SIMULATION OF HETEROGENEOUSLY CATALYSED ESTERIFICATION FOR THE BIODIESEL PRODUCTION USING REACTIVE DISTILLATION COLUMN

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A report submitted in partial fulfillment of the requirements for the award of the degree of Bachelor of Chemical Engineering

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STUDENT DECLARATION

I declare that this plant design project entitled "Simulation of Heterogeneously Catalysed Esterification for the Biodiesel Production using Reactive Distillation Column" is the result of my own research except as cited in the references. The project has not been accepted for my any degree and is not concurrently summated in candidature of any other degree.

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To my beloved mother and father

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ABSTRACT

Biodiesel has become an attractive focus due to its environmental friendliness and benefits. Waste and non-edible raw materials have been employed for producing biodiesel in order to make it competitiveness with the petroleum-based diesel. Waste raw materials can contain substantial amount of free fatty acids (FFAs). Esterification reaction is one of the major routes to produce biodiesel from the raw material with high FFAs. However, the conventional process is facing several problems. Therefore, the development of an efficient continuous process for biodiesel manufacturing is required in which the use of a solid catalyst is highly desirable in order to suppress costly chemical processing steps and waste treatment. In the present study, an innovative esterification process of fatty acids based on reactive distillation was proposed for the biodiesel production. Process simulation was performed to study the feasibility of producing biodiesel using reactive distillation column, to identify the important operating and design factors (reactant ratio, reflux ratio, pressure, distillate-to-feed ratio, number of stages, and catalyst weight), and to propose a suitable configuration of the pilot plant for the biodiesel production. The esterification process was modelled by the esterification of oleic acid with methanol. The reaction was catalysed heterogeneously by sulfonic exchange acid resin. A pragmatic kinetic based on pseudohomogeneous model was incorporated into the reactive distillation model. From the simulation, it was found that it is feasible to produce biodiesel using reactive distillation column. The distillate-to-feed is best suited at 0.4 while the reflux ratio is best-suited in the range of 0.04 to 0.10. Pressure can be up to 3 bar. The changes in catalyst weight apparently contribute to the scale of production for biodiesel. The catalyst weight used is in the range of 250 to 500 gm. Finally, a suitable reactive distillation column configuration was proposed.

ABSTRAK

Biodisel telah menjadi satu tarikan kerana ia bersifat semulajadi and mempunyai pelbagai kebaikan. Sisa buangan and bahan mentah yang tidak boleh dimakan boleh digunakan untuk menghasilkan biodiesel supaya dapat bersaing dengan diesel daripada petroleum. Sisa buangan mentah mengandungi kandungan asid lemak yang tetap. Esterifikasi merupakan salah satu cara untuk menghasilkan biodiesel daripada sisa buangan mentah yang mengandungi asid lemak yang tinggi. Walau bagaimanapun, proses konveksional mengalami beberapa masalah teknikal. Sedemikian, penciptaan proses gabungan yang lebih efisien untuk biodiesel produksi yang memerlukan penggunaan pemangkin heterogen kerana permintaan yang tinggi justeru merendahkan kos langkah pemprosesan kimia dan kos rawatan bahan buangan. Kajian masa kini, satu inovasi dalam proses esterifikasi asid lemak telah melibatkan penyulingan bertindak balas dicadangkan untuk menghasilkan biodiesel. Proses simulasi telah dijalankan untuk mengkaji kebolehan menggunakan "reactive distillation" untuk menghasilkan biodiesel, menentukan kepentingan operasi dan faktor rekabentuk (nisbah bahan tindak balas, nisbah refluk, tekanan, nisbah bahan tersuling kepada suapan, bilangan peringkat dan berat pemangkin), dan mencadangkan konfigurasi yang sesuai untuk pembinaan logi berpandu bagi menghasilkan biodiesel. Proses esterifikasi dimodelkan sebagai esterifikasi asid oleik dengan metanol. Tindak balas dimangkin dengan menggunakan pemangkin heterogen "sulfonic exchange acid resin". Satu pragmatik kinetik yang menggunakan "pseudohomogeneous" model digabungkan dengan model penyulingan bertindak balas. Daripada simulasi, keputusan yang diperolehi menunjukkan biodiesel dapat diproduksi dengan menggunakan "reactive distillation" ruangan. Nilai yang sesuai untuk nisbah bahan tersuling kepada suapan ialah 0.4 manakala nisbah refluk boleh menggunakan nilai antara 0.04 hingga 0.10. Tekanan boleh dinaikkan sehingga 3 bar. Perubahan dalam berat pemangkin didapati memberi kesan kepada perubahan dalam

penghasilan biodiesel. Berat pemangkin yang digunakan adalah antara 250 hingga 500 gm. Akhirnya, satu konfigurasi yang sesuai untuk penghasilan biodisel melalui penyulingan bertindak balas telah dicadangkan.

TABLE OF CONTENT

CHAPTER

TITLE

PAGE

TITLE	i
STUDENT DECLARATION	ii
DEDICATION	iii
ACKNOWLEDGEMENT	iv
ABSTRACT	v
ABSTRAK	vi
TABLE OF CONTENT	viii
LIST OF TABLES	ix
LIST OF FIGURES	xi
LIST OF SYMBOLS/ABBREVIATION	xiv
LIST OF APPENDICES	xvi

1. INTRODUCTION

1.1 Introduction	1
1.2 Identification of problems	3
1.3 Objectives	4
1.4 Scope of study	4
1.5 Rationale and Significance	5

2. LITERATURE REVIEW

2.1 Introduction	7
2.2 General esterification system	8
2.3 Biodiesel system	9
2.4 Catalysis in esterification	10
2.4.1 Homogeneous	11
2.4.2 Heterogeneous	12
2.5 Reactive distillation technology	13
2.5.1 Introduction	13
2.5.2 Reactive distillation process development	21
2.5.3 Challenges in process design for reactive	26
distillation	
2.5.3.1 Feasibility analysis	26
2.5.3.2 Catalyst and hardware selection	27
2.5.3.3 Column scale-up	28
2.6 Reaction kinetics	29
2.7 Phase equilibrium model	34
2.8 Reactive distillation model	40
2.8.1 Equilibrium (EQ) stage model	41
2.8.2 Non-equilibrium (NEQ) stage model	42
2.8.3 Choice of modelling	44

3. METHODOLOGY

3.1 Introduction	46
3.2 Methodology flow chart	46
3.3 Incorporation of kinetic, thermodynamics and	
reactive distillation model	

4. RESULTS AND DISCUSSIONS

4.1 Introduction	57
4.2 Results	58
4.2.1 Reactant ratio	58
4.2.2 Reflux ratio	60
4.2.3 Distillate-to-feed ratio	62
4.2.4 Pressure	64
4.2.5 Number of stages	66
4.2.6 Catalyst weight	67
4.3 The optimised process	69

5. CONCLUSION AND RECOMMENDATIONS

5.1 Introduction	70
5.2 Conclusion for overall dissertation	71
5.3 Suitable Configuration of the pilot plant	72
5.4 Recommendation	73

REFERENCES

APPENDICES A – G 78-117

75

LIST OF TABLES

TABLE NO.	TITLE	PAGE
2 1	Biodiesel production via esterification	10
2.2	Industrially important reactions using RD.	15
2.3	Examples of kinetic models used for esterification process	30
	in biodiesel production.	
2.4	Kinetic parameters used in the model.	34
2.5	Commonly used approaches to VLE by simulation packages.	39
4.1	Number of stages affects conversion value.	66

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
2.1	Interaction of reaction and separation.	22
2.2	Design with respect to residence time and relative	24
	volatility.	
2.3	Equipment suitable for combining reaction and	25
	distillation (heterogeneous catalysis).	
2.4	Principles of the choice of equipment (heterogeneous	25
	catalysis).	
2.5	Relationship of scale-up tools and design parameters	29
2.6	Chemical equilibrium of reaction $A + B \rightleftharpoons P$.	36
	Stoichiometric lines emerge from a pole.	
2.7	Design of reactive distillation curve of an ideal ternary	37
	mixture.	
2.8	Model complexity in simulation of reactive distillation.	40
2.9	Equilibrium-based stage model without feed and side streams.	42
2.10	Non-equilibrium-based stage model without feed and side	43
	streams.	
3.1	Methodology flow chart.	48
3.2	Process flow chart.	49
3.3	Reactive distillation model.	52
3.4	Incorporation of kinetic model.	53
3.5	Incorporation of thermodynamics model.	54
3.6	Property methods decision for the selection of thermodynamic	s 55
	model.	

3.7	Incorporation of catalyst weight.	56
4.1	Conversion as a function of reactant ratio.	59
4.2	Conversion as a function of reflux ratio.	61
4.3	Conversion as a function of distillate-to-feed ratio.	62
4.4	Conversion and reboiler duty as the function of distillate-	63
	to-feed ratio.	
4.5	Conversion as a function of pressure.	64
4.6	Conversion and reboiler duty as the function of column pressure.	65
4.7	Conversion as a function of catalyst weight.	67
4.8	A suitable configuration proposed for the production of	69
	biodiesel using RD column.	
5.1	A suitable configuration proposed for the production of	73
	biodiesel using RD column.	

LIST OF SYMBOLS/ABBREVIATION

SYMBOL DEFINITION

a	liquid activity
A	pre-exponential factor in Arrhenius equation, units according
	to k
С	molar concentration in liquid phase, mol m ⁻³
C _{cat}	catalyst hold-up per unit of liquid phase volume, kg m ⁻³
C_{ref}	reference concentration for Damköhler number, mol m ⁻³
Da_1	Damköhler number for non-catalysed reaction
Da_2	modified Damköhler number for catalysed reaction
E_a	activation energy, kJ mol ⁻¹
Facid	molar flow rate of oleic acid, kmol h ⁻¹
G_V	volumetric flowrate, m ³ s ⁻¹
k_c	rate constant for the catalysed reaction, $m^6 s^{-1} mol^{-1} kg^{-1}$
<i>k</i> _{ref}	rate constant for the non-catalysed reaction, $m^6\ s^{\text{-1}}\ mol^{\text{-1}}\ kg^{\text{-1}}$
Ka	concentration-based reaction equilibrium constant
K_γ	ratio of liquid activity coefficients
K_x	activity-based reaction equilibrium constant
n	molar feed ratio of methanol : oleic acid
n_1, n_2	reaction orders for non-catalysed reaction
Р	pressure, Pa
r	reaction rate per unit of liquid volume, mol s ⁻¹ m ⁻³
R	gas constant, J mol ⁻¹ K ⁻¹
V	total liquid hold-up in the RD column, m ³
V_M	liquid molar volume, m ³ mol ⁻¹

Т	temperature, K
W _{cat}	catalyst hold-up in RD column, kg

Subscripts

acid	oleic acid
alcohol	methanol
cat	sulfonic exchange acid resin
ester	methyl oleate
0	initial or at zero conversion
ref	reference variable

Superscripts

*	modified, by including liquid activity coefficients
eq	at chemical equilibrium
liq	in liquid phase

Greek letters

$\Delta^r G_{P,T}^{liq}$	Gibbs free energy of reaction at P and T , kJ mol ⁻¹
φ_1	ratio of non-catalysed to catalysed reaction rate
φ_2	ratio of the product of liquid activities to K_a
γ	liquid activity coefficient

LIST OF APPENDICES

TITLE

APPENDIX

А	Results summary from simulation runs	78
	for different reactant ratio values.	
В	Results summary from simulation runs	85
	for different reflux ratio.	
С	Results summary from simulation runs	95
	for different distillate-to-feed ratio.	
D	Results summary from simulation runs	102
	for different pressure.	
E	Results summary from simulation runs	105
	for different number of stages.	
F	Results summary from simulation runs	111
	for different catalyst weight.	
G	Results summary for suitable configuration	117
	for biodiesel production using RD column.	

PAGE

CHAPTER 1

INTRODUCTION

1.1 Introduction

Biodiesel has become attractively focus and important because of the fastpaced depleting of petroleum reserves and also of its environmental friendliness and benefits. Biodiesel is an alternative fuel produced from renewable source (Berchmans et al., 2007; Santacesaria et al., 2007) which has low emission profile property minimising carbon dioxide emission. Thus, this fuel can be regarded as mineral diesel substitute with the benefit of lowering greenhouse emissions because it is a renewable resource (Felizardo et al., 2006). However, the high cost of biodiesel is the major obstacle for its commercialisation; the biodiesel produced from vegetable oil or animal fat is usually more expensive than petroleum-based diesel fuel from 10 to 50% (Leung et al., 2006). Alternatively, the production costs can be reduced using less expensive feedstocks containing fatty acids such as non-edible oils, animal fats and oils, fritter away oil and byproducts of the refining vegetables oils (Veljkovic' et al., 2006). Biodiesel has many environmental beneficial properties. Biodiesel can be described as 'carbon neutral' which means the fuel produces no net output of carbon in the form of carbon dioxide (CO_2) . Studies shows that the effect is caused by the oil crop absorbed the same amount of CO_2 when it grows and releases when the fuel is combusted. However, the amount of carbon dioxide cannot be properly associated as there are contributors to the green house gases such as the

production of the fertiliser. Biodiesel is a rapid biodegradable and completely nontoxic, meaning spillages represent far less of a risk than fossil diesel spillages. Besides that, biodiesel has a higher flash point than fossil diesel and so is safer in the event of a crash.

Most biodiesel produced nowadays are from waste vegetable oil sourced from restaurant, chip shops, industrial food producers. Currently, the usage of oil directly from the agricultural industry has the greatest potential source being not commercially produced as the raw oil is too pricy. The cost of converting raw oil from agricultural sources can be too expensive to compete with fossil diesel. Therefore, waste vegetable oil can often be sourced for free or sourced already treated for a small price.

Biodiesel has many environmental beneficial properties. Biodiesel can be described as 'carbon neutral' which means the fuel produces no net output of carbon in the form of carbon dioxide (CO_2). Studies shows that the effect is caused by the oil crop absorbed the same amount of CO_2 when it grows and releases when the fuel is combusted. However, the amount of carbon dioxide cannot be properly associated as there are contributors to the green house gases such as the production of the fertiliser. Biodiesel is a rapid biodegradable and completely non-toxic, meaning spillages represent far less of a risk than fossil diesel spillages. Besides that, biodiesel has a higher flash point than fossil diesel and so is safer in the event of a crash.

There are five primary ways of producing biodiesel: (i) direct use and blending of vegetable oil (Maa *et al.*, 1990), (ii) the usage of microemulsions with short-chain alcohols (Maa *et al.*, 1990), (iii) thermal cracking of vegetable oils (Charusiri *et al.*, 2005), (iv) transesterification of triglycerides catalysed by acids, bases or enzymes, and (v) esterification of fatty acids with alcohols, using acids catalysts, solids acids (Kiss *et al.*, 2006a, Kiss *et al.*, 2006b) or bioenzymes (Foresti

et al., 2007). Using transesterification reaction, biodiesel production is normally catalysed by alkaline homogeneous catalyst to form a mixture of fatty acid methyl esters (Santacesaria *et al.*, 2007). Alkaline catalyst could result soap formation if the feedstock used contains substantial amount of free fatty acids. The acid catalysed esterification reaction is one of the suitable routes to solve the problem.

Production of biodiesel is believed to be economical as it derives from biological sources such as vegetable oils or recycled cooking grease or oils. Biodiesel is an alternative source of energy produced by either esterification or transesterification process by converting oils or fats with appropriate alcohols. In orlder days, production of biodiesel uses separated reactor and distillation column which needs high capital costs. As technology advances, the combination of reaction and distillation within one unit operation called reactive distillation is widely used in industry for processes.

For scaling-up and optimizing the production of biodiesel, reactive distillation has a solid approach and compromise for the process. Besides that, the use of reactive distillation is a better choice as the combination of reaction and distillation offers a lower capital cost compared to the usage of a reactor and a distillation column.

1.2 Identification of Problems

Steinigeweg *et al.* (2003), Omota *et al.* (2003), Kiss *et al.* (2007;2008) and Matallana *et al.* (2000) have carried out experiments for the heterogeneously catalysed esterification for the production of biodiesel using reactive distillation

column. The outcome of these researchers is mostly in experimental works. Therefore, a simulation must be run to ensure the validity of data.

A simulation must be carried out to predict the results and study the possibilities before a plant can be built for production purposes. Simulation also useful for the preliminary design before a pilot plant is being built for experiment study. In the present study, the performance of the esterification of oleic acid and methanol catalysed by sulfonic exchange acid resin in the reactive distillation will be simulated by incorporating the thermodynamics model, kinetic model, and the reactor model.

Aspen-Plus simulator will be used as a tool for the simulation by incorporating the appropriate thermodynamics and kinetic models. The influence of important operating and design factors (reactant ratio, reflux ratio, pressure, distillate-to-feed ratio, size of the reactive section and catalyst weight) will be identified.

1.3 Objectives

The objectives of the studies are:

- 1. To study the feasibility of producing biodiesel using reactive distillation column.
- To identify the important operating and design factors for the reactive distillation process.
- 3. To propose a suitable configuration of the pilot plant for the biodiesel production.

In order to achieve the objectives of this project, the scopes of study are as below:

- 1. The thermodynamics model, kinetic model and reactive distillation model of the selected chemical biodiesel equation, i.e. esterification of oleic acid and methanol using sulfonic exchange acid resin will be analysed and screened.
- Using Aspen-Plus version 12.1, the models are inserted to run simulation. Results obtained are to verify the feasibility of reactive distillation for production in real industry.
- 3. The important operating parameters such as reactant ratio, reflux ratio, pressure, distillate-to-feed ratio, number of stages and catalyst weight will be studied.

