Integral analysis of feedstocks and technologies for Biodiesel production in tropical and subtropical countries

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Abstract: In this work different methodologies from process engineering based on conceptual design and process simulation with ASPEN PLUS, life cycle assessment and waste reduction algorithm are used for energy, and environmental impact assessment of 5 different feedstocks (Palm, Jatropha, Microalgae, Tallow, Waste Cooking Oil) using 3 different technological configurations from industry, such processes with acid catalysis, basic catalysis and cogeneration, at Colombian and Peruvian context. It was found how productivities for process catalyzed with NaOH are comparatively higher (1.007-1.014 kg of Biodiesel per kg of Crude Oil), than those catalyzed with H_2SO_4 (0.845-0.949 kg of Biodiesel per kg of Crude Oil). The Production costs for basic catalyzed processes (USD/L 0.408-0.505) were higher than those for acid catalyzed processes (USD/L 0.219-0.257). The PEI (Potential Environmental Impact) generated for basic catalyzed, had a PEI per kg between -0.078 and -0.033, while acid catalyzed -0.031 and -0.025. Finally LCA for jatropha and palm oil process, evidence Ecosystem Quality damage, a Resources damage, a Human Health damage lower for Jatropha oil in comparison to Palm oil. The Jatropha oil, in a basic catalyzed configuration with energy cogeneration is the best alternative of process, environmental and economics by biodiesel production.

Keywords: *Integral Analysis, Biodiesel, WAR algorithm, LCA, Economic Evaluation*

1. Introduction

Biodiesel is produced from various fat and oils with vegetable, animal or algae origin. These Feedstocks (mainly composed by triglycerides), through transesterification reaction with short chain alcohols and in presence of catalyst, yields to fatty alkyl esters and glycerol as byproduct [1]. Almost 95% of vegetable oils used in biodiesel production are edible (palm, soybean, rapeseed oils). Different positive characteristics are related to Biodiesel: improvement of the environment, reduction of foreign oil imports, increase in rural job and energy self-sufficiency in rural areas. However, not all the above mentioned advantages are reached for all biodiesel feedstocks. Edible crops have food competition; possibly leading to food shortages and increase in their prices. Moreover, an expansion of these crops could require monoculture plantation, affecting water resources and biodiversity. Tropical and subtropical countries are called to be the future world suppliers of feedstocks and biodiesel given the high productivity in crops and algae. Most of these countries are involved in a difficult decision of what kind of feedstock should be used, and then the policies to be developed for encouraging new projects, with new feedstocks. Non-edible oils (jatropha and microalgae oil), allows the employment at massive scale of agricultural/degraded/waste lands, preserving most productive lands for food production. Animal fat (tallow oil) and waste cooking oil are valuable alternatives due their low market prices and availability. Additionally, aiming to increase competitiveness of oilseed based biodiesel plants is an actual trend to use cogeneration plants. Last allows the satisfaction of local heat and power requirements, while surplus electricity is sold to central grid [2]. In this work different methodologies from conceptual design and process simulation with ASPEN PLUS, life cycle assessment and waste reduction algorithm are used for energy, and environmental impact investigation of 5 different feedstocks using 3 different technological configurations from industry, such as process with acid catalysis, basic catalysis and cogeneration. The study was developed in the framework of two countries Colombia and Peru. As a result, two feedstocks and one technological configuration are defined as the more convenient for biodiesel production in these countries.

