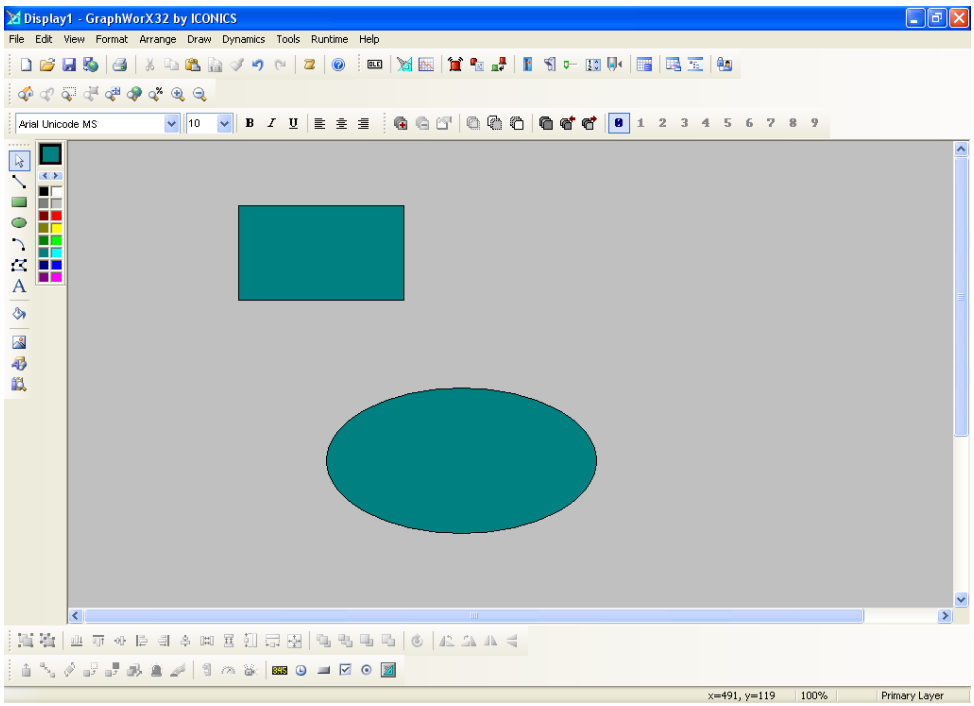
In this work, we applied the SCADA software, named, GENESIS32. It is the industry's first and only fully scalable suite of OPC, SNMP, Web-enabled HMI and SCADA applications. Designed from the ground up to take advantage of the entire range of Microsoft® Windows® operating systems, the GENESIS32 Automation Suite delivers unparalleled performance and cost savings due to its design around open standards. GENESIS 32 is ideally suited for many applications requiring Visualization, Supervisory Control, Data Acquisition, Advanced Alarming, SPC/SQC, Report and Recipe Management and much more. It seamlessly integrates with Batch, MES, MRP, MS Office and Information systems. Create enterprise and distributed applications using the latest OPC and Web enabling technology (Saenate, 2007).

GENESIS 32 includes many tools:

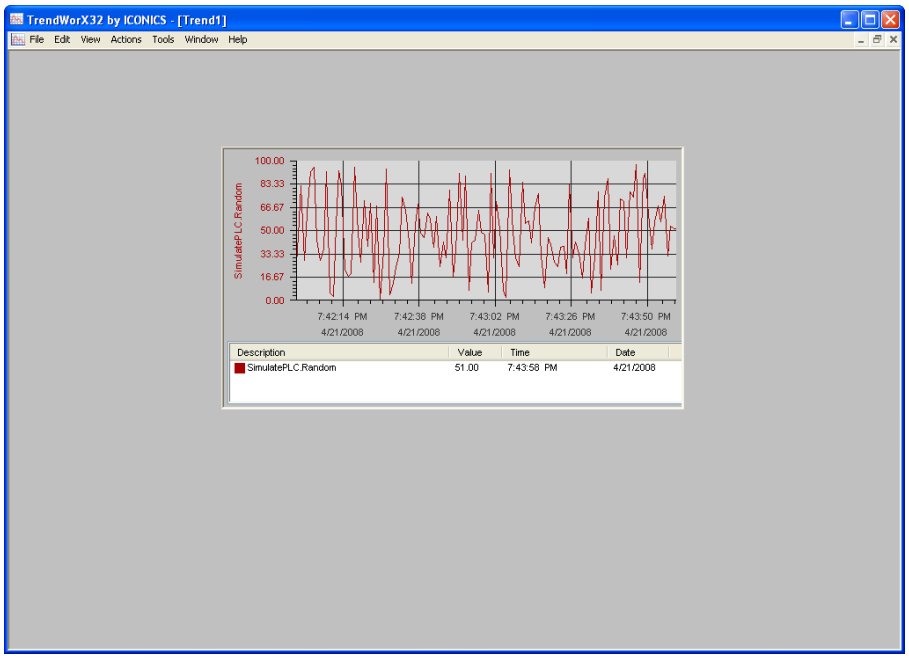
- GraphWorX32 is a major tool, is a human-machine interface (HMI) software package for process control. It helps create dazzling animated graphics.

- TrendWorX32 is a powerful collection of real-time trending, historical data logging, reporting, and analysis tools that seamlessly integrates with enterprise-wide information systems. It offers an open solution to applications requiring scalable and distributed real-time performance.

- AlarmWorX32 is a distributed enterprise-wide alarm and events management system. It offers the tools you need to deliver real-time alarm information throughout your system. These tools are shown in Figure 31.

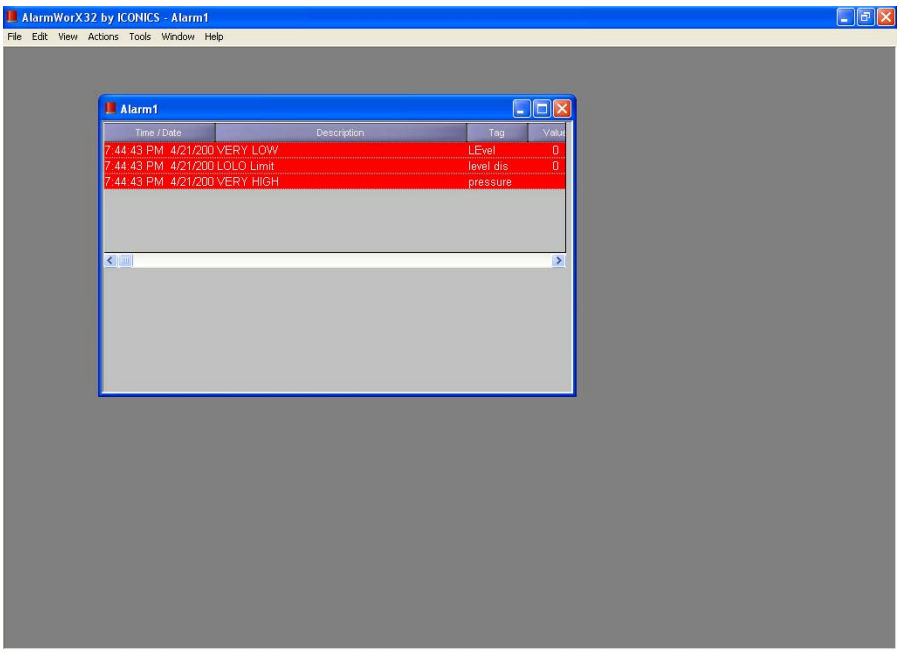


(a)



(b)

Figure 31 (a) The illustration of GraphWorX32, (b) The illustration of TrendWorX32 (c) The illustration of AlarmWorX32



(c)

Figure 31 (Continued)

Due to the speed and flexibility of computers, there is an increasing use of software in industry to control or manage systems that are safety-critical. In some cases, as systems become more and more complex, and faster and faster response time is required, the use of computer and application software is the only feasible approach. In this work, a safety-critical system refers to a system which, if it malfunctions, may cause injury to people, loss of life or serious damage to property (Saenate, 2007).

Visual Basic 6.5 is used to connect with ASPEN PLUS and bring results to interface of Genesis 32. The interface module can show results and change the input parameter of process. Alarm condition is shown when the input parameter is less or more than control period. Since the process is out of control, it may be dangerous. Additionally, the conversion will not be maximum. Figure 32 shows diagrams of this work.

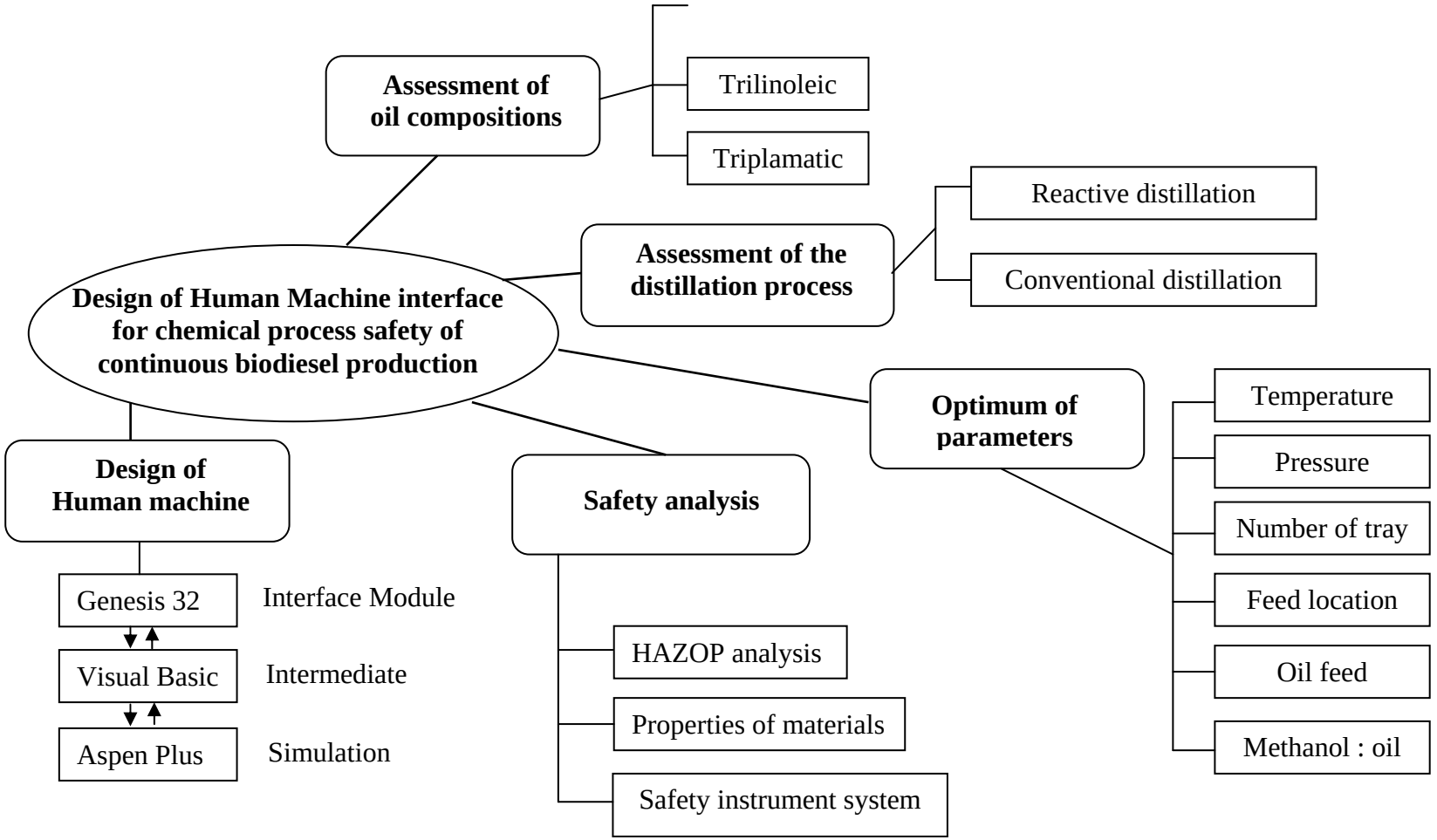


Figure 32 Diagrams of this work

RESULTS AND DISCUSSION

This thesis incorporated the simulation of biodiesel production with safety analysis. It can be divided into two parts. The first part was the simulation of biodiesel from conventional and reactive distillation processes. The second part performed the safety analysis having a feature to work with the first part, seamlessly.

All simulations of biodiesel process have been performed by commercial simulator named ASPEN Plus version 2006.5. The simulation consists of six case studies covering both conventional and reactive distillation processes. In addition, various oil compositions are studied in each experiment. Case study contains of six types of biodiesel process. That is shown in Table 7.

Table 7 The case study of biodiesel process

Case study	Compositions of oil
Conventional process of biodiesel	Trioleic
	Trioleic, Trilinoleic
	Trioleic, Trilinoleic, Triplamatic
Biodiesel production by reactive distillation	Trioleic
	Trioleic, Trilinoleic
	Trioleic, Trilinoleic, Triplamatic

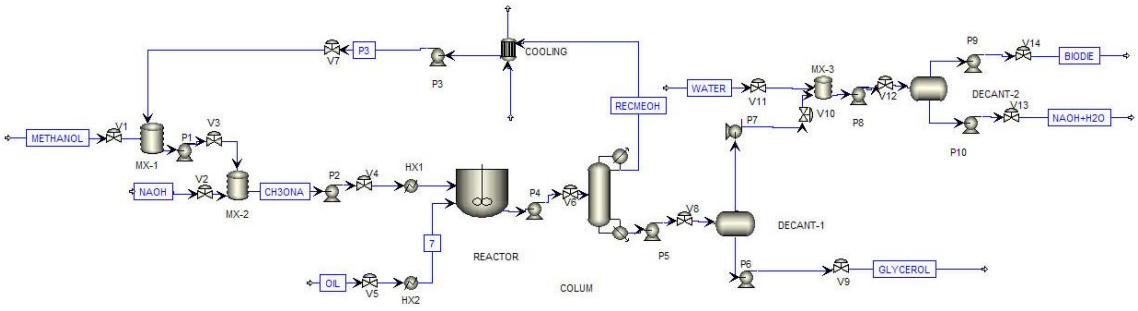


Figure 33 The conventional process of biodiesel production from ASPEN PLUS
Source : Modified from Warasak (2007)

Figure 33 shows the simulation in conventional process using ASPEN PLUS. The detail of units in the conventional process is shown in the Table 8.

Table 8 The unit in the conventional process

ILLUSTRATION	UNIT	NUMBER OF UNIT
	Reactor	1
	Distillation	1
	Heat exchanger	3
	Decanter	2

Table 8 (Continued)

ILLUSTRATION	UNIT	NUMBER OF UNIT
	Mixer	3
	Pump	10
	Valve	14

Operating conditions, specifications and assumptions of the conventional biodiesel process (Zhang *et al*, 2003) are as followed.

1. Temperature in Reactor is 60 ^{o}C and pressure is 1 bar.
2. Distillation column has 10 stages. Reflux ratio and boilup ratio are 1 and 0.6, respectively.
3. Temperature is heated to 60 ^{o}C in heat exchanger.
4. Decanters set pressure at 1 bar and 60 ^{o}C .
5. Mixer is no pressure.
6. Pumps discharge pressure to 3 bar.
7. Pressure drop in valve is 2 bar.

1. Case study

Case 1. The conventional process of biodiesel from one component of oil

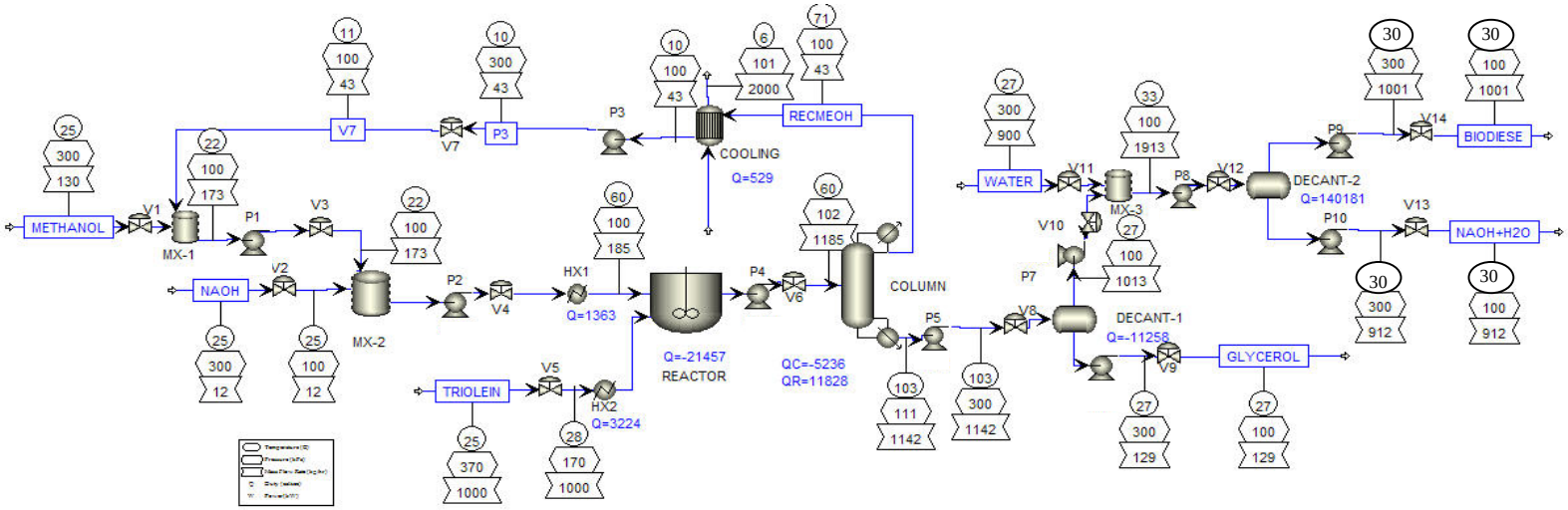
In the first simulation, the conventional process is used to simulate with only trioleic oil as a reactant. This simulation can produce methyl oleate or biodiesel. In this work, we feed 1000 kg/hr of trioleic. We can receive 999 kg/hr of methyl oleic and 101.9 kg/hr of glycerol. The conversion of oil is 99.877 wt%. Purity of biodiesel and glycerol are 99.80 wt % and 72.86 wt %, respectively.

Case 2. The conventional process of biodiesel from two components of oil

In this case, 1000 kg/hr of feed oil includes 55.6 % of trioleic and 44.3 % of trilinoleic in 1000 kg/hr of oil. The results show 556.8 kg/hr of trioelic and 443.2 kg/hr of trilinoleic can produce 557.0 kg/hr of methyl oleate and 443.1 kg/hr of methyl linoleate, respectively. Therefore, this simulation can receive glycerol at 102.4 kg/hr. The conversion of oil is 99.878 wt%. Purity of biodiesel and glycerol are 99.82 wt % and 71.59 wt %, respectively.

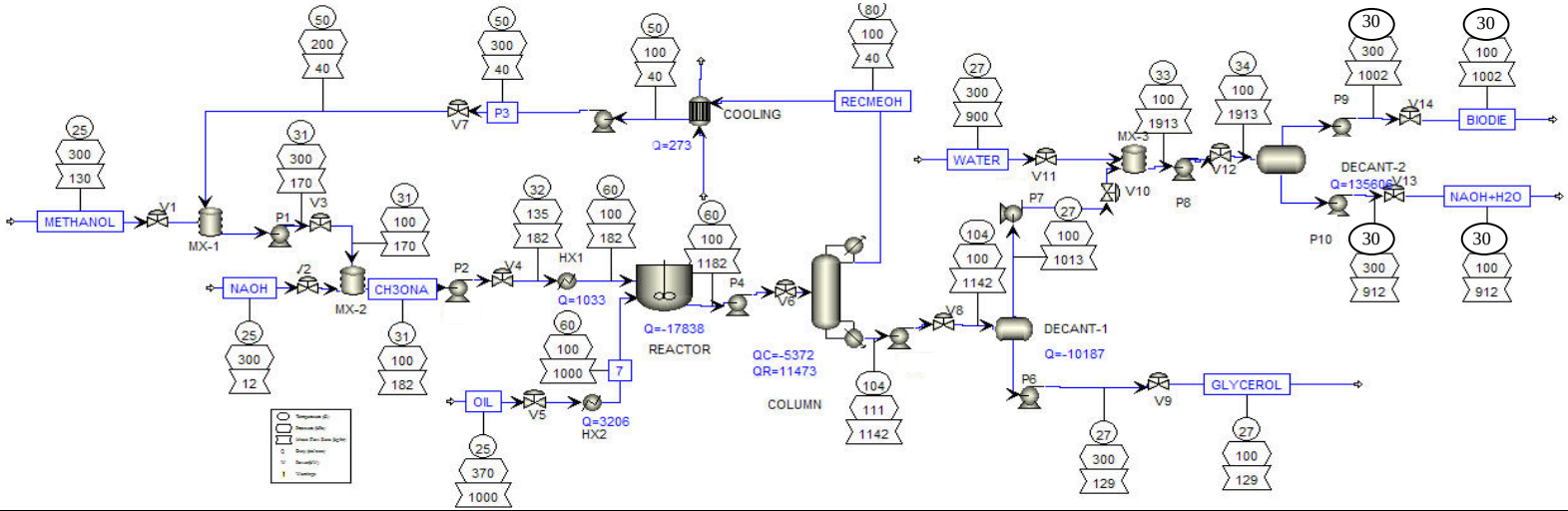
Case 3. The conventional process of biodiesel from three components of oil

Trioleic, trilinoleic and triplamatic are used in this case. 500 kg/hr of trioleic, 300 kg/hr of trilinoleic and 200 kg/hr of triplamatic can produce 533.1 kg/hr of methyl oleate, 303.1 kg/hr of methyl linoleate and 155 kg/hr of methyl plasmatic; respectively. Glycerol is 102.5 kg/hr. Purity of biodiesel and glycerol are 99.82 wt % and 71.98 wt %, respectively. The conversion of oil is 99.868 wt%. In case 3, the amount of biodiesel is lower than cases 1 and 2. Therefore, component of oil is influence for this biodiesel process. The simulation results of three conventional cases are shown in Figures 34, 35 and 36.



