

Sustainable Production of Renewable Aviation Fuel through Intensification Strategies

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In the transportation industry, aviation is one of the most dynamic sectors. The forecast indicates that aviation will grow at 4.8% until 2036, which implies that fuel requirements will double along with CO₂ emissions. Therefore, the sustainable development of aviation sector faces great challenges and relies on a four-pillar strategy, which includes increasing engine efficiency, optimization of flight trajectories, and alternative fuels. Renewable jet fuel, also known as biojet fuel, consists of hydrocarbons in the range of boiling point of fossil jet fuel, C8-C16, obtained from the biomass processing. There are different pathways to produce biojet fuel, being the hydroprocessing of triglyceride feedstock one of the most reliable and advanced. The hydrotreating process consists of three main steps: hydrodeoxygenation, cracking and isomerizing, and finally purification; also, it allows obtaining biojet fuel with the required properties from different renewable oils. Nevertheless, it has several opportunity areas to decrease energy consumption and environmental impact.

Therefore, in this work an analysis of hydrotreating processes to produce biojet fuel is presented in terms of energy consumption, total annual costs, and CO₂ emissions. Different renewable raw materials of high productive potential in Mexico are considered; along with the implementation of process intensification strategies for the separation train. Results show that the use of thermally coupled distillation sequences allows designing sustainable processes for the production of biojet fuel economically competitive with fossil jet fuel.

1. Introduction

Nowadays, aviation sector faces big challenges. Forecasts indicate that aviation sector will grow at 4.8% per year until 2036 (OACI, 2011), which implies, at least, doubling the fuel requirements. This increasing in the fuel demand could be not satisfied due to the depletion of oil wells production. On the other hand, in 2016 aviation sector contributes with 2% of the world CO₂ emissions (IATA, 2017), percentage that can be also increased due to the predicted growth. Thus, the four-pillar strategy has been proposed to allow the sustainable development of the aviation sector (IATA, 2017), being the renewable aviation fuel the most promissory option. Nevertheless, the economic and environmental sustainability are largely dependent on the feedstock origin and characteristics (Chiaromonti et al., 2016). Therefore, the aviation industry has made it clear that it is only looking at sustainable biofuels and is determined not to repeat the mistakes made with first-generation sources in the road transportation, expecting any supply to be fully sustainable (Sandquist and Güell, 2012).

Renewable aviation fuel, also known as biojet fuel or biokerosene, consists of hydrocarbons in C8-C16 boiling point range. Triglyceride, lignocellulosic, sugar and starchy feedstock can be processed through different routes to obtain biojet fuel (Gutiérrez-Antonio et al., 2017). Among these pathways, hydroprocessing of triglyceride feedstock is one of the most advanced and mature technologies. In the hydrotreating process, triglyceride feedstock is transformed, through hydrodeoxygenation, hydrocracking and hydroisomerization reactions, in light gases, naphtha, biojet fuel and green diesel, which are purified by distillation. Different triglyceride feedstock can be used to produce biojet fuel, such as vegetable oil, waste oil and animal fats. In Mexico, jatropha curcas and microalgae oils are the second and third generation raw materials, respectively,

with higher productive potential (Gutiérrez-Antonio et al., 2016; Atabania et al., 2012). Thus, in this work the implementation of intensification strategies in the separation zone of the hydrotreating process are presented, using as raw materials the aforementioned oils. An analysis of hydrotreating conventional and intensified processes to produce biojet fuel is presented in terms of energy consumption, total annual costs, and CO₂ emissions.

2. Modelling of hydrotreating processes

2.1 Raw materials composition

The hydrotreating processes, both conventional and intensified, are modelled in Aspen Plus process simulator. In these processes vegetable oil and hydrogen are required, whose flows are 100 kg/h and 1500 ml NPT H₂/oil ml, respectively. *Jatropha curcas* oil is composed of oleic acid (42 wt%), linoleic acid (44 wt%), palmitic acid (11 wt%) and stearic acid (3 wt%) (Gutiérrez-Antonio et al., 2016); the yield of this raw material is 1590 kg oil/ha (Gui et al., 2008). The composition of micro-algae oil from the specie *Chlorella sp* is oleic acid (36%), linoleic acid (22%) and linolenic acid (42%) (Verma et al., 2011); the yield of micro-algae oil is 42 mg/L*day (Heredia-Arroyo et al., 2011). According to Handler et al. (2008), the greenhouse gas emissions for the cultivation of *jatropha curcas* and microalgae are 0.3 and 0.1-4.4 kg CO₂eq/kg feedstock, respectively; for the microalgae the range is function of the energy consumption and the management of nutrients. The thermodynamic parameters for the modelling of the oil components are taken from Aca-Aca et al. (2009).

