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# Integrated production of biodiesel from palm oil using *in situ* produced bioethanol

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#### **Abstract**

Liquid biofuels as a source of renewable energy represents an important alternative to the fossil fuels. Currently, these biofuels (mainly biodiesel and bioethanol) are produced from oilseed crops and from sugar and starch containing materials. The integration of the production of these two biofuels using a single source of biomass as a raw material may allow the intensification of liquid biofuels production offering attractive alternatives for lowering production costs. In this work and using process simulation tools, the integrated production of biodiesel from palm oil including the in situ production of bioethanol is explored. Lignocellulosic residues obtained during the extraction of crude palm oil are utilized for ethanol production. For this, an integrated process involving the pretreatment of biomass by dilute acid and simultaneous saccharification and co-fermentation is simulated. The oil extracted from Fresh Fruit Bunches was considered as the feedstock for biodiesel production taking into account an integrated process of extractive reaction using the ethyl alcohol produced from the lignocellulosic residues for the transesterification reaction. Overall process was simulated employing Aspen Plus. The integration of material flows between these two production lines allowed a 4.7% reduction in energy costs, whereas the material and energetic integration leaded to 21.3% decrease in these costs. This kind of integrated configuration will become an important option when the technology for ethanol production from biomass reaches such a degree of maturity that its production costs be comparable with those of the process from starch or sugars.

Keywords: pharmaceutical synthesis, green chemistry, green engineering, solvent selection

## 1. Introduction

Colombian government has encouraged the utilization of renewable biofuels for national transport sector in order to achieve several goals: Diminish the volume of

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polluting emissions improving the air quality in our cities, reduce the dependence on fossil fuels through the decrease of diesel and gasoline imports, and boost the development of Colombian rural sector through the consolidation of agro-industrial chains for biofuels production. Colombian Congress issued the Act 693 of 2001, which made mandatory the utilization of fuel ethanol as a gasoline oxygenate (Congreso de la República de Colombia, 2001). In a similar way, the Act 939 of 2004 (Congreso de la República de Colombia, 2004) offers tax exemptions for both biodiesel production and oilseed cropping intended to the production of this biofuel. Thus, Colombia has a legislation promoting the production and utilization of liquid biofuels.

A wide variety of plant materials containing the sugars required for fermentation process can be utilized for fuel ethanol production from biomass (bioethanol). Among these materials, sucrose-containing feedstocks like sugar cane juice and cane or beet molasses should be highlighted as well as starchy materials (corn, cassava, sorghum) and lignocellulosic biomass mainly agricultural and agro-industrial wastes. It is considered that lignocellulosic biomass is the most promising feedstock at mid term for ethanol production due to its availability and low cost.

The biological diesel is a mixture of methyl or ethyl esters of fatty acids that can be utilized as a fuel for diesel engines. The ester group increases the oxygen content of diesel-biodiesel blends improving the efficiency of the combustion of the conventional fossil diesel. For producing biodiesel, the transesterification of vegetable oils with low molecular weight alcohols like methanol or ethanol is necessary. This reaction is accomplished with the help of acid, basic or enzymatic catalysts. Usually, biodiesel production in the world is carried out employing methanol and basic catalysts (mostly KOH). The European countries are the leaders in the production of biodiesel, specifically Germany. The most utilized vegetable oils are rapeseed, soybean and sunflower oils. The oil from palm (*Elaeis guineensis*) is considered as an excellent feedstock for biodiesel production.

Currently, Colombia does not produce methanol and it is imported for domestic needs. On the contrary, this country is becoming an important producer of ethanol in the American continent. On the other hand, Colombia is the fourth world producer of oil palm due to its favorable agro-ecological conditions. Considering the abovementioned, Colombia has the material basis for high-scale production of both bioethanol and biodiesel. Biodiesel production in the Colombian context of selfsufficiency requires the domestic supply of ethanol, which is mostly produced from sugar cane. The extraction of palm oil generates significant amounts of lignocellulosic residues, which may be employed as feedstock for ethanol production. If, in addition, the integration of lines for processing palm oil and lignocellulosic biomass is considered, the synthesis of an integrated technological scheme for biodiesel production is feasible. In this case, the purchase of ethanol is not involved; in its place, production of ethanol inside the same process is contemplated. The aim of this work is the preliminary evaluation of integrated production of biodiesel and bioethanol through process engineering tools (process synthesis, analysis and simulation).

# 2. Process Description

#### 2.1. Oil Extraction

Processing of palm for oil extraction leads to the formation of several by-products and residues that have an economical potential. The overall process for oil extraction using as feedstock the fresh fruit bunches (FFB) of palm is depicted in Fig. 1. FFB are cooked in an direct contact sterilizer using saturated steam. This operation favors the removal of fruits from bunches and prepares the pulp for the further extraction of oil.

