



ADDIS ABABA UNIVERSITY
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SCHOOL OF GRADUATE STUDIES
DEPARTMENT OF MECHANICAL ENGINEERING

**MODELING & SIMULATION OF SMALL-SCALE BIODIESEL PLANT
AND DESIGN OF EXCESS ETHANOL RECOVERY SYSTEM**

BY
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Declaration I, the undersigned, declare that this thesis is my original work, has not been presented for a degree in this or other university and that all sources of materials used for this have been acknowledged.

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Abstract

Rising world fuel prices, the growing demand for energy, depletion in fossil fuel, and concerns about global warming are the key factors driving the increasing interest in renewable energy sources and in biofuels in particular that can be used as an alternative fuel in CI engines. The aim of this study was modeling and simulation of the small-scale biodiesel plant under construction at Addis Ababa institute of technology and design of excess ethanol recovery mechanism for the plant.

Experimentally determined reaction conditions (Reaction temperature 80°C, Ethanol to Oil molar ratio 9:1, catalyst concentration 1% w/w, reaction time 3.5Hours) for optimal Biodiesel production were used for the design of the plant. Aspen Plus software version 8.4 was used for the simulation of the Transesterification. The simulation was done by initially determining the reaction kinetics of the Transesterification process from a biodiesel yield vs time graph obtained from a defended thesis titled “Emission and Performance Characteristics of Jatropha Ethyl Ester and its blends with Diesel Fuel in a C.I. Engine” done by Haymanot Baynesagn at Addis Ababa institute of technology from which the reaction conditions for the plant design are taken. From the biodiesel yield vs time graph, the amount of biodiesel obtained at a point of 30 min interval time for temperatures of 60°C, 70°C, 80°C and 90°C was calculated. Then, the amount (in gram, mole & litter) and concentration of other components in the reaction process at every time interval for the specified temperatures were calculated. From the determined concentration values, the integrated form of the transesterification reaction was plotted so that from slope of the plot, the forward and reverse rate constants determined. The Arrhenius equation is an equation that shows the dependency of the rate constant on temperature. Thus, the natural logarithm of the rate constants determined for the specified temperatures above was plotted against the invers of the temperatures and from the slope of which the kinetic parameters; Activation Energy and Frequency factor (input parameters to the simulation) determined as; for forward reaction $E_{af}=25.769\text{KJ/mol}$ and Frequency factor $A_f = 60.26/\text{min}$ and for the revers reaction $E_{ab}=22.934\text{KJ/mol}$ and Frequency factor $A_b=4.69/\text{min}$.

Aspen software consists of property database for lots of materials. However, Triglyceride oils such as Jatropha oil have not been yet added to the database. Thus, it was a must to select a similar material from the existing once to represent Triglyceride oils. Triolein oil is the mostly

selected model to represent Triglyceride oil. Accordingly, the transesterification reaction was modeled with Triolein in place of Triglyceride and the simulation done. The simulation result obtained was 91.4% yield of biodiesel which was higher than the experimentally determined value of 85.24%.

As the Transesterification reaction is a reversible, excess alcohol is normally added to force the reaction towards the forward. Thus, after the completion of the reaction the amount of alcohol being consumed in the reaction is much lower and much amount to remain unreacted that is termed as excess alcohol. The amount of ethanol that remains unreacted at the end of transesterification reaction was nearly 73%. If this excess amount of ethanol is left uncollected and reused, the process cannot be economical. Thus, inclusion of a mechanism for recovering of excess ethanol in a transesterification process is mandatory. For biodiesel production plant of higher capacity, distillation column is the mostly used alcohol recovery system. However, a reflux condenser is used for smaller production capacity of plant. In this paper, a design of vertical helical coil heat exchanger with dimensions of height 510mm, Shell Diameter 285mm, copper tube of $\text{Ø}7.94\text{mm}$ (5/16 inch) with coil pitch of 17mm was designed for use as reflux condenser.

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Table of Contents

Abstract	i
Acknowledgement.....	iii
List of Figures	vi
List of Tables.....	vii
Nomenclature	viii
1 Introduction	1
1.1 Background	2
1.2 Statement of the problem	3
1.3 Objectives of the Study	3
1.4 Significance of the Study	4
1.5 Scope and Limitations	4
1.5.1 Scope	4
1.5.2 Limitations.....	4
2 Literature Review	5
2.1 Biodiesel Feedstock.....	5
2.2 The Jatropha Plant.....	6
2.3 Physical and Chemical Properties of Jatropha Biodiesel	7
2.4 Biodiesel Production Techniques	8
2.4.1 Esterification	8
2.4.2 Transesterification (alcoholysis)	8
2.5 Main factors affecting the yield of biodiesel.....	9
2.6 Previous works	12
3 Methodology and Kinetics of the Transesterification	14
3.1 Methodology	14
3.2 Kinetics of the Transesterification of JCT.....	14
3.3 Determination of rate constant	15
3.3.1 Determination of TG Concentration.....	17
3.3.2 Activation Energy and Frequency Factor	20
4 Modeling and Simulation	24
4.1 Conceptual Design	24
4.2 ASPEN plus Software	29
4.3 Transesterification Reaction modeling.....	30

4.4.	Thermodynamic Models in Aspen	31
4.5.	Physical and Chemical properties	32
4.6.	Material Balance Calculation of the Reaction.....	33
4.7.	Reactor Modeling in Aspen Plus.....	34
4.8.	Aspen plus Unit Operation Blocks Used in the Biodiesel Plant Model	36
4.9.	Modeling of the Transesterification plant	36
4.9.1.	Modeling Using RStoic reactor model.....	37
4.9.2.	Modeling Using RBatch reactor model.....	39
4.10	Residence time	43
4.11	Sensitivity Analysis.....	46
5	Excess Ethanol Recovery	49
5.1.	Recovery system process Description.....	50
5.2.	Helical coil heat exchanger for the Condenser.....	51
5.2.1.	Design analysis.....	52
5.2.2.	Mass flow rate of evaporated ethanol.....	56
6	Conclusion and Recommendations	59
6.1.	Conclusion.....	59
6.2.	Recommendations	60
	References	61
	Appendix A1: Yield, Amount and Concentration of reaction components for Transesterification reaction of Jatropa oil with Ethanol for temperatures T=60°C, 70°C, 80°C and 90°C.....	64
	Appendix A2: Yield, Amount and Concentration of reaction components for Transesterification reaction of Sunflower oil with Ethanol for temperatures T=35°C, 80°C and 90°C	68
	Appendix A3: Yield, Amount and Concentration of reaction components for Transesterification reaction of Jatropa oil with Methanol for temperature T= 30°C, 40°C and 50°C.....	72
	Appendix B1: Matlab program for the stoichiometric chemical reaction mass balance.....	76
	Appendix B2: Matlab Program for the design of Helical Coil Heat Exchanger for Recovery of Excess Ethanol	77
	Appendix C: Helical Coil Heat Exchanger (Condenser) part drawings.....	79

List of Figures

Figure 2-1: Jatropha Fruit in the tree, ripe and seeds [28].....	6
Figure 2-2: General reaction diagram for Transesterification of Triglycerides with ethanol under an alkali catalyst to form FAEE and glycerol	9
Figure 2-3: Transesterification of Triglyceride to produce esters	9
Figure 2-4: The effect of methanol to JCO molar ratio at various temperatures (catalyst loading at 1% w/w)[21]	11
Figure 2-5: The effect of ethanol to JCO molar ratio at various temperatures (catalyst loading at 1% w/w)[21]	11
Figure 2-6: The effect of reaction time on the concentration of Jatropha curcas methyl and ethyl esters at various temperatures (amount of catalyst loading is 1% w/w)[21]	12
Figure 3-1: Plot of the reversible first order reaction [25]	16
Figure 3-2: Ethyl Ester Yield vs time graph at different temperatures [15]	17
Figure 3-3: Ethyl Ester Yield vs Time graph with added gridlines	20
Figure 3-4: Reaction component concentration verses Time graph	20
Figure 3-5: Reaction rate temperature dependence [25]	22
Figure 3-6: Plot of LN (K_f , forward rate constant) against 1/T for experimental data	23
Figure 3-7: Plot of LN (K_b , reverse rate constant) against 1/T for experimental data.....	23
Figure 4-1: Three-dimensional view of the small-scale Biodiesel plant	25
Figure 4-2: Biodiesel Flowsheet diagram for RStoic Reactor model in Aspen Plus.....	37
Figure 4-3: Simulation results for the model using RStoic reactor model	38
Figure 4-4: Biodiesel Flowsheet diagram for Rbatch Reactor model in Aspen Plus	39
Figure 4-5: Simulation results for the model using Rbatch reactor model.....	40
Figure 4-6: Ethyl ester yield (%) verses Time(hour) at temperatures of 35, 80 and 90 °C, NaOH to oil mass ratio, 1.0%; ethanol/oil molar ratio, 12:1[22].....	41
Figure 4-7: Triglyceride conversion at temperatures of 30, 40 and 50°C. Reaction conditions: Jatropha oil 50 g, catalyst amount 1%, Oil to Methanol Molar Ratio 1:9 [23].....	42
Figure 4-8: Molar composition of feed oil and Ethyl ester produced as a function of time	44
Figure 4-9: Ethyl Ester (Biodiesel) yield as a function of reaction time	45
Figure 4-10: Ethyl Ester (Biodiesel) yield as a function of reaction temperature	46
Figure 4-11 Ethyl Ester (Biodiesel) yield as a function of ethanol feed	47
Figure 4-12: Molar composition of feed oil and Methyl ester produced as a function of time	47
Figure 4-13: Methyl Ester (Biodiesel) yield as a function of reaction time	48
Figure 5-1: Schematic representation of Ethanol Recovery Unit.....	50
Figure 5-2: Helical Coil Heat Exchanger	53
Figure 5-3: Schematic cutaway view of the HCHE	53

List of Tables

Table 2-1: Composition and Characteristics of Jatropha Curcas oil	5
Table 2-2: Fatty acid composition for different vegetable non-edible oils [1].....	7
Table 2-3: Physicochemical Properties of Diesel and Biodiesel.....	7
Table 2-4: Alkali catalyzed transesterification of Jatropha curcas oil with optimized reaction variables ..	12
Table 3-1: Forward and backward reaction rate constants at different temperatures	22
Table 4-1: Biodiesel production process activities as determined on the design phase by the designer.....	26
Table 4-2: Summary of process activities time starting from ethanol catalyst mixing and reactor preparation to drying of pure biodiesel	28
Table 4-3: Reactions Components used in the model for the simulation.....	31
Table 4-4: Physical and chemical properties of the components in the Transesterification process.....	32
Table 4-5: The stoichiometric quantity to produce biodiesel.....	33
Table 4-6: Material and Mass balance for 80% conversion efficiency; Ethanol to Oil molar ratio 9:1	34
Table 4-7: Unit Operation Blocks for the Transesterification process modeling.....	36
Table 4-8: Reacting component amounts for Ethanol to Oil molar ratio 9:1	37
Table 4-9: Heat and Material balance generated by Aspen simulation for RStoic reactor model	38
Table 4-10: Heat and Material balance generated by Aspen simulation for Rbatch reactor	40
Table 4-11: Transesterification reaction parameters for the three cases, the one considered in this study and the other two included for comparison.	43
Table 4-12: Molar composition of the reacting component and products generated by Aspen plus	44
Table 4-13: Biodiesel produced in kmol/hr and percentage yield at selected resident time	45
Table 5-1: Physical property and other assumed values for condenser design	52
Table 5-2: Ethanol recovery condenser parameters, Matlab output for evaporation time t=15min.....	57
Table 5-3: Ethanol recovery condenser parameters, Matlab output (alternative-1)	58
Table 5-4: Ethanol recovery condenser parameters, Matlab output (altenative-2)	58

Nomenclature

K_f	Rate Constant for forward reaction
K_b	Rate constant for reverse reaction
A_f	Arrhenius Constant (/min) for forward reaction
A_b	Arrhenius Constant (/min) for reverse reaction
E_{af}	Activation Energy (kJ/mol) for forward reaction
E_{ab}	Activation Energy (KJ/mol) for revers reaction
R	Universal Gas Constant (J/mol. K)
T	Temperature (K)
D_1	Outside diameter of inner cylinder (m)
D_2	Inside diameter of outer cylinder (m)
D_c	Average (Pitch) diameter of the helix (m)
D_{ci}	Inner diameter of the helix (m)
D_{co}	Outer diameter of the helix (m)
R_c	Average (Pitch) radius of the helix (m)
P	Pitch of the helix (m)
d_o	Outer diameter of the coil (m)
d_i	Inner diameter of the coil (m)
L_c	Length of the coil (m)
N	Coil number of the helix (m)
V_c	Volume of coiled tube (helix) (m ³)
V_a	Volume of annulus (m ³)
D_e	Shell side equivalent (Hydraulic) diameter of the coil (m)
Q	Heat load (KJ)
\dot{Q}	Heat Power (KJ/s)
h_{fg}	Latent heat of vaporization of coil side fluid (KJ/Kg)
m_c	Mass flow rate of coil side fluid (kg/s)
m_s	Mass flow rate of fluid in the annulus (kg/s)
C_{pc}	Specific heat capacity of coil side fluid (KJ/Kg k)
C_{ps}	Specific heat capacity of fluid in the annulus (KJ/Kg k)
V_c	Mean velocity of Coil side fluid (m/s)
V_s	Mean velocity of fluid in the annulus (m/s)
ρ_c	Density of fluid in the coil (Kg/m ³)
ρ_s	Density of fluid in the annulus (Kg/m ³)

K_c	Thermal conductivity of fluid in the coil (KJ/s.m. $^{\circ}$ C)
K_s	Thermal conductivity of fluid in the annulus (KJ/s.m. $^{\circ}$ C)
K_p	Thermal conductivity of coil wall (KJ/s.m. $^{\circ}$ C)
V_{dc}	Dynamic viscosity of fluid in the coil (Kg/m.s) or (N-s/m 2)
V_{ds}	Dynamic viscosity of fluid in the annulus at mean bulk fluid temperature (Kg/m.s) or (N-s/m 2)
V_{dsw}	Dynamic viscosity of fluid in the annulus at pipe wall temperature (Kg/m.s) or (N-s/m 2)
Nuc	Nusselt number of fluid in the coil
Nus	Nusselt number of fluid in the annulus
Rec	Reynolds number of fluid in the coil
Res	Reynolds number of fluid in the annulus
Prc	Prandtl number of fluid in the coil
Prs	Prandtl number of fluid in the annulus
f_c	Friction factor inside coil
f_s	Friction factor inside annulus
h_c	Heat transfer coefficient of fluid in the coil (W/m 2 $^{\circ}$ C)
h_{ic}	Corrected heat transfer coefficient in the coil (W/m 2 $^{\circ}$ C)
h_o	Heat transfer coefficient of fluid in the annulus (W/m 2 $^{\circ}$ C)
F_c	Fouling factor of fluid in the coil
F_s	Fouling factor of fluid in the annulus
U	Overall heat transfer coefficient (W/m 2 $^{\circ}$ C)
A_h	Area of heat transfer (m 2)
T_{ci}	Inlet temperature to condenser of ethanol vapor ($^{\circ}$ K)
T_{co}	Outlet temperature to condenser of ethanol vapor ($^{\circ}$ K)
T_{si}	Inlet temperature to condenser of water ($^{\circ}$ K)
T_{so}	Outlet temperature to condenser of water ($^{\circ}$ K)
ΔT_{lm}	Log mean temperature difference ($^{\circ}$ K)
H	Condenser height (m)

1 Introduction

Knowing of the importance to the national economy in general and to the energy sector in particular, the Ethiopian government has given due attention for the development of biofuels with the objective of achieving energy security via diversifying the energy sources in the country and lowering exposure to the price volatility in international oil markets.

Biofuels are considered to be viable alternative fuels for fossil fuels that can be manufactured from crops, vegetable oils or animal fats, being a renewable and biodegradable fuel with absence of toxicity, providing many environmental benefits as, reduction of greenhouse gas, less pollution of air, water and soil, when compared to the use of petroleum-based fuels.

There are two common modern strategies of producing liquid and gaseous biofuels. One is to grow crops high in sugar (sugar cane, sugar beet, and sweet sorghum) or starch (maize, cassava, yam), and then make use of yeast fermentation to produce ethyl alcohol (ethanol) that has the potential to be a sustainable transportation fuel for gasoline engines. The second is to grow plants that contain high amounts of vegetable oil, such as oil palm, groundnut, soybean, castor oil, algae, *Jatropha*, or *Pongamiapinnata*. When these oils are heated, their viscosity is reduced, and they can be burned directly in a diesel engine, or they can be chemically processed to produce fuels such as biodiesel.

Among the vegetable oils, production from *Jatropha* becomes a worldwide issue for its multi-dimensional advantage including its drought-resistant, growing ability in marginal/poor soil, and its potential for high oil productivity per hectare per year [1, 2].

The production of biodiesel involves oil extraction, oil purification, and processing of oil [2]. Transesterification is the most used processing of biodiesel production. Transesterification is a class of organic reactions that comprises a transformation of an ester into another through an exchange of acyl groups between esters and acid (acidolysis), esters and other esters (interesterification) or esters and alcohols (alcoholysis). The transesterification reaction typically occurs in batch reactors and requires several minutes or hours to achieve high yield [3]. In this process the oil will be trans-esterified with alcohol (methanol or ethanol) using suitable base catalysts such as potassium hydroxide/sodium hydroxide. The variables that can affect the performance of the transesterification reaction are the type and amount of catalyst, the reaction temperature, the molar ratio of alcohol (alcoholysis) and the purity of the reagents

[3]. For a better yield of biodiesel or conversion of the fat or oil to its esters, using convenient reactor is necessary.

1.1 Background

Rising world fuel prices, the growing demand for energy, and concerns about global warming are the key factors driving the increasing interest in renewable energy sources, and in biofuels in particular. Ethiopia imports its entire petroleum fuel requirement and the demand for petroleum fuel is rising rapidly due to a growing economy and expanding infrastructure. This is more relevant for countries like Ethiopia that spend a considerable share of foreign currency reserves on fuel imports and consumes considerable biomass for domestic energy consumption. In 2017/18 fiscal year, Ethiopia used 81.6% of total export earnings on fuel imports (National Bank of Ethiopian, Annual Report 2017/18). In most developing countries, the emerging bio-fuels industry is perceived as an opportunity to enhance economic growth and create or maintain jobs, particularly in rural areas.

Apart from the ever-growing price of petroleum, the world is also suffering from its emission related problems such as global warming, ozone layer depletion and the consequence of climate change: drought, and flooding. It is also a belief of many experts that in the future the world will be exhausted of fossil fuels due to the depletion of the oil reserves. Hence, a far-reaching decision may need to be taken to address this problem.

The most important renewable energy options identified as mitigation measures to reduce the level of greenhouse gas emissions caused by over dependency on energy derived from fossil fuel include the development of bio-energy, hydropower, solar and wind energy.

Biofuel development in Ethiopia consists of projects using sugar cane for ethanol and *Jatropha* and castor beans for biodiesel production. Ethanol production is linked with the public sugar estates and biodiesel with private investment [4]. Biodiesel has attracted considerable attention during the past decade as a renewable, biodegradable and non-toxic fuel alternative to fossil fuels. Biodiesel can be obtained from vegetable oils (both edible and non-edible) and from animal fat. *Jatropha curcas* Linnaeus, a multipurpose plant, contains high amount of oil in its seeds which can be converted to biodiesel. *J. curcas* is probably the most highly promoted oilseed crop in the world [5]. The availability and sustainability of sufficient supplies of less expensive feedstock in the form of vegetable oils, particularly *J. curcas* and efficient processing technology to biodiesel will be crucial determinants of delivering a competitive biodiesel [5].

1.2 Statement of the problem

Ethiopia imports its entire fossil fuels to satisfy its energy demand, and with population growth and economic development the demand will continue to increase. Fossil fuels are limited energy resources and if alternative fuel energy couldn't share part of the fossil fuel, the resources will eventually be exhausted. Furthermore, the use of fossil fuels has a severe impact on climate change. In combination with the increasing global demand for renewable energy forms, the need to secure energy supply in developing countries has created a demand for biomass energy, such as biofuels.

One of the most common biofuel energy systems is production of biodiesel through Transesterification of non-petroleum-based oils. Biodiesel can be used in unmodified diesel engines, either alone or blended with conventional petro diesels [6].

Conventional biodiesel production involves transesterification of plant oil with methanol in combination with a suitable catalyst [1]. In this study, the application of *Jatropha curcas* L. (*Jatropha*) oil for biodiesel synthesis with ethanol as an alcohol source is considered. A better yield of biodiesel needs a time to time improvement on the production process and technology of conversion of the *Jatropha* oil to biodiesel. A device that integrates reaction of *Jatropha* oil and Ethanol and then separation of the two reactants is said to be a reactor.

In this paper, the liquid-phase biodiesel production using batch reactor in the Small-Scale Biodiesel plant being studied and under fabrication by Sine Girma (Co advisor), a PHD candidate at AAIT was studied in order for modeling and simulation of its transesterification reaction to predict and validate conversions at the outlet reactor.

1.3 Objectives of the Study

The objectives of this study are;

- To molecularly model the transesterification process of mixture of *Jatropha* oil and ethanol,
- To use computational tool Aspen plus software to simulate the process of biodiesel production (transesterification process of the small-scale biodiesel plant) and validate the predetermined conversion value of the raw material to biodiesel
- To design a system for recovering of excess alcohol (Ethanol) after reaction completion,

1.4 Significance of the Study

A study of biodiesel synthesis is vital because it provides information that will enable to have better knowledge for future development on the technology and incites effective measures to be undertaken so as to improve the conversion efficiency of the Jatropha oil to biodiesel.

1.5 Scope and Limitations

1.5.1 Scope

The scope of this study is to model and simulate the transesterification process of the small-scale biodiesel plant, estimate the conversions or yield of the raw material (Jatropha Oil) to biodiesel and compare the result to experimentally demined value. In addition, this study includes the design of reflux condenser for recovery of excess ethanol.

1.5.2 Limitations

As the main objective of this study was modeling and simulation of the transesterification process of the biodiesel production system using Aspen plus software and the Aspen unit blocks for reactor model require known kinetics of the reaction. Most researches performed on the biodiesel production process are with the use of methanol as an alcohol and therefore no literature was found on the kinetics of transesterification with ethanol as an alcohol.

Though ASPEN Plus is equipped with a large database of known compounds with various thermodynamic data, the compounds that make up Jatropha oils are not present due to which the simulation result could vary from the experimentally determined value.

2 Literature Review

Biodiesel is a clean burning engine fuel made from vegetable oils or animal fat. It is obtained from addition of alcohol to any source of complex fatty acids through a process called transesterification. The term biodiesel; refers to 100percent pure fuel (B100) that meets the American Society for Testing and Material (ASTM) requirement for biodiesel in its D6751 standards.

2.1. Biodiesel Feedstock

A variety of oil can be processed in to fuel for compression ignition internal combustion engines. Soybean, sunflower, and coconut oils have been the main raw materials for biodiesel production. More than 95% of biodiesel production feedstock comes from edible oils in developed countries because the properties of biodiesel produced from these oils are very similar to petroleum-based diesel. In view of their several advantages, vegetable oils have a great potential to replace petroleum-based fuels in the long run [1]. Non-edible plant oils such as *Jatropha curcas* and castor beans may provide better alternatives. Table 1 shows the fatty acid composition for different vegetable oils [1].

Biodiesel could be used directly in diesel engines or blended with petro diesel. However, their high viscosity leads to problems in the engine. Kinematic viscosity is one of the parameters specified in biodiesel and petro-diesel standards that require compliance especially for *Jatropha* raw oil which reaches to 37.0-54.8 cSt at 30°C (Table 1). It is extremely viscous with a kinematic viscosity about 22 times greater than that of diesel fuel [19]. Reducing viscosity is therefore the major reason for processing plant oils to make them suitable for use as biodiesel. Table 2.1 tabulates the composition and characteristics of *Jatropha curcas* oil.

Table 2-1: Composition and Characteristics of *Jatropha Curcas* oil

Characteristic	Range
Specific gravity (gcm ⁻³)	0.860–0.933
Calorific value (MJ kg ⁻¹)	37.83–42.05
Pour point (°C)	–3
Cloud point (°C)	2
Flash point (°C)	210–240
Cetane value	38.0–51.0
Saponification number (mg g ⁻¹)	102.9–209.0
Viscosity at 30 °C (cSt)	37.0–54.8
Free fatty acids % (kg kg ⁻¹ ×100)	0.18–3.40

2.2. The Jatropha Plant

The scientific name of Jatropha is *Jatropha Curcas* L. and Jatropha oil is one such kind of non-edible vegetable oil. Not only does Jatropha have a yield of well, it also increases the fertility of the land on which it is grown so that it can potentially be used for food crops in subsequent years.

Jatropha is a perennial which can grow in arid conditions on any kind of ground and does not suffer in droughts or require irrigation. It is easy to establish, grows relatively quickly and lives, producing seeds for 50 years.



Figure 2-1: Jatropha Fruit in the tree, ripe and seeds [28]

Jatropha has received tremendous attention in most African countries and has emerged as one of the most promising feedstock candidates for the production of liquid biofuels, both at small-scale and large-scale commercial level. Hence, the governments of most developing countries who aim to attract foreign investments in biofuels, and those in the developed world, are promoting claims that there is ample “marginal” land in Africa and that Jatropha can be successfully grown on “marginal” land without affecting food security or the livelihoods of rural communities [20]

Depending on soil quality and rainfall, oil can be extracted from the Jatropha nuts after two to five years. Jatropha Curcas oil is a free fatty acid Triglyceride derived from Jatropha plant seed that contains about 78.9% unsaturated compounds [1]. Triglycerides are chemically tri esters of fatty acids and glycerol. They are formed by combining glycerol with three fatty acid molecules.

The oil content of Jatropha seed ranges to 55% by its weight. The fatty acid composition of Jatropha classifies it as a linoleic or oleic acid type, which are unsaturated fatty acids. The fatty acid composition of Jatropha oil consists of myristic, palmitic, stearic, Palmitoleic, oleic and linoleic acids. From the fatty acid composition of Jatropha oil the major constituent is the unsaturated fatty acid Oleic acid with 43.1% (Table 2-2) [1].

The seeds and oil are toxic for feeding due to the presence of curcive and curcasive. The oil can be combusted as a fuel without being refined. It burns with clear smoke and free flame. It

is tested successfully as fuel for simple diesel engine. The by-product is press cake which is a good organic fertilizer. The oil also contains insecticide. It can grow in areas, rugged in nature, and can survive with minimum input and easy to propagate.

Table 2-2: Fatty acid composition for different vegetable non-edible oils [1]

Fatty acid composition in%	Molecular formula	Jatropha oil	Pongamia (Karanja oil)	Sunflower oil	Soybean oil	Palm oil
Lauric (C12/0)	C ₁₂ H ₂₄ O ₂	-	-	0.5	-	-
Myristic (C14/0)	C ₁₄ H ₂₈ O ₂	-	-	0.2	0.1	-
Palmitic (C16/0)	C ₁₆ H ₃₂ O ₂	14.2	9.8	4.8	11.0	40.3
Palmitoleic (C16/1)	C ₁₆ H ₃₀ O ₂	1.4	-	0.8	0.1	-
Stearic (C18/0)	C ₁₈ H ₃₆ O ₂	6.9	6.2	5.7	4.0	3.1
Oleic (C18/1)	C ₁₈ H ₃₄ O ₂	43.1	72.2	20.6	23.4	43.4
Linoleic (C18/2)	C ₁₈ H ₃₂ O ₂	34.4	11.8	66.2	53.2	13.2
Linolenic (C18/3)	C ₁₈ H ₃₀ O ₂	-	-	0.8	7.8	-
Arachidic (C20/0)	C ₂₀ H ₄₀ O ₂	-	-	0.4	0.3	-
Behenic (C22/0)	C ₂₂ H ₄₄ O ₂	-	-	-	0.1	-
Saturates (%)		21.1	16	11.6	15.5	43.4
Unsaturates (%)		78.9	84	88.4	84.5	56.6

2.3. Physical and Chemical Properties of Jatropha Biodiesel

The quality of biodiesel is very important for the performance and emission characteristics of a diesel engine. The basic properties that determine the quality of Jatropha biodiesel are kinematic viscosity, density, specific gravity, flash point, cloud point, and Cetane number. Various researches have been conducted for determining these characteristics. The American Society for Testing and Materials (ASTM) standards controls the physical and chemical properties of diesel and biodiesel (B100). ASTM D975 for diesel fuel and ASTM D6751 for biodiesel B100. The Physicochemical Properties of Diesel and Biodiesel as determined by Afaf Ghais Abadi and Salwa Malik Omer [18] are presented in Table 2-3.

Table 2-3: Physicochemical Properties of Diesel and Biodiesel

Physicochemical Property	Diesel ASTM D 975	Biodiesel(B100) ASTM D6751
Specific gravity	0.85	0.87-0.89
Density 15 °C , g.cm ³	0.82-0.87	0.88
Kinematic Viscosity (40°C) cSt	1.3-4.1	1.9-6.0
Flash Point(°C)	60-80	130 (min)
Cloud Point (°C)	-15 to5	-3 to12
Carbon Residue (10% distillation)	0.15	0.3 (max)
Cetane No.	40-55	47 (min)

2.4. Biodiesel Production Techniques

Biodiesel production from natural vegetable oils and animal fats undergoes certain processes. Natural vegetable oils and animal fats are pressed to obtain crude oil which contains free fatty acids, phospholipids, sterols, water, odorants and other impurities. Because of these compounds; high viscosity, low volatility and the polyunsaturated character of the vegetable oils, they cannot be used as fuel directly in compression ignition engines [8].

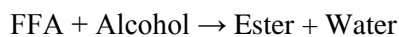
2.4.1. Esterification

Jatropha oil contains 6%- 20% (wt) free fatty acids. The ester is produced by chemically reacting Jatropha oil with an alcohol (methyl/ethanol...), in the presence of catalyst. The amount of free fatty acid in triglyceride plays a very important role in biodiesel production. FFAs act as a potential contaminant. They react with alkali catalyst to form soap. Soap can cause glycerol separation problem. The production of biodiesel from high FFAs containing feedstock needs a pretreatment to convert the FFAs to ester. This pretreatment process is known as esterification [10].

Therefore, the production of biodiesel process from low-quality feedstock consists of two steps esterification and transesterification. This two steps approach is also known as acid catalysis followed by alkali catalysis [10].

The first stage (acid catalyzed) of the process is to reduce the free fatty acids (FFA) content in Jatropha oil by esterification with alcohol and acid catalyst (sulfuric acid) in a closed reactor vessel. When the FFA is reduced to an acceptable value, the reaction will be stopped. After dewatering, the esterified oil will be fed to the transesterification process.

Esterification Reaction (Acid Catalyst)



2.4.2. Transesterification (alcoholysis)

Transesterification of vegetable oils is the most popular method of producing biodiesel. Transesterification (alternatively alcoholysis) is the reaction of a fat or oil (triglyceride) with an alcohol to form fatty acid alkyl esters; methyl and ethyl esters (which are excellent substitutes for biodiesel) and glycerol [8]. General Transesterification process is as shown in figure 2-2, where the R's are to represent the unsaturated fatty acids.

Transesterification Reaction (Base Catalyst)

Oil/Fat + Alcohol → Biodiesel + Glycerol

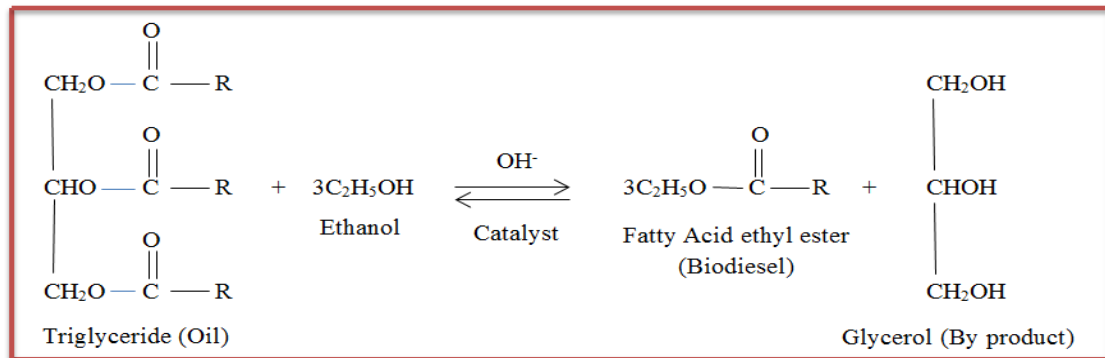


Figure 2-2: General reaction diagram for Transesterification of Triglycerides with ethanol under an alkali catalyst to form FAEE and glycerol

The above Transesterification reaction form can be rewritten as below with R's are replaced with molecular structure of the unsaturated fatty acids.

