Comparison between Biodiesel Production from Soybean Oil and Palm Oil with Ethanol: Design and Economic Evaluation

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Biodiesel production by homogeneous alkali catalysis was simulated in PRO/II ® from crude soybean oil and crude palm oil at industrial level, with ethanol. Actual compositions were assumed for both vegetable oils from the literature and thermodynamic properties were estimated by a group contribution method. Because of the higher content of free fatty acids in crude palm oil, it was demonstrated that some changes in the ethanol content and in the equipment specifications are needed to reach a fuel in agreement with the international quality laws, if compared to biodiesel from soybean oil. A same plant could process both raw materials, because the main structural differences are in vessel volumes and temperatures and not in distillation columns or heat exchangers specifications. An economic evaluation was performed to compare the relative potential of both the oilseeds. In the case of Brazil in the mid-2014, it was not profitable to produce biodiesel from these oilseeds and ethanol. Palm oil had the highest manufacturing cost in that scenario, mainly because of the higher demand for ethanol in the pre-treatment step. However, due to the big contribution of raw materials costs in the total manufacturing cost, this scenario could easily change with tax reductions, subsidy or the simple expansion of palm production in the country. The authors expect that the same methodology could be applied to other technologies and/or other raw materials to update the available information about biodiesel production alternatives in Brazil and elsewhere.

1. Introduction

Biodiesel arises as an alternative for the uncertainty of worldwide petroleum production and attending the environmental concerns that emerged in the last few years. The Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP) defines biodiesel as a fuel composed of long chain fatty acids alkyl esters, derived from vegetable oils or animal fats. It is a renewable fuel, normally produced through transesterification of these components with an alcohol, usually methanol or ethanol. It is biodegradable, nontoxic and its burning emits fewer pollutants than traditional petroleum diesel burning.

Regarding the raw material, vegetable oils and animal fats consist mainly in triglycerides (glycerol and fatty acids esters). They can be obtained from a wide variety of sources. In Brazil, special attention is given to soybean, which corresponded to 78 % of the total raw material used in May 2014 (ANP, 2014). Planting of palm, which is the second most used feedstock to biodiesel production in the world, has tripled in Brazil in the last four years (Neher, 2014). Compared to soybean oil, palm oil has a higher content of free fat acids (FFA), which must be removed before transesterification for biodiesel production (Zhang et al., 2003a).

With respect to the alcohol, the most used to biodiesel production is methanol, mainly because of its higher activity and lower costs. When ethanol is used, besides the higher cost of the feedstock, larger quantities are usually required to obtain the same conversions (Freedman et al., 1984; Garnica, 2009a). Difficulties in the separation processes are also expected and have been studied in the last years (Garnica et al., 2009b; França et al., 2011). However, the biodiesel from ethanol has the commercial advantage of being totally renewable. With appropriate technology and investment, it could become a valuable product for countries like Brazil and United States, which have a large and well stablished ethanol industry. While for biodiesel

production with methanol there are many studies in the literature, there are a small number of studies regarding biodiesel production with ethanol, and that is why it was the choice for this work.

2. Process Design and Simulation

The simulations were performed in PRO/II ®, developed by Invensys Systems, Inc. Although there are little information about the use of PRO/II ® for biodiesel production simulation in the literature, this simulator is preferred due to its biofuels databank, which provides properties for a large number of individual fatty compounds. However, to better represent each vegetable oil, the fatty components (triglycerides, FFA and biodiesel) from both the raw materials were simulated as pseudo-components. Cunico et al. (2013) have pointed the potential of group contribution methods to fatty compounds properties estimations. Thus, the individual critical properties, boiling point and acentric factor were estimated by the Constantinou-Gani group contribution method (Constantinou and Gani, 1994) and the Lee-Kesler mixing rules were used to estimate the properties of the mixtures. Because the compositions of the oils can vary, average compositions, based on literature data, were assumed (Knothe et al., 2005). The other properties were estimated based on the linoleic compounds for soybean derivatives and based on the palmitic compounds for palm derivatives, obtained in PRO/II ® biofuels databank.