2. Feedstocks for biodiesel production

In this work five feedstocks for biodiesel production, are analyzed, which can be potentially used in tropical and subtropical countries. i) **Oil Palm,** is one of the largest supply of edible oil in the world, extended throughout tropics, among major producers are Malaysia, Indonesia and Colombia with 83% of global production [3]. It is a high yield crop that requires small areas to be cultivated. ii) **Jatropha Curcas**, a Native American tropical crop, is a small tree belonging to the family of *Euphorbiaceae*. This crop is highly resistant plant capable of surviving in fallowed agricultural lands and low to high rainfall areas, being easily cultivated with little effort to sustain [4]. iii) **Microalgae**, is a promising feedstock, due to its ability to accumulate lipids and their high photosynthetic yields. Those used in biodiesel production are comprised by up to 40% of overall mass by fatty acids, among its representative species are: *Chlorella, Spirulina maxima,* and *Nannochloropsis sp.* They are fast growers in aquatic habitats, under autotrophic and heterotrophic conditions [5]. iv) **Waste oil**, includes residues from frying oils, soap stocks, yellow and brown greases, obtained from restaurants, hotels and industries; Their Free fatty acid content range between 10 and 25%, as result of frying process where heating in presence of air and light increase viscosity and specific heat, also changing surface tension, color and tendency to fat formation. This feature makes necessary a pretreatment stage before be converted in biodiesel [6]. Finally, v) **Tallow oil**, is a term referred to those fat and greases obtained in slaughter processing facilities from animals. Human consumption of tallow oil is low due its effect on health, finding its main use in the soap industry. However, when its market is overloaded, this oil is incinerated or disposed in landfills [7]. Because of that its use as biodiesel feedstock, is an attractive alternative due its easy availability and historical low prices.

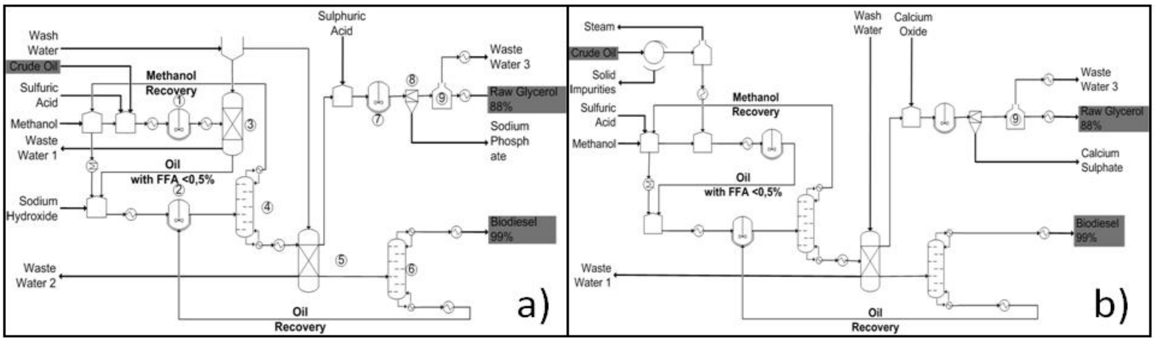

Fig. 1. Process flow diagram for Biodiesel production Using: a) Acid Catalysis; b) Basic Catalysis.

3. Technologies for Biodiesel Production

Biodiesel production can be described, in a general way, by three main sequential stages: i) **Pretreatment,** where undesired elements content in feedstock oil are withdraw. Particles, colloidal mater, pigment, extraction residues and other impurities can be removed using filtration. When water content (>0,06%) and free fatty acid (FFA) content (>4%), a saponification reaction can be induced, generating a gel soap instead of biodiesel. To avoid this is necessary dry the oil, and eliminate free fatty acids, using: Presterification or neutralization. ii) **Reaction,** in this stage, the oils suffer a transesterification reaction. Methanol is the most extensively used alcohol because its low cost and physical and chemical properties. The main catalysts, employed in transesterification process are: acids (sulphuric, phosphoric) or bases (sodium and potassium hydroxide) [8]. iii) **Separation and Purification**

stage is employed to produce biodiesel with high quality requirements. Biodiesel purification is performed by either of two main routes: 1) separating first esters and glycerin, before recover non c onverted alcohol or 2) using vacuum distillation to separate non c onverted alcohol, using then a decanter to separate glycerin and biodiesel [8]. Obtained biodiesel is then purified, removing excess of alcohol, catalyst, neutralization salts and possible soaps formed. The Selected technology for biodiesel production determines main process variables, such as: reaction time, phase, catalyst, as well as energy consumption (see Fig 1).

