MULTIPLICITY ANALYSIS AND CONTROL STRUCTURE DESIGN OF REACTIVE DISTILLATIONS FOR ETHYL TERT-BUTYL ETHER AND BIODIESEL PRODUCTION

By

MR. Kritsanawat PHOLPRASAN

A Thesis Submitted in Partial Fulfillment of the Requirements

for Master of Engineering (CHEMICAL ENGINEERING)

Department of CHEMICAL ENGINEERING

Graduate School, Silpakorn University

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การวิเคราะห์สภาวะคงตัวหลากหลายและการออกแบบโครงสร้างการควบคุมของหอกลั่นแบบมีปฏิกิริยาสำหรับการผลิตเอทิลเทอร์เชียรีบิวทิลอีเทอร์และไบโอดีเซล

โดย
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Title	Multiplicity analysis and control structure design of reactive distillations for Ethyl tert-butyl ether and Biodiesel production
By	Kritsanawat PHOLPRASAN
Field of Study	(CHEMICAL ENGINEERING)
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Reactive distillation column is a combination of reactor and distillation column into a single unit resulting in reduction of equipment and operating cost and higher reaction conversion. However, this also introduces a more complex behavior of the column. This research focuses on multiplicity analysis and control structure design of reactive distillation column. The processes considered include the reactive distillation column for ethyl tert-butyl ether (ETBE) and biodiesel production. Steady-state simulation is performed using Aspen Plus. Sensitivity analysis tool in Aspen Plus is used as detection tools for existence of multiplicity. Aspen Plus Dynamics is used to perform dynamic simulation for the validation of the proposed control structure.

In the study of reactive distillation of ETBE production, input multiplicity can be obviously detected in Aspen Plus while output multiplicity cannot be obviously detected but tentatively appear. In control structure design, the most sensitive stage temperatures are chosen as controlled variables to ensure ETBE product composition. Two control structures including single temperature control and dual temperature control are proposed and validated under disturbance changes of ±5 percent of ethanol feed flowrate. Dynamic simulation shows both control structures can keep the temperatures at the desired value. However, for dual temperature, tight control of ETBE mass fraction is possible.

In the study of reactive distillation of biodiesel production, input multiplicity can be obviously detected in Aspen Plus while output multiplicity is not detected. In control structure design, the most sensitive stage temperatures are chosen as controlled variables to ensure methanol composition in distillate stream.

Two control structures including single temperature control and dual temperature control are proposed and validated under disturbance changes of ±5 percent of free fatty acid feed flowrate. Dynamic simulation shows both control structures can keep the temperatures at the desired value. However, for dual temperature, tight control of methanol mass fraction is possible.

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Kritsanawat PHOLPRASAN

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CHAPTER I

INTRODUCTION

1.1 Motivation

Reactive distillations combine chemical reactions and distillations together in one unit. This results in several advantages such as reduction of a unit operation, improvement of selectivity and conversion by continuously removal of products. However, this may yield a more challenging task for control system design. Furthermore, the interaction between reactions and distillations can exhibit highly non-linear behavior resulting in multiple steady-states or multiplicity.

There are two types of multiplicities including output multiplicity and input multiplicity (Kumar and Kaistha 2008). Output multiplicity refers to the case when the fixed inputs correspond a multiple set of outputs. The set may establish stable or unstable behavior. On the other hand, input multiplicity indicates that for fixed outputs, a multiple set of inputs are possible. Output multiplicity may cause a drifting of system to an undesired region while input multiplicity can lead to wrong control action or reversal signal of controller due to the change of sign of process gain. These types of multiplicities should be explored and understood when designing control structure in a reactive distillation.

Dynamic behavior of the whole plant may change considerably from the behavior of individual units. In design of control structure of an integrated process, a plantwide perspective is needed. Plantwide control design are interesting in an industry. Under a number of disturbances and complex behavior in an integrated plant, it is a challenging task to design control structure for safety, smooth operation, satisfaction of product quality in an optimal manner.

In this research, the analysis of multiplicity and control structure design of reactive distillations will be conducted. In particular, the reactive distillation of ethyl tert-butyl ether (ETBE) and supercritical biodiesel production will be focused.

Reactive distillation of ETBE production can exhibit highly nonlinear behavior resulting in both output and input multiplicities and hence is a good benchmark for the multiplicity study. For biodiesel production, up to the author's knowledge, multiplicity of biodiesel production via reactive distillation has not been investigated in the literatures.

1.2 Objective of Research

1.2.1 Analysis of multiplicities of reactive distillations for ETBE and biodiesel productions.

1.2.2 Control structure design of reactive distillations for ETBE and biodiesel productions.

1.3 Scope of research

1.3.1 Perform steady-state flowsheeting of reactive distillations for Ethyl tert-butyl ether (ETBE) process and biodiesel production via Aspen Plus.

1.3.2 Investigate multiplicity behavior of reactive distillations for Ethyl tert-butyl ether (ETBE) process and biodiesel production.

1.3.3 Design control structure of the reactive distillations for Ethyl tert-butyl ether (ETBE) process and biodiesel production.

1.3.4 Perform dynamic simulation to test the proposed control structure via Aspen Plus Dynamics.

1.4 Contribution of Research

1.4.1 Understanding of output and input multiplicity of reactive distillations.

1.4.2 Control structure of reactive distillations for Ethyl tert-butyl ether (ETBE) process and biodiesel production.

CHAPTER II

THEORY AND REVIEW OF LITERLATURES

2.1 Theory

2.1.1 Control structure

The control structure aspect on design for complete chemical plants is known as plantwide control. The targets of control structure design usually concerns product quality, smooth and safety operation and pollution emission. Many articles proposed various methods for plantwide control design. However, these methods can be categorized into two groups including heuristic design and mathematical design methods.

Heuristic design methods are based on various experiences and understanding of processes. A heuristic step by step approach, integrated framework of simulation and heuristics (Zhang, Vasudevan et al. 2010) proposed and implemented for control structure design and evaluation of ammonia synthesis plant and biodiesel production from waste cooking oil (Patle, Ahmad et al. 2014).

Another method is mathematical design method. The article of control structure design for complete chemical plant (Skogestad 2004) proposed concept of mathematics in systematic design produce including top-down analysis and bottom up design. Top-down analysis includes definition of operational objective and determination of available control degree of freedoms in the plants. Bottom up design section starts with the stabilizing control layer and moving up supervisory control layer. The procedure can be iterative until the design from top-down and bottom-up converge together.

Perspective is also important for control structure design and can be used for systematic analysis (Downs and Skogestad 2011). (Downs and Skogestad 2011)proposed an industrial and academic perspective on control structure design consisting of three decisions: *decision 1*: select controlled variables and determine

the manipulated variables, *decision 2*: determine throughput manipulator (TPM) and *decision 3*: determine control configuration by pairing of controlled variables and manipulated variables.

Determination of control degree of freedoms (CDOF) is one of important step about control structure design. (Luyben 1996) proposed a simple method for determination of control degree of freedom or independent variables by counting the number of control values. A more comprehensive method is proposed by (Konda, Rangaiah et al. 2006).). It is based on the concept of restraining number. Control degree of freedoms are total number of streams in that process subtract sum of the restraining numbers for all the units in process, where restraining number is minimum number of flow rate that cannot be manipulated.

2.1.2 Input-Output Multiplicities

From the perspective for improve the control design on input and output multiplicity or nonlinear behavior can be divided between input and output multiplicity. The concept of input multiplicity is more output are results from the same input demonstrated in this figure 1 and concept of output multiplicity is more input are results from the same output demonstrated in figure 2

Multiplicities are often established in this complicate unit then complicate unit have more multiplicity consists input multiplicity and output multiplicity or nonlinearity behavior is reactive distillation because reactive distillation are combine between separation unit and reaction unit in one unit therefore identify complicated unit. In complicate unit have sensitive for input and output multiplicity or nonlinearity behavior are more difficult to develop scenario in reactive distillation for design controller since it send the command signal are reversal action or wrong action in feedback controller.

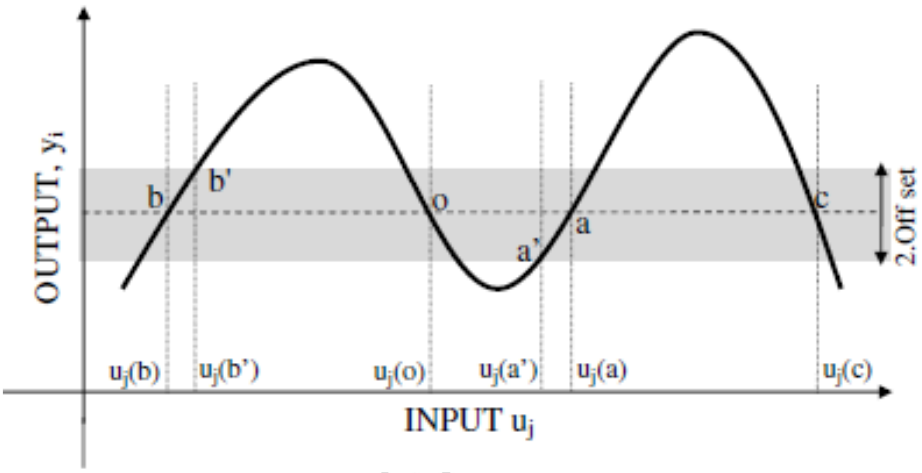


Figure 1 Input-Output relation with input multiplicity (Kumar and Kaistha 2008).

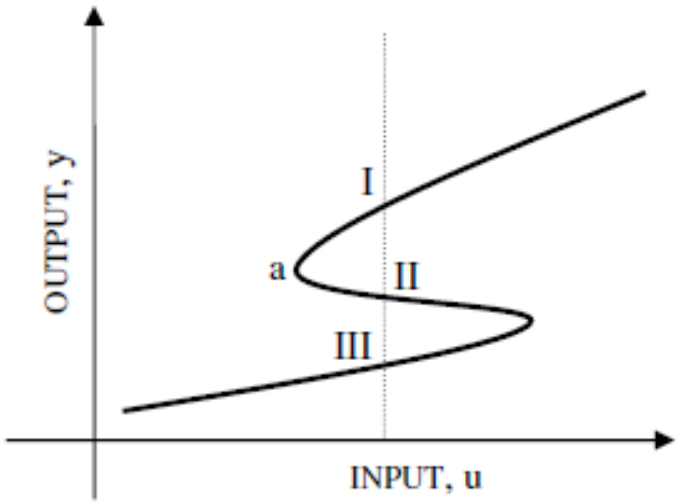


Figure 2 Input-Output relation with output multiplicity (Kumar and Kaistha 2008).

Therefore affect to controller action send reversal or wrong signal to complicate unit operation especially reactive distillation are more interested. Since signal from controller reversal or wrong when controller are detected disturbance in this process then controller control manipulated variable adjust to controlled variable for tracking set point especially in input multiplicity. Input and output multiplicity are problem of controller so in this article was studied about role of multiplicity in reactive distillation control system design (Kumar and Kaistha 2008) propose concept in control system design for avoid input and output multiplicity or nonlinear behavior in reactive distillation because variables section affect to behavior

in this process if select the right variable can be improve the process for avoid input and output multiplicity.

Common variables affect to input and output multiplicities are in section manipulated variables fresh feed rates, reboiler duty and reflux rate or reflux ratio. And controlled variables are tray temperature or composition. In this article propose when avoid output multiplicity by offer range of reboiler duty establish output multiplicity whenever selected fixed reflux ratio so reflux ratio is manipulated variable policy eliminate output multiplicity. And propose range ability calculation in this input multiplicity in this process for prevent controller send reversal control signal. In additional article investigated about multiplicity analysis in reactive distillation column using Aspen plus (Bolun, Jiang et al. 2006).

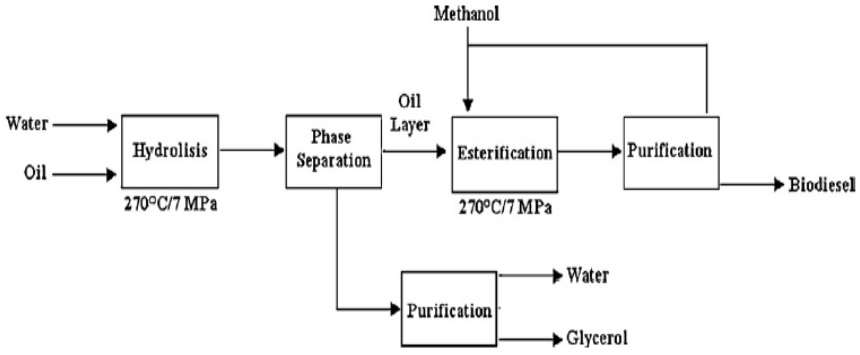


Figure 3 Simplified diagram of the two-step supercritical methanol process (Gomes Castro et al., 2010)

Consider multiplicity in reactive distillation under sensitivity analysis of aspen plus program by study each important parameter affect mole fraction of desire product then design controller send controller action avoid range arise input-output multiplicity.

2.1.3 Biodiesel production

Biodiesel are renewable and sustainable process fuel since biodiesel are produced from free fatty acid such as vegetable oil. Since biodiesel are alternative diesel fuel that attracted increase interest because biodiesel friendly environmental. Conventional biodiesel production consists transesterification of triglyceride to

produce free fatty acid and second reaction section are free fatty acid react with methanol to produce biodiesel and both reaction using catalyst. Consequently in recently articles are improve biodiesel production process in supercritical condition for avoid catalyst and reduces the number of separation of catalyst in figure 3 of biodiesel process (Gomes Castro et al., 2010)

2.1.4 Ethyl tert-butyl ether (ETBE) production

Ethyl tert-butyl ether (ETBE) is increase octane enhancer agent and a gasoline oxygenate in engine. ETBE are produced from isobutene react with ethanol so two raw materials in this process are biomass renewable source and friendly environmental and no pollution then ETBE more interested in this present. In additional ETBE production process was improved by use reactive distillation substitute reactor and separator. By reactive distillation are combine reaction section in isobutene react with ethanol and separation section are separate ETBE product and contaminate in this process.

2.2 Review of literature

2.2.1 Control structure

The control perspective are more importance in an industrial since in chemical plant are perform to maintain conditions of process in target.

Skogestad (2004) studied model of systematic control structure design for chemical plant consists two steps are step (I): Top-down analysis main concern about definition and step by step to found operating target, manipulated variable, controlled variable and production rate in chemical plant another step are step (II): Bottom-up design main concern behavior of process, control loop in this process consist algorithm of model(PI, PID, etc.), type of control loop (centralized or decentralized) include input-output pairing of variables.

Downs and Skogestad (2011) investigated perspective on plantwide control base on economic production by created step on plantwide control design consider in three decision are decision 1: selection of controlled variables affect to good performance and stable operation by identify the objective in operation and

constraints in this process consists two mode maximum throughput is operate at maximum performance since will know high production in process and optimal throughput is operate in condition depend on plant economic then select controlled variables are follow the objective after that determine the manipulated variables, decision 2: determine local of throughput manipulator (TPM) by concept of location throughput manipulator are input of bottleneck unit and inside the recycle system decision 3: determine control configuration pairing with interconnects between controlled variables and manipulated variable by good CVs and MVs are direct connect when adjust MV affect to CV immediate.

Luyben (1996) studied about design and control degree of freedom. In this work the degree of freedom are more importance of chemical process because it leads to determine manipulated variables. Design of degrees of freedom are find number of variables in this process subtract number of equation. So in this individual unit in this way are easy to find it but in this complex plant are difficult to find design degree of freedoms. Therefore in article is purpose the control degrees of freedoms are variables can be controlled in this process from discussion in only steady-state process as variables of stream flow rate so stream flow rate in this process depend on control valve. Whenever control degrees of freedoms was determined by count the number of control valve in this plant.

Konda, Rangaiah et al. (2006) studied about the control degree of freedom (CDOF). Since control degree of freedom is one of importance in control structure system. In this work purpose find equation maximum number of control degree of freedom (maximum number of flow rate can be manipulated in process) because control degree of freedom was founded from count control valve (Luyben 1996) are difficult practical solution at plantwide control design since process flow diagrams needs to be known the control degree of freedom before placing the control valves in this process. The point of article is restraining number is minimum number of flow rate cannot be manipulated in unit (total number of independent and overall material balance with no associated inventory). Equation for explain the control

degree of freedom are total number of streams in that process subtract sum of the restraining numbers for all the units in process.

Skogestad (2000) investigated real time steady state optimization. Determine in optimal operation consider in stabilize and keep the controlled variables within constraints of process. By define the objective function is cost operate was minimized then respect on loss in implementation of process so loss (L) is defined actual value of cost operate function (J(Cs)) minus truly optimal value of cost operate function (Jopt). Therefore in this article is respected on the self-optimization control is achieve acceptable of loss with depend on constant set point value (Cs) for controlled variables.

Jagtap and Kaistha (2012) investigated in the topic economic plantwide control C4 Isomerization. By follow concept of plantwide control system design respect on economic operation at large throughput of rage C4 isomerization process consists two mode are optimum throughput (Mode I) and maximum throughput (Mode II). So Mode I throughput is fixed because depend on demand or supply then consequent decrease one degree of freedom and mode II are operated at maximum throughput remain degree of freedom more than mode I is one variable.

Hung, Chen et al. (2010) studied control plantwide of reactive distillation for hydrolysis transesterification and two-stage esterification. In this work produced follow control structure respect on temperature and temperature-composition control deal with the two disturbance scenario as changes in the feed flow rate and reactant composition to find good robustness control and dynamic performance. In this article implement under feedback control with maintain stoichiometric balance. The control structure produced by seven step are establish control objective, determine the degree of freedom, setting the throughput, find ratio of recycle flow of the reactant to limit fresh feed, maintain composition balance via feedback control, operate the temperature and temperature-composition control and tune the controller of the process under two scenario disturbance, optimize the control objective.

Wang, Wong et al. (2008) investigated design and control of transesterification via reactive distillation with thermal coupling for the methanol and n-butyl acetate production. Since reactants of process consists methanol and methyl acetate are formed azeotope point so in this process must be operated ate high energy consumption for normal reactive distillation. Therefore in this work must be reduce to energy consumption by using the reactive distillation with thermal coupling as the partial thermal coupling are eliminate the condenser in the second column if preparation with conventional process. The design of reactive distillation with thermal couple have four designs degree of freedoms: reflux ratio and boil up flow of the reactive distillation column and boil up flow of side stripper column and liquid split ratio in only two product component reverse into reactive distillation column. In article reflux and liquid split are used minimize boiler duties in both column while remain two degree of freedoms are used for respect on purity specifications. The result reactive distillation with thermal couple is not only reduce the energy consumption but can be operate and control are better.

Shen, Cheng et al. (2011) studied in this topic design and control of biodiesel production processes with phase split and recycle in the reactor system. In this work propose two processes are conventional process and process modified of biodiesel production. Both processes are different conventional process not instead recycle glycerol section but another process are instead recycle glycerol section. The result from the article process modified of biodiesel production (instead glycerol section) are reduction 20% of total annual cost since recycle glycerol phase back to the reactor will have increase amount of methanol to react with the triglyceride. Therefore instead recycle glycerol section are reduced cist because decrease cost of feed methanol react with triglyceride. In part of control design are selection of temperature tray control in 4th tray since from sensitivity analysis was performed 4th tray are more sensitive on composition control by manipulated variable is reboiler duty of reactor. Type of controller are using PI decentralized control mode.

Zhang, Vasudevan et al. (2010) investigated plantwide control system design and performance evaluation for ammonia synthesis process. The article was followed

from formulated the integrated framework of simulation and heuristics (IFSH) for design of plantwide control. By divide two mode were studied mode I optimum throughput and mode II maximum throughput. Article proposed follow step level 1-2 are compile the detail before select control loops, level 3-5 are study the controlled variables and pairing with manipulated variables, level 6-7 are investigated effect each loops and level 8 is implement on control system performance. Descript of each step are level 1.1: Define PWC objective, level 1.2: Determine control degrees of freedom (CDOF), level 2.1: Identify and analysis plantwide disturbances, level 2.2: Set performance and tuning criteria, level 3.1: Production rate manipulator selection, level 3.2: Production Quality manipulator selection, level 4.1: Selection of manipulator for more severe controlled variables. Level 4.2: Selection of manipulators for less severe controlled variables, level 5: Control of unit operation, level 6: Check material composition balances, level 7: Investigate the effects due to integration, level 8: Enhance control system performance with remaining CDOF. After the followed formulated the integrated framework of simulation and heuristics (IFSH) are performs better in term control production rate.

2.2.2 Input and Output multiplicities

The control structure design are determine condition of unit operation and value of manipulated variables and controlled variables are paired for avoid multiplicity or nonlinearity behavior and high production performance.

Kumar and Kaistha (2008) studied about role of multiplicity in reactive distillation control system design. Since multiplicities were problem in control structure design of reactive distillation because when controller detect disturbance and set point tracking then send the signal for tuning manipulated variable if in this process establish multiplicity behavior the controller action from controller is “reversal or wrong”. Therefore multiplicity are more problem for reactive distillation so must studied value of variables affect to multiplicity then improve controller for avoid multiplicity in reactive distillation process. The first result from case study is methyl acetate production via reactive distillation from the case studied have a two importance variables test affect to avoid multiplicity for controller design are reflux

rate and reflux ratio. From article fixed reflux ratio are eliminate output multiplicity from reactive distillation by manipulated variable is reboiler duty and controlled variable is temperature of 18th tray. Second investigated from case study are aspect on three cases candidate control structure from sensitivity analysis from aspen plus program: CS1 (CV-MV) T18 - acetic acid, T34 – methanol and production rate handle from reboiler duty, CS2 (CV-MV) T18 – reboiler duty, T34 – methanol and production rate handle from acetic acid and last candidate CS3 (CV-MV) T18 – reboiler duty, T34 – acetic acid and production rate handle from methanol. Result from second section CS2 is leading to sensitive fast response from controller action very well.

Kim and Han (2012) studied dynamics and control of reactive distillation under multiple steady state based on a nonlinear wave theory. From the article propose alternative way for suppose avoid multiple steady state or multiplicity in reactive distillation are wave theory since multiple steady state have more reactive distillation processes. Wave theory from this work are propose material balance, local and direction for each component to determine the wave position then improve controller when action on manipulated variable with controlled variable for avoid multiplicity. In this work are respect on methyl acetate production via reactive distillation under multiple steady state condition. The result are fixed reflux ratio and fixed different temperature on through each zone of reactive distillation (rectifying section and stripping section) can be inhibit multiplicity behavior in reactive distillation. The result from modified control structure are fast and smooth response from controller action.

