The Effect of Reactor Configuration and Performance on Biodiesel Production from Vegetable Oil

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Abstract

In this paper, to express the effect of reactor performance and configuration of biodiesel production on subsequent process parameters (including mass & energy consumption, required facilities, etc.) two diverse biodiesel production processes (from plant oil) were designed with using Aspen HYSYS V7.2 software. Two series of reactors were taken into account in these designs, where in the first and second processes, the overall conversion were set to be 97.7% and 70% respectively. Comparative analysis of the results showed that, in the second design, further amount of 10% oil and 28.16% methanol were obtained. In addition, cold and hot utilities were increased to almost 204.48% and 151.74% respectively, while a few numbers of facilities like distillation tower and heat exchangers amended merely. To reduce mass & energy consumption, mass/thermal integration method was employed. In the mass integration, the optimum operation condition and the reduction of material loss were the major points of focus; while in thermal integration, pinch technology were used for exchanger network design. Moreover , integration method showed that in the first design, material, cold and hot utilities were decreased by 49.81%, 17.46% and 36.17%, respectively; while in the second design, oil, methanol, cold energy and hot utilities were decreased by 9%, 60.57% 19.62% and 36.58%, respectively.

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Introduction

Fossil fuels as well as their derivatives have been the greatest energy sources. The imminent depletion of their overuse has motivated researchers around the world to looking for renewable, less pollutant, cost-effective and reliable source of energy. Biological fuel has received a critical attention among renewable energy sources e.g. solar and wind energy.

According to the International Energy Agency (IEA), by 2030 the global demand for transportation fuel will increase to almost 55% comparing to that of 2004; hence companies have started to implement their bio-energy plans [1]. At least three critical goals can be attained through governmental investment on bio-energy, such as: (*a*) to decrease the mounting concerns towards greenhouse gasses, (*b*) less relying on conventional fossil energy and (*c*) improving the agricultural 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 bio-energy industry today [2].

A simple comparison between biodiesel and conventional diesel indicates showed that it has not only dramatically decreases the main greenhouse gas (CO_2), by 78% over a life-cycle [3], but also can contribute to reduction of toxic gases by combustion (CO) [4]. It can be simply used in current diesel engines and can be blended (in any proportion) with diesel to improve fuel properties [2].

Nevertheless, the final cost of biodiesel is almost 1.5-3 times higher than the conventional diesel [5], constituting the main obstacle for its production in industrial scale. These costs are mainly associated with high energy consumption, low reactor efficiency, and material/energy loss at various extraction/separation processes.

In this paper, the process of biodiesel production from oleaginous products has been designed, optimized and finally the effect of reactor configuration and performance on process parameters including energy and mass consumption and required facilities etc. were examined.

Biodiesel

Biodiesel is a mixture of fatty acid esters which can be used as fuel in diesel engines. The acid esters compounds of the biodiesel increases the oxygen content in fuel, leading to higher combustion yield and reduction of air pollution [2]. It can be produced from animal fat, waste oil and plant oils, that extracted from Soya, Sunflower, Palm and Canola [6]. Animal fats as side products of fish industry can be obtained basically from livestock. The most important problem, is in-continuity of these products; therefore it cannot be considered as consistent source for biodiesel production [7].
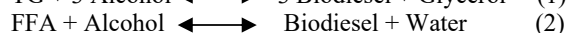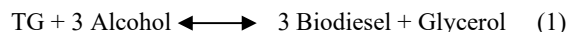
Wasted oil is not also in a reliable quantity; but it needs an extra pretreatment steps [8]; therefore among various alternatives, the oil from oleaginous crops can be introduced as one of the most reliable sources for biodiesel production. Apart from the reliability of the source in question, Fatty Acids (FA) from oleaginous crops, though, cannot be used directly in engines due to it's low volatility and high viscosity since it may lead to piston knocking,

sedimentation, cocking and other technical troubles [9, 10]. To tackle this, researchers have proposed numerous solutions e.g. trans-esterification which keeps the thermal value of the FA, while increasing the volatility and decreasing viscosity index [11, 12]. Trans-esterification (Eq.1) is the reaction of Alcohol with Tri-Glyceride (TG) that producing Glycerin [13]. Both of TG and 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) [14, 15].