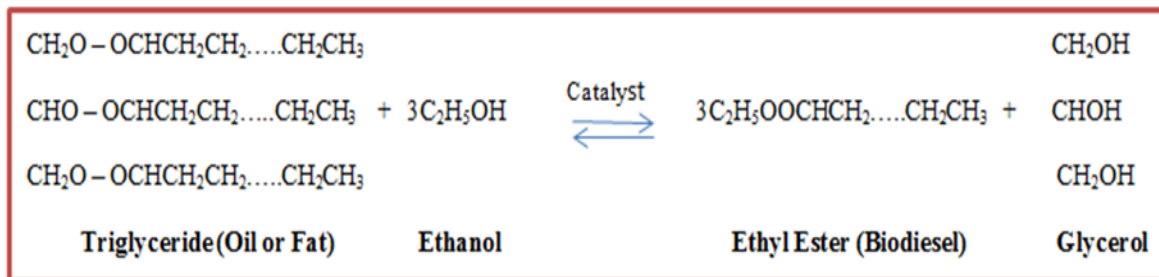


Figure 2-3: Transesterification of Triglyceride to produce esters

Transesterification as an industrial process is usually carried out by heating an excess of the alcohol with vegetable oils under different reaction conditions in the presence of an inorganic catalyst. The reaction is reversible and therefore excess alcohol is used to shift the equilibrium to the products side. The alcohols that can be used in the transesterification process are methanol, ethanol, propanol, butanol and amyl alcohol, with methanol and ethanol alcohol being frequently used [8].

2.5. Main factors affecting the yield of biodiesel

There are few important variables that influence the transesterification reaction. In order to obtain maximum yield of biodiesel, these variables must be at their optimum condition.

a) Reaction temperature

The rate of reaction is strongly affected by the reaction temperature. A higher reaction temperature can decrease the viscosities of oils and result in an increase in reaction rate as more energy is being supplied for the reaction to occur. Thus, the yield of the biodiesel product is improved. However, the reaction temperature must be less than the boiling point of

alcohol (boiling point of methanol is at 60–70°C at atmospheric pressure) to ensure the alcohol will not be lost through vaporization. Also, the yield of biodiesel decreases if the reaction temperature goes beyond its optimum level because a higher reaction temperature will accelerate the saponification reaction which results in a lower yield. Depending on the types of oil, the maximum yield is obtained at temperatures ranging from 60 to 80 °C [1].

b) Molar ratio of alcohol to oil

The stoichiometric ratio for the transesterification reaction involves three moles of alcohol and one mole of triglyceride to produce three mole of fatty acid ester and one mole of glycerol. Excess alcohol is used during transesterification to ensure that the oils will be completely converted to ester due to the forward reaction being more favorable. Furthermore, a higher alcohol to triglyceride ratio can result in a greater ester conversion in a shorter time. The molar ratio is associated closely with the type of catalyst used. For base-catalyzed transesterification where the free fatty acids are less than 1% after pretreatment, a molar ratio of ethanol to oil of 5:1 or 6:1 is sufficient to convert Jatropha oil to biodiesel. However, where the percentage of free fatty acids in oils is high, a molar ratio as high as 20:1 or 24:1 is needed when using acid-catalyzed transesterification [1]

c) Concentration of catalyst

Catalyst concentration can affect the yield of the biodiesel produced. As mentioned earlier, basic catalysts are usually preferred to acid catalysts because of the higher reactivity and the lower process temperature required. Freedman et al (1984), found that sodium methoxide was more effective than sodium hydroxide because of the reduced amount of water produced upon mixing sodium hydroxide with methanol. As the catalyst concentration increases, the conversion of triglycerides and the yield of biodiesel also increased. A concentration of NaOH in the range of 1.0–1.4% (w/w) has been found to produce 90–98% conversion from Jatropha oil to methyl ester. As for the concentration of KOH ranging from 0.55 to 2.0% (w/w), 95–99% of Jatropha biodiesel has been obtained. However, the yield of biodiesel was reduced if the alkali catalysts were added above their optimum concentration as this causes more soap formation [1].

d) Reaction time

The conversion rate increases with reaction time [1]. The reaction time in biodiesel production is an exceptionally crucial parameter due to its role in mass transfer between the two phases of reactants [27]. Figure 2.6 displays the effect of reactants resident time on the percentage of ester yield (65 °C & 70°C for methyl ester and 75°C and 80°C for ethyl ester) [21]. For base-catalyzed transesterification, the yield of biodiesel reaches the maximum yield

with time less than for acid catalyzed transesterification because base catalysts usually exhibit a higher reactivity than acid catalysts. An excess reaction time will lead to a reduction in the product yield due to the backward reaction of transesterification, causing more fatty acids to form soaps [1].

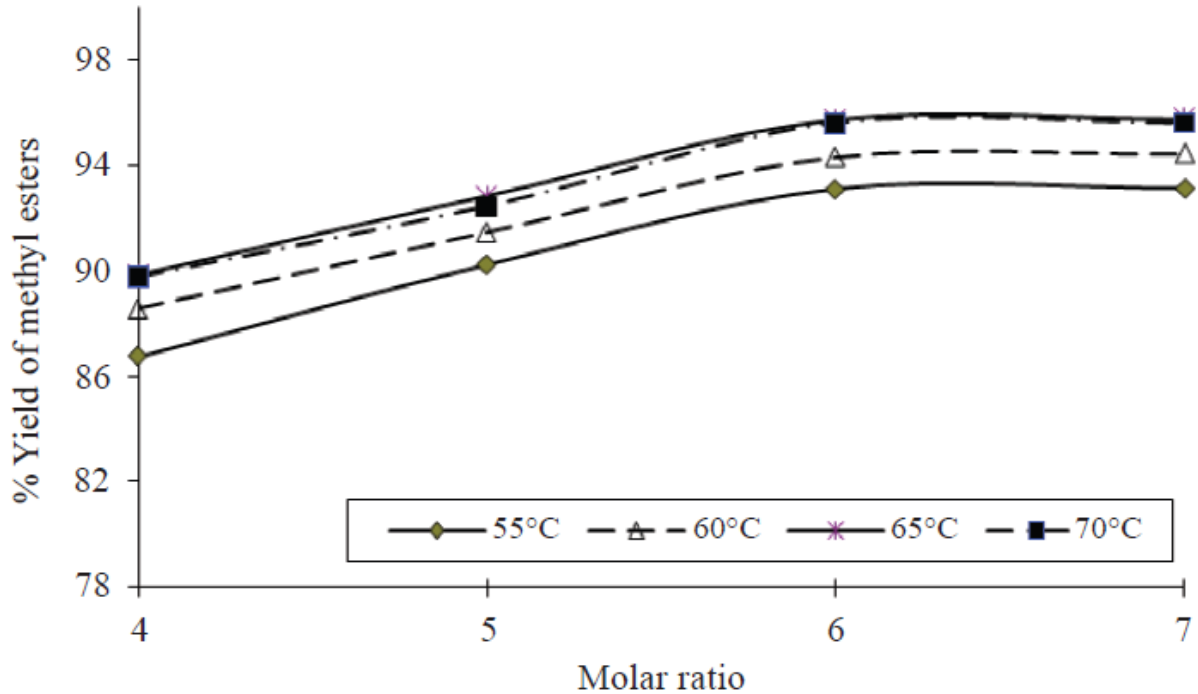


Figure 2-4: The effect of methanol to JCO molar ratio at various temperatures (catalyst loading at 1% w/w) [21]

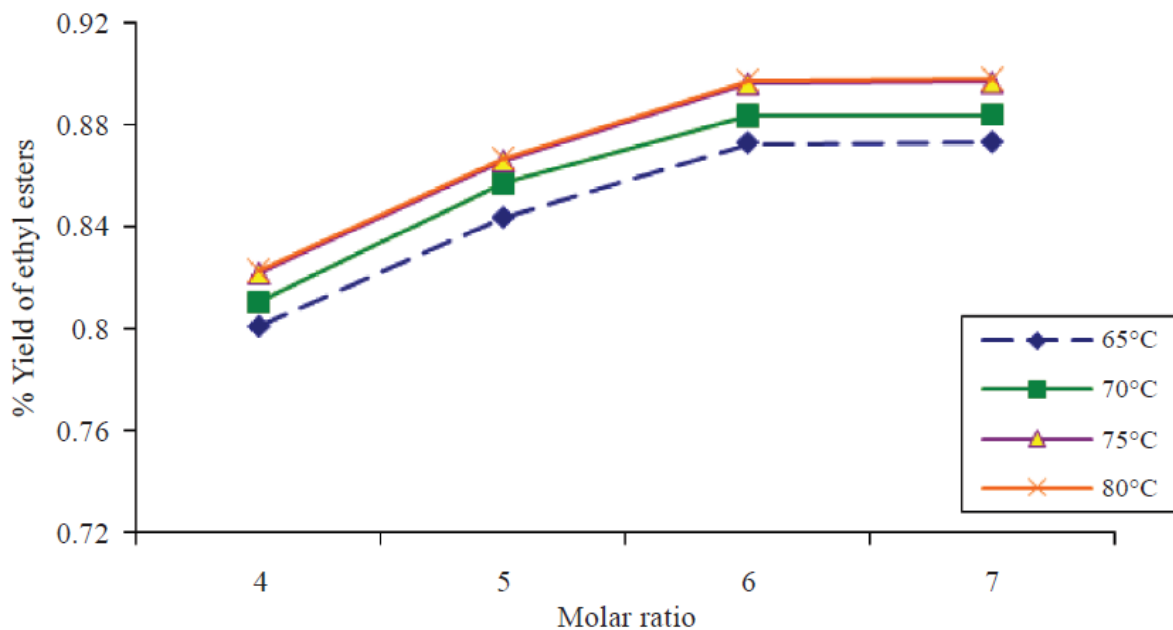


Figure 2-5: The effect of ethanol to JCO molar ratio at various temperatures (catalyst loading at 1% w/w) [21]

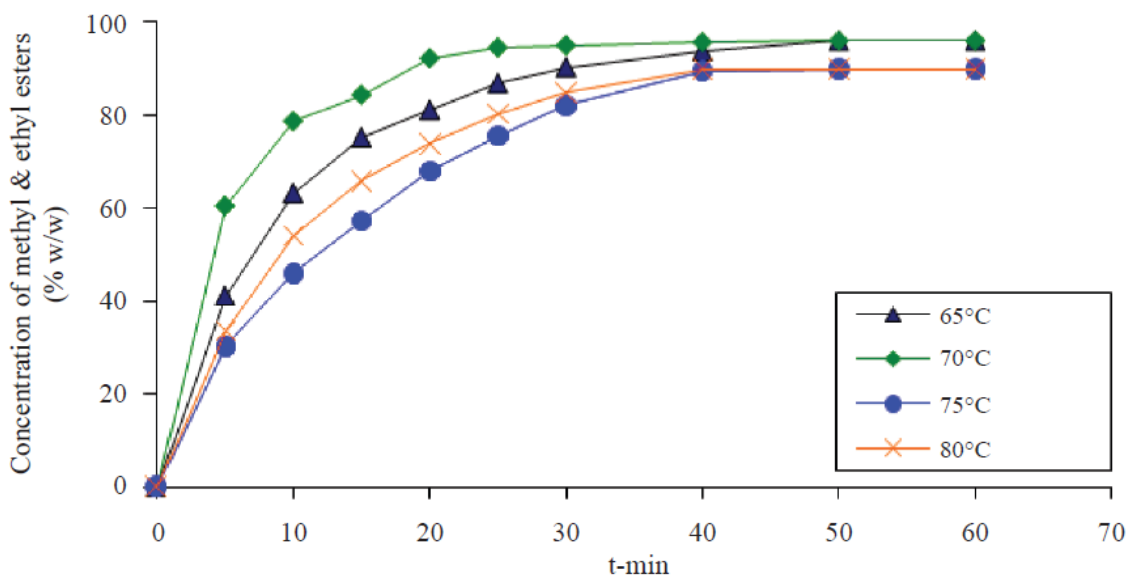


Figure 2-6: The effect of reaction time on the concentration of *Jatropha curcas* methyl and ethyl esters at various temperatures (amount of catalyst loading is 1% w/w) [21]

2.6. Previous works

Various researches have been conducted to determine the kinetics and yield of the transesterification reaction in laboratory and simulations performed to determine the optimal parameter that can contribute to the best performance of a process to conduct a trial plant because it is very costly, and many tests needed to predict the optimal condition for maximizing the yield of biodiesel production.

The alkaline catalyzed transesterification of *Jatropha curcas* oil with optimized reaction conditions of transesterification conducted by some authors and the respective optimum yield obtained have been summarized and tabulated in Table 2.4 [1].

Table 2-4: Alkali catalyzed transesterification of *Jatropha curcas* oil with optimized reaction variables

Alcohol	Molar ratio	Catalyst	Catalyst amount %wt of oil	Optimum reaction condition	Alkaline ester yield %	Reference
Methanol	5:1	NAOH	1.0	60°C, 90min	98	Chitra P, Venkatachalam P, (2005)
Methanol	4.2:1	NAOH	1.4	65°C, 120min	90	Berchmans HJ, Hirata S., (2008)
Methanol	9:1	KOH	2.0	60°C, 120min	95	Patil PD, Deng S., (2009)
Methanol	6:1	KOH	1.0	65°C, 60min	99	Syam AM, Yunus R, (2009)
Methanol	11:1	KOH	1.1	66°C, 120min	93	Sahoo PK, Das LM. (2009)
Methanol	5:1	KOH	0.55	60°C, 24min	99	Tiwari AK, Kumar A, Raheman H., (2007)
Ethanol	9:1	NAOH	1.0	80°C, 180min	85	Haymanot Baynesagn, (2014)

Chemical process characteristics such as flow rates, compositions, temperatures, pressures, properties, equipment sizes, etc. are predicted using several analysis techniques that include mathematical models, empirical correlations and computer-aided process simulation. The experimental means of determining and characterizing results are modeled using computer-aided process simulation tools (Aspen plus and ChemCAD) and results are compared for similarity. Simulation works performed by some researches for transesterification of Biodiesel from different feed stock are; (1)Simulation of the catalytic reaction of transesterification of palm oil with methanol employing an alkaline catalyst to obtain methyl esters (biodiesel) and glycerol under different conditions (oil/methanol feed rates, reaction temperatures, catalyst concentrations) at the pilot plant reaction (PPR) by *L.I. Orificia, C.D. Bahla,b, M.C. Gelya, A. Bandonic and A.M. Paganoa (2013)*, (2) Simulation for Transesterification of Triolein with Methanol in Reactive Distillation Column done by *Chokchai Mueanmas, Kulchanat Prasertsity and Chakrit Tonguraiz [9]*, (3) Transesterification, Modeling and Simulation of Batch Kinetics of Non-Edible Vegetable Oils for Biodiesel Production by *Pankaj Tiwari, Rajeev Kumar and Sanjeev Garg [6]*, (4)Simulation of Biodiesel Production by Transesterification of Vegetable Oils by *Chavdar Chilev, Evgeni Simeonov(2014)* using ChemCAD 6.0 to predict production of biofuel from pure vegetable oil with an alkaline catalyst

3 Methodology and Kinetics of the Transesterification

3.1. Methodology

For the achievement of the objectives mentioned in section 1.3, the below methods were employed:

- Literature survey on biodiesel synthesis from Jatropha oil with Ethanol as alcohol. A broad review of different literatures from different sources on the subject matter.
- Literature survey on various research publications on a small-scale plant designs for biodiesel production.
- For simplicity and shortening of the time for completing this study, previously determined yield of biodiesel at different residence time and temperature was used to determine the rate constant of the transesterification process of Jatropha oil with ethanol
- Applying Matlab, AutoCAD, Catia, and ASPEN software for analysis, two-dimensional drawing, three-dimensional modeling and simulation respectively.

3.2. Kinetics of the Transesterification of JCT

The kinetics of a reaction studies how fast a reaction proceeds. The mechanism proposed for transesterification of Jatropha oil is composed of a series of three consecutive reversible decompositions of triglyceride to diglyceride, diglyceride to monoglyceride, and monoglyceride to glycerol. The kinetics of such reactions is first order with respect to the reacting components' concentration as shown in Equations (3.1) to (3.3) [5].



Where; k_1 , k_3 and k_5 represent rate constants for forward reactions in equation (3.1), (3.2) and (3.3) respectively. Similarly, k_2 , k_4 and k_6 represent rate constants for backward reactions in Equations (3.1), (3.2) and (3.3) respectively. TG = concentration of triglyceride, AL = concentration of alcohol, DG = concentration of diglyceride, EE = concentration of ethyl ester, MG = concentration of monoglyceride, GL = concentration of glycerol. This rate equation has six unknown parameters (four order of the reaction with respect to two reactants and two products each and two rate constants for forward and backward directions). Each step consumes 1 mole of alcohol and produces 1 mole of ester and the overall equation and the

overall reaction, assumed to be a single step (ignoring/ neglecting intermediate steps), was considered to develop kinetic rate equation shown in Equation 3.4 [6].



The kinetics rate for transesterification process using Ethanol as alcohol couldn't be found from literature and become a must to determine the parameters in laboratory or from previous work. In this work, the above overall reversible kinetics mathematical model has been used to fit previously determined experimental values (yield) at different time and temperature to solve the rate equation.

3.3. Determination of rate constant

The rate constant of a reaction can be determined based on the increase in the amount of a product or alternatively based on the decrease in the amount of the limiting reactant. The determination of a rate constant also depends on the order of the reaction. Using experimental data, the correct order can be determined by the rate equation which best fits the linear requirement. Once the order of the reaction is established, the rate constant is estimated from the slope of the linear plot. The order of a reaction can be determined from integrated rate equation. The integrated rate law solutions for zero, first and second order expressions are different functions, but all can be written in the form of a straight line [4]. In many researches, the order of transesterification reaction is determined to be first order reaction. Next the integrated form of rate equation for first order reaction is described.

For the reversible first order reaction $\text{TG} \rightleftharpoons_{k_b}^{k_f} \text{EE}$ the integrated form of the rate equation for a constant volume batch system is given by [25]:

$$-\ln \left\{ \frac{\left(\frac{k_f + 1}{k_b} \right) C_{\text{TG}} - (C_{\text{TGO}} - C_{\text{EE0}})}{\left(\frac{k_f}{k_b} C_{\text{TGO}} + C_{\text{EE0}} \right)} \right\} = (k_f + k_b)t \quad 3.5$$

Where,

- TG in the above equation represents the limiting reactant, Triglyceride in the case of transesterification reaction and EE is the product Ester (Biodiesel).
- k_f and k_b are the forward and backward reaction constants.
- C_{TG} , C_{TGO} , C_{EE0} , and t are Concentration of the triglyceride at time t , initial concentration of Triglyceride, Biodiesel and time reaction

At equilibrium with concentrations of TG and EE as C_{TGe} and C_{EEe} respectively, because $dC_{\text{TG}}/dt=0$ at equilibrium, then $k_1C_{\text{TGe}} = k_2C_{\text{EEe}}$. This implies

$$\frac{k_f}{k_b} = K = \frac{C_{EEe}}{C_{TGe}} \quad 3.6$$

Substituting equation 3.6 in equation 3.5 gives

$$-\ln \left\{ \frac{\left(\frac{C_{EEe}}{C_{TGe}} + 1 \right) C_{TG} - (C_{TGO} - C_{EE0})}{\left(\frac{C_{EEe}}{C_{TGe}} C_{TGO} + C_{EE0} \right)} \right\} = (k_f + k_b)t \quad 3.7$$

This means that if the concentration of TG and EE are determined and inserted in place of C_{TG} and C_{EE} in equation $-\ln \left[\frac{(C_{EEe}/C_{TGe})C_{TG} - (C_{TGO} - C_{EE0})}{((C_{EEe}/C_{TGe})C_{TGO} + C_{EE0})} \right]$ and plotted against time t gives a straight line with the slope $(k_f + k_b)$. From the slope and the equilibrium constant K , k_f and k_b can be determined. Figure 3.1 shows a plot of the reversible first order reaction. However, if the plot had not revealed straight line, it would have been a must to go for the second order integrated rate equation.

Once the rate constant for a group of samples at different temperature is determined, the kinetic parameters (Activation energy and Frequency factor) can be determined from Arrhenius equation as discussed in the next section 3.3

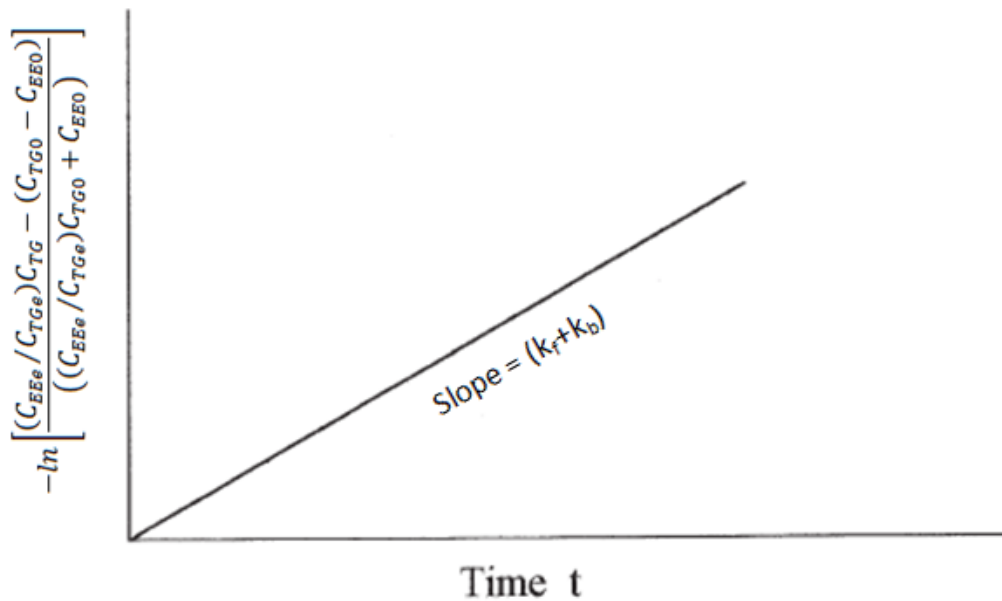


Figure 3-1: Plot of the reversible first order reaction [25]

To determine the rate constant and then the kinetic parameters, measured concentration of TG and EE for groups of experimental data of the reversible transesterification reaction corresponding to a given time points are needed to be known. Therefore, the experimental data can be collected either from carrying out experimental work or to determine it from

previous work. For this paper, the C_{TG} data are to be determined from Ethyl Ester yield graph of previous thesis by Haymanot Baynesagn[15], as shown on figure 3.2. It is a plot of experimentally determined ethyl ester yield against time to study the effect of reaction temperature on ethyl ester yield with catalyst NaOH to oil mass ratio 1.0% and ethanol to oil molar ratio, 9:1

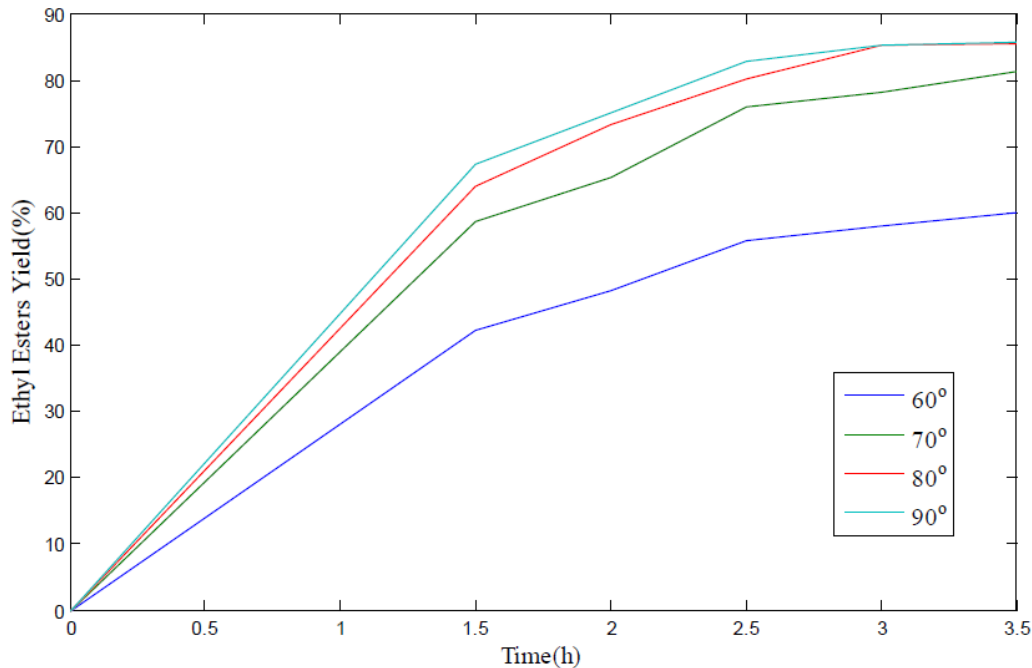


Figure 3-2: Ethyl Ester Yield vs time graph at different temperatures [15]

3.3.1. Determination of TG Concentration

The above Yield (%) vs Time (hr) graph is used to determine the concentration of the Triglyceride (TG). The amount of pretreated or neutralized Jatropha oil sample used when conducting the experimental work of the above graph is $200\text{ml} = 200\text{ml} * 916.2\text{g/ml} = 183.24\text{g} = 183.24\text{g}/885.432\text{g/mol} = 0.20695\text{moles}$ (moles of Triglyceride fed).

Yield of a reaction is defined as the ratio of moles of a certain product to the maximum possible moles of that product which can be formed.

$$\text{Yield} = \frac{\text{Moles of ester produced}}{\text{Stoichiometric moles of ester produced}} * 100 \quad 3.8$$

Or

It is the ratio of moles of a certain product to the moles consumed of the limiting reactant.

$$\text{Yield} = \frac{\text{Moles of ester produced}}{\text{Moles of TG fed} - \text{Moles of TG@t}} * 100 \quad 3.9$$

Or

It is the ratio of moles of a certain product to the moles of the limiting reactant fed.

$$\mathbf{Yield} = \frac{\mathbf{Moles\ of\ ester\ produced}}{\mathbf{Moles\ of\ TG\ fed}} * \mathbf{100} \quad 3.10$$

The maximum possible moles of the product are the stoichiometric moles of the ester which can be determined from equation 3.9.

For the general reversible reaction;



Occurring in the process, the fraction conversion of the limiting reagent is defined as:

$$\mathbf{X}_i = \frac{\mathbf{n}_{i0} - \mathbf{n}_i}{\mathbf{n}_{i0}} \quad 3.12$$

Where X_i ranges from 0 to 1

Then the outlet molar flow rate of the component can be determined by rearranging equation (3.12) to give;

$$\mathbf{n}_i = \mathbf{n}_{i0}(\mathbf{1} - \mathbf{X}_i) \quad 3.13$$

Using stoichiometry, the outlet for other components can be calculated. For the general reaction given in equation 3.11; if the conversion of A, (X_A) is known, then the outlet flow rates of A and other components can be written as [7]:

$$\mathbf{n}_A = \mathbf{n}_{A0}(\mathbf{1} - \mathbf{X}_A) \quad 3.14$$

$$\mathbf{n}_B = \mathbf{n}_{B0} - \frac{\beta}{\alpha} \mathbf{X}_A \mathbf{n}_{A0} \quad 3.15$$

$$\mathbf{n}_C = \mathbf{n}_{C0} + \frac{\gamma}{\alpha} \mathbf{X}_A \mathbf{n}_{A0} \quad 3.16$$

$$\mathbf{n}_D = \mathbf{n}_{D0} + \frac{\delta}{\alpha} \mathbf{X}_A \mathbf{n}_{A0} \quad 3.17$$

Then,

Let

- A be the triglyceride (TG, purified oil), B be the alcohol (Ethanol E_{TH}), C be the Ethyl ester (EE, Biodiesel) and D be the Glycerol; so that
- n_{A0} is the molar flow rate of the Triglyceride entering the reaction. For stoichiometry, the initial mole of Triglyceride or moles fed = 0.20695mole and n_A is the Triglyceride leaving the reaction after the process (unreacted oil)
- n_{B0} is the molar flow rate of the Ethanol entering the reaction and n_B is the Ethanol at each percentage conversion of the Triglyceride and leaving the reaction after the process (Excess Ethanol) completed

- n_{c0} is the molar flow rate of the Ethyl Ester entering the reaction ($=0$) and n_c is the Ethyl ester (Biodiesel) produced at each percentage conversion of the Triglyceride in the reaction process and final product (Biodiesel) leaving the reaction after the process completion
- n_{D0} is the molar flow rate of the Glycerol entering the reaction ($=0$) and n_D is the Glycerol produced at each percentage conversion of the Triglyceride and final Glycerol leaving the reaction after the process completion
- α, β, γ and δ are stoichiometric coefficients of the Triglyceride, Ethanol, Ester and Glycerol respectively

For stoichiometric reaction, the value of α and γ is 1 and 3 respectively so that $\gamma/\alpha=3$ and the fractional conversion of Triglyceride (X_A) is 100%. Thus, the stoichiometric moles of the product (Ester), which is the maximum, possible Ester that can be produced is determined from equation 3.16. That is $n_c = 0 + 3/1 * 1 * 0.20695 = 0.6209$ moles

Once the maximum possible produced amount of ester, and the yield at every time points from the graph in figure 9 are known, the actual amount of moles of the ester at every time point are calculated using equation 3.8

For better tracing of the percentage yield at each time points and temperatures from figure 8, the graph was redrawn with AutoCAD 2012 as in figure 9 adding minor grid lines between each given percentage. Following the actual amount of moles of the ester at every time point is calculated, the fractional conversion of Triglyceride at each time point also is calculated using equation 3.9. Then the other components (n_A, n_B and n_D) at each time point are also calculated for all the temperatures using equations 3.14, 3.15 and 3.17 respectively. Apart from mole calculation, moles per unit volume (Concentration) of each component C_{TG}, C_{ETH}, C_{EE} , and C_{GL} at every time point are also calculated. The determined data (moles and concentrations) of transesterification components and the corresponding plot of first order reaction for the temperatures ($60^\circ\text{C}, 70^\circ\text{C}, 80^\circ\text{C}$ and 90°C) are presented in appendix A1. Figure 3.4 shows the graph of the concentration in moles per liter of the reacting components against resident time determined and plotted using Matlab software.

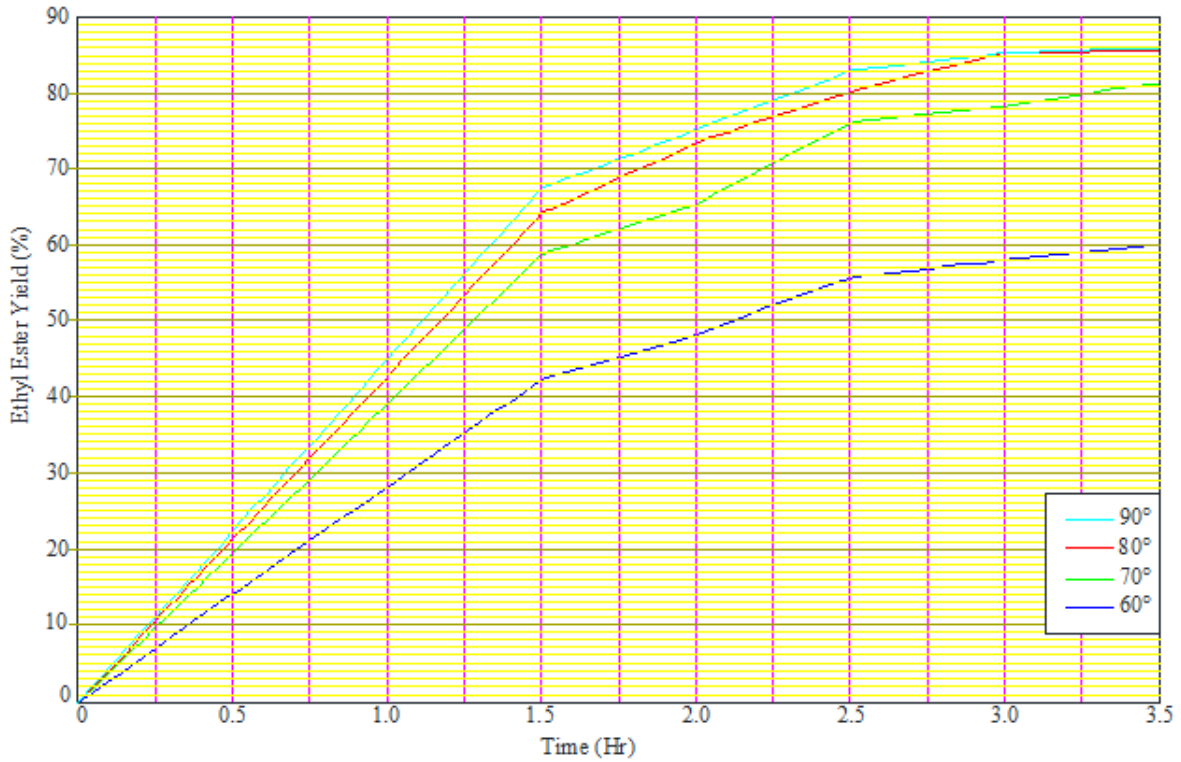


Figure 3-3: Ethyl Ester Yield vs Time graph with added gridlines

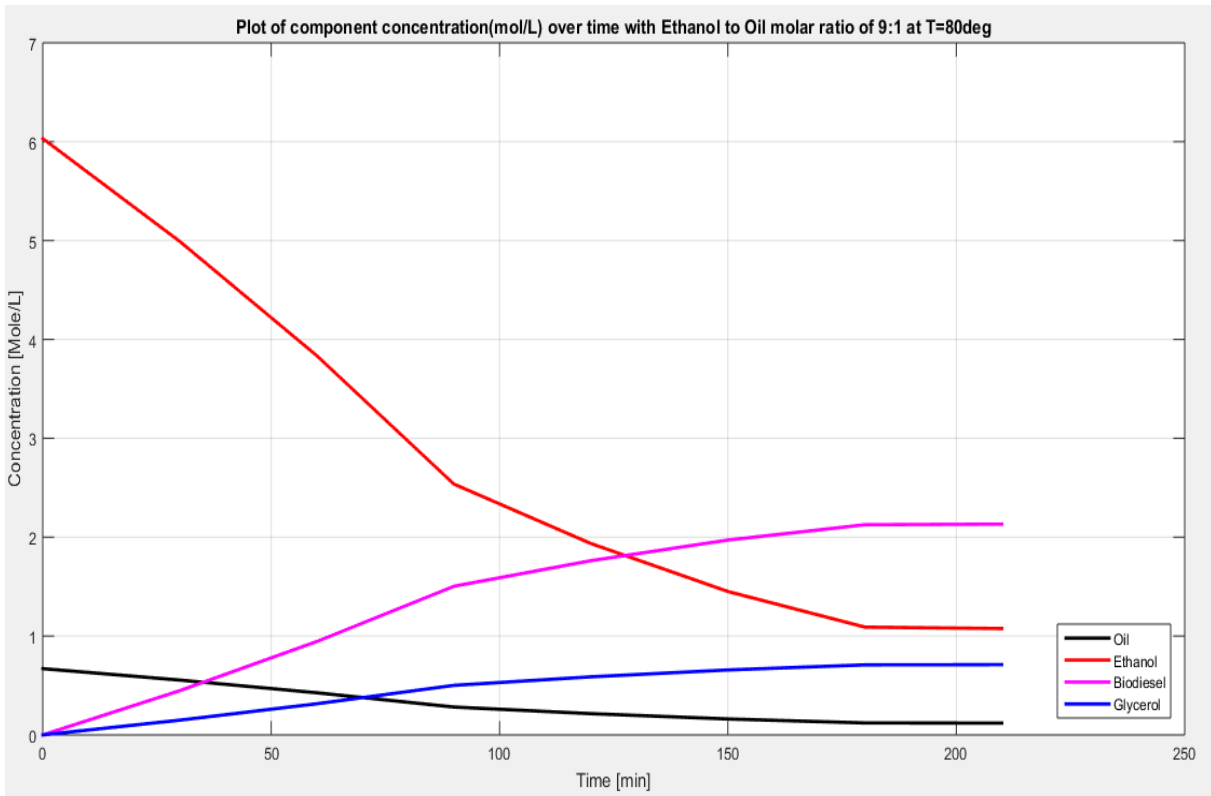


Figure 3-4: Reaction component concentration verses Time graph

3.3.2. Activation Energy and Frequency Factor

It has been reported that the rate constant for any reaction depends on two factors, namely the frequency of collisions between the reactant molecules and the value of the activation energy.