1.5 Rationale and Significance

Rationale. The objective of the present study is to simulate a heterogeneously catalysed esterification for the production of biodiesel using reactive distillation. Laboratory experiments have proven the reactivity of oleic acid and methanol using sulfonic exchange acid resin as catalyst to produce biodiesel. In this research, the results obtained from simulation for the feasibility studies on reactive distillation column can be used to replicate into dynamic business reality.

Significance. Simulation is one of many engineering design method used to study feasibility of a process. From the studies on the feasibility of reactive distillation column, the results can be used to setup an optimised reactive distillation

pilot plant. The pilot plant is built based on the suitable configuration results which then use to generate experiment data. The experiment data that generated from reactive distillation pilot plant is then used to build a production plant using reactive distillation for the production of biodiesel.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Reactive distillation is a hybrid process that combines the reaction and separation in single equipment. The combination of reaction and separation into one single unit provides distinct advantages over the conventional, sequential approach. A reactive distillation includes a distillation column, flashers, strippers and condensers.

The combination (reactor and distillation) is advantageous as when the rate of chemical reaction is decreased by the reaction equilibrium resulting into poor yield, selectivity and conversion. The combination of separation process within the reactor induces better reaction products removal from the reaction zone thus improving the overall yield, selectivity and conversion compared to a conventional process.

Industrial reactive distillation systems comprise homogeneous and heterogeneous catalysed, irreversible and reversible reactions, covering large ranges of reactions, notably hydrogenations, hydrosulfurisation, esterifications, and etherification. The

system may contain multiple catalyst systems, gas and liquid internal recycle traffic over these catalyst systems, separation, mass flow, and enthalpy change.

2.2 General Esterification System

Esterification is a chemical reaction process involving two reactants typically an alcohol and an acid to form an ester as a product. Esters have characteristic pleasant and fruity odour. Esterification is a reversible reaction that therefore, the reactions are equilibrium reactions and need to be driven to completion according to Le Chatelier's principle.

- 1. Esterification of acetic acid with ethanol, catalysed both homogeneously by the acetic acid, and heterogeneously by Amerlyst-15 (Calvar *et al.*, 2007).
- 2. Heterogeneously catalysed esterification of acetic acid with isoamyl alcohol with cation-exchanged resin catalyst, Purolite CT-175 (Teo *et al.*, 2004).
- Esterification of acetic acid with butanol in a heterogeneous reaction system using solid acid catalysts such as Smopex-101, Amberlyst-12, sulphated ZrO₂, H-USY-20, H-BETA-12.5, H-MOR-45, Nb₂O₅, H-ZSM-5-12.5 (Peters *et al.*, 2006).

2.3 Biodiesel System

Biodiesel is the newest attraction to substitute the diesel fuel due to its environment benefits, but also for being a renewable and sustainable source of energy. Biodiesel is produced nowadays mainly by the transesterification of vegetable oils in the presence of basic homogeneous catalysts (NaOH, KOH, or related alkoxides), according to Santacesaria *et al.* (2007). Acids oils have become a new raw material for biodiesel production beside vegetable oils or animal fat but the amount of free fatty acid contains in acid oils exceed the maximum allows for conventional homogeneous basic technology. Because of this, heterogeneous catalyst can be used to perform the esterification reaction of the free fatty acid as well as transesterification of the triglycerides. Table 2.1 shows studies that have been done on biodiesel system via esterification process.

Reactant System Used	Reference
Esterification of decanoic acid with methanol	Sven Steinigeweg and Jurgen Gmerhling.
using strong acidic ion-exchange resin.	(2003)
Esterification of palm fatty acids using	Donato A.G. Aranda, Rafael T.P. Santos,
homogeneous acid catalysts in a batch reactor.	Neyda C.O. Tapanes, Andre Luis Dantas
	Ramos, Octavio Auqusto C. Antunes (2007)
Esterification of free fatty acids using sulphuric	J. M. Marchetti, A.F. Errazu (2008)
acid as catalyst in the presence of triglycerides.	
Esterification of free fatty acids in sunflower oil	J. Ni, F.C. Meunier (2007)
over solid acid catalysts using batch and fixed	
bed-reactors	
Esterification of dodecanoic acid with methanol,	Anton A. Kiss, Alexandre C. Dimian and Gadi
propanol or 2-ethylhexanol using sulphated	Rothenberg (2007)
metal oxides (zirconia, titania, and tin oxide)	
The heterogeneous catalyst system for the	Young-Moo Park, Dae-Won Lee, Deog-Keun
continuous conversion of free fatty acids in used	Kim, Jin-Suck Lee, Kwan-Young Lee
vegetable oils for the production of biodiesel	

Table 2.1 : Biodiesel production via esterific	ation.
--	--------

2.4 Catalysis in Esterification

In general, catalysis can be divided into autocatalytic, homogeneous or heterogeneous and it is meticulously applicable to the reactive distillation column.

Autocatalysis only occurs when a single chemical reaction whose reaction product is itself the catalyst for the reaction. Autocatalysis reactions' reaction velocity is much compliance to be influenced by the reaction temperature, in other words, the pressure plays a proportion role to the effect of temperature of equipment.

Homogeneous catalysis on the other hand is likely to be influenced by the changing of concentration to enhance or lower the reaction velocity. Meanwhile, Heterogeneous catalysis requires a structure to pack the catalyst particles on the reaction zone in the RD column. Reaction catalysed by heterogeneous catalysts is very limited in the changes of its reaction velocity because it can only be enhanced to a certain concentration range and higher temperature or pressure will degrade the effectiveness of the catalyst as it contains ion-exchange particles, whose temperature range is limited.

2.4.1 Homogeneous

Fundamentally, homogeneous catalysis is a chemistry term describing the catalyst is in the same phase (solid, liquid or gas) as the reactants. The catalysts use in biodiesel production using homogeneous catalyst is less-preferred compare to

heterogeneous catalyst. The reactions proceed over an intermediate complex and are often highly selective, but separation of the products and the catalyst is difficult.

Homogeneous catalysts can be divided to two types:

- a) Base catalysts: sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium methoxide (NaMeO);
- b) Acid catalysts: sulphuric acid (H₂SO₄), p-toluene sulfonic acid (PTSA), MSA, phosphoric acid (H₃PO₄), calcium carbonate (CaCO₃);
- c) Typical base concentrations are:
 - a. NaOH/KOH 0.3 to 1.5%
 - b. NaMeO -0.5% or less

The usage of homogeneous catalyst in biodiesel production will eventually constrain the developing of the yield as the catalyst is sensitive to free fatty acids (FFAs) and water content of the feedstock; the removal of catalyst after production; during the reaction, formation of soap with high FFA feedstock; large quantity of effluent water as a result of removal of catalyst; necessities pre-treatment of oil in case FFA content are higher; and no scope for regeneration or re-utilisation of the catalyst.

2.4.2 Heterogeneous

Heterogeneous catalysis is basically a catalyst in different phase (i.e. solid, liquid and gas, also oil and water) to the reactants. Heterogeneous catalysts provide a platform or surface for the chemical reaction to take place on. Separation of catalyst and products is easy, but the reaction is often less selective, because the catalyst material is not homogeneous.

Heterogeneous catalysts are such as sulphated zeolites and clays, hetro-poly acids, metal oxides, sulphates, and composite materials. Contradict to homogeneous catalyst, heterogeneous catalyst is preferred and beneficial as the catalyst can be regenerated thus reduces the catalyst cost; utilization of lower quantity feed stocks for biodiesel production; simplification of separation process thus reduces capital cost; and as well decrease in wastewater which develops environmental friendly process.

2.5 Reactive Distillation Technology

2.5.1 Introduction

Reactive distillation (RD) is a combination of a reaction and separation in a single unit. It is not a new concept application which includes the functions of enhancement and overall performance in the chemical engineering world. Overall, the production of propylene oxide, ethylene dichloride, sodium methoxide, and various esters of carboxylic acids are some examples of processes in which RD found similarity in application and gains not much attractive attention.

Reactive distillation has proven to able in rendering cost-effectiveness and compactness to a chemical plant which the evidence from the Eastman Kodak process that compacted the whole chemical plant methyl acetate in a single RD unit. In this chapter, the overview of an RD column will be discussed in its direction and suggestion on its potential. The objectives of using an RD are to: surpass equilibrium limitation, achieve high selectivity towards a desired product, achieve energy integration, perform difficult separations, and so on.

Table 2.2 gives a wide-ranging list of the reactions that have been investigated as candidates for RD.

Reaction	Catalyst/Column	Remarks on motives and achievements
	internals etc.	
Etherification		
methanol + isobutene = methyl tert butyl ether	Amberlyst 15	To enhance the conversion of isobutene and achieve
(MTBE)		separation if isobutene from C ₄ stream
methanol + isoamylene = <i>tert</i> amyl methyl ether	Ion-exchange resin	To enhance the conversion of isoamylene
(TAME)		
Esterification with alcohols/olefins		
acetic acid + methanol = methyl acetate + water	Dowex 50 W X-8	Recovery of acetic acid from dilute streams $(30 - 60\%)$
		w/w)
	Amberlyst 15	Recovery of acetic acid from dilute streams $(2.5 - 10\%)$
	(baskets on tray)	w/w)
	Katamax packing	
	Sulphuric acid	Recovery of dilute acetic acid in carbonylation process
		Manufacture of methyl acetate; overcomes azeotrope

Table 2.2 : Industrially important reactions using RD.

		formation; enhances conversion (>99%)
Synthesis of vinyl acetate		
acetaldehyde + acetic anhydride = vinyl acetate		Improved safe process with high yields
Hydrolysis		
methyl acetate + water = methanol + acetic acid	Ion-exchange resin	Recovery of acetic acid and methanol in polyvinyl
	bags	alcohol (PVA) and terephthalic acid (PTA) manufacture
	Fluidized RD	
	Cation exchanger on	Recovery of acetic acid in PVA manufacture
	inert	
Acetalisation		
methanol + aqueous formaldehyde = methylal +	Ion-exchange resins	To surpass equilibrium conversion; to remove
water	zeolites, ion-	formaldehyde as an impurity (e.g., from 1,2-butyene
	exchange resins	diol)
ethanol + aqueous formaldehyde = ehtylal + water	Ion-exchange resins	Recovery of formaldehyde and synthesis of ethylal
Aldol condensation followed by dehydration		

acetone to diacetone alcohol (DAA) and mesityl Anion exchange resin High selectivity towards DAA; enhanced conversion

avida		laval
oxide		level
n-butaraldehyde to 2-ethyl hexenal	Aqueous alkaline	Formation of trimers/tetramers of aldehyde is avoided
	solution	
Hydration/dehydration		
ethylene oxide + water = ethylene glycol	Cationic/anionic	To enhance selectivity towards MEG and avoid
	exchanger resins	formation of diethylene glycol (DEG); attain better
		temperature control over the exothermic reaction
hydration of cyclohexane to cyclohexanol	SiO ₂ /Ga ₂ O ₃	Surpass equilibrium conversion
Alkylation/trans-alkylation/dealkylation		
benzene + propylene = cumene	Union Carbide- LZY-	Use of exotherm of reaction; high purity cumene
	82 molecular sieves	
isobutene + propylene/butylenes = highly branched	Lewis acid promoted	Selectivity for C_7/C_8 branched alkanes
paraffins	inorganic oxide	
	catalyst	
Isomerisation		
α -isophorone = β -isophorone	Adipic acid, ZSM-5,	To surpass the equilibrium conversion

	alumina	
n-paraffin to <i>iso</i> -paraffins	Chlorinated alumina	To increase the octane value of paraffin stock
	catalyst, presence of	
	hydrogen (< 8 bar)	
Chlorination		
dichlorobenzene to trichlorobenzene		To increase selectivity towards trichlorobenzene
dichlorodimethyl silane to dichloro (chloromethyl)	photochlorination	Increased yield towards monochlorinated product
silane		
Hydrogenation/hydrodesulfurization/		
dehydrogenation		
hydrogenation of benzene to cyclohexane	Alumina supported	Avoids formation of methyl cyclopentane and cracking
	Ni catalyst	products; used for removal of benzene from light
		reformate
hydrogenation of acytelene		For removal of butadiene from crude C ₄ stream
Metathesis/disproportionation		
butene-1 = propylene + pentene or	Activated metal oxide	To surpass equilibrium limitation, increase in selectivity
butene-1 = ethylene + trans hexene-2		and operation under mild conditions
---	-----------------------	---
Condensation of aldehydes		
formaldehyde to trioxane	Strong acid catalyst	To enhance conversion
	hydrophobic shape	
	selective (modified	
	ZSM-5)	
Dimerisation/Oligomerisation		
oligomerisation of C ₄ iso-olefins	Solid phosphoric	To produce octane boosting oligomers; alternative to HF
	acid, cation exchange	alkylation process
	resins	
Carbonylation		
methanol/dimethyl ether $+ CO = acetic acid$	Homogeneous system	Production of high purity acetic acid

(Source: Reactive distillation: status and future directions, Kai Sundmacher and Achim Kienle (Eds.))

Apart from functioning as a reactor and distillation, RD column can be an efficient separator to enhance the recovery rate and further purification of chemicals. Reactions such as esterification and acetalisation are suitable to be used in the RD column. Theoretically, the production of biodiesel through esterification using reactive distillation as proposed in this study can be fully-exploited. Furthermore, component to be removed is allowed to react in the distillation column and the resultant product can be separated simultaneously.

Reactive distillation (RD) has many distinctive advantages over sequential processing, such as fixed-bed reactor followed by a fractionating column, in which the distillate or bottom of the reaction mixture is recycled to the reactor inlet. The most crucial advantage in use of RD for equilibrium-controlled reactions is the elimination of conversion limitations by continuous removal of products from the reaction zone. Apart from increased conversion the following benefits can be obtained:

- 1. An important advantage of RD technology is a reduction in capital investment, because two process steps are able to be carried out in the same device. This integration leads to lower costs in pumps, piping and instrumentation.
- If RD is applied to exothermic reaction, the reaction heat can be used for vaporisation of liquid and thus leads to saving of energy costs by the reduction of reboiler duties.
- 3. The maximum temperature in the reaction zone is limited to the boiling point of the reaction mixture, so that the danger of hot spot formation on the catalyst is reduced significantly. A simple and reliable temperature control can be achieved.
- 4. Product selectivities can be improved due to a fast removal reactants or products from the reaction zone. By this, the probability of consecutive reactions, which may occur in the sequential operation mode, is lowered.
- If the reaction zone in the RD-column is placed above the feed point, poisoning of the catalyst can be avoided. This leads to longer catalyst lifetime compared to conventional systems.

When RD-technology is to be applied in industry scale, there are three constraints need to be fulfilled for harmonisation:

- RD technology can be used only there is a possibility that the temperature window of the vapour-liquid equilibrium is equivalent to the reaction temperature. If the column operating pressure is to be changed, the temperature window will be altered as well. The thermal stability of the catalyst can limit the upper operation temperature of the distillation column.
- 2. Moreover, the necessity of wet pellets the chemical reaction has to occur entirely in the liquid phase.
- 3. It is extreme costly to change the catalyst in a structured catalytic packing catalysts with a long lifetime.

2.5.2 Reactive Distillation Process Development

As described earlier, reactive distillation (RD) may stand the chance in chemical industries in improving the structure of a process. By rule of thumb, the combination of distillation and reaction is plausible, only if the conditions of both operations are met and synchronised. Supporting argument claims that the reactions have to provide reasonable conversions in ascertain temperature and pressure levels which these data are comprehensively acceptable in a distillation column conditions.

Besides that knowing the important of the operating pressure and temperature in RD, catalyst types play a deeper measurement to understand RD column. The difference in using homogeneous and heterogeneous catalysts in the column also determine the cost of recycle back the catalyst. Homogeneous catalysts are widely used in most processes

however it is vitally need a separation step to recycle back the catalyst which increases the cost of recycling. It nonetheless can be avoided by using heterogeneous catalysts.

esterification:
$$alcohol + acid \leftrightarrow ester + water$$
 (2.1)

$$\frac{d[ester]}{dt} = k^{+}[alcohol][acid] - k^{-}[ester][water]$$
(2.2)



Figure 2.1 Interaction of reaction and separation.

From equation 2.1 and equation 2.2, it can be deduced that both equations will favour more products if the reaction is accelerated forward. According to Le Chatelier's principle, reactions can be influenced by temperature and amount of catalyst used. By increasing the temperature or the amount of catalyst, the forward reaction is accelerated by means of more removal of products in avoidance a change in concentrations in the production stream. The measurement of the product concentration (intensity of the product) and column efficiency are respectively termed as separation performance and reactor performance (Sundmacher and Kienle, 2003).

The maintainability of the reactive distillation column will be purely based on the separation performance but also the ratio of separation performance/reactor performance in order to measure the extent of the main and secondary reactions proceed to a comparable of an industrial-scale reaction column. To achieve the construction by means of separating reaction and product separation, it can be done when the reaction is carried out in the presence of a heterogeneously catalysed at the downcoming stream or with side reactors at the column.

Besides that, the use of reactive distillation column is most effective to be considered in reactions that are extremely fast in achieving a significant conversion in the residence time range of such columns.

For a simple equilibrium reaction, the reaction equation can be described like this as shown in equation 2.3 below:

$$A_1 + A_2 \leftarrow \frac{k_1}{k_{\min 1}} \rightarrow A_3 + A_4 \tag{2.3}$$

The rate constants for the forward and reverse reaction may be different from each other. Equation 2.3 shows a general reversible equation that applicable to certain chemical equilibrium. However, the equilibrium state (when the reaction velocity goes to zero) can be described using the law of mass action as shown in equation 2.4 below:

$$\frac{c_3^* c_4^*}{c_1^* c_2^*} = \frac{k_1}{k_{\min 1}} = K_c \tag{2.4}$$

While the conversion of the stoichiometrically limiting reactant, for example component 1, in the equilibrium state is shown in equation 2.5 as below:

$$U_1^* = 1 - \frac{V c_3^* c_4^*}{V_0 c_1^* c_2^* K_c}$$
(2.5)

In reactive distillation column, there are two distinguishable operating parameters can be considered:

- 1. Range of conversion which is influenced mainly by the concentration of the product removed in the product stream, which is known as 'controlled by distillation'.
- 2. Range of conversion which is influenced mainly by the residence time and the reaction constant, which is known as 'controlled by kinetics'.

