

Biodiesel production from vegetable oil: Process design, evaluation and optimization

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To investigate the effect of reactor performance/configuration of biodiesel production on process parameters (mass & energy consumption, required facilities etc.), two diverse production processes (from vegetable oil) were implemented/designed using Aspen HYSYS V7.2. Two series reactors were taken into account where overall conversion was set to be 97.7% and 70% in first and second processes respectively. Comparative analysis showed that an increase in conversion yield caused to consumption reduction of oil, methanol, cold energy and hot energy up to 9.1%, 22%, 67.16% and 60.28% respectively; further, a number of facilities (e.g. boiler, heat exchanger, distillation tower) were reduced. To reduce mass & energy consumption, mass/heat integration method was employed. Applying integration method showed that in the first design, methanol, cold and hot energy were decreased by 49.81%, 17.46% and 36.17% respectively; while in the second design, oil, methanol, cold and hot energy were decreased by 9%, 60.57%, 19.62% and 36.58% respectively.

Keywords: Process Design, Heat & Mass Integration, Biodiesel, Pinch Technology, Heat Exchanger Network.

INTRODUCTION

Fossil fuels as well as their derivatives have been the greatest energy source over the recent two centuries. Their imminent depletion as well as environmental consequence of their overuse has motivated researchers around the world to look for renewable, less pollutant, cost-effective and reliable source of energy. Biological fuel has received an attention among other renewable energy sources e.g. energy from sun and wind energy, taking into account both greenhouse issue and reliability.

According to International Energy Agency (IEA), in 2011, the global bioenergy use were 1.3 MBOE/D (million barrels of oil equivalent per day), which will reach to 2.1 MBOE/D and 4.1 MBOE/D by 2020 and 2035 respectively; Furthermore in the year 2035, bioenergy fuel will account for almost 8% of all transportation fuel consumed in the world¹; indicating global rise in implementing their bio-energy plans over the coming decades.

At least three critical goals can be attained through governmental investment on bioenergy, including: (a) lessening the mounting concerns towards greenhouse gasses, (b) less relying on conventional depleting fossil energy and (c) improving the agriculture sector in rural areas to produce the feed for bio-energy industry. It is to be noted that European countries (and Germany at the top of the list) are the pioneers of bioenergy industry today². Significant deal of research is being carried out throughout the world to apply different sources for bio-energy production as photocurrent generation, biodiesel and bioethanol and bio-hydrogen production and etc³⁻⁴.

Comparison between biodiesel and conventional diesel indicates that it has not only decreases the main greenhouse gas (CO₂), by 78% over a life-cycle⁵, but also can contribute to reduction of CO through combustion⁶. It can be simply used directly in current diesel engines directly and can be blended (in any proportion) with diesel to improve fuel properties².

The final cost of biodiesel is 1.5–3 times higher than that of the conventional diesel⁷. Nevertheless, it constitutes

the main obstacle for its production in industrial scale. Some of drawbacks are mainly high energy consumption, low reactor efficiency, and material/energy loss at various extraction/separation processes⁸.

With the aim of minimization of energy/material consumption and reduction of facility usage, the effect of reactor performance on processing parameters was investigated in this paper. Therefore, in primary optimizations, the materials and streams which were used to lose in the process, were collected and recycled back to the process input/feed; further, to prevent energy loss, pinch method – as one of efficient methods in integration approach – were employed. In this method the extra energy available in the process were partially used to reduce the utility energy uptake. As such, using identical material load and facilities (with different reactor efficiency), two different processes were sketched where trans-esterification reaction under 60 and 1 atm. carried out with overall yield of 97.7% and 70% at each.

BIODIESEL

Biodiesel is a combination of fatty acid esters which can be used as fuel in diesel engines. The ester acid compounds of the biodiesel increase the oxygen content in fuel, leading to higher combustion yield and reduction of air pollution². It can be produced from animal fats, waste oil and plant oils extracted from Soya, Sunflower, Palm and Canola⁹.

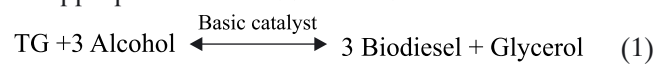
Among various candidates mentioned above, oil from oleaginous crops was found to be reliable, source taking into account the quantity, consistency and continuity of the flow which should be fed into a biodiesel production plant¹⁰.