Due to the nature of the trans-esterification reactions and low solubility of alcohols in FA and more importantly, low reaction rate, using catalysis [8] e.g. acid, alkali and enzyme catalysts has been proposed. For trans-esterification of FA obtained from oleaginous crops, homogeneous alkali catalysts is being conventionally used [16] and enzymatic catalysts has not been proved to be appropriate choice due to low reaction rate [17].

The produced biodiesel should also possess a number of standards which has been clearly elaborated in ASTM 6751-02 along with their testing methods [8].

$$TG + 3\ Alcohol \longleftrightarrow 3\ Biodiesel + Glycerol \quad (1)$$
$$FFA + Alcohol \longleftrightarrow Biodiesel + Water \quad (2)$$

Production process

Production of biodiesel can be carried out over both batch and continuous procedures. In Batch process (Fig.1) a stirred reactor operates with residence time of 20 min to more than an hour. In batch design, the stirring rate is high at initial, but over time, it is reduced to provide an initial bi-phasic separation of glycerin (higher density) to obtain final conversion of 85-94%. To further increase of conversion (up to 95%), two-step series reactor that at which glycerin was removed between two stages, were followed. To separate produced esters and glycerin, a settler or centrifuge can be employed; furthermore, the remaining alcohol in both streams can 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 [18, 19].

One of common modifications in batch production, is the application of series of the Completely Stirred Tank Reactors (CSTR – of course, not essentially with similar volume and residence time) to improve heat transfer and production yield. 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 only (Fig. 2) [18].

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 phase (light) and glycerin phase (heavy) in centrifuge, decanter or hydro-cyclone. The alcohol content of the reactor products (mainly methanol) is the key parameter in mutual miscibility of the two phases [18].

Alcohol separation

Alcohol separation helps to 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, as has been noted earlier, alcohol content, prevent the binary-phase separation of ester-glycerol mainly due to practical interaction with water [18].

Biodiesel treatment

Separation and purification of the produced biodiesel is important in overall economy of biodiesel production since the cost associated with these steps covers 60-80% of the total processing cost; furthermore, it may cause a number of serious subsequent technical difficulties when using in engine e.g. filter plugging, engine failure, higher soot agglomeration, oil adhesion, engine knocking and oil coagulation [20].
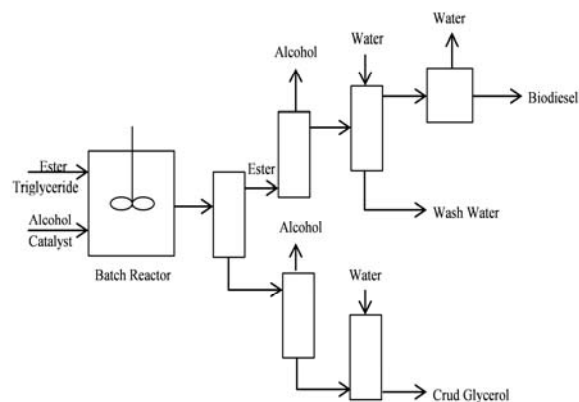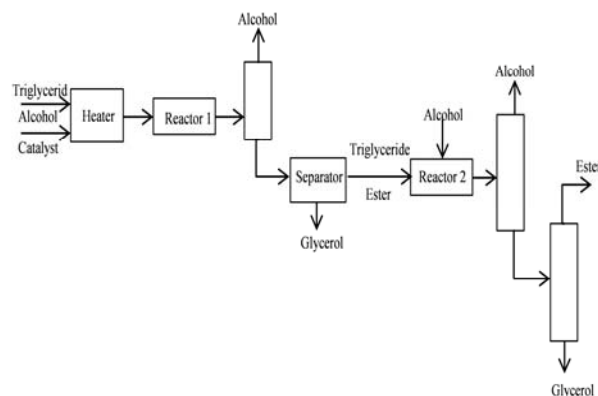

Figure 1. Batch process in biodiesel production.

