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SIMULATION AND PROCESS DESIGN OF BIODIESEL PRODUCTION

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Abstract*- To meet the increasing demand for energy throughout the whole world, non-renewable fuels are widely used. But, as a consequence of spiraling demand and diminishing supply, these fuels are costly. Biodiesel is gaining recognition worldwide as an alternative fuel, to reduce dependency on conservative fuels. Biodiesel, a combination of fatty acid methyl esters, is usually derived from animal and vegetable oils For this paper, production of biodiesel by transesterification of vegetable oil with methanol in presence of an acid catalyst has been studied. Using Aspen HYSYS 2006 software, a continuous process was designed with a capacity of 6,600 tons/yr biodiesel production. Also, the relationships among various process parameters influencing the production process, which are crucial for proper understanding of the whole operation, have been studied and reported via graphical representation in the paper. Furthermore, using HYSYS Optimizer, maximum annual profit was found to be 7.437 million dollars at optimum conditions.*

Keywords: Biodiesel, triolein, alternative fuel, simulation, optimization

1. INTRODUCTION

Owing to the high rate of fuel consumption, increasing oil crisis and detrimental effect of fossil fuels on environment, the necessity and demand of using alternative fuels have been increasing worldwide. Biodiesel, a mixture of monoalkyl esters of fatty acids, can be produced from renewable domestic resources, and, is gaining acceptance as a substitute of petro-diesel since it has many biological benefits and possesses physical properties similar to diesel fuel [1].

Biodiesel has improved cetane number, viscosity, oxidative stability [2], combustion efficiency, biodegradability (biodiesel is 90% more bio-degradable than diesel), lower sulfur & aromatic content and toxicity than petroleum diesel [3]. It reduces emission of GHGs and most exhaust gases except NO_x [4], for example, biodiesel reduces emission of CO_2 by 78% [5], SO_2 by 99%, CO by 20%, hydrocarbons by 32%, soot by 50% and particulate matters by 39% [6].

A number of methods have been implemented for the production of biodiesel, such as– direct use and blending of raw oils, micro-emulsions, thermal cracking and transesterification [3]. Transesterification of animal fats or vegetable oils is the most commonly used method to convert these to biodiesel [4]. The quality of biodiesel is directly related to the quality of the raw oil [7], which can be– vegetable oil (edible or non-edible); animal fat [4]; non-edible plant biomass such as algae and seaweeds, and even animal biomass [3]. The costs of the biodiesel feedstocks are very high, and therefore, more than 95% of biodiesel production feedstocks comes from edible oils since vegetable oils are renewable in nature, produced in many regions on a large scale and environmentally friendly [4].

The transesterification reaction can be accomplished by a number of different methods– alkali catalysis, acid catalysis, non-catalytic supercritical and ultrasound aided alcohol, using heterogeneous catalysts, enzyme catalysis etc. It has been found that, the one step acid-catalyzed process, which has been used in this project, is the most economically attractive one [3] [5]. In transesterification, an alcohol, methanol in this case, is used to separate the vegetable oil's molecules, and replace them with radicals from the alcohols used, by removing glycerol from the triglycerides in presence of a catalyst. In this reaction, the triglyceride, having a branched molecular structure attached to glycerol backbone, is transformed to a monoglyceride, containing a straight chain of smaller molecular structure [8].

In this paper, a simulation software, Aspen HYSYS 2006, which provides the thermodynamic and fluid properties for basic chemical compounds, has been used for simulation and process design of biodiesel production by homogeneous acid catalyzed transesterification [9].

2. METHODOLOGY

2.1 Process description

The complete process involved the transesterification reaction to convert triolein to biodiesel, the recovery of unreacted methanol, neutralization and removal of acid catalyst, separation of by-product and finally biodiesel purification. For the homogeneous acid catalyzed transesterification of triolein, first, methanol (CH_3OH) was mixed with sulfuric acid (H_2SO_4) and the mixed feed was compressed before combining with the recycle stream. The mixed feed reacted with triolein in Reactor-1 to form methyl ester (biodiesel), which is the main product of the process and glycerol as by-product.

