



Supercritical biodiesel production: Feasibility of energy integration with a bioethanol production process

Producción supercrítica de biodiésel: Factibilidad de integración energética con un proceso de producción de bioetanol

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Abstract

Biodiesel can be obtained from raw materials with high content of free fatty acids through supercritical processes, which allows obtaining high-quality fuel; nevertheless, such processes imply operating under high pressure and temperature. On the other hand, low-cost lignocellulosic biomass can be converted to bioethanol. Both processes can be integrated through energy flows, expecting reductions on the total energy requirements and environmental impact. Therefore, in this work the integration through energy flows between biodiesel and bioethanol processes is performed, along with its impact in terms of total annual cost and environmental impact. The processes are first integrated as separated entities, then the effect of integrating both processes in a biorefinery scheme is analyzed. According to the results, the heat integration of both processes allows reducing around 15% of the total annual cost associated to heat exchangers. Moreover, the integration even allows reductions in the capital costs for the supercritical process.

Keywords: supercritical biodiesel production, lignocellulosic bioethanol, energy integration, techno-economic analysis.

Resumen

El biodiésel puede obtenerse a partir de materias primas con alto contenido de ácidos grasos libres, empleando procesos supercríticos. Este tipo de procesos permiten obtener combustible de alta calidad, pero implican operar bajo condiciones de alta presión y temperatura. Por otra parte, la biomasa lignocelulósica puede convertirse en bioetanol. Ambos procesos pueden integrarse para aprovechar los flujos de energía, por medio de lo cual se esperan reducciones en los requerimientos totales de energía, así como en el impacto ambiental. En este trabajo se propone la integración energética entre los procesos de producción de biodiésel y bioetanol, analizando el impacto de la integración en términos del costo total anual y el impacto ambiental. Inicialmente se integran los procesos por separado; después se analiza el efecto de integrar ambos procesos en un esquema de biorrefinería. De acuerdo con los resultados, la integración energética de ambos procesos permite reducir aproximadamente 15% del costo total anual asociado a los intercambiadores de calor. Adicionalmente, la integración permite incluso reducir los costos de capital asociados al proceso supercrítico.

Palabras clave: producción supercrítica de biodiésel, bioetanol lignocelulósico, integración energética, análisis tecno-económico.

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1 Introduction

The use of fossil fuels is still the main way to reach the energy demand of mankind. By 2017, 81% of the worldwide required energy was produced through fossil fuels (International Energy Agency, 2018). Nevertheless, the use of fossil fuels has a high environmental impact due to the many greenhouse gases released, including carbon dioxide and monoxide, methane, nitrous oxide, among others; such anthropogenic emissions are partially responsible for the climate change. The concern on the need of promoting public policies for the mitigation of greenhouse gases has been reflected in international agreements as the Kyoto Protocol and the Paris Agreement (Hellvig and Flores-Sahagun, 2021). Moreover, the petroleum is a non-renewable energy source and, although it is difficult to predict when the reserves will be over, its price is variable, mainly due to political issues. Due to all these factors, the production of renewable energy has taken importance in the last years, with an annual average growth rate of 2.6% (U.S Energy Information Administration, 2016); from which the liquid biofuels have been extensively studied. The liquid biofuels are renewable energy alternatives, which can be used in the transport sector; among these, bioethanol and biodiesel are the most known.

Bioethanol is an alcohol obtained from sources as corn and sugar cane. Nevertheless, to avoid competence with the food sector, other raw materials have been proposed, as agricultural residues, wood, paper, yard waste (Brethauer *et al.*, 2010), sawdust and livestock manure (Avilés-Martínez *et al.*, 2012). Using those sources as material to produce bioethanol allows obtaining a fuel/additive from wastes, which otherwise would rot or would be directly burnt. The conversion of lignocellulosic materials to bioethanol implies four basic steps: pretreatment, hydrolysis, co-fermentation, and bioethanol dehydration (Conde-Mejía *et al.*, 2013). There are still several challenges on the first three steps, related with increasing the yield of bioethanol and reducing the sensitivity of the fermentation yeasts to stress conditions (Haq *et al.*, 2020). In the case of the dehydration step, one of the main issues is related with the presence of the ethanol-water azeotrope, which occurs at a composition close to 95 wt% (Vázquez-Ojeda *et al.*, 2013); the presence of the azeotrope makes difficult reaching a bioethanol purity higher than 99.8 wt%. Such purity is necessary

for ethanol to be used as fuel additive in spark ignition engines. Among the technologies proposed to overcome the azeotrope, the use of pervaporation membranes (Vane, 2005), pressure-swing distillation (Arifeen *et al.*, 2007), as well as azeotropic and extractive distillation (Kiss *et al.*, 2012) can be mentioned. In the case of extractive distillation, an entrainer is used to change the thermodynamic equilibrium, interacting with the components, and modifying their relative volatilities (Gutiérrez *et al.*, 2012). It has been reported that glycerol can be used as entrainer for bioethanol dehydration via extractive distillation (Navarrete-Contreras *et al.*, 2014); this solvent has environmental and operational advantages as low toxicity, low price, renewability, high boiling point, and low vapor pressure (Gu *et al.*, 2010).

On the other hand, biodiesel is a mixture of alkyl esters, obtained from materials with high content of triglycerides and fatty acids, as vegetable oils and animal fats. It has a higher cetane number than fossil diesel, and almost no sulphur (Brusamarello *et al.*, 2020). Biodiesel can be used to power diesel engines, usually mixed with fossil diesel. The production of biodiesel implies the transesterification of triglycerides and esterification of free fatty acids, using basic or acid catalysts. Nevertheless, basic catalysts are quite sensitive to the presence of free fatty acids in the raw material, leading to saponification of the oil and further difficulties in the purification of the biodiesel (Gomez-Castro *et al.*, 2013). Acid catalysts can be used in a pretreatment step, but corrosion issues may occur (Lotero *et al.*, 2005). Such limitations are of importance because waste oils contain high concentrations of free fatty acids, and those oils represent a low-cost raw material for biodiesel production (Igliński *et al.*, 2015). It has been estimated that the use of waste oils or fats may reduce up to 60-80% the total cost on the biodiesel production (Glišić *et al.*, 2009; Lee *et al.*, 2011). To allow the use of such waste oils, avoiding the saponification reaction, the use of supercritical alcohols, particularly methanol, has been proposed to perform the transesterification and esterification reactions (Kusdiana *et al.*, 2001; He *et al.*, 2007; Samniang *et al.*, 2014). The use of ethanol as supercritical reactant has also been reported (Demirbas, 2009), and it may represent a more sustainable alternative than methanol for such processes. Other supercritical processes have been reported, as the two-steps methanol process (Saka, 2005), the methyl acetate process (Saka *et al.*, 2009) and the acetic acid process (Saka *et al.*, 2010). Nevertheless, it has been reported that the one-step

methanol process is the best alternative in terms of total annual cost and environmental impact (Gómez-Castro *et al.*, 2015). One of the main issues of the supercritical processes for the production of biodiesel relies on its operational conditions. Sawangkeaw *et al.*, (2010) and Tan *et al.*, (2011) mentioned that the supercritical processes could be competitive if their energy requirements are reduced; such reduction could be achieved through process intensification or process integration.

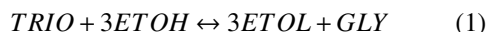
Process intensification alternatives may involve reactive distillation; nevertheless, the high operational pressure turns difficult such approach. On the other hand, process integration could be performed within the process or even with a second process. e.g. the bioethanol process, which implies planning both processes in a biorefinery scheme. Previous studies have reported the energy integration for biofuels production processes. Severson *et al.*, (2013) reported the energy integration for different biodiesel production schemes, including alkali catalysis, enzymatic catalysis, heterogeneous catalysis, and supercritical conditions, employing response surface models and short-cut methodologies for the analysis. Brunet *et al.*, (2015) presented the energy integration of biodiesel production process using basic catalysis, and the energy integration of a bioethanol production process. Petersen *et al.*, (2015) reported the energy integration of a process based on hydrolysis followed by fermentation for bioethanol production; and a process based on simultaneous saccharification and fermentation. Song *et al.*, (2015) presented the energy integration for a microalgae-based biodiesel production process, including an exergy analysis. Aboelazayem *et al.*, (2018) reported the mass and energy integration for the production process of biodiesel with supercritical methanol. Aboelazayem *et al.*, (2021) presented a proposal for the integration of the supercritical production process for biodiesel using an organic Rankine cycle. Most of the described works propose the energy integration for the streams in a given process. Only few works have described the integration two production schemes, as the work of Kralj, (2008), where two biodiesel production processes are integrated; or the work of Gutiérrez *et al.*, (2009), where a bioethanol production process is integrated with an extractive reaction process for the production of biodiesel, including only the heat in the condensers of the distillation columns on the integration scheme. Martín *et al.*, (2013) reported the integration between a bioethanol production process from microalgal biomass and a biodiesel production

process, either by alkali or enzymatic catalysts. Nevertheless, to the authors' knowledge, the potential of energy integration between the supercritical biodiesel production process and other biofuels' production schemes has only been explored in a preliminary way (Gómez-Castro *et al.*, 2017). Thus, in this work the feasibility of energy integration between the supercritical biodiesel and the lignocellulosic bioethanol processes is studied; this integration is performed through the pinch point methodology to assess the minimal utilities required after integration, proposing arrangements to achieve such requirements. The effect of energy integration is determined in terms of total annual costs and environmental impact for the non-integrated and the integrated processes. In this way, energy integration could be a helpful tool to reduce the high-pressure steam requirements on the supercritical biodiesel production process, while promoting the use of less cooling water in the bioethanol production scheme. Nevertheless, it is necessary assessing how the capital costs are affected when the integration takes place. Therefore, two integration scenarios are studied: (I) integrating each process as an independent entity; (II) integrating both processes with interaction among all the streams.