Bolun, Jiang et al. (2006) studied multiplicity analysis in reactive distillation column using aspen plus. In this wok respect on multiplicity in reactive distillation combine between reactor and separator since recently reactive distillation are most interested because reduce the total cost however reactive distillation are combine both unit so complicate unit can be exhibit nonlinear phenomena or multiplicity. Multiplicities are divide two case base on multiple value of input or output by multiplicities affect to control action when detect the problem in this process under multiplicities rang then it send reversal signal so reversal signal is “wrong” the

control action. Therefore in this article are studied the multiplicities rang then avoid multiplicities rang and determine value of parameter for suppose avoid multiplicity. In this case study from article is ethylene glycol production from hydration of ethylene oxide (EO) in reactive distillation from this case in conventional process. The condition established are output multiplicity. The result from ethylene glycol production arise output multiplicity was a produced with various and rang of operation parameters are liquid holdup and reflux ratio. The parameter setup for avoid output multiplicity is boil-up ratio and operate in another rang of operation parameter do not establish output multiplicity in this process.

2.2.3 Biodiesel production

Biodiesel production are a renewable and sustainable substitute of the diesel fuel more than petroleum fuel. Since feedstock from biodiesel is free fatty acids are produced from triglyceride by hydrolysis reaction. And free fatty acid react with methanol are produce biodiesel production.

Marchetti and Errazu (2008) studied about techno economic study of supercritical production plant. In this work are respect on supercritical biodiesel production so supercritical production can be operate in high temperature, high pressure and not used catalyst is comparison with three different catalyst processes were studied : homogeneous alkaline catalyst with acid pre- esterification, only homogeneous acid catalyst and heterogeneous solid catalyst. In this work propose on objective about economic operation consist cost of raw material, equipment, utilities and the price of biodiesel. The result from this work the supercritical biodiesel productionis suitable in alternative aspect for biodiesel production because in this process not used catalyst. However in this term economic comparison with three different catalyst processes then supercritical biodiesel production is high energy consumption and high annual cost.

Cho, Kim et al. (2012) investigated about techno economic study of a biodiesel production from palm fatty acid distillate. The process of biodiesel production is operated in severe value of condition are high temperature and high

pressure and large molar ratio of methanol. The reaction are interest in free fatty acid react with methanol. Beside in this work aspect on economic operation. The result evaluation by sensitivity analysis in economic operation in noncatalystic of esterification method produce biodiesel and respect in economic parameters are value of Net present value (NPV) and payback period (PBP) base on global price consists raw material cost, utilities cost and price biodiesel product in the commercial. The value of economics are exhibit in this article.

Gomez-Castro, Rico-Ramirez et al. (2010) investigated about topic feasibility study of a thermally coupled reactive distillation process for biodiesel production. In this work offer improve process from conventional process of biodiesel via reactive distillation. Since conventional process consists of biodiesel are consist transesterification of triglyceride and esterification of fatty acid produce biodiesel. The modified process improve in esterification of reactive distillation unit by operate at supercritical condition eliminate catalyst in this process and reduction of separation catalyst unit. However only supercritical of reactive distillation must need the energy consumption of the process. Thus in this work are improve supercritical reactive distillation to thermally coupled reactive distillation for biodiesel process. By intended prefractionator column for decrease energy consumption since prefractionator is recycle the component into the main column for rise reaction. The result in this work are save energy consumption and high purity of biodiesel; product.

Patle, Ahmad et al. (2014) studied about plantwide control of biodiesel production from waste cooking oil using integrated framework of simulation and heuristics (IFSH). In this work are find control structure design biodiesel process from follow step by step from integrated framework of simulation and heuristics (IFSH) method. Since biodiesel process are interested in recently because biodiesel is friendly environmental than fossil fuel since sources of biodiesel made from vegetable oil animal fat and waste cooking oil are produce biodiesel. Therefore biodiesel must to improve performance of process by IFSH method. Proposes from this work step level 1-2 are explore the data before choose control design, level 3-5 are investigate the controlled variables and pairing with manipulated variables, level

6-7 are studied effect each loops and level 8 is implement on control system performance. The result from step are level 1.1 define plantwide control objective about minimum operating cost, level 1.2 find the number of control degrees of freedom are 67 of control degrees of freedoms, level 2.1 identify and analyze plantwide disturbance so disturbance from biodiesel process are flow rate was defined, level 2.2 setting the performance and tuning criteria on each controller, level 3.1 selection of production rate manipulator location in this biodiesel process in recycle loop, level 3.2 selecting the manipulator for control product quality in biodiesel process, level 4.1 find the more severe controlled variables and selection manipulated variables directly affect to more severe control value, level 4.2 find the less severe controlled variables and selection manipulated variables directly affect to less severe control value, level 5.2 test biodiesel process by testing from individual unit, level 6.2 recheck component material balances, level 7 study effect of integration cover biodiesel process, level 8 improve enhance control system performance with remaining of control degrees of freedom. Consequently from follow IFH method the implement in this biodiesel process are suitable control loop.

Gomes Castro et al., (2013) investigated in this topic about simulation study on biodiesel production by reactive distillation with methanol at high pressure and high temperature: impact on costs and pollutant emissions. The supercritical biodiesel production are interest process since supercritical biodiesel process not used catalyst so friendly environmental than biodiesel conventional process and supercritical biodiesel process have advantage than biodiesel conventional process are reduce separation catalyst in process and decrease pollution emission. In this work are divide in simulation of each section are hydrolysis step, esterification step involving reactive distillation and the last section purification of glycerol. And estimate pollution emissions. The result from studied in this work are interest in cost are conventional process of biodiesel production less than supercritical biodiesel production process because conventional process operate at normal condition. However result in this pollution emission section of the supercritical biodiesel

production are have a little bit of pollution emission when prepare with conventional biodiesel production.

Gómez-Castro, Rico-Ramírez et al. (2011) studied about esterification of fatty acids in thermally coupled reactive distillation column by the two-step supercritical methanol method. This work compare four processes are fist process biodiesel production by the conventional supercritical methanol method, second process biodiesel production use supercritical methanol method via reactive distillation, third process is biodiesel production by supercritical methanol method using reactive Petlyuk column and the last process of this work is biodiesel production by the supercritical methanol method using the reactive thermally coupled direct sequence by in this work respect on operating cost and estimate carbon dioxide emission. The result from this work biodiesel production by the supercritical methanol method using the reactive thermally coupled direct sequence are lower than in this topic carbon dioxide emission and operating cost when prepare with three processes.

2.2.4 Ethyl tert-butyl ether (ETBE) production

Jhon and Lee (2003) studied topic dynamic simulation for reactive distillation with ETBE synthesis. Since Ethyl tert-butyl ether (ETBE) is a high octane enhancer agent and a gasoline oxygenate so ETBE more interested. In this work are divide two section interested are steady-state and dynamic using aspen plus program and sensitivity analysis mode for find important parameter and study behavior of each parameter affect to Ethyl tert-butyl ether (ETBE) production process in this work. In addition article are determine configuration and condition for optimal operating of reactive distillation column.

CHAPTER III

METHODOLOGY

In chapter, the methodology for multiplicity analysis and control structure design of reactive distillations for Ethyl tert-butyl ether (ETBE) process and biodiesel production will be described.

3.1 Steady-state flowsheeting

For analysis of multiplicity, it is needed to have steady-state flowsheeting of a process. In this research, Aspen Plus is chosen for this purpose. The flowsheet of ETBE production process will be taken from (Luyben and Yu 2009) as shown in Figure 4 while the flowsheet of biodiesel production process will be taken from (Gomez-Castro, Rico-Ramirez et al. 2013) as shown in Figure 5.

In the flowsheet of biodiesel process via supercritical reactive distillation reported by (Gomez-Castro, Rico-Ramirez et al. 2013), reactant fed into reactive distillation column for production of methyl oleate (biodiesel) are oleic acid and methanol. Supercritical condition in this reactive distillation process are operated at 270oC and 70 bar. This can avoid use of catalyst and eliminate step of catalyst separation.

In the flowsheet of ethyl tert-butyl ether (ETBE) process via reactive distillation reported by (Luyben and Yu 2009), two components considered in feedstock are isobutene (chemically inert n-butene) and ethyl alcohol for production of Ethyl tert-butyl ether (ETBE) in distillation column. Operating condition are 61oC and 7.6 bar.

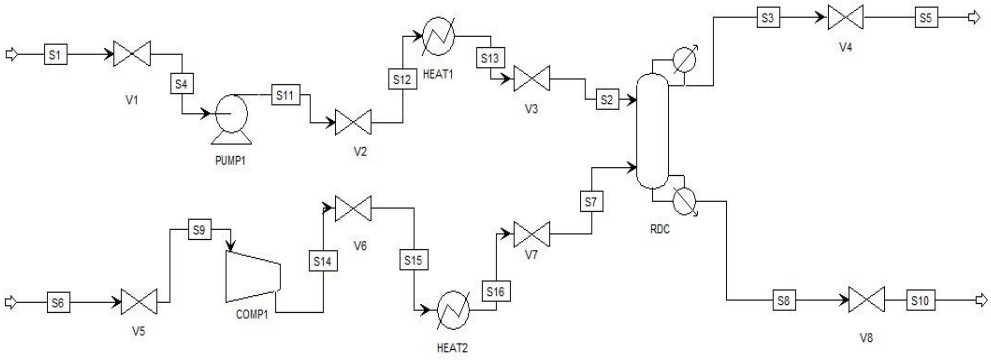


Figure 4 Reactive distillation process for Ethyl tert-butyl ether (ETBE) production (Luyben and Yu 2009)

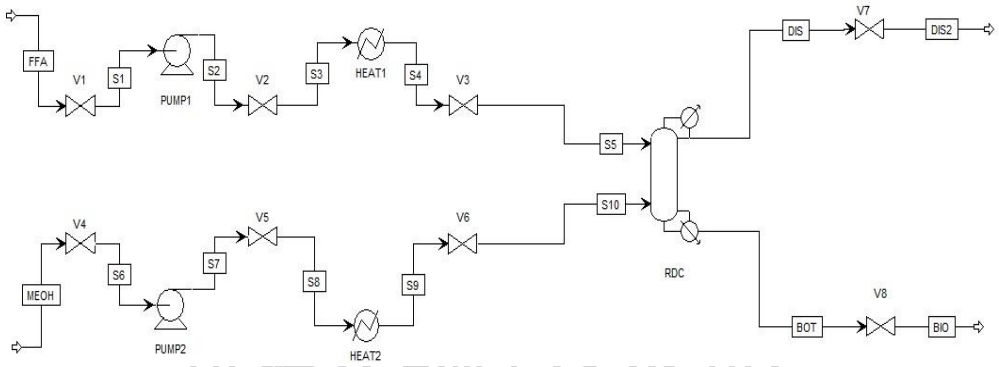


Figure 5 Reactive distillation process for supercritical biodiesel production (Gomez-Castro, Rico-Ramirez et al. 2013)

3.2 Investigation of process behavior

After steady-state flowsheeting, the process behavior will be focused, Steady-state effect of inputs to outputs in reactive distillation will be performed using sensitivity analysis tool in Aspen Plus. The inputs to be considered might include reflux ratio and reboiler duty. Some techniques (Bolun, Jiang et al. 2006) might be required for tracing the existence of input and output multiplicity. Furthermore, effect of equipment design such as number of stages in reactive zone, feed location will also be conducted in this work.

3.3 Preparation for dynamic simulation

The flowsheet created in Aspen Plus can only give insight of process in terms of steady-state simulation. For dynamic simulation, Aspen Plus Dynamics is required.

However, in moving from Aspen Plus to Aspen Plus Dynamics, some additional tasks are required. This includes (a) flowsheet preparation for P-driven mode, and (b) entering of dynamic information such as equipment geometry or size.

To make the dynamic simulation more realistic, Aspen suggests to run in P-driven mode. In flowsheet preparation for P-driven mode, valves must be installed in all process streams for manipulation. Furthermore, Pressure drop of valves must be determined. For dynamic information of reactive distillation, this includes diameter, height, liquid or catalyst holdup and residence time

The parameters required for reactive distillation (RadFrac unit) before exporting to aspen dynamics includes,

1. Reflux drum: vessel geometry consists head type, length and diameter.
2. Sump: same vessel geometry of reflux drum however differ calculate sizing.
3. Hydraulics: tray geometry consists define stage operation and diameter.

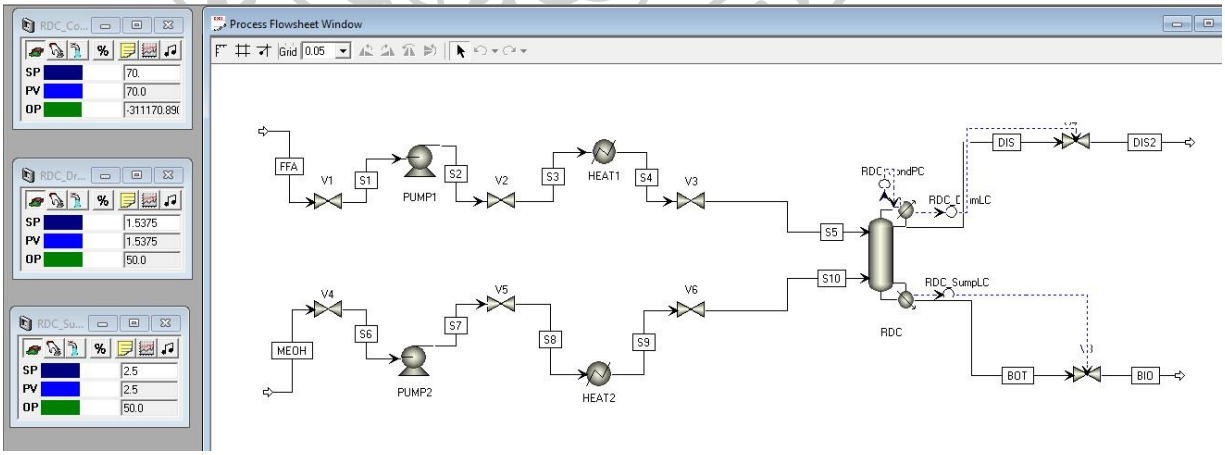


Figure 6 Aspen Plus Dynamics flowsheet of reactive distillation process for supercritical biodiesel production

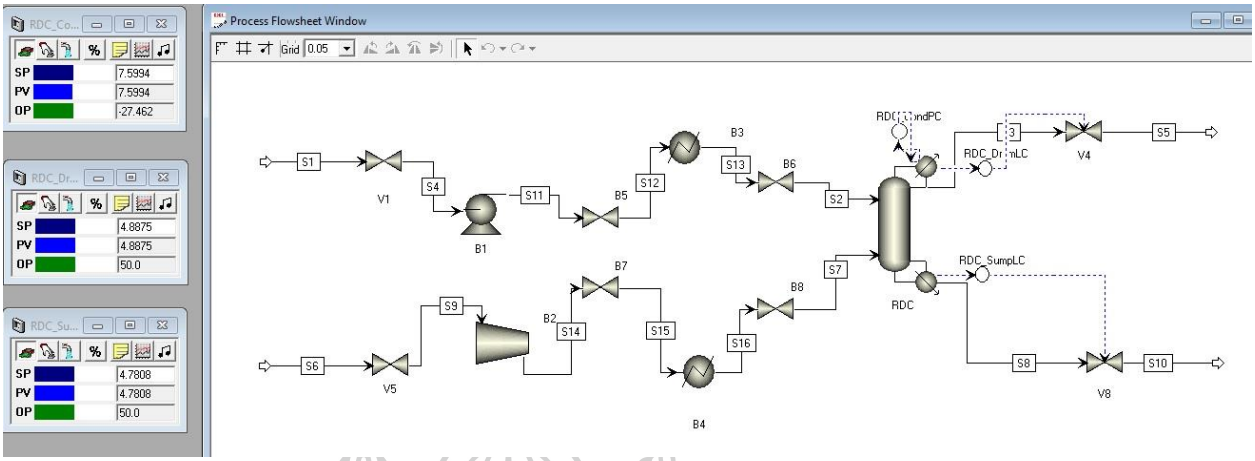


Figure 7 Aspen Plus Dynamics flowsheet of reactive distillation process for Ethyl tert-butyl ether (ETBE) production

3.4 Control structure design

In design of control structure, this research might follow the design procedure of (Skogestad 2004). The procedure consists of 8 steps including Top-down and Bottom-up analysis.

Top-down analysis

1. Definition of operational objective.

2. Manipulated variables and degree of freedom.

3. Primary controlled variable.

4. Production rate.

Bottom-up analysis

5. Regulatory control layer.

    5.1 Stabilization

    5.2 Local disturbance rejection

6. Supervisory control layer.

7. Optimization layer.

8. Validation.

3.5 Dynamic simulation

After control structure design of the processes, dynamic simulation under a set of scenarios will be performed.

Chapter IV

Result and discussion

Steady-state flowsheeting, multiplicity analysis and control structure of the two processes including ETBE and biodiesel production via reactive distillation will be discussed in this chapter

4.1 Ethyl tert-butyl ether (ETBE) process

Sine Ethyl tert-butyl ether via reactive distillation process is complex process and many literatures showed that this process can exhibit multiplicity behaviors, it is a good benchmark for multiplicity study. Ethyl tert-butyl ether via reactive distillation processes reported by (Luyben and Yu 2009) will be studied in this research. The configuration of the column is showed in Figure 8 and Table 1.

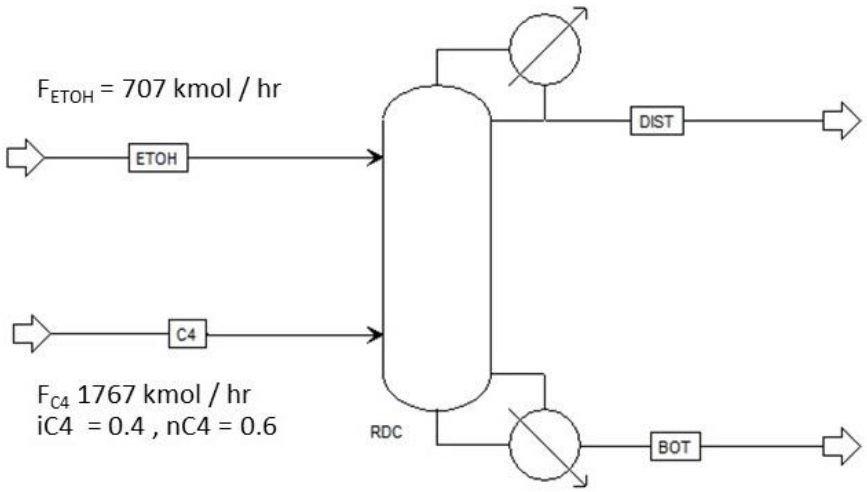


Figure 8 Configuration of Ethyl tert-butyl ether via reactive distillation processes reported by (Luyben and Yu 2009)

Table 1 Configuration of Ethyl tert-butyl ether (ETBE) process via reactive distillation.

Parameter information	Value
Number of stages	25
Ethanol feed stage	6
Butene feed stage	20
Reactive stage	6-20
Liquid holdup (Kg)	1,000
Diameter (m)	4.6
Height (m)	9.14
Pressure on top (atm)	7.5
Reflux Ratio	3
Reboiler duty (MW)	15.2

Table 2 Comparison result between this research and (Luyben and Yu 2009)

Result	Mass fraction of product	Conversion
This research	0.99	99%
(Luyben and Yu 2009)	0.99	99%

Steady-state flowsheeting of the reactive distillation column is performed using Aspen Plus. The property method used is UNIFAC model. The flowsheet is validated with the result from (Luyben and Yu 2009) as shown in Table 2 that mass fraction of ETBE at product stream and conversion of ethanol are equivalent.

4.1.1 Multiplicity analysis

In search of multiplicity, sensitivity analysis toll in Aspen Plus will be used. Reflux ratio and reboiler duty will be system inputs to be varied while output to be observed

4.1.1.1 Effects of reflux ratio and reboiler duty to mass fraction of Ethyl tert-butyl ether

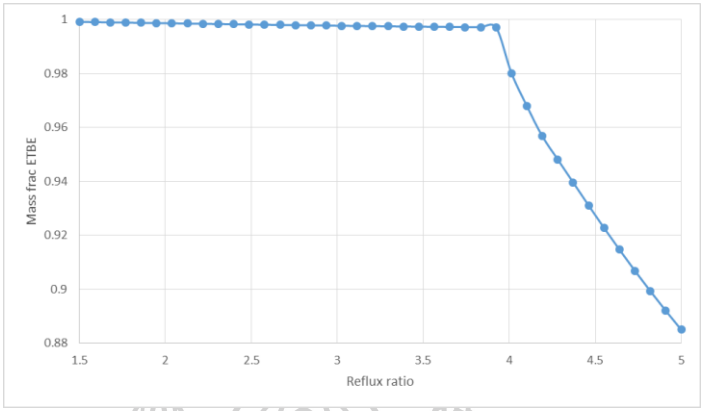


Figure 9 Effect of reflux ratio to mass fraction ETBE for given reboiler duty 15.2 MW

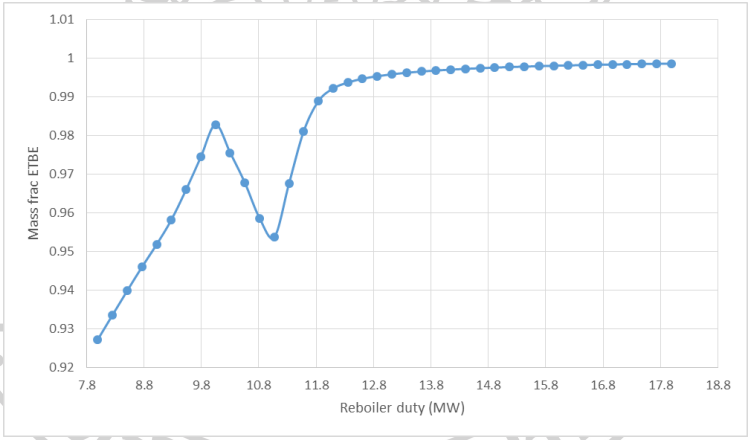


Figure 10 Effect of reboiler duty to Mass fraction ETBE for given reflux ratio 3

Effects of reflux ratio and reboiler duty to mass fraction of ETBE are shown in Figures 9 and 10. In Figure 9, under variation of reflux ratio from 1.5 to 5, there is no establishment of output/input multiplicity behavior. However, in Figure where reboiler duty is varied from 8 to 18 input multiplicity can be observed in range of reboiler duty 9.8-11.8.