Apart from the reliability of the source in question, Fatty Acids (FA) from oleaginous crops, though, cannot be used directly in engines due to its low volatility and high viscosity since it may lead to piston knocking, sedimentation, cocking and other technical troubles¹¹⁻¹². To tackle this, researchers have proposed numerous

solutions e.g. trans-esterification which increases the volatility and decreases viscosity index maintaining the heating value of FA¹³⁻¹⁴.

Trans-esterification (Eq. 1) is the reaction of Alcohol with Tri-Glyceride (TG) producing Glycerin¹⁵. Together with TG, Free Fatty Acid (FFA) can be found in animal and plant oils. If the FFA content would be higher than 1%, it should be removed or converted to biodiesel (Eq. 2)¹⁶⁻¹⁷.

Application of catalyst is of key importance in Eq. 1 and 2 due to the nature of the trans-esterification reactions and low solubility of alcohols in FA, and more importantly, low reaction rate, using catalysis has been proposed¹⁰ e.g. acid, alkali and enzyme catalysts. For trans-esterification of FA obtained from oleaginous crops, homogeneous alkali catalysts are being conventionally used in batch and continuous processes¹⁸⁻¹⁹, Alkali catalysts are preferred for biodiesel production because it is faster than acid catalyzed trans-esterification reaction²⁰. However, enzymatic catalysts have not been proved to be appropriate choice due to insufficient reaction rate²¹.



The produced biodiesel should also possess a number of standards which has been clearly elaborated in ASTM 6751-02 along with their testing methods¹⁰.

Production process

Production of biodiesel can be carried out through both batch and continuous procedures. In batch process (Fig. 1) the reactor stirrer operates for 20 min to more than an hour as residence time starting from a vigorous rate down to zero to provide an initial bi-phasic separation of glycerin (higher density) to obtain the final conversion of 85–94%. To further increase the conversion (up to 95%), a two-step series reactor was followed at which glycerin was removed between two stages as can be seen in Figure 1. To separate produced esters and glycerin, a settler or centrifuge can be employed; furthermore, the remaining alcohol in both streams can also be removed by Flash evaporation. Finally, to remove the remaining impurities e.g. salts, catalyst and alcohol, the obtained biodiesel and glycerin were rinsed with water and acid^{14,22}.

One of the common modifications in batch production is the application of a series of Completely Stirred Tank Reactors (CSTR) to improve heat transfer and production yield. As can be seen in Figure 2, the CSTR series can also be replaced by a Plug Flow Reactor (PFR) to increase conversion fraction as well as total processing time which drops to 6–10 minutes only²³. The choice of alternative, however, depends on potential technical