2 Case study

As case study, two processes are considered: the one-step supercritical process for the production of biodiesel and the lignocellulosic bioethanol process. In the case of the biodiesel process, the one-step supercritical process has been chosen for this study, since it has been reported as the alternative with the lowest total annual costs among four supercritical processes (Gómez-Castro *et al.*, 2015). In the one-step process, the transesterification and esterification reactions take place in a single vessel. The plant is designed to produce 12,000 t/y of biodiesel, which is on the upper bound to be considered a small-scale plant (Skarlis *et al.*, 2012). To obtain such production, 1,284 kg/h of vegetable oil are fed to the process, whose composition is a mixture of triolein (70 mol%) and oleic acid (30 mol%). Varma *et al.*, (2010) reported an ethanol/oil mole ratio of 40 to obtain high conversions to biodiesel, using mustard oil and sesame oil. This value is similar to the optimal ratio of 33 reported by Gui *et al.*, (2009) for palm oil, thus, the value of 40 is taken as appropriate for this study. This implies that 3,358 kg/h of ethanol are

required to perform the reaction. Both reactants, the oil and the ethanol, are taken to 200 bar and 330°C, which are the reaction conditions that would allow high conversions to biodiesel (Varma *et al.*, 2010). The reactants are taken to the reactor, where the following reactions occur:



where TRIO is the triolein, ETOH represents the ethanol, ETOL stands for ethyl oleate, GLY is glycerol, OLAC represents oleic acid and H₂O represents water. The experimental data reported by Varma *et al.* (2010) has been adjusted to the following first-order kinetic model:

$$-r_{ETOL(TRANS)} = kC_{TRIO} \quad (3)$$

$$-r_{ETOL(EST)} = kC_{OLAC} \quad (4)$$

where the subscript ETOL(TRANS) indicates that the ethyl oleate is produced in the transesterification reaction, where the subscript ETOL(EST) implies that the ethyl oleate is produced in the esterification reaction. Since the experimental data is reported for the global conversion of the oil, it is assumed that k is the same for both, transesterification and esterification, where:

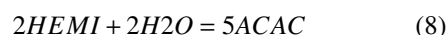
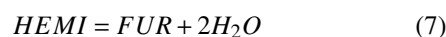
$$k = A_0 \exp(-E_a/RT) \quad (5)$$

The data reported by Varma *et al.* (2010) is regressed, obtaining $A_0 = 5,283.17 \text{ min}^{-1}$ and $E_a = 60,290.60 \text{ kJ}$.

Once the reaction takes place, the pressure is reduced to 1 bar to perform the purification of biodiesel. First, the ethanol is recovered in a distillation column (DD-1). The recovered ethanol

is recycled as reactant. Then, two liquid phases are formed, which are separated in a decanter (DECD-1). Here, the desired product (biodiesel, represented as ethyl oleate) is obtained. Finally, the glycerol is refined in a second distillation column (DD-2). A representation of the full process is shown in Figure 1.

The bioethanol production process has been taken from the work of Conde-Mejía *et al.*, (2013), where only the conversion steps are reported. In this proposal, the purification train is added to obtain the complete flowsheet. This process is designed to produce 3,358 kg/h of ethanol, which is the quantity required to satisfy the reactant requirements in the biodiesel process. The raw material consists of agricultural wastes. The inlet flowrate is 12,127 kg/h with a composition of 45 wt% of cellulose, 30 wt% hemicellulose and 25 wt% of lignin (Garrote *et al.*, 1999). That flowrate allows producing the quantity of ethanol required to perform the transesterification/esterification reactions in the biodiesel process. It is important to mention that the agricultural wastes contain 40 wt% of moisture. In the first step, a pre-treatment of the agricultural wastes is performed with hot diluted sulfuric acid solution and steam to transform most of the hemicellulose (RE-1). The reactions occurring in the pre-treatment are:



where HEMI is the hemicellulose, XYL is xylose, FUR is furfural, ACAC represents acetic acid, CEL stands for cellulose and GLUC is glucose.

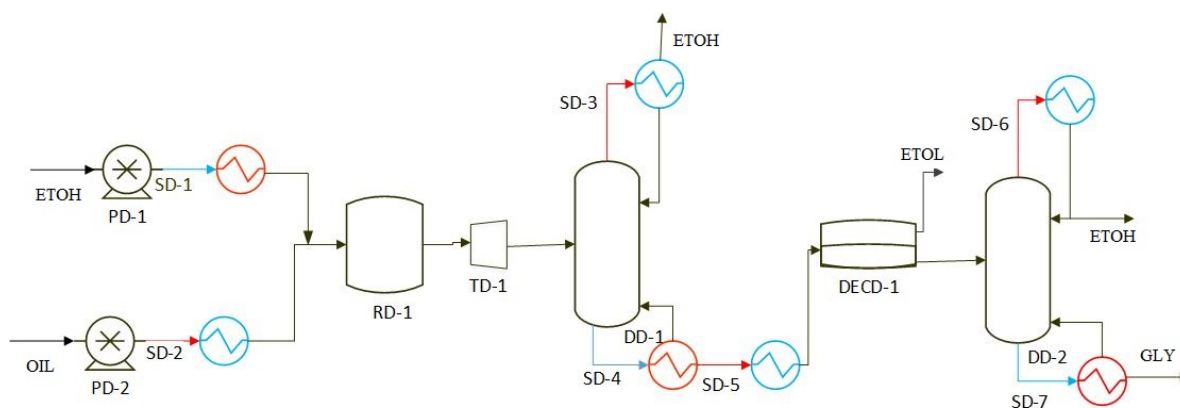


Figure 1. Biodiesel production process. Cold streams in blue, hot streams in red.

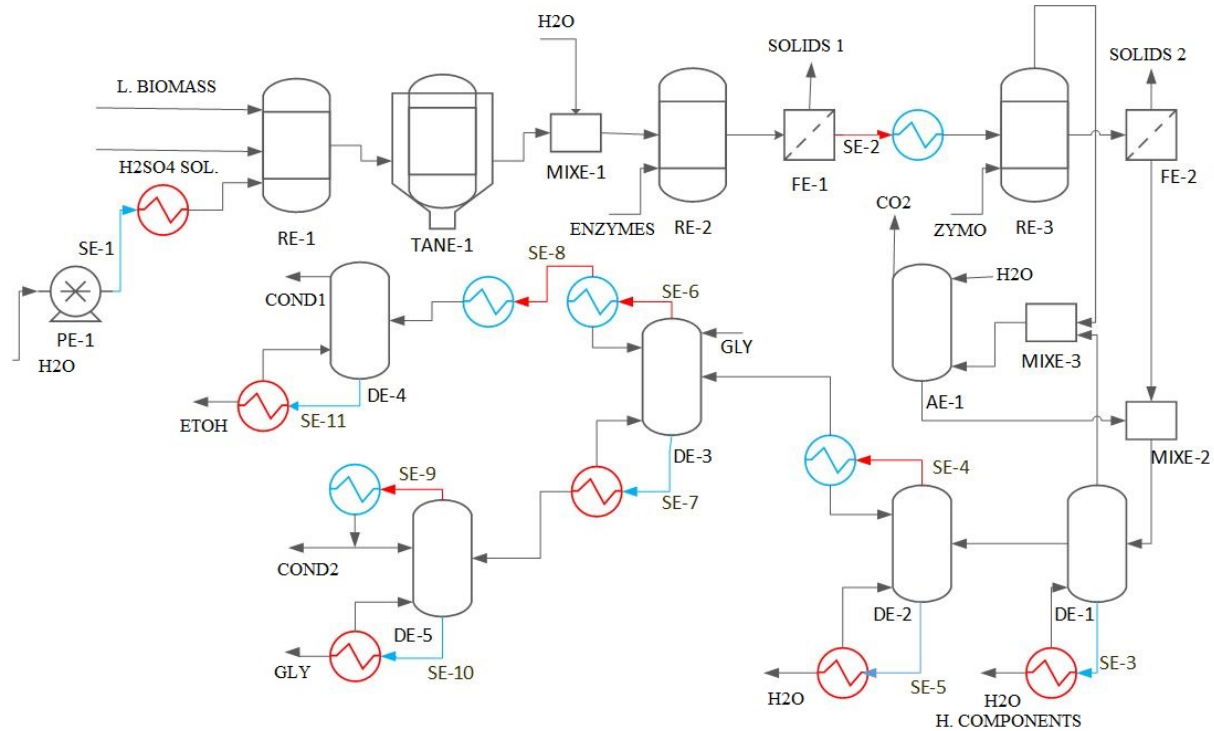
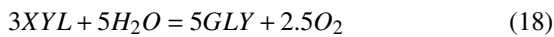
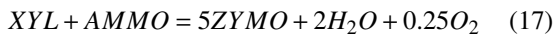
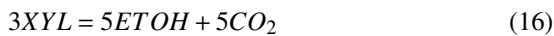
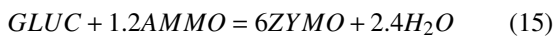
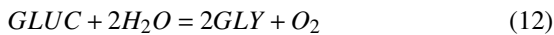
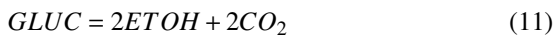
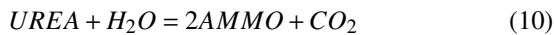


Figure 2. Bioethanol production process. Cold streams in blue, hot streams in red.

The stream leaving the pre-treatment reactor is conditioned and enters to an enzymatic hydrolysis reactor (RE-2), where sugars are completely released. In this equipment, reactions (6), (8) and (9) occur. From the stream leaving the hydrolysis reactor, the remainder solids are separated in a filter, and the sugars enter to a co-fermentation reactor (RE-3). Urea is added to the fermenter as nitrogen source for the microorganisms. In this reactor, the following reactions occur:



where AMMO is ammonia, CO₂ is carbon dioxide, SUCAC represents succinic acid, O₂ is oxygen,

ZYMO represents the *Zymomonas mobilis* used for the co-fermentation. This particular sequence of reactive steps has been reported by Conde-Mejia *et al.* (2013). A stream containing carbon dioxide, water, oxygen and some ethanol is purged, and it goes to an absorber (AE-1), where the ethanol is recovered using water as external agent. The other stream leaving RE-3 contains ethanol, carbon dioxide, furfural, acetic acid, remaining sugars, sulfuric acid and water, among others. This mixture is separated in a stripping column with a side stream (DE-1). The vapor leaving for the top column contains CO₂ and ethanol, and it is sent to the absorber AE-1; while the side stream contains mainly ethanol and water, and most of water with heavy components are separated for the bottoms. The ethanol-water mixture coming from the absorber is fed to the stripping column DE-1. The side stream is sent to a pre-concentration column (DE-2), where in the top the ethanol reaches a composition close to the azeotrope. Then, the ethanol is further purified in an extractive distillation column (DE-3), using glycerol as entrainer. The glycerol is recovered in other distillation column (DE-5). Finally, a low concentration of ammonia remains in the ethanol stream, which is separated in a stripping column (DE-4). The whole process is shown in Figure 2.

