OPTIMIZATION OF BIODIESEL PRODUCTION USING ASPEN PLUS

A Thesis submitted in partial fulfillment of the requirements for the degree of

Bachelor of Technology

in

Chemical Engineering

by

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CERTIFICATE

This is to certify that the thesis entitled "Optimization of biodiesel production using Aspen Plus" submitted by K. Vivek Raja (111CH0482) as a scholastic venture in partial fulfillment of the requirements for the award of BACHELOR OF TECHNOLOGY degree in the Department of Chemical Engineering, National Institute of Technology, Rourkela is an authentic record of bona fide work completed by him under my direction and supervision.

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ABSTRACT

With the continuous increase in energy demand and also simultaneously depletion of fossil fuels made it necessary to research of other alternative sustainable sources of energy. The most promising alternatives include biofuels, especially biodiesel. Here ASPEN Plus software is utilized for a better understanding of models, procedures associated with producing biodiesel. Analyses were also conducted by varying operating parameters to find out how they affect separation throughout the process.

In this project, different models and configurations for producing biodiesel are considered. Models for both trans-esterification and esterification process are designed. In each model, parametric study is done to find optimum parameters at which maximum conversion is obtained and also process is modeled such that heat duty is minimized. Sensitivity analyses are also carried to analyze behavior of all components.

Keywords: Biodiesel, Process simulation, Trans-esterification, Esterification, Optimization

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Nomenclature

$\dot{D}$	Distillate flow rate, kmol/h
e_X	Molar exergy, kW/kmol
E_X	Total exergy, kW
$\dot{F}$	Feed flow rate, kmol/h
h	Enthalpy, kJ/kmol
H	Total enthalpy, kJ
$\dot{Q}$	Heat flow (heat transfer rate), kW
$\dot{L}$	Liquid flow rate, kmol/h
$\dot{n}$	Molar flow rate, kmol/h
$\dot{Q_C}$	Condenser duty, kW
$\dot{Q_R}$	Reboiler duty, kW
R	Reflux ratio
s	Molar entropy, kJ/kmol K
T	Temperature, K
x	Liquid mole fraction
y	Vapor mole fraction
$\dot{V}$	Vapor flow rate, kmol/h
$\dot{W}$	Work, kW

The requirement to meet the world's developing energy requests in an economical way is a key worldwide need, requiring escalated innovative work of cutting edge renewable energy frameworks for oil-based energy and other fossil powers. Energy security, ecological concerns, outside trade reserve funds, and financial issues have made clean biofuels gotten from biomass or organic sources an interesting issue. Among the different option fuel choices, biodiesel has spurned much intrigue and fame. Synthetically, biodiesel is a mixture of unsaturated fatty alkyl-esters (FAAEs), got from triglyceride particles. Triglycerides and liquor are changed over to alkyl esters (biodiesel) through a catalyzed trans-esterification process, as showed in Figure.1 (Nghi Nguyen, 2012)
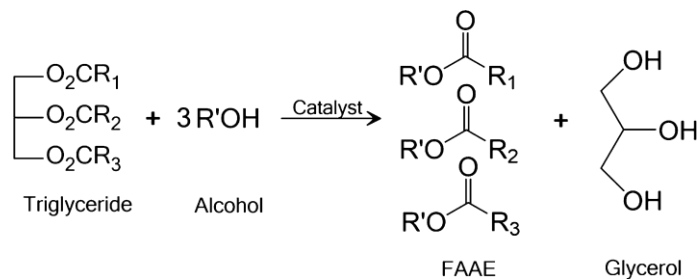
Fig 1.1 Transesterification reaction of triglyceride molecule to form biodiesel.

Glycerol and FAAEs are then differentiated and refined. Rapeseed and soybean oils are the main vegetable oils for biodiesel generation. The ordinary catalysts for the trans-esterification reaction of these vegetable oils are dominatingly fundamental generally antacid or basic earth oxides or alkoxides. Biodiesel is exceptionally appealing as a renewable and naturally agreeable fuel alternative for residential motors, aside from being nontoxic and biodegradable, biodiesel brings

about lesser air pollution and gives energy more than diesel and an expected 93% more energy than the energy put resources into delivering it. Biodiesel likewise has a higher flash point temperature of 150 °C, making its taking care of, utilization, and transport more secure than petroleum diesel and better greasing up properties that minimize motor wear and tear. A promising different option for petroleum, biodiesel utilization and production is subsequently anticipated that would rise fundamentally significantly.

The world's oil supply is foreseen to drain by 2060 because of the increment in interest for energy coupled with exhaustion of petroleum oil. Accordingly, looking for a feasible energy pathway to meet the energy needs without bounds era is attractive. Biodiesel is renewable, nontoxic, biodegradable, and basically free of sulfur and aromatics may be a standout amongst the most suitable contender for future bio fuel. Alongside, U.S. Branch of Energy life cycle examination on biodiesel demonstrates that biodiesel produces 78.5% less net carbon dioxide outflows contrasted with petroleum diesel. In 2011, the United States delivered pretty nearly 1.1 billion gallons of biodiesel and the volume of production is required to increment to 1.9 billion gallons in 2015. Significant downsides of biodiesel production utilizing vegetable oil are the expense of assembling and the high cost of oil since it contends with nourishment. As of now, biodiesel production plants rely on upon government appropriations to keep their plants in operation. Accordingly, looking for a more financial biodiesel generation methodology to lessen the reliance of government appropriations and advance extension of biodiesel industry is desired.

Distillation is considered as an adult innovation and it is utilized for the partition of numerous mixtures; on the other hand, a few enhancements are being made with a specific end goal to decrease the energy and cooling water requests, since it is no doubt understood its high energy prerequisites. These days, the tricky related to the energy prerequisites is more extreme on account of the decreases in fossil powers and strategies in nursery gasses

outflows. Therefore, vital advancements have been completed in biofuels, for example, bioethanol, biodiesel, bio turbo sine and others. On account of the biodiesel production, reactive distillation and responsive retention have been considered to accomplish higher transformations and lower prerequisites of energy and cooling water.

Process Overview:

Since straight vegetable oil (SVO), a triglyceride, is excessively gooey and does not have other needed properties to proficiently fuel cutting edge diesel motors without decreasing motor life, the SVO must experience a methodology of trans-esterification whereby one of its R-gatherings is supplanted by the R-gathering of a liquor, normally methanol, consequently shaping alkyl esters, or biodiesel. A basic catalyst, normally NaOH, is utilized to deprotonate the methanol making it a stronger nucleophile that wills all the more openly responds with the triglyceride. Through this process, the breaking point of the recently created biodiesel is much lower, as it stands its thickness and propensity to polymerize. All things considered, it can be utilized as a part of customary diesel motors without gambling motor wellbeing. It is additionally frequently blended with ordinarily extricated diesel because of its predominant lubricity. Given the undeniably strict laws on sulfur content in traditional diesel for ecological reasons, the expansion of biodiesel gives a significant advantage in supplanting the ointment. Glycerol is additionally framed through the procedure and is effortlessly tapped. It can then be refined and sold for utilization in the production of cleansers and other nonessential and pharmaceutical items. In a run of the mill persistent procedure biodiesel plant, the reaction happens in two stages and the general methodology can be compressed in the accompanying steps:

Vegetable Oil Pretreatment

Waste oil is gotten into capacity. Water is emptied and sent to waste water stockpiling or treatment. The oil is gone through a coarse channel to uproot polluting influences and sent to a dryer to evacuate further overabundance water. In the wake of drying, the oil is for the most part gone through extra channels to guarantee the evacuation of all particulate matter.

Trans-esterification

Vegetable oil, methanol and an antacid catalyst are bolstered into the reactor with methanol in sums reasonably higher than the stoichiometric proportion (more than 3 moles methanol to 1 mole triglycerides) furthermore, the reaction happens at a generally low temperature and weight.

Settling

The stream leaves the reactor into a settling tank where the glycerol is emptied and further decontaminated. The remaining results of methanol, triglycerides, biodiesel and different contaminations are killed, generally with hydrochloric acid, and are then bolstered to a distillation section.

Distillation

The stream leaves the reactor into a distillation column. Unreacted methanol is dissipated and recycled back to capacity or straightforwardly into the second reactor. The remaining mixture is bolstered to a second reactor.

Trans-esterification II

Methanol and the unreacted triglycerides are sustained into a second reactor and the reaction is again base catalyzed. The settling and balance steps are rehashed with items from the second reactor.

Distillation II

The items from the second balance tank are refined and the dissipated methanol is once more recycled back to capacity. The biodiesel is gathered and put away and for the most part has a change rate of 80-95% (Hillion, Delfort, le Pennec, Bournay, & Chodorge, 2003). It ought to be noticed that a acid catalyst can likewise be utilized. Its utilization would help avoid undesirable reactions from happening between the hydroxyl radical and alkyl esters (saponification). On the other hand, the reaction can occur without a catalyst by any means, wherein the triglyceride is responded with methanol in a supercritical state, at a high temperature and weight such that the two reactants are in a solitary stage and the reaction continues suddenly. With the end goal of improving the methodology in Aspen, and catalyst was excluded simultaneously.

LITERATURE REVIEW

According to (Nghi Nguyen, 2012), these days, biodiesel generation methodologies use waste vegetable oil (WVO), creature fats, and virgin oil as feedstock. When in doubt, the higher the nature of the feedstock, the more lavish it will be. Refined soybean, palm, assault and canola oils, contain more than 99% of triglycerides, are samples of probably the most costly oils. WVO and creature fats are the least expensive feedstock yet the expense of generation may be most astounding because of high substance of free unsaturated fats and contaminants (water, particles, phospholipids, and so forth.) in triglycerides. Table 2-1 gives the rough centralization of free unsaturated fat in refined vegetable oils, unrefined vegetable oils, eatery waste oil, creature fat, and trap oil. In the United States, soybean oil is most usually utilized for biodiesel production. Presently, roughly 90% of biodiesel in the United States is gotten from soybean oil. The present cost of oil is about $60.0/barrel and it is records for more than 50% of the expense of biodiesel production.

Table 2-1. Free fatty acid content in biodiesel feed stocks. [8]

Feedstock	Free fatty acid content (%)
Refined vegetable oils	<0.05
Crude vegetable oils	0.3-0.7
Restaurant waste grease	2-7
Animal fat	5-30
Trap grease	10-100

Table 2-2 gives the unsaturated fat synthesis of some usually utilize oils. As indicated by the

United States Department of Agriculture (USDA), 6.18 million metric huge amounts of coconut oil is created worldwide in 2011. At present, coconut oil is being utilized to create biodiesel in Philippines. Biodiesel delivered from coconut oil gel point is around 10°C, accordingly, utilization of immaculate biodiesel is conceivable just in calm atmospheres. Cool stream improvers, for example, poly homo polymer, ethanol, and olefin-ester copolymers, can be mixed to enhance the chilly stream properties of biodiesel.