Reactions that take place inside a reactive distillation column can be divided into two consecutive reaction paces i.e. slow reaction and fast reaction. A reaction is considered slow when the reaction time is slow which correlate to the low residence time. A fast reaction does not require long residence time as the reaction is capable to reach equilibrium in the residence time range that is typical for column internals. Basically, relative volatility plays a role in determining the type of separation steps needed based on the reaction paces. This can be shown in Fig. 2.2 below:



Figure 2.2 Design with respect to residence time and relative volatility.

Meanwhile, Fig. 2.3 lists the equipment alternatives for heterogeneous catalysis. Fig. 2.4 shows the reaction velocity as a function of relative volatility. In here, the relationship between the two functions will be used to describe the principles of the choice of the equipment for specifically heterogeneous catalysis.

nete	erogeneous catalysis
	rectification column with catalytic
	packings
	internals in the downsomers
	rectification column with side stream
	reactors
	column and reactor with pumparound
	evaporator and reactor with pumparound

Figure 2.3 Equipment suitable for combining reaction and distillation (heterogeneous catalysis).



Figure 2.4 Principles of the choice of equipment (heterogeneous catalysis).

For the usage of conventional distillation, a compilation of knowledge is abundantly available in the process synthesis, design, and scale up to be solved. However, study for the development of RD to the extent is not in a crucial stage. Process synthesis and design have been developed to a considerable extent. As RD column has been seen as a potential column certain process, the scaling-up works should considerably improve as the combination of reaction and distillation govern lot of benefits.

2.5.3 Challenges in Process Design for Reactive Distillation

The major challenges in the process design for reactive distillation basically comprises of three factors: feasibility analysis, catalyst and hardware selection, and column scale-up.

2.5.3.1 Feasibility Analysis

To understand the feasibility of the reactive distillation column, the stronghold of fundamental knowledge on equilibrium is essentially needed. The knowledge of equilibrium is the assurance to the effective development of non-reactive as well as reactive distillation process. However, the knowledge of equilibrium applied is not easy as the complexity occurs when the chemical equilibrium is superimposed on the vapourliquid equilibrium. Reactive azeotropes only produce under certain condition in a distillation column. However, the combination of reaction and distillation has the possibilities of forming reactive azeotropes. The formation of reactive azeotropes can be described theoretically (Ung *et al.*, 1995) and experimentally (Song *et al.*, 1997) which a new consideration for the study of feasibility of RD column (Malone *et al.*, 2000). Reactive azeotropes reduce the efficiency and effectiveness (cause difficulties and limitations) in reactive distillation. Depending on the type of reaction carries out, the establishment of physical and chemical equilibrium will be at its limitation when the application of thermodynamic methods is assessed into RD column.

The feasibility of a RD column is majorly depending on the severity of the kinetic limitations (Taylor & Krishna, 2000) which comprising of finite reaction rates, mass transfer limitations and/or slow side-reactions. Therefore, there is a number of studies need to be carried to identify the feasibility of RD column.

2.5.3.2 Catalyst and Hardware Selection

Some unit operations, such as reactors, are easily miniaturised and incorporated into high throughout equipment such as robotic platforms. However, there are currently no units that can replicate stage-wise unit operations such as distillation or reactive distillation on a small scale. Reactive distillation combines chemical synthesis with separation by distillation, but this leads to a non-trivial system; the hardware selection, the components present in the system, the mode of operation and the operating conditions all affect the performance that can be achieved. An important issue in the design of reactive distillation systems is the identification of new catalysts that perform well under reactive distillation conditions. Catalysts are crucial in increasing reaction rate when the operating temperature range is limited by the evaporation processes taking place. The main goal of this research is to develop a method, utilising high throughout technology, which can be used to assess potential catalysts for batch or semi-batch reactive distillation systems.

The key to achieving this target will be the ability to identify whether a candidate catalyst could be suitable as early as possible, ideally using information available from knowledge of the catalyst structure. Basically, the major task of catalytic packing structure is to certify an adequate contact coated/impregnated random packing materials, catalysts wrapped in fabric, and various methods of placing the catalyst in tray columns. Evident requirement in catalyst selection is a comparatively long duration since the entire catalytic structure has to be taken away during catalyst replacement.

2.5.3.3 Column Scale-Up

Fig. 2.5 depicts the most important issues of scale-up for the design of industrial columns, i.e., diameter and height of the column and the column internals, following successful feasibility testing through theoretical and/or experimental investigations of reactive distillation. Besides the essential question to the type of column internals (packing, random packings, trays), various criteria such as location of the reactive zone, catalyst volume and size, must be taken into account particularly in the case of heterogeneous reactive distillation.



Figure 2.5 Relationship of scale-up tools and design parameters.

To decide these issues, the three design aids – simulation, experiments, and references – can be used in close linkage with each other. Simulation might be the decisive basis when all major data are present. Experiments and the references thus provide essential data for the simulation or for verification thereof. Based on the general differences, one must differentiate between homogeneous (dissolved or fluid catalyst) and heterogeneous (solid catalyst fixed in the column) reactive distillation.

2.6 Reaction Kinetics

Kinetic model is a simultaneous system of differential equations and associated algebraic equations that defines the state variables and rate laws for a particular chemical system. Kinetic model is a quantitative statement used to illustrate how a real life system operates.

Table 2.3 shows selected examples of kinetic models used in reactive distillation column proposed by others research studies.

Reference	System Used	Kinetic model Used
Swen Steinigeweg and Jurgen Gmerhling (2003)	Esterification of the fatty acid decanoic acid with methanol catalysed heterogeneously by strong acidic ion- exchange resin	i) Langmuir-Hinshelwood-Hougen-Watson model $r = \frac{1}{v_i} \frac{dn_i}{dt}$ $= m_{cat} \times \left(\frac{k_1^* K_{DecH} a_{DecH} K_{MeOH} a_{MeOH} - k_{-1}^* K_{MeDec} a_{MeDec} K_{H_2O} a_{H_2O}}{1 + \left(K_{DecH} a_{DecH} + K_{MeOH} a_{MeOH} + K_{MeDec} a_{MeDec} + K_{H_2O} a_{H_2O} \right)^2} \right)$
		ii) Pseudo-homogeneous model $r = \frac{1}{v_i} \frac{dn_i}{dt} = m_{cat} \left(\frac{k_1 a_{DecH} a_{MeOH}}{\left(K_{Sorb} a_{H_2O}\right)^2} - \frac{k_{-1} a_{MeDec}}{K_{Sorb} a_{H_2O}} \right)$
		Nomenclature
		a_i = activity of component <i>i</i> (mol m ⁻³)
		K_i = reaction rate coefficient of component i (m ³ kg _{cat} ⁻¹ s ⁻¹)
		$K_{Sorb} = singular$

Table 2.3 : Examples of kinetic models used for esterification process in biodiesel production.

		m_{cat} = mass of the catalyst	
		r = reaction rate	
		Subscriptes	
		<i>DecH</i> = decanoic acid	<i>MeDec</i> = methyl decanoate
		<i>MeOH</i> = methanol	H_2O = water
M. Brehelin, F.	Production of n-propyl	i) Pseudo-homogeneous model	
Forner, D.	acetate by reactive	$1 dn_i$	$(a_{PrOH}a_{H_2O})$
Rouzineau, JU Renke X Meyer	distillation.	$r = \frac{1}{v_1} \frac{1}{dt} = n_H + K_f$	$\left(a_{HOAc} a_{PrOH} - \frac{1}{K_a}\right)$
M. Meyer and G.	Theoretical Study		
Wozny		Nomenclature	
		a = liquid phase activity	
		Δn = molar transformation, mol	

	n = molar amount, mol
	K_f = forward (esterification) equilibrium constant
	K_a = equilibrium constant
	Subscripts
	HOAc = acetic acid
	<i>PrOH</i> = 1-propanol
	PrAc = propyl acetate

The kinetics of oleic acid esterification with methanol has been studied by using sulfonic exchange acid resin as the heterogeneous catalyst. The experiment data obtained have been interpreted from pseudo-homogeneous second order equilibrium model.

The esterification reaction between oleic acid and methanol can be represented in the following schematic form:

$$oleic acid + methanol \rightleftharpoons methyl oleate + water$$
(2.6)

The modelling for the experiment runs, a pseudo-homogeneous second order equilibrium model has been used with an expression of the reaction rate, for equation 2.7, that is as follows and Table 2.3 tabulates the value of parameters used in the equation 2.7.

$$r = \frac{k_c x_A x_M}{1 + K_M x_M + K_W x_W} \left(1 - \frac{1}{K_{eq}} \frac{x_E x_W}{x_A x_M} \right) c_{cat}$$
(2.7)

Equation 2.7 uses kinetic equation which is derived from the Langmuir-Hinshelwood mechanism, ultimately considering additionally the competitive inhibition of methanol. The number of parameters involved in the kinetic equation, the evolution of the denominator of equation. 2.7 was analysed terms by terms. The results of the analysis demonstrated that some terms were several orders of magnitude lower than others. It was found that the second term of the denominator of equation 2.7 is the most significant. Based on the analysis, the complex kinetic of equation 2.7 is reduced to an expression with only two apparent kinetic parameters. The newly-derived kinetic modelling for the esterification of oleic acid and methanol is as follows:

$$r = k_1 x_A x_M \left(1 - \frac{1}{K_{eq}} \frac{x_E x_W}{x_A x_M} \right) c_{cat}$$

$$\tag{2.8}$$

Parameters	Pre-exp factor (k_0)	Active energy (E_a)	Heat of reaction
		(kcal/mol)	(ΔH_r) (kcal/mol)
k_1	12.93 ± 2.87	14.00 ± 0.99	
$(\text{mol.cm}^3/\text{g}_{\text{cat}}^2.\text{min})$			
k _{eq}	4.17 ± 0.04		2.68 ± 0.05

Table 2.4 : Kinetic parameters used in the model.

The list of symbols for the given above equilibrium model are as follows:

 c_{cat} = catalyst concentration in the reactive distillation column (g/cm³)

$$k_1$$
, k_{eq} = kinetic and equilibrium parameters (k_1 = mol.cm³/g².min)

r = reaction rate (mol/min.g_{cat})

 x_A = liquid molar fraction for A = oleic acid

 x_E = liquid molar fraction for E = ester

 x_M = liquid molar fraction for M = methanol

 x_W = liquid molar fraction for W = water

2.7 Phase Equilibrium Model

Thermodynamics plays an important key in understanding and designing all these processes. Reaction and separation are two processes that occur simultaneously give rise to special challenge both in experimental investigations and modelling the processes. Thermodynamics provides the basis relations, such as energy balances of equilibrium conditions, used in the process models, which are the key to reactive separation design. Furthermore, thermodynamics provides models and experimental methods for the investigations of the properties of the reacting fluid that have to be known for any successfully process design.

In reactive distillation, as in conventional distillation, knowledge of the vapourliquid equilibrium is vital. When this equilibrium is superimposed on a chemical reaction, the concentration curve in a distillation column is appreciably influenced. In an equilibrium reaction of the type

$$v_a A + v_b B + \dots \rightleftharpoons v_p P + \dots, \tag{2.8}$$

with the stoichiometric coefficients v_i , the chemical equilibrium of educts A and B with product P can be described using equibrium constant K_x according to Equation. 2.5.

$$K_{x} = \frac{x_{p}^{\nu_{p}}}{x_{A}^{\nu_{A}} x_{B}^{\nu_{B}}}$$
(2.9)

According to Frey and Stichlmair (1998), they have shaped out stoichiometric lines as shown in Fig. 2.6 to illustrate the direction of the concentration change due to the chemical reaction.



Figure 2.6 Chemical equilibrium of the reaction $A + B \rightleftharpoons P$. Stoichiometric lines emerge from a pole (Frey & Stichlmair, 1998).

Changes in composition of the reaction mixture due to distillation become perceptible with the help of the distillation curves. The superposition of the two processes is able to determine the reactive distillation curves in clarifying the concentration profile in a reaction column assuming a fast reaction. Fig. 2.7 shows that the direction of the concentration change due to reaction can sometimes be the opposite of that due to distillation, thereby resulting the production of reactive azeotropes, which cannot be overcome in a reaction column.

In Fig. 2.7, point 1 is assumed to be the chemical equilibrium in the liquid phase while the concentration of the corresponding vapour composition is given by point 1^{*}.



Figure 2.7 Design of reactive distillation curve of an ideal ternary mixture (Frey & Stichlmair, 1998).

The condensation of the vapour generates a liquid which is converted by chemical reaction into the chemical equilibrium state given by point 2. The stoichiometric lines represent the direction of conversion. Various application of this procedure directs to a reactive distillation line that runs from the starting point 1 to the low boiler A and coincides with the chemical equilibrium. From point 10, the reactive distillation line leads to the intermediate boiler B. The different direction of movement is due to different gradients of the distillation curve. Reactive azeotrope exists at point A. From Fig. 2.7 above, the co-linearity of the vapour/liquid equilibrium or distillation curve and the stoichiometic line, the liquid state remains unchanged.

Thermodynamics model can be divided into steady-state and unsteady-state model. This paper presents a thermodynamic model containing the combinatorial and energetic contributions to the excess Gibbs energy for correlating/predicting of the vapour-liquid equilibrium (VLE) for esterification process.

Thermodynamics property package selection is, appropriately, necessity for process simulation. The packages include EOSs, activity (solution) models and other specialised models for considering non-idealities in vapour and liquid mixtures. Table 2.5 summarises the parameters that are calculated in these approaches.

Anton *et al.* (2007) in their research of biodiesel by catalytic reactive distillation powered by metal oxides has successfully using the application UNIQUAC property model (UNIFAC (Dortmund modified)) as the phase equilibrium model.

In the proposed study done by Dossin *et al.* (2006), MOSCED method could not be applied to solve the Wilson equation since data for glycerine molecules are not tabulated. Therefore, UNIFAC method was used to calculate the activity coefficients.

Approach	Equation	Interpretation
EOS	$\hat{f}_{iV} = \hat{f}_{iL}$	Condition of Equilibrium between a Vapour and Liquid.
	$\hat{\phi}_{iV} y_i P = \hat{\phi}_{iL} x_i P$	$\hat{\phi}_{iV}$ and $\hat{\phi}_{iL}$ are calculated using the EOS to solve for y _i
		and/or x_i when solving for the equilibrium condition.
Solution Model	$\hat{\phi}_{iV} y_i P = \hat{\gamma}_i x_i \phi^s{}_i P^s{}_i (PF)_i$	$\hat{\gamma}_i$ are calculated using the solution model. An EOS is
		still needed to calculate $\hat{\phi}_{iV}$ and ϕ^{s}_{i} . Pure component
		vapour pressure (P^{s}_{i}) calculations are preformed with a
		vapour pressure model, and the Poynting factor
		corrections (PF) are optionally calculated with liquid
		density data.
	$y_i P = \hat{\gamma}_i x_i P^s{}_i$	Modified Raoult's law form of solution model.
Henry's Constant	$\widehat{\phi}_{iV} y_i P = H_i x_i$	Henry's constant form of equilibrium equation for use
		with gases having low solubility in the liquid phase. H_{i}
		is specific to the gas-liquid combination.

Table 2.5 : Commonly used approaches to VLE by simulation packages.

(Adopted from: Galen J. Suppes, Selecting Thermodynamic Models for Process Simulation of Organic VLE and LLE

Systems, University of Missouri-Columbia, 2007)

2.8 Reactive Distillation Model

Reactive distillation model can be divided into two subsequently models known as equilibrium (EQ) stage model and non-equilibrium (NEQ) stage model. The selection of models is depend on the depth of the model, various combinations of models including reaction and mass transfer can used to calculate the reactive distillation as shown in Fig. 2.8.



Figure 2.8 Model complexity in simulation of reactive distillation.

Mass transfer can be described with an equilibrium equation or with mass transfer kinetics. For simplicity, the reaction is expressed with an established chemical equilibrium or with reaction kinetics and thus the complexity of the modelling is greatly increased if the mass transfer and/or reaction kinetics are considered.

2.8.1 Equilibrium (EQ) Stage Model

For equilibrium stage model, RADFRAC is used as for its capability in handling both equilibrium reactions as well as kinetically limited reactions. By using RADFRAC, one can adjust the Murphree efficiency to obtain the best possible agreement brween the plant data and the simulations. The advantage of RADFRAC is that existing algorithms and programs can be used to solve the equations. RADFRAC fails to properly account for the influence that chemical equilibrium has on vapour-liquid equilibrium (and vice versa).

In Fig. 2.9 below depicts an equilibrium stage j which is described using the known MESH-equations (material, equilibrium, summation and heat equations). The molar change in the number of moles of component i due to the proceeding reaction must be considered. On the other hand, this equation will not accurately describe the achievement of reaction to chemical equilibrium. The behaviour of a real tray (non-ideal) may be described using of an efficiency method such as Murphree efficiency η (Lockett, 1986).



Figure 2.9 Equilibrium-based stage model without feed and side streams.

2.8.2 Non-Equilibrium (NEQ) Stage Model

Non-equilibrium (NEQ) model for reactive distillation (RD) is related to philosophy of rate-based models for conventional distillation. For NEQ, RATEFRAC mode for rate-based multi-component separation modelling was introduced by Aspen Technology (Sivasubramaniam & Boston, 1990). RATEFRAC appears to be based on the NEQ model of Krishnamurthy and Taylor (1985) with the addition of equations for the effect of reaction on mass transfer and chemical equilibrium constraints (if needed). The non-equilibrium based stage model is illustrated in Fig. 2.10 showing the balance vapour and liquid streams separately and contains component balances, thermal balances and summation equations for both control volumes. For conventional distillation without reaction the mass transfer rate between vapour and liquid phase is described by the matrix of mass transfer coefficients $[k_j]$, the specific interfacial area a_j and the total molar stream N_{tj} (Taylor & Krishna, 1993).