3 Methodology

3.1 Process simulation

First, information about conversions and purities is required, together with the design parameters of the equipment required to obtain the desired biofuels. To obtain such data, both processes have been simulated in Aspen Plus V. 8.0. For the biodiesel process, the streams are first pressurized using *Pump* modules, then heated through *Heater* modules. Then, the streams enter to a *RPlug* module, which represents the reactor RD-1. The reactions are defined as *POWERLAW*, with a kinetic type. Parameters of the reactor (length and diameter) are manipulated until a conversion higher than 99.9 mol% is obtained for triolein. Such conversion would ensure almost total conversion of free fatty acids. Then, the stream leaving the reactor goes to a turbine, where the pressure is reduced to 1 bar, and electricity is generated. Then, the streams enter to a distillation column with a partial condenser (DD-1), simulated with the *RadFrac* module, where ethanol is obtained at the top with purity and recovery higher than 99 mol%. Once the purity is fixed, the number of stages and the feed stage are manipulated to reduce as much as possible the heat duty. Then, a *Heater* module is introduced to reduce the temperature of the bottoms stream to 25 °C, to enter to a *Decanter* module, where two phases are formed: one containing mainly ethyl oleate (which represents the biodiesel), and the other one containing ethanol and glycerol. Glycerol is further purified in a second distillation column (DD-2), to reach a purity of 99.5 mol%. Once more, the purity is fixed and the effect of the number of stages and the location of the feed stream on the heat duty is analyzed. Once the process is complete, the biodiesel stream is revised to ensure that it accomplishes with the international standards (Gómez-Castro *et al.*, 2013). The phase equilibrium for the high-pressure section is represented through the RK-Aspen model (Glisic *et al.*, 2014), while the UNIFAC-LL model is used for the low-pressure zone.

In the case of the bioethanol process, water is heated in a *Heater* module, and then is fed to the pre-treatment reactor RE-1, together with the raw material and the sulfuric acid. This reactor is simulated using a *RStoic* module, operating at 160 °C, where a fractional conversion of 0.623 is fixed for the reaction given by equation (6), 0.0297 for the reaction (7), 0.01235 for the reaction (8) and 0.0626 for the reaction (9). Such conversions have been taken from the work of

Lloyd *et al.*, (2005). The hydrolysis reactor (RE-2) is also simulated as a *RStoic* reactor, which operates at 1 bar and 45 °C. In this case, fractional conversions are defined as 0.1644 for reaction (6), 0.106 for reaction (8) and 0.9112 for reaction (9). Hydrolysis conversions are taken from the work of Wyman *et al.*, (2005). The co-fermentation reactor (RE-3) is simulated with a *RStoic* module, operating at 1 bar and 34 °C. Fractional conversions for reactions (10) to (20) are defined as 0.99, 0.92, 0.002, 0.008, 0.022, 0.027, 0.756, 0.029, 0.029, 0.009 and 0.024, respectively, which have been reported by Dimian *et al.*, (2008) and Kazi *et al.*, (2010). The stream leaving the co-fermentation reactor, RE-3, enters to a purge; this purge is simulated with a *Flash* module, where the CO₂ stream enters to an absorber, simulated through the *RadFrac* module. Carbon dioxide is obtained as top product in the absorber with a purity higher than 93 mol%. The bottoms stream is mixed with the liquid stream on the purge, and the resulting stream enters to the stripping column with a side stream DE-1, represented with the module *RadFrac*; in the stripping column carbon dioxide is the main product at the top, with a purity higher than 93 mol%. The side stream is taken in vapor phase, and it must contain mainly water and ethanol, with an ethanol recovery higher than 99 mol%. The bottoms stream is basically water with heavy components. The side stream goes to the pre-concentration column with a partial condenser DE-2, where ethanol is obtained at the top with purity of 92 wt% (81.7 mol%), which is close to the azeotropic composition. The top stream enters to the extractive distillation column DE-3, where a purity of 98.5 wt% for ethanol was obtained, with recovery higher than 99.5 mol%. The bottoms stream of the extractive column enters to the distillation column DE-5, where the glycerol is obtained as bottoms product with more than 99 mol% of purity and recovery. A small ammonia fraction remains in ethanol stream, and a stripping column is used in order to remove it, achieving a final ethanol concentration higher than 99.8 wt%. For all the distillation columns, a sensitivity analysis is performed over the main manipulated variables; once the desired purities are fixed, the objective is to determine the design with the lowest heat duty. For the bioethanol process, the NRTL model has been used to represent the phase equilibrium.

3.2 Energy integration

Once the simulations are performed, the analysis for energy integration takes place. First, the streams of

each process are characterized in terms of temperature, mass flow rate and enthalpy; also, the equipment releasing or requiring energy are identified. The pinch point methodology is used to perform the analysis (Linnhoff *et al.*, 1983). A selection of the equipment with the highest energy requirements is done, to avoid include them in the analysis streams with a very small change on enthalpy. Once the streams to be studied are selected, a heat cascade is constructed using $\Delta T = 10$ °C. Then, the pinch point is identified, and the minimal heating and cooling requirements are estimated. The streams are then ordered, and the intervals of temperature defined by the heat cascade are located, together with the pinch point for the cold and the hot streams. Then, feasible exchanges are proposed between the hot and cold streams, avoiding crossing the pinch temperature and avoiding potential temperature crossing on the exchangers. Once all the feasible exchanges are obtained, the network is completed with the necessary coolers and heaters, verifying if the network accomplishes the cooling and heating requirements predicted by the heat cascade. Such study has been performed for two scenarios:

- (i) Scenario I. The processes are treated as separated schemes; this implies that the streams in the bioethanol process are integrated among them, while the streams in the biodiesel process are treated similarly.
- (ii) Scenario II. All the streams for both processes are integrated simultaneously.

3.3 Performance assessment

To evaluate the advantages of applying process integration to the studied processes, three parameters will be computed: total heating/cooling requirements, total annual cost and total carbon dioxide emissions. Total heating/cooling requirements are computed directly from the results of the simulations, as the sum of negative heat duties for cooling, and positive heat duties for heating. This information would indicate how much energy can be saved through process integration, and also if the cooling and heating requirements predicted by the heat cascade are accomplished.

Total annual cost (*TAC*) can be computed as the sum of the annualized equipment costs and the operational costs (*OC*), associated with the utilities, i.e.:

$$TAC = \frac{CC}{n} + OC \quad (21)$$

where *CC* represents the capital cost, associated with total equipment cost and *n* is the payback period, which has been assumed as 5 years. Equipment costs are computed using the Guthrie's method, as reported by Turton *et al.*, (2012), and updated with the Chemical Engineering Cost Index of 2018, with a value of 556.8. Utilities costs are computed by using the unitary cost and the utilities requirements for water, steam and electricity, which can be calculated taking as basis the heat duties reported by the simulation software. The unitary costs for utilities used in this work are as follows: cooling water at 20°C, 0.0000148 USD/kg (Turton *et al.*, 2012). Cooling water at 10°C, 0.0000655 USD/kg (Sinnott, 1993). Steam at 15 bar, 0.02959 USD/kg (Turton *et al.*, 2012). Steam at 150 bar, 0.03054 USD/kg (Turton *et al.*, 2012). Electricity, 0.07927 USD/kWh (CFE, 2020). Calculation of total annual costs is important since integrated processes usually require additional equipment; thus, it is necessary to evaluate if the energy savings are reflected as an economic improvement to overpass the increase on capital cost.

The estimation of CO₂ emissions considers its generation due to the use of a fuel to produce the steam that provides heat to the process. Thus, CO₂ emissions are directly related to the heat duty of each equipment and the pressure required for the steam. Gadalla *et al.*, (2006) proposed the following equation to estimate emissions of carbon dioxide:

$$[CO_2]_{em} = 3.67 \left(\frac{Q_{fuel}}{NHV} \right) \left(\frac{C\%}{100} \right) \quad (22)$$

where $[CO_2]_{em}$ are the carbon dioxide emissions, in kg/s, Q_{fuel} (kW) is the duty of fuel burnt to produce the steam, NHV (kJ/kg) is the net heating value of the fuel, and $C\%$ is the carbon content of the fuel. In this work it is assumed that natural gas is used as fuel, for which NHV is 51,600 kJ/kg and $C\%$ is 75.4. According to Gadalla *et al.* (2006), the heat duty delivered by the fuel can be related with the heat duty of the process as follows:

$$Q_{fuel} = \frac{Q_{proc}}{\lambda_{proc}} (h_{proc} - 419) \frac{T_{FTB} - T_0}{T_{FTB} - T_{stack}} \quad (23)$$

where λ_{proc} and h_{proc} are the latent heat and enthalpy of the steam delivered to the process, in kJ/kg, which are related to the required temperature for the steam. T_{FTB} is the flame temperature of the boiler flue gases, which can be taken as 1,800 °C, T_{stack} is the stack temperature, which can be assumed as 160 °C, and T_0 is the ambient temperature, which is assumed to

be 25 °C. Calculation of CO₂ emissions is important to ensure that process integration will allow reducing the environmental impact, in comparison with the non-integrated processes.

4 Results

4.1 Simulation results

Simulations of the individual processes have been performed. Table S-1 in supplementary material shows the detailed results for the reactors of both processes. The pre-treatment reactor in the bioethanol process (RE-1) has the highest energy requirements (2,020.41 kW); all the other reactors are releasing energy. On the other hand, the hydrolysis (RE-2) and fermentation (RE-3) reactors require high volumes; thus, the operation must be performed in a battery of reactors to allow more realistic dimensions. On the other hand, Table S-2 shows the results for the separation columns. The purification train for the bioethanol process has the highest energy requirements among

both processes, with 13,103.102 kW against 459.76 kW on the separation train for the biodiesel process. It must be mentioned that the absorption of carbon dioxide in the column DE-2 required 1,400 kg/h of water, while the ethanol dehydration in column DE-4 required 2,850 kg/h of glycerol. Moreover, Table S-3 shows the characteristics of the pumps for both processes. The pressure levels needed in the biodiesel process makes it the major contribution to the electricity requirements. The characteristics of the heat exchangers are not shown here, since they will be discussed in the energy integration section.