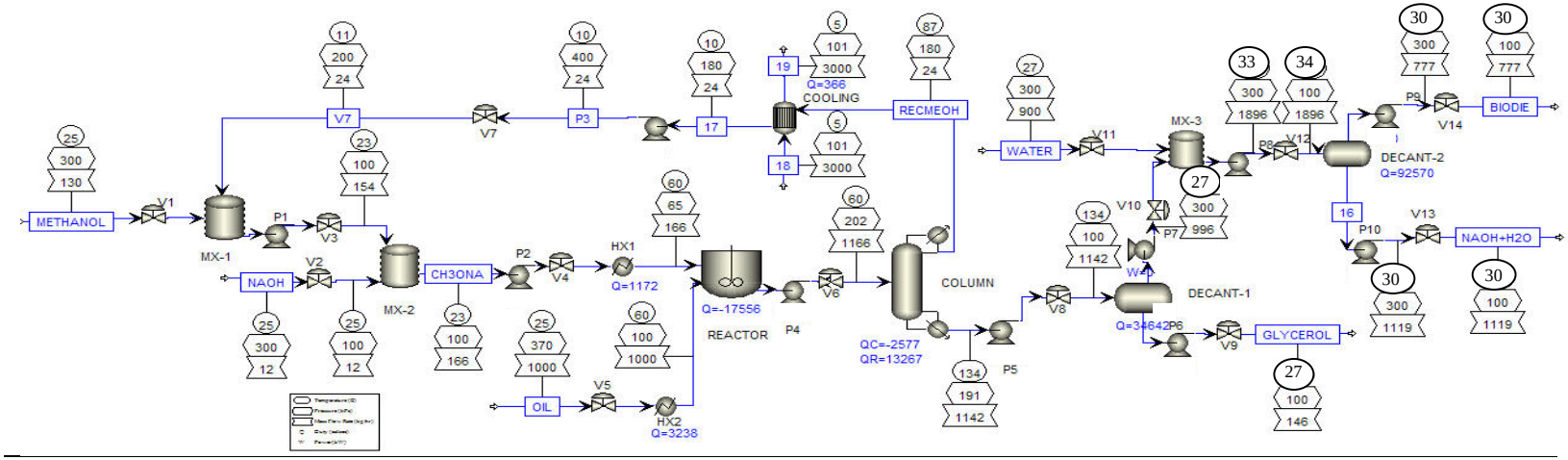
Stream name	TRIOLEIN	METHANOL	NAOH	CH3ONA	BOTTOM-COLUMN	RECMEOH	WATER	GLYCEROL	NAOH+H2O	BIODIESE
Temperature (C)	25.0	25.0	25.0	21.7	103.1	71.3	27.0	27.3	30.0	30.0
Pressure (bar)	3.7	3.0	3.0	1.0	1.1	1.0	3.0	1.0	1.0	1.0
Mole Flow (kmol/hr)	1.1294	4.0572	0.3000	5.5173	5.4866	1.1601	49.9576	1.7909	50.2583	3.3950
Mass Flow (kg/hr)	1000	130	12	185	1142	43	900	129	912	1001
Volume Flow (cum/hr)	20.4995	0.1640	0.0063	0.2622	1.3525	0.1098	0.9076	0.1050	1.4951	1.5837
Mass Fraction										
TRIOLEIN	1	0	0	0.0300	0.0013	0.1302	0	0.0007	0.0001	0.0012
METHANOL	0	1	0	0.9050	0.0191	0.8698	0	0.1030	0.0086	0.0006
NAOH	0	0	1	0.0650	0.0105	0	0	0.0804	0.0017	0
MET-OLE	0	0	0	0	0.8770	0	0	0.0137	0.0005	0.9981
GLYCEROL	0	0	0	0	0.0907	0	0	0.7896	0.0018	0
WATER	0	0	0	0	0	0	1	0	0.9872	0.0001
NA2SO4	0	0	0	0	0	0	0	0	0	0
DI-OLEIN	0	0	0	0	0.0014	0	0	0.0126	0	0
MONO-OLE	0	0	0	0	0	0	0	0	0	0

Figure 34 One component (Triolein) of conventional biodiesel process



Stream name	OIL	METHANOL	NAOH	CH3ONA	BOTTOM-COLUMN	RECMEOH	WATER	GLYCEROL	NAOH+H2O	BIODIE
Temperature (C)	25.0	25.0	25.0	31.3	104.0	80.0	27.0	27.3	30.0	30.0
Pressure (bar)	3.7	3.0	300.0	1.0	1.1	1.0	3.0	1.0	1.0	1.0
Mole Flow (kmol/hr)	1.1328	4.0572	0.3000	5.5735	5.4900	1.2163	49.9576	1.7850	50.2553	3.4073
Mass Flow (kg/hr)	1000	130	12	182	1142	40	900	129	912	1002
Volume Flow (cum/hr)	19.4411	0.1640	0.0063	0.2253	1.3851	0.0712	0.9076	0.1030	1.4933	1.5409
Mass Fraction										
TRIOLEIN	0.5568	0	0	0.0059	0.0005	0.0266	0	0.0003	0.0001	0.0005
METHANOL	0	1	0	0.9257	0.0187	0.9613	0	0.1015	0.0085	0.0006
NAOH	0	0	1	0.0658	0.0105	0	0	0.0802	0.0018	0
MET-OLE	0	0	0	0	0.4887	0	0	0.0074	0.0003	0.5559
GLYCEROL	0	0	0	0	0.0911	0	0	0.7945	0.0019	0
WATER	0	0	0	0	0	0	1	0	0.9872	0.0001
DI-OLEIN	0	0	0	0	0.0006	0	0	0.0054	0	0
MONO-OLE	0	0	0	0	0	0	0	0	0	0
TRI-LINO	0.4432	0	0	0.0027	0.0005	0.0121	0	0	0	0
DI-LINO	0	0	0	0	0.0005	0	0	0.0040	0	0
MONO-LIN	0	0	0	0	0	0	0	0	0	0
MET-LINO	0	0	0	0	0.3889	0	0	0.0067	0.0002	0.4423

Figure 35 Two components (56 % Triolein and 44 % Trilinoleic) of conventional biodiesel process



Stream name	OIL	METHANOL	NAOH	CH3ONA	BOTTOM-COLUMN	RECMEOH	WATER	GLYCEROL	NAOH+H2O	BIODIE
Temperature (C)	25.0	25.0	25.0	23.1	134.0	87.3	27.0	27.3	30.0	30.0
Pressure (bar)	3.7	300.0	3.0	1.0	1.9	1.8	3.0	1.0	1.0	1.0
Mole Flow (kmol/hr)	1.1536	4.0572	0.3000	4.9563	5.5107	0.5991	49.9576	1.2206	51.5949	2.6528
Mass Flow (kg/hr)	1000	130	12	166	1142	24	900	146	1119	1002
Volume Flow (cum/hr)	18.6822	0.1640	0.0063	0.2327	1.4065	0.0768	0.9076	0.1976	2.0599	1.1924
Mass Fraction										
TRIOLEIN	0.5	0	0	0.0223	0	0.1541	0	0	0	0
METHANOL	0	1	0	0.8975	0.0170	0.7914	0	0.0407	0.0114	0.0009
NAOH	0	0	1	0.0723	0.0105	0	0	0.0293	0.0068	0.0001
MET-OLE	0	0	0	0	0.4389	0	0	0.1307	0.0018	0.5321
GLYCEROL	0	0	0	0	0.0927	0	0	0.7020	0.0399	0
WATER	0	0	0	0	0	0	1	0	0.8040	0.0001
DI-OLEIN	0	0	0	0	0.0010	0	0	0.0049	0.0004	0
TRI-LINO	0.3	0	0	0.0070	0	0.0484	0	0	0	0
DI-LINO	0	0	0	0	0.0005	0	0	0.0024	0.0002	0
MONO-LIN	0	0	0	0	0	0	0	0.0000	0	0
MET-LINO	0	0	0	0	0.2634	0	0	0.0782	0.0012	0.3029
TRIPALM	0.2	0	0	0.0009	0.0004	0.0061	0	0.0006	0.0003	0
DIPALM	0	0	0	0	0.0003	0	0	0.0005	0.0002	0
METHPALM	0	0	0	0	0.1754	0	0	0.0037	0.1338	0.1547

Figure 36 Three components (50 % Triolein, 30 % Trilinoleic and 20% Tripalmatic) of conventional biodiesel process

1.1 Optimum parameters of reactive distillation

Due to the limitations and constraints in the experimental, some of the important design parameters such as column pressure, reflux ratio, number of rectifying, number of stripping and number of reaction zones could not be studied experimentally. Therefore, the effect of these parameters on the conversion of biodiesel needs to be evaluated by simulation. The simulations were based on base case of reactive distillation. In this work, reaction zone and feed location of biodiesel process on reactive distillation were investigated.

Normally, the height of reaction zone depends on the type of the catalyst. In the heterogeneous, height of reaction zone depends on the height of catalyst. On the other hand, in the homogeneous catalyst, it depends on the contacting between reactant in the column. In this research, homogeneous catalyst which is sodium hydroxide was used to promote the biodiesel conversion. Therefore, the height of reaction zone was depended on the contacting between oil and methanol. The arrangements of two feed reactants were analyzed in order to find the optimum reaction zone. The heavy reactant feed should be placed at the above position over the light reactant. Because the light reactant will be vaporized into higher position and the heavy reactant will be fallen into lower position, It will be mixed in the middle position. Thus, the methanol which is the light reactant should be fed at the lower and oil should be fed at the higher position of column. However, the light reactant consists of methanol and sodium hydroxide. When the light reactant is fed at the lower, the sodium hydroxide cannot react with oil. Since the boiling point is very high (1390 °C), it does not vaporize to upstairs. Therefore in this simulation, the both light and heavy reactants are fed into same position. The higher reaction is occurred with this procedure.

The column conditions were based on base case. Only number of reaction zone was varied. Figure 37 demonstrates the number of reaction zone. According to this figure, the number of reaction zone increases from one to eight.

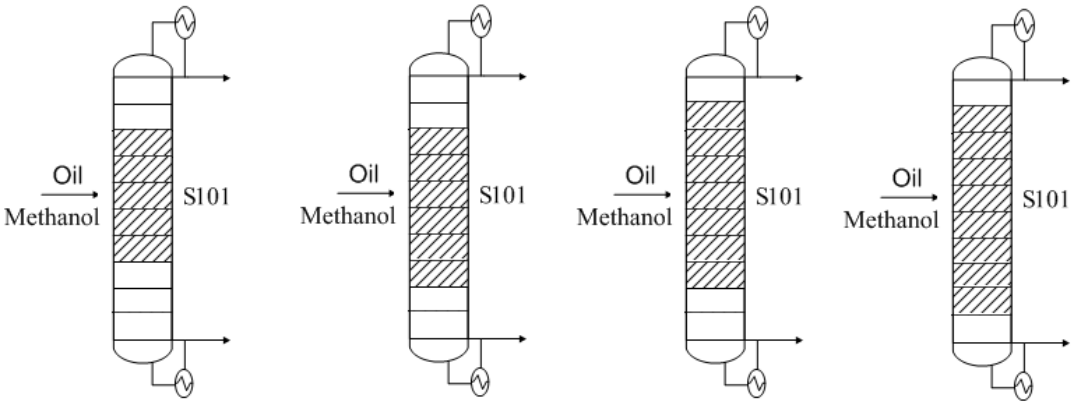


Figure 37 The number of reaction zone in reactive distillation

The effect of reaction zone on the biodiesel conversion was illustrated in the Figure 38. It seems from the figure that the conversion increases as the reaction zone increase because the reaction has more time in distillation. The maximum biodiesel is 787.2 kg/hr at four reaction zone. However, the increasing reaction zone after 4 stages cannot give much the effective conversions. Therefore, the optimum reaction zone could be at 4 stages.

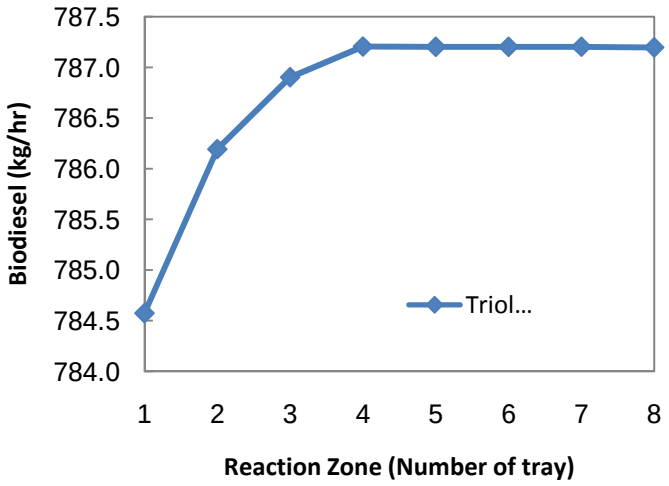


Figure 38 The effect of reaction zone on the biodiesel production

The reactive distillation column could be treated as a tubular reactor with separation units while the reaction zone of a reactive distillation column can view as a cascade-type two phase reactor with the reactor temperature determined from the

bubble-point temperature of the tray liquid phase composition. The composition and temperature profiles could affect the performance of the reactive zone, and the feed tray locations appear to be the important variables. A right choice of feed location ensures high conversion of reactants in the reactive zone. In Figure 39 is illustrated, the feed location is set at tray 5, 6, 7 and 8; respectively. And Figure 40 shows the effect of feed location on biodiesel production.

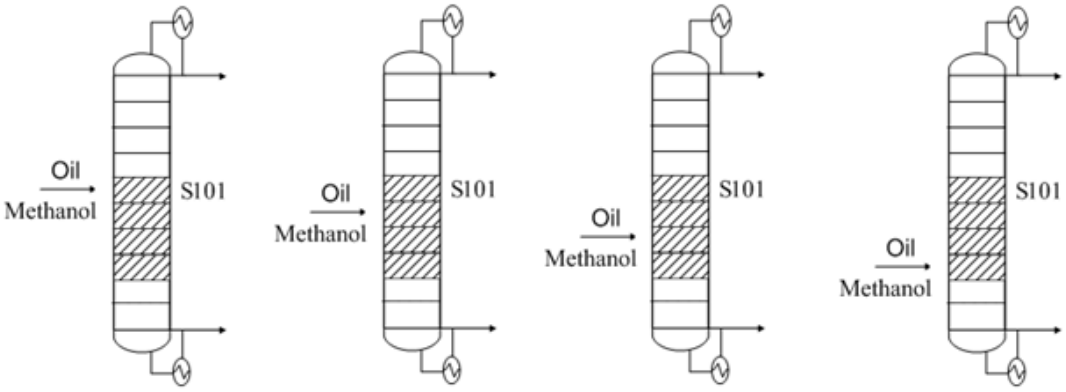


Figure 39 Feed location in reactive zone

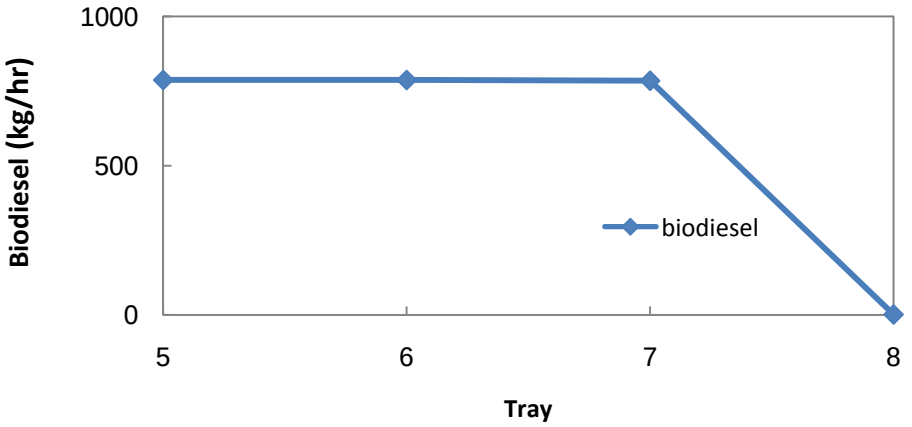


Figure 40 The effect of feed location on biodiesel production

When the reaction zone of this experimental was selected at four trays, the optimal feed location of four trays was verified. Figure 40 shows the four reactive distillation columns with different feed tray location. The effects of feed tray locations

were investigated by comparing the biodiesel production. The result shows that the feed location at tray 5 can receive the maximum biodiesel at 787.2 kg/hr. Therefore, the optimal location is fed into tray 5 that gives the highest production.

Case 4. Biodiesel production by reactive distillation from one component of oil

In this case, we improve the biodiesel production from conventional to reactive distillations in order to propose better performance of biodiesel production. It can decrease the number of units in process. Figure 41 shows simulation process of biodiesel production by reactive distillation from ASPEN PLUS and Table 9 shows the units of reactive distillation process.

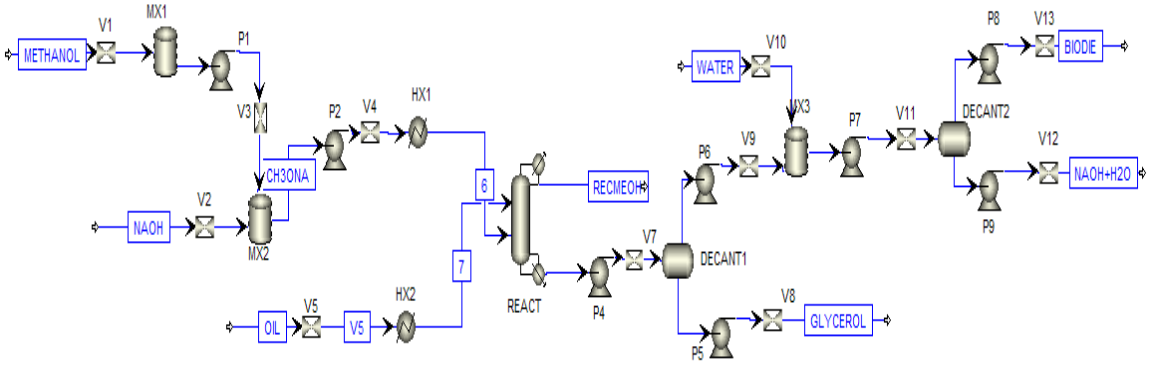


Figure 41 Biodiesel production by reactive distillation from ASPEN PLUS

Table 9 The units of reactive distillation process

ILLUSTRATION	UNIT	NUMBER
	Reactive Distillation	1
	Heat exchanger	2
	Decanter	2
	Mixer	3
	Pump	9
	Valve	13

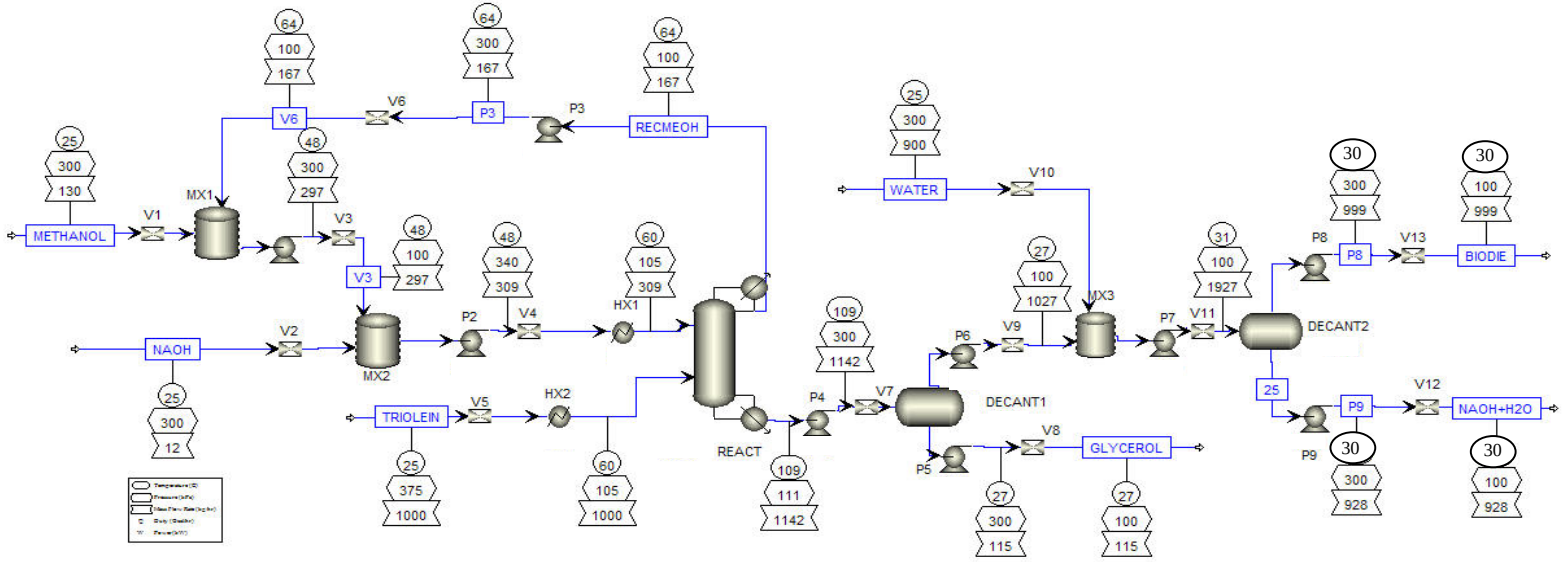
In reactive distillation process can reduce the number of units from 34 to 30. In this process can reduce one reactor, pump, heat exchanger and valve. Component of oil in this simulation is 1000 kg/hr of trioleic. The simulation can produce the methyl oleic at 997.5 kg/hr and glycerol at 96.0 kg/hr. The conversion of oil is 99.963 wt%. Purity of biodiesel and glycerol are 99.84 wt % and 73.15 wt %, respectively.

