MODELLING AND SIMULATION OF BIODIESEL PRODUCTION FROM JATROPHA
A DISSERTATION

Submitted in partial fulfillment of the
Requirements for the award of the degree
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in

CHEMICAL ENGINEERING

(with specialization in Hydrocarbon Engineering)

By

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DECLARATION

I hereby declare that the work being presented in the seminar report entitled "Modelling and Simulation of Biodiesel Production from Jatropha " in partial fulfillment of the requirements for the award of the degree of M.Tech (With Specialization in Hydrocarbon Engineering) and submitted in the department of Chemical Engineering of the Indian Institute of Technology Roorkee, is an authentic record of my own work carried out during the period from January 2015 to May 2016 under the supervision of Dr. V. K. Agarwal, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, India.

The matter presented in this report has not been by me for the award of any other degree of this or any other institute.

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CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

Biodiesel is proving to be an excellent alternative for the conventional diesel fuels. The qualities offered by biodiesel such as being non-toxic, renewable and eco-friendly has motivated many researchers to investigate extensively in the biodiesel production related fields. Edible oils as well as non-edible oils are being used for biodiesel production. Amongst non-edible oils, Jatropha Curcas is being looked upon as a promising source for biodiesel production. This is because Jatropha plant doesn't require fertile lands. They have the ability to grow in a harsh environment. Reaction coupled with distillation in a single vessel is a recent advancement in the biodiesel production. Reactive distillation column (RD column) is the fusion of two major equipment; a reactor and a distillation column. Reactive distillation column has proven to be very effective in terms of energy requirements and operating expenses. The Jatropha oil contains a high percentage of oleic acid and triglycerides. Biodiesel can be produced directly by oleic acid esterification or by triglycerides alcoholysis. This current study focuses on the transesterification of triglycerides from the Jatropha Curcas oil with methanol to produce methyl ester i.e. biodiesel in the reactive distillation column. RADFRAC column from the ASPEN PLUS library has been used for the simulation of the reactive distillation column. Equilibrium stage model has been used for the simulation purpose. The main motive of this work is to study the effect of vital parameters like reflux ratio, condenser pressure, distillate rate etc. on the reactive distillation column performance and suggest the optimum conditions for a reactive distillation column so as to get maximum biodiesel yield.

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NOMENCLATURE

$N = Number\ of\ trays$

$c = Number\ of\ components$

$i = Component\ number$

  $= 1,2,\dots c$

$j = Tray\ number$

  $= 1,2,\dots N-1$

$r = Specific\ reaction\ number$

  $= 1,2,\dots R$

$r_{j,i} = Reaction\ rate\ on\ the\ tray\ j\ for\ component\ i,(mol/s)$

$R_j = Total\ number\ of\ moles\ generated\ or\ disappeared\ through\ reaction\ on\ tray\ j$

$\delta_j = Refers\ to\ reaction\ occurence\ on\ tray\ j$

$$= \begin{cases} 0, when\ no\ reaction\ occurs\ on\ tray\ j \\ 1, when\ reaction\ occurs\ on\ tray\ j \end{cases}$$

$v_{r,i} = Stoichiometric\ coefficient\ of\ component\ i\ for\ reaction\ r$

$H_j = Molar\ holdup\ on\ tray\ j,(moles)$

$k_{fj} = Forward\ rate\ constant\ on\ tray\ j,(kmol\ s^{-1}kmol^{-1})$

$k_{bj} = Backward\ rate\ constant\ on\ tray\ j,(kmol\ s^{-1}kmol^{-1})$

$x_{j,A} = Mole\ fraction\ of\ component\ A\ on\ tray\ j$

$x_{j,B} = Mole\ fraction\ of\ component\ B\ on\ tray\ j$

$x_{j,c} = Mole\ fraction\ of\ component\ D\ on\ tray\ j$

$x_{j,D} = Mole\ fraction\ of\ component\ D\ on\ tray\ j$

$E_f = Activation\ energy\ for\ forward\ reaction,(\frac{kJ}{mol})$

E_b = Activation energy for backward reaction, $\left(\frac{kJ}{mol}\right)$

T_j = Temperature on tray j, (K)

R = Universal gas constant, $\left(\frac{kJ}{mol\ K}\right)$

A_f = Rate constant for forward reaction

A_b = Rate constant for backward reaction

V_j = Vapour flow rate on tray j, $\left(\frac{mol}{s}\right)$

L_j = Liquid flow rate on tray j, $\left(\frac{mol}{s}\right)$

ΔH_v = Heat of vapourization, $\left(\frac{kJ}{mol}\right)$

ΔH^R = Heat of reaction, $\left(\frac{kJ}{mol}\right)$

h^L = Partia molar enthalpy of liquid, $\left(\frac{kJ}{mol}\right)$

h^V = Partial molar enthalpy of vapour, $\left(\frac{kJ}{mol}\right)$

h^f = Partial molar enthalpy of feed, $\left(\frac{kJ}{mol}\right)$

W = Weight of catalyst, (kg)

F_j = Input feed flow rate on feed tray j, $\left(\frac{mol}{s}\right)$

$z_{j,i}$ = Liquid fraction of component i in the feed on tray j, (% mole fraction)

ϕ = Fugacity coefficient(= 1, since here vapour phase is assumed as ideal)

γ = Characteristic liquid phase non − ideality coefficient

P^0 = Saturated vapour pressure

P = Total pressure

INTRODUCTION

1.1) <u>OVERVIEW</u>

In order to develop an economy,energy is the basic requirement. It is needed everywhere in India in areas like agriculture, industry,transport, commercial and household needs. After independence, development plans were made which required a great deal of energy usage. Thus,it leads to a steady rise in the energy consumption in the country . And because of this, we have been greatly dependent on the fossil fuels like crude oil, coal, natural gas [D. Ahuja, 2009]. Excess use of these non-renewable sources is resulting in the environment degradation. Global warming, climate changes etc. are the results of excess use of fossil fuels. Also, there has been a rise in the oil prices all over the world which makes it important to look for an alternative for fossil fuels. Therefore, many researchers from all over the world are seeking alternative sources to replace petrol fuel. And biodiesel is one of the solutions.

Biodiesel fuel recently has attracted a lot of attention throughout the world and has been firmly recommended as a substitute for petroleum diesel [Koh and Ghazi, 2011]. The National Soy Diesel Development Board of U.S.A.in the year 1992 invented biodiesel. Since it has similar characteristics as of petroleum oil, biodiesel can be blended with it [Ramadhas et al., 2004]. Vegetable oils, animal fats are some of the biological sources from biodiesel can be produced [Leung et al., 2009]. Oil from vegetable and animal fats is extracted and is put into use an alternative for fossil fuel. It usually contains free fatty acids, phospholipids, sterols, water, odorants other impurities [Koh et al., 2011]. During transesterification reaction of triglycerides, free fatty acids and water contents causes soap formation, consume catalysts and reduce its effectiveness and result in lower conversion.

Biodiesel reduces overall CO_2 emission because it is produced via plants and thus gets carbon-dioxide from the air during photosynthesis. Life cycle analysis showed that overall CO_2 emissions are reduced by 78% when biodiesel is utilized as opposed to petroleum-based fuel [Van Gerpen, 2005]. Prospects of acid rain has increased greatly due to decomposition of sulphuric, carbonic, and nitric acids into the atmosphere. Further pollutants,like oxygen oxides, sulphur dioxide, turbulent organic compounds and heavy metals, generated by the use of fossil

fuels are very harmful to our health and environment. Sulphur is the main contaminant in petroleum oil. Excessive sulphur levels in petroleum diesel are inimical to the environment via low-level pollution such as smog. The lubricity of fuel is largely decreased because of sulphur removal from diesel oil and in turn results in decrease in engine efficiency. Biodiesel can be used to reclaim appropriate level of lubricity as per study.

1.2) BIODIESEL

Biodiesel is interpreted as mono alkylesters of vegetable oils, animal fats and waste cooking oil produced via transesterification process [Silitonga et al., 2013]. Biodiesel is found to be ecological, bio-degradable, renewable and harmless when set side by side to petroleum diesel. Biodiesel is a variety of ester-based oxygenated fuels derived from natural renewable biological sources like vegetable oils. The name of biodiesel itself advocates its use in the conventional diesel engine. Biodiesel has proven to be advantageous in compression combustion systems that use petroleum diesel and it has also been reported that no need arises for engine modifications in order to use biodiesel [Pinnaret and Savage, 2008]. Also it can maintain the payload capacity similar to conventional diesel oil. Contrary to fossil fuel pure biodiesel is biodegradable, innocuous & free of aromatics. The estimated biodiesel requirement in India is presented in the table 1.1 [Azam et al., 2005].

Table 1.1 Estimated biodiesel requirement in India

Year	Diesel requirement, MMT	Biodiesel requirement blending, MMT		
		5%	10%	20%
2004-05	46.97	2.35	4.70	9.40
2006-07	52.33	2.62	5.23	9.92
2011-12	66.90	3.35	6.69	13.38

Benefits of biodiesel

1. Can be obtained from tenable or inexhaustible biological sources

2. Sulphur free, less CO, HC, particulate matter and aromatic compounds emissions

3. Ecological and oxygenated fuel

4. Fuel properties similar to the conventional fuel

5. Can be managed in existing blunt diesel engines

6. Non-toxic, biodegradable and safe to handle.

The oils that are promising for biodiesel production are vegetable oil, animal fat and used cooking oil. Animal fat is impractical as it gets converted to solid wax at room temperature and thus create complications during reaction [Juan et al., 2011]. Waste cooking oil is a blend of animal and vegetable oils. Impurities like polymers, free fatty acids corrupts the waste cooking. For the biodiesel production, diversified vegetable oils are available. And as they are sustainable in nature, they can be reproduced. Also they are known to be environmental favourable. The diversified edible oils that can be used for biodiesel production include palm oil, sunflower oil, soybean oil etc. But grave issues have arisen due to the excess use of edible oils because it can lead to an increase in vegetable oil demand and because of this, edible oil prices as well as biodiesel oil prices shall increase. The cost of raw material in biodiesel production accounts for 60–80% of the total production cost. Edible oil may become more costly because of the competition between human devouring and biodiesel market [Balat and Mustafa, 2011]. Deforestation can be caused due to mass procreation of plants producing edible oil and it can further lead to environmental degradation. So to overcome these drawbacks, researchers have focused on non-edible oil for biodiesel production. Some e.g. of non-edible, oil-producing plants are Jatropha curcas (Jatropha), Pongamina pinnata, Madhua indica, Calophyllum inophyllum, Rubber etc. [Parawira, 2010]. Among those plants, *Jatropha* has proven to be the most efficient plant for biodiesel production because of its cost effectiveness [Juan et al., 2011 and Ranganathan et al., 2008].

1.3) <u>JATROPHA CURCAS</u>

Jatropha Curcas is a part of Euphorbiaceous family. American tropics are main domestic region *Jatropha plants* but tropical and sub-tropical countries like sub-Sahara Africa, India, South East Asia, and China are also natural growing habitat for *Jatropha plants*. After flowering, it takes 3-4 months for seeds to generally mature and after becoming a grown tree it can continuously produce seeds for next 50 years. Nearly 45% of the seed content can be used to make oil. The table below contains the fatty acid composition of *Jatropha oil*. In India, almost all the state generally grow *Jatropha Curcas* as a live fence to protect their fields .

Table 1.2 Composition of Jatropha Oil [Jain and Sharma, 2010 and Pinzi et al., 2009]

Fatty acid	Systemic name	Structure	Composition (%)
Palmitic acid	Hexadecanoic acid	C_{16}	13.4–15.3
Stearic acid	Octadecanoic acid	C_{18}	6.4–6.6
Oleic acid	Cis-9-octadenoic acid	$C_{18:1}$	36.5–41
Linoleic acid	Cis-9-cis-12-octadecadeneoic acid	$C_{18:2}$	35.3–42.1
Other acids			0.8

Benefits of Jatropha Crop

1. Can be established easily, fast growth and less care required.
2. Can grow in soils with poor nutrients, also in wastelands other flood effected area and waterlogged areas.
3. Wasteland and degraded land can be restored through its plantation. Fertile lands provide higher yield.
4. Plantation of Jatropha, oil extraction and nursery raising, can be rural based hence it can promote rural economy and also ensure energy security.
5. Favourable for averting soil erosion.
6. Jatropha increases the yield hence it is not a competitor of any other crop.
7. Due to *mycorrhizal* value in *Jatropha* roots, it receives phosphate from soil which is useful for the plant.
8. Boosts the soil fertility throughout their life cycle.
9. Possesses medicinal as well as other multiple uses.
10. Provide the locals villagers with jobs, mitigate the need to migrate to cities for employment.

