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# Stand-alone and Biorefinery ways to produce bioenergy from solid biodiesel wastes in Colombia

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## Abstract

A techno-economic assessment for the production of butanol, hydrogen, biogas, biodiesel and ethanol from oil palm was studied taking into account the biorefinery and stand-alone concept. An experimental analysis involved the physicochemical characterization of the palm empty fruit bunches (EFB) obtained as a solid residue in Palm Biodiesel Industry to. The experimental results for this raw material were used to feed the simulation procedure, which was the basis for the techno-economic assessment on a biorefinery concept according to the Colombian conditions. For the biorefinery the obtained economic margin was 45.42%. Production costs of butanol, hydrogen, biogas, biodiesel and ethanol were 1.41 USD/Kg, 1.35 USD/Kg, 0.76 USD/Kg, 0.74 USD/Kg and 0.56 USD/Kg, respectively.

Keywords bioenergy, biorefinery, techno-economic assessment, oil palm.

## 1. Introduction

Last years the interest for the development and production of sustainable, renewable, clean and energetic efficient fuels is increasing dramatically (Cherubini, 2010), (EIA, 2013). Currently, the population growth has caused an increase in energy demand especially in the transportation sector. According to (U.S. Department of Energy, 2014) the world consumption of fuel is 190 million per day approximately. This great volume indicates the necessity of the inclusion of alternative fuels.

In the past decade, the production of biofuels from feedstocks with low production cost which do not compete with the worldwide food security have been studied (Rincón et al., 2014a). These feedstocks play an important role in mitigation of environmental pollution. According to the Colombian commercial chamber PROEXPORT, Colombia is the fifth producer of palm oil worldwide and the number one in Latin-America due to its favorable agro-ecological conditions (Rincón et al., 2014b). Oil from palm and residues of palm leads to the formation of products that have an economic potential. Oil palm fresh fruit bunches (FFB) are harvested and processed in an extraction plant to produce palm oil. The FFB contains crude palm oil (15–18%), shells (5–6%), kernels (5–6%), palm fiber (12–14%), and empty fruit bunches (25–27%) (FAO, 2002). An average yield of 230 Kg EFB per Ton of FFB can be obtained. There is a large potential of transforming EFB into renewable energy resource that could meet the existing energy demand of palm oil mills or other industries. However, pre-processing is necessary before EFB can be considered as a good fuel since the moisture content in EFB is around 67%.

This work develops a design and analysis strategy for the production of biofuels from oil palm by means of technoeconomic assessment. All the integrated processes to produce energy from biomass are projected in a profitable and sustainable vision within the biorefinery concept. Energy biorefineries is a new concept that highlights the only production of different types of bioenergy (either direct, such as from combustion of biomass, or indirect, for instance through biofuel production). Aspen plus V8.2 was used as computational tool for the techno-economic evaluation of energy biorefinery. The products of biorefinery are: ethanol, butanol, hydrogen, biogas and biodiesel. Biodiesel was obtained from palm oil (Maria et al., 2009). Ethanol was produced from glycerol as residue of biodiesel production by fermentation using *Escherichia coli* (Chaudhary et al., 2011). Empty fruit bunch of palm as lignocellulosic raw material was used in the production of butanol, hydrogen and biogas. Butanol production was obtained by acetone, butanol and ethanol (ABE) fermentation of sugars using *Clostridium beijerinckii* (Merwe, 2010). Hydrogen was made by dark fermentation using anaerobic digestion model (ADM1) using as substrate glucose (Gadhamshetty et al., 2010). As a result, a prefeasibility study of ethanol, butanol, hydrogen, biogas and biodiesel was developed to demonstrate that the biorefinery concept can be an interesting option for the production of fuels.

## 2. Materials and Methods

## 2.1 Raw material

Empty fruit bunches (EFB) were obtained from an oil palm extraction plant (Palmar Santa Elena) located at Tumaco town (1° 48' 24" N, 78° 45' 53" W), in the southwest cost of Colombia, which altitude is 2 meters above sea level.

The physicochemical characterization was performed with two replicates. Drying was carried on in an oven at 75°C during 6 hours until constant weight. Finally, dried material was ground to pass 10 mesh (2 mm) using a mill blade (Thomas Model 4 Wiley® Mill).