2.2 Modelling of conventional and intensified hydrotreating processes

The modelling of conventional hydrotreating process for *jatropha curcas* oil is realized according to Gutiérrez-Antonio et al. (2016), where the reactions are carried out at 320 °C and 80 bar (hydrodeoxygenation) and 480 °C and 80 bar (hydrocracking and hydroisomerizing). The renewable hydrocarbons are purified through a direct conventional distillation sequence, considering recoveries of 99% of the key components, which is designed with shortcut methods. On the other hand, the modelling of conventional hydrotreating process for microalgae oil is realized according to Gómez-De la Cruz et al. (2017), where the reactions are carried out at 410 °C and 50 bar (hydrodeoxygenation, hydrocracking and hydroisomerizing). The renewable hydrocarbons are purified through a direct conventional distillation sequence, considering recoveries of 99% of the key components, which is designed with shortcut methods.

For both vegetable oils, the reactants must be conditioned to be fed to the reactor; for this a heat exchanger and a pump are used for the oil, whilst a compressor and a heat exchanger are utilized for hydrogen. Also, the outlet stream of the reactive zone has high pressure and temperature; therefore, before it is fed to the distillation train is passed through a turbine to generate electricity. The shortcut design of the distillation columns is performed in DSTW module, while Radfrac module is used for rigorous simulation of the distillation columns; moreover, all the reactors are modelled in RPlug model of Aspen Plus. After the conventional processes are modelled, the intensification is performed in the separation zone through the use of thermally coupled distillation columns. For this, the methodology proposed by Rong and Errico (2012) is applied. It is worth to mention that the reaction zones are not considered in the intensification of the process.

The conventional and intensified hydrotreating process are evaluated in terms of three parameters. The first one is the total annual cost, which is calculated with the Guthrie method (Turton et al., 2008) as follows:

$$\text{Total annual cost (TAC)} = \text{Annual operating cost} + \text{Annual capital cost} \quad (1)$$

The second one is the CO₂ emissions due to steam and electricity generation, which are calculated with emission factors and the amount of used fuel according to the mass balance. The emission factor for steam production is 2.15 kg CO₂/kg burned fuel, while for electricity generation is 0.166 kg CO₂/kWh (Gutiérrez-Antonio et al. 2016). Finally, the estimation of the price of the products, third parameter, is realized with the methodology proposed by Gutiérrez-Antonio et al. (2016), where the mass fraction of each product along with its price and density are employed.

2.3 Analysis of results

With base on the information presented in Sections 2.1 and 2.2 the modelling and simulation of the hydrotreating process was performed. For all the simulated processes, the convergence setting was the one established by default in the Aspen Plus process simulator.

Figures 1 and 2 show the conventional hydrotreating process considering *jatropha curcas* oil (CJC) and micro-algae oil (CMA) as renewable raw materials, respectively. In both processes we can observe a conditioning zone where the reactants are heated and pressurized to reach the operating conditions inside the reactor. The vegetable oil is available at 25 °C and 1.014 bar; thus, the pressure and temperature are increased through a

pump and a heat exchanger. On the other hand, the initial conditions of hydrogen are the commercially available (-234.58°C and 10 bar) according to Guervós-Sánchez (2016); and they are elevated using a compressor and a heat exchanger. After the conditioning of both reactants, they are mixed, since the Rplug module only have available one input stream. In the case of CJC process we can observe two reactors, and after the first one there is one equipment to remove water and carbon dioxide. After the second reactor another equipment is included to remove the excess hydrogen that accompanies the hydrocarbons generated. In the case of the CMA process there is just one reactor, because it is a multifunctional reactor where all the hydrotreating reactions are performed (Verma et al., 2011); so, CMA process is more compact than CJC process. After this reactor, water, carbon dioxide and excess hydrogen are removed. For both process, the hydrocarbons stream is passed through a turbine, to decrease the pressure of the stream and generate electricity. As result, 3.36 kW and 0.049 kW of electrical energy is produced in CJC and CMA processes.