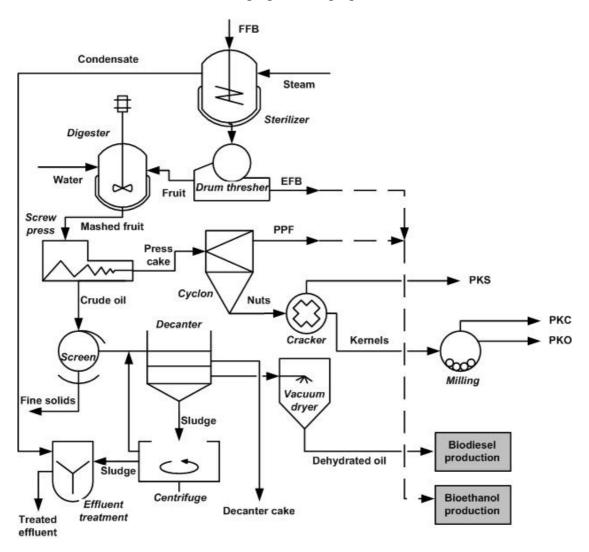


Fig. 1. Schematic diagram of oil extraction from palm. FFB – fruit fresh bunches, EFB – empty fruit bunches, PPF – palm press fiber, PKS – palm kernel shell, PKC – palm kernel cake, PKO – palm kernel oil.

Fruit removal is generally carried out in rotary drum threshers. Fruits undergo digestion in cylindrical vertical tanks with stirring at 100°C. In this step, the mashing

of fruits takes place that leads to the separation of pulp from the nuts (Observatorio Agrocadenas Colombia, 2006). Mashed fruits are sent to screw press where the crude oil is separated from the cake. The oil is passed through vibrating screens for removing fine solids. Then, the oil is clarified in decanters where hot water at 90°C is added for accelerating the process. In this step, decanter cake is obtained. The sludge from decanter is centrifuged for recovering oil and sent to the effluent treatment step. The clarified oil contains about 1% of water. For this reason, it is dehydrated in a vacuum dryer and sent to oil storage tanks. The press cake is directed to a cyclone where the separation of the nuts and palm press fiber (PPF) occurs. The nuts are cracked to separate the kernels from the palm kernel shell (PKS). The kernels undergo milling for extracting palm kernel oil (PKO) obtaining palm kernel cake (PKC) as well.

During oil extraction from palm, several solid and liquid residues are generated besides the main products (palm oil and PKO). These products, by-products and residues are illustrated in Fig. 2 along with their current and potential applications.

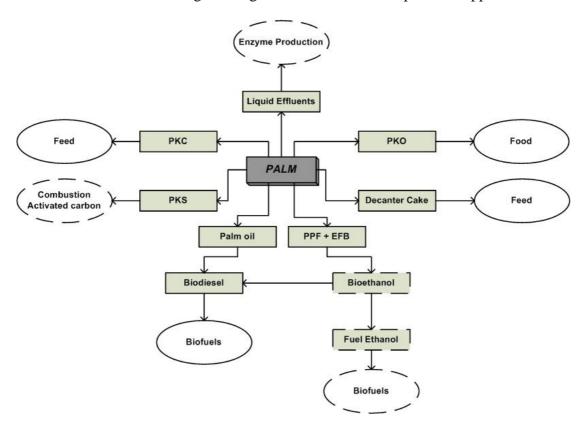


Fig. 2. Products, by-products and residues obtained during the processing of oil palm. Figures with continuous edges correspond to the current applications of products and by-products from oil palm. Figures with dashed edges correspond to potential applications.

The solid residue that is produced in the highest amount corresponds to the EFB whose composition is shown in Table 1. Due to its high moisture content, this material is not appropriate as a fuel; for this reason, it is mostly used as manure (Observatorio Agrocadenas Colombia, 2006). Composting of EFB is also carried out

in order to enhance their value as manure since their volume is reduced in 50% as well as their transport costs (Chavalparit *et al.*, 2006). The utilization of EFB as substrate for cultivation of mushrooms has been proposed; in this case, previous treatment of this material is not required (Prasertsan and Prasertsan, 1996; Chavalparit *et al.*, 2006). In addition, the remaining material after mushroom harvest presents better fertilizing properties. The fiber resulting from separation of press cake (PPF) has an important content of lignocellulosic complex and a lower content of moisture (see Table 1). The oil retained in the fiber makes this material to be a good solid fuel. When palm processing facilities produce both process steam and electricity, the totality of PPF undergoes combustion. However, if only steam is to be produced, 70% of PPF remains without utilization and becomes a waste (Prasertsan and Prasertsan, 1996).