Table 2-2. Fatty acid composition of different oils [7]

Fatty acid component	Crude soybean oil (%)	Food grade soybean	Waste cooking oil	Crude palm oil (%)	Crude algae oil (%)	Crude corn oil from	Crude coconut oil
C 12:0	0	0	0	0	0	0	49.13
C 14:0	0.27	0	0	0.21	2.72	0	19.63
C 16:0	13.05	11.07	11.58	41.92	20.91	11.50	10.12
C 16:1	0.39	0.09	0.18	0.23	10.62	0	1.79
C 18:0	4.17	3.62	4.26	3.85	6.95	4.77	2.83
C 18:1	22.75	20.26	24.84	42.44	33.33	26.26	7.59
C 18:2	52.78	57.60	53.55	11.30	18.45	56.20	2.75
C 18:3	6.59	7.36	5.60	0.04	1.16	1.27	0.15
Others	0	0	0	0	6.86	00	6.01

2.1 Biodiesel Production Process [1]

2.1.1 Biodiesel Production from Triglyceride

Triolein is utilized to speak to triglyceride in this study for reproduction purposes. Every one of the three unsaturated fat chains of triolein are oleic acid. The atomic weight of triolein is 885.46 g/mol, which is like the sub-atomic weight of soybean oil.

2.1.2 Trans-esterification Reaction

The trans-esterification reaction component comprises of three back to back and reversible reactions [2]. Notwithstanding, the disentangled manifestation of the trans-esterification reaction can be depicted by
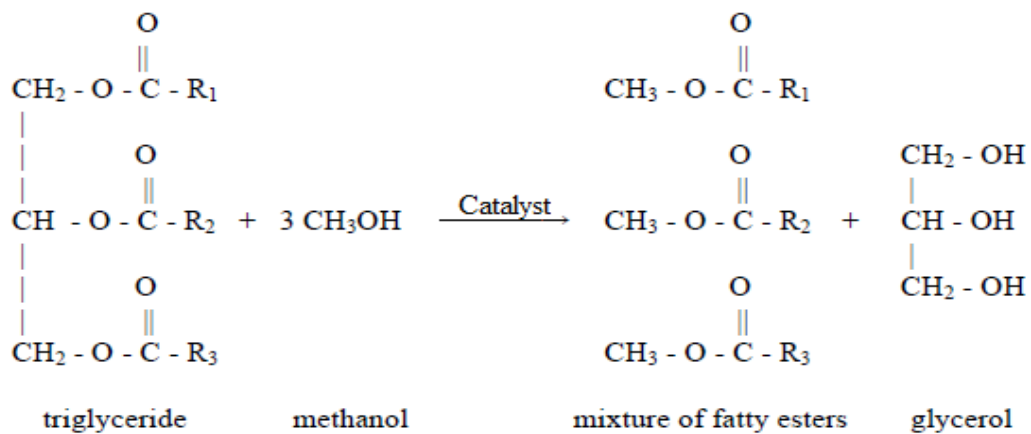
Fig 2.1 Trans-esterification Reaction (Nghi Nguyen, 2012**)**

Here R1, R2, and R3 are the unsaturated fat chains, which makes out of carbon and hydrogen particles. Most biodiesel production methods use sodium hydroxide (NaOH) or potassium hydroxide (KOH) as a catalyst to launch the trans-esterification reaction. The catalyst is obliged essentially to enhance the dissolvability of methanol in the oil stage. A solid mineral acid is utilized to kill the base catalyst after the reaction.

2.2 Biodiesel Production by Trans-esterification

Presently, most biodiesel production plants use triglyceride, methanol and NaOH or KOH as the three essential crude materials. Fig. 2-1 demonstrates the least difficult biodiesel production prepare by trans-esterification. The trans-esterification reaction generally continues at 6:1 methanol

to oil molar proportion, 65°C and utilize 0.3% to 1.5% of sodium hydroxide. Free unsaturated fats respond with a base catalyst and structure cleanser and water, in this manner, it focus must be kept underneath 1% so as to keep the cleanser and water impacts. The reactor outlet is sent to the decanter for stage division in the middle of glycerol and biodiesel. Both stages contain liquor, hence, an evaporator or a flash unit is utilized to expel liquor from both the glycerol and ester. Water is utilized to kill and wash the glycerol stream. Water is additionally used to wash and kill the ester stream to evacuate salts and lingering methanol. A dryer unit is utilized to expel water from biodiesel.
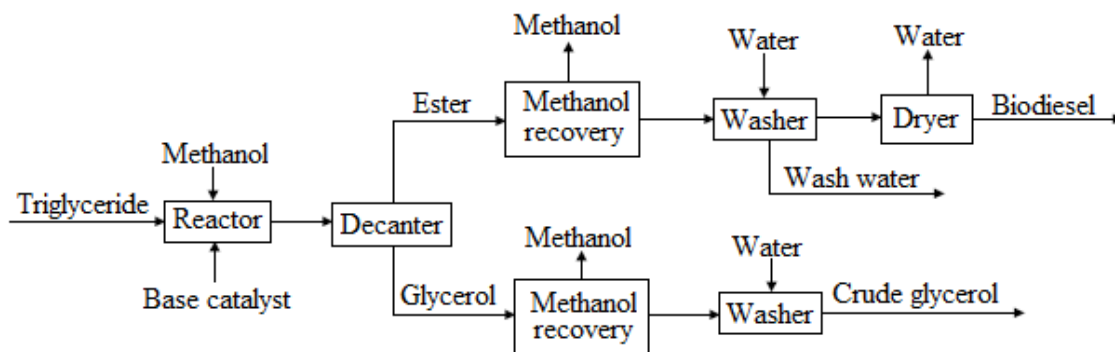
Fig. 2-2. Biodiesel production by trans-esterification.(Nghi Nguyen, 2012)

2.2.1 Biodiesel Production from Free Fatty Acid[3]

Oleic acid, a soaked medium chain unsaturated fat with 12-carbon particle chain, is utilized to speak to free unsaturated fats in this study for reproduction purposes in light of the fact that the reaction active information is promptly accessible in writing. Oleic acid is the significant part of soya bean oil as demonstrated in Table 2-2.

2.2.2 Esterification Reaction

Esterification of free unsaturated fat with methanol is given by

$$H-O-\overset{\overset{\displaystyle O}{\|}}{C}-R_1 \ + \ CH_3OH \ \xrightarrow{\text{Catalyst}} \ CH_3-O-\overset{\overset{\displaystyle O}{\|}}{C}-R_1 \ + \ H_2O$$

free fatty acid   methanol   mixture of fatty esters   water
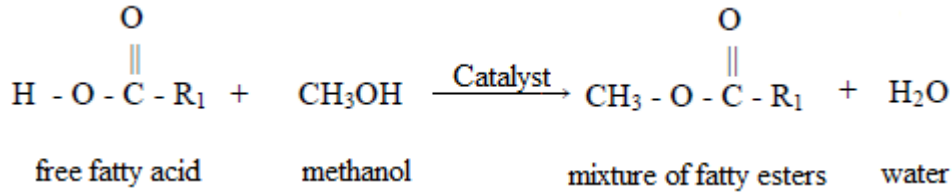
Fig 2.3 Esterification reaction (Nghi Nguyen, 2012)

Here, water is delivered as the by-item rather than glycerol. A solid homogeneous acid catalyst, for example, sulfuric acid (H2SO4) or sulfonic acid, is ordinarily used to catalyze the esterification reaction since base catalysts respond with free unsaturated fats to frame cleanser and water.

2.3 Biodiesel Production by Esterification

Some biodiesel plants e.g. BTK&S Biodiesel utilize almost unadulterated free unsaturated fat, methanol and a solid acid catalyst as crude materials for biodiesel generation. A basic methodology stream graph of biodiesel production by esterification is displayed in Fig. 2-3. A solid base is utilized to kill the acid catalyst after the reaction. The item stream is then sent to the methanol division unit to recuperation methanol. Further, water and different debasements are evacuated by utilizing a dryer unit.
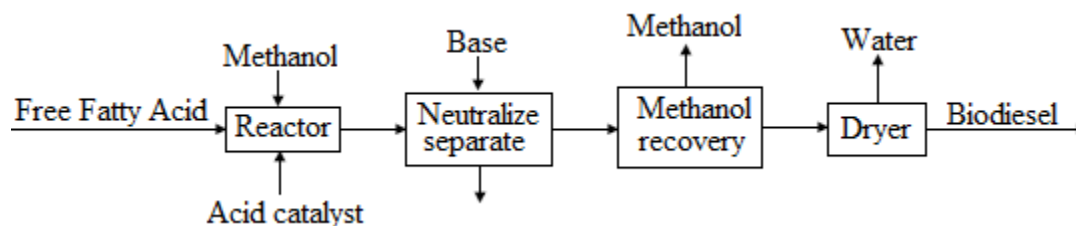
Fig. 2.4 Biodiesel production by esterification.(Nghi Nguyen, 2012)

2.4 American and European Biodiesel Quality Standards (ASTM D-6751) (Nghi Nguyen, 2012)

Parameters that must be met to acquire ASTM D6751 biodiesel quality standard are:

1. Flash point must be greater than $93^{o}C$.

2. Water and sediment must be under 0.05% by volume.

3. Kinematic viscosity at $40^{o}C$ is between 1.9 - 6.0 mm^{2}/s.

4. Sulfated ash must be under 0.02% by mass.

5. Total sulfur must be under 0.05 wt%.

6. Copper strip erosion must be less than No. 3.

7. Methanol content must be under 0.20% by volume.

8. Cetane number must be more than 47.

9. Cloud point must report in ^{o}C to client.

10. Carbon residue must be under 0.50% by mass.

11. Acid number must be lower than 0.50 mg KOH/g.

12. Free glycerine must be under 0.02% by mass.

13. Total glycerin must be under 0.24% by mass.

14. Phosphorus must be under 0.001 wt%.

15. Vacuum distillation end point must be under $360^{o}C$.

16. Oxidatione stability must be more than 3 hours.

ASTM Internationl has complete duplicates of ASTM g

Aspen Plus reproduction utilizes fundamental building connections, for example, mass and energy offsets, to gauge the conduct of a compound procedure. Aspen Plus reenactment permits methodology specialists to outline and test a synthetic process in brief time of time. Likewise, it can be utilized to explore the impacts of diverse configuration parameters of the synthetic process and give comes about that are hard to acquire in research center. By utilizing test thermodynamic information and practical working conditions, the real process conduct can be reenacted. Also, transform reenactment empowers methodology architects grow better methodologies by utilizing devices, for example, affectability investigation, adding machine square, enhancement piece, benefit examination and outline particular. Aspen Plus methodology reproduction can be utilized by the accompanying steps: [4]

Step 1: Identify the unit operations and the procedure streams that stream to and from them in the process flow sheet. Name all streams and associate them to the unit operation models.

