Feasibility of Reactive Distillation for Transesterification Process of Palm Oil

Chokchai Mueanmas

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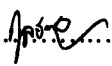**Doctor of Engineering in Chemical Engineering**
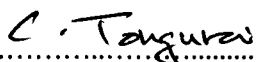
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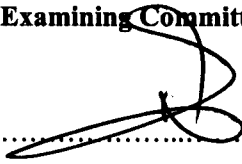
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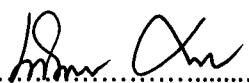
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ชื่อวิทยานิพนธ์	ความเป็นไปได้ของการใช้หอกลั่นแบบมีปฏิกิริยาสำหรับกระบวนการทรานซ์เอสเตอริฟิเคชันของน้ำมันปาล์ม
ผู้เขียน	นายโชคชัย เหมือนมาศ
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บทคัดย่อ

ปัจจุบันไบโอดีเซลยังคงมีราคาค่อนข้างสูง เป็นผลจากต้นทุนของกระบวนการผลิต งานวิจัยนี้จึงได้ทำการศึกษาความเป็นไปได้ในการผลิตไบโอดีเซลจากปฏิกิริยาทรานซ์-เอสเตอริฟิเคชันด้วยหอกลั่นแบบมีปฏิกิริยาของน้ำมันปาล์ม เพื่อปรับปรุง และลดต้นทุนในกระบวนการผลิต โดยแบ่งการศึกษาออกเป็น 3 ส่วน คือ ศึกษาการจำลองกระบวนการด้วยโปรแกรม Aspen Plus เพื่อศึกษาปัจจัยต่าง ๆ ที่มีผลต่อกระบวนการผลิต และประเมินผลทางเศรษฐศาสตร์ จากนั้นจึงนำผลการจำลองกระบวนการที่ได้มาใช้เป็นแนวทางในการออกแบบการทดลอง เพื่อยืนยันผลที่ได้จากการจำลองกระบวนการ และส่วนสุดท้ายเป็นการจำลองระบบควบคุมในการผลิตไบโอดีเซลด้วยหอ กลั่นแบบมีปฏิกิริยา

จากการศึกษาด้วยการจำลองกระบวนการพบว่า ผลที่ได้จากการจำลองกระบวนการ และการทดลอง มี 3 ปัจจัยที่สอดคล้องกัน ได้แก่ อัตราส่วนเชิงโมลของเมทานอลต่อน้ำมัน เท่ากับ 4.0:1 เวลาของสารที่อยู่ในหอกลั่น 5 นาที และตัวเร่งปฏิกิริยา 1% โดยน้ำหนักของน้ำมัน ส่วนปัจจัยอื่น ๆ จะให้ผลที่แตกต่างกันคือ อุณหภูมิของหม้อต้มซ้ำ และอัตรารีฟรักซ์สำหรับการจำลองกระบวนการเท่ากับ 150°C และ 25 ตามลำดับ ส่วนในการทดลองเท่ากับ 90°C และมีการป้อนกลับเมทานอลทั้งหมด โดยความบริสุทธิ์ของเมทิลเอสเตอร์ที่ได้เท่ากับ 97.36% และ 92.27% ตามลำดับ ส่วนต้นทุนการผลิตของกระบวนการแบบหอกลั่นแบบมีปฏิกิริยาจะต่ำกว่ากระบวนการผลิตแบบดั้งเดิม 25.44 เปอร์เซ็นต์

สำหรับการจำลองระบบควบคุมในการผลิตไบโอดีเซลด้วยหอกลั่นแบบมีปฏิกิริยาด้วยการใช้ระบบควบคุมแบบ P สำหรับการรักษาระดับของของเหลวในหม้อต้มซ้ำ และตัวควบคุมแบบ PI ในการควบคุมอุณหภูมิของหอกลั่น หรือองค์ประกอบของสารในกระบวนการ พบว่าระบบควบคุมสามารถที่จะกำจัดตัวรบกวน และปรับกระบวนการให้เข้าสู่จุดที่กำหนดเอาไว้ใหม่ได้ นอกจากนี้ยังพบว่า การควบคุมอุณหภูมิในหอกลั่นสามารถใช้แทนการควบคุมองค์ประกอบของสารได้

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Abstract

Current cost of biodiesel is expensive as a result from the cost of production processes. This research studies the feasibility of using reactive distillation (RD) column for biodiesel production by transesterification reaction of palm oil. The hypothesis of using RD column was efficiency improvement and process cost reduction of the process. This study divided into three parts: First, a study of using RD column for biodiesel production process by Aspen Plus simulation program and comparing the cost of using conventional and RD process. Then the simulation results were used into the next part which was the experimental design to confirm the results of the simulation process. Finally, the simulation of control system for biodiesel production with RD column was studied.

The results of the simulation and the experiment gave the similar for 3 factors that were a molar ratio of methanol to oil at 4.0:1, the residence time in the column 5 minutes and 1% (wt) KOH catalyst. But for the reboiler temperature and reflux ratio in the simulation were 150°C and 25, respectively while for the experiment, the reboiler temperature was 90°C and overall methanol reflux. The purity of methyl ester (ME) from simulation and experiment were 97.36% (wt) and 92.27% (wt), respectively. For economic assessment, using RD process can reduced the process cost about 25.44% from the conventional.

For the control system of RD process, using P controller for reboiler level and PI controller for temperature or composition can reject disturbance and drive the process to the new desired set point.

ACKNOWLEDGEMENT

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CHAPTER 1

INTRODUCTION

1.1 Rational/Problem Statement

The scarcity of conventional fossil fuels, growing emissions of combustion-generated pollutants, and their increasing costs will make biomass sources more attractive (Sensoz et al., 2000). Petroleum-based fuels are limited reserves concentrated in certain regions of the world. These sources are on the verge of reaching their peak production. The fossil fuel resources are shortening day by day. The scarcity of known petroleum reserves will make renewable energy sources more attractive (Sheehan et al., 1998).

An alternative fuel to petrodiesel must be technically feasible, economically competitive, environmentally acceptable and easily available. Biodiesel is one of the current alternative diesel fuel which has high heating value a little bit lower than gasoline (46 MJ/kg), petrodiesel (43 MJ/kg), or petroleum (42 MJ/kg), but higher than coal (32–37 MJ/kg) (Demirbas, 2007). Besides that biodiesel is a good lubricant and can improve the lubrication properties of the diesel fuel blend (Extension, 2010).

Biodiesel can be used as a blending component or a direct replacement for diesel fuel in the diesel engines. It is defined as a mixture of monoalkyl esters of long chain fatty acids (FAME) derived from a renewable lipid feedstock, such as vegetable oil or animal fat. Biodiesel typically comprises alkyl fatty acid (chain length C14–C22) esters of short-chain alcohols, primarily, methanol or ethanol. Biodiesel is now mainly being produced from soybean, rapeseed and palm oils.

As stated by Biodiesel Development and Promotion Strategy (18 January 2005), the main feedstock for biodiesel production is palm oil. Because oil palm is a plant with high competitive potential due to its lower production and marketing costs than other plants. Besides that, palm oil can be utilized diversity in consumption goods (Department of alternative energy development and efficiency, 2009)

A present production capacity of biodiesel in Thailand is at 500,000 l/day (Department of alternative energy development and efficiency, 2009) from palm oil left from domestic consumption and the raw palm oil extraction factories with expanding capacity for receiving of increased raw palm almost in double. Due to the total capacity of raw palm oil extraction factories by 10.81 metric ton of fresh palm fruits per year. Comparing to the feedstock, the raw palm oil extraction factories will have capacity of 50 percent in excess.

In 2012, the biodiesel production capacity will be at 850,000 l/day (Department of alternative energy development and efficiency, 2009) due to the cultivation area of oil palm will extend to 10 million rai in 2011. Furthermore, the Stiarin Palm, which is a by-product from palm oil extraction, can also produce the biodiesel.

For biodiesel production, the conventional process consists of many units such as alcohol-catalyst mixer, reactor, glycerin-methyl ester separation tank, distillation column and methyl ester washer. The combination of reactor with distillation column in only one unit called "RD" may lead to an enormous reduction of capital and investment costs. In addition, it may be important for sustainable development due to a lower consumption of resources. The performance in one piece of equipment offers distinct advantages over the conventional approach. Especially when involving in reversible reaction or consecutive reaction, such as vegetable oil transesterification, the conversion can go far beyond its chemical equilibrium as a result of the continuously removal of reaction products from the reactive zone.

Besides designing RD column can improve the process, a control system is important to implement to the process as well. There are several reasons that the process need the control system such as safety, product specification, environment regulations, operation constraints and economic (Stephanopoulos, 1984) so that, the control system is used to minimize the effect of disturbance and improve process stability when process set point and load have changed.

The ultimate goal of this research study is to feasibility study of using RD column for tranesterification of palm oil. In particular, this research can be separated into three separations but related studies: steady state design simulation, experimental of transesterification with RD column and dynamic control simulation. The objectives and details of these studies are discussed in the next section.

1.1.1   Steady state simulation

The RD process requires the experiment data for design and construction. In order to reduce tradition 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 V7.1 (2006).

1.1.2   Experimental of transesterification with reactive distillation column.

RD column is a combination of a reactor reaction and distillation column in a single vessel. The advantages of using RD column are improving the selectivity and reaction conversion, better heat control, effective utilization of reaction heat, scope for difficult separations and the avoidance of azeotropes. The suitability of RD for reaction depends on various factors such as volatilities of reactants and products along with the feasible reaction and distillation temperature. The transesterification of palm oil with methanol fall in a typical class of reacting systems. Reactive distillation has become one of the extensively researched process intensification methods due to its ability to reduce energy consumption and number of process units.

1.1.3   Dynamic control simulation

After process simulation in the steady-state regime, ASPEN PLUS DYNAMICS V7.1 (2008) can be used for the dynamic simulation of the process. The dynamic simulation of such a system enables the understanding of its behavior after changing an input or output parameter. In a biodiesel process, the system behavior can be affected by the dynamics of individual unit. Due to this fact, a rigorous and complete simulation of the system is required. Process control and safety analysis are the two main areas of using dynamic simulations.

In this research, ASPEN Dynamics was applied in dynamic control simulation of methyl ester production process using RD column.

1.2 Research Objective

1) To study the biodiesel production in RD column.

2) To design appropriate control structure for the RD column.

1.3 Scopes of Research Work

1) Reaction is transesterification of refined palm oil with methanol in the presence of KOH as catalyst with RD column.

2) Simulation the process for biodiesel production and the control system for the RD column by Aspen Plus and Aspen Dynamic.

3) Triolein is used representative of oil composition.

4) Design controller structure using PID for the RD column and compare the performance of each structure.

5) The criterion is used to evaluate the performance of a control system is the integral of the absolute value of error (IAE).

1.4 Expected Benefits

1) The biodiesel production with RD and its control system will improve the effective of biodiesel production process.

2) This knowledge can be applied to the use of other raw material such as Jatropha oil or other chemical process such as chemical synthesis.

3) The product that we get will be value added for the raw material and it will decrease fuel imports from foreign countries.

4) This fuel releases less pollution into the environment than the petroleum diesel.

CHAPTER 2

THEORIES AND LITERATURE REVIEWS

2.1 Theoretical Background

2.1.1 Palm Oil

Palm oil is a form of edible vegetable oil obtained from the fruit of the oil palm tree. The oil palm is a tropical palm tree. The fruit is reddish, about the size of a large plum and grows in large bunches. The weight of each fruits bunch is approximately 10-40 kilograms (kg). Each fruit contains a single seed (the palm kernel) surrounded by a soft oily pulp. Oil is extracted from both the pulp of the fruit (palm oil, edible oil) and the kernel (palm kernel oil, used mainly for soap manufacture). For every 100 kg of fruit bunches, it is typically extracted 22 kg of palm oil and 1.6 kg of palm kernel oil.

The appearance of palm oil, obtained from refining crude palm oil, is a light yellow liquid or semi-solid at room temperature, melting to clear yellow liquid on slightly heating.

Palm oil is the second most traded vegetable oil crop in the world, after soy, and over 90% of the world's palm oil exports are produced in Malaysia and Indonesia. Palm oil is still mostly used in the manufacture of food products. However, palm oil is now starting to be used as an ingredient in bio-diesel and as a fuel to be burnt in power stations to produce electricity. This is a new market for palm oil which has the potential to dramatically increase global demand for this commodity.

Like all oils, Triglyceride (TG) is the major constituents of palm oil. Over 95% of palm oil consists of mixtures of TG, that is, glycerol molecules, each esterified with three fatty acids. During oil extraction from the mesocarp, the hydrophobic TG attracts other fat- or oil-soluble cellular components. These are the minor components of palm oil such as phosphatide, sterol, pigment, tocopherol, tocotrienol and trace metals. Other components in palm oil are the

metabolites in the biosynthesis of TG and products from lipolytic activity. These include the monoglyceride (MG), diglyceride (DG) and free fatty acid (FFA).

$$
\begin{array}{c}
H \qquad O \\
| \qquad \parallel \\
H - C - O - C - R_1 \\
| \qquad\quad O \\
\qquad\quad \parallel \\
H - C - O - C - R_2 \\
| \qquad\quad O \\
\qquad\quad \parallel \\
H - C - O - C - R_3 \\
| \\
H
\end{array}
$$

Figure 2.1 The structure of TG

From Figure 2.1, R_1, R_2 and R_3 represent the hydrocarbon chain of the fatty acid element of the TG. Note that there is a three-carbon chain called the glycerol backbone that runs along the left side of the molecule. Extending away from this backbone are the three long fatty acid chains.

In their free from, the fatty acids have the configuration shown in Figure 2.2.

$$
\begin{array}{c}
O \\
\parallel \\
R - C - OH
\end{array}
$$

Figure 2.2 The structure of fatty acid

R is a hydrocarbon chain of greater than 10 carbon atoms.

The fatty acids are any of a class of aliphatic acids, such as palmitic (16:0), stearic (18:0) and oleic (18:1) in animal and vegetable fats and oils. The major fatty acids in palm oil are myristic (14:0), palmitic, stearic, oleic and linoleic (18:2). The typical fatty acid composition of palm oil is presented in Table 2.1. Palm oil has saturated and unsaturated fatty acids in approximately equal amounts. The percentages of each fatty acid present in common oils and fats are shown in Table 2.2.

Table 2.1 Typical fatty acid composition (%) of palm oil (Americanpalmoilcouncil, 2004)

Type of fatty acid	Systematic name	Structure	Formular	Percent
Lauric	Dodecanoic	C12:0	$C_{12}H_{24}O_2$	0.3
Myristic	Tetradecanoic	C14:0	$C_{14}H_{28}O_2$	1.1
Palmitic	Hexadecanoic	C16:0	$C_{16}H_{32}O_2$	43.5
Palmitoleic	cis-9- Hexadecanoic	C16:1	$C_{16}H_{30}O_2$	0.2
Stearic	Octadecanoic	C18:0	$C_{18}H_{36}O_2$	4.3
Oleic	cis-9- Octadecanoic	C18:1	$C_{18}H_{34}O_2$	39.8
Linoleic	cis-9,cis-12- Octadecanoic	C18:2	$C_{18}H_{32}O_2$	10.2
Alpha Linolenic	cis-9,cis-12-,cis-15- Octadecanoic	C18:3	$C_{18}H_{30}O_2$	0.3
Arachidic	Eicosanoic	C20:0	$C_{20}H_{40}O_2$	0.2

Table 2.2 Composition of various oils and fats (Gerpen et al., 2004)

Oil or fat	14:0	16:0	18:0	18:1	18:2	18:3	20:0	22:1
Soybean		6-10	2-5	20-30	50-60	5-11		
Corn	1-2	8-12	2-5	19-49	34-52	trace		
Peanut		8-9	2-3	50-60	20-30			
Olive		9-10	2-3	73-84	10-12	trace		
Cottonseed	0-2	20-25	1-2	23-35	40-50	trace		
Hi linoleic Safflower		5.9	1.5	8.8	83.8			
Hi Oleic Safflower		4.8	1.4	74.1	19.7			
Hi Oleic Rapeseed		4.3	1.3	59.9	21.1	13.2		
Hi Erucic Rapeseed		3.0	0.8	13.1	14.1	9.7	7.4	50.7
Butter	7-10	24-26	10-13	28-31	1-2.5	0.2-0.5		
Lard	1-2	28-30	12-18	40-50	7-13	0-1		
Tallow	3-6	24-32	20-25	37-43	2-3			
Linseed Oil		4-7	2-4	25-40	35-40	25-60		

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 problems (Agarwal, 2007). To solve the problems, there are many techniques for converting the vegetable oil to biodiesel such as transesterification, pyrolysis, enzyme lipase, super critical fluid extraction.

A summary of the advantages and disadvantages of each technological possibility to produce biodiesel could be found in Table 2.3.

Table 2.3 Comparison of the different technologies to produce biodiesel (Marchetti et al., 2007)

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 materials	Saponified products	Methyl esters	Esters	Esters
Water in raw materials	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

2.1.2 Biodiesel

2.1.2.1 Biodiesel

Biodiesel is the monoalkyl esters of long chain fatty acids derived from renewable feed stocks, such as vegetable oil or animal fats, for use in compression ignition engines (Barnwal and Sharma, 2005). Biodiesel, which is considered as a possible substitute of conventional diesel fuel is commonly, composed of fatty acid methyl esters that can be prepared from TG in vegetable oils by transesterification with methanol. The resulting biodiesel is quite similar to conventional diesel fuel in its main characteristics (Meher et al., 2006). One of the advantages of this fuel is that the raw materials used to produce it are natural and renewable. All these types of oils come from vegetables or animal fat, making it biodegradable and nontoxic (Marchetti et al., 2007)

There are 2 chemical processes for obtaining ester as follows (Department of alternative energy development and efficiency, Ministry of Energy, 2009).

1. Esterification: a process using of acid as catalyst

2. Transesterificaion: a process using of alkaline as catalyst to form up ester by its equation.

Technology of commercial biodiesel production can be classified by 3 production processing, i.e. batch, on-line by transesterification and on-line by 2 stages (esterification and transesterification)

1. Batch Technology

Advantage is the low cost but the product quality may not be steady and a production capacity per round is not large

2. On-line Technology by Transesterification

A process with a steady product quality required an installation space less than the batch technology at equal capacity but at higher investment cost.

3. On-line Technology by 2 stages

Apply the esterification process at first stage and then transesterification process at a second stage. This technology is suitable with all raw materials, esp. oil with a high value of free fat acidic.

The potential raw materials or feedstock for biodiesel production in Thailand are the used cooking oil and new extracted vegetable oil such as oil from palm, coconut, soy bean, ground nut, castor, sesame, sunflower and jatropha.

The plant oils usually contain free fatty acids, phospholipids, sterols, water, odorants and other impurities. Because of these, the oil cannot be used as fuel directly. To overcome these problems the oil requires slight chemical modification mainly transesterification, pyrolysis and emulsification. Among these, the transesterification is the key and foremost important step to produce the cleaner and environmentally safe fuel from vegetable oils (Meher et al., 2006). Transesterification (also called alcoholysis) is the reaction of a fat or oil with an alcohol to form esters and glycerol. The reaction can be represented in equation 2.1 (Ma and Hanna, 1999):

$$
\begin{array}{llll}
CH_2-OOC-R_1 & & R_1-COO-R' & CH_2-OH \\
| & & & | \\
CH-OOC-R_2 & +\ 3R'OH \rightleftharpoons & R_2-COO-R' \ + & CH-OH \qquad (2.1) \\
| & & & | \\
CH_2-OOC-R_3 & & R_3-COO-R' & CH_2-OH \\
\text{Glyceride} & \text{Alcohol} & \text{Esters} & \text{Glycerol}
\end{array}
$$
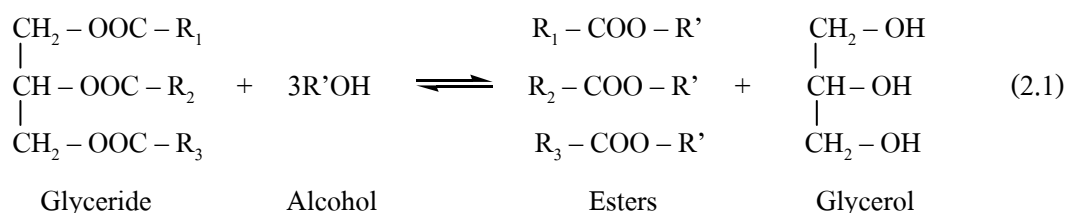
The reaction consists of a number of consecutive, reversible reactions as shown by the following reaction scheme.

Step 1: Triglyceride (TG) + Methanol $\rightleftharpoons$ Methyl Ester + Diglyceride (DG) (2.2)

Step 2: Diglyceride (DG) + Methanol $\rightleftharpoons$ Methyl Ester + Monoglyceride (MG) (2.3)

Step 3: Monoglyceride (MG) + Methanol $\rightleftharpoons$ Methyl Ester + Glycerol (GL) (2.4)
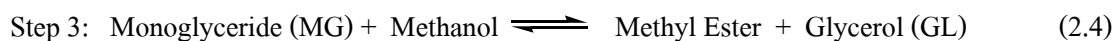
The first step is the conversion of TG to DG, which is followed by the conversion of DG to MG and of MG to GL, yielding one methyl ester molecule from each glyceride at each step (De Filippis, 1995).

A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the products side (Ma and Hanna, 1999).

2.1.2.2 Biodiesel Production Process

The step of biodiesel production (The National Biodiesel Board, 2002):

1. Mixing of alcohol and catalyst: The catalyst is typically sodium hydroxide (caustic soda, NaOH) or potassium hydroxide (potash, KOH). It is dissolved in the alcohol using a standard agitator or mixer.

2. Reaction: The alcohol/catalyst mixture is then charged into a closed reaction vessel and the oil or fat is added. The system from here on is totally closed to the atmosphere to prevent the loss of alcohol. The reaction mixture is kept just above the boiling point of the alcohol (around 71°C) to speed up the reaction and the reaction takes place. Recommended reaction time varies from 1 to 8 hours, and some systems recommend the reaction to take place at room temperature. Excess alcohol is normally used to ensure total conversion of the fat or oil to its esters which concerned the amount of water and free fatty acids in the incoming oil or fat. If the free fatty acid level or water level is too high it may cause problems with soap formation and the separation of the glycerin by-product downstream.

3. Separation: Once the reaction is complete, two major products exist: glycerin and biodiesel. Each has a substantial amount of the excess methanol that was used in the reaction. The reacted mixture is sometimes neutralized at this step if needed. The glycerin phase is much denser than biodiesel phase and the two can be gravity separated with glycerin simply drawn off the bottom of the settling vessel. In some cases, a centrifuge is used to separate the two materials faster.

4. Alcohol Removal: Once the glycerin and biodiesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation. In others systems, the alcohol is removed and the mixture neutralized before the glycerin and esters have been separated. In either case, the alcohol is recovered using distillation equipment and is reused. Care must be taken to ensure no water accumulates in the recovered alcohol stream.

5. Glycerin Neutralization: The glycerin by-product contains unused catalyst and soaps that are neutralized with an acid and sent to storage as crude glycerin. In some cases the salt formed during this phase is recovered for use as fertilizer. In most cases the salt is left in the glycerin. Water and alcohol are removed to produce 80-88% pure glycerin that is ready to be sold

as crude glycerin. In more sophisticated operations, the glycerin is distilled to 99% or higher purity and sold into the cosmetic and pharmaceutical markets.

6. Methyl Ester Wash: Once separated from the glycerin, the biodiesel is sometimes purified by washing gently with warm water to remove residual catalyst or soaps, dried, and sent to storage. In some processes this step is unnecessary. This is normally the end of the production process resulting in a clear amber-yellow liquid with a viscosity similar to petrodiesel. In some systems the biodiesel is distilled in an additional step to remove small amounts of color bodies to produce a colorless biodiesel.

7. Product Quality and Registration: Prior to use as a commercial fuel, the finished biodiesel must be analyzed using sophisticated analytical equipment to ensure it meets ASTM specifications. Additionally, all biodiesel produced must be registered with the Unites States Environmental Protection Agency under 40 CFR Part 79. The most important aspects of biodiesel production to ensure trouble free operation in diesel engines are:

- Complete Reaction
- Removal of Glycerin
- Removal of Catalyst
- Removal of Alcohol
- Absence of Free Fatty Acids

2.1.2.3 The Mechanism and Kinetics

Transesterification consists of a number of consecutive, reversible reactions as shown in equation 2.2 – 2.4. The TG is converted stepwise to DG, MG and finally GL (Ma and Hanna, 1999).

The reaction mechanism for alkali-catalyzed transesterification was formulated as three steps. The first step is an attack on the carbonyl carbon atom of the TG molecule by the anion of the alcohol (methoxide ion) to form a tetrahedral intermediate. In the second step, the tetrahedral intermediate reacts with an alcohol (methanol) to regenerate the anion of the alcohol (methoxide ion). In the last step, rearrangement of the tetrahedral intermediate results in the formation of a fatty acid ester and a DG. When NaOH, KOH, K_2CO_3 or other similar catalysts were mixed with alcohol, the actual catalyst, alkoxide group is formed. A small amount of water,

generated in the reaction, may cause soap formation during transesterification. Figure 2.3 summarizes the mechanism of alkali-catalyzed transesterification.

Pre-step: OH + R'OH $\rightleftharpoons$ R'O$^-$ + H$_2$O

or   NaOR' $\rightleftharpoons$ R'O$^-$ + Na$^+$

Step 1:

$$ROOCR_1 + {}^-OR' \rightleftharpoons R_1 - \underset{\underset{OR'}{|}}{\overset{\overset{OR}{|}}{C}} - O^-$$

Step 2:

$$R_1 - \underset{\underset{OR'}{|}}{\overset{\overset{OR}{|}}{C}} - O^- + HOR' \rightleftharpoons R_1 - \underset{\underset{OR'}{|}}{\overset{\overset{ROH^+}{|}}{C}} - O^- + {}^-OR'$$

Step 3:

$$R_1 - \underset{\underset{OR'}{|}}{\overset{\overset{ROH^+}{|}}{C}} - O^- \rightleftharpoons R_1COOR' + HOR$$
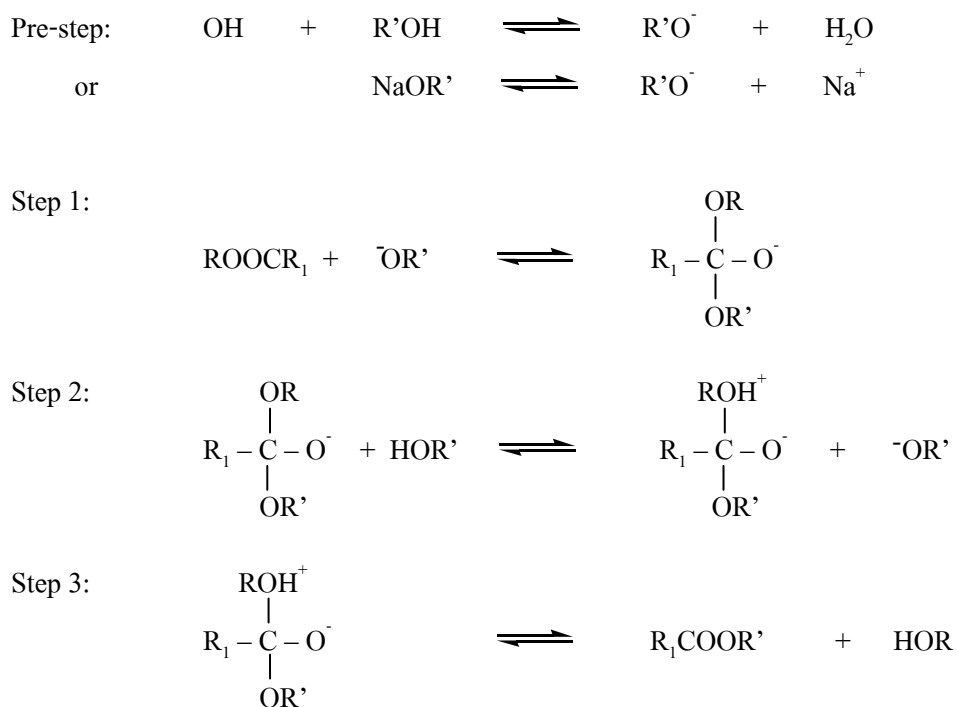
Figure 2.3 Mechanism of alkali-catalyzed transesterification of TG with alcohol

(Ma and Hanna, 1999).

Where R – OH methanol, R$_1$ long chain alkyl group and R' short alkyl group

The governing sets of second-order rate equations characterizing the stepwise reactions (equation 2.2 – 2.4) for transesterification of TG, without shunt reaction, are shown in equation 2.5 – 2.10 as following (Leevijit et al., 2004).

$$\frac{d[TG]}{dt} = -k_1[TG][A] + k_2[DG][E] \tag{2.5}$$

$$\frac{d[DG]}{dt} = k_1[TG][A] - k_2[DG][E] - k_3[DG][A] + k_4[MG][E] \tag{2.6}$$

$$\frac{d[MG]}{dt} = k_3[DG][A] - k_4[MG][E] - k_5[MG][A] + k_6[GL][E] \tag{2.7}$$

$$\frac{d[GL]}{dt} = k_5[MG][A] - k_6[GL][E] \tag{2.8}$$

$$\frac{d[E]}{dt} = k_1[TG][A] - k_2[DG][E] + k_3[DG][A] - k_4[MG][E]$$
$$+ k_5[MG][A] - k_6[GL][E] \tag{2.9}$$

$$\frac{d[A]}{dt} = \frac{-d[E]}{dt} \tag{2.10}$$

Kinetics parameter was estimated using the equation

$$k(T) = A\exp^{-Ea/RT} \tag{2.11}$$

For this kinetics at 60 °C were suggested to use values of k given in Table 2.4.

Table 2.4 Values of the kinetics parameter (Leevijit et al., 2004)

Kinetics parameter	Value (L/mol.s)
k_1	1.057×10^{-2}
k_2	0.000
k_3	1.184×10^{-1}
k_4	8.187×10^{-2}
k_5	1.310×10^{-1}
k_6	2.011×10^{-3}

2.1.2.4 Variables Affecting Transesterification Reaction

The process of transesterification is affected by various factors depending upon the reaction condition used (Meher et al., 2006). The effects of these factors are described below.

1. Effect of free fatty acid and moisture

The free fatty acid (FFA) and moisture content are key parameters for determining the viability of the vegetable oil transesterification process. To carry the base catalyzed reaction to completion; a FFA value lower than 3% is needed. The higher the acidity of the oil causes low conversion efficiency. Both, excess as well as insufficient amount of catalyst may cause soap formation.

Ma et al. (1998) studied the transesterification of beef tallow catalyzed by NaOH in presence of FFA and water. Without adding FFA and water, the apparent yield of beef tallow methyl esters (BTME) was highest. When 0.6% of FFA was added, the apparent yield of BTME reached the lowest, less than 5%, with any level of water added. The products were solid at room temperature, similar to the original beef tallow. When 0.9% of water was added, without addition of FFA, the apparent yield was about 17%. If the low qualities of beef tallow or vegetable oil with high FFA are used to make biodiesel fuel, they must be refined by saponification using NaOH solution to remove free fatty acids. Conversely, the acid catalyzed process can also be used for esterification of these FFA.

Most of the biodiesel is currently made from edible oils by using methanol and alkaline catalyst. However, there are large amounts of low cost oils and fats that could be converted to biodiesel. The problems with processing these low cost oils and fats are that they often contain large amounts of FFA that cannot be converted to biodiesel by using alkaline catalyst. Therefore, two-step esterification process is required for these feed stocks. Initially, the FFA of these can be converted to fatty acid methyl esters (FAME) by an acid catalyzed pretreatment and in the second step transesterification is completed by using alkaline catalyst to complete the reaction (Canakci and Gerpen, 2001). Initial process development was performed with synthetic mixture containing 20 and 40% FFA prepared by using palmitic acid. Process parameters such as molar ratio of alcohol to oil, type of alcohol, amount of acid catalyst, reaction time and FFA level were investigated to determine the best strategy for converting the FFA to

usable esters. The work showed that the acid level of the high FFA feed stocks could be reduced to less than 1% with a two step pretreatment reaction. The reaction mixture was allowed to settle between steps so that the water containing phase could be removed. The two-step pretreatment reaction was demonstrated with actual feedstocks, including yellow grease with 12% FFA and brown grease with 33% FFA. After reducing the acid levels of these feedstocks to less than 1%, the transesterification reaction was completed with an alkaline catalyst to produce fuel grade biodiesel.

The starting materials used for base catalyzed alcoholysis should meet certain specifications. The TG should have lower acid value and all material should be substantially anhydrous. The addition of more sodium hydroxide catalyst compensates for higher acidity, but the resulting soap causes an increase in viscosity or formation of gels that interferes in the reaction as well as with separation of glycerol. When the reaction conditions do not meet the above requirements, ester yields are significantly reduced. The methoxide and hydroxide of sodium or potassium should be maintained in anhydrous state. Prolonged contact with air will diminish the effectiveness of these catalysts through interaction with moisture and carbon dioxide.

2. Effect of catalyst type and concentration

Catalysts used for the transesterification of TG are classified as alkali, acid, enzyme or heterogeneous catalysts. If the oil has high FFA content and more water, acid catalyzed transesterification is suitable. Sodium methoxide (NaOMe) causes formation of several by-products mainly sodium salts, which are to be treated as waste. In addition, high quality oil is required with this catalyst. This was different from the previous reports in which ester conversion at the 6:1 molar ratio of alcohol/oil for 1% NaOH and 0.5% NaOMe were almost the same after 60 min. Part of the difference may be attributed to the differences in the reaction system used.

As a catalyst in the process of alkaline methanolysis, mostly NaOH or KOH have been used, both in concentration from 0.4 to 2% w/w of oil. Refined and crude oils with 1% either NaOH or KOH catalyst resulted successful conversion. Methanolysis of soybean oil with the catalyst 1% KOH has given the best yields and viscosities of the esters (Tomasevic and Siler-Marinkovic, 2003).

Acid catalyzed transesterification was studied with waste vegetable oil. The reaction was conducted at four different catalyst concentrations, 0.5, 1.0, 1.5 and 2.25 M HCl in presence of 100% excess alcohol and the result was compared with 2.25 M H_2SO_4 and the decrease in viscosity was observed. H_2SO_4 has superior catalytic activity in the range of 1.5–2.25 M concentration (Al-Widyan and Al-Shyoukh, 2002).