4.1.1.2 Effects of reflux ratio and reboiler duty to stage temperatures

In distillation column, stage temperatures are also important outputs. Hence, effects of reflux ratio and reboiler duty to stage temperatures will be explored in this section.

As showed in Figure 11, when reflux ratio is varied from 1.5 – 5 for given reboiler duty 15.2 MW, input multiplicity are not observed. Although output multiplicity is not clearly observed, it is likely to occur due to sharply change of some stage temperatures at reflux ratio around 4.

For given reflux ratio=3, when reboiler duty is varied from 8 to 18 MW, input multiplicity is detected with one and two turning points as shown in Figure 12. Note that input multiplicity is observed for the stage after reaction zone (stage 6).

Figure 13 shows input multiplicity of the 6th 7th 9th 10th 14th and 15th stage temperatures. 3 The turning point is around 10.5 MW. Figure 14 shows input multiplicity of the 18th 20th and 22nd stage temperatures with clearly two turning point. The first turning point is around 10 MW while the second turning point is around 10.5 MW. Another observation is that input multiplicity can be observed only in the range of low reboiler duty (9-11 MW).

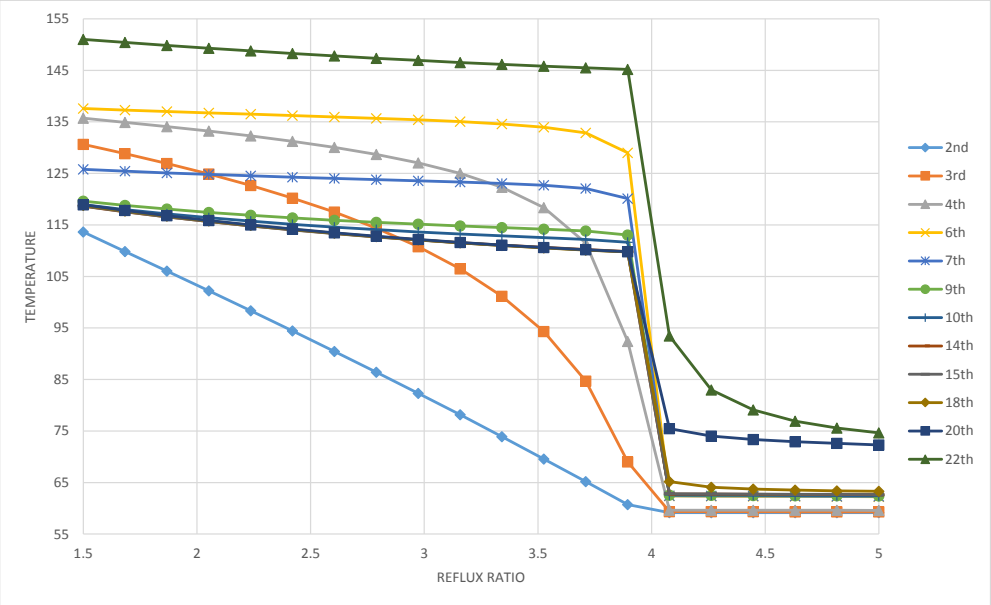


Figure 11 Effects of reflux ratio to stage temperatures for given reboiler duty 15.2 MW.

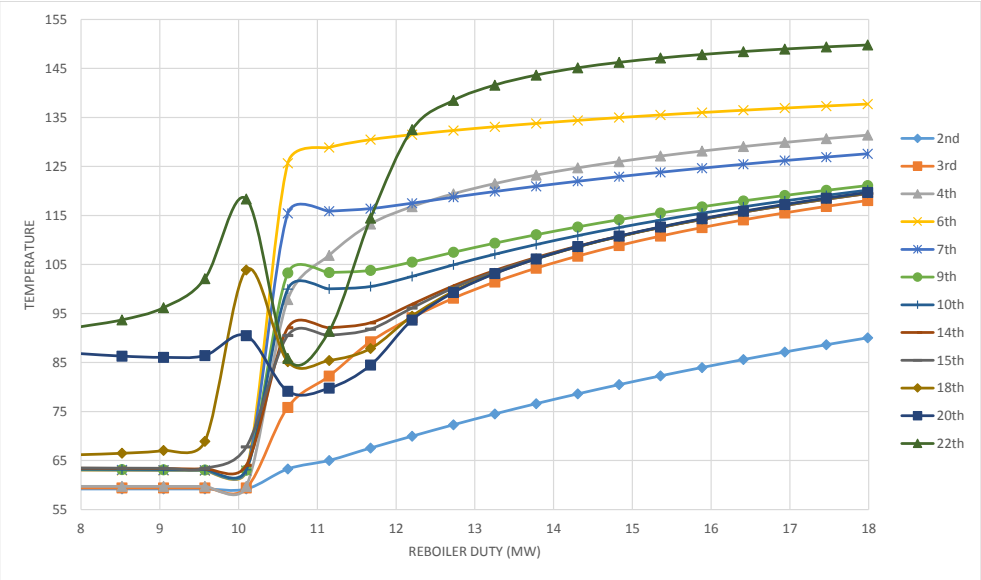


Figure 12 Effects of reboiler duty to stage temperature for given reflux ratio 3.

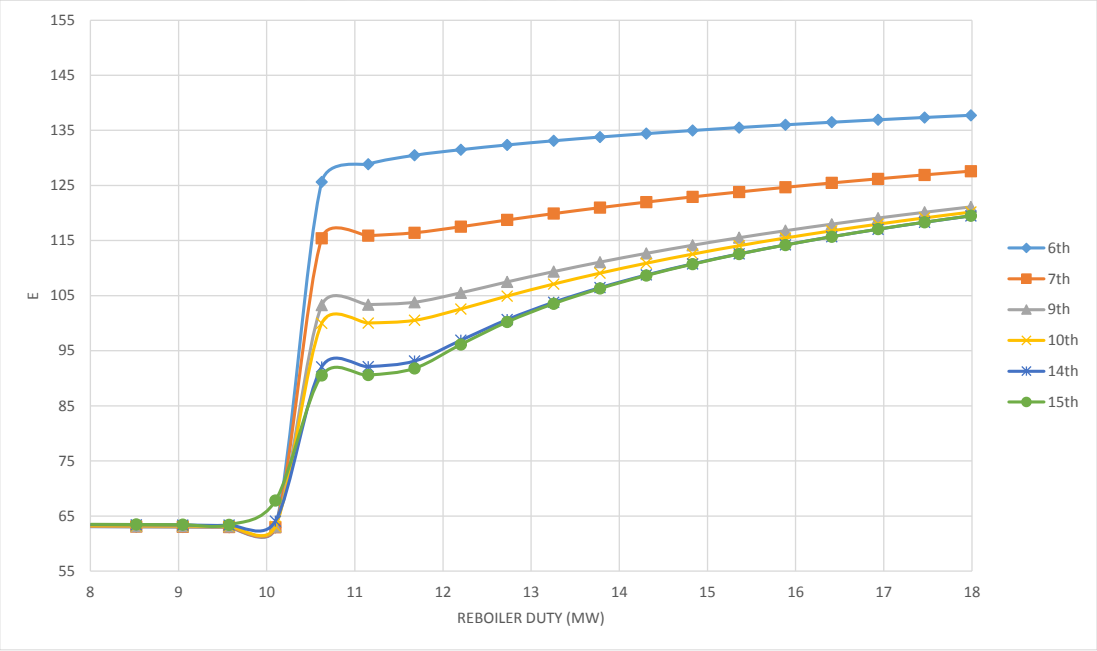


Figure 13 Effects of reboiler duty to the 6th 7th 9th 10th 14th and 15th stage temperature for given reflux ratio 3.

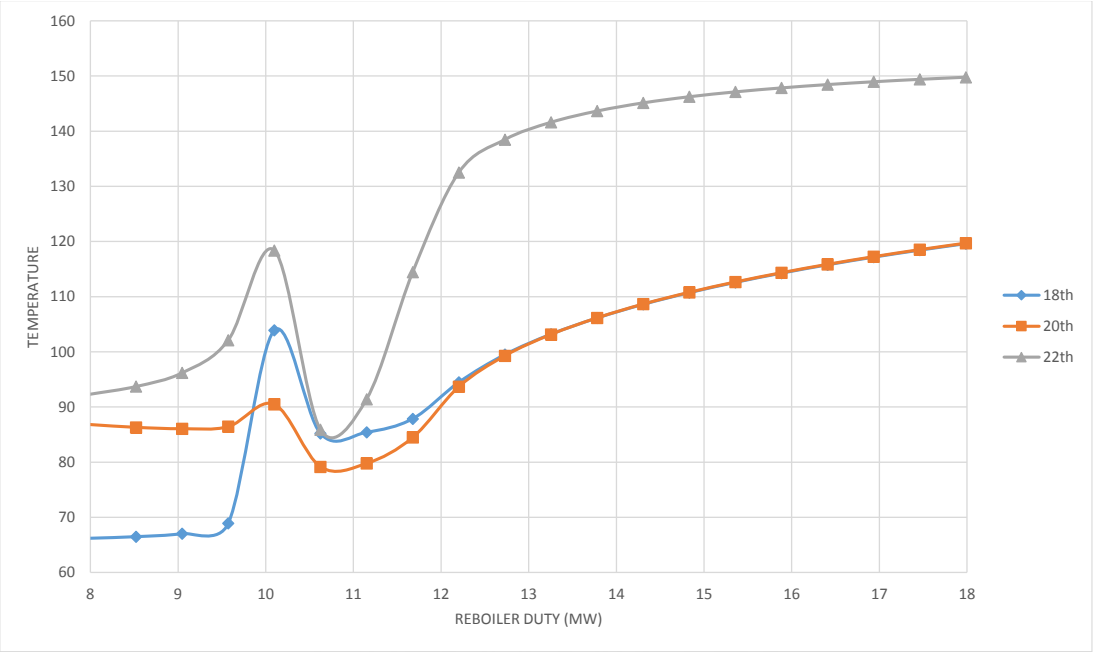


Figure 14 Effects of reboiler duty to the 18th 20th and 22nd stage temperature for given reflux ratio 3.

4.1.1.3 Effect of reflux ratio and reboiler duty to stage temperature for given operating parameter.

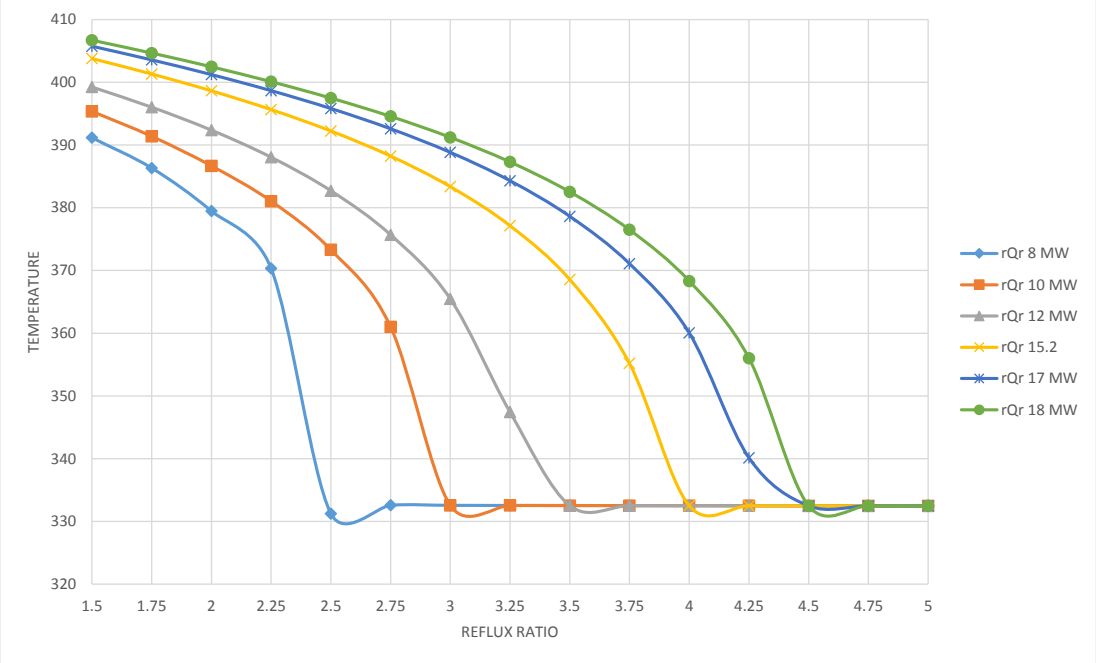


Figure 15 Effects of reflux ratio to the 3rd stage temperature for given reboiler duty.

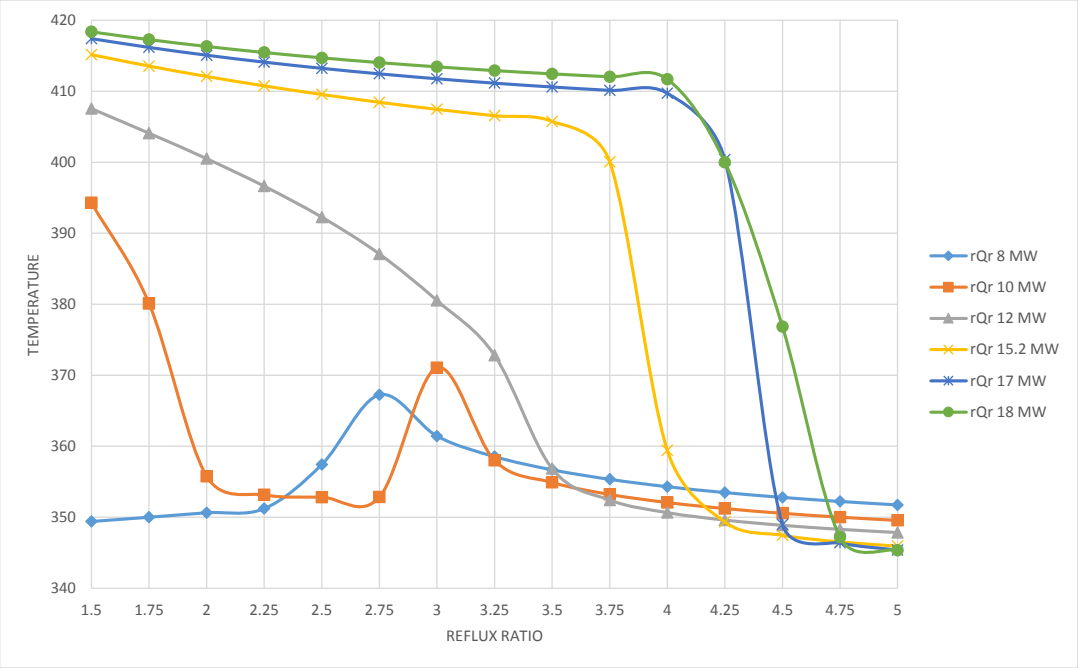


Figure 16 Effect of reflux ratio to the 21st stage temperature for given reboiler duty.

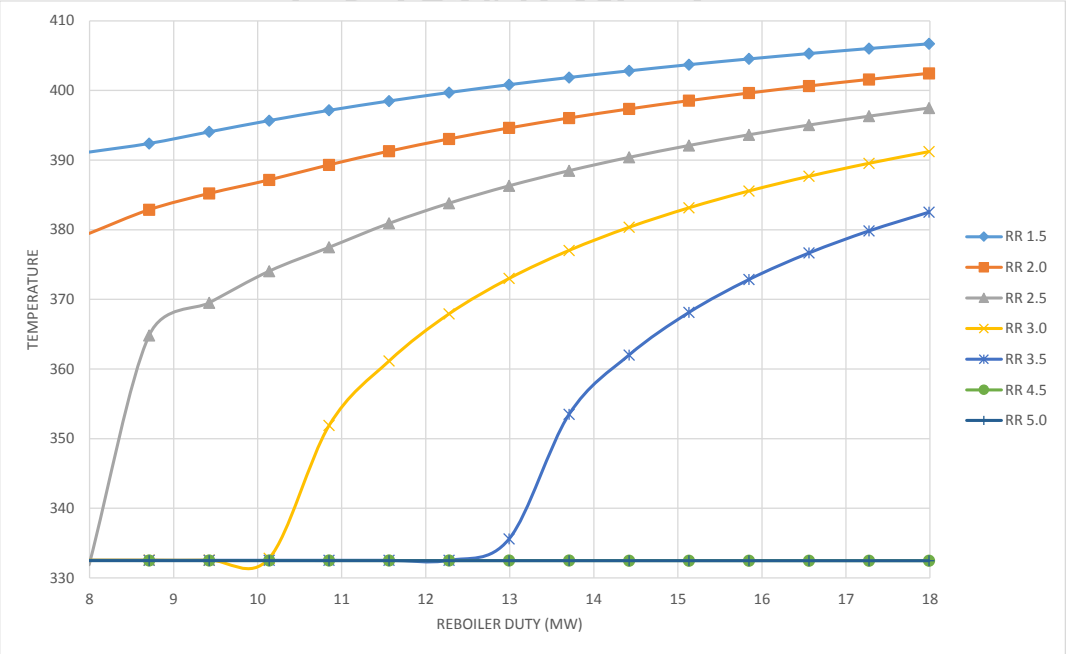


Figure 17 Effects of reboiler duty to the 3rd stage temperature for given reflux ratio.

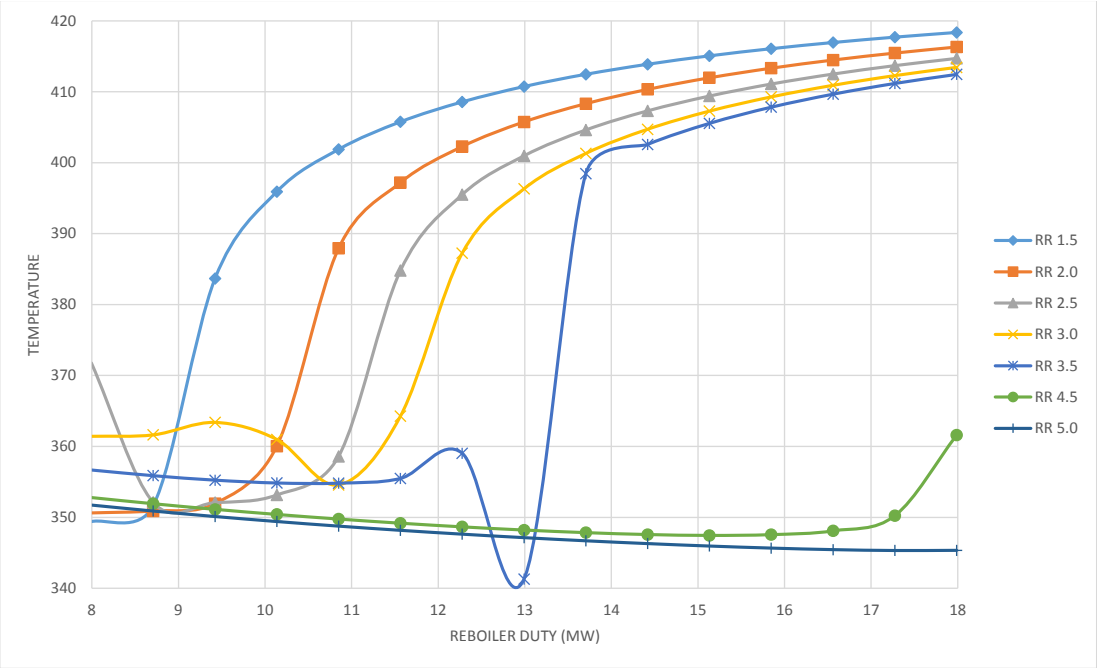


Figure 18 Effects of reboiler duty to the 21st stage temperature for given reflux ratio.

Figures 15 and 16 demonstrate effects of reflux ratio to the 3rd stage and the 21st stage temperatures for given reboiler duty. For the 3rd stage temperature input multiplicity cannot be observed while for the 21st stage temperature, input multiplicity is detected in the range of low reboiler duty (8-10 MW). For given reboiler duty=8 MW, input multiplicity occurs at around reflux ratio = 2.5 – 3.0.For given reboiler duty =10 MW, there are two turning points in the ranges of reflux ratio = 1.76 – 2.0 and 2.75 – 3.25.

Effects of reboiler duty to the 3rd and the 21st stage temperatures for given reflux ratio are illustrated in Figures 17 and 18. For the 3rd stage temperature, input multiplicity cannot be observed while for the 21st stage temperature, input multiplicity with two turning points occurs for given reflux ratio = 3 and 3.5. For reflux ratio = 3, the turning points are at around 9 – 10 and 10 – 11.5 MW. For reflux ratio = 3.5, two turning points are at around 11.5 – 12.5 MW and 12.5 – 13.5 MW. Effect of reflux ratio to 21st stage temperature form input multiplicity for given reboiler duty = 3-3.5 MW.

As shown above that using sensitivity analysis tool in Aspen Plus can clearly detect input multiplicity. However, this is not easy for output multiplicity where the challenge is to find multiple solutions, especially a middle turning curve of output for a given value of input. As shown in Fig 11 that output multiplicity might happen for some stage temperatures with sharp changes at reflux ratio around 4. For the 21st stage temperature as shown in Fig 19, this research attempts to find output multiplicity by gradually increase/decrease of reboiler duty around the point of reflux ratio=4 but output multiplicity cannot be detected. Other attempts based on use of design specification tool is by giving temperatures between upper and lower bound and finding reflux ratio to satisfy given temperature. However, Aspen cannot converge to the desired given temperature.