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

Triolein Methanol Methyl oleate Glycerol

The unreacted methanol was separated from the product stream of Reactor-1, in a distillation column as the distillate, to be used as the recycle stream. The rest of the materials, *i.e.*, methyl ester, glycerol and unreacted triolein, entered another reactor where calcium oxide (CaO) was added, to neutralize the acid by formation of calcium sulfate ($CaSO_4$).

$$\mathbf{CaO + H_2SO_4 \rightarrow CaSO_4 + H_2O}$$

Calcium Oxide Sulfuric acid Calcium Sulfate Water

The $CaSO_4$ precipitate was removed in a splitter. The by-product, *i.e.*, glycerol was separated in another splitter, along with the water produced in the second reaction. The separation was facilitated by the difference in weight between glycerol and methyl ester. The lighter fraction from the second splitter, containing the main product, *i.e.*, methyl ester and the unreacted triolein entered a second distillation column, where most of the biodiesel was separated as the distillate.

2.2 Process Simulation

Complete process simulation for biodiesel production was performed using Aspen HYSYS 2006, to evaluate technological viability and obtain material and energy balances. HYSYS was selected as a process simulator for both its simulation capabilities and its ability to incorporate calculations using the spreadsheet tool. Although, simulation result does not guarantee 100% correct results compared to the real process, simulation provides the opportunity to design and test the unit operations in a short period of time. The major steps involved in the simulation using were –

- Specifying the components involved in the process.
- Selection of a thermodynamic model.
- Drawing the graphical simulation process flow sheet using required unit operations.
- Specifying the operating and input conditions.

The basic components required for this process were triolein, methanol, sulfuric acid, methyl oleate, glycerol, water, calcium oxide and calcium sulfate. HYSYS library contained information for most of these components. Calcium oxide, calcium sulfate and triolein were specified using the ‘Hypo manager’ tool. Since triolein is a crucial component of the process and is involved in operations requiring data for vapor-liquid equilibria, the property values were specified with great care. As the property package for the simulation, non-random two liquid (NRTL) thermodynamic/activity model was selected because of the presence of polar compounds, such as, glycerol and methanol.

The simulation was performed on the basis of 1000 kg/h biodiesel production. For this, stoichiometric amount of methanol (CH_3OH) and triolein ($C_{57}H_{104}O_6$) were provided, along with 110.3 kg/h sulfuric acid (H_2SO_4) as the catalyst, at 25°C and 1 atm. First, 108.1 kg/h methanol was mixed with the acid, then the mixed feed was pressurized to 2 atm with a pump. This pressurized feed and the recycle stream containing almost pure methanol (99.99%), from the top of Distillation column-1 were mixed before entering the Reactor-1. On the other hand, 1026 kg/h triolein was pressurized to 2 atm, and then, heated to 60°C before entering Reactor-1, where it reacted with the mixed feed to reactor. For the transesterification reaction, a general conversion reactor was selected where 97% conversion of the oil was achieved.

The liquid product stream from Reactor-1 containing glycerol ($C_3H_8O_3$), methyl oleate ($C_{19}H_{36}O_2$) and a little amount of unreacted methanol, oil and all of the acid, entered Distillation column-1. From the top of the distillation column, all of unreacted methanol was recovered and sent back as the recycle stream. The bottom product containing glycerol, methyl oleate with unreacted oil and H_2SO_4 at 300.9°C was cooled to 200°C before entering Reactor-2, which was also a general conversion reactor for complete conversion of sulfuric acid. The acid reacted with 3 kgmole/hr CaO to produce $CaSO_4$, which along with glycerol, methyl oleate and oil entered into the first component splitter, Splitter-1.
From the bottom of this splitter, $CaSO_4$ was removed at 25°C as precipitate and the top product entered the second component splitter, Splitter-2, where 95% solution of glycerol was collected at the bottom as the heavy fraction. The top product containing oil and methyl oleate was passed to Distillation column-2, where all of the biodiesel was separated at 99.99% purity.

The methyl-ester purification column was operated under vacuum conditions, condenser pressure 10 kPa and reboiler pressure 15 kPa, to keep the temperature of the distillate and bottom stream at low levels, since biodiesel is subject to distillation at temperature greater than 250°C. The process flow diagram is shown in Fig. 1.

3. OPTIMIZATION

Optimization is a process or methodology, by which, a design, system, or a decision is made fully perfect, functional or as effective as possible. It is a mathematical procedure, executed to find the maximum of one or more desired function or functions and the minimum of the undesired ones. In this simulation, optimization was performed using HYSYS optimizer tool to find the optimum parameters for optimum production and the maximum profit that can be achieved. For this process, several assumptions were made-

- The simulation was based on a plant capacity of 6,600 tonnes of biodiesel production per year considering 330 days of operation per year with operating hour set at 20 hours per day.
- The oil used was assumed to be waste cooking oil with 30% triolein content.
- Electricity was used as heating and cooling medium. Cost of heating and cooling was assumed to be equivalent to the cost of electrical energy consumed. The selling prices of biodiesel and glycerol and cost of raw materials & electricity have been given in Table 1.