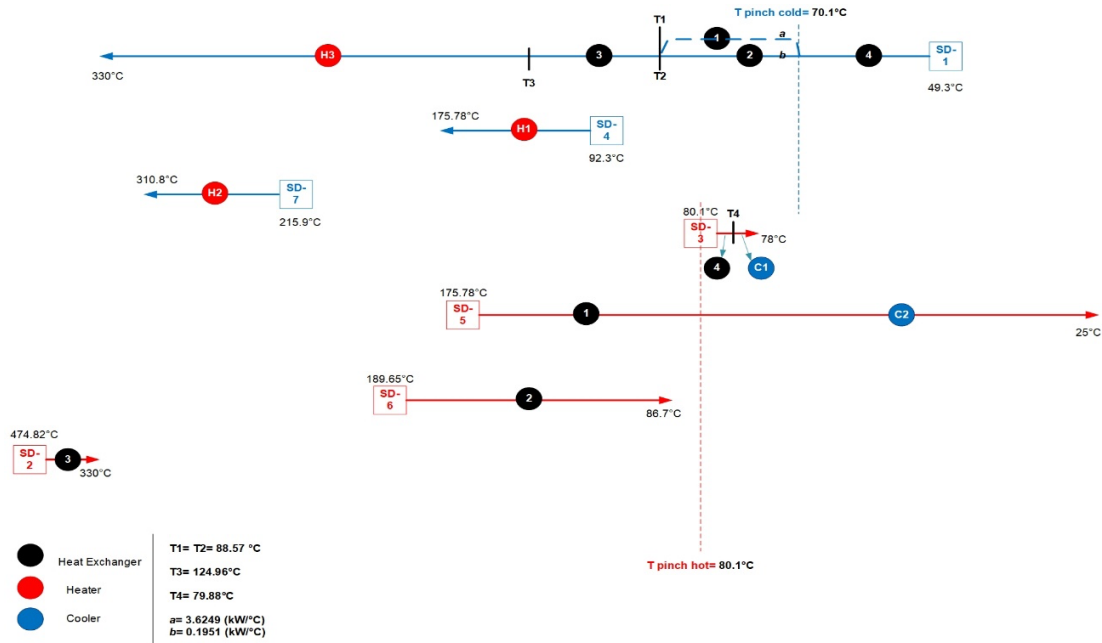
Once the simulation results are obtained, the streams requiring or releasing energy are identified to perform the energy integration. The involved streams and their characteristics are shown in Table 1, while Figures 1 and 2 show the location of those streams on each process.

4.2 Energy integration results

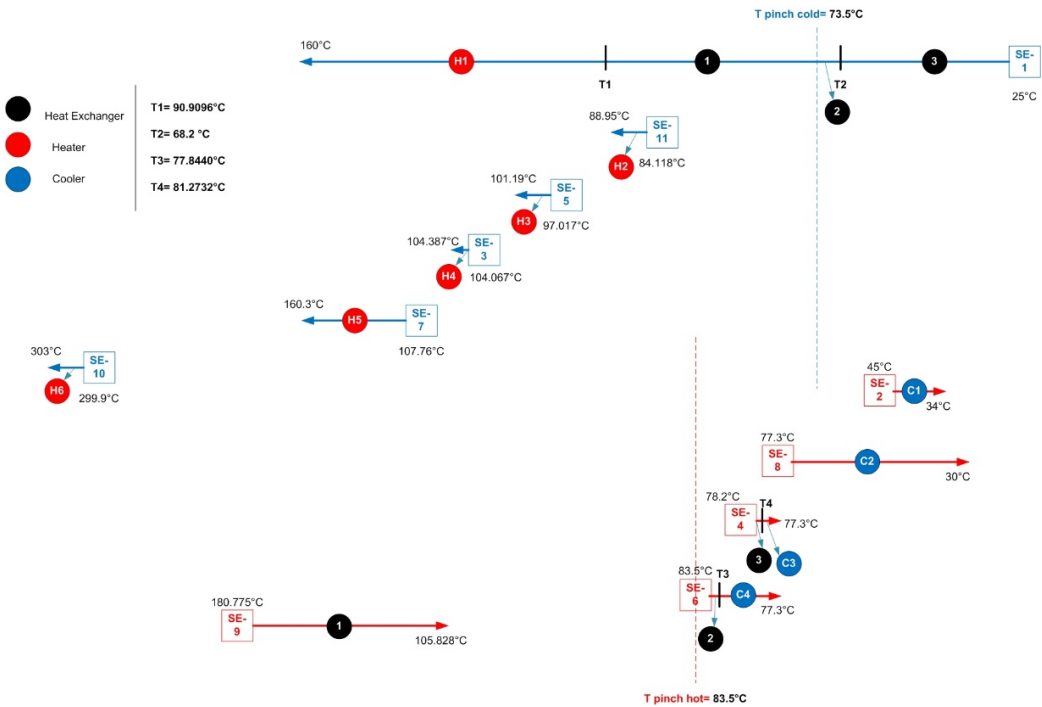
The bioethanol process has higher heating requirements (blue line) than biodiesel process, which must be covered through utilities.

Table 1. Streams for energy integration.

BIODIESEL PROCESS					
Stream ID	Stream description	Initial Temperature (°C)	Target Temperature (°C)	w*Cp (kW/°C)	Classification
SD-1	Ethanol for heating	49.3	330	3.82	Cold
SD-2	Oil for cooling	474.82	330	0.96	Hot
SD-3	Top of the column DD-1	80.1	78	357.7	Hot
SD-4	Bottoms of the column DD-1	92.3	175.78	5.16	Cold
SD-5	Stream entering the decanter DECD-1	175.78	25	0.7	Hot
SD-6	Top of the column DD-2	189.65	86.7	0.035	Hot
SD-7	Bottoms of the column DD-2	215.9	310.8	0.3	Cold
BIOETHANOL PROCESS					
SE-1	Water entering pretreatment reactor	25	160	45.46	Cold
SE-2	Stream entering co-fermentation reactor	45	34	67	Hot
SE-3	Bottoms of the column DE-1	104.067	104.387	25,249	Cold
SE-4	Top of the column DE-2	78.2	77.3	5,516.60	Hot
SE-5	Bottoms of the column DE-2	97.017	101.19	705.2	Cold
SE-6	Top of the column DE-3	83.5	77.3	108.2	Hot
SE-7	Bottoms of the column DE-3	107.76	160.3	15.28	Cold
SE-8	Stream entering DE-4	77.3	30	20.1	Hot
SE-9	Top of the column DE-5	180.775	105.828	10.56	Hot
SE-10	Bottoms of the column DE-5	299.9	303	351.3	Cold
SE-11	Bottoms of the column DE-4	84.118	88.95	38.84	Cold



(a)



(b)

Figure 3. Heat exchanger networks, scenario I (a) biodiesel process, (b) bioethanol process.

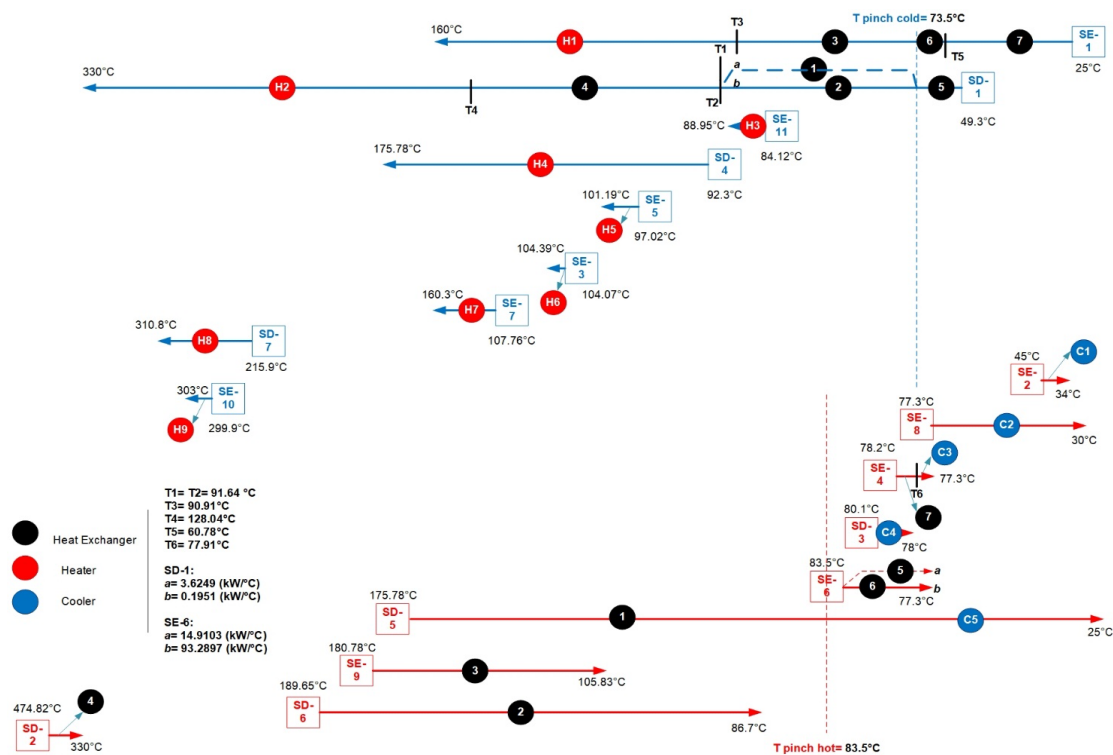
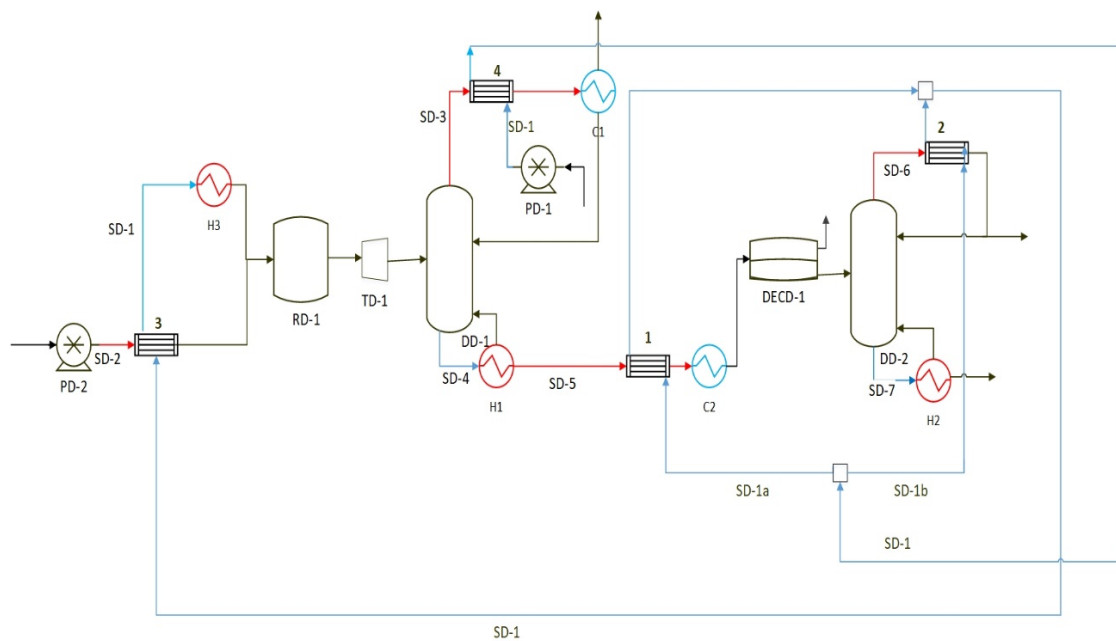


Figure 4. Heat exchanger network, scenario II.