Although chemical transesterification using an alkaline catalysis process gives high conversion levels of TG to their corresponding methyl esters in short reaction times, the reaction has several drawbacks: it is energy intensive, recovery of glycerol is difficult, the acidic or alkaline catalyst has to be removed from the product, alkaline waste water require treatment, and FFA and water interfere the reaction. Enzymatic catalysts like lipases are able to effectively catalyze the transesterification of TG in either aqueous or non-aqueous systems, which can overcome the problems mentioned above (Fukuda et al., 2001). In particular, the by-products, glycerol can be easily removed without any complex process, and also that FFA contained in waste oils and fats can be completely converted to alkyl esters. On the other hand, in general the production cost of a lipase catalyst is significantly greater than that of an alkaline one.

3. Effect of molar ratio of alcohol to oil and type of alcohol

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to TG. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of TG to yield three moles of fatty acid alkyl esters and one mole of glycerol (Demibas, 2007; Refaat et al., 2008). However, transesterification is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction to the right. For maximum conversion to the ester, a molar ratio of 6:1 should be used. The molar ratio has no effect on acid, peroxide, saponification and iodine value of methyl esters. However, the high molar ratio of alcohol to vegetable oil interferes with the separation of glycerin because there is an increase in solubility. When glycerin remains in solution, it drives the equilibrium backward, lowering the yield of esters. The transesterification of Canary oil with ethanol was studied at molar ratios between 3:1 and 15:1. The ester yield increased as the molar ratio increased up to a value of 12:1. The best results were for molar ratios between 9:1 and 12:1. For molar ratios less than 6:1, the reaction was incomplete. For a molar ratio of 15:1, the separation of glycerin is difficult and the

apparent yield of esters decreased because a part of the glycerol remains in the biodiesel phase. Therefore, molar ratio 9:1 seems to be the most appropriate (Enciner et al., 2002).

The base catalyzed formation of ethyl ester is more difficult than the formation of methyl esters. Specifically, the formation of stable emulsion during ethanolysis is a problem. Methanol and ethanol are not miscible with TG at ambient temperature, and the reaction mixtures are usually mechanically stirred to enhance mass transfer. During the course of reaction, emulsions usually form. In the case of methanolysis, these emulsions quickly and easily break down to form a lower glycerol rich layer and upper methyl ester rich layer. In ethanolysis, these emulsions are more stable and severely complicate the separation and purification of esters (Encinar et al., 2007). The emulsions are caused in part by formation of the intermediates MG and DG, which have both polar hydroxyl groups and non-polar hydrocarbon chains. These intermediates are strong-surface active agents. In the process of alcoholysis, the catalyst, either NaOH or KOH is dissolved in polar alcohol phase, in which TG must transfer in order to react. The reaction is initially mass-transfer controlled and does not conform to expected homogeneous kinetics. When the concentrations of these intermediates reach a critical level, emulsions form. The larger non-polar group in ethanol, relative to methanol, is assumed to be the critical factor in stabilizing the emulsions. However, the concentrations of MG and DG are very low, and then the emulsions become unstable. This emphasizes the necessity for the reaction to be as complete as possible, thereby reducing the concentrations of MG and DG (Meher et al., 2006).

4. Effect of reaction time and temperature

The conversion rate increases with reaction time. Peanut, cotton-seed, sunflower and soybean oils were transesterified under the condition of methanol–oil molar ratio 6:1, 0.5% NaOMe catalyst and 60°C. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1 h, the conversion was almost the same for all four oils (93–98%) (Meher et al., 2006).

Ma et al. (1999) studied the effect of reaction time on transesterification of beef tallow with methanol. The reaction was very slow during the first minute due to mixing and dispersion of methanol into beef tallow. From one to five minute, the reaction proceeds very fast. The production of BTME reached the maximum value at about 15 min.

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Transesterification can occur at different temperatures, depending on the oil used. For the transesterification of refined oil with methanol (6:1) and 1% NaOH, the reaction was studied with three different temperatures (Freedman et al., 1984). After 0.1 h, ester yields were 94, 87 and 64% for 60, 45 and 32°C, respectively. After 1 h, ester formation was identical for 60 and 45°C runs and only slightly lower for the 32°C run. Temperature clearly influenced the reaction rate and yield of esters (Ma and Hanna, 1999).

5. Effect of mixing intensity

Mixing is very important in the transesterification reaction, as oils or fats are immiscible with NaOH–methanol solution. Once the two phases are mixed and the reaction is started, stirring is no longer needed. Initially the effect of mixing on transesterification of beef tallow was studied (Ma and Hanna, 1999). The result showed that no reaction was observed without mixing and when NaOH–MeOH was added to the melted beef tallow in the reactor while stirring, stirring speed was insignificant. Reaction time was the controlling factor in determining the yield of methyl esters. This suggested that the stirring speeds investigated exceeded the threshold requirement of mixing.

6. Effect of using organic cosolvents

The methoxide base catalyzed methanolysis of soybean oil at 40^{0}C (methanol–oil molar ratio 6:1) shows that to form methyl esters proceeds approximately more slowly than butanolysis at 30^{0}C. This is interpreted to be the result of a two phase reaction in which methanolysis occurs only in the methanol phase. Low oil concentration in methanol causes the slow reaction rate; a slow dissolving rate of the oil in methanol causes an initiation period. Intermediate MG and DG preferentially remain in the methanol, and react further, thus explaining the deviation from second order kinetics. The same explanations apply for hydroxide ion catalyzed methanolysis.

In order to conduct the reaction in a single phase, cosolvents like tetrahydrofuran (THF), 1,4- dioxane and diethyl ether were tested. Although, there are other cosolvents, initial study was conducted with tetrahydrofuran. At the 6:1 methanol–oil molar ratio the addition of 1.25 volume of tetrahydrofuran per volume of methanol produces an oil dominant one phase system in which methanolysis speeds up dramatically and occurs as fast as butanolysis. In particular, THF is chosen because its boiling point of 67^{0}C is only two degrees higher than that of methanol. Therefore at the end of the reaction the unreacted methanol and THF can be co-distilled and recycled (Boocock et al., 1996).

An improved process was investigated for methanolysis and ethanolysis of fatty acid glycerides such as those found in naturally occurring fats and oils derived from plant and animals. The processes comprise solubilizing oil or fat in methanol or ethanol by addition of a cosolvent in order to form a one-phase reaction mixture, and adding an esterification catalyst. The processes proceed quickly, usually in less than 20 min, at ambient temperatures, atmospheric pressure and without agitation. The co-solvent increases the rate of reaction by making the oil soluble in methanol, thus increasing contact of the reactants. The lower alkyl fatty acid monoesters produced by the process can be used as biofuels and are suitable as diesel fuel replacements or additives.

2.1.3 Reactive Distillation Column (RD)

RD is a chemical unit operation in which chemical reaction and product separation occur simultaneously in one unit (Figure. 2.4 and 2.5) and offers the possibility to overcome restrictions given by chemical and phase equilibrium.
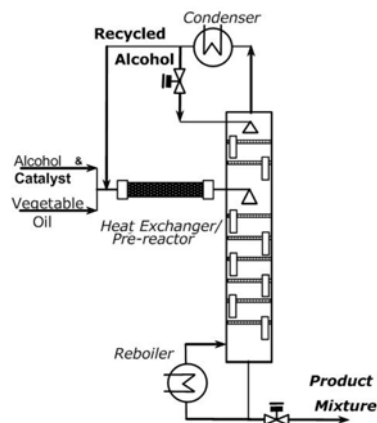
Figure 2.4 Diagram of the RD process (He, 2006)
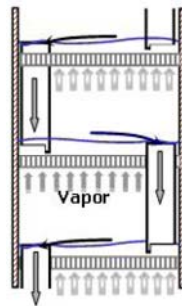
Figure 2.5 Close-up of the perforated plates (He, 2006)

The integration of reaction and separation into one apparatus reduces the investment cost and facilitates utilizing the heat of reaction. Moreover, removing the products from the liquid reaction zone into the vapor phase overcomes conversion restrictions given by the reaction equilibrium.

The excess alcohol in conventional process which consists of reactor and distillation column is remain unreacted and is contained in the crude biodiesel and the glycerol

by-product streams. It has to be recovered and purified for reusing by rectification and distillation, which are energy-consuming processes.

In the RD process, the reaction between vegetable oil and alcohol in a ratio close to stoichiometric while excess alcohol is created by internal alcohol recycling. The RD reactor consists of packing material that holds certain amount of reacting liquid on it. Unreacted alcohol is vaporized from the reboiler, flows upward constantly, and bubbles through the pack bed, which provides a uniform mixing. The thru-vapor is condensed at the top of the RD column and refluxes partially back to the column and the rest combines with the feeding stream. It is this portion of the recycled alcohol that creates a locally excess alcohol to oil ratio, which drives the reactions forward. Therefore, the excess alcohol needed at the input stream is considerably reduced. Combined with elevated operating temperature, the RD technique shortens the reaction significantly from that of a conventional process, and greatly increases the productivity (He, 2006).

To summarize, the RD reactor system has the following major advantages over the traditional processes (He, 2006):

1. RD reactor system requires much less feeding alcohol. Compared to other systems, the alcohol feed input can be reduced by 66 percent.

2. The RD system requires short reaction and provides high productivity since the elevated temperatures enhance high reaction rates. Experimental results showed that the overall reaction time was reduced to 10 to15 min and productivity was increased 6 to 9 times.

3. The RD reactor system greatly reduces the load of downstream alcohol recovery processes, which significantly reduces initial capital and also operating costs. The use of reactor/mixer prior to the reactive column is found to be very effective to increase the overall productivity. High reaction rates at initial stage in the pre-reactor significantly reduce the reaction duty on the reactive column.

Model Equations for RD column

The following assumptions are made during the model formulation of RD process for biodiesel production (Chin et al., 2006).

• Constant liquid holdups.

• Ideal vapour behaviour.

• Equimolar overflow except in the reaction zone where vapor boilup changes due to heat of reaction, which vaporizes some liquid on each tray.

• Constant relative volatilities.

• Fixed heat of reaction and vaporization.

• Saturated methanol feed and reflux flowrates.

• Oil feed at same temperature as methanol.

• The vapor and liquid are in equilibrium on each stage with negligible heat of mixing of liquid and vapor mixtures.

• Liquid phase reaction, perfectly mixed stirred-tank reactor (CSTR) for each stage in reaction section.

• Negligible the vapor holdup.

The model equations including mass and energy balances, vapor-liquid equilibrium and summation equation (MESH equations, eq 2.12 – 2.34) are shown in Figure 2.5 (Chin et al., 2006).

Figure 2.6 show schematic diagram of a RD unit (Olanrewaju and Al-Arfaj, 2005). The column is considered to consist of five interconnected subsystems, which are: the reboiler, stripping section, reactive section, rectifying section and the condenser. The reactive section contains N_{RX} trays. The rectifying section contains N_R trays, and the stripping section below the reactive section contains N_S trays
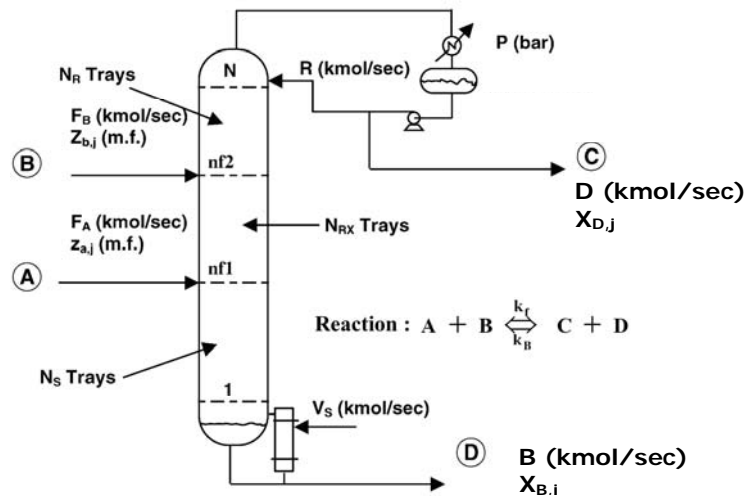
Figure 2.6 Schematic diagram of RD column (Chin et al., 2006)

Mass Balance

- Reboiler $(i = 1)$:

$$\frac{dx_{1,j}}{dt} = \frac{L_2(x_{2,j} - x_{1,j}) + V_S(x_{1,j} - y_{1,j})}{M_1} \tag{2.12}$$
$$j = 1,...,N_C$$

- Stripping section $(2 \leq i \leq N_S + 1)$:

$$\frac{dx_{i,j}}{dt} = \frac{L_{i+1}(x_{i+1,j} - x_{i,j}) + V_S(y_{i-1,j} - y_{i,j})}{M_i} \tag{2.13}$$
$$j = 1,...,N_C$$

- Reactive section $(nf_1 \leq i \leq nf_2)$, $F_i = 0$ except at $i = nf_1, nf_2$:

$$\frac{dx_{i,j}}{dt} = \frac{L_{i+1}(x_{i+1,j} - x_{i,j}) + V_{i-1}(y_{i-1,j} - x_{i,j}) + V_i(x_{i,j} - y_{i,j}) + R_{i,j} + F_i(Z_{i,j} - x_{i,j})}{M_i} \tag{2.14}$$
$$j = 1,...,N_C$$

- Rectifying section $(nf_2 + 1 \leq i \leq N_S + N_{RX})$:

$$\frac{dx_{i,j}}{dt} = \frac{L_{i+1}(x_{i+1,j} - x_{i,j}) + V_n(y_{i-1,j} - y_{i,j})}{M_i} \tag{2.15}$$

$$j = 1,..., N_C$$

- Condenser:

$$\frac{dx_{N,j}}{dt} = \frac{V_n(y_{N-1,j} - x_{N,j})}{M_N} \tag{2.16}$$

$$j = 1,..., N_C$$

The vapor and liquid flow rates on tray i of the reactive section are given as:

$$V_i = V_S + \frac{\lambda}{\Delta H_V} \sum_{k=1}^{i-N_S-1} R_{N_S+1+k,j} \tag{2.17}$$

$$L_i = L_{i-1} + \frac{\lambda}{\Delta H_V} \sum_{k=1}^{i-N_S-1} R_{N_S+1+k,j} \tag{2.18}$$

The reaction rate (kmol/s) of component j on tray i is given as:

$$R_{i,j} = M_i(k_{f,i}x_{i,A}x_{i,B} - k_{B,i}x_{i,C}x_{i,D}) \tag{2.19}$$

The forward and backward specific reaction rates (kmol s^{-1} kmol^{-1}) on tray i are:

$$k_{F,i} = a_F e^{-E_F/RT_i} \tag{2.20}$$

$$k_{B,i} = a_B e^{-E_B/RT_i} \tag{2.21}$$

The vapor–liquid equilibrium equations are:

$$y_{i,j} = \frac{\alpha_j x_{i,j}}{\sum_{k=1}^{N_C} \alpha_k x_{i,k}} \tag{2.22}$$

$$T_i = \frac{B_{vp,1}}{A_{vp,1} - \ln\left(\alpha_1 P \Big/ \sum_{k=1}^{N_C} \alpha_k x_{i,k}\right)} \tag{2.23}$$

Energy Balance

$$
\begin{aligned}
&F_j \sum_{i=1}^{M} z_{j,i}(h_{j,i}^f - h_{j,i}^L) + L_{j-1} \sum_{i=1}^{M} x_{j-1,i}(h_{j-1,i}^L - h_{j,i}^L) + V_{j+1} \sum_{i=1}^{M} y_{j+1,i}(h_{j+1,i}^V - h_{j,i}^L) \\
&- \delta_j W_j \sum_{r=1}^{R} (\Delta\Delta_{j,r}^R) r_{j,r} = V_j \sum_{i=1}^{M} y_{j,i}(h_{j,i}^V - h_{j,i}^L)
\end{aligned}
\tag{2.24}
$$

Phase Equilibrium

$$\varphi P y = \gamma P^o x$$

In the present study, the vapor phase is assumed to be ideal so that the entire fugacity coefficients φ for the system are equivalent to unity. The liquid phase non-ideality is characterized by the activity coefficients γ calculated from the Universal Functional Activity Coefficient (UNIFAC) method. The saturated vapor pressure P^o is calculated from the Antoine equation and P is the total pressure of the system.

Antoine equation $\qquad \ln P^o = A + \dfrac{B}{C + T} \qquad$ Pa, T(K) $\hfill (2.25)$

The UNIFAC contribution method was used to calculate activity coefficients (Reid et al., 1977). The activity coefficient is separated into two parts (Dossin et al., 2006) one

part provides the contribution due to molecular size and shape and is defined as the combinatorial contribution ($\ln \gamma_i^C$), and the other provides the contribution due to molecular interactions, known as the residual contribution ($\ln \gamma_i^R$):

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{2.26}$$

Where

$$\ln \gamma_i^C = \ln \frac{\Phi_i}{x_i} + 5q_i \ln \frac{\theta_i}{\Phi_i} + 1_i - \frac{\Phi_i}{x_i} \sum_j^{\text{all comp.}} x_j 1_j \tag{2.27}$$

$$\ln \gamma_i^R = \sum_k^{\text{all groups}} \nu^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \tag{2.28}$$

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j}, \qquad \Phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \tag{2.29}$$

$$r_i = \sum_k \nu_k^{(i)} R_k, \qquad q_i = \sum_k \nu_k^{(i)} Q_k, \qquad 1_i = 5(r_i - q_i) - (r_i - 1) \tag{2.30}$$

$$\ln \Gamma_k = Q_k \left\{ 1 - \ln \left(\sum_m^{\text{all comp.}} \theta_m \Psi_{mk} \right) - \sum_m^{\text{all comp.}} \frac{\theta_m \Psi_{km}}{\sum_n^{\text{all comp.}} \theta_n \Psi_{nm}} \right\} \tag{2.31}$$

$$\Psi_{mn} = \exp\left(-\frac{a_{mn}}{T} \right) \tag{2.32}$$

Summation

$$\sum_{i=1}^{M} x_{i,j} - 1 = 0, \quad j = 1,..., N \tag{2.33}$$

$$\sum_{i=1}^{M} y_{i,j} - 1 = 0 \quad j = 1,..., N \tag{2.34}$$

To produce high quality products from a biodiesel production, it is necessary to be able to control the production process. The basic requirement that a control system should be able to fulfill is stability. This means that a controlled process should remain stable in all circumstances. The accuracy, speed and robustness of each control structure should be considered for a quality of the control system.

2.1.4 Control System

Feedback control is used in practice in many control applications. The benefits of feedback control are that it is possible to keep some physical quantity at the desired e.g. pressure, temperature etc, and quickly despite of the disturbances (d) that might occur (Helsinki University of Technology, 2002). The Figure 2.7 shows the principal structure of feedback control. In feedback control, controlled variable is measured and can be defined as output signal (y) or measurement signal (y_m) from sensor. The y_m is compared with reference signal (r) or set point (y_{sp}) of the controlled variable. The difference between y_{sp} and y_m is an error variable (e) signal. The controller creates the control signal (based on the error signal) and controls the process (actually the controller controls an actuator which controls the process).
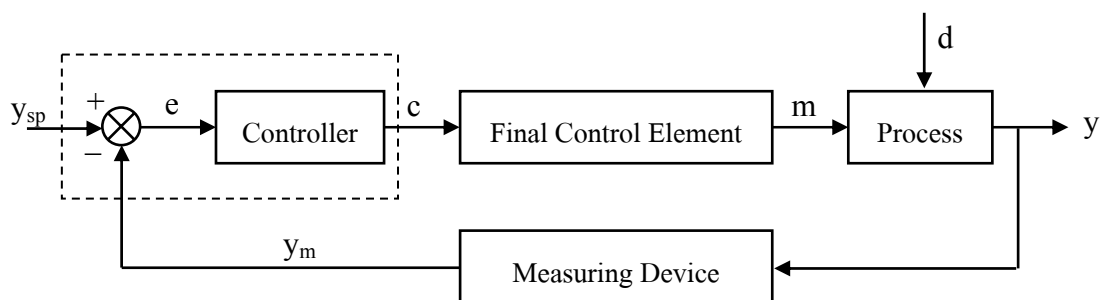
Figure 2.7 Principal structure of feedback control (Seborg et al., 2004)

2.1.4.1 Different Controllers

There are three basic types of feedback controllers.

1. P-controller

For proportional control, the controller output, $u(t)$, is proportional to the error signal, $e(t)$, by a factor of K, the dimensionless controller gain.

$$u(t) = Ke(t) \tag{2.35}$$

The controller gain is adjusted to increase or decrease the sensitivity of the controller output to the deviations between set point and the controlled variable (CV).

2. PI-controller

In PI-controller, there is another term in the controller equation.

$$u(t) = K\left(e(t) + \frac{1}{\tau_I}\int_0^t e(t)dt\right) \tag{2.36}$$

Where τ_I is integration time constant. If the controller is tuned to be slow and τ_I is large, then the controller first acts like P-controller, but later the as the integration starts to affect, the steady-state deviation goes slowly to zero. In PI-control, the steady-state deviation will finally go to zero. If the controller is tuned to be fast and τ_I is small, then both terms (P and I) affect the control signal all the way from the beginning. The system becomes faster, but the output signal might oscillate.

3. PID-control

The equation of PID-controller has three terms, P, I and D-terms.

$$u(t) = K\left(e(t) + \frac{1}{\tau_I}\int_0^t e(t)dt + \tau_D\frac{de(t)}{dt}\right) \tag{2.37}$$

Where τ_D is derivation time constant. The derivation term acts like predictor, because the speed of change of the error signal affects the control signal. The derivation term has a large effect in systems where disturbances are present, because disturbances are often fast. This means that fast changes in error signal (disturbances) might even push the process to unstable state. On the other hand, the D-term might speed up the controlled system.

2.1.4.2 Tuning the Controller

Several methodologies exist for autotune controllers. One scheme is to create a "relay response" in which a hardwired relay circuit is placed in series with the controller and apparatus call that autotune variation method (ATV).

The ATV method is a classical automatic tuning method first proposed by Aström and Hägglung (1984). This method identifies important characteristics of the response of a monovariable process using a simple relay experiment (Litrico et al., 2007). It has been applied in conjunction with tuning rules based on ultimate cycle analysis. The relay experiment identifies with a single straightforward experiment the ultimate cycle parameters (ultimate gain K_u and ultimate period P_u) of a monovariable process represented by a linear transfer function. Once these parameters are obtained, any classical tuning rule based on the ultimate cycle can be used to obtain a P, PI or PID controller (Litrico et al., 2007).

The pulsing of this circuit creates a square wave in the manipulated variable (MV) of the system and a corresponding oscillating response in the process variable (PV). The oscillating response seen in the PV simulates the process under Ziegler-Nichols (ZN) ultimate control conditions, that is, it is an undamped oscillation, from which measurements of both ultimate controller gain (K_u) and ultimate period (P_u) can be made, as seen in Figure 2.8.
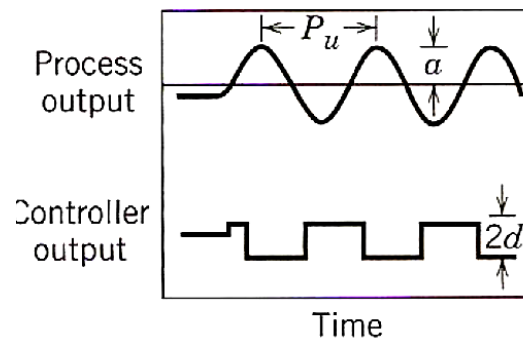
Figure 2.8 Graphical representation response of a system undergoing an ATV test

(Seborg et al., 2004)

The ultimate gain is calculated according to Equation 2.38:

$$K_u = \frac{4d}{a\pi}$$

(2.38)

Where d = relay amplitude

a = amplitude of the process output.

The usefulness of this method lies in the ability to obtain controller parameters from a running process with a minimal disturbance to the system.

After the type of feedback controllers has been select, all process variables (CV, MV and disturbance) are defined, the controlled parameters (K_C, τ_I and τ_D) must be determined for the appropriate value. There are method approaches that can be used for tuning the controller parameters:

1. Step response method

The step response method can be used to tune the parameters of a controller, if it is possible to feed a step into open system (neither control nor feedback). If a step of height K_1 is fed into the system and the output of the system behaves as in Figure 2.8, one can draw a tangent to the turning point of the output signal. The height of the output signal is then K_2. Delay (t_1) and rising time (t_2) are calculated as in Figure 2.9. The parameters of the controller are presented in Table 2.5.
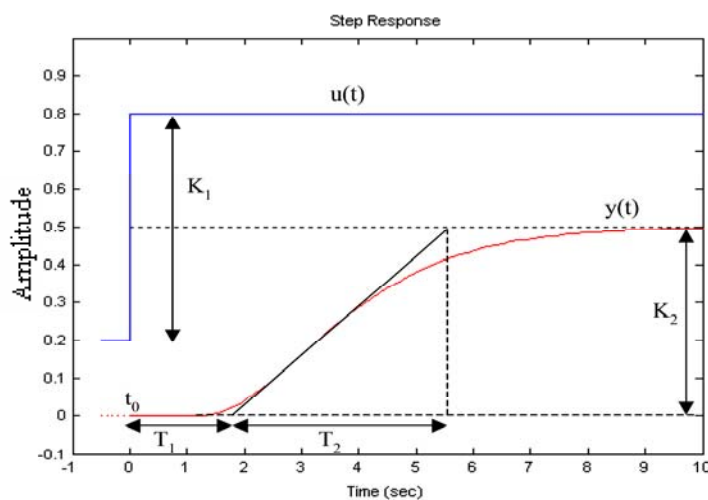
Figure 2.9 Step response method measurements (Helsinki University of Technology, 2002)

Table 2.5 Controller parameters in step response method

Controller	Gain (K_C)	Integration time (τ_I)	Derivation time (τ_D)
P	$\dfrac{K_1}{K_2}\dfrac{t_2}{t_1}$		
PI	$0.9\dfrac{K_1}{K_2}\dfrac{t_2}{t_1}$	$3t_1$	
PID	$1.2\dfrac{K_1}{K_2}\dfrac{t_2}{t_1}$	$2t_1$	$0.5t_1$

2. Ziegler-Nichols (ZN) criterion

The method is straightforward. First, set the controller to P mode only. Next, set the gain of the controller (K_c) to a small value. Make a small set point (or load) change and observe the response of the controlled variable. If K_c is low the response should be luggish. Increase K_c by a factor of two and make another small change in the set point or the load. Keep increasing K_c (by a factor of two) until the response becomes oscillatory. Finally, adjust K_c until a response is obtained that produces continuous oscillations. This is known as the K_u and the period of the oscillations is P_u. The control law settings are then obtained from the following Table 2.6.

Table 2.6 Controller parameters in ZN criterion

Controller	Gain (K_C)	Integration time (τ_I)	Derivation time (τ_D)
P	$\dfrac{K_u}{2}$		
PI	$\dfrac{K_u}{2.2}$	$\dfrac{P_u}{1.2}$	
PID	$\dfrac{K_u}{1.7}$	$\dfrac{P_u}{2}$	$\dfrac{P_u}{8}$

3. Tyreus-Luyben (TL) tuning method

The TL tuning method is demonstrated to tend to reduce oscillatory effects and give more robust control for this type of system than the ZN method. The controller parameters in TL tuning are shown in Table 2.7.

Table 2.7 Controller parameters in TL tuning method

Controller	Gain (K_C)	Integration time (τ_I)	Derivation time (τ_D)
PI	$\dfrac{K_u}{3.2}$	$2.2P_u$	
PID	$\dfrac{K_u}{2.2}$	$2.2P_u$	$\dfrac{P_u}{6.3}$

Generally the criterion might not work in all processes, but it gives a good initial value for the parameters when tuning a more complex system. It is also possible that overshoots are not approvable in some systems and the method can not be used.

2.1.4.3 Criteria for Selecting Temperature Control Trays in Distillation Columns

The use of tray temperatures to infer compositions is widespread in distillation control. A number of criteria have been proposed for selecting which trays to hold at constant temperature (Luyben, 2006).

1. Slope criterion: Select the tray where there are large changes in temperature from tray to tray

The temperature profile at design conditions is plotted, and the ''slope'' of profile is examined to find the tray where this slope is the largest. Large changes in temperature from tray to tray indicate a region where compositions of important components are changing. Maintaining a tray temperature at this location should hold the composition profile in the column and prevent light components from dropping out the bottom and heavy components from escaping out the top.

2. Sensitivity criterion: Find the tray where there is the largest change in temperature for a change in the manipulated variable

A very small change (0.1%) is made in one of the manipulated variables (for example, reflux flow rate). The resulting changes in the tray temperatures are examined to see which tray has the largest change in temperature. The procedure is repeated for the other manipulated variable (for example, reboiler heat input). Dividing the change in the tray temperature by the change in the manipulated variable gives the openloop steady-state gain between temperature on that tray and each manipulated variable. The tray with the largest temperature change is the most ''sensitive'' and is selected to be controlled. A large gain indicates that the temperature on that tray can be effectively controlled by the corresponding manipulated variable. A small gain indicates that valve saturation can easily occur and the operability region could be limited.

3. Singular value decomposition (SVD) criterion:

The steady-state gains between all the tray temperatures and the two manipulated variables are calculated as described in the previous section. A gain matrix K is formed, which has N_T rows (the number of trays) and two columns (the number of manipulated variables). This matrix is decomposed using standard SVD programs (for example, the ''svd'' function in Matlab) into three matrices: $K = U\sigma V^T$. The two U vectors are plotted against tray number. The tray or trays with the largest magnitudes of U indicate locations in the column that can be most effectively controlled. The σ matrix is a 2x2 diagonal matrix whose elements are the singular values. The ratio of the larger to the smaller is the condition number, which can be used to assess the feasibility of dual-temperature control. A large condition number (or small minimum singular value) indicates a system that is difficult to control. The controller is the inverse of the plant gain matrix, and a singular value of zero means the matrix is ''singular'' and cannot be inverted.

4. Invariant temperature criterion: With both the distillate and bottoms purities fixed, change the feed composition over the expected range of values. Select the tray where the temperature does not change as feed composition changes

The difficulty with this method is that there may be no constant-temperature tray for all feed compositions changes. This is particularly true in multi-component systems where the amounts of the non-key components can vary and significantly affect tray temperatures, especially near the two ends of the column.

5. Minimum product variability criterion: Choose the tray that produces the smallest changes in product purities when it is held constant in the face of feed composition disturbances

Several candidate tray locations are selected. The temperature on one specific tray is fixed, and a second control degree of freedom is fixed such as reflux ratio or reflux flowrate. Then the feed composition is changed over the expected range of values, and the resulting product compositions are calculated. The procedure is repeated for several control tray

locations. The tray is selected that produces the smallest changes in product purities when it is held constant in the face of feed composition disturbances.

This criterion corresponds to exactly what we would like to achieve in the operation of a distillation column. However, it involves significantly more effort since there are a large number of alternative trays to evaluate.

2.1.4.4 Controller Performance

Most operators of processes know what they want in the form of a response to a change in set point or disturbance (load). For example, a response that gives minimum overshoot and 1/4 decay ratio is often considered as a satisfactory response. In many cases, tuning is done by trial and error until such a response is obtained. In order to compare different responses that use different sets of controller parameters, a criterion that reduces the entire response to a single number, or a figure of merit, is desirable.

One criterion that is often used to evaluate a response of a control system is the integral of the square of the error with respect to time (ISE). The definition of ISE is as follows (Coughanowr, 1991):

Integral of the square of the error (ISE)

$$\text{ISE} = \int_0^\infty e^2 dt \tag{2.39}$$

where e is the usual error (i.e., set point – control variable). For a stable system for which there is no offset (i.e., $e(\infty)=0$), Eq. 2.39 produces a single number as a figure of merit. The objective of the designer is to obtain the minimum value of ISE by proper choice of control parameters. A response that has large errors and persists for a long time will produce a large ISE. For the cases of P and PD control, where offset occurs, the integral given by Eq. 2.39 does not converge. In these cases, one can use a modified integrand, which replaces the error $r(t) - c(t)$, by $c(\infty) - c(t)$. Since $c(\infty) - c(t)$ does approach zero as t goes to infinity, the integral will converge and serve as a figure of merit.

Two other criteria often used in process control are defined as follows:

Integral of the absolute value of error (IAE)

$$IAE = \int_{0}^{\infty} \left| e \right| \, dt \qquad (2.40)$$

Integral of time-weighted absolute error (ITAE)

$$ITAE = \int_{0}^{\infty} \left| e \right| t \, dt \qquad (2.41)$$

Each of the three figures of merit given by Eqs. 2.39, 2.40 and 2.41 have different purposes. The ISE will penalize (i.e., increase the value of ISE) the response that has large errors, which usually occur the beginning of a response, because the error is squared. The ITAE will penalize a response which has errors that persist for a long time. The IAE will be less severe in penalizing a response for large errors and treat all errors (large and small) in a uniform manner. The ISE figure of merit is often used in optimal control theory because it can be used more easily in mathematical operations (for example; differentiation) than the figures of merit, which use the absolute value of error.

2.1.5 Aspen Plus

Aspen Plus is a component of the Aspen Engineering Suite which is a chemical process simulation program. It is an integrated set of products designed specifically to promote best engineering practices and to optimize and automate the entire innovation and engineering workflow process throughout the plate and across the enterprise. The program automatically integrates process models with engineering knowledge databases, investment analyses, production optimization and numerous other business processes. Aspen Plus contains data, properties, unit operation models, built-in defaults, reports and other features (Sahapatsombut, 2004).

Aspen Plus is powerful and flexible engineering tool for the steady-state design and optimization of process. Process simulation with Aspen Plus can predict the behavior of a process using basic engineering relationships such as mass and energy balances, phase and chemical equilibriums and reaction kinetic. Given reliable thermodynamic data, realistic operating conditions and the rigorous Aspen Plus equipment models, actual plant behavior can be simulated. Aspen Plus can help design better plants and increase profitability in existing plants.

2.2 Literature review

The conventional biodiesel process is studied both batch and continuous reactor, many researches focus to study optimum condition and kinetic of reaction, such as

Foon et al. (2004) studied the kinetics of base-catalyzed transesterification of palm oil based on parameters such as oil and alcohol ratio, catalyst concentration and reaction temperature. The result showed that both NaOH and NaOMe had high kinetic constants depicting fast formation of palm oil methyl esters with conversions above 99%. Fast formation of palm oil methyl esters with a rate constant of 0.163 litre mole min^{-1} was obtained when the reaction parameters were: molar ratio of oil to methanol, 1:10; catalyst concentration, 0.125 mole kg^{-1} oil; and temperature, 60°C.