Figure 2.10 Non-equilibrium-based stage model without feed and side streams.

2.8.3 Choice of Modelling

Equilibrium stage model is a very good pragmatic approach suitable particularly in the early stage of process development to carry out feasibility studies.

Influential of model parameters on model accuracy (Kreul *et al.*, 1999) proves to have significant differences in concentration profiles comparing the equilibrium- and rate-based model, thus kinetic approach are recommended for packed columns. Besides that, detailed modelling is not necessarily straightforward as in most cases a consideration of interaction phenomena (e.g. diffusional and direct reaction-mass transfer interaction) that would lead only to small improvements in calculated concentration profiles.

In present time, many chemical industries mainly large-scale industrial columns are rarely produced without simulation, and in fact, facilities are now increasingly being set up without experiments. For this reason, simulation is a vital part in development and optimisation of separation sequences and the designing of individual columns. This applies in particular to reactive distillation because of the greater complexity.

Reactive distillation combines the functionality of a continuous reactor with a conventional distillation process. Implementation of model equations and all simulations are to be carried out using the model RADFRAC from the steady-state simulator Aspen Plus version 12.1, which is based on rigorous equilibrium-stage model for solving the MESH (Material balance, vapour-liquid Equilibrium, mole fraction Summations and Heat balance) equations.

The model is both rigorous enough to represent the process complexity and simple enough to ensure feasibility of the process simulation. To validate the reactive distillation model, the simulation results are compared with experimental results published by Santacesaria *et al.* (2007) for the synthesis of oleic acid.

A pseudo-homogeneous second order equilibrium model with an expression of reaction rate-based kinetic models proposed by Santacesaria *et al.* has been used to design the Reactive Distillation column i.e. weight of the catalyst required for each section, subsequently the weight of the catalyst that calculated has been used to simulate the performance of Reactive Distillation column.

The key results of simulation i.e. typical profiles of temperature, composition of liquid and vapour phases, molar flow rates of liquid and vapour phase will be evaluated using different figures. The simulation results of these models will be studied to understand the RD process design and operational features by studying how different process parameters can affect overall column performance. The different process parameters include reflux ratio, number of catalyst used, reaction kinetics employed, operating pressure of the column and the number of reactive and separation sections.

CHAPTER 3

METHODOLOGY

3.1 Introduction

Chapter 4 discusses methodology of the project in general, with a specific focus on running the simulation using Aspen-Plus version 12.1.

3.2 Methodology Flow Chart

Methodology flow chart is used as the guidelines and the sequences to make the present project go with a swing. As illustrated in Fig. 3.1, literature review will be carried out with the field that regards to this project. Simultaneously, the author needs to identify the problem in this research paper before the further research can be carried out. The identified problem is there is a scarce experiment data for biodiesel production using reactive distillation column. Therefore, simulation should be done before a real pilot plant can be built. Once the problem has been identified, the search for appropriate

model such as kinetic model, thermodynamics model, and reactive distillation model should be identified. The kinetic model used for the esterification of oleic acid and methanol can be seen in equation 2.8, Chapter 2 while the thermodynamics model used is UNIQUAC.

Next, the important operating parameters that need to be studied are incorporated in Aspen Plus. The operating parameters are to be studied are reactant ratio, reflux ratio, pressure, distillate-to-feed ratio, number of stages, and catalyst weight. After that, the author will generate an initial estimate for column pressure, reactive zone location, catalyst mass, reactant fuel location, reactant ratio, reflux ratio, column diameter, number of equilibrium stages and packed height. Lastly, a suitable reactive distillation configuration is proposed.



Figure 3.1 Methodology flow chart

3.3 Incorporation of Kinetic, Thermodynamics and Reactive Distillation Model

Process flow chart can be used to illustrate the sequence for the incorporation of kinetic and thermodynamics models in reactive distillation model in Aspen Plus version 12.1. Fig. 3.2 shows the process flow diagram, kinetic model for the esterification of oleic acid and methanol, thermodynamics model (UNIQUAC) and important operating parameters are incorporated in the reactive distillation model.



Figure 3.2 Process Flow Chart

Fig. 3.3 shows the selection of reactive distillation model. To start the simulation, the Columns tab from the selection of pieces of equipment is clicked, then, RadFrac is selected. Fract1, the second picture from the left in the top row is clicked. Next, the cursor is moved into the white area and the desired position for the column is clicked on. After that, the "Material Streams" box is clicked which located at the bottom left corner of the window. Red and blue arrows will appear around the column. A red arrow signifies a stream that is required for a design specification; blue arrows signify an optional stream.

Fig 3.4 shows the incorporation of kinetic model in Aspen Plus. The kinetic model can be inserted in the Reactions box. The type of kinetic model used is based on power law rather than Langmuir-Hinshelwood Hougen-Watson kinetics. The important data need to insert in the reactions box are: (i) chemical equations for esterification of oleic acid and methanol; (ii) pre-exponential factor (k_o) and (iii) activation energy (E_a).

Fig 3.5 shows the incorporation of thermodynamics model. The thermodynamics model can be inserted in Aspen Plus through the 'Property Specifications' sheet. In 'Property Specifications' sheet, the author can choose the base method to use for the calculations Aspen Plus will perform. Based on Fig. 3.6, the 'Property Methods Decision Program', the UNIQUAC has been selected for this simulation. In the property method choice, the mixture is firstly identified as polar or $T < T_{cr}$, then, the next selection will be based whether the mixture has electrolyte property. The mixture contains no electrolyte in it, thus the third property selection will be based on $P_r < 0.1 \& T < T_{cr}$. The mixture has been identified to have property between ' $P_r < 0.1 \& T < T_{cr}$, and the next selection property will be based on the availability of interaction parameters. The reaction used has interaction parameters available and the following property method selection will be based whether the mixture is in liquid-liquid phase. Hence, the mixture has been identified to be in liquid-liquid phase. From Fig 3.6, the route taken from above decision will lead to the thermodynamics decision box 'NRTL, UNIQAC

and etc', then to point A. From point A, the mixture has no vapour-phase association, which lead to the final decision thermodynamics box consists of thermodynamics models such as WILSON, WILS-RK, WILS-LR, WILS-GLR, NRTL, NRTL-RK, NRTL-2, UNIQUAC, UNIQ-RK, UNIQ-2, UNIFAC, UNIF-LL, UNIF-LBY, UNIF-DMD. Anton *et al.* (2007) in their research of biodiesel by catalytic reactive distillation powered by metal oxides has successfully using the application UNIQUAC property model (UNIFAC (Dortmund modified)) as the phase equilibrium model. Therefore, UNIQUAC has been selected as the thermodynamics model for this simulation.

Fig 3.7 illustrates the incorporation of catalyst weight in Aspen-Plus. The catalyst weight can be incorporation by going to Reactions folder under Block box. Under the tab name 'Holdups', the author can insert the specified reactive stages that can hold the amount of catalysts and amount of catalyst weight in kilogram can be inserted at liquid holdup column.



Figure 3.3 Reactive distillation model

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Figure 3.4 Incorporation of kinetic Model

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Figure 3.5 Incorporation of thermodynamics model


Figure 3.6 Property methods decision for the selection of thermodynamics model

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Figure 3.7 Incorporation of catalyst weight

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

The presentation and discussion of the results is the heart of the thesis. Many readers, of course, are interested only in obtaining the quick review of the work afforded by the Summary and the concluding section. But readers who have reason to study the entire text of a report will normally spend most of their time on the Results and Discussion section.

The first purpose of this section is a well-organised and objective presentation of the results. Tables and figures that show the results should have sufficient supporting description to permit the reader to interpret them quickly and accurately. There should be no repetition in words which already apparent from examination of the tables and figures. The second purpose of this section is a discussion of the results with analysis, to show that the conclusions are acceptable. Each major conclusion should be clearly explained and compared with the results of similar work by other investigators.

4.2 Results

The results section is basically to illustrate the end-result based on the operating parameters mentioned in the objectives section in graphical format. The operating parameters such as reactant ratio, reflux ratio, distillate-to-feed ratio, pressure, number of stages, and catalyst weight (sulfonic exchange acid resin) have been studied through the sensitivity analysis in Aspen-Plus version 12.1 and the value has been converted as graph illustration to ease readers.

4.2.1 Reactant Ratio

The reactant ratio is the ratio between molar flowrate of oleic acid over molar flowrate of methanol. It is illustrated in Fig. 4.1. The reactant ratio studied is in the range from 1.0 to 4.0. The increment value is by 0.5. Figure 4.1 illustrates the conversion as a function of reactant ratio.



Figure 4.1 Conversion as a function of reactant ratio.

From Fig. 4.1, an excess of oleic acid in the feed stream results in higher acid conversions. When the reactant ratio is 1.0, the conversion is approximately 84%, sequentially 1.5 (91%), 2.0 (93%), 2.5 (94.2%), 3.0 (94.4%), 3.5 (94.6%) and 4.0 (94.8%). As the reactant ratio increases from 1.5 to 4.0, there is no significant change in the conversion. However, there is a significant jump when a change from 1.0 to 1.5. The increase in the stoichiometric value of oleic acid is thus increases the amount methyl esters in the production stream by approximately 7%. The advantage of using reactive distillation is the reactant ratio can be decreased to its stoichiometric value. There is a continuous removal of products at the bottom stream which direct the reaction to the right, thus the stoichiometric value can be decreased. Besides that, acid catalysed reaction of a carboxylic acid and an alcohol to form an ester and water is a reversible process. The value of *K* will depend on the particular carboxylic acid and alcohol and is determined experimentally by allowing the reaction mixture to reach equilibrium and analysing for reactants and products. In general, the numerical value of the esterification constant varies between 1 and 10 for various primary and secondary alcohols and

carboxylic acids. The primary alcohols have a higher value than secondary alcohols. Tertiary alcohols are generally much less than unity, and direct esterification with a carboxylic acid is not practical since dehydration of the alcohol will generally occur much more readily than esterification. Therefore, for all calculations a total feed ratio of oleic acid:methanol of 1:1 is applied. Results summary for each change in reactant ratio value can be found in Appendix A.

4.2.2 Reflux Ratio

Reflux is the liquid condensed from the rising vapour which returns to the pot flask. The reflux ratio is the ratio between the boil up rate and the take-off rate. Or in other words, it is the ratio between the amount of reflux that goes back down the distillation column and the amount of reflux that is collected in the receiver (distillate).

If 5 parts of the reflux go back down the distillation column and 1 part is collected as distillate then the reflux ratio is 5:1. In the case where all the reflux is collected as distillate the reflux ratio would be 0:1. If no distillate is collected then a reflux ratio is not assigned. Instead it is called "total reflux" or equilibration.

The higher the reflux ratio, the more vapour/liquid contact can occur in the distillation column. So higher reflux ratios usually mean higher purity of the distillate. It also means that the collection rate for the distillate will be slower. Figure 4.2 illustrates the conversion as a function of reflux ratio.



Figure 4.2 Conversion as a function of reflux ratio.

From Fig. 4.2, it is can be clearly seen that there is no significant increase in the conversion as the reflux ratio is increased. Reflux ratio does not play a crucial role in increasing the conversion of methyl esters. The boiling point of methyl oleate is 353^oC while boiling point for water is 100^oC. The difference in boiling point between methyl oleate and water proved that reflux ratio does not affect the conversion of esters as the product is formed as the bottom stream. Any value of reflux ratio can be used and thus 0.04 is selected for further calculations. Results summary for each change in reflux ratio value can be found in Appendix B.

4.2.3 Distillate-to-Feed Ratio

Distillate-to-feed ratio is the measurement amount of distillate flow out over the total amount of feed to the column. Distillate-to-feed ratio or in short D:F ratio corresponds to the reboiler duty of the reactive distillation column. A higher D:F value needs a larger reboiler duty to boil up the raffinate back to the column to enhance the amount of distillate. However, a small increase in the D:F value would unconditionally increase the reboiler duty significantly which the end-result increase a small amount of conversion of methyl esters. Meanwhile, the increases in reboiler duty will increase the capital cost of the entire production plant. Figure 4.3 below illustrates the conversion as a function of distillate-to-feed ratio.



Figure 4.3 Conversion as a function of distillate-to-feed ratio.



Figure 4.4 Conversion and reboiler duty as the function of distillate-to-feed ratio.

From Fig. 4.3, the distillate-to-feed ratio can be divided into two ranges which are 0.01 to 0.10 and 0.10 to 0.40. The increment value for the range 0.01 to 0.10 is 0.01 while the increment value for the range 0.10 to 0.40 is 0.05. There is no significant increase in the conversion value for the range of 0.10 to 0.10. However, for the range 0.10 to 0.40, the increase in conversion value shows a linearity change. When the distillate-to-feed ratio is 0.40, the conversion is approximately 94%. As the distillate to feed ratio increases, the conversion and reboiler duty increases. However, the increase in conversion is 0.978. If D:F ratio at 0.4, the reboiler duty is approximate 390 kW and the conversion is 0.978. If D:F ratio is changed to 0.5, the reboiler duty increases tremendously to 1054 kW but the conversion does not increase significantly. Therefore, any further increase of D:F ratio above 0.4 is not advisable because the conversion remains non-significant. Results summary for selection value in distillate-to-feed ratio can be found in Appendix C.

4.2.4 Pressure

For a reactive distillation column, pressure plays a role in increasing or decreasing the conversion of a product. However, if heterogeneous catalyst is used in a reactive distillation column, elevating the pressure will affect the activity of the catalyst used. Increasing pressure thus increasing temperature of the column and will obstruct the catalyst. Figure 5.4 below shows the conversion as a function of pressure.



Figure 4.5 Conversion as a function of pressure.

Elevating the column pressure leads to higher temperature and hence higher reaction rates for kinetically controlled reactions. Otherwise, using sulfonic exchange acid resin it is not possible to operate at temperatures above 398K since this is the maximum operating temperature the catalyst can operate. Simulation studies show that temperature below 398K can be realised when pressures up to 3 bar are realised. Results summary for each change in pressure value can be found in Appendix D.



Figure 4.6 Conversion and reboiler duty as the function of column pressure.

From Fig. 4.6, it can be seen that as the column pressure is increased, the conversion and reboiler duty increases. Both conversion and reboiler duty increase linearly as the higher pressure is applied. In accordance to PVT theory, as the pressure increases, the boiling point of methyl oleate and water increase. Thus, the increase in boiling point of methyl oleate and water will need a higher reboiler duty to boil up the bottom stream to comprehend the higher boiling point of methyl oleate and water.

4.2.5 Number of Stages

It can be deduced that the increase in number of stages will increase the efficiency of separation. The number of stages varies is the stripping section. Table 4.1 shows the number of stages affecting the conversion unit.

Number of stages	Conversion
11	0.91
12	0.92
13	0.93
14	0.94
15	0.95
16	0.98

 Table 4.1 : Number of stages affects conversion value.

From table 5.1, it can be seen that the conversion increases as the number of stages increase. This is because reactive distillation column acts as an efficient and effective separation unit that enhances the product productivity. The separation efficiency is crucial for the success of the process since water has to be removed from the reactive section not only to shift the chemical equilibrium to higher conversions but also to avoid its detrimental sorption effect on reaction kinetics. Not only the reactive

section is crucial for effective separation, the number of stages that acts as stripping section to further purify the product and enhance the conversion. Results summary for each change in number of stages can be found in Appendix E.

4.2.6 Catalyst Weight

Varying the catalyst weight will thus increase the conversion of the methyl esters in the bottom stream. Figure 5.5 illustrates the conversion as a function of catalyst weight.



Figure 4.7 Conversion as a function of catalyst weight.

From Fig. 4.7, it can be seen that as the catalyst weight increases by 0.05 kg, the conversion of methyl esters increases as well. The starting value of catalyst weight is 0.25 kg because it is in accordance to a batch study proposed and proportionally to the total feed amount.

Catalysis reactions are preferred in environmentally friendly green chemistry due to the reduced amount of waste generated, as opposed to stoichiometric reactions in which all reactants are consumed and more side products are formed. Catalyst works by providing an alternative reaction pathway to the reaction product. The rate of reaction is increased as this alternative route has lower activation energy than the reaction route not mediated by the catalyst.

As mentioned above, the catalyst provides an alternative pathway involving a different transition state and lower activation energy. Consequently, more molecular collisions have the energy needed to reach the transition state. Hence, catalysts can enable reactions that would otherwise be blocked or slowed by a kinetic barrier. The catalyst may increase reaction rate or selectivity, or enable the reaction at lower temperatures. The catalysts do not change the extent of a reaction: they have no effect on the chemical equilibrium of a reaction because the rate of both the forward and the reverse reaction are both affected. The fact that a catalyst does not change the equilibrium is a consequence of the second law of thermodynamics. Results summary for each change in catalyst weight value can be found in Appendix F.

4.3 The Optimised Process

After the studies of the operating parameters, a further study on the optimised process has been carried out to propose a suitable configuration for the reactive distillation model. Fig. 4.8 shows the suitable optimised process for biodiesel production using reactive distillation column. Result summary for the suitable configuration for the production of biodiesel using reactive distillation column can be found in Appendix G.



Figure 4.8 A suitable configuration proposed for the production of Biodiesel using RD column.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Introduction

Generally, introductions and conclusions can be the most difficult parts of papers to write. While the body is often easier to write, it needs a frame around it. An introduction and conclusion frame the author's thoughts and bridge the author's ideas for the reader.