Table 1. Average composition of two solid residues obtained during palm oil extraction.

Component	Content, % (w/w)		
	EFB	PPF	
Cellulose	15.47	24.00	
Hemicellulose	11.73	14.40	
Lignin	7.14	12.60	
Ash	0.67	3.00	
Oil	-	3.48	
Others	-	2.52	
Moisture	65.00	40.00	

Source: Abdul Aziz et al. (2002a; 2002b), Wan Zahari and Alimon (2004).

PKS is another residue generated in lower amounts than EFB and PPF. This material is the most difficult residue to decompose. For this reason, it is not usually utilized and disposed of by landfill method. PPF has a high energy value, but its use in burners or boilers designed for wood or fossil fuels implies a substantial modification of these equipments. This explains why it is not widely utilized as a fuel. It has been proposed its use for the production of activated carbon (Prasertsan and Prasertsan, 1996; Chavalparit *et al.*, 2006).

# 2.2. Production of Bioethanol

Lignocellulosic biomass is a difficult to degrade feedstock for ethanol production, hence pretreatment and hydrolysis steps are required in order to obtain the fermentable sugars required by the fermentation process. During the pretreatment, lignocellulose matrix is broken down releasing its three main components (cellulose, hemicellulose and lignin); in addition, crystallinity degree of cellulose is decreased leading to the increasing of the fraction of amorphous cellulose, which is more susceptible to hydrolysis. At the same time and depending on the pretreatment

method, the hemicellulose is partially hydrolyzed forming pentoses (mainly xylose) and hexoses (including glucose).

There exist different pretreatment methods of lignocellulosic biomass that differ in their physical, chemical or biological principle, in the type of utilized equipments, and in the degree of maturity of employed technologies (Sánchez and Cardona, 2005). In the present work, dilute acid method was selected for its analysis since it is considered a mature technology and allows the hydrolysis of the main part of hemicellulose as well as an adequate level of amorphous cellulose. Pretreatment reactor operates at 190°C and 12.2 atm. Solid fraction resulting from pretreatment steps is mostly composed by cellulose and lignin, whereas the liquid fraction contains dissolved pentoses and hexoses (hemicellulose hydrolyzate), besides products of the thermal degradation of these sugars and lignin. These products may inhibit the subsequent fermentation. For this reason, this fraction should be directed to the detoxification step employing ionic exchange columns that remove these inhibitory substances.

Cellulose hydrolysis is a key step in the production of ethanol from lignocellulosic materials. It is generally carried out using cellulolytic enzymes (cellulases). Most process flowsheets consider an enzymatic reactor where the solid fraction from pretreatment step makes contact with fungal cellulases obtaining a cellulose hydrolyzate with a significant concentration of glucose. Then, this hydrolyzate is fermented towards ethanol using conventional yeast (*Saccharomyces cerevisiae*). In a parallel way, detoxified liquid fraction, which contains pentoses and hexoses, is sent to a fermentor where pentose-assimilating yeasts convert this mixture into ethanol. Among this type of yeasts, *Pichia stipitis*, *Candida shehatae* and *Pachysolen tannophilus* are the most utilized microorganisms. Unfortunately, these microorganisms have lower efficiency in ethanol production and reduced tolerance to this alcohol related to conventional yeast (Claassen *et al.*, 1999).

Process integration is an alternative approach to undertake the biomass-to-ethanol conversion. In fact, process design has been boosted thanks to process intensification through the development of simultaneous or coupled configurations. When several operations are carried out in a single unit, the possibilities for improving the performance of overall process are increased (Cardona and Sánchez, 2007). In particular, process integration of biomass conversion through the integration of enzymatic hydrolysis of cellulose and ethanolic fermentation makes possible the improvement of the process due to the reduction of end product inhibition characteristic of cellulases. When these two processes are simultaneously accomplished in a same unit, the glucose formed during cellulose hydrolysis is immediately assimilated by the microorganisms converting it into ethanol and reducing the inhibitory effect of glucose over cellulases. This process is called simultaneous saccharification and fermentation (SSF).

An option that offers an even higher degree of integration is the utilization of genetically modified microorganisms with the ability of assimilating both pentoses and hexoses formed during the pretreatment and enzymatic hydrolysis of

lignocellulosic biomass. In this way, cellulose hydrolysis using cellulases and fermentation of hexoses and pentoses using engineered microorganisms may be carried out in the same unit, process known as simultaneous saccharification and cofermentation (SSCF) (Cardona and Sánchez, 2007). Among the microorganisms capable of co-fermenting glucose and xylose, genetically modified strains of the bacterium *Zymomonas mobilis* should be highlighted.

