

# **BIOFUELS: GENERAL ASPECTS,** TECHNOLOGICAL DEVELOPMENT AND **ECONOMIC VIABILITY**

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Abstract- This paper presents general aspects about the importance of technological development of biodiesel as well as environmental considerations, production, consumption and sustainability. Because of the need to have a source of sustainable and renewable energy, there is significant increase worldwide in the biodiesel bearing and marketing. Comparatively, it was shown in 2012 that Argentina surpassed the levels of biodiesel demand previously observed for Germany; since 2014 the United States remained in the lead and Brazil came to occupy the second position. Actually the biodiesel production in Brazil is sufficient to meet domestic and some external demand. Originally it was driven in an attempt to overcome economic crises and have at the same time, energy independence. However, the positive result can be proven by the number of vehicles using B100 (biodiesel obtained from sugar cane or soy) has had an importante role. In general, 75.57% of the biodiesel produced in Brazil become from soybean, while in other countries from palm oil (32%). Biodiesel has the advantage of reducing majority of offencive gases to the environment and less energy dependence on fossil fuels, among other benefits and its blends provide beneficial effects on the consumption of fuel and wast materials wear. However, a barrier to the large production of biodiesel on a commercial scale is the fact that its final cost still higher than that of diesel oil added to stagnation of soil with long term reduction in production capacity. Most countries already have been using blends of biodiesel in diesel with significant reductions in environmental impact and meet the demand for fuel consumption.

keyworlds: Biodiesel; Historical and technological aspects; Worldwide production and consumption; Environmental impact.

#### I. INTRODUCTION

Biodiesel is a generic name for biodegradable fuels in which chemical composition do not have sulfur or aromatic compounds, largely evidenced on diesel. This alternative fuel type derived from renewable sources, especially vegetable oils, and can be used in mixtures with diesel aiming advantage to reduce toxicological risk. Biodiesel blends can be used as B2 (2% biodiesel and 98% diesel), B5 (5% biodiesel and 95% diesel), B7 (7% biodiesel and 93% diesel), B20 (20% biodiesel and 80% diesel) onwards. Biodiesel mixtures volumetric proportions among 5% to 20% are the most used and stands out biodiesel with lower sulfur amounts producing excellent lubricant products. Biodiesel B5 provides burning with reduction of environmental impacts and for car engines application none adjustment become necessary [1, 2].

Biodiesel 100% type is produced through a chemical process called transesterification affording semi-synthetic esters and glycerin as a secondary compoun, widely utilized in the manufacture of soap. The biofuel quality is directly related to the content of hydrocarbons for good lubricity and by residual levels of sulfur that prevents biodiesel industrial applications, at high percentages [3-9]. Transesterification reactions carried out in the biodiesel industry is widely conduced for oleaginous plants, because of its high oil content. In that, triglycerides react with a short chain alcohol in the presence of a catalyst (as acid or basic medium), preferably ethanol to provide a satisfactory lubricant product with low corrosive power [9, 10-12].

agronomic aspects (pests, diseases and weeds) Aiming to reduce recurring problems in this industrial sector biofuels programs were implemented in several countries. Brazil successfull highlight lies in the production and marketing of ethanol. In fact, bioethanol is commercialized as a fuel in many countries, such as Brazil, USA, China and Thailand This present paper emphasises specific aspects of biodiesel in a general approach. Specifically, historical comments, technological development, global consumption, economic and environmental viability, as well advantages and disadvantages of biofuels production are herein

conmented.

Currently biodiesel production increases worldwide due

the advantages of energy production from renewable sources.

