Current Processes in Brazilian Biodiesel Production

Donato A. G. Aranda, Carla C. C. M. da Silva, Chaline Detoni

Abstract – Brazilian biodiesel production has experienced a very fast growing. After the first plant in 2005, more than 60 plants are running and producing about 2 million tons/year in less than 4 years of the national biodiesel program. In addition to regular transesterification plants, there is a commercial esterification plant running with heterogeneous catalysis producing biodiesel from palm fatty acids. A new process denominated hydroesterification is becoming more important since it is able to use any acid fatty material integrating hydrolysis and esterification reactions. In addition to an European standard biodiesel, hydroesterification produces a very pure glycerol during hydrolysis step. Pure glycerol is a multiple application molecule including hydrogen production to be applied with fatty acid reactions producing high valued bioproducts.

Keywords: Biodiesel, Transesterification, Esterification, Hydroesterification

I. Introduction

Biodiesel is defined by ASTM International as a fuel composed of monoalkyl esters of long-chain fatty acids derived from renewable vegetable oils or animal fats complying the requirements of ASTM D6751 [1]. Finding an alternative fuel has attracted considerable attention in recent years due to limitation of traditional fossil resources and increasing of crude oil prices as well as concern over greenhouse gas emissions. Biodiesel, a biodegradable and renewable form of energy, has cardinal potential as alternative fuels [2].

About one hundred years ago, Rudolf Diesel tested vegetable oil as fuel for his engine [3]. He operated his engine with peanut oil in the Paris Exhibition of 1900, it is seen that the use of vegetable oils as a diesel fuel is as old as diesel engine. Vegetable oils had been used as a diesel fuel in 1930s and 1940s as a diesel fuel is as old as diesel engine. Vegetable oils had been used as a diesel fuel in 1930s and 1940s but generally in emergency conditions such as World War II [4]. Although positive results were obtained at first, a number of severe engine problems were observed when the usage durations were extended [5].

With the advent of cheap petroleum, appropriate crude oil fractions were refined to serve as fuel and diesel fuels and diesel engines evolved together. However, as a result of oil crisis in 1970, the investigations on the vegetable oils for diesel engines started again.

Recently, because of increasing in crude oil prices, limited resources of fossil oil and environmental concerns there has been a renewed focus on vegetable oils and animal fats to make biodiesel fuels. Continued and increasing use of petroleum will intensify local air pollution and magnify the global warming problems caused by CO₂ [3]. In a particular case, such as the emission of pollutants in the closed environments of underground mines, biodiesel fuel has the potential to reduce the level of pollutants and the level of potential or probable carcinogens [6].

Different varieties of vegetable oils such as, canola [7], [8], palm [9], jatropha [10], palm kernel [11], sunflower [12], coconut [11] and soybean [13], [14], [15] have been studied as precursors for biodiesel production. The main concern about biodiesel production is the high price of vegetable oils compared to that of fossil based diesel fuel. As a result, in some countries, non-edible oils such as jatropha or waste cooking oils [16] are preferred due to their low price. Microalgae, as biomass, are a potential source of renewable energy, and they can be converted into energy such as biofuel oil and gas [17]. Microalgae contains as your cell components lipids and fatty acids storage products, metabolites and sources of energy.

Blending of biodiesel with diesel fuel is another option to mitigate the high price of biodiesel and in this case, the blended product is designated as Bx (B30, 30% biodiesel in 70% diesel fuel) [18]. Use of bio-diesel is catching up all over the world especially in development countries.

II. International Scenario

U.S. currently has about 170 biodiesel plants, with this number continuing to grow [19]. At present, soy oil is the dominant feedstock, but numerous other seed oils are being investigated – including canola, sunflower, safflower, cottonseed, palm, jatropha, and others. In addition, many biodiesel plants utilize animal fats and waste cooking oils as feedstock. Though not yet widely practiced commercially, there is also interest in
utilizing algal oils as a biodiesel feedstock. Algae offers the promise of much higher oil production per acre, and growth with low quality water. Most biodiesel in the U.S. is used as low concentration blends with petroleum diesel – typically 5% blends (B5) or 20% blends (B20). Some early usage of biodiesel has led to poor engine operability and/or fuel handling difficulties [20].