Step 2: Identify the substance columns from the Aspen Plus databanks or characterize them all the while.

Step 3: Identify thermodynamic models incorporated with Aspen Plus to gauge the physical properties of the parts and mixtures simultaneously.

Step 4: Identify the thermodynamic conditions and the part stream rates of the info streams.

Step 5: Identify the working conditions for the unit operation models.

Users can change the majority of the above information details to dissect option forms. Besides, Aspen Plus can be utilized to fit plant information to reproduction models,

foresee and relapse physical properties, create even yield results, and interface results to spreadsheets. In this undertaking, different models are contrasted with produce biodiesel and parameters are improved such that greatest transformation and least warmth obligation is gotten.

Now, for trans-esterification reaction, let us consider different models to study.

3.1 Model 1: (using Distillation column)

This model is designed with reference to (Nghi T. Nguyen, 2012) with considerable modifications.

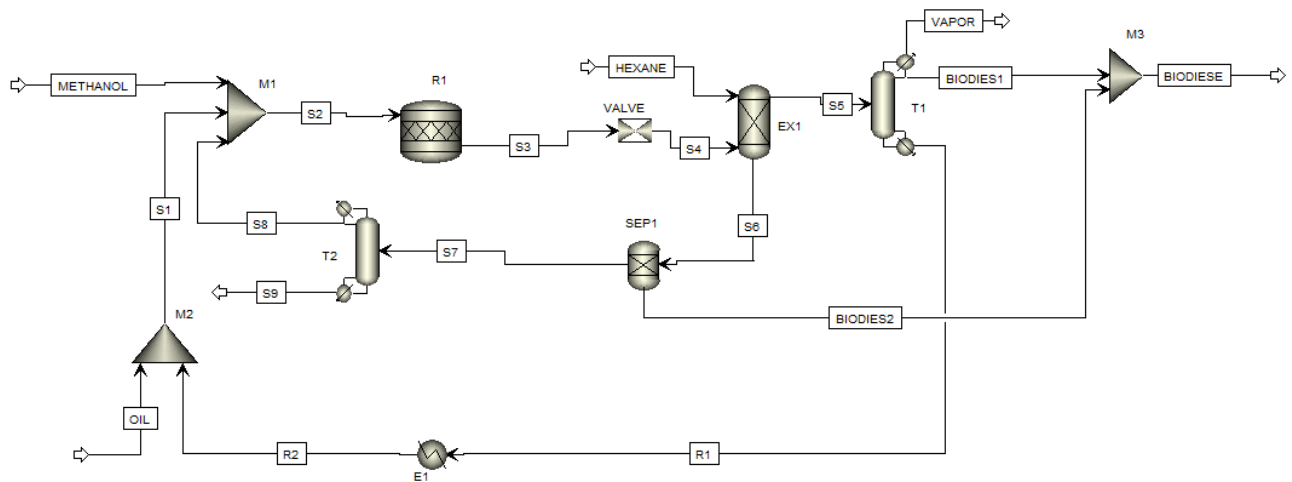**Fig. 3-1.** Process flow diagram for trans-esterification process model 1

Stiochiometric Equation for reaction taking place:

$$C_{57}H_{104}O_6 + 3CH_3OH \longrightarrow 3C_{19}H_{36}O_2 + C_3H_8O_3$$

(Triolein)   (methanol)   (Biodiesel)   (Glycerol)
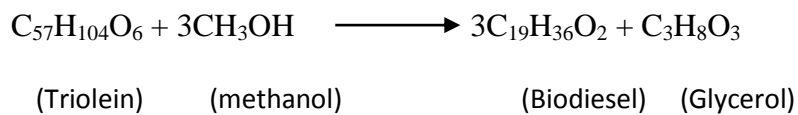
Table 3.1 Operating conditions of Distillation Columns

Conditions & Configuration	Design
No. of stages	4
Feed stage	2
Feed temperature, ^{o}C	60
Pressure, bar	0.08
Reflux ratio	1
Condenser duty, kW	-4081.06
Distillate rate, kmol/hr	37.09
Condenser temperature, ^{o}C	49.98
Reboiler duty, kW	4135.89
Boil up rate, kmol/hr	127.79
Bottoms rate, kmol/hr	0.87
Reboiler temperature, ^{o}C	297.70

Fig. 3.1 demonstrates the procedure flow diagram (PFD) of a routine biodiesel plant with retrofitted distillation sections. The biodiesel plant uses methanol, oil, NaOH and hexane as the essential food streams, and produces 2,175.40 kg/h and 96.3% pure unsaturated fat methyl ester (FAME). The byproducts are 94.7% pure 134.55 kg/h glycerol. Recycle and new methanol and oil are blended in blender M2 before sending to the RStoic reactor, R1, as indicated in Fig.3.1. The FAME synthesis happens in an RStoic reactor by trans-esterification reaction catalyzed by NaOH at 60°C with a byproduct of glycerol. The methanol/oil molar proportion is 6:1 and 95% percent oil transformation was assumed. The reactor outlet contains FAME, methanol, oil, hexane, NaOH, and glycerol is pumped into the extractor EX1 that uses hexane as a solvent to in part extricate polar parts from the mixture. The top item is encouraged to distillation column T1 at stage 2 where the FAME is cleaned. This section works with four stages, a fractional vapor-fluid condenser and a pot reboiler. The base item containing some FAME and basically oil is recycled to the reactor. The vapor stage stream containing little measures of hexane/methanol is a

waste stream while the distillate is the item FAME. Tables 4-1 demonstrate the stream results of the above plant as shown in Fig. 3.1.

The bottom stream of the extractor EX1 and phosphoric acid (H3PO4) are fed to the separator where biodiesel separates from other components. The top stream contains about immaculate glycerol while the distillate is cooled to $80^{\circ}C$ and encouraged to stage 9 of distillation column T2 for filtration of methanol. Column T2 has 12 stages, an aggregate condenser and a pot re boiler. The base item is basically hexane and other impurities and the distillate methanol is recycled through blender M1.

3.2 Model 2: (without using distillation column)

This model is designed with reference to (David Houghton et al., 2014). The methodology was demonstrated in Aspen to focus ideal conditions to expand the change of vegetable oil to biodiesel. Vegetable oil is an intricate arrangement which was spoken to as triolein in the reproduction. Biodiesel was spoken to as methyl oleate. Triolein is responded with methanol to create methyl oleate and glycerol as per the reaction underneath.

Stiochiometric Equation for reaction taking place:

$$C_{57}H_{104}O_6 + 3CH_3OH \longrightarrow 3C_{19}H_{36}O_2 + C_3H_8O_3$$

(Triolein)   (Methanol)   (Biodiesel) (Glycerol)
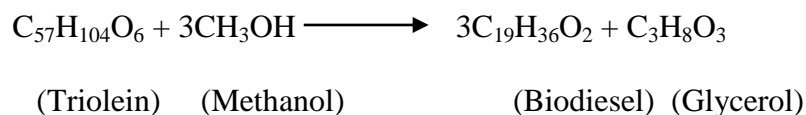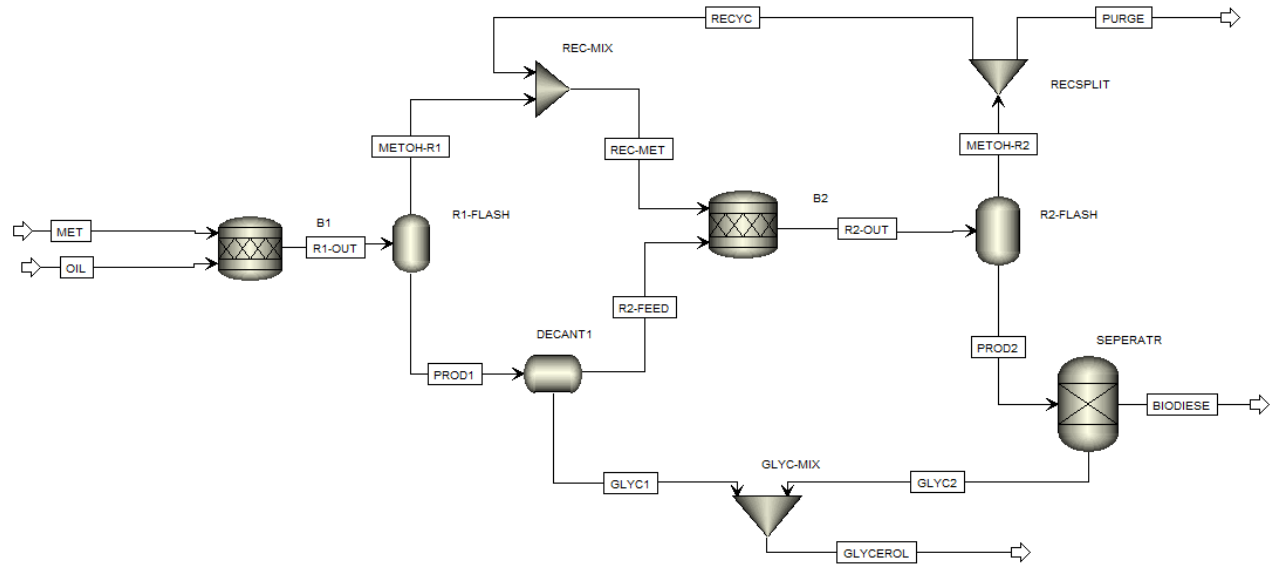
Figure 3.2: Biodiesel production process flow sheet of model 2

The process model included two RStoic reactors worked in arrangement, as indicated in the process stream sheet above. Triolein (FEED-OIL) of 100lbmol/hr and methanol (FEED-MET) 300lbmol/hr were fed into the first RStoic reactor (R1) in stoichiometric sums. The outlet of this reactor (R1-OUT) was divided in a flash drum (R1-FLASH) to uproot unreacted methanol (METOH-R1) to be gone to the second reactor. The two stage fluid leaving the first flash drum (PROD1) was then divided in a decanter into glycerol (GLYC1) and a mixture of the unreacted triolein and biodiesel (R2-FEED). The triolein-biodiesel mixture then entered the second RStoic minister (R2) with recycled methanol (REC-MET). The second reactor item stream (R2-OUT) was then flashed to uproot and recycle methanol (METOH-R2), this stream was part (RECSPLIT) to permit a cleanse stream (PURGE). The bottoms fluid (PROD2) was emptied (DECANT2) to split the (BIODIESEL) of around 299lbmol/hr and glycerol (GLYC-2). The glycerol streams were consolidated (GLYC-MIX) to create the last glycerol item as a procedure yield.

