Process integration possibilities for biodiesel production from palm oil using ethanol obtained from lignocellulosic residues of oil palm industry

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Oil palm
Lignocellulosic residues
Process integration

1. Introduction

Biodiesel and bioethanol are the most important liquid biofuels employed in the transportation sector. These biofuels can be utilized as a sole fuel in special motor engines or as additives in diesel and gasoline blends in order to enhance the oxygen content of such fuels. These oxygenated blends allow the reduction of polluting gases mostly aromatic hydrocarbons and CO.

The biodiesel is a mixture of methyl or ethyl esters of fatty acids. The ester group increases the oxygen content of diesel–biodiesel blends improving the combustion efficiency 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, world biodiesel production is carried out employing methanol and basic catalysts (mostly KOH). In such case, the biodiesel produced is considered as partially renewable since methanol is mainly obtained from natural gas. The European countries are the leaders in the production of biodiesel being Germany the first world producer. The most employed vegetable oils are rapeseed, soybean and sunflower oils. On the other hand, the oil from palm (Elaeis guineensis) is considered an excellent feedstock for biodiesel production in tropical countries as Thailand, Malaysia and Colombia.

Processing of palm for oil extraction leads to the formation of several by-products and residues that have an economical potential. These products, by-products and residues are illustrated in Fig. 1 along with their current and potential applications. The empty fruit bunches (EFB) are the solid residue that is produced in the highest amount. Their composition is shown in Table 1 according to the data of Abdul Aziz et al. (2002a,b) and Wan Zahari and Alimon (2004). Due to its high moisture content, this material is not appropriate as a fuel. For this reason, it is mostly used as a manure (Observatorio Agrocadenas Colombia, 2006). Composting has been suggested as an option for producing high quality manure from EFB. This microbial process allows the reduction of the volume of the obtained manure in 50% as well as its transport costs (Chavalparit et al., 2006). The utilization of EFB as a substrate for cultivation of mushrooms by solid-state fermentation has been proposed. In this case, previous treatment of this material is not required (Chavalparit et al., 2006; Prasertsan and Prasertsan, 1996). In addition, the remaining material after mushroom harvest presents better fertilizing properties. On the other hand, the fiber resulting from separation of press cake (palm press fiber, PPF) has an important content of the 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 total amount 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). The lignocellulosic complex...
biomass contained in both EFB and PPF can be used for ethanol production as described below.

The palm kernel shell (PKS) is another residue generated in lower amounts than EFB and PPF during palm oil extraction (see Section 2.1.1). This material is the most difficult residue to decompose. For this reason, it is usually disposed of by landfill method. PKS 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. Its use has been proposed for production of activated carbon (Chavalparit et al., 2006; Prasertsan and Prasertsan, 1996). The palm kernel cake (PKC) is a waste from palm processing obtained during the extraction of oil contained in the kernels produced after nuts cracking. It also contains significant amounts of lignocellulosic materials.

All solid palm residues containing lignocellulosics (EFB, PPF, PKC, PKS) can be potentially converted into different biofuels using inorganic catalyst as stated by Chew and Bhatia (2008). In particular, bio-oil may be obtained through pyrolysis. The resulting liquid product is a mixture of acids, alcohols, aldehydes, ketones, esters, heterocyclic derivatives and phenolic compounds (see Fig. 1). When fast pyrolysis is performed, hydrogen can be generated using a low residence time and proper catalysts in the reactor. Other valuable fuel products can be produced if biomass undergoes gasification. This process implies the generation of the synthesis gas in a first step. Then, the gas mixture can be converted into liquid hydrocarbon fuels like gasoline, naphta and diesel via Fischer–Tropsch synthesis. Alcohols like methanol, ethanol and others, can be produced using a catalytic process named higher alcohol synthesis (HAS). Finally, synthesis gas is a feedstock for producing hydrogen by steam reforming followed by a water-gas-shift (WGS) reaction as shown in Fig. 1.

The use of liquid effluents generated during palm oil extraction (see Fig. 1) as a culture medium for obtaining lignocellulolytic enzymes is a perspective potential method to diminish the organic load of these effluents (Prasertsan and Prasertsan, 1996). On the other hand, different liquid biofuels may be produced from the palm oil by catalytic cracking. In this case, hydrocarbons like bio-gasoline, kerosene and diesel can be obtained (Chew and Bhatia, 2008). Palm oil is the main feedstock for biodiesel production as described below.