Kinetic obtained from laboratory unit are usually played an important role in modeling and scale up designs for new biodiesel production units [3]. Various researchers conducted laboratory study to estimate the rate constant of a reaction and estimated various result for the rate constant K, Activation Energy Ea and the Arrhenius constant A.

- *Robiah Yunus a & Azhari Muhammad Syam* [5], have estimated the activation energies for the transesterification of TG with methanol as an alcohol to be 27.38 kJ/mol. The molar ratio of methanol to JCT and the amount of catalyst fixed were at 6:1 and 1.0% w/w, respectively.
- The Activation energy for *Jatropha curcas* oil with stirring rate of 750rpm, molar ration 6:1 and 0.5% catalyst estimated by *Pankaj Tiwari, Rajeev Kumar and Sanjeev Garg* [6] was 4.808 Kcal /mol = 20.12kJ/mol and with stirring rate of 300rpm is 10.792 kcal /mol = 45.15 kJ/mol.
- *T.Thananchayan* [2] on his study for *Jatropha* oil the Experimental and Kinetic results obtained are plotted on excel sheet and the Arrhenius parameters; Activation energy and Frequency factor are evaluated using Arrhenius equation as 14.930kJ/mol and 20.359/sec respectively
- The study by *Mu'azu K.I, Mohammed ...*[5], the kinetic of the reaction for *Jatropha curcas* Seed Oil Using Heterogeneous Catalyst with Methanol to Oil ration 10:1 revealed first order (n=1) having Activation energy and frequency factor of 14.80kJ/mol and 20.697 respectively

The dependency of the rate constant, K, on temperature follows the Arrhenius equation [4]:

$$\mathbf{K} = \mathbf{A}e^{\frac{-E_a}{RT}} \quad 3.18$$

Where:

- **K** is the rate constant defined as the change in the molar mass of the reactant with respect to time
- **A** is a frequency factor describes the number of potential elementary reactions per unit time
- **Ea** is the activation energy that describes the energy barrier that must be exceeded in order for a reaction to occur
- **R** is the universal constant (8.314J/mol.k)
- **T** is the reaction temperature (°K)

Activation Energy (E_a) is the minimum energy required so that a collision leads to breaking bonds and to obtain products

Frequency factor or pre-exponential factor or stearic factor (A) is embedment of rate at which molecules come into contact and the orientation of the molecule in space at the moment of collision

The dependence of K on T is more clearly seen when we linearize the equation by taking the natural logarithm on both sides; we get:

$$\ln K = \frac{E_a}{RT} + \ln A \quad \text{or} \quad \ln K = \frac{-E_a}{R} \left(\frac{1}{T} \right) + \ln A \quad 3.19$$

Which looks like $y=mx+b$; where: $y=\ln k$; $m= -E_a/R$ and $x=1/T$; $b= \ln A$. That is when plotting experimentally determined reaction rate constants as a function of temperature (i.e., $\ln K$ against $1/T$), a straight line is obtained of with $\frac{-E_a}{R}$ equal to the slope and the intercept $\ln A$. Equation 3.19 indicates that for high activation energy, reaction rate is highly sensitive to temperature and for small activation energy; reaction rate is less sensitive to temperature [25].

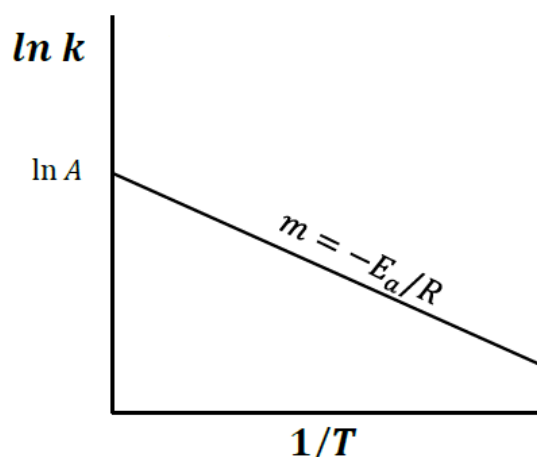


Figure 3-5: Reaction rate temperature dependence [25]

Table 3.1 shows the rate factors determined for forward and backward reaction at specified temperatures to determine the Activation energy and the frequency factor.

Table 3-1: Forward and backward reaction rate constants at different temperatures

T		x=(1/T)	K_f	K_b	y= (lnk_f)	y= (lnk_b)
°C	°K					
60	333.15	0.00300	0.004831	0.00117	-5.3326	-6.7536
70	343.15	0.00291	0.008413	0.00078	-4.7780	-7.1599
80	353.15	0.00283	0.010116	0.00058	-4.5936	-7.4570
90	363.15	0.00275	0.010573	0.00061	-4.5495	-7.4063

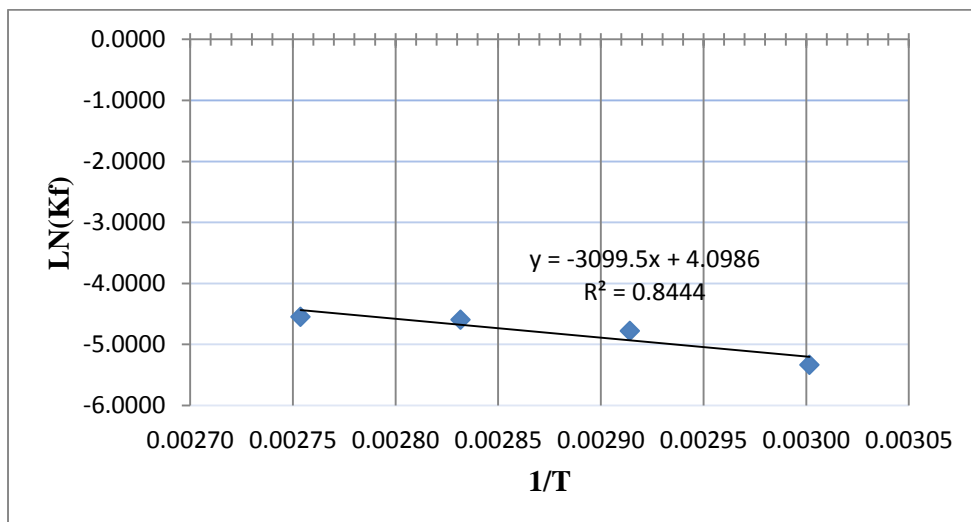


Figure 3-6: Plot of LN (K_f , forward rate constant) against $1/T$ for experimental data

From the graph, the activation energy for the forward reaction is $E_a = -m \cdot R = -(-3099.5) \cdot 8.314 \text{ J/mol} = 25769.2 \text{ J/mol} = 25.769 \text{ KJ/mol}$ and Frequency factor $A = \text{invLN}(4.0985) = 60.26/\text{min}$.

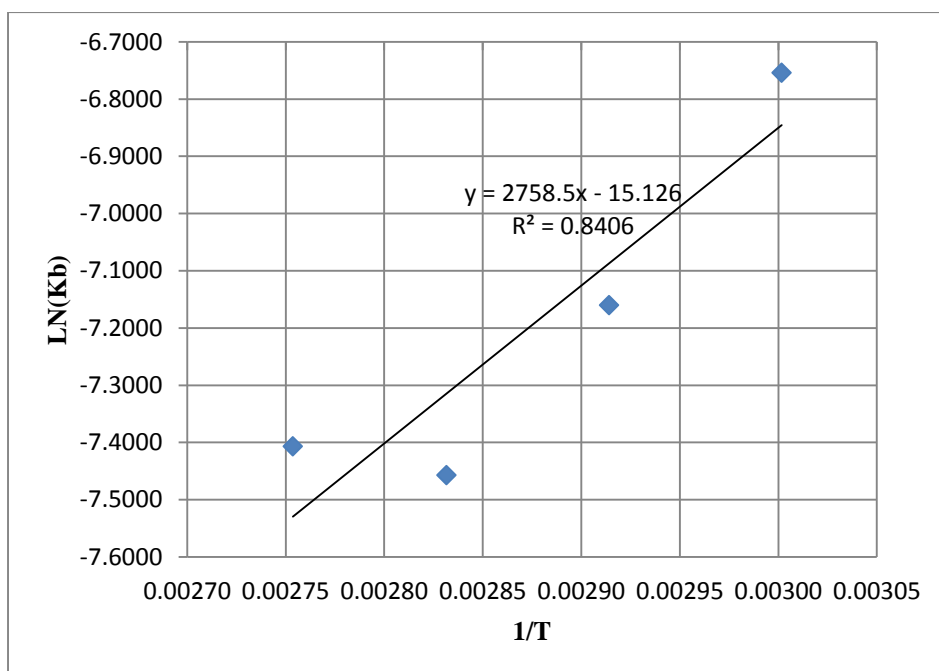


Figure 3-7: Plot of LN (K_b , reverse rate constant) against $1/T$ for experimental data

The reverse activation energy is $E_a = m \cdot R = 2758.5 \cdot 8.314 \text{ J/mol} = 22934 \text{ J/mol} = 22.934 \text{ KJ/mol}$. And the frequency factor in this case is calculated using the formula in equation 3.19. Taking one of the temperature $T = 60^\circ\text{C} = 333.15^\circ\text{K}$, the frequency factor is $A = 4.69/\text{min}$

4 Modeling and Simulation

Modeling exists for various fields to help engineers visualize object, system design and or formulation. In chemical reaction engineering, modeling helps virtually to understand the chemistry, optimal size, and design of the system, and how it interacts with other physics that may come in play. 3-Dimensional (3D) Modeling is a technique in computer graphics for producing a 3D digital representation of any object or surface. It is used in a wide range of fields including engineering architects and entertainment. The art of translating problems from an application area in to traceable mathematical formulation where it's theoretical and numerical analysis provides insight, answers, and guidance useful for the originating application is termed Mathematical Modeling.

These models are used in this paper as found to be appropriate for the determination of important parameters for the simulation work intended and demonstration and description of the system process in this study. The 3D modeling of the Biodiesel synthesis plant is presented in section 4.1 so as to visualize the process flow and various lists of equipment involved in the system. In section 4.2, the Transesterification reaction process model is discussed in detail appropriate to the simulation work. The flow sheet diagram, basic step of the simulation work of the process modeled using Aspen software is also shown in section 4.9.1 and 4.9.2

4.1. Conceptual Design

The three-dimensional representation of the transesterification plant equipment layout modeled using CATIA software is shown in figure 4-1 below. The process for this small-scale plant is made to start with storage tanks for the raw oil (Jatropha oil) (A1) and ethanol (A5). The raw oil is drawn by gravity to caustic pretreatment tank (A2) followed by washing and drying tanks (A3) from which the neutralized oil is pumped to purified oil storage tank (A4). Ethanol is directed to flow by gravity to ethanol-catalyst mixing tank (A6) where the two components are thoroughly mixed. The purified oil and ethanol mixed with catalyst are pumped to the reactor transesterification tank (B), where the mixture is heated up to 80°C and continuously stirred for about 3&1/2 hours. After the transesterification reaction process is completed, it is pumped to washing and settling tank (C) at which the produced raw oil is allowed to settle for glycerol separation and after separation, it is washed by hot distilled water. The separated biodiesel is then pumped to drying tank (D) where it is heated up to 110°C to vaporize any remaining ethanol residue. Finally, the purified biodiesel is pumped to

its storage tank E where it is stored and made ready for use. The detailed processes descriptions of this plant at all equipment are presented in table 4.1.

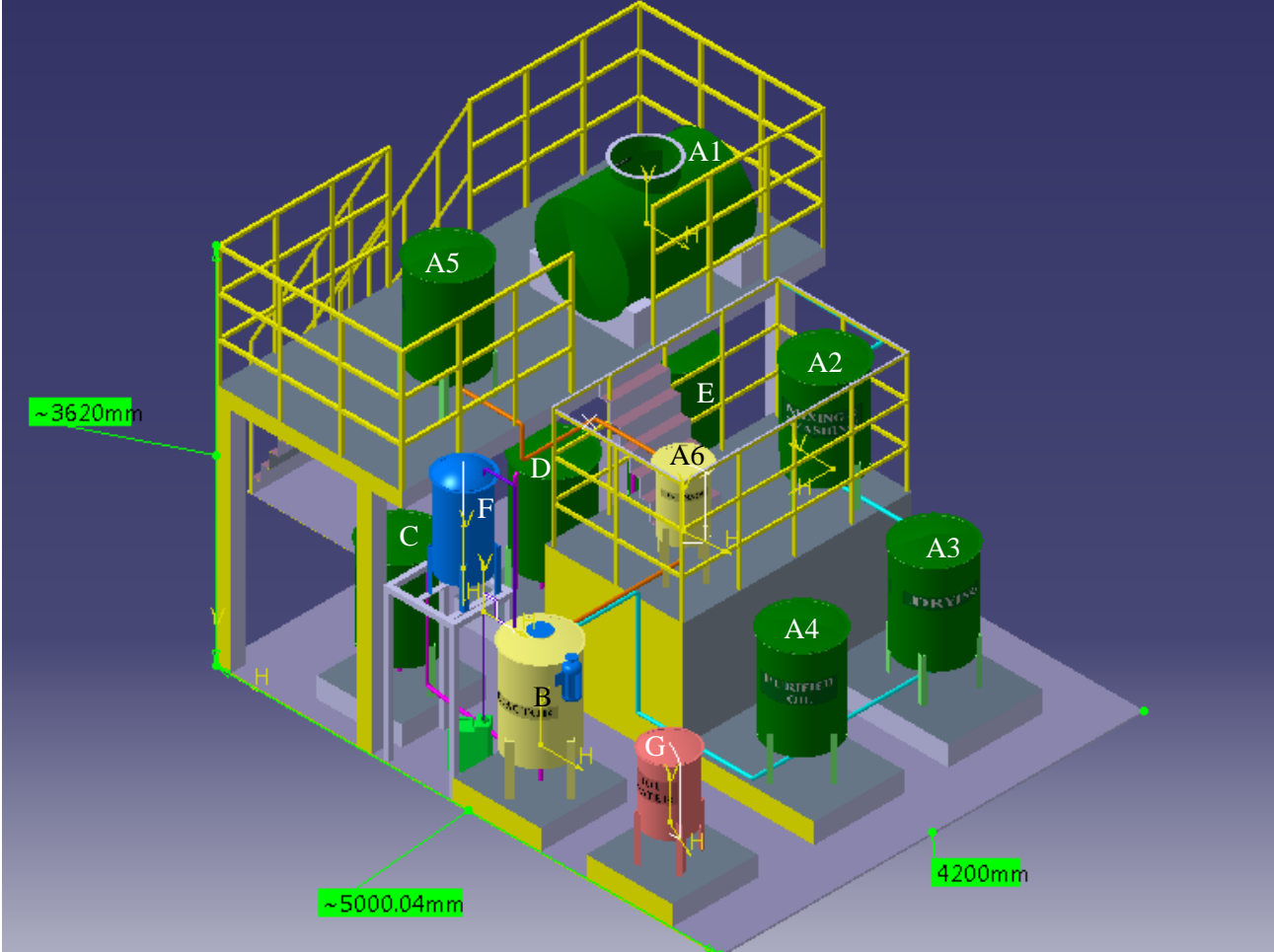


Figure 4-1: Three-dimensional view of the small-scale Biodiesel plant

Process activity and time frame of the Transesterification

Once the pretreatment /purification process is completed the purified Jatropha oil will be ready to undergo further process that is called the transesterification process to yield the intended product ‘Biodiesel’. The transesterification process activities that take place and the required time for each are presented in the table 4.1 and activities time summary in table 4.2.

Table 4-1: Biodiesel production process activities as determined on the design phase by the designer

Task	Activities	Tank Specification	Tank ID	Volume of liquid (Lit)	Time taken (Min)	Pumping to	Total pumping time (Min)	Total time of batch process (Min)
Raw oil preheating	Preheating, to decrease the viscosity of the oil for ease of pumping	Raw Oil storage tank	A1	2005	60	Neutralization tank (A2)	10	70
Caustic Pretreatment (Storage)	Step-1: The crude oil will be pre heated up to 65°C and the mixture of sulphuric acid and ethanol is added to pre heated Jatropa oil and thereafter, stirred continuously maintaining a steady temperature of 65°C for 1 hour.	Neutralization tank	A2	418	60	Washing and Drying tank (A3)	20	60
	Step 2: The reaction product will be kept in Tank and left for 4 hr to separate into two phases: a top phase (the oily phase, consisting of oil) and a bottom phase (the waste phase or black phase, consisting of water, un-reacted ethanol, sulfuric acid and gummy material). The bottom phase will be drained out while the top oil phase will be pumped to washing and drying tank which the draining and pumping to drying tank may take up to 20 min				240			280
Washing (Oil) and Drying	(Washing oil): After cooling the oil will be centrifuged to separate the formed soaps and washed with the half amount of distilled water (w: w) for three times Drying: This will be dried to 100C for 0.5h by using drier	Washing and Drying tank	A3	418 351	30	Purified oil storage tank (A4)	10	40

Task	Activities	Tank Specification	Tank ID	Volume of liquid (Lit)	Time taken (Min)	Pumping to	Total pumping time(Min)	Total time of batch process (Min)
Purified Oil Storage Tank	After the oil is washed and dried, it will be stored in a tank where it will be ready to be pumped to the transesterification/reactor tank	Purified oil storage tank	A4			Reactor tank (B)		
Alcohol Storage Tank	This is a tank where a received alcohol (Ethanol/Methanol) is stored and from where it will be pumped to the mixing tank with catalyst	Mixing Tank	A5			Mixing Tank (A6)		
Mixing Ethanol and catalyst	Ethanol and Sodium hydroxides are mixed together till the system homogenizes	Ethanol and Catalyst mixing tank	A6	91	10	Reactor tank (B)	10	20
Preparation for transesterification process	The reactor will be heated to 75°C prior to transesterification process to avoid any moisture present in the reactor tank for 10 min,	Reactor tank	B	91.+167 =258	10			10
Transesterification process	When the reactor reached the temperature (80°C) established for the reaction, the ethanol - catalyst mixture and the purified oil will be added in the amounts established for each batch process and the stirring started. The mixture will be stirred and refluxed for 180min.				180	Settling and washing tank	10	190
Excess Ethanol recovery	After the ethanolysis reaction is completed, the excess ethanol will be distilled off under vacuum or any distillation mechanism. In this particular case, the reactor will be heated up to 110°C to vaporize the excesses ethanol leading it to a reflux condenser where it will be condensed and recollected for reuse.				30			30

Task	Activities	Tank Specification	Tank ID	Volume of liquid (Lit)	Time taken (Min)	Pumping to	Total pumping time (Min)	Total time of batch process (Min)
Settling and Washing of Raw Biodiesel	The trans esterified product will then be allowed to settle for glycerol separation. This will take 1 hour for glycerol to separate from ester. Then after separation of the layers of ester layer and glycerol layer, the crude ester will be washed several times (up to 10 times) with hot distilled water (50C) until a neutral PH is achieved	Settling and washing tank	C	337	120	Drying tank	10	130
Drying of Pure Biodiesel	The pure biodiesel will then be dried by 110°C for 30-60 min	Drying Tank	D	183	60	Biodiesel storage tank	10	70
Total Time (Min) starting from reactor preparation to drying of pure biodiesel								450

Table 4-2: Summary of process activities time starting from ethanol catalyst mixing and reactor preparation to drying of pure biodiesel

Activities	Time taken for individual tasks in the batch process																								Total time (Hrs)																					
	20		230										130						70																											
Time (min)	20	20	20	20	20	20	20	20	20	20	20	30	20	20	20	20	20	20	10	20	20	20	10																							
Mixing Ethanol and catalyst																									0.33																					
Transesterification process																									3.83																					
Settling and Washing of Raw Biodiesel																									2.17																					
Drying of Pure Biodiesel																									1.17																					
Grand total time taken to produce 150 Lit of Biodiesel																																														7.50

The purpose of simulation in general is to determine the optimal parameter that can contribute to the best performance of a process. It involves the decomposition of the process into its constituent units for individual study of performance. The process characteristics (flow rates, compositions, temperatures, pressures, properties, equipment sizes, etc.) are predicted using several analysis techniques. These techniques include mathematical models, empirical correlations and computer-aided process simulation tools (such as ASPEN Plus software). In addition, process analysis may involve the use of experimental means to predict and validate performance. Therefore, in process simulation, the process inputs and flow sheet are required to predict process outputs.

4.2. ASPEN plus Software

ASPEN stands for “**Advanced System for Process Engineering**”. It is based on a flowsheet simulation. A flowsheet simulation is computer software that is used to quantitatively model a chemical processing plant, which, in addition to the core reactor unit, also includes pre and post-treatment steps. Thus, simulation of an entire chemical process, starting from the raw material to the final finished product, is symbolically represented by different icons where each icon stands for a unit operation, chemical process, input/output material stream, input/output energy stream, or input/output electric/pneumatic signal. In latest version Aspen was replaced by Aspen Plus. Aspen Plus is a computer-aided software a very powerful tool that can be used to tackle different chemical process and unit operation calculation-based tasks, in the form of modeling, simulation, optimization, data regression, design specifications, sensitivity analysis, solids handling, dynamics and control, energy saving, safety compliance, and finally process economic analysis.

Since to conduct a trial plant is very costly and many tests needed to predict the optimal condition for maximizing the yield of biodiesel, ASPEN Plus will become a beneficial tool to determine the parameter that can affect the biodiesel production.

The process flow sheets are constructed by selecting and connecting proper unit operations such as mixing tanks, reactors, distillation columns, heat exchangers, pumps, etc. Then, conditions for each unit operation such as temperature, pressure, flow rates and composition of the input and output streams in each stream are specified. The major steps involved in simulation using ASPEN PLUS software are:

Major Steps

- Drawing the graphical simulation process flow sheet
- Specifying the components involved in the process
- Selection of a thermodynamic model
- Specifying the operating condition (flow rate, temperature, pressure, composition etc.)

Input data of reactants

Process input data of the biodiesel production of Jatropha oil ethyl esters by transesterification of crude Jatropha oil (CJO) with ethanol using alkaline catalysts in a batch reactor considered under the study are:

- Catalyst: sodium hydroxide (NaOH)
- Catalyst consideration: Kg of oil
- Reaction temperature: 80°C
- Ratio of oil to ethanol: 1:9
- Intended biodiesel output amount: 150Lit

The above parameters are considered because they are the conditions at which the optimal biodiesel yield was obtained per the experiment done by Haymanot and the small scale biodiesel plant also was based on these parameters.

4.3. Transesterification Reaction modeling

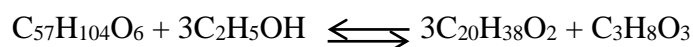
Although ASPEN Plus is equipped with a large database of known compounds with various thermodynamic data, the compounds that make up a large portion of the triglycerides found in the oils used as feedstock for biodiesel production are not present. Thermodynamic properties for those compounds can be estimated by one of three ways [12].

- One method is to choose compounds that exist in the database that have comparable molecular weights. The large assumption is that for compounds sharing similar molecular weights, their thermodynamic properties will be comparative.
- A second possibility is to manually enter in the thermodynamic properties using a user defined method, if the thermodynamic properties for the unlisted compounds happen to be available. However, the availability of unlisted thermodynamic properties is not always an option.
- A preferable way to estimate thermodynamic properties is to draw the molecular structures using the ISIS draw patch to ASPEN Plus. An ISIS/Draw is a chemical structure drawing program for Windows, published by MDL Information Systems

(Wikipedia, 2019). The ISIS draw program will import the molecular structure into a user defined method and will estimate thermodynamic properties by using ASPEN's UNIFAC group contribution factor evaluation system. While ISIS is limited in the types of molecular configurations a compound can have, it can still provide a fairly decent prediction of an unlisted compounds thermodynamic properties.

With the use of the first method i.e choosing compounds that exist in the database that have comparable molecular weight; the Triglyceride for Biodiesel production from Jatropha Oil is represented by Triolein in process analysis and simulation. Triolein is a symmetrical triglyceride derived from glycerol and three units of the unsaturated fatty acid oleic acid (Wikipedia, 2019) the major constituent of Jatropha oil. The molecular formula of Triolein is $C_{57}H_{104}O_6$ and that of the Biodiesel (Ethyl ester) produced is $C_{20}H_{38}O_2$.

Therefore, the chemical reaction diagram shown on figure 2.2 and 2.3 of the Transesterification process can be expressed using the balanced molecular formula of the components as;



The reaction components for the transesterification reaction presented in the chemical formula above are as presented in table 4.3

Table 4-3: Reactions Components used in the model for the simulation

ID	Type	Name	Formula
ETHANOL	Conventional	ETHANOL	$3C_2H_5OH$
OIL	Conventional	TRIOLEIN	$C_{57}H_{104}O_6$
FAEE	Conventional	Ethyl ESTER	$C_{20}H_{38}O_2$
GLYCEROL	Conventional	GLYCEROL	$C_3H_8O_3$
SODIUM HYDROXIDE	Conventional	SODIUM HYDROXIDE	NAOH

FAEE, Ethyl-Oleate is the biodiesel product, with glycerol as a by-product. Sodium hydroxide is used as the catalyst

4.4. Thermodynamic Models in Aspen

All unit operation models need property calculations to generate results. A few different physical property packages were used to develop the biodiesel simulation. These physical property packages allow ASPEN Plus to calculate ideal and non-ideal Vapor-Liquid Equilibria, estimate thermodynamic properties of components, calculate precise predictions for component

separations, and provide close approximations for energy requirements for the various unit operations employed in the simulation.

For chemical process, Aspen Plus property method selection assistance in general suggests selection of an activity coefficient-based property method is appropriate, such as the NRTL, WILSON, UNIQUAC, and their variances. For preliminary designs, one of the UNIFAC-based property methods: the original UNIFAC, or the Dortmund modified UNIFAC (UNIF-DMD) can be used and for process at high pressures (>10 bars), an equation of state method with advanced mixing rules, such as the Wong-Sandler, MHV1, MHV2 or Mathias-Klotz-Prausnitz mixing rules are used. Options include SR-POLAR, PRWS, RKSWS, PRMVH2, RKSMVH2, SRK, PSRK, and HYSGLYCO.

In present studies, the simulation was carried out by using equilibrium stage model and NRTL model was used to model the reactor. In this model the property method used is NRTL (Non-Random Two Liquid) which would probably give more accurate results, though requires estimation of NRTL binary interaction parameters.

There was Lack of information on Triolein (oil). Therefore, all the information was estimated by using Aspen Plus estimation parameter and UNIQUAC thermodynamic property method was used to estimate all the missing parameters.

4.5. Physical and Chemical properties

The Important physical and chemical properties of the component involved in the Transesterification reaction for the analysis carried out in this paper are described in table 4.4.

Table 4-4: Physical and chemical properties of the components in the Transesterification process

Properties	Component				
	Triolein Liquid	Ethanol		Ethyl ester Liquid	Glycerol Liquid
		Liquid	Vapor		
Use in the process	Raw material, main reactant	Reactant		Main product	Secondary product
Molecular Formula	C ₅₇ H ₁₀₄ O ₆	C ₂ H ₅ OH		C ₂₀ H ₃₈ O ₂	C ₃ H ₈ O ₃
Molar Mass (g/mol)	885.432	46.09		310.54	92.09
Boiling Point (°C)	554.2	78.29		367.85	287.85
Density(kg/m ³)	950	789	1.624	860	1260
Heat Capacity (KJ/Kg °k)	1.67		1.600	2.09	2.43

4.6. Material Balance Calculation of the Reaction

When studying chemical reactions, we need to determine what the reactants are and what products are needed, what amount of the reactants is required to produce a desired amount of products, to what extent will the reaction proceed, and how fast it will proceed.

From the design parameters of the biodiesel plant in this study, the Ester (biodiesel) yield of the Transesterification is 150lit per batch process. This amount in mass and mole can be expressed as; $150\text{Lit} = 150\text{Lit} \times 860\text{g/Lit} = 129,000\text{g} = 129\text{kg} = 129,000\text{g}/310\text{g/mole} = 415.4322\text{mole}$

Similar method to the above is used to determine the amount of other components in units of Litter, Mole and gram.

To determine the stoichiometric amount of Triglyceride and ethanol required to deliver the intended amount of the ester and other product Glycerol, the equations defined in equation 3.4 to 3.10 in section 3.1 for the general reversible reaction are reconsidered.

The value of the X_i (fractional conversion of Triglyceride) in equation 3.5 to 3.10 for stoichiometric reaction is 1. These equations determine the amount of reactants and obtained final output results. For the easiness of the calculation, the equations are rewritten in Matlab software M-script file. Two cases are considered; the first is for a stoichiometric reaction where X_i is 1 and no addition of excess ethanol. The second is with addition of excess ethanol with Ethanol to Oil molar ration of 9:1 and 80% conversion of Triglyceride that is $X_i = 0.80$. The Matlab programs for both cases are annexed in Appendix-. The result of the mass balance for the stoichiometric reaction and estimated conversion is presented in table 4.5 and 4.6 respectively.

Table 4-5: The stoichiometric quantity to produce biodiesel

Parameters =						
	PurifiedOil	Ethanol	Ester	Glycerol	UnreactedOil	ExcessEtanol
Amount in Moles	138.48	415.43	415.43	138.48	0	0
Mass in Kg	122.61	19.147	129	12.752	0	0
Design Volume in Lt	133.83	24.268	150	10.121	0	0

MassBalance =		
	Rightside	Leftside
MassBalance	141.76	141.75

The calculation is repeated for Mass balance with 20 % inefficiency during conversion the reaction and with addition of excess ethanol with Ethanol to Oil ratio of 9:1. That means the conversion of the purified oil (Triglyceride) to Ester (Biodiesel) is assumed to be 80%

Table 4-6: Material and Mass balance for 80% conversion efficiency; Ethanol to Oil molar ratio 9:1

Parameters =						
	PurifiedOil	Ethanol	Ester	Glycerol	UnreactedOil	ExcessEthanol
Amount in Moles	173.1	1557.9	415.43	138.48	34.619	1142.4
Mass in Kg	153.27	71.802	129	12.752	30.653	52.655
Design Volume in Lt	167.28	91.004	150	10.121	33.457	66.736

MassBalance =		
	Rightside	Leftside
MassBalance	225.07	225.06

4.7. Reactor Modeling in Aspen Plus

There are seven blocks for reaction modeling in Aspen that can perform calculations based on the stoichiometry, yield, equilibrium, and Gibbs minimization, plus the kinetics models for CSTR and PFR. In addition, a batch model is available for batch reactors.