In a previous work, several integrated schemes for producing ethanol from lignocellulosic biomass considering different variations in conversion technologies were analyzed (Cardona and Sánchez, 2006). The configuration with the best performance from energy viewpoint involved the SSCF process. For this reason, this alternative is analyzed in the present work considering the integration of ethanol production with biodiesel production.

Culture broth exiting SSCF bioreactor has an ethanol concentration of about 6% by weight. This stream is concentrated up to 42% of ethanol in a distillation (concentration) column, and then, it is concentrated up to 92,3% in another distillation (rectification) column. The dehydration of ethanol is accomplished by adsorption with molecular sieves. Stillage obtained in the bottoms of concentration column is evaporated with the aim of reducing its volume and diminishing the costs of its further treatment (see Fig. 3). The lignin is separated by centrifugation in order to employ it as a fuel for co-generation of process steam and electricity whose surplus can be sold to the grid.

## 2.3. Production of Biodiesel

Main feedstock for biodiesel production analyzed in this work is palm oil consisting of a mixture of triglycerides. Through transesterification reaction, this mixture is contacted with an excess of ethanol (oil:ethanol molar ratio from 1:5 to 1:9) forming the ethyl esters of the fatty acids that made part of the structure of triglycerides contained in the oil. These esters are the biodiesel. Glycerol is formed as a by-product of this reaction. Then, the mixture of products and unreacted reagents is sent to a decanter where two liquid phases are separated: biodiesel-enriched and glycerol-enriched phases. Non-converted ethanol is distributed between these two phases. The reaction is reversible and occurs at 70°C under atmospheric pressure using KOH as the catalyst (Montoya *et al.*, 2006).

The application of extractive reaction is one of the integration approaches that can be utilized for the intensification of biodiesel production. This process consists in the combination of the chemical reaction and liquid-liquid extraction in the same unit achieving such synergistic effect, that the increase of selectivity, conversion, productivity, and purity of final product may be attained (Rivera and Cardona, 2004). In this case, two liquid phases are formed during the reaction. These phases are separated in the same reactor-extractor by an adequate control of agitation. For this reason, the decanter is not needed. The system works in continuous regime at the same temperature of the sequential (conventional) process.

Biodiesel-enriched liquid phase is continuously removed from the reactor-extractor and sent to a flash unit where ethanol is recovered and recycled to the reaction zone. Thus, a high purity biodiesel is obtained (see Fig. 3). Glycerol-enriched phase is directed to another flash unit where part of ethanol is recovered and recycled as well. The second stream from this unit, which contains glycerol and the other part of ethanol, is fed to a distillation column in order to separate their components. In this column, high purity glycerol is obtained in the bottoms whereas a stream with a high content of ethanol is removed as distillate.

## 2.4. Integrated Configuration

Proposed integrated configuration for production of biodiesel and bioethanol from oil palm is depicted in Fig. 3. The FFB are the feedstock for crude oil production; in addition, different solid lignocellulosic residues are generated. The utilization of these residues, particularly the EFB and PPF, is proposed as raw materials for ethanol production. They enter the pretreatment reactor where react with dilute acid at high pressure. Then, the pretreated lignocellulosic biomass undergoes the transformations described in section 2.2 obtaining dehydrated ethanol with purity greater than 99.5% by weight. This stream of ethanol, along with crude oil, is fed to reactor-extractor where transesterification reaction is accomplished by reactive extraction process using KOH.

There exit several level of integration in the proposed scheme. Bioethanol production implies the reaction-reaction integration of cellulose hydrolysis, hexose fermentation and pentose fermentation through the SSCF process. In a similar way, an integration of the reaction-separation type is verified in the reactor-extractor leading to the improvement of the biodiesel production process. Other level of integration corresponds to the recirculation of material streams in order to achieve a better utilization of sugars, e.g. by implementing the recycling of water streams. In this case, the bottoms of rectification column and a fraction of the thin stillage (see Fig. 3), which mostly contain water but also a low content of non-utilized by microorganisms sugars, are recycled to the step of washing of lignocellulosic biomass that leaves the pretreatment reactor. Thus, non-utilized pentoses and hexoses return to the SSCF reactor to be converted into ethanol. In addition and with the aim of reducing the volume of wastewater that should be treated, secondary steam from evaporators is condensed and recycled to the pretreatment reactor where it is used as process water.

The mentioned streams correspond to the ethanol production process, but it is also possible the recirculation of streams between the biodiesel production line and ethanol production line increasing the integration of the overall process. In this work, the recirculation of the distillate from the distillation column utilized for glycerol separation is proposed. This stream contains ethanol with a low content of water; for this reason, it cannot be used as gasoline oxygenate. Considering this, this stream is fed to the rectification column in the ethanol production line. Moreover, this column

is fed with the regenerate resulting of the adsorption in the molecular sieves (see Fig. 3).