Fuel ethanol is the most employed liquid biofuel worldwide. A broad variety of plant materials containing the sugars required for fermentation process can be utilized for fuel ethanol production like sugar cane juice and cane or beet molasses. Starchy materials are also used for these purposes. The United States has become the first world producer of ethanol (Sánchez and Cardona, 2008).

**Table 1**

<table>
<thead>
<tr>
<th>Component</th>
<th>Content, % (w/w) EFB</th>
<th>PPF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>15.47</td>
<td>24.00</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>11.73</td>
<td>14.40</td>
</tr>
<tr>
<td>Lignin</td>
<td>7.14</td>
<td>12.60</td>
</tr>
<tr>
<td>Ash</td>
<td>0.67</td>
<td>3.00</td>
</tr>
<tr>
<td>Oil</td>
<td>–</td>
<td>3.48</td>
</tr>
<tr>
<td>Others</td>
<td>–</td>
<td>2.52</td>
</tr>
<tr>
<td>Moisture</td>
<td>65.00</td>
<td>40.00</td>
</tr>
</tbody>
</table>

Sources: Abdul Aziz et al. (2002a,b); Wan Zahari and Alimon (2004).
which is produced from corn. Ethanol can be produced from lignocellulosic biomass as well. It is considered that lignocellulosic biomass is the most promising feedstock at mid term for ethanol production due to its availability and low cost.

Many countries have implemented or are implementing programs for addition of ethanol to gasoline (Sánchez and Cardona, 2008) or biodiesel to diesel. For instance, European Union has issued different directives about the addition of renewable oxygenates to fuels. The oxygenation target of fuels consider the addition of 2 wt.% by 2005 and 5.75 wt.% by 2010. However, the implementation of these directives varies too much among the different countries. Spain and France are leading the production of bioethanol in Europe. In contrast, Germany has developed the production of biodiesel from rapeseed. For this country, it is considered that the production of fuel ethanol is not economically feasible in comparison to gasoline due to the high costs of feedstocks (grains, sugar beet) (Henke et al., 2005; Rosenberger et al., 2002).

Colombian government has encouraged the utilization of renewable biofuels for national transport sector in order to achieve several goals: Diminish the volume of polluting emissions improving the air quality in Colombian 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 oil-seed cropping intended to the production of this biofuel.

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. In addition, Colombia is the fourth world producer of oil palm due to its favorable agro-ecological conditions. Considering the above-mentioned, Colombia has the material basis for large-scale production of both bioethanol and biodiesel.

This work appoints to the integral assessment of the integrated production of biodiesel from palm oil using in situ produced bioethanol. For this, the lignocellulosic wastes generated during the extraction of palm oil (empty fruit bunches and palm press fiber)
are considered as feedstocks for ethanol production. In order to provide evaluation data for making decisions on the commercial scale implementation of this integrated configuration, the aim of this paper is to demonstrate whether such process is economically viable taking into account energy consumption considerations.

2. Methods

In this paper, a first approximation to an oil-palm-based biorefinery with biodiesel as the main product is analyzed. Such biorefinery involves the use of in situ produced ethanol, which is obtained from some of the lignocellulosic residues generated during the extraction of crude palm oil. The analysis was based on process simulation applying the integration principle described elsewhere (Cardona et al., 2008). To carry out this analysis, the involved processes are briefly described in the following section.

2.1. Process description

2.1.1. Oil extraction

The overall process for oil extraction using as feedstock the fresh fruit bunches (FFB) of oil palm is depicted in Fig. 2. FFB are cooked in a direct contact sterilizer using saturated steam. This operation favors the removal of fruits from bunches and prepares the pulp for further extraction of 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 leading 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.

2.1.2. 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 increase 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 used equipments, and in the degree of maturity of employed technologies (Sánchez and Cardona, 2008). In the present work, dilute acid method was selected for its analysis since it is considered a mature technology that 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 ion 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 cel lulolytic 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-fermenting yeasts convert this mixture into ethanol. Among this type of yeasts, Pichia stipitis, Candida shehatae and Pachysolen tannophilus are the most employed 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 allows the improvement of the process due to the reduction of end product inhibition that is 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 co-fermentation (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. The culmination of reaction-integration integration for transforming biomass into ethanol is the consolidated bioprocessing (CBP). In this process, only one microbial community is employed both for the production of cellulases and fermentation, i.e., cellulase production, cellulose hydrolysis, and fermentation are carried out in a single step. It is expected that new advances in genetic engineering will allow the development of highly efficient recombinant microorganisms for CBP of cellulose in the mid term.