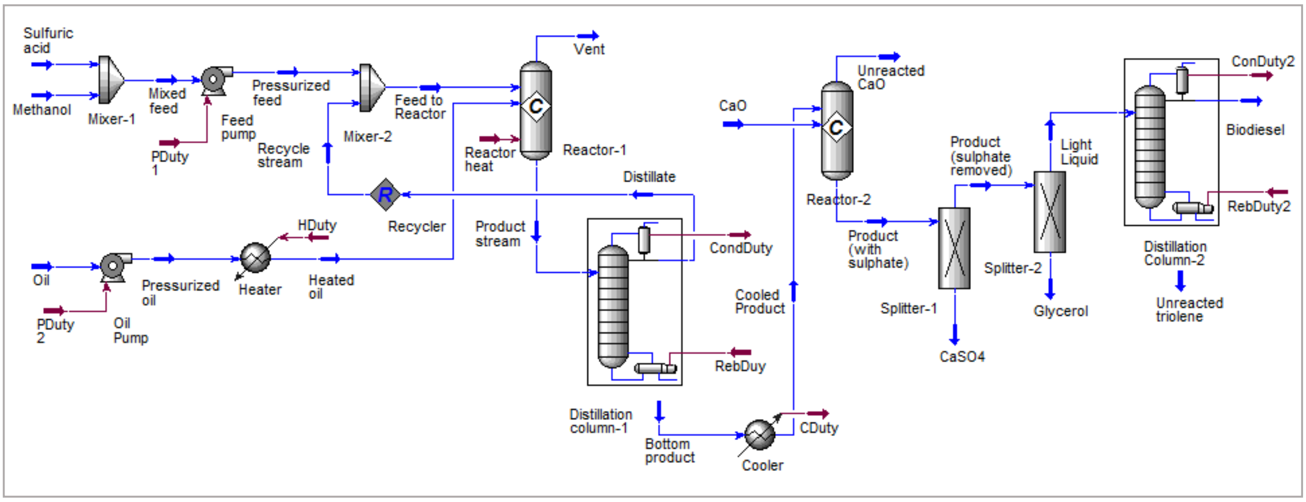


Fig.1: Process flow diagram of biodiesel production

Table 1: Price and cost assumptions

Item	Cost/ Price $/tonne	Item	Cost/ Price
Methanol	180 [5]	Biodiesel	$6/gallon [10]
Oil	200 [5]	Glycerol	$1200/tonne [5]
H_2SO_4	60 [5]	Electricity	$0.12/kWh [11]
CaO	40 [5]		

3.1 Profit function

In this simulation process, to perform the optimization, an optimization function was used. This is a function for calculating profit that showed a relation between the selling prices with the costs of reactant materials and the electricity bill for using the energy to run the process, ultimately giving the profit obtained. To calculate profit, HYSYS spreadsheet tool was used. The function is given in Eq. (1) –

$$\mathbf{Profit} = \mathbf{V_B S_B + M_G S_G - M_M C_M - M_S C_S - M_C C_C - M_O C_O - \frac{C_E}{3600} \times (Q_{FP} + Q_{OP} + Q_c + Q_H + Q_{CD_1} + Q_{RD_1} + Q_{CD_2} + Q_{RD_2} + Q_R)} \quad (1)$$

Here, S_B = Selling price of Biodiesel ($/m^3)
V_B = Rate of Biodiesel production (m^3)
S_G = Selling price of Glycerol ($/kg)
M_G = Mass flow rate of Glycerol produced (kg/h)
C_M = Cost of Methanol ($/kg)
M_M = Mass flow rate of Methanol used (kg/h)
C_S = Cost of Sulfuric acid ($/kg)
M_S = Mass flow rate of Sulfuric acid used (kg/h)
C_C = Cost of CaO ($/kg)
M_C = Mass flow rate of CaO (kg/h)
C_O = Cost of waste cooking oil ($/kg)
M_O = Mass flow rate of waste cooking oil used (kg/h)
Q_{FP} = Energy required to pressurize the mixed feed in Feed pump (kJ/h)
Q_{OP} = Energy required to pressurize the feed oil in Oil pump (kJ/h)
Q_C = Energy required to cool the bottom product from Distillation column-1 in Cooler (kJ/h)
Q_H = Energy required to heat the pressurized oil from oil pump in Heater (kJ/h)
Q_{CD1} = Condenser duty in Distillation column-1 (kJ/h)
Q_{RD1} = Reboiler duty in Distillation column-1 (kJ/h)
Q_{CD2} = Condenser duty in Distillation column-2 (kJ/h)
Q_{RD2} = Reboiler duty in Distillation column-2 (kJ/h)
Q_R = Energy required in Reactor-1 (kJ/h)
C_E = Cost of electricity per kWh ($/kWh)