The United States, Brazil, some European Union (EU)

countries (Germany, for example) and Argentina lead the

mundial rank production [13-15]. In that, blend biodiesel

added biotechnological value on fuel production with

reduction of costs been economically viable. On matters

giving rise to discussions on technologies and renewable

energy sources some aspects are highlighted such as

increases demand for fuel consumption, exhaustion of oil

reserves, worsening pollution, acid rain, global warming and

global economic crises. In this context, biofuels world

production suffers limitations correlated to high productivity

demand, seasonal issues, adverse weather occurences and

ISSN (Online):2278-5299

#### **Publication History**

Manuscript Received : 19 July 2015 Manuscript Accepted : 1 August 2015 Revision Received : 26 August 2015 Manuscript Published : 31 August 2015

#### II. HISTORICAL ASPECTS

Fuel history regarding to oils and fats as well its derivatives began in 1900 when Rudolph Diesel (inventor of the engine internal combustion) essayed crude oil and peanut oil. Meanwhile, other countries have developed research in this purpose. The French Petroleum Institute for exemple, conducted in 1940 several tests using palm oil to produce biodiesel [21, 22]. Currently, biodiesel studies has been focused in biodiesel blends because their optimal performance in vehicles with greenhouse gas emissions reduction.

According to standard legislative British Standard BS EN 590, biodiesel blends smaller than B10 present warranty manufacturers in EU countries such as United Kingdom, Germany, Croatia, Iceland, Norway and Switzerland [23].

Respect to biofuels marketing in Latin America, the pioneer is Brazil. The first attempts began in the 1970s and were not motivated by environmental issues but as a strategy to overcome economic crises, aiming energy independence which was supported by agronomic aspects of regional raw materials [20, 24]. In 1983, in other to allow industrial biodiesel production, Brazilian Government determined the implementation of the Vegetable Oil Program (OVEG) focusing in replace fossil fuels. In this way, biodiesel become applied in internal combustion engines with compression ignition as well as for power generation. As the positive result of the OVEG program, in 2005, the Law 11.097 enabled biodiesel in the Brazilian energy matrix and establish from January 2008 onwards that diesel should contain biodiesel 2% blend (B2) and also established blend reach (B5) until 2013 year. However, the Resolution No.2 of the National Energy Policy Council (CNPE) published in 2008 year, determined that from July 1th, 2008, the mandatory content of biodiesel in a mixture had to increase up to 3%.

Nowadays, despite of the discovery of large oil reserves in the pre-salt layer, this percentage has been expanded and the Brazilian Federal Government maintained the prior biodiesel blendes approval. The industrial production of B5 and B7 blends were established before 2013 year [1].

Aiming to control biodiesel pollution indexes from any raw material, international specifications must be considered, for example, ASTM D6751 norm. In USA, biodiesel represent a significant fuel alternative to obtain strong approval in the Clean Air Act of 1990 and its sale or distribution is authorized by the USA Environmental Agency (EPA). The National Agency of Petroleum, Natural Gas and Biofuels (ANP) is the Brazilian agency control. Beside the ethanol marketing consolidation in Brazil, an other successful example of Brazilian biodiesel is the soybean B100 which had been used in Curitiba city (Paraná State) in bus fleet reducing 70% of opacity rates and 30% carbon monoxide at environment [25].

# III. RAW MATERIAL ADVANTAGES TO OBTAINING BIODIESEL

Brazil has one of the highest biodiversity in the world with a 55.000 known species flora and numerous other non-cataloged vegetals or even unknown to botanical science. In fact, Brazilian biodiversity products account for 31% of exports demand, specifically for coffee, soy and orange. This richness is due mainly to Brazil privileged geographical position, suitable climate and humidity and many biotic and abiotic factors. However, this genetic diversity has not always naturally existed but was constituted over the centuries, through the migration of plants and animals coming from other countries [26]. This is the case of many other countries, the United States, for example, with thousand varieties grown from it 99.7% of the green reserve are not native, except for artichokes-of-jerusalem, the wild cherry trees and sunflower [27].

Worldwide the vegetable raw materials used as biodiesel productivity originates from soybean, babassu, castor bean, sunflower, corn, peanut, jatropha, palm, rapeseed (canola), among other minor species, being the most used soybean and palm oils.

Among the alternatives of raw materils for biodiesel production there are other possibilities such as animal origin, in which bovine fat, pig and poultry. In addition, frying oils used can also be recovered to produce biodiesel. Table 1 shows the main potencial of various oils for brazilian biodiesel production in which biodiesel (monoalkyl esters) were obtained by chemical processes of transesterification (Figure 1) according to its industrial importance and viability, in which advances on agricultural and seasonal phenomena for oils cultivations and for biodiesel development process and applications were included [4, 7, 8, 24, 28-35].