In Europe the most important biofuel is biodiesel [21]. In the European Union (EU) Biodiesel is the most used biofuel and represents 82% of the biofuel production [22]. Germany led production followed by France and Italy [21]. Biodiesel production uses around 1.4 million hectares (ha) of arable land in the EU. The most important biodiesel producer is Germany (with about 40% of the production). There are approximately 40 plants in the EU, however, the number of plants and the crushing capacity is growing quite fast. The plants are mainly located in Germany, Italy, Austria, the Czech Republic, France and Sweden [22]. In France, biodiesel production started in 1992. In 2004, the production capacity was 520,000 tons, which makes France the second largest biodiesel producer in Europe. In contrast to Germany, French biodiesel is exclusively sold as a mix with either up to 5% or up to 30% biodiesel added to fossil diesel [23].

India is producing only 30% of the total petroleum fuels required. The remaining 70% is being imported. It is estimated that India will be able to produce 41% of the total demand of diesel fuel consumption in India by 2012. The planning commission of India has released a bio-fuel project in 200 districts from 18 states in India. It has recommended two plant species: jatropha (Jatropha curcas) and karanja (Pungamia pinnata) for biodiesel production [19].

During this century, great progress has been made in biodiesel production in China. However, some barriers hinder biodiesel development in practice. Among these, two important barriers are a stable supply of cheap feedstock and the high production cost of biodiesel [24]. Total diesel fuel consumption in China reached 140 million tons in 2005, of which 40 million tons were imported [25]. In September 2001, the first biodiesel production factory was established in Hebei province with an annual output of 10,000 tons [24]. In 2005, the annual production of biodiesel was about 85,000 tons in China, and this output increased sharply to about 0.2 million ton by 2006. In 2007, more biodiesel corporations have been established in China including a few foreign enterprises, and together they produced more than 1.0 million tons of biodiesel [25]. In December 2006, the first enzymatic process for biodiesel production was implemented in Hunan with an output of 2×104 tons/yr [26].

### III. Brazilian Scenario

At 2005 Biodiesel was officially introduced in the Brazilian energy matrix. From this resolution the ANP (Agência Nacional de Petróleo) established rules specifying the mix of biodiesel and diesel fuel. Production and use of biodiesel on Brazil favoring development of a sustainable energy source about environmental, economic and social aspects and also shows the perspective in a reduction of diesel fuel importation. At 2008 the use of biodiesel on Brazil avoided importation of 1.1 billion of liters of diesel fuel resulting in a economy around US$ 976 million. In addition to reducing dependence on imported diesel, biodiesel has other indirect effects of their production and use, such as the increase in local and regional economies, both in the agricultural stage and industry.

Since July 1, 2009, all diesel fuel sold in Brazil contains 4% of biodiesel. The continued rise in the percentage of biodiesel added to diesel demonstrates the success of the National Production and Use of Biodiesel and experience gained by Brazil in the production and large-scale use of biofuels. Brazil is among the largest producers and consumers of biodiesel in the world with an annual production in 2008 of 1.2 billion liters and an installed capacity in 2009 to 3.7 billion liters.

Brazilian Biodiesel Program requires:
- B2 mandatory at Jan/2008 (850,000 ton/year);
- B3 mandatory at Jul/2008 (1,300,000 ton/year);
- B4 mandatory at Jul/2009 (1,700,00 ton/year);
- B5 mandatory at Jan/2010 (2013, originaly).

On Brazil 62 biodiesel plants are working (> 3,000,000 ton/year, capacity), 35,000 gas stations providing B4 and some transportation companies using B20, B30 (more than 2,000 buses).

In other hand this capacity can be larger as the available land for new crops is more than 90 millions hectares. See Table I.