Just as the author's introduction acts as a bridge that transports the readers from their own lives into "place" of the author's analysis, the author's conclusion can provide a bridge to help the readers make the transition back to their daily lives. Such a conclusion will help them see why all the author's analysis and information should matter to them after they put the paper down.

The author's conclusion is his/her chance to have the last word on the subject. The conclusion allows the author to have the final say on the issue the author has raised in the author's paper, to summarise the author's thoughts, to demonstrate the importance of the author's ideas, and to propel the reader to a new view of the subject. It is also the author opportunity to make a good final impression and to end on a positive note.

The author's conclusion can go beyond the confines of the assignment. The conclusion pushes beyond the boundaries of the prompt and allows the author to consider broader issues, make new connections, and elaborate on the significance of the author's findings.

The author's conclusion should make the readers glad they read the author's paper. The author's conclusion gives the reader something to take away that will help them see things differently or appreciate the author's topic in personally relevant ways. It can suggest broader implications that will not only interest the readers, but also enrich the reader's life in some way. It is the author's gift to the reader.

5.2 Conclusion for Overall Dissertation

From the simulation data achieved, it can be concluded that biodiesel can be produced using reactive distillation column and concluding the achievement of the first objective of this dissertation which to study the feasibility of biodiesel production using reactive distillation column.

From Chapter 5, Results and Discussions, simulation has been run and the study on the operating parameters has been carried out. The results show the reactant ratio, distillate-to-feed ratio, pressure, number of stages and catalyst weight are the important operating parameters that affect the condition of a reactive distillation column. Meanwhile, reflux ratio does not play any significant role in reactive distillation column for product enhancement. Therefore, this concludes the second objective of this dissertation which is to identify the important operating and design factors for the reactive distillation column.

Lastly, a suitable configuration for pilot plant has been proposed in the next subchapter to adhere the last objective of this dissertation which is to propose a suitable configuration of the pilot plant for the biodiesel production.

5.3 Suitable Configuration of the Pilot Plant

A thorough study and analysis have been carried out using the simulation software Aspen Plus version 12.1 to fulfil the three main objectives of this dissertation. First and second objectives have been carried out by inserting the kinetic model, thermodynamic model and reactive distillation model in Aspen-Plus version 12.1 followed by the important operating parameter to be studied. Through the simulation, the first and second objectives have been successfully determined and illustrated in graphical format as shown in Chapter 5. As for this subchapter, a suitable configuration for the pilot plant of the biodiesel production has been proposed and as illustrated in Fig. 6.1 below:



Figure 5.1 A suitable configuration proposed for the production of Biodiesel using RD column.

5.4 Recommendation

There is always space for improvement in every research work and projects. The simulation study for the biodiesel production using reactive distillation column uses Aspen-Plus, one of many engineering simulation tool to study its feasibility. Besides that, the kinetic model which has been incorporated is modelled by power law and equilibrium (EQ) stage model is used for reactive distillation column.

The improvements that the author proposed for this simulation study are as follows:

- 1. Using HYSYS. HYSYS is a user-friendly computer software package developed by Hyprotech. The package combines comprehensive data regression, thermodynamic database access (TRC, DIPPR, DDB, API, DBS) and the Mayflower distillation technology to enable the design and analysis of separation systems, including azeotropic and extractive distillation and non-ideal, heterogeneous and multiple liquid phase systems. Besides that, HYSYS is a powerful engineering simulation tool, has be uniquely created with respect to the program architecture, interface design, engineering capabilities, and interactive operation. Moreover, HYSYS has integrated steady state and dynamic modelling capabilities, where the same model can be evaluated from either perspective with full sharing of process information, which represents a significant advancement in the engineering software industry.
- 2. Using MATLAB. Although there are numerous tools available, many of them free, the modelling and simulation MATLAB can be used in the engineering. Through MATLAB, there are a collection of MATLAB functions to construct and solve ODEs for deterministic simulation and to implement realisations of CMEs for stochastic simulation using advanced MATLAB coding.
- 3. Power law equation has been incorporated into Aspen Plus simulation tool software to test the feasibility of reactive distillation column for the biodiesel production. However, other kinetic models such as Langmuir-Hinshelwood-Hougen-Watson for the esterification of oleic acid and methanol can be incorporated to study the effect of different type of kinetic models used.
- 4. This simulation study used equilibrium (EQ) stage model which is RADFRAC to obtain the experiment data and results. Therefore, it is proposed that further study on the esterification of oleic acid and methanol using sulfonic exchange acid resin should use the non-equilibrium (NEQ) stage model to study the effect on the operating parameters and the conversion value.

REFERENCES

- Bock, H.; Wozny, G.; Gutsche, B. Design and Control of a Reaction Distillation Column Including the Recovery System. *Chem. Eng. Process.* 1997, 36, 101.
- Charusiri, W.; Vitidsant, T. Kinetic Study of Used Vegetable Oil to Liquid Fuels over Sulfated Zirconia. *Energy & Fuels*, 2005, 19, 1783-1789.
- Chemseddine, B.; Audinos, R. Use of ion-exchange membranes in a reactor for esterification of oleic acid and methanol at room temperature. *Journal of Membrane Science* 115 (1996) 77-84.
- Clark, J.H. Solid Acids for Green Chemistry. Acc. Chem. Res. 2002, 35, 791-797.
- Combes, D. Kinetics of lipase catalysed reaction in nonconventional media, in: F.X. Malcata (Ed.), Engineering of/with Lipases, NATO ASI Series, *Kluwer Academic Publishers*, Dordrecht, The Netherlands, 1996, p. 289.
- Cornish-Bowden, A.; Eisenthal, R. Statistical considerations in the estimation of enzyme kinetic parameters by the direct linear plot and other methods, *Biochem. J.* 139 (1974) 721.
- Dosin, Tanguay F.; Marie-Francoise Reyniers; Berger, Rob J.; Marin, Guy B. Simulation of heterogeneously MgO-catalysed transesterification for finechemical and biodiesel industrial production. *Applied Catalysis B: Environmental* 67, 2006, 136-148.
- Eisenthal R.; Cornish-Bowden, A. The direct linear plot: a new graphical procedure for estimating enzyme kinetic parameters, *Biochem. J.* 139 (1974) 715.
- Fangrui Ma and Hanna Milford A. Biodiesel Production: a review. Bioresource Technology 70, 1999, 1-15.

- Felizardo P, Neiva Correia MJ, Raposo I, Mendes JF, Berkemeier R, Bordado JM. Production of biodiesel from waste frying oils. *Waste Manage* 2006;26: 487-94.
- Foresti, M.L.; Pedernera, M.; Ferreira M.L.; Bucala, V. Kinetic modelling of enzymatic ethyl oleate synthesis carried out in biphasis systems. *Applied Catalysis A: General*, 334, 2008, 65-72.
- Goddard, R.; Bosley, J.; Al-Duri, B. Esterification of oleic acid and ethanol in plug flow (packed bed) reactor under supercritical conditions. Investigation of kinetics. *Journal of Supercritical Fluids*. 18, 2000, 121-130.
- Hammond, D.A.; Karel, M.; Krukonis V.J. Enzymatic reactiosn in supercritical gases, Appl. *Biochem*. Biotechnol. 11 (1985) 393.
- Hazarika, S.; Goswami, P.; Dutta, N.N.; Hazarika, A.K. Ethyl oleate synthesis by *Porcine pancreatic* lipase in organic solvents. *Chemical Engineering Journal* 85 (2002) 61 – 68.
- Jan Harmsen, G. Reactive Distillation: The front-runner of industrial process intensification. A full review of commercial applications, research, scale up, design and operation. *Chemical Engineering and Processing* 46, 2007, 774-780.
- Kiss, Anton A.; Dimian, Alexandre C.; and Rothernberg Gadi. Biodiesel by Catalytic Reactive Distillation Powered by Metal Oxides. *Energy & Fuels*, 2008, 22, 598-604.
- 17. Kiss, Anton A.; Dimian, Alexandre C.; and Rothernberg, Gadi. Biodiesel Production by Integral Reactive-Separative Design. 17th European Symposium on Computer Aided Process Engineering – ESCAPE17, 2007, 1283-1288.
- Oliveira, A.C.; Rosa, M.F.; Aires-Barros, M.R.; Cabral, J.M.S. Enzymatic esterification of ethanol and oleic acid – a kinetic study. *Journal of Molecular Catalysis B: Enzymatic 11* (2001) 999 – 1005.
- Omota F.; Dimian A.C.; and Bliek, A. Fatty acid esterification by reactive distillation Part 2 – kinetics-based design for sulphated zirconia catalysts. *Chemical Engineering Science* 58, 2003, 3175-3185.

- Popken, T.; Steinigeweg, S.; Gmehling, J. Systhesis and Hydrolysis of Methyl Acetate by Reactive Distillation Using Structured Catalytic Packings: Experiments and Simulation. *Ind. Eng. Chem. Res.* 2001, 40, 1566.
- Predojević, Z.J. The production of biodiesel from waste frying oils: A comparison of different purification steps. *Fuel* 87 (2008) 3522-3528.
- Santacesaria, E.; Di Serio, M.; Tesser, R. Gas-Liquid and Gas-Liquid-Solid reactions performed in spray tower loop reactors. *Ind. Eng. Chem. Res.* 2005, 44, 9461.
- Santacesaria, E.; Tesser, R.; Di Serio, M; Guida, M; Gaetano D.; Garcia Agreda, A.; and Cammarota, F. Comparison of Different Reactor Configurations for the Reduction of Free Acidity in Raw Materials for Biodiesel Production. *Ind. Eng. Chem. Res.* 2007, *46*, 8355-8362.
- 24. Steinigeweg, S.; and Gmehling, J. Esterification of a Fatty Acid by Reactive Disitllation. *Ind. Eng. Chem. Res.* **2003**, *42*, 3612-3619.
- 25. Steinigeweg, S.; Gmehling, J. n-Butyl Acetate Synthesis via Reactive Distillation: Thermodynamic Aspects, Reaction Kinetics, Pilot Plant Experiments, and Simulation Studies. *Ind. Eng. Chem. Res.* 2002, 41. 5483.
- 26. Taylor, R. and Krishna, R. Modelling reactive distillation. *Chemical Engineering Science* 55, 2000, 5183-5229.
- Tesser, R.; Di Serio, M.; Guida, M.; Natasi, M.; Santacesaria, E. Kinetics of Oleic Acid Esterification with Methanol in the Presence of Triglycerides. *Ind. Eng. Chem. Res.* 2005, 44, 7978.
- Tesser, R.; Di Serio, M.; Nastasi, M.; and Santacesaria, E. Kinetics of Oleic Acid Esterification with Methanol in the Presence of Triglycerides. *Ind. Eng. Chem. Res.* 2005, 44, 7978-7982.
- Veljkovic' V.B.; Lakic'evic', S.H.; Stamenkovic', O.S.; Todorovic', Z.B.; Lazic', M.L. Biodiesel production from tobacco (*Nicotiana tabacum* L.) seed oil with a high content of free fatty acids. *Fuel* 85 (2006) 2671-2675.
- 30. Yong, Y.P.; Al-Duri, B. Kinetic studies on immobilised lipase esterification of oleic acid and octanol, J. Chem. Technol. *Biotechnol.* 65 (**1996**) 239.

APPENDIX A

Operating Parameters Condition:

Reactant ratio = 1.0 Distillate-to-feed ratio = 0.05

Reflux ratio = 0.04

Pressure = 1 bar Catalyst = 0.35 kg Number of stages = 16

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	6.90E-07	1.552231
METHA-01	0	10	3.94E-03	1.548289
METHY-01	0	0	2.44E-07	8.447768
WATER	0	0	0.9960567	7.451712
Total Flow	10	10	1	10
kmol/hr	10	10	1	17
Total Flow kg/hr	2824.668	320.4216	18.07083	3127.018
Total Flow 1/min	53.26892	6.735048	0.3284301	62.95467
Temperature K	298.15	298.15	372.0365	345.0088
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy	-1 96E+05	-56989 17	-6688/113	-1 21E+05
cal/mol	-1.90E+05	-50505.17	-00004.15	-1.2111+05
Enthalpy	-694 1013	-1778 568	-3701 221	-732 4654
cal/gm	071.1015	1770.500	5701.221	752.1051
Enthalpy	-5 45E+05	-1 58E+05	-18578 93	-6 36E+05
cal/sec	5.151.05	1.502+05	10570.95	0.501+05
Entropy	-433 7462	-57 54022	-34 9993	-243 3665
cal/mol-K	100.7102	07.01022	51.5555	215.5000
Entropy	-1 535565	-1 795766	-1 936784	-1 478713
cal/gm-K	2.125.02	0.00.1-1.11	0.050514	5.007.00
Density mol/cc	3.13E-03	0.0247461	0.0507464	5.03E-03
Density gm/cc	0.8837759	0.7929208	0.9170307	0.8278492
Average MW	282.4668	32.04216	18.07083	164.5799
Lig Vol 60F l/min	53.27933	6.722433	0.3023024	59.52338

 Table A.1 Results summary for reactant ratio at 1.0.

Reactant ratio $= 1.5$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.05$	Catalyst = 0.35 kg
Reflux ratio $= 0.04$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	15	0	9.18E-07	5.890236
METHA-01	0	10	3.57E-03	0.8866654
METHY-01	0	0	1.55E-07	9.109763
WATER	0	0	1.246427	7.863336
Total Flow	15	10	1.25	22 75
kmol/hr	15	10	1.23	25.75
Total Flow kg/hr	4237.001	320.4216	22.56949	4534.854
Total Flow 1/min	79.90339	6.735048	0.4100422	91.04649
Temperature K	298.15	298.15	372.2478	349.9829
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy cal/mol	-1.96E+05	-56989.17	-66893.02	-1.35E+05
Enthalpy cal/gm	-694.1013	-1778.568	-3704.837	-706.9183
Enthalpy cal/sec	-8.17E+05	-1.58E+05	-23226.74	-8.90E+05
Entropy cal/mol-K	-433.7462	-57.54022	-34.98061	-279.8811
Entropy cal/gm-K	-1.535565	-1.795766	-1.937384	-1.465798
Density mol/cc	3.13E-03	0.0247461	0.0508077	4.35E-03
Density gm/cc	0.8837759	0.7929208	0.9173645	0.8301352
Average MW	282.4668	32.04216	18.05559	190.9412
Liq Vol 60F l/min	79.919	6.722433	0.3773737	86.07418

Table A.2 Results summary for reactant ratio at 1.5.

Reactant ratio $= 2.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.05$	Catalyst = 0.35 kg
Reflux ratio $= 0.04$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	20	0	1.11E-06	10.75432
METHA-01	0	10	4.99E-03	0.7493313
METHY-01	0	0	1.64E-07	9.245674
WATER	0	0	1.495004	7.75067
Total Flow	20	10	1.5	28.5
kmol/hr	20	10	1.3	28.3
Total Flow kg/hr	5649.335	320.4216	27.09332	5942.663
Total Flow 1/min	106.5378	6.735048	0.4923129	119.251
Temperature K	298.15	298.15	372.1629	355.0531
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy cal/mol	-1.96E+05	-56989.17	-66889.01	-1.45E+05
Enthalpy cal/gm	-694.1013	-1778.568	-3703.257	-693.2399
Enthalpy cal/sec	-1.09E+06	-1.58E+05	-27870.42	-1.14E+06
Entropy cal/mol-K	-433.7462	-57.54022	-34.98829	-303.5804
Entropy cal/gm-K	-1.535565	-1.795766	-1.937099	-1.45592
Density mol/cc	3.13E-03	0.0247461	0.0507807	3.98E-03
Density gm/cc	0.8837759	0.7929208	0.9172119	0.8305539
Average MW	282.4668	32.04216	18.06221	208.5145
Liq Vol 60F l/min	106.5587	6.722433	0.4531115	112.6353

Table A.3 Results summary for reactant ratio at 2.0.

Reactant ratio $= 2.5$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.05$	Catalyst = 0.35 kg
Reflux ratio $= 0.04$	Number of stages $= 16$

	1	2	3	4
	B1	B1	5	•
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	25	0	1.30E-06	15.69703
METHA-01	0	10	7.06E-03	0.6899737
METHY-01	0	0	1.86E-07	9.302965
WATER	0	0	1.742937	7.560028
Total Flow	25	10	1 75	33.25
kmol/hr	23	10	1.75	55.25
Total Flow kg/hr	7061.669	320.4216	31.62619	7350.464
Total Flow 1/min	133.1723	6.735048	0.5748215	147.6066
Temperature K	298.15	298.15	372.0347	359.7785
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy cal/mol	-1.96E+05	-56989.17	-66883.06	-1.51E+05
Enthalpy cal/gm	-694.1013	-1778.568	-3700.9	-684.1031
Enthalpy cal/sec	-1.36E+06	-1.58E+05	-32512.6	-1.40E+06
Entropy cal/mol-K	-433.7462	-57.54022	-35.00007	-320.0921
Entropy cal/gm-K	-1.535565	-1.795766	-1.93669	-1.447944
Density mol/cc	3.13E-03	0.0247461	0.0507403	3.75E-03
Density gm/cc	0.8837759	0.7929208	0.9169857	0.8299612
Average MW	282.4668	32.04216	18.07211	221.0666
Liq Vol 60F l/min	133.1983	6.722433	0.5290886	139.1978

Table A.4 Results summary for reactant ratio at 2.5.