Soybean (Glycine max L. Merr.), stands out in biodiesel production, even with a relatively low income compared to other oils. It is justified by its resistance function to climate changes and pluviometric precipitation annual of 700-1200 mm well distributed perfectly meet their water needs and the optimal temperature for the best soybean development are between 20 °C to 35 °C. Regions with high humidity are not suitable for its cultivation [4, 8, 33-35]. For sunflower (Helianthus annus L.) its optimum temperature for development around 27 °C to 28 °C. Elaeis guineensis Jacq. (palm) reaches up to 15 m high, making the production bunches started 3.5 years after planting with minimum average temperatures exceeding 24 °C. Brassican napus L. (canola) requires moist soils mosto of the year, limiting its large-scale cultivation. Ricinnus Communis L. (castor bean) is considered very viscous not being viable for biodiesel production [33-35].

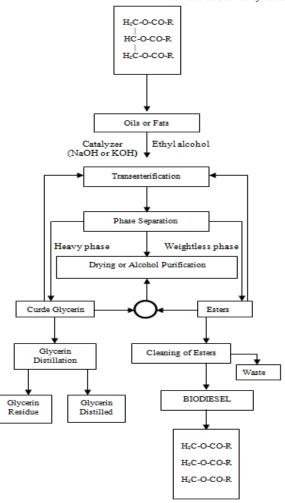


Figure 1. Oil transesterification process [31].

Table 1. Caracteristics for main Biodiesel oils [32].

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Species	Commom Name	Oil Source	Oil Content (%)	Yield (t.ha <sup>-1</sup> )
Attalea Speciosa Mart.	babassu	Seed	66	0.1 – 0.3
Brassica napus L.	canola	Bean	40 – 48	0.5 - 0.9
Cocos nucifera L.	coconut	Fruit	55 – 60	1.3 – 1.6
Elaeis guineensis Jacq.	Palm	Seed	22	3.0 – 6.0
Glycine max (L.) Merr.	soybean	Seed	18	0.2 - 0.6
Gossypium hirsutum L.	cotton	Seed	15	0.1 - 0.2
Helianthus annuus L.	sunfower	Seed	38 – 48	0.5 - 1.9
Persea americana Mill.	avocado	Fruit	7.0 – 35	1.3 – 5.0
Ricinus communis L.	castor bean	Seed	45 – 48	0.5 – 1.0

Regarding to the increased productivity of coconut oil (*Cocos nucifera* L.) the average temperature should be around 27 °C with monthly minimum temperature less than 18 °C and insolation season should be between 1800 h to 2000 h per year. Pluviometric precipitation considered ideal must be between 1500 mm to 1800 mm per year with a monthly distribution not less than 130 mm to 150 mm. The largest Brazilian plantations of *Cocos nucifera* L. are long the coast northeast which accounts for approximately 81% of Brazilian national production [33-35].

# IV. PHYSICAL AND CHEMICAL PARAMETERS AND COMPOSITION OF BIODIESEL

Austria was the first country to set and aprove biodiesel standards of quality which was applied to methyl esters of *Brassica napus* L. (canola). Subsequently, standards of quality were established in other countries based on the so called regulations ASTM D6751 (from EU) and EN 14214 (from USA) as shown in Table 2 [33].

Parameters such as kinematic viscosity, flash point, among other ones, aiming to reduce combustion emissions, safe transport and handling, provide very enlightening results about the quality of biodiesel production. These parameters undergo variation according to the presence of contaminants from raw material, biodiesel production process or chemical modification formed during biodiesel storage. The common contaminants coming from raw materials are phosphorus, sulfur, calcium and magnesium [7]. Esters molecular structure is directily corraleted with the vegetal oil material in the biodiesel production. In this context, esters structures suffer varying in both carbon chain size by the presence of substituent groups and also by the position and quantity of insaturation bonds. Hydroxyl carbonic chain linked to the alkyl ester derivative of ricinoleic acid is the main characteristic for castor bean biodiesel.