Case 5. Biodiesel production by reactive distillation from two components of oil

In this case, trioleic and trilinoleic are the components of oil in reactant. 554.9 kg/hr of Methyl oleate, 441.6 kg/hr of methyl linoleate and 97 kg/hr of glycerol are produced in this simulation. The conversion of oil is 99.959 wt%. Purity of biodiesel and glycerol are 99.86 wt % and 73.45 wt %, respectively.

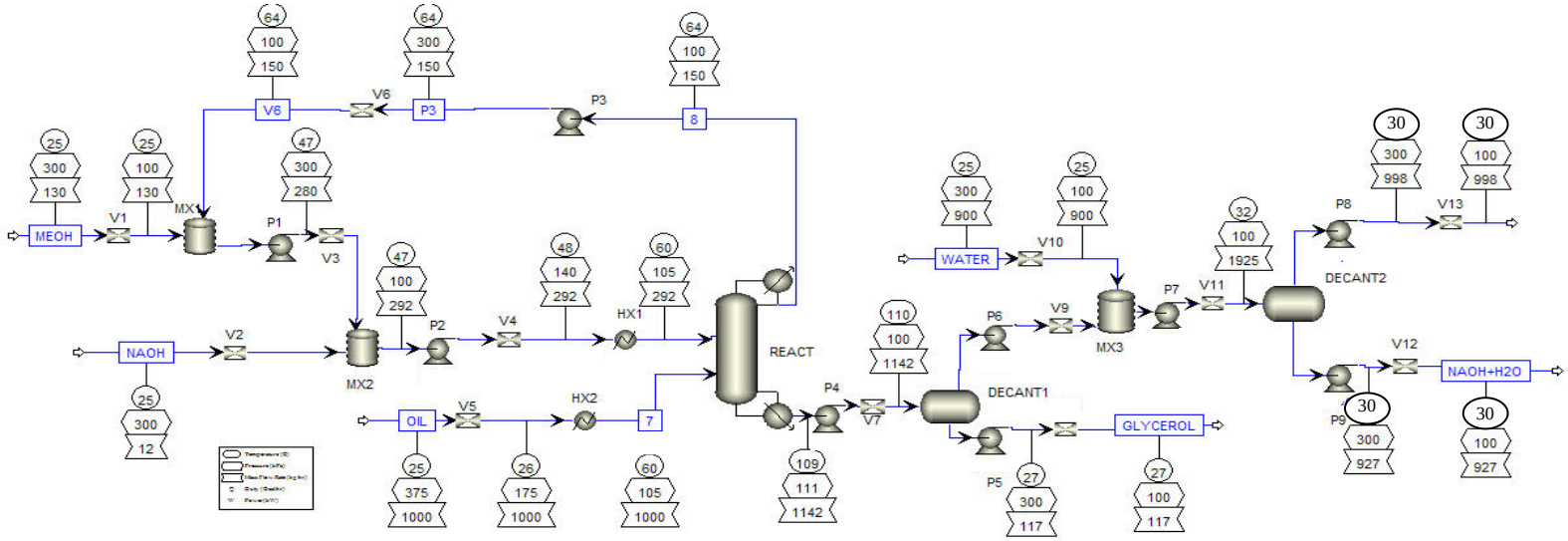
Case 6. Biodiesel production by reactive distillation from three components of oil

500 kg/hr of trioleic, 300 kg/hr of trilinoleic and 200 kg/hr of triplamatic can produce 502.1kg/hr of methyl oleate, 301.3 kg/hr of methyl linoleate and 198.4 kg/hr of methyl plamatic, respectively. Glycerol is 106.5 kg/hr. Purity of biodiesel and glycerol are 99.84 wt % and 74.52 wt %, respectively. The conversion of oil is 99.955 wt%. Figures 43, 44 and 45 perform the results of reactive distillation processes.



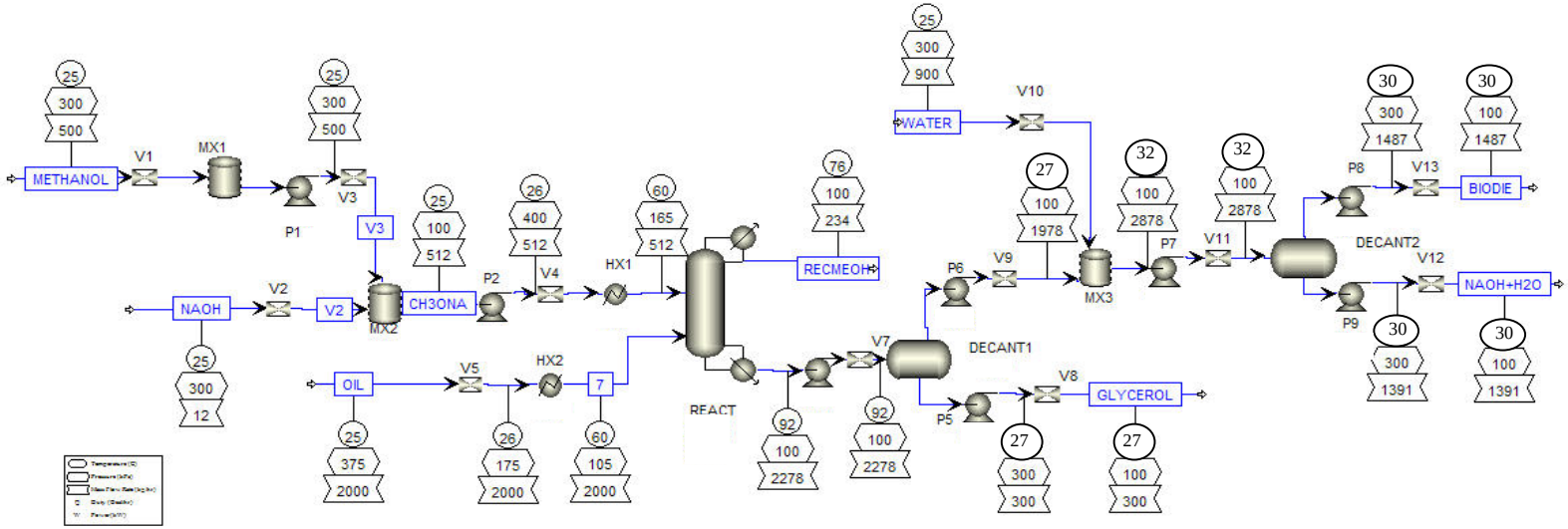
Stream name	TRIOLEIN	METHANOL	NAOH	CH3ONA	BOTTOM-COLUMN	RECMEOH	GLYCEROL	NAOH+H2O	BIODIE
Temperature (C)	25.0	25.0	25.0	48.2	108.5	64.2	27.3	30.0	30.0
Pressure (bar)	3.7	3.0	3.0	1.0	1.1	1.0	1.0	1.0	1.0
Mole Flow (kmol/hr)	1.1294	4.0572	0.3000	9.5698	5.4868	5.2124	1.4430	50.5981	3.4033
Mass Flow (kg/hr)	1000	130	12	309	1142	167	115	928	999
Volume Flow (cum/hr)	1.1017	0.1640	0.0063	0.3781	1.3408	0.2243	0.0940	1.2177	1.4020
Mass Fraction									
TRIOLEIN	1	0	0	0	0.0002	0	0.0002	0.0001	0.0001
METHANOL	0	1	0	0.9612	0.0188	1	0.0849	0.0119	0.0007
NAOH	0	0	1	0.0388	0.0105	0	0.0257	0.0091	0.0006
MET-OLE	0	0	0	0	0.8793	0	0.0549	0.0005	0.9985
GLYCEROL	0	0	0	0	0.0910	0	0.8343	0.0085	0.0000
WATER	0	0	0	0	0	0	0	0.9698	0.0001
DI-OLEIN	0	0	0	0	0.0001	0	0	0	0.0001
MONO-OLE	0	0	0	0	0	0	0	0	0

Figure 42 One component (Triolein) of reactive distillation biodiesel



Stream name	OIL	METHANOL	NAOH	CH3ONA	BOTTOM-COLUMN	RECMEOH	GLYCEROL	NAOH+H2O	BIODIE
Temperature (C)	25.0	25.0	25.0	47.2	109.3	64.2	27.3	30.0	30.0
Pressure (bar)	3.7	3.0	3.0	1.0	1.1	1.0	1.0	1.0	1.0
Mole Flow (kmol/hr)	1.1328	4.0572	0.3000	9.0380	5.4900	4.6808	1.4535	50.5825	3.4116
Mass Flow (kg/hr)	1000	130	12	292	1142	150	117	927	998
Volume Flow (cum/hr)	5.4843	0.1640	0.0063	0.3558	1.3785	0.2016	0.0962	1.2167	1.3846
Mass Fraction									
TRIOLEIN	0.5568	0	0	0	0	0	0	0	0
METHANOL	0	1	0	0.9589	0.0185	0.9999	0.0833	0.0116	0.0007
NAOH	0	0	1	0.0411	0.0105	0	0.0260	0.0091	0.0006
MET-OLE	0	0	0	0	0.4897	0	0.0327	0.0003	0.5561
GLYCEROL	0	0	0	0	0.0913	0	0.8299	0.0082	0.0000
WATER	0	0	0	0	0	0	0	0.9706	0.0001
DI-OLEIN	0	0	0	0	0	0	0	0	0
MONO-OLE	0	0	0	0	0	0	0	0	0
TRI-LINO	0.4432	0	0	0	0	0.0001	0	0	0
DI-LINO	0	0	0	0	0	0	0	0	0
MONO-LIN	0	0	0	0	0	0	0	0	0
MET-LINO	0	0	0	0	0.3898	0	0.0280	0.0002	0.4425

Figure 43 Two components (56 % Triolein and 44% Trilinoleic) of reactive distillation biodiesel



Stream name	OIL	METHANOL	NAOH	CH3ONA	BOTTOM-COLUMN	RECMEOH	GLYCEROL	NAOH+H2O	BIODIE
Temperature (C)	25.0	25.0	25.0	40.6	98.2	76.2	27.3	30.0	30.0
Pressure (bar)	3.7	3.0	3.0	1.0	1.1	1.0	1.0	1.0	1.0
Mole Flow(kmol/hr)	1.1535	4.0571	0.3000	9.3278	5.5072	4.9741	0.9834	54.0035	2.6632
Mass Flow (kg/hr)	1000	130	12	301	1141	159	121	51.818	998
Volume flow(m^3/hr)	6.0779	0.1639	0.0063	0.3649	1.3578	0.2099	0.3985	2.1198	2.0765
Mass Fraction									
TRIOLEIN	0.5	0	0	0	0	0	0.0001	0.0002	0.0001
METHANOL	0	1	0	0.9600	0.0166	0.8773	0.0028	0.0364	0.0005
NAOH	0	0	1	0.0398	0.0105	0	0.0084	0.0063	0.0005
MET-OLE	0	0	0	0	0.4397	0	0.8525	0.0225	0.5031
GLYCEROL	0	0	0	0	0.0930	0	0.0144	0.0676	0.0000
WATER	0	0	0	0	0	0	0	0.6470	0.0001
DI-OLEIN	0	0	0	0	0	0	0	0	0
MONO-OLE	0	0	0	0	0	0	0	0	0
TRI-LINO	0.3	0	0	0	0	0.0001	0	0	0
MET-LINO	0	0	0	0	0.2639	0	0.076	0.010	0.3016
TRIPALM	0.2	0	0	0	0	0.0155	0	0	0
METPALM	0	0	0	0	0.1760	0	0.008	0.210	0.1958

Figure 44 Three components (50 % Triolein, 30 % Trilinoleic and 20% Tripalmatic) of reactive distillation biodiesel

1.2 Effect on flow of oil in simulation biodiesel process.

In this work, the effect on quantity of oil in reaction is investigated. In the conventional process, the flow of oil is varied from 100 kg/hr to 1200 kg/hr. The methanol feed is fixed at 130 kg/hr. Figures 45 to 47 perform the effect of oil flow on three cases of conventional process and three cases of reactive distillation.

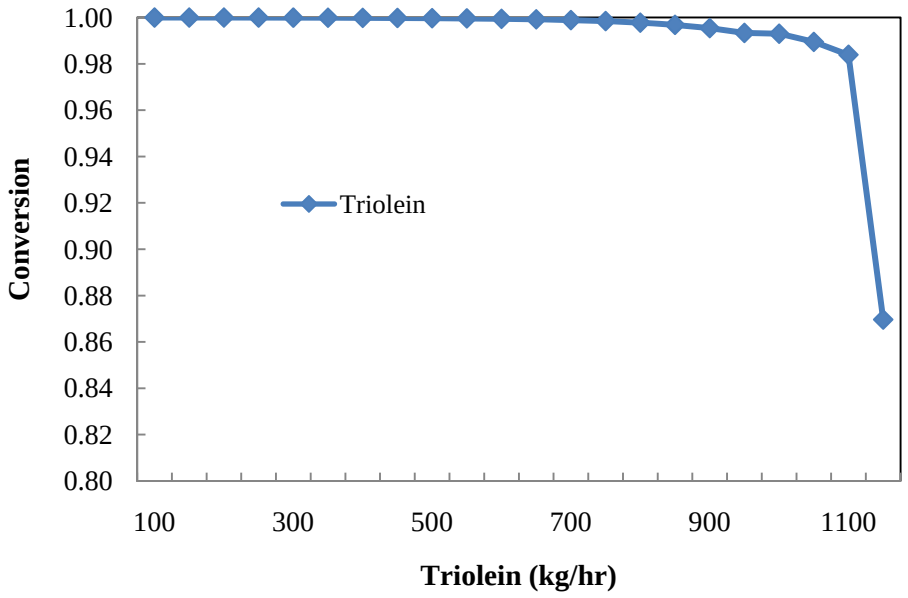


Figure 45 Effect of oil flow in conventional process from one component of oil

In Figure 45, when the flow of triolein is between 100 and 1000 kg/hr, the conversion of triolein is about 0.99. However, the conversion will decrease when the oil feed is more than 1000 kg/hr. Because the quantity of methanol is not enough for quantity of oil. This simulation selected the optimal feed oil between 350 and 750 kg/hr. Because it gives the high conversion of triolein at 0.99. The other reason for selecting this range is the optimal ratio of methanol to oil in the reation. In general, ratio of methanol to oil is 6:1 (Noureddini and Zhu, 1997). Therefore, range of methanol to oil in this case is used 6:1 to 12:1. Since increasing ratio of methanol to oil after 12:1 does not affect to the converion of oil. The ratio of methanol to oil from 12:1 to 6:1 is the range of feed oil at 350 to 750 kg/hr, respectively.

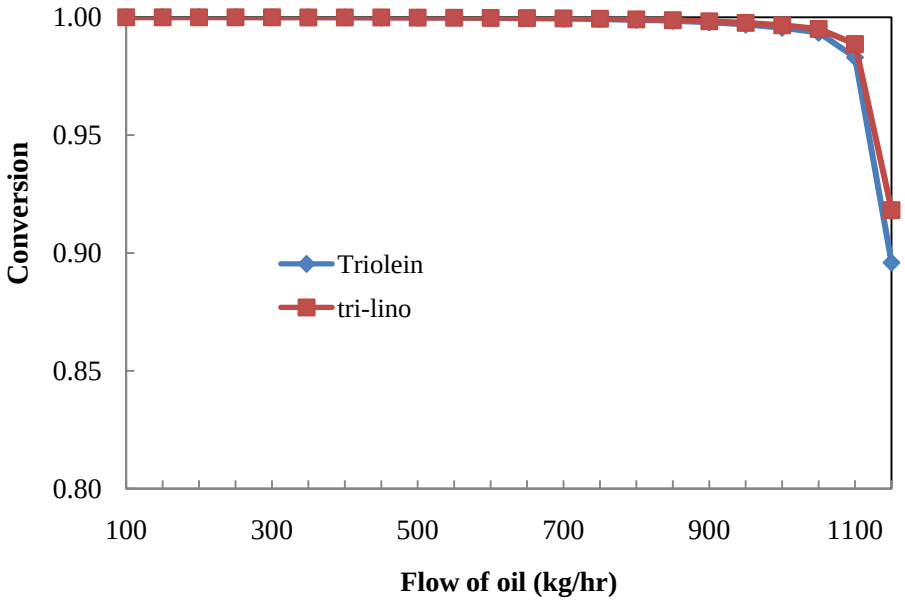


Figure 46 Effect of oil flow in conventional process from two components of oil

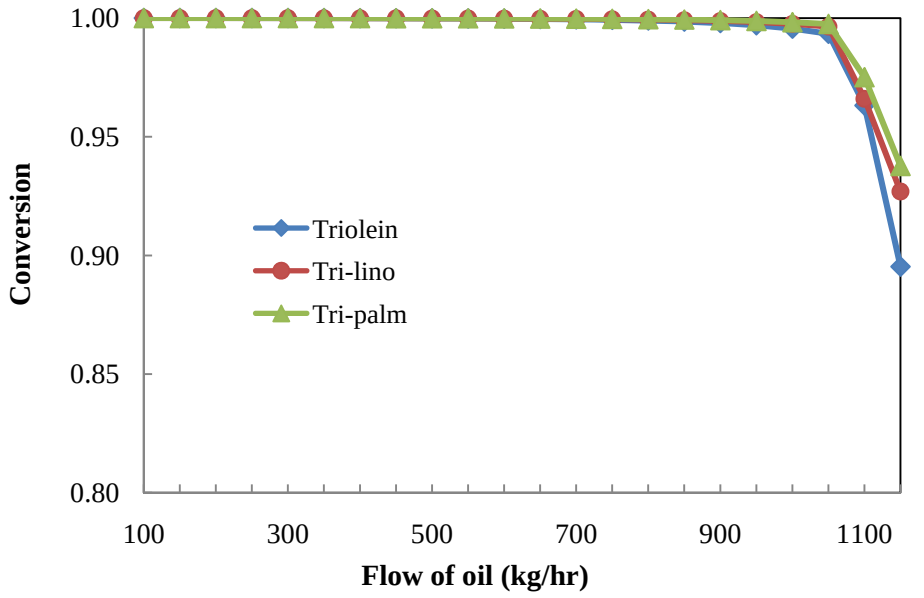


Figure 47 Effect of oil flow in conventional process from three components of oil

In Figures 46 and 47, the conversion of oil will also decrease when flow of oil is more than 1000 kg/hr. The effect of oil flow on three conventional process is alike. The optimal ratio of methanol to oil is 12:1 to 6:1 and the optimal range of feed oil is also 350 to 750 kg/hr in two and three components of oil.