For the Esterification reaction, only one simple model is considered:

3.3 Model:
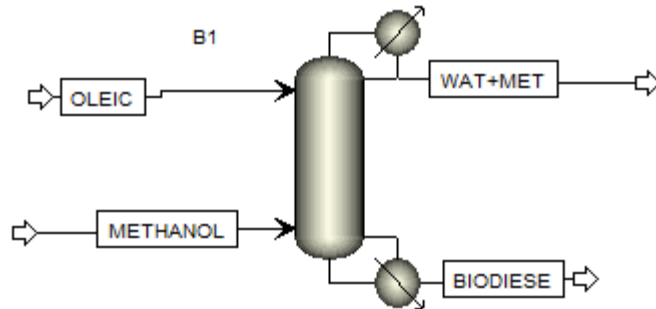
Fig 3.3 Process flow sheet for esterification process

Esterification of oleic acid with methanol may be described by

Methanol + oleic Acid ⟶ Ester (Biodiesel) + Water
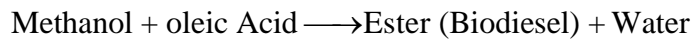
  The reactive distillation column uses methanol and oleic acid as essential feedstock to deliver methyl oleate and water. The section comprises of 30 stages with two partition zones at every end and a reaction zone in the center, and works with an aggregate condenser and a pot reboiler. Stream oleic comprises of 100 kmol/hr of oleic acid, which is warmed to 100°C preceding entering top of the reaction zone of the column at stage 3. Stream METH comprises of 199 kmol/hr of methanol and 1 kmol/hr of water, which is warmed up near to methanol's immersion point and encouraged into the base of the reaction zone of the section at stage 29. The ester with a 104 kmol/hr stream rate is the base item, while the distillate is the mixture of water and methanol with a stream rate 196 kmol/hr. The action coefficient model UNIQUAC is utilized to gauge the stage balance in the section.

The test system of Aspen Plus is utilized to perform the reproduction esterification of oleic acid with methanol. Oleic acid originates from soya bean oil. The main period of this work is to diminish the centralization of water in the reaction zone by conforming the reflux proportion and obligation of a side warmer in a balance plan. The outcomes are then utilized as starting data values for the non-harmony plan. Under indistinguishable setups and conditions, non-balance configuration has yielded lower transformation because of complex warmth and mass exchange rates between the vapor and fluid stages. Accordingly, number of stages and weight expected to be balanced keeping in mind the end goal to attain to the same level of change.

RESULTS AND DISSCUSION

4.1 For Model 1: (Stream Results)

	OIL	METH	R1	R2	R3	S1	S2	S3	S4
Mass Flow kg/hr									
METHANO	0.00	1125.92	0.00	0.00	1045.33	0.00	2171.25	1139.91	1139.91
OIL	9639.09	0.00	360.92	360.91	0.00	10000.00	10000.00	500.00	500.00
METHY-01	0.00	0.00	140.00	140.00	0.00	140.00	140.00	9683.26	9683.26
GLYCEROL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	988.09	988.09
NAOH	0.00	0.00	0.00	0.00	0.00	0.00	95.99	95.99	95.99
HEXANE	0.00	0.00	0.00	0.00	8.40	0.00	8.40	8.40	8.40
Mass Frac									0.0918
METHANO	0.0000	1.0000	0.0000	0.0000	0.9920	0.0000	0.1749	0.0918	0.0403
OIL	1.0000	0.0000	0.7205	0.7205	0.0000	0.9862	0.8054	0.0403	0.7799
METHY-01	0.0000	0.0000	0.2795	0.2795	0.0000	0.0138	0.0113	0.7799	0.0796
GLYCEROL	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0796	0.0077
NAOH	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0077	0.0077	0.0007
HEXANE	0.0000	0.0000	0.0000	0.0000	0.0080	0.0000	0.0007	0.0007	0.0000
Total Flow kg/hr	9639.09	1125.92	500.92	500.91	1053.73	10140.00	12415.64	12415.64	60.11
Temperature C	25.00	25.00	297.91	25.00	64.53	25.00	29.46	60.00	1
Pressure bar	1	1	0.18	1	1	1	1	4	

	HEXAN	S5	S6	VAPOR	BIODIES	S7	BIODIES	BIODIES
Mass Flow kg/hr								
METHANOL	0.00	88.73	1051.18	70.50	0.00	1051.18	1051.18	1045.40
OIL	0.00	500.00	0.00	0.16	0.00	0.00	0.00	0.00
METHY-01	0.00	9682.11	1.14	0.00	0.00	1.14	1.14	1.12
GLYCEROL	0.00	0.00	988.09	0.00	0.00	988.09	988.09	16.12
NAOH	0.00	0.00	95.99	0.00	0.00	0.00	0.00	0.00
HEXANE	0.00	33.50	124.90	27.37	0.00	168.13	168.13	167.36
Mass Frac								
METHANOL		0.0086	0.4649	0.7191	0.0000	0.4493	0.4760	0.8499
OIL	0.0000	0.0485	0.0000	0.0016	0.0000	0.0000	0.0000	0.0000
METHY-01	0.0000	0.9396	0.0005	0.0000	0.0000	0.0005	0.0005	0.0009
GLYCEROL	0.0000	0.0000	0.4370	0.0000	0.0000	0.4223	0.4474	0.0131
NAOH	0.0000	0.0000	0.0424	0.0000	0.0000	0.0000	0.0000	0.0000

HEXANE	0.0000	0.0033	0.0552	0.2792	0.0000	0.0719	0.0761	0.1361
Total Flow	0.0000	10304.35	2261.29	98.03	131.15	2339.69	2208.54	1230.00
Temperature C	78.40	60.40	60.19	53.67	50.00	50.00	50.00	100.00
Pressure bar	25.00	1	1	0.08	1	1	1	0.05
	1							

Fig 4.1 Stream Results of model 1

The biodiesel plant uses methanol, oil, NaOH and hexane as the essential food streams, and produces 2,175.40 kg/h and 96.3% pure unsaturated fat methyl ester (FAME). The byproducts are 94.7% pure 134.55 kg/h glycerol. Recycle and new methanol and oil are blended in blender M2 before sending to the RStoic reactor, R1, as indicated in Fig.3.1. The FAME synthesis happens in an RStoic reactor by trans-esterification reaction catalyzed by NaOH at 60°C with a byproduct of glycerol. The methanol/oil molar proportion is 6:1 and 95% percent oil transformation was assumed.
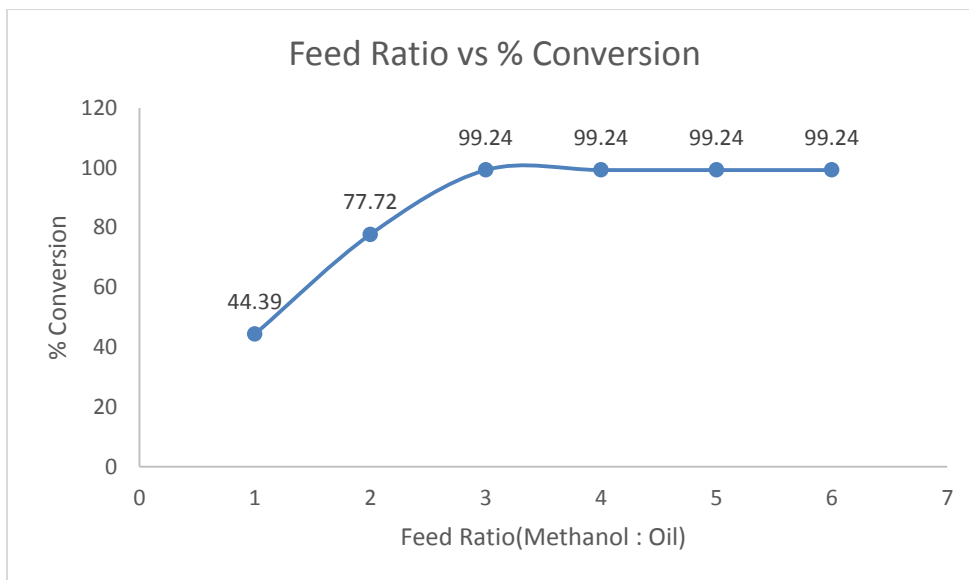

Fig 4.2 Change of conversion with feed ratio

Table 3-1 shows the base case design (Model 1) operating conditions and design parameters for distillation column T1, which operates with four equilibrium stages. Here we can observe that after obtaining a feed ratio of 3 i.e. ratio of methanol to oil in feed to 3, there is no significant

increase in conversion rate. Hence 3:1 is considered as optimum feed ratio.

Table 4.1 Product Configuration

Key Product	Stream	Total Flow (kmol/hr)	Composition (Mol %)				
			Hexane	Methyl-Oleate	Glycerol	Methanol	Triolein
Biodiesel (Methyl-oleate)	BIODIESEL	4.829	0.24	85.5	14.06	0.323	0.006
Glycerol	GLYCEROL	1.252	1.09	0.013	94.53	2.168	2.199
Hexane	VAPOR	0.02	96.88	0.005	0.0003	3.11	0.002

Table 4.2 Heat duty Calculation

Process	Block	Duty (kW)
Reactor 1	R1	-128.681
Distillation Column 1	T1	-338.208
Separator 1	SEP1	0.1127
Cooler	E1	-17.781
Distillation Column 2	T2	334.557
TOTAL		-150.16

In above table, we can observe that biodiesel of purity 94% is produced with a heat duty of 150KW