3.2 Method of optimization

The primary variables that were varied to determine the optimum condition using HYSYS optimizer tool, have been given below –

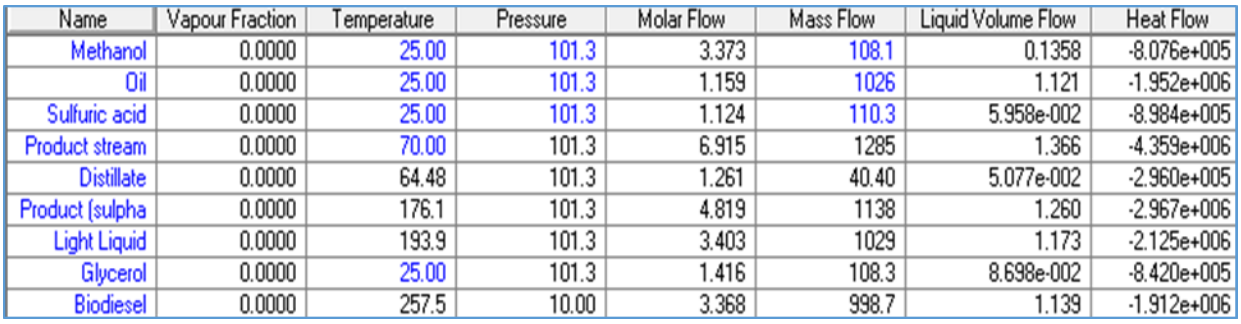
- The percentage of conversion of triolein in Reactor-1;
- The pressure of the feed containing fresh methanol, sulfuric acid & recycled methanol before entering Reactor-1;
- The pressure of the oil before heating;
- The temperature to which triolein (oil) was heated before entering Reactor-1;
- Pressure of mixed feed before combining with recycle stream in Mixer-2;
- The reflux ratio in Distillation column-1;
- The fractional recovery of biodiesel in Distillation column-2;
- The temperature at which $CaSO_4$ was removed from Splitter-1.

The optimization process involved several steps. Variables included in the profit function were imported from the simulation or entered manually. Profit and annual profit were determined using the profit function. The primary variables were added and their ranges were selected, with the help of the graphs that were plotted to understand the flexibility of the variables. Using HYSYS optimizer tool, optimum conditions for the maximum profit were attained.

4. RESULTS & DISCUSSIONS

4.1 Optimized Workbook

The major streams of the complete process were, the



Name	Vapour Fraction	Temperature	Pressure	Molar Flow	Mass Flow	Liquid Volume Flow	Heat Flow
Methanol	0.0000	25.00	101.3	3.373	108.1	0.1358	-8.076e+005
Oil	0.0000	25.00	101.3	1.159	1026	1.121	-1.952e+006
Sulfuric acid	0.0000	25.00	101.3	1.124	110.3	5.958e-002	-8.984e+005
Product stream	0.0000	70.00	101.3	6.915	1285	1.366	-4.359e+006
Distillate	0.0000	64.48	101.3	1.261	40.40	5.077e-002	-2.960e+005
Product (sulpha	0.0000	176.1	101.3	4.819	1138	1.260	-2.967e+006
Light Liquid	0.0000	193.9	101.3	3.403	1029	1.173	-2.125e+006
Glycerol	0.0000	25.00	101.3	1.416	108.3	8.698e-002	-8.420e+005
Biodiesel	0.0000	257.5	10.00	3.368	998.7	1.139	-1.912e+006

Fig.2: Final condition of major streams

input streams, *i.e.*, methanol, oil and sulfuric acid streams, the product stream from Reactor-1 after conversion of triolein to biodiesel, the distillate from Distillation column-1 that formed the recycle stream, the product obtained after neutralization and removal acid catalyst, the product after removal of glycerol, the final products to be sold, *i.e.*, the biodiesel and glycerol streams. The final conditions the major streams have been shown Fig. 2.