Figure 2. Continuous process in biodiesel production.

Glycerin treatment

Glycerin is considered to be the most important by-product of the biodiesel production process with its global consumption quantity that growing to 600Ktonnes per year used for cosmetics (almost 28%) and medical purposes [21]. 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 production [22].

By employing chemical, thermo-chemical and biological methods, it can be converted to highly added-value products e.g. propylene glycol, propionic acid, acrylic acid, propanol, i-propanol and allyl alcohol [23, 24]. By using Fisher-Trops and catalyst, the glycerin can be converted to fuel and hydrogen over relatively low temperatures (225-300°C) [25, 26].

The separated glycerin mainly includes catalyst, soap and ester along with negligible quantities of phosphate, sulfur, protein, aldehyde, ketone and dissoluble inorganic compounds. Vacuum distillation as well as physic-chemical techniques can be employed for glycerin separation [18]. The obtained glycerin may be also used as a feed for various industries including food, cosmetics, lubricant etc.

Materials and Methods

Process design

The simulation was carried out with using Aspen HYSYS V7.2 software employing Triolein (as TG), Oleic acid (as FFA), and m-Oleate as biodiesel [19, 27, 28]. To avoid side-stream reactions such as trans-esterification, the FFA content was taken to be 0.05% (mass ratio) [29]. Feed stream was taken as product of NaOH-catalyzed bioreactor system operating at 60°C and 1atm [30-32] with the overall conversion of 97.7%. Using two series reactors has already been investigated in previous researches [33, 34].

Although the type of employed alcohol does not cause difference in chemical structure of final obtained biodiesel, methanol was used in this investigation due to low cost, accessibility and handling considerations [35, 36]

In Eq. (1), the ratio of TG to Alcohol is 1:3, though it was taken 1:6 to appropriate reactor performance in practice [37, 38]. The design was mainly intended to produce 20 m^3/h biodiesel with mass concentration of 99.65%. As the pressure drop of exchanger is about 50 kpa, the pressure in pumps increases in a level so that the overall pressure would be remain almost 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 decanters SRK were used [28, 33, 39].

Thermal Integration

Today reducing processing costs is one of the major challenges of chemical engineers; 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 solves modeling problems e.g. Mixed Integer Non-Linear Programming (MINLP) and Mixed Integer Linear Programming (MILP) equations through classical or stochastic methods [40]. Thermodynamic methods e.g. Pinch Technology is based on thermo-kinetic principals and exergy loss reduction [41]. Pinch technology was first introduced by Linhoff et al., in 1978 for the optimization of heat exchanger networks and lodged pinch point as the critical point of energy consumption [42]. This method has been used here to design exchanger network to reduce energy consumption and losses. The energy

consumption reduction, number of used exchangers, required effective area and 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.

Results and Discussion

As can be clearly seen in Fig. 3, feed streams reacts in Reac.1 and the downstream lines flows to Sep.1 to separate unreacted oils like the extra methanol. The separator operating condition is 25°C and 1atm and the outlet (Reac.2 feed) possess the ratio of methanol: oil that this ratio would not be lower than 6:1. Also Freedman et al., have concluded that to obtain maximum ester formation by transesterification of vegetable oils, the alcohol should be moisture free. A molar ratio of alcohol to oil of 6:1 gives optimum conversion to the ester [29]. While Portha et al., simulations have shown that the use of a high molar ratio of methanol to triolein (about 25) is necessary to shift equilibrium such as the triolein conversion reaches 80%. The simulations indicate that a conversion of triolein of 87% can be reached with a methanol to triolein molar ratio of 36 [20].