4.2 Model 2: (Stream Results)

|	BIODIESE GLYC-MIX SEPERATR LIQUID	GLYC1 GLYC-MIX DECANT1 LIQUID	GLYC2 GLYC-MIX SEPERATR LIQUID	GLYCEROL GLYC-MIX LIQUID	MET B1 LIQUID	METOH-R1 REC-MIX R1-FLASH VAPOR	METOH-R2 RECSPLIT R2-FLASH VAPOR	OIL B1 LIQUID
Substream: MIXED								
Mole Flow lbmol/hr								
TRIOL-01	7.23632E-3	1.197104	0.0	1.197104	0.0	.1044997	.1925373	100.0000
METHA-01	2.434978	3.927854	0.0	3.927854	600.0000	308.7835	2.96827E+5	0.0
GLYCE-01	0.0	93.58480	4.488159	98.07296	0.0	.7509376	730.7379	0.0
METHY-01	296.2032	.1020354	0.0	.1020354	0.0	.0853488	83.06660	0.0
Mole Frac								
TRIOL-01	2.42305E-5	.0121149	0.0	.0115886	0.0	3.37396E-4	6.46878E-7	1.000000
METHA-01	8.15341E-3	.0397508	0.0	.0380237	1.000000	.9969625	.9972652	0.0
GLYCE-01	0.0	.9471015	1.000000	.9493998	0.0	2.42454E-3	2.45510E-3	0.0
METHY-01	.9918224	1.03262E-3	0.0	9.87759E-4	0.0	2.75564E-4	2.79084E-4	0.0
Total Flow lbmol/hr	298.6454	98.81179	4.488159	103.2999	600.0000	309.7243	2.97641E+5	100.0000
Total Flow lb/hr	87906.80	9834.750	413.3357	10248.09	19225.30	10081.08	9.60306E+6	88544.92
Total Flow cuft/hr	1720.873	158.7130	5.375922	164.1093	408.1030	1.53924E+6	1.47919E+9	5413.316
Temperature F	211.6315	212.0000	211.6315	211.9646	140.0000	212.0000	212.0000	140.0000
Pressure psi	14.50377	14.50377	14.50377	14.50377	14.50377	1.450377	1.450377	14.50377
Vapor Frac	0.0	0.0	0.0	0.0	0.0	1.000000	1.000000	0.0
Liquid Frac	1.000000	1.000000	1.000000	1.000000	1.000000	0.0	0.0	1.000000
Solid Frac	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Enthalpy Btu/lbmol	-2.9216E+5	-2.7958E+5	-2.8045E+5	-2.7961E+5	-1.0095E+5	-85555.63	-85322.74	-8.0355E+5
Enthalpy Btu/lb	-992.5398	-2808.961	-3045.240	-2818.491	-3150.589	-2628.553	-2644.522	-907.5094
Enthalpy Btu/hr	-8.7251E+7	-2.7625E+7	-1.2587E+6	-2.8884E+7	-6.0571E+7	-2.6499E+7	-2.540E+10	-8.0355E+7
Entropy Btu/lbmol-R	-418.1944	-315.3006	-135.2963	-307.4765	-54.79990	-29.21064	-24.08366	-15284.39
Entropy Btu/lb-R	-1.420730	-3.167891	-1.469099	-3.099341	-1.710244	-.8974477	-.7464572	-17.26174
Density lbmol/cuft	.1735430	.6225817	.8348631	.6294582	1.470217	2.01219E-4	2.01219E-4	.0184729
Density lb/cuft	51.08268	61.96563	76.88648	62.44671	47.10893	6.54938E-3	6.49211E-3	16.35687
Average MW	294.3517	99.53013	92.09472	99.20707	32.04216	32.54857	32.26395	885.4492
Liq Vol 60F cuft/hr	1618.260	131.5088	5.262792	136.7716	387.6590	202.4812	1.93092E+5	1560.190
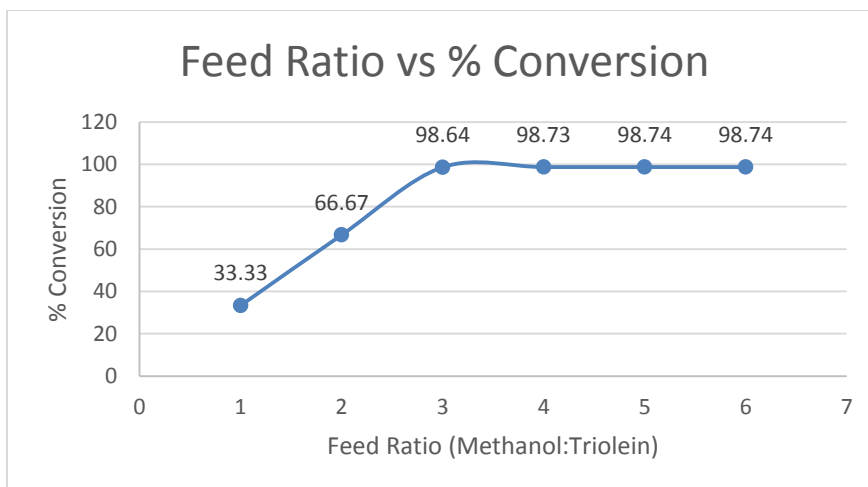
Fig 4.4 Change in conversion with feed ratio

	PROD1 DECANT1 R1-FLASH LIQUID	PROD2 SEPERATR R2-FLASH LIQUID	PURGE RECSPLIT MIXED	R1-OUT R1-FLASH B1 LIQUID	R2-FEED B2 DECANT1 LIQUID	R2-OUT R2-FLASH B2 LIQUID	REC-MET B2 REC-MIX MIXED	RECYC REC-MIX RECSPLIT MIXED
Substream: MIXED								
Mole Flow lbmol/hr								
TRIOL-01	4.895461	7.23632E-3	1.29376E-6	5.000000	3.698358	.1997735	.2971125	.1925360
METHA-01	6.219672	2.434978	1.994530	315.0000	2.291818	2.96829E+5	2.96838E+5	2.96825E+5
GLYCE-01	94.24861	4.488159	4.91020E-3	95.00000	.6638134	735.2260	730.7665	730.7330
METHY-01	284.9120	296.2032	5.58167E-4	285.0000	284.8100	379.2668	83.06973	83.06605
Mole Frac								
TRIOL-01	.0125436	2.38717E-5	6.46878E-7	7.14286E-3	.0126889	6.70508E-7	9.98186E-7	6.46878E-7
METHA-01	.0159366	8.03269E-3	.9972652	.4500000	7.86313E-3	.9962587	.9972648	.9972652
GLYCE-01	.2414923	.0148058	2.45510E-3	.1357143	2.27752E-3	2.46767E-3	2.45510E-3	2.45510E-3
METHY-01	.7300274	.9771376	2.79084E-4	.4071429	.9771705	1.27295E-3	2.79083E-4	2.79084E-4
Total Flow lbmol/hr	390.2757	303.1336	2.000000	700.0000	291.4640	2.97944E+5	2.97652E+5	2.97639E+5
Total Flow lb/hr	97688.37	88320.14	64.52790	1.07770E+5	87853.62	9.69138E+6	9.60353E+6	9.60300E+6
Total Flow cuft/hr	1939.644	1726.813	1003.169	2091.851	1780.931	2.04962E+5	1.49298E+8	1.49291E+8
Temperature F	212.0000	212.0000	220.6408	140.0000	212.0000	140.0000	220.6411	220.6408
Pressure psi	1.450377	1.450377	14.50377	14.50377	14.50377	14.50377	14.50377	14.50377
Vapor Frac	0.0	0.0	.9964539	0.0	0.0	0.0	.9964537	.9964539
Liquid Frac	1.000000	1.000000	3.54606E-3	1.000000	1.000000	1.000000	3.54626E-3	3.54606E-3
Solid Frac	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Enthalpy Btu/lbmol	-2.9376E+5	-2.9192E+5	-85322.74	-2.1347E+5	-2.9857E+5	-1.0166E+5	-85323.00	-85322.74
Enthalpy Btu/lb	-1173.614	-1001.935	-2644.522	-1386.524	-990.5456	-3125.324	-2644.506	-2644.522
Enthalpy Btu/hr	-1.1465E+8	-8.8491E+7	-1.7065E+5	-1.4943E+8	-8.7023E+7	-3.029E+10	-2.540E+10	-2.540E+10
Entropy Btu/lbmol-R	-532.1429	-413.9102	-28.64799	-329.8022	-605.6565	-55.45589	-28.65332	-28.64799
Entropy Btu/lb-R	-2.125969	-1.420628	-.8879258	-2.142164	-2.009331	-1.704890	-.8880827	-.8879258
Density lbmol/cuft	.2012100	.1755451	1.99368E-3	.3346318	.1636582	1.453654	1.99368E-3	1.99368E-3
Density lb/cuft	50.36407	51.14633	.0643240	51.51906	49.33017	47.28380	.0643246	.0643240
Average MW	250.3060	291.3571	32.26395	153.9574	301.4219	32.52755	32.26425	32.26395
Liq Vol 60F cuft/hr	1745.863	1623.523	1.297487	1948.357	1614.354	1.94716E+5	1.93102E+5	1.93091E+5

Fig 4.3 Stream Results of model 2

From above figures we can observe that an optimum feed ratio of 3:1 is maintained to obtain 98.7% conversion and 99% purity. From Tables 4.3 and 4.4, we can also observe that a minimum heat duty of 75KW is consumed for the process to run.

Table 4.3 Product Configuration of model 1

Key Product	Stream	Total Flow (Kmol/hr)	Composition (Mol %)			
			Methyl-Oleate	Glycerol	Methanol	Triolein
Biodiesel (Methyl-oleate)	**BIODIESEL**	2.96	99	0.1	0.7	0.2
Glycerol	**GLYCEROL**	1.04	0.01	94.9	3.8	1.18

Methanol	PURGE	0.06	0.03	0.25	99.7	0.02

Table 4.4 Heat duty Calculation of model 1

Process	Block	Duty(kW)
Reactor 1	R1	-167.495
Reactor 1 Flash Drum	R1-FLASH	100.513
Reactor 1 Decanter	DECANT 1	0
Reactor 2	R2	-364.199
Reactor 2 Flash Drum	R2-FLASH	356.537
Reactor 2 Separator	SEPERATR	-0.292
Total		**-74.936**
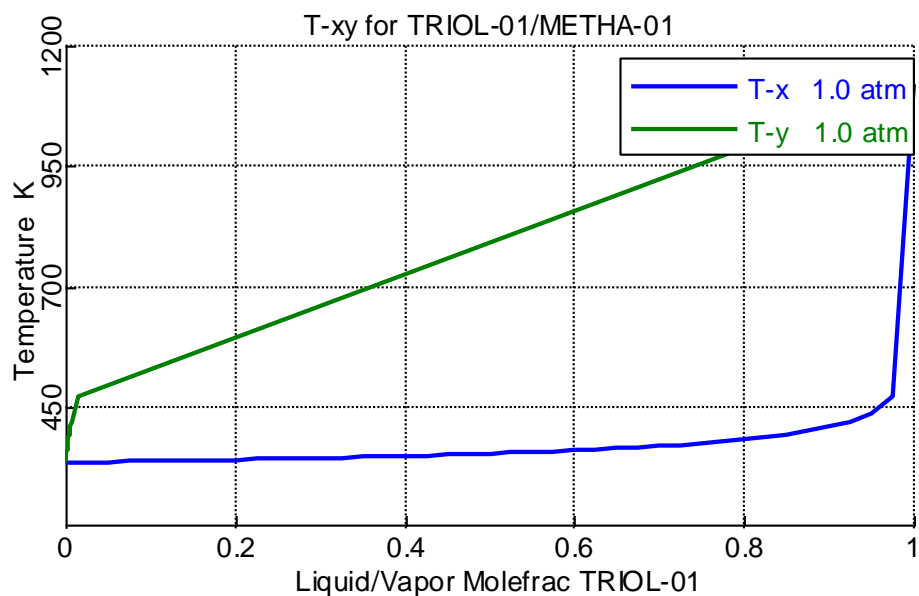
Fig 4.4 Temperature profiles with change in mole fraction of oil