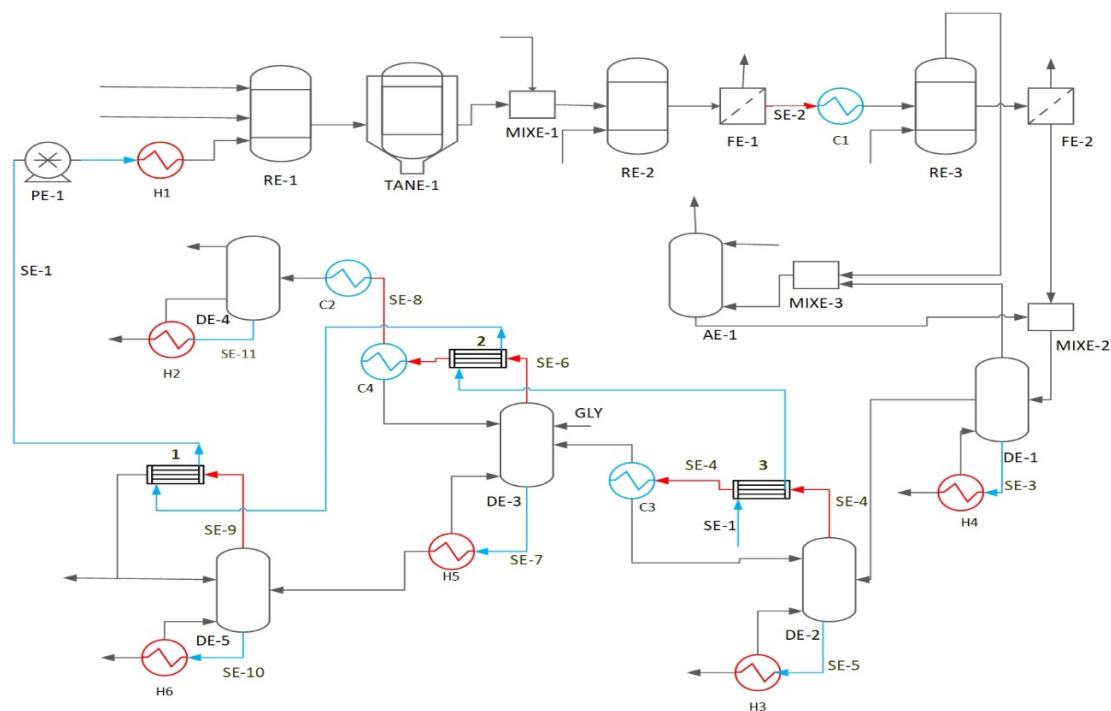
This can be observed in the grand composite curves, shown in Figure S-1 for the separated processes and in Figure S-2 for the case when the streams for both processes are included. From the heat cascades for scenario I, it is obtained that the minimum heating requirements for the biodiesel process are 1,242.44 kW; while the minimum cooling requirements are 710.29 kW, with the pinch point for hot streams located at 80.1 °C. In the case of the bioethanol process, the minimum heating requirements are 16,243.53 kW; while the minimum cooling requirements are 5,118.7 kW, with the pinch point for hot streams located at 83.5°C. For scenario II, the minimum heating requirements are 17,473.81 kW; while the minimum cooling requirements are 5,818.38, with the pinch point for hot streams located at 83.5 °C.

Once the heat cascades are constructed, the exchange networks are proposed. The resulting networks for scenario I are shown in Figure 3, while Figure 4 presents the network for scenario II. On the other hand, Figure 5 shows the integrated process schemes for scenario I, while Figure 6 presents the integrated processes for scenario II. In the biodiesel production process for scenario I, the stream SD-1 is

first heated up to the cold streams' pinch temperature of 70.1 °C by exchanging heat with the stream SD-3, which requires an additional cooler to reach its objective temperature of 78 °C. Stream SD-1 is then divided into two sub-streams, SD-1a and SD-1b. The stream with the highest WCP, SD-1a, exchanges heat with the stream SD-5, reaching the hot streams' pinch temperature (80.1 °C). A cooler is used to reach the desired temperature of SD-5 (25 °C). The second sub-stream of SD-1 exchanges heat with the stream SD-6, leading it to its objective temperature, 86.7 °C. After their corresponding exchange, sub-streams SD-1a and SD-1b are mixed. The exchanges have been established so the final temperature of both sub-streams is the same. Then, SD-1 exchanges heat with the stream SD-2, reaching the desired temperature for the hot stream (330 °C). The final temperature of SD-1, 330 °C, is obtained through a heater. Heating needs for the streams SD-4 and SD-8 are completely fulfilled with steam. Similarly, cooling needs for stream SD-6 are satisfied with cooling water. In the case of the bioethanol process for scenario I, stream SE-1 is first heated up with stream SE-4, which requires additional cooling to reach its final temperature (77.3 °C).



(a)



(b)

Figure 5. Integrated processes, scenario I (a) biodiesel process, (b) bioethanol process.

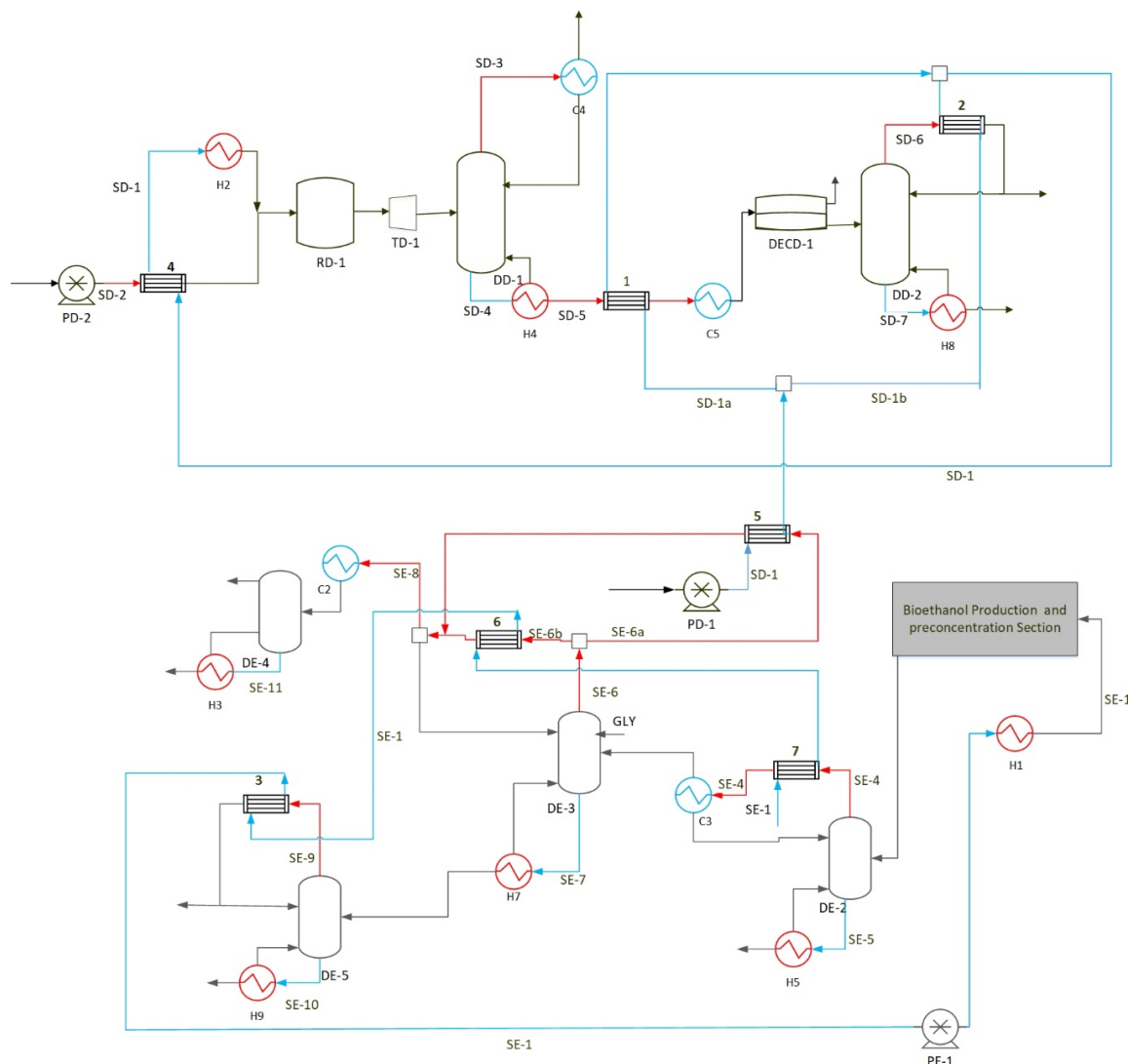


Figure 6. Integrated processes, scenario II.

Then, stream SE-1 exchanges heat with stream SE-6, which then enters to a cooler to reach its desired temperature ($77.3\text{ }^{\circ}\text{C}$). SE-1 reach the cold streams' pinch temperature, $73.5\text{ }^{\circ}\text{C}$; then, it exchanges heat with SE-9, which reaches its final temperature ($105.828\text{ }^{\circ}\text{C}$). SE-1 reaches its desired temperature ($160\text{ }^{\circ}\text{C}$) in a heater. Heating requirements for all the other cold streams are satisfied with steam. Similarly, cooling needs for streams SE-2 and SE-8 are satisfied with cooling water.