RStoic; described as Stoichiometric reactor: When the reaction stoichiometry is known but information on kinetics is not available (or not important). The block must have one or more feed streams, one required output stream. Optional connections are the water decant and input and output heat streams.

RYield; described as Yield reactor: The second block in the Reactors library, RYield, performs the calculations based on the yield. The block takes similar streams as that for the RStoic block. This block does not require exact information about the stoichiometry or kinetics. Similar input to that of RStoic is needed here for the exit stream. The output of the reaction is defined based on the yield in the Setup. The yield is defined as mole or mass of each component per total mass input to the block. Inert components can be defined in the same form and will not be included in the yield calculations. No heat of reaction can be calculated here because the stoichiometry of the reaction is not known.

REquil; described as Equilibrium reactor: When one or more reactions involved are equilibrium reaction, the REquil block can be used.

The block requires knowledge of the reaction stoichiometry and performs chemical and phase equilibrium reactions. Unlike the previous blocks, the REquil block has a vapor and liquid phase product streams (both are required). The only required information for this block is the output stream and the reaction. With this input, all the required calculations are made based on thermodynamics calculations

RGibbs; Equilibrium reactor with Gibbs energy minimization: The fourth block provides reaction calculations without the need for detailed stoichiometry or yield. The calculations are based on minimizing the Gibbs energy for the system. The block takes one or more input and one or more output streams, and an optional heat input and/or output stream. The input form requires two variable specifications. The block can be used to calculate phase and/or chemical equilibrium and allows constraining the equilibrium value with specific heat duty and/or temperature approach in the Setup | Specifications form. If restricted equilibrium is selected, reactions can be defined for the system. The block also allows specifying the number of phases, which components present in each phase, and how to distribute the phase on the outlet streams (when multiple output streams are used) in the Setup | Products and Setup | Assign Streams forms. Inert components can be defined in the Setup | Inerts form.

RCSTR and RPlug; described as Continuous stirred tank reactor and Plug flow reactor respectively

When rigorous simulation of reactors is needed, the RCSTR and RPlug are used. These two blocks perform simulation of ideal reactors operated under specific conditions. For the CSTR, two design variables are needed (pressure and temperature or heat duty), specification of the valid phases, and a reactor specification. For the plug reactor, a specification is needed for the type of the reactor (specific temperature, adiabatic, or cooled). Depending on the type choice, the required specification will vary: temperature or temperature profile, no specifications are needed, or heat transfer coefficient. The configuration for the reactor is input in the Setup /Configuration form which includes the reactor geometry. The pressure drop can be specified in the Setup Pressure form. Unlike the previous blocks, detailed information on the reaction and its kinetics

must be input for these blocks. The reactions are defined in the Reactions folder. Two types of reactions present: chemistry (used for ions forming systems) and reactions (for reactions in general).

RBatch; described as Batch reactor: One, two, or three-phase batch and semi-batch reactors with rate-controlled reactions in any phase based on known stoichiometry and kinetics. *RBatch Models* batch or semi-batch reactor: Aspen Plus provides these several libraries to model the reactor. The selection of the model depends on the amount of information available and the type of simulation. In this study the reactor models selected to be used are *RStoic* with assumption on the conversion amount of the oil to biodiesel and *RBatch* with known values of reaction kinetic properties determined for the process and obtained from certain similar studies.

4.8. Aspen plus Unit Operation Blocks Used in the Biodiesel Plant Model

For the batch biodiesel (ethyl ester) production, two types of reactor models are used out of the seven blocks for reaction modeling available in Aspen data bank by analogy of behavior with the ideal stirred batch reactor with constant density. Two tanks; one for raw *Jatropha* oil and the other for ethanol and sodium hydroxide are installed at the reactor inlet to provide the reactants streams with the prefixed molar relation followed by two pumps; one for pumping the oil and the other for pumping ethanol-catalyst mixture to the reactor. Lines that connect one-unit block to the other are termed as streams. Streams represent the material and energy flows in and out of the process. Streams can be of three types: Material, Heat, and Work. Feeds to the biodiesel model are oil, ethanol, sodium hydroxide, water and acid.

Table 4-7: Unit Operation Blocks for the Transesterification process modeling

Unit Operation	ASPEN-PLUS "Block"	Comments / Specifications
Raw oil storage Tank	Mixer	
Ethanol-Catalyst mixing Tank	Mixer	
Pumps	Pump	
Transesterification	<i>RStoic</i> /	Simplified simulation with stoichiometric reactions
Transesterification	<i>RBatch</i>	Simulation with Known stoichiometric & reaction

4.9. Modeling of the Transesterification plant

As stated in section 4.5, from the several reactor models Aspen provides, the models used in this study are the *RStoic* and *RBatch*.

4.9.1. Modeling Using RStoic reactor model

For using this model, the reaction stoichiometry must be known and the percentage conversion of the limiting reactant (Triolein) shall be known or assumed. In this case, similar assumption is considered as in section 4.4. That is the reaction is 20% inefficient.

For convenience; input to the reactor model for the simulation in ASPEN software, the amount of the reactants was presented based on molar flow rate. Hence, the molar flow rate of the reactants for the set amount of yield (150lit) per unit time for the batch process is presented in table 4.8.

Table 4-8: Reacting component amounts for Ethanol to Oil molar ratio 9:1

Reactants	Volume	Mass	Mole	Molar flow rate	
	Liters	Kg	Mole	Mol/hr	Kmol/hr
Purified oil ($C_{57}H_{104}O_6$)	167.28	153.27	173.1	173.1	0.1731
Ethanol ($3C_2H_5OH$)	91.004	71.802	1557.9	1557.9	1.5579
Catalyst (NAOH)		1.533	38.326	38.326	0.0383

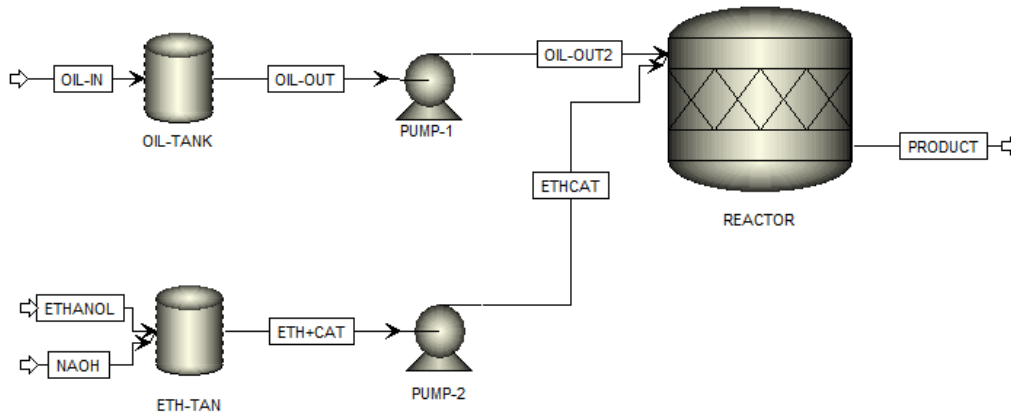


Figure 4-2: Biodiesel Flowsheet diagram for RStoic Reactor model in Aspen Plus

Simulation Results

As seen from figure 4.3 of next page; under the product column the value of CETYL-01(Ethyl ester) is 0.415kmol/hr = 415mol/hr. Multiplying this value by a unit time and molecular weight of Ethyl ester (310.54 g/mol) gives 128,874g=128.874kg (result obtained by Matlab for the stoichiometry and assumed percentage inefficiency analysis). This indicates that Aspen simulation with modeling using RStoic reactor model delivers pre-assumed conversion efficiency. Practically, the final reaction value shall not be a value that can be obtained by assumption rather; Aspen consists of other type of reactor model where the final reaction output is nearly the actual value with the use of certain experimentally determined parameters of the

reaction. RBatch model discussed next is a model used for modeling and simulation of reaction based on known stoichiometry and kinetics.

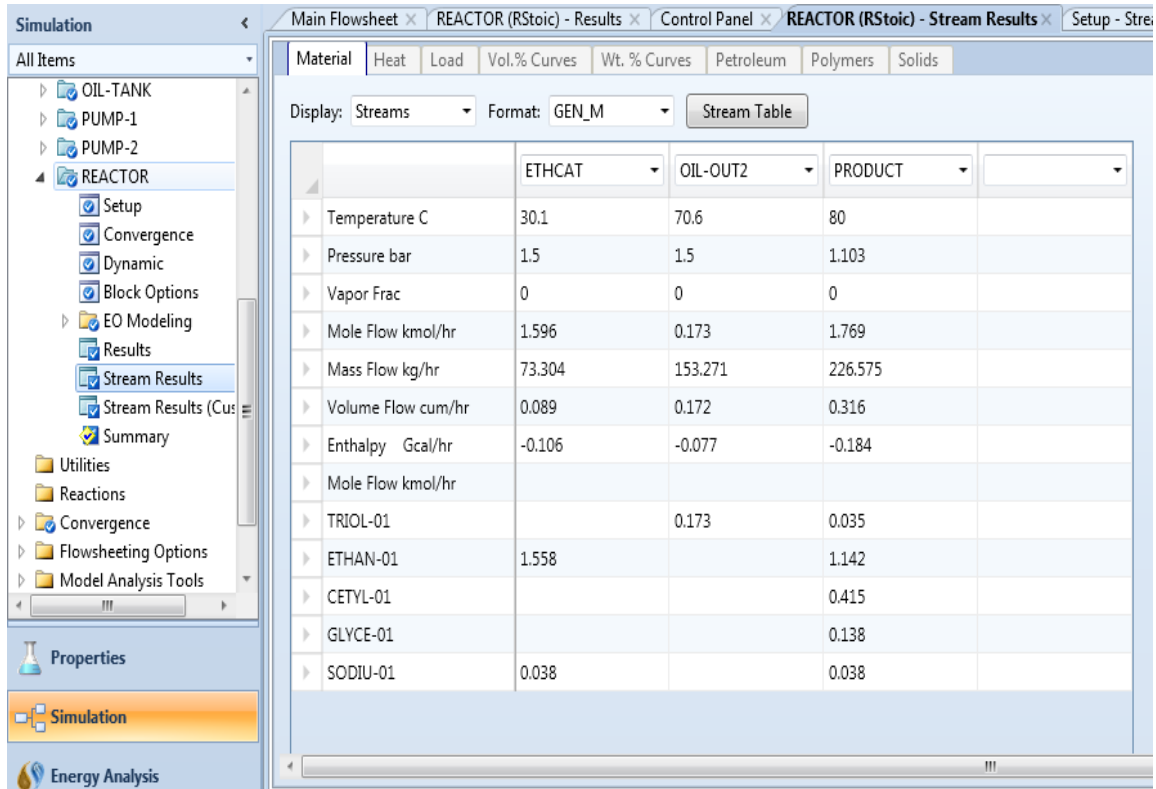


Figure 4-3: Simulation results for the model using RStoic reactor model

Figure 4.3 is the screen shoot direct from the Aspen menu which again generated in stream tables presented in table 4.9.

Table 4-9: Heat and Material balance generated by Aspen simulation for RStoic reactor model

Heat and Material Balance Table				
Stream ID		ETHCAT	OIL-OUT2	PRODUCT
Temperature	C	30.1	70.6	80.0
Pressure	bar	1.500	1.500	1.103
Vapor Frac		0.000	0.000	0.000
Mole Flow	kmol/yr	1.596	0.173	1.769
Mass Flow	kg/yr	73.304	153.271	226.575
Volume Flow	cum/yr	0.089	0.172	0.316
Enthalpy	Gcal/yr	-0.106	-0.077	-0.184
Mole Flow	kmol/yr			
TRIOI-01			0.173	0.035
ETHAN-01		1.558		1.142
CETYL-01				0.415
GLYCE-01				0.138
SODIU-01		0.038		0.038

4.9.2. Modeling Using RBatch reactor model

As described in section 4.8, this model is used for reactions in any phase based on known stoichiometry and kinetics. Thus, the purpose of the topic discussed in section 3 about the kinetics of Transesterification reaction to determine the values for Frequency factor and the Activation energy is to use this block for modeling of the transesterification reactor. The values of Activation Energy $E_a=27.815\text{KJ/mol}$ and Frequency factor $A= 118/\text{min}$ determined in section of 3.1.2 are used for this transesterification reactor simulation model.

The amount of reactants entering the reaction for the simulation for delivering of the intended biodiesel amount (150Lt) are now assumed based on the maximum experimentally determined yield percent (85.24%). That is for 150Lt of yield of biodiesel, $150\text{lt} \times 860\text{gm/lt} = 129000\text{gm} = 129000\text{gm}/310.54\text{gm/mol} = 415.4322\text{mole}$.

The maximum theoretical amount of biodiesel using equation 3.1 is;

$$85.24\% = \frac{\text{Moles of Ester produced}}{\text{Stoicheometric moles of Ester produced}} * 100$$

This implies,

$$\text{Stoicheometric} = \frac{\text{Moles of Ester produced}}{85.24} * 100 = \frac{415.4322}{85.24} * 100 = 487.37\text{mole}$$

Then, the amount of triglyceride oil per the stoichiometric reaction is $487.37/3 = 162.46\text{mol} = 0.162\text{kmol}$ and the amount of Ethanol with 9:1 ratio to oil is $0.162\text{kmol} \times 9 = 1459.4\text{mol}$.

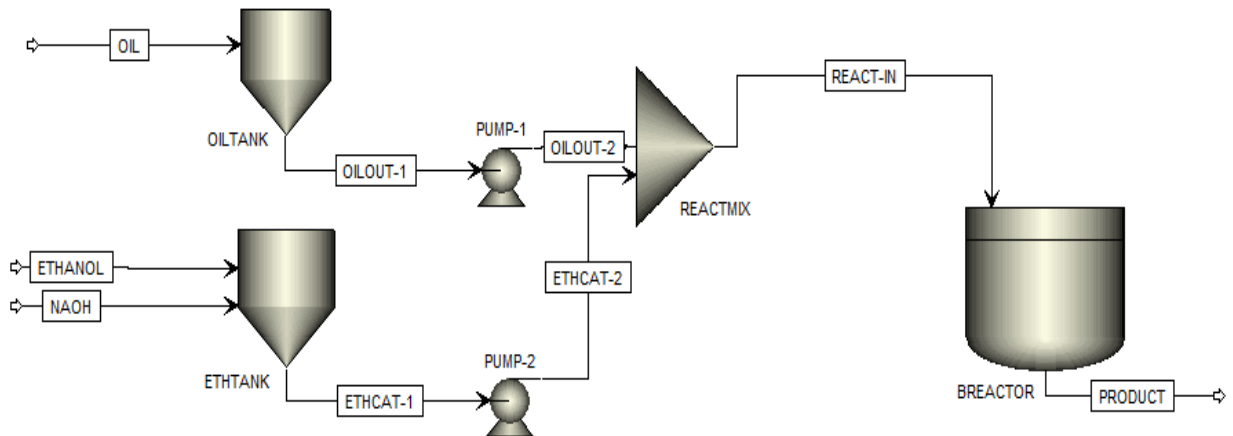


Figure 4-4: Biodiesel Flowsheet diagram for Rbatch Reactor model in Aspen Plus

Simulation Result

From both the chart in figure 4.5 and table 4.10, the amount of biodiesel (CETYL-01) produced is $0.446\text{Kmol/hr} = 446\text{mol/hr} \times 1\text{hr} = 446\text{mol}$. Then, the yield as per the simulation result is =

$\frac{445.57}{487.37} * 100 = 91.4\%$, which is about 6.16% higher than the experimentally determined yield.

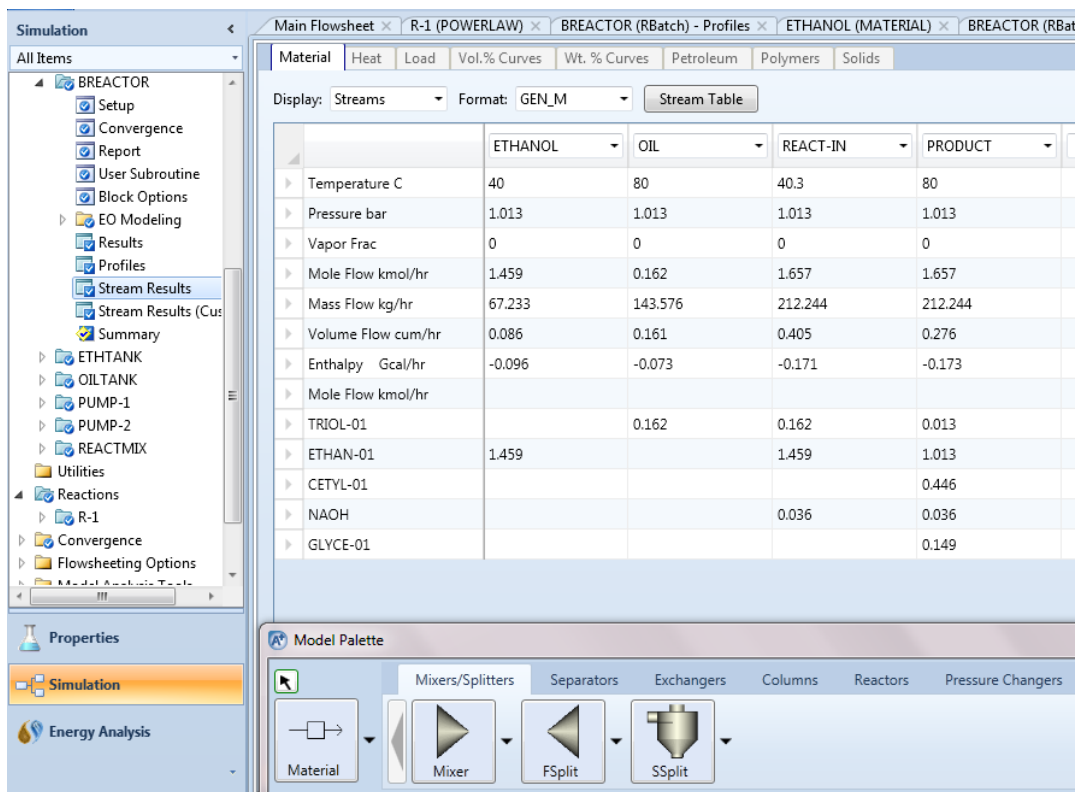


Figure 4-5: Simulation results for the model using Rbatch reactor model

Table 4-10: Heat and Material balance generated by Aspen simulation for Rbatch reactor

Heat and Material Balance Table					
Stream ID		ETHANOL	OIL	REACT-IN	PRODUCT
Temperature	C	40.0	80.0	40.3	80.0
Pressure	bar	1.013	1.013	1.013	1.013
Vapor Frac		0.000	0.000	0.000	0.000
Mole Flow	kmol/hr	1.459	0.162	1.657	1.657
Mass Flow	kg/hr	67.233	143.576	212.244	212.244
Volume Flow	cum/hr	0.086	0.161	0.405	0.276
Enthalpy	Gcal/hr	-0.096	-0.073	-0.171	-0.173
Mole Flow	kmol/hr				
	TRIOL-01		0.162	0.162	0.013
	ETHAN-01	1.459		1.459	1.013
	CETYL-01				0.446
	NAOH			0.036	0.036
	GLYCE-01				0.149

For the purpose of evaluating the difference resulted from the simulation result, two additional cases were considered so that the simulation result is compared to the experimentally determined value. The first case (figure 4.6) was a research conducted by George Anastopoulos, Ypatia Zannikou, Stamoulis Stournas and Stamatis Kalligeros at National Technical University of Athens, School of Chemical Engineering [22]. The transesterification reactions were conducted with Sunflower oil and ethanol as an alcohol, where ethanol to oil molar ratio 12:1, NaOH as a catalyst, with catalyst amount 1% (wt/wt), 3 hours of reaction time, for temperatures of 35°C, 80°C and 90°C. and the second case (figure 4.7) was a research conducted by Amish P. Vyas, Jaswant L. Verma, Nandula Subrahmanyam, Chemical Engineering Department, Nirma University, Ahmedabad, India. A transesterification of Jatropha Oil with Methanol under Ultrasonic Irradiation with reaction conditions Methanol to oil molar ratio of 9:1, catalyst amount 1% (wt/wt) NaOH, reaction time 45min and reaction temperatures 30°C, 40°C, and 50°C. The nearly equilibrium conversion was found to be about 93.5% at 45 minutes of reaction time.

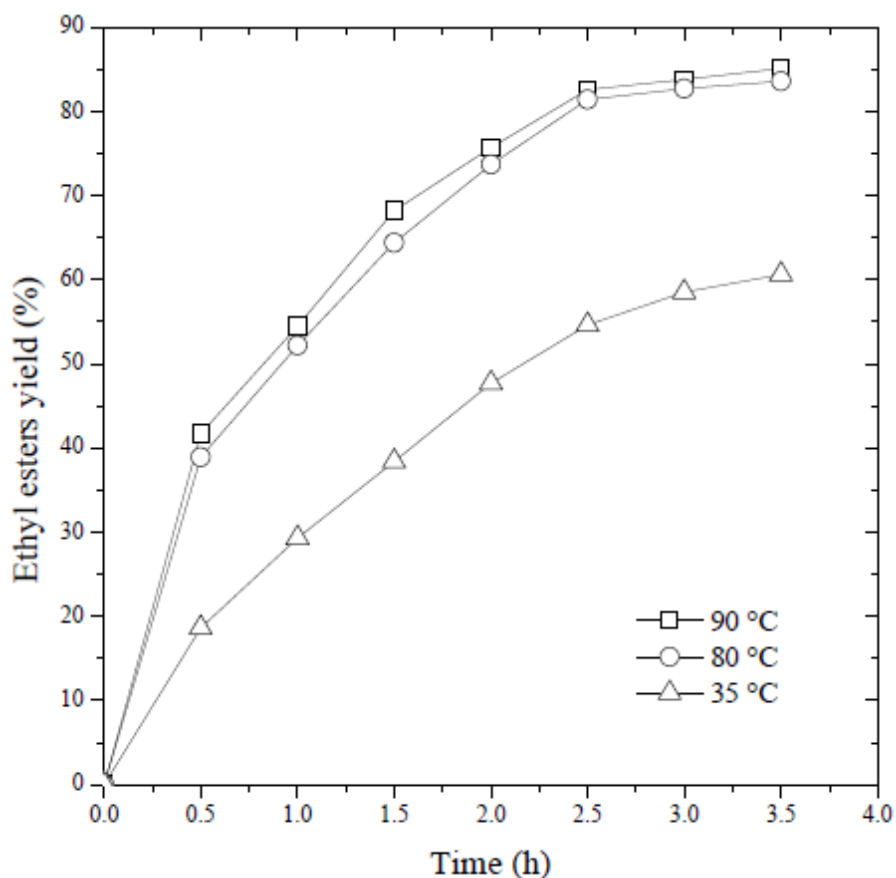


Figure 4-6: Ethyl ester yield (%) versus Time (hour) at temperatures of 35 °C, 80 °C and 90 °C, NaOH to oil mass ratio, 1.0%; ethanol/oil molar ratio, 12:1[22]

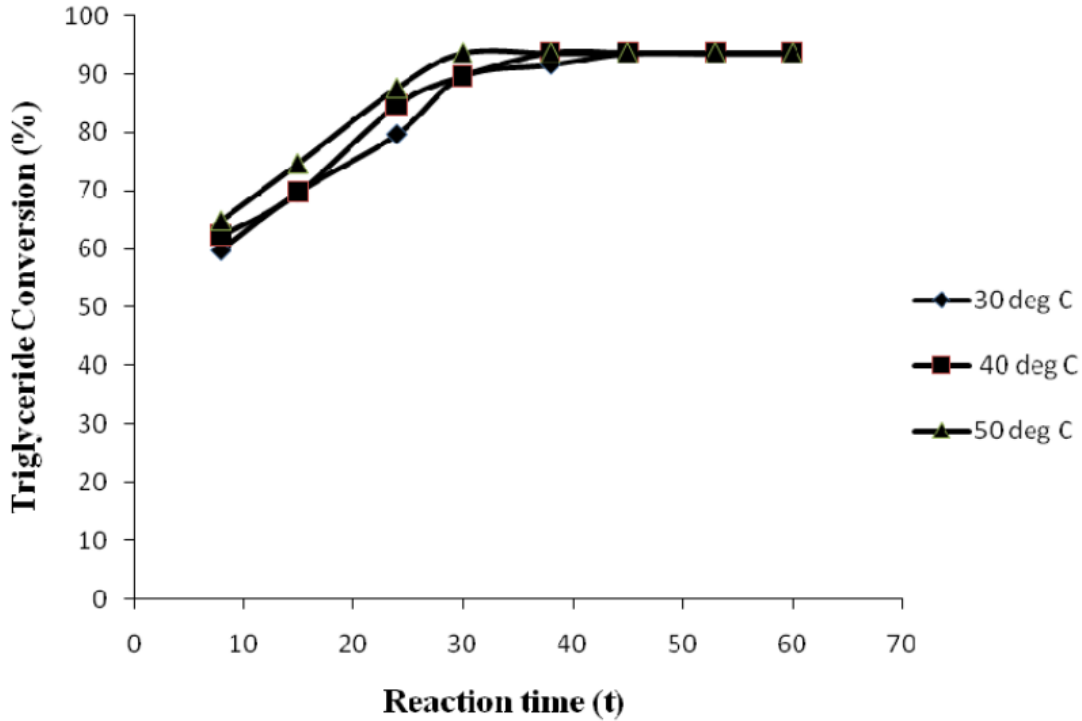


Figure 4-7: Triglyceride conversion at temperatures of 30, 40 and 50°C. Reaction conditions: Jatropha oil 50 g, catalyst amount 1%, Oil to Methanol Molar Ratio 1:9 [23]

The yield, amount and concentration of reaction components for Transesterification reaction of Sunflower oil with Ethanol for temperatures $T=35^{\circ}\text{C}$, 80°C and 90°C and of Jatropha Oil with Methanol for temperatures $T= 30^{\circ}\text{C}$, 40°C and 50°C with the corresponding plot of $-\ln \left[\frac{(C_{EEe}/C_{TGe})C_{TG} - (C_{TG0} - C_{EE0})}{((C_{EEe}/C_{TGe})C_{TG0} + C_{EE0})} \right]$ verses time, the determined forward & revers rate factors at each temperature are presented in appendix A2 and A3 respectively.

From which the activation energy (E_a) and the frequency factor (A) of each case for forward and revers reaction calculated as;

- ✓ For Sunflower oil with Ethanol $E_a = 14.087\text{kJ/mol}$, $A=2.70$ (forward) and $E_a = 8.255\text{kJ/mol}$, $A=0.141$ (revers)
- ✓ For Jatropha Oil with Methanol $E_a= 9.512\text{kJ/mol}$, $A=2.70$ (forward) and $E_a = 9.438\text{kJ/mol}$, and $A=0.019$ (revers)

Table 4-11: Transesterification reaction parameters for the three cases, the one considered in this study and the other two included for comparison.

Reaction parameters	Condition		
	1	2	3
Oil source	Jatropha oil	Sunflower oil	Jatropha oil
Alcohol	Ethanol	Ethanol	Methanol
Alcohol to oil molar ration	9:1	12:1	9:1
Catalyst	NaOH	NaOH	NaOH
Catalyst amount % wt/wt	1%	1%	1%
Reaction temperature (°C)	80	80	50
Reaction time (min)	180	180	40
Activation energy (forward)	25.769kJ/mol	14.0781kJ/mol	9.512kJ/mol
Activation energy (backward)	22.9342kJ/mol	8.2547kJ/mol	9.438kJ/mol
Frequency factor (forward)	60.26 /min	2.70 /min	2.70 /min
Frequency factor (backward)	4.69 /min	0.141 /min	0.019 /min
Yield (Wt %) Aspen simulation	91.51%	90.0%	93.13%
Yield (wt %) Experimental	85.24%	82.9%	93.5%
Difference	6.27	7.1	-0.37
Error %	7.4%	8.6%	0.4%
Reference	[15]	[23]	[22]

As seen from table 4.11, for the first two cases the alcohol used was ethanol, the yield obtained from aspen simulation is slightly higher than the value obtained experimentally while the case where the alcohol used was methanol, the obtained value from the simulation and experimentally determined value was nearly equal.

4.10 Residence time

Residence time of a reaction is time for the reacting component stay in the reaction process. It influences the molar composition of produced biodiesel from the reactor. Fig. 4.8 and Table 4.12 show the molar composition of the produced biodiesel at different residence times.

The residence time is crucial for the produced component. Increased residence gives a higher Biodiesel and Glycerol concentration, while the feed oil (Triolein) and Ethanol concentrations decrease with residence time. The residence time used to this project to evaluate the reaction in Aspen Plus is 220min. Table 4.13 shows that as per this simulation result, resident time beyond 150min does not show significant increase in the product. Hence, it is better to consider the optimum resident time for the reaction to be 150min.

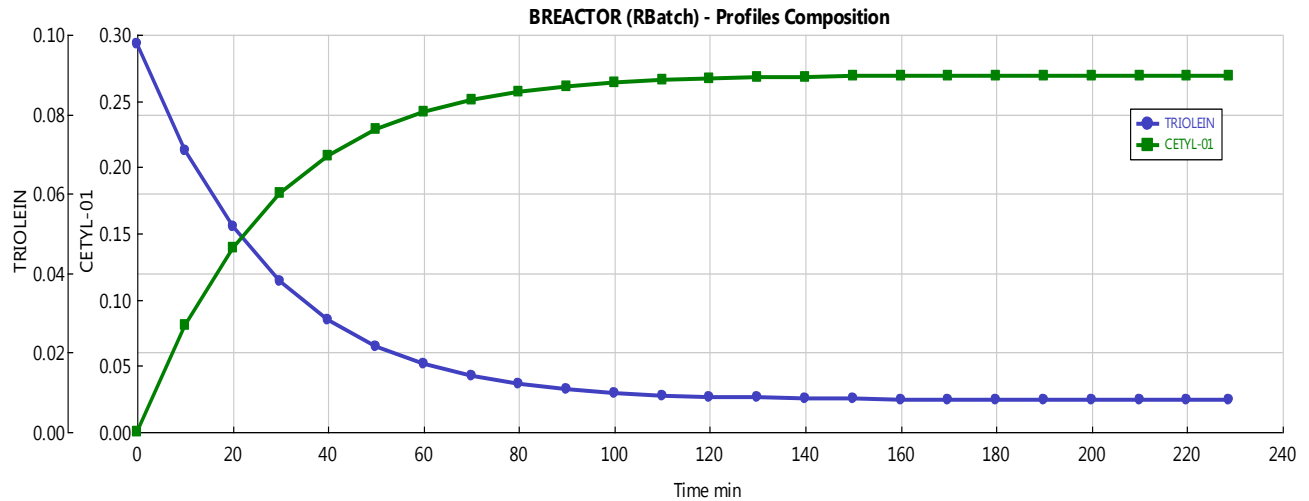


Figure 4-8: Molar composition of feed oil and Ethyl ester produced as a function of time

Table 4-12: Molar composition of the reacting component and products generated by Aspen plus

Time(min)	TRIOLEIN	ETHAN-01	CETYL-01	GLYCE-01	SODIU-01
0	0.097767049	0.88050694	0	0	0.021726011
10	0.07090457	0.799919502	0.080587438	0.026862479	0.021726011
20	0.051569958	0.741915667	0.138591274	0.046197091	0.021726011
30	0.037824794	0.700680177	0.179826763	0.059942255	0.021726011
40	0.028221092	0.671869071	0.208637869	0.069545957	0.021726011
50	0.021609968	0.652035697	0.228471243	0.076157081	0.021726011
60	0.017112122	0.638542159	0.241964781	0.080654927	0.021726011
70	0.014080355	0.629446859	0.251060082	0.083686694	0.021726011
80	0.012053538	0.623366408	0.257140532	0.085713511	0.021726011
90	0.01070545	0.619322144	0.261184796	0.087061599	0.021726011
100	0.00981144	0.616640113	0.263866827	0.087955609	0.021726011
110	0.00921947	0.614864203	0.265642737	0.088547579	0.021726011
120	0.008828167	0.613690295	0.266816645	0.088938882	0.021726011
130	0.008570392	0.612916971	0.26758997	0.089196657	0.021726011
140	0.008400662	0.612407779	0.268099162	0.089366387	0.021726011
150	0.008288508	0.612071317	0.268435623	0.089478541	0.021726011
160	0.008214289	0.61184866	0.26865828	0.08955276	0.021726011
170	0.008165206	0.611701412	0.268805529	0.089601843	0.021726011
180	0.008132954	0.611604655	0.268902285	0.089634095	0.021726011
190	0.008111837	0.611541304	0.268965636	0.089655212	0.021726011
200	0.008097863	0.611499382	0.269007558	0.089669186	0.021726011
210	0.008088675	0.611471818	0.269035123	0.089678374	0.021726011
220	0.008082416	0.611453042	0.269053899	0.089684633	0.021726011
228	0.008078986	0.611442752	0.269064188	0.089688063	0.021726011

The molar composition of the reacting and produced components at different residence time is shown in table 4.12 The amount of reacting component in moles is Ethanol= 1.459, Oil=0.162 (with ethanol to oil ratio 9:1) and for NaOH = 0.036 that gives a total of 1.459+0.162+0.036= 1.657.

