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Simulation and optimization of a biojet fuel production process

Claudia Gutiérrez-Antonio[a*], Fernando Israel Gómez-Castro[b], Juan Gabriel Segovia-Hernández[b], Abel Briones-Ramírez[c]

[a] *Ingeniería de Plantas, CIATEQ, A.C., Av. Manantiales 23a, Parque Industrial Bernardo Quintana, El Marqués, Querétaro, México 76000,* claudia.gutierrez@ciateq.mx

[b] *Universidad de Guanajuato, Campus Guanajuato, División de Ciencias Naturales y Exactas, Departamento de Ingeniería Química, Noria Alta s/n, Guanajuato, Guanajuato, México 36050*

[c] *Exxerpro Solutions, Av. del Sol 1B Interior 4B, Plaza Comercial El Sol, Querétaro, Querétaro, México 76134*

Abstract

Aviation sector contributes with 2% of the total CO_2 emissions due to human activities. Moreover, predictions estimate that air traffic will duplicate in the next 20 years, with the corresponding increasing in CO_2 emissions. The International Air Transport Association (IATA) has established four strategies to reduce CO_2 emissions; one strategy is the development of aviation fuel from renewable feedstocks, known as biojet fuel. In 2009 UOP Honeywell received a patent for its process to produce aviation fuel from renewable feedstocks. The process considers the transformation of vegetable oil through hydrogenating, deoxygenating, isomerizing and selective hydrocracking to generate propane and hydrocarbons fuels. The resulting aviation fuel is very similar to the fossil one, with the only difference that the first one does not contain aromatic compounds. Due to this, the ASTM standard established the use of biojet fuel in mixtures with fossil jet fuel with up to 50% of the bio-fuel. Also, it is important to remark that in this moment the process of UOP Honeywell is the only one certified for the production of aviation fuel from renewable feedstocks. In this work we propose a model for the production of biojet fuel, obtaining an estimation of the conversion of the reactions of the process of UOP Honeywell. Also, the optimization of the purification stage is performed using a multiobjective genetic algorithm with constraints, which is coupled to Aspen Plus process simulator, in order to generate results considering the complete models of the process. Results show a high conversion of the vegetable oil (castor oil) to biofuels (biojet fuel and green diesel); also, energy can be generated in the process as result of the conditioning of the stream that is fed to the distillation train.

Keywords: biojet fuel, genetic algorithms, aviation fuel, renewable feedstocks.

1. Introduction

In the transport sector, the aviation industry is responsible for 2% of total annual emissions of CO_2, about 623 million tons in 2009 [1]. Although the overall percentage is low, the aviation sector is growing rapidly, together with CO_2 emissions. It is estimated that by 2020, global emissions of international aviation will be approximately 700% higher than in 2005, even if the engine efficiency will increase by 2% per year

[2]. The International Civil Aviation Organization, ICAO, forecasts that by 2050 they could grow to 300-700% [2], if nothing is done to prevent this increase. ICAO estimates that this growth is due to air traffic will grow at a rate of 4.8% per year until 2036 [3], this finding is consistent with that of the International Air Transport Association, IATA, which estimates that air traffic will double by 2020 compared to 2005, Figure 1 [4].

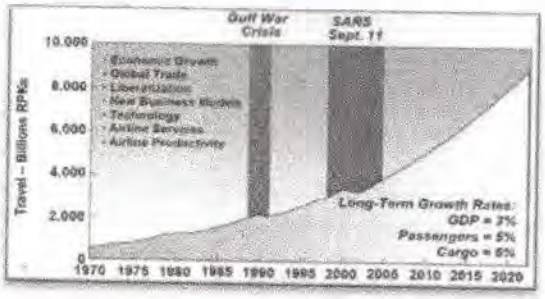


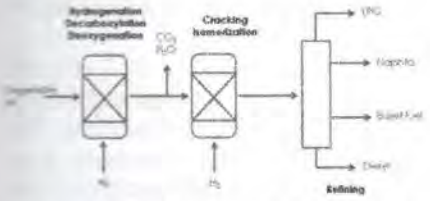
Figure 1. Anthropogenic emissions of CO_2 associated with aviation sector.