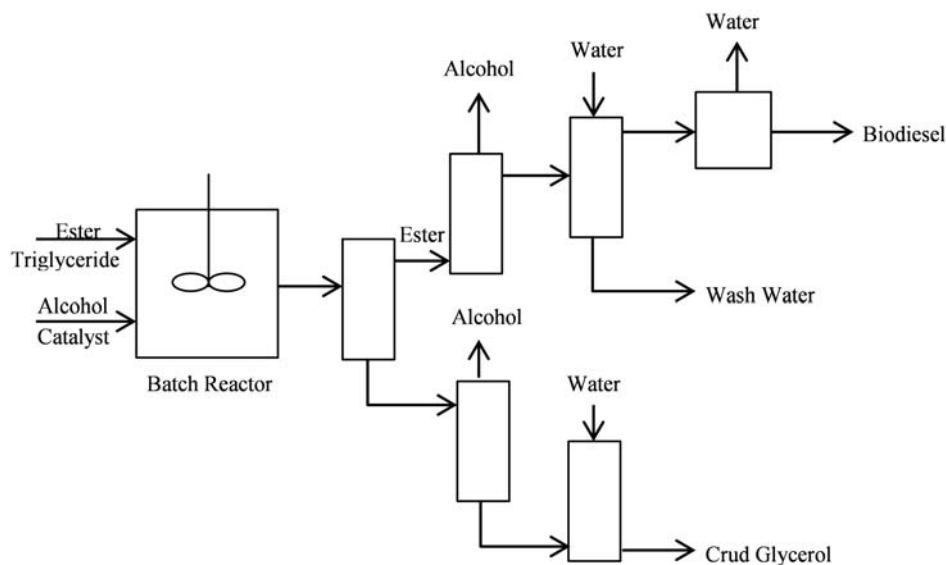


Figure 1. Batch process in biodiesel production

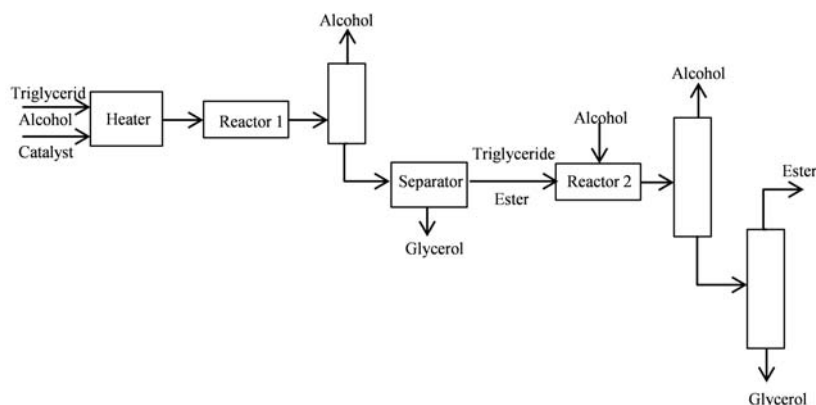


Figure 2. Continuous process in biodiesel production

troubles, material handling's manner as well as cost/benefit balance.

Separation of ester and glycerin

The separation of ester and glycerin carries out after the production of biodiesel in the reactor (chain) based on the density difference among ester (light phase) and glycerin (heavy phase) in centrifuge, decanter or hydro-cyclone. The alcohol content of reactor products (mainly methanol) is the key parameter in mutual miscibility of the two phases²⁴.

Alcohol separation

Alcohol separation contributes the whole process to be more cost-effective and environmentally-friendly since it enters to the reactor in extra proportions and is mainly volatile, flammable and harmful. Moreover, the separation should be carried out prior to ester-glycerol separation, since as has been noted earlier, alcohol content prevents the binary phase separation of ester-glycerol due mainly to practical interaction with water²⁵.

Biodiesel treatment

Separation and purification of the produced biodiesel is of critical importance in overall economy of biodiesel production since the cost associated with this steps amounts to 60–80% of the total processing cost; furthermore, it may cause a number of serious subsequent technical difficulties when using e.g. filter plugging, higher soot agglomeration, oil adhesion, oil coagulation, engine knocking and failure²⁶.

Glycerin treatment

Glycerin is considered to be the most important by-product of the biodiesel production process with its global consumption quantity mounting to 600 Ktonnes per year being used mainly for cosmetics (almost 28%) and medical purposes²⁷. The final price, however, dropped dramatically to 7.5 US\$/ton from 110 US\$/ton between 2004 and 2011 due to significant increase in global biodiesel production²⁵.

Employing thermo-chemical and biological methods, it can be converted to highly value-added products e.g. propylene glycol, propanoic acid, acrylic acid, propanol, i-propanol and allyl alcohol^{28–29}. Using Fisher-Trops method in presence of catalyst, the glycerine may be converted to fuel and hydrogen over relatively low temperatures i.e. 225–300°C^{29–30}.

The separated glycerin includes mainly catalyst, sapon and ester along with negligible quantities of phosphate, sulfur, protein, aldehyde, ketone and dissoluble inorganic compounds. Vacuum distillation as well as physico-chemical techniques can be employed for glycerin separation³¹. The

obtained glycerin may also be used as feed in various industries including food, cosmetics, lubricant etc³².