1.4) REACTIVE DISTILLATION

In reactive distillation viz. RD column, chemical reaction is coupled with distillation of the components. In one part of the column there is a reaction taking place and in the other part distillation takes place which in turn offers distinctive advantages over the conventional, sequence wise approach. Because of the continuous letting out of reaction products from the reactive zone, this RD column proves to be very beneficial; specifically for equilibrium limited reactions like esterification, hydrolysis etc. And also it leads to an increase in conversion. This in turn reduces capital and operations costs [Kiss et al., 2012]. Also it can play a vital role in sustainable development. It also helps in decreasing the consumption of resources like heat

requirements etc. The working of a RD column is affected by various parameters like reflux ratio, feed location, stage pressure, stage temperature, size of trays, packing used in the trays, location of reactive column sections as well as location of non-reactive column sections. While performing simulation of a RD column, sensitivity analysis is generally performed. This makes it easier for us to know the optimum conditions required for getting the desired biodiesel yield. Then it can further be scaled-up.

Benefits of reactive distillation

1. Processing speed is increased
2. Energy requirements, operational costs are decreased
3. Fewer waste products are formed
4. Enhanced product quality
5. Heat expelled can be reused for the reboiler
6. Increase in product selectivity
7. Fewer by-products formation

1.5) CATALYSTS

1.5.1) Homogeneous Catalysts

Homogeneous catalyst is the catalyst which is in the same phase as that of the reactants i.e. if the reactants are in liquid phase then the catalyst is in liquid phase, if the reactant is in gaseous phase then the catalyst is also in gaseous phase. In biodiesel production, heterogeneous as well as homogeneous catalyst are used. But, generally heterogeneous catalyst are preferred over homogenous catalyst in biodiesel production [Melero et al., 2009]. Because removal of impurities and by-products is difficult in case of homogeneous catalyst compared to heterogeneous catalyst. The reactions are proceeded unto an intermediate complex. Also the reactions are often highly selective. Separation is what makes its use difficult.

1.5.1.1) Homogeneous Base-Catalyst Transesterification

Alkaline metal hydroxides are generally preferred for transesterification reaction to produce biodiesel [Leung et al., 2010]. Metal alkoxides, metal carbonates can also be used. Study has shown that alkaline catalysts show a better performance over alkoxides and carbonates [Lee et al., 2009]. Alkaline oxides gave a better yield for raw materials having high free fatty acid

contents (FFA < 1 wt. %) and moisture content < 0.5 wt. % [Sharma et al., 2008]. Sodium and Potassium hydroxides are generally preferred. When alkaline hydroxides like NaOH and KOH are used, reaction time is increased. But when we use metal alkaline alkoxides like sodium alkoxide, yield greater than 98 % can be obtained, as per the study. Alkaline alkoxides are the most reactive catalysts and reaction can be completed in a very short time as short as half an hour [Demirbas, 2008]. Alkaline hydroxides are cheaper but show lesser reactivity whereas alkaline alkoxides are costlier but show greater reactivity. In order to increase the yield of methyl oleate or biodiesel, we have to increase the quantity of alkaline hydroxides. Typical base concentrations for optimum biodiesel yield is 0.3 to 1.5 % for alkaline hydroxides while for alkaline alkoxides the concentration should be 0.5% or less. Although base catalyst is cheaper, it cannot directly be used when oil or fats contains high quantity of FFAs i.e.>1 wt. % [Ma & Hanna, 1999]. It is only suitable for oils having FFA content < 1 wt. %. It is the major disadvantage of base catalyst. This happens because if a large amount of FFA is present in the oil, the neutralization reaction between acid and base produces soap. And because of the saponification problem, the catalyst activity decreases. Also, the soap formation hinders the glycerol separation from the reaction mixture. And also it interferes with the biodiesel purification. On commercial scale though, base catalysts are preferred over acid catalysts in case oils containing low FFA contents.

1.5.1.2) Homogeneous Acid-Catalyst Transesterification

They can be used in the transesterification reaction of oils containing high FFA contents like Jatropha oil, waste cooking oil, tobacco oil, rubber etc. Strong acids like sulfuric, hydrochloric and phosphoric acids are generally favoured over base catalyst for oils having high FFA contents i.e. > 1 wt. %. Because they don't form soap like the base catalysts. However, acid-catalysts are very sensitive to the water. Even if the water content in the oil is as less as 0.1 wt. %, the biodiesel was decrease [Vicente et al., 2004]. Various studies have revealed that on using acid catalyst for the transesterification of Jatropha oil with methanol with Jatropha oil having some moisture content, then its yield was affected. Other drawbacks of using acid catalyst for transesterification include high temperature requirement and long reaction time. Acids also corrode the vital equipment parts. Generally, acid-catalyst transesterification is usually preferred at the following conditions: a high molar ratio of methanol to oil of 12:1; high temperatures of 80–100 °C; and a strong acid viz. sulfuric acid. For this operating conditions, biodiesel yield as high as 95% was obtained.

1.5.2) Heterogeneous Catalyst

In heterogeneous catalysis, the catalyst is in different phase as opposed to the phase of reactants. They can be in solid, liquid or gaseous phase. Oil and water are also considered as heterogeneous catalysts. Heterogeneous catalysts subdue the disadvantages of the homogeneous catalysts like product separation, biodiesel purification etc. There are various solid catalysts like zeolites, metal oxides, hydrotalcites, composite materials, clays etc. Heterogeneous catalysts are divided into acid catalysts and base catalysts. In heterogeneous catalyst case also, solid base catalyst prove superior to solid acid catalyst [Jothiramalingam & Wang, 2006]. Examples of solid base catalysts are oxides of Ca, Mg, Ba etc., and alkaline modified zirconia catalysts like Mg/ZrO_2, Ca/ZrO_2, Sr/ZrO_2 etc., tri potassium phosphate, tri sodium phosphate and metal oxides supported on silica. Whereas, solid acid catalyst include sulphated zirconia, Nafion-NR50, tungsted zirconia etc.

1.6) BIODIESEL PRODUCTION PROCESS OVERVIEW

1) Pre-treatment of Jatropha oil: Raw Jatropha Curcas Oil is firstly filtered to remove all the impurities. Then the filtered Jatropha Oil is heated so as to remove the moisture content, if any, from the oil.

2) Transesterification reaction: The treated Jatropha Curcas Oil is then reacted with alcohol esp. methanol or ethanol in presence of a catalyst. The catalyst used can be a homogeneous catalyst or a heterogeneous catalyst. The transesterification reaction produces fatty acid methyl esters (FAME) and glycerol. FAME is basically the biodiesel.

The transesterification reaction is as follows [Burno et al., 2006]:
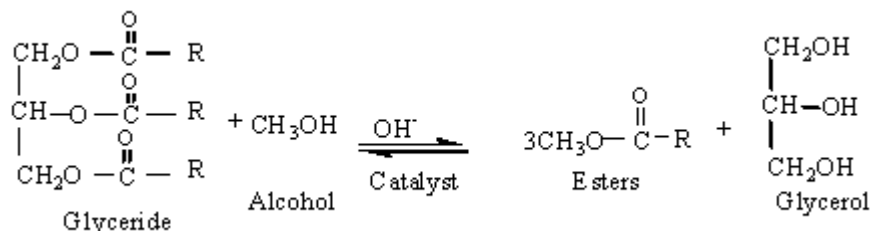
3) Separation: The biodiesel and glycerol produced are separated usually in distillation column.

4) <u>Removal of alcohol</u>: The alcohol that is left in the product stream is removed. Flash evaporation technique or fractionation is used generally to remove the alcohol.

5) <u>Neutralizing Glycerol</u>: Some part of catalyst goes into the glycerol stream, so the catalyst needs to be removed. So, the stream is acid treated so as to neutralize any basic catalyst. Also the glycerol stream may contain some quantities of soap and hence the soap is removed by acid treatment.

6) <u>Biodiesel wash</u>: Residual catalysts or soaps are removed by washing the obtained biodiesel with warm water.

7) <u>Biodiesel quality</u>: The quality of biodiesel produced depends on the completion of reaction, proper neutralization of soaps and leftover catalyst, complete removal of glycerol, no presence of free fatty acids and complete removal of alcohol.

1.7) **GAPS**

Today, different approaches are used for the production of biodiesel. Vegetable oils, non-edible oils are being used as the feedstocks. Amongst the non-edible oils, Jatropha has proven to be an important feedstock for the biodiesel production. Research papers have shown that different methods can be used for the biodiesel production. Some have reported that biodiesel can be produced in a single step if FFA content < 1%, while for FFA content > 1%, a two-step transesterification process has been proposed. Biodiesel can be produced from the transesterification of oleic acids or transesterification of triglycerides without the initial step of hydrolysis of triglycerides. But problems have also been noted while using catalysts like, on using base catalyst for the transesterification for Jatropha oil having high free fatty acid contents lead to the formation of soap thus lower yield of biodiesel [Juan et al., 2011]. While on using acid catalyst for transesterification, reaction temperature and pressure, methanol to oil ratio had to be increased in order to increase the rate of transesterification reaction [Avhad and Marchetti, 2015]. Though vast research has not been done on enzyme catalysed transesterification, studies have shown that it's a costly process. Heterogeneous catalysts like $SiO_2.HF$, CaO etc have proven to be beneficial compared to the homogenous catalysts as biodiesel yield was increased. Still, extensive work research needs to be done in the field of heterogeneous catalysts.

LITERATURE REVIEW

Anton A. Kiss (2011) considered reactive distillation column for biodiesel production from Jatropha. He suggested that reactive distillation column coupled with heterogeneous catalyst proves beneficial as it helps in lower capital investment and better yield. He used heat integration in his model which further decreased the energy requirements thus decreasing operating costs. He used Aspen Plus for his simulation work and reactive distillation column was simulated using RADFRAC unit in Aspen Plus library. Waste vegetable oil and methanol with high free fatty acid content were used for simulation purpose. He used sulphated zirconia as the catalyst. With heat integration in place, he found that heat requirements were 45% lower – only 108.8 kWh/ton biodiesel – as compared to previous RD processes without heat integration. Capital investment cost remained the same as no additional instrument was required.

Chen et al. (2010) investigated about the process of biodiesel production from Jatropha Curcas oil. They worked on the supercritical carbon dioxide (SC-CO_2) abstraction of triglycerides from the crumbled Jatropha seeds. After supercritical extraction, they performed supercritical hydrolysis which was further followed by supercritical methylation to produce biodiesel. Highly pure biodiesel (98.5%) was obtained. This process gave a biodiesel yield of 99%. They conducted a parametric study on reaction temperature, reaction time. Solvent to feed ratio was also varied. Activation energies of hydrolysis reaction and transesterification reaction were found to be 68.5 and 45.2 kJ/mole, respectively. Thus their study concluded that a two-step process of hydrolysis and consequent methylation was a convenient way of producing biodiesel from Jatropha seeds.

Corro et al. (2010) produced a high quality biodiesel from Mexican Jatropha crude oil using a two-step process. In the first step, free fatty acids (FFA) were reacted with methanol in the molar ratio of 1:12 (FFA: methanol) in presence of a solid catalyst SiO_2.HF (SiO_2.HF/Jatropha

oil mass ratio of 10%) at 60ºC for 2h. The conversion of FFA was 96 %. They carried out 30 esterification runs and found out that the catalyst activity remained unchanged. Also the catalyst showed a high esterification activity, high stability, high number of Lewis acid surface sites and showed no CO_2 or H_2O adsorption activity. First step gave a mixture of the esterified free fatty acids and the unreacted triglycerides. The second step was the transesterification step which consisted the reaction of unreacted triglycerides with methanol in the molar ratio of 1:6 catalysed by 1 wt. % NaOH under the reaction conditions of 60ºC for 2h with stirring at 400 rpm. Chromatographic analysis of the biodiesel obtained revealed that the use of solid catalyst led to a very high quality of biodiesel and also amount of sulphur and aromatic compounds were very low. But halogenated compounds and dicyclopentadiene were also discovered.

Deng et al. (2010) studied a two-step biodiesel production process in an ultrasonic reactor at 60ºC. Firstly, only NaOH was used as a catalyst for biodiesel production which gave a biodiesel yield of only 47.2% along with saponification problem. Secondly, they used H_2SO_4 as catalyst which increased the yield to 92.8% but increased the reaction time (4h) and also the product was unstable. Then a two-step biodiesel production process was employed viz. acid-esterification and base-transesterification. After acid-esterification with H_2SO_4 (4 vol.%) of Jatropha oil with 40% vol. methanol at 60ºC for 1h in the first step in the ultrasonic reactor, the acid value of oil was decreased from 10.45 to 1.2 mg KOH/g. Then in the second step, base-transesterification using NaOH (1.4 wt. %) of Jatropha oil having methanol/oil volume ratio of 24% for 0.5 h, a biodiesel yield of 96.4% was obtained along with the reduction in the acid value of oil to 0.32 mg KOH/g and also the biodiesel obtained was stable. They hence concluded that a two-step biodiesel production process in an ultrasonic reactor took only 1.5h for completion and also it is a time efficient method for biodiesel production.