Therefore, both the IATA as ICAO have established a four-pillar strategy to combat climate change problem [5]: 1) Technological improvements; 2) Operational improvements; 3) market-based measures; and 4) Alternative fuels. IATA estimates that this strategy will allow a 50% reduction in CO_2 emissions by 2050, relative to 2005 emissions levels, and be neutral growth in CO_2 emissions from 2020 [1]. From the above alternatives, IATA identifies the development of biofuels as one of the most promising, and will allow reducing more significantly CO_2 emissions to the atmosphere. The aviation fuel from renewable feedstocks, also known as biojet fuel, must be drop in, since changes in motor structures are not desirable; in other words, it has to present the same properties and chemical composition of the jet fuel [4]. Thereby, compounds known as synthetic paraffinic kerosene (SPK's) have been developed, and they are very similar to the jet fuel in energetic density and physical properties [6]. Also, the SPK's contains small amounts of sulfur, generating less contaminant emissions in comparison with the conventional jet fuel. The only inconvenient of the SPK's is that they do not contain aromatics, so that they must be used in mixtures up to 50% of biojet fuel with the conventional jet fuel according to standard ASTM D7566. The SPK's can be produced from biomass in two ways [7]. The first one considers the gasification of the biomass, which is introduced to a Fischer-Tropsch process where the SPK's are generated. The second one considers the extraction of vegetable oils, which are chemically modified to produce the SPK's. In both cases, purification of the product stream is required to obtain the biojet fuel.

In 2009, UOP Honeywell received a patent for its process to produce aviation fuel from renewable feedstocks [8]. The process considers the transformation of vegetable oil to generate biojet fuel and hydrocarbons fuels. In this work we propose a model for the production of biojet fuel, obtaining an estimation of the conversion of the reactions of the process of UOP Honeywell. Also, the optimization of the purification step is performed using a multiobjective genetic algorithm with constraints, which is coupled to Aspen Plus process simulator, in order to generate results considering the complete models of the process. Results show a high conversion of the vegetable oil (castor oil) to biofuels (biojet fuel and green diesel); also, energy can be generated in the process as result of the conditioning of the stream that is fed to the distillation train.

2. Biojet fuel production process

At this moment, there are several technologies developed for producing SKP's, for instance: Centia Process (North Carolina University and Diversified Energy Corporation), Greasoline Process (Fraunhofer Institute, UMSICHT), Bio-synfining process (Syntroleum) and Fischer-Tropsch Process (Sasol) [9]; however, we select the process of UOP Honeywell since is the only one certified for the production of aviation fuel from renewable feedstocks. The process of UOP Honeywell considers the transformation of vegetable oil through hydrogenating, deoxygenating, isomerizing and selective hydrocracking to generate hydrocarbons fuels [8]. Later, the stream of hydrocarbons is separated to obtain biojet fuel and green diesel, Figure 2.



- Maximum conversion to biojet fuel: 36%
- Meets the requirements of ASTM D7566
- Flexibility in the raw materials that can be used
- Energy generated in the first reaction can be used in the following reactions
- Elevated costs of the catalyst
- High amounts of hydrogen required
- It is possible to avoid coke formation

Figure 2. UOP Honeywell process for production fo biojet fuel and its mains characteristics.

An important aspect in the production of biojet fuel is eliminating the oxygen to ensure the thermal stability of the fuel; due to this the first reaction is the deoxygenation. From this reaction we obtain paraffins, but not in the range of the distillation curve of the biojet fuel. In a second step, reactions of catalytic cracking and isomerizing occur to cut the hydrocarbons chain in the required range for the biojet fuel; also, the chain is branched to improve the freezing point of biojet fuel. The obtained product is a kerosene equivalent to jet fuel, but without aromatics compounds. The reaction system is a fixed bed reactor, and the reaction is exothermic. In general, the cracking conditions are lower than those for a traditional cracking process. The process uses a multifunctional catalyst to transform the vegetable oil into biofuels. It is important to mention that the quality of the SPK's is independent of the raw material employed, plant (jatropha, camelina, algae, castor) or animal (tallow or fish oils) oils [8].

3. Model of the biojet fuel production process

We consider as renewable feedstock castor oil with a flow stream of 100 kg/h, which composition was taken from Demirbas [10], and it is: palmitic acid (1.1 kg/h), estearic acid (3.1 kg/h), oleic acid (4.9 kg/h), linoleic acid (1.3 kg/h) and ricinoleic acid (89.6 kg/h). It is important to mention that there is no information available for the kinetic model or type of catalyst involved in the UOP Honeywell process due to confidential issues. Therefore, we estimate the hydrotreating reaction with the kinetic model develop by Sebos et al [11] for the hydrotreating of cottonseed oil:

$$(-r_{HDO}) = k_{HDO} \cdot C_{esto} \cdot (1 - x) \quad (1)$$

$$k_{HDO} = -\ln(1 - x) \cdot \dot{m}/m_{cat} \quad (2)$$

Where the subindex HDO implies hydro-deoxigenation, $\dot{m}$ is the feed stream flow and m_{cat} is the catalyst mass. Equation (2) is obtained for a feed of 10% of cottonseed oil in fossil diesel, with temperatures between 305 and 345 °C, a pressure of 30 bar in a Al_2O_3 catalyst. Using the values reported by Sebos et al. [11] and eq. (2) we estimate the conversion of the castor oil in order to select the optimal catalyst mass; the result was