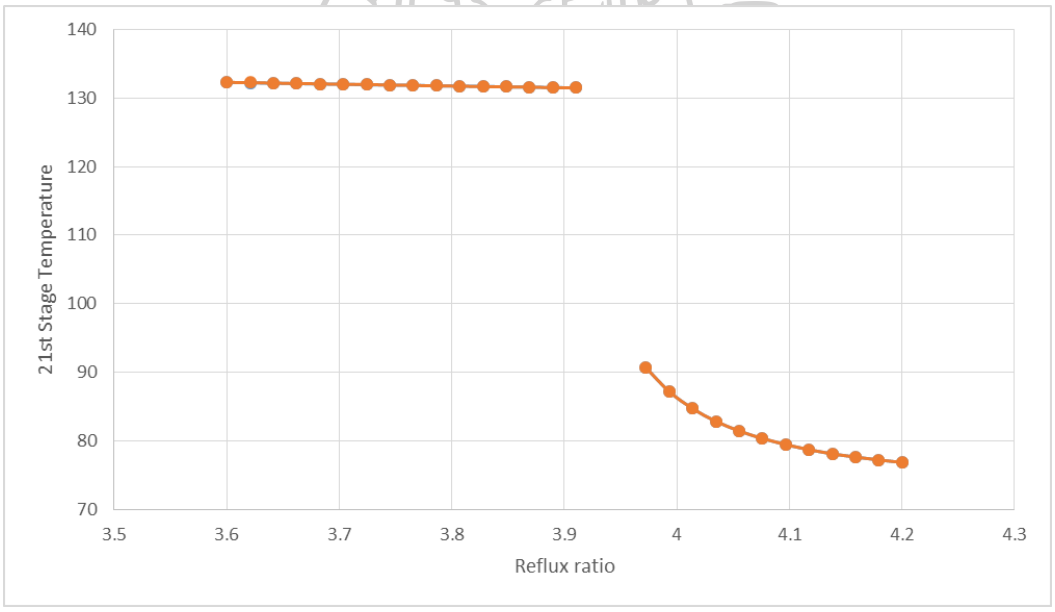


Figure 19 Output multiplicity at 21st Stage temperature varied reflux ratio 3.6 – 4.2 given reboiler duty equal 15.2 MW

4.1.2 Control structure design of Ethyl tert-butyl ether process via reactive distillation

4.1.2.1 Control degree of freedom analysis

Performing DOFs analysis (Konda, Rangaiah et al. 2006), ethyl tert-butyl ether process has seven control degrees of freedom including MV1: Flowrate of the inlet stream of the isobutene, MV2: Flowrate of the inlet stream of the ethanol, MV3: Flowrate of distillate stream, MV4: Flowrate of reflux stream, MV5: Flowrate of bottom stream, MV6: Reboiler duty, MV7: Condenser duty. To ensure production rate, flowrate of ETOH and the ratio of ETOH/C4 must be controlled. For stability, the integrating modes of levels in reflux drum and column base must be controlled. To have safe operation, column pressure should be controlled. Table 3 lists manipulated variables, controlled variables and pairing between them.

Pressure in reactive distillation column

Pressure in column must be selected controlled variable because avoid weeping and flooding in distillation column, in addition pressure in column can control vapor inventory in column.

The liquid levels in reflux drum

Liquid level in reflux drum must be controlled variable, since liquid level affect to stability in column. Hence liquid level must be kept in limit value.

The production of biodiesel

Production rate of biodiesel process is one in purpose of reactive distillation more important. Also flow rate of ETOH and ratio of ETOH/C4 would be controlled variables because ETOH affect to production rate and conversion was C4

Table 3 Pairing of Controlled and Manipulated Variables

Manipulated Variables	**Controlled Variable**
Flow rate of ETOH stream	Production rate
Flow rate of Isobutene stream	Ratio of ETOH/C4
Distillate rate	Level in reflux drum
Bottom rate	Level in column base
Condenser duty	Column pressure

Reflux ratio	
Reboiler duty	

From Table 3, there are two remaining CDOFs: reflux ratio and reboiler duty which can be used for other purposes and in this research they will be used for control of product composition. However, due to lack of reliability of composition measurement, temperature control will be chosen instead. A further task required is the selection of stage temperatures to be controlled. For control performance, the most sensitive stage temperatures should be chosen for control. Sensitivity of reflux ratio and reboiler duty to stage temperatures are shown in Figures 20 and 21.

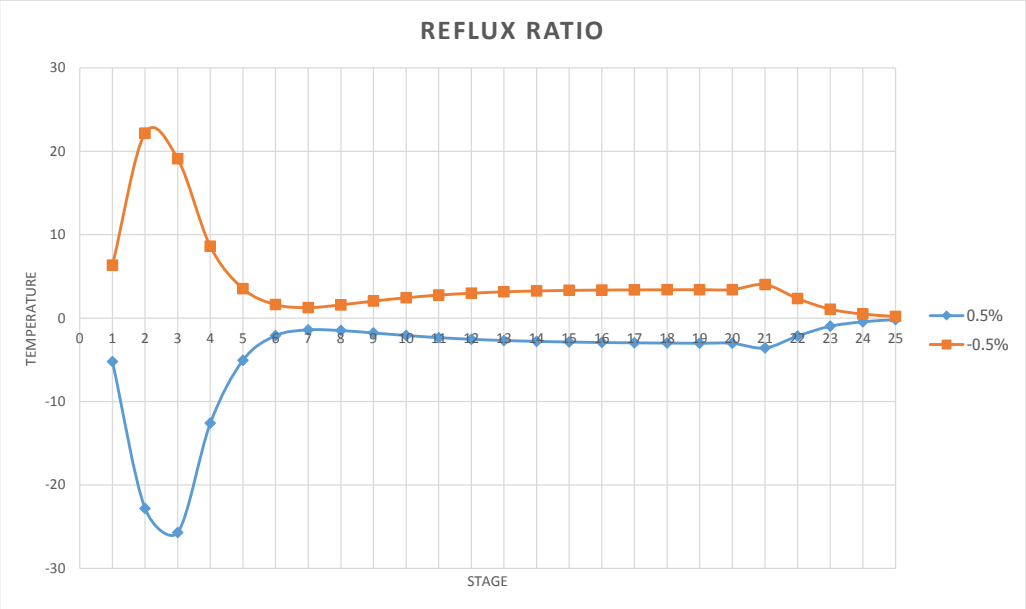


Figure 20 Sensitivity stage temperatures with respect to reflux ratio.

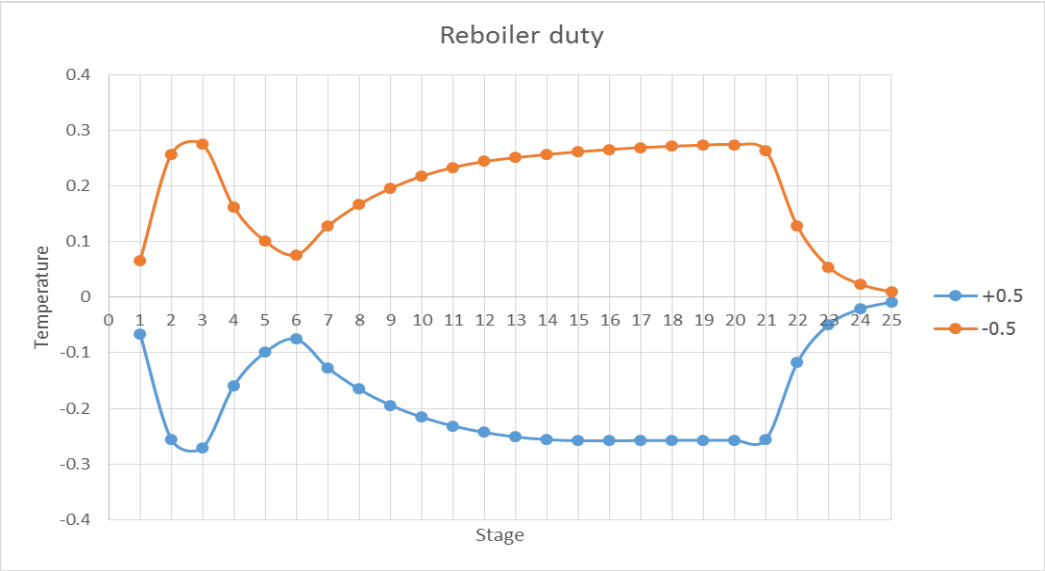


Figure 21 Sensitivity of stage temperature with respect to reboiler duty.

From Figures 20 and 21, the sensitive stage temperature that will be chosen as controlled variables are the 3rd stage temperature and the 21st stage temperature. For the control pairing, the 3rd stage temperature will be manipulated using reflux ratio while the 21st stage temperature will be manipulated using reboiler duty.

4.1.2.1 Dynamic simulation in Ethyl tert-butyl ether process

From the previous section, two control structures are proposed, that is, control structure I (CSI) with single temperature control where reboiler duty is used for control of the 21st-stage temperature, and control structure II (CSII) with dual temperature control where additional control loop is using reflux ratio for control of the 3rd-stage temperature. Note that implementation of temperature control is for satisfying bottom ETBE composition at the desired value.

4.1.2.1a Single temperature control (CSI)

Table 4 shows control pairing of control structure CSI. Note that reflux ratio is unused and can be used for other purposes such as self-optimizing variable (Skogestad 2004)or for tight control with dual temperature control as the proposed CSII.

Table 4 Control paring of control structure CSI with single stage temperature control (CSI)

Manipulated Variables	Controlled Variable
Flow rate of ETOH stream	Production rate
Flow rate of Isobutene stream	Ratio of ETOH/C4
Distillate rate	Level in reflux drum
Bottom rate	Level in column base
Condenser duty	Column pressure
Reflux ratio	
Reboiler duty	21st stage temperature

Table 5 Control paring of control structure CSII with dual temperature control (CSII)

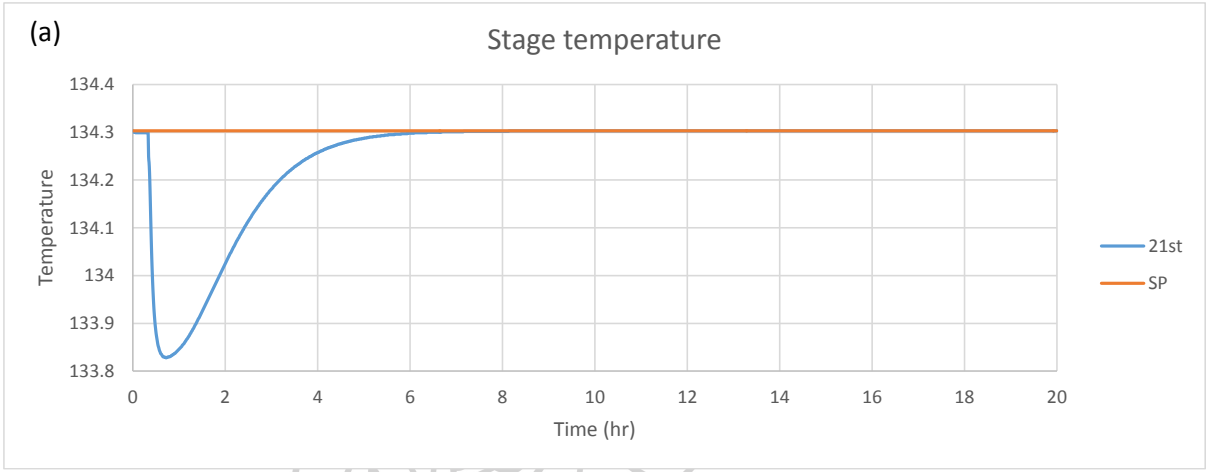
Manipulated Variables	**Controlled Variable**
Flow rate of ETOH stream	Production rate
Flow rate of Isobutene stream	Ratio of ETOH/C4
Distillate rate	Level in reflux drum
Bottom rate	Level in column base
Condenser duty	Column pressure
Reflux ratio	3rd stage temperature
Reboiler duty	21st stage temperature

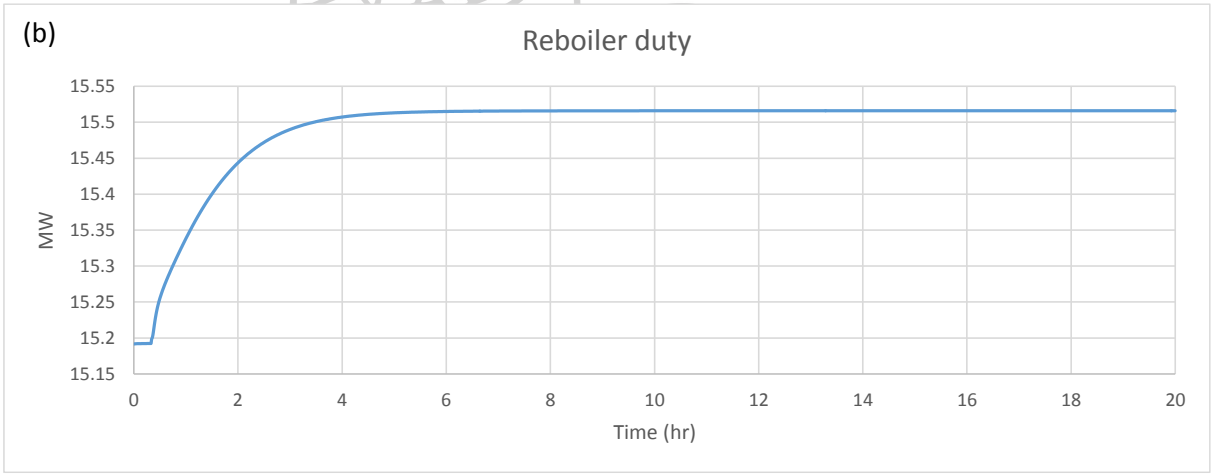
4.1.2.1.b Dual temperature control (CSII)

Table 5 shows control pairing of control structure CSII. The product composition is tightly controlled using dual temperature control of the 3rd-stage and 21st stage temperatures.

4.1.2.1c Controller action type in process

Aspen dynamics is equipment that studied control structure design performance. Program proposed consists two controller action type. Direct action mean that output variable increase if input variable increase. Reverse action mean that output variable increase if input variables decrease.





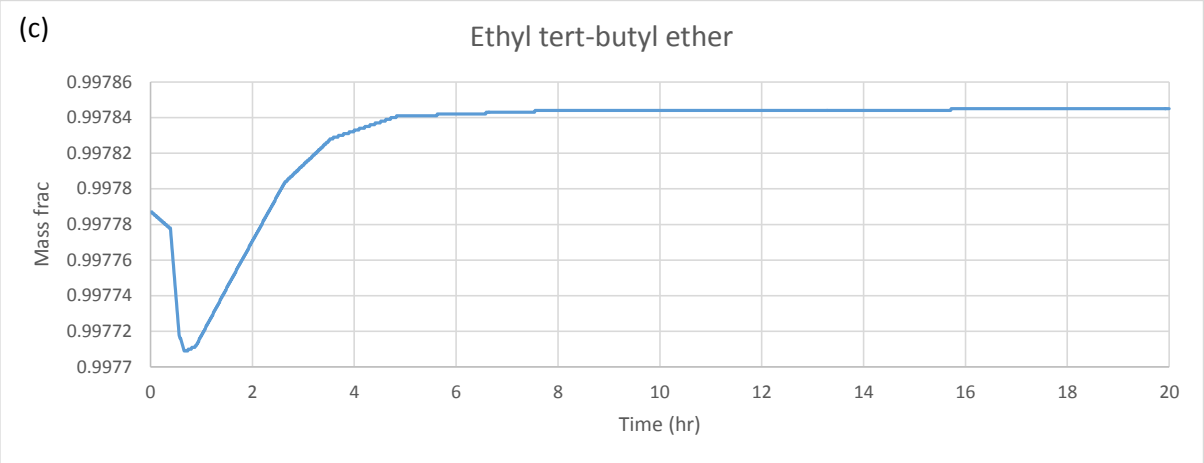


Figure 22 Dynamic response from control structure CSI: (a) response of the 21st stage temperature (CV),and (b) Reboiler duty, and (c) Mass fraction of Ethyl tert-butyl ether, when increase of 5% in ETOH feed flowrate.

4.1.2.2 Control performance

The proposed control structures CSI and CSII are validated using dynamic simulation performing in Aspen Plus dynamic disturbances of changes of ±5% ETOH feed flowrate.

Dynamic responses under change of ±5% of ETOH feed flowrate when the control structure CSI with single temperature control is used are shown in Figures 22 and 23. The result shows CSI can keep the 21st-stage temperature at the desired value. However, observation of ETBE mass fraction shows that small offset cannot be eliminated.

Dynamic responses under change of ±5% of ETOH feed flowrate when the control structure CSII with dual temperature control is used are shown in Figures 24 and 25. The result shows CSII can keep both the 3rd-stage and the 21st-stage temperature at the desired values. Furthermore, observation of ETBE mass fraction shows that offset can be eliminated.

Under the operating windows of ±5% of ETOH feed flowrate, the operation is not inside the regions of multiplicity. Hence, both control structures CSI and CSII can control the reactive distillation column very well.

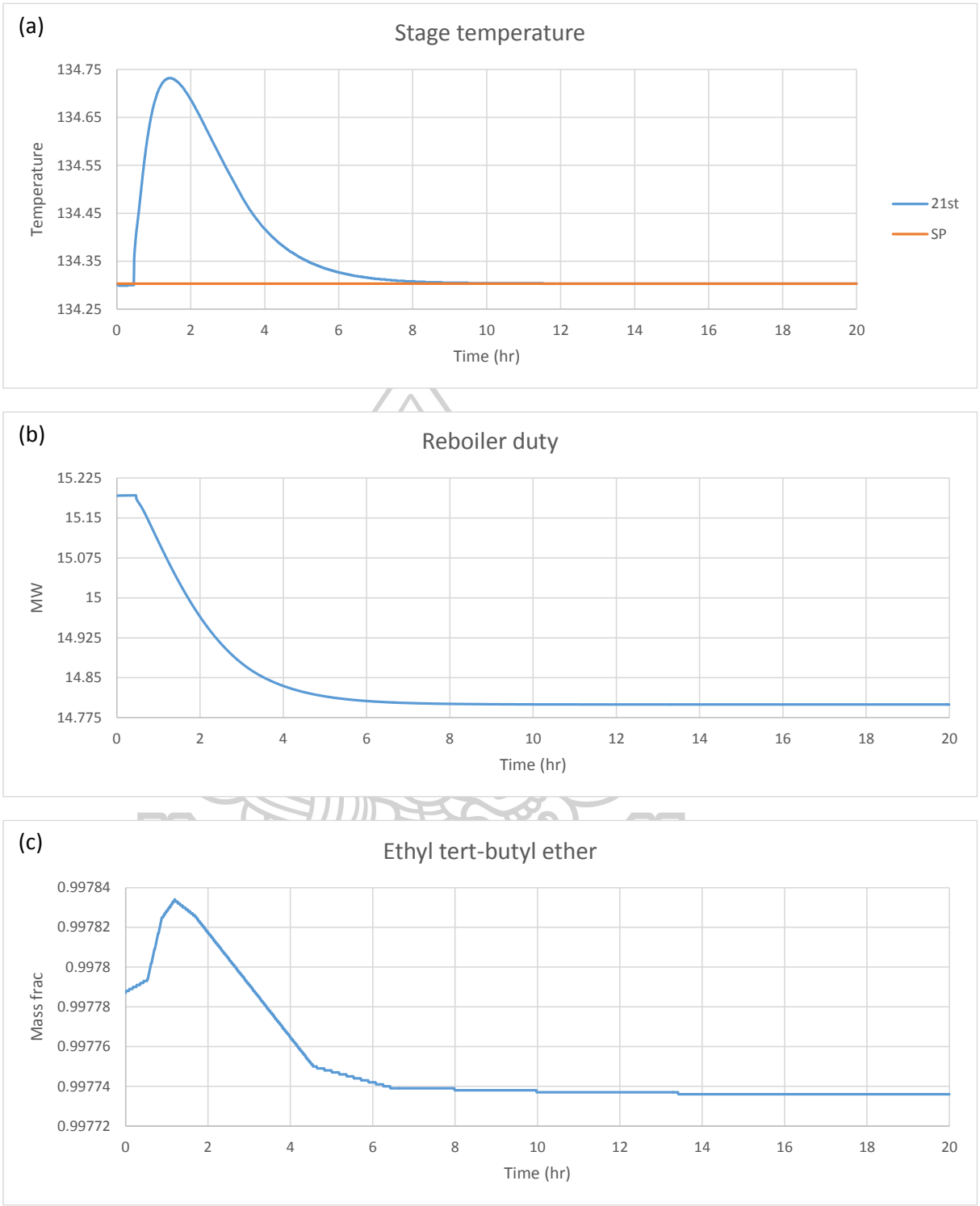
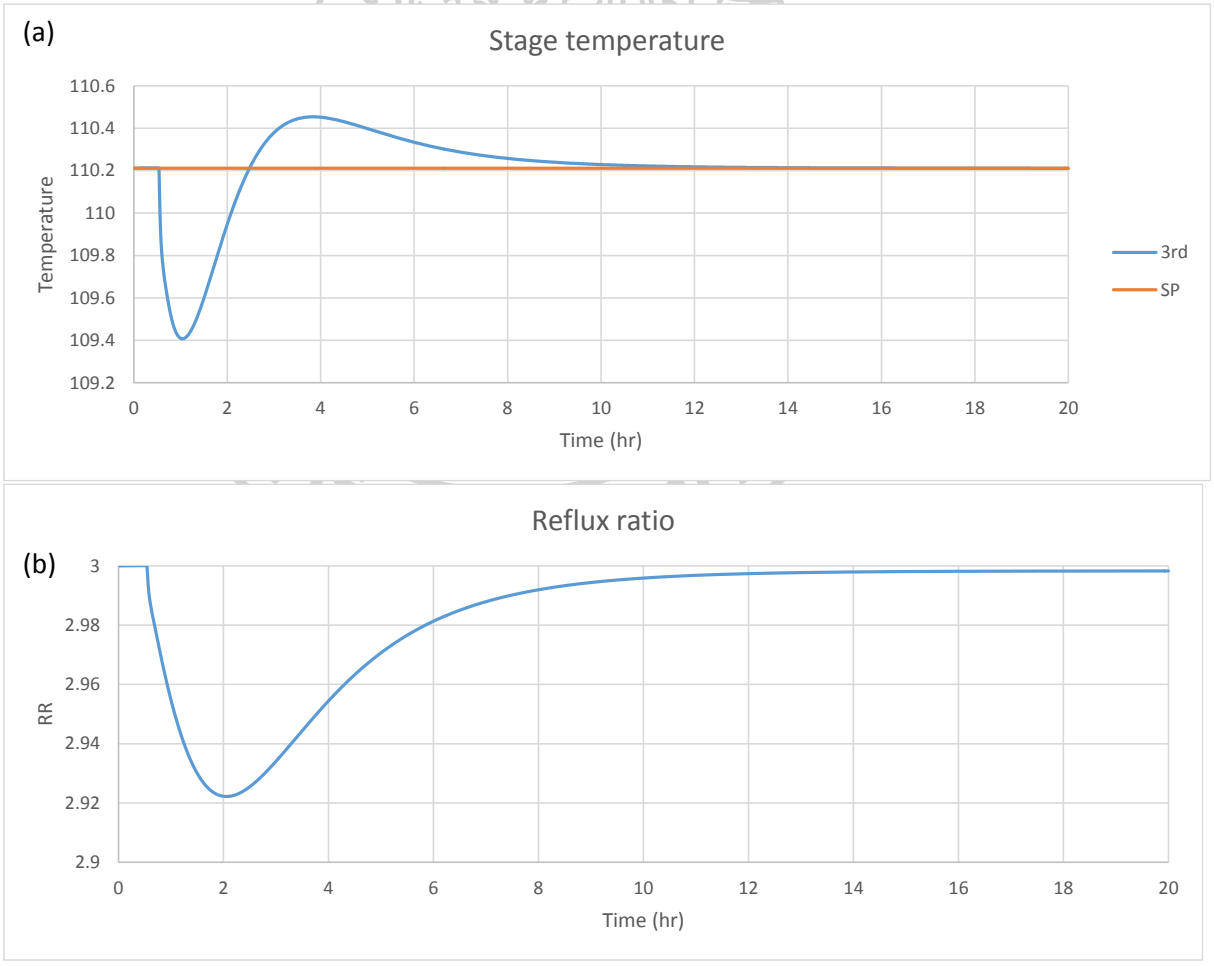


Figure 23 Dynamic response from control structure CSI: (a) response of the 21st stage temperature (CV),and (b) Reboiler duty, and (c) Mass fraction of Ethyl tert-butyl ether, when decrease of 5% in ETOH feed flowrate.