Leevijit et al. (2004) studied transesterification of palm oil with methanol at molar ratio 6:1, temperature 60°C, NaOH concentration 1 %wt of oil in an ideal CSTR. That could produce the highest purity at 97.8 %wt. For number of reactor greater than 1 and for plug flow reactor, they could produce the same highest purity at 98.7 %wt. However, the required residence times were different. For yield conversion that is less than 98.0 %wt, increasing of number of reactor gave a significant decrease of required residence time up to number of reactor equal to 6. In addition, for more than 98.5 %wt, number of reactor that is greater than 6, it still gave some significant decrease of required residence time. As a result, to produce saleable biodiesel, the optimum mixing performance of a continuous reactor was 6 ideal CSTRs in series. The predicted residence times of 6 ideal CSTRs in series to produce palm methyl esters at purities of 96.5, 97.0, 97.5, 98.0 and 98.5 %wt were 2.85, 3.15, 3.61, 4.32 and 6.24 min, and the efficiencies of this reactor were 66%, 64%, 62%, 59% and 53%, respectively.

Darnoko and Cheryan (2000) studied methyl ester production by transesterification of palm oil with methanol in the presence of a catalyst (KOH). The rate of transesterification in a batch reactor increased with temperature up to 60°C. Higher temperatures did not reduce the time to reach maximum conversion. The conversion of TG, DG and MG appeared to be second order up to 30 min of reaction time. Reaction rate constants for TG, DG

and MG hydrolysis reactions were 0.018-0.191 (wt %. min)$^{-1}$, and were higher at higher temperatures and higher for the MG reaction than for the TG hydrolysis. Activation energies were 14.7, 14.2 and 6.4 kcal/mol for the TG, DG and MG hydrolysis reactions, respectively. The optimum catalyst concentration was 1% KOH.

Moreover, many researchers tried to improve the production by focus on the process with RD, such as

Singh et al. (2005) studied to synthesis biodiesel on a continuous RD system. Effects of six process variables were evaluated on the reaction conversion, productivity and soap formation. An inline static-mixer type pre-reactor was using prior to the RD column that achieved a substantial portion of the reaction duty. Potassium methoxide was found to be significantly better catalyst than KOH for achieving high conversion while low Reboiler temperatures were favorable for lower soap formation. The condenser in total reflux mode was found to be better than in total recycle mode. Moreover, the feed molar ratio and overall flow rate was not highly correlated to overall product conversion or soap formation. The result showed that reaction conversion achieved on the RD reactor ranges from 41.46-94.94% with an average of 76.32%. Similarly, the productivity varies from 16-55.8 kmol/m$^3_{reactor}$-h with and average of 32 kmol/m$^3_{reactor}$-h.

He (2006) developed and studied to use a manufactured (glass) RD column in biodiesel production processes to reduce the use of excess alcohol and still produce a quality fuel was proven. The process was to scale-up the system to a production rate of 80 to 100 ml/min and measured its effectiveness. A 20 sieve-tray RD reactor system was designed. This model was used to produce biodiesel. The product parameters such as methyl ester content and total glycerol were analyzed. Preliminary results showed that process parameters of methanol-to-oil ratio of 4:1 (molar) and a column temperature of 65°C produced a biodiesel that was 90.71% converted in 5 min.

He and Peterson (2004) studied the use of RD technique for biodiesel preparation from yellow mustard seed oil. The goal was to significantly reduce the use of excess alcohol while maintaining a high alcohol-to-oil molar ratio inside the RD reactor by recycling a small amount of methanol within the system. In this study, the effects of process parameters, including operating temperature, feeding methanol to oil ratio and reaction time were conducted on a laboratory scale sieve-tray RD reactor system. Product parameters such as methyl ester content, glycerides, total glycerol and methanol content were analyzed as per ASTM methods. This study indicated that total resident time in the pre-reactor and RD column was about 3 min, which was 20-30 times lower than in typical batch processes. The productivity of the RD reactor system is about 6.6 m^3 biodiesel/m^3 reactor volume/hour, which was 6-10 times higher than that of a batch process. Preliminary results showed that biodiesel produced with methanol-to-oil ratio 4:1 (molar) and 10 min retention time in the RD reactor met the ASTM standards for total glycerol and viscosity.

He and Peterson (2006) found the RD reactor process had to be feasible for the continuous production of biodiesel from seed oils and making the process more efficient by reducing the alcohol-to-oil molar ratio. A 66% reduction to the industrial standard of 6:1 alcohol to oil molar ratio was achieved with good results. From the experimental results he concluded that the operating condition the RD system at 65°C with a 4:1 molar ratio and a pre-reactor was the optimum point for producing biodiesel from among the parameters examined in this study.

He et al. (2005) studied of biodiesel preparation from canola oil was performed on a continuous flow RD reactor system. Optimization of six process variables was studied experimentally and analyzed statistically on the overall performance of the RD reactor system. These variables include the feed methanol to triglycerides molar ratio, reaction time, Reboiler temperature, catalyst concentration, methanol circulation mode, and catalyst formulation. The following optimum ranges were found that feed molar ratio from 3.65:1 to 4.50:1, reaction time from 3.76 to 5.56 min, reboiler temperature from 100°C to 130°C, and catalyst concentration from 0.13 to 0.24 mol/mol. Although the process variable individually affected the system performance to a certain extent, the interactive effect of the process variable combinations affected the system

efficiency more significantly. When maximized, the product yields and productivity were 98.8% and 55.6 kmol/m^3.h (18.5 m^3/m^3.h), respectively. However, when soap formation was minimized, the yield and productivity were 72% and 9.3 kmol/m^3.h (3.1 m^3/m^3.h), respectively. It is recommended that the optimization of the RD reactor system be based on the maximization of product yield and reactor productivity.

Anyway, the control system is used for biodiesel production to prevent the process changes that occur. The control structure of biodiesel process with RD is still investigated. Many researches show that appropriate control structure can reject disturbance very well such as

Al-Arfaj and Luyben (2002a) focused on the design and control of a methyl acetate RD column. Several steady-state multiplicities were found. The impact of these multiplicities on the openloop stabilities is discussed. The systems that are openloop unstable are harder to control than openloop stable systems. Several control structures were studied. The CS1 control structure, in which three compositions are measured and controlled. The purities of the distillate and bottoms are controlled by manipulating reflux and reboiler heat-input, respectively. A composition inside the reactive zone of the column is measured and controlled by manipulating one of the fresh feeds, is effective provided loop interaction and system nonlinearity are not complex. However, this structure requires three composition analyzers, so it is less practical than the CS5 control structure, in which only one composition is controlled (the column internal composition) and a temperature is controlled in the stripping section.

The interaction between the design and control was examined by changing the conversion level. Low-conversion designs are less nonlinear and are easier to control. It is important to consider both design and control together in the design stage. The control of the methyl acetate reactive column process is very difficult if a CS1 structure is implemented on the high-conversion design.

The CS7 control structure, in which temperature controllers on two trays in the column manipulate the two fresh feed flow rates. The reflux drum level is controlled by the reflux flow rate and the base level by the bottoms flow rate. The distillate flow rate is adjusted to give a constant RR, uses only temperature measurements and provides effective control, provided the

disturbances are not too large and the column has been designed for higher-than-required purity levels. The methyl acetate system is compared to an ideal system with similar chemistry. The two systems have some differences and similarities. It is found that some control structures can be used on both systems.

Also, Al-Arfaj and Luyben (2002b) investigated the design and control of a RD column in which one reactant is consumed and two products are formed (A $\leftrightarrow$ B+C). The volatility (α) of the reactant is intermediate boiling between the two products ($\alpha_B > \alpha_A > \alpha_C$). The metathesis of 2-pentene is considered as the demonstrative example. The column has a single feed of the intermediate boiling reactant. The distillate contains mostly light component and the bottoms mostly heavy.

Three designs were considered: the base case (low-conversion/low-pressure), a low-conversion/high-pressure case and a high-conversion/high-pressure case. The base design is obtained from the literature, and the other two steady-state designs are optimized with respect to the total annual cost. All the designs are found to be openloop stable. Five control structures are studied for the base design. This category of RD exhibits less challenging problems than other categories since it uses a single feed, which eliminates the need for the control structure to perfectly balance two fresh feeds.

Simulation results demonstrate that effective dynamic control is provided by a control structure that uses two temperature controls to maintain the purities of both product streams. No internal composition measurement is required. This structure is found to be robust and stable. It can reject loads and tracks set points very well.

Lai et al. (2007) designed for two RD processes with azeotropic feed. The two processes are for the production of ethyl acetate (EtAc) and isopropyl acetate (IPAc). A systematic design procedure is presented to improve the quantitative design based on the total annual cost (TAC). The ternary minimum boiling azeotrope and ranking of the boiling points leads to a RD column with a reactive zone and a rectifying section followed by a stripper. For alcohol feeds below azeotrope composition (87 mol% for EtOH and 65 mol% for IPOH), the

TACs only increase by a factor of 5% for EtAc system and 8% for IPAc system. This offers attractive alternatives for EtAc and IPAc productions.

Next, the issue of control strategies for RD was studied. Two control structures, dual-temperature control and one-temperature-one-composition control, are considered. The non-square relative gain (NRG) is used to determine sensor locations and the relative gain array (RGA) is used to characterize the interaction and, subsequently, determine corresponding controller structure. The autotune variation test is employed to determine K_u and P_u, and the TL tuning is used to find controller parameters. Since steady-state offsets in product composition may result in temperature control, the composition control is also devised. Good disturbance rejection is observed for these control schemes. From the simulation results of control, it comes to a conclusion that the processes are resilient for moderate-size rate as well composition disturbances and decentralized PI control perform reasonably well for these dynamically decoupled systems.

Singh et al. (2005) studied the systematic analysis of the steady-state input–output (IO) relationships for synthesizing effective control structures for RD columns. Such control structures are necessary to provide robust, stable, safe and economical column operation to tide over disturbances entering the column. Effective control structures can be obtained by identifying IO pairings that avoid multiplicities and allow a sizeable nearly linear operating region around the base case. The methyl tertiary butyl ether (MTBE) case study shows that input and output multiplicity in the IO relations occurs in the steady-state relationships. It also shows that the occurrence of multiplicity depends on the control strategy implemented. For the MTBE example, a control structure that uses the reboiler duty to control Tray 11 temperature in the stripping section and the butene feed to control Tray 10 isobutene composition in the reactive section is found suitable. Proper choice of the manipulated variables and the tray locations for the measurements in the two loops is especially critical for effective column regulation. At a more general level, the results showed that maintaining the stoichiometric balance of the fresh feeds is needed for the effective control of doublefeed RD columns.

However, RD still is studied in many fields to find the optimal condition of each reaction for improve the effective of process such as

Bhatia et al. (2007) studied the esterification of palmitic acid with isopropanol in a RD column using zinc acetate supported on functionalized silica gel as a catalyst in Katapak-SP structured packing. The RD column performance was evaluated by running the column at different operating conditions. The operating parameters include total feed flow rate, reboiler temperature, palmitic acid feed composition, palmitic acid feed temperature, molar ratio of isopropanol feed to palmitic acid feed and reflux ratio. The equilibrium stage and rate-based models were used for the simulation studies. The simulation studies show that the equilibrium stage model could describe the column profiles only qualitatively while the rate-based model was capable in describing the column profiles quantitatively and qualitatively. The experimental data were in good agreement with the simulated results obtained from rate-based model. The important design parameters were also investigated with the aid of simulation studies. Finally, a technically optimized RD process for the production of isopropyl palmitate was proposed based on the experimental and simulation results. The nonreactive zones are of minor importance to the process performance. Furthermore, the additional unit operations are needed in the process for the recovery of isopropanol from water and isopropyl palmitate before recycling back to the column.

Cheng and Yu (2005) studied the effects of feed locations to the design of RD. And ideal RD systems are used to illustrate the advantage of feedtray optimization. RD columns with various process parameters were explored. The parameters were included relative volatilities between reactants, relative volatilities between products, column pressure, activation energies and pre-exponential factors. The results from all studied system indicate 6% to 47% energy saving, which can be achieved by simply rearrange the feed locations. Because the temperature and composition profiles play a vital role for the effective utilization of the reactive section, the optimal feed locations are essential to obtain improved performance. Qualitatively, heuristics are also given to place the feeds at the vicinity of optimal locations. Quantitatively, a systematic procedure is proposed to find the appropriate feed trays. Finally, the idea of optimal feedtrays can be carried over to the control of RD system. First, steady state analysis is performed to find the optimal feedtrays as the measurable load variable changes. Then, a coordinated control structure is proposed to rearrange the feeds as the disturbance comes into the system. The results indicated

that, again, substantial energy can be saved during process operation by feed rearrangement while showing improved closed‑loop dynamics.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Transesterification of Triolein with Methanol in RD Column: Simulation Studies

3.1.1 Abstract

Biodiesel is one of the most famous alternative petroleum diesel fuels. It is a clean fuel that causes less pollution than petroleum diesel does. To produce biodiesel by the conventional process, a biodiesel plant requires at least a reactor and a distillation column. Therefore, this work focuses on a feasibility study of using RD, the combination of a reactor with a distillation column in one unit, to produce biodiesel from palm oil. The hypothesis of using RD is to reduce the amount of excess alcohol in the feed stream bringing its stoichiometric ratio close to that of oil. That causes less energy to be required for the methanol recovery process. Aspen Plus 2006 has been used to simulate this process. The kinetic constants of the conventional process need to be modified for the RD process. The preliminary results show a molar ratio methanol to oil of 4:1 and the reboiler temperature at $150\,^{\circ}\mathrm{C}$ produces a 97.36 %(wt) methyl ester in 5.6 minutes. It can be concluded that using the RD process is more efficient and more feasible than using the conventional process to produce biodiesel from palm oil.

3.1.2 Introduction

Biodiesel is an interesting alternative as a renewable energy from vegetable oil and seems to be the best supplement to fossil-based fuels (He, 2006) due to its being clean burning, biodegradable, nontoxic, and essentially free of sulfur and aromatics. Biodiesel contains no petroleum, but it can be blended with any level of petroleum diesel. It can be used in compression-ignition (diesel) engines with little or no modifications.

The plant oils usually contain FFA, phospholipids, sterols, water, odorants and other impurities. Because of these, the oil cannot be used as a fuel directly. To overcome these problems the oil requires a slight chemical modification, mainly transesterification, pyrolysis and emulsification. Among these, the transesterification is the key and the foremost important step to produce the cleaner and environmentally safe fuel from vegetable oils (Meher et al., 2006). Transesterification (also called alcoholysis) is the reaction of a fat or oil with an alcohol. The TG within these fats and oils are transesterified with methanol or ethanol in the presence of usually a basic catalyst to form esters and glycerol as a byproduct.

The reaction is shown in Figure 3.1. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is a consecutive reaction (Noureddini and Zhu, 1997; Danoko and Cheryan, 2000), excess alcohol is therefore used to shift the equilibrium to the products side (Ma and Hanna, 1999). Alcohol remaining in the product must be purified and recycled in the recovery process. This process increases energy consumption and process time for the reaction.

$$
\begin{array}{lllll}
CH_2-OOC-R_1 & & & R_1-COO-R' & CH_2-OH \\
| & & & & | \\
CH-OOC-R_2 & + \ 3R'OH & \xrightarrow{\text{catalyst}} & R_2-COO-R' \ + & CH-OH \\
| & & & & | \\
CH_2-OOC-R_3 & & & R_3-COO-R' & CH_2-OH
\end{array}
$$

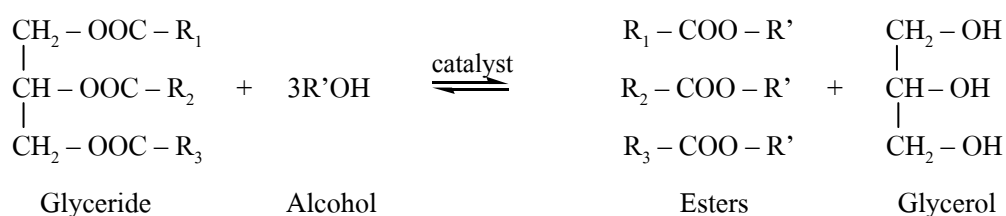   Glyceride   Alcohol   Esters   Glycerol

Figure 3.1 Transesterification of TG to produce esters

Fatty acid esters are conventionally produced in batch or a continuous stirred tank reactor by homogeneous catalysis. The conventional processes are penalized by a number of shortcomings and these are:

(1) Product quality degradation due to relatively long exposure to heat.

(2) Catalyst neutralization and removal after the reaction.

(3) Back reaction during alcohol removal.

(4) Relatively high alcohol demand.

These have accelerated the development of process intensification technologies such as the RD column for the production of fatty acid esters.

RD column as shown in Figure 3.2 is a combination of reactor and distillation column in one unit in which chemical reaction and product separation occur simultaneously. This technique is especially useful for equilibrium-limited reactions such as transesterification and esterification reactions. Conversion can be increased far beyond what is expected by the equilibrium due to the continuous removal of the products from the reactive zone. RD seems to be an attractive option for both economical and environmental reasons (Omota et al., 2003).This helps to reduce capital and investment costs, and may be important for sustainable development due to a lower consumption of resources. RD has several advantages (Sahapatsombut, 2004) such as:

- Increased speed and improved process efficiency and selectivity
- Lower costs – reduced equipment and energy use
- Less waste and fewer byproducts
- Improved product quality– reduced opportunity of product degradation because of lower temperature production
- Reacting away azeotropic mixtures

The concept of RD allows achieving a 100% conversion of theoretical amount of inputs. RD is a special type of gas-liquid reaction where the distribution of components in liquid and gas phase depends upon their reaction kinetics, mass transfer and vapor-liquid equilibrium. Both packed and tray columns can be used for this application. However, a sieve-tray type column was chosen in this study in order to achieve higher liquid holdup.
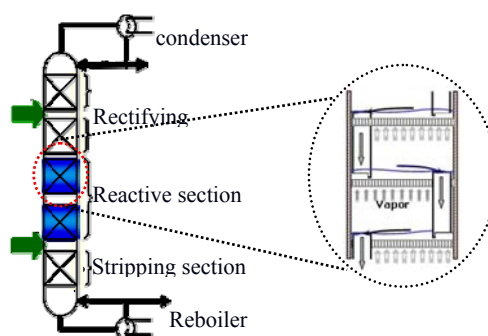
Figure 3.2 RD column (He, 2006)

3.1.3 Methodology

3.1.3.1 Adjusting the kinetics constant of the reaction

The kinetics constant of the biodiesel production process is still reported in conventional process. It must be adjusted to use in the simulation of RD process. The elementary reaction of transesterification for triolein with alcohol is shown in equation (1)-(3)

$$TG + MeOH \xrightarrow{k_1} DG + ME \qquad (3.1)$$

$$DG + MeOH \xrightarrow{k_2} MG + ME \qquad (3.2)$$

$$MG + MeOH \xrightarrow{k_3} GL + ME \qquad (3.3)$$

The set of second-order rate equations characterizing the stepwise reactions for transesterification of triolein are as follows (Leevijit et al., 2004)

$$\frac{d[TG]}{dt} = -k_1[TG][MeOH] \tag{3.4}$$

$$\frac{d[DG]}{dt} = k_1[TG][MeOH] - k_2[DG][MeOH] \tag{3.5}$$

$$\frac{d[MG]}{dt} = k_2[DG][MeOH] - k_3[MG][MeOH] \tag{3.6}$$

$$\frac{d[ME]}{dt} = k_1[TG][MeOH] + k_2[DG][MeOH] + k_3[MG][MeOH] \tag{3.7}$$

$$\frac{d[GL]}{dt} = k_3[MG][MeOH] \tag{3.8}$$

$$\frac{d[MeOH]}{dt} = k_1[TG][MeOH] + k_2[DG][MeOH] + k_3[MG][MeOH] \tag{3.9}$$

where k_1, k_2, and k_3 are reaction rate constants; [TG], [DG], [MG], [MeOH], [ME] and [GL] are molar concentration of Triglyceride, Diglyceride, Monoglyceride, Methanol, Methyl ester and Glycerol, respectively. The concentration profile calculates by Euler's integration.

The Euler's integration method is a first-order numerical procedure for solving ordinary differential equations (ODEs) with a given initial value. It is used for calculate the changing of species in the system by equation.

$$\frac{d(x)}{dt} = f(t, x(t)) \tag{3.10}$$

$$x(t_0) = x_0 \tag{3.11}$$

$$t_{n+1} = t_n + h \tag{3.12}$$

$$x_{n+1} = x_n + h * f(t_n, x_n) \tag{3.13}$$

where $f(t, x(t))$ is a known function and the values in the initial condition are also known numbers.

t_0 is an initial time

x_0 is an initial value

h is step size

The temperature dependency of the rate constant is expressed by the Arrhenius equation.

$$k = A e^{\frac{-Ea}{RT}}$$

(3.14)

where   k   is reaction constant

                      A   is pre-exponential factor

                      Ea   is Activation Energy

                      R   is gas constant

                      T   is temperature

3.1.3.2 Simulation of the biodiesel production process by the Aspen Plus (2006) program.

In this study, the Radfrac model in Aspen plus, a commercial program for process simulation, is applied for RD simulation for the methyl ester production with an alkaline catalyst. The base case study of simulation uses 12 stage-sieve RD trays and 1 atm. The RD process consists of a total condenser and a kettle reboiler. They are considered as two separation stages. The RD column had a diameter of 48.26 mm, a weir height of 35.03 mm and a tray spacing 25.4 mm. The residence time is 4.63 minutes. The feed stage is at the 2nd stage from the top. The top column and the reboiler temperatures are 65°C and 150°C, respectively which is close to the experiment of He (2004). The Non Random Two Liquids (NRTL) method is used to determine the thermodynamic property due to the highly polar components, methanol and glycerol. The process diagram for this process is shown in Figure 3.3.

The model assumes adiabatic operation of the column and the ideal reaction take place in the liquid phase. Each reactive stage is treated as a perfectly mixed continuous stirred tank reactor (CSTR). The vapour and liquid leaving any stage are in phase equilibrium with negligible. The hydrodynamic effects are neglected in this work in order to simplify the modeling complexities.
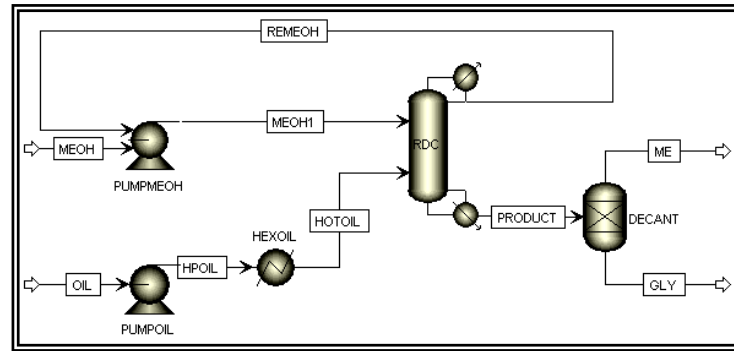
Figure 3.3 The RD column of biodiesel production process in simulation

3.1.4 Simulation result and Discussion

3.1.4.1 Adjusting the kinetic constant of the reaction.

The least square method was used to adjust kinetic constant for RD based on the experimental results of He et al. (2004). The results are shown in table 3.1.

Table 3.1 The kinetic constants of conventional and RD process

kinetic constant	Conventional[*]	RD
A_1	1.52×10^8	7.46×10^{16}
A_2	1.47×10^8	1.00×10^{15}
A_3	2614.24	6.17×10^8
Ea_1	14,700	33,870
Ea_2	14,200	29,850
Ea_3	6,400	19,470

* Danoko et al. (2000)

The adjusted kinetic constants for the RD process have higher values than those of the conventional process because of elevated temperatures and a higher alcohol to oil ratio in the RD.

Figure 3.4 shows the comparison of methyl ester (%wt) produced by the experiment and the calculation which are similar. It can be use to explain the reaction rate and mechanism of reaction in the RD process.
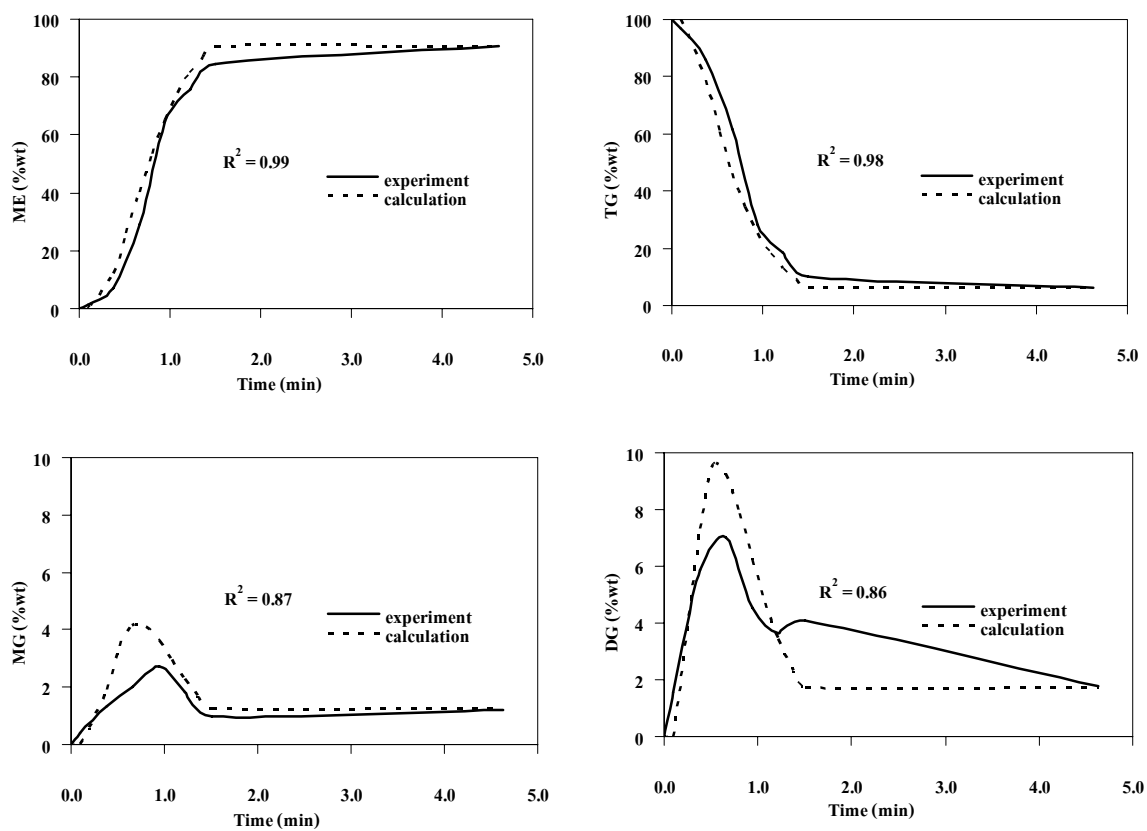
Figure 3.4 The comparison of experimental results and calculated by Euler's integration method

at varying residence times

3.1.4.2 Base case simulation

The simulation results obtained from Aspen Plus are compared with the experimental results of He and Peterson (2006). The comparison of results in table 3.2 indicates that the results are identical with the standard deviations of 0.02 – 4.60.

Table 3.2 Comparison of results obtained by simulation and experimental

| Ratio | Composition (% wt) | | | | | | | | | |
| | Experimental results | | | | | Simulation results | | | | |
	ME	MG	DG	TG	MeOH	ME	MG	DG	TG	MeOH
3.0:1	79.90	2.30	3.00	12.70	2.10	74.28	2.35	3.31	19.21	0.85
3.5:1	79.00	1.40	3.60	14.60	1.40	84.60	1.30	1.91	11.26	0.93
4.0:1	92.00	0.40	0.90	5.80	0.90	91.84	0.59	0.93	5.66	0.98
4.5:1	93.80	0.60	0.70	3.40	1.50	95.51	0.26	0.45	2.76	1.01
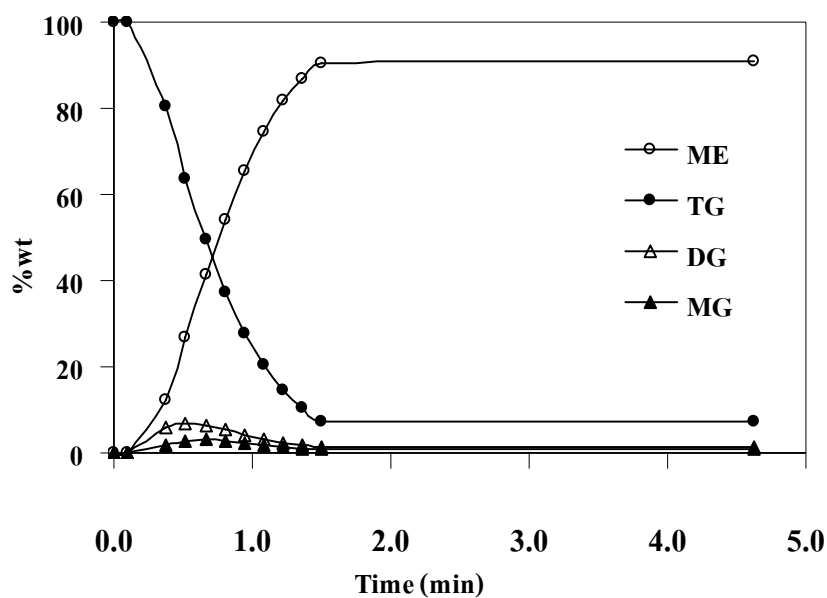
Figure 3.5 Concentration profile of bottom products at standard operating condition of the base case (ratio 4:1)

The %weight profiles for the bottom products plotted with residence time are shown in Figure 3.5. The concentration profiles obtained from the RD column have the same pattern as in batch reactors obtained by various researchers (Noureddini and Zhu, 1997; Darnoko and Cheryan, 2000; Foon, et al., 2004).

Considering the temperature profile in RD column (Figure 3.6), this work found that the temperature of each stage in the RD column is higher than in the reactor of the conventional process. The elevated operating temperature would augment the reaction rate and affect it by shortening the reaction time. The objective of using higher temperature is to remove the excess methanol in product. The more remaining methanol is higher cost loss.
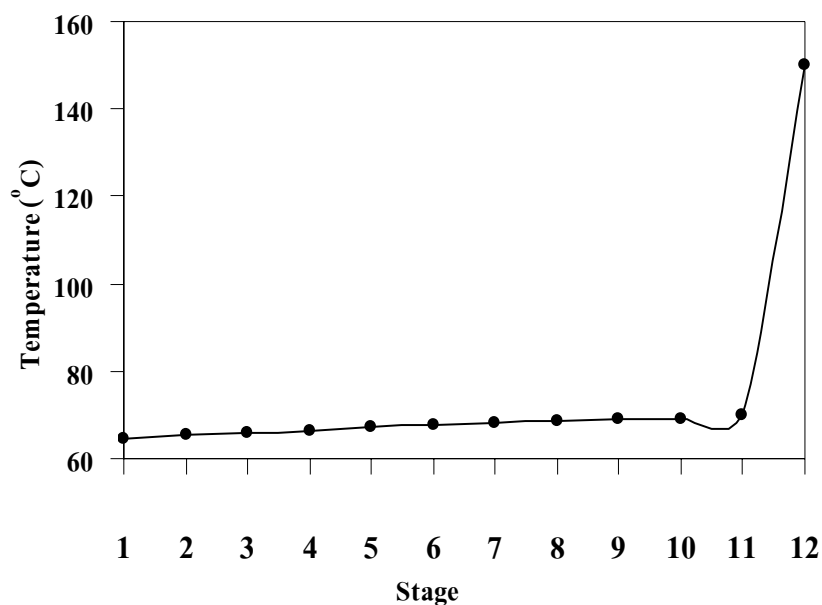
Figure 3.6 Temperature profile of the RD column

3.1.4.3 Effects of parameter

1. Effects of molar ratio of alcohol to oil

For batch kinetic studies of the conventional process, the methanol to oil molar ratio of feed has been considered as an important factor for determining equilibrium conversion (Darnoko et al., 2000). On the other hand for this study, the molar ratio which is higher than the theoretical has significantly less effect on the equilibrium ‑ since the unreacted methanol is vaporized from the reboiler to the top of the column and increases the methanol concentrations locally for each tray. The feed molar ratio always has a positive effect on the reaction conversion because a higher molar ratio can drive the reaction to a higher yield.