18 kg to get almost a total conversion (99.35%). According with Donis et al [12], when a triglyceride molecule is broken by a deoxygenation reaction the byproducts are water (6 mol by triglyceride mol) and one mol of propane. Also, it is possible that a decarboxilation reaction occurs, generating propane and carbon dioxide. We consider that both reactions ocurr: 50% of the triglycerides react by deoxygenation and 50% by decarboxilation. We assume that all fatty acids in castor oil are present as triglycerides.
For the reactions of isomerizing and cracking we take the results showed by Steijns et al [13] for the isomerization and hydroracking simultaneous of n-dodecane. This implies that we are assuming that the n-alcanes from 15 to 18 carbons present a similar reactive behavior of the n-dodecane. According to Steijns [13], for pressures between 50-60 bar and temperatures of 240 °C the maximum conversion to isomers is around 32%, for a total conversion for n-dodecane of 50%. We take this conversion for estimation of the streams leaving the second reactor of the biojet fuel production process.
The generated hydrocarbon stream, at 240 °C and 60 bar, is conditioned at 19.7 psia and 27.22 °C in order to be fed to a conventional distillation sequence, for the separation of the biojet fuel. We have design two schemes: direct and indirect separations. We consider recoveries of 99% in the key components to generate three products: light hydrocarbons (C3 to C7), biojet fuel (C8 to C16) and green diesel (C17 and C18). The distillation sequences are optimized using a multiobjective genetic algorithm with constaints, coupled to Aspen Plus process simulator, and accelerated through neural networks, [14]. The algorithm generates a set of optimal designs that represent the best trade-off between the selected objetives; it manages several objectives simultaneously, manipulating integer and continue variables, and the link to Aspen Plus allows consider the complete model of the distillation columns. The algorithm works as follow: the first generation is created from an initial design, and all individuals are sent to Aspen Plus to simulate them and get data about objectives and constraints; then, individuals are ranked in subpopulations, according with the number of satisfied constraints. The best individuals are selected to be the new parents of the second generation, and so on; the process ends when the maximum number of generations has been reached. For the distillation sequences analyzed, the objectives are the number of stages (associated with capital costs) and energy consumption (associated with operating costs) in each column, that achieving the recoveries and purities specified.

4. Analysis of results

With the proposed model, we simulate the biojet fuel production process, taking as raw material castor oil (100 kg/h) For the hydrotreating reaction we consider that the operating conditions are 345 °C, 30 bar, 18 kg of Al_2O_3 catalyst, and the kinetic model described in eqs. (1) and (2). Table 1 shows the material balance of the hydrotreating reactor, where a high conversion, 99.36%, of the triglycerides to hydrocarbons plus water and carbon dioxide is observed. Notice that, among the generated hydrocarbons, the major proportion corresponds to those in the range of a diesel (C17 and C18) instead of biojet fuel (C8 to C16). Therefore, the hydrocarbons must be separated from water and carbon dioxide, and fed to the second reactor where the isomerization and cracking are performed. For these reactions we consider that the operating conditions are 240 °C and 60 bar. The material balance of the isomerizing/cracking reactor is showed in Table 2, where we note an important modification of the hydrocarbons to generate biojet fuel. There is a total conversion to hydrocarbons of 82%, while the conversion to biojet fuel is 22%; conversion to biojet fuel is low, but consistent with the maximum conversion of 36% reported by UOP Honeywell [8].

Table 1. Material balance in the hydrotreating reactor

Component	Input flow (kmol/h)	Output flow (kmol/h)	Output flow (kg/h)
Triricinolein	0.0959	0.00062	0.5800
Triolein	0.0055	0.00003	0.03172
Tristearin	0.0035	0.00002	0.02007
Trilinolein	0.0015	0.000009	0.008416
Tripalmitin	0.0014	0.000009	0.007121
Propane	0.0	0.1071	4.7239
n-pentadecane	0.0	0.002031	0.4313
n-hexadecane	0.0	0.002031	0.4598
n-heptadecane	0.0	0.158686	38.1592
n-octadecane	0.0	0.158686	40.3839
Water	0.0	0.60348	10.8686
Carbon dioxide	0.0	0.15869	6.9838

Table 2. Material balance in the isomerizing/cracking reactor

Component	Input stream (kg/h)	Output stream (kg/h)
n-propane to n-heptane	4.7239	10.1255
n-octane to n-tetradecane	0	21.6061
n-pentadecane	0.4313	0.2157
n-hexadecane	0.4598	0.2299
n-heptadecane	38.1592	19.0796
n-octadecane	40.3839	20.1919
i-pentadecane	0	0.06901
i-hexadecane	0	0.0736
i-heptadecane	0	6.1055
i-octadecane	0	6.4614

In order to feed the hydrocarbon stream to the distillation sequence in adequate conditions, we propose a turbine to take advantage of the pressure on the stream. Simulations show that 74.5 Watts are generated during the process; which can contribute to decrease the operating costs of the process.