Table 2. Biodiesel standards of quality [41]

Characteristic	Unit	Brazil ANP	EU EN 14214	USA ASTM D6751
Kinematic Viscosity (40 °C)	mm <sup>2</sup> /s	3.0 - 6.0	3.5 -5.0	1.9 -6.0
Flash point minimum	°C	100	120	130
Copper Corrosiveness (50 °C/, 3 h) maximum	mg/kg	1	1	3
Total sulfur maximum	mg/kg	50	10	15
Phosphorus maximum	mg/kg	10	10	10
Oxidation stability ( 110°C) minimum	h	6	6	-

### Kinematic viscosity at 40 °C

The viscosity of the biodiesel increases with carbon chain lenght and also degrees of saturation which interfer on the burning process in the engine combustion chamber. High viscosity causes heterogeneity in the combustion of biodiesel due to the decrease efficiency of atomization in the combustion chamber, causing deposition of residues on internal engines parts. The residual soaps and the unreacted

carbohydrate (mono-, di- and triglycerides) and oxidative products of the biodiesel degradation process increase its viscosity [7].

#### Flash point

The flash point is the lowest temperature where release of vapor is observed from a liquid in suficiente quantity to form a flammable mixture with air. The flash point values for biodiesel is considerably higher than values observed on mineral diesel. For B100 fuel the flash point is about 170 °C, however, small amounts of alcohol added to the B100 give rise to significant decrease [35].

#### Phosphorus and sulfur content and corrosion

The transesterification of crude vegetable oil without prior degumming treatment will result in reaction yield loss and higher phosphorus content. Additionally, emissions will produce large amount of particulate matter. From that, sulfur compounds which affect the automotive catalytic converters process. Sulfur matter is formed during fuel oxidation and also damage catalytic converters, increases emission of particulate matter, and cause corrosion on the automotive engine [36-38].

A parameter set to determine the fuel corrosive potential is the corrosiveness of copper metal which could be found into automotive engine or storage tank. The fuel corrosive property is associated with the presence of acids or sulfur compounds. Since in biodiesel the sulfur content is lower the need for search this parameter had been discussed, being only necessary to essay acidity [7, 35].

Diesel with low sulfur content present loss of lubricity due to the reduction of nitrogen and oxygen compounds during the desulfurization process. Biodiesel, however, has very low amounts of sulfur and excelent lubricity, so can act as lubricity additive for correction of the mineral diesel [39].

#### Oxidation stability at 110 °C

Diesel fuel is a mixture of hydrocarbons with long carbon chain (15 to 20 carbon atoms) and other chemical components considered impurities. Positions and quantities of double bonds in the carbon chain of the fuel compounds are factors that influence the oxidative stability. The presence of water can promote the hydrolytic biodiesel oxidation and the concentration of alkyl esters with a high degree of insaturation varies depending on the raw material. In fact, it was observed the greater the number of insaturations the greater the reactivity, and therefore, the molecule is more susceptible to termal or oxidative degradation affording insoluble products and its deposits and clogging affect fuel injection in the automobile engines. Palm biodiesel compared to soybean biodiesel has fewer insaturations therefore is stable to oxygen processes. The high temperature and exposure to air are also important factors that affect the stability of biodiesel, which is significantly affected when these two factors are present at the same time [40-43]. In Table 3 physical and chemical parameters are focused for B100 obtained from palm oil and soybean.

Table 3. Physical and chemical properties of biodiesel obtained from palm and soybean [41, 42].

Characteristic	B100 Palm	B100 Soy bean
Kinematic Viscosity at $40 ^{\circ}\text{C}  (\text{mm}^2/\text{s})$	4.76	4.37
Flash point (°C)	170	202.5
Copper corrosiveness (50 °C/3 h)	1	1
Total sulfur	1.81	0.86
Oxidation stability ( 110 °C/h)	23.56	6.086

The molecule of methyl oleate, one example among alkyl esters present in biodiesel, is significantly oxygenated and becomes a rich source of oxygen radical and its combustion chamber conditions, been much more oxidant than the oxygen gaseous air, providing higher flash point than mineral diesel. All the cited abouve fuel properties produce a positive effect on fuel consumption and vehicle wear parts that use different proportions diesel/biodiesel. Figure 2 shows the profile of the diesel consumption, as well as mixtures with biodiesel.