4.2 Results from simulation

For production of 1000 kg biodiesel per hour, with 97% conversion of input triolein to biodiesel, it was found that 3420 kg/h oil, containing 30% triolein, and 108.1 kg/h methanol are required. The process has been designed for recovery of unreacted methanol with 99.99% purity and complete recovery of produced biodiesel with also 99.99% purity. As a byproduct, 95% glycerol solution was obtained. The process also resulted in the production of 153.1 kg/h calcium sulfate.

The process might be improved by recycling the unreacted oil from the final stage of purification and can be made more energy efficient if heat produced in the transesterification reaction and during cooling of bottom product from Distillation column-1 were used to preheat the oil and methanol.

4.3 Case studies

From Fig. 3, Case study 1, it can be seen that, the mass flow rate of $CaSO_4$ increases with mass flow rate of H_2SO_4 until the provided amount of CaO is exhausted. At this stage, the amount of $CaSO_4$ produced becomes constant.

From Fig. 3, Case study 2, heat produced in the transesterification reaction starts fluctuating when the temperature of the oil is greater than 80°C and the rate at which heat has to be removed from the reactor changes, which complicates the overall process. In this simulation, oil was heated to 60°C before entering the reactor.

From Fig. 3, Case Study 3, heat flow of bottom product of the Distillation column-1 remains constant at 3.361×10^6 kJ/h with increasing temperature of the liquid stream from the Reactor-1 until it becomes greater than 175°C. At this stage, it becomes impossible to achieve required recovery of methanol in Distillation column-1. In this simulation, the liquid stream from Reactor-1 was drawn at 25°C, for which the vapor stream mass flow rate became zero and it was possible to recover all unreacted methanol in the distillation column.

From Fig. 3, Case Study 4, mass flow of bottom product of Distillation column-2 remains constant at 30.75kg/h with increasing temperature of the inlet stream to Splitter-2 until it becomes greater than 185°C. At this stage, it becomes impossible to separate $CaSO_4$ from the products of Reactor -2. In this simulation, the $CaSO_4$ was separated at 25°C from Splitter-1 and the remaining stream from the splitter was obtained at 176.1°C.

From Fig. 3, Case Study 5, mass flow rate of biodiesel in the liquid product from Reactor-1, *i.e.*, biodiesel production, decreases with temperature of the oil fed to the reactor above 80°C. In the simulation, the heated oil temperature was kept at 60°C.

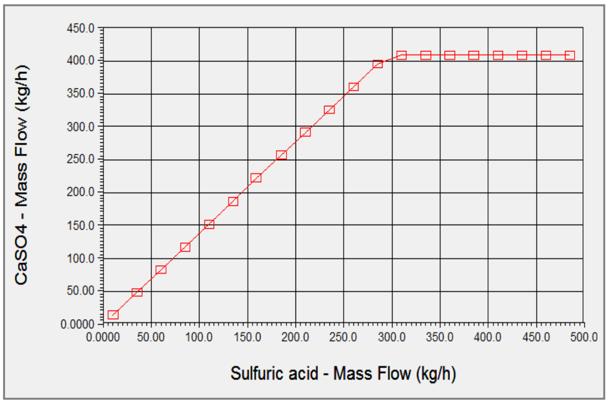
From Fig. 3, Case study 6, the change in heat flow of the liquid product from Reactor-2 with increasing temperature of CaO, shows fluctuation when the temperature is below 18°C or greater than 44°C. Therefore, the temperature of CaO should be in between these two values. In this simulation, the temperature of CaO was set at 25°C, for which heat flow of the liquid product from Reactor-2 was 3.616×10^6 kJ/h.

4.4 Optimization

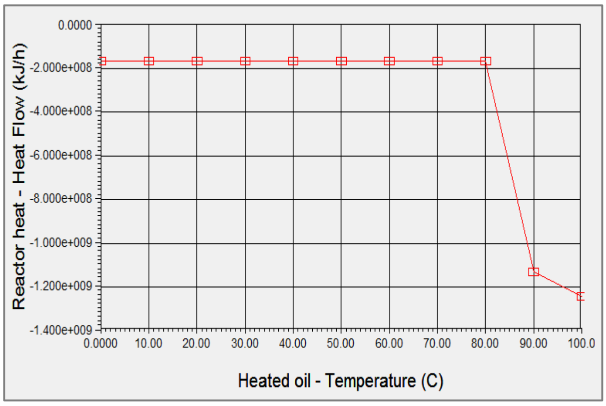
At the initial process condition, the profit was determined using HYSYS spreadsheet tool to be $1119/hr and the annual profit was $\$7,385\times10^6$. Optimum condition for maximum profit was obtained using HYSYS optimizer tool. During the optimization process, only two iterations were needed to find the optimum situation.