PROCESS DESIGN

HYSYS is a software for steady-state and dynamic process simulation created by Hyprotech as an interactive and flexible process modeling software^{22, 31}. The simulation was carried out using Aspen HYSYS V7.2 employing Triolein (as TG), Oleic acid (as FFA), and m-Oleate as biodiesel as has already been used in previous communications as model representatives^{22, 31, 33}. To avoid side-stream reactions as well as trans-esterification, the FFA content was taken to be 0.05% – mass ratio³⁴. Feed stream was taken as product of NaOH-catalyzed bi-reactor system operating at 60°C and 1atm^{35–37} with the overall conversion of 97.7%, using two series reactors has already been investigated in previous researches^{38–39}.

Taking into account the low cost, accessibility and handling considerations, methanol was employed in this investigation as the model-type alcohol, since it may not cause difference in chemical structure of final obtained biodiesel^{39–40}.

In Eq. 1, the TG:Alcohol ratio is 1:3, though it was taken in extra 1:6 for appropriate reactor performance in practice^{41–42}. The design was mainly intended to produce 20 m³h⁻¹ biodiesel with mass concentration of 99.65%. As exchanger pressure loss is about 50 kpa, the increase of pressure in pumps were taken in a level so that the overall pressure would remain almost at 1 atm. all along the process since higher pressure may cause dramatic effects on reactions and costs. NRTL was taken as the governing Equation of State (EOS) for the process, while for decanters; SRK was used^{31, 43–44}.

As has been showed in Figure 3, feed-streams reacts in Reac. 1 and the downstream lines flows to Sep. 1 (Separator 1) to separate un-reacted oils as well as the extra methanol. The separator operates at 25°C (1 atm) and the separation carries out in a proportion at which the outlet (Reac. 2 feed) possesses of methanol: oil ratio of higher than (or equal to) 6:1.

Reac. 2 products including glycerin, methanol, biodiesel and oil were flown to Sep. 2 (Separator 2) (25°C) to separate ester (light) and glycerin (heavy). Light phase (ester) was directed to a recycled distillation column (Dist. 1) with R = 1.5 and 6 trays to obtain extra-pure methanol (100%) from biodiesel. Biodiesel-containing flow then entered to Sep. 3 (Separator 3) to improve purity and remove remaining catalysts via HCl-NaOH neutralization reaction. HCl and catalyst are fed with identical molar flow and reacts with 95% conversion fraction to give 99.65% ultra-pure biodiesel (Table 1).

Table 1. Inlet/Outlet material in biodiesel production process

Stream	T [°C]	\dot{m} [kg h ⁻¹]	P [kPa]	Mass fraction								
				Triolein	Methanol	M-oleate	Glycerol	H ₂ O	Oleic Acid	HCl	NaCl	NaOH
NaOH	25.0	174.8	101.3	0	0	0	0	0	0	0	0	1
Methanol	25.0	1905	101.3	0	0	0	0	0	0	0	0	0
Oil	25.0	17420	101.3	0.9995	0	0	0	0	0.0005	0	0	0
Methanol rec	64.4	1894	101.3	0	1	0	0	0	0	0	0	0
Glycerol-2	283.4	1816	110	0	0.0005	0	0.9995	0	0	0	0	0
HCl	25.0	158.8	101.3	0	0	0	0	0	0	1	0	0
Biodiesel	27.6	17600	101.3	0.0005	0.0001	0.9965	0	0.0015	0.0005	0.0005	0	0.0005
HLD-3	27.6	291.2	101.3	0	0.0001	0	0.0037	0.1659	0	0	0.8303	0