Deng et al. (2011) studied biodiesel production using a solid base catalyst derived from hydrotalcites with Mg/Al molar ratio of 3/1 and they were synthesized by a coprecipitation method using urea as precipitating agent in an ultrasonic reactor and with microwave-hydrothermal treatment (MHT) followed by calcination. In the first step, esterification of the jatropha oil was carried out using H_2SO_4 as catalyst at 318 K in an ultrasonic reactor for 1.5h. The acid value of the pretreated oil was reduced to 0.7 mg KOH/g. In the second step, the pretreated oil was reacted with methanol (methanol to oil molar ratio of 4:1) in presence of 1

wt. % calcined hydrotalcite catalyst at 318 K for 1.5 h with 210 W ultrasonic power. Biodiesel yield obtained was 95.2%. They used this catalyst in the second step because of its strong basicity. They concluded that glycerol absorption on the surface formed during.the reaction was the main reason for the catalyst deactivation. Further, after the removal of glycerol from.the catalyst surface, they reused the catalyst for eight times.

Guo et al. (2013) studied biodiesel production using ionic.liquids (ILs) with metal chlorides. For this they used various ILs and amongst them they found highest catalytic activity of 1-butyl-3-methylimidazolium tosylate {[BMIm][TS]}**.** Firstly, they carried out esterification of oleic acid using 9 mmol of {[BMIm][TS]} as catalyst with methanol having methanol: oleic acid ratio of 2:1 on mole-mole basis at 140ºC for 5h and they had had obtained methyl oleate yield of 93%. But they had obtained a very low Jatropha biodiesel yield of 63.7% at 200 ºC in absence of metal chlorides. Then, they added several metal chlorides like $FeCl_3$, $CuCl_2$, $ZnCl_2$, $MnCl_2$, $AlCl_3$, $CoCl_2$ and LiCl in {[BMIm][TS]} and found out increase in the conversion rate of oleic acid. After that they performed one step biodiesel production without esterification step using high acid valued Jatropha (13.8 mg KOH/g) in presence of {[BMIm][TS]} doped with metal chloride and obtained a maximum biodiesel yield of 92.5% on addition of $ZnCl_2$ at 180 ºC. They further suggested that metal ions in ILs were useful in promoting reactions and that metal ions from transition period showed higher activity than Group A elements.

H.J. Berchmans, S. Hirata (2008) crafted a process to produce biodiesel from Jatropha Curcas oil. The oil had had high FFA (15%) content. They used two steps for pre-treatment of Jatropha Curcas oil. The pre-treatment caused the reduction in FFA to below 1%. In the first step, they treated the oil with methanol (0.6 w/w methanol to oil ratio) along with H_2SO_4 (1% w/w) as the acid catalyst at 50ºC for 1 hour reaction time. Then the reaction mixture was left for 2 hours as it was and after that CH_3OH-water mixture was separated at the top layer which was evacuated afterwards. In the next step, they carried out transesterification reaction using 1.4% w/w NaOH to oil as the alkaline catalyst and 0.24 w/w methanol to oil at 65ºC. It produced biodiesel. Finally, they found out that oil to biodiesel conversion was 90% in 2 hours.

Hawash et al. (2009) carried out transesterification of Jatropha oil using supercritical methanol and in the absence of the catalyst. They studied transesterification under different conditions of 512 to 613 K temperature, 5.7 to 8.6 MPa pressure, and 10 to 43 mole alcohol per mole oil. Experimental results showed that 100% yield of methyl ester could be obtained with supercritical methanol within 4 min only at reaction condition of 593 K, 8.4 MPa and 43:1 methanol to oil ratio. Use of supercritical methanol for transesterification showed advantages like very short reaction time (4 min) and ease in separation of products and by-products. Also, the purification was easy since it required only the removal of methanol (as catalyst is absence). High performance liquid chromatography (HPLC), thin layer chromatography (TLC) and titration against KOH were used to analyse the contents of residual triglycerides, glycerol, monoglycerides, diglycerides, esters and free acids in the reaction products.

Huaping et al. (2006) produced biodiesel from Jatropha oil using heterogenous catalyst CaO after dipping in ammonium carbonate. They found an increase in the activity of CaO after being dipped in ammonium carbonate solution followed by calcination. After carrying out the reaction of Jatropha oil with methanol (methanol: oil molar ratio 9:1) with catalyst dosage of 1.5% at reaction temperature of 70ºC for 2.5h and with catalyst calcination temperature of 900 ºC, they had obtained a maximum biodiesel yield of 93%. They then found out remains of cations in the products after the use of basic catalyst. So, cations needed to be removed. Using water washing to remove the impurity, showed only 50% decalcification rate and the quality of biodiesel did not meet the standard. So they studied three kinds of decalcifying agents' viz. oxalic acid, critic acid and EDTA to remove calcium and found out that decalcification rate was increased compared to water as decalcifying agent. Critic acid showed the highest decalcification rate. They concluded that this whole process was simple, repeatable and exhibited standard biodiesel properties.

Juan et al. (2011) studied about the biodiesel production processes from Jatropha oil via catalytic and non-catalytic approaches. Their paper stressed on the importance for using biodiesel in place for conventional diesel fuels. But they also suggested that use of vegetable oils for biodiesel production can cause steep increase in demand for vegetables and in turn would disturb the food market. So, they suggested that non-edible oils and especially Jatropha should to put to use for producing biodiesel because of its ability to grow in infertile or

wastelands. Further, they studied about the transesterification process and stated that for FFA content < 1 %, base catalyst should be preferred and while for FFA content > 1 %, a two-step transesterification process should be used. Also they suggested that using enzymatic approach for transesterification can be a better alternative.

Kaewcharoensomabt et al. (2011) studied biodiesel production from Jatropha from Thailand. They laid importance on the design alternatives for biodiesel production from Jatropha. Impact on the environment through various production process was their main motive. They used two catalysts; sodium hydroxide and potassium hydroxide and different design processes were designed for them. Processes were then compared to each other considering environmental impact and also the through the optimum operation point of view. Process simulation was performed using Aspen Plus software. Whereas, environmental impacts were calculated using Eco-indicator 99 in SimaPro 7. They then performed Life Cycle Assessment (LCA) to guess the environmental impacts. Parameters for the LCA were; human health, ecosystem quality and resource exhaustion. The results showed that the process using NaOH had greater environmental impacts i.e. on the human health and the ecosystem. However, the process using KOH caused greater resource depletion. They concluded neither of the two catalysts made any significant difference.

Lu et al. (2009) developed a two-step process for biodiesel production using Jatropha oil. In the pre-esterification step, free fatty acids (FFA) in the oil were converted to methyl esters (biodiesel) using H_2SO_4 or the solid catalyst SO_4^{2-}/TiO_2. With 1 wt. % of H_2SO_4 in oil along with 12 wt. % of methanol at 70ºC, reduction in the acid value of oil from 14 mg-KOH/g-oil to below1.0 mg-KOH/g-oil in 2 h was observed. They showed that phospholipids contents could be eliminated during pre-esterification operation and separate degumming operation was unrequired. Using 4 wt. % solid acid catalyst along with a molar ratio of methanol to FFAs of 20:1 at 90ºC for 2h converted FFAs to more than 97 %. After that, in the transesterification process 98 % biodiesel yield was obtained using 1.3 % KOH as catalyst along with a molar ratio of methanol to oil 6:1 in 20 min at 64 ºC.

Luu et al. (2014) conducted a two-step co-solvent method to produce high quality biodiesel from Jatropha oil. The Jatropha oil contained a high free fatty acid (FFA) content of 15.93 %. In the first stage, esterification reaction was carried out using 1 wt. % H_2SO_4, methanol to FFAs molar ratio of 6:1 at 65°C along with 30 % (wt/wt) acetonitrile as co-solvent which caused the reduction in FFA contents of the oil from15.93 to 2 wt. % in 60 min. They showed that using acetonitrile as co-solvent in the first stage decreased the reaction time significantly and also a small amount of acid catalyst was required in comparison to that which didn't use co-solvent. In the second stage, using 20% (wt/wt) acetone as co-solvent along with 1 wt. % KOH and methanol-to-oil molar ratio of 6:1 at 40°C produced biodiesel with 99% efficiency in 30 min. They concluded that, use of co-solvent method for second stage showed a high transformation efficiency, shorter reaction times and lower production costs in the production of biodiesel.

M.Y. Koh, T.I. Mohd. Ghazi (2011) studied various techniques and approaches to produce biodiesel from Jatropha. They discussed about the need to search alternatives for conventional fossil fuels. They discussed about the primary methods for biodiesel production viz. blending, micro emulsion, pyrolysis and transesterification. They pointed out that we should look for non-edible oils like Jatropha oil rather than edible oils for biodiesel production. They also studied about transesterification reaction, carried out using homogenous catalysts, heterogeneous catalysts, enzymes etc. And lastly, they also stated that biodiesel produced from Jatropha has analogous properties to that of petroleum based diesel.

Mu'azu K. et al. (2015) developed a mathematical model that described chemical kinetics of transesterification of jatropha *curcas* oil using calcium oxide as heterogeneous catalyst. The Model is based on the reverse mechanism of transesterification reactions. They studied the reaction at the following reaction conditions: methanol to oil ratio (10:1); catalyst concentration (8wt %); time (1hr); temperature (55°C) and stirrer speed (700rpm). They observed that the changes in concentration of all0reactants and products as a function of time and temperature and they were highly significant between 0-25 minutes. Their study also disclosed that conversion of triglyceride to diglyceride was the rate determining step (RDS) and the effective rate constants for all the six reactions (reversible and irreversible) were favoured by high temperature. Kinetics was of first order and the Activation energy was found to be 14.80 kJ/mol and frequency factor of $20.697s^{-1}$.

N.N.A.N. Yusuf, S.K. Kamarudin (2013) produced biodiesel from Jatropha oil via supercritical methanol process. They also performed the economic evaluation of the biodiesel produced from Jatropha. They also presented a conceptual design for the production process. Process they used consisted of four major units, namely transesterification unit, methanol recovery unit, glycerol recovery unit and biodiesel purification unit. They considered biodiesel production of 40,000 tonnes per year for their case study. They found out that using supercritical transesterification process with methanol, highly pure biodiesel (99.96 %) was obtained. Also, highly pure glycerol (96.49 %) was obtained as the by-product. After performing economic evaluation, they stated that manufacturing and capital investment costs were in the proximity of 25.39 million $ per year and 9.41 million $ per year, respectively. They also reported that the biodiesel produced could be sold at 0.78 $ per kg, after performing the economic evaluation. Also the total production cost was found to be 31.20 million $ per year.

Nizah et al. (2014) studied simultaneous esterification and transesterification of Jatropha Curcas oil in presence of a bifunctional catalyst Bi_2O_3 supported on La_2O_3. They synthesized the catalyst using wet impregnation method. They characterized the catalysts using X-ray diffraction and Brunauer–Emmett–Teller (BET) surface area. Also the catalysts acidity and basicity was studied using temperature programmed desorption with NH_3 as probe molecule (TPD-NH_3) and CO_2 as probe molecule (TPD-CO_2), respectively. At the optimum reaction conditions of methanol/oil molar ratio of 15:1, catalyst amount 2 wt. %, reaction temperature of 150ºC and reaction time of 4h, the highest fatty acid methyl ester conversion obtained was 93%. Also, they found out that the catalysts maintained 87% fatty acid methyl esters conversion after 3 successive runs of reuse. They also concluded that the catalyst possesses strong acid and basic strengths favouring simultaneous esterification and transesterification reactions since they contain more active sites.

Phuenduang et al. (2012) studied a two-step process viz. hydrolysis and esterification in biodiesel production from jatropha. In the first step, triglycerides in jatropha oil were hydrolysed using water in the hydrolysis reactor to give fatty acids and glycerol. In the second step, esterification reaction takes place in which methyl oleate i.e. a biodiesel product and water and it was formed by the reaction of fatty acids with methanol. Instead of a conventional

distillation process, they used reactive distillation in second step. Simulation was carried out for the hydrolysis section and esterification section with and without reactive distillation. Results showed an increase in the biodiesel production in case`of reactive distillation instead of conventional distillation process. They also considered heat integration of reactive distillation so as to minimize the energy requirements. Results showed a significant reduction in cooling and heating requirements by 20% and 35.7% respectively when they were compared to reactive distillation without heat integration.

Reddy et al. (2015) carried out transesterification reaction to produce biodiesel using Jatropha Oil as the feedstock. They used nano-CaO as the heterogeneous catalyst. The catalyst was incorporated from P. erosa seashells through a calcination−hydration−dehydration technique. Fourier transform infrared spectroscopy, transmission electron microscope, XRD, and BET methods were used to evaluate the CaO catalyst's spectral and fundamental characteristics. A response surface methodology was used to study the reaction kinetics of Jatropha biodiesel. At the optimized conditions of 0.02:1 (w/w) catalyst ratio, 133.1 min reaction time, and 5.15:1 mol/mol of methanol to the pre-treated feed, a 98.54% biodiesel yield was obtained. When the catalyst was reused for 6th cycle, an average of 95.8% biodiesel yield was obtained. Fuel property test results of JB matched with the standard referred biodiesel.