Due to the presence of highly polar components, like ethanol and glycerol, the NRTL (Non-Random Two Liquid) model was used to predict the activity coefficients. Binary interaction parameters not included in the simulator's databank were estimated from the UNIFAC structure of the compounds (Zhang et al., 2003a; West et al., 2008).

The plant capacity was specified as the average production per plant in Brazil in the mid-2014. In June, there were 61 licensed production plants, producing a total of 21,167.79 m³/d. It corresponds to about 12,625 kg/h per plant, based on the soy biodiesel density (ANP, 2014).

2.1 Pre-treatment: esterification

Alkali catalysis is the most common way to produce biodiesel. However, before entering the transesterification reactor, the FFA content and humidity must be removed, to avoid the production of soap. Lepper and Frisenhagen (1986) developed a process to esterify the FFA present in vegetable oils, which was first reproduced in a process simulator by Zhang et al. (2003a) and, later, by other authors (West et al. 2008; Morais et al., 2010). This was the process adopted in this work, which is exposed in Figure 1.

The catalyst chosen for the esterification step was H_2SO_4, because of its low cost and high activity. A pure ethanol stream is firstly mixed with the catalyst and then conducted to the esterification reactor, which works continuously at 70 °C and 400 kPa. The esterification kinetics was assumed to be of reversible second order, based on the work of Pisarello et al. (2010). The quantity of ethanol added in the reactor was equal to 15 % in volume of the quantity of crude soybean oil (0.5 % FFA), which is the lower limit of the optimum range determined by Lepper and Friesenhagen (1986). But for palm, a quantity of ethanol equivalent to 45 % in volume of the quantity of crude palm oil (5 % FFA) was used. It was needed to displace the equilibrium in the products direction, based in an equilibrium constant value of 0.62 provided by Pisarello et al. (2010). A residence time of 0.3 h was necessary for the conversion of 50 % of the FFA in soybean oil and 7.1 h were necessary for the conversion of 95 % of the FFA in palm oil.

After esterification, the oil goes to a sequence of four mixers and settlers (simulated as flash vessels) where a glycerol washing is performed. The objective is to remove all the catalyst and humidity. A flash vessel operating under vacuum (30 kPa) is used to separate glycerine and ethanol. The same type of equipment was indicated by Garnica et al. (2009b). For the soybean oil process, the ethanol obtained in this step is under
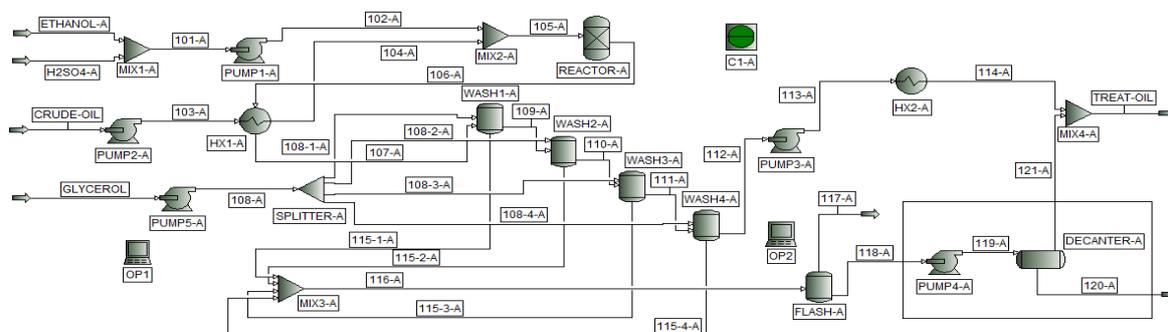

Figure 1: Pre-treatment module, with (palm) and without (soy) the decanter, indicated by the rectangle

specifications to be sold as anhydrous fuel in Brazil (ANP, 2011). But even with this small content of water, it is not recommended to recycle this alcohol to the esterification reactor, because the water could accumulate and be carried to the transesterification reactor. The ethanol obtained in the palm oil process could only be sold in Brazil, without a specific treatment step, as hydrated ethanol fuel, because of the higher quantity of water generated in the esterification reactor.