Reac.2 products including glycerin, methanol, biodiesel and oil were directed to Sep.2 (25°C) to separate ester and glycerin. The light phase (ester) was directed to the recycled distillation column (Dist.1) with R=1.5 and 6 trays to obtain extra-pure methanol (100%) from biodiesel. Then biodiesel-containing flow enters to Sep.3 to improve purity and removing remaining catalysts via HCl-NaOH neutralization reactions. HCl and catalyst enters with identical molar flow and reacts with 95% conversion fraction to give 99.65% ultra-pure biodiesel (Table 1). This percent of purification is comparable with Fumnanya et al., results that with the optimization of the process they could increase the purity from (0.648) to 0.7995 only.

They have also revealed the Aspen HYSYS model developed in their research work can be used to represent, simulate and optimize a reactive distillation process successfully, while Freedman et al., in their simulation found that ester conversions of 96-98% can be obtained by transesterifying refined oils with methanol, ethanol and butanol [29]. This should be mention that use of 0.05 % free fatty acid content and sodium hydroxide as a catalysts in this study are in corporation with other researchers finding [29, 34] which for example Freedman et al., demonstrated that either 0.5% sodium methoxide (for laboratory use) or 1% sodium hydroxide (for larger-scale reactions) are effective catalysts while a free fatty acid content is less than 0.5% [29]. Second effluents from Sep.1 and Sep.2 including 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 purity of 100% and 99.54% respectively; considering their significant difference in boiling points. The obtained methanol recycles back to the beginning of process as a feed; while glycerin was sent out to downstream as by-product. It has been revealed that recovery of glycerol, the by-product, is also

important. Glycerol has many industrial uses. An estimate has been made that the cost of the transesterification processing could be paid for if suitable markets can be found for the glycerol [29]. Sanchez *el al.*, have reported that methanol obtained in esterification reaction can be used inside the overall process to reduce external water consumption to remove catalyst and impurities from the biodiesel stream [39].

Table 1. Inlet/outlet material of the biodiesel production process.

Stream	T (°C)	$\dot{m}$ (kg h⁻¹)	P (kPa)	Triolein	Methanol	M-oleate	Glycerol	H₂O	Oleic Acid	HCl	NaCl	NaOH
												Mass fraction
NaOH	25	174.8	101.3	0	0	0	0	0	0	0	0	1
Methanol	25	1905	101.3	0	0	0	0	0	0	0	0	0
Oil	25	17420	101.3	0.9995	0	0	0	0	0.0005	0	0	0
Methanol rec	64.43	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	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

The cold and hot required energies to whole processes were calculated to be 6194kw and 6884kw respectively. These results are in corporation with Gomez-Castroa *et. al.*, finding where their study also considered aspects of energy, costs and environmental impact, It has been found that, in terms of energy requirements for the conventional alternatives, the use of two reactors represents lower energy requirements for the feed flow rate considered also in terms of costs, a similar result was found. They have found that the use of a reactive distillation column with a mass purity of 80% for the biodiesel represents the lower costs for the process [19].

Ye *et al.*, conducted that although glycerol exists in the methyl ester–methanol mixture, the content of glycerol is usually very small because of removal of most of glycerol before the second transesterification, and it has no significant effect on the liquid–liquid phase equilibrium of the methanol–methyl ester–water ternary system. Furthermore, this small amount of glycerol can also be removed by water washing because glycerol is apt to solve in water. Therefore, the water washing operation could be utilized to replace the traditional costly methyl estermethanol distillation operation, and the corresponding improved separation process is worthy of further study [34].

Table 2 demonstrates the thermal characteristics of all streams such as source and demand-streams, regardless of the outlet streams like glycerol streams. HR-1, HR-2, HD-1 and HD-2 represent cooling water that leaving reactors and condensers respectively which flew subsequently to utility to drop water temperature to 25°C. Cp is also indicating thermal capacity of each line which calculated with using Eq. (3): $CP = (cp_{in} + cp_{out}) * / m\,2$ (3)

Table 2. Source and demand streams and their thermal characteristics.