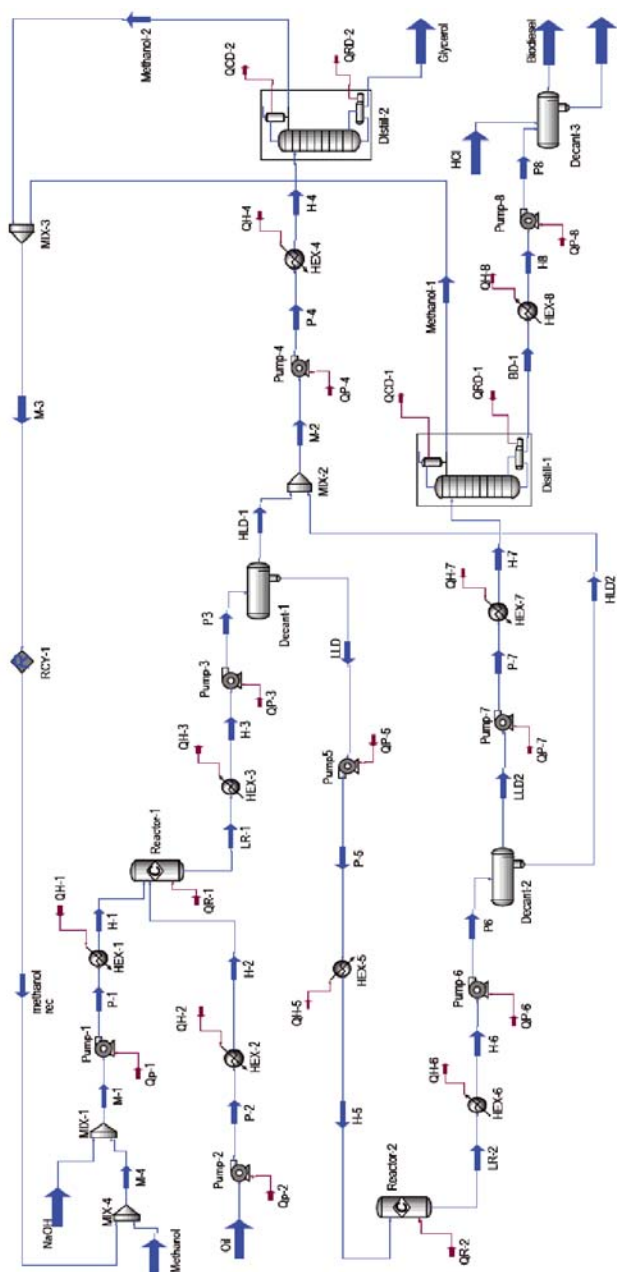


Figure 3. PFD of biodiesel production from vegetable oil

Effluents from Sep. 1 and Sep. 2 having large quantities of methanol and glycerin were directed to second distillation tower (Dist. 2) with 5-tray and $R = 1.5$ to yield pure methanol and glycerin with 100% and 99.54% purity respectively, considering their significant difference

in boiling points. The obtained methanol recycled back to the beginning of process as a feed; while glycerin was sent out to downstream as by-product.

Finally, the cold energy (sum of cooler and condenser energies) and the hot energy (sum of heater and boiler energies) required for the process were calculated to be 6194 kw and 6884 kw respectively.

HEAT INTEGRATION

Reducing the processing costs is one of the major challenges for chemical engineers today; which mainly deals with utility costs. Energy consumption can be balanced partially using heat exchangers where energy exchanges between the cold and hot streams. Optimization as well as integration methods based generally on thermodynamic and mathematic approaches. Mathematic methods solve modeling problems e.g. Mixed Integer Non-Linear Programming (MINLP) and Mixed Integer Linear Programming (MILP) equations through classical or stochastic methods⁴⁴.

Thermodynamic methods e.g. Pinch Technology based on thermo-kinetic principals and exergy loss reduction⁴⁵. Pinch technology was first introduced by Linhoff et al. in 1978 to the optimization of heat exchanger networks and lodged pinch point as the critical point of energy consumption⁴⁶.

The method was used here to design exchanger network to reduce energy consumption and loss. Energy consumption reduction, number of used exchangers, required effective area etc., can be assigned as the scope of pinch approach as the first step in pinch design. Energy consumption was taken as the basis of optimization in this study; thereafter, source and demand streams (which can be defined as emission and receiving of energy respectively) were determined. Table 2 demonstrates the thermal characteristics of all streams including source and demand, regardless of the outlet streams like glycerol line. HR-1, HR-2, HD-1 and HD-2 represent cooling water leaving reactors and condensers respectively which flew subsequently to utility to drop water temperature to 25. C_p is also indicating heat capacity of each line which can be calculated using Eq. 3:

$$C_p = (C_{p_{in}} + C_{p_{out}}) \cdot m/2 \quad (3)$$

Where m is the flux and $C_{p_{in}}/C_{p_{out}}$ are the heat capacity of inlet/outlet streams. Minimum approach temperature (ΔT_{min}) was also taken as 10 in the following calculations.