Result of control structure I (CSI) from figure 22 effect of increase disturbance 5% of ETOH feed, (a) 21st stage temperature (CV) decrease then reverse back to setpoint after controller detected error of CV consequently send controller signal to manipulated variable is reboiler duty (MV) that handle CV is increase value for CV tracking to setpoint. In additional composition of Ethyl tert-butyl ether in process was reversed and higher than original value by demonstrate in figure 22 (c). And the effect of -5% feed of ETOH is reboiler duty decrease for handle 21st stage temperature back to setpoint however composition of Ethyl tert-butyl ether is lower than original composition, was demonstrated in figure 23.



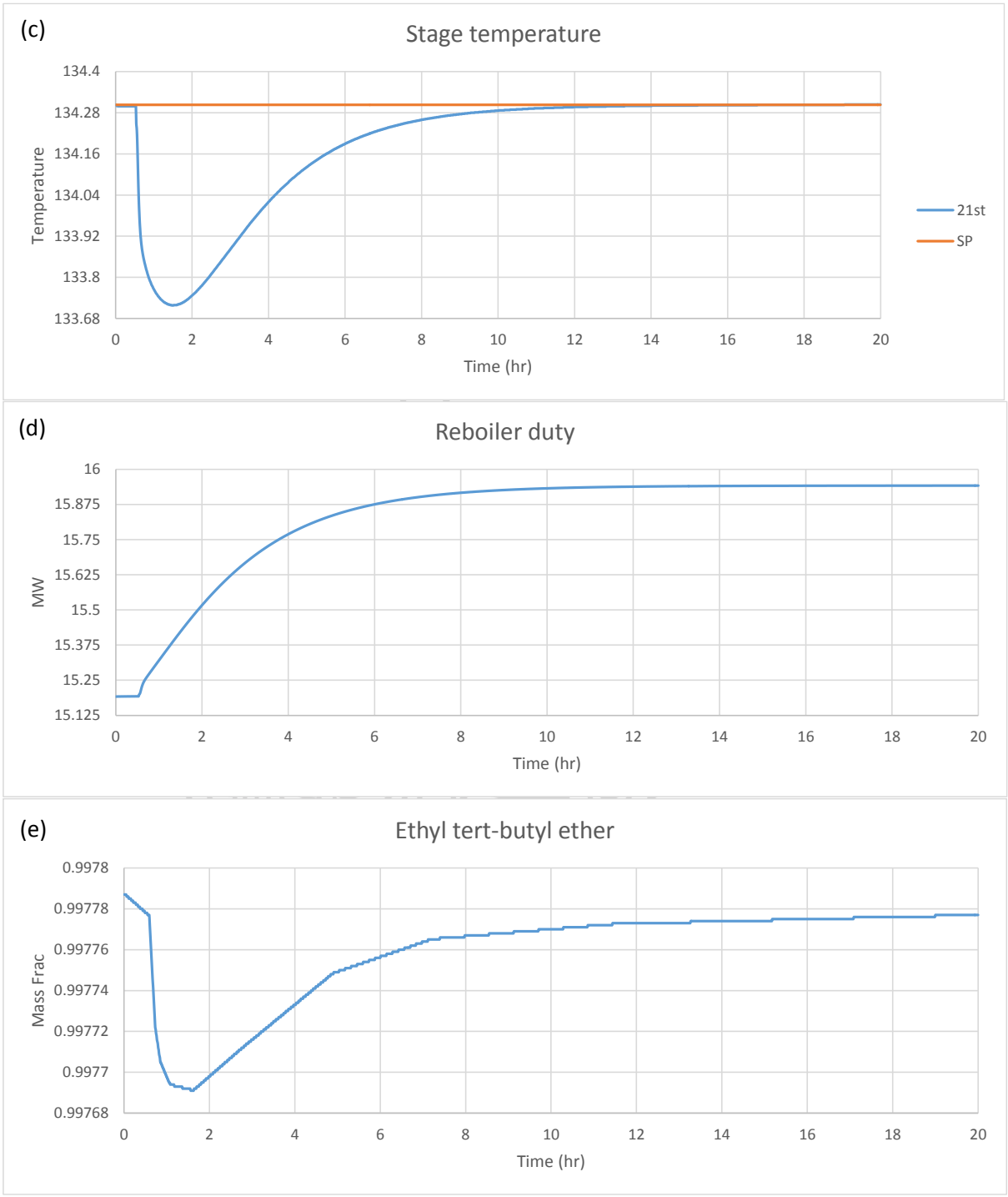
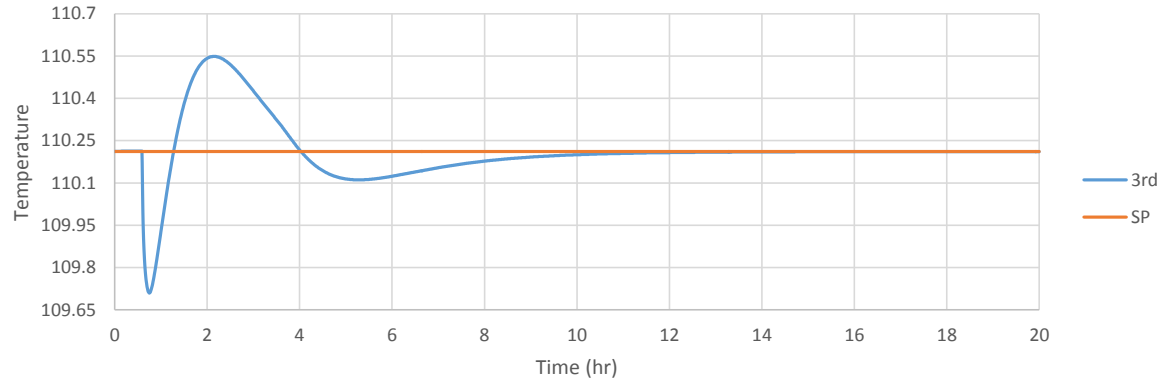
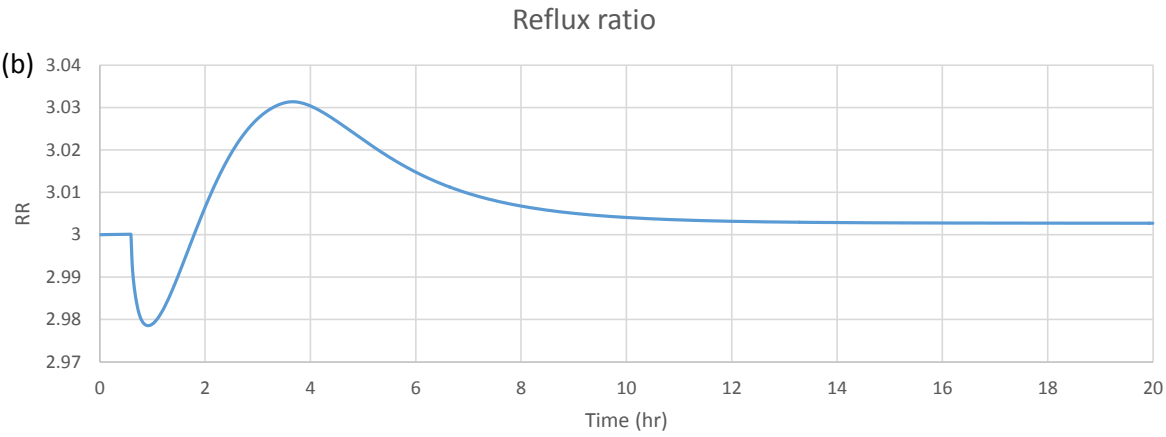


Figure 24 Dynamic response from control structure CS II: (a) 3rd stage temperature (CV-1),(b) Reflux ratio (MV-1) (c) 21st stage temperature (CV-2) (d) Reboiler duty (MV-2) and (e) Mass fraction of Ethyl tert-butyl ether, when increase of 5% in ETOH feed flowrate.

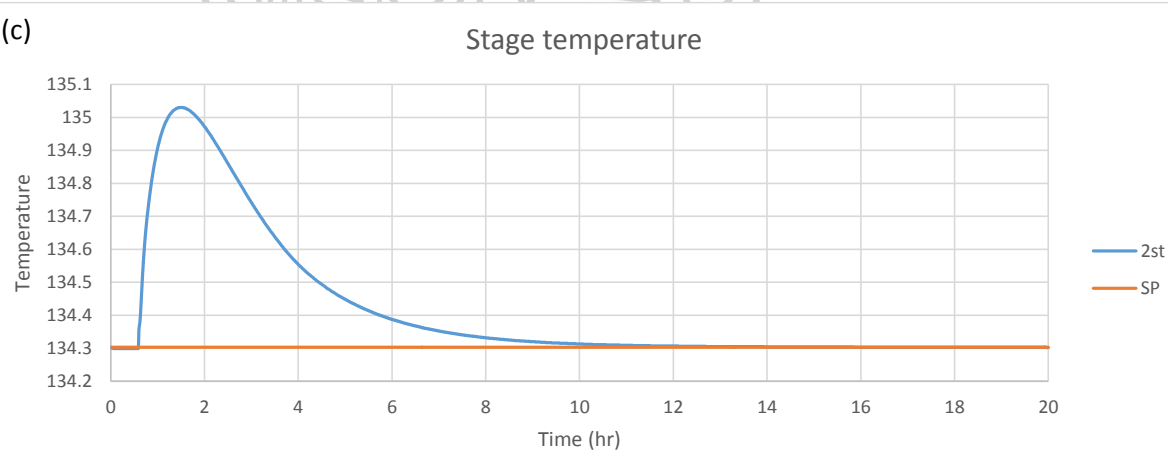
(a)


Stage temperature
Temperature
110.7
110.55
110.4
110.25
110.1
109.95
109.8
109.65
0
2
4
6
8
10
12
14
16
18
20
Time (hr)
3rd
SP

(b)


Reflux ratio
RR
3.04
3.03
3.02
3.01
3
2.99
2.98
2.97
0
2
4
6
8
10
12
14
16
18
20
Time (hr)

(c)


Stage temperature
Temperature
135.1
135
134.9
134.8
134.7
134.6
134.5
134.4
134.3
134.2
0
2
4
6
8
10
12
14
16
18
20
Time (hr)
2st
SP

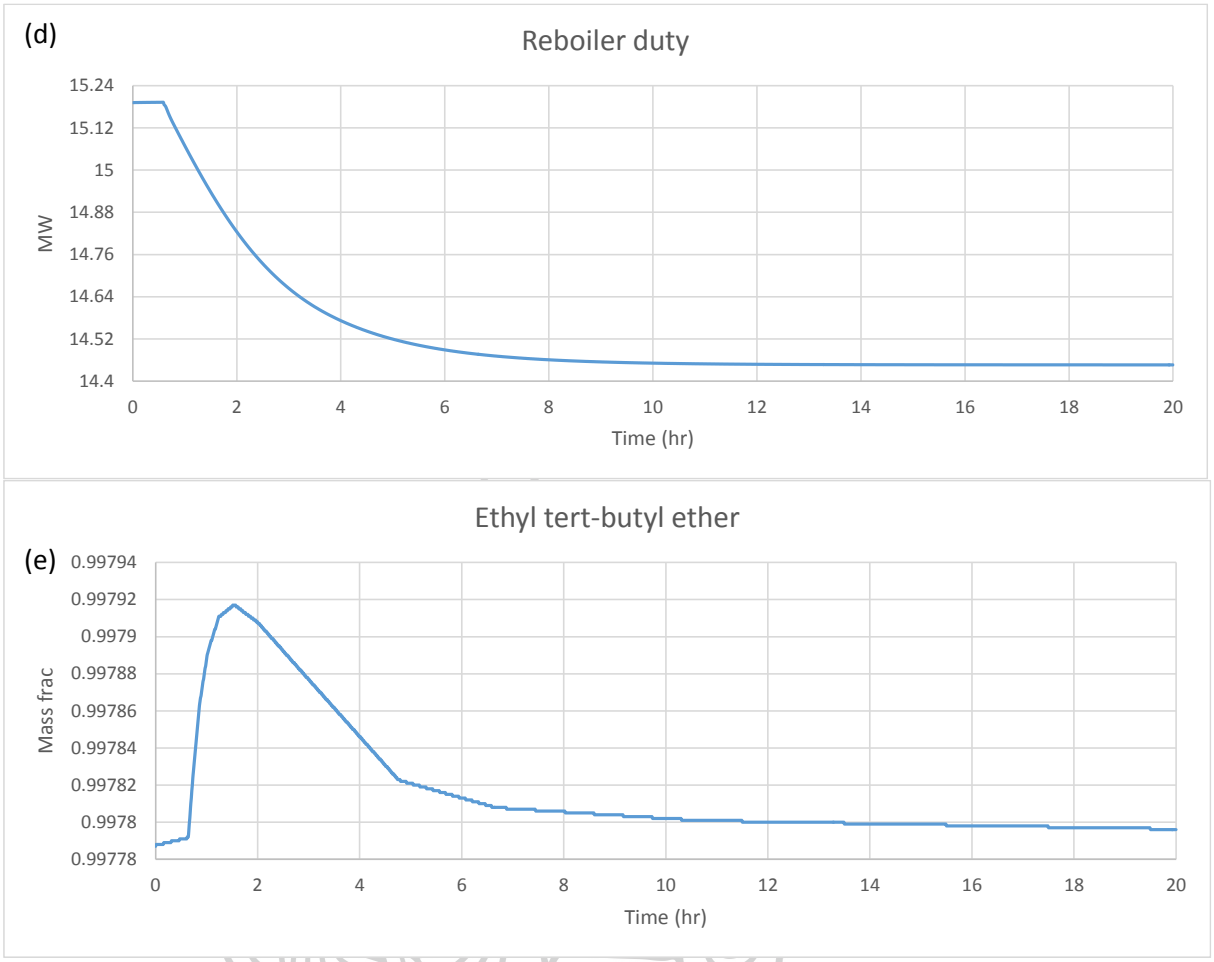


Figure 25 Dynamic response from control structure CS II: (a) 3rd stage temperature (CV-1),(b) Reflux ratio (MV-1) (c) 21st stage temperature (CV-2) (d) Reboiler duty (MV-2) and (e) Mass fraction of Ethyl tert-butyl ether, when decrease of 5% in ETOH feed flowrate.

4.2 Biodiesel process

In this section, multiplicity analysis and control structure design of supercritical biodiesel production process adapted from Wang, Wong et al. (2003) will be studied. (Gomez-Castro, Rico-Ramirez et al. 2013) processes involved two-step methods where oils is hydrolyzed to free fatty acid (FFA) then FFA is esterified with excess methanol to fatty-acid methyl ester (FEME). The FAME stream will be further purified to meet biodiesel standard using a distillation column. However, in this research, only the part of reactive distillation column with supercritical esterification will be studied. Data of the column is shown in Table 6.

Table 6 Data of supercricritical esterification reactive distillation column for biodiesel production

Parameter information	Value
Number of stages	10
Free fatty acid feed stage	3
Methanol feed stage	6
Reactive stage	6-9
Residence time (h)	0.3
Diameter (m)	1.36
Height (m)	3.16
Pressure on top (bar)	70
Reflux Ratio	0.1194*
Reboiler duty (MJ/h)	8,714

* Reflux ratio is adjusted to 4 for higher methanol fraction in recovery distillate stream

The flowsheet of the reactive distillation column for biodiesel production is simulated using Aspen Plus. The property method used is COSMOSAC. The simulation result is compared with the result from (Gomez-Castro, Rico-Ramirez et al. 2013) that is in an agreement as shown in Table 7.

Table 7 Comparison results between this research and (Gomez-Castro, Rico-Ramirez et al. 2013)

Result	Mass fraction of FAME in product stream	Conversion of FFA
This research	0.85	99%
Gomez-Castro et al., (2013)	0.90	99%

In (Gomez-Castro, Rico-Ramirez et al. 2013) flowsheet, the distillate stream with rich methanol is recovered for the reaction. However, the methanol fraction in the distillate is only 0.76. To have higher methanol fraction, the nominal reflux ratio will be adjusted to 4.

4.2.1 Multiplicity analysis

4.2.1.1 Effects of reflux ratio and reboiler duty to methanol mass fraction

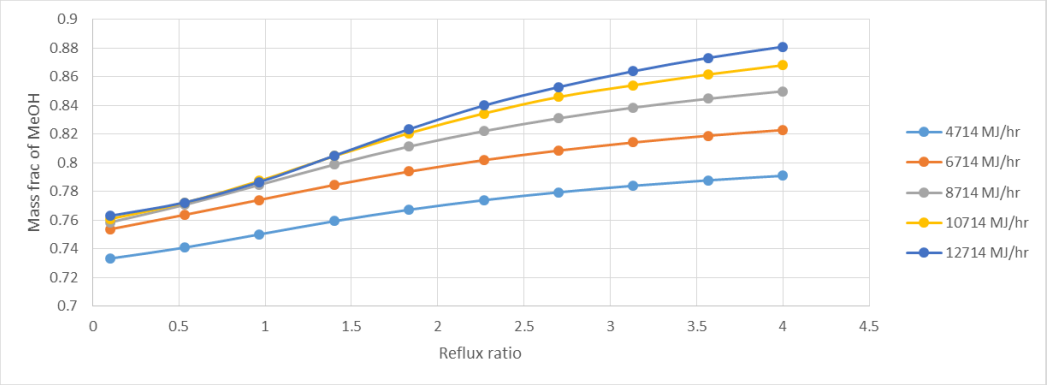


Figure 26 Effects of reflux ratio to mass methanol fraction for given reboiler duty 8,714 MJ/hr

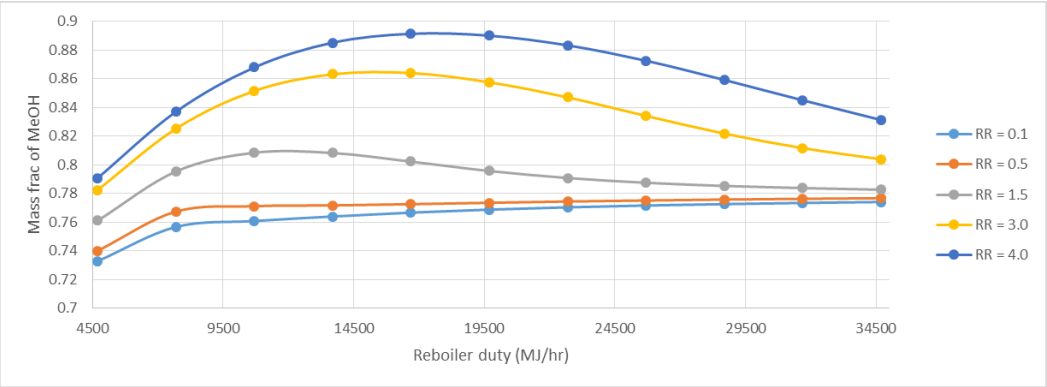


Figure 27 Effects of reboiler duty to methanol mass fraction for given reflux ratio 4

Figures 26 and 27 show effect of reflux ratio and reboiler duty to methanol mass fraction. Under our investigation with reflux ratio 0.016-4 and reboiler duty 4,500-34,500 MJ/hr, output multiplicity cannot be observed but input multiplicity is detected, especially at higher reflux ratio operation.

4.2.1.1 Effects of reflux ratio and reboiler duty to stage temperatures

Figure 28 shows effects of reflux ratio in the range of 0.1-6 to stage temperatures for given reboiler duty = 8,714 MJ/hr. No multiplicity can be observed. Figure 29 shows effects of reboiler duty in the range of 4,714-32,714 MJ/hr to stage temperatures for given reflux ratio = 4. Input multiplicity is observed.

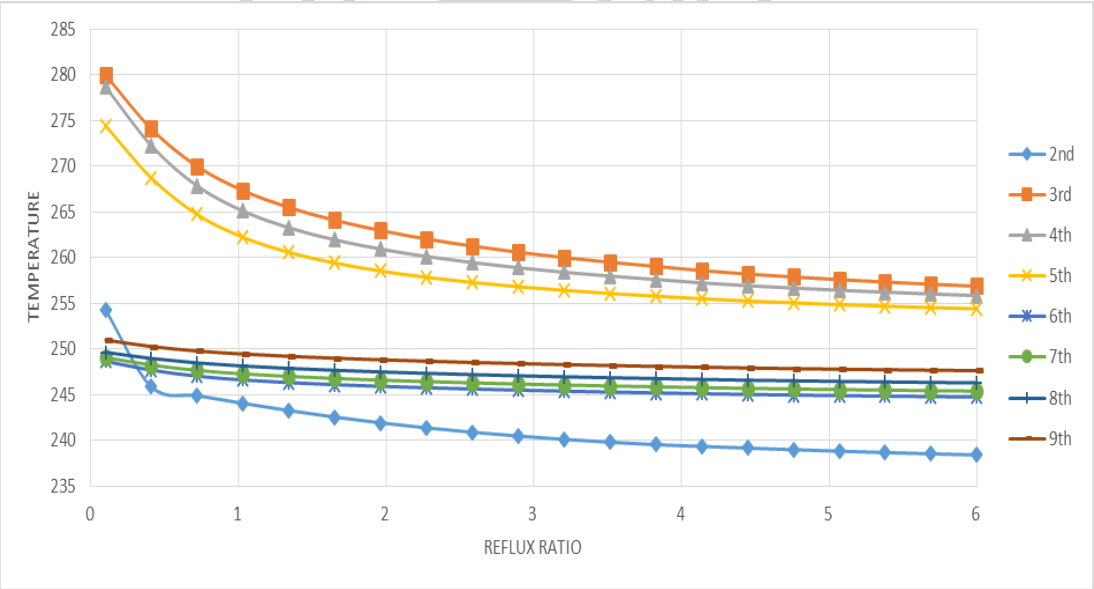


Figure 28 Effects of reflux ratio to stage temperatures for given reboiler duty 8,714 MJ/hr.