To evaluate the biodiesel produced in moles and percentage yield, certain residence times from table 4.12 are selected and values tabulated in table 4.13.

The amount of biodiesel produced in kmol/hr and percentage yield is calculated as (for example at residence time of 120min) from table 17= 0.266816645*1.657= 0.44212 Kmole/hr. and from section 4.9.2, the maximum achievable (stoichiometric) amount is 0.48737 kmole/hr. Then, the percentage yield = $0.44212 \times 100 / 0.48737 = 90.71\%$. Similarly, the values for the remaining selected resident times (0, 30, 60, 90, 120, 150, 180, and 210) are shown in table 4.13 and graphically the percentage yield against reaction time is plotted on excel is shown on figure 4.9.

Table 4-13: Biodiesel produced in kmol/hr and percentage yield at selected resident time

Time (hr)	0	0.5	1.0	1.5	2	2.5	3.0	3.5
Biodiesel (Kmol/hr)	0.0	0.29797	0.40094	0.43278	0.44212	0.44480	0.44557	0.44579
Yield (%)	0.0	61.1	82.3	88.8	90.7	91.3	91.4	91.5

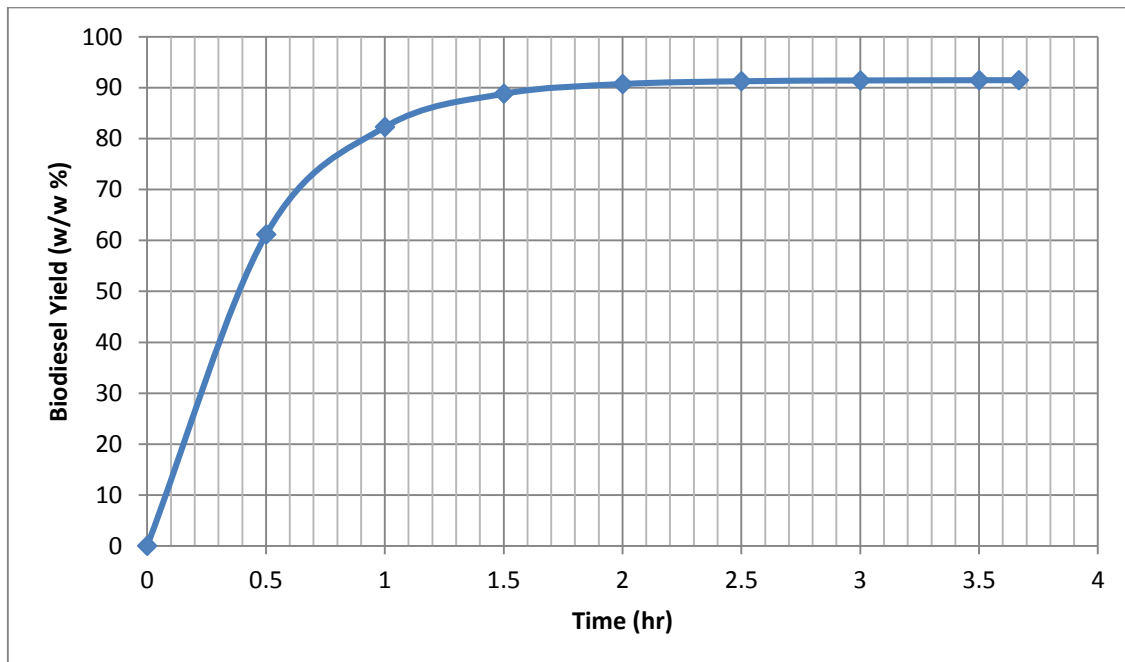


Figure 4-9: Ethyl Ester (Biodiesel) yield as a function of reaction time

4.11 Sensitivity Analysis

Sensitivity analysis is a tool for determining how a process reacts to varying key operating and design variables. It can be used to vary one or more flowsheet variables and study the effect of that variation on other flowsheet variables. It is a valuable tool for performing “what if” studies. The flowsheet variables that are varied must be inputs to the flowsheet. They cannot be variables that are calculated during the simulation. Sensitivity analysis can be used to verify if the solution to a design specification lies within the range of the manipulated variable, it can also be used to perform simple process optimization. Sensitivity blocks are used to generate tables and/or plots of simulation results as functions of feed stream, block input, or other input variables [24].

In this study, the sensitivity analysis tool in Aspen plus is carried out to analyze the dependency of biodiesel production with the variation of parameters such as temperature and ethanol feed flow. Figure 4.10 and 4.11 plotted by Aspen shows the graph of biodiesel yield against reaction temperature, and ethanol feed flow, respectively.

As seen from figure 4.10, the biodiesel yield increases with temperature from 30°C (0.408Kmol/hr = $0.408/0.487.27 = 83.7\%$ w/w yield) until the reactor temperature reaches 80°C (91.5% yield) and from then onwards, it is not sensitive to the increase of temperature. And from figure 4.11, the yield increases with increase in ethanol amount yielding 0.15kmol/hr = 30.8%w/w with ethanol to oil ratio 1:1 and reached 0.446kmol/hr at ethanol to oil ratio of 9:1 (0.1459kmol/hr) and from then onwards, it was less sensitive to the increase in the molar ratio with nearly constant yield.

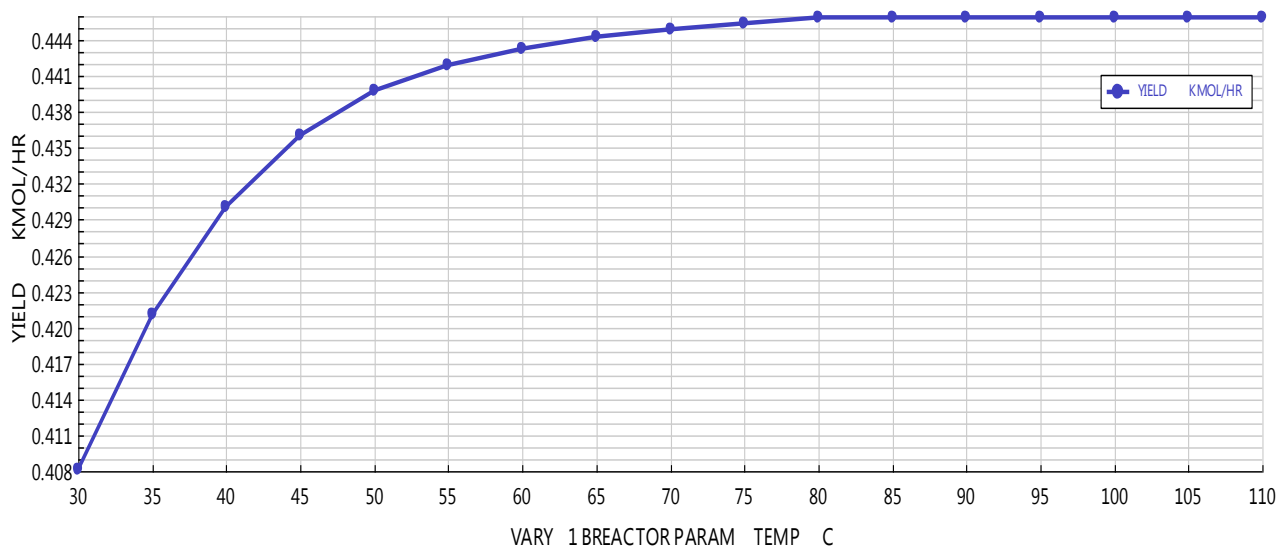


Figure 4-10: Ethyl Ester (Biodiesel) yield as a function of reaction temperature

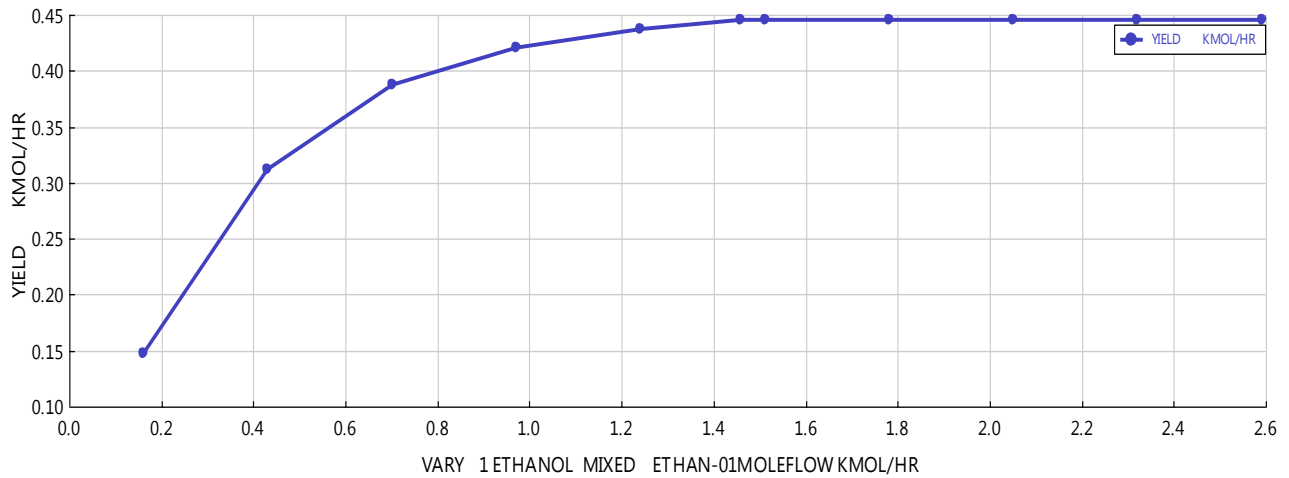


Figure 4-11 Ethyl Ester (Biodiesel) yield as a function of ethanol feed

Similarly to the above case, the yield for transesterification reaction with methanol as an alcohol (for 3rd condition, from table 4.11) at different reaction resident time evaluated and the results shown in figure 4.12, a graph showing the molar composition of feed oil and methyl ester produced with resident time. And the percentage yield (w/w %) of the methyl ester is shown in figure 4.13, plotted by excel. The yield increases rapidly with time in the first 10 to 15min and gradual increment up to nearly 30min from which onwards it remains constant. The final simulation result is in agreement to the laboratory result presented in figure 4.7.

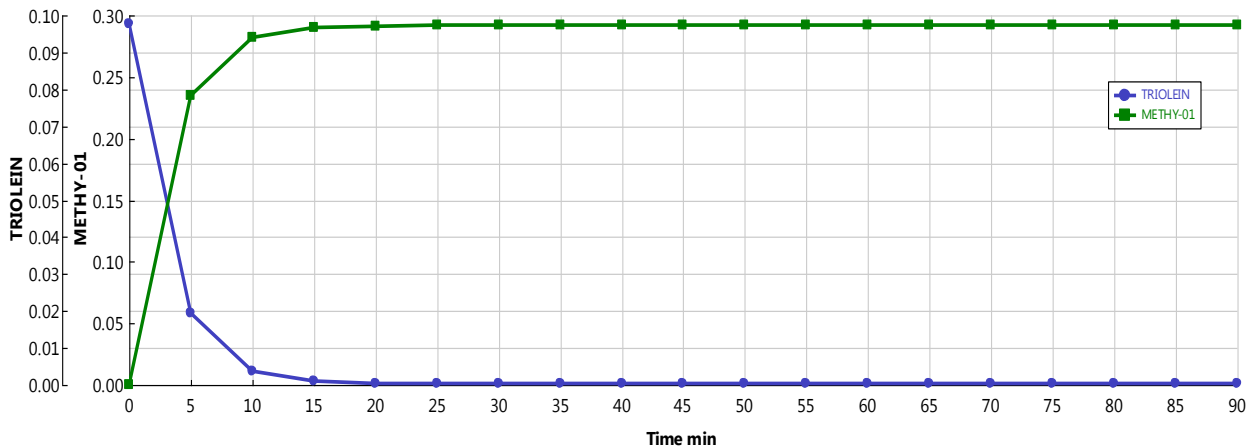


Figure 4-12: Molar composition of feed oil and Methyl ester produced as a function of time

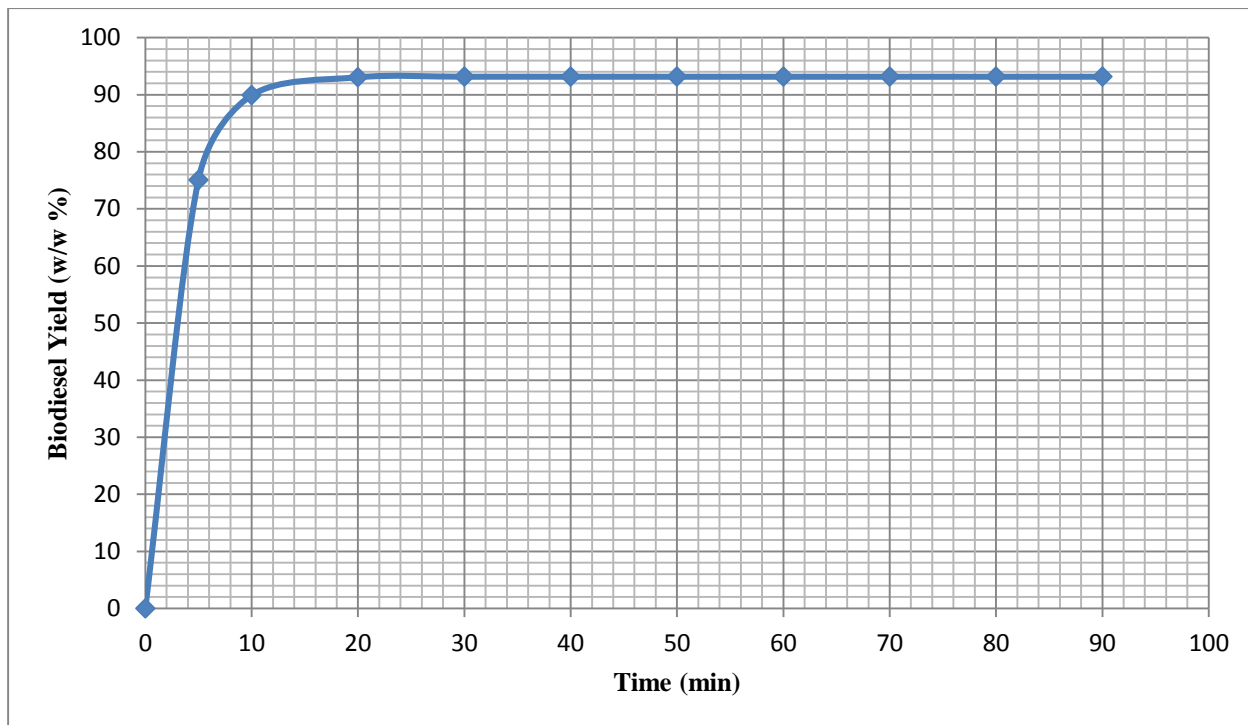


Figure 4-13: Methyl Ester (Biodiesel) yield as a function of reaction time

5 Excess Ethanol Recovery

The biodiesel production process produces two products: Ethyl ester (biodiesel) and glycerol. The stoichiometric ratio for the transesterification reaction involves 3mole of Ethanol and 1mole of triglyceride to produce 3 mole of fatty acid ester (ethyl ester) and 1mole of glycerol. However, most biodiesel production process uses excess alcohol to force reaction to completion or to get high yield.

After the completion of transesterification and esterification reactions the excess ethanol is distributed to the mixture of the products (biodiesel and glycerol). Usually this mixture is separated by gravity separation, as they have different densities [10]. After the biodiesel process is complete, a lot of alcohol is available for recovery and reuse. Ethanol recovery can make the biodiesel production process more efficient from both economic and environmental point of view, as it can save the input costs for the process as well as helps to maintain the specific standard.

The recovery may be done within biodiesel reactor or in stand-alone recovery units, before phase separation [11]. The unreacted ethanol acts as a phase stabilizer and reduces the rate of phase separation. Besides, ethanol recovery can be carried out immediately following transesterification to reduce the load in downstream units [10].

There are several different methods of extracting ethanol from biodiesel and glycerol: vacuum flash evaporation, distillation, and water washing [15].

- If a simple flash evaporation operation is performed based solely on the vapor pressure of ethanol, only a portion of the ethanol will be removed which means more ethanol may remain in the biodiesel than desired. To remove the final amounts of ethanol to the low levels of ASTM requirements is more complex.
- Biodiesel water washing to remove the total amount of methanol from biodiesel generally is a lower equipment cost method of extraction; however, the separation of ethanol from the resulting ethanol-water mix becomes expensive.
- Distillation of ethanol from biodiesel can be performed in a single column; however, the column is relatively complex in design, control and operation, and more expensive.

As our plant in concern is Small Scale Biodiesel plant and knowing the relatively low boiling point of ethanol, it is possible to recapture the ethanol via a simple still. The mix of biodiesel, glycerol and ethanol, still liquid following the reaction stage, can be heated to vaporize the ethanol. These vapors can then be condensed and recycled; maximizing use, reducing waste, and lowering overall processing cost [16].

Therefore, for the ethanol recapture system based on the above statement a design of water-cooled Helical Coil Heat Exchanger (condenser) where ethanol vapor enters at one end and liquid ethanol coming out at the other end is presented next. The system can be constructed from items that can be found easily at any plumbing store in Addis Ababa. Schematic of the ethanol recapturing system is shown in figure 5.1.

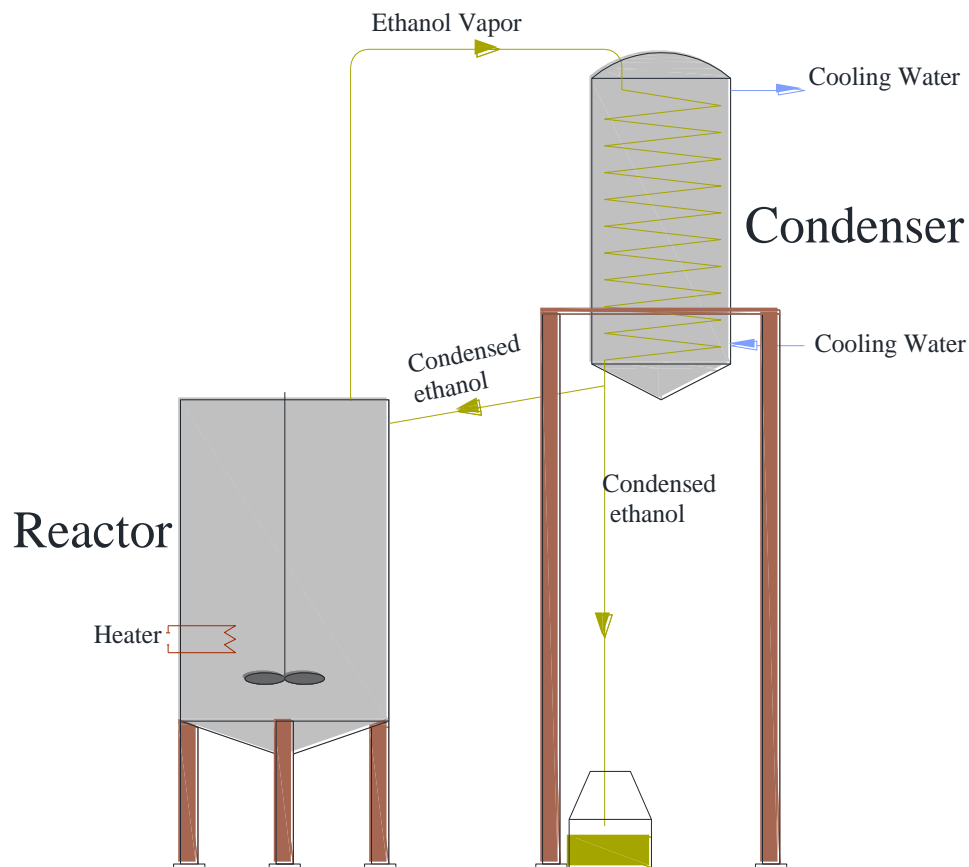


Figure 5-1: Schematic representation of Ethanol Recovery Unit

5.1. Recovery system process Description

The system illustrated in Figure 5.1 above is suitable alternative for an easy ethanol recovery system. The reactor tank is made to have an opening to a tube to allow the evaporated ethanol

pass through it while the reaction is in progress. The tube is connected to a copper tube that is coiling as it enters the condenser. Cold tap water passes through the condenser, cooling the ethanol vapors to a liquid. The condensate falls through the copper tubing where it is refluxed back to the reactor to compensate the evaporated amount so that the ethanol added in excess to forces the equilibrium to the right will not be reduced and ensure the reaction consumes all of the oil. The cooling water comes from and goes to a cooling tower (its design not included in this study but part of the project) where it is cooled to be used continuously for the next process.

Once the reaction is completed, to evaporate the ethanol a substantially amount of energy under atmospheric pressure is added to the product beyond the boiling temperature of ethanol (78.26°C), perhaps to 110 °C. This time the ethanol condensate will be diverted to fall in the other direction where it is collected at the bottom. Once the liquid ethanol stops flowing, the process is complete, and the remained product will be processed to the next step where the final Biodiesel and Glycerol are separated.

5.2. Helical coil heat exchanger for the Condenser

Heat exchangers are used in a wide variety of applications including power plants, nuclear reactors, refrigeration and air-conditioning systems, automotive industries, heat recovery systems, chemical processing, and food industries. Besides the performance of the heat exchanger being improved, the heat transfer enhancement enables the size of the heat exchanger to be considerably decreased. In general, the enhancement techniques can be divided into two groups: active and passive techniques. The active techniques require external forces like fluid vibration, electric field, and surface vibration. The passive techniques require special surface geometries or fluid additives like various tube inserts. Both techniques have been widely used to improve heat transfer performance of heat exchangers. Due to their excellent heat transfer performance and compact structure as compared to straight tube heat exchangers, helically coiled tubes have been introduced as one of the passive heat transfer enhancement techniques [13].

Helical coil heat exchangers are used in *evaporators* and *condensers* in the food, pharmaceutical, modern energy conversion and power utility systems, air conditioning and heating ventilating engineering and chemical industries.

Helical coil heat exchangers are frequently used to attain a large heat transfer area per unit volume and to improve the heat transfer coefficient of the tube internal surface. As compare to straight tube, helically coiled tube shows higher heat transfer coefficient due to the enhanced

turbulence (since constantly varying flow direction). The centrifugal forces induce in a coiled tube give rise to secondary flow pattern because of this swirl flow, which consists of two vertices perpendicular to the axial flow direction. Therefore, the heat transfer takes place by diffusion in the radial direction and as well as by convection. The contribution of such secondary convective transport prevails the overall process and significantly improves the heat transfer rate per unit length of the tube in comparison with a straight tube of equal length [14].

In general, helical coil heat exchanger has many benefits that make it a good choice [17]:

- ✓ where space is limited, and highly efficient use of space is needed, especially when it's limited, and not enough straight pipe can be laid
- ✓ Under conditions of laminar flow or low flow rates, where a shell and tube heat exchanger would become uneconomical because of the resulting low heat transfer coefficient.
- ✓ When there is low pressure in one of the fluids, usually from accumulated pressure drops in other process equipment
- ✓ When one of the fluids has components in multiple phases (solids, liquids, and gases), which tends to create mechanical problems during operations, such as plugging of small-diameter tubes. Cleaning of helical coils for these multiple-phase fluids can prove to be more difficult than its shell and tube counterpart; however, the helical coil unit would require cleaning less often

5.2.1. Design analysis

For designing the Helical Coil Heat exchanger indicated on figure 5.2, the existing formulas available in the literatures are used to carry out the analysis.

Table 5-1: Physical property and other assumed values for condenser design

Descriptions	Ethanol Vapor	Coolant (water)
Mass flow rate (kg/s)	0.036215	0.6425
Heat Capacity (KJ/Kg °c)	1600	4200
Density (Kg/m ³)	1.624	996
Thermal conductivity (KJ/s.m.°c)	0.0199	0.615
Dynamic Viscosity (Kg/m.s)	1.03*10 ⁻⁵	0.891*10 ⁻³
Enthalpy of vaporization (KJ/Kg)	838.3	2256.4
Inlet temperature (°c)	110	22
Outlet temperature (°c)	78	34

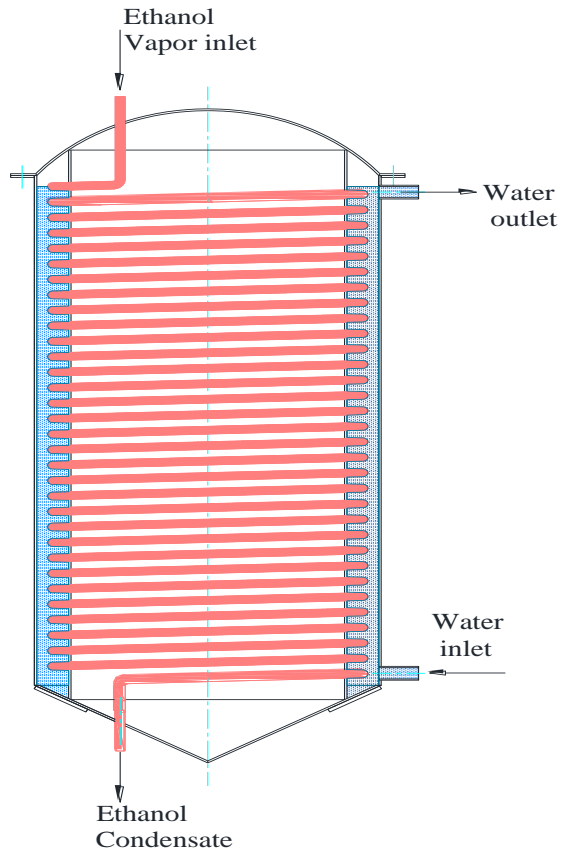


Figure 5-2: Helical Coil Heat Exchanger

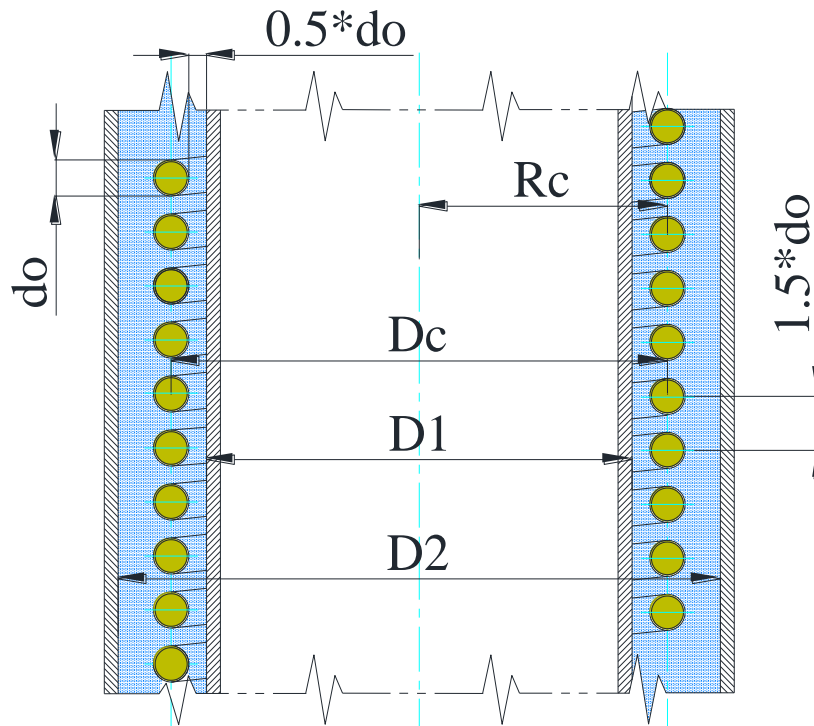


Figure 5-3: Schematic cutaway view of the HCHE

I. Determining the heat transfer coefficient

To calculate the heat transfer coefficients in the coil and annulus, the following parameters need to be known

a) The length of coil L_c need to make N turns and it is given by

$$L_c = N\sqrt{(2\pi R)^2 + P^2} \quad 5.1$$

The volume occupied by the coiled tube V_c given by;

$$V_c = \frac{\pi}{4} d_o^2 L_c \quad 5.2$$

The volume of the annulus V_a given by;

$$V_a = \frac{\pi}{4} (D_2^2 - D_1^2) P N \quad 5.3$$

Then, the volume available for the flow of fluid in the annulus outside the coil is $V_a - V_c$

b) The shell side hydraulic diameter of the coil is defined by;

$$D_e = \frac{4*(V_a - V_c)}{\pi d_o L_c} = \frac{(D_2^2 - D_1^2) P}{d_o \sqrt{(2\pi R)^2 + P^2} - d_o} \quad 5.4$$

The heat Load, which can be obtained from

$$\dot{Q} = \dot{m}_c * (C_{pc} * (T_{ci} - T_{co}) + h_{fg}) \quad 5.5$$

And

$$\dot{m}_s = \frac{\dot{Q}}{C_{ps}(T_{so} - T_{si})} \quad 5.6$$

c) The fluid mean velocity and the Reynolds number can be obtained from

$$V_s = \frac{4*\dot{m}_s}{\pi S_s (D_2^2 - D_1^2) - (D_{co}^2 - D_{ci}^2)} \quad 5.7$$

$$R_{es} = \frac{D_e V_s S_s}{\mu_s} \quad 5.8$$

d) The heat transfer coefficient in the annulus h_o can be calculated from the equation;

$$\frac{h_o D_e}{K_s} = N_{us} \quad 5.9$$

Where for;

Reynolds number R_{es} in the range of 50 to 10,000

$$N_{us} = 0.6 R_{es}^{0.5} P_r^{0.31} \quad 5.10$$

Reynolds number R_{es} over 10,000

$$N_{us} = 0.36 R_{es}^{0.55} P_r^{\frac{1}{3}} \left(\frac{V_{ds}}{V_{dsw}} \right)^{0.14} \quad 5.11$$

e) The heat transfer coefficient inside the coil h_i ;

The average fluid velocity inside the coil and the Reynolds number are;

$$v_c = \frac{4 \cdot m_c}{\pi S_c d_i^2} \quad 5.12$$

$$Re_c = \frac{d_i v_c S_c}{\mu_c} \quad 5.13$$

Then, the heat transfer coefficient inside the coil can be calculated from the equation

$$\frac{h_i d_i}{K_c} = N_{uc} \quad 5.14$$

Where;

$N_{uc} = 4.36$ or $N_{uc} = 3.36$ for Reynolds number less than 2300, fully developed flow and constant surface heat flux & temperature respectively. Or

$$N_{uc} = \frac{(f_s/8)(Re_s - 1000)Pr_s}{1 + 12.7 \left(\frac{f_s}{8}\right)^{1/2} (Pr_s^{2/3} - 1)} \quad 5.15$$

a correlation, valid over a large Reynolds number range including the transition region, provided by Gnielinski; where the friction factor may be obtained from the Moody diagram, or, for smooth tubes, from equation (5.16);

$$f_s = (0.79 \ln Re_s - 1.64)^{-2} \quad 5.16$$

a single correlation that encompasses a large Reynolds number range developed by Petukhov. The correlation is valid for $0.5 \leq Pr \leq 2000$ and $3000 \leq Re \leq 5 \times 10^6$.

The corrected inside heat transfer coefficient h_{ic} for the coil is

$$h_{ic} = h_i \left(1 + 3.5 \frac{d_i}{D_c}\right) \quad 5.17$$

f) Overall heat transfer coefficient

The overall heat transfer coefficient is given by

$$U = \frac{1}{\frac{1}{h_{io}} + \frac{1}{h_{ic}} + \frac{t}{k_p} + F_s + F_c} \quad 5.18$$

II. Log mean temperature difference ΔT_{lm} for counter flow heat exchanger is,

$$\Delta T_{lm} = \frac{(T_{ci} - T_{so}) - (T_{co} - T_{si})}{\log \left(\frac{T_{ci} - T_{so}}{T_{co} - T_{si}}\right)} \quad 5.19$$

III. Determining the required heat transfer area

$$A = \dot{Q}/(U\Delta T_{lm}) \quad 5.20$$

IV. Determining the number of coils of the tube

Since $A = \pi d_o L_c$ from which the length of the coil $L_c = \frac{A}{\pi d_o}$ and from equation (1) the number of turns of the coil is

$$N = \frac{L_c}{\sqrt{(2\pi R)^2 + P^2}} \quad 5.21$$

V. Height of the condenser needed to accommodate the number of the coil is then

$$H = N * P + d_o \quad 5.22$$

Using the above heat transfer design equations to get the condenser parameters, the calculation needs iteration and doing this manually is tedious. Hence, to ease the calculation work Matlab software is used for programming the analysis. The Matlab program is presented in Appendix 2.

To start the calculation, the mass flow rate of the evaporated ethanol is needed to be determined.