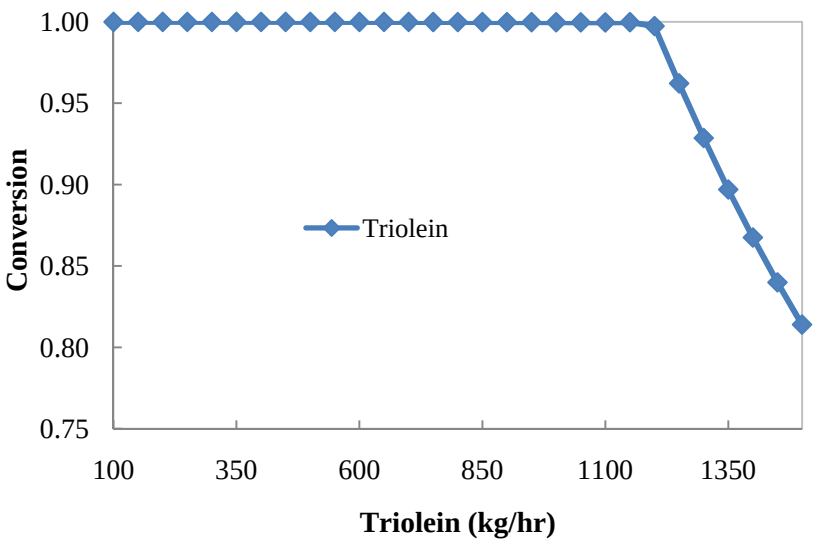


Figure 48 Effect of oil flow in reactive distillation from one component of oil

For the reactive distillation, the flow of oil varied from 100 to 1500 kg/hr and methanol flow is 130 kg/hr in the simulation. The results are shown in Figures 48 to 50. In Figure 48, the conversion of oil becomes lower, when the oil feed increases. The maximum of flow in this process should not be over 1200 kg/hr. Since, it will rapidly decrease when the flow is more than 1200 kg.hr. Because the quantity of oil is more than quantity of methanol for reaction, Some quantity of oil are unreacted. Therefore, the conversion of oil becomes lower, the optimal feed oil is 650 to 1200 kg/hr that receives the high conversion.

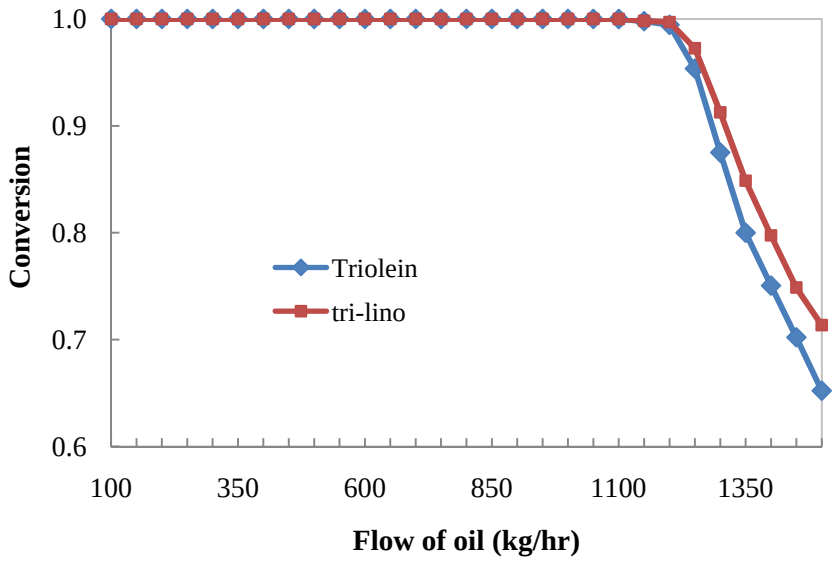


Figure 49 Effect of oil flow in reactive distillation from two components of oil

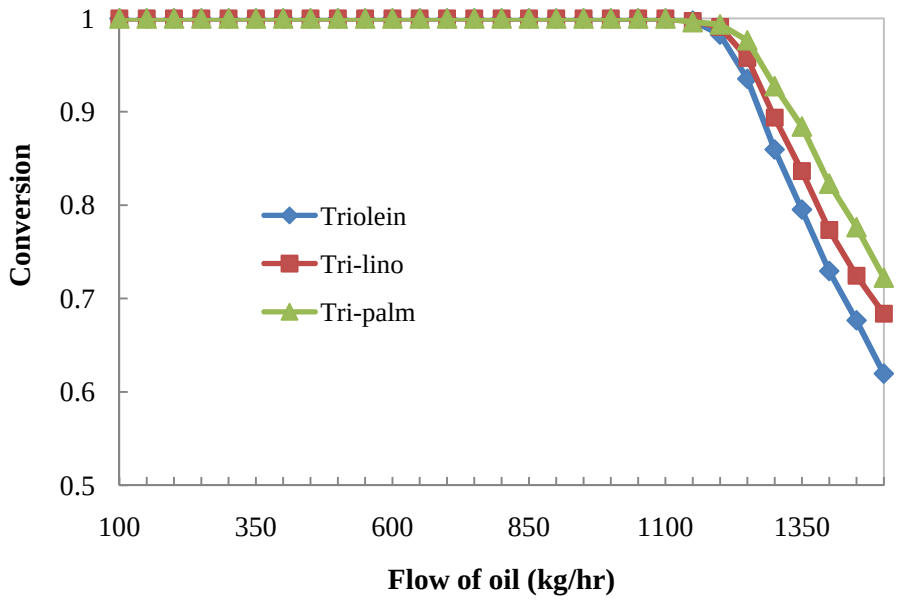


Figure 50 Effect of oil flow in reactive distillation from three components of oil

The reactive distillation from two and three components of oil, the conversion of oil will also decrease at high flow. Therefore, the optimal feed in two and three components should not be over 1150 and1200 kg/hr, respectively. The

optimal range for maximum conversion of oil in two and three components is 500 - 1150 kg/hr and 550-12000 kg/hr, respectively.

1.3 Effect on ratio of methanol to oil in simulation biodiesel process.

The biodiesel process, the ratio of methanol to oil is 3:1 in theory. However, in the real biodiesel process about 6:1 of methanol to oil or more are practiced. Figures 51 to 56 perform the effect of methanol to oil on six cases of biodiesel process.

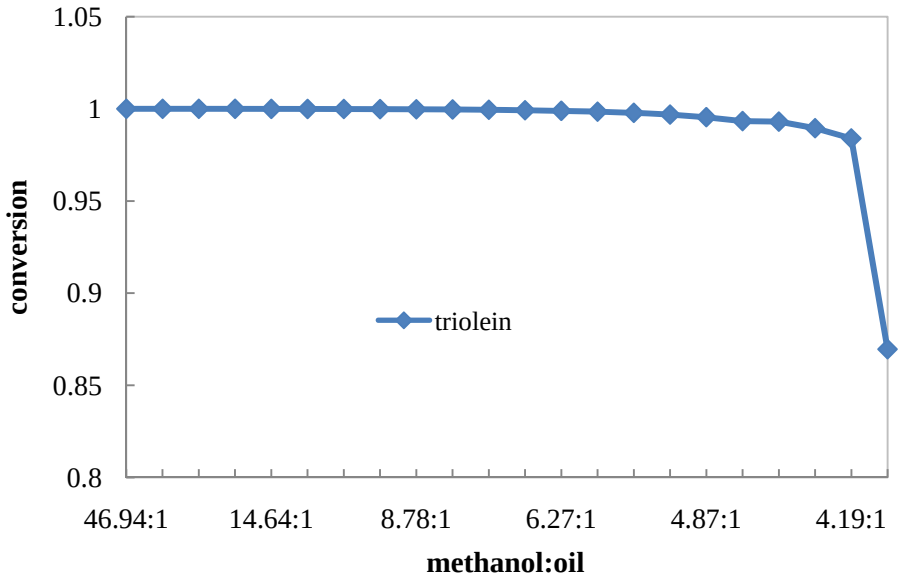


Figure 51 Effect on ratio of methanol to oil in conventional process of biodiesel from one component of oil

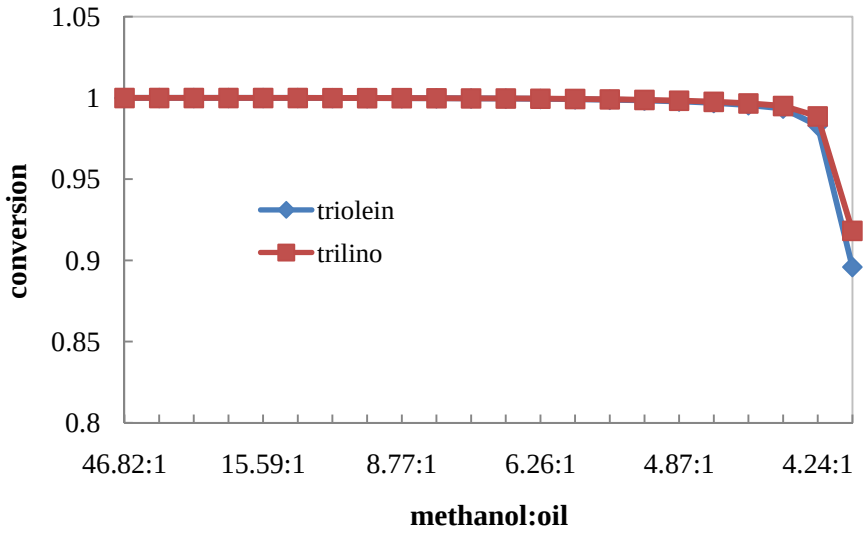


Figure 52 Effect on ratio of methanol to oil in conventional process of biodiesel from two components of oil

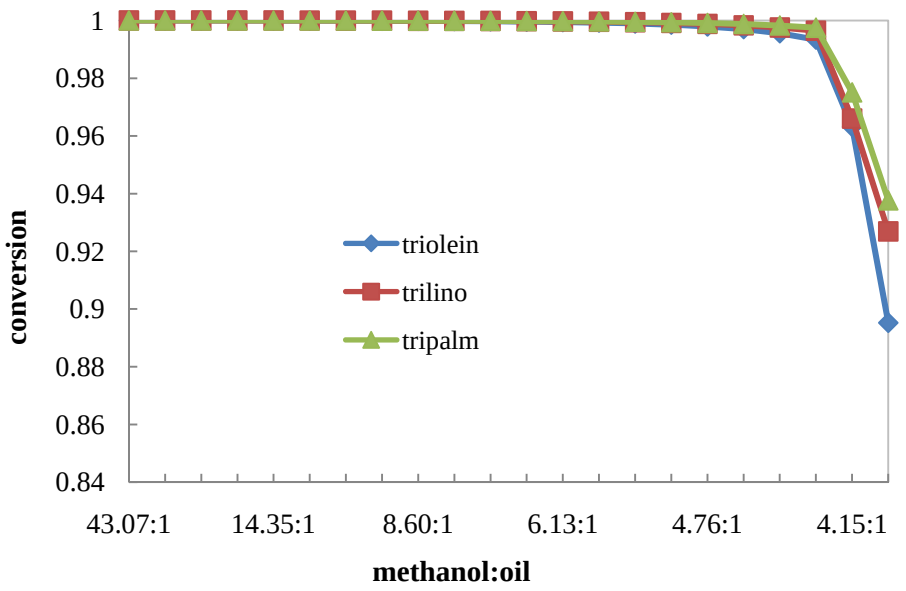


Figure 53 Effect on ratio of methanol to oil in conventional process of biodiesel from three components of oil

Three cases of conventional process, ratio of methanol and oil affects to the reaction. It decreases the conversion when the ratio of methanol is low. The optimal ratio of methanol to oil in three cases of conventional process is 6:1 to 12:1.

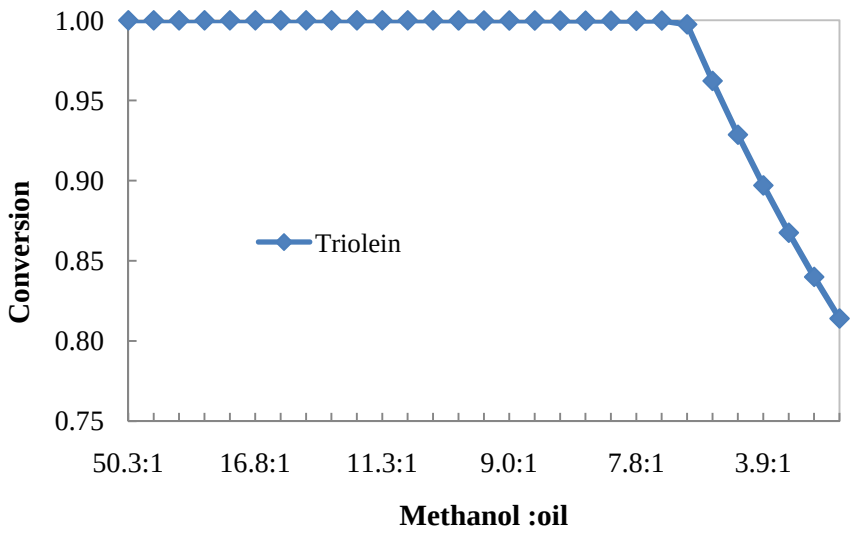


Figure 54 Effect on ratio of methanol to oil in reactive distillation process of biodiesel from one component of oil

Figure 54, the conversion of oil decreases when the ratio of methanol is less than 8:1 because the quantity of methanol is not sufficient for oil in the reaction. Therefore the optimal ratio is 8:1 to 12:1 in this case.

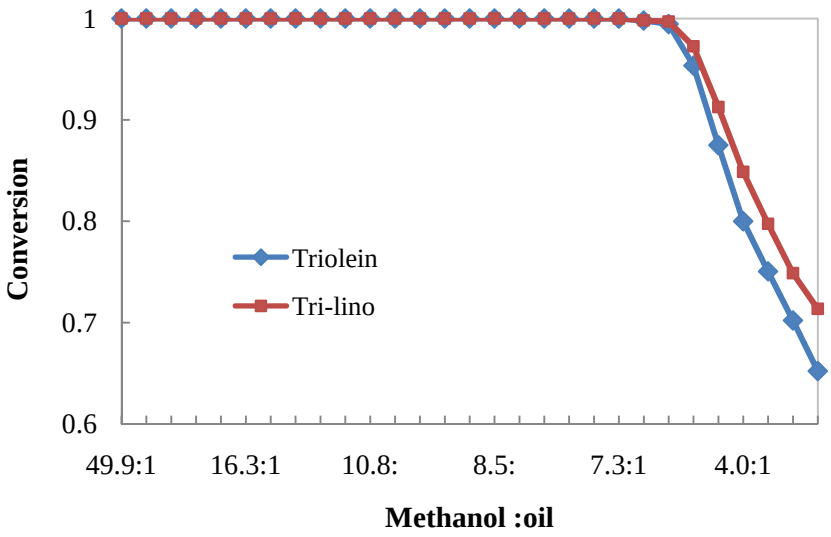


Figure 55 Effect on ratio of methanol to oil in reactive distillation process of biodiesel from two components of oil

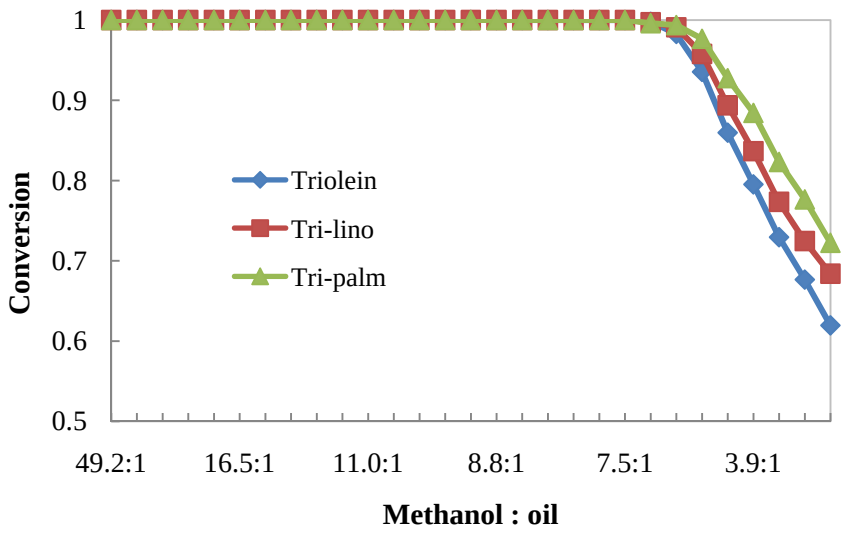


Figure 56 Effect on ratio of methanol to oil in reactive distillation process of biodiesel from three components of oil

The ratio of methanol to oil in two and three components in reactive distillation is 12:1 to 6:1. The high conversion is performed in this range.

1.4 Effect of Temperature on the simulation biodiesel

This process is the endothermic reaction. Temperature in reactor can affect the efficiency of reaction. The effect of temperature on reaction is carried out at a constant pressure of 1 bar. Figure 57 shows the effect of the temperature on conversion of oil. Since endothermic reaction is good in higher temperature. When temperature increases, the conversion will increase. Since the boiling point of methanol is 64.7 ^{o}C, this simulation is operated at 60 ^{o}C to maintain methanol in the liquid phase. The optimal reactor temperature was found in the range of 58 – 64 ^{o}C.

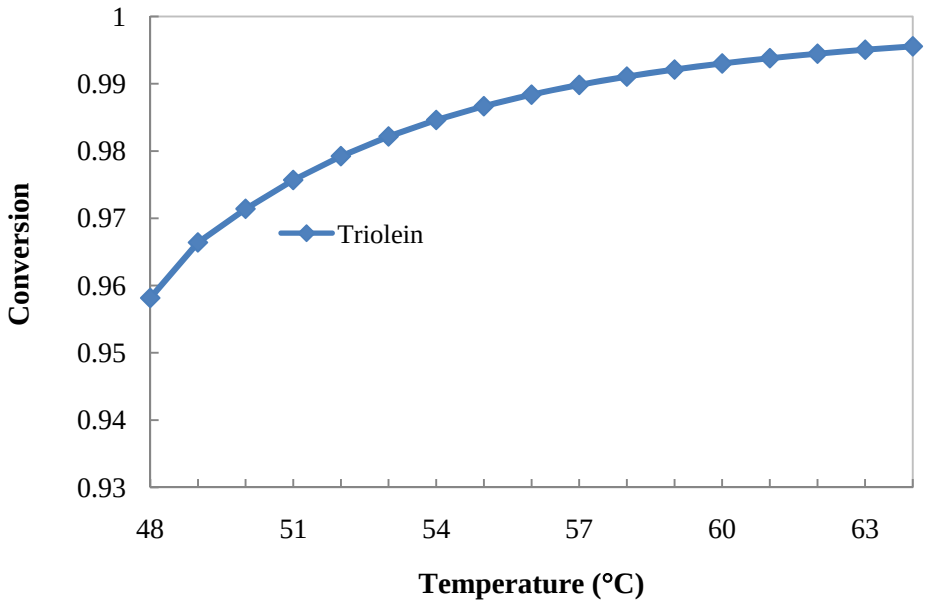


Figure 57 Effect of temperature in conventional process from one component of oil

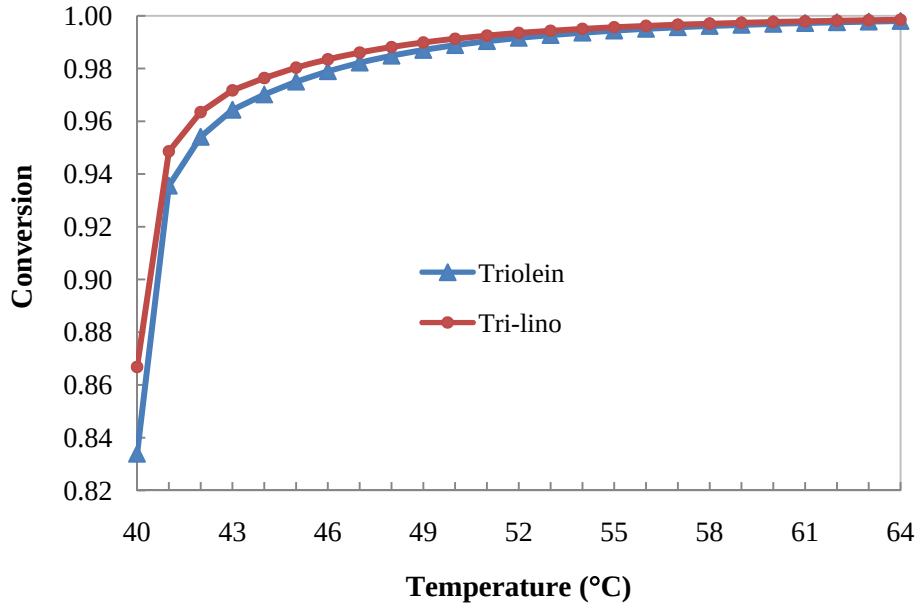


Figure 58 Effect of temperature in conventional process from two components of oil

And the effect of temperature in conventional process from two components of oil is shown in Figure 58. Conversion is higher when temperature increases. The optimal range of temperature is between 58 and 64 ^{o}C.