There is another difference between the soybean oil process and the palm oil process. In the second one, because of the higher quantity of ethanol and solvent needed for washing, some volume of biodiesel is lost in the extract. This behaviour has already been described by França et al. (2011). To recover this volume, the glycerine goes to a decanter, where a simple gravitational separation could happen. The biodiesel and the oil recovered meet the raffinate stream and go to transesterification. In the soybean oil process the decanter is not necessary.

2.2 Transesterification

The process adopted to perform the homogeneous alkali transesterification is similar to the process used by Zhang et al. (2003a) and is shown in Figure 2. Although in the process with methanol an alcohol to oil ratio of 6:1 is recommended (Freedman et al., 1984), when the vegetable oil is processed with ethanol, a higher ratio is generally used. A molar ratio of 9:1 was adopted in this work. The transesterification reactor works continuously at 50 °C and 400 kPa. The kinetics of the reaction was assumed to be of irreversible second order, based on the work of Shahla et al. (2012).

The catalyst chosen for the transesterification was NaOH, because of its low cost and high activity. It is firstly dissolved in pure alcohol and the mixture is added in the reactor. The same occurs with the pre-treated oil. Based on the contribution of Garnica (2009a), who studied these reactions for soybean oil and palm oil in the same conditions, the residence time for 95 % conversion was obtained from simple component molar balances for the batch experiments and for the continuous reactor simulated in this study. For soybean, the residence time was estimated as 6.6 h, while for palm it was 8.9 h.

The product of the reaction goes to a distillation column, to recover the excess of ethanol. The column operates with six theoretical stages, including condenser and reboiler, and reflux ratio of two. Vacuum operation (10 kPa at the top and 30 kPa at the bottom) is necessary to avoid degradation of the biodiesel or the glycerol (Zhang et al., 2003a). Almost 99 % of the ethanol present in the product stream could be recycled to the reactor.

Then the product goes to a water washing, in a sequence of four mixers and settlers (simulated as flash vessels). The objective is to separate the catalyst and glycerine. Biodiesel goes to a purification column, which operate with five theoretical stages and under vacuum. The biodiesel produced in the condenser has a purity of 99.7 %, a water content of 0.02 %, an alcohol content of 0.03 % and a FFA content below 0.25 % in mass. All other components are in a negligible scale. It satisfies the Brazilian and the American specifications. The effluent at the top consists of ethanol and water, and must be properly disposed. The effluent at the bottom consists mainly of unreacted oil.

Crude glycerine goes to a neutralizer reactor, which also receives the glycerine used in the esterification and an extra load of H_2SO_4. The reactor works continuously at 60 °C and 110 kPa. After a residence time of five minutes, it is assumed that all the sodium hydroxide reacts with the sulphuric acid, forming sodium sulphate (Na_2SO_4). The solid is separated in a clarifier and the glycerine can be sold.
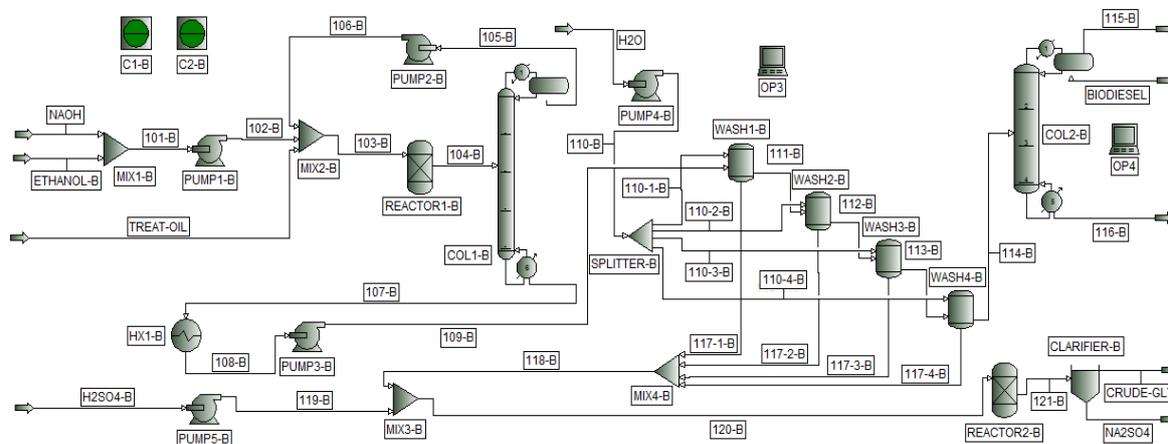