Figure 3.7 shows the effect of molar ratio of alcohol to oil in feed. The ratio of 3.0:1, 3.5:1, 4.0:1 and 4.5:1 were investigated. The methyl ester content in the product increased from 74.96% to 96.51% as the methanol to oil molar ratio increased from 3.0:1 to 4.5:1. The simulation result shows that the optimum ratio in this study is 4.0:1 because increasing the methanol to oil ratio to 4.5:1 makes %wt ME increase only 3.99% from 4.0:1, whereas a 41.33% increase in energy consumption cost would not benefit the methyl ester significantly.
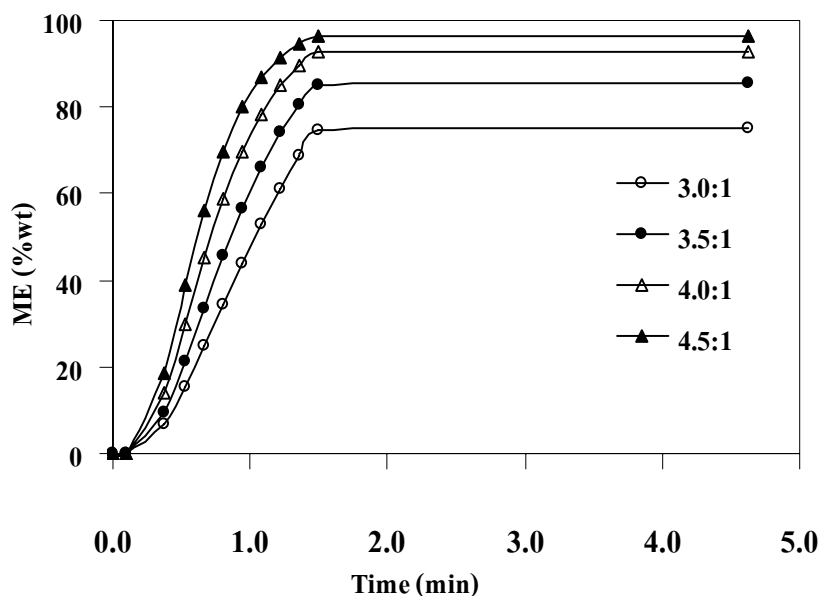

Figure 3.7 Effect of methanol to oil ratio on methyl esters content in product

2. Effect of residence time

Figure 3.8 shows the effect of residence time on methyl ester content in the product. The %weight of methyl ester increases with an increase in residence time because the reactants have a longer contact time. At about 5.6 minutes was the optimum residence time for producing because at this point the quantity of methyl ester reaches its standard, while beyond that point it slightly increases %wt of methyl ester.
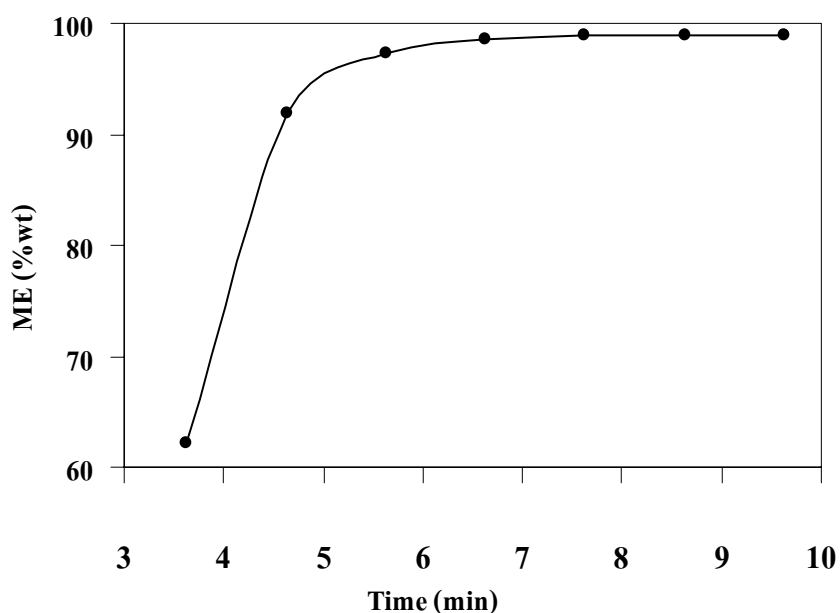

Figure 3.8 Effect of residence time on methyl ester content in product

3. Effect of reboiler temperature

The function of the reboiler is to vaporize the residual liquid methanol present in the bottom of the column. Figure 3.9 shows the effect of reboiler temperature on the methyl ester content in the product and reboiler duty. The %weight of methyl ester is increased as the temperature increases which is due to an increasing reboiler duty. Higher than 150°C, the temperature has only a slight effect on the %weights of methyl ester, because the bottom product has little vaporized methanol which means the methanol in each tray minimally accrued.
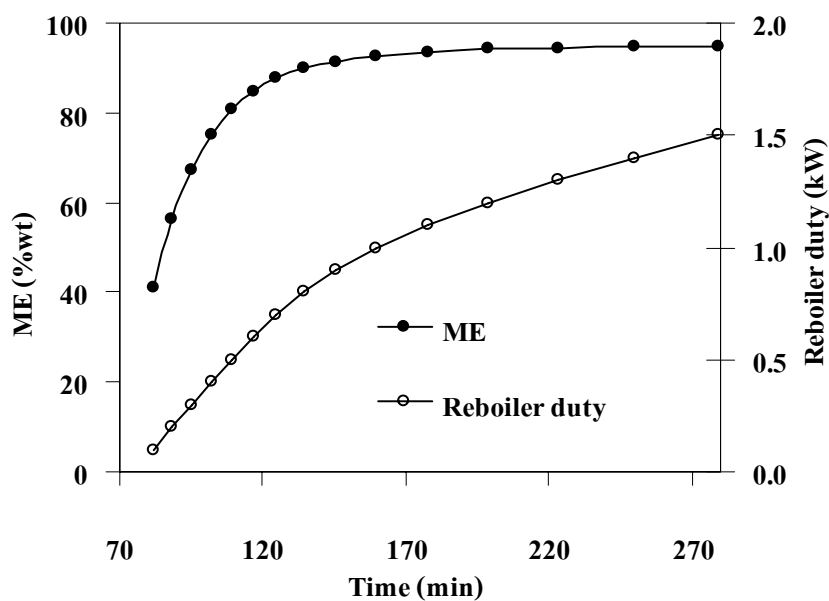
Figure 3.9 Effect of reboiler temperature on methyl ester and heat duty

Figure 3.10 shows the effect of reboiler temperature on methanol content in the product. The %weight of methanol content decreased if the temperature of the reboiler was increased due to higher reaction and its increased vaporization from the reboiler.
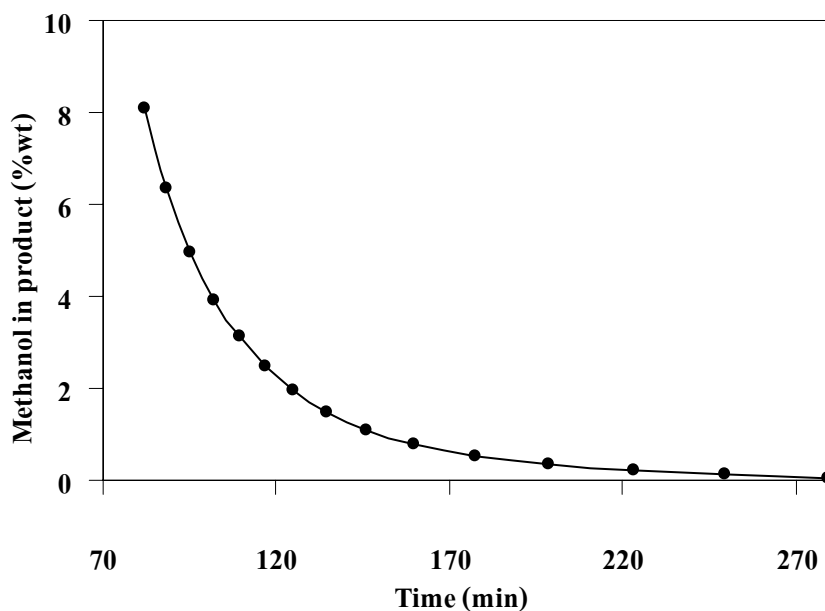

Figure 3.10 Effect of reboiler temperature on methanol content in product

4. Effect of methanol feed location

The feed location depends upon feed composition and reactive zone location. As the methanol's volatility (boiling point) and other component volatilities vary greatly, there is no need to provide any stripping trays for distillation performance other than a condenser. And the inlet feed has to be in the liquid phase, because the reaction will take place in the liquid phase only.

The result in figure 3.11 shows the effect of methanol feed stage on methanol content in the product. The upper stage has lesser temperature than the lower stage so that the methanol in liquid phase is higher than the vapor phase. Therefore the methanol must feed into the top of the RD.
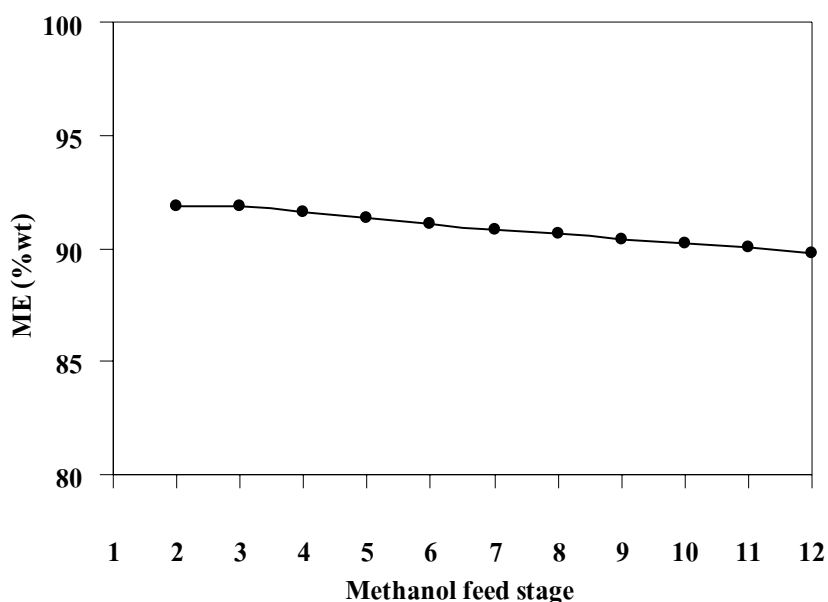

Figure 3.11 Effect of methanol feed stage on methyl ester content in product

5. Effect of reflux ratio

The reflux ratio is defined as the reflux liquid flow from the condenser divided by the total distillate flow. Figure 3.12 shows the effect of reflux ratio on methyl ester content in the product. Increasing the reflux ratio from 1 to 50 raised the %weight methyl ester. Increasing the reflux ratio increased the quantity of reactant (MeOH) on the top of the column. It creates excess alcohol to shift the reaction to the products side. However, a high reflux ratio is economically unattractive as it adds to the energy requirement. The optimum reflux is 25 because after that it has little effect on the methyl ester.
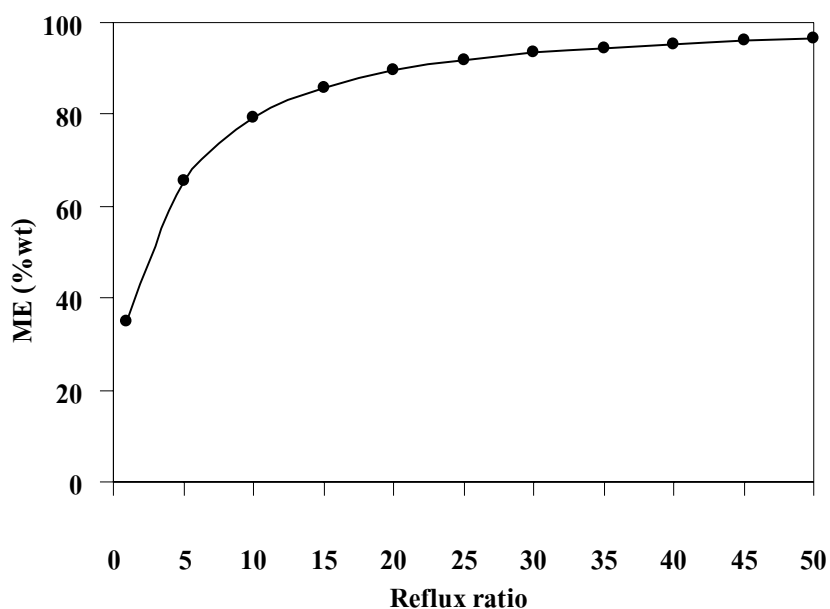

Figure 3.12 Effect of reflux ratio on methyl ester content in product

3.1.5 Conclusion

From the simulation of the biodiesel production process with the kinetic constants adjusted, the optimum condition for producing biodiesel is 4.0:1 molar ratio at 150°C of reboiler temperature and a residence time of 5.6 minutes. Based on the results of the experiment it can be concluded that the RD process is probably more efficient than the conventional process because (1) the excess alcohol at the input was reduced by 66%. (2) Reaction time was shortened by 5 times. (3) Elevated temperature enhanced a high reaction rate.

Therefore, the RD process has been found to be feasible for the continuous production of biodiesel from palm oil.

3.2 Economic Evaluation of a RD Column for Biodiesel Production

3.2.1 Abstract

Biodiesel is a long chain alkyl ester that is typically produced by esterification or transesterification of oil and alcohol. In a conventional process, the cost of the biodiesel plant is high because it involves recycled methanol, and the rate for this process is an extremely expensive. A distillation unit causes a sufficient amount of energy to be used in order to separate methanol from other products. RD columns can be a high-quality alternative process used for biodiesel production because this technique leads to an enormous capital-investment due to cost reduction. The goal of this work is to compare the costs involved in biodiesel production through conventional and RD processes. Results of this study show that the estimated cost of biodiesel production through the RD process is cheaper than the conventional process by approximately 25.44%. In addition, the price of reactants is found to be the most significant factor affecting the economics of biodiesel manufacturing.

Keyword: Biodiesel, RD, economic, conventional process, simulation
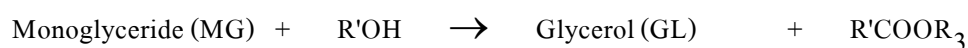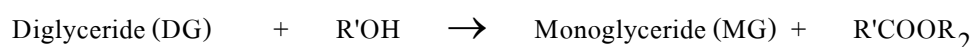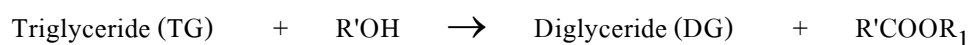
3.2.2 Introduction

The increasing demand for energy combined with the decreasing supply of fossil fuels has led to great interest in alternate energy production technologies. Biodiesel is an alternative, renewable, and biodegradable fuel with similar properties as petroleum diesel (Ma and Hanna, 1999; Bowman et al., 2006). It can be used alone or blended with conventional petrodiesel in unmodified diesel-engine vehicles (Balat and Balat, 2008). Biodiesel is a liquid that varies in color from golden to dark brown, depending on the feedstock; however, it is more expensive than traditional petroleum diesel because of the higher costs of feedstock and processing (Behzadi and Farid, 2009). The conventional process for biodiesel production consists of at least two types of equipment, reactor and distillation units, and requires 100% of the excess methanol to complete the reaction. These are a few of the factors that elevate the cost of biodiesel production.

Most of the current researches intend to reduce costs, consider environmental protection techniques, and increase simplicity of biodiesel production. Currently, the production of chemical engineering equipment that integrates several functions in a single apparatus is studied more frequently than in the past. In this field, multifunctional reactors can be defined as reactors that also perform other operations, like heat exchange or separation, in order to enhance the chemical conversion (Thery et al., 2005). The RD column, that combines both distillation and chemical reaction in only one unit, is one of the most significant examples used in this process. The integration of reaction and separation in a single apparatus presents numerous advantages; reducing capital investment costs, facilitating the use of heat from reactions (Zhu et al., 2009), reducing energy usage and catalyst requirements (Chen et al., 2000; Rakesh et al., 2006), improving conversion, selectivity, and avoidance of azeotropes (Svandov et al., 2006). Moreover, RD column can be applied to various areas of chemical engineering, such as esterification reactions (Bildea et al., 2004), transesterification (Fang and Xiao, 2004), hydrolysis (Lin et al., 2008) and etherification (Aiouache and Goto, 2003). The use of RD column for biodiesel production should make the price of biodiesel more competitive with respect to fossil fuels (Ma and Hanna, 1999; Srivastava and Prasad, 2000; Gerpen, 2005).

The purpose of the present study is to quantitatively compare the economics of two different process flow sheets: (1) a conventional process that consists of reactor and separation units and (2) an RD column process. The design of the flow sheets are based on experimental results from Noureddini and Zhu (1997) and He and Peterson (2006).

3.2.3 Process studies

The basic process of the present study included a transesterification reaction of trioleic acid and methanol in the presence of KOH as catalyst. The reaction consisted of a number of consecutive reactions. The TG was converted by steps to DG to MG and finally to glycerol, as shown below:

$$\text{Triglyceride (TG)} \quad + \quad \text{R'OH} \quad \rightarrow \quad \text{Diglyceride (DG)} \quad + \quad \text{R'COOR}_1$$

$$\text{Diglyceride (DG)} \quad + \quad \text{R'OH} \quad \rightarrow \quad \text{Monoglyceride (MG)} + \quad \text{R'COOR}_2$$

$$\text{Monoglyceride (MG)} \quad + \quad \text{R'OH} \quad \rightarrow \quad \text{Glycerol (GL)} \quad + \quad \text{R'COOR}_3$$

The simulation of the conventional process corresponded to a study by Noureddini and Zhu (1997), which demonstrated one reactor and one distillation column applied to the process. The conventional process is shown in Figure 3.13(a). The conventional process began by mixing methanol with KOH to produce KOMe, which was heated to 60°C and sent to the reactor. At the same time, palm oil was heated to 60°C and sent to the reactor, as well. The reactor effluent was sent to a distillation column to remove the excess methanol. The bottom stream containing biodiesel, glycerol, and remaining reactant was sent to the purification process.

The RD process was slightly different than the conventional process. The reactor unit was not necessary because the reaction already occurred in the RD. The process is shown in Figure 3.13(b).
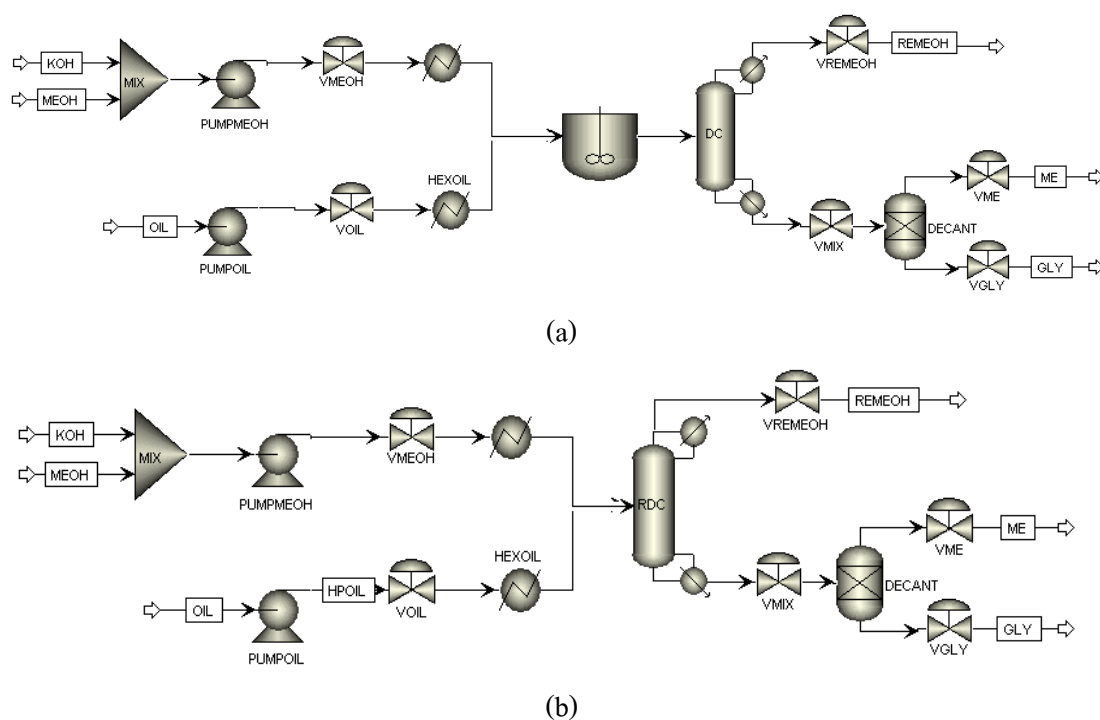
(a)

(b)

Figure 3.13 Steady state biodiesel process flowsheet: (a) Conventional process (b) RD process

3.2.3 Process simulation

Aspen Plus is a computer program that was used to simulate the chemical process in this study. Unit block operating conditions and chemical components were selected based on a previous experiment by He and Peterson (2006). The Radfrac model was applied during the RD simulation for the methyl ester production with alkaline catalyst. The components for reaction were available in the data banks, and Aspen Plus estimated the thermodynamic properties. Currently, kinetic constants, frequency factors, and activated energy were reported in the conventional process and adjusted before being used in the RD process. Details of the operating conditions for RD in the base case process are listed in Table 3.3.

Table 3.3 Detail of the RD column in base case process

Transesterification	Catalyst		KOH
	Temperature (°C)	Reboiler	150
		Condenser	64
	Methanol to oil molar ratio		4:1
	Feed oil temperature (°C)		60
	Residence time (min)		5.63
Column	Type		Tray
	Number of stages		10
	Position of the feed stage		2
	Pressure (atm)		1

3.2.5 Economic assessment

An economic assessment of biodiesel production processes using conventional and RD processes involved a calculation of total annual cost (annual capital and operating cost). The operating cost consists of raw materials and utility. The capital (equipment) cost depends on the size of material related to the plant capacity. The current study was based on a biodiesel plant with a capacity of 200,000 liters per day. This was the demand of biodiesel for blending and distributing B5 (95% diesel and 5% biodiesel) and B2 (98% diesel and 2% biodiesel) in Thailand (Department of Alternative Energy Development and Efficiency, 2010).

The total annual cost (TAC) is defined as

$$TAC = operating \ cost + \frac{capital \ cost}{payback \ period}$$

Equations 3.15 − 3.17 (Douglas, 1988) show the capital cost correlation of equipment (column, reactor and tray) with correspond to the Guthrie's correlations.

$$\text{Purchased cost, \$} = \frac{(M \& S)}{280}(101.9D^{1.066}H^{0.82}F_c) \tag{3.15}$$

$$\text{Column and reactor installed cost, \$} = \frac{(M \& S)}{280}(101.9D^{1.066}H^{0.802}(2.18 + F_c)) \tag{3.16}$$

$$\text{Trays installed cost, \$} = \frac{(M \& S)}{280}(4.7D^{1.55}HF_t) \tag{3.17}$$

Where $M \& S$ is the Marshall and Swift index, an index of 1,468.6 (ChemicalEngineering, 2010) was used in this study. D is diameter in feet, H is height in feet, and F_c and F_t correspond to the correction factors for materials, pressure, etc., F_c of 1.15 and F_t of 1 were also used in this study.

The terms involved in the TAC equations were calculated from the following set of assumptions and equations:

(i) The diameter (D_R) and height (H_R) of the reactor were calculated from the known volume and an aspect H_R / D_R ratio. Aspect ratios of various vessels varied from 1 to 4. However, the value of 2 was typical used (Luyben, 2002).

(ii) The column height (H_C) was calculated by assuming 2 feet (0.61 m) of tray space and allowing 20% more height for base-level volume (Luyben, 2002).

$$H_C = 2.4 N_T \tag{3.18}$$
$$N_T = \text{number of trays in the column}$$

(iii) The two processes were assumed to operate for 24 hours per day and 365 days per year (Kaymak and Luyben, 2004). The payback period was approximately 11 years (Peters and Timmerhaus, 1991).

(iv) The source of energy was electricity. The time of use rate (TOU) was used to calculate the cost of utility (ProvincialElectricityAuthority, 2010).

3.2.6 Results and Discussion

3.2.6.1 Base case simulation

Figure 3.14 presents the composition profile of the RD column in the base case simulation. The simulation results indicate that the reaction occurred rapidly through an observation of fast changes in substance and product. The mass fraction of methanol in the reaction zone is almost uniform at 0.4 – 0.5. Therefore, the methanol drove the reaction to accrue the methyl ester. A small amount of methanol remained because the high temperature of the reboiler vaporized most of it. The triglyceride fell from top to bottom, and it was mostly consumed in the upper part of the column. This change increased the biodiesel accumulation in the column, as the residence time increased. The reaction rate increased in the upper part of the column (Figure 3.15) more than in the lower part because the major composition in the upper part is TG, which reacts easily with methanol, and the high ratio of methanol to oil was vaporized from the bottom. The higher methyl ester in the lower part of the column makes it more difficult to shift the equilibrium of the reaction to the product side at a higher temperature (Figure 3.16). As a result, the system had a lower quantity of methanol.
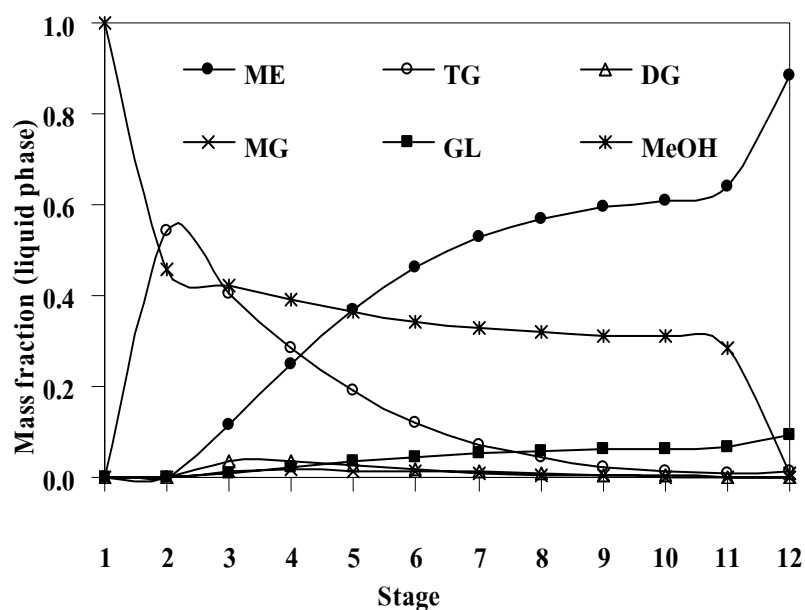
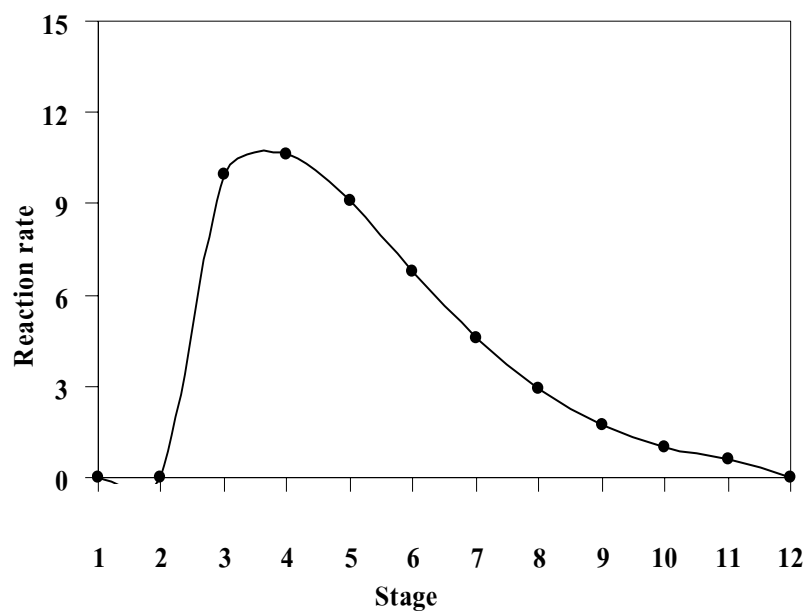Figure 3.14 Composition profile of the RD column

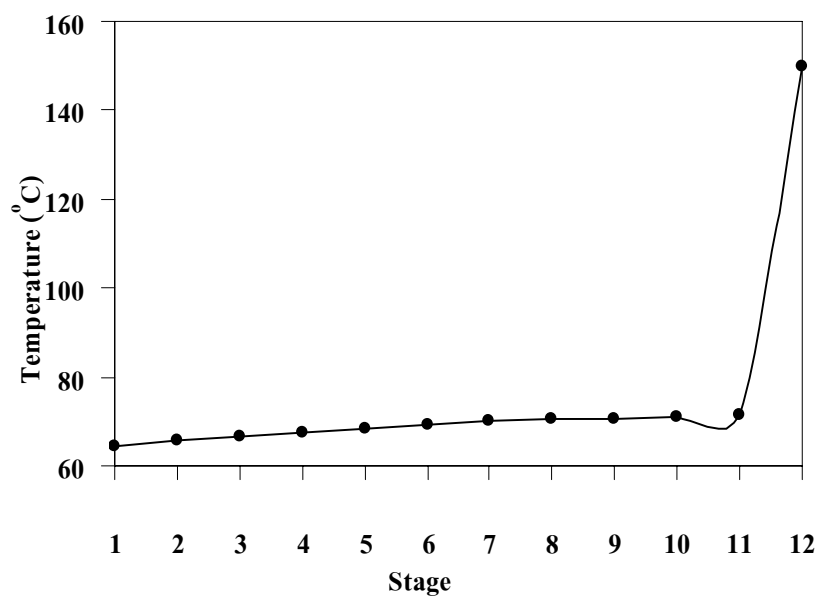Figure 3.15 Reaction rate profile of the RD column

Figure 3.16 Temperature profile of the RD column
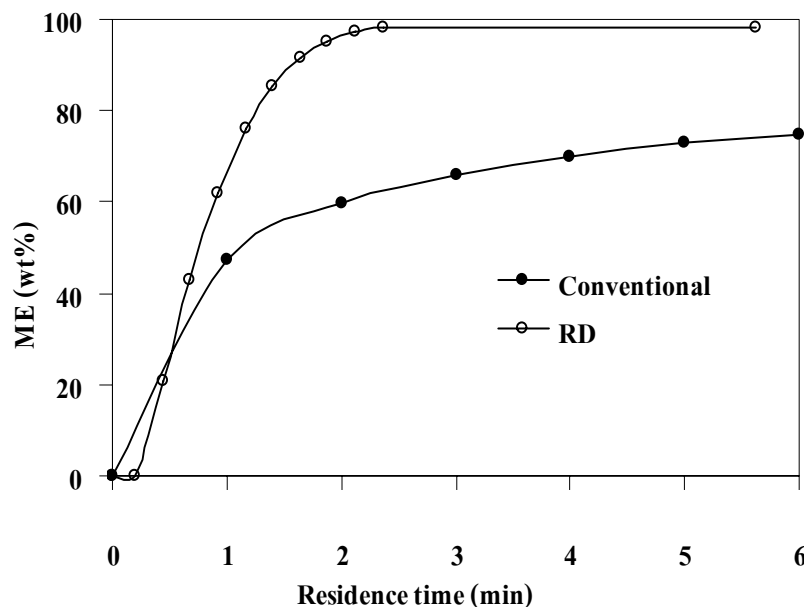
3.2.6.2 Comparison of conventional and RD

Figure 3.17 Comparison of methyl ester (%wt) between conventional and RD

The comparison of methyl ester products using two methods is shown in Figure 3.17. The reaction is shown to be faster in the RD process than in the conventional process because of the higher temperature and methanol ratio used in the RD column. In the RD column, the high temperature of the reboiler to the top of the column caused the methanol to vaporize. The partial vapor was condensed at each stage and created a local excess alcohol to drive the reaction close to completion. The rise in temperature caused the reaction rate to increase. As a result, the process had a shorter reaction time and productivity was augmented.

Table 3.4 shows the comparison between streams from the conventional and RD processes. The ratio of fresh feed of methanol to oil in the RD process is lower than in the conventional process, but the quantity of biodiesel in the RD process is higher than in the conventional process. Because the products are continuously removed from the RD, the reaction can extend far beyond its chemical equilibrium, and the higher temperature enhances reaction rates. This result indicates that the RD process has a more efficient performance level than the conventional process.

Table 3.4 Comparison of components and flow rates between conventional and RD processes

Method	Conventional		RD	
Component	Distillate (kg/hr)	Bottom (kg/hr)	Distillate (kg/hr)	Bottom (kg/hr)
Triolein	trace	983.24	trace	80.22
Diolein	trace	461.39	trace	13.87
Monoolein	trace	240.45	trace	9.95
Methanol	537.15	336.46	175.95	67.65
KOH	trace	64.26	trace	64.26
Methyloleate	trace	4827.11	trace	6353.03
Glycerol	trace	435.57	trace	655.38

3.2.6.3 Assessment of biodiesel production costs

The reaction section of biodiesel production was designed and employed to estimate the capital and operating cost for producing biodiesel with purity greater than 96.5 %, according to the European standards for biodiesel production (EN 14214). In this study, the reactant that was representative of palm oil was triolein because it was a major component and already contained in the library of programs. The raw material and capital costs are listed in Table 3.5 and Table 3.6, respectively.

Table 3.5 Annual raw material costs for the annual production of 7.30×10^7 L of biodiesel

Raw materials	Process	Price/Unit* (US\$/kg)	Annual use (kg)	Annual cost (US\$/year, million)
Palm oil		0.46	5.63×10^7	26.00
Methanol	Conventional	0.60	1.22×10^7	7.30
	RD		8.15×10^6	4.86
Potassium Hydroxide		2.47	5.63×10^5	1.39

*Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops, 2010

Table 3.6 Capital costs for the 7.30×10^7 L/year of biodiesel production

Process	Equipment	Size (ft)		Cost (US\$)	
				Purchased	Installed
Conventional	Reactor	D_R	1.25		
		H_R	2.49	1641.46	4675.67
	Distillation column	D_C	5.26		
		H_C	24.00	48909.88	133751.66
	Trays				7766.32
RD	Distillation column	D_C	3.18		
		H_C	24.00	28598.94	78208.25
	Trays				3559.24

The estimated total annual costs of conventional and RD processes are summarized in Table 3.7.

Table 3.7 Comparison of the production costs between conventional and RD processes

Process	Cost (US\$, million)					
	Raw materials	Equipment	Utility		Operating	TAC
Conventional	34.69	0.20	11.64 { reactor 0.36 / distillation column 11.28		46.33	46.35
RD	32.25	0.11	2.30		34.55	34.56
% Reduce	7.03	45.00	80.24		25.43	25.44

The results in Table 3.7 show that the TAC of the RD process is less than in the conventional process by about 25.44% (capital and operating costs are reduced by 45.00% and 25.43%, respectively). Application of the RD process can reduce the capital and utility costs corresponding to Gomez‑Castro et al. (2010) and Kiss (2009).

Figure 3.18 shows that the major cost of both processes is raw material, which can be reduced by changing to a new source. Furthermore, the operating cost in RD process was cheaper than in the conventional process. The energy in conventional process used more than in RD process around 3.76 times because of the energy was used in reactor (0.36 time) and used to remove the excess methanol (11.28) that had more than RD process about 4.55 times (fresh feed 0.30 and reflux 4.25). Therefore, the major energy cost in conventional process is used for stripping and purifying of methanol.

(a)   (b)
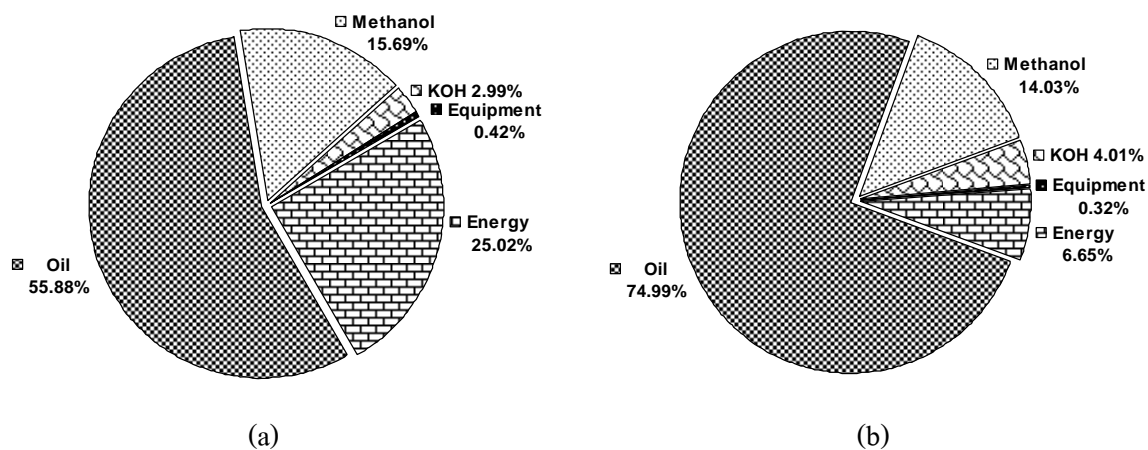
Figure 3.18 Comparison of proportional costs of biodiesel production between

(a) the conventional process and (b) the RD process

3.2.7 Conclusion

The economic assessment of biodiesel production through the RD process was examined and developed in this research study. The simulation results show that using RD is more efficient than using the conventional process, as it can increase the conversion of the reaction with a lower ratio of fresh feed methanol to oil. In addition, RD can reduce the capital and operating costs.