It is observed that the integration procedure is mainly based on streams SD-1 (which is the ethanol stream to be heated to act as a reactant in the transesterification/esterification reactor), and SE-1 (which is the water to be heated to enter to

the pretreatment reactor). This is because they are the streams with the wider change in temperature. Although there are other streams with high WC_p , their temperature change is small. This is reflected in scenario II, where the integration is once more focused on streams SD-1 and SE-1. Here, SE-1 first exchanges heat with SE-4, which then enters to a cooler to reach its final temperature of $77.3\text{ }^{\circ}\text{C}$. Stream SE-6 is divided into two sub-streams, SE-6a and SE-6b. SE-1 is heated up to the cold streams' pinch temperature ($73.5\text{ }^{\circ}\text{C}$) by heat exchange with SE-6b, reaching the desired temperature for the hot stream ($77.3\text{ }^{\circ}\text{C}$). Then, SE-1 is used to satisfy the cooling needs of stream SE-9. Finally, SE-1 reaches its final temperature ($160\text{ }^{\circ}\text{C}$) by using steam. Stream SD-1 starts with an exchange with

the sub-stream SE-6a, reaching its final temperature (77.3 °C), as occurred with SE-6b. SD-1 leaves the exchanger at the cold streams' pinch temperature. Then, it is divided into two sub-streams, SD-1a and SD-1b. SD-1a is used to take stream SD-5 to the hot streams' pinch temperature (83.5 °C); then, cooling water is used to take SD-5 to its final temperature (25 °C). On the other hand, SD-1b is used to satisfy the cooling requirements of SD-6. Both sub-streams, SD-1a and SD-1b, leave their respective exchangers at the same temperature, and are mixed to obtain the complete stream SD-1. This stream is used to fulfill the cooling needs of stream SD-2. Finally, steam is used to reach the final temperature of SD-1 (330 °C). Heating requirements of all the other cold streams (SE-3, SE-5,

SE-7, SE-10, SE-11, SD-4 and SD-8) are satisfied with steam. Similarly, the cooling needs for the hot streams SE-2, SE-8 and SD-3 are fulfilled with cooling water.

Table 2 presents the equipment and utilities costs for the heaters and coolers required in the non-integrated processes. The annual cost due to heat exchangers for the bioethanol process is 9,935,359.6 USD/y, from where 95.2% is due to the utilities, mainly steam. For the biodiesel process, the annual cost due to heat exchangers is 1,713,904.9 USD/y, where the utilities contribute with 71.7% to the TAC. In the case of the biodiesel process, a high-resistance material is necessary for the two high-pressure heaters ED-1 and ED-2.

Table 2. Equipment and utilities costs for the non-integrated processes.

BIODIESEL PROCESS			
Equipment	Area (m ²)	Equipment cost (USD)	Utility cost (USD/y)
Heater SD-1	8.1	234,806.77	1,001,354.83
Reboiler SD-4	5.3	157,079.94	200,396.89
Reboiler SD-7	0.3	783,249.60	26,587.02
Condenser SD-3	14.6	150,627.62	1.5
Cooler SD-5	877.6	984,388.05	1,434.44
Condenser SD-6	0.03	5,597.81	0.007
Cooler SD-2	0.4	104,900.25	0.27
BIOETHANOL PROCESS			
Equipment	Area (m ²)	Equipment cost (USD)	Utility cost (USD/y)
Heater SE-1	45.7	159,562.09	2,855,104.71
Reboiler SE-11	1.1	221,711.50	87,310.20
Reboiler SE-5	19.8	224,521.97	1,369,050.69
Reboiler SE-3	57.3	462,639.73	3,758,832.74
Reboiler SE-7	8.8	168,123.78	373,484.22
Reboiler SE-10	17.8	274,263.59	1,017,002.60
Cooler SE-2	61.9	171,973.70	1.48
Cooler SE-8	42.4	157,083.64	1.9
Condenser SE-4	99.5	203,585.81	9.94
Condenser SE-6	12.7	153,376.71	1.34
Condenser SE-9	6.9	175,948.34	1.58

Table 3. Equipment and utilities costs for the integrated processes, scenario I.

BIODIESEL PROCESS			
Equipment	Area (m ²)	Equipment cost (USD)	Utility cost (USD/y)
Exchanger SD-5/SD-1A	1.9	111,767.13	—
Exchanger SD-6/ SD-1B	0.08	173,209.46	—
Exchanger SD-2/SD-1	0.5	129,760.28	—
Exchanger SD-3/SD-1	4.31	141,975.29	—
Heater SD-1	7.34	223,550.25	731,437.79
Reboiler SD-4	5.3	157,079.94	200,396.89
Reboiler SD-7	0.3	783,249.60	26,587.02
Condenser SD-3	13.1	152,668.04	1.34
Cooler SD-5	1.13	18,407.05	1.02
BIOETHANOL PROCESS			
Equipment	Area (m ²)	Equipment cost (USD)	Utility cost (USD/y)
Exchanger SE-9/SE-1	14.06	151,460.65	—
Exchanger SE-4/SE-1	76.31	183,968.88	—
Exchanger SE-6/SE-1	21	147,645.51	—
Heater SE-1	31.25	150,424.06	1,461,187.67
Reboiler SE-11	1.1	221,711.50	87,310.20
Reboiler SE-5	19.8	224,521.97	1,369,050.69
Reboiler SE-3	57.3	462,639.73	3,758,832.74
Reboiler SE-7	8.8	168,123.78	373,484.23
Reboiler SE-10	17.8	274,263.59	1,017,002.60
Cooler SE-2	61.9	171,973.70	1.48
Cooler SE-8	42.4	157,083.64	1.9
Condenser SE-4	60.4	170,652.49	6.01
Condenser SE-6	8.3	167,282.12	0.86

For calculation purposes, stainless steel is used, as reported for a heat exchanger at 200 bar by Seo *et al.*, (2020). On the other hand, the stream SD-5 requires using refrigerated water, which slightly increases the contribution of the cooling utilities to the cost; but the use of steam still represents the highest contribution (71.6%). This analysis is focused only on the heat exchangers, since it is where the impact of energy integration will be reflected. Nevertheless, when all the equipment is included, the TAC for the bioethanol process is 31,403,413.49 USD/y, while the TAC for the biodiesel process is 2,519,740.48 USD/y.

Table 3 shows the costs for heaters, coolers and heat exchangers obtained for scenario I; subscripts A and B indicate that the stream has been divided into two sub-streams. When integration is performed, the annual cost due to heat exchangers for the bioethanol process is 8,597,228.7 USD/y, with a contribution of 93.8% due to steam. In comparison with the non-integrated process, the equipment cost increases about 10.5%, but it is compensated with a reduction of 14.7% in the utilities' costs. Thus, the annual cost due to heat exchangers is reduced by 13.5% when energy integration is applied.

Table 4. Equipment and utilities costs for the integrated processes, scenario II.

BIODIESEL PROCESS			
Equipment	Area (m ²)	Equipment cost (USD)	Utility cost (USD/y)
Exchanger SD-5/SD-1A	1.85	111,438.08	—
Exchanger SD-6/ SD-1B	0.08	165,175.19	—
Exchanger SD-2/SD-1	0.48	129,636.86	—
Heater SD-1	7.3	223,010.89	720,465.70
Reboiler SD-4	5.3	157,079.94	200,396.89
Reboiler SD-7	0.28	783,249.60	26,587.02
Condenser SD-3	14.6	150,627.62	1.5
Cooler SD-5	1.16	18,547.71	1.09
BIOETHANOL PROCESS			
Equipment	Area (m ²)	Equipment cost (USD)	Utility cost (USD/y)
Exchanger SE-9/SE-1	14.06	151,460.76	—
Exchanger SE-4/SE-1	50.91	163,395.86	—
Exchanger SE-6B/SE-1	44.53	158,681.66	—
Heater SE-1	31.25	150,424.07	1,461,189.71
Reboiler SE-11	1.1	221,711.50	87,310.20
Reboiler SE-5	19.8	224,521.97	1,369,050.69
Reboiler SE-3	57.3	462,639.73	3,758,832.74
Reboiler SE-7	8.8	168,123.78	373,484.23
Reboiler SE-10	17.8	274,263.59	1,017,002.60
Cooler SE-2	61.9	171,973.70	1.48
Cooler SE-8	42.4	157,083.64	1.9
Condenser SE-4	67.1	176,140.15	6.69
INTEGRATION BETWEEN PROCESSES			
Exchanger SE-6A/SD-1	5.3	153,897.29	—

In the case of the biodiesel process, the annual cost due to the heat exchangers network is 1,336,757.49 USD/y, where steam cost represents a contribution of 71.7%. In this case, equipment cost is reduced by 21.8% since in the non-integrated process, the heat exchangers require high-pressure for both tubes and shell because steam is at 150 bar. When performing heat integration, the size of such equipment is reduced, and the additional exchangers have high-pressure requirement only on one side of the exchanger; thus, a carbon steel-stainless steel combination can be used, which allows reducing the investment. On the other hand, utilities' costs are reduced by 22.1%. It is important to mention

that when integration occurs, the need for refrigerated water is considerably reduced. Thus, the annual cost due to heat exchangers in the biodiesel process is reduced by 22% when integration is applied. If all the equipment on the processes is included, the TAC for the bioethanol process is 30,065,282.60 USD/y, while the TAC for the biodiesel process is 2,142,593.07 USD/y. Thus, savings of 4.3% and 14.9% are obtained in total annual cost for the whole bioethanol and biodiesel processes, respectively.

Table 4 presents the costs for heaters, coolers and heat exchangers obtained for scenario II.

Table 5. Results for the emissions analysis.

	CO ₂ emissions (kg CO ₂ /h)		
	Non-integrated case	Scenario I	Scenario II
Bioethanol process	5,120.43	4,357.42	4,357.42
Biodiesel process	613.47	481.19	475.81
Total	5,733.90	4,838.61	4,833.23
CO ₂ emissions (kg CO ₂ /kg product)			
Bioethanol process	1.52	1.29	1.29
Biodiesel process	0.43	0.34	0.336

Table 6. Results summary.

