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PART A

Edited by
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Mass and energy integration for the supercritical process for biodiesel production and a bioethanol dehydration train

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Abstract

Biofuels have taken importance on the last years, due to the concern on the environmental impact of the transport sector. One of the most known liquid biofuels is biodiesel. The use of supercritical alcohols to produce biodiesel has been studied recently because of its advantages over the methods with homogeneous catalysts. Nevertheless, due to the high pressure and temperature conditions under which the supercritical process operates, the energy demand is considerable high. In addition, glycerol is produced as by-product, and it is expected that the price of glycerol falls; because of its high production on the biodiesel processes reducing the incomes for its commercialization. On the other hand, bioethanol is other well-known biofuel. To overcome the azeotrope between water and ethanol and produce high-purity bioethanol, extractive distillation is usually employed, where glycerol may be used as entrainer.

Therefore, in this work it is proposed the mass and energy integration between supercritical biodiesel production process and bioethanol purification train. For the energy integration, a pinch analysis will be used to integrate the two processes, aiming to reduce the external energy demand by using the energy released by the chemical reactions. By this approach, reductions on the total annual costs can be obtained if compared with the individual processes. Also, since the energetic requirements are partially satisfied by the energy delivered in the processes, global environmental impact is reduced as well.

Keywords: Biodiesel, supercritical processes, bioethanol, extractive distillation, process integration.

1. Introduction

It is well known that the use of fossil fuels to satisfy the energetic demand causes an increment on the concentration of greenhouse gases in the atmosphere. Moreover, the variations on the production of petroleum cause instability on the prices of fossil fuels. This is the reason why the production of biofuels have taken importance on the last years. One of the most known liquid biofuels is biodiesel, which consists basically on a mixture of alkyl esters obtained from biomass rich in triglycerides (vegetable oils or animal fats). Among the different processes to produce biodiesel, the use of supercritical alcohols is an alternative with some advantages over the traditional base-catalyzed process. The supercritical method increases considerably the reaction rate. Furthermore, no undesired reactions occurs when the raw material has high concentration of free fatty acids, thus this method allows using low-cost raw materials with no need of the pre-treatment section (Saka, 2011), reducing, as consequence, the total cost of biodiesel production (Lee et al., 2011). Nevertheless, due to the high pressure and temperature conditions under which the supercritical process operates, the energy demand is considerable high. In addition, glycerol is obtained as by-product, and the price of glycerol is expected to fall because of its high production on the biodiesel processes, reducing the incomes for its commercialization (Johnson and Taconi, 2007).

On the other hand, bioethanol is other well-known biofuel, which is produced through the conversion of raw materials containing cellulose or lignocellulose. Once the ethanol is obtained, it must be separated from water to produce high-purity bioethanol. This implies a technical challenge, due to existence of an azeotrope between water and ethanol at compositions of about 95 wt% of ethanol (Váquez-Ojeda et al., 2013). An alternative to solve the azeotrope problem is using extractive distillation, on which an entrainer is used to modify the volatilities of the binary mixture ethanol-water; thus obtaining fuel-grade ethanol (at least 99.8 wt%) at the top of the column, and a mixture of water and the entrainer at the bottoms. The use of glycerol as entrainer for the dehydration of bioethanol has been recently proposed, and it has been established that it can properly separate the mixture ethanol-water (Navarrete-Contreras et al., 2014). Furthermore, glycerol has lower environmental impact than the commonly used ethylene glycol. Glycerol is also a by-product in the biodiesel production for both, homogeneously catalysed and supercritical methods. Therefore, in this work the mass and energy integration between supercritical biodiesel production process and a bioethanol purification train is proposed. Regarding to mass integration, the glycerol obtained in the supercritical biodiesel process is going to be used to reduce the requirement of fresh glycerol on the dehydration stage of the bioethanol process. Also, produced ethanol can be used as fuel or as reactant for the production of ethyl esters. With respect to the energy integration, a pinch analysis will be used to integrate the two processes, aiming to reduce the external energy demand by using the energy released by the chemical reactions. By this approach, reductions on the total annual costs can be obtained if compared with the individual processes. Also, since the energetic requirements are partially satisfied by the energy delivered in the processes, global environmental impact is reduced as well.