Finally, other option for integrating the whole process is the energy integration between both production lines. For this, it is proposed the utilization of the heat released during the condensation of vapors exiting the concentration and rectification columns. This heat is employed to provide the required energy for the operation of the flash unit processing the glycerol-enriched stream exiting the reactor-extractor. In this way, the supply of steam generated in boilers is not needed decreasing the total energy costs.

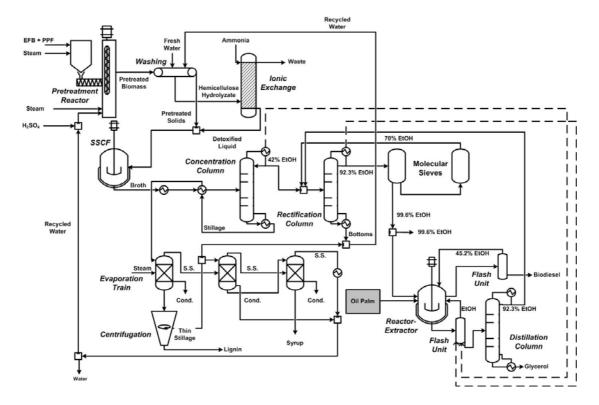


Fig. 3. Integrated technological configuration of the combined production of biodiesel and bioethanol. S.S. – secondary steam. Material streams are represented by continuous lines whereas dashed lines represent energy streams

## 3. Simulation Procedure

Material balance of the oil extraction process was based on the data reported by Prasertsan and Prasertsan (1996) for processing FFB until crude palm oil. The data on volume and composition of the analyzed lignocellulosic residues (EFB and PPF) were employed for the simulation of bioethanol production scheme as well as the amount of crude oil required for biodiesel production.

The simulation of the global technological scheme was performed using the process simulator Aspen Plus v. 11.1 (Aspen Technologies, Inc. USA). For process units

corresponding to the ethanol production line, NRTL thermodynamic model was utilized for calculating the activity coefficients of the liquid phases. For units related to the biodiesel production line, UNIFAC model was employed for the simulation of the properties of the two formed liquid phases. In particular, modified values of the group interaction parameters were utilized for the substances involved in the transesterification reaction; these values were taken from Batista *et al.* (1998). Part of the data of physical properties of the components required for the simulation were obtained from Wooley and Putsche (1996).

Enzymatic hydrolysis and co-fermentation processes were simulated based on a stoichiometric approach that considered the conversion of cellulose into glucose as well as the transformation of glucose and pentoses (modeled as xylose) into cell biomass, ethyl alcohol and other fermentation by-products as aldehydes, succinic acid and glycerol, among others. Similar approach was utilized for the analysis of the preatreatment of lignocellulosic biomas.

The simulation of biodiesel production in the reactor-extractor was performed employing a kinetic approach. For this, the values of reaction rate constants reported by Marchetti *et al.* (2005) were utilized. Analyzed transesterification reactions include the conversion of triglycerides into diglycerides, followed by the conversion of diglycerides into monoglycerides and the conversion of monoglycerides into glycerol. During each reaction stage, a molecule of the ethyl ester (biodiesel) is produced. For the simulation, the triolein was considered as the model triglyceride. Consequently, obtained biodiesel was represented by the molecule of ethyl oleate. In this paper, the simulation procedure for biodiesel production by extractive reaction describe in a previous work (Montoya *et al.*, 2006) was applied.

For the simulation of distillation columns, residue curves maps was analyzed applying the principles of thermodynamic topology (analysis of the statics) (Pisarenko et al., 2001) with the help of software developed by our research group and Aspen Split (Aspen Technologies, Inc., USA). For defining the preliminary specifications of distillation columns, the DSTWU short-cut method included in Aspen Plus was employed; this method utilizes the Winn-Underwood-Gilliland method providing an initial estimate of the minimum number of theoretical stages, the minimum reflux ratio, the localization of the feed stage, and the products split of the column. With this information and the results of the analysis of the statics, the rigorous calculation of the distillation columns was performed using the RadFrac module that is based on MESH equations and utilizes the inside-out calculation algorithm. Sensitivity analyses were carried out in order to study the effect of the main operation variables (reflux ratio, feed temperature, number of stages, etc.) on the composition of products and corresponding energy costs. The estimation of energy consumption was carried out based on the results of simulation corresponding to the thermal energy required by the heat exchangers, reboilers and flash units. Likewise, the electric energy needed for the operation of pumps was considered as well.