From above fig 4.4, varying of liquid and vapor mole fractions of oil with increasing temperature is observed and analyzed.
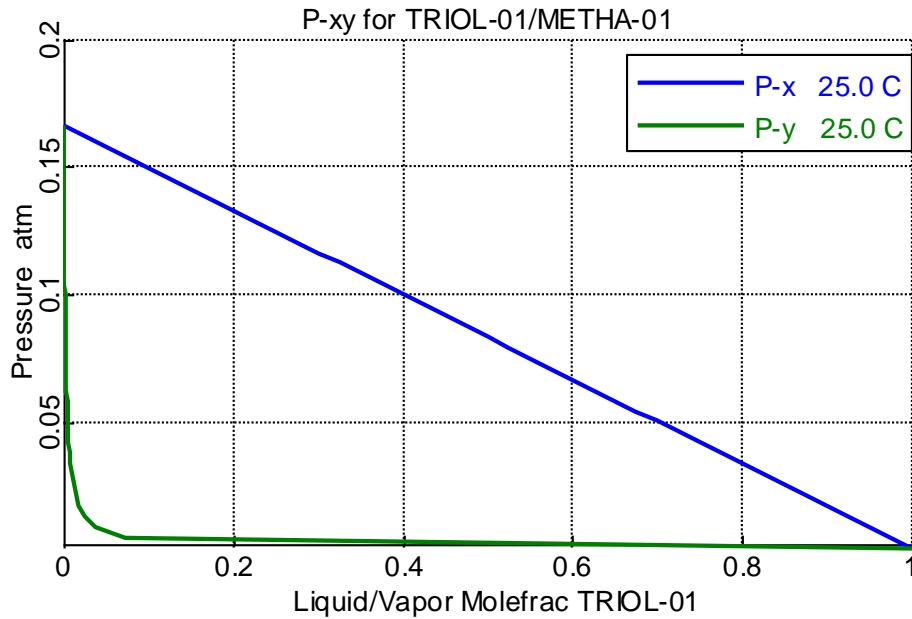
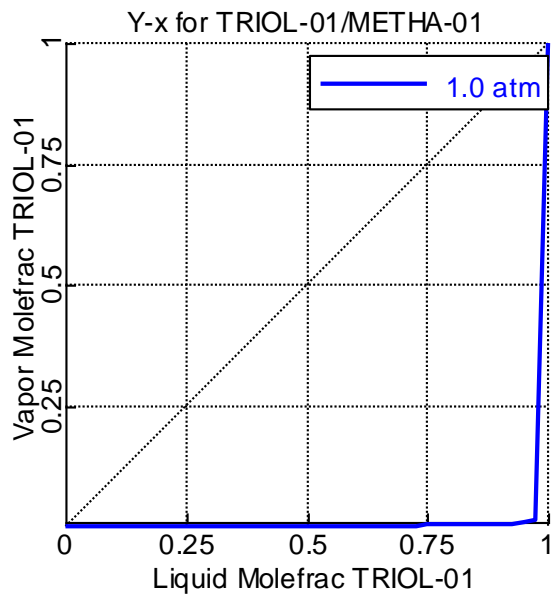**Fig 4.5** Pressure profiles with change in mole fraction of oil

Fig 4.6 Change of Y with X

From above figures 4.5, 4.6 we can observe and analyze the variation of mole fractions of oil with change in pressure.

Parameter Optimization:

Reactor Temperature and Pressure vs Conversion

The beginning quality for the temperature of both reactors was chosen taking into account writing survey and thusly examined with an affectability investigation. The reaction of triolein to methyl oleate was investigated to expand change while making the methodology as gainful as could be expected under the circumstances. An affectability examination was led on the transformation proportion with changing minister temperatures and the outcomes are shown in Fig 4.7. As can be seen, the change does not expand essentially up to 100°C. The minimal increment in change was insufficient to legitimize the additional warmth obligation, equal to cost, for the reactors. This investigation was done at 1 bar which is the working weight of the reactor.
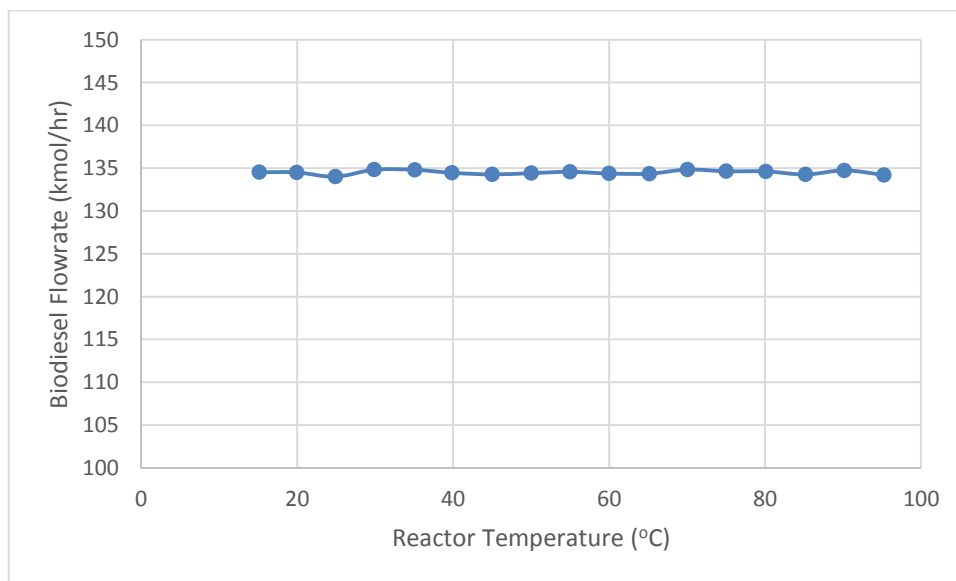

Fig 4.7: Dependence of temperature of conversion in the reactors at 1 bar. Blue line is the molar flow rate of methyl oleate in the R1-OUT stream measured on the outside vertical axis.

From above fig 4.7, we can observe that flow rate of product is slightly increasing with

increase in temperature of reactor. The weight of both reactors was picked in view of methanol's

vapor weight at the reactor temperature. Methanol's vapor weight at 60°C is 0.85 bar so a higher

weight is obliged to keep up methanol in the fluid stage. An affectability examination was

completed to focus the impact of weight on transformation of triolein to methyl oleate; the

outcomes are demonstrated in Fig 4.8. The diagram demonstrates no adjustment in transformation

at weights somewhere around 0 and 5 bars. A reactor weight of 1 bar was chosen to minimize cost
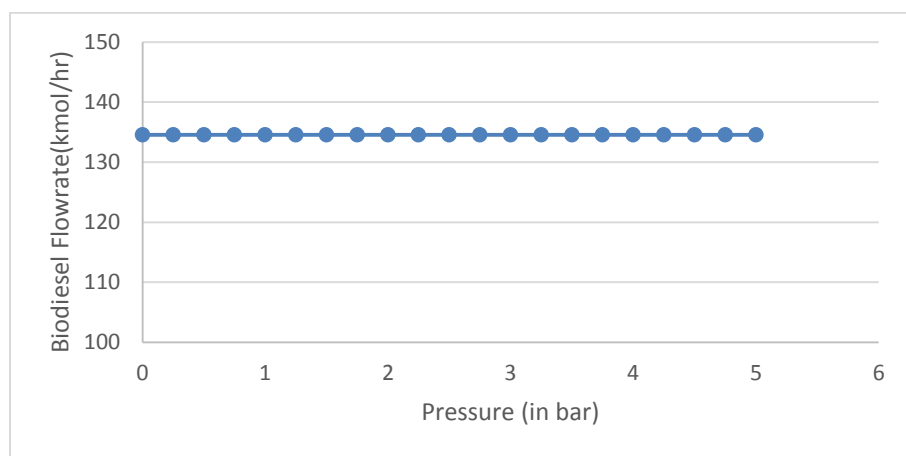
and augment security.

Fig 4.8: Dependence of pressure of conversion in the reactor at 60°C. Blue line is the molar flow
rate of methyl oleate in the R1-OUT stream.

From above fig 4.8, we can observe that there is no change in flow rate of biodiesel with variation

of pressure.

Flash Temperature and Pressure vs Product Purity

 The flash drums were at first worked at a temperature of 60 C and a weight of 0.5 bar which is

beneath the vapor weight of methanol at 60 C (0.85 bar). An affectability examination was done to

figure out whether an adjustment in temperature and/or weight could enhance the virtue of the

flash items by uprooting more of methanol. The aftereffects of the affectability investigation are

demonstrated in Figure 6 to Figure 9. Methanol flow rate increases with increasing temperature

and diminishing weight while the methanol mole fraction stays at 1. Consequently, more of methanol can be differentiated while keeping up recycle stream virtue by increasing temperature and diminishing the weight. The flash drums were worked at 0.1 bar and 100° C.
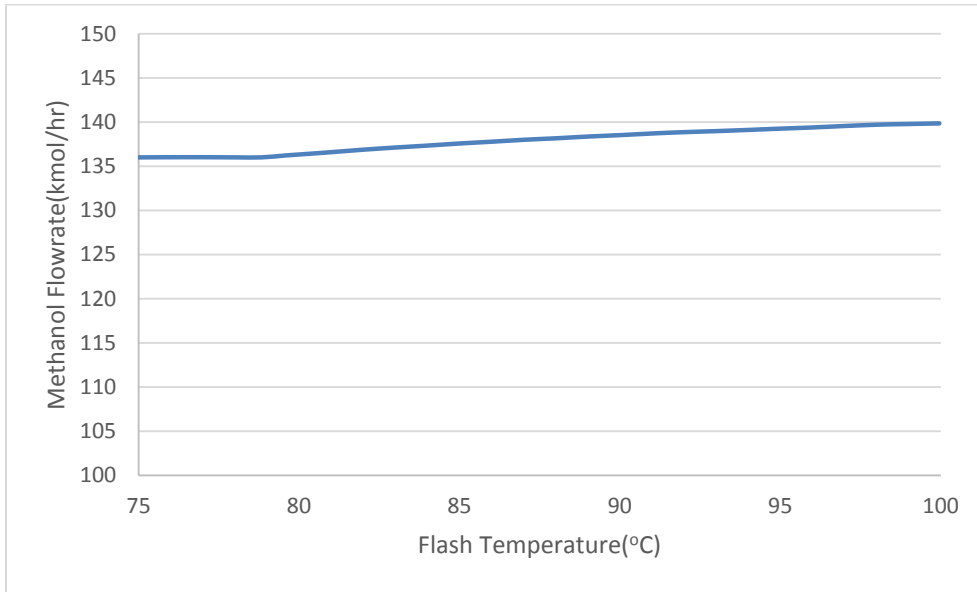

Fig 4.9: Dependence of temperature of separation in the flash at 1 bar. Blue line is the molar flow rate of methanol in the METOH-R1 stream.