Reactant ratio $= 3.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.05$	Catalyst = 0.35 kg
Reflux ratio $= 0.04$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	30	0	1.48E-06	20.66207
METHA-01	0	10	9.61E-03	0.6524624
METHY-01	0	0	2.11E-07	9.337927
WATER	0	0	1.990388	7.347539
Total Flow	20	10	2	20
kmol/hr	30	10	2	38
Total Flow kg/hr	8474.003	320.4216	36.16582	8758.259
Total Flow 1/min	159.8068	6.735048	0.6575086	176.1159
Temperature K	298.15	298.15	371.8955	364.1922
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy cal/mol	-1.96E+05	-56989.17	-66876.54	-1.56E+05
Enthalpy	(04.1012	1770 5 (0	2(00.220	(77.0101
cal/gm	-694.1013	-1//8.568	-3698.329	-677.3121
Enthalpy	1.62E+06	1 59E±05	27152 62	1.65E±06
cal/sec	-1.03E+00	-1.38E+03	-5/155.05	-1.03E+00
Entropy	133 7167	57 54022	35.01318	337 1387
cal/mol-K	-435.7402	-37.34022	-55.01518	-332.1382
Entropy	-1 535565	-1 795766	-1 936258	-1 //1069
cal/gm-K	-1.555505	-1.//0/00	-1.750250	-1.771007
Density mol/cc	3.13E-03	0.0247461	0.0506964	3.60E-03
Density gm/cc	0.8837759	0.7929208	0.9167388	0.8288349
Average MW	282.4668	32.04216	18.08291	230.4805
Liq Vol 60F l/min	159.838	6.722433	0.6052447	165.7606

Table A.5 Results summary for reactant ratio at 3.0.

Reactant ratio $= 3.5$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.05$	Catalyst = 0.35 kg
Reflux ratio $= 0.04$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
	-			
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	35	0	1.67E-06	25.63658
METHA-01	0	10	0.0125779	0.6239999
METHY-01	0	0	2.36E-07	9.363422
WATER	0	0	2.23742	7.126002
Total Flow kmol/hr	35	10	2.25	42.75
Total Flow kg/hr	9886 337	320 4216	40 71132	10166.05
Total Flow 1/min	186,4412	6.735048	0.7403511	204.7785
Temperature K	298.15	298.15	371.7549	368.359
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy cal/mol	-1.96E+05	-56989.17	-66869.88	-1.60E+05
Enthalpy cal/gm	-694.1013	-1778.568	-3695.71	-671.9084
Enthalpy cal/sec	-1.91E+06	-1.58E+05	-41793.68	-1.90E+06
Entropy cal/mol-K	-433.7462	-57.54022	-35.02674	-341.2194
Entropy cal/gm-K	-1.535565	-1.795766	-1.935829	-1.434887
Density mol/cc	3.13E-03	0.0247461	0.0506516	3.48E-03
Density gm/cc	0.8837759	0.7929208	0.9164867	0.827402
Average MW	282.4668	32.04216	18.09392	237.8023
Liq Vol 60F l/min	186.4777	6.722433	0.6815562	192.3234

Table A.6 Results summary for reactant ratio at 3.5.

Reactant ratio $= 4.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.05$	Catalyst = 0.35 kg
Reflux ratio $= 0.04$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	40	0	1.85E-06	30.61607
METHA-01	0	10	0.0159193	0.600153
METHY-01	0	0	2.61E-07	9.383927
WATER	0	0	2.484078	6.899849
Total Flow	40	10	2.5	47 5
kmol/hr	10	10	2.5	17.5
Total Flow kg/hr	11298.67	320.4216	45.26206	11573.83
Total Flow 1/min	213.0757	6.735048	0.8233329	233.5944
Temperature K	298.15	298.15	371.6168	372.3347
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy cal/mol	-1.96E+05	-56989.17	-66863.27	-1.63E+05
Enthalpy cal/gm	-694.1013	-1778.568	-3693.119	-667.3956
Enthalpy cal/sec	-2.18E+06	-1.58E+05	-46432.82	-2.15E+06
Entropy cal/mol-K	-433.7462	-57.54022	-35.04033	-348.2314
Entropy cal/gm-K	-1.535565	-1.795766	-1.935414	-1.429172
Density mol/cc	3.13E-03	0.0247461	0.0506073	3.39E-03
Density gm/cc	0.8837759	0.7929208	0.9162366	0.8257781
Average MW	282.4668	32.04216	18.10482	243.6596
Liq Vol 60F l/min	213.1173	6.722433	0.7580067	218.8862

Table A.7 Results summary for reactant ratio at 4.0.

APPENDIX B

Operating Parameters Condition:

Reactant ratio = 1.0 Distillate-to-feed ratio = 0.40

Reflux ratio = 0.01

Pressure = 1 bar Catalyst = 0.35 kg Number of stages = 16

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.76E-06	0.5393088
METHA-01	0	10	0.2762807	0.2630309
METHY-01	0	0	9.62E-06	9.460679
WATER	0	0	7.723707	1.736981
Total Flow kmol/hr	10	10	8	12
Total Flow kg/hr	2824.668	320.4216	148.001	2997.088
Total Flow 1/min	53.26892	6.735048	2.719562	60.40557
Temperature K	298.15	298.15	367.2719	355.7826
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy cal/mol	-1.96E+05	-56989.17	-66612.49	-1.50E+05
Enthalpy cal/gm	-694.1013	-1778.568	-3600.651	-600.0464
Enthalpy cal/sec	-5.45E+05	-1.58E+05	-1.48E+05	-5.00E+05
Entropy cal/mol-K	-433.7462	-57.54022	-35.56663	-360.9989
Entropy cal/gm-K	-1.535565	-1.795766	-1.922507	-1.445398
Density mol/cc	3.13E-03	0.0247461	0.0490275	3.31E-03
Density gm/cc	0.8837759	0.7929208	0.907015	0.8269348
Average MW	282.4668	32.04216	18.50013	249.7574
Liq Vol 60F l/min	53.27933	6.722433	2.509346	57.29523

Table B.1 Results summary for reflux ratio at 0.01

Reactant ratio $= 1.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.35 kg
Reflux ratio $= 0.02$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.74E-06	0.5371927
METHA-01	0	10	0.2768015	0.260394
METHY-01	0	0	9.64E-06	9.462795
WATER	0	0	7.723186	1.739618
Total Flow	10	10	Q	10
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	148.0083	2997.081
Total Flow 1/min	53.26892	6.735048	2.719761	60.40518
Temperature K	298.15	298.15	367.2634	355.7659
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy cal/mol	-1.96E+05	-56989.17	-66611.89	-1.50E+05
Enthalpy	-694.1013	-1778.568	-3600.44	-600.0503
Enthalmy				
cal/sec	-5.45E+05	-1.58E+05	-1.48E+05	-5.00E+05
Entropy				
cal/mol-K	-433.7462	-57.54022	-35.56785	-361.0063
Entropy		1 -0 ((4	
cal/gm-K	-1.535565	-1.795766	-1.922479	-1.445432
Density mol/cc	3.13E-03	0.0247461	0.0490239	3.31E-03
Density gm/cc	0.8837759	0.7929208	0.9069933	0.8269382
Average MW	282.4668	32.04216	18.50104	249.7567
Liq Vol 60F l/min	53.27933	6.722433	2.509539	57.29499

Table B.2 Results summary for reflux ratio at 0.02.

Reactant ratio $= 1.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.35 kg
Reflux ratio $= 0.03$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.72E-06	0.5349739
METHA-01	0	10	0.2772247	0.2577519
METHY-01	0	0	9.67E-06	9.465014
WATER	0	0	7.722763	1.74226
Total Flow	10	10	8	12
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	148.0143	2997.075
Total Flow 1/min	53.26892	6.735048	2.719923	60.40479
Temperature K	298.15	298.15	367.2564	355.7486
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy cal/mol	-1.96E+05	-56989.17	-66611.4	-1.50E+05
Enthalpy cal/gm	-694.1013	-1778.568	-3600.269	-600.0534
Enthalpy cal/sec	-5.45E+05	-1.58E+05	-1.48E+05	-5.00E+05
Entropy cal/mol-K	-433.7462	-57.54022	-35.56886	-361.0142
Entropy cal/gm-K	-1.535565	-1.795766	-1.922456	-1.445466
Density mol/cc	3.13E-03	0.0247461	0.0490209	3.31E-03
Density gm/cc	0.8837759	0.7929208	0.9069757	0.8269418
Average MW	282.4668	32.04216	18.50178	249.7562
Liq Vol 60F l/min	53.27933	6.722433	2.509696	57.29479

Table B.3 Results summary for reflux ratio at 0.03.

Reactant ratio $= 1.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.35 kg
Reflux ratio $= 0.04$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.70E-06	0.5326841
METHA-01	0	10	0.2775801	0.2551067
METHY-01	0	0	9.70E-06	9.467304
WATER	0	0	7.722408	1.744906
Total Flow	10	10	8	12
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	148.0192	2997.07
Total Flow 1/min	53.26892	6.735048	2.720059	60.40441
Temperature K	298.15	298.15	367.2504	355.7309
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy cal/mol	-1.96E+05	-56989.17	-66610.98	-1.50E+05
Enthalpy cal/gm	-694.1013	-1778.568	-3600.126	-600.0559
Enthalpy cal/sec	-5.45E+05	-1.58E+05	-1.48E+05	-5.00E+05
Entropy cal/mol-K	-433.7462	-57.54022	-35.5697	-361.0223
Entropy cal/gm-K	-1.535565	-1.795766	-1.922437	-1.445501
Density mol/cc	3.13E-03	0.0247461	0.0490185	3.31E-03
Density gm/cc	0.8837759	0.7929208	0.906961	0.8269456
Average MW	282.4668	32.04216	18.5024	249.7558
Liq Vol 60F l/min	53.27933	6.722433	2.509828	57.29461

Table B.4 Results summary for reflux ratio at 0.04.

Reactant ratio $= 1.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.35 kg
Reflux ratio $= 0.05$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.69E-06	0.5304866
METHA-01	0	10	0.2779823	0.2525069
METHY-01	0	0	9.73E-06	9.469501
WATER	0	0	7.722005	1.747505
Total Flow	10	10	8	12
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	148.0249	2997.064
Total Flow 1/min	53.26892	6.735048	2.720212	60.40403
Temperature K	298.15	298.15	367.2437	355.7138
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy	1.06E+05	-56989.17	-66610.52	-1.50E+05
cal/mol	-1.90E+03			
Enthalpy	-694 1013	-1778 568	-3500 063	-600 0589
cal/gm	-074.1015	-1//0.000	-3377.705	000.0507
Enthalpy	-545E+05	-1.58E+05	-1.48E+05	-5.00E+05
cal/sec	-5.45L+05			
Entropy	-433 7462	-57.54022	-35.57065	-361.0301
cal/mol-K	455.7462			
Entropy	-1 535565	-1 795766	-1 922415	-1 445535
cal/gm-K	1.555505	1.75700	1.722715	1.773333
Density mol/cc	3.13E-03	0.0247461	0.0490157	3.31E-03
Density gm/cc	0.8837759	0.7929208	0.9069444	0.8269493
Average MW	282.4668	32.04216	18.50311	249.7554
Lia Vol 60F l/min	53.27933	6.722433	2.509978	57.29441

Table B.5 Results summary for reflux ratio at 0.05.

Reactant ratio $= 1.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.35 kg
Reflux ratio $= 0.06$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
				-
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.67E-06	0.528431
METHA-01	0	10	0.2784857	0.249948
METHY-01	0	0	9.75E-06	9.471557
WATER	0	0	7.721502	1.750064
Total Flow	10	10	0	12
kmol/hr			8	
Total Flow kg/hr	2824.668	320.4216	148.0319	2997.057
Total Flow 1/min	53.26892	6.735048	2.720405	60.40365
Temperature K	298.15	298.15	367.2355	355.6976
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy cal/mol	-1.96E+05	-56989.17	-66609.93	-1.50E+05
Enthalpy cal/gm	-694.1013	-1778.568	-3599.76	-600.0626
Enthalpy cal/sec	-5.45E+05	-1.58E+05	-1.48E+05	-5.00E+05
Entropy cal/mol-K	-433.7462	-57.54022	-35.57184	-361.0374
Entropy cal/gm-K	-1.535565	-1.795766	-1.922387	-1.445567
Density mol/cc	3.13E-03	0.0247461	0.0490123	3.31E-03
Density gm/cc	0.8837759	0.7929208	0.9069234	0.8269526
Average MW	282.4668	32.04216	18.50399	249.7548
Liq Vol 60F l/min	53.27933	6.722433	2.510165	57.29418

Table B.6 Results summary for reflux ratio at 0.06.
Reactant ratio $= 1.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.35 kg
Reflux ratio $= 0.07$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.66E-06	0.5263007
METHA-01	0	10	0.2789121	0.2473913
METHY-01	0	0	9.78E-06	9.473687
WATER	0	0	7.721075	1.752621
Total Flow	10	10	8	12
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	148.0379	2997.051
Total Flow 1/min	53.26892	6.735048	2.720568	60.40327
Temperature K	298.15	298.15	367.2284	355.681
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy cal/mol	-1.96E+05	-56989.17	-66609.44	-1.50E+05
Enthalpy cal/gm	-694.1013	-1778.568	-3599.588	-600.0657
Enthalpy cal/sec	-5.45E+05	-1.58E+05	-1.48E+05	-5.00E+05
Entropy cal/mol-K	-433.7462	-57.54022	-35.57285	-361.0449
Entropy cal/gm-K	-1.535565	-1.795766	-1.922364	-1.445601
Density mol/cc	3.13E-03	0.0247461	0.0490093	3.31E-03
Density gm/cc	0.8837759	0.7929208	0.9069057	0.8269561
Average MW	282.4668	32.04216	18.50474	249.7543
Liq Vol 60F l/min	53.27933	6.722433	2.510323	57.29398

Table B.7 Results summary for reflux ratio at 0.07.

Reactant ratio $= 1.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.35 kg
Reflux ratio $= 0.08$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.64E-06	0.5241161
METHA-01	0	10	0.27928	0.2448387
METHY-01	0	0	9.81E-06	9.475871
WATER	0	0	7.720707	1.755174
Total Flow	10	10	8	12
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	148.0431	2997.046
Total Flow 1/min	53.26892	6.735048	2.720709	60.40291
Temperature K	298.15	298.15	367.2222	355.6641
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy cal/mol	-1.96E+05	-56989.17	-66609.02	-1.50E+05
Enthalpy cal/gm	-694.1013	-1778.568	-3599.439	-600.0684
Enthalpy cal/sec	-5.45E+05	-1.58E+05	-1.48E+05	-5.00E+05
Entropy cal/mol-K	-433.7462	-57.54022	-35.57372	-361.0527
Entropy cal/gm-K	-1.535565	-1.795766	-1.922344	-1.445634
Density mol/cc	3.13E-03	0.0247461	0.0490068	3.31E-03
Density gm/cc	0.8837759	0.7929208	0.9068905	0.8269597
Average MW	282.4668	32.04216	18.50539	249.7538
Liq Vol 60F l/min	53.27933	6.722433	2.51046	57.2938

Table B.8 Results summary for reflux ratio at 0.08.

Reactant ratio $= 1.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.35 kg
Reflux ratio $= 0.09$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
			,	~
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.63E-06	0.5219923
METHA-01	0	10	0.2796797	0.2423152
METHY-01	0	0	9.84E-06	9.477995
WATER	0	0	7.720308	1.757697
Total Flow	10	10	8	12
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	148.0487	2997.04
Total Flow 1/min	53.26892	6.735048	2.720862	60.40254
Temperature K	298.15	298.15	367.2156	355.6476
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy cal/mol	-1.96E+05	-56989.17	-66608.55	-1.50E+05
Enthalpy cal/gm	-694.1013	-1778.568	-3599.278	-600.0713
Enthalpy cal/sec	-5.45E+05	-1.58E+05	-1.48E+05	-5.00E+05
Entropy cal/mol-K	-433.7462	-57.54022	-35.57467	-361.0602
Entropy cal/gm-K	-1.535565	-1.795766	-1.922322	-1.445667
Density mol/cc	3.13E-03	0.0247461	0.049004	3.31E-03
Density gm/cc	0.8837759	0.7929208	0.9068739	0.8269632
Average MW	282.4668	32.04216	18.50609	249.7534
Liq Vol 60F l/min	53.27933	6.722433	2.510609	57.2936

Table B.9 Results summary for reflux ratio at 0.09.

Reactant ratio $= 1.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.35 kg
Reflux ratio $= 0.10$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.61E-06	0.5198852
METHA-01	0	10	0.2800763	0.2398115
METHY-01	0	0	9.87E-06	9.480102
WATER	0	0	7.719911	1.760201
Total Flow	10	10	0	10
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	148.0543	2997.035
Total Flow 1/min	53.26892	6.735048	2.721013	60.40217
Temperature K	298.15	298.15	367.209	355.6312
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy	-1.96E+05	-56989.17	-66608.09	-1.50E+05
Enthology				
cal/gm	-694.1013	-1778.568	-3599.118	-600.0742
Enthalpy	-5 45E+05	-1 58E+05	-1 48E+05	-5 00E+05
cal/sec	0.102 00	11002 00	1.102 00	0.002 00
Entropy	-433.7462	-57.54022	-35.57561	-361.0677
cal/mol-K				
Entropy cal/gm-K	-1.535565	-1.795766	-1.922301	-1.4457
Density mol/cc	3.13E-03	0.0247461	0.0490013	3.31E-03
Density gm/cc	0.8837759	0.7929208	0.9068575	0.8269666
Average MW	282.4668	32.04216	18.50678	249.7529
Liq Vol 60F l/min	53.27933	6.722433	2.510756	57.29341

Table B.10 Results summary for reflux ratio at 0.10.