Figure 2: Alkali-catalysed transesterification module

3. Equipment Sizing and Economic Analysis

All the equipment was sized according to empirical guidelines described by Seider et al. (2003). The flash vessels were designed according to Towler and Sinnott (2008). The reactors volumes were obtained multiplying the entering flow rate with the residence time. A headspace of 20 % of the liquid volume was considered. The columns were packed with 2 inches carbon steel Pall rings. The height equivalent to theoretical plate (HETP) was obtained from empirical formulas and their diameters were calculated from Leva correlation. Heat exchangers were designed as single pass shell and tube. The pump type was chosen to minimize the cost, between centrifugal or external gear pumps. Equipment that work with sulphuric acid were designed with stainless steel and all the other equipment with carbon steel.

The equipment costs were calculated with empirical formulas proposed by Seider et al. (2003). The formulas consider experimental data collected from several sources. The equipment costs were updated from the year of 2000 to 2014 with the Chemical Engineering Plant Cost Index. Table 1 shows the size and costs of the main equipment present in the plants.

The economic evaluation was similar to the work of Zhang et al. (2003b) and West et al. (2008), except by the inclusion of a Lang factor of 4.8, following the guidelines proposed by Seider et al. (2003). Table 2 shows the price scenario considered in this work. These were the medium prices practiced in Brazilian foreign and internal trades in the first semester of 2014. The main parameters evaluated were total investment, total manufacturing cost, the annual net profit and biodiesel break-even price. Table 3 shows these results.

Table 1: Main equipment size and cost

Main Process Equipment		Soy	Palm
Reactors	Esterification		
	Size (D x H), m	1.37 x 4.11	4.21 x 12.64
	Cost, ($ x 10^{-3})	380.27	2057.59
	Transesterification		
	Size (D x H), m	3.94 x 11.82	4.64 x 13.92
	Cost, ($ x 10^{-3})	1752.67	2155.20
	Neutralization		
	Size (D x H), m	0.49 x 1.48	0.54 x 1.63
	Cost, ($ x 10^{-3})	148.05	159.51
Columns	Ethanol Recovery		
	Size (D x H), m	1.61 x 12.42	1.60 x 12.41
	Cost, ($ x 10^{-3})	219.93	217.56
	Biodiesel Purification		
	Size (D x H), m	2.95 x 13.70	2.92 x 13.64
	Cost, ($ x 10^{-3})	372.31	374.15
Separators	Flash Vessel		
	Size (D x H), m	1.37 x 2.30	2.26 x 3.51
	Cost, ($ x 10^{-3})	74.09	151.10
	Decanter		
	Size (D x L), m	-	0.23 x 0.93
	Cost, ($ x 10^{-3})	-	11.67
	Glycerol Washing Vessels		
	Size (mixers), m	1.21 x 1.21	1.31 x 1.31
	Size (settlers), m	0.59 x 2.35	0.66 x 2.64
	Cost, ($ x 10^{-3})	247.79	280.99
	Water Washing Vessels		
	Size (mixers), m	1.22 x 1.22	1.22 x 1.22
	Size (settlers), m	0.59 x 2.35	0.59 x 2.38
	Cost, ($ x 10^{-3})	119.56	125.79
	Clarifier		
	Sedimentation Area, m²	25.04	24.79
	Cost, ($ x 10^{-3})	68.08	67.68

Table 2: Price scenario in Brazil mid-2014. Medium prices of foreign and internal trades (US$/kg)

RM and Products	Prices	Catalysts and Solvents	Prices	Utilities	Prices
Soybean Crude Oil	0.8790	Tec. Grade Glycerol	0.7900	Superheated Vapour	0.0100
Palm Crude Oil	0.8690	Crude Glycerine	0.3300	Vapour 400 psi	0.0015
Anhydrous Ethanol	0.7461	NaOH	0.5100	Natural Water	0.00005
Hydrated Ethanol	0.6993	H_2SO_4	0.2000	Ammonia 34 °F	0.0005
Biodiesel	0.9600	Na_2SO_4	0.1200	Electricity (US$/KWh)	0.1375
Effluent Disposal	0.1500	Ethylene Glycol	0.9100		