Stream	Supply Temp (°C)	Target Temp (°C)	CP (kW/°C)	ΔH (kW)
		Cold stream		
HEX-1	43.9	60	4.1	65.6
HEX-2	25	60	0.64	21.8
HEX-4	25	60	2.2	76.7
HEX-5	25	60	10.7	373
HEX-7	25	60	10.9	380
		Hot stream		
HEX-3	60	25	12.8	-0.42
HEX-6	60	25	10.9	-0.36
HEX-8	343.5	25	12.3	-3930.6
HD1-1	50	25	31.25	-784.2
HD2-1	50	25	26.3	-659.2
HR-1	120.4	25	7.1	-657.6
HR-2	100	25	0.36	-20.1

Where m˙ is the flux and Cp_{in}/Cp_{out} are the thermal capacity ratio of inlet/outlet streams. Minimum approach temperature (ΔT_{min}) was also taken at 10°C in the following calculations.

As the next step to calculate temperature interval, the inlet and outlet temperatures of hot flow must be diffracted 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. Interval enthalpy can also be calculated with using Eq. (4).

$$\Delta H_{interval} = \Delta T_{interval} [C_{PCold} - C_{PHot}] \quad (4)$$

According to table 3., the hot and cold required energy for the network were found to be zero and 5988.4kw respectively; where the number "zero" indicates that the source stream is able to providing all required energy by demand stream, whereas 5988.4kw 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 it can be clearly seen, there is no pinch temperature among interval temperatures confirming of no limitation for energy transfer between streams, according to pinch principals. A caution should be taken here, that the exchanger approach temperature should not be less than the minimum selected approach temperature.
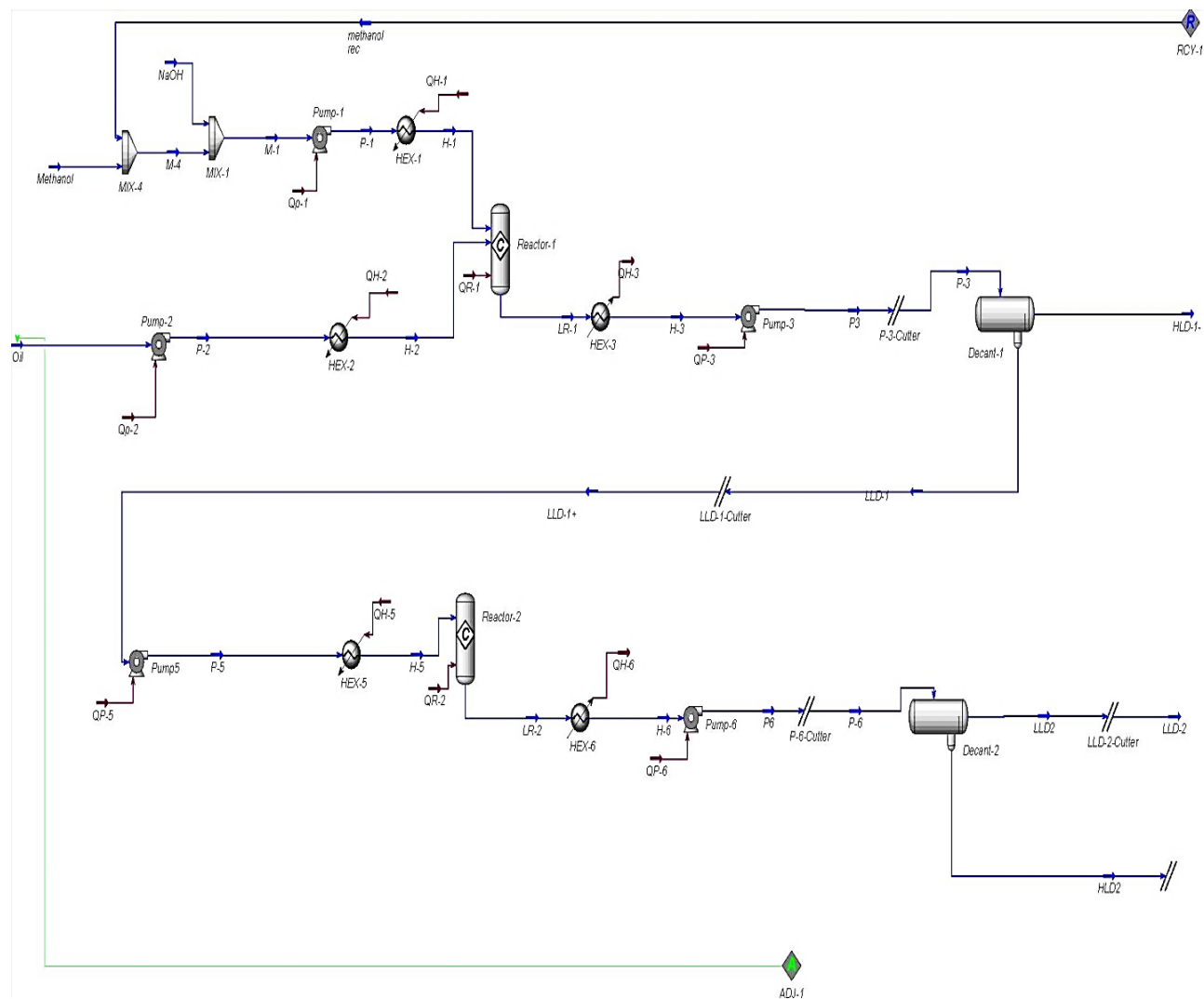