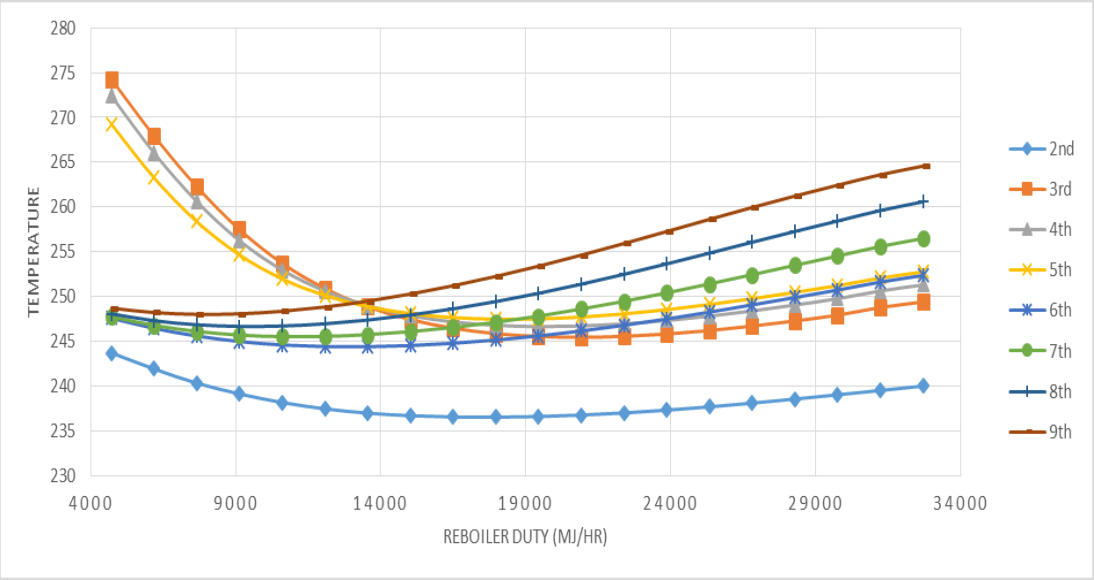


Figure 29 Effects of reboiler duty to stage temperatures for given reflux ratio 4.

In Figure 29, at lower reboiler duty, the 3rd, 4th, and 5th stage temperatures are higher comparing with others because the temperature of the FFA feed is almost 270°C. Furthermore, the esterification is endothermic and makes lower temperatures of the 6th, 7th, 8th, and 9th stage.

Effects of reboiler duty for given reflux ratio 4 to the 2nd, 3rd, 4th, and 5th stage temperatures that are temperatures in rectifying section are shown in Figure 30 while the effects to the 6th, 7th, 8th, and 9th stage temperatures that are temperatures in reaction section are shown in Figure 31. Note that the turning points of the temperatures in reaction occurs at lower values of reboiler duty.

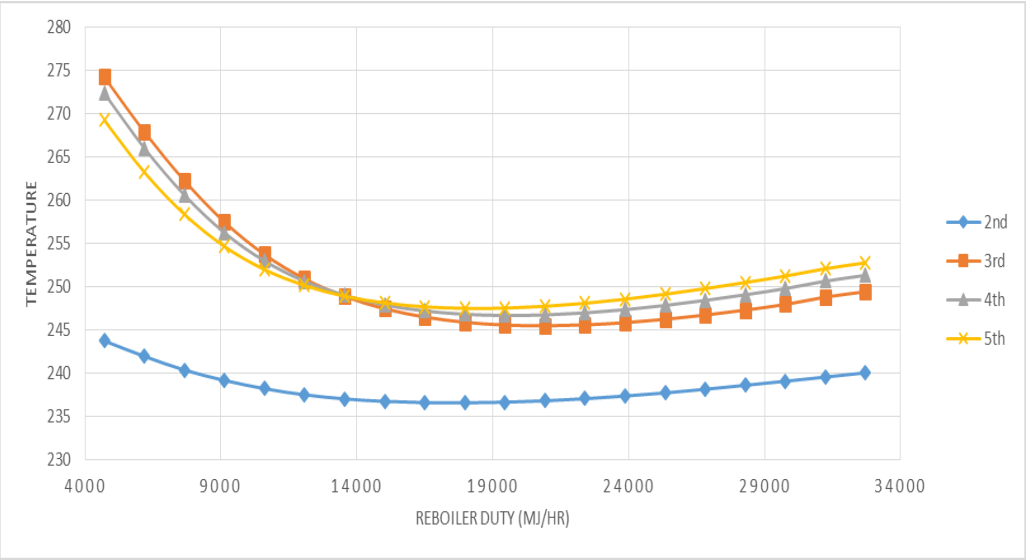


Figure 30 Effects of reboiler duty to the 2nd , 3rd , 4th and 5th stage temperatures for given reflux ratio 4.

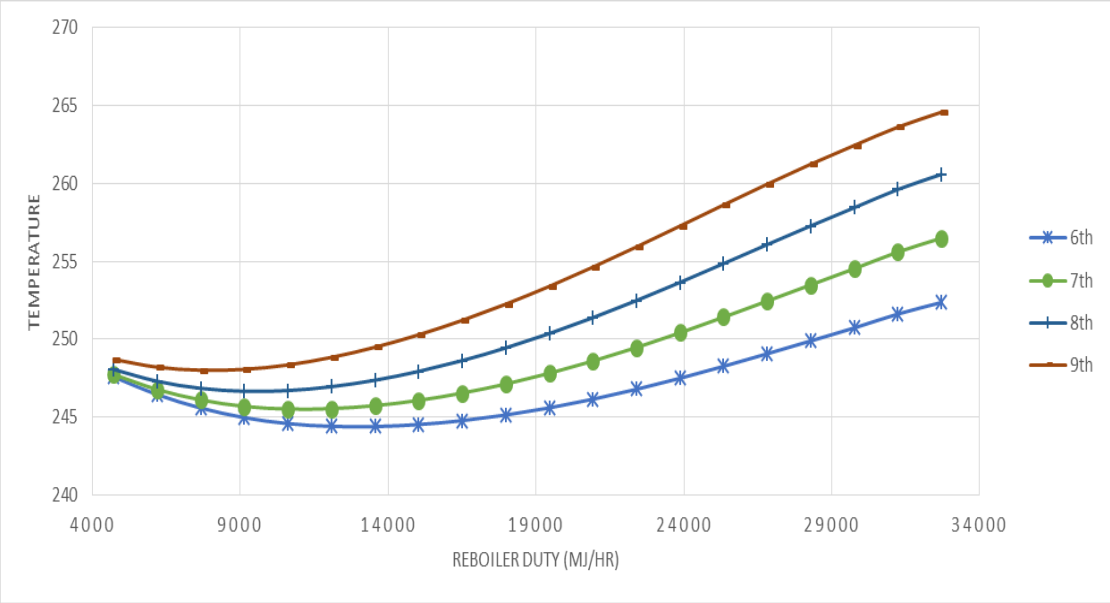


Figure 31 Effects of reboiler duty to the 6th , 7th , 8th and 9th stage temperatures for given reflux ratio 4.

4.2.1.2 Effects of reflux ratio and reboiler duty to stage temperatures for given operating parameters.

Further study of multiplicity for each stage temperature will be focused in this section. Effects of reflux ratio to the 2nd-6th stage temperatures for various reboiler duty are shown in Figures 32-35. As shown in Figure 35, there is an existence of input multiplicity for the 6th stage temperature when operating at high reboiler duty. Furthermore, under the range of reflux ratio 0.1-6, input multiplicity has two turning points, changing from negative effects to positive effects, and then to negative effects again.

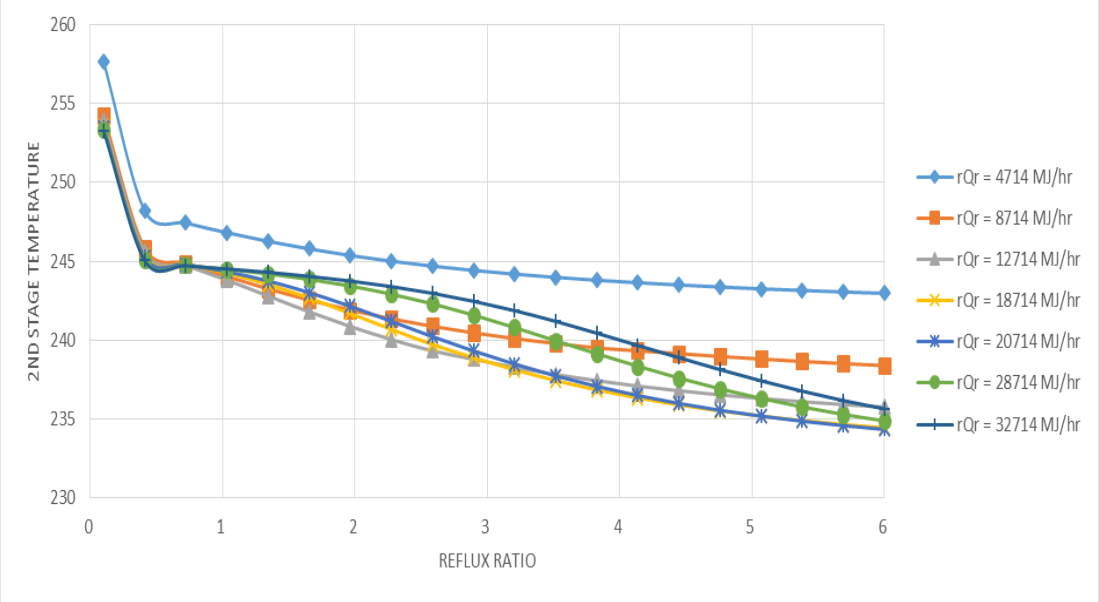


Figure 32 Effects of reflux ratio to the 2nd stage temperature for given reboiler duty.

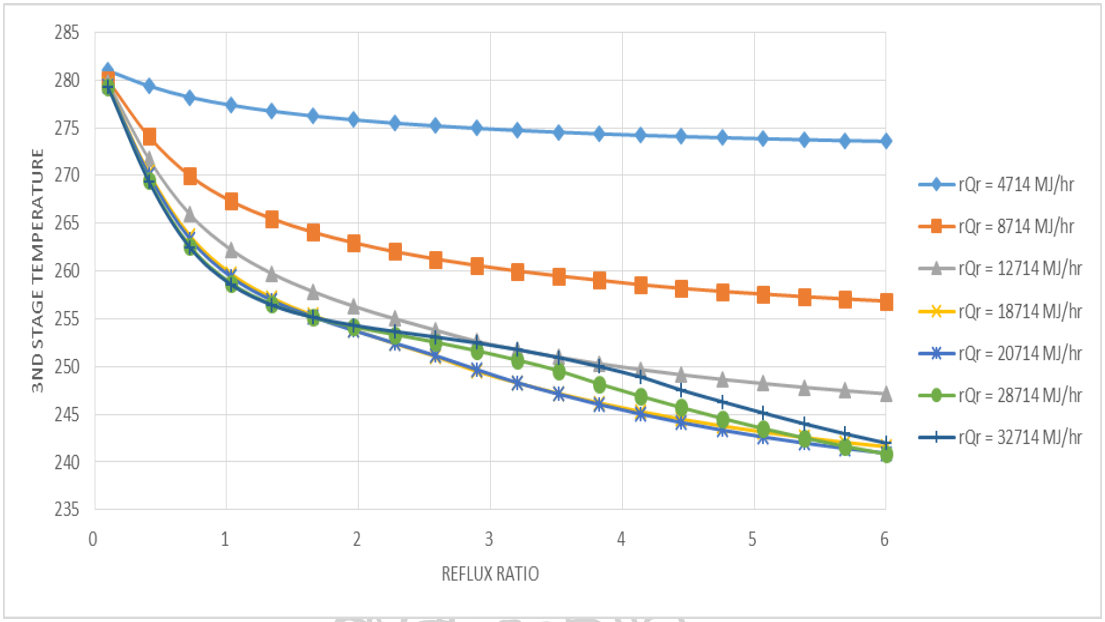


Figure 33 Effects of reflux ratio to the 3rd stage temperature for given reboiler duty.

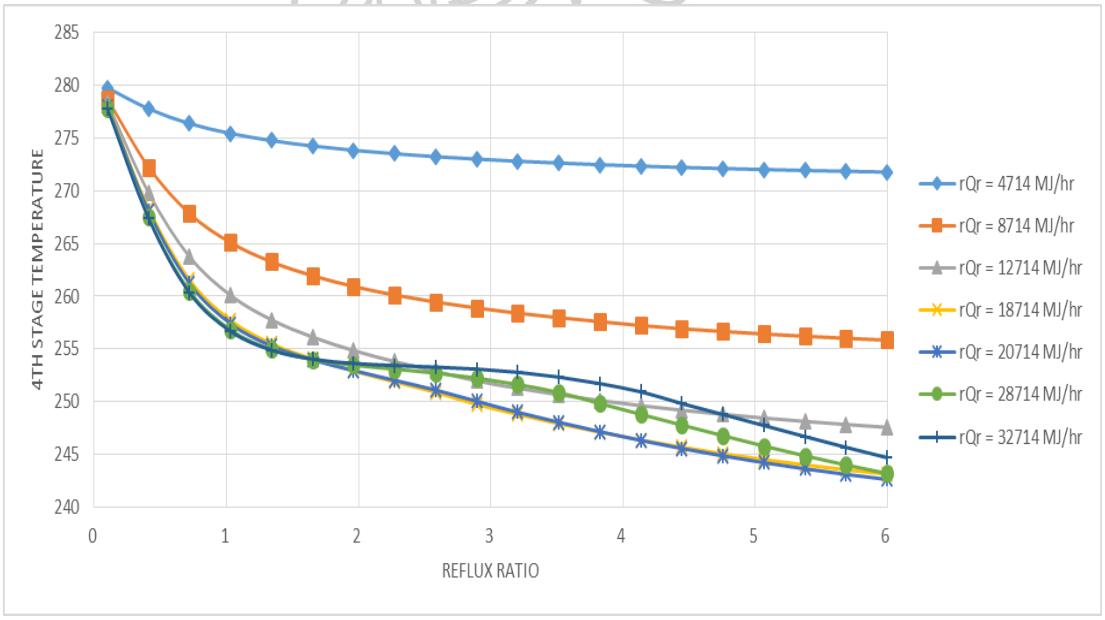


Figure 34 Effects of reflux ratio to the 4th stage temperature for given reboiler duty.

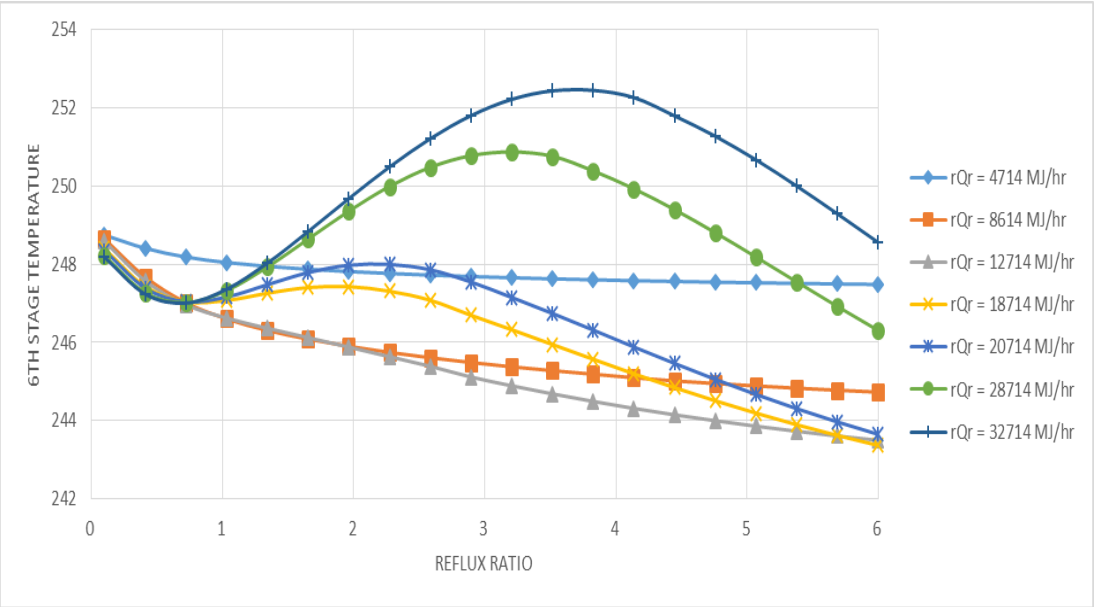


Figure 35 Effects of reflux ratio to the 6th stage temperature for given reboiler duty.

Effects of reboiler duty to the 2nd-6th stage temperatures for various reflux ratio are shown in Figures 36-39. There is an existence of input multiplicity for every stage temperature, especially when operating at high reflux ratio. Further observation is that the 6th stage temperature tends to exhibit higher effect of input multiplicity.

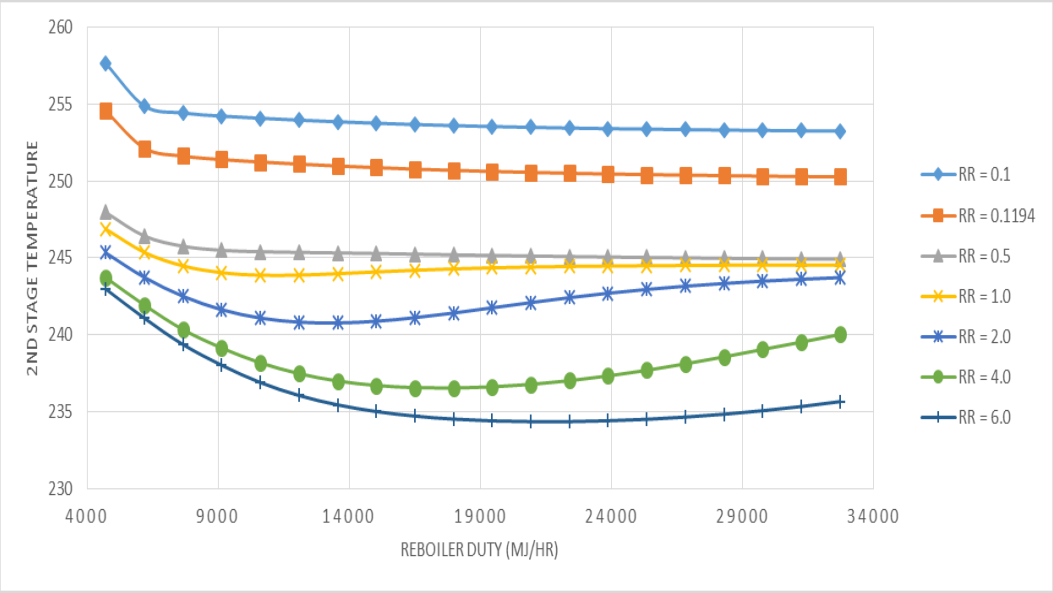


Figure 36 Effects of reboiler duty to the 2nd stage temperature for given reflux ratio.

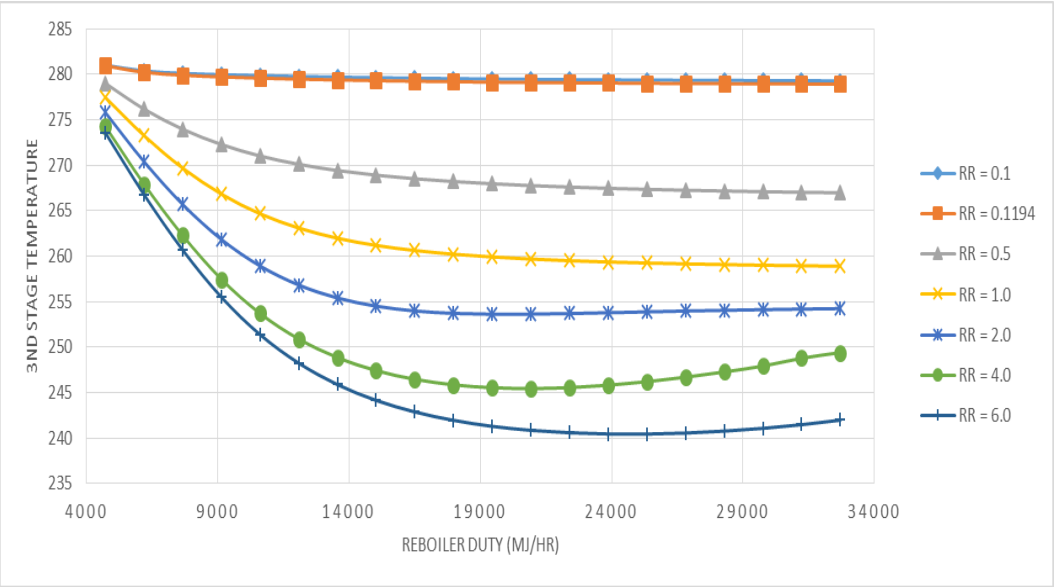


Figure 37 Effects of reboiler duty to the 3rd stage temperature for given reflux ratio.