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
of ethyl esters of palm oil, the separation of two liquid phases is achieved. Stillage obtained from the bottoms of concentration column is evaporated with the aim of reducing its volume and diminishing the costs of its further treatment. The lignin is separated by centrifugation in order to employ it as a fuel for co-generation of process steam and electricity. The power surplus can be sold to the electric network.

2.1.3. Production of biodiesel

The palm oil and ethanol were the selected feedstocks for biodiesel production analyzed in this work. In this paper, alkali catalyzed transesterification was considered. The corresponding transesterification reaction is as follows:

\[
\text{Triglyceride} + \text{Ethanol} \rightarrow \text{Ethylesters} + \text{Glycerol}
\]

Through this reaction, the oil is contacted with an excess of ethanol forming the ethyl esters of the fatty acids of palm oil (biodiesel). Taking into account the reversibility of the transesterification, an excess of ethanol is required to favor the direct reaction leading to an increased conversion. Thus, an oil:ethanol molar ratio of 1:6 is recommended (Marchetti et al., 2007; Van Gerpen, 2005). 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. In this specific case, the formation of these liquid phases is very slow and may take up to two days in a batch regime (Gutiérrez, 2008). This conventional configuration is depicted in Fig. 3a. The reaction occurs at 70 °C under atmospheric pressure using KOH as the catalyst (Van Gerpen, 2005).

The application of extractive reaction is one of the integration approaches that can be used for 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). Thus, two liquid phases are formed during the reaction. For this reason, the decanter is not needed. For the case of ethyl esters of palm oil, the separation of two liquid phases is not possible using a conventional stirred tank reactor in continuous regime. To attain such separation, a compact system consisting of one reaction stage and several separation stages working at non-isothermal conditions put together in a single unit (multi-stage reactor–extractor) have been developed and is currently being patented. This system was used to carry out the reactive extraction process intended to the biodiesel production using palm oil and ethanol in continuous regime. The results obtained (Gutiérrez, 2008) showed that a biodiesel-enriched liquid phase (65% of ethyl esters) and a glycerol-enriched liquid phase (44% of glycerol) can be continuously removed from the above-mentioned multi-stage reactor-extractor, which is continuously fed with ethanol and palm oil at a molar ratio of 6:1, respectively. In this way, the principle of reaction-separation integration can be applied to the production of ethyl esters using palm oil and even castor oil (Gutiérrez, 2008; Montoya et al., 2006). Biodiesel-enriched liquid phase is continuously removed from the reactor-extractor and sent to a separation unit where ethanol is recovered. This integrated configuration is shown in Fig. 3b. In order to obtain a high purity biodiesel, this stream is washed with hot water to extract the excess of KOH and the soap that could have been formed during the reaction. Glycerol-enriched phase is directed to another separation unit where part of ethanol is recovered.

2.2. Integration approach

Proposed integrated configuration for production of biodiesel and bioethanol from oil palm is depicted in Fig. 4. 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 2.1.2 obtaining dehydrated ethanol with purity greater than 99.5% by weight. This stream of ethanol, along with crude oil, is fed to a multi-stage reactor–extractor (see Section 2.1.3) where transesterification reaction is continuously accomplished by reactive extraction process using KOH.

There exist several levels 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, the reaction-separation integration is considered in the multi-stage reactor–extractor leading to the improvement of the biodiesel production process as exposed above. Other level of integration corresponds to the recirculation of material streams in order to achieve a better exploitation 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. 4), which mostly contains water but also a low content of non-sterilized by microorganisms sugars, are recycled back to the washing step of lignocellulosic biomass leaving the pretreatment reactor. Thus, non-consumed pentoses and hexoses return to the SSCF reactor to be converted into ethanol. In addition and with the aim of reducing the volume of waste-water that should be treated, the secondary steam from evaporators is condensed and recycled back to the pretreatment reactor where it is used as process water.

The above-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 degree of the overall process. In this work, the recirculation of the distillate from the distillation column used for glycerol separation is proposed. This stream contains ethanol with a low content of water. For this reason, it cannot be used as a gasoline oxygenate. This stream is fed to the rectification
column in the ethanol production line. In addition, this column is also fed with the regenerate resulting from the adsorption in the molecular sieves. The corresponding flowsheet involving the mentioned ways of material integration is called Configuration 1 in Table 4.