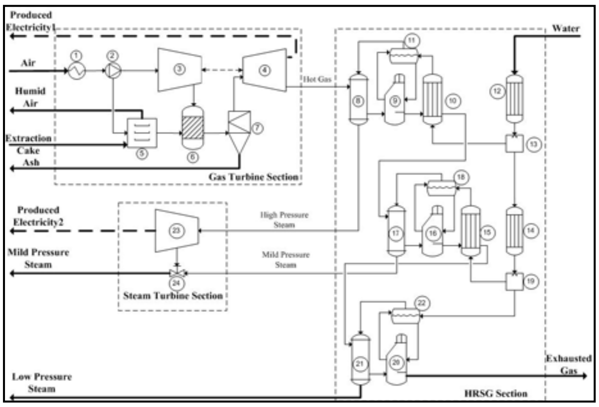

Fig. 2. Process flow diagram for Cogeneration system based on extraction cake residues

Cogeneration plants integrated to biodiesel production facilities usually employs extraction cakes and other biomass residues as fuel in a configuration called biomass fired cogeneration. Combined production of mechanical and thermal energy has remarkable cost and energy savings. Among available technologies for biomass fired cogeneration, the combined cycle gas turbine (CCGT), is considered as the most energy efficient. CCGT configurations are composed by: Gas Turbine, Heat steam recovery generator (HSRG) and Steam Turbine (see Fig. 2) [9].

4. Methodology

The simulations of biodiesel production and heat and power cogeneration were carried out in Aspen Plus 2006.5 (Aspen Technologies Inc., USA). This scheme allows obtaining data of mass and energy balances; as well as, basic engineering estimations of equipment size and its energy consumption. Feedstocks (Palm, Jatropha, Microalgae, Tallow and Waste cooking oils) for biodiesel production, were modeled as a sort of pseudocomponents, created to represent triglycerides and methyl esters; according to Chang and Liu methodology [10]. Conversely, Palm oil cake, jatropha oil cake and microalgae paste were introduced to simulator database as non conventional components according to its elemental and immediate analysis. Physicochemical properties for pseudocomponents, were estimated using the Marrero and Gani Method [11]. UNIFAC Dortmund for liquid phase, Soave Redlich Kwong with the Bosto Mathias modification for the vapor phase; water enthalpy calculated with NBS steam tables, were used as base methods. The Kinetic model for acid and basic catalysis, employed in this work, was reported by Granjo et al. [12], as first order and second order expressions, respectively. Biodiesel simulated process use a same flow rate input of 1000 kg/h, to make a comparison among yields for all processes. Additionally, from these values, was calculated a residue flow rate for palm oil cake, jatropha oil cake and microalgae paste; using it as input for the biomass fired cogeneration system. The economic analysis was performed using Aspen Icarus Process Evaluator package (Aspen Technology, Inc., USA), to calculate a mean cost in US dollar per liter for biodiesel produced with the selected feedstocks. This analysis was performed using the design information provided by Aspen

Plus, under the economic conditions of Colombia (annual interest rate of 17% and tax rate of 33%) and Peru (annual interest rate of 18% and tax rate of 30%). A straight Line depreciation method, at 12 year of analysis period, was considered. For feedstock prices, were employed the international reports from ICIS pricing; while, operative charges such operator and supervisor labor cost were defined for both countries at USD 2.14/h and USD 4.29/h, respectively. Electricity, potable water, low and high steam pressure costs were USD 0.0304/kWh, USD 1.25/m^3, USD 8.18/ton. The environmental impact was assessed with WAR, Waste Reduction algorithm (EPA, USA), to estimate the potential environmental impact (PEI) generated in the biodiesel production process. Considering eight environmental impact categories: Human toxicity potential by ingestion (HTPI), Human toxicity potential by exposure both dermal and inhalation (HTPE), Terrestrial toxicity potential (TTP), Aquatic toxicity potential (ATP), Global warming potential (GWP), Ozone depletion potential (ODP), Photochemical oxidation potential (PCOP), and Acidification potential (AP). The mass flow rate of each component in the process streams is multiplied by its chemical potency; determining its contribution to the potential environmental impact categories [13]. To compare the environmental profiles for all process, total PEI was determined by the sum of all (eight) potential environmental impact categories as follows: $\sum_{i=1}^{n} \propto_i \varphi_i$, where α_i is the weighting factor for potential environmental impact category *i*, and φ_i represents the potential environmental impact for category *i*. In this work all of the weighting factors were set equal to 1. Finally, Life cycle assessment was performed for those process with a potential impact in land change use (LCU), such palm and jatropha; using a demo version of SimaPro 7, with Eco-indicator 99 (E) as base method. The LCA study consists of four steps: Defining the goal and scope of the study; making a model of the product life cycle with all the environmental inflows and outflows; understanding the environmental relevance of all the inflows and outflows and finally the interpretation of the study [14].