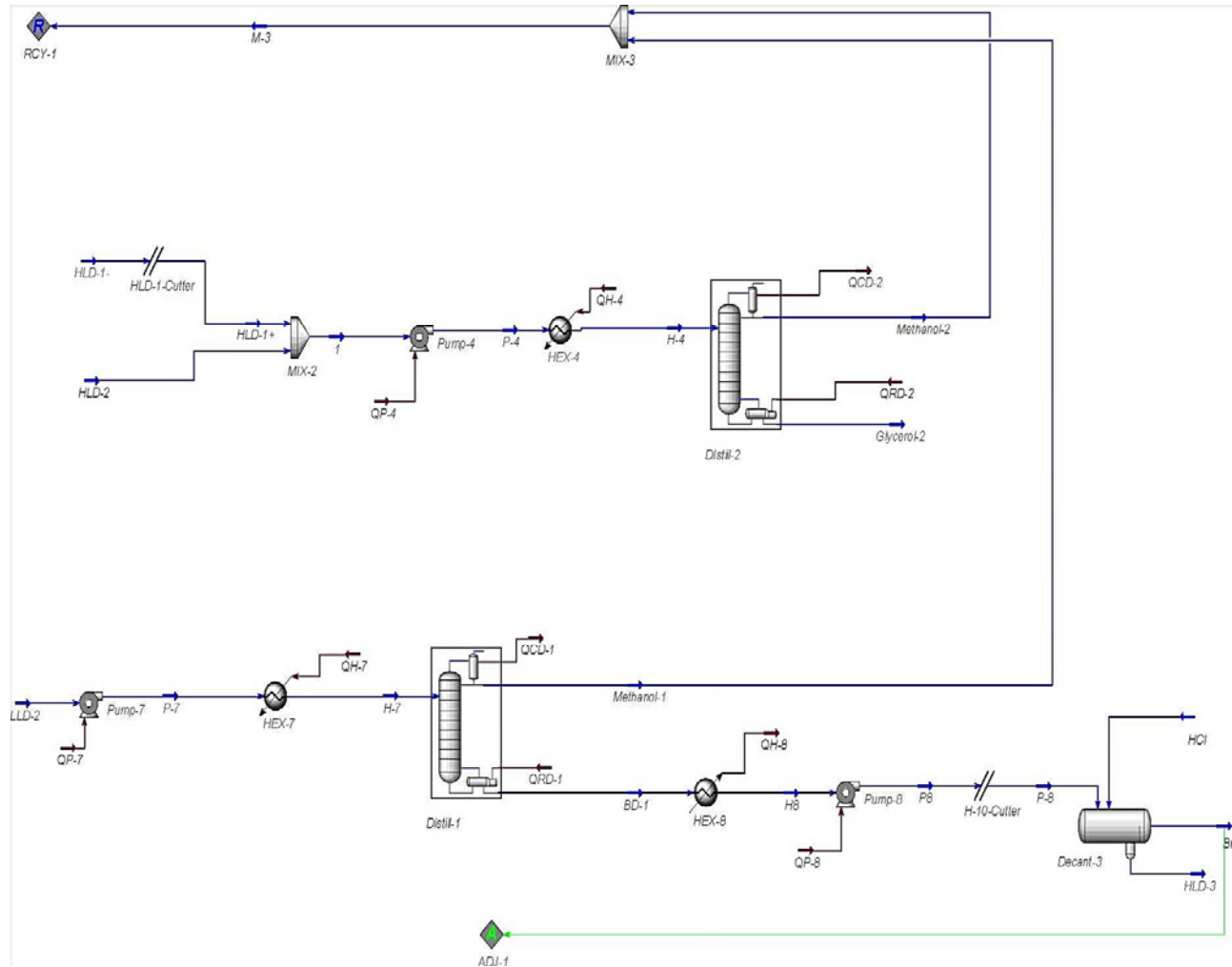**Figure 3.** PFD of biodiesel production from vegetable oil (Continue).