APPENDIX C

Operating Parameters Condition:

Reactant ratio = 1.0 Distillate-to-feed ratio = 0.01

Reflux ratio = 0.04

Pressure = 1 bar Catalyst = 0.35 kg Number of stages = 16

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	1.43E-07	1.691162
METHA-01	0	10	5.91E-04	1.690571
METHY-01	0	0	3.76E-08	8.308838
WATER	0	0	0.1994084	8.109429
Total Flow	10	10	0.2	10.8
kmol/hr	10	10	0.2	19.0
Total Flow kg/hr	2824.668	320.4216	3.611399	3141.478
Total Flow 1/min	53.26892	6.735048	0.0656136	63.28352
Temperature K	298.15	298.15	372.2223	345.105
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy	1 06E+05	56080 17	66802 32	1 18E+05
cal/mol	-1.90E+05	-30787.17	-00872.52	-1.16L+05
Enthalpy	-694 1013	-1778 568	-3704 51	-746 6152
cal/gm	094.1015	1770.500	5704.51	740.0152
Enthalpy	-5 45E+05	-1 58E+05	-3716.24	-6 52E+05
cal/sec	5.151.05	1.501+05	5710.21	0.521+05
Entropy	-433 7462	-57 54022	-34 98262	-234 9486
cal/mol-K	133.7102	07.01022	51.90202	23 1.9 100
Entropy	-1 535565	-1 795766	-1 937344	-1 480826
cal/gm-K	1.000000	1.755700	1.557511	1.100020
Density mol/cc	3.13E-03	0.0247461	0.0508024	5.21E-03
Density gm/cc	0.8837759	0.7929208	0.9173401	0.8273554
Average MW	282.4668	32.04216	18.057	158.6605
Liq Vol 60F l/min	53.27933	6.722433	0.0603872	59.76819

Ope	rati	ing	Para	ameters	Condition:
D			. •	1.0	

Reactant ratio $= 1.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.04$	Catalyst = 0.35 kg
Reflux ratio $= 0.04$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	5.57E-07	1.58744
METHA-01	0	10	2.94E-03	1.584503
METHY-01	0	0	1.83E-07	8.412559
WATER	0	0	0.7970612	7.615498
Total Flow	10	10	0.8	10.2
kmol/hr	10	10	0.8	19.2
Total Flow kg/hr	2824.668	320.4216	14.45363	3130.636
Total Flow 1/min	53.26892	6.735048	0.2626647	63.03684
Temperature K	298.15	298.15	372.0871	345.0285
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy	-1.96E+05	-56989.17	-66886.38	-1.20E+05
cal/gm	-694.1013	-1778.568	-3702.121	-736.0174
Enthalpy		1 505 05	1.10.60.61	6 40E 0 E
cal/sec	-5.45E+05	-1.58E+05	-14863.64	-6.40E+05
Entropy	133 7167	57 54022	3/ 00/60	2/1 1060
cal/mol-K	-435.7402	-57.54022	-34.99409	-241.1909
Entropy	-1 535565	-1 705766	-1 936935	-1 479246
cal/gm-K	-1.555505	-1.//5/00	-1.750755	-1.4/7240
Density mol/cc	3.13E-03	0.0247461	0.0507618	5.08E-03
Density gm/cc	0.8837759	0.7929208	0.9171156	0.8277264
Average MW	282.4668	32.04216	18.06704	163.0539
Liq Vol 60F l/min	53.27933	6.722433	0.2417617	59.58466

Table C.2 Results summary for distillate-to-feed ratio at 0.04.

Operating Parameters Condition:	
Reactant ratio $= 1.0$	
Distillate-to-feed ratio $= 0.08$	

Reflux ratio = 0.04

Pressure = 1 bar Catalyst = 0.35 kg Number of stages = 16

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	1.07E-06	1.445901
METHA-01	0	10	7.79E-03	1.438116
METHY-01	0	0	4.72E-07	8.554098
WATER	0	0	1.592213	6.961886
Total Flow	10	10	1.6	10.4
kmol/hr	10	10	1.0	18.4
Total Flow kg/hr	2824.668	320.4216	28.93407	3116.155
Total Flow 1/min	53.26892	6.735048	0.5260323	62.70831
Temperature K	298.15	298.15	371.8648	344.973
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy	1.0(E + 0.5)	5(000 17	((07(41	1.2201-05
cal/mol	-1.90E+05	-30989.17	-008/0.41	-1.22E+05
Enthalpy	604 1012	1770 560	2609.14	721 7520
cal/gm	-094.1015	-1//8.308	-3098.14	-/21./339
Enthalpy	5 45 E±05	1 59E±05	20722.85	6 25E±05
cal/sec	-3.43E+03	-1.36E+03	-29/22.83	-0.23E+03
Entropy	122 7167	57 54022	25.01527	250 1541
cal/mol-K	-435.7402	-37.34022	-33.01327	-230.1341
Entropy	1 525565	1 705766	1 026270	1 477088
cal/gm-K	-1.555505	-1./95/00	-1.930279	-1.4//000
Density mol/cc	3.13E-03	0.0247461	0.0506939	4.89E-03
Density gm/cc	0.8837759	0.7929208	0.9167394	0.8282143
Average MW	282.4668	32.04216	18.0838	169.3563
Liq Vol 60F l/min	53.27933	6.722433	0.484233	59.33924

 Table C.3 Results summary for distillate-to-feed ratio at 0.08.

Operating	Parameters	Condition:
Operating	Parameters	Condition:

Reactant ratio $= 1.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.10$	Catalyst = 0.35 kg
Reflux ratio $= 0.04$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	1.31E-06	1.374129
METHA-01	0	10	0.0111769	1.362953
METHY-01	0	0	6.65E-07	8.625869
WATER	0	0	1.988821	6.637049
Total Flow	10	10	2	10
kmol/hr	10	10	2	18
Total Flow kg/hr	2824.668	320.4216	36.18787	3108.901
Total Flow 1/min	53.26892	6.735048	0.6580732	62.5443
Temperature K	298.15	298.15	371.7321	344.971
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy cal/mol	-1.96E+05	-56989.17	-66870.34	-1.23E+05
Enthalpy cal/gm	-694.1013	-1778.568	-3695.733	-714.5652
Enthalpy cal/sec	-5.45E+05	-1.58E+05	-37150.19	-6.17E+05
Entropy cal/mol-K	-433.7462	-57.54022	-35.02793	-254.9265
Entropy cal/gm-K	-1.535565	-1.795766	-1.935893	-1.47598
Density mol/cc	3.13E-03	0.0247461	0.0506529	4.80E-03
Density gm/cc	0.8837759	0.7929208	0.9165107	0.8284531
Average MW	282.4668	32.04216	18.09393	172.7167
Liq Vol 60F l/min	53.27933	6.722433	0.605828	59.21615

Table C.4 Results summary for distillate-to-feed ratio at 0.10.