Other option for integrating the whole process is the energy integration between both production lines. For this, the utilization of the heat released during the condensation of overhead vapors exiting the concentration and rectification columns is proposed. This heat is employed to provide the energy required by the flash unit processing the glycerol-enriched stream that leaves the reactor–extractor. In this way, the supply of steam generated in boilers is not needed decreasing the total energy costs. This flowsheet involving both material and energy integration is named Configuration 2 in Table 4 and is depicted in Fig. 4.

An alternative way of integration is also studied. For this case (Configuration 3), the purification of the two streams exiting the multi-stage reactor–extractor undergoes distillation using two columns. The first column is aimed at separating the biodiesel, which is removed from the bottoms, and an ethanol-enriched stream that is removed from the top (see Fig. 5). The second column purifies the glycerol contained in the heavy stream from the multi-stage reactor–extractor. As in the first column, the distillate contains high amounts of ethanol. These two ethanol-enriched streams are recycled back to the reactor–extractor unlike the Configuration 1 where ethanol is recirculated to the concentration column in the bioethanol production line. Finally, the Configuration 4 is based on Configuration 3 and includes the energy integration possibilities by using the available heat of the condensers of both concentration and rectification columns in the ethanol production line. In this case, these heat streams are directed to the distillation column employed for glycerol purification (see Fig. 5).

2.3. Simulation procedure

Material balance of the oil extraction process was based on the data reported by Prasertsan and Prasertsan (1996) for processing FFB towards crude palm oil. The data on composition of the analyzed lignocellulosic residues (EFB and PPF) shown in Table 1 were employed for simulating bioethanol production scheme.

The simulation of the global technological scheme including both material and energy integration was performed using the process simulator Aspen Plus v. 11.1 (Aspen Technologies, Inc., USA). Main process data of such simulation are presented in Table 2. For ethanol production line, the approach and principles employed for simulation were mostly taken from a previous work (Cardona and Sánchez, 2006). For process units involved in ethanol production, NRTL thermodynamic model was utilized to calculate the activity coefficients of the liquid phases. For units related to the biodiesel production, 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. (1999). Part of the data on physical properties of the components required for the simulation was 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 used for analyzing the pretreatment of lignocellulosic biomass.

The simulation of biodiesel production in the multi-stage reactor–extractor was performed employing a kinetic approach. For this, the values of reaction rate constants reported by Marchetti et al. (2007) were employed. Studied transesterification reactions included 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 formed. During the calculations, the triolein was considered as the model triglyceride. Consequently, obtained biodiesel was represented by the molecule of ethyl oleate. In this paper, the approach to simulate the biodiesel production by extractive reaction described in a previous work (Montoya et al., 2006) was employed.

For the simulation of distillation columns, residue curves maps were 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 uses the Winn–Underwood–Gilliland procedure 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, which is based on the MESH equations and employs 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 calculation of the energy consumption was based on the thermal energy required by the heat exchangers, reboilers and flash units. The electric energy needed for the operation of pumps was considered as well.

3. Results and discussion

Under Colombian conditions, the installed processing capacity of an average facility for production of crude palm oil is of 122 tonnes per day of FFB (Espinal et al., 2005). In general, these facilities
operate during a single work shift of eight hours. Based on this capacity and according to the material balance of an oil extraction plant as the one depicted in Fig. 2, the volume of lignocellulosic residues selected for bioethanol production was determined: 28.06 tonnes/day of EFB and 17.98 tonnes/day of PPF. The total volume of crude oil available for biodiesel production in the above-mentioned facility reaches 21.76 tonnes/day. These data, along with the composition of EFB and PPF, allowed simulating the integrated process for biodiesel production using the composition of EFB and PPF, allowed 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. The first integrated flowsheet analyzed corresponds to the Configuration 1 (see Fig. 4). 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.

Through sensitivity analyses, a value of 3.9 for the molar ratio between ethanol and palm oil leading to a better conversion of feedstocks during biodiesel production was identified. This ratio is referred to the streams of crude oil and fresh ethanol (not recycled) entering the multi-stage reactor–extractor. In this way, the principle of energy integration is applied. These heat streams are indicated by dashed lines in Fig. 4. 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.