Table 1. Simulation Results for Biodiesel Production using Basic or Acid Catalysis

	Basic Catalysis			Acid Catalysis	
	Palm Oil	**Jatropha Oil**	**Microalgae Oil**	**Tallow Oil**	**Waste Cooking Oil**
Materials (kg/h)					
Crude Oil	1000.00	1000.00	1000.000	1000.00	1000.00
FFA content (% wt)	6%	4%	4%	15%	10%
Water content (% wt)	0%	0%	0%	8%	12%
Methanol	160.21	214.75	207.77	1579.07	1772.44
NaOH	9.40	9.60	9.29	-	-
Water	1400.00	1400.00	1400.00	1250.00	1400.00
H_2SO_4	21.00	21.45	20.75	35.00	41.20
CaO	-	-	-	30.00	29.60
Products (kg/h)					
Biodiesel @>99% wt	1007.46	1009.69	1014.62	949.85	847.63
Glycerol @>88% wt	113.05	117.34	127.33	81.95	82.07
Waste Water	1010.95	942.77	1062.20	2163.03	1836.84
$CaSO_4$	-	-	-	104.51	95.27
Na_2SO_4	10.64	17.03	17.03	-	-

5. Results

In the simulation of biodiesel production for acid and basic catalyzed processes using palm, jatropha, microalgae, tallow and waste cooking oils, as feedstocks (see Table 1), was found how productivities for process catalyzed with NaOH are comparatively higher (1.007-1.014 kg of Biodiesel/kg of Crude Oil), than those catalyzed with H_2SO_4 (0.848-0.949 kg of Biodiesel/kg of Crude Oil). Otherwise, Methanol consumption as well as global energy consumption (heating and electricity) is higher for acid catalyzed process, requiring 1.579-1.772 kg of Methanol/kg of crude oil and heating of 53.389 - 69.112 MW respectively. About process residues, acid catalyzed processes also have higher production rates for waste water (1.863-2.163 kg of Water/kg of crude oil). Simulation results for the biomass fired cogeneration plant using palm oil cake, jatropha oil cake and microalgae paste as fuels (see Table 2), reveals how heating energy production from jatropha cake (31.34 MW) is higher than produced with Microalgae paste (33.82 MW) and palm oil cake (20.61 MW). Consequently, only heating requirements for biodiesel production from jatropha (26.59 MW) are fully satisfied. Biodiesel from palm oil and microalgae oil meet only 68.13% and 74.15%, respectively of its Heating requirements. Regard to electricity, all cogeneration processes cover at 100% biodiesel plant requirements, with a surplus able to be sold. However, among three residues consider, was microalgae paste who cogenerates more electricity (8.34 MW) than jatropha oil cake (7.06 MW) and Palm Oil Cake (4.88 MW).

Table 2. Cogeneration Results for Extraction residues Based Biomass fired cogeneration system

	Jatropha Oil Cake	Palm Oil Cake	Microalgae Oil Paste
Available Residue [kg/h]	3092	2304	3964
Calorific Value [MJ/kg]	15.77	12.32	14.21
Total Cogenerated Heating [MW]	31.34	20.61	33.83
Total Cogenerated Electricity [MW]	7.66	4.88	8.34

Table 3. Economic Evaluation Results for Biodiesel Production using Basic Catalysis

