Technical-Economic Study of the Esterification Process of Used Vegetable Oils (UVOs) Using Heat Exchange Networks (HENs)

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Abstract. The objective in this study was to conduct a technical-economic study of the esterification process of used vegetable oils (UVOs) for the production of biodiesel from the point of view of energy savings achieved by implementing heat exchange networks (HENs). Used vegetable oils (UVOs) can be employed as an input in the production of biodiesel by catalytic transesterification. But, previously it is necessary to reduce its level of free fat acids (FFA) by the acid-catalyzed esterification process in order to prevent undesirable saponification reaction. To carrying out an optimal design of the technology required in the process, simulation tools have an important role for process engineering and optimization of resources. Computer programs such as Aspen Plus[™] and Aspen Energy Analyzer[™] provide an environment to perform process modeling and network design optimal heat exchange. In this paper, from the Aspen PlusTM simulation of the process of catalytic esterification in acid medium of UVOs, the technical-economic evaluation process was conducted with and without network of heat exchange in order to analyze the different investment options. The comparison of the two projects (with and without the implementation of HENs) was performed by determining the net present value (NPV). On the scale set for the project, the total cost of the equipment of heat exchange for the esterification process designed with HENs was US\$ 4,782.50 higher than the corresponding to the process without HENs application. However, it should be noted that the cost of services decreased by 30% annually, and on the other hand, comparing the process, it was observed that the NPV of the HENs process was 29.5% higher, which leads to the conclusion that the project which includes heat exchange networks is technically and economically feasible.

Introduction

Biodiesel is a monoalkyl ester of long-chain fatty acids that is an alternative to fossil fuels because it is natural, it is produced from renewable resources and has lower toxic emissions [1]. It is obtained by catalytic reaction of transesterification of triglycerides with short-chain alcohols at a temperature close to the boiling point of alcohol reaction. The most important factor biodiesel production is the raw material selected. The use of used vegetable oils (UVOs) as raw material for biodiesel provides a reduction to problems such as water pollution and obstructions in drainage systems [2], as it is estimated that one liter of UVOs pollutes about 1000 liters water [3]. Moreover, although the use of a residue as UVOs reduces the the raw material costs involved, it must be considered that the frying process at elevated temperatures (180-190°C) [4] has negative influences on the properties of oil by the formation of free fatty acids (FFA), incorporation of impurities and

increase in water content [2,5]. To carry out the catalytic transesterification reaction smoothly in the production of biodiesel, it is necessary to reduce the level of FFA, thus avoiding the occurrence of an undesirable saponification reaction. The necessary treatment that must be applied in order to decrease the initial percentage of of FFA in UVOs is catalytic the esterification process, which involves reacting the UVOs with an alcohol in the presence of an acid catalyst.

Most economic studies on the production of biodiesel are based on the process simulation, which can be seen as one of the best ways to perform economic assessments [6,7]. In order to realize the energy integration of the process streams, the methodology of Pinch Method is one of the best tools that can be used for efficient energy use. Pinch Method technology was developed in 1982-1983 designing heat exchanger networks for individual processes [8,9]. Today computer programs such as Aspen Energy Analyzer[™] and Aspen Plus[™] provide an excellent environment to simulate the network design optimal heat exchange.

The objective of the present work was to realize a technical-economic study of the biodiesel production by esterification of UVOs based on the simulation of the process with applying of heat exchange networks, in order to optimize the energetic consumption.

Methodology

It was made the technical-economic evaluation of the UVOs esterification process for obtaining biodiesel for a plant with a processing capacity of 680.7 kg/h UVOs located in the center of the Province of Buenos Aires (Argentina) [10].

The UVOs composition was considered as consisting of 23% sunflower oil and 77% soybean oil according to information referring to local consumer habits in Argentine markets. For modeling the UVOs it was considered that them were mainly comprised by the triglycerides trilinolein ($C_{57}H_{98}O_6$) and triolein ($C_{57}H_{104}O_6$) due that these components are present in soybean oil (70% and 30%, respectively) and in sunflower oil (78% and 22%, respectively) [11]. Consequently, the fraction of free fat acids (FFA) present in the oils were assumed such as linoleic and oleic acids. Then, from this information it was determined that the UVOs were composed of 67.53% trilinolein, 26.47% triolein, 4.31% linoleic acid and 1.69% oleic acid.