Table 2. Source and demand streams and their heat characteristics

Stream	Supply temperature [°C]	Target temperature [°C]	CP [kW/°C]	ΔH [kW]
Cold stream				
HEX-1	43.9	60.0	4.1	65.6
HEX-2	25.0	60.0	0.64	21.8
HEX-4	25.0	60.0	2.2	76.7
HEX-5	25.0	60.0	10.7	373
HEX-7	25.0	60.0	10.9	380
Hot stream				
HEX-3	60.0	25.0	12.8	-0.42
HEX-6	60.0	25.0	10.9	-0.36
HEX-8	343.5	25.0	12.3	-3930.6
HD1-1	50.0	25.0	31.25	-784.2
HD2-1	50.0	25.0	26.3	-659.2
HR-1	120.4	25.0	7.1	-657.6
HR-2	100.0	25.0	0.36	-20.1

To calculate interval temperature as the next step, the inlet and outlet temperatures of hot flow must be diffractioned from the half of minimum approach temperature of exchangers; and the inlet and outlet cold temperatures should be summed with the half of minimum of approach temperature of exchangers (Eq. 4 and Eq. 5). Interval enthalpy can also be calculated using Eq. 6.

$$\text{Hot Interval Temperature} = \text{Hot Tem.} - \Delta T_{\min} \quad (4)$$

$$\text{Cold Interval Temperature} = \text{Cold Tem.} + \Delta T_{\min} \quad (5)$$

$$\Delta H_{\text{interval}} = \Delta T_{\text{interval}} [C_{P\text{Cold}} - C_{P\text{Hot}}] \quad (6)$$

According to Table 3, the required hot and cold energy for the network were found to be zero and 5988.4 kw respectively; where the number “zero” indicates that the source stream is able of providing all energy required by demand stream, whereas 5988.4 kw shows that a make-up energy with this magnitude should be transferred from utility to process in furtherance of the energy given by source stream to the demand. Moreover, as can be seen, there is no pinch temperature among interval temperatures confirming of no limitation for energy transfer between streams, according to pinch principals. Care should be taken that the exchanger approach tem-

perature should not be less than the minimum selected approach temperature.

According to Table 2, since the considered source streams were able of providing required network energy, the energy from the rebuilders heat source were not taken into account; additionally, utilization of energy from source stream possessing “300°C and 1 MPa” merely to warm other streams to the maximum of 60°C is not cost-effective and it should be saved for essential cases e.g. boilers. Taking all Pinch principals and processing issues into consideration, the plant demonstrated in Figure 4 was plotted and re-characterized.

Applying the new system (Fig. 4) in the process, cold and hot energy reduced to 5991.4 kw and 5273.6 kw respectively at which the hot energy is consumed merely for heating the distillation reboilers. From Table 4 and Figure 4, HEX-8 can be used as energy source for the second distillation tower’s reboilers which result in 14.68% reduction of cold energy and 16.67% reduction in hot energy consumption. Table 5 provides a comparative report on the effect caused by applying the integration method.

To investigate the effect of conversion on process, similar 20 m³ h⁻¹ production unit was designed using

Table 3. Cold and Hot utility calculation of exchanger network

		$\Sigma [C_{P\text{Cold}} - C_{P\text{Hot}}]$ [kW°C ⁻¹]	ΔH [kW]	0
340				
115.4		-12.3	-2762.6	2762.6
95		-19.4	-395.8	3158.8
65		-19.8	-594	3752.4
55		8.8	88	3664.4
48.9		-14.9	-90.9	3755.3
45		-19	-74.1	3829.4
30		-76.6	-1149	4978.4
20		-101	-1010	5988.4