#### TABLE I

**LAND USE IN BRAZIL**

<table>
<thead>
<tr>
<th>National territory 8,51 million Km²</th>
<th>Millions of hectares</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amazon forest</td>
<td>350</td>
</tr>
<tr>
<td>Breeding pastures</td>
<td>210</td>
</tr>
<tr>
<td>Protected areas</td>
<td>55</td>
</tr>
<tr>
<td>Annual cultures</td>
<td>47</td>
</tr>
<tr>
<td>Permanent cultures</td>
<td>14</td>
</tr>
<tr>
<td>Cities, lakes, roads and swamps</td>
<td>20</td>
</tr>
<tr>
<td>Cultivated forests</td>
<td>5</td>
</tr>
<tr>
<td>Other uses</td>
<td>60</td>
</tr>
<tr>
<td>Total</td>
<td>761</td>
</tr>
<tr>
<td>Unexploited area still available</td>
<td>90</td>
</tr>
</tbody>
</table>

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IV. Processes for Biodiesel Production

Transesterification

In the Brazilian context, biodiesel is conventionally produced from the transesterification reaction (Fig. 1). In this process the reaction occurs between one mole of triglyceride and three moles of alcohol in the presence of a catalyst, generally basic and homogeneous, generating 3 moles of mono-alkyl ester (biodiesel) and 1 mole of glycerol [28].

![Fig. 1. Transesterification reaction](image)

Although transesterification is a technology that is at public domain, is fast and requires low temperature, there are some limitations on the specification of the raw material. The use of this process is limited to the use of oils or fats with acidity below 1% and low humidity. This is because these two parameters favor the undesired reaction of saponification. In the saponification reaction the homogeneous basic catalyst reacts directly with the oil or fat to form soap, so there is a catalyst consumption and difficulty in washing, because the soap acts as a surfactant in aqueous and organic phases[29].

Decantation of the generated glycerol is slow and expensive, besides having impurities such as alcohol, catalyst and soap, which lower the value and increases the number of operations for purification and reuse of the glycerol [30].

It’s possible to perform transesterification using acid catalysts, heterogeneous or homogeneous, but this process, due to corrosion problems in the reactors and use of high temperature, isn’t used industrially. In this case, the transesterification process is catalyzed typically by Brønsted acids, preferably by sulfonic and sulfuric acids. These catalysts give very high yields to alkyl esters, but the reactions are slow, requiring temperatures above 100 °C and more than 3 h to reach complete conversion [31]. Pryde et al. [32] showed that the methanolysis of soybean oil, in the presence of 1 mol% of H$_2$SO$_4$, with an alcohol/oil molar ratio of 30:1 at 65 °C, takes 50 h to reach complete conversion of the vegetable oil (> 99%), while the butanolysis (at 117 °C) and ethanolysis (at 78 °C), using the same quantities of catalyst and alcohol, take 3 and 18 h, respectively.

The transesterification reaction using heterogeneous basic catalysts, has been studied by several authors. The catalysts used are magnesium oxide, potassium loaded on alumina, zinc oxide and mixed oxides derived from hydrotalcite. The number of works on the latter has greatly increased because of its bifunctional properties, i.e. it has active basic and acidic sites [33], [34], [35]. However, there aren’t many studies on the reuse of catalysts.

Bournay et al (2005) described a continuous process of transesterification by heterogeneous catalysis using mixed oxides of zinc and aluminum, where the reaction occurs at temperatures and pressures higher than in homogeneous catalysis, in addition to excess methanol. This alcoholic excess is removed by vaporization. The desired conversion is obtained with two successive stages of reaction and separation of glycerol [36].

V. Esterification

Esterification is another process for biodiesel that is also used industrially in Brazil. It is the reaction of one mole of fatty acid with one mole of alcohol to form a mole of ester and one mole of water [37].

This process is bound to use industrial by-product, such as Agropalma (Fig. 2) using the palm fatty acid obtained from the crude palm oil refining. In this process, niobic acid pellets are used as heterogeneous acid catalyst in fixed bed reactor [38].

![Fig. 2. Agropalma biodiesel plant](image)

Gonçalvez, J. studied the esterification reaction with the palm oil fatty acids at a molar ratio alcohol / fatty acid equal to 4, at 200 °C using 10% (wt/wt) acid niobic powder, obtained 88% of conversion, during one hour of reaction [39].