Table 3: Cost, revenues, annual net profit and biodiesel break-even prices ($ x 10^{-6})

			Soy	Palm
Capital Cost				
	Total Equipment Cost		3.61	5.86
	Fixed Capital Cost, C_{FC}		18.21	29.53
	Working Capital, $C_{WC} = 0.15C_{FC}$		3.41	5.54
Total Capital Investment, $C_{TC} = C_{FC} + C_{WC}$			21.63	35.06
Direct Costs				
	Feedstock			
		Crude Oil	88.11	86.51
		Ethanol	20.02	34.77
	Catalysts and Solvents			
		Glycerol	14.48	15.94
		H_2SO_4	0.25	0.24
		NaOH	0.51	0.51
		Washing Water	0.0001	0.0001
	Operating Labour, C_{OL}		0.44	0.44
	Supervisory and Clerical Labour, $C_{SC} = 0.15C_{OL}$		0.07	0.07
	Utilities			
		Superheated Steam	9.29	8.70
		Saturated Steam	0.15	0.15
		Cooling Water	0.33	0.31
		Electricity	0.18	0.47
	Effluents Disposal		0.83	0.81
	Maintenance and Repairs, $C_{MR} = 0.06C_{FC}$		1.09	1.77
	Operating Supplies, $C_{OS} = 0.15C_{MR}$		0.16	0.27
	Laboratory Charges, $C_{LC} = 0.15C_{OL}$		0.07	0.07
	Patents and Royalties $C_{PR} = 0.03C_{TP}$		5.03	5.61
	Subtotal		141.02	156.63
Indirect Costs				
	Overhead, Packaging and Storage, $C_{OPS} = 0.60(C_{OL}+C_{SC}+C_{MR})$		0.96	1.37
	Local Taxes, $LT = 0.015C_{FC}$		0.27	0.44
	Insurance, $IN = 0.005C_{FC}$		0.09	0.15
	Subtotal		1.33	1.96
General Expenses				
	Administrative Costs, $C_{AD} = 0.25C_{OPS}$		0.24	0.34
	Distribution and Selling Costs, $C_{DS} = 0.10C_{TP}$		16.77	18.70
	Research and Development, $C_{RD} = 0.05C_{TP}$		8.39	9.35
	Subtotal		25.40	28.39
Total Production Cost, C_{TP}			167.74	186.98
Revenues				
	Annual Biodiesel Sales		95.99	95.99
	Annual Glycerine Credit		10.59	11.61
	Annual Na_2SO_4 Credit		0.21	0.21
	Annual Ethanol Credit		7.87	19.86
Total Revenue			114.66	127.67
Annual Net Profit			- 53.09	- 59.31
Biodiesel Break-even Price (US$/kg)			1.53	1.62

It was not profitable to produce biodiesel from ethanol in Brazil in the considered scenario. Compared to the work of Zhang et al. (2003b), it is possible to see how much the high costs related to the use of ethanol contribute to the higher biodiesel price. The higher content of FFA makes palm biodiesel more expensive than soy biodiesel, because of the higher content of ethanol and the higher equipment volumes needed to deal with it. The cost of vegetable oil corresponds to 46-53 % of the total costs and 55-62 % of the direct costs. Therefore, crude palm oil and crude soybean oil prices are important factors and palm could become advantageous if the palm planting growth in Brazil result in price reductions, as expected.

4. Conclusions

This work compares soybean oil and palm oil as feedstock for biodiesel production with ethanol in Brazil, mid-2014. The economic analysis showed that palm biodiesel is more expensive than soy biodiesel and biodiesel with ethanol is not profitable without subsidy. A proposed solution is to focus subsidies and tax reductions in the vegetable oil acquisition, because of its big contribution to the total production cost. A vertical integration of the process, with refiners purchasing directly the seeds and extracting the oil should contribute to lower biodiesel prices. Another option to cost reduction is the treatment and recycle of the process effluents, composed mainly by unreacted oil, ethanol and glycerol. This study is been performed as a development of this work.

Acknowledgements

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