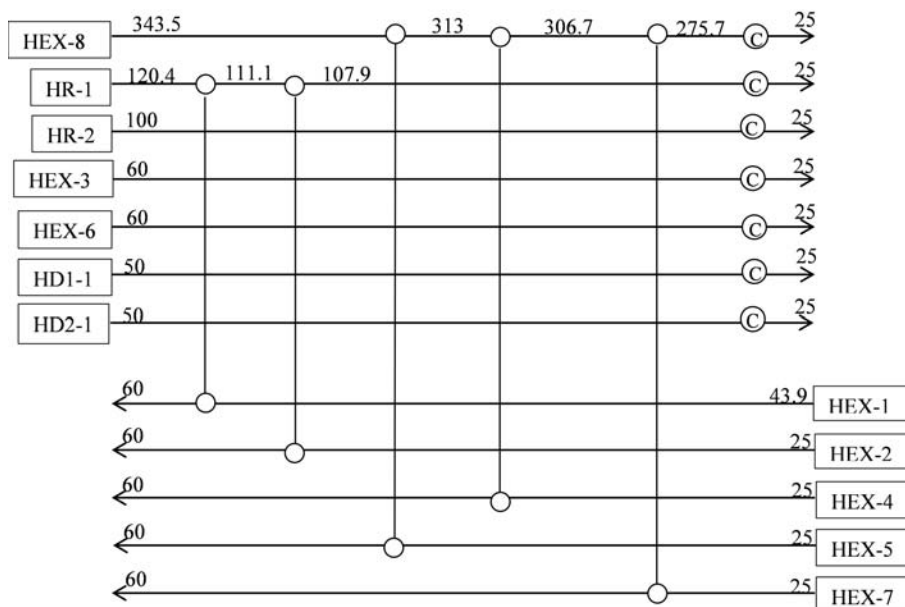


Figure 4. Heat exchanger network in the biodiesel production process

Table 4. Heat characteristics of distillation tower reboilers

Reboiler	T _{in} [°C]	T _{out} [°C]	ΔH [kW]
First column	162.1	343.5	4394
Second column	81.0	231.7	879.7

Table 5. Obtained results from first and second results

process parameters	First design		Second design	
	before integration	after integration	before integration	after integration
Inlet oil [kg h ⁻¹]	17420	17420	19170	17440
Inlet methanol [kg h ⁻¹]	3788	1901	4855	1914
Outlet Glycerol [kg h ⁻¹]	1818	1818	1834	1834
No. Distillation column	2	2	3	3
No. of heat transfer equipment	8	10	9	14
No. of pump	8	8	9	9
Total pump power [kW]	2.6	4.9	2.7	5.9
Cold energy [kW]	6194	5112.2	18860	15160
Hot energy [kW]	6884	4394	17330	10990

same facilities and materials. In the new design, however, two series reactors ($X = 70\%$) were employed. In these conditions, the output biodiesel concentration (mass fraction) in Sep. 3 is 90.8% which was sent to another distillation tower with 5 trays and recycle flow ratio 1.5 directly to further increase biodiesel concentration.

The upstream line on top of this tower includes biodiesel with appropriate purity, whereas downstream contains a great deal of triolein because more than 30% of the feed remains un-reacted. Therefore purification reactors for triolein treatment were used as has been used in the earlier design. The downstream line for increasing in purity and recycle to the feed stream sent to separator at 25°C; this operation resulted in triolein with 99.51% mass concentration. Hence, in this new process, a distillation tower, a heat exchanger, a pump and another separator were added after Sep. 3.

In this design, to reduce energy consumption, exchanger networks have been designed applying pinch method with the minimum approach temperature of 10°C; the results were shown in Table 5.

CONCLUSION

Application of recycle stream and mass integration has reduced methanol consumption up to 49.81% and 60.57% in first and second design respectively. In the second design, since there is still a significant quantity of un-reacted oil, it can be recycled back into feed and reduce the oil consumption up to 9%. Cold and Hot energies were also reduced 17.46% and 36.17% respectively in first and 19.6% and 36.6% in second design respectively. The number/capacity of used facilities increased in some cases as a result of application of integration method; this item can be also optimized depending on relative price of feed, used facilities or other technical considerations.

From the results, it can be deduced that the increase of reactor conversion from 70% to 97.7%, caused a significant reduction in consumed oil (9.1%), methanol (22%), cold energy (67%) and hot energy (60.3%); in addition to reduction of a number of used facilities e.g. distillation tower and exchangers, were reduced.

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