S. Jain, M.P. Sharma (2010) studied about the promising future of biodiesel production from Jatropha oil in India. They studied the effects of increasing industrialization and modernization on the fossil fuel reserves. They studied vastly about Jatropha and its use in the biodiesel production. They investigated the performance of 2 kVA DG set on concoction of straight vegetable oil (SVO) with CH_3OH. Also the fusion of biodiesel from Jatropha with CH_3OH was studied at various loads. The experiment advocated that biodiesel can take over from the diesel completely for the working in the IC engine. They also stated that engine didn't experience any problems while using biodiesel in place for the conventional diesel. They further laid the importance on the cultivation of Jatropha in India. Discussed about the advantages of using Jatropha and also stated that Jatropha can be a more desirable substitute for biodiesel production on account of its ability to give excelling outcome regarding quality and quantity of oil.

S. Jain, M.P. Sharma (2010) studied the kinetics of acid base catalysed transesterification of Jatropha curcas oil. They did the kinetic study for the two-step biodiesel production process. Their study was carried out at an optimized temperature of 65 ºC for the esterification reaction and 50 ºC for the transesterification reaction. Other optimized conditions included 3:7 (v/v) methanol to oil ratio, 1% (w/w) concentration of H_2SO_4 and NaOH. Parametric study was done by using the obtained quantity of biodiesel. The results showed that both esterification and transesterification reaction were of first order and their specific rate constant were reported to be 0.0031 min^{-1} and 0.008 min^{-1} respectively. A maximum yield of 21.2% of methyl ester was obtained during esterification and a 90.1% yield of methyl oleate was obtained during the transesterification.

Tiwari et al. (2007) used Response Surface Methodology (RSM) based on central composite rotable design (CCRD) to optimize methanol quantity, acid concentration&and reaction time for the reduction of free fatty acid (FFA) from the Jatropha Curcas crude oil. They developed models for first and second step. According to the model for first step, the optimum conditions for the acid value reduction of Jatropha oil containing high FFA (14%) to less than 1% were: 0.28 v/v methanol to oil ratio, 1.43% v/v H_2SO_4 catalyst, 88 min reaction time at 60ºC. For this step, they used a five-level-three-factor CCRD for the optimization study to reduce acid value of the oil requiring 34 experiments. According to the model for second step, the optimum conditions for producing biodiesel having an average yield of more than 99% with KOH as catalyst were: 0.16 v/v methanol to pre-treated oil ratio, 24 min of reaction time at 60ºC. For the second step, they employed a five-level-three-factor CCRD that required 21 experiments. The feasibility of the predicted models were confirmed by performing the verification experiments. Biodiesel quality obtained was found to be compatible with the American and European standards.

Wu et al. (2014) developed a technique to produce biodiesel from Jatropha oil by using a solid base catalyst. Methanol was used for the transesterification reaction. The catalyst they used was based on potassium salts (K_2CO_3, K_2SiO_3 and KAc). The catalyst was bedded on mesoporous silicas (SBA-15 & AlSBA-15). The catalysts were prepared by absorption method. For characterizing the catalysts, they used various techniques like XRD, BET, transmission electron microscopy and temperature programmed desorption of CO_2. They performed parametric study on catalytic activity and biodiesel yield. They found out that Aluminium

dopant in SBA-15 was able to protect the pore structure of the bedded catalyst. After loading potassium compounds, they found out that the basic and catalytic activity of AlSBA-15 was boosted further. Moreover, the catalytic activity of K_2SiO_3 was found to be exceptional than that of K_2CO_3 and KAc impregnated catalysts. On using K_2SiO_3/AlSBA-15 catalyst with 30 wt. % of K_2SiO_3 loading on AlSBA-15 as support, oil to methanol ratio of 1:9, catalyst to oil 3 w/w % at a temperature of 60ºC for 150 min gave a biodiesel yield of 95%. After reusing of 5th cycle, a slight decrease in its catalytic activity took which decreased the biodiesel yield by mere 6%. They concluded that the decrease in the catalytic activity was because of the potassium being leached on the portion of the catalyst as well as the deposition of the organics on the exterior. The study also suggested that K_2SiO_3/AlSBA-15 had uniform catalytic activity as distinguished to conventional potassium hydroxide and K_2CO_3 catalysts.

Xue et al. (2014) studied biodiesel production process from Jatropha oil and soybean oils. They used heterogeneous base catalyst $CaFe_2O_4$-$Ca_2Fe_2O_5$ for the transesterification reaction. The heterogeneous catalyst was prepared by co-precipitation and calcination. XRD, X-Ray photoelectron spectroscopy and temperature programmed desorption method were used to characterize the catalyst. The catalyst had weak magnetism initially which was further boosted by reduction of its component of Fe_2O_3 to Fe_3O_4-Fe under hydrogen atmosphere for better magnetic separation. For the optimum conditions of 373 K, 15:1 methanol to oil molar ratio, 4 wt% catalyst and 30 min, the highest biodiesel yield obtained for soybean oil was 85.4 % for weak magnetic activity catalyst and 83.5 % for strong magnetic activity catalyst. Reusability for these catalysts was reported to be three times. For biodiesel production from Jatropha, $CaFe_2O_4$-$Ca_2Fe_2O_5$-Fe_3O_4-Fe magnetic catalyst was used and 78.2 % biodiesel yield was obtained. They concluded that reaction time and temperature had weighty impact on the biodiesel yields.

Yingying et al. (2012) produced biodiesel from.Jatropha oil using trace sulphuric acid catalyst (0.04% to 0.08% by mass). Temperature range was 135 to 184 ºC. Esterification and transesterification were carried out simultaneously using.supercritical transesterification. By the reaction of Jatropha oil with methanol in presence of sulphuric acid catalyst under the optimum conditions of 20:1 methanol to oil molar ratio, 0.06% by mass H_2SO_4 at 165ºC, 1.6 MPa for 2h, the glycerol yield obtained was 84.8%. They further studied the effect of addition

of free fatty acid (FFA) and fatty acid methyl esters (FAME) during biodiesel production and concluded that optimum amount of FFA and FAME helped the transesterification reaction in.a positive way by improving the miscibility.between Jatropha oil and methanol. Effect of water content in the oil was also studied and concluded that water below 1% (by mass) did not affect the transesterification reaction. They also studied the reaction kinetics in the temperature of 155ºC to 175ºC.

Yun et al (2013) studied about biodiesel production with Jatropha as the catalyst. They simulated a continuous enzyme-catalyzed biodiesel pilot plant with production capacity of 6482 ton/yr, using Aspen Plus. Operating conditions and equipment design were obtained from previous works. They applied five reactions to present the transesterification for biodiesel production. Simulation data matched with the real data. They then proposed five optimization processes in order to enhance methanol recovery and also save energy. Pinch technology was also used to develop heat exchange networks. Highly pure biodiesel (>98.5%) was obtained even after several intensifications.

2.1) <u>MOTIVATION</u>

The strongest motivation is regarding the exhaustive supply of non-renewable conventional diesel fuels for the transit sector with ever increasing demand. Also, there has been an increase in the expenses for the agricultural products which are used for biodiesel production. So today, biodiesel production from non-edible sources has become an important aspect. However, environmental concerns about global and local pollution have taken the lead as a motivational factor.

Various methods have been put to use for the biodiesel production. Nowadays, reactive distillation columns are being put to use instead of conventional process of reaction which then is followed by distillation. Reactive distillation column have proved to be very beneficial in terms of operating expenses and energy requirements. Also it is reported that the reactions are occurring in a short period of time and also by-products are formed in less amounts. Hence, the current study is an attempt to study to the reactive distillation column thoroughly and find ways to put its use in a more efficient way.

In this present study, esterification reaction of oleic acid and methanol is being studied. Reactive distillation column is being used for this purpose. Solid acid catalyst, Calcium Oxide (CaO), is being used for the esterification reaction. Simulation is being done of this process. And APSEN PLUS has been used for the simulation of the biodiesel production from Jatropha.

2.2) OBJECTIVES

1) To perform the parametric study of the reactive distillation column involving changes in reflux ratio, condenser pressure, oleic acid feed rate.

2) To perform sensitivity analysis for studying the effects of the above parameters.

3) To propose an optimum configuration regarding triglycerides conversion and biodiesel purity for a reactive distillation column.

MODELLING

The reactive distillation column involves the complex procedure of reaction as well as distillation while conventional columns consists only distillation. Also the designing of a reactive distillation column is complex as compared to conventional distillation columns. The design of a reactive distillation column has reactive trays in between rectifying section at the top and stripping section at the bottom. The reactive trays are the ones where the reactions take place. The reactive trays can be loaded with the catalyst. Whereas, the rectifying section trays and stripping section trays are non-reactive.

The mechanism proposed for transesterification of Jatropha oil to biodiesel [Burno et al, 2006] is as follows:

$$TG + AL \leftrightarrow DG + BD$$
$$DG + AL \leftrightarrow MG + BD$$
$$MG + AL \leftrightarrow BD + GLY$$
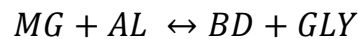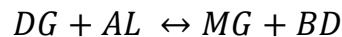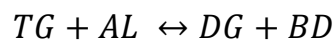
Where, TG = Triglycerides, DG = Diglycerides, MG = Monoglycerides, AL = Methanol
        BD = Biodiesel, GLY = Glycerol

The overall mechanism proposed for the biodiesel production is

$$TG + 3AL \leftrightarrow BD + GLY$$
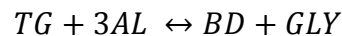
The reaction kinetics proposed by Mu'azu K. et al. (2015) has been used in this work. The authors considered the transesterification reaction of Jatropha oil with methanol for the biodiesel production using CaO as the catalyst. The reaction they considered involved the same reaction steps as reported by Burno et al. (2006). For determining the reaction kinetics, they assumed MeOH to be abundant with respect to triglycerides. After calculations, they concluded that the forward reaction followed a 1st order kinetics, whereas, the backward reaction followed

a 2nd order kinetics. Their proposed rate expression has been incorporated in modelling of the RD column in this present work.

Their proposed rate expression for the forward reaction is as follows:

$$r_{TG} = \frac{dC_{TG}}{dt} = -k_f C_{TG}$$

Fig 3.1 Schematic of a reactive distillation column [Murat et al., 2003]
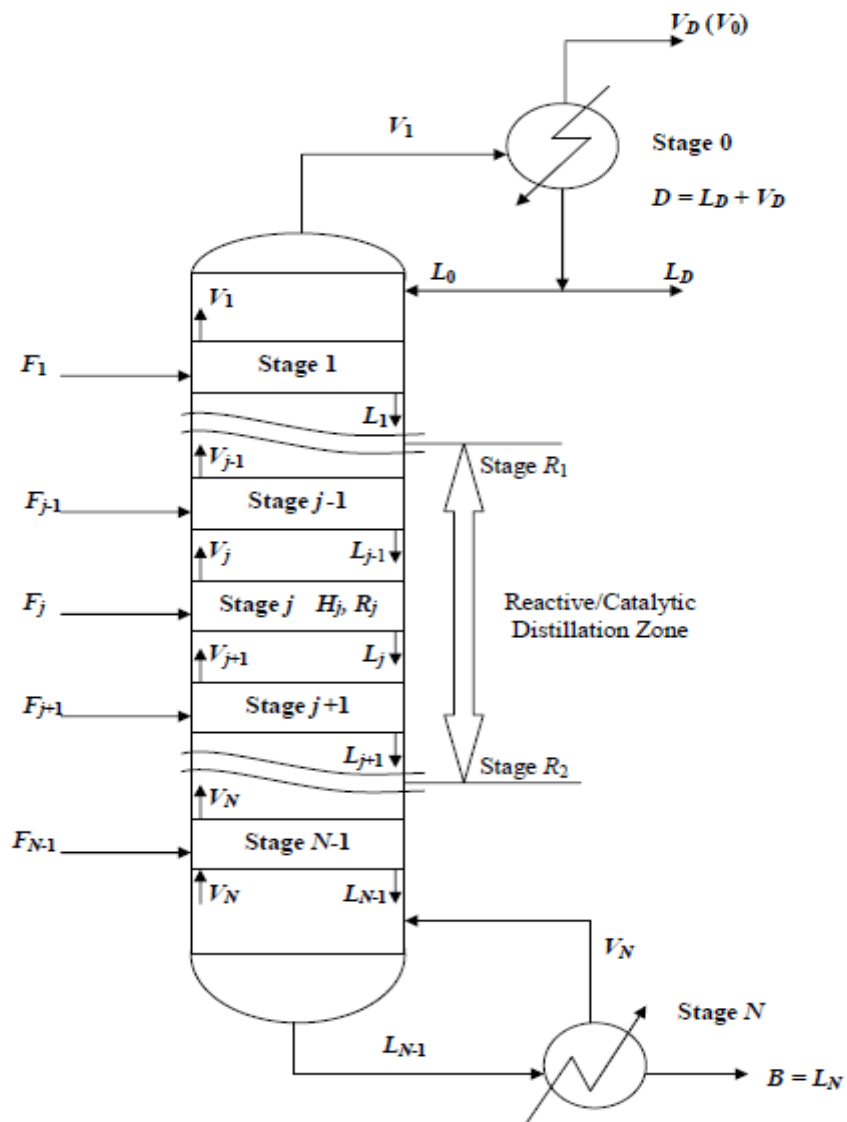
3.1) MODELLING ASSUMPTIONS

The mathematical model used in this work has the following assumptions:

1) Equimolal flow is assumed.