The 20% biodiesel addition to diesel causes a decrease in performance of automotive engine, however, diesel/biodiesel amount maintained above 20% increases its consumption. For B100 it was observed similar diesel thermal efficiency but B100 due to its low calorific power shows higher consumption [44]. Several biodiesel blend were analyzed and among them B20 showed 2.5% at maximum greenhouse gas reduction [45].

Analysis performed for viscosity, presence of water and iron content in the lubricant oil, showed acceptable changes deemed and do not compromisse the automobile engine performance [46]. When the regular diesel automotive engine was analyzed by running biodiesel B10 (obtained from frying oil) without any adaptation, it was successfull without any apparent damage to engine components [47].

Potential of biodiesel to diesel studies indicated that replacement of the various mixtures ester/diesel burned more efficiently, resulting in an improved thermal efficiency of the automotive engine. In addition, mixtures of carbon monoxie were less produced than those observed on mineral diesel. Automobile engines running B100 and B75 performed best, while B50 resulted in lower emissions at all tested velocities

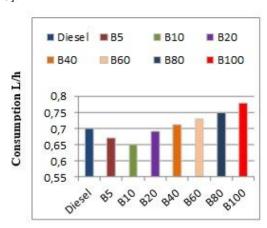


Figure 2. Profile fuel consumption measured for diesel, biodiesel and blends on eletricity generator [33].

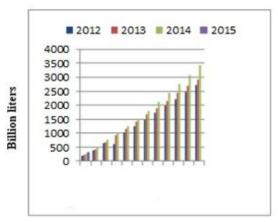
Diesel/biodiesel

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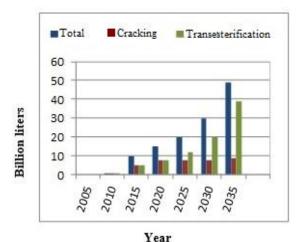
# V. BIODIESEL ADVANCES AND PERSPECTIVIES IN BRAZIL

Since 1980s Brazil won prominent place on the world biodiesel market. Brazil emerged for sustainable development with expansive grounds such as good weather (tropical or subtropical climate) favoring the large cultivation variety of biodiesel raw materials. In 2014, 3.40 billion liters of biodiesel were consumed in Brazil, representing an increase of 6.5% compared with previously year. As expected, biofuel production increased in the same amount, about 3.42 billion liters (Figure 3). Therefore, Brazil has become the second largest biodiesel producer and consumer worldwide, surpassing Germany, that had been the largest representative country [47].

Due to the growing demand of global consumption it is estimated that Brazil could produce biodiesel to meet both domestic and foreign markets with majority production (80%) via transesterification process [31] and minority via cracking, which consist in break molecules at temperatures above 450 °C in the absence of air or oxygen, affording a rich mixture of chemical compounds with properties very similar to diesel [48, 49]. Figure 4 shows estimates for biodiesel production in Brazil by different processes [49].