EFB were characterized to determine extractive, ash, holocellulose, cellulose and lignin content. Both, extractives and ash content were determined using an ethanol-water mixture and total ignition of samples respectively according to the procedures reported by National Renewable Energy Laboratories (NREL/TP-510-42619 and NREL/TP-510-42622) (Sluiter, Ruiz, Scarlata, Sluiter, & Templeton, 2008) (Sluiter, Hames, et al., 2008). Holocellulose content was determined with the chlorination method described by the ASTM Standard D1104 (Han & Rowell, 1997). Cellulose content was calculated after holocellulose content determination in pursuit of the ultimately pure form of fiber (Han & Rowell, 1997). Finally, hemicellulose content was calculated by subtracting the cellulose content from the holocellulose content. This chemical characterization was used as the initial composition of EFB in the simulation of the process to obtain hydrogen, butanol and biogas.

According to (Gui et al., 2008), the oil of palm is composed mainly by palmitic and oleic acid with 35.9 and 41.1% respectively. This chemical composition was fed to simulation to produce biodiesel.

## 2.2 Process simulation description

The simulation of biorefinery includes all the processing steps to obtain biofuels from EFB and palm. The objective of this procedure was to generate the mass and energy balances from the requirements for raw material, consumables, utilities and energy. The main computational tool used was the commercial package Aspen Plus v8.0 (Aspen Technologies Inc., USA). Specialized package for performing mathematical calculations especially for kinetic analysis such as Matlab was also used. Non-Random Two-Liquid (NRTL) thermodynamic model was chosen to calculate the activity coefficients of the liquid phase while the Hayden-O'Conell equation of state is used for description of the vapor phase. Also the UNIFAC-DORTMUND and Soave Redlick Kwong models for liquid and vapor phases were needed when the NRTL model do not predict properties.

Same methodology was used to describe the simulation of each stand-alone process; however, each process was taken individually in order to generate the mass ad energy balances. Sugar extraction procedure for each individual process was performed due to the use of lignocellulosic material that would need to increase its biodegradability.

## 2.2.1 Sugar extraction

EFB were submitted to a process consisting in two stages as follow described: i) size reduction and pretreatment and ii) enzymatic hydrolysis. The first stage of the process involved a size reduction stage in which the expected final particle diameter was 1 mm. After milling and sieving, in the second stage the cellulose fraction was hydrolyzed based on kinetics expressions reported by (Morales-Rodriguez et al., 2011) at 35°C to obtain a rich-hexoses liquor and a solid residue rich in hemicellulose and lignin. Rich-hexoses liquor was sent to hydrogen and butanol production and resulting solids were sent to the biogas production.

## 2.2.2 Hydrogen production

Hydrogen is obtained from the 50% of rich- hexose liquor via dark fermentation using Anaerobic Digestion Model (ADM1). Fermentation process is carried out based on the kinetics expressions reported by Gadhamshetty et al., 2010 at 37°C. Afterwards, cell biomass and solids are separated from the culture broth. Finally, PSA (pressure swing adsorption) was used for hydrogen separation (Biswas et al., 2010).

## 2.2.3 Butanol production

The remaining 50% rich-hexose liquor was sent to sterilization process at  $121^{\circ}$ C in which the biologic activity is neutralized. Then, the ABE fermentation process is carried out based on the kinetic expressions reported by (Merwe, 2010) at 33°C using *C. acetobutylicum* as microorganism. Afterwards, cell biomass is separated from the culture broth containing approximately 5% (wt/wt) of butanol. The resulting stream is taken to the separation zone, which consists of three distillation columns. In the first column, some organic components and the most of the water are removed, concentrating the butanol up to 53%. The second column removes acetone and ethanol, obtaining butanol is at 69%. Finally, in the third column of the mixture water-butanol is separated for obtaining butanol at a concentration of 90% by weight (Merwe, 2010).

## 2.2.4 Biogas production

The process started with the pretreatment of the stream with ammonia in order to remove part of the lignin and to enhance the hydrolysis of the biomass, preserving the most of the fermentable fraction. The pretreatment process was performed at 51°C, with ammonia at 14.8% in a 1:10 solid to liquid ratio and a residence time of 27 h (Li et al., 2014). After the pretreatment, the resulting streams are filtered and the remaining solids were used to obtain biogas through anaerobic digestion at 35°C during 20 days. Anaerobic digestion process was carried out based on the kinetics expressions reported by (Borja et al., 2005).