#### 4. Results and Discussion

Under Colombian conditions, the average installed capacity of production facilities of crude palm oil is of 122 tonnes per day (Espinal *et al.*, 2005). In general, these facilities operate during a single work shift of eight hours. Based on this production volume and according to the material balance of an oil extraction plant as the one depicted in Fig.1, the volume of lignocellulosic residues selected for bioethanol production was determined: 28.06 tonnes/day of EFB and 17.98 tonnes/day of PPF. For biodiesel production, the total volume of produced crude oil was considered: 21.76 tonnes/day. These data along with the composition of EFB and PPF allow simulating the integrated process for biodiesel production using *in situ* produced bioethanol for the case of a production facility working in a continuous regime during three shifts per day (see Fig. 3). The results of the simulation are presented in Table 2.

Table 2. Simulation results of the integrated scheme for biodiesel production for some process streams.

Streams	Lignocell. biomass	Broth	Recycled water for washing	Rectific. Column distillate	BioEtOH	Biodiesel	Glycerol
T, °C	20.0	30.0	77.4	93.4	25.0	52.4	254.7
p, bar	1.013	1.013	1.793	1.793	1.000	0.200	0.400
Mass flow, kg/h	1,913.1	4,185.0	667.3	347.1	260.1	959.4	95.7
Cellulose, % <sup>(1)</sup>	18.38	1.52	0.04	-	-	-	-
Hemicellulose, %	12.52	1.31	0.03	-	-	-	-
Lignin, %	9.05	3.72	0.09	-	-	-	-
Glucose, %	-	0.56	0.50	-	-	-	-
Xylose, %	-	0.67	0.89	-	-	-	-
Water, %	56.84	80.47	97.78	7.66	0.41	0.01	-
Triolein, %	-	-	-	-	-	0.44	-
Diolein, %	-	-	-	-	-	0.34	1.88
Monoolein, %	-	-	-	-	-	0.03	2.10
Ethanol, %	-	5.59	0.01	92.34	99.57	1.32	0.03
Ethyl oleat, %	-	-	0.01	-	-	97.84	-
Glycerol, %	-	-	0.02	-	-	0.02	95.94

<sup>(1)</sup> Percentages by weigth.

The proposed scheme allows the production of high-purity biodiesel that is verified by the elevated level of ethyl oleat in the corresponding stream. This integrated configuration makes possible the production of the necessary amount of anhydrous ethanol required by the conversion of the extracted crude oil into biodiesel from 122 tonnes/day of FFB. The ethanol required by the process is obtained from the lignocellulosic residues generated during the extraction of palm oil (excluding the PKS). In addition, a remaining amount of anhydrous ethanol for sale as fuel ethanol is produced (78.0 kg/h).

A value of 3.9 for the molar ratio between ethanol and palm oil leading to a better conversion of feedstocks for biodiesel production was identified through sensitivity analyses. This ratio is referred to the streams of crude oil and fresh ethanol (not recycled) entering the reactor-extractor. In fact, the excess of ethanol reaches higher values inside the reactor-extractor due to the recirculation of ethanol recovered from the two liquid phases formed during the extractive reaction process. This ratio reaches a value of 20 for the process that considers the material integration (see below), and a value of 60 for the process that considers both the material and energy integrations. The higher the ratio between ethanol and oil, the greater the conversion of feedstocks and the purity of biodiesel. For the proposed configuration, the conversion of triolein reaches 99.9%, and the purity of produced ethyl oleat achieves a value of 97.8%.

These obtained values for the integrated process through extractive reaction can be compared to those of the conventional (sequential) process where the decantation of the liquid phases is accomplished after the reaction in a separate unit. In this case and utilizing a molar ratio between ethanol and oil of 12, the same oil conversion can be achieved (99.9%), but the purity of the biodiesel is reduced to 94% according to the simulation performed in a previous work (Montoya et al., 2006). Moreover, it is necessary to consider that the conventional process implies a greater number of process units and is less compact related to the extractive reaction (integrated) process. Therefore, extractive reaction represents a viable technological alternative for biodiesel production due to its higher conversion and yields obtained thanks to the integration of reaction and separation. This integration allows the removal from the reaction zone of the products due to the achieved synergy as a result of the immiscibility present in the system (liquid extraction). The continuous extraction of the product provokes a perturbation of the chemical equilibrium; for returning to the equilibrium state, the system consumes a greater amount of reagents increasing process conversion and productivity.

Data of Table 2 indicate that the recirculation stream employed for washing the lignocellulosic biomass after its pretreatment may be utilized as recycled water. In addition, this stream makes possible a higher conversion of the sugars formed during the process allowing a higher ethanol concentration in the culture broth exiting the SSCF rector. If a 5% increase in the conversion of both glucose and xylose into ethanol is considered, ethanol concentration in the broth reaches 6.11% by weight that implies lower costs in the separation and dehydration steps.