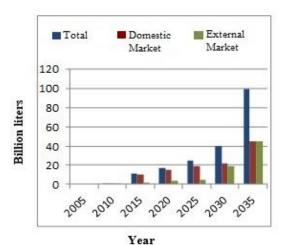


**Figure 3.** Improvement of biodiesel production in Brazil [47].

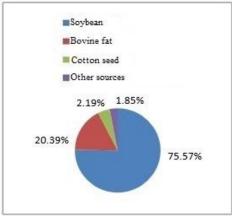


**Figure 4.** Estimate for biodiesel production by different processe [49].

According to estimatives biodiesel porduction for domestic and export markets it will be equivalent in a long term (Figure 5). Currently, 75.57% of the biodiesel produced in Brazil comes from soybean, overcoming the United States that produces 89.5 million tons [50]. In 2014, it was 2.20 billion liters higher than in 2013 (2.11 billion lliters) resulting in a market increase from 82 million tons to 92 million tons, becoming the largest producer. The participation of this raw material supplies in basket fell from 80.6% to 75.2%, which characterize a future sustainability problem. Alternatively, in the percentage amount of biofuel obtained from frying oils, the recycled soybean oil records up production of 18 million liters in 2013 and 40 million liters in 2014 [51]. Figure 6 shows the whole raw material used in Brazil to produce biofuel along with the major soybean biofuel production (75.57%), 20.39% derived from bovine fat, 2.19% comes from cotton seed oil and 1.85% other sources such as sunflower (a raw material utilized in the midwest region), canola (south region), palm (north region) and castor bean (northeast region) [52].



**Figure 5.** Estimate for biodiesel production by consumer demand [49].



**Figure 6.** Biodiesel raw materials used in Brazil [52].

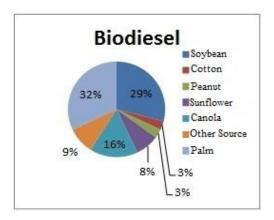
In Brazil the midwest region stands out as the largest biodiesel producer, accounting for about 40% of the national demand [30]. Due to the increase of the biodiesel blended (ranging from 5% to 6% in July 2014 and 6% to 7% in November 2014) the biofuel sale increased 16.45% (3.41).

billion liters per year). Actually, cross the country there are in operation 86 biodiesel stations, which are concentrated in greater numbers in the Brazil midwest, south and southeast regions. Specifically, in Mato Grosso State there are 20 biodiesel stations, in Góias 7 units, in São Paulo 8 and in Rio Grande do Sul 5, among other ones [53].

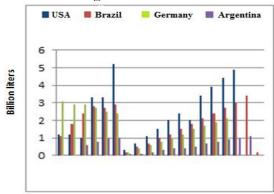
# VI. WORLD REPRESENTATION OF BIODIESEL AND ITS ENVIRONMENTAL CONSIDERATIONS

Many countries have had employing efforts on biodiesel industries development along with United States, Brazil and European Union, arises Argentina, Canada, Philippines, Japan, India, Indonesia, Malaysia and Taiwan [50]. According to the International Energy Agency (IEA) the global projections for 2020 predict significant substitution of fuel sources from fossil fuels to renewable biomass sources, especially sugar cane and corn, aiming at ethanol production and for major biodiesel demand soybean, palm and canola.

In 2014 the production and consumption of biodiesel in the United States was 4.8 billion liters, almost of the same amount produced in 2013. As pointed out above, in 2014 3.40 billion liters were consumed in Brazil representing 6.5% of increase compared to 2012 and biodiesel production increased in the same amount (3.42 billion liters). Germany produced 3.0 billion liters in 2013 and in 2014 it was about 3.1 billion liters. The United Kingdom countries consumed 195 million liters of biodiesel during the first months of 2014 representing an increase of 52.3% over the 128 million liters consumed in the same period of the previous year (2013) [47, 54, 55]. Indonesia leads the biodiesel production from palm oil, overtaking Malaysia. In 2014 were produced 31 million tons and reached approximately 52% of global production [33]. Figure 7 shows the raw materials used worldwide in the production of biofuel [50] and Figure 8 biofuel consumption [47].