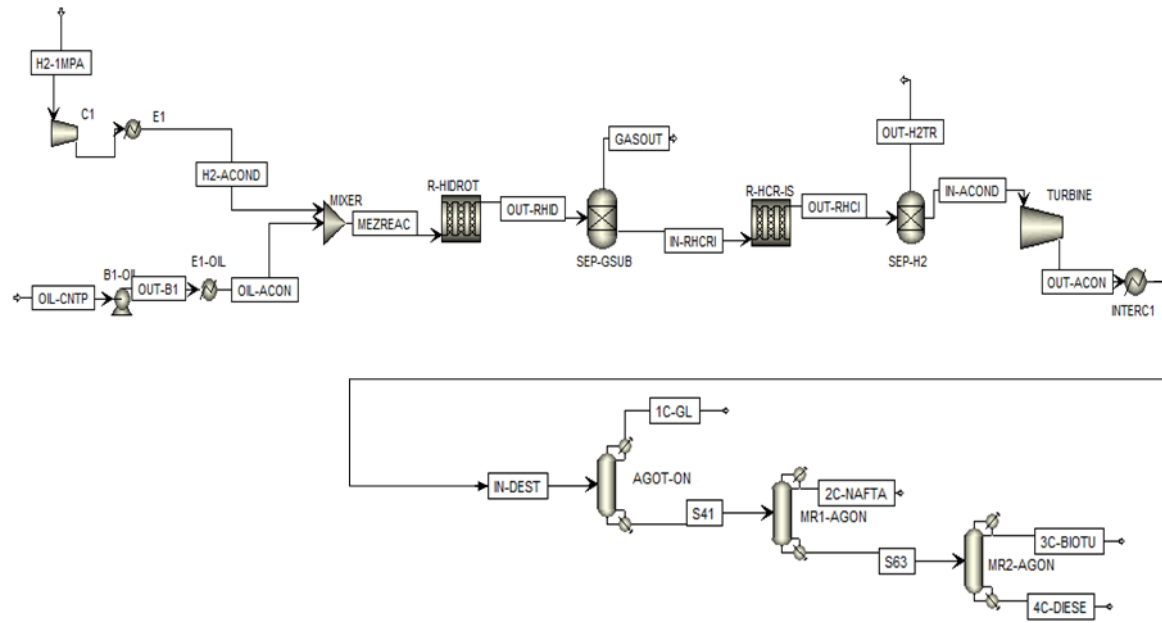


Figure 1: Processing of *jatropha curcas* oil through conventional hydrotreating process.

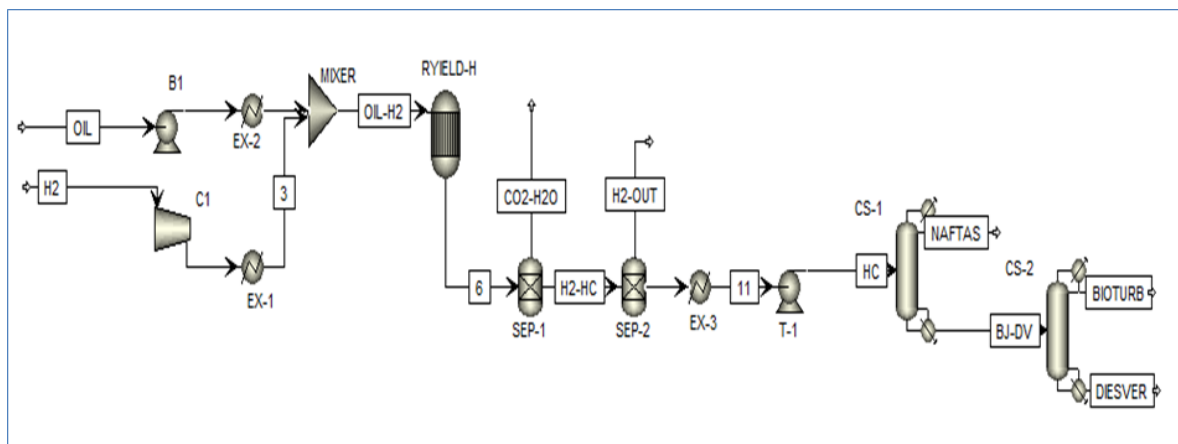


Figure 2: Processing of microalgae oil through conventional hydrotreating process.

Later, the hydrocarbons stream is fed to the direct conventional distillation train. At this point, a significant difference between processes is found. For CJC process, light gases, naphtha, biojet fuel and green diesel are obtained as products. In counterpart, naphtha, biojet fuel and green diesel are obtained as product in the CMA process. Thus, in the CMA process a major yield to biojet fuel can be expected, since light gases are not generated. Table 1 shows the yields of the products for both processes.