Table 2

<table>
<thead>
<tr>
<th>Feature</th>
<th>Value</th>
<th>Feature</th>
<th>Value</th>
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<tbody>
<tr>
<td>Feedstocks</td>
<td>EFB + PPF</td>
<td>Composition</td>
<td>Product Composition</td>
</tr>
<tr>
<td>Feed flow rate</td>
<td>1913.1 kg/h</td>
<td>Flow rate</td>
<td>959.35 kg/h</td>
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<tr>
<td>Feed flow rate</td>
<td>903.15 kg/h</td>
<td>Flow rate</td>
<td>959.35 kg/h</td>
</tr>
<tr>
<td>Co-product</td>
<td>Ethanol</td>
<td>Co-product</td>
<td>Glycerol</td>
</tr>
<tr>
<td>Composition</td>
<td>Ethanol 99.56%, water 0.41%</td>
<td>Composition</td>
<td>Glycerol 95.98%, ethanol 0.03%, diolein 1.88%, monolein 2.10%</td>
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<td>Flow rate</td>
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<td>Flow rate</td>
<td>95.65 kg/h</td>
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<td>Pressure of columns</td>
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<tr>
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<td>Cycle time</td>
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<tr>
<td>Bioreagents</td>
<td>T. reesei cellulases and recombinant Z. mobilis</td>
<td>Number of stages</td>
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<td>Temperature</td>
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<tr>
<td>Streams</td>
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</table>

* All the percentages are expressed by weight.
Configuration 1. In addition, the ethanol concentrations in the streams recycled back to the reactor–extractor are higher than in Configurations 1 and 2 (see Fig. 5). In this way, all the ethanol required by the reaction is recirculated to the reaction step allowing the elimination of the recirculation stream to the concentration column in the ethanol production line. This makes possible the reduction in the size of this column and a better utilization of material streams. This can be verified by the reduction of the value of molar ratio between ethanol and palm oil inside the reactor–extractor that is 28.7. This ratio is less than in the case of Configuration 2 and equal to the value of Configuration 4. In addition, the decrease in the products concentration (biodiesel and glycerol) of these recirculation streams allows the reduction of the volume of the reactor–extractor, which has a positive effect on the capital costs of the extractive reaction process.

The different levels of integration analyzed in this work have a strong influence on the energy consumption of the global process. The results of the evaluation of energy costs for the process flow-sheets simulated are shown in Table 4 (the energy costs of oil extraction process are not included). The base case defined consisted in the production of biodiesel from crude palm oil employing ethanol as a feedstock. This base case includes the expenditure of ethanol production from lignocellulosic residues of oil palm, but without any integration between both production lines, e.g. the recycling of recovered ethanol is not considered. This configuration corresponds to two independent plants producing bioethanol and biodiesel in an autonomous way.

If the base case is taken as a reference, the simulation data show a 3.4% reduction in the unit energy costs in terms of MJ/L of produced biodiesel for the scheme involving the biodiesel production integrated with the production of ethanol from lignocellulosic residues of palm industry (Configuration 1 in Table 4). When the energy integration between both production lines (see dashed lines in Fig. 4) is considered (Configuration 2 in Table 4), the reduction of energy costs reaches a value of 13.6%. This demonstrates the integration benefits of these two configurations from energy viewpoint.

The analysis through process simulation carried out in this work confirmed the advantages of simultaneous integrated process related to conventional sequential configurations in the case of biodiesel production. Thus, simulation results for 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 (see Fig. 3a). In a previous work (Montoya et al., 2006), the sequential non-integrated process for biodiesel production was assessed following the same simulation guidelines as in the present article. The results obtained in that paper indicated that a 99.9% conversion can be achieved using a molar ratio between ethanol and oil of 12. Nevertheless, the purity of the produced biodiesel is reduced to 94% compared to the purity of the integrated process studied in this work (97.8%) using a molar ratio of 3.9 for Configuration 1, and to 98.9% purity using a molar ratio of 4.0 for Configuration 3. This implies a lower consumption of ethanol and a higher efficiency of the global process. It should be noted 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, yield, and productivity. The integration of reaction and separation allows the improvement of these process indicators since the products formed are removed from the reaction zone because of the formation of two liquid immiscible phases. This situation leads to the perturbation of both types of equilibrium present in the system (chemical and liquid–liquid equilibria). 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. In addition, the simultaneous process leads to a significant increase in the main product concentration in one of the two liquid phases (the extract), which is not possible to attain in a conventional configuration.