**Figure 7.** Raw materials used worldwide in the production of biofuel [50].



**Figure 8.** Worldwide biodiesel consumption [47].

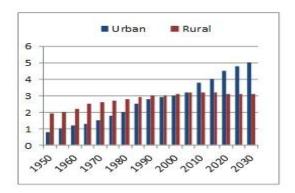
In Brazil, the Sustainable Production Program for Palm Oil was created in 2010, delimiting few suitable areas at regions that suffered human action. This program is based on the guidelines of preservation of native vegetation and also by the integrated production for family agriculture, emphasised in the regulation for conversion of areas used for sugar cane and also include limitations correlated to degraded Amazon Brazil areas [56]. Taking in acount the biodiesel blended demand as well as sugar cane in Brazil to produce ethanol, the trend correspond to a large area of reserve for planting oleaginous. About ethanol production to run flexfuel cars, in 2020 it could add 75% of the fleet [51]. Concerning to this subject and based on deforestation prohibition in the native areas throughout the country for planting, the total of suitable areas fell from 232.8 million to 31.8 million hectares [56]. So, in Brazil from the whole 96.3% country regions for native planting it is not allowed for palm cultivation and palm oil for biofuel still little explored. In fact, nowadays around the world planting palm is considered one of the main reasons for destructive deforestation. Despite of that, the palm biodiesel production increases is explained by its good results, one hectare of palm produces on average 5 tons of oil which is greater than soybean production (0.5 ton per hectare) [33].

Due to the fuel industry competitiveness it is important to equalize biodiesel supply and the food quantitative needs, to avoide rises prices on food products. Table 4 shows perspectivies for vegetal oil production during 2013 to 2022 years. Certainly there will be competitiveness in the consumption of vegetal oils to supply food and fuel industries which increases agricultural improvement [56, 57].

As a result of the world rural exous will increases fuel consumption been estimated that in 2030, 60% of the worldwide population will reside in cities. Figure 9 shows the rural world exodus data. The distance between the countryside and cities has been reduced and the technology becomes more accessible day by day, beyond the obvious purchase of land of small farmers by landowners with a drastic reduction in the supply of food products, including oils in general [53, 54].

**Table 4.** Annual world perspectivies for cereal and biofuel demand [57].

Country	Cereal	Oils	Ethanol	Biodiesel
Brazil	1.1	2.4	5.1	2.9
United States	1	1.2	3.8	1.7
European Union	-	1.9	-	6.3
World	1.4	2.0	4.1	4.5



**Figure 9**. Rural world exodus data [53, 54].

Despite of the environmental advantages conferred to biodiesel, one has to consider the part of productivity and its environmental issues. The biodiesel blend content provides increasing in water consumption. So, generates a loss in biodiversity and food habitats and the tendency to monoculture causing soil stagnation with a reduction in the long term production capacity. Actually, many growing plants land for biotechnoogical purposes were originally tropical forests with great capacity for CO<sub>2</sub> aborption and reduction effects that contribute to global warming. In the other hand, the world population has to deal with the improvement of biotechnology aiming at sustainability and better environmental living conditions [58-62]. In this context it is known that addition of biodiesel to diesel reduces vehicle emissions and increases the lubricity of the fuel (motor parts lubricating capacity). Among the petroleum-based fuels, diesel is one of the most susceptible to the presence of biological and chemical origin sediments and the higher biodiesel content in the mixture, the greater biodegradability, affording new probems such as clogging of filters, emergence of dregs and bacteria proliferation [62, 63]. In fact, biodiesel allows security in safer handling and storage by having lower flash point (100 °C to 210°C) compared to diesel (50 °C) with better lubricity and little or no change in automobile engines. Biofuel degrade about 4 times faster than petroleum diesel and biodiesel blends degrades up to three times faster than diesel. Table 5 shows the percentage of emissions of particulate pollutants from the biofuels B20 (biodiesel in a mixture with 80% diesel) and B100 (pure biodiesel), evaluated by comparing the percentage of emissions of diesel particulate pollutants which is considered as the main responsible for global warming [57, 64, 65].

**Table 5.** Particulate pollutant emissions B20 and B100 [65].

	Biodiesel B20	Biodiesel B100
Particles	-12%	-47%
Carbon monoxide	-12%	-48%
Dióxido de carbono		-78%
Hydrogen sufide	-20%	-100%
Sulfur dioxide	-20%	-100%
Nitrogen oxide	+2 a -2%	+10 a -15%

Estimatively, a run biodiesel car makes on average 581 km with emissions of 6.7 kg of  $CO_2$  per 100 km; run diesel car (fuel with sulfur content up to 10 mg/kg) 524 km with emission of 21.7 kg of  $CO_2$ ; a car running 368 km with ethanol emits 10.2 kg of  $CO_2$  and gasoline emits 24 kg of  $CO_2$  by running 329 km [33].