Table 1: Product flows for the hydrotreating processes

Process	Light gases (kg/h)	Naphtha (kg/h)	Biojet fuel (kg/h)	Green diesel (kg/h)
CJC	14.30	16.92	18.61	35.65
CMA	-	13.12	76.61	0.46

Moreover, as result of the simulations the yield to biojet fuel is 18.61% and 76.6% for CJC and CMA processes, respectively. As it can be observed, the difference in the yields is high, which is result of a combination of the oil composition and the effectiveness of the catalyst. It is important to remark that for both renewable raw materials a flow of 100 kg/h is considered, with a hydrogen flow of 1500 ml NPT H₂/oil ml. The flow of hydrogen is the reported in the experimental studies where the kinetic models were presented (Sharma et al., 2012; Verma et al., 2011), and also, this flow rate avoid the coke formation in the catalyst according to MCall et al. (2009). It is important to remark that in the hydrotreating process energy is released as result of the reactions; thus, this energy can be used to satisfy the requirements of the processes.

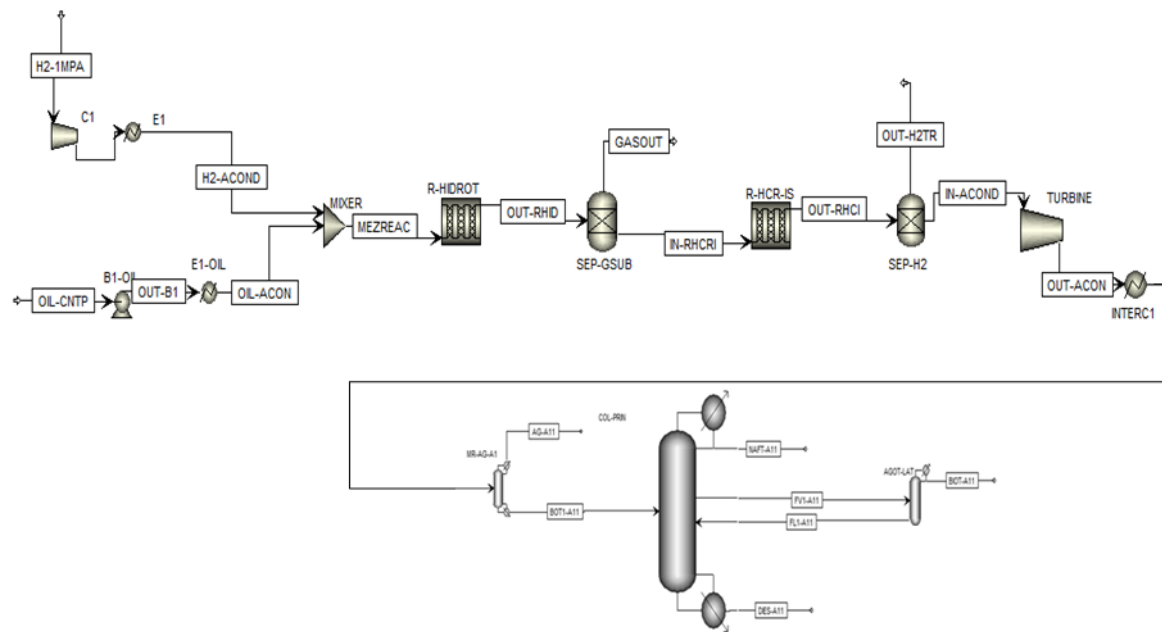


Figure 3: Processing of jatropha curcas oil through intensified hydrotreating process