VI. Hydroesterification

Recently a new method to obtain biodiesel was developed, it is called hydroesterification (scheme 1) and it integrates the process of esterification similar to the one used in Agropalma with the process of hydrolysis of fats and oils, which is well known industrially. Hydroesterification occurs in two steps, the first is the hydrolysis of (mono, di and tri) glycerides present in the raw material producing fatty acids and glycerin. Fatty materials are heated and feed at the base of the column. Molar excess water enters into the top of the same column in a countercurrent process. On this step, water and glycerol of high purity are obtained at the base of the...
successful. This conversion level is obtained at 260 °C even with no catalyst. Glycerin generated during this stage is removed and sent to concentration. If the raw material has a high content of unsaponifiable materials, a vacuum distillation is necessary immediately after the hydrolysis [40].

The hydroesterification has many operational and environmental advantages [43] over other methods, such as:
- There is no concern with the acidity of the raw material, because in the hydrolysis reaction all the raw material is transformed into fatty acids.
- There is no problem with the water content of the raw material, because water is a reagent to hydrolysis.
- Glycerin has no contact with a catalyst or alcohol, which can make it be the so-called "food grade".
- It is possible to use really any fat material like lard, fish oil, chicken oil, sewage, etc. which the conventional transesterification does not comply.
- It is better under the environmental point of view because the transesterification generates waste (soap, glycerin salts derived from the neutralization) and hydroesterification tries to reuse liabilities of industries.

Two industrial hydroesterification plants are working in Brazil. USDA is a 10,000 metric ton/year facility at Parana state and Biobrax is a 60,000 mton/year in Bahia state (Figures 3a and 3b) [44].

VII. Glycerin

For each 100 tons of biodiesel produced by transesterification, about 10 tons of glycerin are generated. It is estimated that in 2013 there will be a surplus of glycerin in the order of 250,000 tons per year in Brazil. Therefore, the study of glycerol-chemistry is important for viable production of biodiesel, avoiding the accumulation of glycerol as waste [45].

- There are studies on the literature about the use of glycerine. Most of them involves pure glycerol like obtained in the hydroesterification process. Some solutions to the application of glycerin in the industry are showed next. Glycerol + Alcohols → Ethers [45]
- Plastics from Glycerol [46]
- Hydrogen from Glycerol Reforming (low temp, low CO concentration) [47]

Hydrogen generated from glycerin could be used in the industry itself for the following processes.
- \( \text{H}_2 + \text{Fatty acids} \rightarrow \text{Low iodine number Fatty Acids} \) [46]
- \( \text{H}_2 + \text{Fatty acids} \rightarrow \text{Hydrocarbons} \) [49]
- \( \text{H}_2 + \text{Fatty acids} \rightarrow \text{Fatty alcohols} \)

Figs. 3. USDA plant (a) Biobrax plant (b)

VIII. Conclusions

Biodiesel is a commercial reality in Europe and US. In Brazil, it is a very important issue in the national biofuel policy. As mandatory use, brazilian biodiesel...
production is growing very fast with more than 3 millions tons/year capacity in less than four years.

Transesterification process is still the most important industrial process. Hydroesterification is a more flexible process able to use any acid fatty material as industrial process. Hydroesterification is a more flexible process allows multiple applications including hydrogen production, a key component to extend biodiesel plants to biorefineries.

References


Authors’ information

Brazil CEP: 21941-909 email: donato@eq.ufrj.br

Chaline Detoni: Graduated in Chemistry (2006). Chaline has experience in inorganic chemistry, catalysis and biofuels focusing mainly on the following topics: zeolites, synthesis, MCM-22, oxidation, biodiesel, biogasoline and heterogeneous catalysis. M. Sc. obtained at Escola de Química - UFRJ (2008) and currently a Ph.D student at the same university.

Carla C. C. M. Silva: Graduated in Chemistry (2005). Carla has experience in catalysis and biofuels developing projects in the following topics: catalyst synthesis, hydrotalcites, catalyst characterization, biodiesel, biorefineries and heterogeneous catalysis. M. Sc. obtained at Escola de Química - UFRJ (2008) and currently a Ph.D student at the same university.

Donato A. G. Aranda: Ph D (1995, Chemical Engineering - UFRJ) Professor at Chemical Eng Department of Federal University of Rio de Janeiro. Donato has received the main award of Brazilian Catalysis Society (2007) and the main scientific award from brazilian government from Pres. Lula (2006). Main research topics are: biodiesel, biorefineries, heterogeneous catalysis and scale-up of catalytic reactors. Website: www.grentec-ufrj.com