The recirculation of some process streams can be considered as another way of integration for the analyzed process. Data of Table 3 show that the aqueous streams from the bottoms of the rectification column and from the centrifuge processing the stillage (see Fig. 4) may be used as recycled water for washing the lignocellulosic biomass after its pretreatment due to their low contents of soluble solids. In addition, this recirculation makes possible a higher conversion of the sugars formed during the process, which leads to a higher ethanol concentration in the culture broth exiting the SSCF reactor. If a 5% increase in the conversion of both glucose and xylose into ethanol during the SSCF is considered, ethanol concentration in the broth reaches 6.11% by weight that implies lower costs in the separation and dehydration steps.

Other interesting integration possibility indicated by the simulation consists in the recirculation of the ethanol-enriched streams exiting from the top of the two columns employed for purification of both biodiesel and glycerol (Configuration 3). Thus, the recovered ethanol can be utilized again for transesterification reaction.

The heat integration also plays an important role in the improvement of the overall process. The results obtained illustrate how a simple utilization of the energy available in the overhead vapors of the concentration and distillation columns may entail significant reductions in energy consumption of the glycerol
Table 4  
Energy consumption of different technological configurations for biodiesel production using in situ produced ethanol

<table>
<thead>
<tr>
<th>Processes</th>
<th>Energy consumption, MJ/h</th>
<th>Unit energy cost of biodiesel, MJ/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-integrated production of biodiesel</td>
<td>1,210</td>
<td>–</td>
</tr>
<tr>
<td>Ethanol production from EFB and PPF</td>
<td>6,918</td>
<td>–</td>
</tr>
<tr>
<td>Base case</td>
<td>8,128</td>
<td>6.62</td>
</tr>
<tr>
<td>Configuration 1*</td>
<td>7,895</td>
<td>6.40</td>
</tr>
<tr>
<td>Configuration 2b</td>
<td>7,059</td>
<td>5.72</td>
</tr>
<tr>
<td>Configuration 3c</td>
<td>7,863</td>
<td>6.56</td>
</tr>
<tr>
<td>Configuration 4d</td>
<td>4,775</td>
<td>3.98</td>
</tr>
</tbody>
</table>

* Biodiesel production considering material integration using flash units for biodiesel and glycerol purification with ethanol recirculation to concentration column.  
** Biodiesel production considering material and energy integration using flash units for biodiesel and glycerol purification with ethanol recirculation to concentration column.  
† Biodiesel production considering material integration using distillation columns for biodiesel and glycerol purification.  
‡ Biodiesel production considering material and energy integration using distillation columns for biodiesel and glycerol purification.

recovery step (see Table 4). This is explained by the enhanced efficiency of the distillation column employed for separation of glycerol-enriched stream leaving the multi-stage reactor–extractor (stream 8 in Fig. 5). This tower exploits the heat contained in the overhead vapors leading to a better recovery of ethanol and to the decrease of ethanol content in the glycerol product stream exiting from that column. Consequently, the energy required to separate the ethanol from the glycerol is less than in the case when no energy integration is applied. If comparing energy consumption for Configurations 3 and 4, the reduction of energy requirements for the heat integrated case reaches 39.3%. Other possibilities for heat integration can be taken into account. 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 azotropic 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 agro-industrial wastes are higher than production costs from sugar cane or starch materials. For instance, McAloon et al. (2000) have calculated that production costs of a gallon of anhydrous ethanol from corn are of US$0.88 whereas these costs reach US$1.50 per gallon when ethanol is produced from lignocellulosic biomass. The cost of cane ethanol is even lower reaching near US$0.82 per gallon according to data obtained in a previous work (Quintero et al., 2008). However, it is expected that these costs decrease at mid-term being comparable to those of grain ethanol. Among the trends for improving this process, 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 biomass pretreatment technologies allowing a lower formation of inhibitors and a reduction of the energy consumption should be highlighted.

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 energy sources. Practically, each country has a wide availability of lignocellulosic materials (woody and forestry wastes, agricultural and agro-industrial residues, cellulosic fraction of municipal solid waste, among others) whose production do not imply the substitution of farming lands already used for food production. It is expected that this technology for fuel ethanol production will replace the utilization of other feedstocks that do have importance as foods (sugar cane, sugar beet, corn, wheat, sorghum, etc.). In this context, the production of biodiesel employing biomass ethanol represents a valuable opportunity for the production and global utilization of renewable liquid fuels. 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.

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 by-products.

4. Conclusions

Biodiesel production from oil palm by a configuration that uses 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 produced during oil extraction have a high content of lignocellulosic biomass making them very suitable materials for their conversion into ethanol.

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