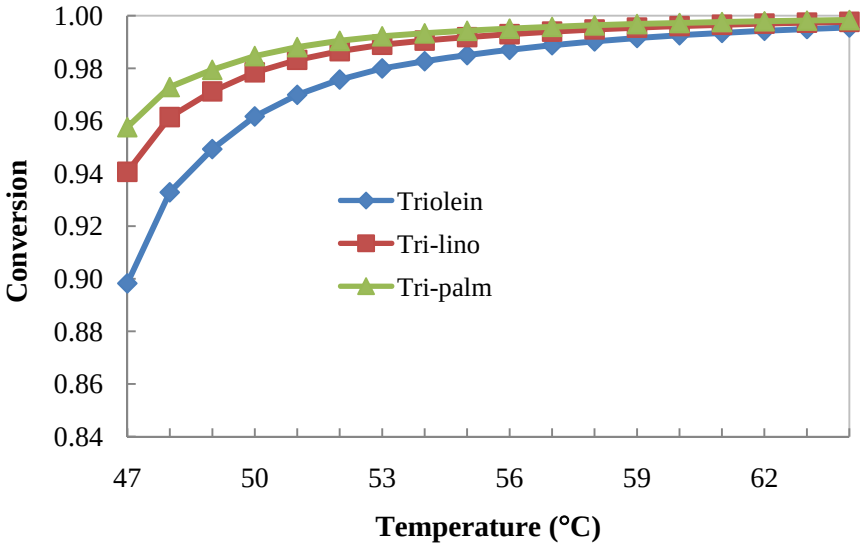


Figure 59 Effect of temperature in conventional process from three components of oil

Figure 59 shows the effect of temperature. Results are the corresponding in three case of conventional process. The conversion will increase in higher temperature. 58-64 ^{o}C is the optimal temperature in reactor for all cases.

1.5 Effect of Pressure on the simulation biodiesel

The effect of pressure on the transesterification of soybean oil to methyl esters, was experimentally investigated at a constant temperature of 60 ^{o}C. The effect of pressure on conventional process was shown in the following figures.

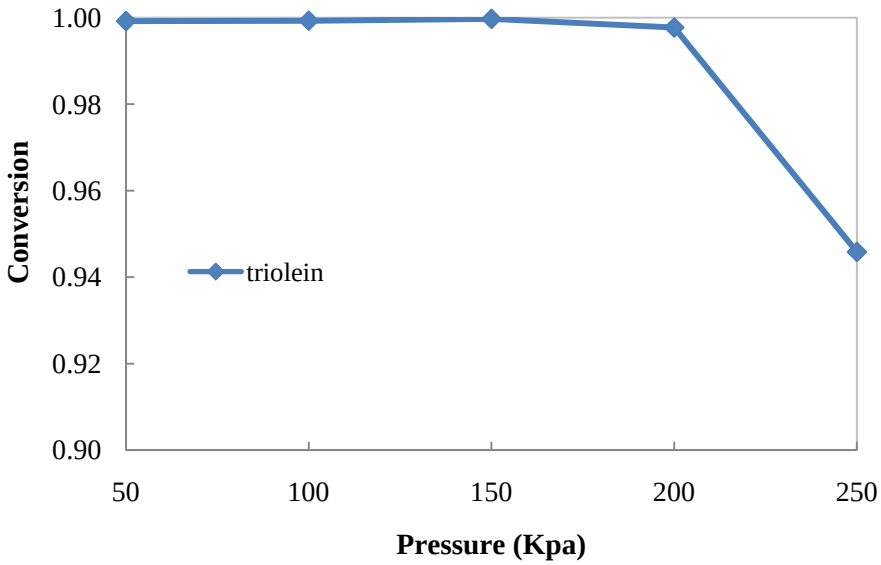


Figure 60 Effect of pressure in conventional process from one component of oil

Figure 60 shows the decreasing conversion at high pressure. The separated methanol from distillation will decrease due to separation in column will be difficult in high pressure. It causes the total quantity of methanol return into reactor that decreases in high pressure. Because the separation in high pressure is complicated, the optimal range in all cases of conventional process is 50- 200 KPa.

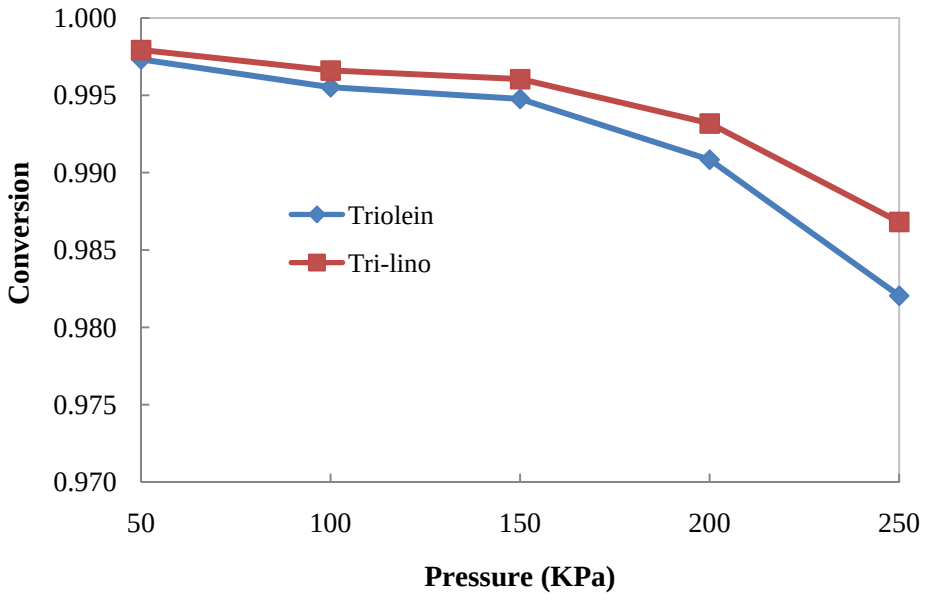


Figure 61 Effect of pressure in conventional process from two components of oil

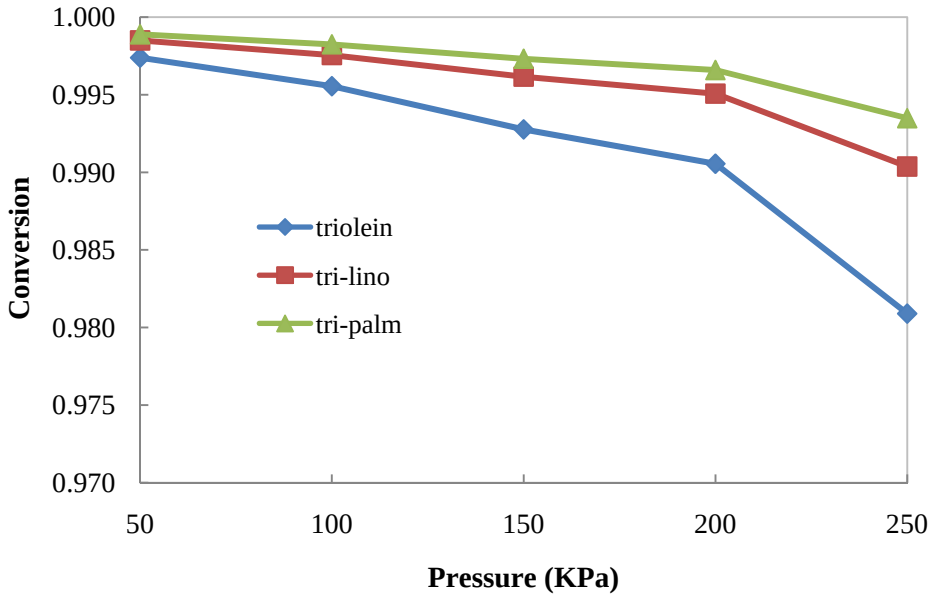


Figure 62 Effect of pressure in conventional process from three components of oil

The typical distillation column, operating pressure in distillation column is always less than the critical pressure of top product or temperature of cooling medium of overhead condenser cannot be greater than critical temperature of top product (methanol). The separation in column is also easy in lower pressure. High pressure in column will decrease the recycle of methanol from top product. In addition, it decreases the consumption of oil due to lower quantity of methanol in reaction.

Pressure is also a key design parameter in reactive distillation because of impact on phases and reaction equilibrium and on reaction kinetics. Lower pressures often make separation easier, but lower pressures mean lower temperatures and smaller reaction rates. Therefore, the results of effect on pressure in reactive distillation are shown in Figures 63, 64 and 65. When the pressure in reactive column decreases, the reaction rate will decrease. The conversions become lower in lower pressure. The optimal pressure is 100-250 KPa.

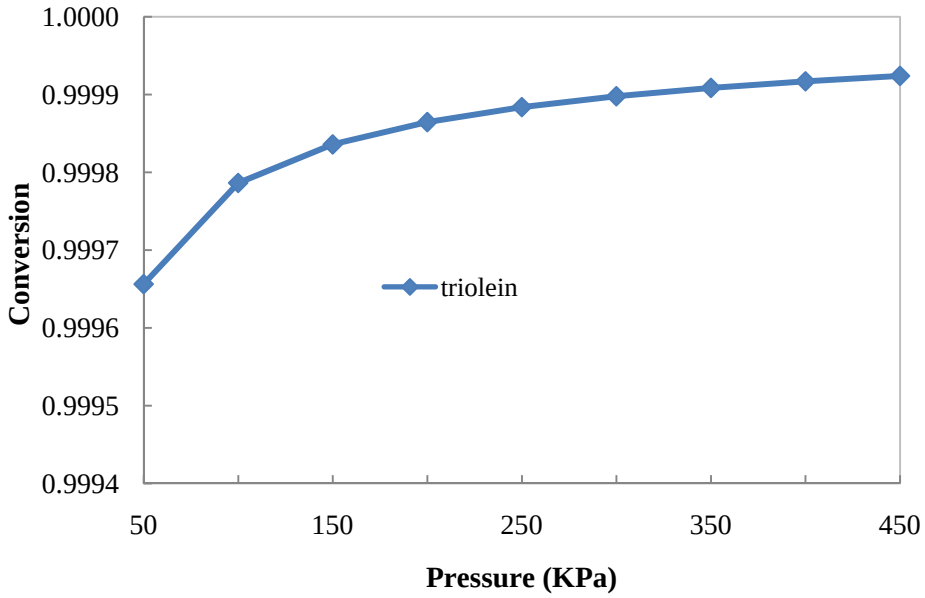


Figure 63 Effect of pressure in reactive distillation process from one component of oil

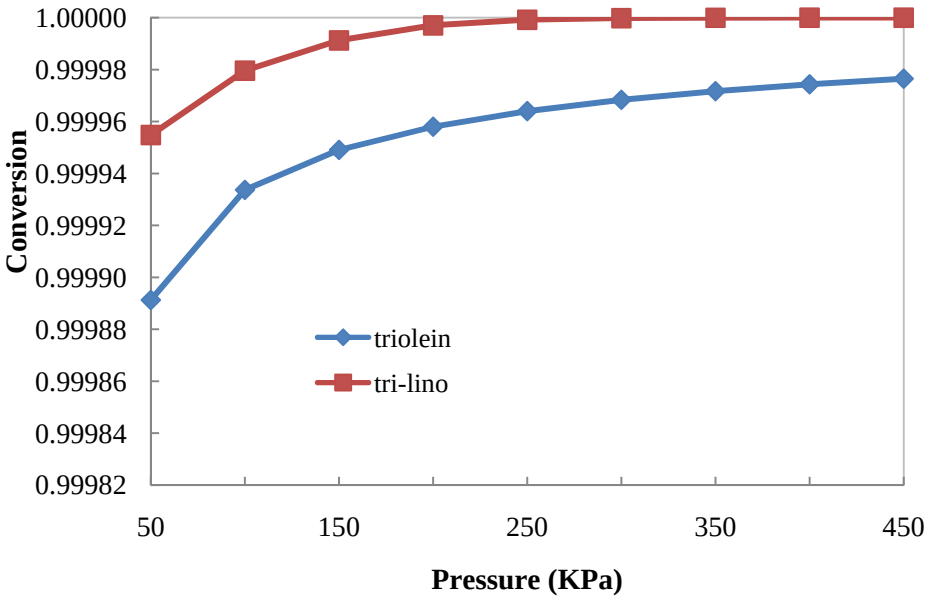


Figure 64 Effect of pressure in reactive distillation process from two components of oil

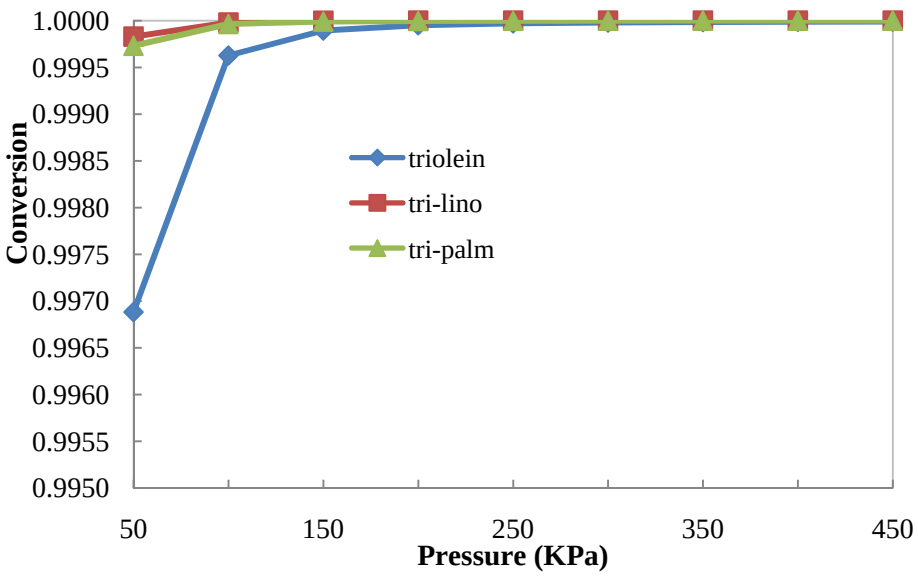


Figure 65 Effect of pressure in reactive distillation process from three components of oil

In the simulation of biodiesel process, the effect of parameters is performed. Flow of oil, ratio of methanol to oil, reactor temperature and pressure in column are investigated. The results on effect of these parameters to biodiesel process, we can select the optimal condition for the process. And the safety analysis is used to operate the process.

2. Safety analysis

In general, the process material susceptibilities for hazardous consequences are used for HAZOP analysis. The process material models only indicated whether a material is flammable or toxic in nature without quantifying these properties. Whenever the consequences of the process variable deviations in a process unit are considered, the susceptibilities of the process materials present in that process unit are consulted and the corresponding hazards will be found. This approach always considers the worst case scenario and hence will always find the hazardous consequence whenever there is a process variable deviation corresponding to the

process material susceptibility. For example, whenever there is a high temperature in any process unit, and if the unit has a flammable process material, the earlier approach will always conclude that there will be a fire hazard. If the normal operating temperature of the process unit is given, then it can be determined whether there might actually be a fire hazard as a consequence of the high temperature deviation.

In this work, the quantification of the flammable nature of the process material by specifying the flash-point or the toxic nature of the process material by specifying the exact health hazard, will enable the expert system to identify the hazards similar to the HAZOP team. For example, if the operating temperature of the process units and the flash-points of the process materials are given, then the hazardous consequence that the release of a flammable material above its flash-point into the plant area will lead to a fire hazard can be found.

Table 10 Properties of methanol

Methanol, a process-material	
Names	METHANOL
Material type	Reactant
Physical state	Colorless liquid
Corrosive	Corrosive
Flammable	Flammable
Volatile	Volatile
Toxic	Toxic
Molecular weight	32.04
Boiling point	64.7 ^{o}C
Flash point	11 ^{o}C
Auto ignition temperature	470 ^{o}C

Table 11 Properties of sodium hydroxide

Sodium hydroxide, a process-material	
Names	SODIUM HYDROXIDE
Material type	Reactant
Physical state	White solid
Corrosive	Strong corrosive
Flammable	Not-flammable
Volatile	Not-volatile at room temperature
Toxic	Toxic
Molecular weight	39.99
Boiling point	1390 ^{o}C
Flash point	-
Auto ignition temperature	-

Table 12 Properties of glycerol

Glycerol, a process-material	
Names	GLYCEROL
Material type	Product
Physical state	Viscous colorless liquid
Corrosive	Strong corrosive
Flammable	Flammable
Volatile	Not-volatile at room temperature
Toxic	Toxic
Molecular weight	92.09
Boiling point	290 ^{o}C
Flash point	160 ^{o}C
Auto ignition temperature	370 ^{o}C

For example, properties of the process material methanol, sodium hydroxide and glycerol are shown in Tables 10, 11 and 12. In addition to the qualitative process

material susceptibility information, like the material-type, normal physical-state, corrosive, flammable, volatile, and toxic nature, the quantitative properties like molecular weight, normal boiling point, flash-point and auto ignition temperature are incorporated.

During the last two decades, great emphasis has been placed on improving management of technological risks in the process industry. Process Industry refers to those processes involved the production, generation and manufacture. These efforts have resulted in the development of performance-based standards from the International Electro technical Commission (IEC, 1997), the Instrument Society of America (ISA), ANSI/ISA S84.01 (ISA, 1996), and national (USA) regulations from Occupational Safety and Health Agency (OSHA, 1992) and the Environmental Protection Agency (EPA, 1995).

This thesis has been developed to support biodiesel process that uses Safety Instrumented Systems (SIS) to protect against hazardous events. A Safety Instrumented System is composed of sensors, logic solvers, and final control elements for the purpose of taking the process to a safe state when predetermined conditions are violated. SIS is used in ANSI/ISA S84.01 to refer to E/E/PE SRSs, a term used in IEC 61508 (IEC, 1997). For the remainder of this work the term SIS will be used. The emerging performance-based standards and regulations were applied to the biodiesel process. It proposes an assessment scheme, for the risk associated with a process and the reliability of a safety system, consistent with the standards, in order to generate data and information to meet the requirements of the standards and regulations.

The objective of this work is to identify the required safety instrumented functions and implement them in an SIS in order to achieve the desired safety level for the process. The safety analysis is demonstrated on biodiesel process case studies. The safety team normally ranks the adverse consequences found in a study based on the frequency and severity of the hazards they cause in the plant. The consequences which have a high frequency of occurrence and high severity will have a high priority for mitigation. This ranking facilitates the HAZOP team to concentrate on the major

hazards in the plant. The severity level of consequences is divided into three levels (Venkatasubramanian, 1995).

Severity Level 1: Process deviations which cause process upsets downstream, and minor process upsets due to process conditions (e.g. less of material, higher temperature).

Severity Level 2: Equipment failures, and other consequences due to process material properties which will cause plant shut down, major process upset.

Severity Level 3: Fire/explosion hazards in process units caused by temperature higher than auto-ignition temperatures of the process materials, which will lead to fatalities, injuries, and severe plant damage.

The SIS operation is designed to provide automatic responses after alarms indicate potentially hazardous situations. The objective is to have the process reach a safe condition. The automatic responses are implemented interlocks and automatic shutdown.

For reactor system, the level must stay above a minimum value in order to avoid pump damage. The solenoid-operated valve is normally closed. If the level drops below the specified limit, the low-level switch (LSL) and a solenoid (S), which acts as a relay and turns the pump off. But if the level in reactor exceeds a specified limit, the high-level switch (LSH) activates an alarm and causes the valve to open fully for reducing the level in the reactor. Figure 67 shows the interlock system including, (a) The level interlock system, (b) The temperature interlock system and (c) The pressure interlock system.