2. Case study

For the biodiesel production, the process with supercritical ethanol has been selected as case study. In this process, ethanol and oil enters to a reactor under high pressure, high temperature conditions. A small-scale biodiesel process is studied, treating 1,284 kg/h of oil. The oil has been modelled as a mixture of triolein (70 mol%) and oleic acid (30 mol%). This composition has been selected since triolein and free oleic acid are common components in many vegetable oils. In the reactor, the triolein is converted into ethyl oleate and glycerol. At the same time, oleic acid reacts with ethanol to obtain ethyl oleate and water. This reactions occurs at 200 bar and 300 °C The pressure of the stream leaving the reactor is reduced to normal conditions, and enters to a purification train where ethanol is recovered, while biodiesel and glycerol are obtained as products. In Figure 1 a representation of the process is presented.

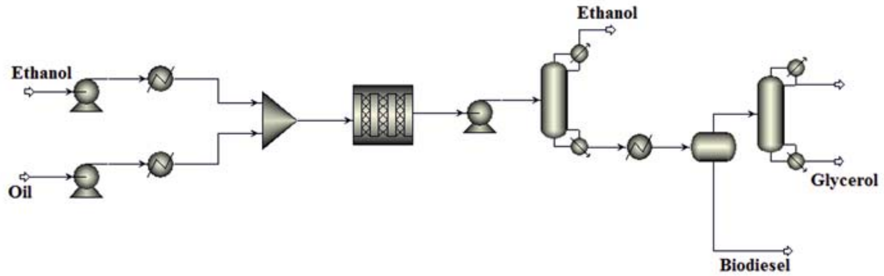

Figure 1. Supercritical process for biodiesel production.

In the case of the bioethanol purification train (Figure 2), a sequence of conventional distillation/extractive distillation of ethanol has been analysed, aiming to obtain 1620 kg/h of fuel-grade bioethanol. The sequence must dehydrate a stream containing around 5 mol% of ethanol, which is on the typical range reported by Kang et al. (2014). This stream is assumed to come from a previous conversion process for biomass. The first column is expected to achieve a purity of ethanol of 82 mol%, while in the extractive column ethanol with a purity of 99.8 mol% is obtained. In a third column, the entrainer (glycerol) is recovered.

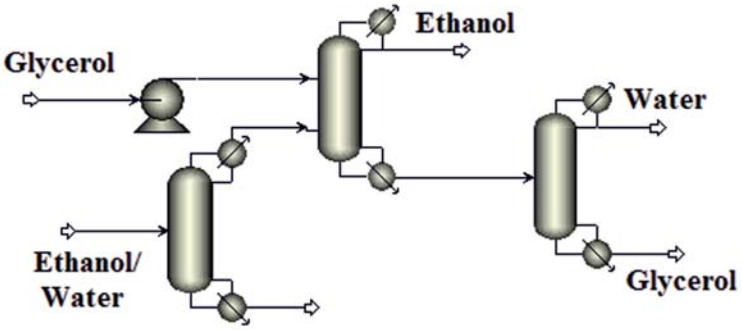

Figure 2. Bioethanol dehydration train.

3. Methodology

The processes have been simulated in the commercial simulator Aspen Plus V. 8.0. For the biodiesel process, ethanol and oil are first pressurized and heated, then entering to the reactor, where the RK-Aspen model is used to represent the phase equilibrium. In order to model the kinetics of the reactions, the following equations are used:

$$-r_{TRIO} = k_1 C_{TRIO} \tag{1}$$

$$-r_{OLAC} = k_1 C_{OLAC} \tag{2}$$

where C_{TRIO} is the concentration of triolein and C_{OLAC} represents the concentration of oleic acid. Kinetic data has been fitted employing the experimental data reported by Varma et al. (2010) for the transesterification of sesame oil. The purification stage consists on distillation columns and a decanter, on which phase equilibrium is modelled through the UNIFAC-LL model. This thermodynamic model is also used to represent phase equilibrium for the distillation columns on the bioethanol purification train.

The processes are simulated, and for each equipment a sensibility analysis is performed, aiming to obtaining the desired purities with heat duty as low as possible. Once the individual processes were simulated, mass integration took place, using the bioethanol produced to partially satisfy the requirements of the biodiesel process. In a similar way, the glycerol produced in the biodiesel process was used to satisfy the entrainer requirements in the extractive distillation column of the bioethanol process. To achieve energetic integration between both processes, a pinch analysis has been performed, obtaining which hot streams can be used to satisfy heating requirements and which cold streams can satisfy cooling requirements. All the heating/cooling requirements that cannot be fulfilled by the process streams is supplied by steam or cooling water. Heat exchangers are then introduced in the simulator to perform the integration between the streams. Finally, equipment and utilities costs are computed for both, non-integrated and integrated processes.