Operating Parameters Cond	ition:
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Reactant ratio $= 1.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.20$	Catalyst = 0.35 kg
Reflux ratio $= 0.04$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
	```	`		`
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.24E-06	1.020244
METHA-01	0	10	0.044188	0.9760579
METHY-01	0	0	2.32E-06	8.979752
WATER	0	0	3.955807	5.023947
Total Flow	10	10	4	16
kmol/hr	10	10	4	10
Total Flow kg/hr	2824.668	320.4216	72.68218	3072.407
Total Flow 1/min	53.26892	6.735048	1.324246	61.73052
Temperature K	298.15	298.15	370.7717	345.4042
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy cal/mol	-1.96E+05	-56989.17	-66823.77	-1.30E+05
Enthalpy cal/gm	-694.1013	-1778.568	-3677.588	-678.0592
Enthalpy cal/sec	-5.45E+05	-1.58E+05	-74248.64	-5.79E+05
Entropy cal/mol-K	-433.7462	-57.54022	-35.12647	-282.2607
Entropy cal/gm-K	-1.535565	-1.795766	-1.933154	-1.469913
Density mol/cc	3.13E-03	0.0247461	0.0503431	4.32E-03
Density gm/cc	0.8837759	0.7929208	0.9147615	0.8295214
Average MW	282.4668	32.04216	18.17055	192.0254
Liq Vol 60F l/min	53.27933	6.722433	1.219769	58.59483

Table C.5 Results summary for distillate-to-feed ratio at 0.20.

Reactant ratio $= 1.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.30$	Catalyst = 0.35 kg
Reflux ratio $= 0.04$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.65E-06	0.7186065
METHA-01	0	10	0.1263168	0.5922923
METHY-01	0	0	5.47E-06	9.281385
WATER	0	0	5.873675	3.407716
Total Flow	10	10	6	14
kmol/hr	10	10	0	17
Total Flow kg/hr	2824.668	320.4216	109.8657	3035.223
Total Flow 1/min	53.26892	6.735048	2.008903	60.95462
Temperature K	298.15	298.15	369.1714	347.5131
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy	-1 96E+05	-56989 17	-66735 63	-1 39E+05
cal/mol	-1.90E+05	-50505.17	-00755.05	-1.571-05
Enthalpy	-694 1013	-1778 568	-3644 574	-640 4806
cal/gm	0,11015	1770.000	5011.571	010.1000
Enthalpy	-5 45E+05	-1 58E+05	-1 11E+05	-5 40E+05
cal/sec	0.102 00	1.002 00		0
Entropy	-433 7462	-57 54022	-35 31272	-316 9044
cal/mol-K		0,.0.010		0100000
Entropy	-1.535565	-1.795766	-1.928502	-1.461725
cal/gm-K				
Density mol/cc	3.13E-03	0.0247461	0.0497784	3.83E-03
Density gm/cc	0.8837759	0.7929208	0.9114902	0.8299135
Average MW	282.4668	32.04216	18.31096	216.8017
Liq Vol 60F l/min	53.27933	6.722433	1.851958	57.95635

Table C.6 Results summary for distillate-to-feed ratio at 0.30.

Reactant ratio $= 1.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.35 kg
Reflux ratio $= 0.04$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.70E-06	0.5327417
METHA-01	0	10	0.2776189	0.2551255
METHY-01	0	0	9.70E-06	9.467246
WATER	0	0	7.722369	1.744887
Total Flow	10	10	Q	12
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	148.0198	2997.069
Total Flow 1/min	53.26892	6.735048	2.720074	60.40441
Temperature K	298.15	298.15	367.2498	355.7312
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy	1 06E±05	56080 17	66610.04	1 50E±05
cal/mol	-1.90E+05	-30989.17	-00010.94	-1.30E+03
Enthalpy	60/ 1013	1778 568	3600 11	600 0563
cal/gm	-094.1015	-1//8.308	-3000.11	-000.0303
Enthalpy	-5 45E+05	-1 58E+05	-1 48E+05	-5.00E+05
cal/sec	-3.43E+05	-1.561+05	-1.401+03	-5.001+05
Entropy	-433 7462	-57 54022	-35 56979	-361 0221
cal/mol-K	-+33.7+02	-37.34022	-33.30777	-501.0221
Entropy	-1 535565	-1 795766	-1 922434	-1 445501
cal/gm-K	1.555505	1.795700	1.722454	1.445501
Density mol/cc	3.13E-03	0.0247461	0.0490182	3.31E-03
Density gm/cc	0.8837759	0.7929208	0.9069594	0.8269456
Average MW	282.4668	32.04216	18.50247	249.7558
Liq Vol 60F l/min	53.27933	6.722433	2.509843	57.29459

Table C.7 Results summary for distillate-to-feed ratio at 0.40.

APPENDIX D

Operating Parameters Condition:

Reactant ratio = 1.0 Distillate-to-feed ratio = 0.40

Reflux ratio = 0.04

Pressure = 1 bar Catalyst = 0.35 kg Number of stages = 16

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.70E-06	0.5326841
METHA-01	0	10	2.78E-01	0.2551067
METHY-01	0	0	9.70E-06	9.467304
WATER	0	0	7.722408	1.744906
Total Flow	10	10	8	12
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	148.0192	2997.07
Total Flow 1/min	53.26892	6.735048	2.720059	60.40441
Temperature K	298.15	298.15	367.2504	355.7309
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy	-1 96E+05	-56080 17	-66610.98	-1 50E+05
cal/mol	-1.901-105	-50707.17	-00010.78	-1.501-05
Enthalpy	-694 1013	-1778 568	-3600 126	-600.0559
cal/gm	094.1015	1770.500	5000.120	000.0557
Enthalpy	-5 45E+05	-1 58E+05	-1 48E+05	-5.00E+05
cal/sec	5.152.05	1.501+05	1.101-05	5.001+05
Entropy	-433 7462	-57 54022	-35 5697	-361 0223
cal/mol-K	100.7102	07.01022	55.5097	501.0225
Entropy	-1 535565	-1 795766	-1 922437	-1 445501
cal/gm-K	1.000000	1.798766	1.922 137	1.110001
Density mol/cc	3.13E-03	0.0247461	0.0490185	3.31E-03
Density gm/cc	0.8837759	0.7929208	0.906961	0.8269456
Average MW	282.4668	32.04216	18.5024	249.7558
Liq Vol 60F l/min	53.27933	6.722433	2.509828	57.29461

Table D.1 Results summary for pressure at 1 bar.

Reactant ratio $= 1.0$	Pressure = 2 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.35 kg
Reflux ratio $= 0.04$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	1.19E-05	0.2658127
METHA-01	0	10	3.02E-02	0.2356181
METHY-01	0	0	1.32E-05	9.734162
WATER	0	0	7.969768	1.764407
Total Flow	10	10	8	12
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	144.5528	3000.536
Total Flow 1/min	53.26892	6.735048	2.691187	61.55426
Temperature K	298.15	298.15	392.3789	375.6694
Pressure atm	1.973847	1.973847	1.973847	1.973847
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy	-1.96E+05	-56988.55	-66495.16	-1.47E+05
cal/mol				
Enthalpy cal/gm	-694.0801	-1778.549	-3680.049	-587.3017
Enthalny				
cal/sec	-5.45E+05	-1.58E+05	-1.48E+05	-4.90E+05
Entropy	100			
cal/mol-K	-433.7517	-57.54139	-33.98439	-354.6613
Entropy	-1.535585	-1.795803	-1.880802	-1.418392
cal/gm-K	0.105.00	0.00/5///	0.0405444	
Density mol/cc	3.13E-03	0.0247461	0.0495444	3.25E-03
Density gm/cc	0.8837759	0.7929208	0.8952231	0.8124367
Average MW	282.4668	32.04216	18.06909	250.0447
Lıq Vol 60F l/min	53.27933	6.722433	2.418016	57.38086

Table D.2 Results summary for pressure at 2 bar.

Reactant ratio $= 1.0$	Pressure = 3 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.35 kg
Reflux ratio $= 0.04$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.62E-05	0.2171773
METHA-01	0	10	5.79E-03	0.2114173
METHY-01	0	0	1.05E-05	9.782786
WATER	0	0	7.994177	1.788619
Total Flow	10	10	8	12
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	144.2133	3000.876
Total Flow 1/min	53.26892	6.735048	2.726355	62.30187
Temperature K	298.15	298.15	406.1798	388.9498
Pressure atm	2.96077	2.96077	2.96077	2.96077
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy cal/mol	-1.96E+05	-56987.93	-66258.92	-1.45E+05
Enthalpy cal/gm	-694.0589	-1778.53	-3675.608	-579.995
Enthalpy cal/sec	-5.45E+05	-1.58E+05	-1.47E+05	-4.83E+05
Entropy cal/mol-K	-433.7573	-57.54257	-33.29119	-350.2075
Entropy cal/gm-K	-1.535605	-1.795839	-1.846775	-1.400421
Density mol/cc	3.13E-03	0.0247461	0.0489053	3.21E-03
Density gm/cc	0.8837759	0.7929208	0.8815997	0.8027785
Average MW	282.4668	32.04216	18.02666	250.073
Liq Vol 60F l/min	53.27933	6.722433	2.409004	57.38886

Table D.3 Results summary at pressure at 3 bar.

APPENDIX E

Operating Parameters Condition:

Reactant ratio = 1.0 Distillate-to-feed ratio = 0.40

Reflux ratio = 0.04

Pressure = 3 bar Catalyst = 0.30 kg Number of stages = 11

Table E.1	Results summar	v when nur	nber of stages	s is 11.
		2	0	

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.65E-05	0.3080296
METHA-01	0	10	6.10E-03	0.3019531
METHY-01	0	0	9.51E-06	9.191934
WATER	0	0	7.993861	2.808066
Total Flow	10	10	8	12
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	144.2175	3000.872
Total Flow 1/min	53.26892	6.735048	2.726599	62.33195
Temperature K	298.15	298.15	406.2088	389.89
Pressure atm	2.96077	2.96077	2.96077	2.96077
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy	-1.96E+05	-56987.93	-66257.84	-1.45E+05
Cal/III01				
cal/gm	-694.0589	-1778.53	-3675.44	-579.8352
Enthalpy	5 45E+05	1.500-05	1.475+05	4.025+05
cal/sec	-5.45E+05	-1.58E+05	-1.4/E+05	-4.83E+05
Entropy	122 7572	57 54257	22 20000	240 7827
cal/mol-K	-455.7575	-37.34237	-33.28988	-349.7827
Entropy	1 525605	1 705830	1 846640	1 208725
cal/gm-K	-1.555005	-1./93039	-1.040049	-1.390/23
Density mol/cc	3.13E-03	0.0247461	0.0489009	3.21E-03
Density gm/cc	0.8837759	0.7929208	0.8815467	0.8023899
Average MW	282.4668	32.04216	18.02719	250.0726
Liq Vol 60F l/min	53.27933	6.722433	2.409118	57.39064

Reactant ratio $= 1.0$	Pressure = 3 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.30 kg
Reflux ratio $= 0.04$	Number of stages $= 12$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.63E-05	0.2898553
METHA-01	0	10	6.56E-03	0.2833222
METHY-01	0	0	1.02E-05	9.710108
WATER	0	0	7.993404	2.789892
Total Flow	10	10	Q	10
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	144.224	3000.865
Total Flow 1/min	53.26892	6.735048	2.726697	62.32556
Temperature K	298.15	298.15	406.1734	389.6969
Pressure atm	2.96077	2.96077	2.96077	2.96077
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy	-1.96E+05	-56987.93	-66257.86	-1.45E+05
cal/mol				
Enthalpy	-694.0589	-1778.53	-3675.274	-579.8734
Entholpy				
cal/sec	-5.45E+05	-1.58E+05	-1.47E+05	-4.83E+05
Entropy				
cal/mol-K	-433.7573	-57.54257	-33.29184	-349.8681
Entropy	1 525(05	1 705920	1.94((72	1 2000/0
cal/gm-K	-1.535605	-1./95839	-1.8466/3	-1.399069
Density mol/cc	3.13E-03	0.0247461	0.0488992	3.21E-03
Density gm/cc	0.8837759	0.7929208	0.8815552	0.8024705
Average MW	282.4668	32.04216	18.028	250.0721
Liq Vol 60F l/min	53.27933	6.722433	2.40929	57.39008

Table E.2 Results summary when number of stages is 12.

Reactant ratio $= 1.0$	Pressure = 3 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.30 kg
Reflux ratio $= 0.04$	Number of stages $= 13$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.61E-05	0.273127
METHA-01	0	10	7.03E-03	0.2661207
METHY-01	0	0	1.09E-05	9.326836
WATER	0	0	7.992931	2.673164
Total Flow	10	10	0	12
kmol/hr	10	10	8	12
Total Flow kg/hr	2824.668	320.4216	144.2308	3000.858
Total Flow 1/min	53.26892	6.735048	2.7268	62.31968
Temperature K	298.15	298.15	406.137	389.5193
Pressure atm	2.96077	2.96077	2.96077	2.96077
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy cal/mol	-1.96E+05	-56987.93	-66257.87	-1.45E+05
Enthalpy cal/gm	-694.0589	-1778.53	-3675.102	-579.9088
Enthalpy cal/sec	-5.45E+05	-1.58E+05	-1.47E+05	-4.83E+05
Entropy cal/mol-K	-433.7573	-57.54257	-33.29385	-349.9469
Entropy cal/gm-K	-1.535605	-1.795839	-1.846699	-1.399387
Density mol/cc	3.13E-03	0.0247461	0.0488973	3.21E-03
Density gm/cc	0.8837759	0.7929208	0.8815634	0.8025444
Average MW	282.4668	32.04216	18.02885	250.0715
Liq Vol 60F l/min	53.27933	6.722433	2.409468	57.38956

Table E.3 Results summary when number of stages is 13.

Reactant ratio $= 1.0$	Pressure = 3 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.30 kg
Reflux ratio $= 0.04$	Number of stages $= 14$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.60E-05	0.2577145
METHA-01	0	10	7.53E-03	0.2502154
METHY-01	0	0	1.16E-05	9.442248
WATER	0	0	7.992437	2.557752
Total Flow	10	10	o	10
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	144.2379	3000.851
Total Flow 1/min	53.26892	6.735048	2.726908	62.31426
Temperature K	298.15	298.15	406.0996	389.3558
Pressure atm	2.96077	2.96077	2.96077	2.96077
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy cal/mol	-1.96E+05	-56987.93	-66257.87	-1.45E+05
Enthalpy	-694.0589	-1778.53	-3674,922	-579.9417
cal/gm				
Enthalpy	-5.45E+05	-1.58E+05	-1.47E+05	-4.83E+05
cal/sec				
Entropy	-433.7573	-57.54257	-33.29594	-350.0199
Entropy				
cal/gm-K	-1.535605	-1.795839	-1.846724	-1.399682
Density mol/cc	3.13E-03	0.0247461	0.0488954	3.21E-03
Density gm/cc	0.8837759	0.7929208	0.8815716	0.8026122
Average MW	282.4668	32.04216	18.02973	250.0709
Liq Vol 60F l/min	53.27933	6.722433	2.409654	57.38905

Table E.4 Results summary when number of stages is 14.

Reactant ratio $= 1.0$	Pressure = 3 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.30 kg
Reflux ratio $= 0.04$	Number of stages $= 15$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.58E-05	0.2434526
METHA-01	0	10	8.03E-03	0.2354436
METHY-01	0	0	1.23E-05	9.556509
WATER	0	0	7.991927	2.442491
Total Flow	10	10	0	12
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	144.2452	3000.844
Total Flow 1/min	53.26892	6.735048	2.727021	62.30925
Temperature K	298.15	298.15	406.0614	389.2045
Pressure atm	2.96077	2.96077	2.96077	2.96077
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy	-1 96E+05	-56987 93	-66257.86	-1 45E+05
cal/mol	-1.70E+05	-50707.75	-00237.00	-1.431-05
Enthalpy	-694 0589	-1778 53	-3674 736	-579 9725
cal/gm	-074.0507	-1770.55	-3074.730	-517.7125
Enthalpy	-5 45E+05	-1 58E+05	-1 47F+05	-4 83E+05
cal/sec	-5.451-05	-1.50L+05	-1.4712+05	-4.05L+05
Entropy	-433 7573	-57 54257	-33 29809	-350.0876
cal/mol-K	455.7575	57.54257	55.27007	550.0070
Entropy	-1 535605	-1 795839	-1 84675	-1 399957
cal/gm-K	1.555005	1.795059	1.04075	1.577751
Density mol/cc	3.13E-03	0.0247461	0.0488934	3.21E-03
Density gm/cc	0.8837759	0.7929208	0.8815796	0.8026749
Average MW	282.4668	32.04216	18.03065	250.0703
Liq Vol 60F l/min	53.27933	6.722433	2.409846	57.38856

Table E.5 Results summary when number of stages is 15.

Reactant ratio $= 1.0$	Pressure = 3 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.30 kg
Reflux ratio $= 0.04$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.56E-05	0.2303056
METHA-01	0	10	8.57E-03	0.2217604
METHY-01	0	0	1.30E-05	9.769656
WATER	0	0	7.991391	1.778278
Total Flow	10	10	o	12
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	144.2529	3000.836
Total Flow 1/min	53.26892	6.735048	2.727143	62.30461
Temperature K	298.15	298.15	406.0217	389.0649
Pressure atm	2.96077	2.96077	2.96077	2.96077
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy	1.06E±05	56097 02	66257.91	1 45E±05
cal/mol	-1.90E+03	-30987.95	-00237.84	-1.43E+03
Enthalpy	604 0580	1778 52	2674 520	580.0014
cal/gm	-094.0389	-1//8.33	-3074.339	-380.0014
Enthalpy	5 45 E+05	1 58E+05	1 47E+05	1 83E+05
cal/sec	-3.43E+03	-1.30E+05	-1.4/12+03	-4.03E+03
Entropy	-133 7573	-57 54257	-33 30033	-350 1503
cal/mol-K	-+33.7373	-37.34237	-55.50055	-550.1505
Entropy	-1 535605	-1 705830	-1 8/6775	-1 400211
cal/gm-K	-1.555005	-1.75055	-1.040775	-1.400211
Density mol/cc	3.13E-03	0.0247461	0.0488912	3.21E-03
Density gm/cc	0.8837759	0.7929208	0.8815873	0.8027325
Average MW	282.4668	32.04216	18.03161	250.0697
Liq Vol 60F l/min	53.27933	6.722433	2.410048	57.38808

Table E.6 Results summary when number of stages is 16.

APPENDIX F

Operating Parameters Condition:

Reactant ratio = 1.0 Distillate-to-feed ratio = 0.40

Reflux ratio = 0.04

Pressure = 1 bar Catalyst = 0.25 kg Number of stages = 16

Table F.1 F	Results summa	y for catal	yst weight a	t 0.25 kg.
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	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.46E-06	0.7242715
METHA-01	0	10	0.4480114	0.2762625
METHY-01	0	0	1.02E-05	9.275716
WATER	0	0	7.551976	1.72375
Total Flow	10	10	8	12
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	150.4099	2994.679
Total Flow 1/min	53.26892	6.735048	2.785816	60.36508
Temperature K	298.15	298.15	364.7106	356.3455
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy cal/mol	-1.96E+05	-56989.17	-66408.62	-1.50E+05
Enthalpy cal/gm	-694.1013	-1778.568	-3532.14	-601.6163
Enthalpy cal/sec	-5.45E+05	-1.58E+05	-1.48E+05	-5.00E+05
Entropy cal/mol-K	-433.7462	-57.54022	-35.97006	-360.4782
Entropy cal/gm-K	-1.535565	-1.795766	-1.913175	-1.444475
Density mol/cc	3.13E-03	0.0247461	0.0478615	3.31E-03
Density gm/cc	0.8837759	0.7929208	0.8998557	0.8268245
Average MW	282.4668	32.04216	18.80124	249.5566
Liq Vol 60F l/min	53.27933	6.722433	2.57313	57.2353

Reactant ratio $= 1.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.30 kg
Reflux ratio $= 0.04$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.58E-06	0.6127246
METHA-01	0	10	0.3482907	0.2644364
METHY-01	0	0	9.99E-06	9.387263
WATER	0	0	7.651697	1.735576
Total Flow	10	10	o	10
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	149.0111	2996.078
Total Flow 1/min	53.26892	6.735048	2.747224	60.38821
Temperature K	298.15	298.15	366.138	355.9909
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy	-1.96E+05	-56989.17	-66528	-1.50E+05
cal/mol				
Enthalpy cal/gm	-694.1013	-1778.568	-3571.706	-600.7026
Enthalpy		1 505 05	4.405.05	
cal/sec	-5.45E+05	-1.58E+05	-1.48E+05	-5.00E+05
Entropy	-433 7462	-57 54022	-35 73607	-360 7929
cal/mol-K	155.7102	07.01022	55.75007	500.1727
Entropy cal/gm-K	-1.535565	-1.795766	-1.918572	-1.445061
Density mol/cc	3.13E-03	0.0247461	0.0485338	3.31E-03
Density gm/cc	0.8837759	0.7929208	0.9040104	0.8268937
Average MW	282.4668	32.04216	18.62639	249.6732
Liq Vol 60F l/min	53.27933	6.722433	2.536092	57.27001

Table F.2 Results summary for catalyst weight at 0.30 kg.

Reactant ratio $= 1.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.35 kg
Reflux ratio $= 0.04$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.70E-06	0.5326728
METHA-01	0	10	0.2775424	0.2551331
METHY-01	0	0	9.70E-06	9.467315
WATER	0	0	7.722445	1.744879
Total Flow	10	10	0	12
kmol/hr	10	10	8	12
Total Flow kg/hr	2824.668	320.4216	148.0187	2997.07
Total Flow 1/min	53.26892	6.735048	2.720044	60.40443
Temperature K	298.15	298.15	367.2511	355.7311
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy	-1.96E+05	-56989.17	-66611.03	-1.50E+05
cal/mol	1., 02 00	00000000	0001100	1.002 00
Enthalpy	-694.1013	-1778.568	-3600.141	-600.0556
Entholpy				
cal/sec	-5.45E+05	-1.58E+05	-1.48E+05	-5.00E+05
Entropy				
cal/mol-K	-433.7462	-57.54022	-35.56961	-361.0223
Entropy	1 5255(5	1 7057((1.022420	1 445501
cal/gm-K	-1.333303	-1./93/00	-1.922439	-1.445501
Density mol/cc	3.13E-03	0.0247461	0.0490188	3.31E-03
Density gm/cc	0.8837759	0.7929208	0.9069626	0.8269456
Average MW	282.4668	32.04216	18.50234	249.7559
Liq Vol 60F l/min	53.27933	6.722433	2.509814	57.29462

Table F.3 Results summary for catalyst weight at 0.35 kg.

Reactant ratio $= 1.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.40 kg
Reflux ratio $= 0.04$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.83E-06	0.4728448
METHA-01	0	10	0.2253951	0.2474526
METHY-01	0	0	9.38E-06	9.527143
WATER	0	0	7.774593	1.75256
Total Flow	10	10	0	12
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	147.2872	2997.802
Total Flow 1/min	53.26892	6.735048	2.700133	60.41624
Temperature K	298.15	298.15	368.1322	355.5329
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy	-1.96E+05	-56989.17	-66671.21	-1.50E+05
cal/mol				
Enthalpy	-694.1013	-1778.568	-3621.29	-599.5792
Cal/glii Entholmy				
cal/sec	-5.45E+05	-1.58E+05	-1.48E+05	-4.99E+05
Entropy				
cal/mol-K	-433.7462	-57.54022	-35.44692	-361.1959
Entropy	1.525565	1 705766	1.005000	1 4450 42
cal/gm-K	-1.535565	-1./95/66	-1.925323	-1.445843
Density mol/cc	3.13E-03	0.0247461	0.0493802	3.31E-03
Density gm/cc	0.8837759	0.7929208	0.9091353	0.8269857
Average MW	282.4668	32.04216	18.4109	249.8168
Liq Vol 60F l/min	53.27933	6.722433	2.490445	57.31274

Table F.4 Results summary for catalyst weight at 0.40 kg.

Reactant ratio $= 1.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.45 kg
Reflux ratio $= 0.04$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.96E-06	0.4267261
METHA-01	0	10	0.1858439	0.2408852
METHY-01	0	0	9.04E-06	9.573262
WATER	0	0	7.814144	1.759127
Total Flow	10	10	0	12
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	146.7323	2998.357
Total Flow 1/min	53.26892	6.735048	2.685109	60.42508
Temperature K	298.15	298.15	368.8387	355.3768
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy	1.06E±05	56090 17	66716 21	1 50E±05
cal/mol	-1.90E+03	-30989.17	-00/10.21	-1.30E+03
Enthalpy	604 1012	1770 560	2627 127	500 2192
cal/gm	-094.1015	-1//8.308	-3037.437	-399.2182
Enthalpy	5 450+05	1 59E±05	1 485+05	4 00E±05
cal/sec	-3.43E+03	-1.38E+03	-1.40E+05	-4.99E+05
Entropy	-133 7162	-57 54022	-35 35407	-361 3313
cal/mol-K	-+55.7+02	-57.54022	-55.55407	-501.5515
Entropy	-1 535565	-1 705766	-1 027541	-1 1/16117
cal/gm-K	-1.555505	-1.75700	-1.727341	-1.440117
Density mol/cc	3.13E-03	0.0247461	0.0496565	3.31E-03
Density gm/cc	0.8837759	0.7929208	0.9107784	0.8270177
Average MW	282.4668	32.04216	18.34154	249.8631
Liq Vol 60F l/min	53.27933	6.722433	2.475754	57.32647

Table F.5 Results summary for catalyst weight at 0.45 kg.

Reactant ratio $= 1.0$	Pressure = 1 bar
Distillate-to-feed ratio $= 0.40$	Catalyst = 0.50 kg
Reflux ratio $= 0.04$	Number of stages $= 16$

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	3.08E-06	0.3902868
METHA-01	0	10	0.1551644	0.2351254
METHY-01	0	0	8.69E-06	9.609701
WATER	0	0	7.844824	1.764886
Total Flow	10	10	0	12
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	146.3019	2998.787
Total Flow 1/min	53.26892	6.735048	2.673505	60.43185
Temperature K	298.15	298.15	369.4115	355.2507
Pressure atm	0.9869233	0.9869233	0.9869233	0.9869233
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy	-1.96E+05	-56989.17	-66750.69	-1.50E+05
cal/mol	1., 02 00	000000000	00,0000	1.002 00
Enthalpy	-694.1013	-1778.568	-3650.024	-598.9383
Entholpy				
cal/sec	-5.45E+05	-1.58E+05	-1.48E+05	-4.99E+05
Entropy				
cal/mol-K	-433.7462	-57.54022	-35.28233	-361.4395
Entropy	1 525565	1 7057((1 020299	1 44(242
cal/gm-K	-1.333303	-1./93/00	-1.929288	-1.440343
Density mol/cc	3.13E-03	0.0247461	0.0498721	3.31E-03
Density gm/cc	0.8837759	0.7929208	0.9120482	0.8270438
Average MW	282.4668	32.04216	18.28774	249.8989
Liq Vol 60F l/min	53.27933	6.722433	2.464358	57.33711

Table F.6 Results summary for catalyst weight at 0.50 kg.

APPENDIX G

Operating Parameters Condition:Reactant ratio = 1.0Pressure = 3 barDistillate-to-feed ratio = 0.40Catalyst = 0.35 kgReflux ratio = 0.04Number of stages = 16

Table G.1 Results summary for suitable configurations for the biodiesel production using reactive distillation column.

	1	2	3	4
	B1	B1		
			B1	B1
	LIQUID	LIQUID	LIQUID	LIQUID
Substream:				
MIXED				
Mole Flow				
kmol/hr				
OLEIC-01	10	0	2.62E-05	0.2171963
METHA-01	0	10	5.79E-03	0.2114337
METHY-01	0	0	1.05E-05	9.782767
WATER	0	0	7.994174	1.788603
Total Flow	10	10	8	12
kmol/hr	10	10	0	12
Total Flow kg/hr	2824.668	320.4216	144.2133	3000.876
Total Flow 1/min	53.26892	6.735048	2.726357	62.30187
Temperature K	298.15	298.15	406.1799	388.95
Pressure atm	2.96077	2.96077	2.96077	2.96077
Vapor Frac	0	0	0	0
Liquid Frac	1	1	1	1
Solid Frac	0	0	0	0
Enthalpy cal/mol	-1.96E+05	-56987.93	-66258.91	-1.45E+05
Enthalpy cal/gm	-694.0589	-1778.53	-3675.606	-579.9949
Enthalpy cal/sec	-5.45E+05	-1.58E+05	-1.47E+05	-4.83E+05
Entropy cal/mol-K	-433.7573	-57.54257	-33.29118	-350.2074
Entropy cal/gm-K	-1.535605	-1.795839	-1.846775	-1.400421
Density mol/cc	3.13E-03	0.0247461	0.0489053	3.21E-03
Density gm/cc	0.8837759	0.7929208	0.8815995	0.8027784
Average MW	282.4668	32.04216	18.02666	250.073
Liq Vol 60F l/min	53.27933	6.722433	2.409005	57.38886