## 2.2.5 Biodiesel production

Biodiesel production is described by three sequential main stages. Initially, pretreatment where unwanted elements contained in the crude oil were retired and a neutralization or preesterification reaction to remove free fatty acids was carried out. Afterwards, the reaction step wherein the oil undergoes a transesterification reaction with methanol catalyzed by sodium hydroxide. Reaction stage is carried out based on the kinetics expressions reported by (Granjo et al., 2009). Finally, the step of separation and purification is performed using vacuum distillation to remove the alcohol which is not

converted, using a decanter to separate the glycerin and biodiesel (Fangrui et al., 1998). The biodiesel obtained is then purified by removing excess alcohol, catalyst, possible neutralization salts and soaps formed.

## 2.2.6 Ethanol production

Initially the glycerol obtained as byproduct of biodiesel production process is sent to a sterilization process at  $121^{\circ}$ C in which the biological activity is neutralized. Later the fermentation process is carried out based on the kinetic expressions reported by (Chaudhary et al., 2011), at 37°C using *Escherichia coli* as microorganism. Afterwards, cell biomass is separated from the culture broth by a simple gravitational sedimentation technology. After the fermentation stage, the culture broth containing approximately 5-10% (wt/wt) of ethanol is taken to the separation step, which consists of two distillation columns. In the first column, ethanol is concentrated nearly to 45-50% by weight. In the second column, the liquor is concentrated until the azeotropic point (96% wt/wt) to be led to the dehydration step with molecular sieves to obtain an ethanol concentration of 99.6% by weight (Pitt, Haag, & Lee, 1983).

Energy producing biorefinery considered the production of butanol, hydrogen and biogas production from empty fruit bunches and biodiesel and ethanol production from oil. Both raw materials are main components of oil palm. For the analyzed biorefinery, the feedstock corresponds to 1 tonne/h. Figure 1 shows the diagram description of the biorefinery proposed.

Figure 1. Flowsheet for palm biorefinery to produce bioenergy.

## 2.3 Economic Assessment

The capital and operating costs were calculated using the Aspen Process Economic Analyzer software (Aspen Technologies, Inc., USA). This analysis was estimated in US dollars for a 10-year period at an annual interest rate of 17% (typical for the Colombian economy), considering the straight-line depreciation method and a 25% income tax. Prices and economic data used in this analysis as indicated the table 1, correspond to Colombian conditions such as the costs of the raw materials, income tax, labor salaries, among others, were incorporated in order to calculate the production costs per kilogram of product.

 Table 1 Price/cost of feedstock and products used in the economic assessment.

## 3. Results and Discussion

## 3.1 Physicochemical characterization

The chemical composition of the main components in EFB is shown in Table 2. As can be seen, the highest compositional content, in dry basis, was for the cellulosic component. In contrast, lignin content is nearly the half cellulose composition in the material. This fact shows up two important advantages EFB to be used as potential feedstock for butanol, hydrogen and biogas production; First of all, this byproduct is a material enriched in cellulose which can potentially be recovered as reducing sugar source. Secondly, the low lignin content associated with the cellulose makes technical and economically feasible the recovery of almost completely the total cellulose by using a suitable delignification process. Finally, the mean moisture content found in EFB is nearly 65.04% leading to conclude that a previous drying process for the material must be included if a size reduction is need.

Table 2. Empty fruit bunches composition in wet basis.

## 3.2 Process simulation

Simulation of production processes described are used to generate their respective mass and energy balances, which are the basic input for the techno-economic assessment. Table 3 shows the production capacities for processes. The analysis is focused in the influence of raw material on the overall performance of the proposed biorefinery (see, Figure 1).

Table 3. Production capacities and global yields of the products obtained in oil palm biorefinery.