The hydrocarbons stream is fed to a conventional distillation sequence. We consider two alternatives: direct and indirect sequences; these sequences were optimized through a multiobjective genetic algorithm with constraints, accelerated with neural networks, coupled to Aspen Plus process simulator [14]. As a result we obtained the Pareto front of both sequences, which includes a set of optimal designs that represent the best trade-offs between the objectives simultaneously optimized: number of stages and heat duty in each column of the sequence. This set of optimal designs include minimum heat duty, minimum number of stages and all designs that represent the best compromises between these extremes. Table 3 present three optimal designs, taken from the Pareto front, of both distillation sequences with: minimum number of stages, minimum heat duty and an intermediate case with similar energy consumption. From Table 3 we observe that the indirect distillation sequence presents the minimum energy consumption; however, if we choose another optimal with similar energy consumption is clear that the direct sequence is the best option since it has a minor number of stages.

Table 3. Optimal designs of direct and indirect distillation sequences

Sequence	Total stages	Heat duty (Btu/h)	Total stages	Heat duty (Btu/h)	Total stages	Heat duty (Btu/h)
	Minor number of stages		Minor heat duty		Similar heat duty	
Direct	94	98 464.93	127	84 812.31	97	88 017.23
Indirect	144	98 014.72	238	79 241.51	189	88 249.65

5. Conclusions

We propose a model for the production of biojet fuel, based on the process developed by UOP Honeywell. We estimated the proportion of reactions and amount of catalyst with base in other works previously reported. The results show that the proposed model gives good estimations of the conversion to hydrocarbons, 82%, and biojet fuel, 22%. Also, we propose the generation of energy in the process, as a result of the modification of conditions of the stream of the reactor that will be feed to the distillation sequence. The optimization method used has shown to be useful for obtaining distillation sequences with low energy requirements and potentially low investment costs.

Acknowledgments

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References

[1] Internation Air Transport Association, 2009, A global approach to reducing aviation emissions – First stop: carbon neutral growth from 2020, 8 pp, http://www.iata.org/SiteCollectionDocuments/Documents/Global_Approach_Reducing_Emissions_251109web.pdf

[2] European Commission, Reducing emissions from the aviation sector, http://ec.europa.eu/clima/policies/transport/aviation/index_en.htm

[3] Chacin, E., 2010, La OACI y los combustibles alternativos sustentables de aviación, Taller de Financiamiento, Legislación, Logística y Distribución, Plan de Vuelo, 21 pp.

[4] Herrera-Vaillard, A. et al., 2010, Sustainable Aviation Fuel – Global Overviews, Reunión de arranque, Plan de Vuelo, 16 pp.

[5] Tríptico del Plan de Vuelo hacia los biocombustibles sustentables de aviación en México, Plan de Vuelo, Reunión de arranque, 6 pp.

[6] Bertelli, C., 2010, Bioturbosina, Taller de Refinación e Infraestructura, Plan de Vuelo, 16 pp.

[7] Jansen, J.P. et al., 2002, Large-scale production of biofuels through biomass (co-) gasification and Fisher-Tropsch synthesis, Report, TNO Environment, Energy and Process Innovation.

[8] McCall, M. J. et al., 2009, Production of aviation fuel from renewable feedstocks, Patent No. US 8,039,682 B2.

[9] Gutiérrez-Antonio, C. et al., 2010, Estudio de benchmarking para las tecnologías de producción de bioturbosina, Internal technical report, CIATEQ, A.C.

[10] Demirbas, A., 2005, Prog. Energ. Combust., 31, 466-487.

[11] Sebos, I. et al., 2009, Fuel, 88, 145-149.

[12] Donnis, B. et al., 2009, Topics on Catalysts, 52, 229-240.

[13] Steijns, M. et al., 1981, Ind. Eng. Chem. Prod. Res. Rev., 20, 654-660.

[14] Gutiérrez-Antonio, C. et al., 2010, Comp. Aided Chem. Eng., 28, 391-396.