2) Methanol is assumed to be abundant.

3) Heat of vaporization and heat of reaction is kept locked.

4) Heat of mixing is assumed negligible.

5) The different catalyst sites on a catalyst surface doesn't show variations in their catalyst activity.

6) Vapour doesn't accumulate on the trays.

7) The whole liquid solution is assumed to be ideal.

8) Adiabatic conditions are assumed.

9) The reactions are occurring only in liquid state.

10) On each tray, liquid holdup is assumed to be constant.

11) Vapour and liquid are assumed to be in equilibrium.

The equations that describe the reactive distillation column are very complex as they contain a large number of linear and algebraic equations. And also the reaction kinetics involve a high degree of non-linearity. Therefore, equilibrium stage models with unsteady state operations are considered while modelling. With reference to the figure below, the following model equations are used in this work. They are known as MESH equations which includes mass balances, energy balances, phase equilibrium and summation equations.

The equilibrium reaction being incorporated in this work is:

$$A + B \leftrightarrow C + D$$
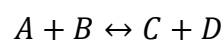
Where, A= 1 mole of triglycerides, B= 3 moles of methanol, C= 3 moles of FAME, D= 1 mole of glycerol

3.2) MESH EQUATIONS

3.2.1) Mass Balance:

  Overall material balance for stage j:

$$F_j + L_{j-1} + V_{j+1} + \delta_j R_j = L_j + V_j$$

Material balance for component i:

$$\frac{H_j dx_{j,i}}{dt} = \left(z_{j,i}F_j + x_{j-1,i}L_{j-1} + y_{j+1,i}V_{j+1}\right) - \left(x_{j,1}L_j + y_{j,i}V_j\right) + \delta \sum_{r=1}^{R}\left(v_{r,i}r_{j,r}\right)$$

3.2.2) <u>Energy Balance:</u>

$$F_j \sum_{i=1}^{c}\llbracket z_{j,i}\left(h_{j,i}^{f} - h_{j,i}^{L}\right)\rrbracket + L_{j-1} \sum_{i=1}^{c} x_{j-1,i}\left(h_{j-1,i}^{L} - h_{j,i}^{L}\right) +$$

$$V_{j+1} \sum_{i=1}^{c} y_{j+1,i}\left(h_{j+1,i}^{V} - h_{j,i}^{L}\right) - \delta_j W_j \sum_{r=1}^{R}\left(\Delta H_{j,r}^{R}\right)r_{j,r} =$$

$$V_j \sum_{i=1}^{c}\llbracket x_{j,i}\left(h_{j,i}^{V}\rrbracket - h_{j,i}^{L}\right) \qquad\qquad \left(\frac{J}{s}\right)$$

3.2.3) <u>Phase Equilibrium:</u>

$$y = \frac{\gamma P^0 x}{\phi P}$$

3.2.4) <u>Summation Equation:</u>

For liquid phase: $\qquad \sum_{i=1}^{c} x_{j,i} = 1.0$

For gaseous phase: $\qquad \sum_{i=1}^{c} y_{j,i} = 1.0$

3.3) <u>REACTIVE TRAYS MODELLING</u>

a) <u>The net of reaction on tray j for any component i in the reactive zone is given by</u>:

$$R_{j,i} = v_i H_j\left(k_{fj}x_{j,A} - k_{bj}x_{j,C}x_{j,D}\right)$$

b) <u>Vapour and liquid flow rates for the reactive trays:</u>

The esterification reaction we are considering is an exothermic reaction and hence the reaction rate is different for each of the reactive trays. As some liquid onto the tray is vaporized due to the exothermic chemical reaction, therefore the flow rate of the liquid which is going downwards is decreasing down through the reactive trays whereas the flow rate of the vapour goes on increasing up through the reactive trays.

$$V_j = V_{j-1} - \Delta H^R * R_{j,C}/\Delta H_v$$

$$L_j = L_{j+1} + \Delta H^R * R_{j,C}/\Delta H_v$$

3.4) **KINETIC MODEL**

For the reactions whose reaction kinetics are known, kinetic model is used. Consider the reversible equation $A + B \leftrightarrow C + D$ whose reaction kinetics are known. The reaction used in this work follows a 1st order kinetics for forward reaction and a 2nd order kinetics for backward reaction.
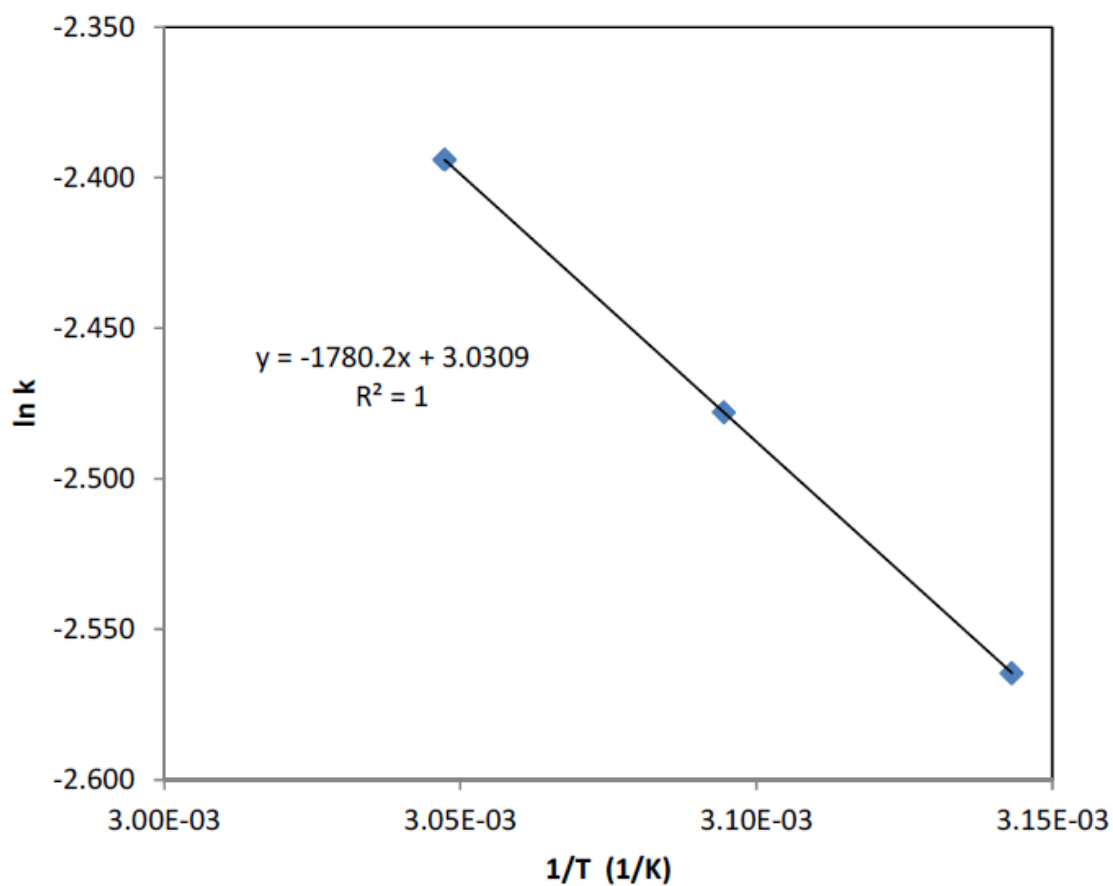
The forward and backward specific reaction rates on tray j follow Arrhenius Law and they are as follows:

$$k_f = A_f e^{(-\frac{E_f}{RT})}$$

$$k_b = A_b e^{(-\frac{E_b}{RT})}$$

The kinetics for the forward reaction of oleic acid with methanol has been taken from Mu'azu K. et al. (2015). The graph taken from the paper is shown on the next page.

Fig. 3.2 Temperature dependency on rate constant [Mu'azu K. et al., 2015]

$$\ln(K) = -1780.2 \left(\frac{1}{T}\right) + 3.0309$$

$$E = 14.8 \left(\frac{kJ}{mol}\right)$$

$$\ln A = 3.0309$$

Where, E = Activation energy,   A = Arrhenius constant,   K = Rate constant

SIMULATION

In this current work, simulation for the biodiesel production from Jatropha oil using CaO as the solid catalyst has been performed. Methanol has been used for the transesterification reaction in the reactive distillation column.

4.1) PROPOSED MODEL

In this work, RadFrac column from the ASPEN PLUS library has been used to simulate the reactive distillation column (RDCOLUMN). Triolein from the ASPEN PLUS library has been used to represent triglycerides in the reaction. The preliminary design shown below has been used for the simulation work.

The design being used in this work is presented on the next page.

Fig. 4.1 Preliminary design for biodiesel production
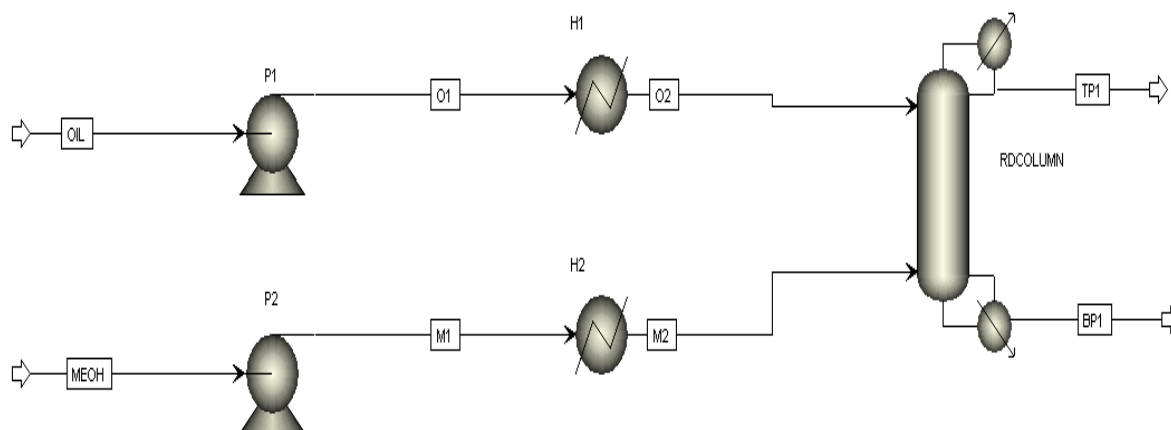
4.2) OPERATING CONDITIONS

Firstly, the methanol (MEOH) and Jatropha oil (OIL) streams were pressurized to 7 atm. Then they were heated to a temprature of 60 ºC as the reaction condition demanded [Reddy et al.,

2015]. A relatively low reflux ratio of 1 has been used for the operation of the reactive distillation column. This is because of the methyl oleate product having higher boiling point as compared to water and methanol and in turn it leads to an ease in seperation.

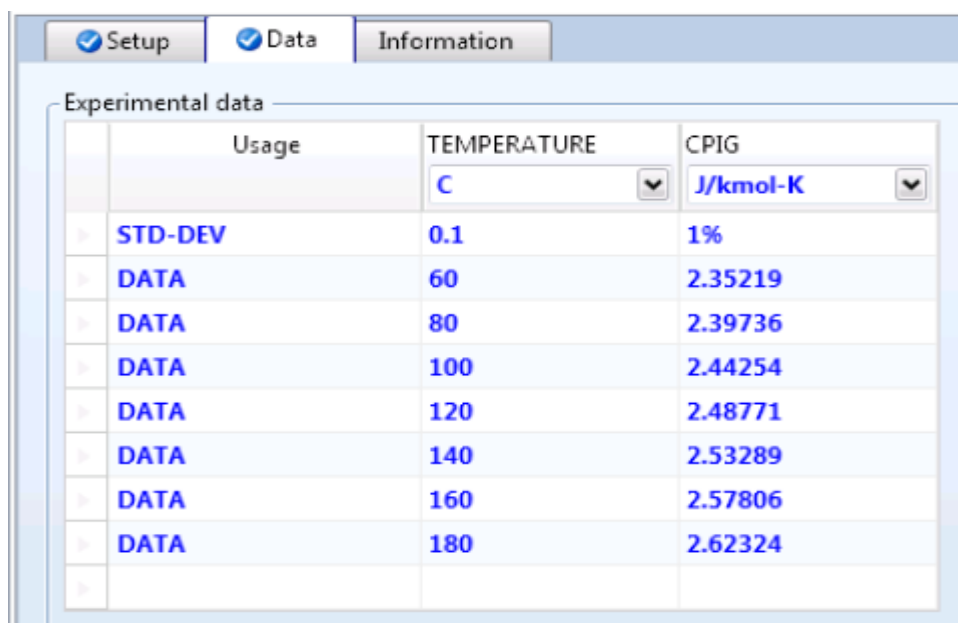The operating conditions used in this work are shown in the table 4.1 below:

Table 4.1 Operating conditions of the RD column

	RD COLUMN
No. of Stages	15
Molar reflux ratio	1
Methanol feed stage	12
Oil feed stage	4
Condenser pressure (atm)	2
Reflux ratio	1
Reactive stages	4-12
Distillate rate (kmol/hr)	290
Bottom rate (kmol/hr)	200
Triolein feed rate (kmol/hr)	150
Methanol feed rate (kmol/hr)	150

An error arose while performing the simulation. Ideal gas property for triolein were shown to be missing and could not be determined through property estimation. So, the ideal gas properties for Triolein had to be entered manually. The missing ideal gas properties for the pure component Triolein were taken from the works of Noor et al (2000).