(Noomtim & Cheirsilp, 2011) studied the effect of the pretreatment in EFB to produce butanol. The yield of butanol that can be obtained from EFB was 0.04 Kg Butanol/Kg sugars. The composition of sugars in the EFB after the hydrolysis step is referred that from 1 Kg of EFB approximately 0.1014 Kg of sugars can be produce. (Chong et al., 2013) studied the production of hydrogen using prehydrolysate EFB as raw material through fermentation n by acclimatized mixed consortia. From 1 Kg of EFB approximately 0.003 Kg of hydrogen can be obtained using acid hydrolysis as pretreatment step. (Nieves, Karimi, & Horváth, 2011) studied the use of ligcellulosic materials (EFB) in the production of biogas. The lignocellulosic material was previously hydrolyzed with NaOH in order to increase it biodegradability. The results shows

that from 1 Kg of EFB, 0.21 Kg of methane can be obtained. Methane and carbon dioxide are the two main gases species that constitute the biogas. Methane corresponds to a fraction between 55 - 65%. From this relation, it ca be calculate the amount of biogas produce per Kg of EFB that corresponds to 0.3 Kg of biogas. (Rincón et al., 2015) evaluated the optimal conditions of the supply chain biodiesel in Colombia using palm oil for biodiesel production. The productivity yield obtained from the evaluation was 1.007 Kg of Biodiesel per Kg of palm oil. (Posada et al., 2012) evaluated the production of ethanol using glycerol as raw material. Glycerol is obtained from biodiesel production process as a residue with high potential for fuel production. According to this analysis, 0.027 Kg of ethanol per Kg of palm oil can be obtained using as raw material the glycerol obtained from the transesterification process in the biodiesel production.

The implementation of the biorefinery concept as a new alternative for the production of a variety of products with high added value taking full advantage all the process streams. This concept provides higher yields than those obtained for stand-alone processes, as can be observed in the previously results.

## 3.3 Economic analysis

The economic assessment aims to calculate production costs and incomes by product sales (see, Table 4). The operating cost includes various aspects inherent to the production process such as raw materials, utilities, labour and maintenance, general and administrative costs, annualized capital costs.

## Table 4. Production cost for each product.

The features that most affect the production cost are raw materials, utilities and capital depreciation (see, Figure 2), which are directly related with feedstock purchasing price and consumables, energy consumption and equipment use respectively. To estimate the costs of raw materials on the biorefinery process, the basic purchasing costs were included. Also materials needed for each biorefinery plant were considered (Figure 1). The current work shows that the share of raw materials is above 30% for biorefinery. This is remarkable since in the majority of industrial processes, raw materials represents approximately more than 50% of total production costs. However, the integrated approach of a biorefinery leads to reductions in costs because material streams from one process can be connected to a subsequent process as shown in Figure 1.

Figure 2. Shares of features for each process production.

To evaluate the entire economic performance of the proposed concepts, the economic margin is used as parameter to assess the economic behavior of bioenergy production on a biorefinery concept (Moncada et al., 2013). This parameter is defined as the ratio of the net incomes (sales – cost) over the total sales, and was applied to bioenergy producing biorefinery. Consequently, in the figure 3 can be seen the individual economic margins for products of the biorefinery, obtaining in this sense a global economic margin for biorefinery of 40% meanwhile the same mass allocation for independent processing plants just 28%.

Figure 3 Individual economic margin for the products of biorefinery.

## 4. Conclusions

A biorefinery that produces different energy carriers seems to be a clear idea for the integral utilization of raw materials such as oil palm for the production of biofuels. The use of biomass as raw materials for different bioenergy sources is encouraged by a reduction of fossil  $CO_2$  emissions, the need for a secure energy supply, and a revitalization of rural areas. A key driver for the development and implementation of energy producing biorefineries is the growth in the demand for energy and fuels. The stand-alone option is weak when comparing it to a biorefinery that produces different energy carriers by the integral utilization of raw materials such as palm for the production of bioenergy.

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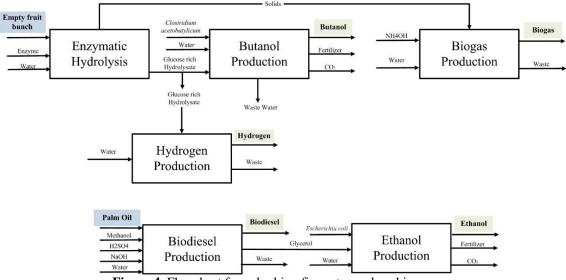


Figure 4. Flowsheet for palm biorefinery to produce bioenergy.

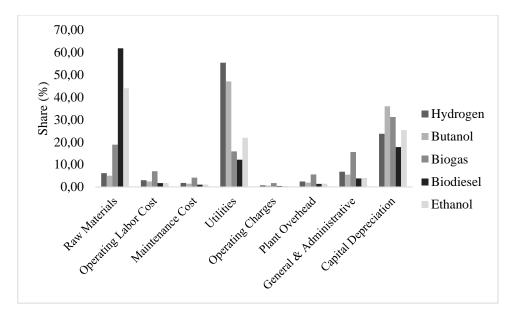


Figure 5. Shares of features for each process production.