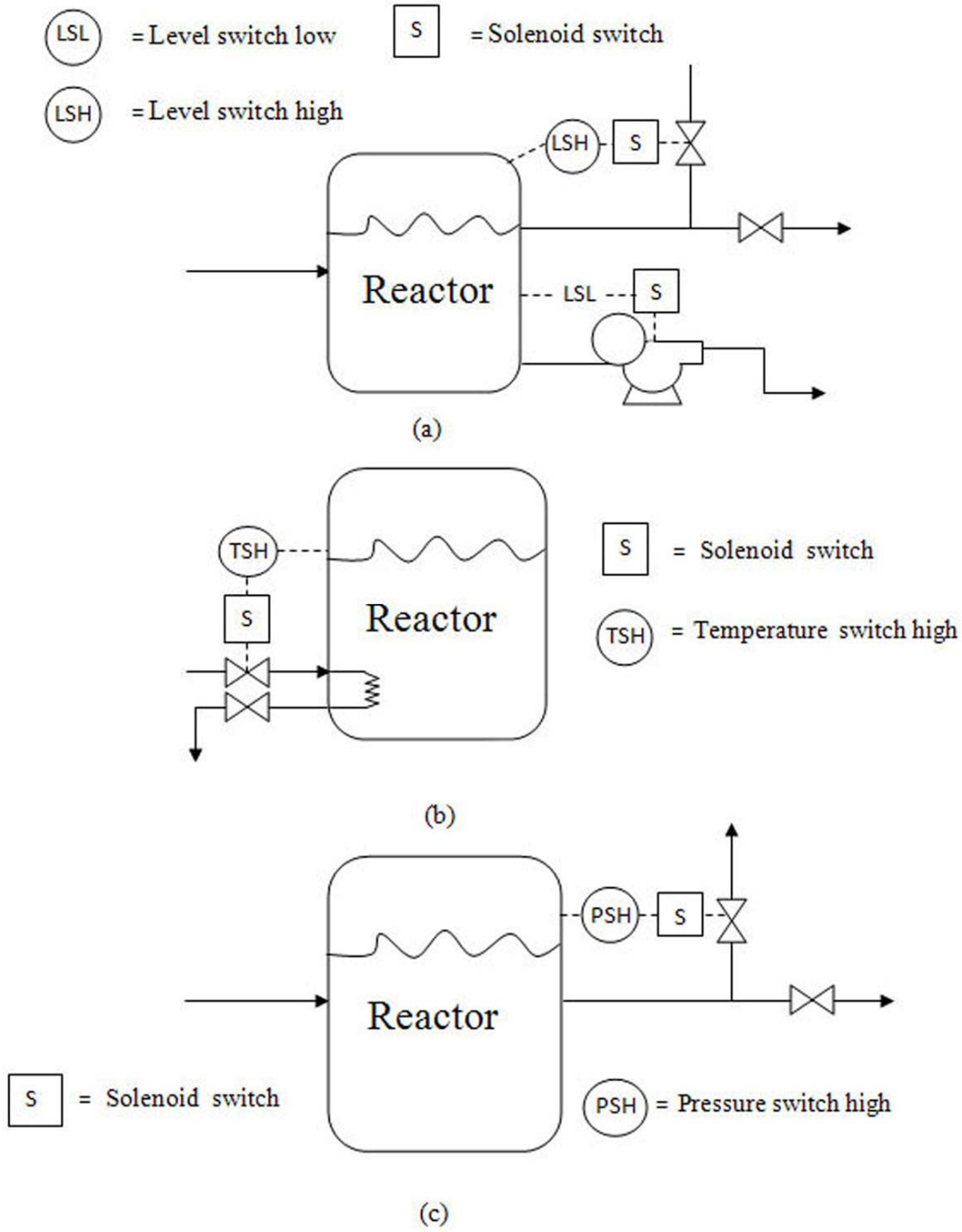


Figure 66 (a) The level interlock system, (b) The temperature interlock system and (c) The pressure interlock system

The temperature and pressure interlock will activate when the values of them are above their specified limit. If the temperature is higher than limited value, the valve will close to stop the heating medium into the reactor. It assists the operators to

reduce temperature that causes the fire or explosion in the reactor. Pressure interlock system, the valve will open when the pressure is higher than specified limit. That can decrease in rapidly when valve is opened.

Safety instrumented systems is implemented when the severity level 3 is performed. Because the severity level 3 is a violent hazard, it will cause to fatalities, injuries and sever plant damage. This system manages the situations when the control operation is failed. It will lock a trouble device or shut down the plant when the situation is terrible. SIS is performed in order to reduce the severe damage in the biodiesel process. For example, when the temperature in the reactor is more than auto-ignition temperature of the process material, it will cause the severe damage in the plant such as firing or explosion hazard in the process. The process will be repaired or shut down in automatically. In summary, SIS can assist/reduce the quantity of damage in the process.

The simulation included the effect of flow, temperature and pressure which can be classified into safety concerns. Therefore, the optimal range of biodiesel processes can be selected. An example, conventional process from one component of oil, the optimal range of oil feed is between 350 and 750 kg/hr. When oil feed is more than 750 or less than 350 kg/hr. The HAZOP analysis is performed and the severity level of this situation is defined at level 1. Because the severity level of event has not serious affect on the process. It just reduces the biodiesel production from the process.

The temperature in the process is an important variable in the process. The severity of hazard level for the temperature deviation is divided into two levels. Level 1 is determined when the temperature is more than 64 °C or less than 58 °C. The reaction rate will be slow if the temperature is less than 58 °C. In addition, the reaction may decrease when temperature is more than 64 °C. Because the methanol is changed to vapor phase, it vaporize at 64.7 °C. The reaction is not complete due to methanol is only react on the oil surface. It affects to the biodiesel production that will be lower. Level 3 is performed when the temperature is more than auto ignition of

glycerol (370 °C). This situation is a critical performance in the process. It will cause the fire or explosion in the plant. Therefore, Level 3 is violently situation in the process. The severity level in HAZOP analysis is shown the order of magnitude for execution. If the severity level 1 and 3 are performed, the first is repair the situation for level 3. Since level 3 causes the high damage in the plant, the problem must be fixed in immediately. Then the lower level is concerned.

The pressure is an insignificant parameter in the process. In the conventional column in biodiesel process, the optimal pressure is 50 to 200 KPa. The severity of level for the pressure is defined at 1 and 2. When pressure is more than 200 KPa or less than 50 KPa, the severity level 1 is performed. In conventional column, the column can obtain the maximum pressure at 1000 KPa. If the pressure in column is more than 1000 KPa, the column will rupture. The severity level 3 is performed for this situation because the plant may be shut down.

The optimal conditions of the conventional process and the reactive distillation of biodiesel are concluded in Tables 13 and 14. These tables also showed the severity level that can be implemented for HAZOP analysis.

Table 13 The optimal conditions of the conventional process of biodiesel

Case 1. Conventional process from one component of oil.				
Deviation / Parameter	Less	Normal	More	Severity level
Oil	< 350 kg/hr	350 – 750 kg/hr	> 750 kg/hr	1
Temperature	< 58 °C	58 – 64 °C	> 64 °C	1,3
Pressure	< 50 KPa	50 – 200 KPa	> 200 KPa	1,2

Table 13 (Continued)

Case 2. Conventional process from two components of oil.				
Deviation / Parameter	Less	Normal	More	Severity level
Oil	< 350 kg/hr	350 – 750 kg/hr	> 750 kg/hr	1
Temperature	< 58 °C	58– 64 °C	> 64 °C	1,3
Pressure	< 50 KPa	50 – 200 KPa	> 200 KPa	1,2
Case 3. Conventional process from three components of oil.				
Deviation / Parameter	Less	Normal	More	Severity level
Oil	< 350 kg/hr	350 – 750 kg/hr	> 750 kg/hr	1
Temperature	< 58 °C	58 – 64 °C	> 64 °C	1,3
Pressure	< 50 KPa	50 – 200 KPa	> 200 KPa	1,2

Table 14 The optimal conditions of the reactive distillation of biodiesel.

Case 4. Reactive distillation process from one component of oil.				
Deviation / Parameter	Less	Normal	More	Severity level
Oil	< 650 kg/hr	650 – 1200 kg/hr	> 1200 kg/hr	1
Temperature	-	60 – 350 °C	> 350 °C	3
Pressure	< 100 KPa	100 – 250 KPa	> 250 KPa	1,2
Case 5. Reactive distillation process from two components of oil.				
Deviation / Parameter	Less	Normal	More	Severity level
Oil	< 500 kg/hr	500 – 1150 kg/hr	> 1150 kg/hr	1
Temperature	-	60 – 350 °C	> 350 °C	3
Pressure	< 100 KPa	100 – 250 KPa	> 250 KPa	1,2

Table 14 (Continued)

Case 6. Reactive distillation process from three components of oil.				
Deviation / Parameter	Less	Normal	More	Severity level
Oil	< 550 kg/hr	550 – 1200 kg/hr	> 1200 kg/hr	1
Temperature	-	60 – 350 °C	> 350 °C	3
Pressure	< 100 KPa	100 – 250 KPa	> 250 KPa	1,2

In the safety module, the severity of level will automatically show in the module. Figure 67 demonstrates the severity level. That is " 2 " in this simulation. Since some equipments fail, it causes plant shut down.

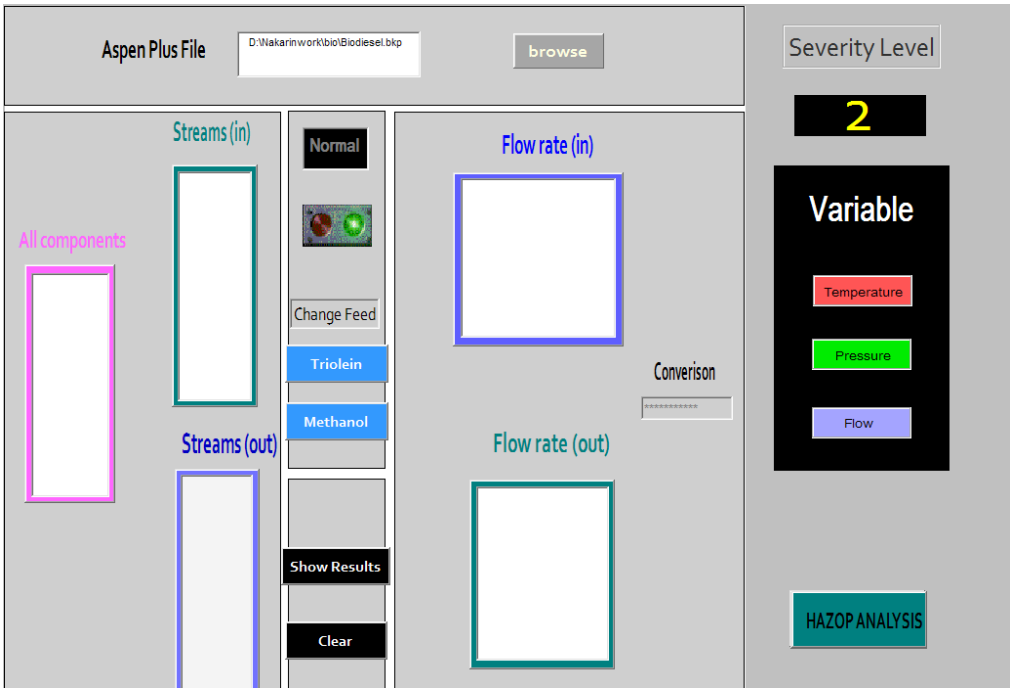


Figure 67 The severity level in the safety module

In order to decide a high temperature deviation in a process unit, a safety alarm is performed in this system. Only when this condition is not satisfied, the hazardous consequence, 'fire/explosion hazard in the process unit due to flammable material at high temperature' is reported as a HAZOP result. Thus, if the normal operating temperature of the process units is much lower than the auto-ignition temperatures of the process materials present in that unit, then fire/explosion hazard will not occur as a consequence of high temperature.

In Table 13, the optimal condition of conventional process from one component of oil is concluded. Therefore, the LOW and HIGH deviations can be selected. For example, 300 – 700 kg/hr of flow oil is optimal condition in the process. When feed oil is less than 300 kg/hr, the LOW deviation is concerned. If the feed oil is more than 700 kg/hr, the HIGH deviation will perform. The results of HAZOP analysis in three cases of conventional process are shown in Table 15. Three cases of reactive distillation are shown in Table 16.

Table 15 The HAZOP results for Case 1, 2 and 3

Unit ID	Variable	Deviation	Causes	Consequences	Severity
REACTOR	FLOW	LOW	LOW of inlet flow to VALVES 4 and 5. The control valve fails.	The consequence for LOW FLOW in REACTOR is loss of production due to loss of reactant.	1
		HIGH	HIGH VALVE-OPENING in VALVES 4 and 5.	The consequence for HIGH FLOW in REACTOR is low reaction rate	1

Table 15 (Continued)

Unit ID	Variable	Deviation	Causes	Consequences	Severity
REACTOR	FLOW	HIGH	High inlet flow.	The consequence for HIGH FLOW in REACTOR is flooding of reactor	2
REACTOR	TEMPERA-TURE	LOW	Controller of heating in reactor fails.	The consequence for LOW TEMPERATURE in REACTOR is low reaction rate due to the endothermic reaction.	1
		HIGH	High inlet flow temperature to reactor. Controller of heating in reactor fails.	The consequence for high TEMPERATURE in REACTOR is a fire hazard due to the presence of the flammable.	3
	PRESSURE	HIGH	HIGH inlet flow pressure to reactor. Controller of pressure in column fails.	The consequence for high PRESSURE in REACTOR is release of flammable into plant area due to leak, causing health hazard in the plant.	3

Table 15 (Continued)

Unit ID	Variable	Deviation	Causes	Consequences	Severity
COLUMN	FLOW	LOW	LOW of inlet flow to VALVE 6. The control valve fails.	The consequence for Low FLOW in COLUMN is loss of production due to loss of reactant.	1
		HIGH	HIGH VALVE-OPENING in VALVE 6. The control valve fails.	The consequence for high FLOW in COLUMN is flooding column and potential tray damage leading to high column pressure drop, incomplete separation.	2
	TEMPERA-TURE	HIGH	HIGH inlet flow temperature to column. Controller of temperature in column fails.	The consequence for high TEMPERATURE in COLUMN is a fire hazard due to the presence of the flammable.	3

Table 15 (Continued)

Unit ID	Variable	Deviation	Causes	Consequences	Severity
COLUMN	PRESSURE	HIGH	HIGH inlet flow pressure to column.	The consequence for HIGH PRESSURE in COLUMN is build up high pressure in the bottom, possible tower rupture.	2
			Controller of pressure in column fails.	The consequence for HIGH PRESSURE in COLUMN is hard separation in column.	1

Table 16 The HAZOP results for Case 3, 4 and 5

Unit ID	Variable	Deviation	Causes	Consequences	Severity
REACTIVE DISTILL-ATION	FLOW	LOW	LOW of inlet flow to VALVES 4 and 5. The control valve fails.	The consequence for LOW FLOW in REACTIVE DISTILLATION is loss of production due to loss of reactant.	1

Table 16 (Continued)

Unit ID	Variable	Deviation	Causes	Consequences	Severity
		HIGH	HIGH VALVE-OPENING in VALVES 4 and 5. The control valve fails.	The consequence for HIGH FLOW in REACTIVE DISTILLATION is low reaction rate due to optimal quantity reactant.	1
				The consequence for high FLOW in REACTIVE DISTILLATION is flooding column and potential tray damage leading to high column pressure drop, incomplete separation.	2

Table 16 (Continued)

Unit ID	Variable	Deviation	Causes	Consequences	Severity
		HIGH	HIGH inlet flow pressure to reactive distillation. Controller of pressure in column fails.	The consequence for high PRESSURE in REACTIVE DISTILLATION is release of flammable into plant area due to leak, causing health hazard in the plant.	3

3. User interface with safety analysis

Genesis 32 and visual basic 6.5 are used to construct the safety module. This module can simulate and develop a control structure of the process. It combines the process with safety analysis. Genesis 32 is used to build the graphical user interface while Visual basic 6.5 is used to communicate with ASPEN PLUS. This work consists of three modules. The first module is concerned about temperature of process. Second module is performed the pressure in the process and final module is the flow rate of the process. Biodiesel process is operated in this module. In Figure 68 shows the main interface of this work. In the module, three of variables in the process are concerned.

1. Temperature in the process.
2. Pressure of the process.
3. Flow rate of the process.

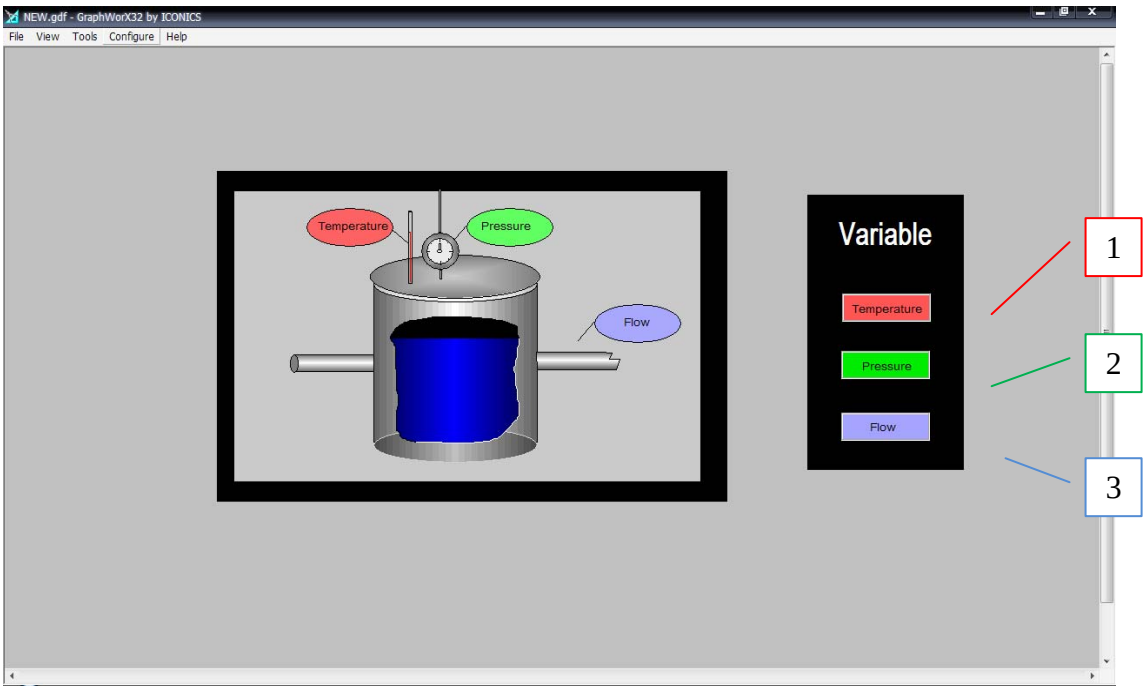


Figure 68 The main module of the process

When you select the variable and click the button (numbers 1, 2 and 3) in the Figure 68. The interface will link to the specific variable of modules. They can show the details of the process, such as temperature of reactor and pressure in pump. And safety analysis is performed in these modules. Figures 69, 70 and 71 show the modules of the temperature, pressure and flow of the process, respectively.

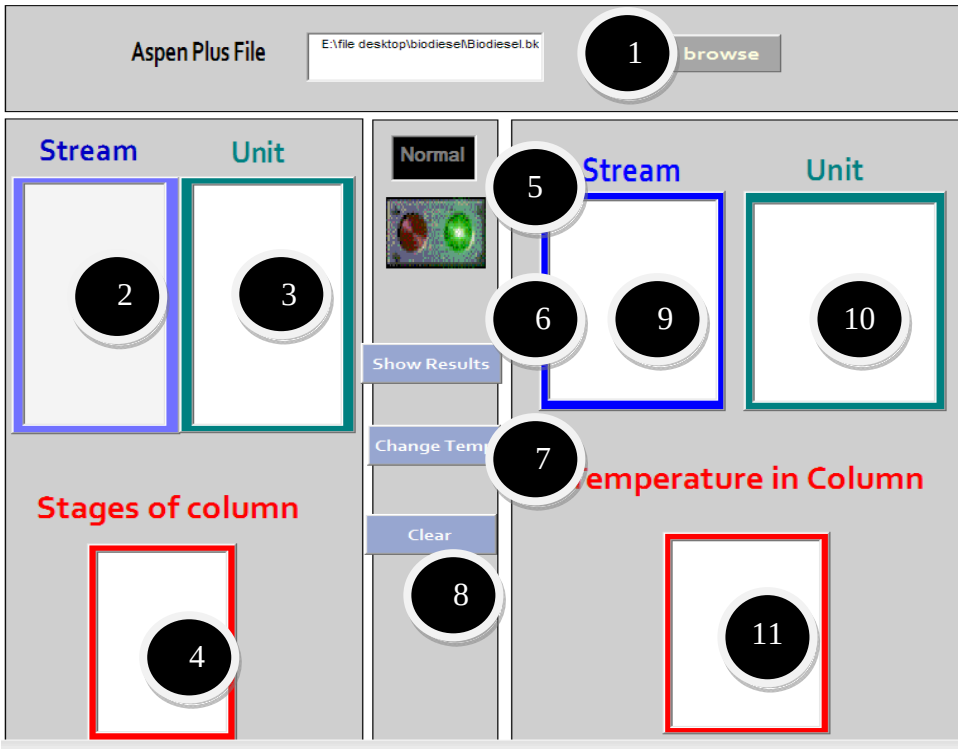


Figure 69 The module of temperature in the process

In this module shows the temperature of streams and units. It consists of 11 parts. Part 1 is used to select the ASPEN PLUS file of biodiesel. Part 2 shows all streams of process. Part 3 shows all units in the process and part 4 shows the numbers of stages in the distillation column. Part 5 shows the condition of the process such as normal and alarm. When condition is alarming, the green light will change to red light. Part 6 is the command click, will show the results when the user selects the streams, units and stages of column (Parts 2, 3 and 4) and then click it. In Part 7, if the user wants to change the input parameter, user can click here. User can clear the all parts by click in Part8. Parts 9 and 10 will show the temperature of selected stream and unit. Part 11 shows the temperature of selected stages of column in part 4.