The pure component data for the Triolein has been shown in the table 4.2.

Table 4.2 Pure component data for Triolein [Noor et al., 2000]

| | Usage | TEMPERATURE | CPIG |
		C	J/kmol-K
	STD-DEV	0.1	1%
	DATA	60	2.35219
	DATA	80	2.39736
	DATA	100	2.44254
	DATA	120	2.48771
	DATA	140	2.53289
	DATA	160	2.57806
	DATA	180	2.62324

4.3) FURTHER SPECIFICATIONS

i) Packing rating: MELLAPAK packing from the vendor SULZER was used for the stages 2-14. Packing specifications used in the column are: Dimension=250 Y, HETP (Height Equivalent to Theoretical Plate) =1 m, Section diameter=7 m.

ii) Reflux drum: Horizontal vessel was used. Head of the reflux drum was elliptical while length and diameter were 2 m and 1 m, respectively.

iii) Sump: Sump of elliptical head was used. Length of the sump was 2.2 m and diameter of the sump was 1.1 m.

iv) Hydraulics: Simple packing was used. Packing geometry for the stages 2-14; 6 m diameter and 1 m HETP.

v) Convergence: Maximum iterations were increased to 200.

vi) Liquid holdup: Liquid molar holdup for the reactive trays 2-14 was assumed to be 1000 moles.

RESULTS AND DISCUSSIONS

5.1) <u>EFFECT OF CONDENSER PRESSURE</u>: The table 5.1 below shows the effect of stage 1 or condenser pressure on the % conversion of triglycerides. It can be seen that as the condenser pressure increases, the conversion of triglycerides also increases. Which in turn also suggests that the concentration of biodiesel in the bottoms of the RD column also increases. This is because the increase in the condenser pressure increases the boiling point of the product thus increasing the separation.

Table 5.1 Effect of condenser pressure on conversion

Condenser Pressure (atm)	Percentage Conversion
1	60.5982
1.5	68.462
2	74.485
2.5	79.827
3	83.045
3.5	85.973
4	87.593
4.5	88.768
5	89.972
5.5	90.883
6	91.598

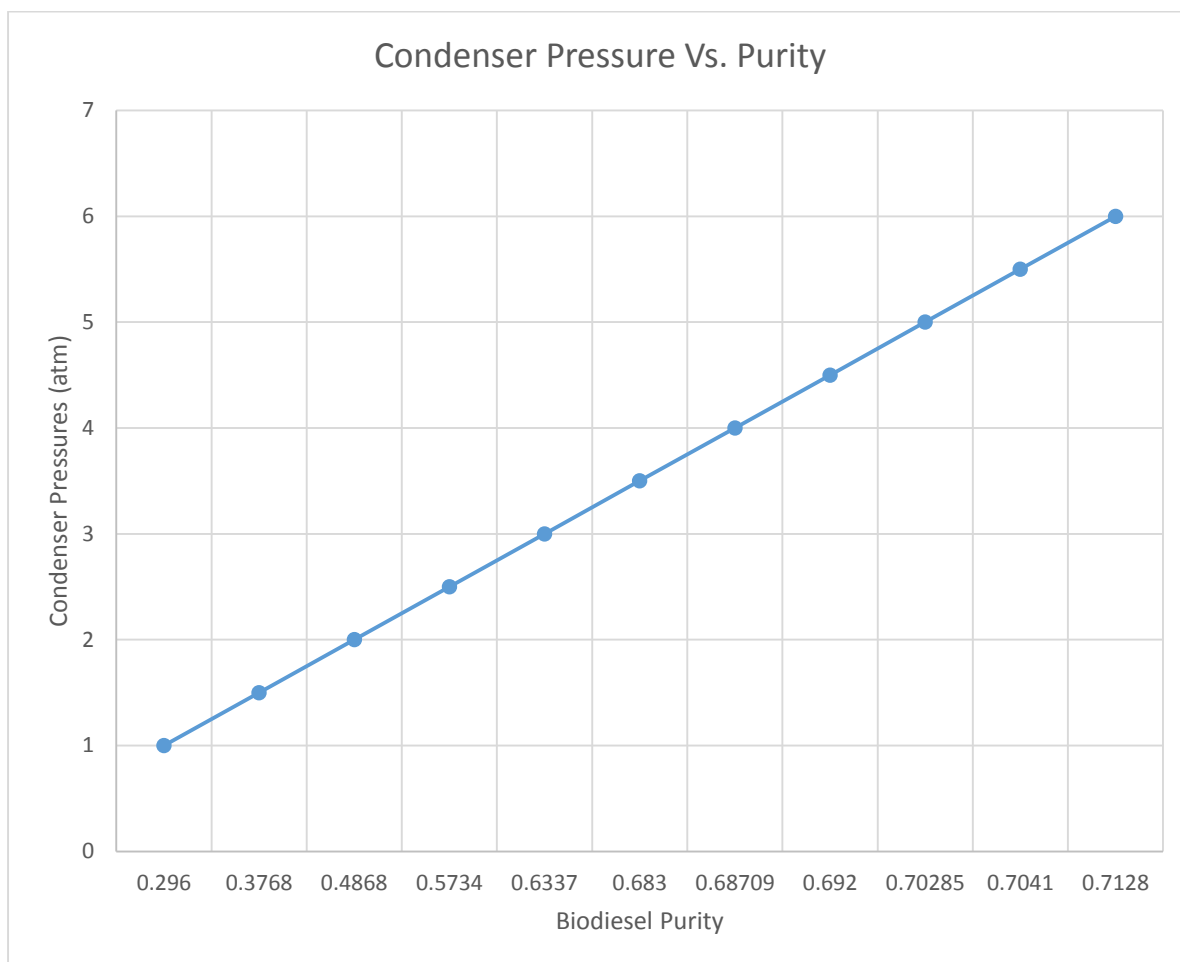Fig. 5.1 Effect of condenser pressure on conversion
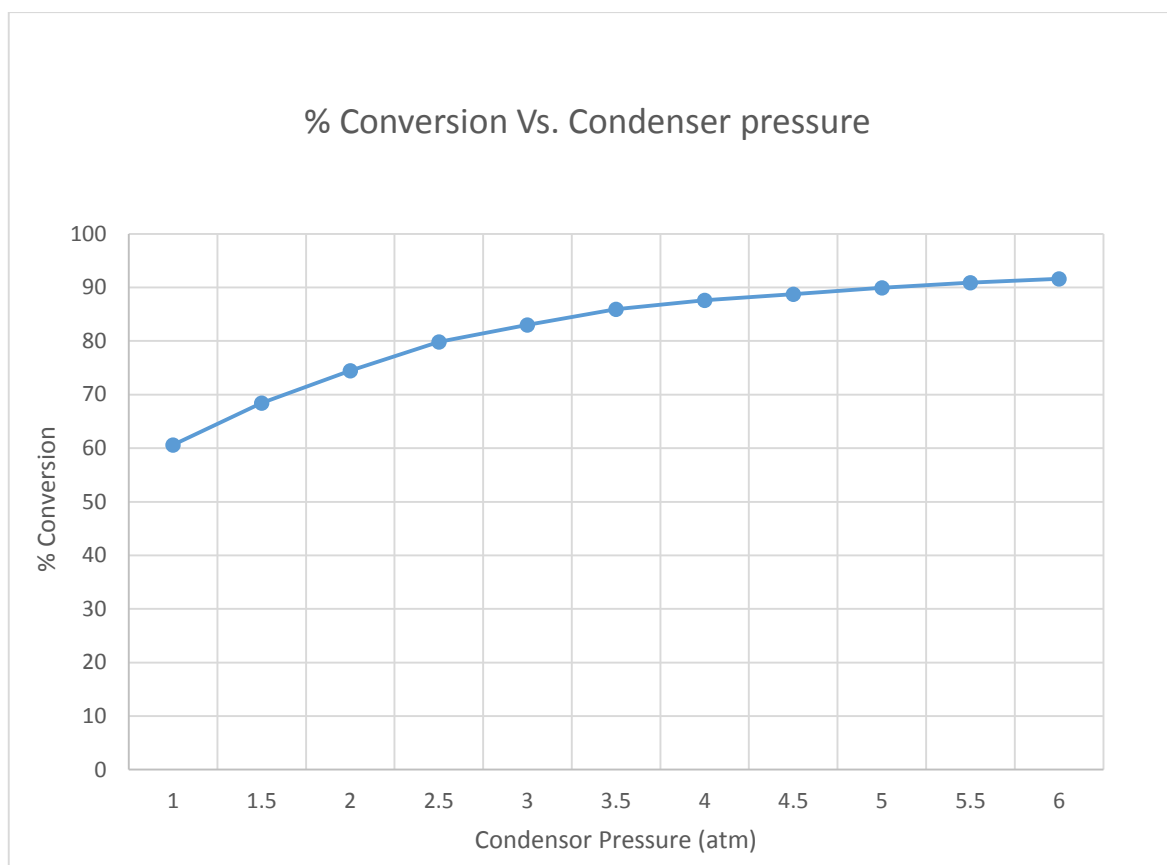
The following table 5.2 and the subsequent graph shows the relationship between condenser pressure and the biodiesel purity.

Table 5.2 Effect of condenser pressure on biodiesel purity

Condenser Presssure (atm)	Biodiesel Purity
1	0.296
1.5	0.3768
2	0.4868
2.5	0.5734
3	0.6337
3.5	0.6835
4	0.6871
4.5	0.6903
5	0.7028
5.5	0.7041
6	0.7128

Fig. 5.2 Effect of condenser pressure on product purity

Condenser Pressure Vs. Purity

(Chart: X-axis "Biodiesel Purity" with values 0.296, 0.3768, 0.4868, 0.5734, 0.6337, 0.683, 0.68709, 0.692, 0.70285, 0.7041, 0.7128; Y-axis "Condenser Pressures (atm)" ranging 0 to 7)
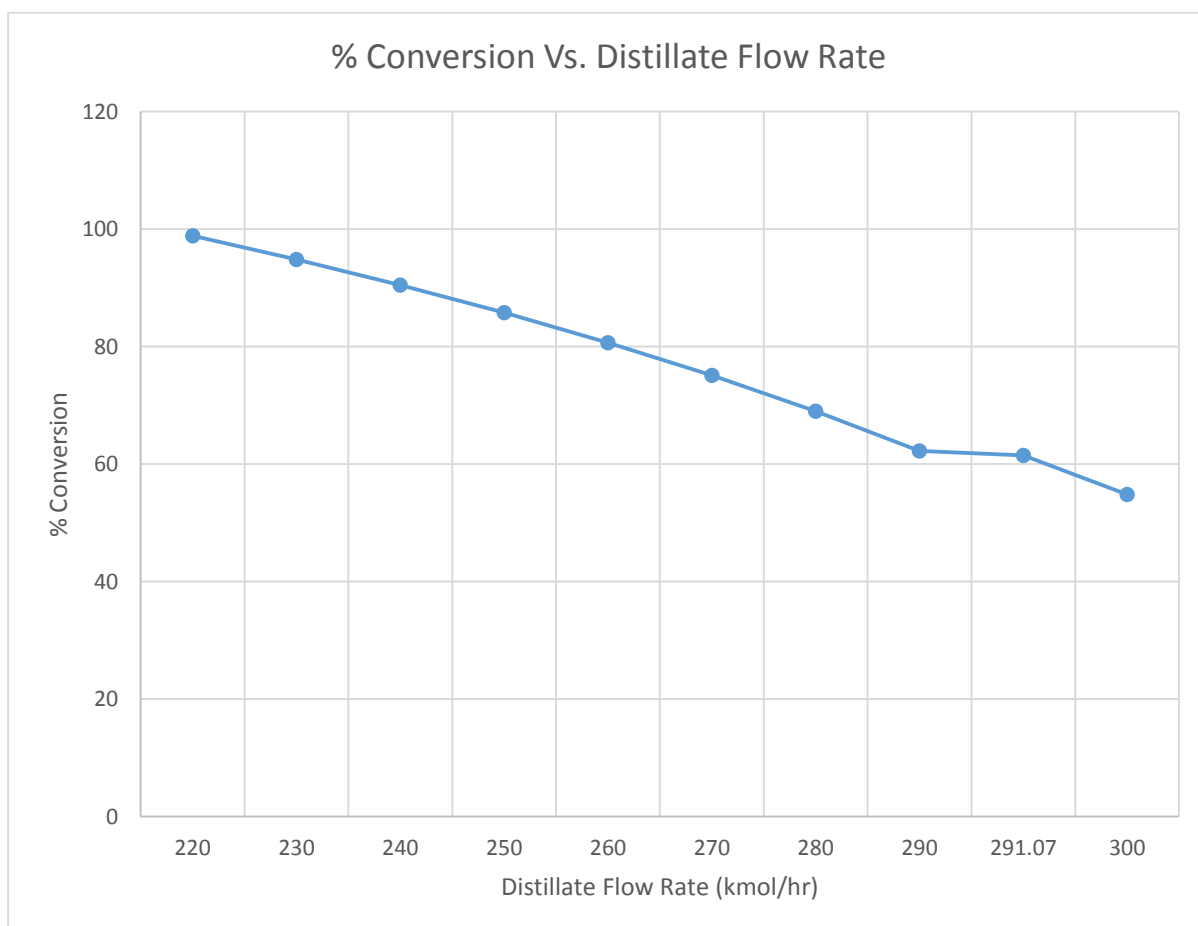
5.2) <u>EFFECT OF DISTILLATE RATE</u>: The tables and graphs under this section shows the effect of distillate rate on the % conversion and the amount of biodiesel in the bottoms of the reactive distillation column. The table 5.3 below shows that as distillate rate is increased from a certain value, the conversion % decreases. % conversion only increases upto a certain value on increasing the distillate flow rate and after that certain value, conversion starts to decrease with the increase in the distillate rate.