3.3 The Experimental of Transesterification of Palm Oil with Methanol in a RD Column

3.3.1 Abstract

The cost of biodiesel is actually significantly higher than petroleum diesel, which is attributed to higher feedstock and processing costs. Applying RD, the combination of a reactor with a distillation column in only one unit, has the advantage of reducing the capital and operating costs of biodiesel production and also produces consistently high-quality biodiesel. This research investigates the feasibility of biodiesel production from palm oil by RD. The hypothesis is to reduce the amount of alcohol in the feed stream to close to its stoichiometric ratio to oil. The effects of process parameters – reactant ratio, reboiler temperature, and residence time – were conducted using a laboratory-scale RD packed column. The results indicated that the system reached a steady state at 8 h. The optimum process parameters of a reboiler temperature 90°C, a methanol to oil molar ratio of 4:1, and 5 min of residence time in the column produced 92.27% biodiesel purity.

Keyword: RD, Transesterification, Palm oil, Biodiesel, Cost

3.3.2 Introduction

The exhaustion of world petroleum resources and increasing environmental concerns (Marchetti et al., 2007) have stimulated the search for alternative sources of fuel, including diesel fuels. Because of its related properties, biodiesel fuel (FAME) obtained from vegetable oil is considered to be the best candidate for a diesel fuel substitute (Kusdiana and Saka, 2002; Enweremadu and Mbarawa, 2009). However, current production costs for biodiesel are not economically competitive with petroleum-based fuel, due to higher capital and operating expenses (Chongkhong et al., 2009). This is because the conventional biodiesel production process consists of many units and requires a high alcohol to oil ratio in order to drive the reaction to completion. To eliminate this problem, a RD column is applied (Miranda-Galindo et al., 2009) instead of the conventional biodiesel production process. The RD method eliminates many inherent problems such as low reaction yield, low product purity, corrosion problems, and high fixed costs and operating costs caused by separate reaction and distillation processes (Kim and Roh, 1996).

RD is an innovative process which combines both distillation and chemical reaction into a single unit (Bhatia et al., 2007; Qiu et al., 2010), thereby saving energy (for heating) and materials (Wang et al., 2008). RD technology therefore offers many benefits over the conventional process of reaction followed by distillation, or other separation approaches. Reduced capital cost (Brehelin et al., 2007), higher conversion, improved selectivity (Venkateswarlu and Kumara, 2006), lower energy consumption, the reduction or elimination of solvents used in the process (Zeng et al., 2006), and avoidance of azeotropes (Thery et al., 2005) are a few of the potential advantages offered by RD. This technique is especially useful for equilibrium-limited reactions (Fang and Xiao, 2004) such as esterification and transesterification reactions. Conversion can be increased far beyond what is expected by the equilibrium, due to the continuous removal of reaction products from the reactive zone. This helps reduce capital and investment costs and may be important for sustainable development due to a lower consumption of resources.

The goal of this work was to study the laboratory-scale continuous-flow in RD column and its applicability to produce biodiesel. The hypotheses were: (1) RD technique could

be applied to biodiesel production; (2) this would reduce the amount of alcohol in the fresh feed, to close to its stoichiometric ratio with oil; (3) high operating temperature would shorten the reaction time.

3.3.3 Materials and methods

3.3.3.1 Chemicals and reagent

Refined palm oil and methanol were used as the reactants, with KOH as the catalyst. The palm oil contained approximately 0.3-0.6% FFA and less than 1% moisture content. Commercial grade methanol was used as the alcohol source in all experiments. The methanol was premixed with 100 g KOH/L methanol before being pumped into the RD column. Pre-mixing of KOH with methanol allows the formation of KOMe needed to catalyze the reaction.

3.3.3.2 Equipment

A continuous-flow RD reactor system (Figure 3.19) was developed and tested on overall process parameters. The RD column was a stainless steel packed column, with heating tape to maintain the temperature at the top of the column at 64°C.
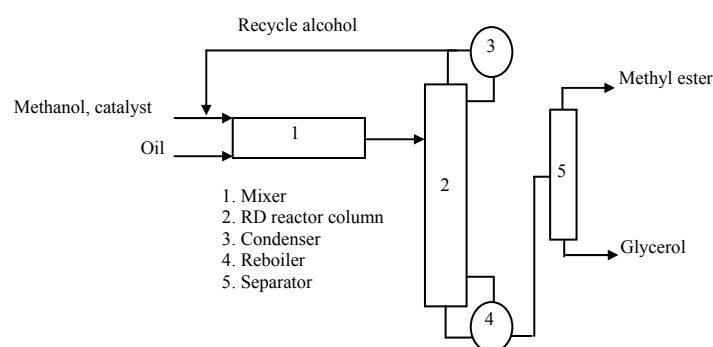
Figure 3.19 Biodiesel production process with RD column

3.3.3.3 Experimental

1. Start-up procedures

To start of each experiment, approximate 2 L of oil and 250 mL of methanol were injected into the column. The reboiler heater was set to 120°C and allowed to heat for approximately 1.5 hours till the temperature of the top column reached 64°C. The actual flow rate, ratio of methanol to oil and temperature profile along the column of each experiment were show in Table 3.8.

Table 3.8 Process parameters used in the preliminary experiments

Trial ID	Molar Ratio	Feed rate (ml/hr)		Temperature (°C)				
		Oil	Methanol	Reboiler	Column height from bottom (m)			
					1	2	3	4
1	3.0:1	900	118.17	85 - 120	70	64	64	64
2	4.0:1	900	157.56	85 - 120	70	64	64	64
3	5.0:1	900	196.94	85 - 120	70	64	64	64
4	6.0:1	900	236.33	85 - 120	70	64	64	64

2. Steady-operation

The inputs, both oil at 85°C and methanol at 30°C, were pumped into a short tube mixer to mix the oil with the methanol/catalyst solution. Then the reactant mixture at 65°C was entered to the top of the RD column. In the RD column, TG in the reactant mixture further reacted with the present methanol. The product mixture was withdrawn from the reboiler section and sent to a glycerol-ester separator, where the glycerol and esters were separated by gravity in a continuous mode. Every hour, samples were collected from reboiler to analyst the biodiesel composition and methanol content.

3.3.3.4 Product analysis

1. Gas Chromatography (GC)

The content of FAME in product was analyzed by a GC-7890 (Agilent 7890A). Its column is a SelectTM Biodiesel for fatty acid methyl ester (FAME) capillary column (length 30 m x 320 μm I.D. x 0.25 μm film thickness, Varian Part No. CP-9080). Initial column temperature was 210°C and kept it for 12 min, then was raised to 250°C at the rate of 20°C/min and maintained this temperature for 8 min. The temperature of the injector and the flame ionization detector (FID) was 290 and 300 °C, respectively. The content of ester FAME was quantitatively determined using the concentration of methyl heptadecanoate (C17:0, internal standard).

Sample Preparation

Accurately weigh approximately 250 mg of sample in a 10 mL vial, then add 5 mL of methyl heptadecanoate solution (10 mg/mL) using a pipette.

Calculations

The ester content (C) expressed as a fraction in percent, is calculated using the following formula:

$$C = \frac{(\sum A) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\% \qquad (3.19)$$

$\sum A$ = the total peak area from the FAME C14:0 to C24:1

A_{EI} = the peak area of methyl heptadecanoate

C_{EI} = the concentration, in mg/mL, of the methyl heptadecanoate solution

V_{EI} = the volume, in mL, of the methyl heptadecanoate solution

m = the mass, in mgr, of the sample

2. Thin Layer Chromatography with flame ionization detector (TLC–FID)

The compositions of the reaction mixture samples were determined by a TLC–FID using an Itronscan MK-6s with Chromarods type S-III quartz rod (Mitshubishi Kagaku Iatron). One microliter of the reaction medium, diluted in hexane at appropriate dilution, was spotted onto chromarods.

- Firstly, chromarods were immersed in a solvent mixture of hexane:diethyl ether:formic acid (50:20:0.3 v/v) until the solvent reaching to 8 cm (approximately 15 min).

- Secondly, the chromarods were immersed in a solvent mixture of benzene:hexane (50:50 v/v) for about 35 min (or until the solvent reach to 10 cm).

- The spotted samples were developed in these two solvent mixtures. The chromarods were then dried at 105°C for 5 min and scanned with TLC–FID.

- Scanning was performed using a 160 ml/min of hydrogen flow rate and 20 l/min of air flow rate to produce a chromatogram.

- The compositions were calculated as wt% based on the peak areas of each component.

3. Methanol content

Unreacted methanol in product, both ester and glycerol, was determined by weighing before and after evaporation in vacuum distillation at 50°C.

3.3.4 Results and discussion

3.3.4.1 A study of the palm oil composition used in biodiesel production

The palm oil obtained from Lian Hoe Trading Company Limited was a clear yellow liquid and some of white solid (unsaturated fatty acid) at room temperature (Figure 3.20).

Figure 3.20 The physical appearance of palm oil at room temperature

The palm oil component studied by TLC is shown in Figure 3.21. It was found that the palm oil consist of 0.58% of FFA (Table 3.9 and Figure 3.22). So, it can use directly to transesterification reaction.
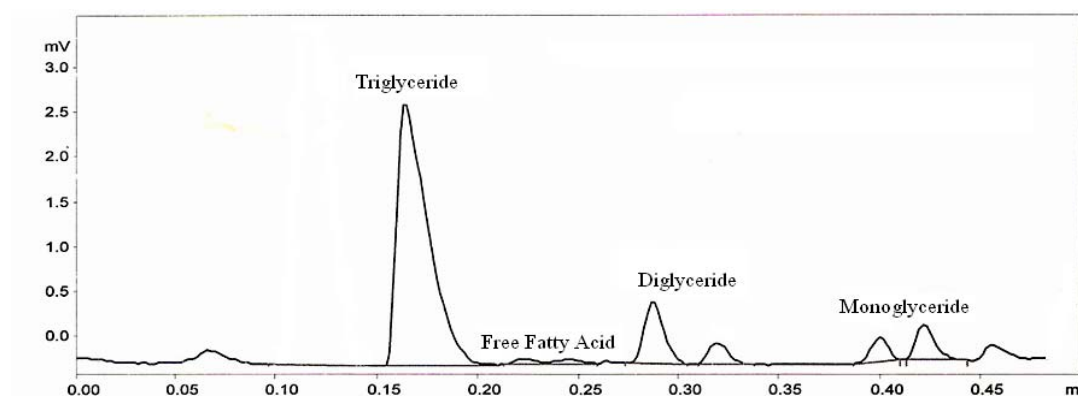
Figure 3.21 The analysis result of palm oil component by TLC

Table 3.9 Acid value of palm oil

Run	Oil (g)	Volume of NaOH(ml)	%Acid value
1	10.00	2.30	0.59
2	9.93	2.30	0.59
3	9.97	2.10	0.54
4	9.96	2.35	0.60
average	9.97	2.26	0.58
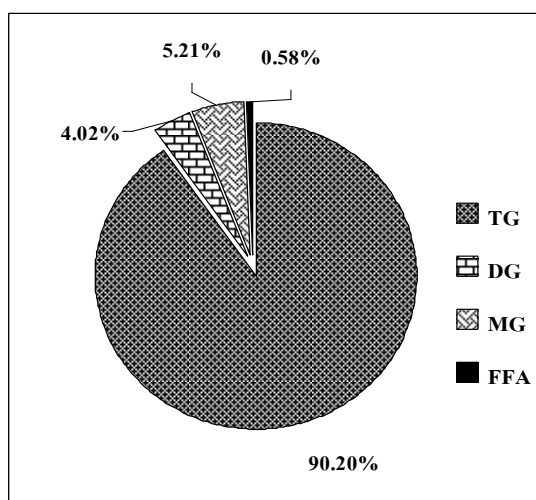
Figure 3.22 The palm oil composition

3.3.4.2 The physical appearance of tranesterified products

       Transesterified products are separated into 2 phase. They are methyl ester in top phase and glycerol in bottom phase. The unreacted methanol dissolves in both phases. The appearance of transesterified product is shown in Figure 3.23. At low temperature, the product was easy separated by gravity but can not separate at high temperature. At the high temperature, the rate of soap formation increases more rapidly than transesterification. The soap is occurred by saponification reaction between oil or biodiesel with catalyst, which consumes the catalyst and causes decrease of reaction conversion. Then, glycerol could dissolve in methyl ester phase.

(a) (b) (c)
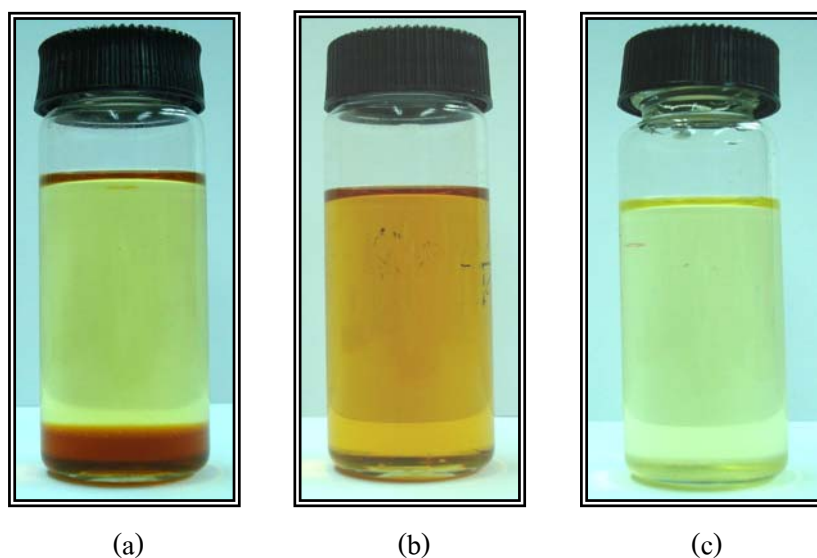
Figure 3.23 The physical appearance of tranesterified products:

(a) low temperature; (b) high temperature; (c) purified methyl ester

The FAME profile from the palm oil was analyzed using the GC method (EN-14103) and is shown in Figure 3.24 and Figure 3.25.
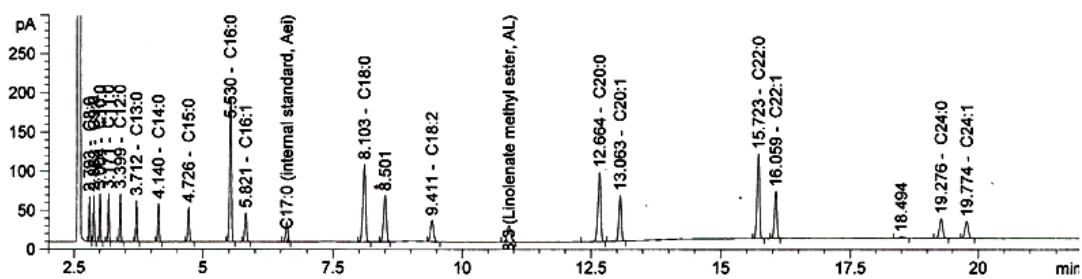
Figure 3.24 Chromatogram of standard FAME ($C_8 - C_{24}$)
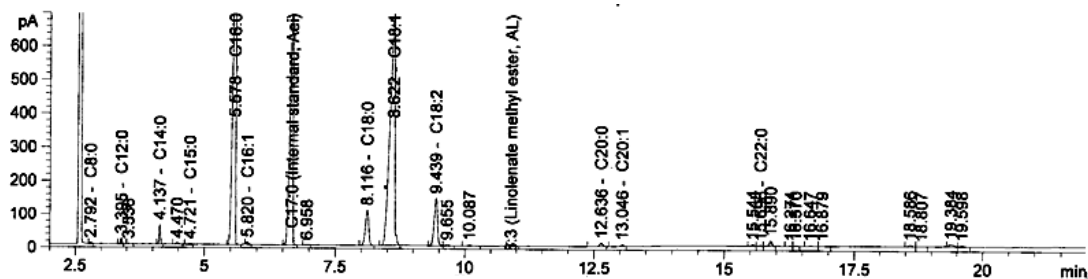
Figure 3.25 Chromatogram of FAME from palm oil

(reboiler temperature 90°C; methanol to oil ratio 4.0:1; residence time 5 minutes)

3.3.4.3 Steady state of biodiesel production by RD column

After the start of each experiment, the % of methyl ester (ME) in the bottom product was checked by gas chromatography to ensure that the system had reached steady state, which was indicated by a constant value. Early of the process start up, the product has slight ME since the oil and the methanol were put into the reboiler without catalyst. Therefore, the oil quietly changed to the ME when the reactant was feed at the top of the RD column. Increasing of ME is a result from the reaction of reactant in the column and of excess reactant (methanol and catalyst) with oil in reboiler. Figure 3.26 shows that the %wt of ME demonstrates rapid formation within the first 8 h. After that, the increasing of ME slows and finally reaches to steady state. Therefore, every experiment spent 8 hours for start up process.
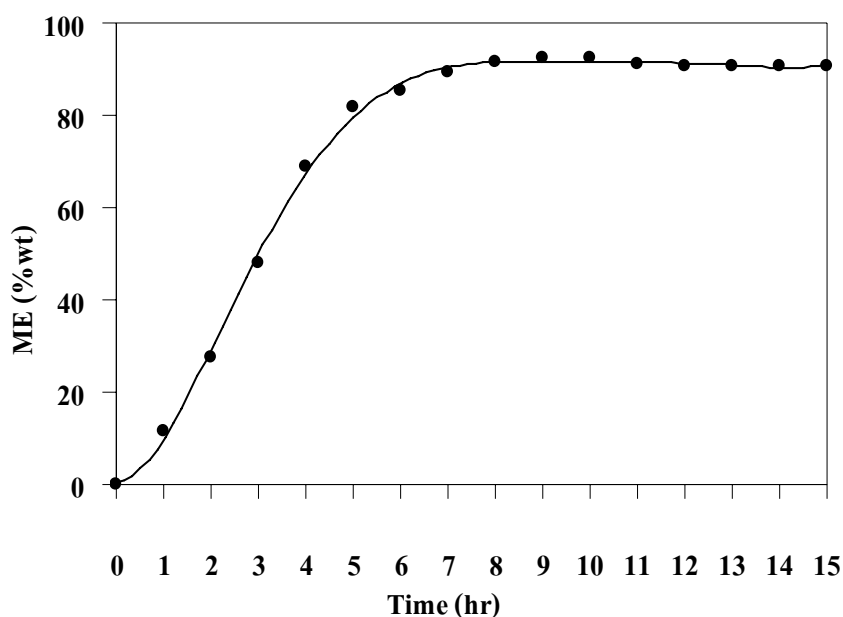
Figure 3.26 The change of %ME at reboiler temperature 90°C; methanol to oil ratio 4.0:1; residence time 5 minutes

3.3.4.4 Effect of flow rate

The feed stream flow rates for the test run were chosen carefully in order to avoid any column flooding problem. The flow rate, which is inversely related to retention time, is used as an experimental factor to interpret the reaction conversion with the liquid retention time. The total column has volume of approximately 75 mL. The flow rate achieved in the experimental varied from 15 to 60 mL/min. The retention time varied from about 5 to 1.25 min. These values may not be the actual reaction time because of some reaction that took place in the reboiler product. Since the concentrations of methanol and catalyst were very small in the liquid phase of the reboiler, it was not possible to determine the actual retention time of reactants and catalyst in the reboiler. Figure 3.27 shows that the %weight of ME decreases while the flow rate increases since the less retention time. To set up the RD operation in this study, the feed flow rate should not be higher 15 mL/min in order to avoid flooding in column and this rate were considered as optimum range of the operation.
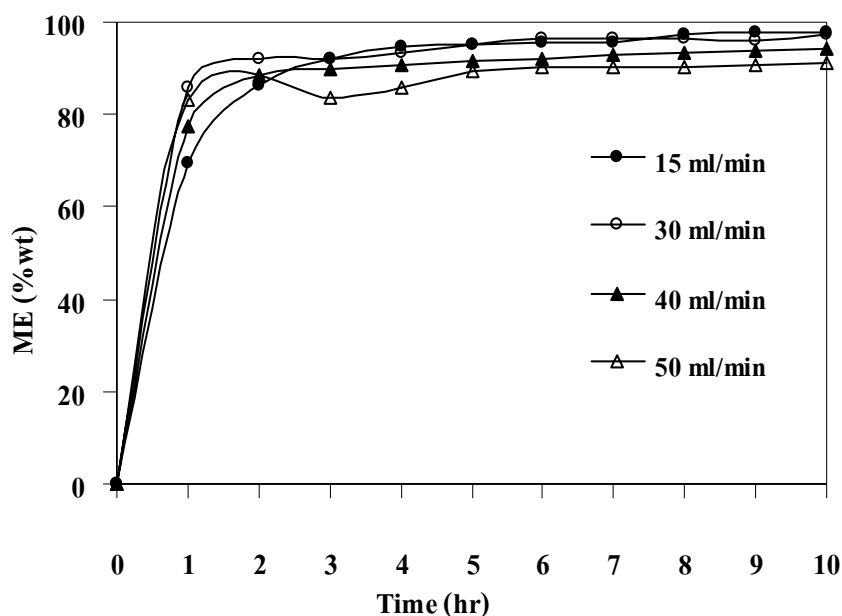
Figure 3.27 Effect of flow rate on ME content in product at varying time

3.3.4.5 Effect of reboiler temperature

The function of a reboiler is to vaporize the residual methanol presenting in the bottom product. Methanol boils at 64.7°C; however, according to the experiments, sufficient methanol vapors were generated only with in a reboiler temperature higher than 90°C. Depending upon the methanol concentration, therefore, reboiler temperatures in the experimental design varied from 85°C to 120°C in order to produce smooth and consistent methanol vapor flow rates. It was found that lower reboiler temperatures were more favorable for better reactor performance as shown in Figure 3.28, corresponding to previous work (Leung and Guo, 2006; Leung et al., 2010; Köse et al., 2002). Because some KOH at a concentration of 1% (weight of KOH/weight of oil) in the high-temperature process were consume to promote a saponification reaction, that produces salts of fatty acids (soaps) and thus inhibits the transesterification reaction (Leung et al., 2010).
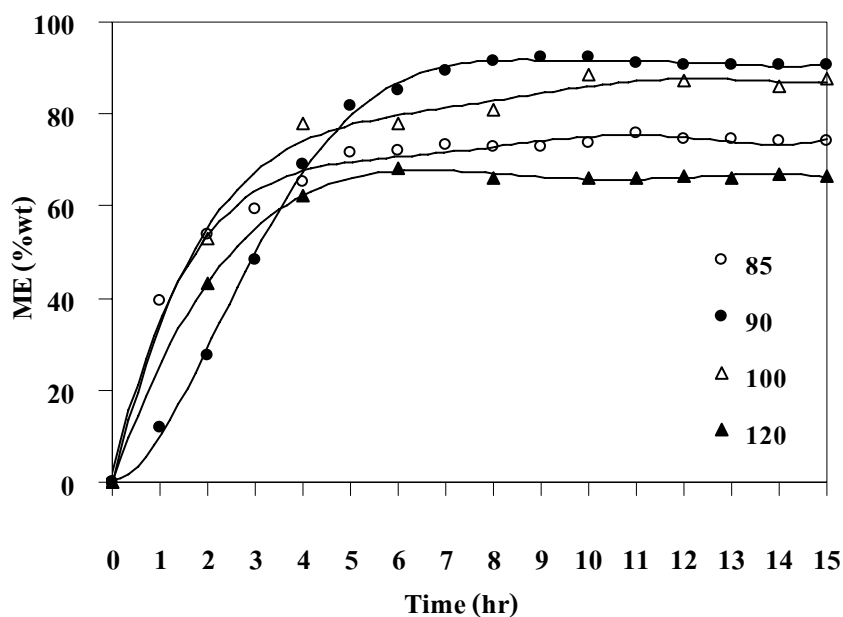
Figure 3.28 Effect of reboiler temperature on ME content
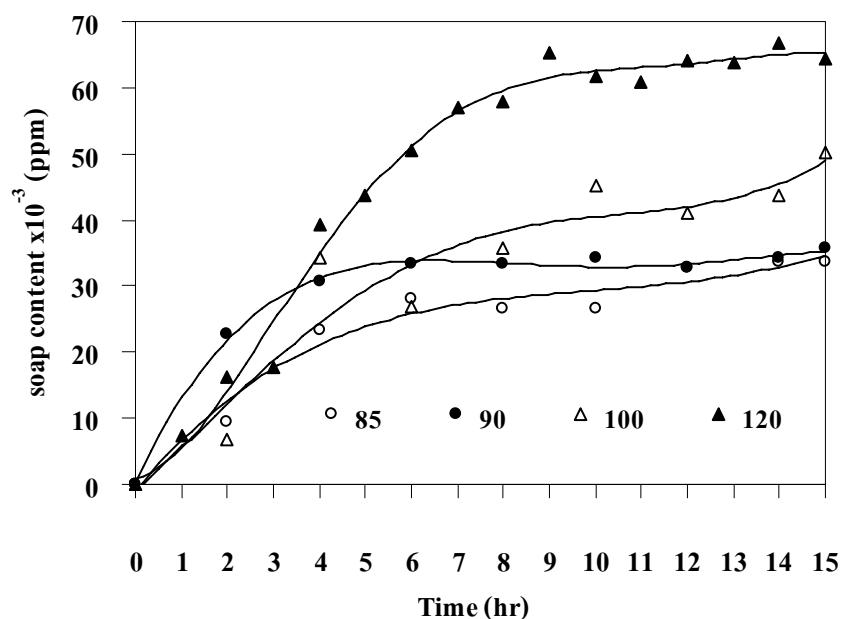
Figure 3.29 Effect of reboiler temperature on soap content

An alkaline catalyst was used in the present experiment. The effect of reboiler temperature on soap content in the product is shown in Figure 3.29. The saponification reaction as shown in the following equation:

$$TG \; + 3\,KOH \; \rightarrow 3\,SOAP + GL$$

$$DG \; + 2\,KOH \; \rightarrow 2\,SOAP + GL$$

$$MG \; + KOH \; \rightarrow SOAP \; + GL$$

$$ME \; + KOH \; \rightarrow SOAP \; + MeOH$$
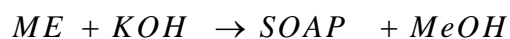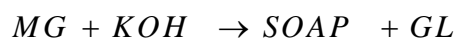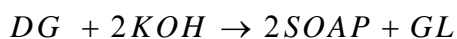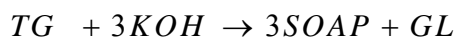
where TG, DG, MG, ME, GL and MeOH are triglyceride, diglyceride, monoglyceride, methyl ester, glycerol and methanol, respectively.
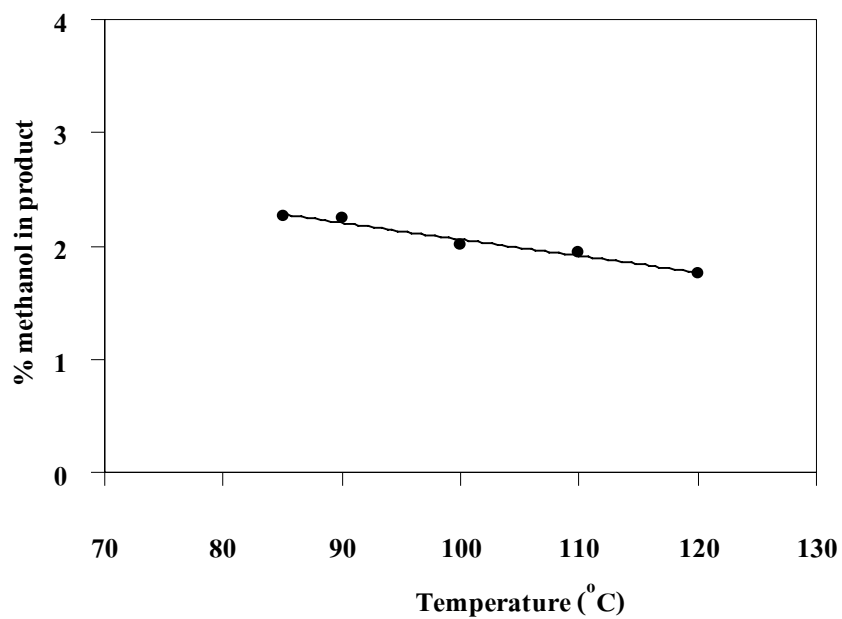
Figure 3.30 Effect of reboiler temperature on methanol content

The residue methanol in biodiesel is shown in Figure 3.30. The methanol content decreased if the reboiler temperature was increased due to a greater reaction and its complete vaporization from the reboiler.

3.3.4.6 Effect of methanol to oil ratio

Figure 3.31 shows the effect of methanol to oil ratio on ME content. The ME content in the product stream increased from 84.09% to 92.37% as the methanol to oil molar ratio increased from 1:3 to 1:5. After that the ME content dropped off due to flooding phenomena in the column. This result was brought by excessive vapor flow, causing liquid to be entrained in the vapor up the column. The result of the RD process shows a reaction of alcohol and palm oil in a ratio close to stoichiometric, while the excess unreacted alcohol is vaporized from the reboiler.
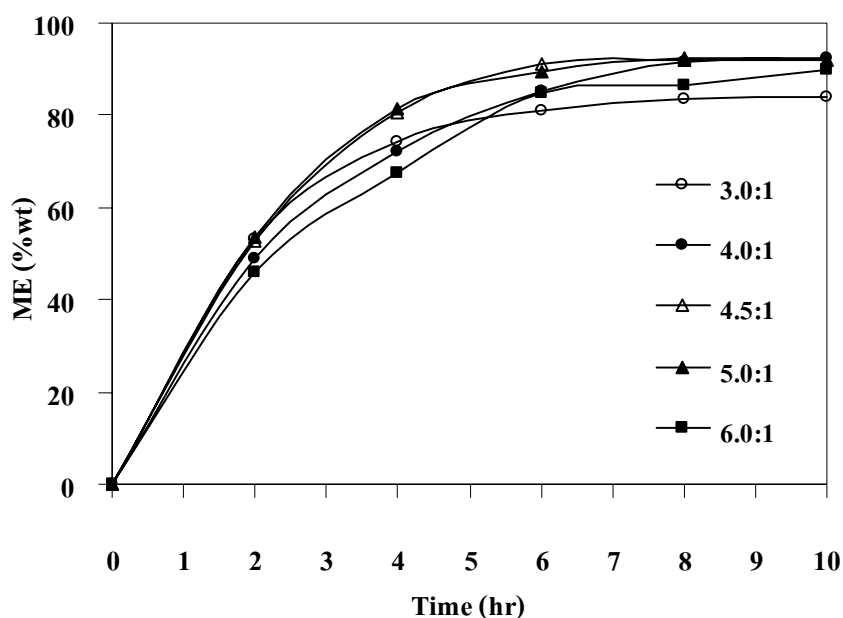
Figure 3.31 Effect of methanol to oil ratio on ME content

3.3.4.7 Effect of catalyst amount

Figure 3.32 shows the effect of the %wt of catalyst to oil. The results indicate that the biodiesel yield was significantly improved with an increase of KOH. The biodiesel yield reached 92.37% after 8 h when the %wt of KOH was 1%. However, only 85.68% and 79.55% yields were obtained at 1.5% and 2%wt KOH/oil, respectively. It was also recognized that the alkalinity of the catalyst particularly influenced the biodiesel yield, but that too high a quantity of KOH had a negative effect on biodiesel yield. This is because conditions with a high concentration of KOH support the side reaction (saponification) more than transesterification (Bournay et al., 2005).
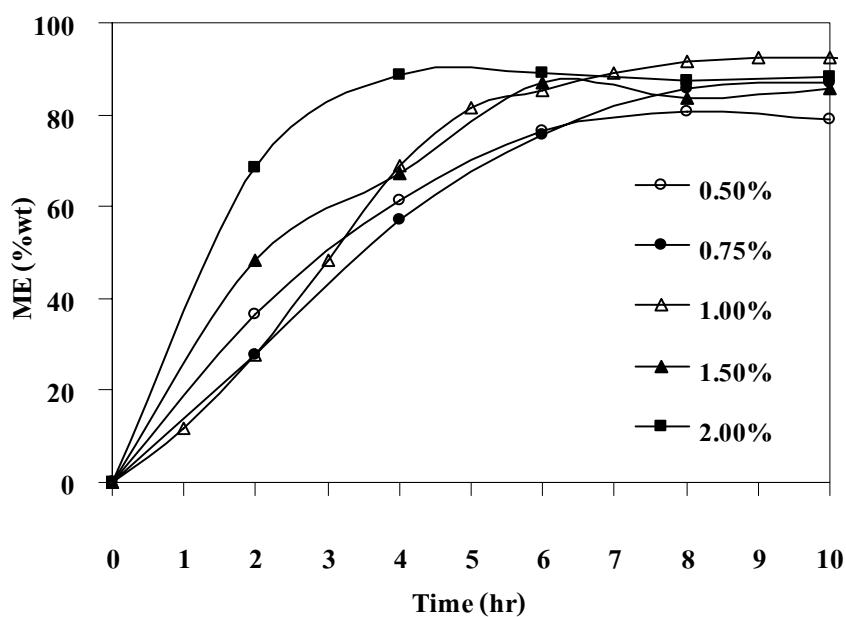
Figure 3.32 Effect of %KOH on ME content

3.3.4.8 Effect of residence time

RD column height significantly influences the residence time, except on the brink of the flooding point of the column. The greater the RD length is, the longer the residence time. Figure 3.33 shows the effect of RD length on ME content in the product stream. The %wt of ME increases with the increase of RD column length or residence time.
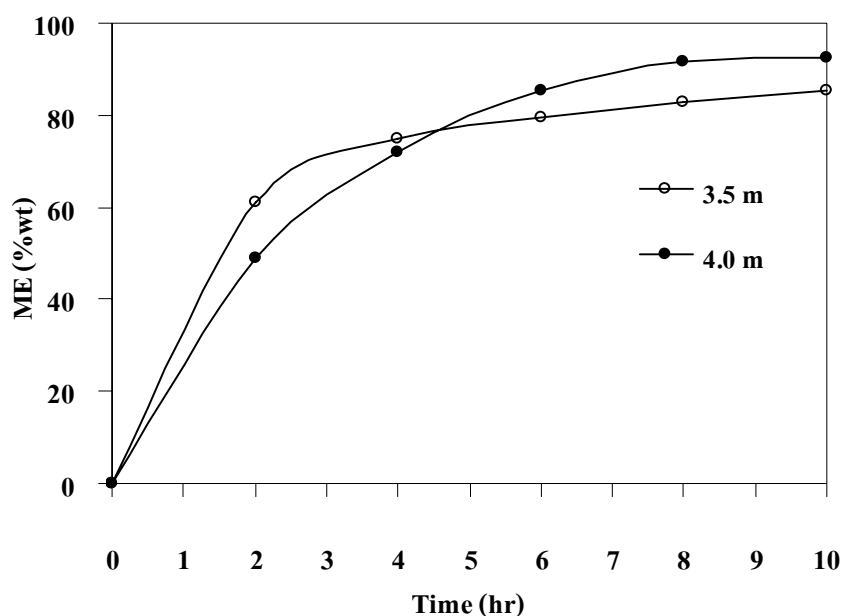