After optimization, significant change seen was in the increase in temperature of the product stream from the Reactor-1 from 25°C to 70°C. Consequently, there were changes in reactor heat, *i.e.*, heat generated in Reactor-1, which decreased from 5.962×10^5 kJ/hr to 4.777×10^5 kJ/hr; condenser duty of Distillation column-1, which changed from 9.077×10^4 kJ/hr to 9.075×10^5 kJ/hr and reboiler duty of Distillation column-1, which decreased from 9.122×10^5 kJ/hr to 7.936×10^5 kJ/hr.

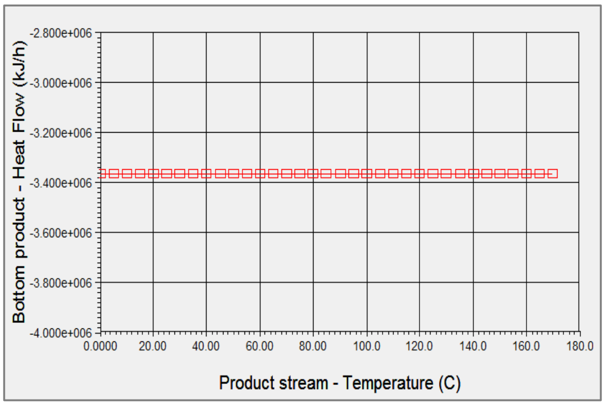
The maximized profit was found to be $1127 per hour which resulted in an annual profit of $7,437,000. The spreadsheet before and after optimization has been shown in Fig. 4.