	Heating requirements (kW)	Cooling requirements (kW)	TAC (USD/y, only heat exchangers)	TAC (USD/y, all the process)	CO ₂ emissions (kg CO ₂ /h)
Non-integrated case	20,770.59	62,942.76	11,649,264.50	33,923,154.00	5,733.90
Scenario I	17,485.31	5,828.96	9,933,986.19	32,207,875.70	4,838.61
Scenario II	17,473.57	5,818.49	9,888,949.20	32,162,838.68	4,833.23

For this scenario, the annual cost due to heat exchangers for both processes is 9,888,949.2 USD/y, with a contribution of 91.1% due to steam. Equipment cost for both processes is reduced by 8.8% in comparison with the non-integrated process. This reduction is explained in terms of the variation of the material required for the heat exchangers in the biodiesel process, as was described before. Additionally, the cost of utilities is reduced by 15.6% in comparison with the non-integrated case; this implies a reduction on 15.1% for the annual cost associated to heat exchangers when the integration considers the streams of both processes. If all the equipment on the processes is included, the TAC is 32,162,838.68 USD/y. Thus, savings of 5.2% are obtained in total annual cost when both processes are integrated by sharing heating/cooling among them. When the processes are integrated as separated entities (scenario I), savings on TAC of 5.06% are obtained, since when performing the integration between the streams of both processes only one exchange takes place among a stream from the bioethanol process (SE-6) and a stream from the biodiesel process (SD-1), see Table 4. All the other exchanges are quite similar to those obtained from scenario I.

4.3 Estimation of CO₂ emissions

Table 5 shows the emissions of carbon dioxide for the non-integrated case and scenarios I and II. Similar to TAC, CO₂ emissions are almost equal for scenarios I and II. Emissions have no change

among those scenarios for the bioethanol process, since the stream of such process interacting with the biodiesel process (i.e., SE-6A) is a hot stream, which requires cooling. On the other hand, the stream from the biodiesel process interacting with stream SE-6A (i.e., SD-1) allows an additional reduction in the steam requirement for scenario II; with the consequent decrease in CO₂ emissions by 1.12% in comparison with scenario I. If the non-integrated case is analyzed, it can be seen that the integration allows reducing around 15% of carbon dioxide emissions, either if the processes are integrated as separated entities, or if they are integrated in a biorefinery scheme. If the emissions for each process are analyzed, integration allows savings in CO₂ emissions in the order of 15% for the bioethanol process, while for the biodiesel process savings are around 22%. Table 5 presents the normalized emissions per kilogram of product. It can be seen that the bioethanol process still has the main contribution in terms of carbon dioxide emissions, even when the biodiesel process requires high-pressure steam for the exchangers ED-1 and ED-2.

Table 6 shows a summary of the obtained results. The benefits of process integration are particularly observed in the reduction of cooling needs, where savings around 90% are obtained when performing the integration. In the case of heating requirements, savings around 16% are produced through energy integration. The effect of process integration in TAC is opposite to what is expected, since reductions around 14% are obtained in the TAC of the heat

transfer equipment when integration occurs. This is mainly due to variations in the material required for the construction of the exchangers when integration is performed. If the TAC of all the processes is considered, there is still a small reduction when energy integration occurs. CO₂ emissions are reduced about 15% when energy integration takes place. Finally, it has been observed that the savings for all the indicators are similar either if the processes are integrated as separated entities or in a combined scheme.

Conclusions

In this work, the feasibility of energy integration between biodiesel and bioethanol production processes has been analyzed. The bioethanol is obtained from lignocellulosic biomass through pretreatment, hydrolysis, and fermentation steps. On the other hand, biodiesel is obtained through the treatment of a vegetable oil with supercritical ethanol. Two integration scenarios are analyzed: I) the processes are integrated as separated entities, and II) both processes are simultaneously integrated, aiming to a biorefinery-like scheme. It has been observed that both cases show similar total annual costs and CO₂ emissions, since the streams of the bioethanol process have low compatibility with those of the biodiesel process. Even so, the integration of both processes in any of the proposed schemes allows reducing heating requirements in 16%, the total annual cost of heat exchangers around 15% and the carbon dioxide emissions in 16%, when compared with the non-integrated case. Additionally, integration allows reducing equipment cost in the supercritical biodiesel production process, due to the reduction in the requirement for high-pressure steam, which implies that a less expensive material is required for one side of the heat exchangers. Moreover, heat integration allows reducing the need for refrigerated water. Benefits of heat integration have been demonstrated, although other processes in a biorefinery scheme must be considered to allow a higher interaction between the streams.

Acknowledgments

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Nomenclature

$C\%$	[] carbon content of the fuel used to produce steam
CC	[USD] capital cost
C_i	[mol/L] molar concentration of component i
$[CO_2]_{em}$	[kg/s] emissions of carbon dioxide
A_0	[1/min] pre-exponential factor
E_a	[kJ/kmol] activation energy
h_{proc}	[kJ/kg] enthalpy of the steam
k_j	[1/min] kinetic constant for reaction j
n	[y] payback period
NHV	[kJ/kg] net heating value of fuel
OC	[USD/y] operational cost
Q_{fuel}	[kJ/s] heat duty of fuel burnt to produce steam
Q_{proc}	[kJ/s] heat duty required by the process
$r_{i(j)}$	[mol of i /min] reaction rate for the component i in the reaction j
TAC	[USD/y] total annual cost
T_0	[°C] ambient temperature
T_{FTB}	[°C] flame temperature of the boiler flue gases
T_{stack}	[°C] stack temperature
GREEK LETTERS	
λ_{proc}	[kJ/kg] latent heat of steam
ΔT	[°C] minimum temperature difference

References

- Aboelazayem, O., Gadalla, M., Alhajri, I. and Saha, B. (2021). Advanced process integration for supercritical production of biodiesel: Residual waste heat recovery via organic Rankine cycle (ORC). *Renewable Energy* 164, 433-443. <https://doi.org/10.1016/j.renene.2020.09.058>
- Aboelazayem, O., Gadalla, M. and Saha, B. (2018). Design and simulation of an integrated process for biodiesel production from waste cooking oil using supercritical methanolysis. *Energy* 161, 299-307. <https://doi.org/10.1016/j.energy.2018.07.139>
- Arifeen, N., Wang, R., Kookos, I. K., Webb, C. and Koutinas, A. A. (2007). Process design and optimization of novel wheat-based continuous bioethanol production system. *Biotechnology*

- Progress 23, 1394-1403. <https://doi.org/10.1021/bp0701517>
- Avilés-Martínez, A., Saucedo-Luna, J., Segovia-Hernandez, J. G., Hernandez, S., Gomez-Castro, F. I. and Castro-Montoya, A. J. (2012). Dehydration of bioethanol by hybrid process liquid-liquid extraction/extractive distillation. *Industrial and Engineering Chemistry Research* 51, 5847-5855. <https://doi.org/10.1021/ie200932g>
- Brethauer, S. and Wyman, C. E. (2010). Review: Continuous hydrolysis and fermentation for cellulosic ethanol production. *Bioresource Technology* 101, 4862-4874. <https://doi.org/10.1016/j.biortech.2009.11.009>
- Brunet, R., Boer, D., Guillén-Gosálbez, G. and Jiménez, L. (2015). Reducing the cost, environmental impact and energy consumption of biofuel processes through heat integration. *Chemical Engineering Research and Design* 93, 203-212. <https://doi.org/10.1016/j.cherd.2014.06.018>
- Brusamarello, C.Z., Di Domenico, M., Da Silva, C. and de Castilhos, F. (2020). A comparative study between multivariate calibration and artificial neural network in quantification of soybean biodiesel. *Revista Mexicana de Ingeniería Química* 19, 123-132. <https://doi.org/10.24275/rmiq/Bio579>
- CFE - Comisión Federal de Electricidad. (2020). Tarifa de alta tensión, nivel transmisión, tarifa intermedia para zona central. In Comisión Federal de Electricidad. Available at: <https://app.cfe.mx/Aplicaciones/CCFE/Tarifas/TarifasCREIndustria/Tarifas/DemandaIndustrialTran.aspx>. Accessed: February 10, 2020
- Conde-Mejía, C., Jiménez-Gutiérrez, A. and El-Halwagi, M. M. (2013). Assessment of combinations between pretreatment and conversion configurations for bioethanol production. *ACS Sustainable Chemistry and Engineering* 1, 956-965. <https://doi.org/10.1021/sc4000384>
- Demirbas, A. (2009). Production of biodiesel fuels from linseed oil using methanol and ethanol in non-catalytic SCF conditions. *Biomass and Bioenergy* 33, 113-118. <https://doi.org/10.1016/j.biombioe.2008.04.018>
- Dimian, A. C. and Bildea, C. S. (2008). *Chemical Process Design: Computer-Aided Case Studies*. Wiley-VCH, Germany.
- Gadalla, M., Olujić, Ž., Jobson, M. and Smith, R. (2006). Estimation and reduction of CO₂ emissions from crude oil distillation units. *Energy* 31, 2398-2408. <https://doi.org/10.1016/j.energy.2005.10.030>
- Garrote, G., Domínguez, H. and Parajó, J. C. (1999). Hydrothermal processing of lignocellulosic materials. *Holz Als Roh- Und Werkstoff* 57, 191-202. <https://doi.org/10.1007/s001070050039>
- Glisic, S. B. and Orlović, A. M. (2014). Review of biodiesel synthesis from waste oil under elevated pressure and temperature: Phase equilibrium, reaction kinetics, process design and techno-economic study. *Renewable and Sustainable Energy Reviews*, 31, 708-725. <https://doi.org/10.1016/j.rser.2013.12.003>
- Glišić, S., Lukic, I. and Skala, D. (2009). Biodiesel synthesis at high pressure and temperature: Analysis of energy consumption on industrial scale. *Bioresource Technology* 100, 6347-6354. <https://doi.org/10.1016/j.biortech.2009.07.024>
- Gómez-Castro, F. I., Aldana-González, M. G., Conde-Mejía, C., Gutiérrez-Antonio, C., Romero-Izquierdo, A. G. and Morales-Rodríguez, R. (2017). Process integration for the supercritical production of biodiesel and the production of lignocellulosic bioethanol. *Computer Aided Chemical Engineering* 40, 931-936. <https://doi.org/10.1016/B978-0-444-63965-3.50157-4>
- Gomez-Castro, F. I., Rico-Ramirez, V., Segovia-Hernandez, J. G., Hernandez-Castro, S. and El-Halwagi, M. M. (2013). Simulation study on biodiesel production by reactive distillation with methanol at high pressure and temperature: Impact on costs and pollutant emissions. *Computers & Chemical Engineering* 52, 204-215. <https://doi.org/10.1016/j.compchemeng.2013.01.007>