Figure 3.33 Effect of RD length on ME content

The average results as mass fractions with cumulative residence time at each sampling location are shown in Figure 3.34. The results show that reactions at the top of the column can occur more quickly than those at the lower part. Because of this, the ratio of oil to methanol is greater at the top of the column than at the lower part. This can be observed from the temperature within the column, where the temperature at the lower part of the column is higher than at the top. The effect of high temperature causes some methanol to remain at the bottom of the column. Moreover, a higher concentration of reactant produces a greater amount of product.
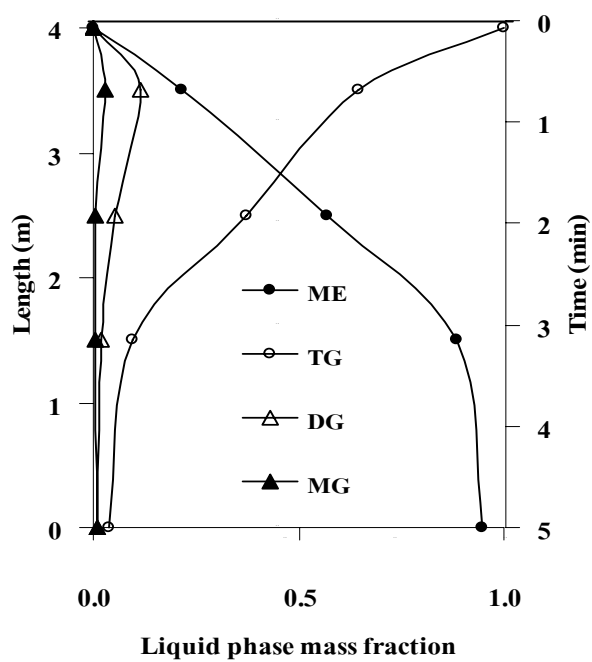
(a)
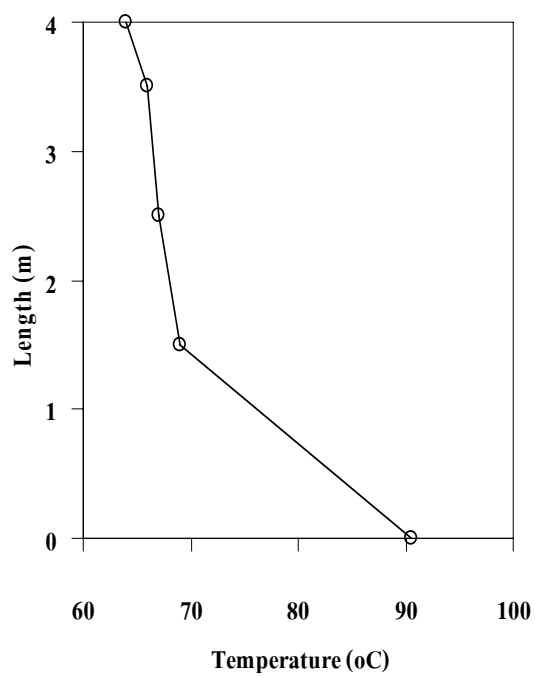
(b)

Figure 3.34 Effect of residence time in column on ME content

(a) Liquid phase mass fraction (b) Temperature

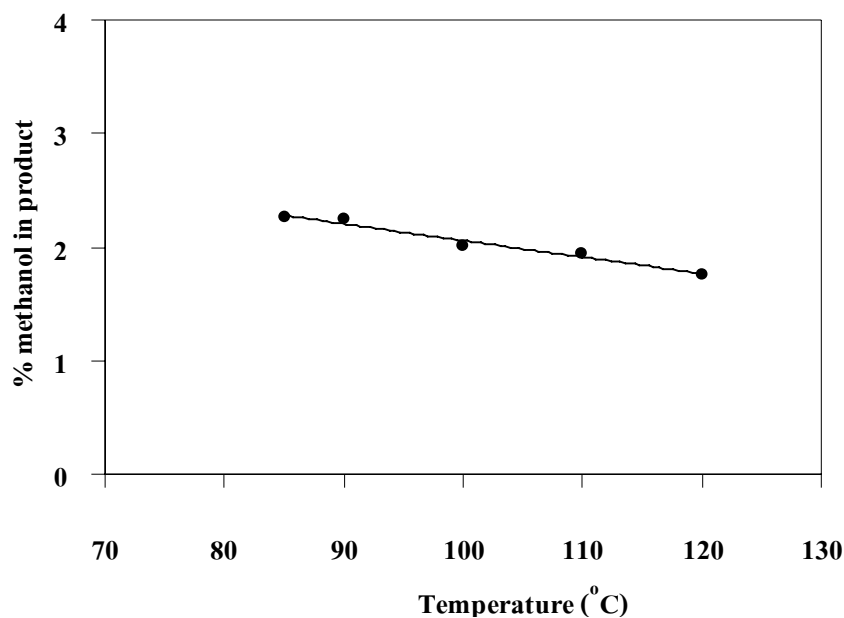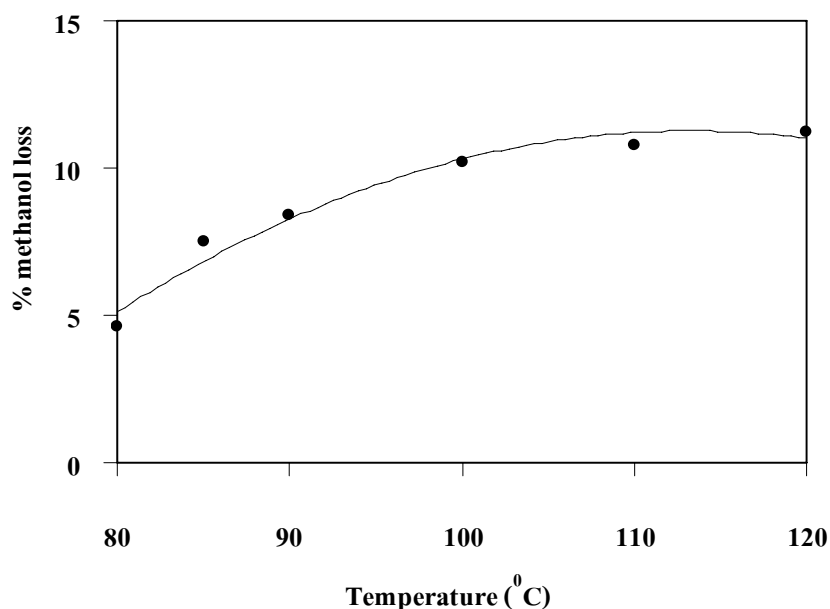**3.3.4.9 Quantity of methanol in product**

Figure 3.35 The effect of reboiler temperature on methanol content in product

Normally, the conventional process requires 100% excess methanol to drive the reaction to complete and to prevent chemical equilibrium. Excess methanol from reactor effluent (mostly ME) is about 3.99% wt at 60 $^{\circ}$C reactor temperature. Then the remainder of the methanol must be recovered for reusing, to reduce operating costs. However, the quantity of residue methanol in the RD process is only 2.25% (Figure 3.35) at 90°C reboiler temperature because the initial amount of methanol in RD was smaller than in the conventional method. The higher reboiler temperature has the fewer methanols in product because high temperature can be vaporized methanol faster than low temperature.

3.3.4.10 Methanol balance of biodiesel production

The transesterification is reversible reaction in which excess alcohol is required to complete reaction. The excess alcohol must be recovered through distillation for reusing in conventional process. However, chemical reaction and methanol separation occur simultaneously in RD process. Unreacted alcohol is vaporized from the reboiler and flows uphill to the top of column. The methanol in vapor phase can be losing from system. Figure 3.36 shows that further increasing of temperature and methanol to oil ratio has significantly increased the percent of methanol loss.

The material balance shows the entire methanol associated in biodiesel production process. The result shows that there is much more mass input than output. In the process, oil and methanol were fed 13.65 and 2.08 g, respectively. However, the methanol was consumed in the reaction of transesterification only 1.56 g so that it should remain in the product stream 0.52 g, however, it remained only 0.44 g in product stream and some of it leaked from the system.
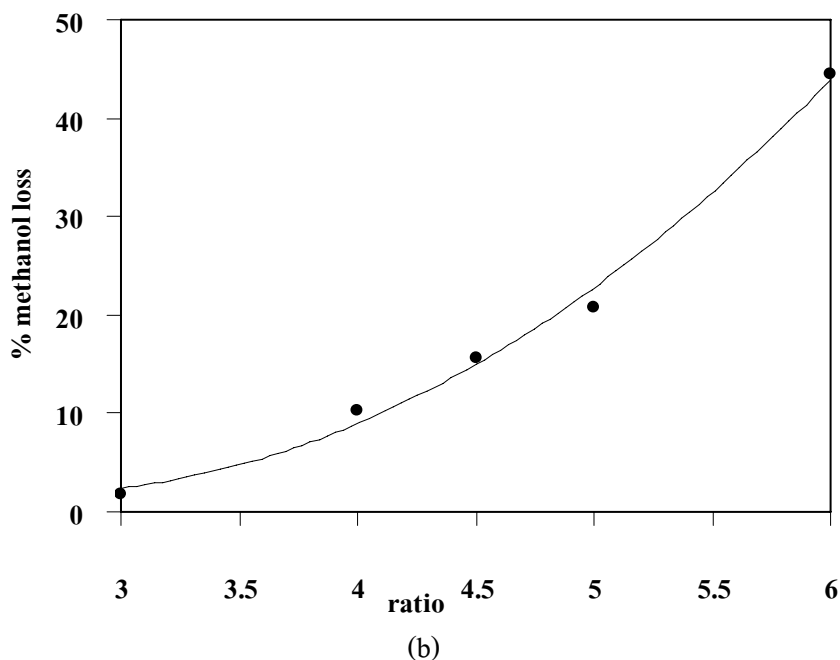

(a)

Figure 3.36 The quantity of methanol loss from system: (a) Temperature, (b) methanol to oil ratio

3.3.5 Conclusion

A RD process was applied for production of biodiesel from palm oil. The original objective was to reduce the capital and investment costs of the production process. Investment cost was reduced by using less methanol than in the conventional process, and without expending additional energy for recovering and purifying the excess methanol.

The results show that the RD process has been found to be feasible for the continuous production of biodiesel. It can be concluded that the operation of the RD process results in efficiency improvement compared to the conventional process. Based on the results of this study, the following conclusions can be made: (1) excess alcohol in the fresh feed input was reduced; (2) reaction time was shortened; and (3) elevated temperature enhanced a high reaction rate.

3.4 Control System Design for Biodiesel Production by RD Column

3.4.1 Abstract

The control strategy of a RD for biodiesel production process by transesterification reaction of triolein and methanol is investigated. The optimum condition at steady state was selected as the base case condition for the control study. Two conventional control structures (feed flow disturbance) have been designed to control the temperature, product composition and level. Autotune variation (ATV) was used to determine ultimate gain and frequency of the process and Ziegler-Nichols (ZN) and Tyreus-Luyben (TL) tuning were used to determine PID parameters. From Aspen Dynamic simulation, the proposed control strategies perform very well in rejecting disturbances. The ZN tuning give the better setting than TL tuning due to TL tuning produced response which were too damped as a result the integral absolute error (IAE) is greater more than ZN tuning. The control structure I (CS1) and II (CS2) are used for control the product composition plus reboiler level and the temperature at 11st stage plus reboiler level, respectively. The result shows that both control structure can reject disturbances and bring the system back to set point. In addition, this study has also founded that the product composition can be controlled by temperature controlling.

Keyword : control, RD, Aspen dynamic simulation, disturbance, biodiesel

3.4.2 Introduction

The RD, a combination of reactor and distillation column in a single unit, provides an attractive alternative for process intensification, especially for reaction/separation systems with reversible reactions. The main advantage of using RD is the reduction of capital and operating costs due to elimination part of equipment, reactant and utility. Also, the overall reactant conversion increases with the constant recycling of reactants and removal of products. RD process also increases energy efficiency due to direct utilization of reaction heat. It easily makes temperature control of reaction and reacts away from azeotrope. To maintain the stability of RD process, the dynamic and control will be studies. Vora and Daoutidis (2001) studied the dynamics and control of an ethyl acetate using RD system and proposed a new feed configuration for two reactants that allowed higher conversion and purity than the conventional configuration, which involves feeding in a single tray. Al-Arfaj and Luyben (2002c) compared the control of an ideal RD column with that of a similar real chemical system of methyl acetate production. A number of control structures were evaluated for both systems. Sneesby et al. (1999) proposed a two-point control scheme of RD which used simple, linear PI controllers to control both the product composition and the reactant conversion where feed rate and set-point changes were disturbances.

The objective of this work is to propose a conventional control structure for the biodiesel production process with RD column. The control objective is to maintain the process stability. Temperature, level of reboiler and product composition were control variables while feed flow rate was disturbance.

3.4.3 Base case column design in dynamic simulation

The RD column shown in Figure 3.37 was used as the base case of the control study. The column consisted of 12 stages, including a total condenser and kattle reboiler. There were two zones in the column, stripping zone and reaction zone. The stripping zone was underside of the column for purifying the bottom product. Biodiesel was formed in the reaction zone. The reactant was fed to the column on stage 2 from the top. The column pressure was 1 atm. The NRTL method was used to determine the thermodynamic option with distinct activity coefficients for vapor-liquid and liquid-liquid equilibriums. Every stage was assumed to be in chemical equilibrium. The reaction which took place in the column had only three consecutive reversible reactions that were the conversion of TG to DG, DG to MG and MG to GL. The product was one methyl ester molecule from each glyceride at each step (Fukuda et al., 2001). The others reaction was assumed to be negligible.
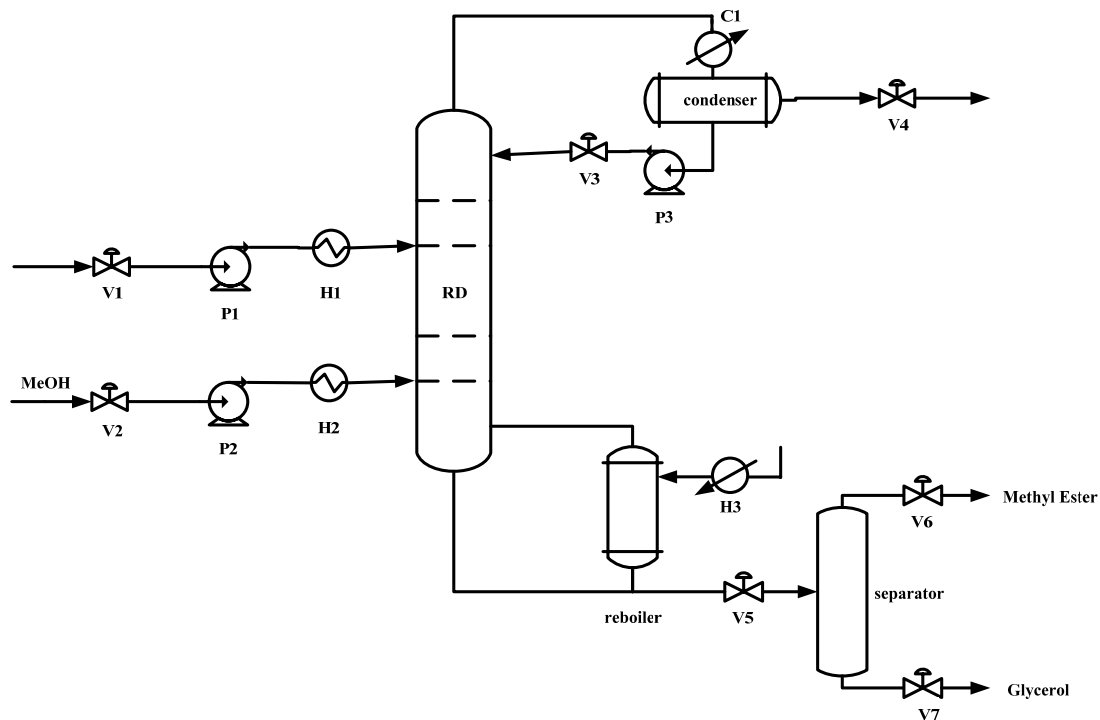
Figure 3.37 RD column configuration for biodiesel production

Table 3.10 shows the operating condition of biodiesel production with RD column. At this condition, the purity of biodiesel was 92.75% (mass basis).

Table 3.10 Base case operating condition of biodiesel production by RD column

Feed condition			Column specification	
Feed	Oil	Methanol	Type	Tray
Feed tray	2	2	Number of stages	10
Temperature (^{o}C)	60	25	Overhead pressure (bar)	1.01
Pressure (bar)	1.01	1.02	Column pressure drop (bar)	0.01
Flow rate (kmol/hr)	7.26	29.03	Reflux ratio	25
Composition (molfraction)	1	1	Reflux rate (kmol/hr)	137.29
			Distillation rate (kmol/hr)	5.49
			Bottom rate (kmol/hr)	30.79
			Reboiler duty (MW)	1.27
			Biodiesel purity (mass %)	92.75

3.4.4 Procedure

In this research, 2 control structures were designed for RD process as shown in Figure 3.38 and 3.39 to reduce the effects of disturbances in order to achieve a desired quantity and quality. The first scheme controls composition plus level with the feed flow rate as disturbance. Another scheme is changed a controlled variable to temperature plus level. The controller types for each structures is shown in Table 3.11

Table 3.11 Control structure of RD column

Control structure	Disturbance	Controlled variable	Manipulated variable	Type of controller
		Flow controller at oil feed	Oil flow rate (V1)	PI
		Flow controller at methanol feed	Methanol flow rate (V2)	PI
CS1	Oil flow rate	Composition controller of product	Heat rate (H3)	PI
		Level controller at reboiler	Product flow rate (V5)	P
CS2	Oil flow rate	Temperature controller at 11st stage	Heat rate (H3)	PI
		Level controller at reboiler	Product flow rate (V5)	P

3.4.4.1 Select tray temperature control.

3.4.4.2 Tune and compare controller type.

3.4.4.3 Test system stability and controllability.
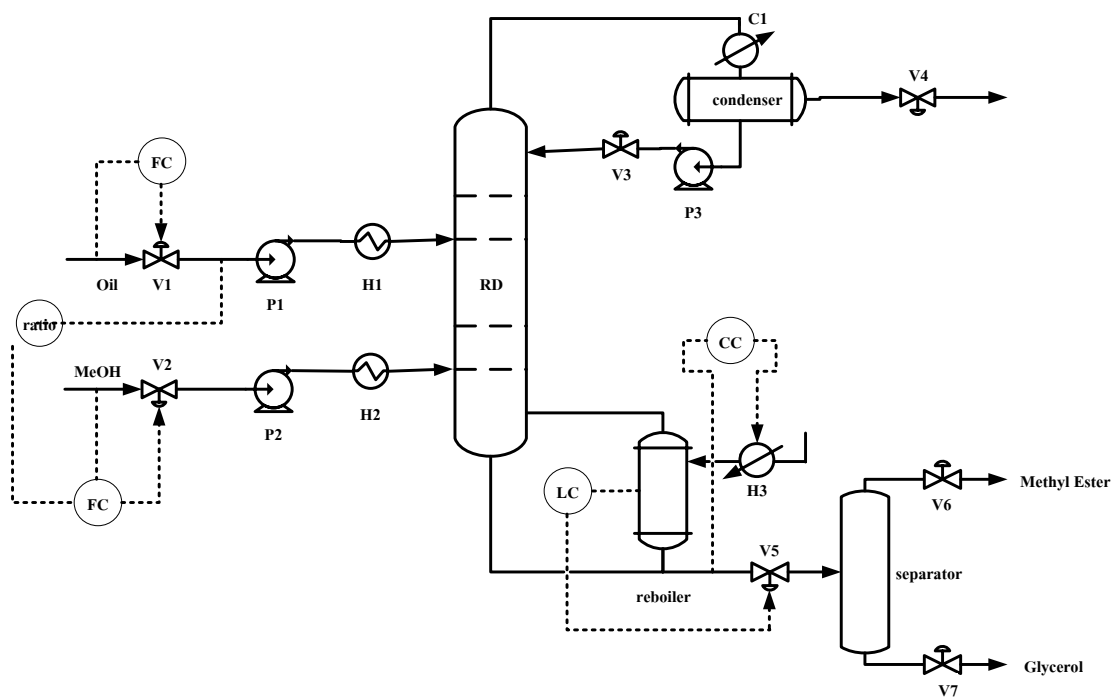
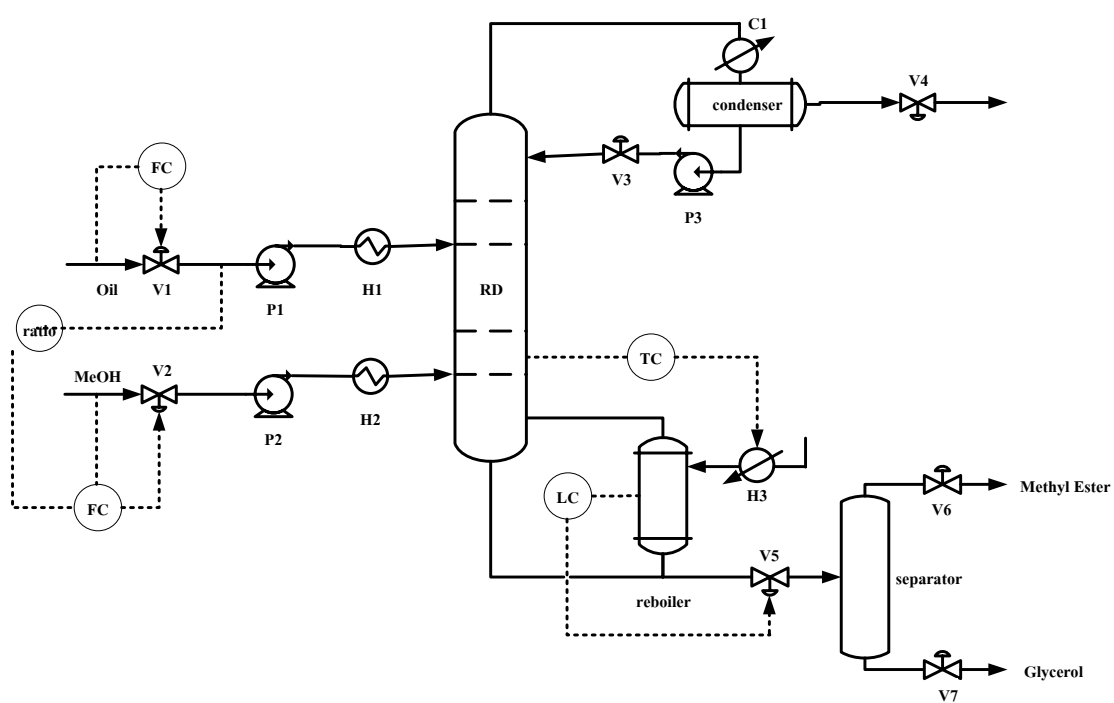Figure 3.38 Designed CS1 of RD process

Figure 3.39 Designed CS2 of RD process

3.4.5 Results and discussion

Figure 3.40, 3.41 and 3.42 show the composition, temperature and reaction rate profiles in the RD column at base case operating condition.
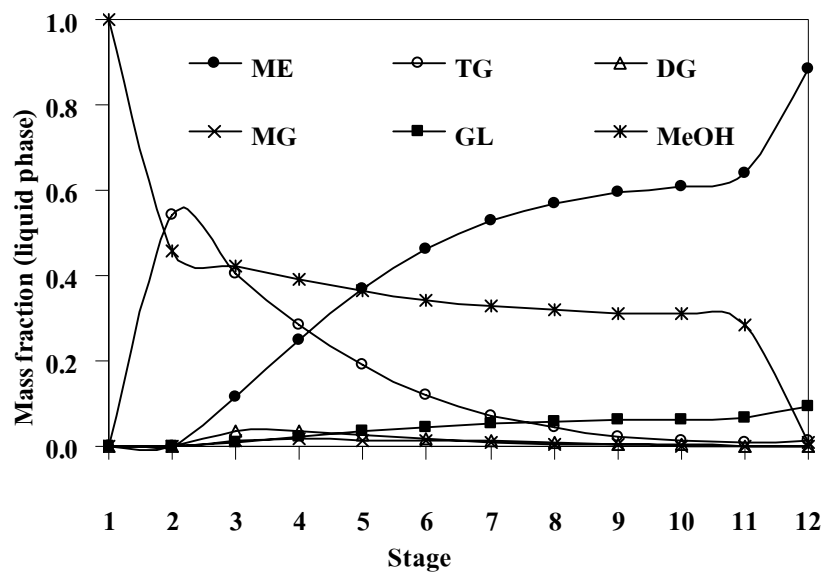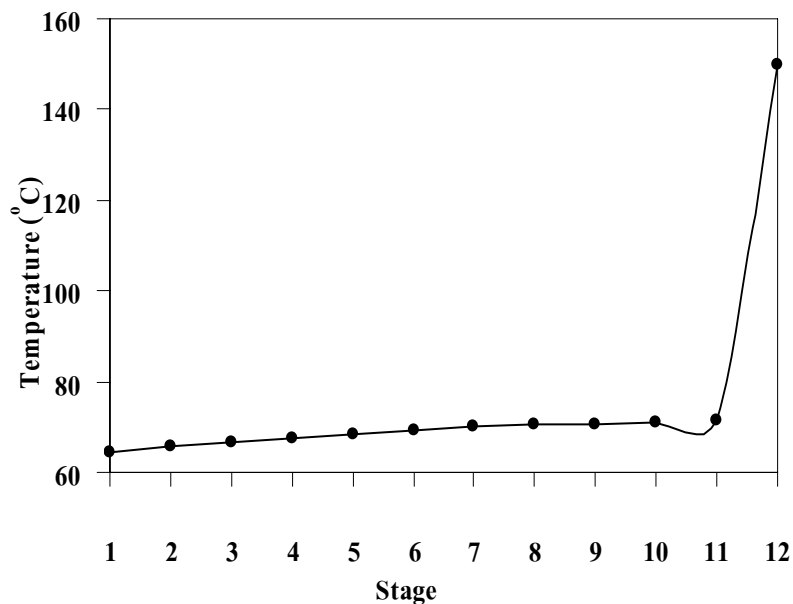

Figure 3.40 Composition profile in the RD column
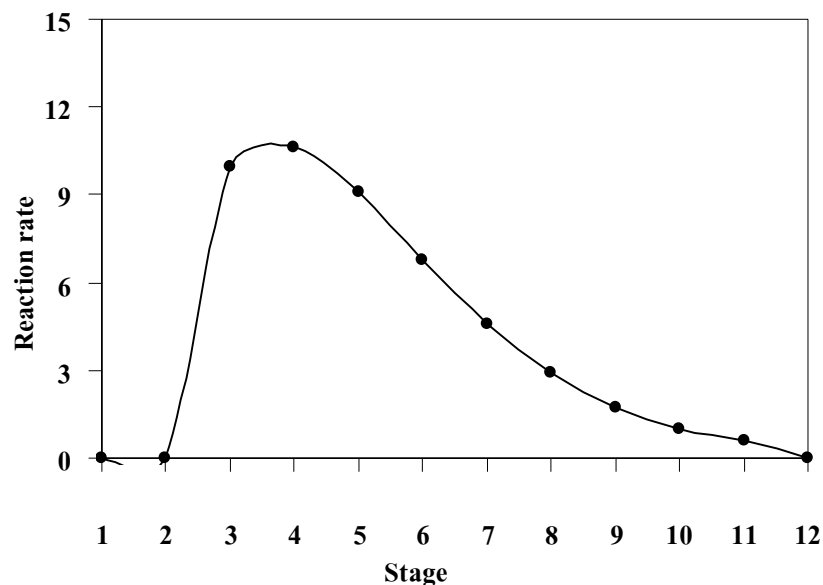

Figure 3.41 Temperature profile in the RD column

Figure 3.42 Reaction rate profile in the RD column

3.4.5.1 Selecting tray temperature control

In this research, temperature control is used instead of composition control. The reason is that most product analyzers, such as gas chromatography, suffer from large measurement delays and high investment and maintenance costs. The composition control can be replaced by a temperature control. Hence the stage temperature selected should have large changes in temperature from tray to tray.

The temperature profile of each tray at design conditions was plotted. The selected tray is the tray which has the largest slope. Large changes in temperature from tray to tray indicate a region where compositions of important components are changing. Maintaining a tray temperature at this location should hold the composition profile in the column, prevent light components from dropping out the bottom and heavy components from escaping out the top (Luyben, 2006).

From Figure 3.41, tray 11 has the largest slope therefore it was a selected tray for tray temperature control.

3.4.5.2 Tune and compare controller type

After the controlled variables and manipulated variables were selected, the controller can be tuned. In this study, a closed loop autotune variation (ATV) was used as the test method to find ultimate gain and frequency of the process. The default value of the relay output amplitude (MV) is 5% (Thyagarajan and Yu, 2003; Shen et al., 1996) which is usually good. For a very nonlinear column, the amplitude may have to be reduced. After several (4–6) cycles or the change has same amplitude and period, test is finished.

ATV, based on relay feedback testing, has proven to be a reliable approach for controller tuning in a non‑linear behavior. Two measurement lags with time constant of 30 s (Al-Arfaj and Luyben. 2002a; Luyben, 2002) are used in all composition or temperature loops. At a steady state, the MV is increased by "h" (h is called the relay height). As the process shows an increase in process variable, the MV is switched to m ‑ h. This procedure is repeated and the continuous cycling of the process variable is shown in Figure 3.43. The K_u and P_u of the process can be expressed as

$$K_u = \frac{4h}{a\pi}$$

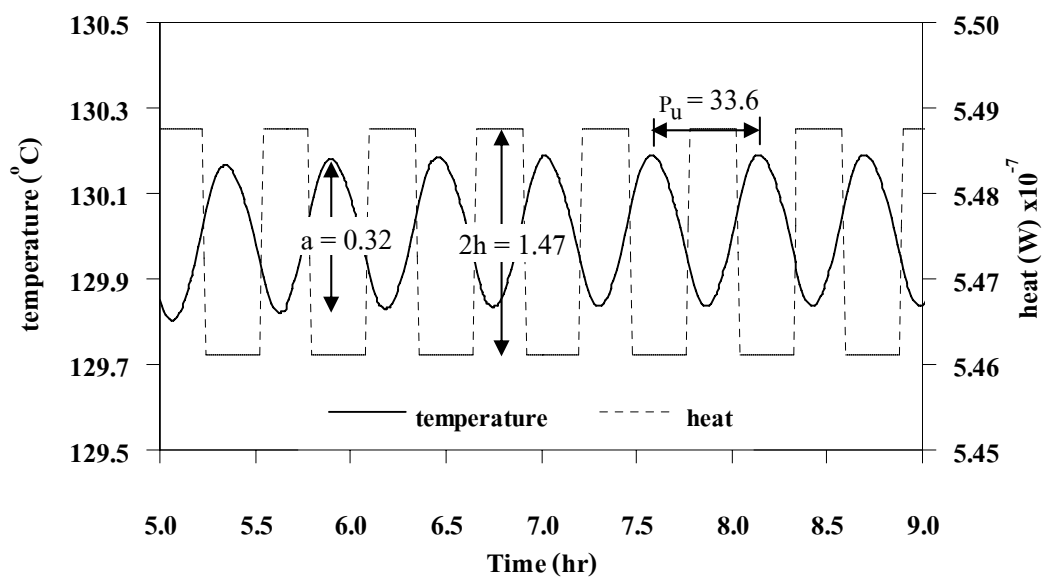where h is the relay height set by the user and a is the amplitude of the oscillation.

Figure 3.43 Input and output from relay feedback test for temperature control by heat input rate

From Figure 3.43 shows the temperature control tuning with heat input rate (MV). This gives $K_u = 2.88$ and $P_u = 33.6$. And using 2 different tuning rules, ZN and TL tuning (Table 3.12), provide PID controller parameters as shown in Table 3.13.