Table 3. Cold and Hot utility calculation of exchanger network.

						$\sum(CP_{Cold} - CP_{Hot})$	ΔH	
340								0
						$(kW°C^{-1})$	(kW)	
115.4						-12.3	-2762.6	2762.6
95				HR-2		-19.4	-395.8	3158.8
65				3	6	-19.8	-594	3752.4
55						8.8	88	3664.4
48.9						-14.9	-90.9	3755.3
	1			HD1-1	HD2-1			
45						-19	-74.1	3829.4
30						-76.6	-1149	4978.4
	2	4 5 7						
20						-101	-1010	5988.4

According to table 2, since the considered source streams were able to providing required network energy, the energy from the heat source of reboiler were not taken into account; additionally, utilization of energy from source stream possessing "300°C and 1MPa" merely to heat other streams to the maximum point of 60°C is not cost-effective and it should be left for essential cases e.g. boilers.

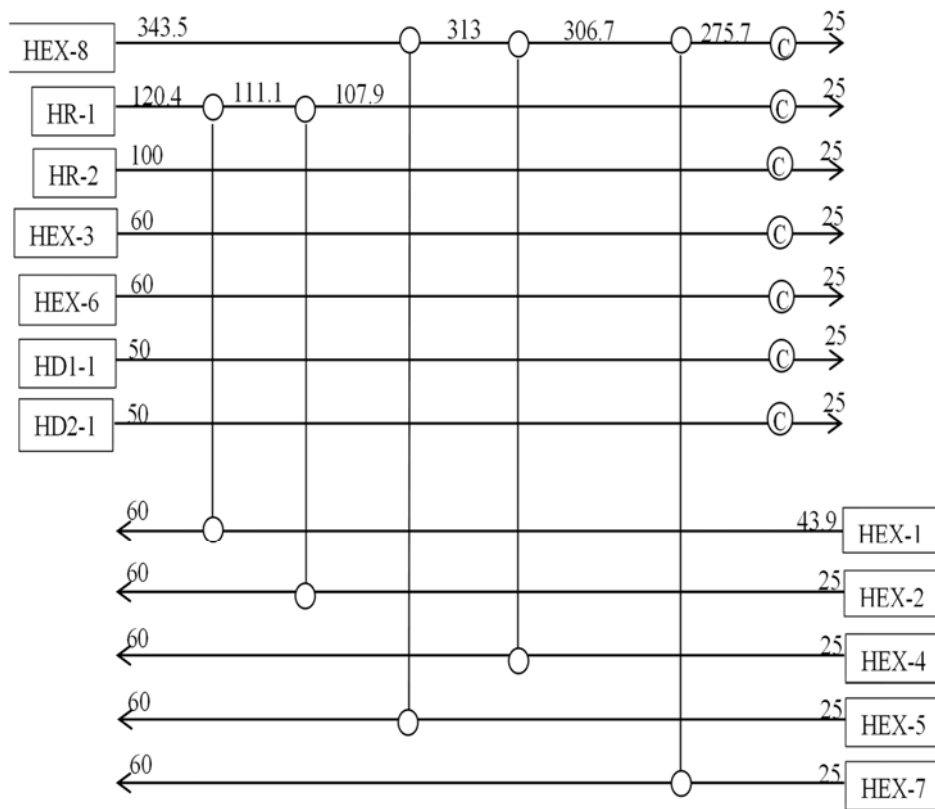**Table 4.** Thermal characteristics of distillation tower reboilers.