The simulation demonstrates the possibility of integrating two production lines in an additional way through the recirculation of the ethanol-enriched stream from the top of distillation column used for glycerol recovery. Thus, recovered ethanol can be utilized again for transesterification reaction. Depending on the composition, this stream is recycled to the rectification column if the ethanol-water mixture has a composition below the azeotropic one (approximately 95.6% by weight) or directly to the molecular sieves if the composition is greater than that of the azeotropic ethanol-water mixture.

The analysis of the process allowed verifying the feasibility of energetically integrating the two production lines. The available heat in the distillate streams of the concentration and rectification columns is enough to supply the energy requirements of the flash unit processing the glycerol-enriched stream leaving the reactor-extractor. In this case, the design of this unit implies the loss of a degree of freedom in the specification of process variables in order to fix the amount of supplied heat.

The different levels of integration analyzed in this work have a strong influence on the energy costs of the global process. The results of the evaluation of energy costs of the simulated process flowsheets are shown in Table 3 (the energy costs of oil extraction process are not included). A base case was defined consisting in the production of biodiesel from crude palm oil employing ethanol as a feedstock. This base case includes the costs of ethanol production from lignocellulosic residues of oil palm, but without any integration between both production lines. This configuration corresponds to two independent plants producing bioethanol and biodiesel in an autonomous way.

Table 1. Energy consumption of different technological configurations for biodiesel production using *in situ* produced ethanol.

Process	Energy consumption, MJ/h	Unit energy costs of biodiesel, MJ/L	
Non-integrated production of biodiesel	1,210	-	
Ethanol production from EFB and PPF	3,821	-	
Base case	5,031	16.77	
Biodiesel production considering material integration	4,791	15.99	
Biodiesel production considering material and energy integration	3,962	13.21	

If the base case is taken as a reference, simulation data show a 4.7% reduction of the energy costs for biodiesel production scheme integrated with the production of ethanol from lignocellulosic residues from palm; this integration is called material integration in Table 3, and comprises the recycling of ethanol between the two production lines, besides the integrated processes within each line (SSCF for bioethanol production, and extractive reaction for biodiesel production). When the energy integration between both production lines (see dashed lines in Fig. 3) is considered, the reduction of energy costs reaches a value of 21.3%. This demonstrates the benefits of the integration of these two processes from energy point of view. Considering the temperature of the cold and hot streams of the whole technological scheme, it is possible to exchange heat among other process units. In this sense, pinch analysis, which allows systematic and optimal energy integration, may provide further energy savings. In a previous work, this analysis was applied to the integration of

separation and purification steps in the case of ethanol dehydration by azeotropic distillation (Grisales *et al.*, 2005).

A very important issue to be considered is that the technology for ethanol production from lignocellulosic biomass is not completely developed at present. In fact, production costs of ethanol from such lignocellulosic materials as wood or agroindustrial wastes are higher than production costs from sugar cane or starchy materials. For instance, McAloon *et al.* (McAloon *et al.*, 2000) calculate that production costs for a gallon of anhydrous ethanol from corn are of US\$0.88 whereas for lignocellulosic biomass these costs reach US\$1.50 per gallon of ethanol. However, it is expected at mid term that these costs decrease and be comparable to those of grain ethanol, or even cane ethanol. Among the trends for improving this process are the development of recombinant microorganisms with higher stability under industrial conditions and with higher yields, the increase of specific activity of cellulases, and the development of pretreatment technologies of biomass allowing a lower formation of inhibitors and a reduction of the energy consumption.

Process integration plays a crucial role in the improvement of the performance indicators of chemical and biotechnological processes not only at economic level, but also considering environmental criteria. Worldwide interest for developing technologies for fuel ethanol production from lignocellulosic biomass is justified by the fact that the lignocellulosic complex is the most abundant biopolymer in nature and that its exploitation makes possible the utilization of renewable sources of energy. Practically, each country has a wide availability of lignocellulosic materials (wood, herbaceous plants, agricultural and agro-industrial wastes, cellulosic fraction of municipal solid waste, among others) that have no food value. It is estimated that this technology will replace the utilization of other feedstocks that do have importance as foods (sugar cane, sugar beet, corn, wheat, sorghum, etc.) for fuel ethanol production. In this context, the production of biodiesel employing biomass ethanol represents a valuable opportunity for the production and global utilization of renewable liquid fuels.

## 5. Conclusions

Employed methodology and obtained results demonstrate that process engineering plays a decisive role for the design of integrated chemical and biotechnological processes. In particular, process simulation represents a powerful tool for the synthesis of integrated technological configurations with high technical and economic performance and that take economical advantage of agro-industrial residues and byproducts.