Figure 70 shows the module of pressure in the process. This module is similar to the temperature module. It also contains 11 parts, but it will show the pressure of the process instead of temperature.

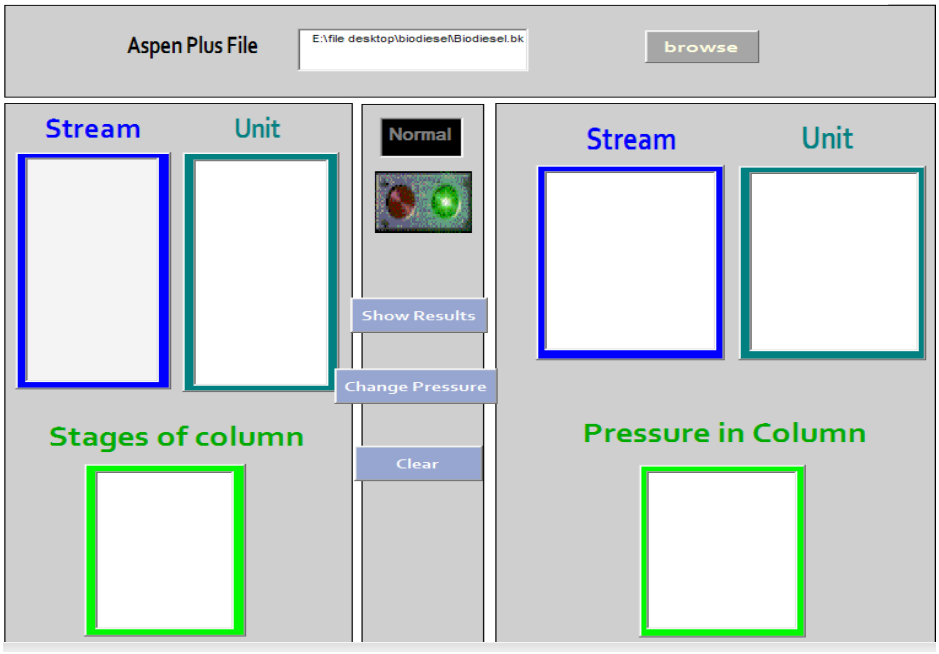


Figure 70 The module of pressure in the process

Part 9 shows the pressure of selected stream in part 2. Part 10 shows the pressure of selected unit in part 3. Part 11 shows the pressure of selected stages of column in part 4.

Figure 71 shows flow of the process and conversion of reactant. This module consists of 11 parts. Part 1 is used to select the ASPEN PLUS file of biodiesel. Part 2 shows all components of process. Part 3 shows all streams flowing into process and part 4 shows all streams flowing out the process. Part 5 shows the condition of the process such as normal and alarm. When condition is alarming, the green light will change to red light. Part 6 is the command click, will show the results when the user selects the streams (Parts 3, 4) and click it. In Part 7, if the user wants to change the input parameter, user can click here. User can clear the all parts by click in Part8. Part 9 shows the all input of flow rate. Part 10 shows the all outputs of flow rate. Part 11 shows the conversion of reactant.

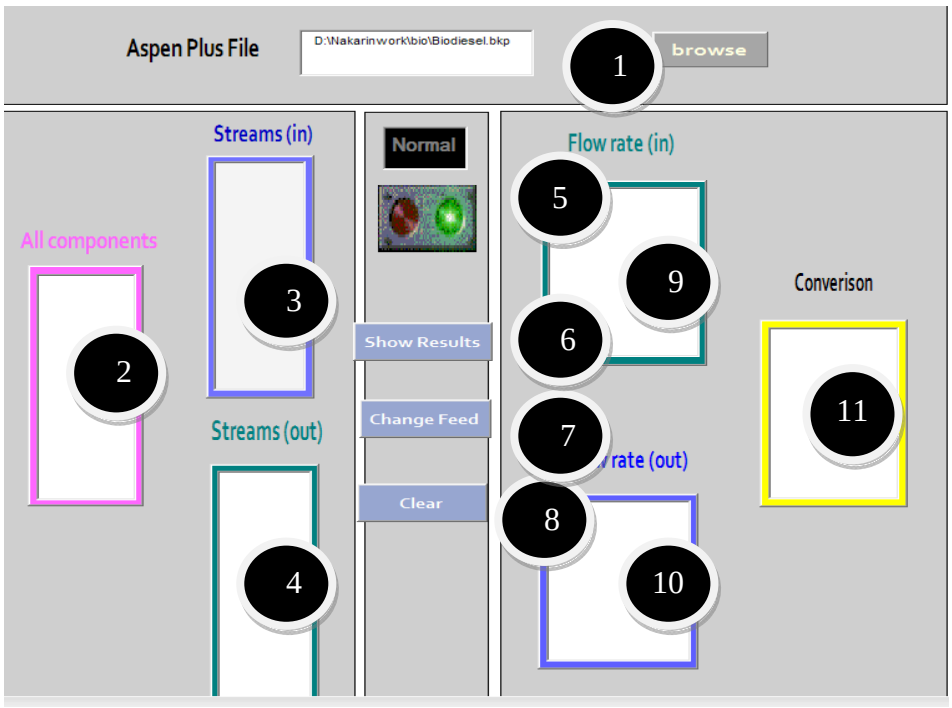


Figure 71 The module of flow of the process

This module will simulate the process by ASPEN PLUS and perform the HAZOP analysis. All steps are illustrated in Figure 72 (a) to (e).

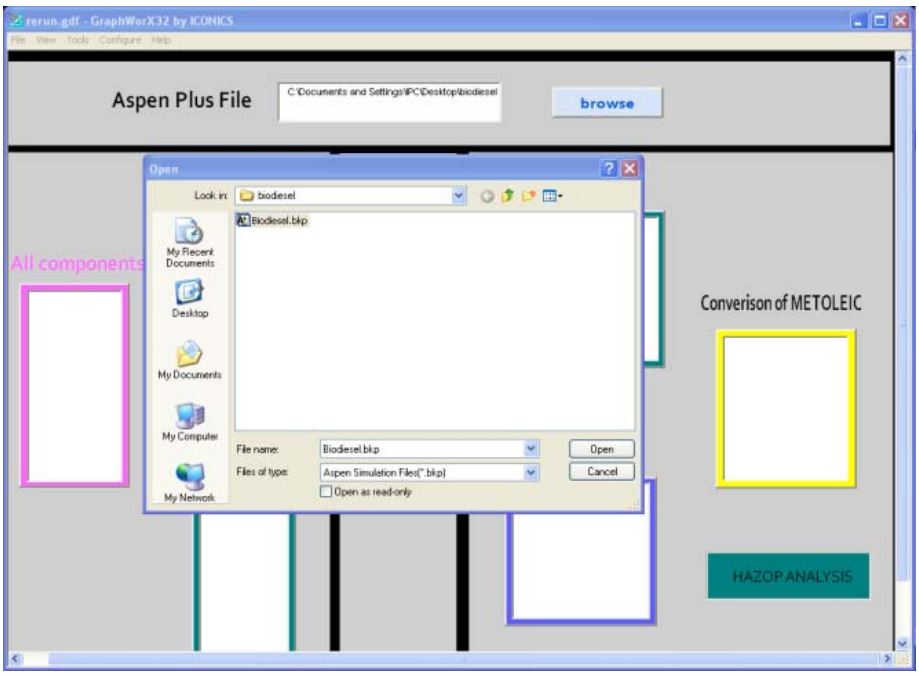
(a) Select the ASPEN PLUS file (*.bkp) from directory “C:\Documents and Settings\IPC\Desktop\biodiesel”. Biodiesel.bkp is selected in Figure 72(a).

(b) When click “open”. ASPEN PLUS is started and then the biodiesel process is simulated. The module will show the all components, inlet and outlet streams of the process, when the simulation of ASPEN PLUS is completed.

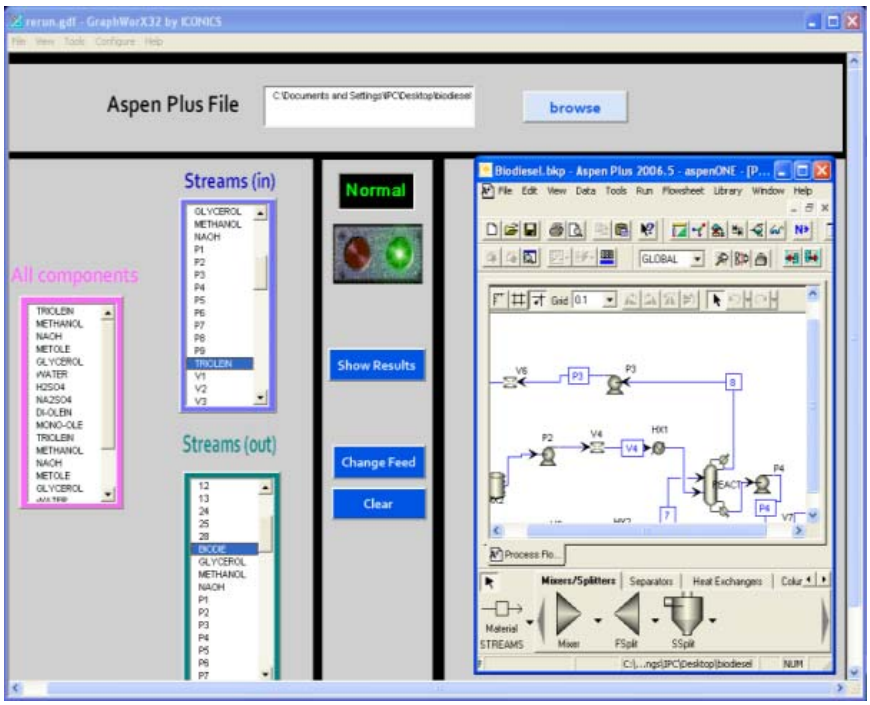
(c) Select the streams that want to see the results. Then, click the “Show Results” button. The results form ASPEN Plus will show in this module.

(d) If the user wants to change the inlet stream, click the “Change feed” button. Add the new number of flow rate that you want to simulate.

(e) If the user wants to see the HAZOP analysis, click “HAZOP analysis” button. In Figure 72(e) shows HAZOP analysis of “no flow” deviation.

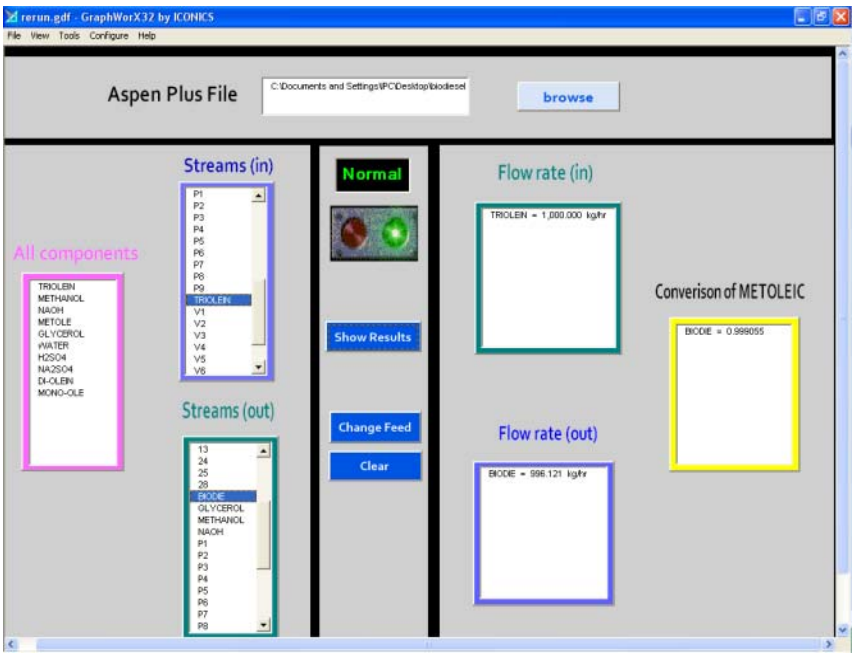


(a)

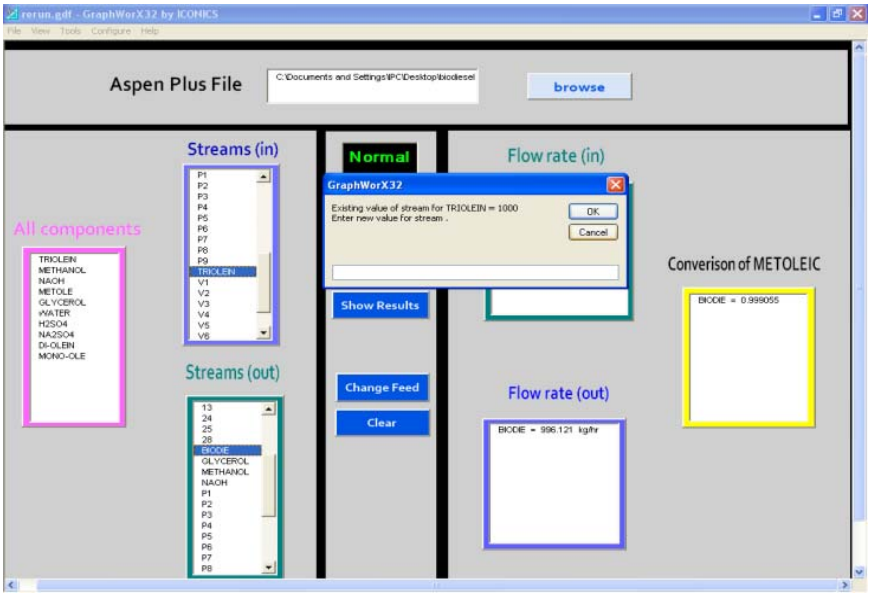


(b)

Figure 72 Schematic of graphical user interface

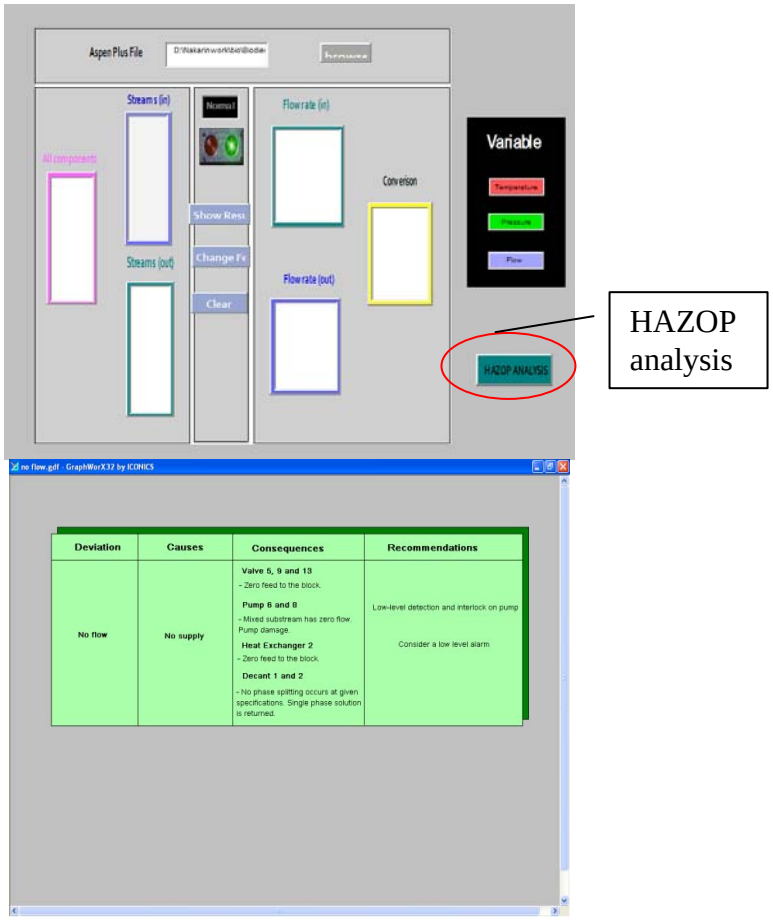


(c)



(d)

Figure 72 (Continued)



(e)

Figure 72 (Continued)

In this work, the conventional and reactive distillation can simulate in high purity of biodiesel. The results on effect of, oil feed, temperature in reactor and pressure in column are performed. Therefore, the optimal condition in each case of biodiesel is selected. When the condition is not normal range, HAZOP analysis is performed. And the severity of level hazard is concerned in this HAZOP analysis. It shows the severity of hazard level. The number of level performs the effect of parameter to the process. High level is severe hazard. Human machine interface is constructed to operate the biodiesel process with HAZOP automatic. It helps for decreasing the hazard and increasing production.

CONCLUSION AND RECOMMENDATION

Conclusion

In this work, the conventional and reactive distillation processes combined with a standard hazard identification method (HAZOP) were performed. Therefore, the integration of the HAZOP study may potentially lead to the identification of some unexpected deviations and may radically decrease the time necessary for the hazard identification process.

The HAZOP analysis and alarm system are used to develop the operation and safety of the process. After optimal condition was addressed from simulator, HAZOP analysis with human machine interface was developed to assist the operators in various conditions under suitable paradigm. Sensitivity analysis was carried out to investigate the effects of operating parameters on column performance. The conventional and reactive distillation of biodiesel processes were chosen for the demonstration of this methodology. Soy bean oil was used for this process and different compositions of oil were simulated. The inlet flow rate of oil into the process was analyzed. In addition, the effect of temperature, pressure and ratio of methanol to oil in the biodiesel process were performed. The steady state analysis showed that the solution diagrams for investigated parameters.

All derived HAZOP deviations along with their consequences may be analyzed in a similar way by the approach presented. The optimal ranges of oil feed, temperature and pressure can be selected to gain the maximum conversion. 350 kg/hr to 750 kg/hr were selected for optimal oil feed in all cases of conventional process. In reactive distillation, 650 - 1200 kg/hr, 500-1150 kg/hr and 550-1200 kg/hr were selected for one, two and three compositions of oil, respectively. Temperature influences to the reaction. Reaction rate will decrease when the temperature decreases. Since transesterification is an endothermic reaction. Their temperature reactors were selected at 58-64 °C. All conventional cases, 50-200 KPa were selected

for optimal pressure. And; 100-250 KPa were selected for all cases of reactive distillation.

The severity level is divided into three parts. Level 1 is process deviations which cause process upsets or less production. Level 2 is equipment failures which will cause plant shut down. Level 3 is fire/explosion hazards in plant cause by temperature higher than auto-ignition temperatures of the process materials. The HAZOP analysis is performed the severity of level for each process deviations. The major contribution of this interface module is that the module can decrease time consuming for hazard identification and propose user friendly environment for the input data for process. In the module, required data of any streams in a chemical process on ASPEN PLUS can be selected and retrieved to calculate automatically. The time consuming is reduced comparing with manually calculation. It can help the operator to know suitable value of all parameters in the process and perform an online monitoring.

Since the real process is not always operated in the control range. It may be occurs many accidents such as damage of valve, damage of pump, leak of pipe, etc. The HAZOP analysis is used to show the causes of problem, the consequences and severity of level. It helps operator to do when process is not be controlled. It reduces the time to find the cause of problem and come back to normal. In this work, we presented alarm signal of the problem unit and table of HAZOP analysis of the process. Therefore, HAZOP analysis can use to operate the process combing safety analysis. It decreases the possibility that several sources of hazard will be overlooked. And this work, Human machine interface was used to operate the process with HAZOP analysis. It can perform the HAZOP analysis when the condition is not optimal.

Recommendation

1. In this work, the process is simulated by Aspen plus simulator. It will give the result that has not any accidents. But real system may occur many accidents and undesirable events. Therefore, the operation of real system is required in next study.

2. HAZOP analysis in this thesis is only shown the process deviation which is operated in the biodiesel. However, the other process cannot use this result of HAZOP. Therefore, the HAZOP programming should combine in the process to analysis the result of HAZOP for any processes.

3. In this experiment, only some of parameters are investigated. However, all of parameters in the process should be investigated because each parameter can affect to the process in some way.

4. HAZOP analysis is used for safety analysis in this thesis. Nevertheless, there are many methods to analysis the safety in the process. Therefore, other methods may be used in next work for comparison such as fault tree analysis.

LITERATURE CITED

Agreda, V.H. and L.R. Partin. 1984. Reactive distillation process for the production of methyl acetate, US Patent 4435595.