From above fig 4.9, we can observe that at 1 bar pressure, with increase in temperature flow rate of methanol vapor flashing out of flash drum increases after remaining constant for a small temperature increase.
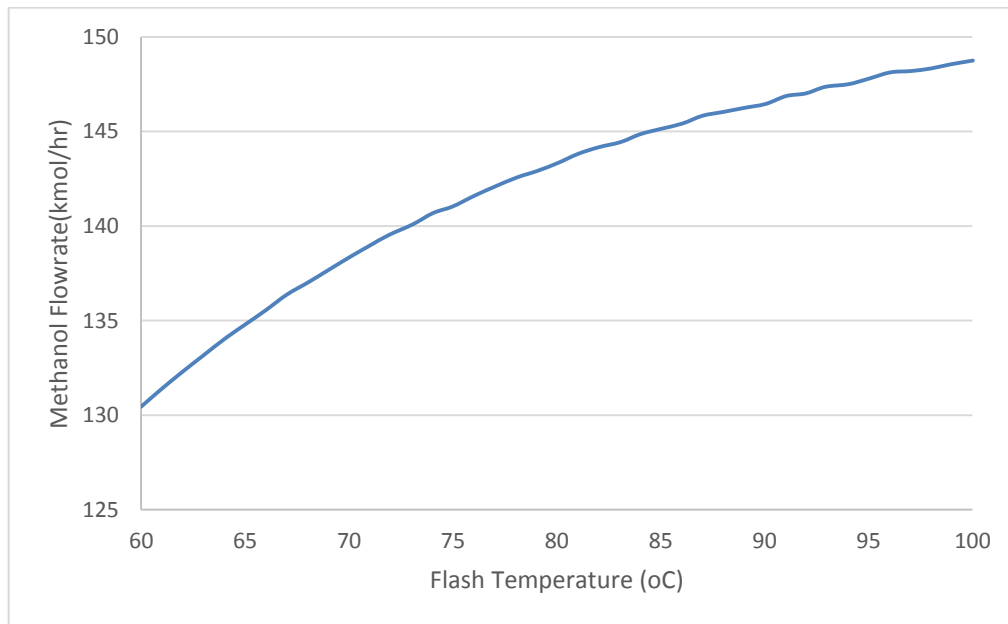
Fig 4.10: Dependence of temperature of separation in the flash at 0.3 bar. Blue line is the molar flow rate of methanol in the METOH-R1 stream.

From above fig 4.10, we can observe that at 0.3 bar pressure, with increase in temperature flow

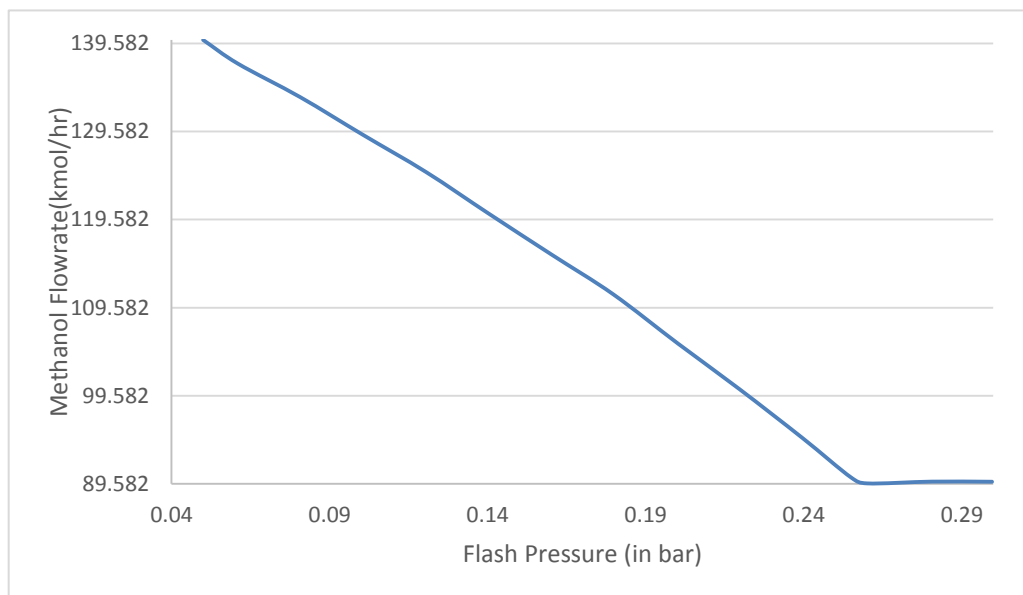rate of methanol vapor flashing out of flash drum increases exponentially.

Fig 4.11: Dependence of pressure of separation in the flash at 60°C. Blue line is the molar flow rate of methanol in the METOH-R1 stream.

From above fig 4.11, we can observe that flow rate of methanol vapor flashing out increases with decrease in pressure at 60°C after remaining constant for some pressure drop.
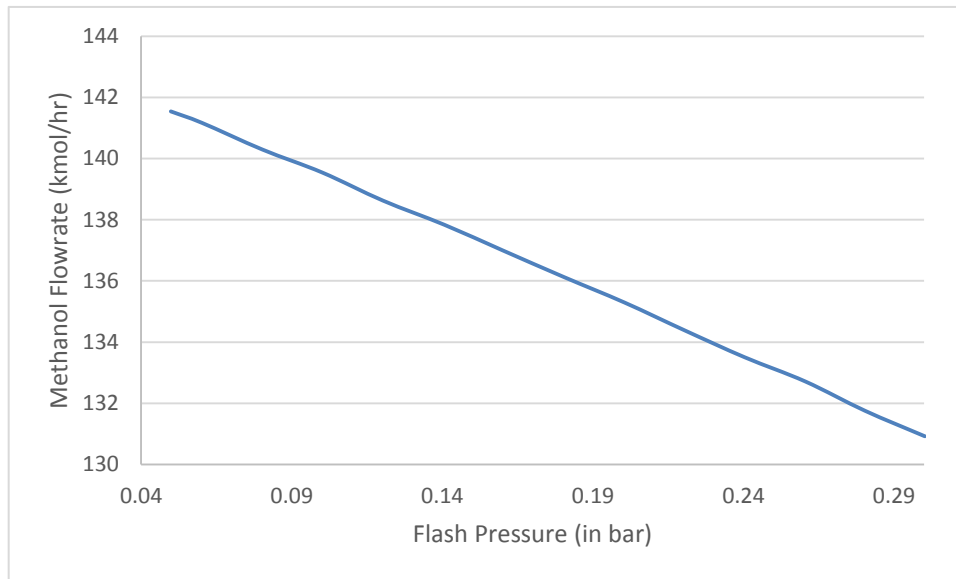

Fig 4.12: Dependence of pressure of separation in flash at 100°C. Blue line is the molar flow rate of methanol in the METOH-R1 stream measured on the outside vertical axis.

From above fig 4.12, we can observe that flow rate of methanol vapor flashing out increases linearly with decrease in pressure at 100°C.

4.3 Esterification process (Stream Results):

Esterfication					
Stream ID		BIODIESE	METHANOL	OLEIC	WAT+MET
From		B1			B1
To			B1	B1	
Phase		LIQUID	VAPOR	LIQUID	VAPOR
Substream: MIXED					
Mole Flow	lbmol/hr				
OLEIC-01		1.3592E-20	0.0	100.0000	1.0447E-31
METHA-01		3.04983E-5	190.0000	0.0	89.99997
METHY-01		93.99997	0.0	0.0	6.000031
WATER		1.4515E-20	0.0	0.0	100.0000
Mole Frac					
OLEIC-01		1.4459E-22	0.0	1.000000	5.3302E-34
METHA-01		3.24450E-7	1.000000	0.0	.4591835
METHY-01		.9999997	0.0	0.0	.0306124
WATER		1.5441E-22	0.0	0.0	.5102041
Total Flow	lbmol/hr	94.00000	190.0000	100.0000	196.0000
Total Flow	lb/hr	27870.39	6088.010	28246.68	6464.292
Total Flow	cuft/hr	753.7443	62126.56	543.8935	88772.66
Temperature	F	684.9740	212.0000	230.0000	458.5333
Pressure	psi	21.75566	22.04392	22.04392	21.75566
Vapor Frac		0.0	1.000000	0.0	1.000000
Liquid Frac		1.000000	0.0	1.000000	0.0
Solid Frac		0.0	0.0	0.0	0.0
Enthalpy	Btu/lbmol	-2.0450E+5	-84883.50	-3.3242E+5	-95600.72
Enthalpy	Btu/lb	-689.7221	-2649.119	-1176.864	-2898.653
Enthalpy	Btu/hr	-1.9223E+7	-1.6128E+7	-3.3242E+7	-1.8738E+7
Entropy	Btu/lbmol-R	-322.1902	-29.24725	-400.4338	-23.83184
Entropy	Btu/lb-R	-1.086668	-.9127739	-1.417632	-.7225912
Density	lbmol/cuft	.1247107	3.05827E-3	.1838595	2.20789E-3
Density	lb/cuft	36.97593	.0979936	51.93421	.0728185
Average MW		296.4936	32.04216	282.4668	32.98108
Liq Vol 60F	cuft/hr	513.0190	122.7587	512.0718	119.8082

Fig 4.13 Stream results for esterification process

Table 4-5. Operating conditions and configurations for reactive distillation column

Conditions & Configurations	Equilibrium-1
Number of stages	30
Oleic acid feed stage	3
Methanol feed stage	29
Side reboiler stage	—
Side reboiler duty, kW	0
Oleic feed temperature, ^{O}C	100
Methanol feed temperature, ^{O}C	90
Molar reflux ratio	1.5
Reaction stages	3-29
Distillate rate, kmol/hr	196
Bottom rate, kmol/hr	104
Bottom ester mass percent	90.23
Liquid holdup, cm^3	0.043
Condenser duty, kW	-5014.33
Condenser temperature, ^{O}C	107.92
Condenser pressure, bar	3.5
Reboiler duty, kW	7029.99
Reboiler temperature, ^{O}C	224.36
Reboiler pressure, bar	4.0
Total Conversion, kmol/hr	90.19
Exergy loss, kW	1385.5