- Gómez-Castro, F. I., Segovia-Hernández, J. G., Hernández, S., Rico-Ramírez, V., Gutiérrez-Antonio, C., Briones-Ramírez, A., Cano-Rodríguez, I. and Gamiño-Arroyo, Z. (2015). Analysis of alternative non-catalytic processes for the production of biodiesel fuel. *Clean Technologies and Environmental Policy* 17, 2041-2054. <https://doi.org/10.1007/s10098-015-0933-x>
- Gu, Y. and Jérôme, F. (2010). Glycerol as a sustainable solvent for green chemistry. *Green Chemistry* 12, 1127-1138. <https://doi.org/10.1039/c001628d>
- Gui, M. M., Lee, K. T. and Bhatia, S. (2009). Supercritical ethanol technology for the production of biodiesel: Process optimization studies. *The Journal of Supercritical Fluids* 49, 286-292. <https://doi.org/10.1016/j.supflu.2008.12.014>
- Gutiérrez, J. P., Meindersma, G. W. and Haan, A. B. De. (2012). COSMO-RS-based ionic-liquid selection for extractive distillation processes. *Industrial and Engineering Chemistry Research* 51, 11518-11529. <https://doi.org/10.1021/ie301506n>
- Gutiérrez, L. F., Sánchez, Ó. J. and Cardona, C. A. (2009). Process integration possibilities for biodiesel production from palm oil using ethanol obtained from lignocellulosic residues of oil palm industry. *Bioresource Technology* 100, 1227-1237. <https://doi.org/10.1016/j.biortech.2008.09.001>
- Haq, I.U., Tahir, A., Nawaz, A., Mustafa, Z., Mukhtar, H. and Rehman, A.U. (2020). Sustainable bioconversion of saccharified agro residues into bioethanol by *Wickerhamomyces anomalus*. *Revista Mexicana de Ingeniería Química* 19, 1477-1491. <https://doi.org/10.24275/rmiq/Bio966>
- He, H., Wang, T. and Zhu, S. (2007). Continuous production of biodiesel fuel from vegetable oil using supercritical methanol process. *Fuel* 86, 442-447. <https://doi.org/10.1016/j.fuel.2006.07.035>
- Hellvig, E.L.F. and Flores-Sahagun, T.H. (2021). The importance of public policies that encourage companies to decarbonize the environment and invest in clean technologies in Brazil. *Revista Mexicana de Ingeniería Química* 20, 899-910. <https://doi.org/10.24275/rmiq/Poly2363>
- International Energy Agency. (2018). World Energy Outlook 2018. Available at: <https://www.iea.org/reports/world-energy-outlook-2018>. Accessed: February 8, 2021
- Igliński, B., Piechota, G. and Buczkowski, R. (2015). Development of biomass in polish energy sector: an overview. *Clean Technologies and Environmental Policy* 17, 317-329. <https://doi.org/10.1007/s10098-014-0820-x>
- Kazi, F. K., Fortman, J. A., Anex, R. P., Hsu, D. D., Aden, A., Dutta, A. and Kothandaraman, G. (2010). Techno-economic comparison of process technologies for biochemical ethanol production from corn stover. *Fuel* 89, S20-S28. <https://doi.org/10.1016/j.fuel.2010.01.001>
- Kiss, A. A. and Suszwalak, D. J.-P. C. (2012). Innovative dimethyl ether synthesis in a reactive dividing-wall column. *Computers & Chemical Engineering* 38, 74-81. <https://doi.org/10.1016/j.compchemeng.2011.11.012>
- Kralj, A. K. (2008). Heat integration between two biodiesel processes using a simple method. *Energy and Fuels* 22, 1972-1979. <https://doi.org/10.1021/ef700710y>
- Kusdiana, D. and Saka, S. (2001). Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol. *Fuel* 80, 693-698. [https://doi.org/10.1016/S0016-2361\(00\)00140-X](https://doi.org/10.1016/S0016-2361(00)00140-X)
- Lee, S., Posarac, D. and Ellis, N. (2011). Process simulation and economic analysis of biodiesel production processes using fresh and waste vegetable oil and supercritical methanol. *Chemical Engineering Research and Design* 89, 2626-2642. <https://doi.org/10.1016/j.cherd.2011.05.011>
- Linnhoff, B. and Hindmarsh, E. (1983). The pinch design method for heat exchanger networks. *Chemical Engineering Science*, 38, 745-763. [https://doi.org/10.1016/0009-2509\(83\)80185-7](https://doi.org/10.1016/0009-2509(83)80185-7)

- Lloyd, T. A. and Wyman, C. E. (2005). Combined sugar yields for dilute sulfuric acid pretreatment of corn stover followed by enzymatic hydrolysis of the remaining solids. *Bioresource Technology* 96, 1967-1977. <https://doi.org/10.1016/j.biortech.2005.01.011>
- Lotero, E., Liu, Y., Lopez, D. E., Suwannakarn, K., Bruce, D. A. and Goodwin, J. G. (2005). Synthesis of biodiesel via acid catalysis. *Industrial and Engineering Chemistry Research* 44, 5353-5363. <https://doi.org/10.1021/ie049157g>
- Martín, M. and Grossmann, I. E. (2013). Optimal engineered algae composition for the integrated simultaneous production of bioethanol and biodiesel. *AIChE Journal* 59, 2872-2883. <https://doi.org/10.1002/aic.14071>
- Navarrete-Contreras, S., Sánchez-Ibarra, M., Barroso-Muñoz, F. O., Hernández, S. and Castro-Montoya, A. J. (2014). Use of glycerol as entrainer in the dehydration of bioethanol using extractive batch distillation: Simulation and experimental studies. *Chemical Engineering and Processing: Process Intensification* 77, 38-41. <https://doi.org/10.1016/j.cep.2014.01.003>
- Öhgren K., Bura R., Lesnicki G., Saddler J. and Zacchi G. (2007). A comparison between simultaneous saccharification and fermentation and separate hydrolysis and fermentation using steam-pretreated corn stover. *Process Biochemistry* 42, 834-839. <https://doi.org/10.1016/j.procbio.2007.02.003>
- Petersen, A. M., Melamu, R., Knoetze, J. H. and Görgens, J. F. (2015). Comparison of second-generation processes for the conversion of sugarcane bagasse to liquid biofuels in terms of energy efficiency, pinch point analysis and Life Cycle Analysis. *Energy Conversion and Management* 91, 292-301. <https://doi.org/10.1016/j.enconman.2014.12.002>
- Saka S. (2005). Biodiesel fuel production by supercritical methanol technology. *Journal of the Japanese Institute of Energy* 84, 413-419.
- Saka, S. and Isayama, Y. (2009). A new process for catalyst-free production of biodiesel using supercritical methyl acetate. *Fuel* 88, 1307-1313. <https://doi.org/10.1016/j.fuel.2008.12.028>
- Saka, S., Isayama, Y., Ilham, Z. and Jiayu, X. (2010). New process for catalyst-free biodiesel production using subcritical acetic acid and supercritical methanol. *Fuel* 89, 1442-1446. <https://doi.org/10.1016/j.fuel.2009.10.018>
- Samniang, A., Tipachan, C. and Kajorncheappungam, S. (2014). Comparison of biodiesel production from crude Jatropha oil and Krating oil by supercritical methanol transesterification. *Renewable Energy* 68, 351-355. <https://doi.org/10.1016/j.renene.2014.01.039>
- Sawangkeaw, R., Bunyakiat, K. and Ngamprasertsith, S. (2010). A review of laboratory-scale research on lipid conversion to biodiesel with supercritical methanol (2001-2009). *The Journal of Supercritical Fluids* 55, 1-13. <https://doi.org/10.1016/j.supflu.2010.06.008>
- Seo, H., Cha, J. E., Kim, J., Sah, I. and Kim, Y.-W. (2020). Design and performance analysis of a supercritical carbon dioxide heat exchanger. *Applied Sciences* 10. <https://doi.org/10.3390/app10134545>
- Severson, K., Martín, M. and Grossmann, I. E. (2013). Optimal integration for biodiesel production using bioethanol. *AIChE Journal* 59, 834-844. <https://doi.org/10.1002/aic.13865>
- Sinnott, R. K. (1993). *Coulson and Richardson's Chemical Engineering*, Vol. 6, 2nd ed., Pergamon Press, New York.
- Skarlis, S., Kondili, E. and Kaldellis, J. K. (2012). Small-scale biodiesel production economics: a case study focus on Crete Island. *Journal of Cleaner Production* 20, 20-26. <https://doi.org/10.1016/j.jclepro.2011.08.011>
- Song, C., Chen, G., Ji, N., Liu, Q., Kansha, Y. and Tsutsumi, A. (2015). Biodiesel production process from microalgae oil by waste heat recovery and process integration. *Bioresource Technology* 193, 192-199. <https://doi.org/10.1016/j.biortech.2015.06.116>

- Tan, K. T. and Lee, K. T. (2011). A review on supercritical fluids (SCF) technology in sustainable biodiesel production: Potential and challenges. *Renewable and Sustainable Energy Reviews* 15, 2452-2456. <https://doi.org/10.1016/j.rser.2011.02.012>
- Turton, R., Bailie, R. C., Whiting, W. B., Shaeiwitz, J. A. and Bhattacharyya, D. (2012). *Analysis, Synthesis, and Design of Chemical Processes*, 4th ed. Prentice Hall, New Jersey.
- U.S Energy Information Administration (2016). International Energy Outlook 2016, Report Number DOE/EIA-0484. Available at: [https://www.eia.gov/outlooks/ieo/pdf/0484\(2016\).pdf](https://www.eia.gov/outlooks/ieo/pdf/0484(2016).pdf). Accessed: June 25, 2021.
- Vane, L. M. (2005). A review of pervaporation for product recovery from biomass fermentation processes. *Journal of Chemical and Technological Biotechnology* 80, 603-629. <https://doi.org/10.1002/jctb.1265>
- Varma, M. N., Deshpande, P. A. and Madras, G. (2010). Synthesis of biodiesel in supercritical alcohols and supercritical carbon dioxide. *Fuel* 89, 1641-1646. <https://doi.org/10.1016/j.fuel.2009.08.012>
- Vázquez-Ojeda, M., Segovia-Hernández, J. G., Hernández, S., Hernández-Aguirre, A. and Kiss, A. A. (2013). Design and optimization of an ethanol dehydration process using stochastic methods. *Separation and Purification Technology* 105, 90-97. <https://doi.org/10.1016/j.seppur.2012.12.002>
- Wyman, C. E., Dale, B. E., Elander, R. T., Holtzapple, M., Ladisch, M. R. and Lee, Y. Y. (2005). Comparative sugar recovery data from laboratory scale application of leading pretreatment technologies to corn stover. *Bioresource Technology* 96, 2026-2032. <https://doi.org/10.1016/j.biortech.2005.01.018>