	Jatropha Oil	Palm Oil	Microalgae Oil	Waste Cooking Oil	Tallow Oil
	USD/L	USD/L	USD/L	USD/L	USD/L
Raw material Cost	0.325	0.426	4.646	0.139	0.186
Total utilities Cost	0.022	0.021	0.022	0.052	0.044
Operating Labor	0.008	0.008	0.008	0.009	0.008
Maintenance	0.005	0.004	0.005	0.002	0.002
Operating Charges	0.002	0.002	0.002	0.002	0.002
Plant Overhead	0.006	0.006	0.006	0.006	0.005
General and Administrative Cost	0.039	0.037	0.038	0.008	0.010
Subtotal Cost	0.408	0.505	4.727	0.219	0.257
Credit by electricity selling	- 0.252	- 0.168	- 0.278	0.000	0.000
Total Cost with Cogeneration	0.157	0.337	4.449	0.219	0.257

Results of economic evaluation for biodiesel production under Colombian and Peruvian contexts were quite similar and because of that, in table 3, average results are presented. As highlights results, Raw material cost for basic catalyzed processes (USD 0.325-4.646/L) were higher than those for acid catalyzed processes (USD 0.139-0.186/L). Otherwise, Utilities costs for acid catalyzed processes (USD 0.044-0.052/L) were higher than basic catalyzed process (USD 0.021-0.022/L). Remaining cost, for both processes were similar. As result, Production costs for basic catalyzed processes (USD 0.408-0.505/L) were higher than those for acid catalyzed processes (USD 0.219-0.257/L). However, considering Potential income for electricity selling at average price between Colombia and Peru, can be seen how total production cost for jatropha, palm and microalgae biodiesels were reduced to 0.157 USD/L, 0.337 USD/L and 4.449 USD/L, respectively.

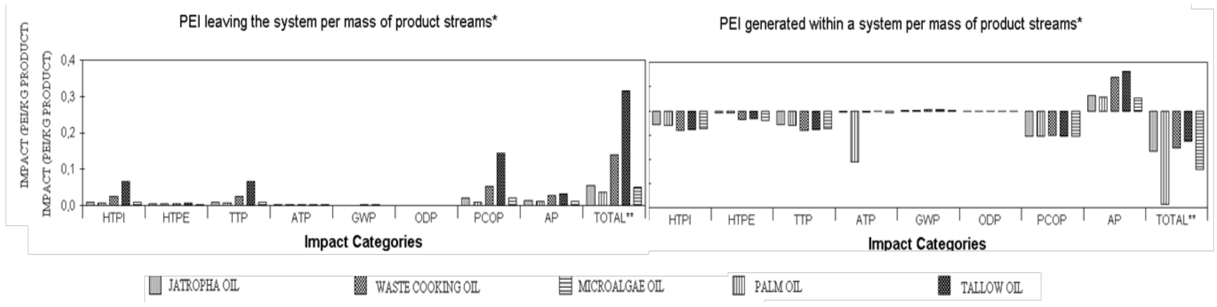

Fig. 3. PEI (Potential Environmental Impact) Analysis for Biodiesel Production from different feedstocks.

Regarding to environmental analysis; WAR analysis results of 5 biodiesel feedstocks, stated analyzing by process, how basic catalyzed had a PEI per kg of product ranging between 0.037 and 5.518e-2, while acid catalyzed catalysis between 0.139 and 0.317 for emissions output. Furthermore, when these feedstocks were analyzed by emission generation, basic catalyzed raw materials, had a PEI per kg between -0.078 and -0.033, while acid catalyzed -0.031 and -0.025 (see Fig. 3). Finally LCA analysis performed with SimaPro 7, for jatropha and palm oil process, evidence a Ecosystem Quality damage of 0.062 and 0.087 PDF*m^2*yr. Besides of a Resources damage of 1.07 and 1.49 MJ surplus, while Human Health damage was of 1.96e-6 y 2.73e-6 Daly, respectively.