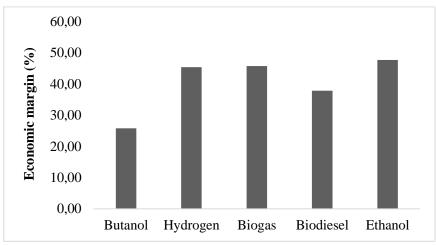


Figure 6 Individual economic margin for the products of biorefinery.

Table 5 Price/cost of feedstock and products used in the economic assessment.

| Item               | Unit                  | Price | Reference                      |
|--------------------|-----------------------|-------|--------------------------------|
| Palm oil           | USD Kg <sup>-1</sup>  | 0.22  | ("ICIS Chemical Pricing" 2010) |
| Methanol           | USD Kg <sup>-1</sup>  | 0.35  | ("ALIBABA 2014")               |
| Sodium hydroxide   | USD Kg <sup>-1</sup>  | 0.635 | ("ICIS Chemical Pricing" 2010) |
| Sulfuric acid      | USD Kg <sup>-1</sup>  | 0.094 | ("ICIS Chemical Pricing" 2010) |
| Ammonium hydroxide | USD Kg <sup>-1</sup>  | 0.21  | ("ALIBABA 2014")               |
| Ethanol            | USD Kg <sup>-1</sup>  | 1.07  | ("FEDEBIOCOMBUSTIBLES", 2014)  |
| Butanol            | USD Kg <sup>-1</sup>  | 1.9   | ("ALIBABA 2014")               |
| Biogas             | USD Kg <sup>-1</sup>  | 1.4   | ("ALIBABA 2014")               |
| Biodiesel          | USD Kg <sup>-1</sup>  | 1.19  | ("ICIS Chemical Pricing" 2010) |
| Hydrogen           | USD Kg <sup>-1</sup>  | 2.47  | ("ALIBABA 2014")               |
| Fuel               | USD/MEGAWatt          | 24.58 | ("NME, N.m.y.E. LyD" 2013)     |
| Water              | USD m <sup>-3</sup>   | 0.74  | *                              |
| Electricity        | USD kWh <sup>-1</sup> | 0.14  | *                              |
| Operator labor     | USD h <sup>-1</sup>   | 2.56  | *                              |
| Supervisor labor   | USD h <sup>-1</sup>   | 5.12  | *                              |

\*Typical prices in Colombia.

| Table 6. Empty fruit bunches composition | in wet basis. |
|--|---------------|
|--|---------------|

| Component     | Content (wt %)   |  |
|---------------|------------------|--|
| Cellulose     | $13.75\pm0.44$   |  |
| Hemicellulose | $12.79\pm0.40$   |  |
| Lignin        | $7.79\pm0.08$    |  |
| Ash           | $0.63 \pm 0.04$  |  |
| Moisture      | $65.04 \pm 1.80$ |  |

Table 7. Production capacities and global yields of the products obtained in oil palm biorefinery.

| Product - | Produ | Productivity |       | Yield                    |  |  |
|-----------|-------|--------------|-------|--------------------------|--|--|
|           | Value | Unit         | Value | Unit                     |  |  |
| Butanol   | 26.7  | Kg/h         | 0.027 | Kg butanol/Kg EFB        |  |  |
| Hydrogen  | 7.60  | Kg/h         | 0.008 | Kg hydrogen/kg EFB       |  |  |
| Biogas    | 17.6  | Kg/h         | 0.018 | Kg biogas/Kg EFB         |  |  |
| Biodiesel | 1146  | Kg/h         | 1.146 | Kg biodiesel/Kg palm oil |  |  |
| Ethanol   | 31.0  | Kg/h         | 0.031 | Kg ethanol/Kg palm oil   |  |  |

 Table 8. Production cost for each product.

| Product   | Cost | Units  |
|-----------|------|--------|
| Butanol   | 1.41 | USD/Kg |
| Hydrogen  | 1.35 | USD/Kg |
| Biogas    | 0.76 | USD/Kg |
| Biodiesel | 0.74 | USD/Kg |
| Ethanol   | 0.56 | USD/Kg |