5.2.2. Mass flow rate of evaporated ethanol

Mass and Heat capacities of final products after reaction completion

- a. Biodiesel
 - ✓ Mass $M_b = 129\text{kg}$
 - ✓ Heat capacity $C_{pb} = 2.09\text{KJ/Kgk}$
- b. Glycerol
 - ✓ Mass $M_g = 12.752\text{kg}$
 - ✓ Heat capacity $C_{pg} = 2.43\text{KJ/kgk}$
- c. Excess Ethanol
 - ✓ Mass $M_e = 52.655\text{kg}$
 - ✓ Heat capacity (vapor phase) $C_{pv} = 1.603\text{kJ/kg k}$
- d. Unreacted Oil
 - ✓ Mass $M_o = 30.653\text{Kg}$
 - ✓ Heat capacity $C_{po} = 1.67\text{KJ/kgk}$

Temperatures at the end of reaction and maximum temperature for evaporating the excess ethanol is $T_i = 80^\circ\text{C}$ and $T_f = 110^\circ\text{C}$

Then the heat load/energy required to raise temperature of the mixture of end reaction to 110°C is taken as

$$Q = Q1 + Q2 + Q3 + Q4$$

Where,

$$Q1 = Mb * Cpb * (Tf - Ti) = 129 * 2.09 * (110 - 80) = 8088 \text{ KJ}$$

$$Q2 = Mg * Cpg * (Tf - Ti) = 12.752 * 2.43 * (110 - 80) = 929.6 \text{ KJ}$$

$$Q3 = Me * Cpv * (Tf - Ti) = 52.655 * 1.603 * (110 - 80) = 2532.17 \text{ KJ}$$

$$Q4 = Mo * Cpo * (Tf - Ti) = 30.653 * 1.67 * (110 - 80) = 1535.7 \text{ KJ}$$

Then

$$Q = 8088 + 929.6 + 2532.17 + 1535.7 = \mathbf{13,085.47 \text{ KJ}}$$

This heat energy can also be written as $Q = \dot{Q} * t$

Where,

\dot{Q} is the heat (power in KJ/sec) supplied to the mixture from electric heater and t is time required for the mixture to reach 110 °C with the supplied power.

Let the time t required for the mixture temperature to reach 110°C is 15min = 900 sec, then the heat power required is $\dot{Q} = Q/t = 13085.47 \text{ KJ} / 900 \text{ sec} = 14.54 \text{ KJ/s} \approx 15 \text{ KJ/s} = 15 \text{ KW}$.

Hence, for the mixture to reach 110 °C in 15min a heater of 15KW capacity is required. And with this heat power the mass flow rate of the vapor ethanol will then be $\dot{m} = 52.655 \text{ kg} / 900 \text{ sec} = 0.05851 \text{ kg/sec}$. This mass flow rate would be equal to the ethanol condensate in the condenser. Then, using this mass flow rate for the design of the condenser, the parameters are calculated using Matlab software and results presented in table below.

Table 5-2: Ethanol recovery condenser parameters, Matlab output for evaporation time t=15min

DesignParameters =	Option1	Option2	Option3	Option4	Option5
Tube outer dia.do in m	0.00635	0.00794	0.00952	0.0127	0.01905
Coil Pitch P in m	0.013595	0.017	0.020382	0.027191	0.040786
Shell side Reynolds No.Res	6250.9	6175.6	6102.4	5960	5693.6
Coil Side Reynolds No.Rec	1.4671e+06	1.1444e+06	8.9293e+05	6.412e+05	4.1978e+05
Inner Dia. D2 of the shell in m	0.2754	0.28176	0.28808	0.3008	0.3262
Coil dia.Dc in m	0.2627	0.26588	0.26904	0.2754	0.2881
Coil lenght Lc in m	32.744	31.667	31.384	31.148	31.367
Height H of the HCHE in m	0.54568	0.65228	0.76612	0.99111	1.4311
Coil side Pumping power Pw in Watt	55.171	16.135	4.8295	0.97064	0.12677

However, the available heaters obtained in the market are with capacities of 5KW and 9KW.

Hence, with $\dot{Q} = 5KW = 5KJ/sec$, time is

$$t = Q/\dot{Q} = 13,085.47 \text{ KJ}/(5KJ/s) = 2617.1\text{sec} = 43.62 \text{ min}$$

(time for the mixture temperature to reach 110°C with heater capacity of 5KW)

And

The mass flow rate of the ethanol vapor will be then $m = 52.655\text{kg}/2617.1\text{sec} = 0.020\text{kg/sec}$. taking this mass flow is the ethanol condensate in the condenser, the design parameters of condenser are as given presented below.

Table 5-3: Ethanol recovery condenser parameters, Matlab output (alternative-1)

DesignParameters =

	Option1	Option2	Option3	Option4	Option5
Tube outer dia.do in m	0.00635	0.00794	0.00952	0.0127	0.01905
Coil Pitch P in m	0.013595	0.017	0.020382	0.027191	0.040786
Shell side Reynolds No.Res	2147.9	2122.1	2096.9	2048	1956.5
Coil Side Reynolds No.Rec	5.0148e+05	3.9119e+05	3.0522e+05	2.1918e+05	1.4349e+05
Inner Dia. D2 of the shell in m	0.2754	0.28176	0.28808	0.3008	0.3262
Coil dia.Dc in m	0.2627	0.26588	0.26904	0.2754	0.2881
Coil lenght Lc in m	17.838	17.732	18.024	18.474	19.264
Height H of the HCHE in m	0.30017	0.36875	0.44405	0.593	0.88625
Coil side Pumping power Pw in Watt	1.6049	0.48288	0.14816	0.03074	0.0041587

And with $\dot{Q} = 9KW = 9KJ/sec$, time is

$$t = Q/\dot{Q} = 13,085.47 \text{ KJ}/(9KJ/s) = 1453.94\text{sec} = 24.23 \text{ min}$$

And

The mass flow rate of the ethanol vapor will be then $m = 52.655\text{kg}/1453.9\text{sec} = 0.036215\text{Kg/sec}$. taking the ethanol condensate in the condenser is this mass flow, the design parameters of condenser are as given presented below.

Table 5-4: Ethanol recovery condenser parameters, Matlab output (altenative-2)

DesignParameters =

	Option1	Option2	Option3	Option4	Option5
Tube outer dia.do in m	0.00635	0.00794	0.00952	0.0127	0.01905
Coil Pitch P in m	0.013595	0.017	0.020382	0.027191	0.040786
Shell side Reynolds No.Res	3869	3822.4	3777.1	3689	3524.1
Coil Side Reynolds No.Rec	9.0806e+05	7.0834e+05	5.5268e+05	3.9687e+05	2.5982e+05
Inner Dia. D2 of the shell in m	0.2754	0.28176	0.28808	0.3008	0.3262
Coil dia.Dc in m	0.2627	0.26588	0.26904	0.2754	0.2881
Coil lenght Lc in m	24.796	24.295	24.367	24.559	25.155
Height H of the HCHE in m	0.41477	0.50229	0.59695	0.78414	1.1515
Coil side Pumping power Pw in Watt	11.196	3.3196	1.0056	0.20528	0.02728

6 Conclusion and Recommendations

6.1. Conclusion

Small scale biodiesel production plants are growing in numbers until a large enough demand exists in the market to support larger scale production facilities, or until fossil fuel prices increase tremendously driving the need for larger scale production. To make biodiesel production more economical for large scale production, design and optimizations have to begin at the simulation scale first. While trials performed at the industry scale are not economical and not sufficient for true process optimization, a great deal of power for process design lies in utilizing simulation software, like the ASPEN Plus. Understanding how to model the complex reactions occurring in the Biodiesel Process with ASPEN Plus was the key focus of this paper. The goal was modeling and simulation of the transesterification reaction to predict and validate conversions at the outlet reactor with ASPEN Plus software.

Kinetics of the Transesterification of Biodiesel production from Jatropha Oil with Ethanol as an alcohol was determined. A model of the batch reactor to simulate the process of biodiesel production was performed in Aspen-Plus environment and validated with experimental data from previous thesis work by Haymanot Baynesagn and two other researchers considered for comparison. Biodiesel yield obtained by the simulation (91.4%) was found to be higher than the experimentally determined value (85.24%) having a difference of 6.16.

Factors affecting the transesterification process such as temperature, molar ratio and reaction time are also evaluated with the simulation. The biodiesel yield reached equilibrium near after 150minutes with operating condition of 80°C and ethanol to oil molar ratio 9:1. It also increased with temperature up to nearly 80°C and increasing beyond this temperature has shown no significant increase in the yield. Keeping constant the oil feed (0.162Kmol/hr), temperature at 80°C and reaction equilibrium time; ethanol feed to the reactor was varied from (0.162kmol/hr to 2.6kmol/hr) that is ethanol to oil molar ration from 1:1 to 16:1. The biodiesel yield was increased with increasing the ethanol feed from 0.162kmol/hr to nearly between 1.4 and 1.6 kmol/hr and keeps constant from then onwards, indicating the maximum yield reached was nearly at ethanol to oil molar ration of 9:1. These parameters (temperature of 80°C, reaction time 150min and ethanol to oil molar ratio 9:1) were operating conditions for optimum biodiesel yield for the transesterification process previously estimated by Haymanot Baynesagn.

The Biodiesel model provides a useful description of the process. The model can be used as a guide for understanding the process and also as a starting point for more sophisticated models for plant design and specifying process equipment.

6.2. Recommendations

Since this study was with regard to small scale biodiesel production plant for a batch process, the reactor model used was batch reactor model where the parameters obtained with the simulation are limited. Had the process was continuous instead of batch reactor, models such as continuous and plug flow could have been used and parameters such as reactor geometry, size and plant capacity could have been determined. Thus, it is recommended that the plant also be designed for continuous production and parameters mentioned determined by the Aspen.

For determination of reactions component concentration in the process from which the kinetics of the reaction is determined in most research is analyzed by a technique known as gas chromatography. The yield data used for this study wasn't conducted and analyzed with the help of the technique described due to which error there exist possibility of error in accuracy of data utilized. Therefore, it is recommended that appropriate standardized technique shall be used for a better estimate of yield value be determined by which the reaction kinetics of transesterification and behavior of the chemical process determined.

Finally, Alcohol recovery system considered in this study was simple reflux condenser where for continuous production process and the plant capacity, the recovery mechanism used in many researches is distillation column and when still the plant capacity increases, and better yield is intended, reactive distillation column are used where both reaction, separation, and recovery system are performed. Thus, studying distillation columns and reactive distillations column and performing the simulation to estimate the behavior of a chemical process is recommended.

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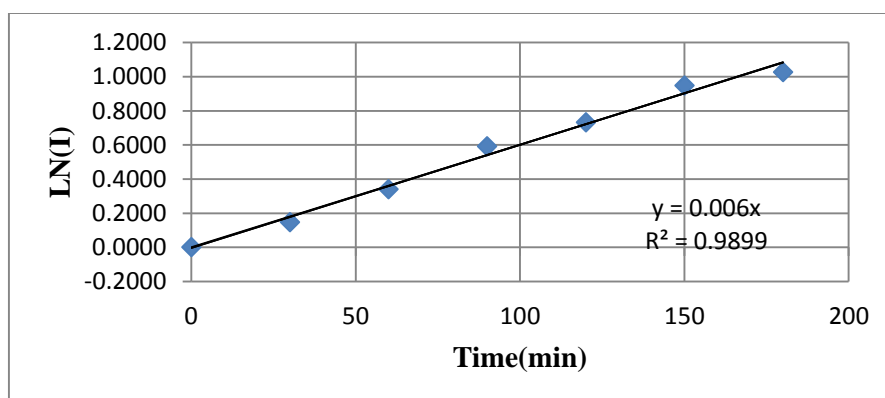
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Appendix A1: Yield, Amount and Concentration of reaction components for Transesterification reaction of Jatropha oil with Ethanol for temperatures T=60°C, 70°C, 80°C and 90°C.

For T=60°C

Triglyceride	ml	gram	mole	Ethanol	mole		
TG ₀	200	183.24	0.20695	ETH ₀	1.863		
T °C	60 °C						
Time (min)	0	30	60	90	120	150	180
yield %	0	13.8	28.05	42.05	48.1	55.65	58
E. ester, (g)	0.00	26.61	54.08	81.07	92.74	107.29	111.82
E. ester N _{EE} (mol)	0.0000	0.0857	0.1741	0.2611	0.2986	0.3455	0.3601
X _{TG}	0.0000	0.1380	0.2805	0.4205	0.4810	0.5565	0.5800
N _{TG} (mol)	0.2069	0.1784	0.1489	0.1199	0.1074	0.0918	0.0869
N _{ET} (mol)	1.8625	1.6055	1.3401	1.0793	0.9667	0.8260	0.7823
N _{GL} (mol)	0.0000	0.0286	0.0580	0.0870	0.0995	0.1152	0.1200
V _{TG} (l)	0.2000	0.1724	0.1439	0.1159	0.1038	0.0887	0.0840
V _{ETH} (l)	0.1088	0.0938	0.0783	0.0631	0.0565	0.0483	0.0457
V _{Bi₀} (l)	0.0000	0.0309	0.0629	0.0943	0.1078	0.1248	0.1300
V _{GL} (l)	0.0000	0.0021	0.0042	0.0063	0.0073	0.0084	0.0088
C _{TG}	0.6702	0.5962	0.5147	0.4290	0.3901	0.3398	0.3238
C _{ETH}	6.0315	5.3659	4.6323	3.8609	3.5106	3.0582	2.9138
C _{EE}	0.0000	0.2864	0.6020	0.9339	1.0845	1.2792	1.3413
C _{GL}	0.0000	0.0955	0.2007	0.3113	0.3615	0.4264	0.4471
I	1.0000	0.8630	0.7120	0.5532	0.4812	0.3881	0.3583
- LN[I]	0.0000	0.1473	0.3397	0.5920	0.7316	0.9466	1.0263

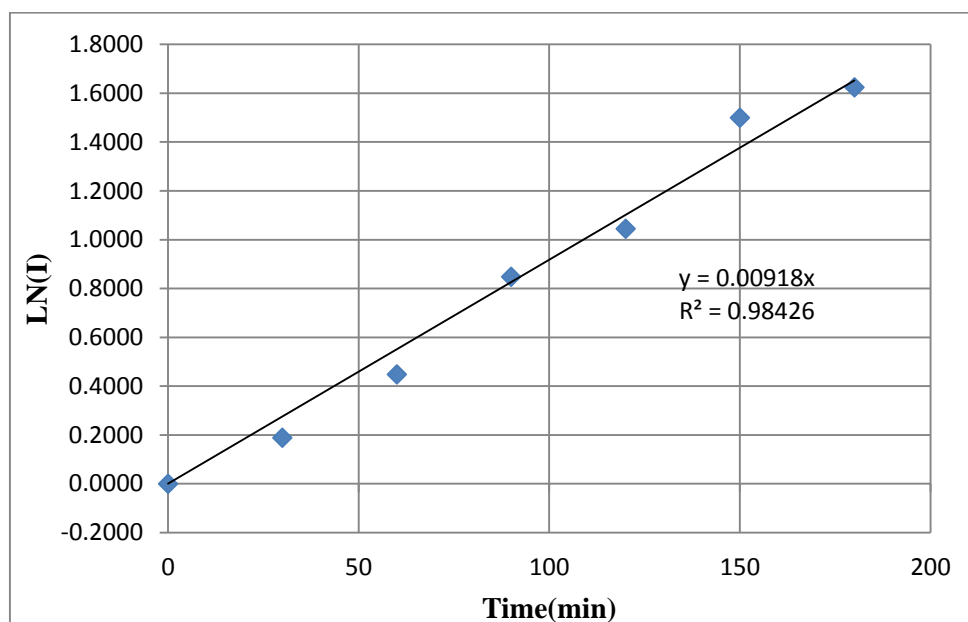


Plot of LN (I) verses Time

From which, Keq=4.14, k_f+K_b=0.006, → k_f=0.00483, K_b=0.00117

For T=70°C

T °C	70 °C						
Time (min)	0	30	60	90	120	150	180
yield %	0	19.45	38.95	58.6	65.3	76	78.11
E. ester Mass (g)	0.00	37.50	75.10	112.98	125.90	146.53	150.60
E. ester N _C (mol)	0.0000	0.1208	0.2418	0.3638	0.4054	0.4718	0.4849
X _{TG}	0.0000	0.1945	0.3895	0.5860	0.6530	0.7600	0.7811
N _{TG} (mol)	0.2069	0.1667	0.1263	0.0857	0.0718	0.0497	0.0453
N _{ET} (mol)	1.8625	1.5003	1.1371	0.7711	0.6463	0.4470	0.4077
N _{GL} (mol)	0.0000	0.0403	0.0806	0.1213	0.1351	0.1573	0.1616
V _{TG} (ml)	0.2000	0.1611	0.1221	0.0828	0.0694	0.0480	0.0438
V _{ET} (ml)	0.1088	0.0876	0.0664	0.0450	0.0378	0.0261	0.0238
V _{bio} (ml)	0.0000	0.0436	0.0873	0.1314	0.1464	0.1704	0.1751
V _{GL} (ml)	0.0000	0.0029	0.0059	0.0088	0.0099	0.0115	0.0118
C _{TG}	0.6702	0.5645	0.4485	0.3196	0.2726	0.1940	0.1780
C _{ETH}	6.0315	5.0809	4.0363	2.8767	2.4538	1.7464	1.6021
C _{EE}	0.0000	0.4090	0.8584	1.3573	1.5392	1.8435	1.9056
C _{GL}	0.0000	0.1363	0.2861	0.4524	0.5131	0.6145	0.6352
I	1.0000	0.8277	0.6383	0.4281	0.3514	0.2232	0.1970
- LN[I]	0.0000	0.1891	0.4490	0.8485	1.0458	1.4997	1.6245

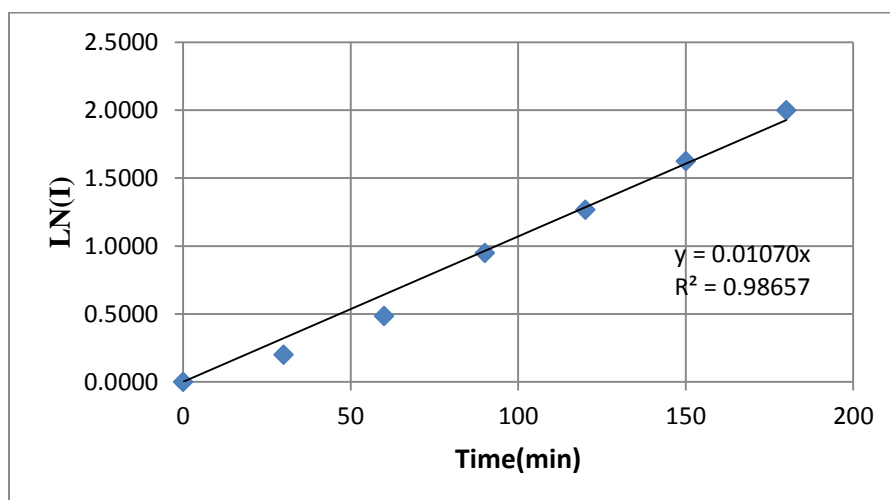


Plot of LN (I) versus Time

From which $K_{eq} = 10.71$, $k_f + K_b = 0.00918$, $k_f = 0.00840$, $K_b = 0.00078$

For T=80°C

T °C	80 °C						
Time (min)	0	30	60	90	120	150	180
yield %	0	21.2	42.5	64	73.2	80.3	85.24
E. ester Mass (g)	0.00	40.87	81.94	123.39	141.13	154.82	164.34
E. ester N _C (mol)	0.0000	0.1316	0.2639	0.3973	0.4545	0.4985	0.5292
X _{TG}	0.0000	0.2120	0.4250	0.6400	0.7320	0.8030	0.8524
N _{TG} (mol)	0.2069	0.1631	0.1190	0.0745	0.0555	0.0408	0.0305
N _{ET} (mol)	1.8625	1.4677	1.0710	0.6705	0.4992	0.3669	0.2749
N _{GL} (mol)	0.0000	0.0439	0.0880	0.1324	0.1515	0.1662	0.1764
V _{TG} (l)	0.2000	0.1576	0.1150	0.0720	0.0536	0.0394	0.0295
V _{ET} (l)	0.1088	0.0857	0.0626	0.0392	0.0292	0.0214	0.0161
V _{bio} (l)	0.0000	0.0475	0.0953	0.1435	0.1641	0.1800	0.1911
V _{GL} (l)	0.0000	0.0032	0.0064	0.0097	0.0110	0.0121	0.0129
C _{TG}	0.6702	0.5546	0.4261	0.2819	0.2151	0.1612	0.1224
C _{ETH}	6.0315	4.9911	3.8352	2.5370	1.9355	1.4505	1.1017
C _{EE}	0.0000	0.4476	0.9449	1.5034	1.7622	1.9709	2.1209
C _{GL}	0.0000	0.1492	0.3150	0.5011	0.5874	0.6570	0.7070
I	1.0000	0.8176	0.6148	0.3872	0.2817	0.1966	0.1355
- LN[I]	0.0000	0.2014	0.4864	0.9489	1.2669	1.6264	1.9989

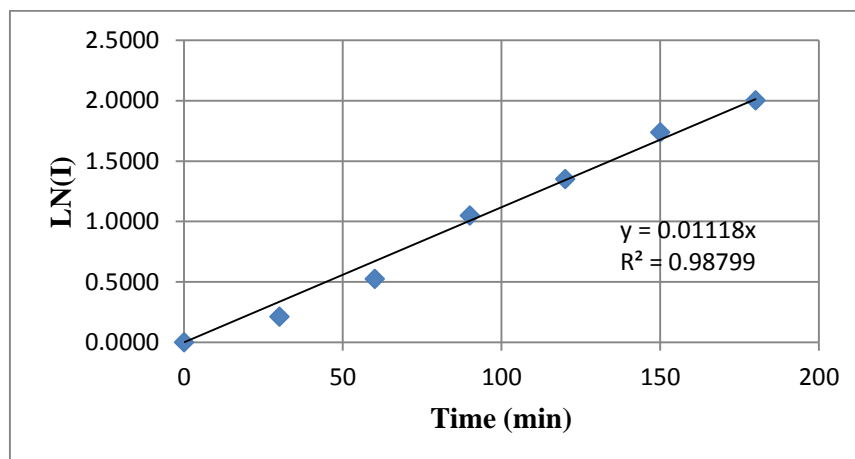


Plot of LN (I) verses Time

From which, $K_{eq} = 17.33$, $k_f + K_b = 0.0107$, $k_f = 0.01012$, $K_b = 0.00058$

For T=90°C

T °C	90 °C						
Time (min)	0	30	60	90	120	150	180
yield %	0	22.2	44.75	67.25	75.15	82	85.3
E. ester Mass (g)	0.00	42.80	86.28	129.66	144.89	158.10	164.46
E. ester (mol)	0.0000	0.1378	0.2778	0.4175	0.4666	0.5091	0.5296
X _{TG}	0.0000	0.2220	0.4475	0.6725	0.7515	0.8200	0.8530
N _{TG} (mol)	0.2069	0.1610	0.1143	0.0678	0.0514	0.0372	0.0304
N _{ET} (mol)	1.8625	1.4491	1.0291	0.6100	0.4628	0.3352	0.2738
N _{GL} (mol)	0.0000	0.0459	0.0926	0.1392	0.1555	0.1697	0.1765
V _{TG} (ml)	0.2000	0.1556	0.1105	0.0655	0.0497	0.0360	0.0294
V _{ET} (ml)	0.1088	0.0846	0.0601	0.0356	0.0270	0.0196	0.0160
V _{bio} (ml)	0.0000	0.0498	0.1003	0.1508	0.1685	0.1838	0.1912
V _{GL} (ml)	0.0000	0.0033	0.0068	0.0101	0.0113	0.0124	0.0129
C _{TG}	0.6702	0.5488	0.4118	0.2586	0.2005	0.1479	0.1219
C _{ETH}	6.0315	4.9395	3.7059	2.3278	1.8041	1.3315	1.0974
C _{EE}	0.0000	0.4698	1.0005	1.5934	1.8187	2.0220	2.1228
C _{GL}	0.0000	0.1566	0.3335	0.5311	0.6062	0.6740	0.7076
I	1.0000	0.8085	0.5923	0.3507	0.2589	0.1760	0.1350
- LN[I]	0.0000	0.2125	0.5238	1.0479	1.3515	1.7373	2.0028



Plot of LN (I) verses Time

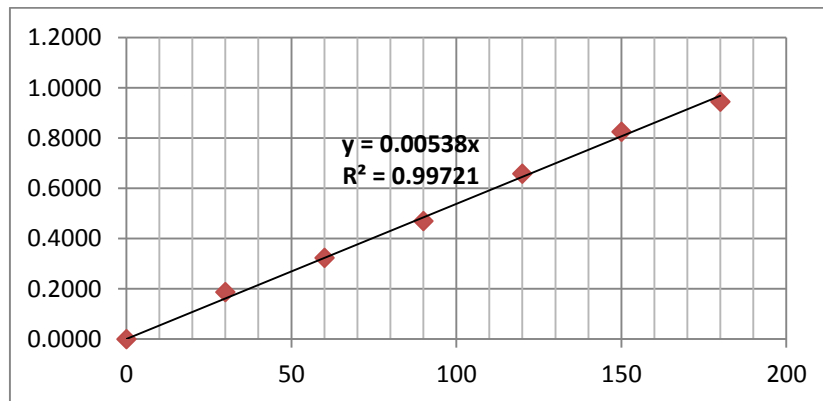
From which, Keq= 17.41, k_f+K_b = 0.01118, k_f = 0.01057, K_b= 0.00061

$$\text{Where in all cases } I = \left\{ \frac{\left(\frac{C_{EEe}}{C_{TGe}} + 1 \right) C_{TG} - (C_{TG0} - C_{EE0})}{\left(\frac{C_{EEe}}{C_{TGe}} C_{TG0} + C_{EE0} \right)} \right\}$$

Appendix A2: Yield, Amount and Concentration of reaction components for Transesterification reaction of Sunflower oil with Ethanol for temperatures $T=35^{\circ}\text{C}$, 80°C and 90°C

For $T=35^{\circ}\text{C}$

Triglyceride	ml	gram	mole	E_{THO}	mole		
TG ₀		250	0.282348		3.3882		
T °C	35 °C						
Time (min)	0	30	60	90	120	150	180
yield %	0	18.8	29.4	38.6	48	54.6	58.5
E. ester Mass (g)	0.00	49.46	77.34	101.55	126.27	143.64	153.90
E. ester N _C (mol)	0.0000	0.1593	0.2491	0.3270	0.4066	0.4625	0.4956
X _{TG}	0.0000	0.1880	0.2940	0.3860	0.4801	0.5461	0.5851
N _{TG} (mol)	0.2823	0.2293	0.1993	0.1733	0.1468	0.1282	0.1172
N _{ET} (mol)	3.3882	2.7511	2.3919	2.0802	1.7617	1.5380	1.4059
N _{GL} (mol)	0.0000	0.0531	0.0830	0.1090	0.1355	0.1542	0.1652
V _{TG} (ml)	0.2729	0.2216	0.1926	0.1675	0.1419	0.1239	0.1132
V _{ET} (ml)	0.1979	0.1607	0.1397	0.1215	0.1029	0.0898	0.0821
V _{bio} (ml)	0.0000	0.0575	0.0899	0.1181	0.1468	0.1670	0.1789
V _{GL} (ml)	0.0000	0.0039	0.0061	0.0079	0.0099	0.0112	0.0120
C _{TG}	0.5997	0.5168	0.4653	0.4176	0.3657	0.3270	0.3033
C _{ETH}	7.1968	6.2012	5.5842	5.0118	4.3879	3.9239	3.6391
C _{EE}	0.0000	0.3590	0.5814	0.7878	1.0128	1.1801	1.2828
C _{GL}	0.0000	0.1197	0.1938	0.2626	0.3376	0.3934	0.4276
I	1.0000	0.8290	0.7230	0.6246	0.5174	0.4377	0.3888
- LN[I]	0.0000	0.1876	0.3244	0.4706	0.6589	0.8262	0.9447

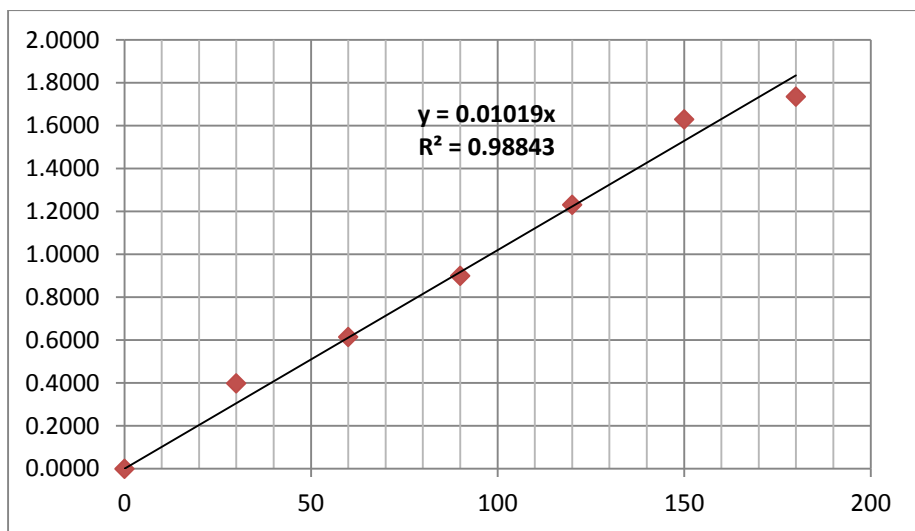


Plot of LN (I) verses Time for $T=35^{\circ}\text{C}$

$$K_{eq} = 4.23, K_f + K_b = 0.00538, K_f = 0.00435, K_b = 0.00103$$

For T=80°C

T	80 °C						
Time (min)	0	30	60	90	120	150	180
yield %	0	39	52.1	64.3	73.9	81.4	82.9
E. ester Mass (g)	0.00	102.60	137.06	169.15	194.41	214.14	218.09
E. ester N _C (mol)	0.0000	0.3304	0.4414	0.5447	0.6260	0.6896	0.7023
X _{TG}	0.0000	0.3900	0.5211	0.6431	0.7391	0.8141	0.8291
N _{TG} (mol)	0.2823	0.1722	0.1352	0.1008	0.0737	0.0525	0.0483
N _{ET} (mol)	3.3882	2.0666	1.6227	1.2093	0.8840	0.6299	0.5791
N _{GL} (mol)	0.0000	0.1101	0.1471	0.1816	0.2087	0.2299	0.2341
V _{TG} (ml)	0.2729	0.1664	0.1307	0.0974	0.0712	0.0507	0.0466
V _{ET} (ml)	0.1979	0.1207	0.0948	0.0706	0.0516	0.0368	0.0338
V _{bio} (ml)	0.0000	0.1193	0.1594	0.1967	0.2260	0.2490	0.2536
V _{GL} (ml)	0.0000	0.0080	0.0107	0.0132	0.0152	0.0168	0.0171
C _{TG}	0.5997	0.4155	0.3419	0.2666	0.2023	0.1486	0.1374
C _{ETH}	7.1968	4.9861	4.1023	3.1997	2.4280	1.7831	1.6493
C _{EE}	0.0000	0.7971	1.1158	1.4412	1.7194	1.9520	2.0002
C _{GL}	0.0000	0.2657	0.3719	0.4804	0.5731	0.6507	0.6667
I	1.0000	0.6717	0.5405	0.4064	0.2918	0.1961	0.1762
- LN[I]	0.0000	0.3979	0.6153	0.9003	1.2315	1.6293	1.7361

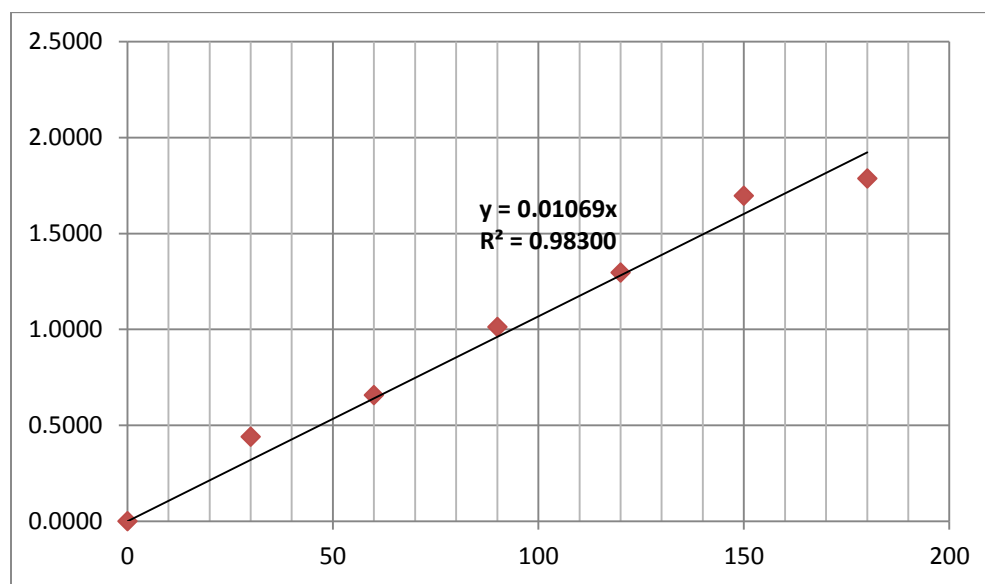


Plot of LN (I) verses Time

Keq= 14.55, Kf+Kb = 0.01019, Kf = 0.00953, Kb = 0.00066

For T=90°C

T	90 °C						
Time (min)	0	30	60	90	120	150	180
yield %	0	42	54.4	68.2	75.6	82.6	83.8
E. ester Mass (g)	0.00	110.49	143.11	179.41	198.88	217.30	220.45
E. ester (mol)	0.0000	0.3558	0.4608	0.5777	0.6404	0.6997	0.7099
X _{TG}	0.0000	0.4200	0.5441	0.6821	0.7561	0.8261	0.8381
N _{TG} (mol)	0.2823	0.1637	0.1287	0.0898	0.0689	0.0491	0.0457
N _{ET} (mol)	3.3882	1.9650	1.5448	1.0772	0.8264	0.5892	0.5486
N _{GL} (mol)	0.0000	0.1186	0.1536	0.1926	0.2135	0.2332	0.2366
V _{TG} (ml)	0.2729	0.1582	0.1244	0.0868	0.0666	0.0475	0.0442
V _{ET} (ml)	0.1979	0.1148	0.0902	0.0629	0.0483	0.0344	0.0320
V _{bio} (ml)	0.0000	0.1285	0.1664	0.2086	0.2312	0.2527	0.2563
V _{GL} (ml)	0.0000	0.0086	0.0112	0.0140	0.0156	0.0170	0.0173
C _{TG}	0.5997	0.3992	0.3282	0.2411	0.1904	0.1397	0.1307
C _{ETH}	7.1968	4.7909	3.9383	2.8931	2.2852	1.6762	1.5682
C _{EE}	0.0000	0.8675	1.1749	1.5517	1.7709	1.9905	2.0294
C _{GL}	0.0000	0.2892	0.3916	0.5172	0.5903	0.6635	0.6765
I	1.0000	0.6442	0.5181	0.3635	0.2736	0.1835	0.1675
- LN[I]	0.0000	0.4398	0.6576	1.0120	1.2961	1.6955	1.7865