Table 5.3 Effect of distillate flow rate on conversion

Distillate Flow Rate (kmol/hr)	Percentage Conversion
220	98.86
230	94.8365

|	
240	90.4929
250	85.7875
260	80.6734
270	75.0952
280	68.9868
290	62.2692
291.07	61.5106
300	54.8471

Fig. 5.3 Effect of distillate rate on conversion

The table 5.4 and the graph shown on the next show that, biodiesel purity becomes as high as 80.15% when the distillate rate is increased but after that, the biodiesel purity starts to decrease.

Table 5.4 Effect of distillate flow rate on biodiesel purity

Distillate Flow Rate (kmol/hr)	Biodiesel Purity
100	0.6729
120	0.6919
140	0.7132
160	0.7370
180	0.7639
200	0.7945
220	0.8015
240	0.7600
260	0.7114
280	0.6534
300	0.6164

Fig. 5.4 Effect of distillate rate on biodiesel purity
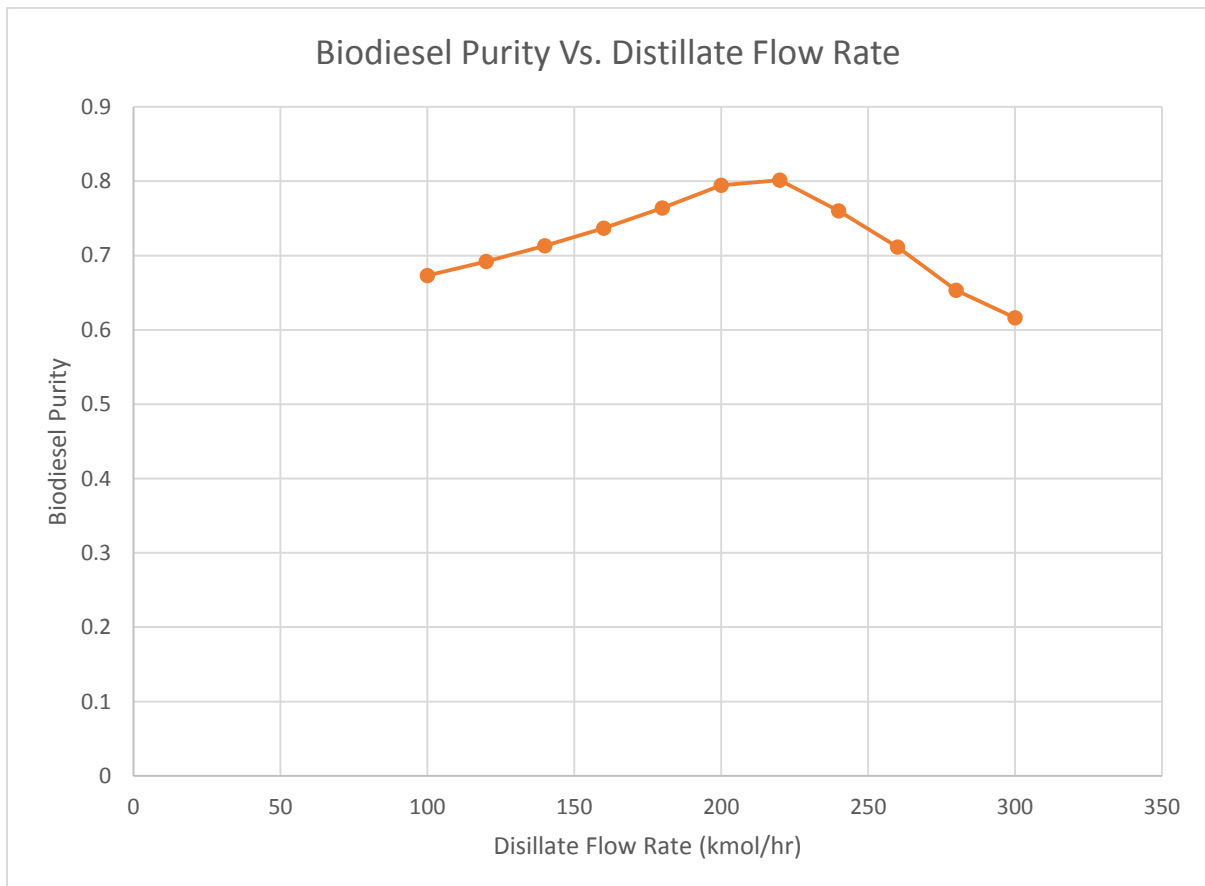
5.3) <u>EFFECT OF TRIGLYCERIDES FLOW RATE</u>: The table and the graph below illustrates the effect of triglycerides flow rate on % conversion of triglycerides. The % conversion of the triglycerides starts to decrease after attaining a point of maximum. At 60 kmol/hr, equilibrium has been attained. So, further increase in the influx of triglycerides causes the equilibrium to shift backwards. Hence, there is a decrease in conversion.

Table 5.5 Effect of triglycerides flow rate on percentage conversion

Triglycerides Flow Rate (kmol/hr)	Percentage Conversion
60	99.14082
65	95.20314
70	91.55945
75	88.18271
80	85.04484
85	82.1214
90	79.39115
95	76.83555
100	74.43839
105	72.18535
110	70.06383
115	68.06264
120	66.17182
125	64.38249
130	62.68669
135	61.07727
137.62	60.26624
140	59.5478
145	58.09246
150	56.70599
155	55.38362
160	54.12101
165	52.91418
170	51.75952
175	50.65373

180	49.59376
185	48.57683
190	47.60036
195	46.66199
200	45.75953

Fig. 5.5 Effect of triglycerides flow rate on percentage conversion
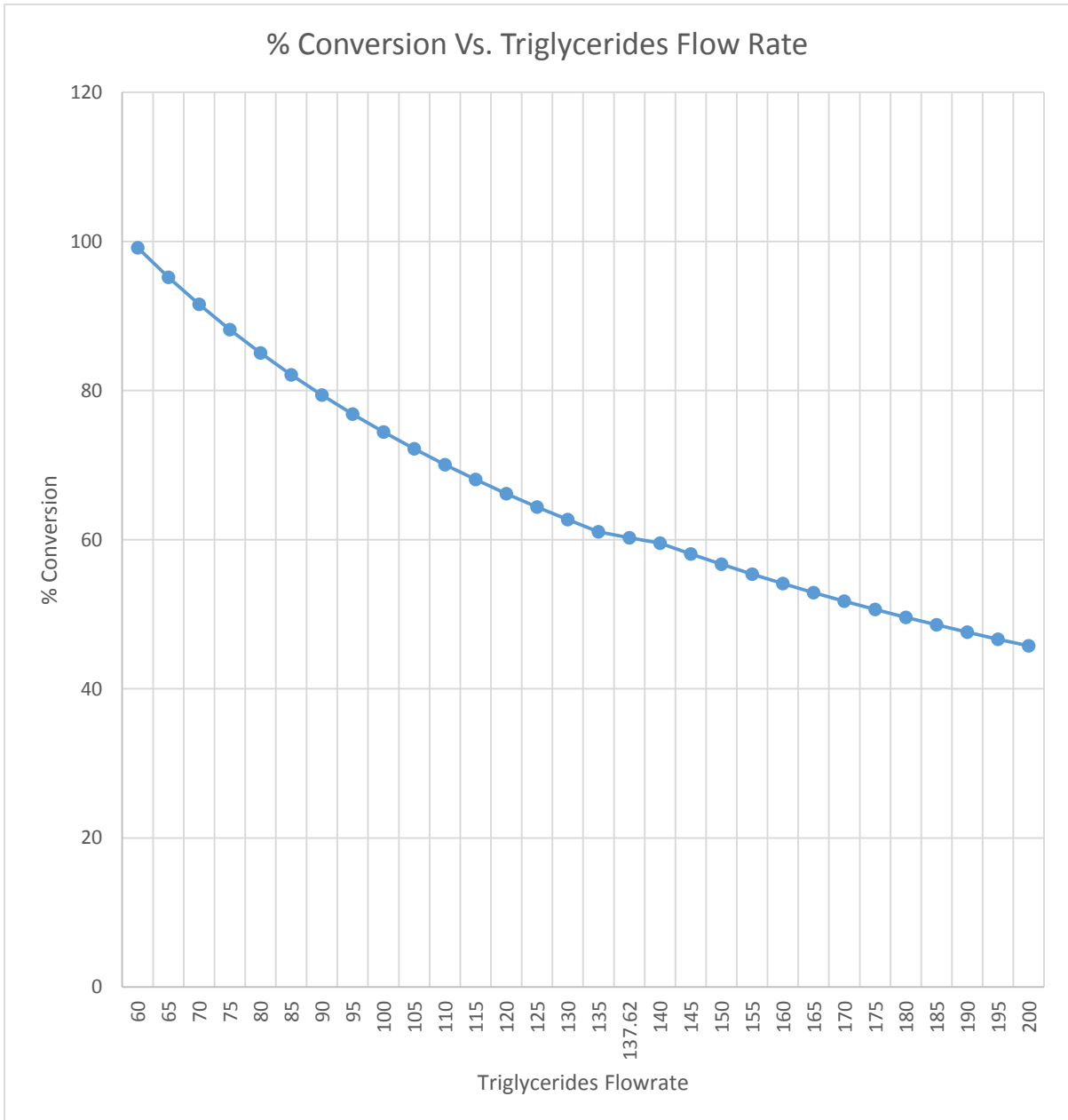
5.4) <u>EFFECT OF REFLUX RATIO</u>: The table and the subsequent graph below shows the influence of reflux ratio on biodiesel purity. It can be seen from the table, that the composition of biodiesel in the bottoms increases unto the point where reflux ratio is 6. And after this point, an increase in reflux ratio causes decrease in the biodiesel composition in the bottoms. Thus, a reflux ratio of 6 should be chosen.