According to this composition of UVOs, it was considered that the products of the esterification reaction were methyl oleate $C_{19}H_{36}O_2$) and methyl linoleate $(C_{19}H_{34}O_2)$. The reaction was carried out at a temperature of 70°C and a pressure of 400 kPa, using a molar ratio of methanol/UVOs of 6/1 [12]. The flow of fresh methanol was 112 kg/h.

The methanol recovery was realized and the 34.15% of the recovered was recirculated. Sulfuric acid catalyst was used in an amount of 6 wt% FFA [13], which represents a flow of 2.45 kg H_2SO_4/h .

The reactor was modeled as a stoichiometric type reactor, with a conversion of the FFA of 0.97 [12]. The product was washed with glycerol (10.5% w/w of the entered UVOs) at 25°C and 200 kPa [12], in order to remove catalyst and water present in the product.

With the aim to study the energy optimization the method of Pinch [14-19] was applied on the simulated process.

To perform the economic analysis of processes with and without HENs, in both cases it was established that the quantities produced and fixed costs are equal. The difference between the two processes lies in the heat exchange equipment (capital costs) and the cost of external cooling and heating services (operating costs) having each. From this information, it was made an economic analysis to assess the feasibility of the application of heat exchange networks.

The capital cost assessment was performed using Eq.º1 [20].

$$C_{BM} = C_P F_{BMa} \tag{1}$$

where C_{BM} is the equipment cost (US\$), C_P is the purchase cost (US\$) and F_{BM} is the is naked factor module that graphically obtained from the product of F_M (material factor) and F_P (pressure factor). The C_P and materials and pressure factors were obtained from the work of Ulrich and Vasudevan [20].

Aspen Energy Analizer[™] software was used to obtain the areas of heaters and coolers for the process without HENs, and the areas of exchanger and heater for the process with HENs.

Exchangers selected for this process are the double tube type because the areas of trade are small [21], the construction material is carbon steel.

Costing of external utilities, water cooling and heating steam used in coolers and heaters, respectively, they were estimated from Eq.^o2 raised by Ulrich and Vasudevan [22].

$$C_{S,u} = a (CE PCI) + b (C_{S,f})$$
(2)

where $C_{S,u}$ is the price of the service (US\$/kg for steam and US\$/m³ water), a and b are coefficients, $C_{S,f}$, is the price of fuel in US\$/gallon and CE PCI is the coefficient of renovation cost.

For cooling water service, the calculation of the coefficient a is presented in Eq.^o3. The coefficient b is 0.003. Both under the condition $0.01 < q < 10 \text{ m}^3/\text{s}$.

$$a = 0.0001 + 3 \times 10^{-5} q^{-1}$$
(3)

where q is the flow of cooling water.

Steam for heating service, Equations (4) and (5) show how respectively a and b coefficients were determined.

$$a = 2.5 + 10^{-5} \,\mathrm{ms}^{-0.9} \tag{4}$$

$$b = 0.0034 \text{ p}^{0.05} \tag{5}$$

for 1 bar and <math>0.06 < ms < 40 kg/s

where p is the pressure (bar), and ms is the mass flow (kg/s).

Differential flow of funds was made to five years considering the investment equals the cost of heat exchange equipment, and variable cost equal to the cost of external services. To compare both processes the differential NPV (net present value) was determined considering a rate of 17%.