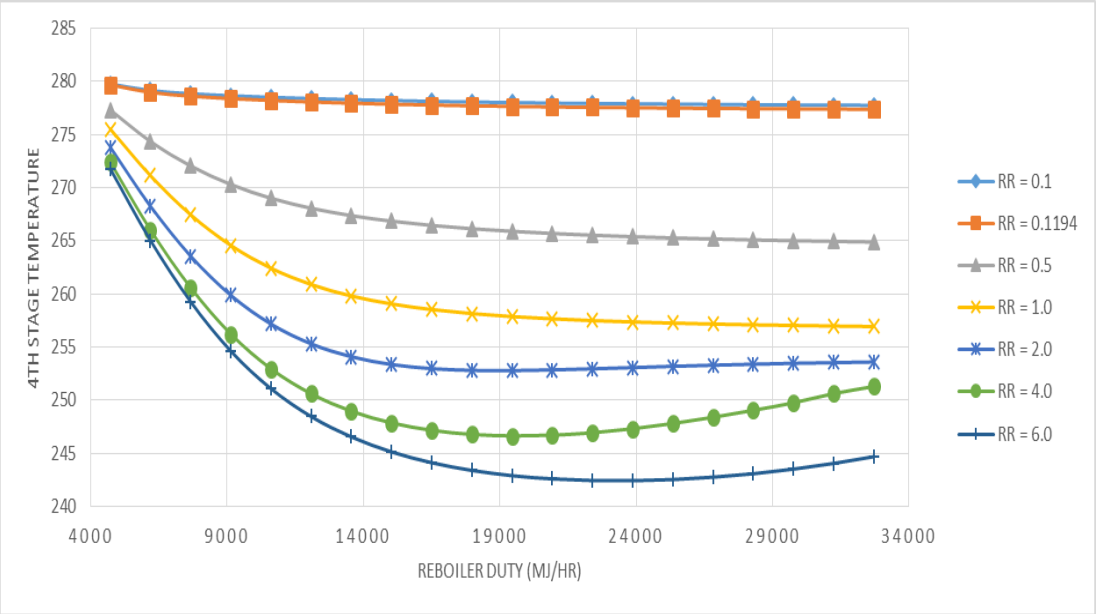


Figure 38 Effects of reboiler duty to the 4th stage temperature for given reflux ratio.

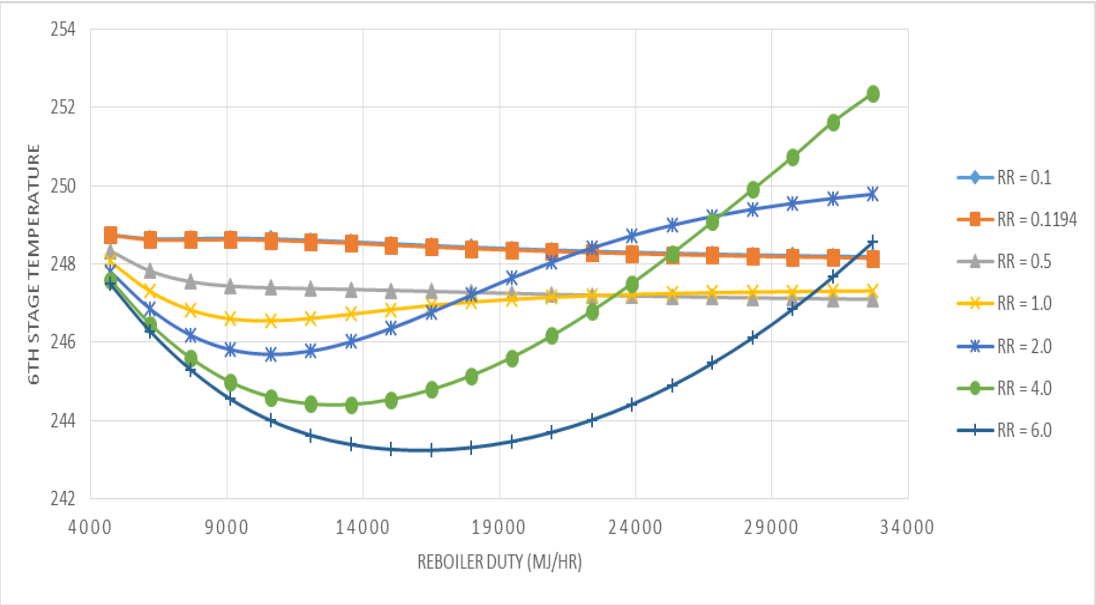


Figure 39 Effects of reboiler duty to the 6th stage temperature for given reflux ratio.

The result in 2nd 3rd 4th and 6th stage temperatures consist multiplicity behavior in effect of reboiler duty given reflux ratio. Multiplicity behavior in 2nd 3rd 4th and 6th stage stared from 8,000 MJ/hr. and high reflux ratio. However 2nd and 6th severe multiplicity behavior because 2nd stage near reflux ratio and 6th stage is one in all reaction zone and near reboiler duty which affect to establish multiplicity easily.

4.2.2 Control structure design of biodiesel process

After multiplicity analysis, control structure design will be studied in this section. The purposes of control structure design are to satisfy production rate, safety, stability, and methanol fraction in process.

4.2.2a Control degree of freedom analysis

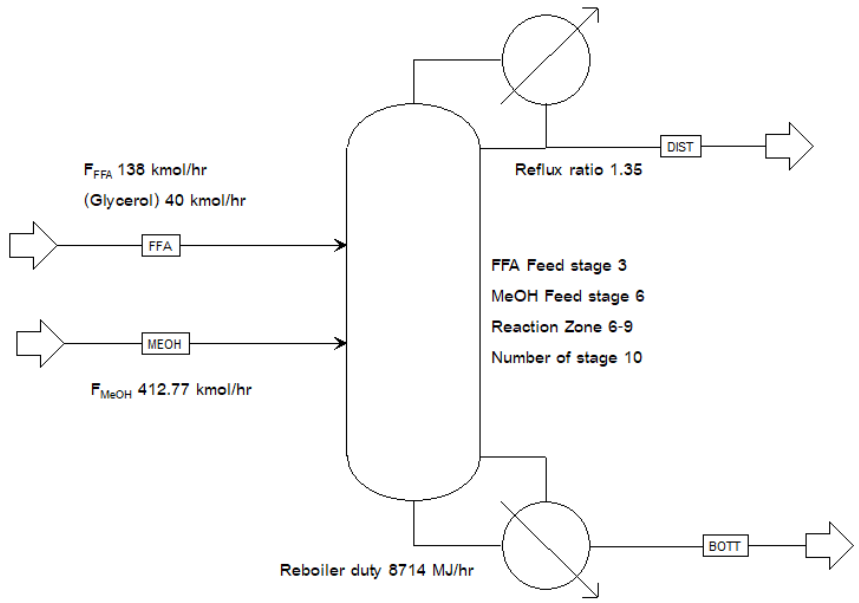


Figure 40 Configuration of biodiesel production by (Gomez-Castro, Rico-Ramirez et al. 2013)

Based on control degree of freedom (CDOF) analysis of (Konda, Rangaiah et al. 2006). , there are eight CDOFs including MV1: feed flowrate of free fatty acid, MV2: feed flowrate of the methanol, MV3: Flowrate of distillate stream, MV4: Reflux ratio, MV5: Flowrate of bottom stream, MV6: Reboiler duty, MV7: Condenser duty.

4.2.2.b Section controlled variables

Table 8 Pairing of Controlled and Manipulated Variables

Manipulated Variables	**Controlled Variable**
Flow rate of FFA stream	Production rate
Flow rate of MEOH stream	Ratio of FFA/MeOH
Distillate rate	Level in reflux drum
Bottom rate	Level in column base
Condenser duty	Column pressure
Reflux ratio	
Reboiler duty	

Pressure in reactive distillation column

Pressure in column must be controlled to avoid weeping and flooding in distillation column. It also implies vapor inventory in column.

The liquid levels in reflux drum

Liquid level in reflux drum must be controlled for stability. Hence, liquid level must be kept within limited values.

The production of biodiesel

To ensure production rate of biodiesel process, flow rate of FFA and ratio of FFA/MeOH must be controlled.

Table 8 shows paring between manipulated variables and controlled variable.

Up to now, there are two remaining CDOFs including reflux ratio and reboiler duty that can be used for control of product specification. Again temperature control will be chosen rather than composition control due to its reliability. The sensitivity to reflux ratio and reboiler duty will be used to find stage temperatures to be controlled as shown in Figures 41 and 42. Note that the most sensitive stage temperatures are the 3rd and the 4th stage temperatures, hence, these temperatures will be used as controlled variables to ensure product specification.

4.2.2.1 Dynamic simulation in Biodiesel process

Two control structures proposed includes single temperature control (CSI) where the 3rd stage temperature is controlled, and dual temperature control (CSII) where additional control loop is the 4th stage temperature controlled by reboiler duty. The control structure CSI is listed in Table 9 while the control structure CSII is listed in Table 10.

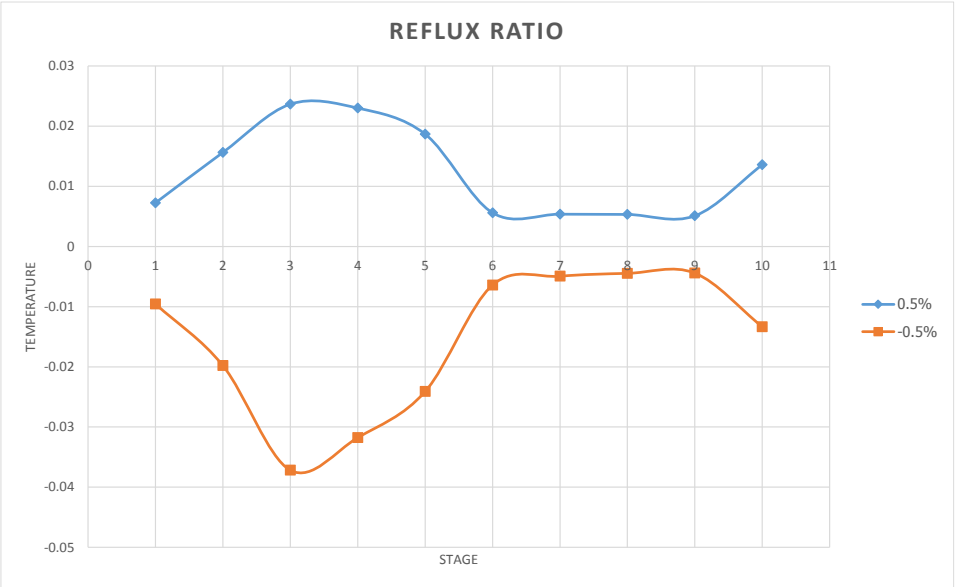


Figure 41 Sensitive stage temperature with respect to reflux ratio.

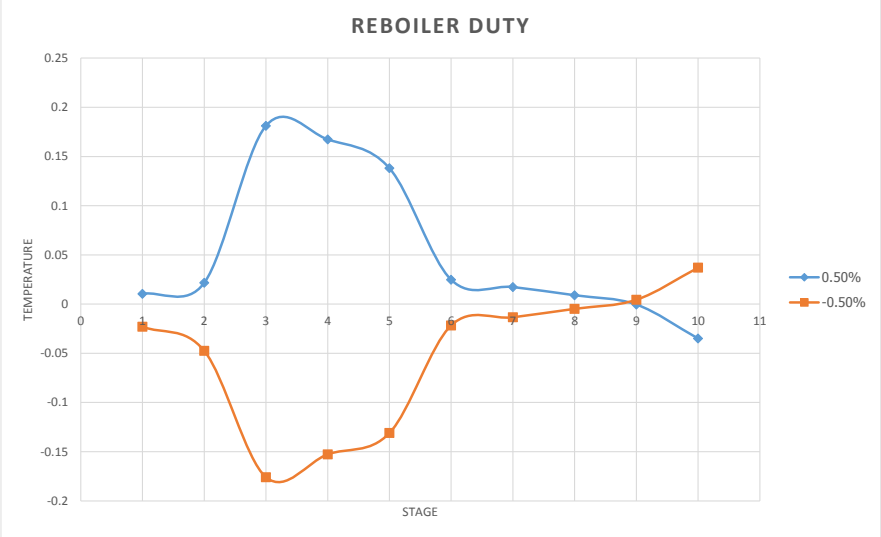


Figure 42 Sensitive stage temperature with respect to reboiler duty.

Table 9 Pairing of Controlled and Manipulated Variables in single temperature control

Manipulated Variables	Controlled Variable
Flow rate of FFA stream	Production rate
Flow rate of MEOH stream	Ratio of FFA/MeOH
Distillate rate	Level in reflux drum
Bottom rate	Level in column base
Condenser duty	Column pressure
Reflux ratio	3rd stage temperature
Reboiler duty	

Table 10 Pairing of Controlled and Manipulated Variables in dual temperature control

Manipulated Variables	Controlled Variable
Flow rate of FFA stream	Production rate
Flow rate of MEOH stream	Ratio of FFA/MeOH
Distillate rate	Level in reflux drum
Bottom rate	Level in column base
Condenser duty	Column pressure
Reflux ratio	3rd stage temperature
Reboiler duty	4th stage temperature

4.2.2.1a Single temperature control

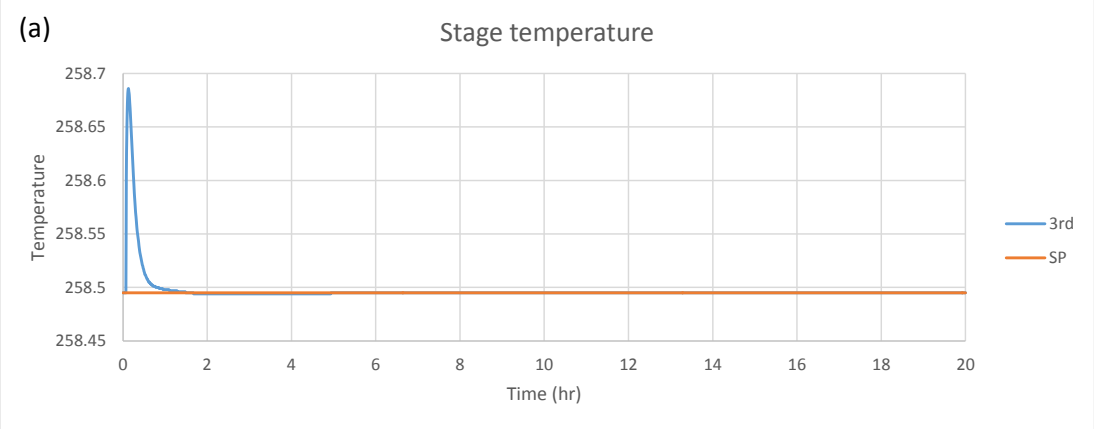
Single temperature control in biodiesel process only used reflux ratio pairing with 3rd stage temperature. Pairing variable was analyzed by location of manipulated variable and controlled variable. Reflux ratio near 3rd stage temperature or one in sensitive tray. In additional 3rd stage temperature close methanol recovery in distillate.

4.2.2.1b Dual temperature control

Dual temperature control used all remaining control degree of freedom are reflux ratio and reboiler duty. Selected between manipulated and controlled variables are reflux ratio pair with 3rd stage temperature and reboiler duty pair with 4th stage temperature.

4.2.2.2 Control performance

The proposed of control structure processes consist CSI and CSII validated in Aspen Plus dynamic. Suppose scenario disturbance change 5% (increase and decrease) occur in process then studied control structure design handle disturbance rejection or robustness control. Result in figure 43 showed control structure I (CSI) effect when increase disturbance 5% of FFA feed (a) 3rd stage temperature (CV) was reversed back to original setpoint after controller detected error in controlled variable then adjusted reflux ratio (MV) that was increase value for disturbance rejection or handle disturbance was occurred in process. In additional composition of methanol rise from original value.



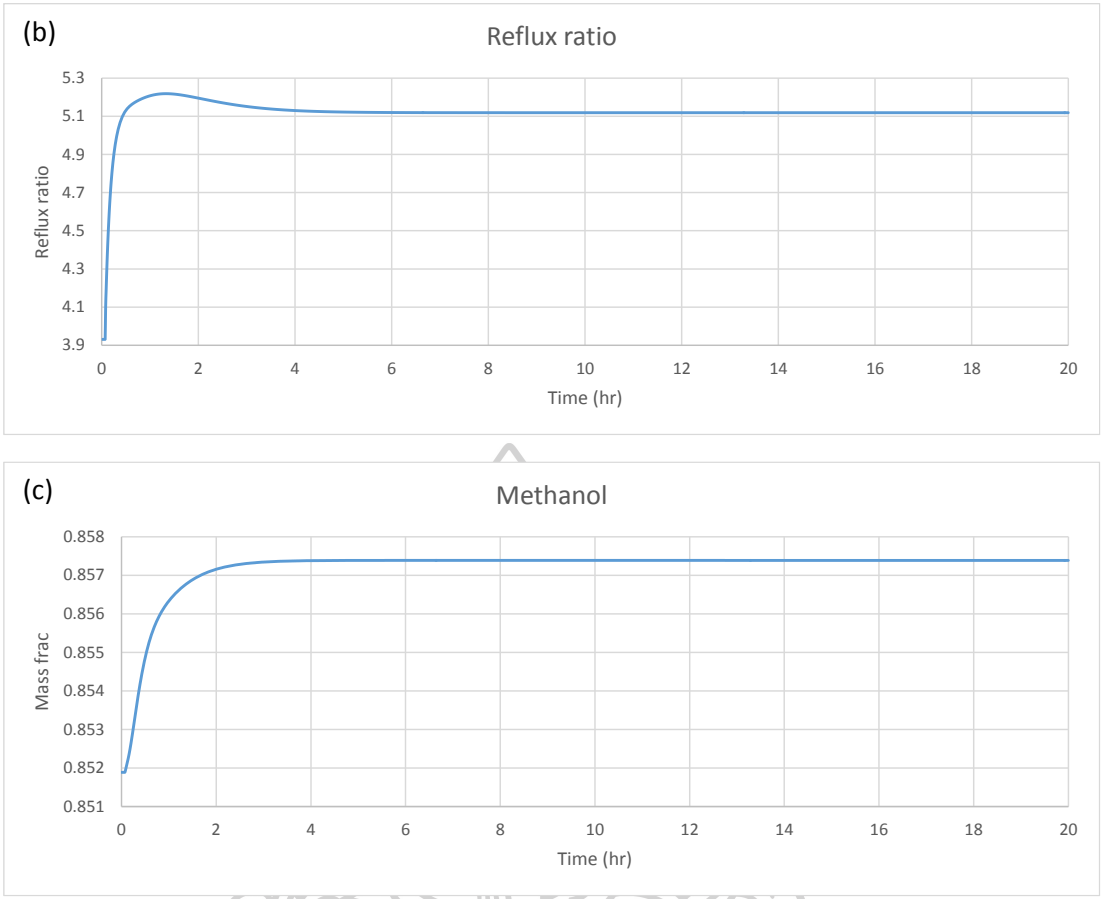


Figure 43 Dynamic response from control structure CSI: (a) response of the 3rd stage temperature (CV),and (b) Reflux ratio, and (c) Mass fraction of MeOH , when increase of 5% in FFA feed flowrate.

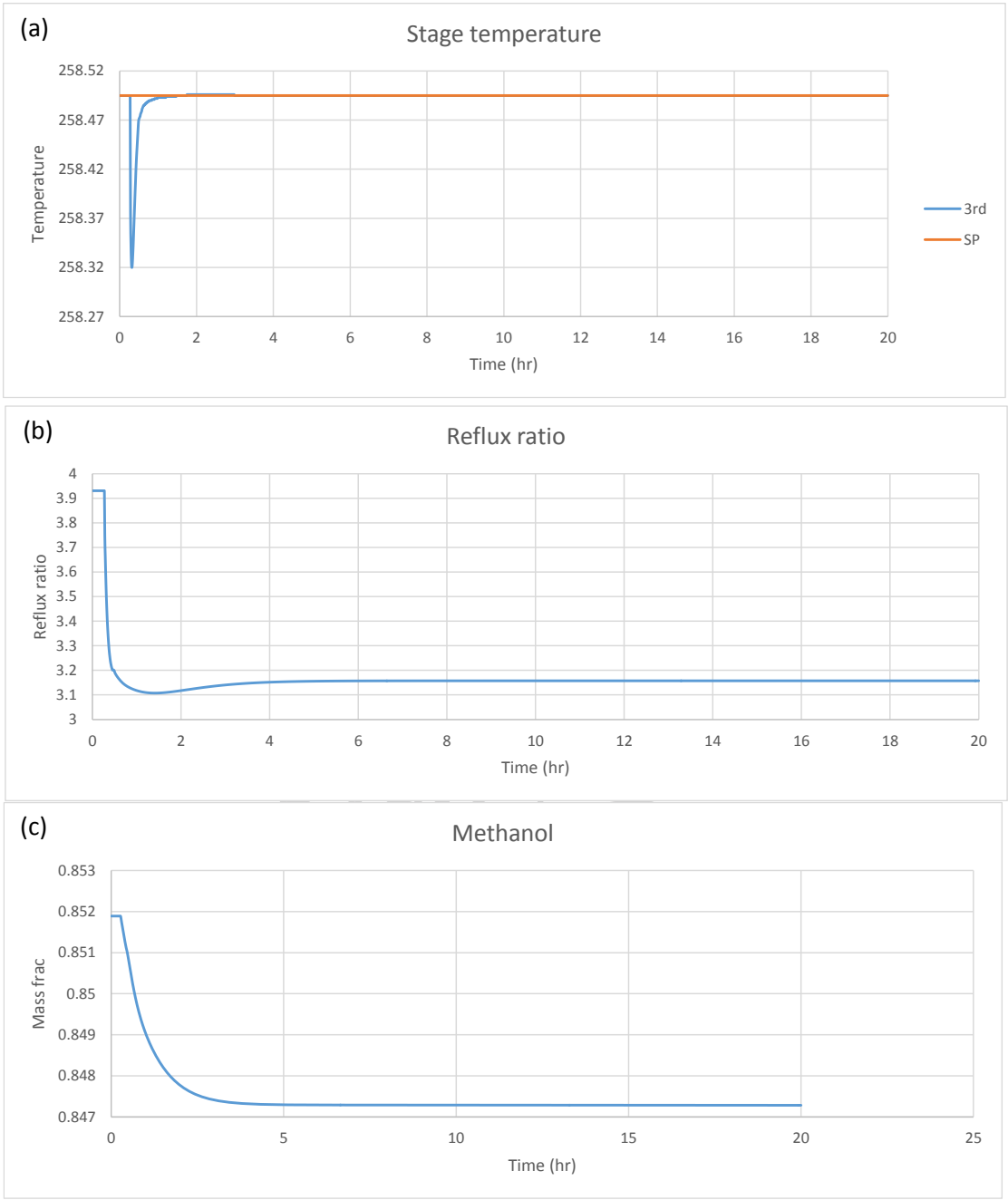
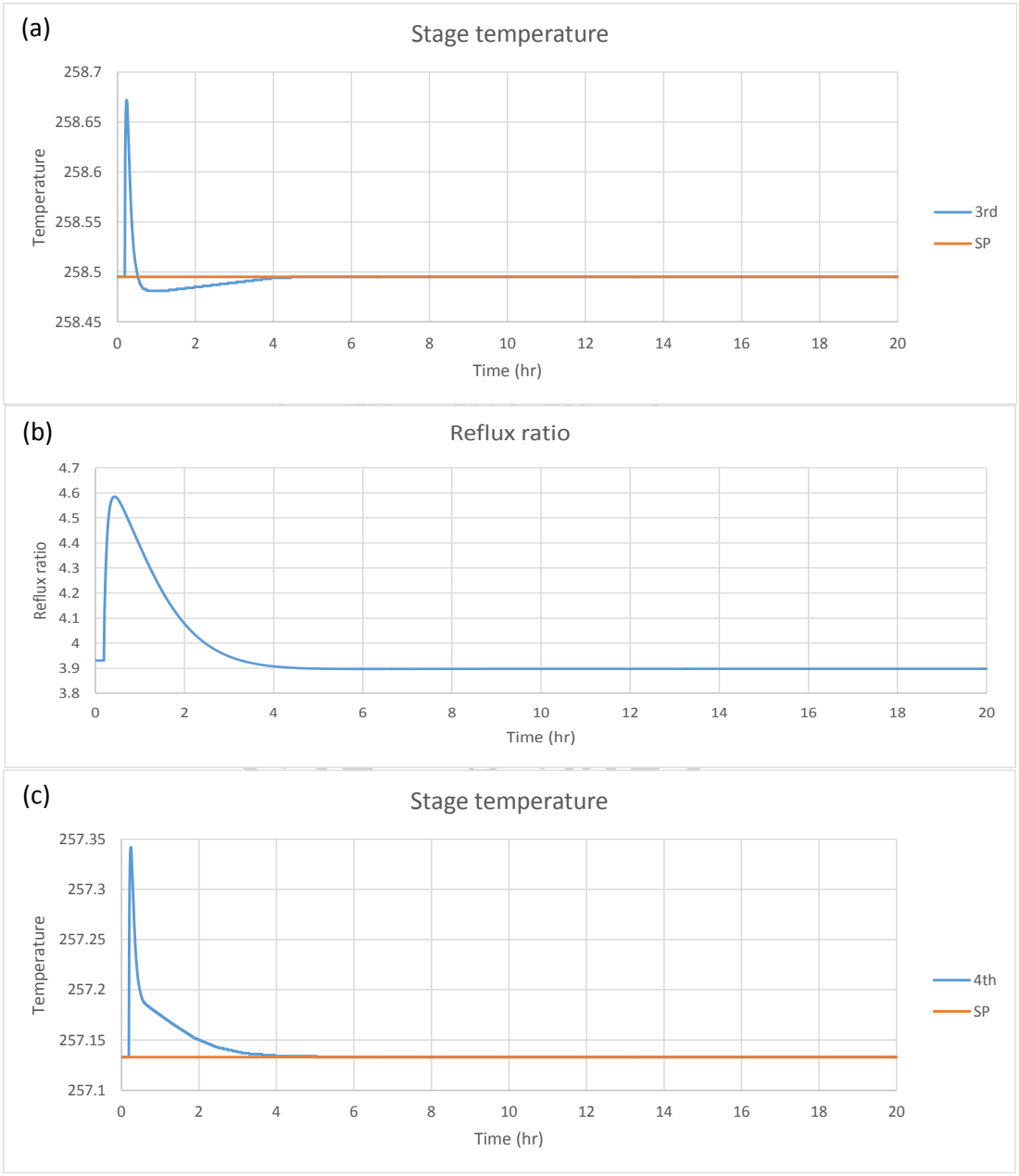