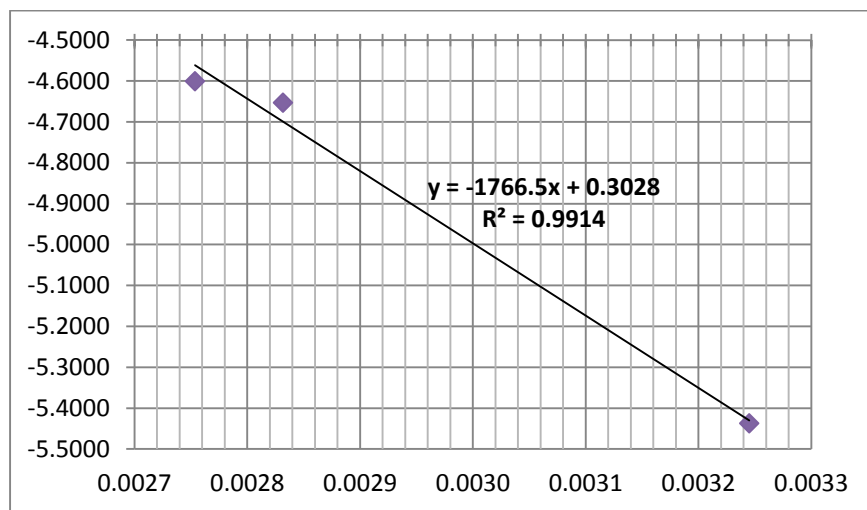


Plot of LN (I) verses Time

Keq= 15.53, Kf+Kb = 0.01069, Kf = 0.01004, Kb = 0.00065

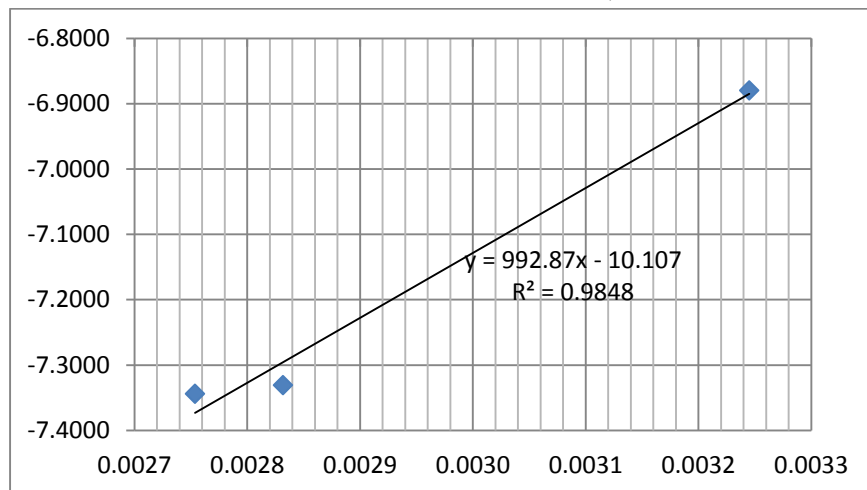
Forward and backward Kinetic rate constants for against reaction temperature

	T	x=(1/T)	K _f	K _b	y= (lnk _f)	y= (lnk _b)
35	308.15	0.0032	0.004351	0.001029	-5.4373	-6.8795
80	353.15	0.0028	0.009535	0.000655	-4.6528	-7.3306
90	363.15	0.0028	0.010043	0.000647	-4.6009	-7.3436



Plot of LN(K) for Forward reaction

$$E_a = 1766.5 \times 8.314 = 14078 \text{ J/mol} = 14.087 \text{ kJ/mol}, A = 2.70$$



Plot of LN(K) for Reverse reaction

$$E_a = 992.87 \times 8.314 = 8254.72 \text{ J/mol} = 8.255 \text{ kJ/mol}, A = 0.141$$

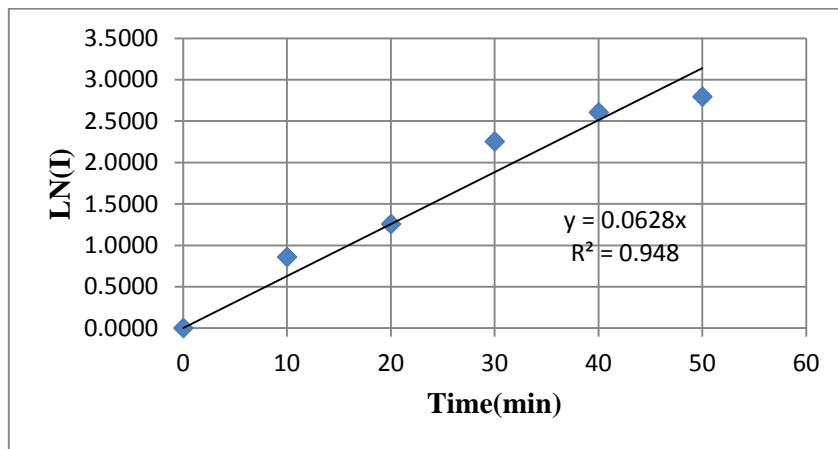
The amount of triglyceride oil per the stoichiometric reaction is $415.4322/3 = 162.15 \text{ mol} = 0.162 \text{ kmol}$ and the amount of Ethanol with 12:1 ration to oil is $0.162 \text{ mol} \times 12 = 1.946 \text{ kmol}$.

The maximum theoretical amount of biodiesel = $415.43 \times 100/82.9 = 501.12 \text{ mol} = 0.501 \text{ kmol}$. The obtained value from the aspen software is 0.451 kmole , implying that $0.451/0.501 = 0.899976$.

Appendix A3: Yield, Amount and Concentration of reaction components for Transesterification reaction of Jatropha oil with Methanol for temperature T= 30°C, 40°C and 50°C

For T=30°C

Triglyceride	ml	gram	mole	Methanol	mole	
TG ₀		50	0.05647	METH ₀	0.508	
T °C	30 °C					
Time (min)	0	10	20	30	40	50
yield %	0	62.5	75	90	92.5	93.5
E. ester, (g)	0.00	31.38	37.66	45.19	46.45	46.95
E. ester N _{EE} (mol)	0.0000	0.1059	0.1271	0.1525	0.1567	0.1584
X _{TG}	0.0000	0.6250	0.7500	0.9000	0.9250	0.9350
N _{TG} (mol)	0.0565	0.0212	0.0141	0.0056	0.0042	0.0037
N _{ET} (mol)	0.5082	0.1906	0.1271	0.0508	0.0381	0.0330
N _{GL} (mol)	0.0000	0.0353	0.0424	0.0508	0.0522	0.0528
V _{TG} (l)	0.0546	0.0205	0.0136	0.0055	0.0041	0.0035
V _{ETH} (l)	0.0297	0.0111	0.0074	0.0030	0.0022	0.0019
V _{Bio} (l)	0.0000	0.0382	0.0459	0.0551	0.0566	0.0572
V _{GL} (l)	0.0000	0.0026	0.0031	0.0037	0.0038	0.0038
C _{TG}	0.6702	0.2925	0.2016	0.0841	0.0635	0.0552
C _{ETH}	6.0315	2.6323	1.8143	0.7565	0.5714	0.4966
C _{ME}	0.0000	1.4624	1.8143	2.2694	2.3491	2.3812
C _{GL}	0.0000	0.4875	0.6048	0.7565	0.7830	0.7937
I	1.0000	0.4234	0.2846	0.1052	0.0738	0.0611
- LN[I]	0.0000	0.8595	1.2567	2.2523	2.6070	2.7957

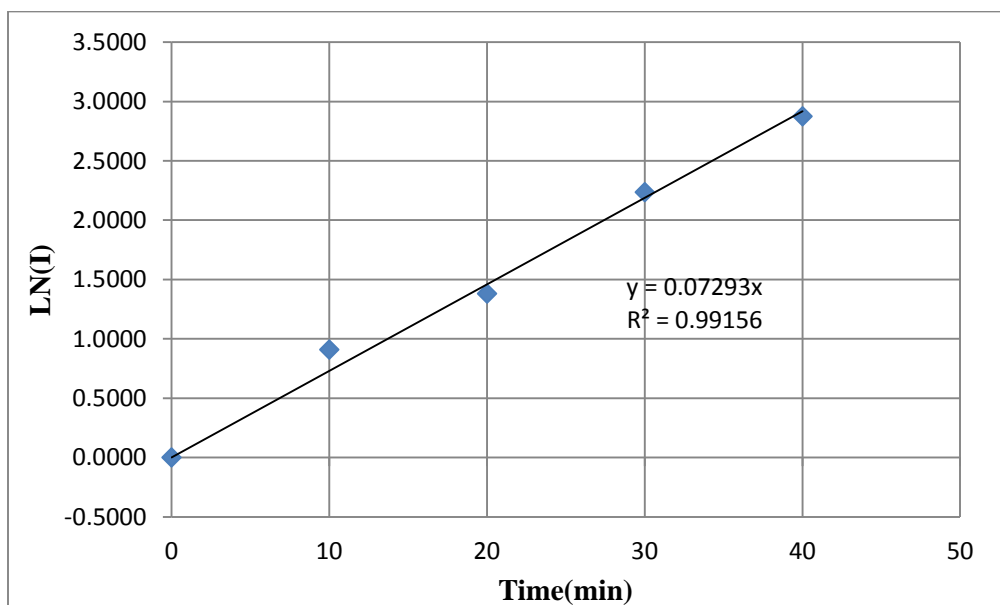


Plot of LN (I) verses Time

Keq= 43.15, Kf+Kb = 0.0628, Kf = 0.06138, Kb = 0.00142

For T=40°C

T °C	40 °C				
Time (min)	0	10	20	30	40
yield %	0	64.5	78	90	94
E. ester Mass (g)	0.00	32.39	39.17	45.19	47.20
E. ester N _C (mol)	0.0000	0.1093	0.1321	0.1525	0.1592
X _{TG}	0.0000	0.6450	0.7800	0.9000	0.9400
N _{TG} (mol)	0.0565	0.0200	0.0124	0.0056	0.0034
N _{ET} (mol)	0.5082	0.1804	0.1118	0.0508	0.0305
N _{GL} (mol)	0.0000	0.0364	0.0440	0.0508	0.0531
V _{TG} (ml)	0.0546	0.0194	0.0120	0.0055	0.0033
V _{ET} (ml)	0.0297	0.0105	0.0065	0.0030	0.0018
V _{bio} (ml)	0.0000	0.0395	0.0477	0.0551	0.0575
V _{GL} (ml)	0.0000	0.0027	0.0032	0.0037	0.0039
C _{TG}	0.6702	0.2783	0.1789	0.0841	0.0510
C _{ETH}	6.0315	2.5051	1.6097	0.7565	0.4591
C _{ME}	0.0000	1.5172	1.9024	2.2694	2.3974
C _{GL}	0.0000	0.5057	0.6341	0.7565	0.7991
I	1.0000	0.4029	0.2513	0.1068	0.0565
- LN[I]	0.0000	0.9091	1.3812	2.2367	2.8743

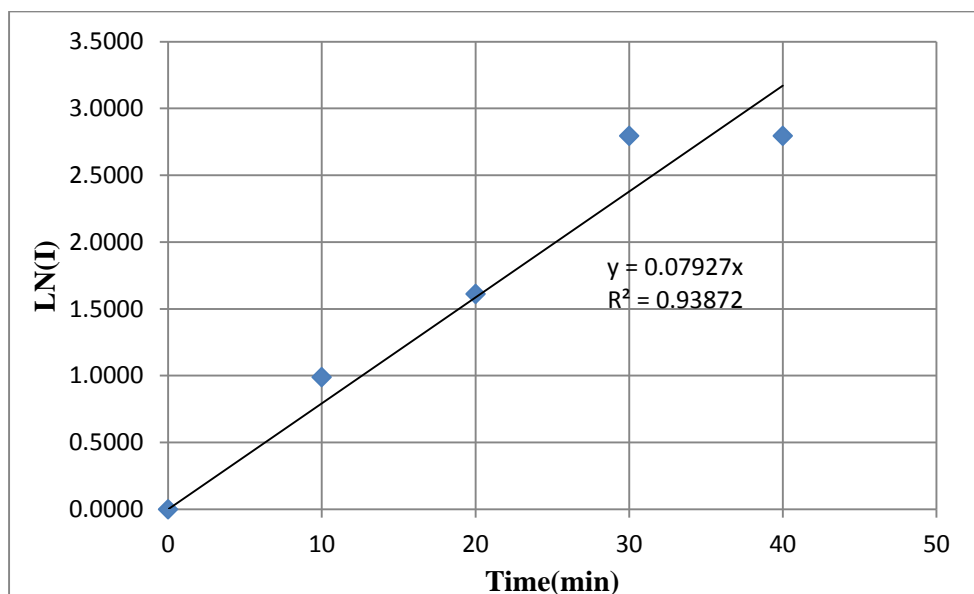


Plot of LN (I) verses Time

Keq= 47.00, Kf+Kb = 0.07293, Kf = 0.07141, Kb = 0.00152

For T=50°C

T °C	50 °C				
Time (min)	0	10	20	30	40
yield %	0	67.25	82.25	93.5	93.5
E. ester Mass (g)	0.00	33.77	41.30	46.95	46.95
E. ester N _C (mol)	0.0000	0.1139	0.1393	0.1584	0.1584
X _{TG}	0.0000	0.6725	0.8225	0.9350	0.9350
N _{TG} (mol)	0.0565	0.0185	0.0100	0.0037	0.0037
N _{ET} (mol)	0.5082	0.1664	0.0902	0.0330	0.0330
N _{GL} (mol)	0.0000	0.0380	0.0464	0.0528	0.0528
V _{TG} (ml)	0.0546	0.0179	0.0097	0.0035	0.0035
V _{ET} (ml)	0.0297	0.0097	0.0053	0.0019	0.0019
V _{bio} (ml)	0.0000	0.0411	0.0503	0.0572	0.0572
V _{GL} (ml)	0.0000	0.0028	0.0034	0.0038	0.0038
C _{TG}	0.6702	0.2587	0.1460	0.0552	0.0552
C _{ETH}	6.0315	2.3279	1.3140	0.4966	0.4966
C _{ME}	0.0000	1.5934	2.0296	2.3812	2.3812
C _{GL}	0.0000	0.5311	0.6765	0.7937	0.7937
I	1.0000	0.3717	0.1997	0.0611	0.0611
- LN[I]	0.0000	0.9896	1.6108	2.7957	2.7957

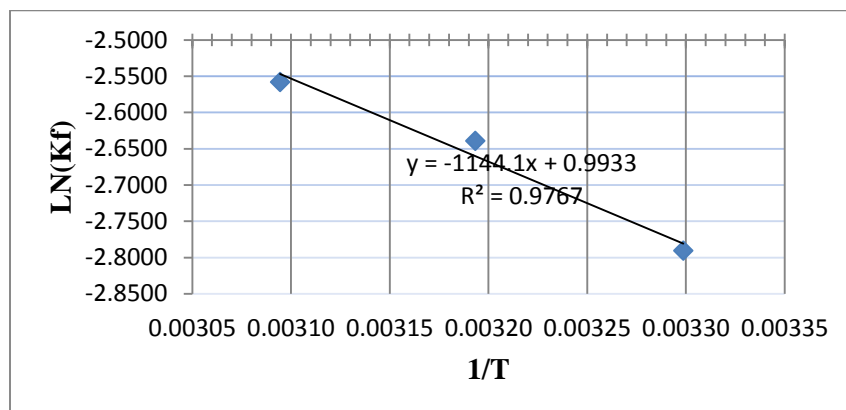


Plot of LN (I) versus Time

Keq= 43.15, Kf+Kb = 0.07927, Kf = 0.07747, Kb = 0.0018

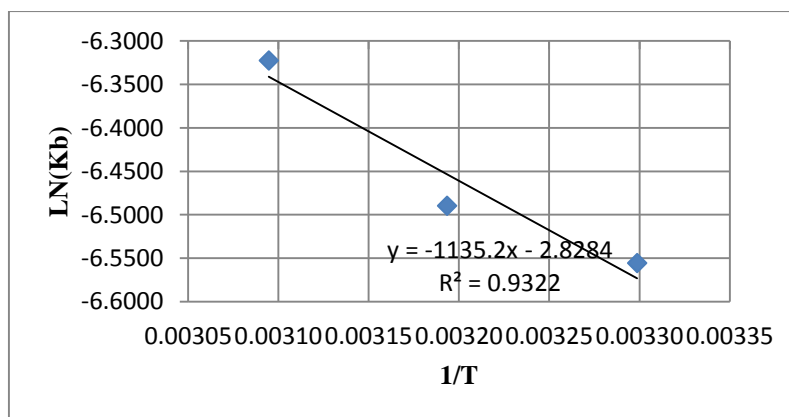
Forward and backward Kinetic rate constants against reaction temperature

	T	x=(1/T)	Kf	Kb	y= (lnkf)	y= (lnkb)	
	30	303.15	0.00330	0.061378	0.001422	-2.7907	-6.5555
	40	313.15	0.00319	0.071411	0.001519	-2.6393	-6.4895
	50	323.15	0.00309	0.077475	0.001795	-2.5578	-6.3226



Plot of LN(K) for Forward reaction

The Activation energy $E_a = 1144.1 \times 8.314 = 9512 \text{ J/mol} = 9.512 \text{ kJ/mol}$, and the Frequency factor $A = 2.70$



Plot of LN(K) for Revers reaction

The Activation energy $E_a = 1135.2 \times 8.314 = 9438 \text{ J/mol} = 9.438 \text{ kJ/mol}$, and the Frequency factor $A = 0.019$

The amount of triglyceride oil per the stoichiometric reaction is $435.2236/3 = 145.074 \text{ mol} = 0.1451 \text{ kmol}$ and the amount of Ethanol with 9:1 ratio to oil is $0.1451 \text{ mol} \times 12 = 1.3057 \text{ kmol}$.

The maximum theoretical amount of biodiesel = $415.43 \times 100/93.5 = 465.5 \text{ mol} = 0.466 \text{ kmol}$. The obtained value from the aspen software is 0.434 kmole , implying that $0.434/0.466 = 0.93133$

Appendix B1: Matlab program for the stoichiometric chemical reaction mass balance

```

a=1; b=3;c=3;d=1;r=3; %coefficients of purified oil,
Ethyl Ester, Glycerol and Molar ratio of Ethanol to Oil
SEt= 789; SOi=916.2; SE=860; SGl=1260; %density of Ethanol, Purified
Oil, Ethyl Ester, and Glycerol respectively in kg/m3 (g/l)
MEt=46.09; MOi=885.432; ME=310.52; MGl= 92.09; %molar mass of Ethanol,
Purified Oil, Ethyl Ester, and Glycerol respectively in g/mole
X=1; VE= 150; %reactor efficiency (conversion
efficiency) of oil and design volume of Ethyl Ester (Biodiesel) resp.
Emo=0; Glmo=0; %Initial amount of Ethyl ester
and Glycerol respectively
Em= Emo+VE*SE/ME; %amount of Ethyl ester
produced in mole
Oim=Em*a/(X*c); %amount of Oil in mole
Etmo=Oim*r; %amount of Ethanol in mole
Glm=Glmo+(Oim*X*d/a); %amount of Glycerol produced
in mole
UOi= Oim*(1-X); %amount of unreacted oil in
mole
ExEt=Etmo-(Oim*X*b/a); %amount of excess ethanol in
mole
Moles =[Oim Etmo Em Glm UOi ExEt];
Mass = [MOi*Oim Etmo*MEt ME*Em MGl*Glm MOi*UOi MEt*ExEt]./1000;
DVolume=[MOi*Oim/SOi Etmo*MEt/SEt ME*Em/SE MGl*Glm/SGl MOi*UOi/SOi
MEt*ExEt/SEt];
R=[(MOi*Oim)+(Etmo*MEt)]./1000;L=[(ME*Em)+(MGl*Glm)+(MOi*UOi)+(MEt*ExEt)]./1000;
A=[Moles;Mass;DVolume];
B=[R L];
Parameters = array2table(A,...

'VariableNames',{'PurifiedOil','Ethanol','Ester','Glycerol','UnreactedOil',...
'ExcessEtanol'},'RowNames',{'Amount in Moles','Mass in Kg','Design Volume
in Lt'})
MassBalace = array2table(B,...
'VariableNames',{'Rightside','Leftside'},'RowNames',{'MassBalance'})

```

Appendix B2: Matlab Program for the design of Helical Coil Heat Exchanger for Recovery of Excess Ethanol

```

mc=0.036215; % mass flow rate of the vapor in kg/sec
Tci=110; Tco=78.26;
Tsi=22; Tso=34;
Prs=5.42; Prc=0.96;
Ks=0.615; Kc=0.0199; Kp=398;
Vds=0.891*10^(-3); Vdsw= 0.653*10^(-3); Vdc=1.03*10^-5;
Ss=996; Sc=1.624;
Cps=4200; Cpc=1600; hfg=838300;
Fs=0.0001; Fc=0.0001;
do=[0.0127, 0.01905, 0.0254, 0.03175];
t=[0.00081, 0.00102, 0.00122, 0.00122];
di=do-(2.*t);
D1=0.35;
Dc=D1+3.15.*do;
Dci=Dc-do; Dco=Dc+do; Rc=Dc./2; P=1.9685.*do;
D2=2.*Dc-D1;
De=((D2.^2-D1.^2).*P)./(do.*sqrt((2*3.1416.*Rc).^2+P.^2))-do;
Q=mc*(Cpc*(Tci-Tco)+hfg);
ms=Q/(Cps*(Tso-Tsi))
Vs=4*ms./(3.1416*Ss*((D2.^2-D1.^2)-(Dco.^2-Dci.^2)));
Res=De.*Vs*Ss/Vds;
if (50<=Res)<=10000
    Nus=0.6.*(Res.^0.5).*(Prs.^0.31);
else
    if Res>10000
        Nus=0.36.*(Res.^0.55).*(Prs.^(1/3)).*(Vds/Vdsw);
    end
end
ho=Nus*Ks./De;
hoi=ho.*(1+3.5.*(di./Dc)); % shell side evaluated
Vc=mc/Sc;
va=4*Vc./((3.1416*di.^2));
Rec=di.*va*Sc/Vdc;
if Rec<3000
    Nus=4.36;
else
    if (3000<=Rec)<=5*10^6
        fc=(0.790.*log(Rec)-1.64).^(-2);
        Nuc=((fc./8).*(Rec-1000).*Prc)./(1+12.7*((fc./8).^0.5)*((Prc^2/3)-1));
    end
end
hi=Nuc*Kc./di; % Coil side heat
transfer coefficient
hic=hi.*(1+3.5.*(di./Dc)); % corrected heat
transfer coefficient for coiled tube
U=((1./hoi)+(1./hic)+(t./Kp)+Fs+Fc).^(-1); % U is Overall
heat transfer coefficient
Tlm=((Tci-Tso)-(Tco-Tsi))/log((Tci-Tso)/(Tco-Tsi)); % Tlm is the Log
mean temperature difference
A=Q./(U*Tlm);
Lc=A./(3.1416.*do);
N=Lc./sqrt((2*3.1416.*Rc).^2+P.^2);