Table 3.12 Controller parameters in ZN and TL criterion

Tuning rule	Controller	Gain (K_C)	Integration time (τ_I)	Derivation time (τ_D)
ZN	P	$\dfrac{K_u}{2}$		
	PI	$\dfrac{K_u}{2.2}$	$\dfrac{P_u}{1.2}$	
	PID	$\dfrac{K_u}{1.7}$	$\dfrac{P_u}{2}$	$\dfrac{P_u}{8}$
TL	PI	$\dfrac{K_u}{3.2}$	$2.2P_u$	
	PID	$\dfrac{K_u}{2.2}$	$2.2P_u$	$\dfrac{P_u}{6.3}$

Table 3.13 Tuned parameter of temperature controller from RD column

Controller	Tuning rule	Type of controller	Tuned parameter			IAE (feed change)
			K_C	τ_I	τ_D	
Temperature	ZN	P	1.441	100,000	0	17.720
controller at 11st stage		PI	1.310	28.0	0	1.464
		PID	1.696	16.8	4.2	0.640
	TL	PI	0.901	73.9	0	4.900
		PID	1.310	73.92	5.333	3.373

Figure 3.44 and 3.45 show control performance of controller which can rejected disturbance and brings CV to its set point. Comparison of effective of the controllers indicated that PI and PID controller types can be used to control the system reach to the set point. PID controller has better performance because its action can eliminate the disturbance faster than PI. However, PI controller is fairly common since derivative action is sensitive to measurement noise. The P controller can not use for temperature control because it has the offset that affected to the system behavior.
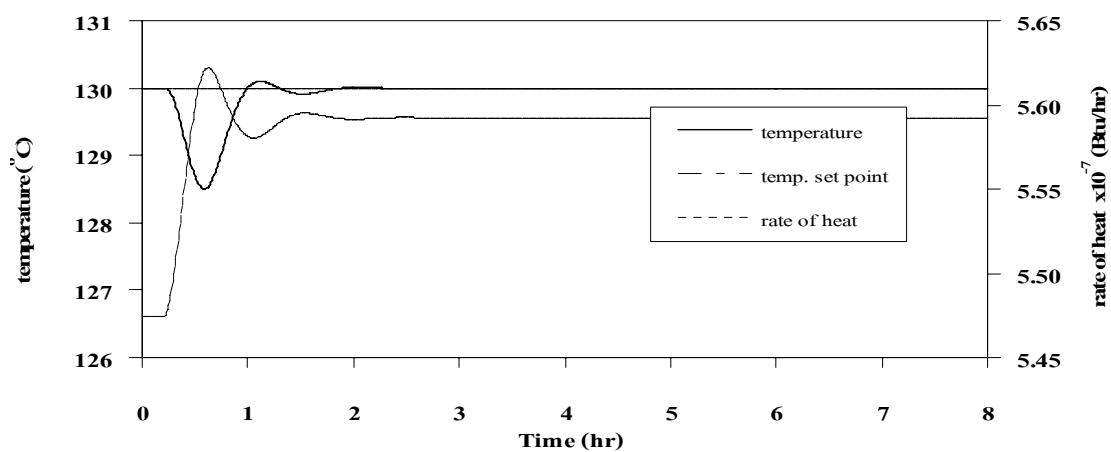
Significant differences are found on effective comparison between ZN and TL tunning rule. The results of this study show that ZN has high performance because it allows the system come to set point faster than another one.
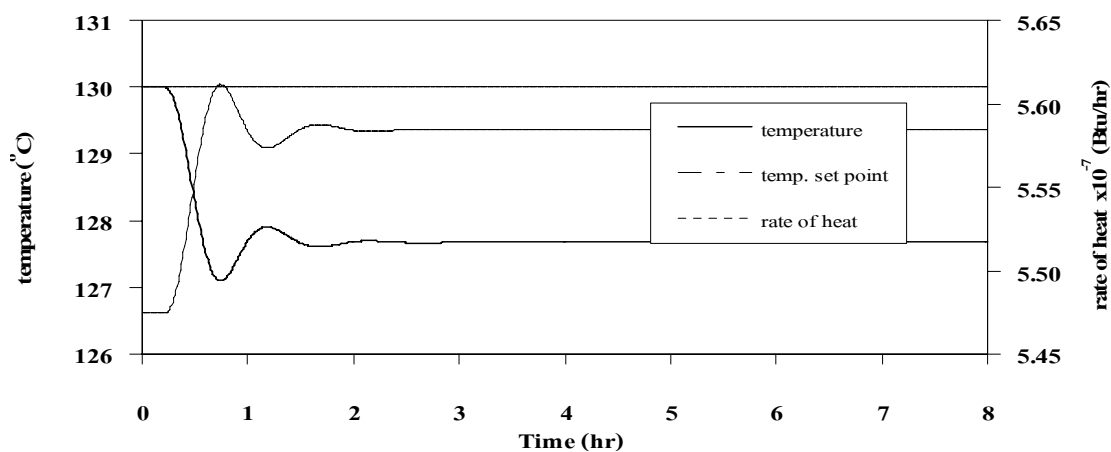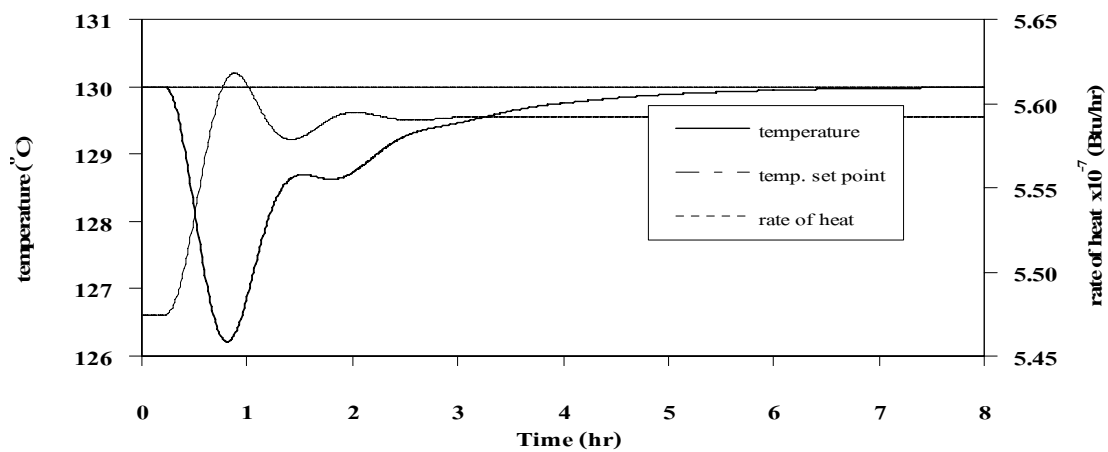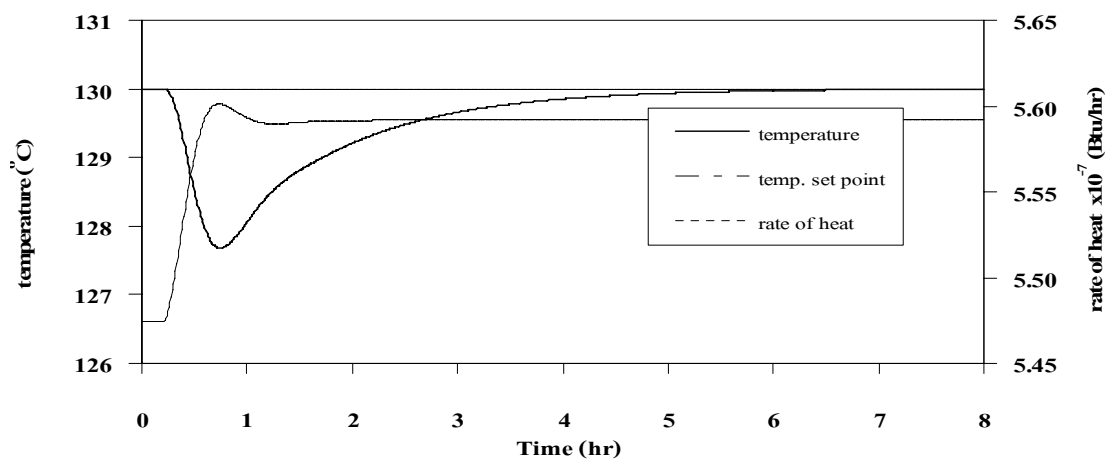
(a) P controller
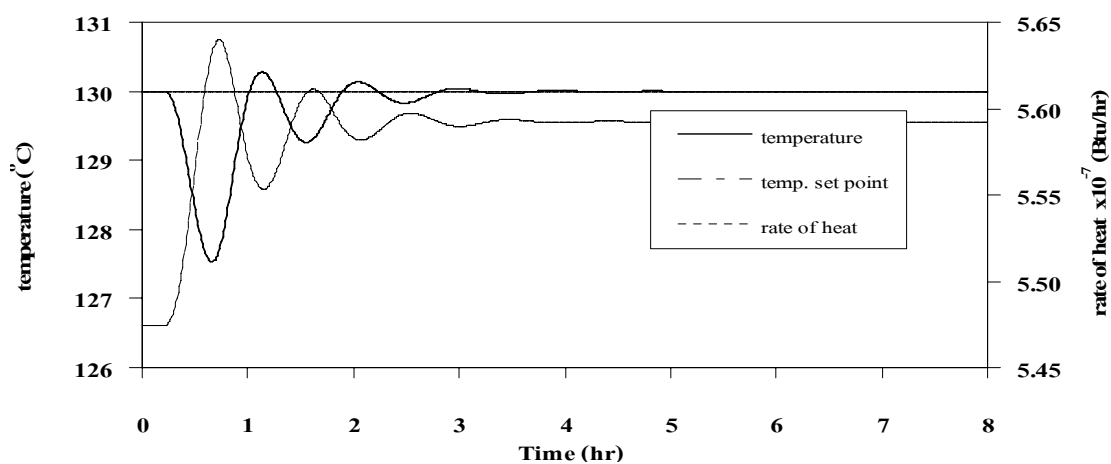
(b) PI controller

(c) PID controller

Figure 3.44 Effect of tuned parameters from ZN tuning rule with feed disturbance
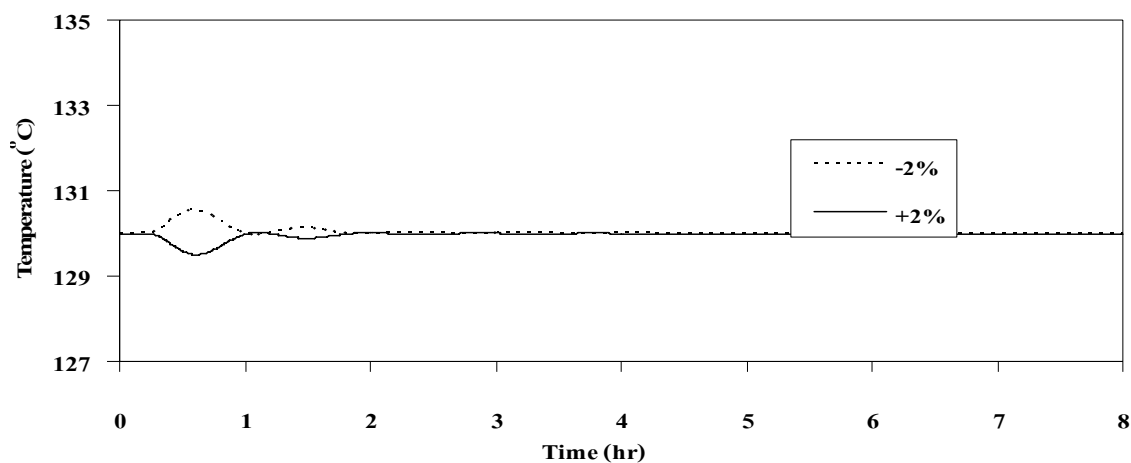
(a) PI controller

(b) PID controller

Figure 3.45 Effect of tuned parameters from TL tuning rule with feed disturbance

3.4.5.3 Test system stability and controllability
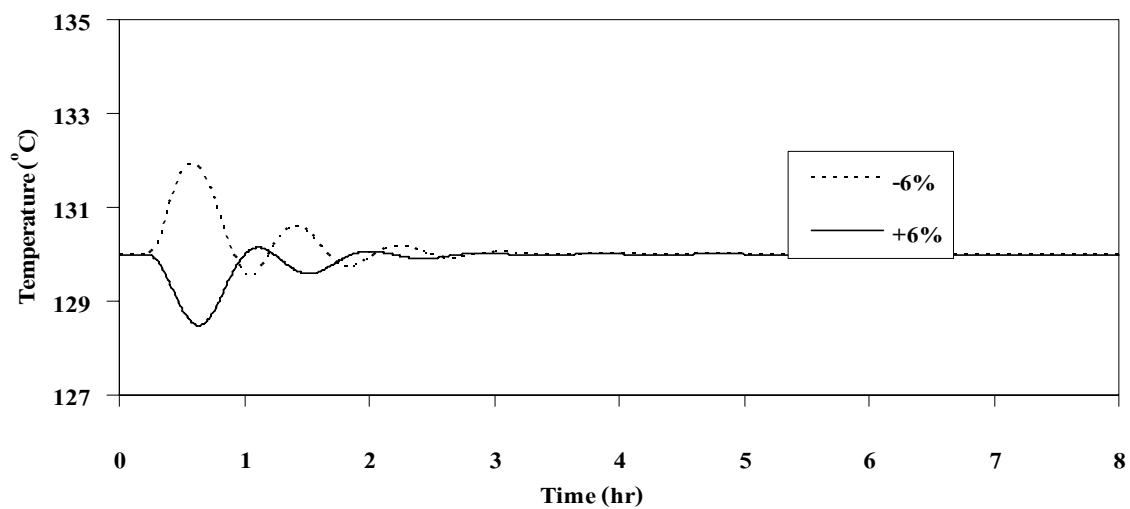
1. Robustness controller

To test the robustness of controller when parameters (disturbance and set point) change, a decreasing and an increasing in oil feed flow rate and in temperature set point were applied. Figure 3.46 and 3.47 show the system response following a step change of feed flow and temperature set point. The results show that robustness characteristic of designed controller for RD process has satisfactory output responses. It is clear that the system equipped with PI controller can cover the changing range of -10 - 50% feed flow and of -17 - 2% temperature set point of the system.
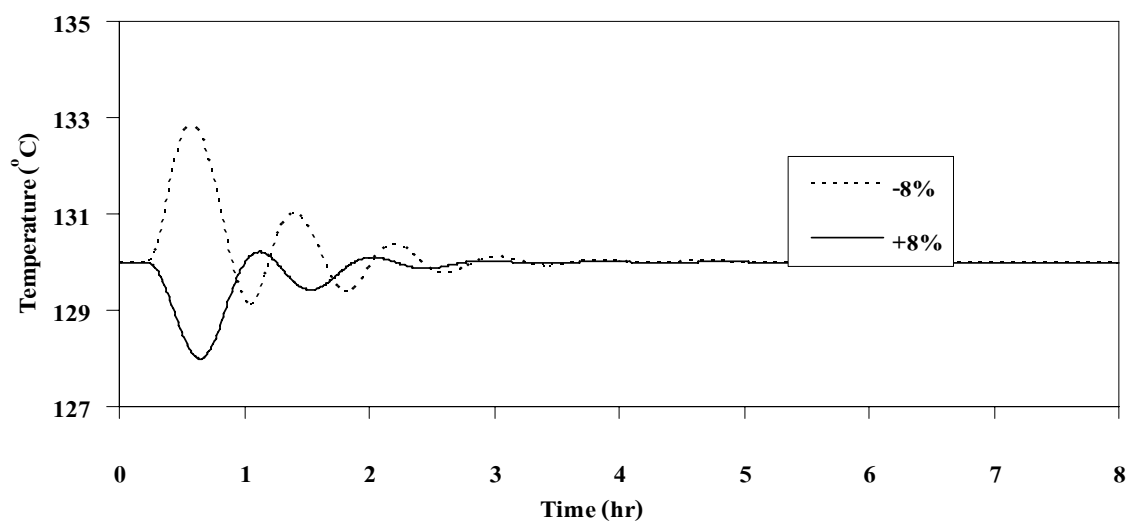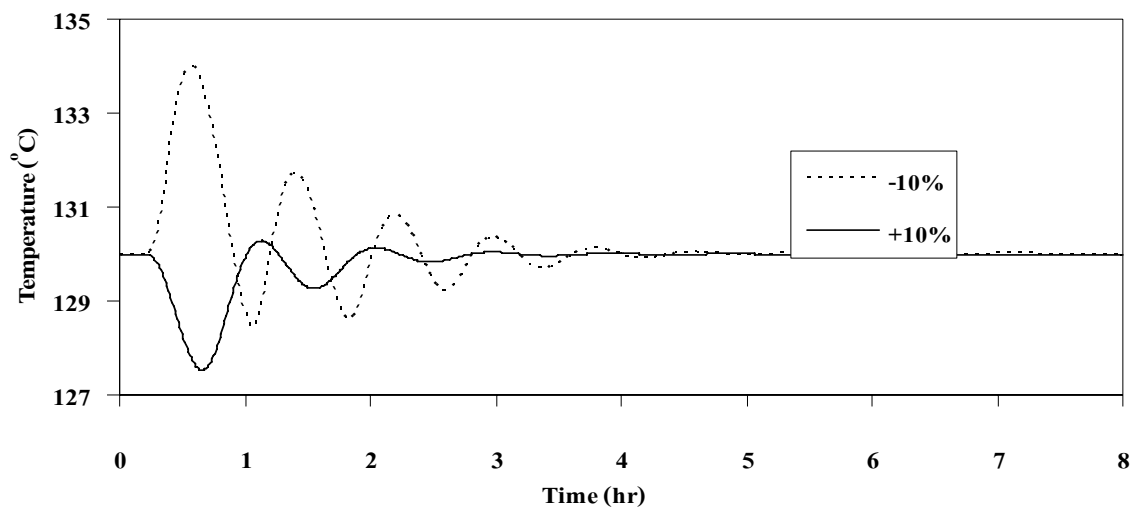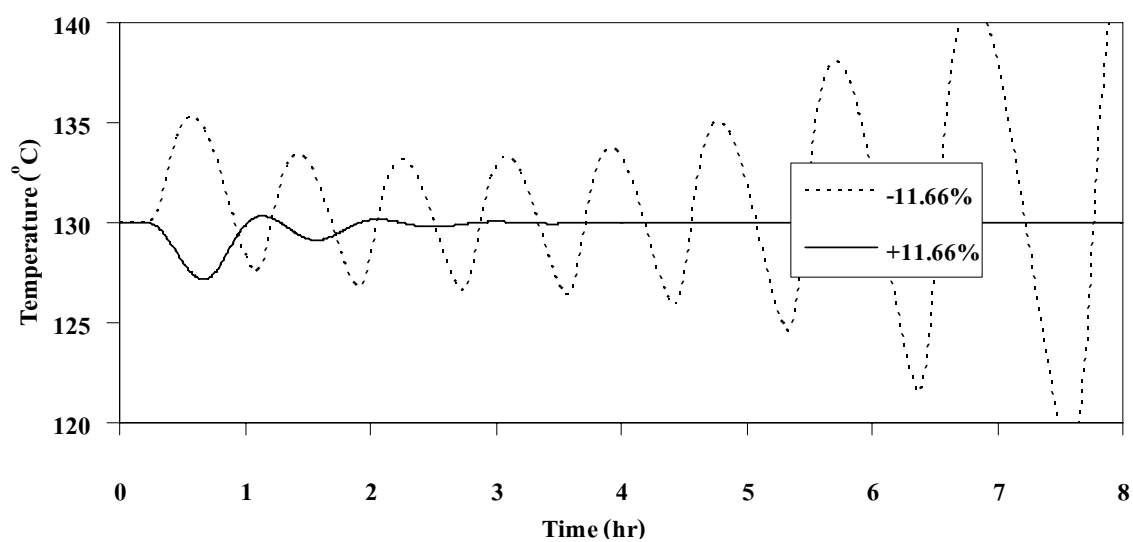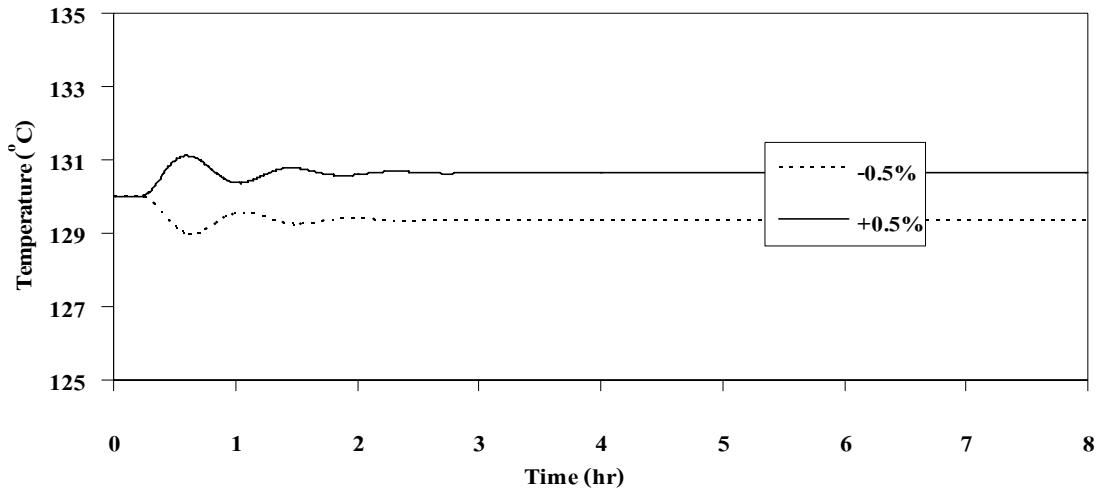
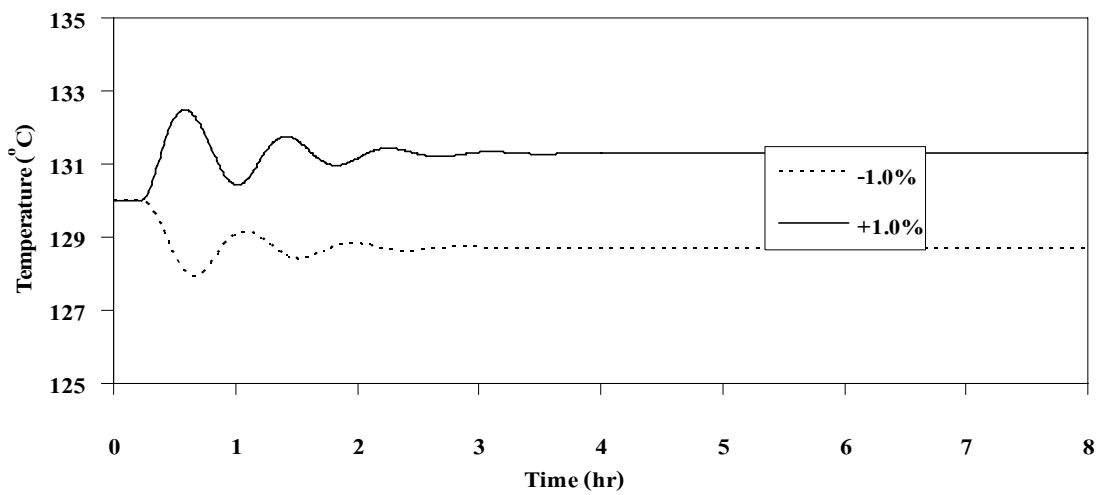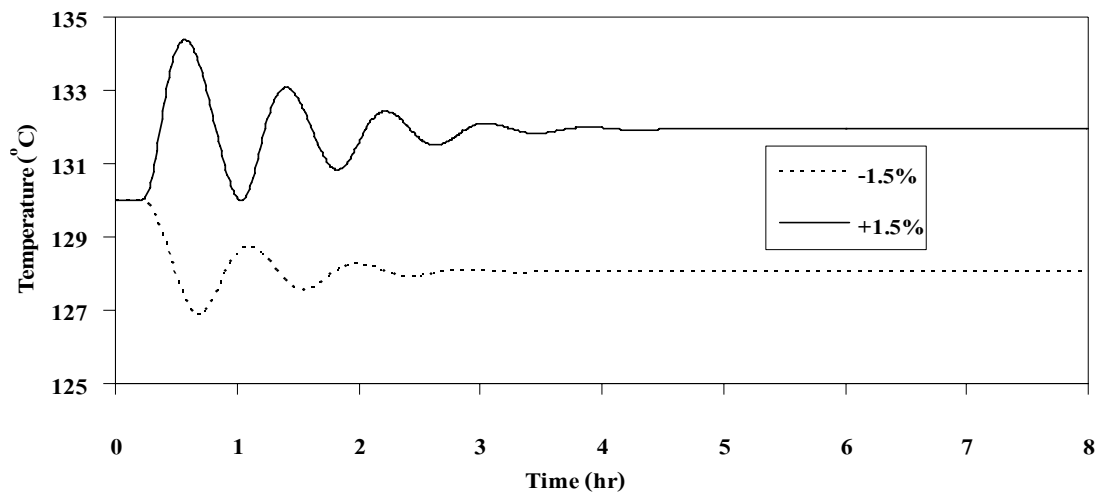

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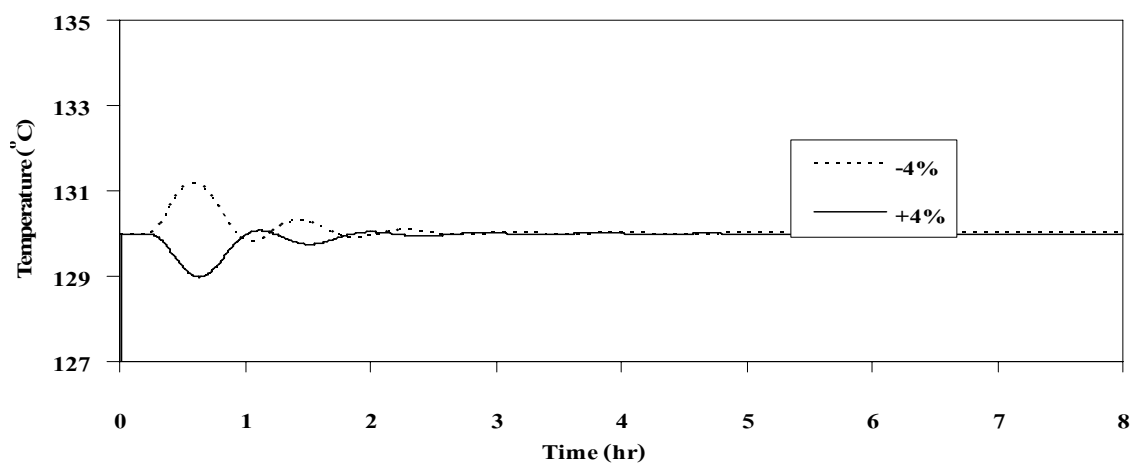
(b)

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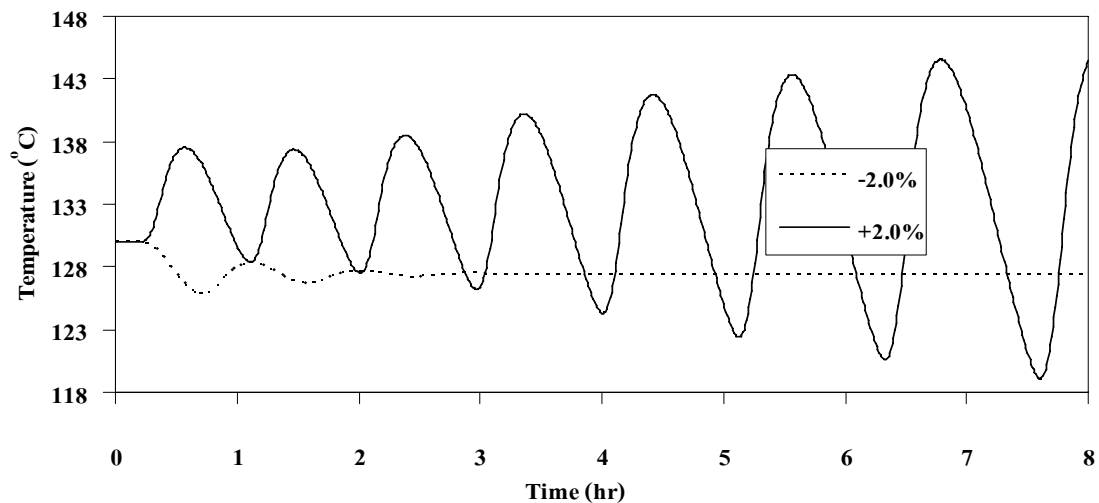Figure 3.46 Robustness of controller with feed change

(a)

(b)

(c)

(d)

Figure 3.47 Robustness of controller with temperature set point change

2. Control individual unit operations

From the previous, ZN method has better performance than TL and PI controller is suitable control structure. All of PI controllers which were installed in the RD column were tuned by ZN tuning. The results of tuning parameters are shown in Table 3.14.

Table 3.14 Tuned parameters of individual unit operation

Control structure	Controller	Tune parameter		
		K_C	τ_I	τ_D
	Flow controller at oil feed	0.755	5.000	0
	Flow controller at methanol feed	0.057	5.000	0
CS1	Composition controller of product	2.113	35.500	0
	Level controller at reboiler	5.790	100,000	0
CS2	Temperature controller at 11st stage	1.310	28.000	0
	Level controller at reboiler	5.790	100,000	0

Table 3.15 and 3.16 show the IAE of controllers. The results show that all controllers have performance to induce the response of system (Figure 3.48) come back to the set point whenever the disturbance and set point are changed. The IAE of feed flow rate, composition and level of CS1 and CS2 have slightly different. However, the IAE for temperature in CS1 is greater than in CS2 since the composition control which has heat rate is MV will affect to temperature change in the RD column.

Table 3.15 Tuned parameters of individual unit operation of CS1

Parameters Changed (%)			IAE			
Feed flow rate[*]	Composition[**]	Level[**]	Feed flow rate[*]	Temperature[**]	Composition[**]	Level[**]
+10	0	0	0.568	23.888	0.003	0.093
-10	0	0	0.533	41.220	0.003	0.110
0	+1.0	0	0.692	193.812	0.004	0.103
0	-1.0	0	0.165	97.113	0.005	0.105
0	0	+10	2.095×10^{-4}	0.331	2.244×10^{-5}	7.924×10^{-4}
0	0	-10	2.072×10^{-4}	0.332	2.244×10^{-5}	7.592×10^{-4}
+10	+1.0	0	0.655	158.521	0.004	0.171
-10	-1.0	0	0.547	71.559	0.004	0.186
0	+1.0	+10	0.702	200.456	0.005	0.104
0	-1.0	-10	0.151	92.605	0.005	0.102
+10	+1.0	+10	0.662	159.395	0.004	0.171
-10	-1.0	-10	0.541	69.707	0.004	0.186

[*] Feed flow rate is disturbance

[**]Tray temperature, composition and level is set point change

Table 3.16 Tuned parameters of individual unit operation of CS2

Parameters Changed (%)			IAE			
Feed flow rate[*]	Temperature[**]	Level[**]	Feed flow rate[*]	Temperature[**]	Composition[**]	Level[**]
+10	0	0	0.568	1.461	0.017	0.031
-10	0	0	0.576	3.299	0.051	0.046
0	+1.5	0	0.115	2.346	0.043	0.016
0	-1.5	0	0.055	1.119	0.029	0.011
0	0	+10	1.999×10^{-4}	1.849×10^{-3}	3.219×10^{-4}	1.825×10^{-4}
0	0	-10	1.897×10^{-4}	1.563×10^{-3}	$3.136 \times^{-4}$	1.078×10^{-4}
+10	+1.5	0	0.548	1.345	0.015	0.039
-10	-1.5	0	0.512	1.337	0.016	0.043
0	+1.5	+10	0.123	2.533	0.045	0.017
0	-1.5	-10	0.053	1.070	0.028	0.011
+10	+1.5	+10	0.548	1.345	0.015	0.039
-10	-1.5	-10	0.511	1.337	0.016	0.043

[*] Feed flow rate is disturbance

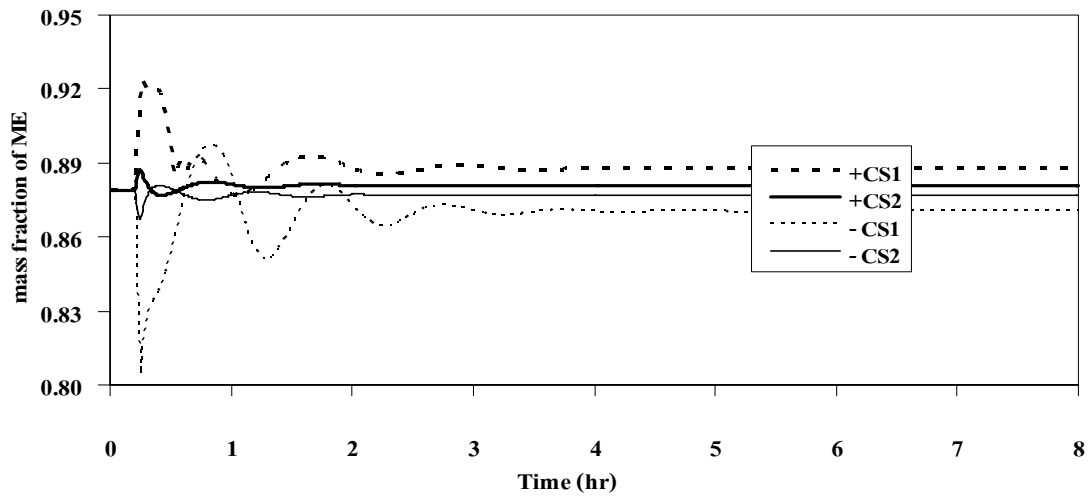[**] Tray temperature, composition and level is set point change
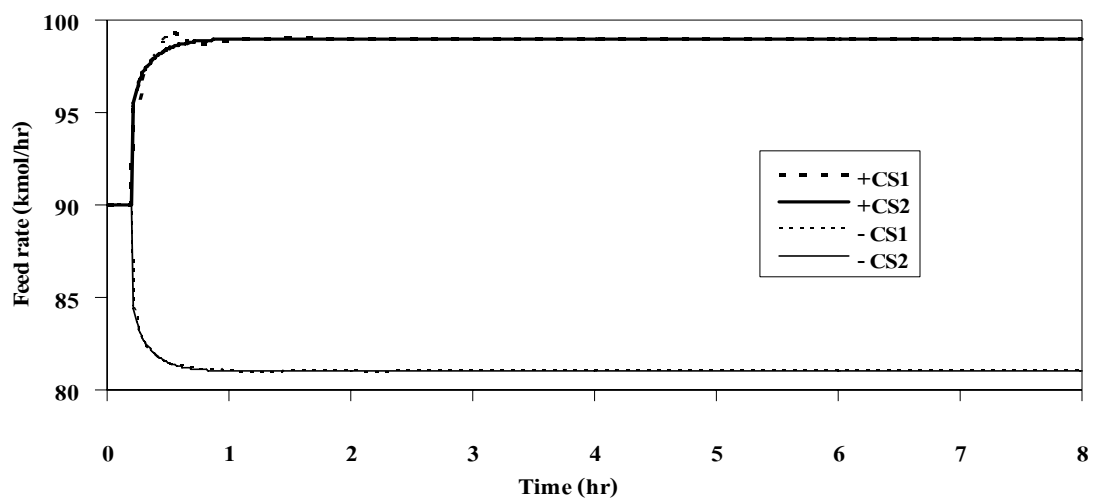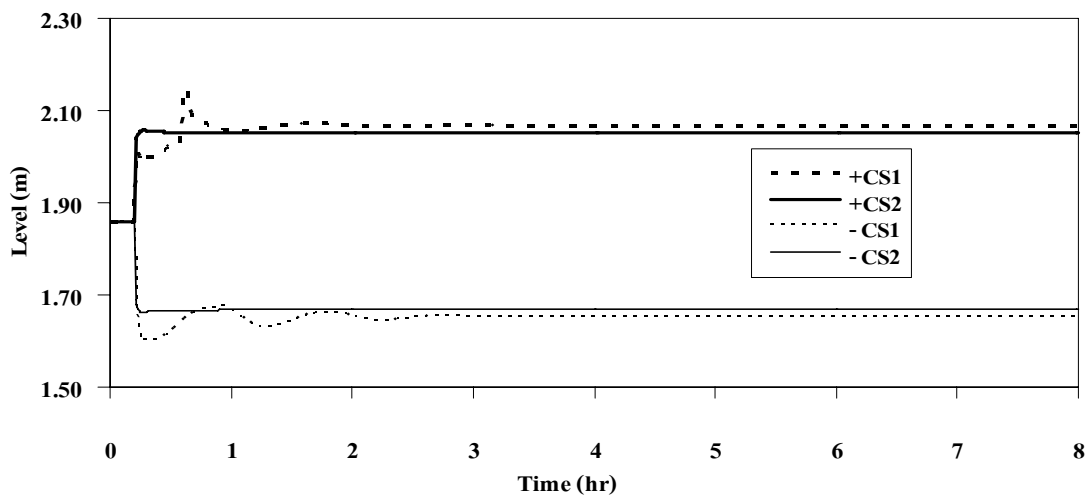
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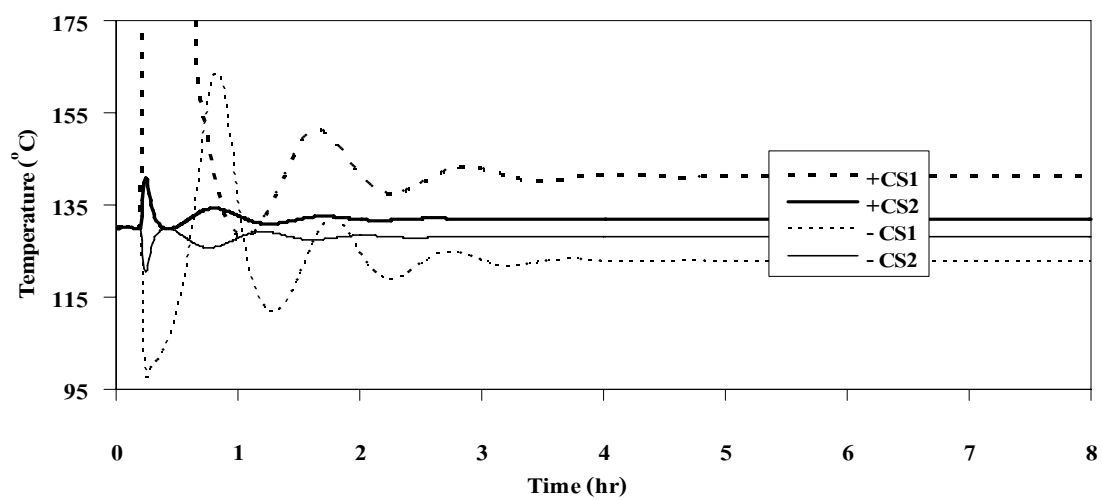
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(c)