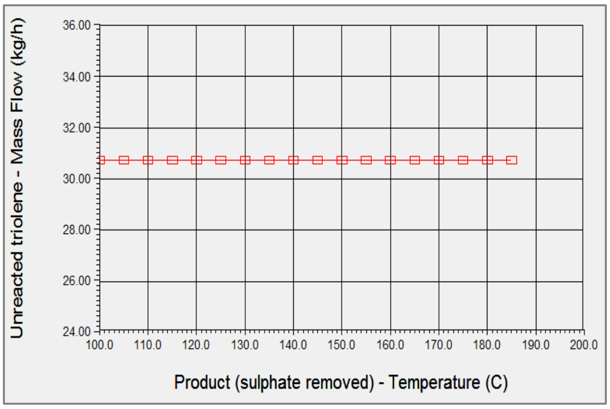
Case Study 1



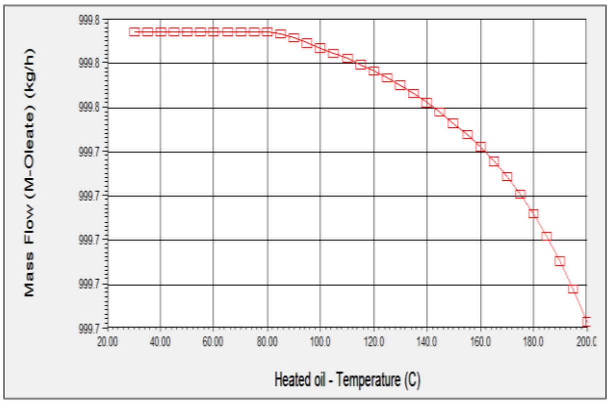
Case Study 2



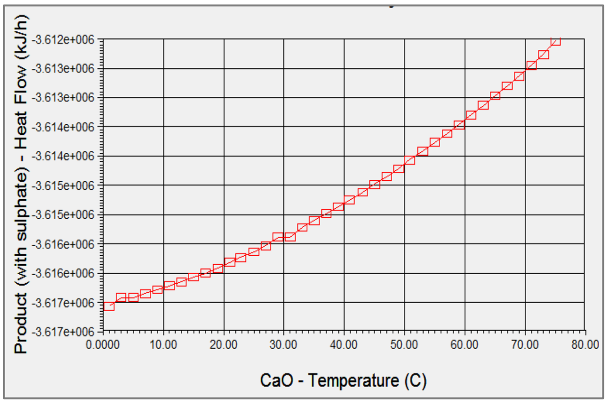
Case Study 3



Case Study 4



Case Study 5

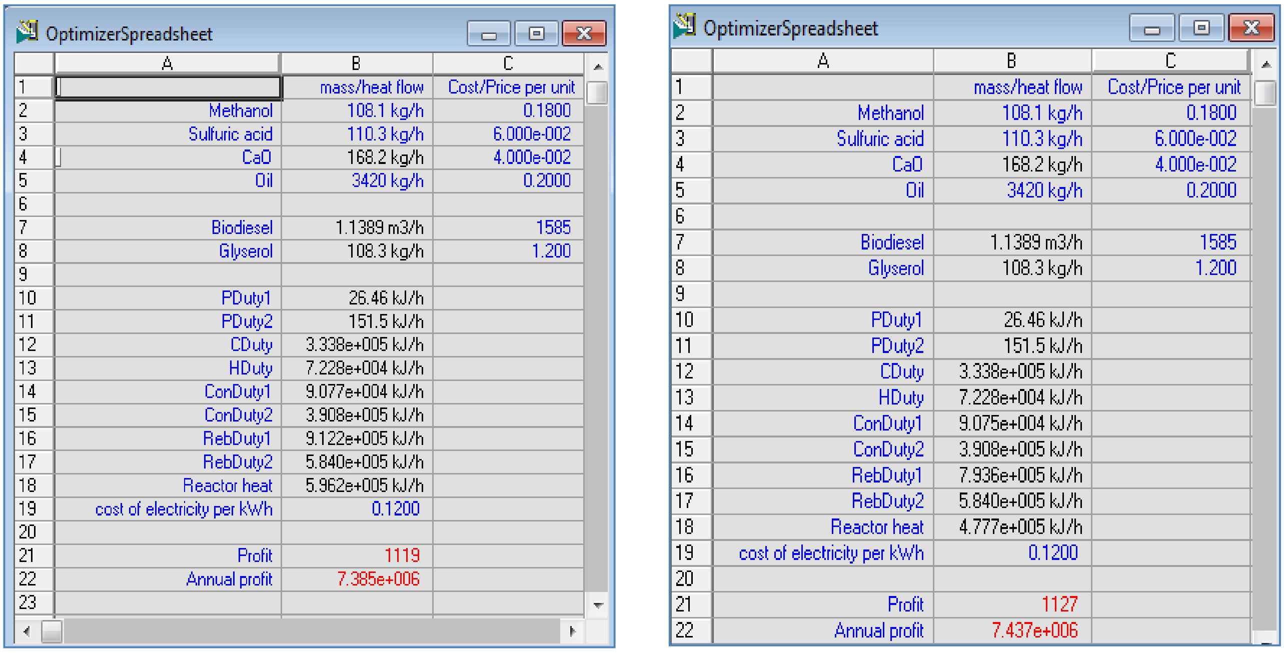


Case Study 6

Fig.3: Case Studies

5. CONCLUSION

For dealing with the worldwide energy crisis, biodiesel is a promising alternative to non-renewable energy sources. In this project, a plant, to produce biodiesel using transesterification of triolein in presence of homogeneous acid catalyst was designed, and also analyzed to assess economic viability. The feasibility of a plant includes both technological and economic aspects, and therefore, various factors, such as, altering reactor specifications, changing reactor temperatures and greater reactivity of raw materials in presence of the acid catalyst as well as accessibility of the raw materials and catalyst and their provision cost, variations in the design conditions of distillation towers, the required extent of purification of the final product etc. have major influence on the quality, and consequently, on the price of the final products. While determining profit, it was found that raw materials consumed in the process accounts for a major portion of the manufacturing cost, and, further modifications such as, recycling of unreacted oil and better utilization of heat generated in the process may yield better economic outcome.