Reboiler	Tin (°C)	Tout (°C)	ΔH (Kw)
First column	161.1	343.5	4394
Second column	81.04	231.7	879.7

Taking all Pinch principals and processing issues into consideration, the pilot demonstrated in Fig. 3 was plotted and re-characterized. By applying the new system in the process, cold and hot energy reduced to 5991.4 kw and 5273.6kw respectively at which the hot energy is consumed just for heating the distillation reboilers. HEX-8 can be used as energy source for the reboilers of second distillation towers, which results in 14.68% reduction of cold energy and 16.67% reduction of hot energy consumption. Gomez *et al.*, have also revealed that using a reactive distillation column further reduces the total heat input required by the process, due to the constant removal of the by-products and the excess methanol [19].

Sanchez *et al.*, also showed that thermal integration minimizes the industrial services for cooling and heating by 11.3 and 13.3%, compared with a no-integrated scheme [39]. Table 5 provides a comparative report on the effects caused by applying the integration method. The traditional distillation separation process of the biodiesel production has the high energy duty due to very high boiling points of methyl ester and glycerol [34].

Figure 4. Heat exchanger network used in the process of biodiesel production.

To investigate the effect of conversion on process, similar 20m3h-1 production unit was designed using same facilities and materials. In the new design, two sequential reactors (X=70%) employed. In these conditions, the output biodiesel concentration (mass fraction) in the separator3 is 90.8% which to increase biodiesel concentration, the flow was directly sent to another distillation tower with 5 trays and with recycle flow ratio 1.5.

Ye *et al.*, have also revealed that the following second transesterification can increase the yield of biodiesel to about 97% and reduce the composition of the intermediate product to 0.5 wt% [34].

Table 5. Obtained results from first and second design.

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

Upstream in top of this tower included biodiesel with appropriate purity, whereas downstream contains a lot of triolein because over than 30% of the feed remains unreacted. Therefore purification reactors for triolein purification were used like reactors have been used in the earlier design. To increasing the purity and recycle to the feed stream, downstream sent to separator at the 25°C, that this operation resulted to 99.51% mass concentration for triolein. In this design to reduce energy consumption, exchanger networks has been designed applying pinch method with the minimum approach temperature of 10°C; the results were showed in table 5. Sanchez *et al*., also showed that Pinch analysis worked properly in the case of producing more biodiesel per kg of oil [39].

Conclusion
Advantages of recycle stream and mass integration have reduced methanol consumption to 49.79% and 60.57% in first and second design. In second design, since there is a significant volume of un-reacted oil, it can be recycled back into feed and reduce the oil consumption up to 10%. Cold and Hot energies were also reduced 17.46% and 36.17% respectively at first and 19.62% and 36.58% in the second design. The number and 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 uncertainties.
Overall, the results from second process showed that reduction in conversion led to significant increase in the number of used facilities as well as the used material load that, by turn, causes dramatic increase in the overall cost of the process.

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