Table 4.6 Product Configuration

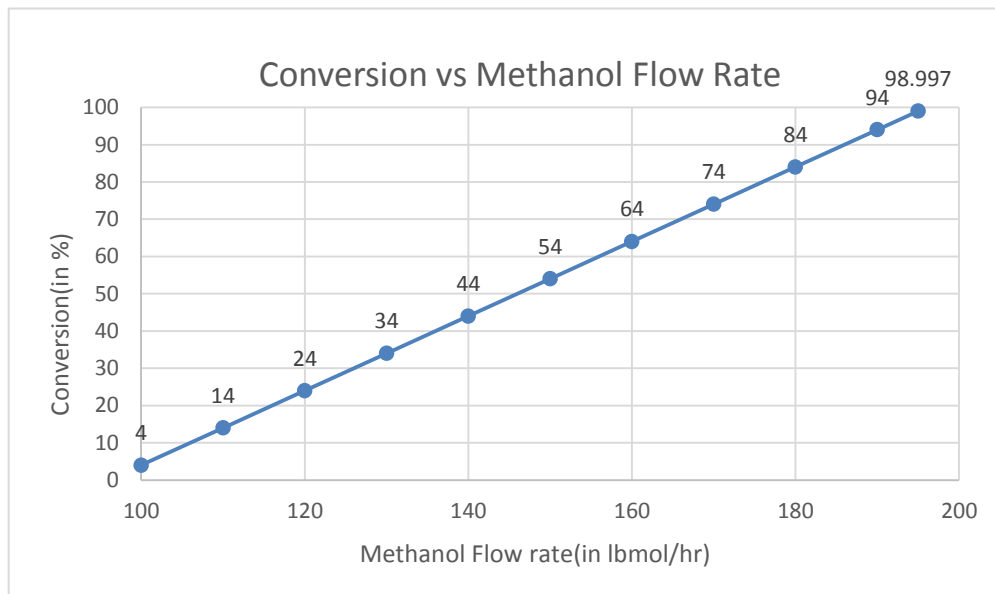| Key Product	Stream	Total Flow (Kmol/hr)	Composition (Mol %)			
			Methyl-Oleate	Water	Methanol	Triolein
Biodiesel (Methyl-oleate)	BIODIESEL	42.64	99.9	0.01	0.03	0.06
Water+Methanol	WAT+MET	88.9	3.06	51	45.9	0.04

Fig 4.14 Change in conversion with feed ratio for model 3
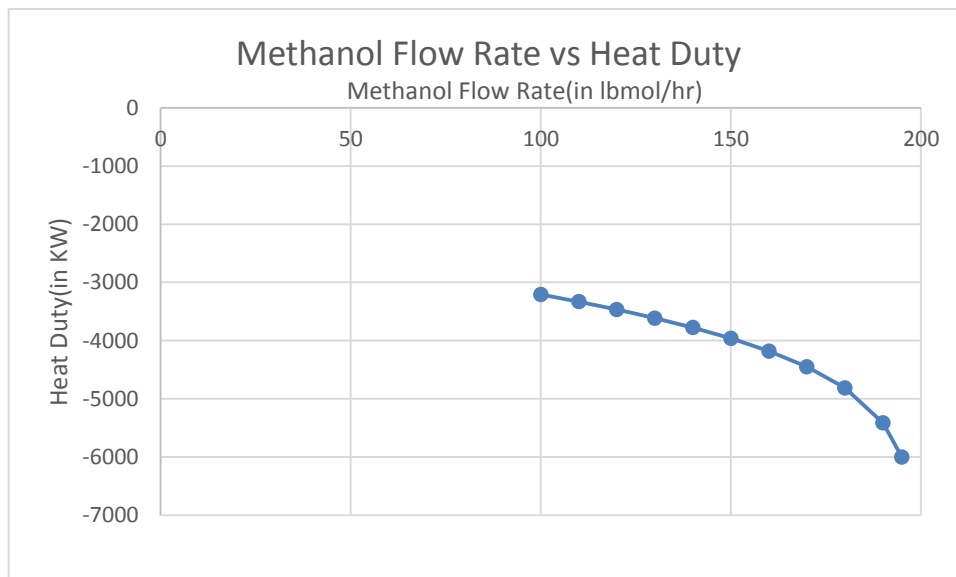

Fig 4.15 Change in Heat duty with increasing methanol flow rate

Analysis with respect to reflux ratio, numbers of stages are also done but there is no significant
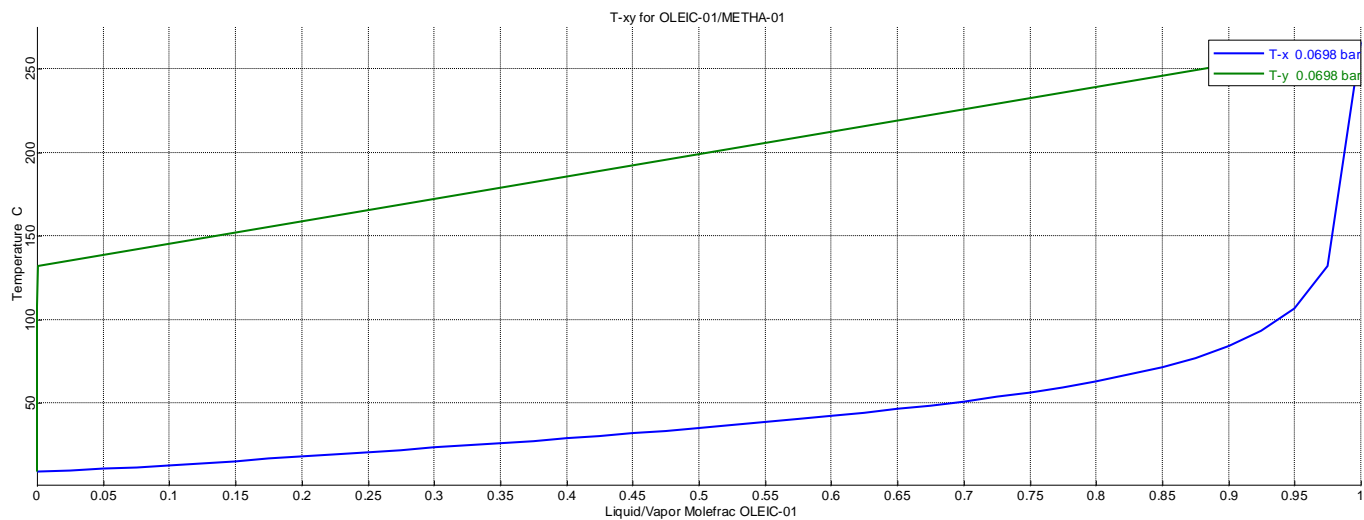
change in product flow rate.

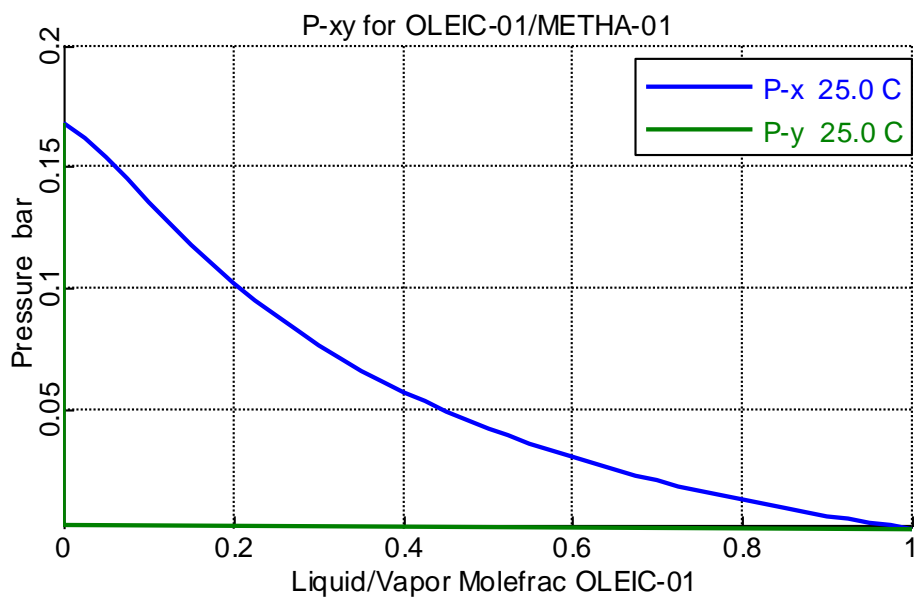**Fig 4.16** Temperature profiles with changing mole fractions of oil

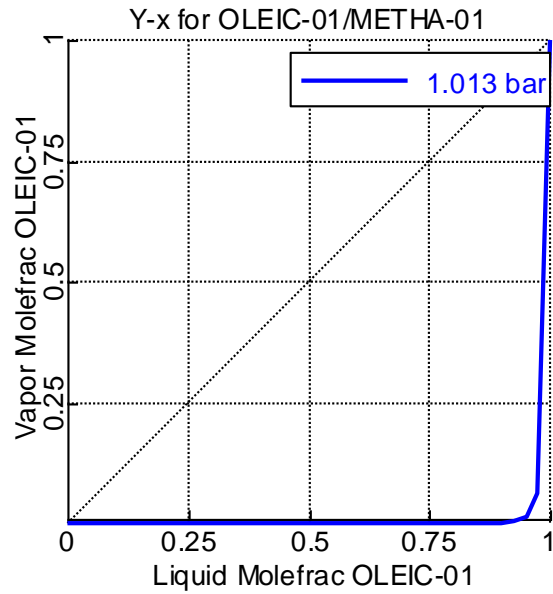**Fig 4.17** Pressure profiles with changing mole fractions of oil

Fig 4.18 Change of Y with X at 1atm pressure

From above fig 4.16,17,18 we can observe variation of mole fractions of oil with temperature and pressure changes.

CONCLUSIONS AND FUTURE SCOPE

Several optimizations were made to improve the conversion of triolein and the purity of the methyl oleate. Sensitivity analyses were conducted on reactor temperature, reactor pressure, flash drum temperature, and flash drum pressure to determine the effect on triolein conversion and methanol removal which controls product purity. The model 1 produces a triolein conversion of 99% and a biodiesel purity of 94% at $60^{o}C$ and 1 bar pressure with a heat duty of 150KW required for process to run.

Similarly, in model 2 triolein conversion of 98.74% and biodiesel of purity 99% is obtained at $60^{o}C$ and 1 bar pressure with a net heat duty of 75KW requirement.

For the process of esterification, a reactive distillation column is used to convert all free fatty acid content to methyl esters at $100^{o}C$ and 1.5 bar pressure

For better and accurate results one should try to run non-equilibrium models with data from literature and get results that are practically accurate. The optimum parameters obtained in above models do not contribute to any deviations or errors theoretically but practically these may not be the optimum parameters. But from these results we can minimize heat duty and maximize conversion.

Future Scope:

As distillation columns require higher heat duties, energy integration methods should be used like thermally coupled distillation columns etc.

Non-equilibrium models should be used for accurate results that does not deviate much than practical values, i.e. rate based models with data.

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