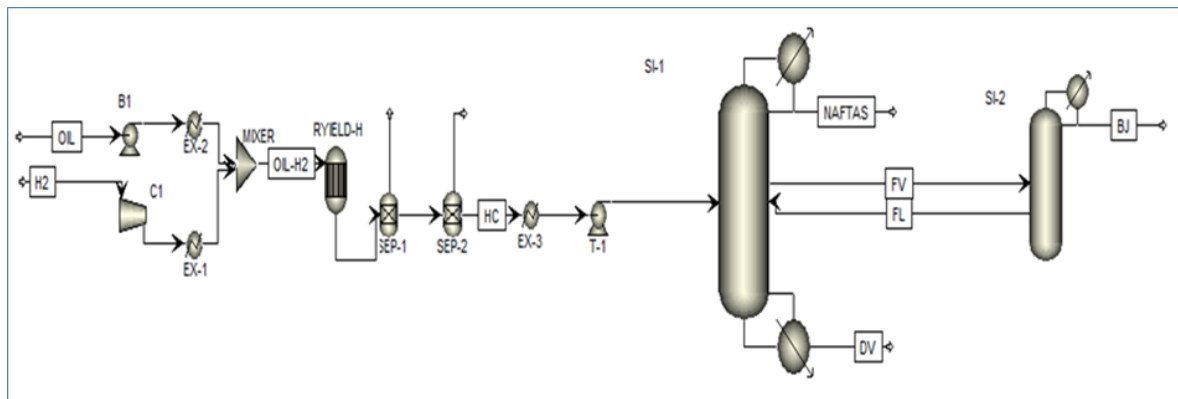


Figure 4: Processing of microalgae oil through intensified hydrotreating process.

With base on the conventional hydrotreating process, the intensified ones were obtained as result of the synthesis methodology proposed by Rong and Errico (2012). Figures 3 and 4 show the intensified

hydrotreating process considering jatropha curcas oil (IJC) and micro-algae oil (IMA) as renewable raw materials, respectively. In both processes, a direct thermally coupled distillation sequence is employed for the separation of the renewable hydrocarbons; however, the configuration is different since three and four products are purified in CMA and CJC processes, respectively. It is worth to mention that conventional and intensified schemes are still not optimized. For the hydrotreating of jatropha curcas oil, the intensification of the separation train is not favourable, since the intensified scheme requires 22.52 kW, while the conventional scheme consumes only 19.90 kW. This is due to the small flows of the key components and the high recoveries established (99%) in the intensified scheme, in comparison with the conventional scheme. On the other hand, for the hydrotreating of microalgae oil, the intensification of the separation train is favourable, since the intensified scheme requires 27.38 kW, while the conventional scheme consumes 28.63 kW. It is important to mention that the total number of stages in conventional and intensified processes is the same. Once the conventional and intensified hydrotreating processes are designed and simulated, the calculation of the economic and environmental parameters is performed, Table 2.

Table 2: Economic and environmental parameters for the hydrotreating processes

Process	Total annual cost (USD/year)	CO ₂ emissions (kg/year)	Biojet fuel price (USD/lt)
CJC	4,749,005.43	280,906,461.11	0.672
IJC	4,761,491.97	326,136,096.10	0.673
CMA	4,468,303.53	241,301,411.08	0.739
IMA	4,557,010.20	159,775,917.48	0.753

From Table 2, it can be seen that the total annual costs are similar, being the minor value found in CMA process. It is worth to mention that according to the results, the major contribution to the total annual costs is the raw material cost. However, the biojet fuel price is slightly higher for in CMA and IMA processes in comparison with CJC and IJC processes. This is due to in both CMA and IMA processes a minor amount of green diesel is produced, being the one with higher price in the market (0.771 USD/liter) than the fossil jet fuel (0.613 USD/liter) according to Petróleos Mexicanos (2017); also, in CMA and IMA processes light gases are not generated, which price for the fossil counterpart is even higher than green diesel (0.986 USD/liter). Therefore, a good balance in the production of byproducts must be searched to obtain a more competitive price for biojet fuel. In spite of this, the biojet fuel price is competitive with the one for fossil jet fuel. Finally, an important aspect is that IMA process has the minor environmental impact, which represents almost 50% less than the CO₂ emissions of the IJC process. Thus, the intensified hydrotreating of microalgae oil allows producing biojet fuel with minimum environmental impact and a competitive price, with respect to the fossil jet fuel.

3. Conclusions

The modelling of conventional and intensified hydrotreating process to produce biojet fuel has been presented. For all the hydrotreating processes jatropha curcas and microalgae oils are considered as renewable raw materials, since they have the higher productive potential in Mexico. The results show that the total annual costs of all hydrotreating process are similar, being the CMA process the one with the minor value. However, the CO₂ emissions of the CMA process are 34% higher than the ones reported for IMA process, being the IMA process total annual costs just 1.9% higher than the CMA process. Therefore, considering both aspects IMA process is the better. On the other hand, the CJC process shows the minor biojet fuel price, with similar total annual costs, but higher environmental impact. Therefore, a good balance in the production of by-products in IMA process must be searched to obtain a more competitive price for biojet fuel. Thus, the intensified hydrotreating of microalgae oil allows producing biojet fuel with minimum environmental impact and a competitive price, with respect to the fossil jet fuel.

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