```

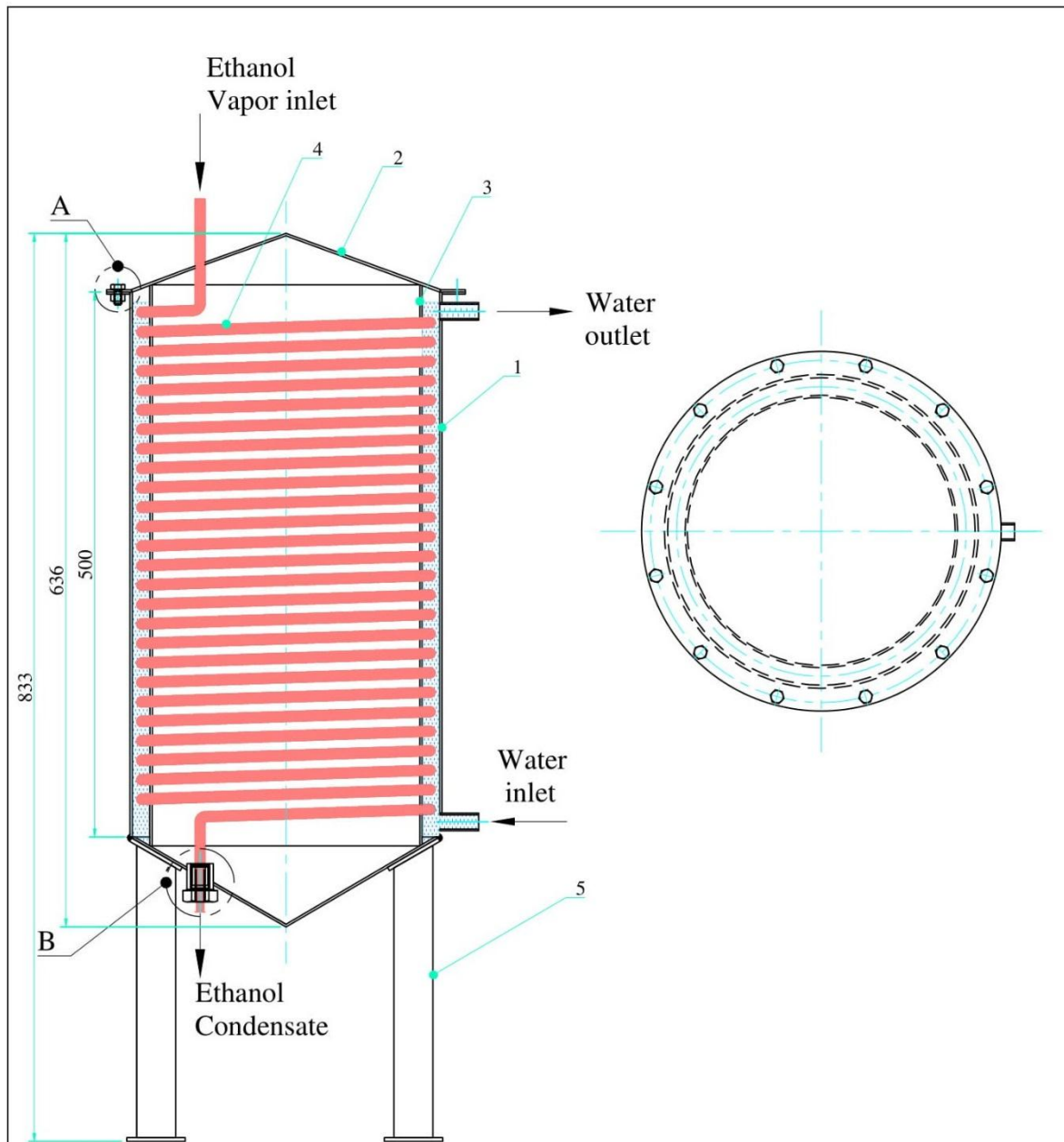
```

H=N.*P+do;
dP=fc.*(Lc+5).*Vdc.*va.^2./(2.*di);
Wp=Vc.*dP;
A=[do; P; Res; Rec; D2; Dc; Lc; H; Wp];
DesignParameters = array2table(A,...

'VariableNames',{'Option1','Option2','Option3','Option4'},'RowNames',{'Tube
outer dia.do in m','Coil Pitch P in m',...
'Shell side Reynolds No.Res','Coil Side Reynolds No.Rec','Inner Dia. D2 of
the shell in m','Coil dia.Dc in m',...
'Coil lenght Lc in m','Height H of the HCHE in m','Coil side Pumping power
Pw in Watt'})

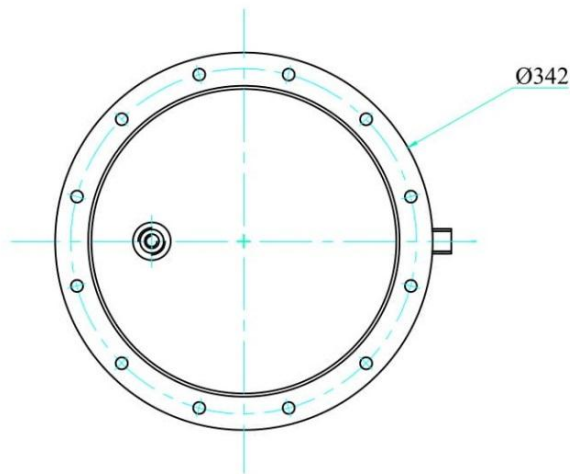
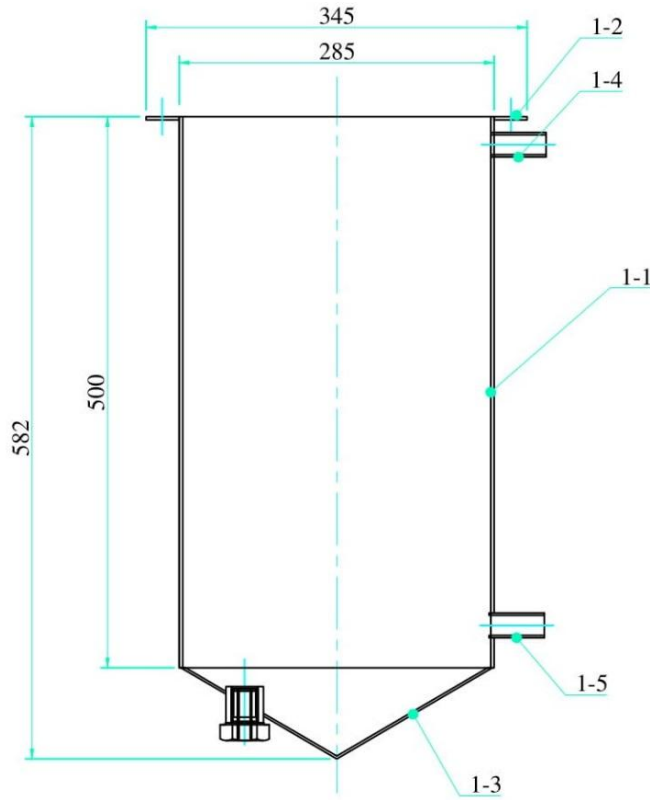
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
Appendix C: Helical Coil Heat Exchanger (Condenser) part drawings

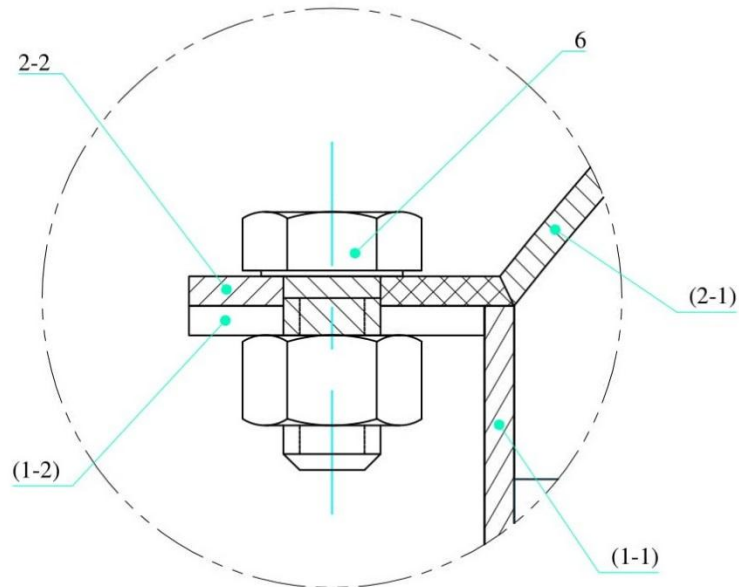


NB. All dimensions are in mm unless specified

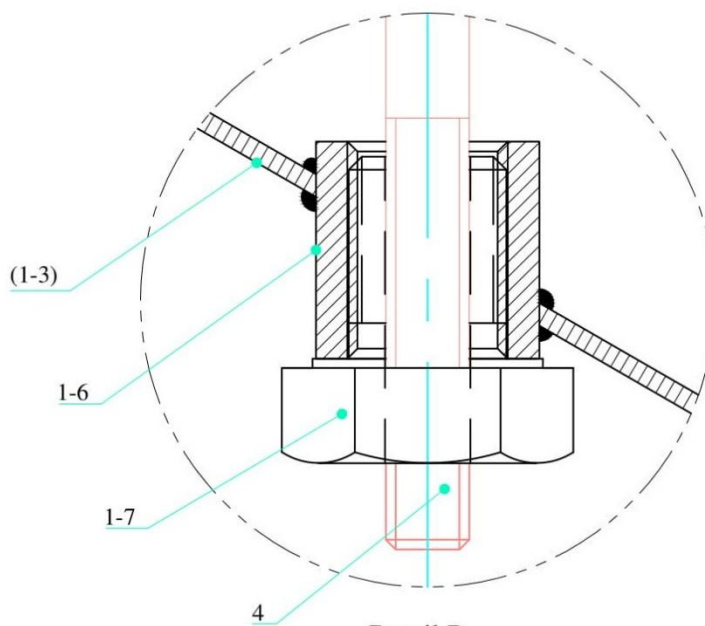
6	Condenser stand	Angle Iron	80x80x5	4
5	Bolt & Nut	Standard	M10	12
4	Helical coil	Copper	$\phi 7.94 \times 25000$	1
3	Condenser shell; inner	Sheet metal	785x516x3	1
2	Shell top cover	Ref. Sub Assy-2		
1	Condenser shell; outer	Ref. Sub Assy-1		
P.No.	Description	Material	DIMENSION	Qty
Client: AAU Mechanical Eng'g Dep't		Reflux Condenser Design	Scale: 1:5	Signature
Project: Small Scale Biodiesel Plant			Designed by: Girma D.	
<p style="text-align: center;">ADDIS ABABA UNIVERSITY ADDIS ABABA INSTITUTE OF TECHNOLOGY</p>		Main Assembly	Checked by: Sine G.	Date: Nov. 2018
			Approved by: Dr. Demis A.	Date: Nov. 2018
		Addis Ababa, Ethiopia	Drawing Number: Mech BD01	



1-5	Coolant/Water inlet	Galvanized steel pipe	1/2"x70	1	
1-4	Coolant/Water outlet	Galvanized steel pipe	1/2"x70	1	
1-3	Outer shell bottom cover	Sheet metal	Ø327x3	1	
1-2	Shell flange	Sheet metal	Ø342x3	1	
1-1	Outer shell	Sheet metal	886x500x3	1	
P.No.	Description	Material	DIMENSION	Qty	
Client:	AAU Mechanical Eng'g Dep't	Reflux Condenser Design	Scale:	1:6	 Signature
Project:	Small Scale Biodiesel Plant		Designed by:	Girma D.	
ADDIS ABABA UNIVERSITY ADDIS ABABA INSTITUTE OF TECHNOLOGY		Sub Assy.-1 outer shell	Date:	Nov.2018	
			Checked by:	Sine G.	
		Date:	Nov. 2018		
		Approved by:	Dr.Demis A.		
		Addis Ababa, Ethiopia	Date:	Nov. 2018	
			Drawing Number:	Mech BD02	



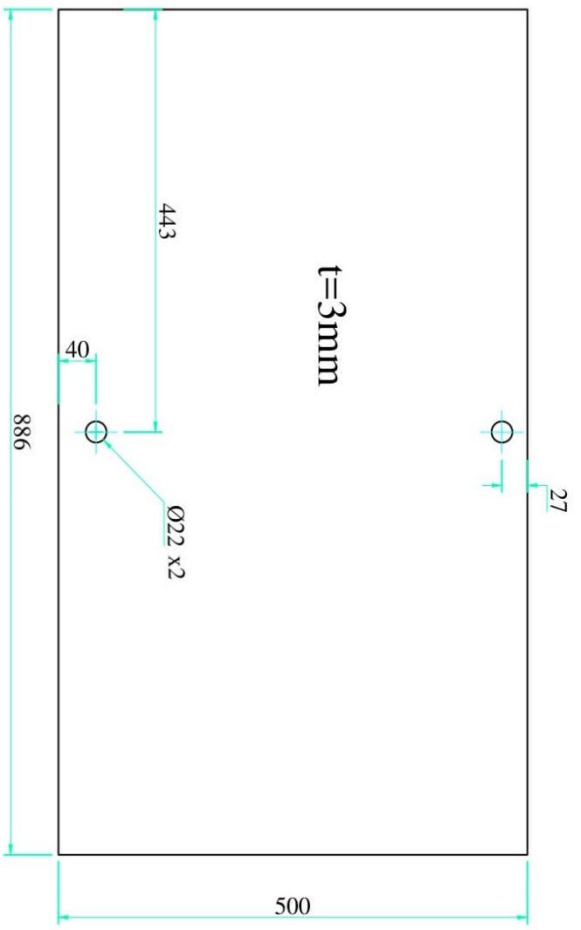
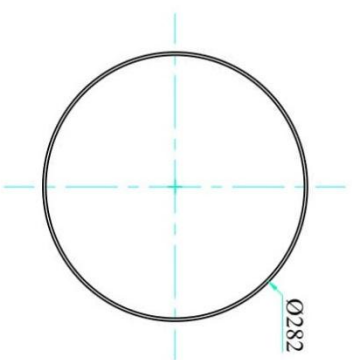
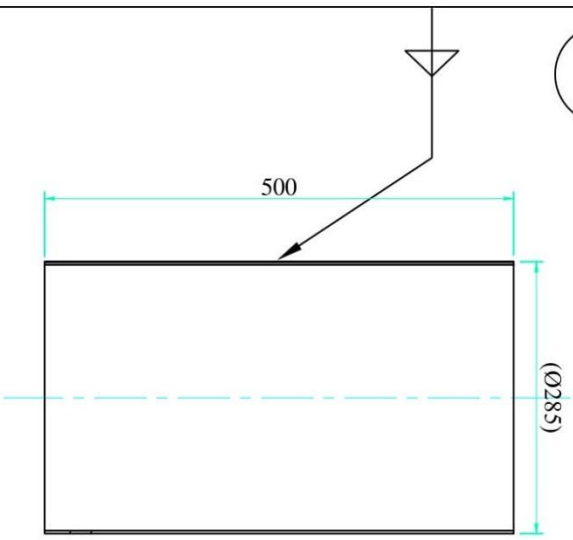
Detail A
Scale: 1.5:1



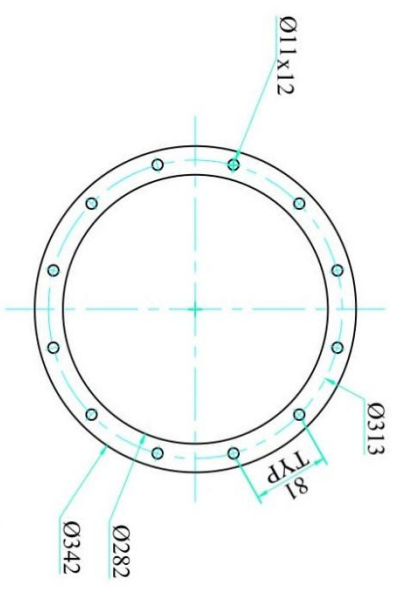
Detail B
Scale: 1:1

1-7	Tube outlet	Bolt, STD	M24	1
1-6	Insert	Round steel rod	Ø34x34	1
P.No.	Description	Material	DIMENSION	Qty
Client: AAU Mechanical Eng'g Dep't		Reflux Condenser Design	Scale: 1:10	Signature
Project: Small Scale Biodiesel Plant			Designed by: Girma D.	
<p align="center">ADDIS ABABA UNIVERSITY ADDIS ABABA INSTITUTE OF TECHNOLOGY</p>		Details	Date: Nov. 2018	
			Checked by: Sine G.	
		Approved by: Dr. Demis A.		
		Addis Ababa, Ethiopia	Date: Nov. 2018	
			Drawing Number: Mech BD03	

1-1

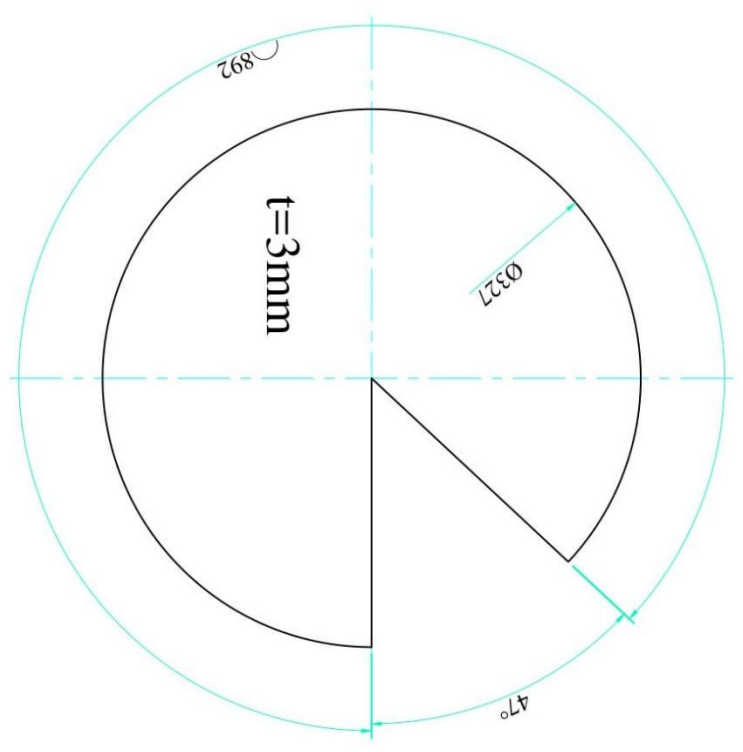
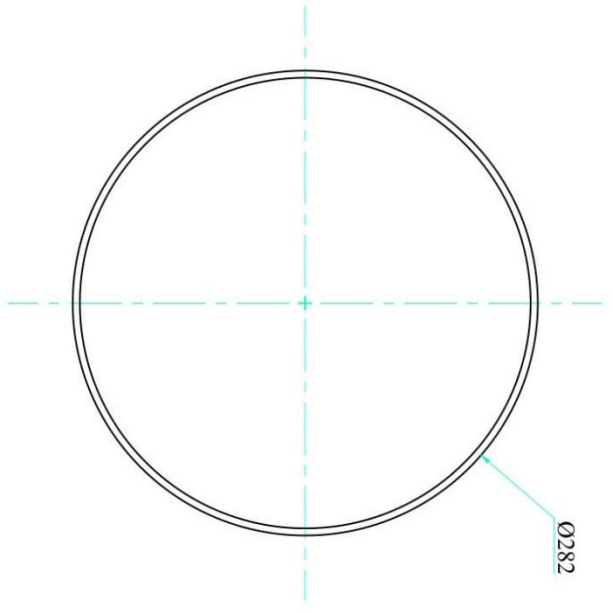
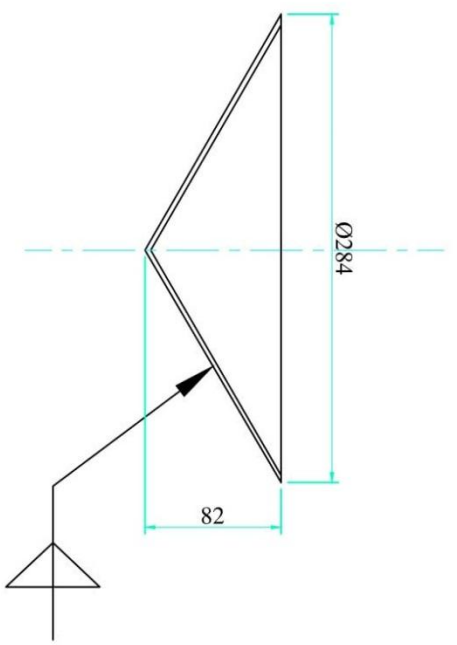


1-2



Client: AAU Mechanical Eng'g Dept		Scale: 1:7		Signature	
Project: Small Scale Biodesign Plant		Designed by: Girma D.		Date: Nov. 2018	
ADDIS ABABA UNIVERSITY ADDIS ABABA INSTITUTE OF TECHNOLOGY		Part Details		Checked by: Sime G.	
		Reflux Condenser Design		Date: Nov. 2018	
Addis Ababa, Ethiopia		Approved by: Dr. Dennis A.		Date: Nov. 2018	
Drawing Number: Mech BD04					

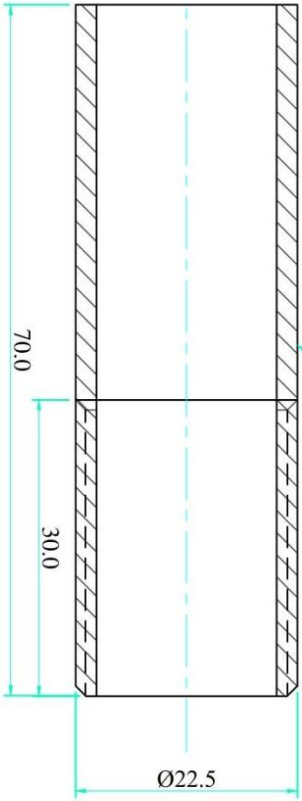
1-3



Client: AAU Mechanical Eng'g Dept'		Scale: 1:4		Signature
Project: Small Scale Biomedical Plant		Designed by: Girma D.		
ADDIS ABABA UNIVERSITY ADDIS ABABA INSTITUTE OF TECHNOLOGY		Reflux Condenser Design		
		Part Details		
		Checked by: Sime G.	Date: Nov. 2018	Approved by: Dr. Demis A.
Addis Ababa, Ethiopia		Drawing Number: Mech BD05		

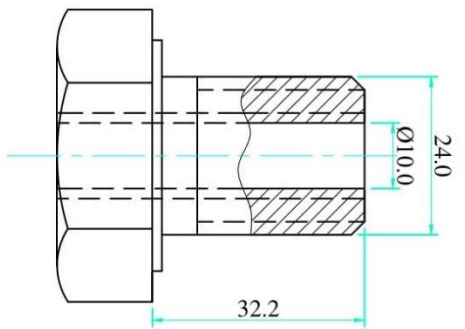
1-4/5

1/2" Galvanized steel pipe

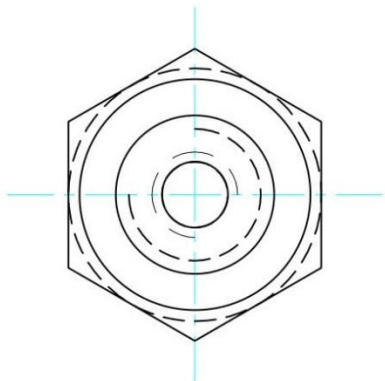


Scale: 3:2

1-7

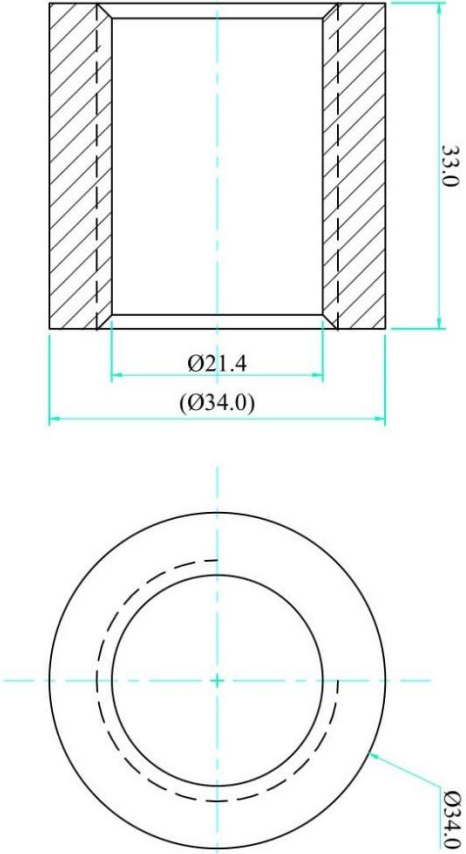


Scale: 1:1

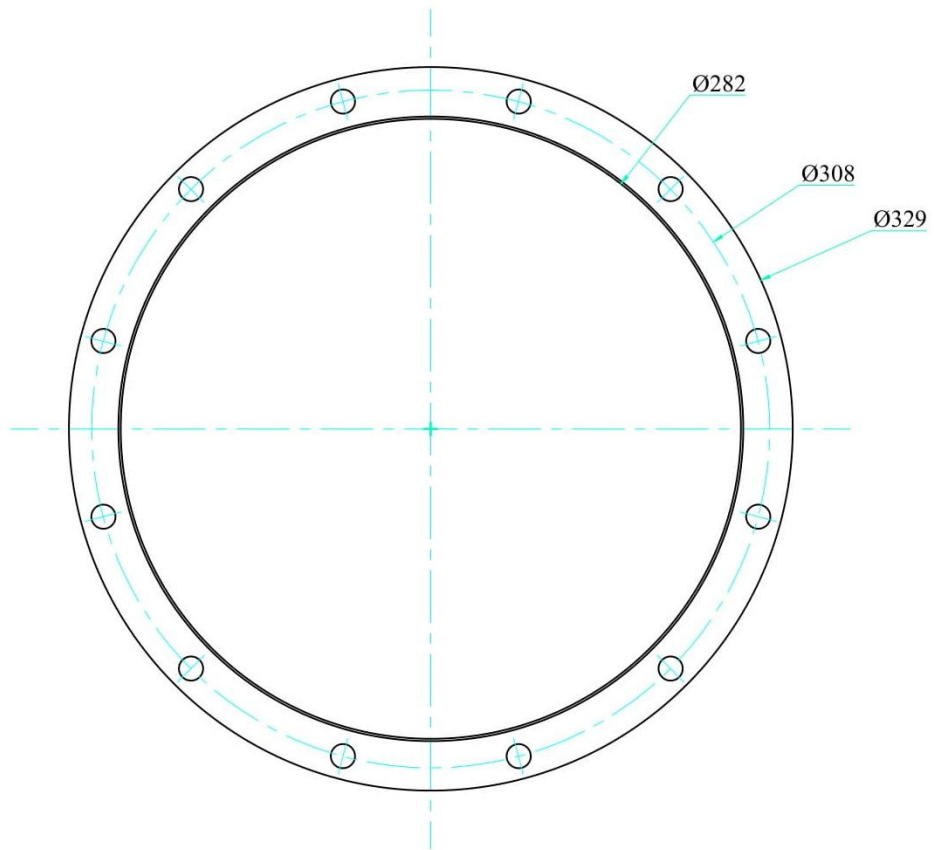
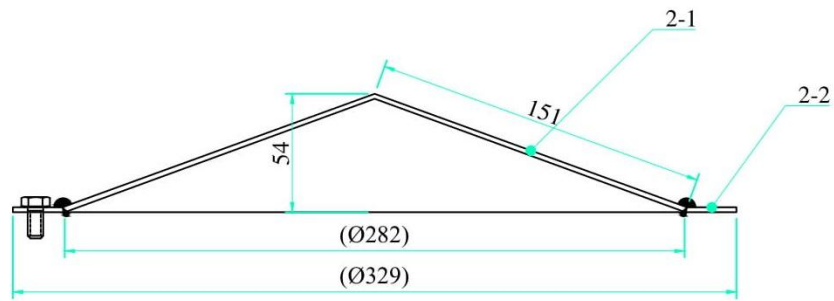


1-6

Scale: 3:2

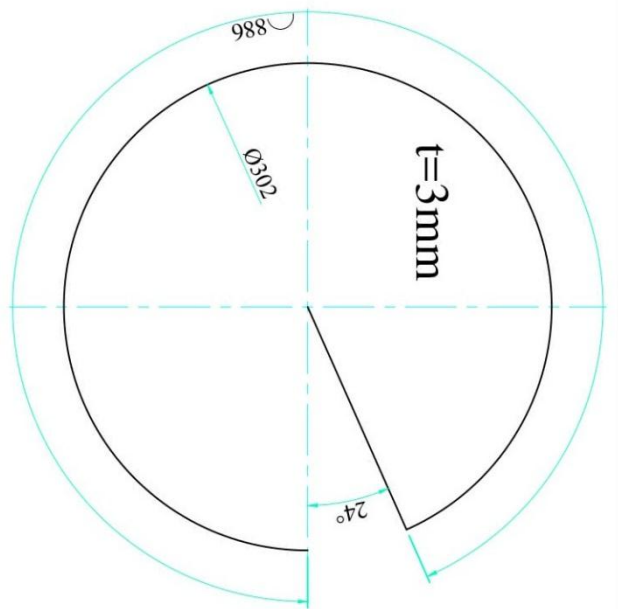
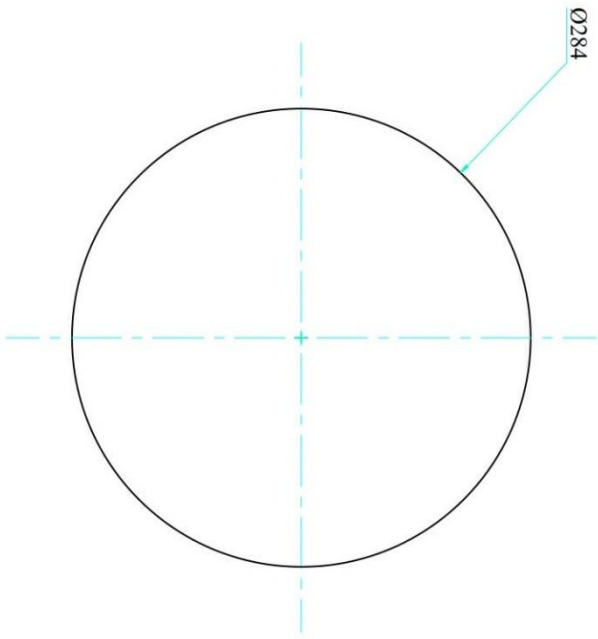
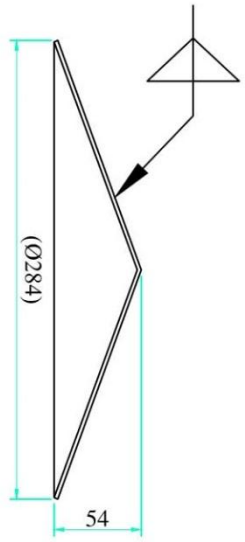


Client:	AAU Mechanical Eng'g Dept'	
Project:	Small Scale Biodesel Plant	
ADDIS ABABA UNIVERSITY ADDIS ABABA INSTITUTE OF TECHNOLOGY		
Reflux Condenser Design Part Details		Scale: 1:10 Designed by: Girma D. Date: Nov. 2018 Checked by: Sime G. Date: Nov. 2018 Approved by: Dr. Dennis A. Date: Nov. 2018 Drawing Number: Mech BD06
Addis Ababa, Ethiopia		Signature

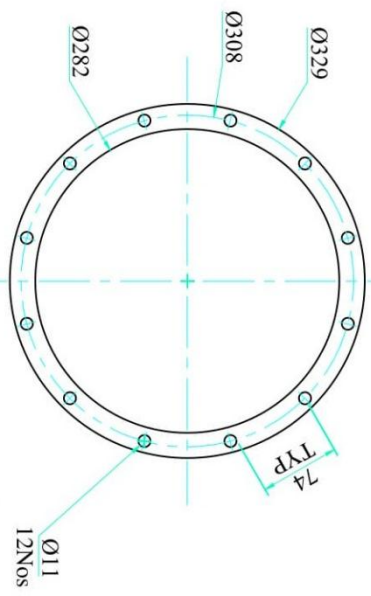





2-2	Cover flange	Sheet metal	Ø329x3	1
2-1	Top cover	Sheet metal	Ø302x3	1
P.No.	Description	Material	DIMENSION	Qty
Client:	AAU Mechanical Eng'g Dep't	Reflux Condenser Design	Scale: 1:3	Signature
Project:	Small Scale Biodiesel Plant		Designed by: Girma D.	
ADDIS ABABA UNIVERSITY ADDIS ABABA INSTITUTE OF TECHNOLOGY		Sub Assy.-2 Top Cover	Date: Nov.2018	
			Checked by: Sine G.	
		Date: Nov. 2018		
		Addis Ababa, Ethiopia	Approved by: Dr.Demis A.	
			Date: Nov. 2018	
			Drawing Number: Mech BD07	

2-1

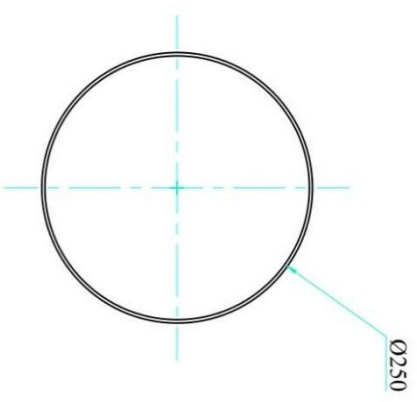
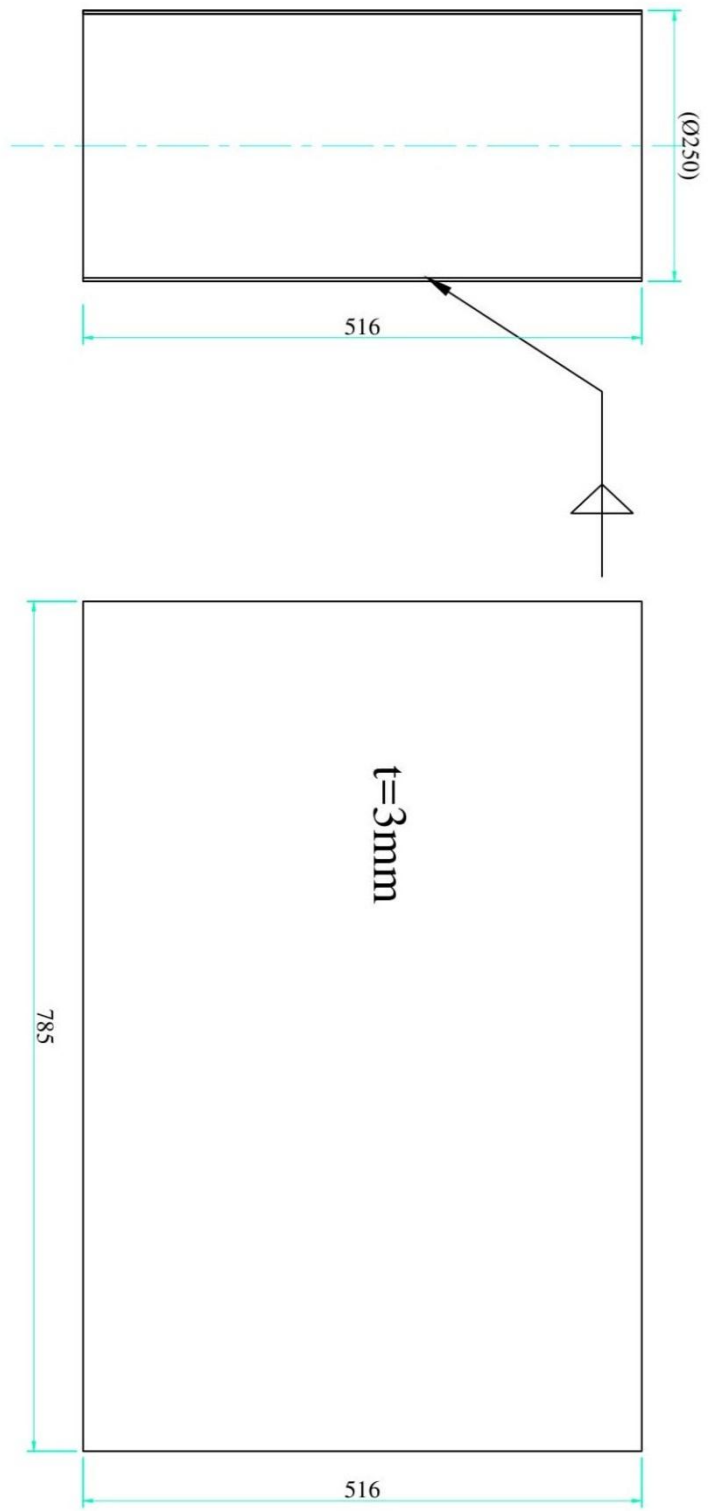


2-2



Client: AAU Mechanical Eng'g Dept		Scale: 1:4		Designed by:  Girma D.		Signature	
Project: Small Scale Biodesel Plant		Date: Nov. 2018		Checked by:  Sime G.		Date: Nov. 2018	
ADDIS ABABA UNIVERSITY ADDIS ABABA INSTITUTE OF TECHNOLOGY		Approved by:  Dr. Demis A.		Date: Nov. 2018		Date: Nov. 2018	
		Addis Ababa, Ethiopia		Drawing Number: Mech BD08			

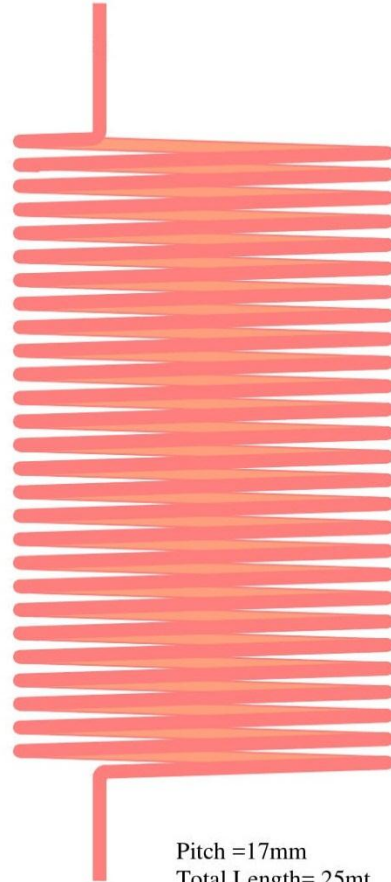
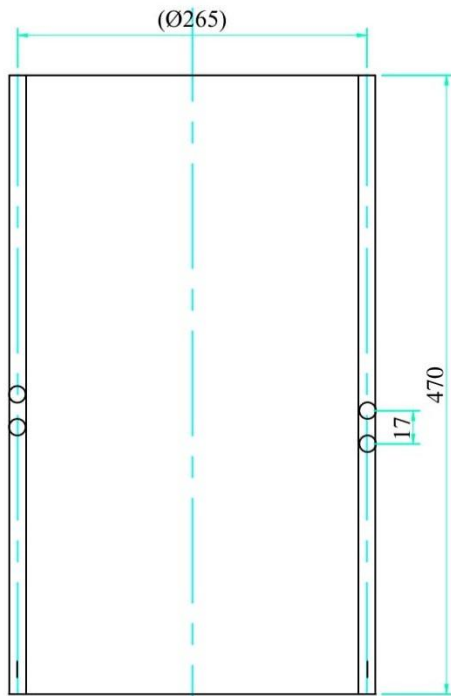
3



Qty=1

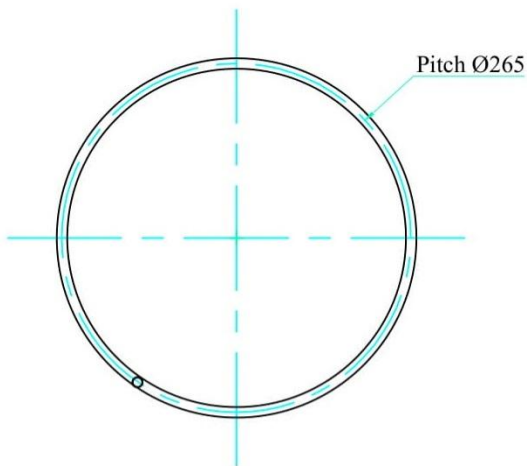
Client: AAU Mechanical Eng'g Dept		Scale: 1:6		Signature	
Project: Small Scale Biodesed Plant		Designed by: Girma D.		Date: Nov. 2018	
ADDIS ABABA UNIVERSITY ADDIS ABABA INSTITUTE OF TECHNOLOGY		Condenser part details		Checked by: Sime G.	
		Addis Ababa, Ethiopia		Date: Nov. 2018	
		Approved by: Dr. Dennis A.		Date: Nov. 2018	
		Drawing Number: Mech BD09			

4



Pitch = 17mm
Total Length = 25mt

Qty=1



Client: AAU Mechanical Eng'g Dep't	Condenser part details	Scale: 1:5		Signature
Project: Small Scale Biodiesel Plant		Designed by: Girma D.		
ADDIS ABABA UNIVERSITY ADDIS ABABA INSTITUTE OF TECHNOLOGY	Copper tube Helical Coil	Date: Nov.2018		
		Checked by: Sine G.		
	Date: Nov. 2018			
	Approved by: Dr.Demis A.			
	Addis Ababa, Ethiopia	Date: Nov. 2018		
		Drawing Number: Mech BD10		