Biodiesel production from oil palm by a configuration that utilizes ethanol produced from the solid residues of the same palm, offers such degree of integration that makes possible the decrease of energy costs compared to the autonomous production of biodiesel and bioethanol. This option is very attractive taking into account not only the energy consumption, but also the decrease of the solid wastes generated during the processing of oil palm. In particular, empty fruit bunches and palm press fiber generated during oil extraction have a high content of lignocellulosic biomass making them very adequate materials for their conversion into ethanol. Nevertheless, this kind of integrated configuration will be viable in palm producing countries, only when the technologies for ethanol production from biomass reaches such a degree of maturity that its production costs be comparable with those of the process from starch or sugars. The joint production of the two analyzed liquid biofuels and their worldwide utilization in transport sector, have clear environmental benefits, but these benefits have a cost that should be assumed by the society in order to achieve a sustainable economic development.

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#### References

Abdul Aziz, A., Das, K., Husin, M., Mokhtar, A., (2002a) *Journal of Oil Palm Research*, 14(2),10-17.

Abdul Aziz, A., Husin, M., Mokhtar, A., (2002b) Journal of Oil Palm Research, 14(1),9-14.

Batista, E., Rodrigues, M. I., Meirelles, A. J., (1998) *Computers and Chemical Engineering*, 22,S737-S740.

Cardona, C. A., Sánchez, O. J., (2006) *Energy*, 31,2447-2459.

Cardona, C. A., Sánchez, Ó. J., (2007) Bioresource Technology, 98,2415-2457.

Claassen, P. A. M., van Lier, J. B., López Contreras, A. M., van Niel, E. W. J., Sijtsma, L., Stams, A. J. M., de Vries, S. S., Weusthuis, R. A., (1999) *Applied Microbiology and Biotechnology*, 52,741-755.

Congreso de la República de Colombia. (2001). Ley 693 de 2001 (septiembre 19) (Act 693 of 2001, in Spanish). Diario Oficial No. 44.564.

Congreso de la República de Colombia. (2004). Ley 939 de 2004 (diciembre 31) (Act 939 of 2004, in Spanish). Diario Oficial No. 45.778.

Chavalparit, O., Rulkens, W. H., Mol, A. P. J., Khaodhair, S., (2006) *Environment, Development and Sustainability*, 8,271-287.

Espinal, C. F., Martínez, H. J., González, E. D. (2005). La cadena de oleaginosas, grasas y aceites en Colombia. Una mirada global de su estructura y dinámica 1991-2005 (The chain of oilseeds, fats and oils in Colombia. An overview of its structure

and dynamics 1991-2005, in Spanish). Documento de Trabajo No. 93. Obervatorio Agrocadenas Colombia, Ministerio de Agricultura y Desarrollo Rural. 54 p.

Grisales, R., Cardona, C. A., Sánchez, O. J., Gutiérrez, L. F. (2005). Heat integration of fermentation and recovery steps for fuel ethanol production from lignocellulosic biomass. En: 2nd Mercosur Congress on Chemical Engineering and 4th Mercosur Congress on Process Systems Engineering, ENPROMER 2005. Rio de Janeiro, Brazil.

Marchetti, J. M., Miguel, V. U., Errazu, A. F., (2005) Renewable and Sustainable Energy Reviews.

McAloon, A., Taylor, F., Yee, W., Ibsen, K., Wooley, R. (2000). *Determining the cost of producing ethanol from corn starch and lignocellulosic feedstocks*. Technical Report NREL/TP-580-28893. Golden, CO (USA): National Renewable Energy Laboratory. 35 p.

Montoya, M. I., Quintero, J. A., Sánchez, O. J., Cardona, C. A., (2006) Revista Facultad de Ingeniería, 36,85-95.

Observatorio Agrocadenas Colombia. (2006). La industria de aceites y grasas en Colombia (Oils and fats industry in Colombia, in Spanish). En: Agroindustria y competitividad. Estructura y dinámica en Colombia 1992-2005. Ministerio de Agricultura y Desarrollo Rural - IICA: Bogotá. p. 29-94.

Pisarenko, Y. A., Serafimov, L. A., Cardona, C. A., Efremov, D. L., Shuwalov, A. S., (2001) *Reviews in Chemical Engineering*, 17(4),253-325.

Prasertsan, S., Prasertsan, P., (1996) Biomass and Bioenergy, 11(5),387-395.

Rivera, M., Cardona, C. A., (2004) Ingeniería y Competitividad, 6(1),17-25.

Sánchez, O. J., Cardona, C. A., (2005) *Interciencia*, 30(11),671-678.

Wan Zahari, M., Alimon, A. R., (2004) Palm Oil Developments, 40,5-9.

Wooley, R., Putsche, V. (1996). *Development of an ASPEN PLUS physical property database for biofuels components*. Report NREL/MP-425-20685. Golden, CO, USA: National Renewable Energy Laboratory. 38 p.