4. Results

In this section, results of the analysis will be presented. In the simulation of biodiesel production, the reactor was designed to obtain a conversion of triolein to methyl oleate higher than 99.5%, so the final biodiesel product accomplishes with the standard. To reach those goals, a reactor with a diameter of 1 m and length of 1.5 m is required. This equipment releases 84.53 kW of thermal energy. Specifications of the distillation columns are presented in the Table 1 for both the biodiesel and the bioethanol processes. It can be seen that in the biodiesel process most of the energy is required to recover the ethanol. In the bioethanol process, the preconcentration column is the one with the highest energy requirements. In the extractive distillation column, a molar flowrate of 20 kmol/h (about 1838 kg/h) of glycerol is required to perform the separation.

The energy released by the reactor in the biodiesel production could be used for the preconcentration column in the bioethanol process, because, as aforementioned, that column has a high heat duty. Thus, the energy integration between the streams has been performed. Furthermore, to reduce the costs of materials, the ethanol produced in the bioethanol process is integrated as reactant for the biodiesel process. Similarly, the glycerol produced in the biodiesel process is used to reduce the requirements of fresh glycerol in the extractive distillation column. The integrated process is shown in Figure 3.

Table 1. Specifications of the distillation columns.

	Biodiesel process		**Bioethanol process**		
	Ethanol recovery	**Glycerol recovery**	**Ethanol preconcentration**	**Extractive distillation**	**Glycerol recovery**
Total number of stages	6	5	9	25	6
Feed stage	5	4	7	2, 19	4
Diameter (m)	0.83	0.07	1.82	0.85	0.24
Heat duty (kW)	531.09	28.22	8759.86	795.83	291.02

In Figure 3, it can be seen that several streams can be used to reduce external steam requirements. In the reactor, the released heat can be used to produce steam, and partially satisfy the energy requirement of a water stream which will be vaporized (dashed line in Figure 3). This vapour is used to satisfy the energy requirements of the reboiler on the glycerol recovery column (marked in a red circle). Both exchangers marked in a red circle are, in fact, the same, buy are shown separated in the Figure for a better visualization of the streams.

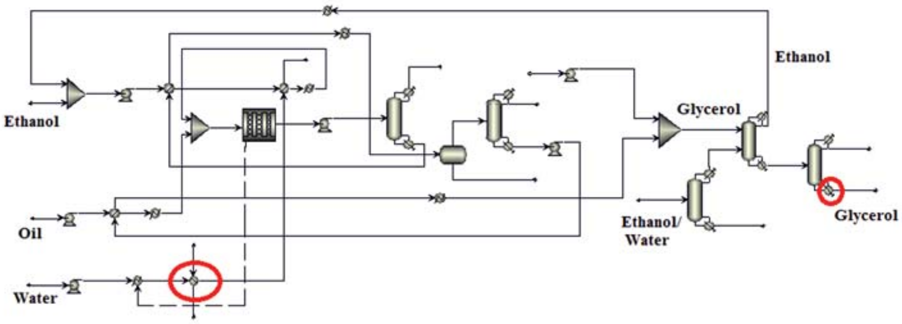

Figure 3. Integrated processes.

Before entering to the extractive distillation column, glycerol obtained on biodiesel process may deliver heat to the oil. Table 2 shows the costs for the individual processes and for the integrated processes, calculated with Guthrie’s method. It can be seen that, when integrating the process, equipment cost is increased in about 26% if compared with the non-integrated process. On the other hand, utilities costs are reduced in a 4.6% when integration occurs. Nevertheless, that reduction is not enough to compensate the cost of the additional equipment, thus, total annual cost (TAC) for the integrated process is higher than that for the individual processes.

Table 2. TAC for the non-integrated and the integrated processes (USDx10^3/year).

Process/Costs	**Separated biodiesel and bioethanol processes**	**Integrated biodiesel + bioethanol**
Equipment	1,796.45	2,450.86
Utilities	5,817.48	5,551.12
TAC	7,613.93	8,001.09

5. Conclusions

Mass and energy integration for a supercritical biodiesel process and the dehydration step of a bioethanol process has been presented. Individual and integrated processes have been simulated and compared in terms of total annual costs. When integrating the processes, savings in utilities costs (mainly steam costs) are obtained. Nevertheless, since additional equipment is required, the cost due to the acquisition of equipment is increased, and the total annual cost for the integrated process results higher than that for the individual processes. This opens an opportunity area for further research to find alternative to reduce energy requirements without increasing considerably the capital costs.

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