	A	B	C
1		mass/heat flow	Cost/Price per unit
2	Methanol	108.1 kg/h	0.1800
3	Sulfuric acid	110.3 kg/h	6.000e-002
4	CaO	168.2 kg/h	4.000e-002
5	Oil	3420 kg/h	0.2000
6			
7	Biodiesel	1.1389 m3/h	1585
8	Glyserol	108.3 kg/h	1.200
9			
10	PDuty1	26.46 kJ/h	
11	PDuty2	151.5 kJ/h	
12	CDuty	3.338e+005 kJ/h	
13	HDuty	7.228e+004 kJ/h	
14	ConDuty1	9.077e+004 kJ/h	
15	ConDuty2	3.908e+005 kJ/h	
16	RebDuty1	9.122e+005 kJ/h	
17	RebDuty2	5.840e+005 kJ/h	
18	Reactor heat	5.962e+005 kJ/h	
19	cost of electricity per kWh	0.1200	
20			
21	Profit	1119	
22	Annual profit	7.385e+006	
23			

Before Optimization

	A	B	C
1		mass/heat flow	Cost/Price per unit
2	Methanol	108.1 kg/h	0.1800
3	Sulfuric acid	110.3 kg/h	6.000e-002
4	CaO	168.2 kg/h	4.000e-002
5	Oil	3420 kg/h	0.2000
6			
7	Biodiesel	1.1389 m3/h	1585
8	Glyserol	108.3 kg/h	1.200
9			
10	PDuty1	26.46 kJ/h	
11	PDuty2	151.5 kJ/h	
12	CDuty	3.338e+005 kJ/h	
13	HDuty	7.228e+004 kJ/h	
14	ConDuty1	9.075e+004 kJ/h	
15	ConDuty2	3.908e+005 kJ/h	
16	RebDuty1	7.936e+005 kJ/h	
17	RebDuty2	5.840e+005 kJ/h	
18	Reactor heat	4.777e+005 kJ/h	
19	cost of electricity per kWh	0.1200	
20			
21	Profit	1127	
22	Annual profit	7.437e+006	

After Optimization

Fig.4: View of optimizer spreadsheet before and after optimization

6. REFERENCES

[1] E. I. Bello, "Methanol and glyceride contents of Egunsi melon oil, its biodiesel and blends with diesel fuel", *Journal of Petroleum Technology and Alternative Fuels*, vol. 4, pp. 119-124, 2013.

[2] A. M. Syam, R. Yunus, T. I. M. Ghazi, and T. C. S. Yaw, "Synthesis of Jatropha curcas-based Methyl Ester and Ethyl Ester as Biodiesel Feedstocks", *Pertanika Journal of Science & Technology*, vol. 20, pp. 165-173, 2013.

[3] M. Okoronkwo, and A. G. Leke, "Advances in Biodiesel synthesis: from past to present", *Elixir Applied Chemistry*, vol. 43, pp. 6924-69451, 2012.

[4] D. Y. Leung, X. Wu, X., and M. Leung, "A review on biodiesel production using catalyzed transesterification", *Applied Energy*, vol. 87, pp. 1083-1095, 2010.

[5] A. H. West, D. Posarac, and N. Ellis, "Assessment of four biodiesel production processes using HYSYS", *Bioresource Technology*, vol. 99, pp. 6587-6601, 2007.

[6] W. Korbitz, "Biodiesel production in Europe and North American, an encouraging prospect", *Renewable Energy*, vol. 16, pp. 1078-1083, 1997.

[7] B. Supple, R. Howard-Hildige, E. Gonzalez-Gomez, and J. Leahy, "The effect of steam treating waste cooking oil on the yield of methyl ester", *Journal of the American Oil Chemists' Society*, vol. 79, pp. 175-178, 1999.

[8] A. C. Pinto et al., "Biodiesel: An overview", *Journal of the Brazillian Chemical Society*, vol. 16, pp. 1313-1330, 2005.

[9] K. Kapilakarn, and A. Peugtong, "A Comparison of Costs of Biodiesel Production from Transesterication", *International Energy Journal*, vol. 8, pp. 1-6, 2007.

[10] http://farmdocdaily.illinois.edu/2013/09/recent-trends-in-biodiesel.html (19 March, 2015)

[11] http://www.eia.gov/electricity/monthly/epm_table_grapher.cfm?t=epmt_5_06_a (19 March, 2015)

7. NOMENCLATURE

Symbol	Meaning	Unit
$C_{x,y,z...}$	Cost of unit material indicated in subscript	(\$/kg, \$/kWh)
$M_{x,y,z...}$	Mass flowrate of material indicated in subscript	(kg/h) (\$/kg, \$/m^3)
$S_{x,y,z...}$	Cost of unit substance indicated in subscript	
$Q_{x,y,z...}$	Heat flowrate of material indicated in subscript	(kJ/h)
$V_{x,y,z...}$	Volumetric flowrate of material indicated in subscript	(m^3/h)