Results and Discussion

First, the esterification process of UVOs without HENs was simulated on Aspen PlusTM for a mass flow of 680.7 kg/h with a content of 6% FFA represented by linoleic and oleic fatty acids [11]. From the simulation model, the service streams requiring heating and cooling were determined. Then, the Pinch Method was applied to those currents. As a result of the application of this technique, an external heating requirement of 59548.99 W was determined without being required cooling services. With this data, the heat exchange network was defined, which was made up of exchanges between the streams UVOs-2 and UVOs, where UVOs-2 satisfies your energetic requirement and UVOs reaches the temperature of $63^{\circ}C$ (335.7 K) (Fig.°1).

From the simulation of the process of UVOs esterification for the production of biodiesel, the currents with need of heating or cooling were selected in order to realize the analysis of the operating cost and so compare the process with and without HENs. These selected currents are: UVOS-2 (p = 1 bar), UVOS (p = 2 bar) and MET-CAT (p = 1 bar).



Figure 1. Esterification process of UVOs aaplying HENs.

From the simulation in Aspen Energy Analyzer[™] software of the heat exchange for processes, the areas and energy requirements of each of the equipment (Table I) were obtained.

The necessary services for the process without HENs were (Te = 289 K-Ts = 290 K, q = 0.003 m^3) with a requirement of 11232.48 J/s and steam heating (Te = 448.1 -Ts = 447.1 K) with a requirement of 70781.47 J/s. Meanwhile, when heat exchange networks are applied, a heater is required to raise the temperature of the stream MET-CATR from 26°C (299.5 K) to 70°C (343.1 K) and a heater to raise the temperature of the stream UVOS from 63°C (335.7 K) to 70°C (343.1 K) with a total energy requirement of 59,548.99 J/s (15.87% lower than the process without heat exchange network).

In Table I the currents involved in each of the processes, associated equipment and their characteristics evaluated from the results of simulations of the process is presented [11].

From the above, the cost of the equipment involved in both processes were determined according to Equation 1 ($F_M = 1$, $F_P = 1$, $F_{MBa} = 3$) and the costs of the services were calculated by Eq.°2. Results are shown in Table 2. The daily price of fuel oil and the CE PCI 2014 were considered 1.63 US\$/gallon and 579.7, respectively.

Process	Equipment	Exchange Área, A [m ²]	Heat Flow, Q [J/s]	Mass Flow, ms [kg/s]
Without HENs	Cooler (UVOS-2)	1.5	11232.48	-
	Heater (UVOS)	0.6	13443.83	3.216
	Heater (MET-CATR)	2.4	57337.64	13.717
With HENs	Exchanger	9.7	-	-
	Heater (UVOS)	0.1	2211.35	0.529
	Heater (MET-CATR)	2.4	57337.64	13.717

Table I. Characteristics of the needed services and equipment.

Table II. Costs of heat exchange equipment and costs of operation.

Process	Equipment	Capital Cost [US\$]	Operative Cost [US\$/year]
Without HENs	Cooler (UVOS-2)	9565.1	546183.82
	Heater (UVOS)	7391.2	1121123.75
	Heater (MET-CATR)	12173.7	2997109.55
With HENs	Exchanger	16086.7	-
	Heater (UVOS)	6956.4	547999.13
	Heater (MET-CATR)	7173.8	3080494.80

In analyzing Table II it is determined that the total cost of processing equipment with HENs exceeds in US\$ 15651.9 the process without HENs diminishing the services involved in 22.21% annually.

Cash flow for processes with and without HENs was performed. By comparing the results the NPV of each process, it was observed that in the case of the process with HENs, the economic index is 22.06% higher, which means that the project is acceptable as it will produce higher profits.

Conclusions

Through energetic optimization of the designed process, the full reduction of the cooling service and the diminishing of 15.87% of the heating service were achieved. This demonstrated that the process integration reduced the energy requirements relative with the non-integrated process.

The total cost of the heat exchange equipment of the designed process for UVOs esterification with HENs was \$ 15651.90 higher the corresponding to the process without HENs, but it should be noted that in the first mentioned process the cost of service decreased by 22.21% annually. Moreover, when comparing the NPV of each process, it was observed that in the case of the process with HENs, the economic factor is 22.06% higher, which means that it is an acceptable project as it will produce higher profits.

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