Figure 44 Dynamic response from control structure CSI: (a) response of the 3rd stage temperature (CV),and (b) Reflux ratio, and (c) Mass fraction of MeOH , when decrease of 5% in FFA feed flowrate.

In the other hand effect of -5 feed of FFA, reflux ratio is decrease after 3rd stage temperature decrease left out of setpoint for handle controlled variable the result was demonstrated in figure 44 is reflux ratio able to handle 3rd stage variable, but methanol composition is lower than original vale. Because effect of reflux ratio adjust stage temperature and composition of methanol.



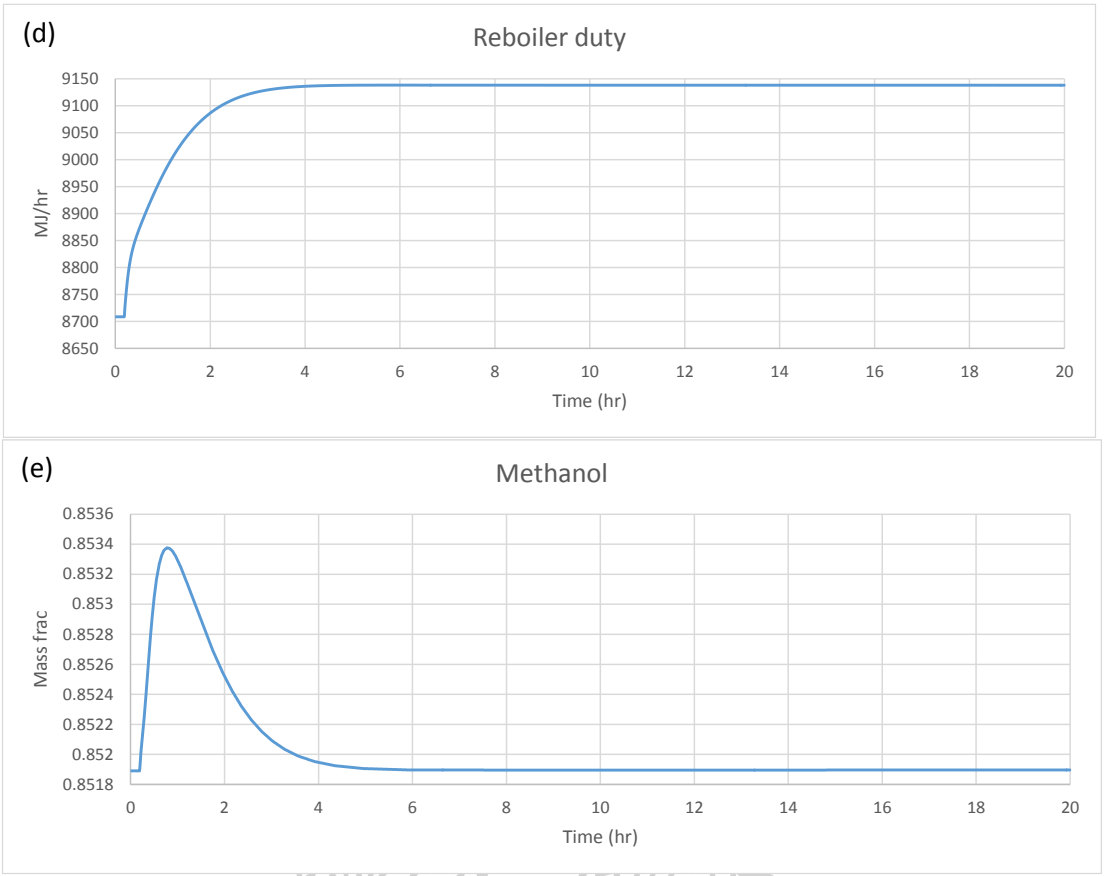
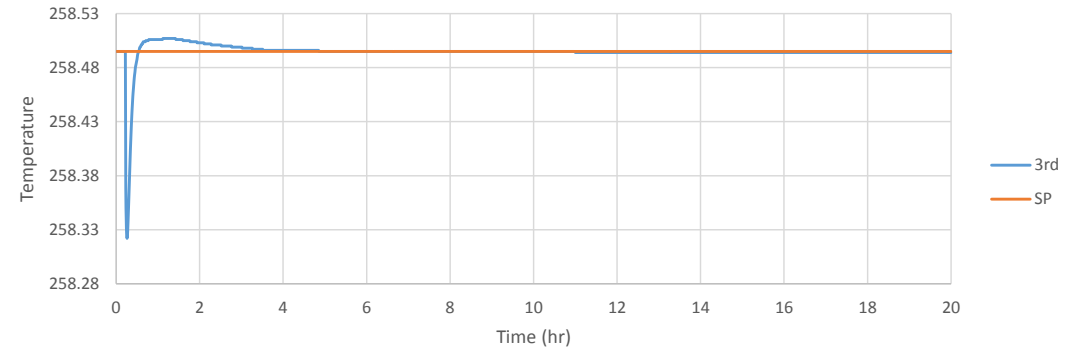
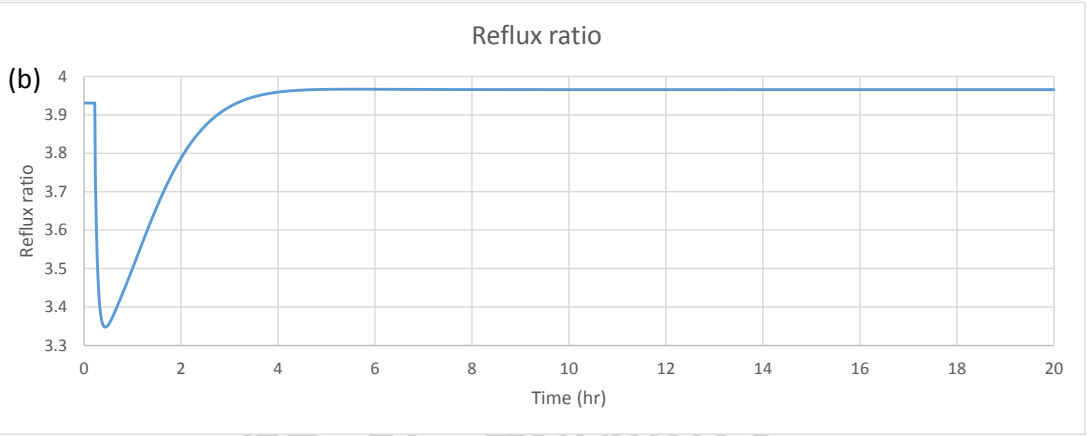


Figure 45 Dynamic response from control structure CS II: (a) 3rd stage temperature (CV-1),(b) Reflux ratio (MV-1) (c) 4th stage temperature (CV-2) (d) Reboiler duty (MV-2) and (e) Mass fraction of MeOH, when increase of 5% in FFA feed flowrate.

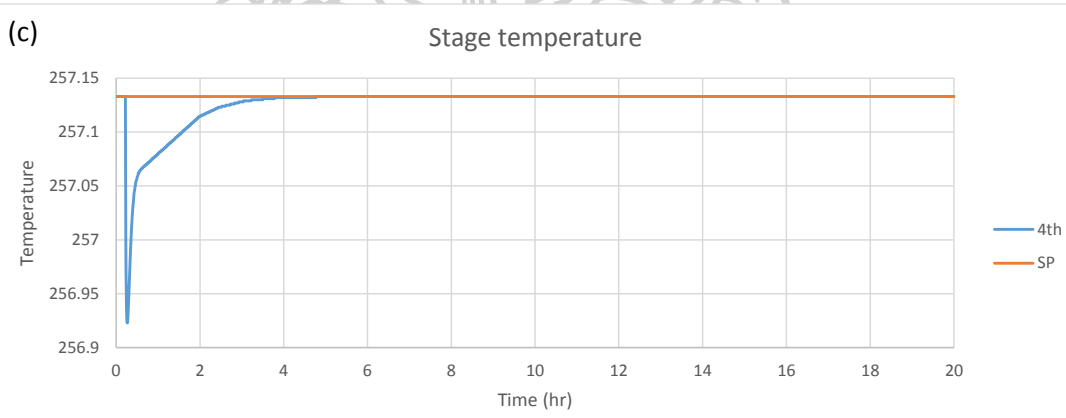
Result from figure 45 were dual temperature control and disturbance was occurred in process by increase 5% of FFA, from figure 45 demonstrated disturbance rejection in both loops control, first loop is 3rd stage (CV-1) and reflux ratio (MV-1), reflux ratio increase then 3rd stage temperature was decrease when disturbance occurred, And another loop reboiler duty (MV-2) increase value for reverse 4th stage temperature (CV-2) back to setpoint or handle disturbance was occurred in process. Methanol composition can back to the original value.

(a)


Stage temperature
Temperature
258.53
258.48
258.43
258.38
258.33
258.28
0
2
4
6
8
10
12
14
16
18
20
Time (hr)
3rd
SP


Reflux ratio
(b)
Reflux ratio
4
3.9
3.8
3.7
3.6
3.5
3.4
3.3
0
2
4
6
8
10
12
14
16
18
20
Time (hr)

(c)


Stage temperature
Temperature
257.15
257.1
257.05
257
256.95
256.9
0
2
4
6
8
10
12
14
16
18
20
Time (hr)
4th
SP

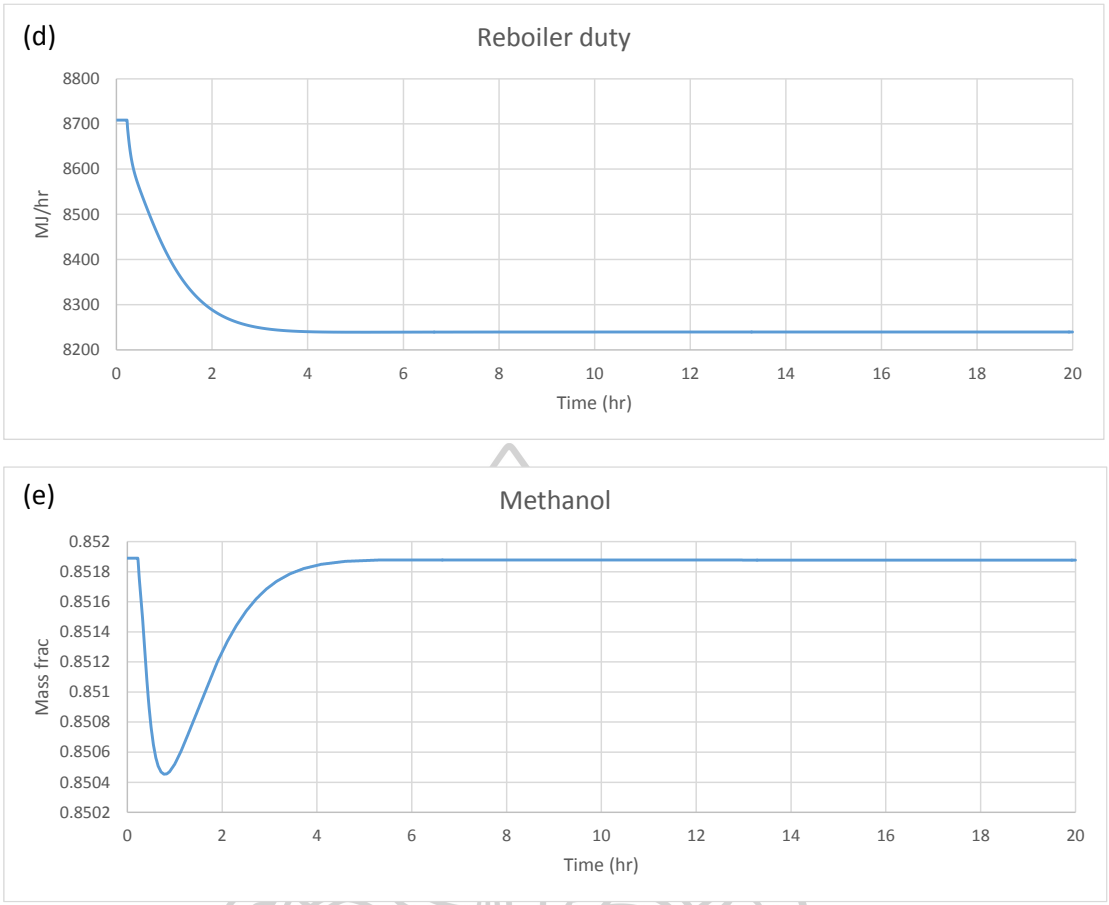


Figure 46 Dynamic response from control structure CS II: (a) 3rd stage temperature (CV-1),(b) Reflux ratio (MV-1) (c) 4th stage temperature (CV-2) (d) Reboiler duty (MV-2) and (e) Mass fraction of MeOH, when increase of 5% in FFA feed flowrate.

Result in figure 46 demonstrated disturbance was occurred scenario that decrease 5% of FFA. The control structure design is dual temperature control had strategy for handled and able rejection of disturbance was occurred in biodiesel process. Nevertheless dual temperature control have more ability for close the methanol composition near the original value more than single temperature control since reboiler duty affect to purity of product composition.

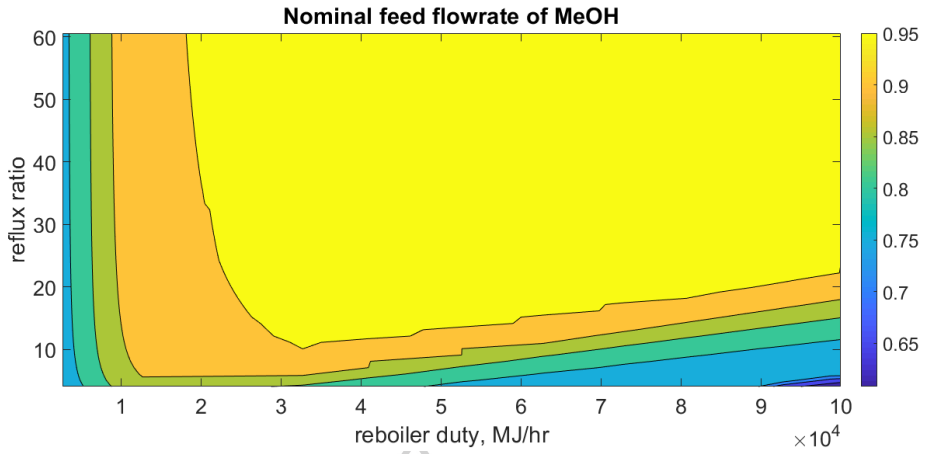


Figure 47 Methanol mass fraction under nominal feed flowrate of methanol

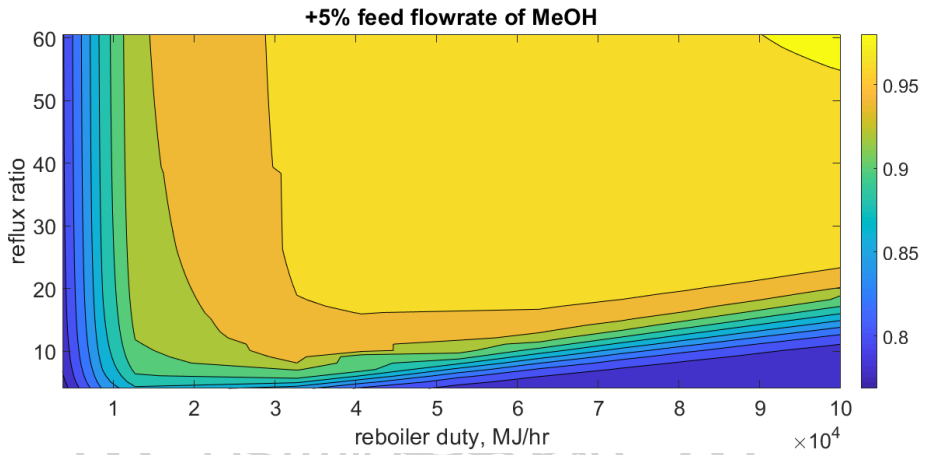


Figure 48 Methanol mass fraction under +5% change of feed flowrate of methanol

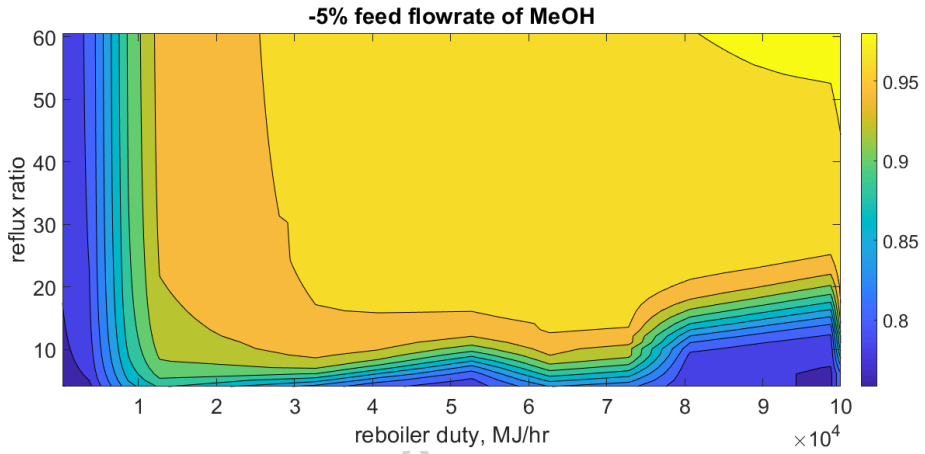


Figure 49 Methanol mass fraction under -5% change of feed flowrate of methanol

When reflux ratio and reboiler duty are used for control, the turning point of input multiplicity may changes as shown in Figure 47. Furthermore, the changes of operating condition also affects the turning points. As shown in Figure 48 and 49, changes of feed flowrate of methanol alter the turning points. Hence, exploration of multiplicity under given operating windows might be needed to ensure satisfactory results.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Analysis multiplicities in reactive distillation of ETBE production which input multiplicity can be obviously detected in Aspen Plus. However output multiplicity cannot be obviously detected but appear tentatively. In biodiesel production via reactive distillation which input multiplicity can be obviously detected while output multiplicity is not detected.

In control structure design, the most sensitive tray temperature are chosen as controlled variable to ensure composition of ETBE product. Two control structures include single and dual temperature control that are proposed and validated under disturbance change from nominal condition ±5 percent of ethanol feed flowrate. Dynamic simulation shows both control structures can keep the temperatures at the desired value. However, for dual temperature, tight control of ETBE mass fraction is possible. Control structure design of biodiesel production, the most sensitive stage temperatures are chosen as controlled variables to ensure methanol composition in distillate stream. Two control structures including single temperature control and dual temperature control are proposed and validated under disturbance changes of ±5 percent of free fatty acid feed flowrate. Dynamic simulation shows both control structures can keep the temperatures at the desired value. However, for dual temperature, tight control of methanol mass fraction is possible.

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