Agreda, V.H., L.R. Partin and W.H. Heise. 1990. High-purity methyl acetate via reactive distillation. **Chemical Engineering Progress.** 86: 40–46.

Andow, P. K., F. P. Lees and C. P. Murphy. 1980. "The Propagation of Faults in Process Plants: a State of the Art Review," Int. ***Chem. Eng. Symp. Ser., 58,*** p. **225.**

Aretz, K., M. Haardt, W. Konhauser and W. Mohr. 2001. The future wireless communications beyond the third generation. Comput. Netw. **37**, 83–92.

Bhatia, S., A.L. Ahmad, A.R. Mohamed and S.Y. Chin. 2006. Production of isopropyl palmitate in a catalytic distillation column: Experimental studies. **Chemical Engineering Science.** 60: 7436-7447.

Center for Chemical Process Safety (CCPS). 1992. Guideline for hazard evakuation procedures (2nd ed.). New York: American Institute of Chemical Engineers.

Chang, Y.A. and J.D. Seader. 1988. Simulation of continuous reactive distillation by a homotopy continuation method, Comput Chem Eng,12: 1243–1255.

Chen, F.R., R.S. Huss, M.F. Doherty and M.F. Malone. 2002. "Multiple steady states in reactive distillation: Kinetic effects", Comput.Chem.Eng.,26, 81-93.

Cheng, Y.C. and C.C. Yu. 2005. Effects of feed tray locations to the design of reactive distillation and its implication to control. **Chemical Engineering Science.** 60: 4661 – 4677.

Chopade, S.P. and M.M. Sharma. 1997. Reaction of ethanol and formaldehyde: use of versatile cation-exchange resins as catalyst in batch reactors and reactive distillation columns. **Reactive & Functional Polymers.** 32:53-64.

Ciric, A.R. and P. Miao. 1994. Steady state multiplicities in an ethylene glycol reactive distillation column, Ind Eng Chem Res, 33(11): 2738–2748.

Crowl, D.A. and J.F. Louvar. 1990. Chemical Process Safety: Fundamental with Application, U.S.A., Prentice Hall, p. 2.

DeKleer, J. 1979. "The Origin and Resolution of Ambiguities in Causal Arguments," ***Proc. IJCAI,* 197.**

Demirbas, A. 2002. Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey. **Energy Conversion & Management.** 44: 2093-2109.

Doherty, M.F. and M.F. Malone. 2001. **Conceptual Design of Distillation Systems.** McGraw-Hill Inc. Singapore.

EPA 40 CFR Part 68, 1995. Risk Management Programs for Chemical Accidental Release Prevention; Proposed Rule, Environmental Protection Agency, Washington, DC.

Fogler, H.S. 1998. Elements of Chemical Reaction Engineering. third ed. Prentice-Hall, Englewood Cliffs, NJ.

Gani, R. and J.B. Jorgensen. 1994. Multiplicity in numerical solution of nonlinear models: separation processes, Comput. Chem. Engng*, 18,* S55.

Gu¨ttinger, T.E. and M. Morari. 1997. Predicting multiple steady states in distillation: Singularity analysis and reactive systems, Comput Chem Eng, 21(1): 995–1000.

Harwood, H.J. 1984. Oleochemicals as a fuel: Mechanical and economic feasibility. **JAOCS.** 61: 315-324.

IEC d61508, 1997. Functional Safety of ElectricrElectronicrProgrammable Electronic Systems, International Electrotechnical Commission, Draft Report.

ISA S84.01, 1996. Application of Safety Instrumented Systems for the Process Industry, Instrument Society of America Standard.

Koppel, L.B. 1982. Input multiplicities in nonlinear, multivariable control systems. A.I.Ch.E. Journal 28 (6), 935–945.

Krawcyk, T. 1996. Biodiesel. **INFORM.** 7: 801-822.

Lee, J.H. and M.P. Dudukovic. 1998. A comparison of the equilibrium and nonequilibrium models for a multicomponent reactive distillation column. **Computers and Chemical Engineering.** 23: 159-172.

Lees, F.P. 1986. Loss Prevention in the Process Industries, London, Buttenvorths, Chapter 13: Control System Design, pp. 342-346.

Lees, F. P. 1984. “Process Computer Alarm and Disturbance Analysis: Outline of Methods for Systematic Synthesis of the Fault Propagation Structure,” ***Comp. Chem. Eng.*, 8, 91.**

Lemos, F., J.M. Lopes and F.R. Ribeiro. 2002. Reactores Qu:micos. IST Press, Lisboa.

Levenspiel, O. 1972. Chemical Reaction Engineering. second ed. Wiley, New York.

Luo, H.P. and W.D. Xiao. 2001. A reactive distillation process for a casde and azeotropic reaction system: Carbonylation of ethanol with dimethyl carbonate. **Chemical Engineering Science**. 56: 403-410.

Magid, K. 1979. Industrial Hazard and Safety Handbook, U.S.A., Butterworth, pp. 12-17.

Mohl, K., A. Kienle, E. Gilles, P. Rapmund, K. Sundmacher and U. Hoffmann. 1999. Steady-state multiplicities in reactive distillation columns for the production of fuel ethers MTBE and TAME: theoretical analysis and experimental verification, Chem Eng Sci, 54(8):1029–1043.

Noureddini, H. and D. Zhu. 1997. Kinetics of Transesterification of Soybean Oil. **JAOCS.** 74: 1457-1463.

Oliveira, N.M.C. 1994. Newton-type algorithms for nonlinear constrained chemical process control. Ph.D. Thesis, Carnegie Mellon University, Pittsburgh, PA.

Ong, Y. S., H.B. Gooi and S.F. Lee. 2001. Java-based applications for accessing power system data via Intranet, extranet and Internet. Int. J. Electr. Power Energy Syst. **23**, 273–284.

OSHA 29 CFR Part 1910, 1992. Process Safety management of Highly Hazardous Chemicals; Explosives and Blasting Agents; Final Rule, Occupational Safety and Health Administration, Washington, DC.

Oyeleye, O. and M.A. Kramer. 1988. "Qualitative Simulation of Chemical Process Systems: Steady-State Analysis," ***AIChE J.*****, 34(9), 1441**.

Pitblado, R. and R. Turney. 1996. Risk Assessment in the Process Industries,Institute of Chemical Engineer, United Kingdom, pp. 1-6.

Qiu, B., H.B. Gooi, Y. Liu and E.K. Chan. 2002. Internet-based SCADA display system. IEEE Computer Applications in Power, pp. 14–19.

Siirola, J.J. 1995. An industrial perspective on process synthesis, AIChE Symp Series, 91(304): 222–233.

Singh, R. 2004. Steady state simulation of reactive distillation columns using Naphtali-Sandholm method, MTech Thesis, Department of Chemical Engineering, IIT Kanpur, India.

Sistu, P.B. and W. Bequette. 1995. Model predictive control of processes with input multiplicities. Chemical Engineering Science 50 (6), 921–936.

Srinivansan, R. and V. Venkatasubramanian. 1998. "Automating HAZOP Analysis of Batch Chemical Plant Part I, The Knowledge Representation Framework," Computer & Chemical Engineering, Vol. 22, No. 9, pp. 1345-1355.

Subawalla, H. and J. R. Fair. 1999. Design guidelines for solid-catalyzed reactive distillation systems. **Industrial Engineering Chemical Research.** 38: 3696-3709.

Sundmacher, K., R.S. Zhang and U. Hoffmann. 1995. Mass transfer effects on kinetics of nonideal liquid phase ethyl tert-butyl ether formation. **Chemical Engineering and Technology.** 18: 26-277.

Taylor, R. and R. Krishna. 2000. Modeling reactive distillation. **Chemical Engineering Science.** 55: 5183-5229.

Umeda, T., T. Kuriyama, E. O'Shima and H. Matsuyama. 1980. "A Graphical Approach to Cause and Effect Analysis of Chemical Processing Systems," ***Chem. Eng. Sci., 35,*** **2379.**

Venkatasubramanian, V. and R. Vaidhyanathan. 1998. "A Knowledge Based Framework for Automating HAZOP Analysis," **AIChE** Journal, Vol. 40, NO. 3, pp. 496-505.

Wayburn, T.L. and J.D. Seader. 1987. Homotopy continuation methods for computer aided process design, Comput Chem Eng, 11: 7–25.

Yang, S.B., B.L. Yang and H.J. Wang. 2001. "Simulation for the reactive distillation process to synthesize ethyl tert-buty ether", J. ***Chem.*** Eng. ***Jpn., 34,*** 1165-1170.

Zhang, Y., M.A. Dub, D.D. McLean and M. Kates. 2003. Biodiesel production from waste cooking oil: 1. Process design and technological assessment. **Bioresource Technology**. 89: 1–16.

Zhou, H., H. Lu and B. Liang. 2006. Solubility of Multicomponent Systems in the Biodiesel Production by Transesterification of *Jatropha curcas* L. Oil with Methanol. **Journal of chemical & Engineering Data.** 51: 1130-1135.

APPENDIX

The Biodiesel Process Module Code in Visual Basic

1. FormsCode

```
Private Sub Command1_Click()
Dim Val_From_Func As Variant
Dim z As Variant
   z = 0.00035
ThisDisplay.List1.Clear
ThisDisplay.List2.Clear
ThisDisplay.List4.Clear
ThisDisplay.List5.Clear
ThisDisplay.List6.Clear
ThisDisplay.List7.Clear
   Val_From_Func = OpenSimulation(z)
   Call Check_Stream(go_simulation)
End Sub

Private Sub Command3_Click()
'Dim ObjCtrl1 As Control
'Set ObjCtrl1 = Thisdisplay.List1
'Dim ObjCtrl2 As Control
'Set ObjCtrl2 = Thisdisplay.List2
'Dim ObjCtrl3 As Control
'Set ObjCtrl3 = Thisdisplay.List3
'Dim ObjCtrl4 As Control
'Set ObjCtrl4 = Thisdisplay.List4


'Dim ObjCtrl5 As Control
'Set ObjCtrl5 = Thisdisplay.List5
Dim i As Integer
```

```
Dim j As Integer
Dim h As Integer
Dim w As Integer
Dim S As Integer
Dim R As Integer
Dim check1() As String
Dim wastevalue() As Variant
Dim wastevalue1() As Variant
Dim bheck1() As String
Dim check2 As String
Dim contaminant_value() As Variant
Dim contaminant_value1() As Variant
Dim check3() As String
Dim delta_m() As Double
Dim delta_m1() As Double
Dim unitName() As Variant
Dim Conc_maxin As Double

S = ThisDisplay.List1.ListCount - 1
ReDim check1(S)
ReDim wastevalue(S)
ReDim wastevalue1(S)
ReDim wastevalue2(S)
ReDim wastevalue3(S)


For i = 0 To S
   If ThisDisplay.List1.Selected(i) = True Then
   check1(i) = ThisDisplay.List1.List(i)
   wastevalue(i) = SendValueConver(check1(i))
   wastevalue1(i) = Format(wastevalue(i), "0.###,###")
   Debug.Print wastevalue1(i)
```

```
    ThisDisplay.List4.AddItem check1(i) & "  " & "=" & "  " & wastevalue1(i) & "  "
    End If
Next i

For i = 0 To S
    If ThisDisplay.List1.Selected(i) = True Then
    check1(i) = ThisDisplay.List1.List(i)
    wastevalue2(i) = SendValueStreams(check1(i))
    wastevalue3(i) = Format(wastevalue2(i), "###,###.000")
    Debug.Print wastevalue3(i)
    ThisDisplay.List5.AddItem check1(i) & "  " & "=" & "  " & wastevalue3(i) & "  "
& "kg/hr"
    End If
Next i

For i = 0 To S
    If ThisDisplay.List6.Selected(i) = True Then
    check1(i) = ThisDisplay.List6.List(i)
    wastevalue2(i) = SendValueflowrate(check1(i))
    wastevalue3(i) = Format(wastevalue2(i), "###,###.000")
    Debug.Print wastevalue3(i)
    ThisDisplay.List7.AddItem check1(i) & "  " & "=" & "  " & wastevalue3(i) & "  "
& "kg/hr"
    End If
Next i
End Sub

Private Sub Command4_Click()
  ThisDisplay.List1.Clear
  ThisDisplay.List2.Clear
  ThisDisplay.List4.Clear
  ThisDisplay.List5.Clear
```

```
  ThisDisplay.List6.Clear
  ThisDisplay.List7.Clear
End Sub

Private Sub Command5_Click()
On Error GoTo error
  CommonDialog1.Filter = "Aspen Simulation Files(*.bkp)|*.bkp|All files(*.*)|*.*"
  CommonDialog1.ShowOpen
  ThisDisplay.Text1.text = CommonDialog1.FileName
  Aspen_FileName = ThisDisplay.Text1.text
  error:
Dim Val_From_Func As Variant
Dim z As Variant
    z = 0.00035
  ThisDisplay.List1.Clear
  ThisDisplay.List2.Clear
  ThisDisplay.List4.Clear
  ThisDisplay.List5.Clear
  ThisDisplay.List6.Clear
  ThisDisplay.List7.Clear
    Val_From_Func = OpenSimulation(z)
    Call Check_Stream(go_simulation)
End Sub

Private Sub Command6_Click()
Call RunExample(go_simulation)
End Sub
```

2. Modules Code

```
Option Explicit
Public go_simulation As IHapp
```

```
Public Aspen_FileName As String

Public Function OpenSimulation(X As Variant) As Variant

'.....................GetVal_Stream Application.............
'-- check to see if simulation is loaded --
       If go_simulation Is Nothing Then
          '-- open the selected Aspen Plus File
          Set go_simulation = GetObject(Aspen_FileName)
          '--set the simulation to Not Visible so it can be closed --
           go_simulation.Visible = True
           go_simulation.Engine.Run
       End If
         Dim tot As Double
         tot = X * 2
         Debug.Print tot
End Function

Public Sub Check_Stream(go_simulation As IHapp)
Dim individual As Variant
Dim allBlock As IHNode
Dim check As String

'Dim ObjCtrl1 As Control
'Set ObjCtrl1 = ThisDisplay.List1
Dim allStreamM As IHNode
Dim checkM As String
Dim streamvalueM As Variant
Dim allComponentsM As IHNode
Dim ComponentM As Variant
Dim componentNameM As String
Dim individualM As Variant
```

```
'Dim ObjCtrl2 As Control
'Set ObjCtrl2 = ThisDisplay.List2
Set allStreamM = go_simulation.Tree.Data.Streams
   For Each individualM In allStreamM.Elements
      checkM = individualM.Name
      Debug.Print checkM,
     ThisDisplay.List1.AddItem checkM
   Next individualM

Set allStreamM = go_simulation.Tree.Data.Streams
   For Each individualM In allStreamM.Elements
      checkM = individualM.Name
      Debug.Print checkM,
     ThisDisplay.List6.AddItem checkM
   Next individualM

Set allComponentsM =
go_simulation.Tree.Data.Components.Specifications.Input.OUTNAME
   For Each ComponentM In allComponentsM.Elements
      componentNameM = ComponentM.Name
       ThisDisplay.List2.AddItem componentNameM
Next ComponentM
End Sub

Public Function SendValueConver(A As String) As Variant
Dim Selectedstream As IHNode
Dim individual1 As Variant
Dim streamvalue1 As Variant
Set Selectedstream = go_simulation.Tree.Data.Streams
For Each individual1 In Selectedstream.Elements
  If individual1.Name = A Then
  streamvalue1 = individual1.Output.MASSFRAC.MIXED.METOLE.Value
```

```
  Debug.Print A, Format(streamvalue1, "0.###,###")
  End If
Next individual1
SendValueConver = streamvalue1
End Function

Public Function SendValueStreams(A As String) As Variant
Dim Selectedstream As IHNode
Dim individual1 As Variant
Dim streamvalue2 As Variant

Set Selectedstream = go_simulation.Tree.Data.Streams
For Each individual1 In Selectedstream.Elements
  If individual1.Name = A Then
  streamvalue2 = individual1.Output.RES_MASSFLOW.Value
  Debug.Print A, Format(streamvalue2, "###,###.000")
  End If
Next individual1
SendValueStreams = streamvalue2
End Function

Public Function SendValueflowrate(A As String) As Variant
Dim Selectedstream As IHNode
Dim individual1 As Variant
Dim streamvalue3 As Variant
Set Selectedstream = go_simulation.Tree.Data.Streams
For Each individual1 In Selectedstream.Elements
  If individual1.Name = A Then
  streamvalue3 = individual1.Input.TOTFLOW.MIXED.Value
  Debug.Print A, Format(streamvalue3, "###,###.000")
  End If
Next individual1
```

```
SendValueflowrate = streamvalue3
ThisDisplay.GetPointObjectFromName("~~V~~").Value = streamvalue3
End Function

Public Sub RunExample(ihAPsim As IHapp)
' This example changes a simulation parameter and re-runs the simulation
Dim ihEngine As IHAPEngine
Dim stream As Variant
Dim strPrompt As String
On Error GoTo ErrorHandler
Set ihEngine = ihAPsim.Engine
EditSimulation:
stream = ihAPsim.Tree.Data.Streams.TRIOLEIN.Input.TOTFLOW.MIXED.Value
strPrompt = "Existing value of stream for TRIOLEIN = " & stream _
& Chr(13) & "Enter new value for stream ."
stream = InputBox(strPrompt)
If (stream = "") Then GoTo finish
' edit the simulation
ihAPsim.Tree.Data.Streams.TRIOLEIN.Input.TOTFLOW.MIXED.Value = stream
' run the simulation
ihAPsim.Run
' look at the status and results
Call Check_Stream(go_simulation)
Call Command3_Click
GoTo EditSimulation
finish:
Exit Sub
ErrorHandler:
MsgBox "RunExample failed with error " & Err & Chr(13) & error(Err)
End Sub

Public Sub Command3_Click()
```

```
'Dim ObjCtrl1 As Control
'Set ObjCtrl1 = Thisdisplay.List1
'Dim ObjCtrl2 As Control
'Set ObjCtrl2 = Thisdisplay.List2
'Dim ObjCtrl3 As Control
'Set ObjCtrl3 = Thisdisplay.List3
'Dim ObjCtrl4 As Control
'Set ObjCtrl4 = Thisdisplay.List4
'Dim ObjCtrl5 As Control
'Set ObjCtrl5 = Thisdisplay.List5
Dim i As Integer
Dim j As Integer
Dim h As Integer
Dim w As Integer
Dim S As Integer
Dim R As Integer
Dim check1() As String
Dim wastevalue() As Variant
Dim wastevalue1() As Variant
Dim bheck1() As String
Dim check2 As String
Dim contaminant_value() As Variant
Dim contaminant_value1() As Variant
Dim check3() As String
Dim delta_m() As Double
Dim delta_m1() As Double
Dim unitName() As Variant
Dim Conc_maxin As Double

S = ThisDisplay.List1.ListCount - 1
ReDim check1(S)
ReDim wastevalue(S)
```

```
ReDim wastevalue1(S)
ReDim wastevalue2(S)
ReDim wastevalue3(S)

For i = 0 To S
   If ThisDisplay.List1.Selected(i) = True Then
   check1(i) = ThisDisplay.List1.List(i)
   wastevalue(i) = SendValueConver(check1(i))
   wastevalue1(i) = Format(wastevalue(i), "0.###,###")
   Debug.Print wastevalue1(i)
   ThisDisplay.List4.AddItem check1(i) & "  " & "=" & "  " & wastevalue1(i) & "  "
   End If
Next i

For i = 0 To S
   If ThisDisplay.List1.Selected(i) = True Then
   check1(i) = ThisDisplay.List1.List(i)
   wastevalue2(i) = SendValueStreams(check1(i))
   wastevalue3(i) = Format(wastevalue2(i), "###,###.000")
   Debug.Print wastevalue3(i)
   ThisDisplay.List5.AddItem check1(i) & "  " & "=" & "  " & wastevalue3(i) & "  "
& "kg/hr"

   End If
Next i

For i = 0 To S
   If ThisDisplay.List6.Selected(i) = True Then
   check1(i) = ThisDisplay.List6.List(i)
   wastevalue2(i) = SendValueflowrate(check1(i))
   wastevalue3(i) = Format(wastevalue2(i), "###,###.000")
   Debug.Print wastevalue3(i)
```

```
    ThisDisplay.List7.AddItem check1(i) & "  " & "=" & "  " & wastevalue3(i) & "  "
& "kg/hr"
    End If
Next i
End Sub
```

CIRRICULUM VITAE

NAME : Mr. Nakkarin Sainyamsatit

BIRTH DATE : January 9, 1983

BIRTH PLACE : Bangkok, Thailand

EDUCATION :

YEAR	**INSTITUTE**	**DEGREE/DIPLOMA**
2002	Saint Dominic	Math-Science
2006	Thammasat Univ.	B.Eng.(Chemical Engineering)

SCHOLARSHIP : Asian Development Bank 2006-2008