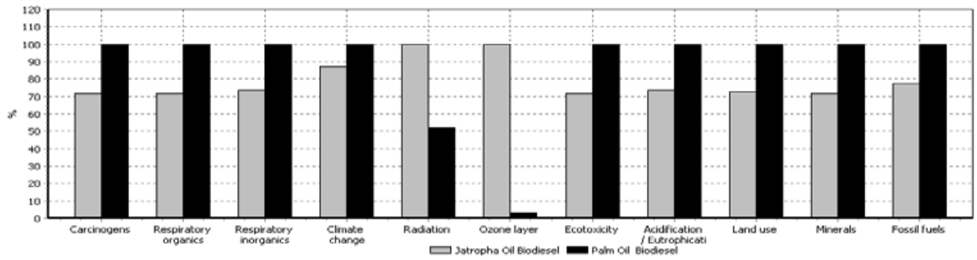

Fig. 4. LCA for Biodiesel Production from Jatropha oil and Palm oil

6. Discussion and Conclusions

In this work, the obtained results reveal how with selected five feedstocks is possible to obtain high quality biodiesel (>99 wt); besides, raw glycerol (88%wt). Among results for chemical processes simulation, can be seen how basic catalyzed processes have higher biodiesel yields (74-78%), than acid catalyzed ones (54-63%), with the consequent reduction in the total biodiesel produced. These results are lower compared with values between 90-95% reported from biodiesel simulations, on literature [15]. This fact can be explained by the lower quality of feedstocks considered, especially tallow and waste cooking oil, where a high FFA content and impurities presence; which, although increase the simulation quality, reduces the amount of initial reactant available for transesterification reaction, reducing also biodiesel produced.

Regard to cogeneration results, these gave an advantage to basic catalyzed processes due to the possibility of employ its extraction residues to generate heat and power. The bigger amount of heating potential was released by jatropha oil cake; while the higher power potential by microalgae oil paste. This result can be partially explained by the high calorific value and available flow of these residues, which increase its potential to generate steam and consequently produce heat and power (see Table 2). Jatropha oil cake results were the best, due its capacity to meet heating requirements of the biodiesel plant generating also an important amount of electricity able to be selling to central grid.

Economic evaluation of biodiesel production process, without cogeneration, shows how production cost for basic catalyzed processes initially were higher than acid catalyzed, despite high methanol consumption of this last. These results were agreed with those reported on literature where biodiesel production cost range between USD $ 0.30 – 0.6/L [16]. The main component of this production cost was the raw material price, which is higher for vegetable oils (jatropha and palm) than for residual oils (waste cooking and tallow), explaining their lower production cost. However, when a cogeneration scheme is included for processes based on vegetable oils, which can employs its extraction residues as fuel in a biomass fired scheme, the total production cost of basic catalyzed process is reduced (see Table 3). Apart mention, deserves microalgae oil, which price as feedstock still today is higher, mainly due the high energy consumption in its processing, either in open pounds or bioreactors; in the future is expected is expected a reduction in its price using better microalgae oil production technologies.

The Environmental analysis results, reveals with WAR algorithm, how despite all processes had a positive PEI, still all of them can generate acid rain because its positive acidification potential produced by the sulphuric acid. In these sense, acid catalyzed processes had more polluting waste streams than basic catalyzed. Particularly, output emissions from process waste streams for waste cooking oil, had the more positive PEI among all simulated processes. This effect could be explained by the substances contained in its process residues, which had a high degree of potential PCOP influenced by acid catalysis, increasing the total values. Otherwise, palm and jatropha oils had the comparatively lesser PEI, revealing them as environmentally friendly feedstocks; because, they are converted to high value products in a cleaner process (basic catalysis) being more environmentally favorable, reducing significantly the aquatic toxicity potential. Regard to LCA analysis performed to jatropha and palm oils as best WAR results, was found that most promising feedstock was the jatropha oil because its comparatively low land use than the palm and its possibility of growth in fallow agricultural lands. Also, its impact on climate change and emissions were lower than palm at every stage, from cultivation to waste scenarios.

In conclusion, the more convenient configuration for biodiesel production in tropical and subtropical countries is employ jatropha oil in a basic catalyzed scheme, integrated to a cogeneration plant fired with jatropha oil cake. This configuration is able to produce high rates of biodiesel with the lower production cost, improved by electricity selling. Also, this configuration proves, be the most environmentally friendly with lesser potential emissions and climate change effect, as well as reduced land use by its ability to be growth in marginal lands.

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