(d)

Figure 3.48 Response of controller for change of flow rate and set point

+ CS1 = +10% feed flow rate, +1.0% composition, +10% level

 - CS1 = -10% feed flow rate, -1.0% composition, -10% level

+ CS2 = +10% feed flow rate, +1.5% temperature, +10% level

 - CS2 = -10% feed flow rate, -1.5% temperature, -10% level

3. Test system controllability

3.1 Flow controller (FC) of feed

The feed flow rate of oil and methanol is increased and decreased by 10% of the steady state condition after 0.2 hr from the previous steady state as shown in Figure 3.49 and 3.50. The previous steady state value of oil and methanol feed were 90 and 360 kmol/hr, respectively. At the new steady state, the value of the oil flow rates were 81 and 99 kmol/hr and the methanol flow rates were 324 and 396 kmol/hr.
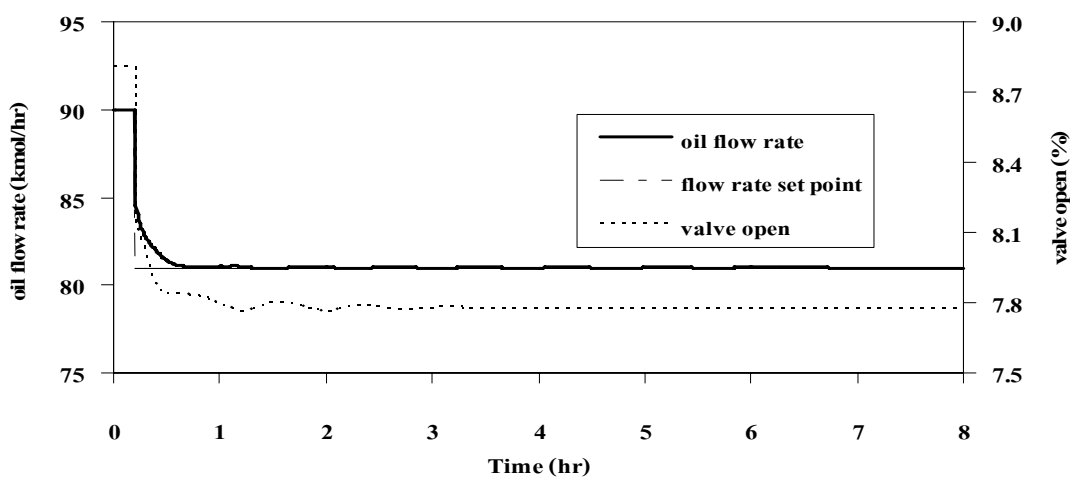
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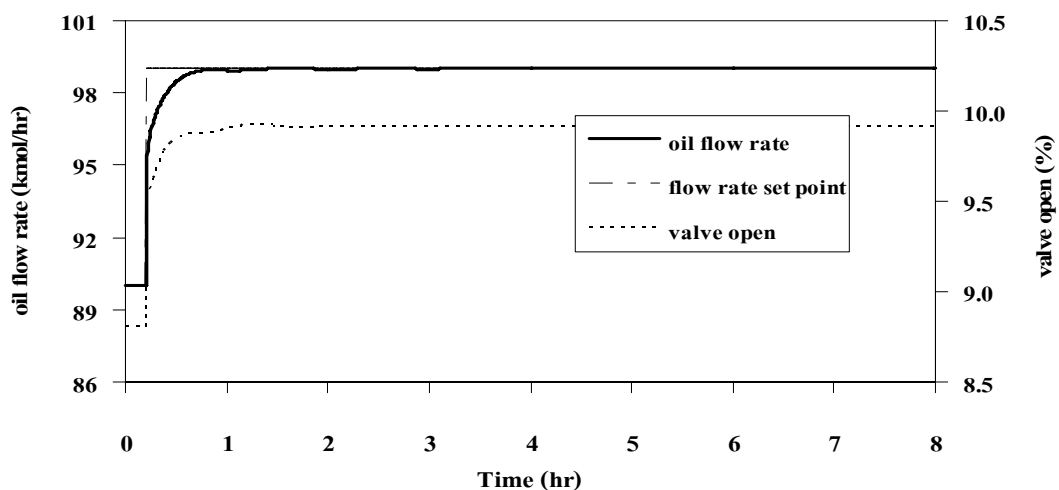
(b)

Figure 3.49 Response of oil flow rate for changing of oil flow rate set point (a) -10% (b) +10%
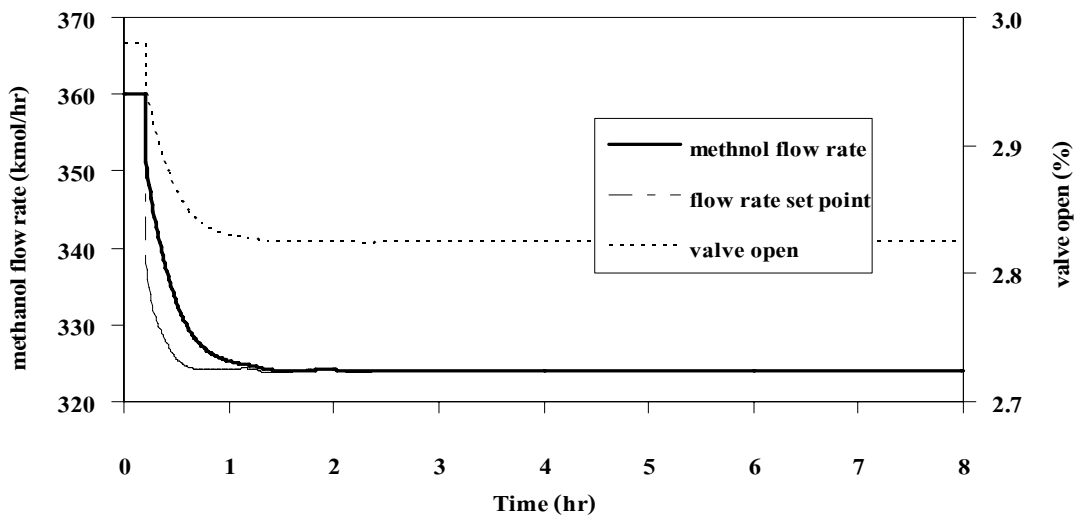
(a)
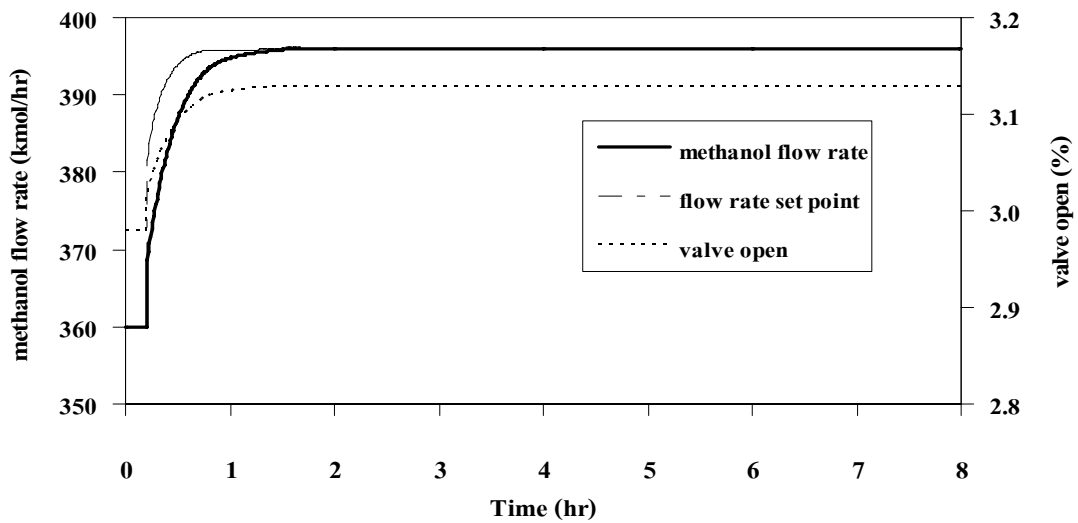
(b)

Figure 3.50 Response of methanol flow rate for changing of methanol flow rate set point

(a) -10% (b) +10%

As the flow rate of the feed has increased, the original % valve open are not sufficient to flow of new set point. Therefore, the controllers sends signals to increase the % valve open. On the other hand, the valves are contrasted action for the feed decreased. The responses of flow controllers are overdamped system as shown in Figure 3.49 and 3.50.

3.2 Control structure I (CS 1)

Base on Figure 3.38, oil flow rate is flowed control by valve V1 and this flow rate affects the flow rate of methanol by ratio control to valve V2. The composition product is controlled by heat input at reboiler (H3). And the reboiler level is controlled by bottom flow rate (V5).

The starting conditions are the base case design where oil flow rate is 90 kmol/hr. Step change of ±10% in set point of oil flow rate after 0.2 hr was made. This action affected to methanol flow rate due to it is ratio with the oil flow rate.

As the flow rate of the feed has increased, the original heat duty in the reboiler is not enough to convert reactant of the new feed flow rate to 0.87 of methyl ester mass fraction. Therefore, the composition controller (CC) sent signal to increase the heat duty. On the other hand, the CC decreased signal for the feed decreased.

Figure 3.51 shows simulation result for changing ±10% feed flow rate of CS1. The mass fraction of ME response (Figure 3.51c) is oscillatory and it comes to set point within 3.4 and 4.5 hr for increasing and decreasing, respectively. Effect from the feed flow change, the temperature at 11st stage (Figure 3.51a) changes because of changing feed flow can disturb the temperature in the column and its heat duty adjusted to maintain the product composition. The temperature response reaches to new set point within 3.9 hr. Figure 3.51b shows the reboiler level response which has offset because effect of P controller. The changing of reboiler level from the original set point to be the new steady state within 4.5 hr is not a problem because it slightly affect to process.
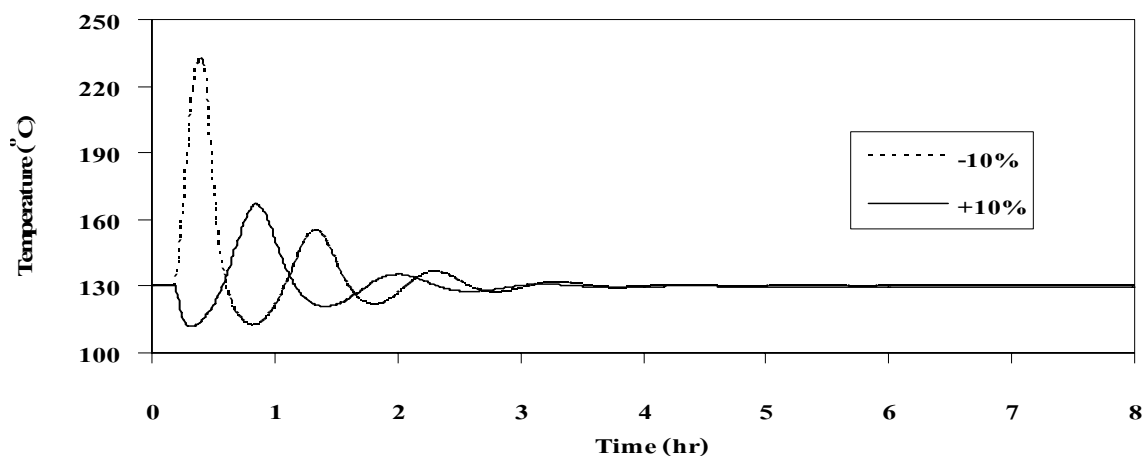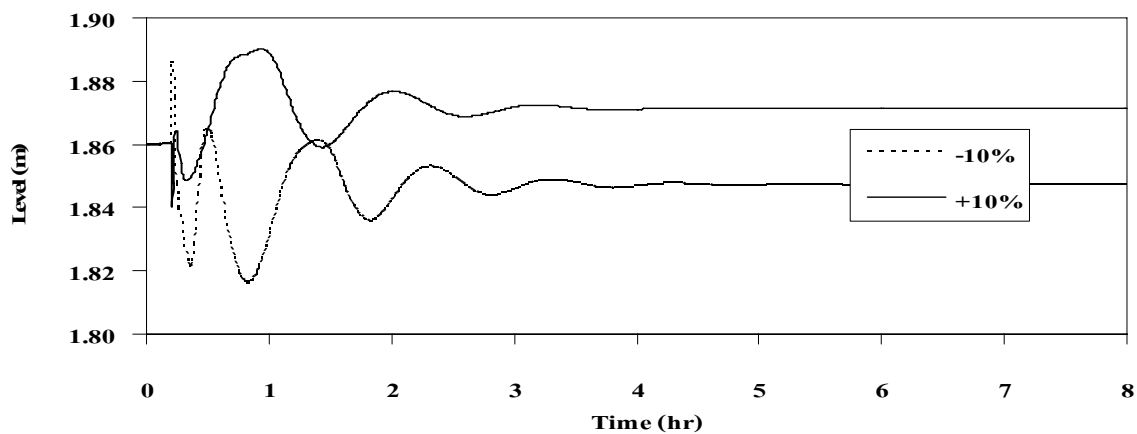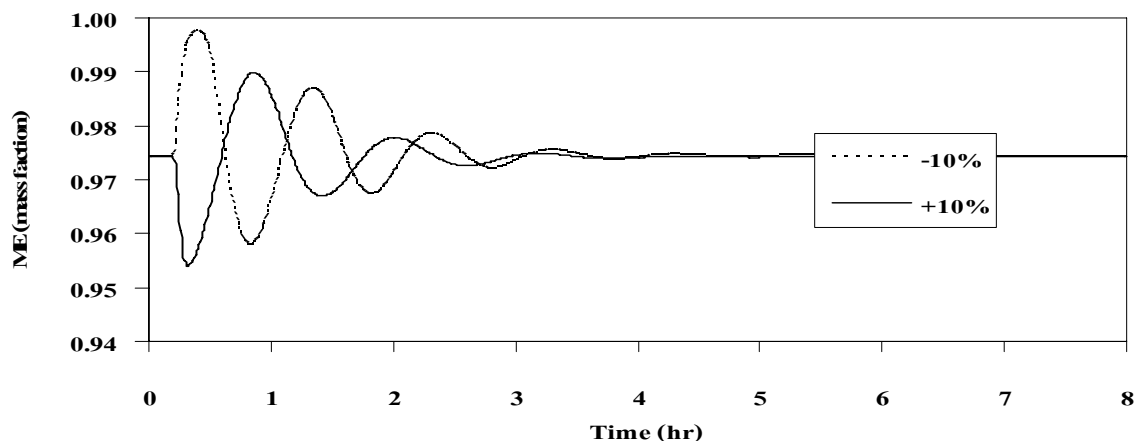
Figure 3.51 Dynamic response of ±10% feed flow rate of CS1

(a) Temperature (b) Level (c) ME (mass fraction)

3.3 Control structure II (CS 2)

This control structure is based on the CS1. The control variable is changed from the product composition plus reboiler level to temperature at 11st stage plus reboiler level. The manipulated is the same with the CS1.

(a)

(b)

(c)
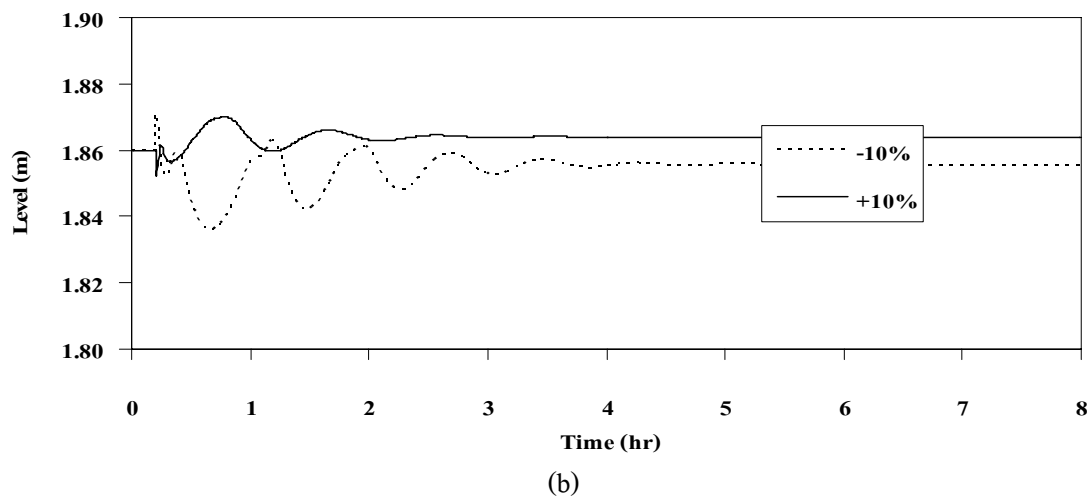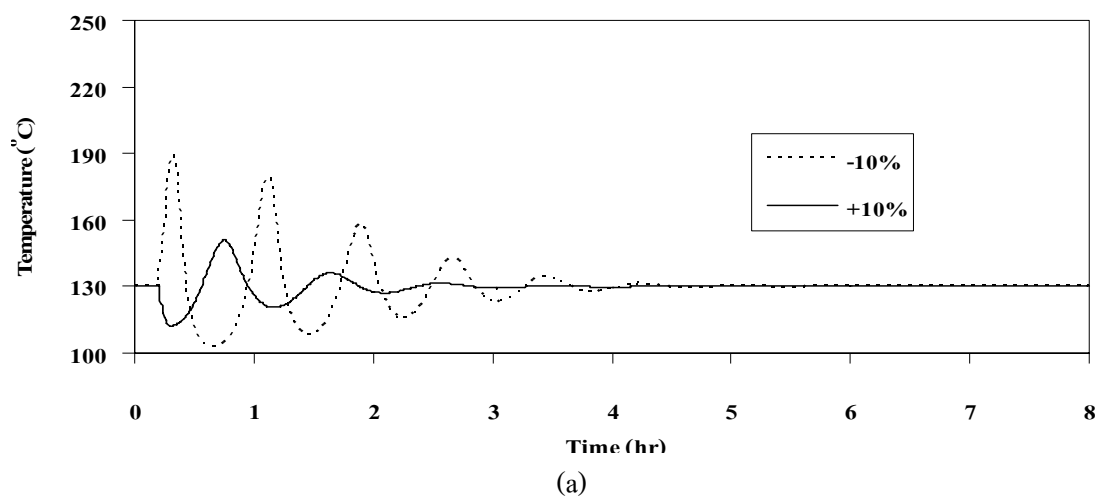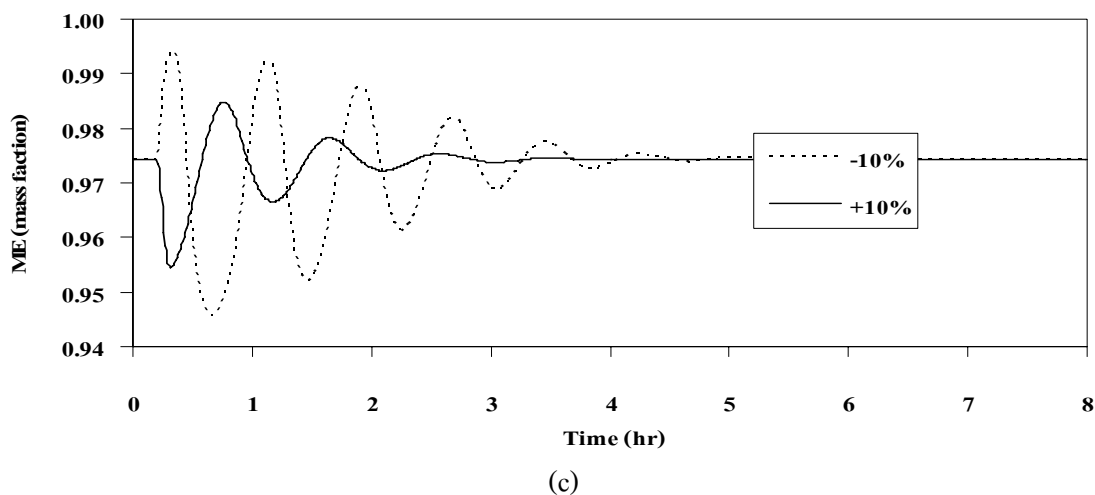
Figure 3.52 Dynamic response of ±10% oil flow rate of CS2

(a) Temperature (b) Level (c) ME (mass fraction)

The parameters changing of CS2 are the same with CS1. All controllers adjusted themselves to eliminate disturbance for maintain stability of system. Figure 3.51 shows simulation result for changing ±10% oil flow rate of CS2. The response of system is oscillatory when the feed is changed. The temperature, level and mass fraction of ME response come to set point within 4.75, 4.85 and 5.22 hr, respectively, when the feed is increased. For the contrast change, the responses reach to steady state within 3.16, 2.64 and 3.63 hr. Although, the response of CS1 is faster than CS2 its response has overshoot more than CS2. From this reason, the higher temperature affect to amount of utility is increased. Furthermore, it may cause material degradation and equipment damage. So, the temperature control can be used for control composition instead of composition control.

3.4.6 Conclusion

The study of the control strategy for a biodiesel production process by RD column is established. Two conventional control structures (feed flow disturbance) have been designed. The keys of controlling the column are to maintain the quality of the bottom product. The result shows that the dynamic performance of both control structure are satisfy. Although the system has both disturbance and set point change, a controller still brings the output back to the set point. However, the temperature controlling of CS2 has overshoot less than the composition controlling of CS1. It is found that the composition can be controlled by temperature controlling.

CHAPTER 4

SUGGESTIONS

4.1 Steady state simulation

1. In this study, kinetic constants are obtained by least square method by solver in Excel. The results from the simulation process are different from the experiment. Therefore, it must be tested to determine the kinetic constants more precisely.

2. The study process is assumed to have only 3 consecutive reactions. In the real, the process also has side reactions. All reaction also affect to the biodiesel production. Therefore, it should be studied increasing the reaction in the process model to the more same real process.

3. The representatives of palm oil composition has only olein that were estimated properties from the molecular weight and structure. The results of the steady state simulation will be more accuracy if the real properties of these representative oils were input. It can be available from experiments.

4.2 Experimental of transesterification with reactive distillation column

1. The purity of product still has lower than the standard. It should improve the process and the equipment to increase the purity of the product.

2. The reactive distillation column in the experiment should be designed to support the operation in a wide range. To reduce the various problems such as reduce the height to the vapor of methanol can easy distillate, increase the width to facilitate the movement of liquids and gases and prevent the problem of flooding.

3. Heat source at the reboiler should be enough efficiency to offer heat to maintain the system temperature. And also, the temperature swings in narrow range.

4. To prevent the glycerol accumulate in the system, pulling the products from the system should be faster than the separation of the product.

5. Before start the experiment, the column must be checked the leakage, the heaters and the thermocouples.

4.3 Dynamic control simulation

1. This process investigation is a potential candidate for feedback control studies. With the feed forward controllers in place for the model, these controllers can be implemented and improve plant operations.

2. Investigation can also be done in finding out if choosing different set of controlled and manipulated variables gives any possible advantage over the present work.

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Appendix

Appendix A

Calibration curve of pump
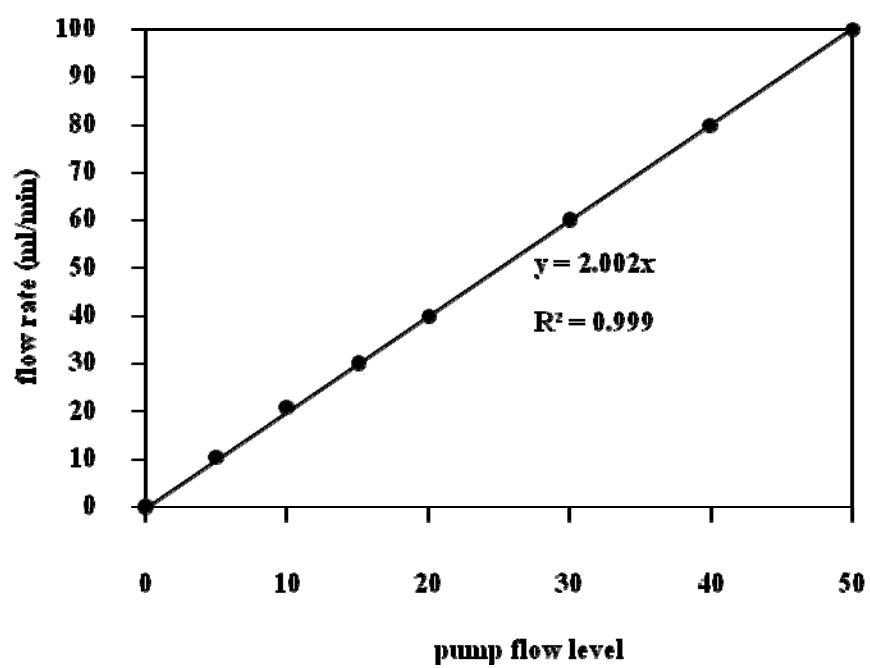
1. The results of calibration bottom product pump.

Figure A1. Calibration curve of product pump
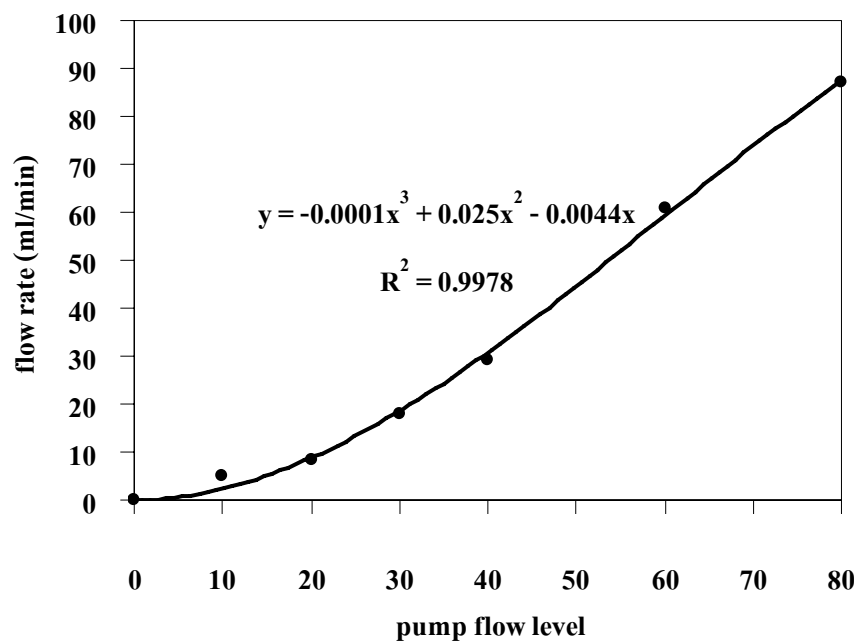
2. The results of calibration palm oil (80°C) pump.

Figure A2. Calibration curve of palm oil (80°C) pump

3. The results of calibration methanol pump.
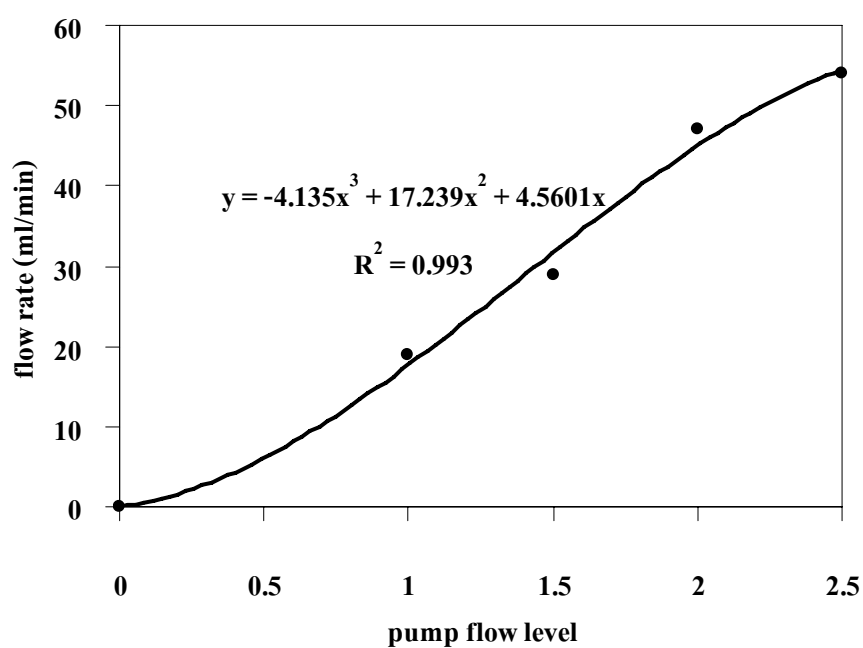

Figure A3. Calibration curve of methanol pump

Appendix B

Material Balance Calculation

1. Calculation of Methanol loss

Material balance of the methanol in total process:

The oil feed rate 900 ml/hr	=	0.973	mol/hr
$\therefore$ The methanol feed (ratio 4:1 by mol)	=	3.894	mol/hr
The methanol is use in the reaction (stoichiometric)	=	2.921	mol/hr
The theory residue methanol	=	0.974	mol/hr
The real residue methanol (20.70 g/hr)	=	0.647	mol/hr

The methanol loss $\quad = \quad 0.974 - 0.647 \quad = \quad 0.327 \quad$ mol/hr

$$\% \text{ methanol loss} \quad = \quad \frac{0.327}{3.894} \text{ x } 100 \quad = \quad 8.39\%$$

2. Calculation of KOH balance

Material balance of the KOH in total process:

The KOH feed rate $\quad = \quad 8.19 \quad$ g/hr

The quantity of theory soap:

$$\text{The maximum soap (g)} \quad = \quad \frac{\text{purity of KOH x KOH (g / hr)}}{\text{MW of KOH}} \text{ x MW of soap}$$

$$= \quad \frac{0.95 \text{ x } 8.19 \text{ g / hr}}{56 \text{ g / mol}} \text{ x } 320.56 \text{ g / mol}$$

$$= \quad 44.54 \text{ g/hr}$$

$$\text{The maximum soap (ppm)} \quad = \quad \frac{\text{max soap (g / hr)}}{\text{mass of (oil + KOH + MeOH) (g / hr)}} \text{x } 10^6$$

$$= \quad \frac{44.54 \text{ (g / hr)}}{900 + 8.19 + 59.84 \text{ (g / hr)}} \text{x } 10^6$$

$$= \quad 46010.97$$

The quantity of real soap (ppm) $\quad = \quad 34193.07$

The residue of KOH in system

$$= \frac{(\text{max soap} - \text{real soap})(\text{ppm}) \text{ x MW KOH (g/mol) x mass of(oil} + \text{KOH} + \text{MeOH})(\text{g/hr})}{\text{purity of KOH x MW soap (g/mol) x } 10^{6} \text{ (ppm)}}$$

$$= \frac{(46010.97 - 34193.07)(\text{ppm}) \text{ x } 56 \text{ g/mol x } (900 + 8.19 + 59.84)(\text{g/hr})}{0.95 \text{ x } 320.56 \text{ (g/mol) x } 10^{6} \text{ (ppm)}}$$

$$= \quad 2.10 \text{ g/hr}$$

The quantity of KOH from tritration (ppm) $\quad = \quad 1797.83$

The quantity of KOH from tritration (g) $\quad = \quad \dfrac{968.03 \text{ (g) x } 1797.83 \text{ (ppm)}}{10^{6}(\text{ppm})}$

$$= \quad 1.74$$

$\therefore$ The KOH loss $\quad = \quad 2.10 - 1.74 \qquad \text{g/hr}$

$$= \quad 0.36 \qquad \text{g/hr}$$

Appendix C

Least Square Method

The method of least squares is a standard approach to the approximate solution of over determined systems, i.e. sets of equations in which there are more equations than unknowns. "Least squares" means that the overall solution minimizes the sum of the squares of the errors made in solving every single equation.

The most important application is in data fitting. The best fit in the least-squares sense minimizes the sum of squared residuals, a residual being the difference between an observed value and the fitted value provided by a model.

The method of least squares assumes that the best-fit curve of a given type is the curve that has the minimal sum of the deviations squared (least square error) from a given set of data.

Suppose that the data points are (x_1, y_1), (x_2, y_2), ..., (x_n, y_n) where x is the independent variable and y is the dependent variable. The fitting curve $f(x)$ has the deviation (error), d, from each data point, i.e., $d_1 = y_1 - f(x_1)$, $d_2 = y_2 - f(x_2)$, ..., $d_n = y_n - f(x_n)$. According to the method of least squares, the best fitting curve has the property that:

$$II = d_1^2 + d_2^2 + ... + d_n^2 = \sum_{i=1}^{n} d_i^2 = \sum_{i=1}^{n} [y_i - f(x_i)]^2 = a \ minimum$$

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Presentations

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