Table 5.6 Effect of reflux ratio on biodiesel purity

Reflux Ratio	Biodiesel Purity
1	0.467
2	0.578
3	0.668
4	0.726
5	0.752
6	0.763
7	0.772
8	0.781
9	0.789
10	0.797

Fig. 5.6 Effect of reflux ratio on biodiesel purity
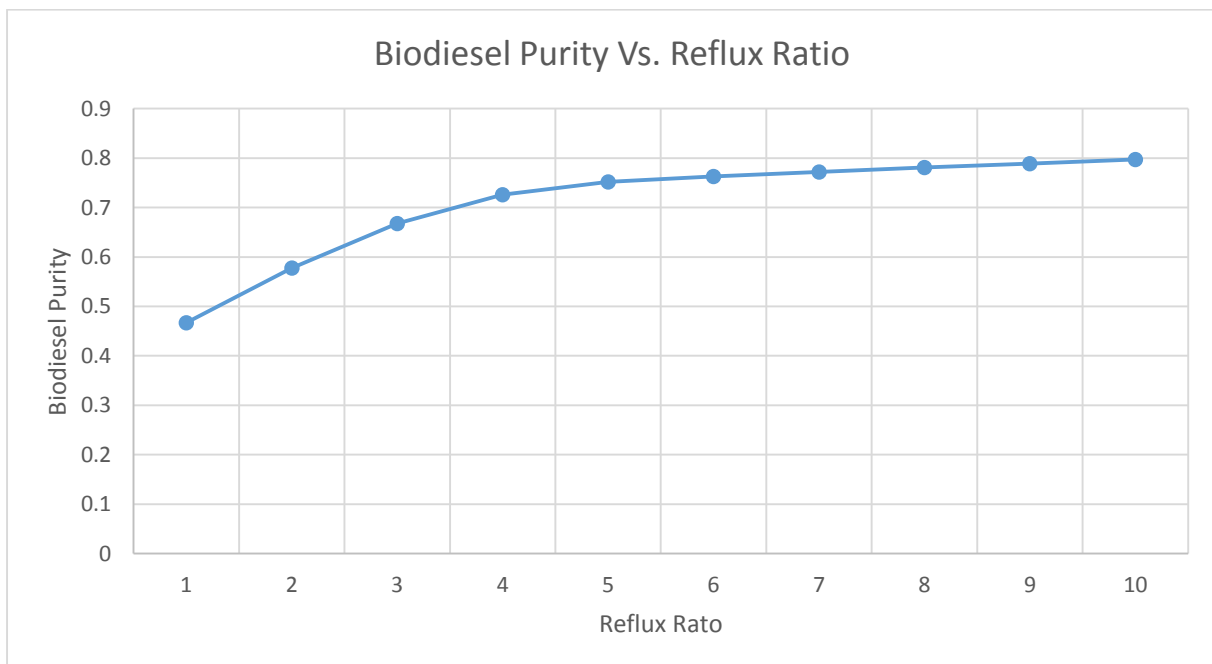
Table 5.7 Effect of reflux ratio on percentage conversion

Reflux Ratio	Percentage Conversion
1	54.3235
2	65.62
3	74.89
4	81.68
5	84.32
6	85.53
7	86.45
8	87.53
9	88.65
10	89.75

Fig. 5.7 Effect of reflux ratio on conversion
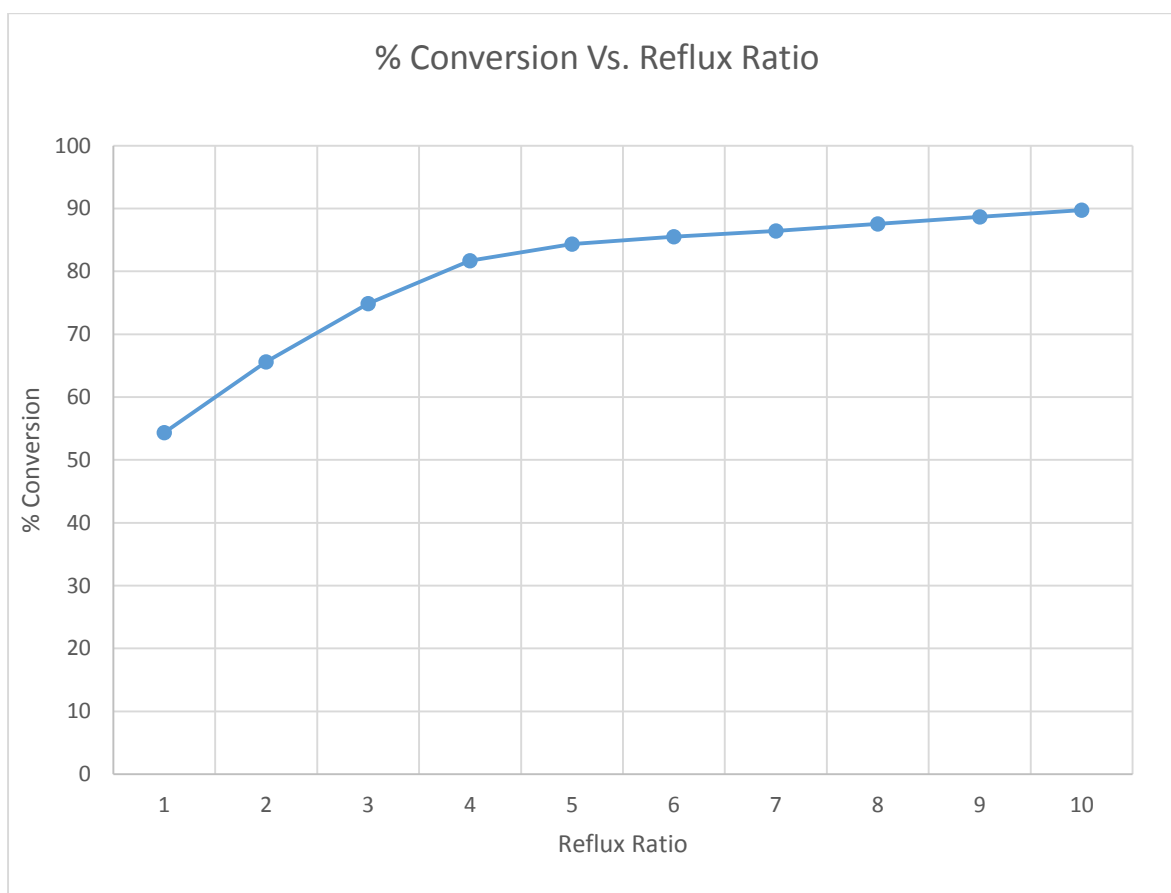
5.5) <u>EFFECT OF NUMBER OF REACTIVE STAGES</u>: Jatropha oil is fed at the top stage 4 while, methanol is fed at the bottom stage 12 of the reactive distillation column. In this work, a total of 15 stages are used and they include 9 reactive stages. Here, the effect of increase in the number of reactive stages on biodiesel purity and % conversion has been studied. Number of stripping and rectifying sections have been kept constant. It can be seen from the below graphs and tables that, with an increase in number of reactive stages, the product purity as well as conversion increase. Purity and conversion increase at a faster rate upto 24 number of stages and after that, rate of increase decreases.

Table 5.8 Effect of increase in number of reactive stages on biodiesel purity

Total Number of Stages	Number of Reactive Stages	Biodiesel Purity
12	6	0.596
15	9	0.628
18	12	0.655
21	15	0.673
24	18	0.705
27	21	0.716
30	24	0.725
33	27	0.738
36	30	0.748

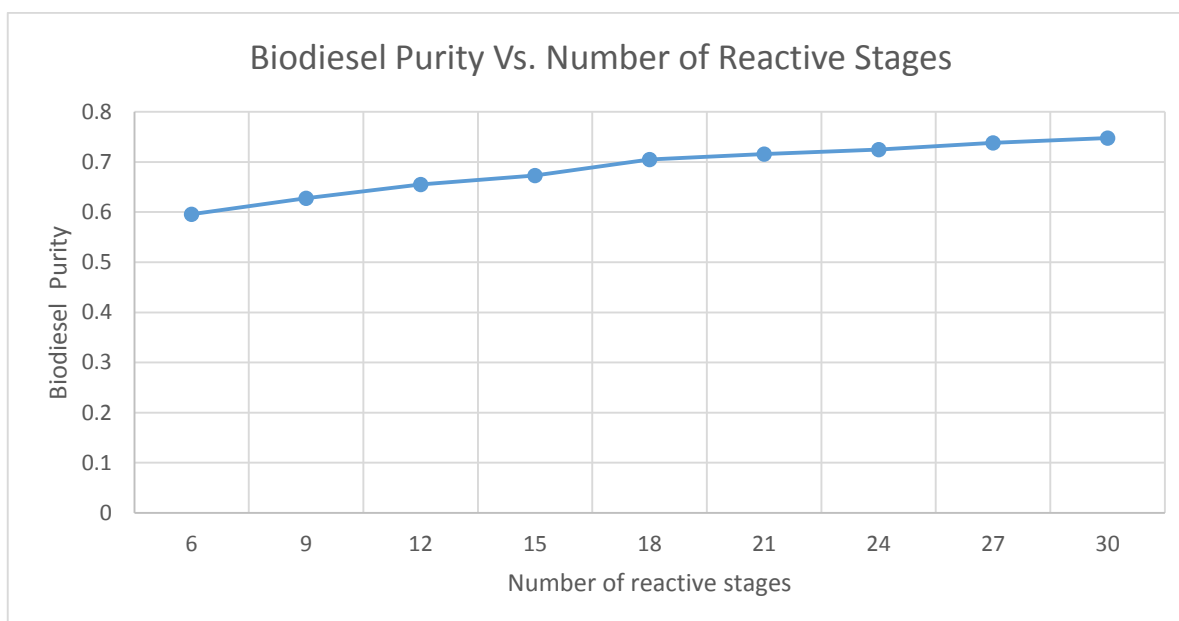Fig. 5.8 Effect of number of reactive stages on biodiesel purity

Table 5.9 Effect of number of reactive stages on percentage triglycerides conversion

Total Number of Stages	Number of Reactive Stages	Percentage Conversion
12	6	64.57
15	9	73.84
18	12	76.32
21	15	77.94
24	18	80.63
27	21	81.65
30	24	82.71
33	27	83.15
36	30	84.19

Fig. 5.9 Effect of number of reactive stages on percentage triglycerides conversion
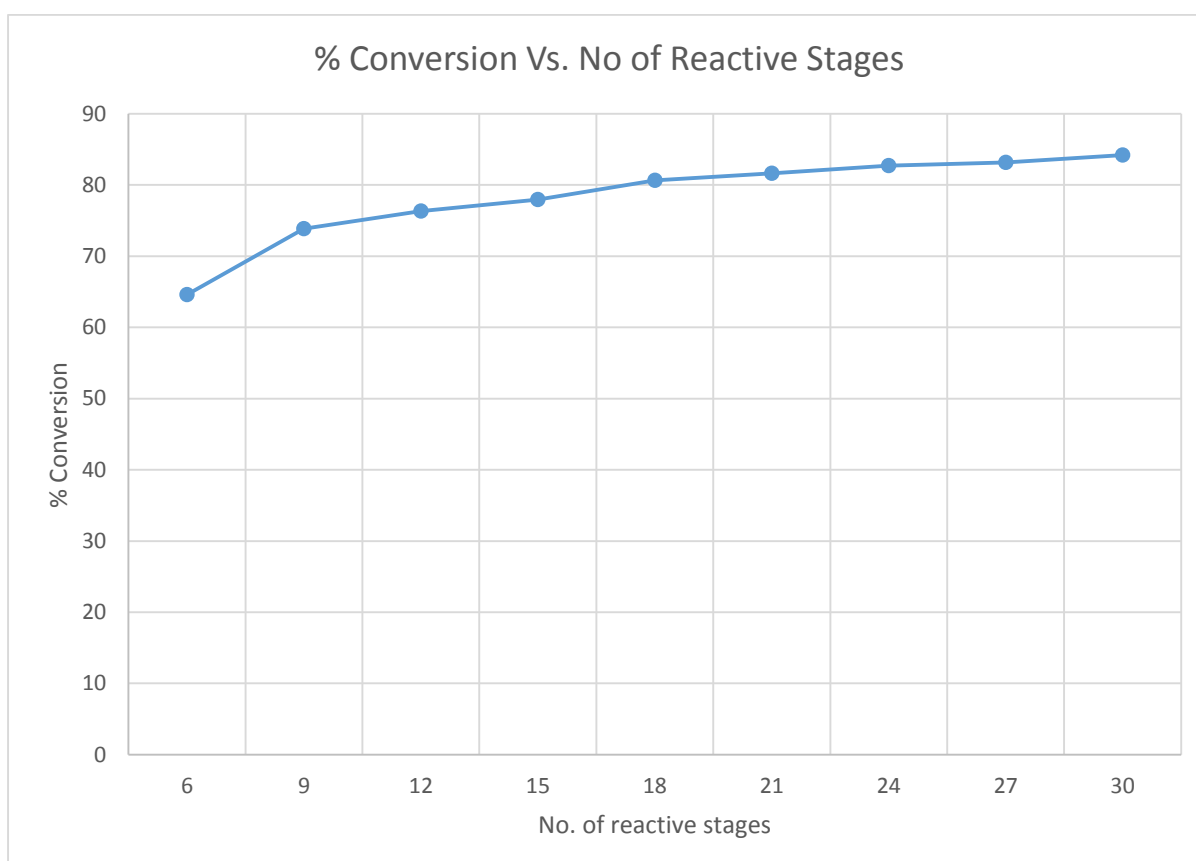
CONCLUSIONS & RECOMMENDATIONS FOR FUTURE WORK

6.1) CONCLUSIONS

In this present work, simulations were performed for the biodiesel production by the transesterification of triglycerides contained in the Jatropha oil using calcium oxide (CaO) as the catalyst. Reactive distillation column was used. Triolein has been used to represent the triglycerides in the simulation work. The results obtained are for the steady state reactive distillation process and they are based on the equilibrium stage model.

The following conclusions can be drawn from the simulations:

1) Biodiesel production in a reactive distillation column proposes several advantages over a conventional reaction column which then is followed by a distillation column in terms of energy savings and biodiesel yield.

2) Parametric study is done to present the optimum configuration required for obtaining maximum triglycerides conversion and subsequent biodiesel's amount in the bottoms.

6.2) RECOMMENDATIONS FOR FUTURE WORK

1) Ethanol can be used instead methanol as ethanol is less toxic than methanol and it is much cheaper than methanol and is easily available.

2) Heat integration of the reactive distillation column can be used in the biodiesel production plants. This can lead to a decrease in the energy requirements.

3) For increasing the yield of biodiesel, a configuration containing distillation column after the reactive distillation column should also be considered.

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