Obtaining biodiesel by transesterification process enables gycerine production which is widely used in the production of cleaning materials. Over recent years, many USA biodiesel manufacturers are reducing the water consumption in the production, avoiding disposal of liquid waste into the environment. It is known that at final stage of biofuel production, the product goes through wash processes (repeating five times washing) as the purpose to eliminate impurities and increase its quality. The wast water is rich in glycerin, fatty acids and alcohols requiring cares before environmental discard. To purify each liter of biodiesel it is consumed at least three liters of water [66-68].

Most countries already use mixtures and tests of volumetric proportions increasing of biodiesel in diesel. The blend use provides significant reductions in environmental impact by reducing greenhouse gases as well as acid rain and meet the demand for fuel consumption. However, it requires a strict control of waste from the production, mainly due to scarcity of water, suitable for consumption. In Brazil, there is no survey or safe estimate on the generation of effluents by biodiesel chain, as each plant has different technologies in its production process, varying the quantity and quality of waste. However with respect to the water consumption it is known that the biodiesel wash water is treated and reused by the Brazilian stations of biodiesel production, as Petrobras Biofuels (PBio) program regulation. As cited before, in 2014 the Brazilian biodiesel production was 3.4 billion liters needing 8.1 billion liters of water consumption to ensure the cleanliness of the product. Comparing it to human being basic needs (110 liters per day), the total volume of water for biodiesel production all long year coud serve 254.100 people [69].

Compensating for this expense and to make the process more effective, PBio uses technology from USA Company, Crown Iron Works, which works in a closed circuit water/whased water that is treated and reused in its own biodiesel purification process and shows efficiency up to 95% and reduces to a minimum the need for more water consumption [69].

Specifically, the biodiesel whased water treatment process is made by coagulation-flocculation in which coagulation corresponds to destabilization of the particles, obtained by reduction of the repulsion forces by the addition of chemicals, the anticoagulants, added during intense agitation to disperse rapidly hydrolyzed species. Flocculation is the agglomeration of coagulated particles and matter in suspension in the liquid mass, forming arger and denser clusters, called flakes [70, 71].

From a technological point of view, reactions to produce biofuel may be caused by conventional process (chemical using chemical, acid or basic catalyzers and non-conventional such as biological process (with biological catalyzers, enzymes or immobilized cells). Through a variety of processes that includes esterification, transesterification, in situ transesterification, cracking, pyrolysis, alcoholysis, enzyme catalysis, microemulsions reactions, microwave assisted biodiesel production, continuous production of biodiesel supercritical ethanol. among methodologies, the development of analytical procedures to valuate transesterification or other process is still a challenge in biofuel production [24, 72-78]. In this context, there is an intense interest in the development of renewable fuels, both clean and economically viable. In fact, current biodiesel production processes face a number of constraints, especially in terms of prices, flexibility and renewability of feedstocks. A barrier to the large production of biodiesel on a commercial scale is the fact that its final cost still higher than that of diesel oil added to stagnation of soil with long term reduction in production capacity. Adding value to the biofuel industry the increasing demand of biodiesel for blending with fossil-derived diesel leads to a great production of residues and co-products. The residues generated in the vegetable oil production are mainly used in animal feeding, manure production and thermal energy generation. On the other hand, the focus on glycerin, the main co-product of biodiesel production, is the chemical transformation into products that can be used in the production of plastics as well as fuel additive [76, 79-81].

#### REFERENCES

- [1] ANP Agência Nacional de Petróleo, Gás Natural e Biocombustíveis. Dados estatísticos mensais. Vendas, pelas distribuidoras, dos derivados combustíveis de petróleo (metros cúbicos). Available in: <a href="http://www.anp.gov.br/">http://www.anp.gov.br/</a>>. Accessed at July 1th, 2014.
- [2] PATIL, K. N.; ROMANA, P. V.; SING, R. N. Performance evalation of natural draff basead agricultural residues charcoal system. Biomass and Bioenergy, 2000, 18.
- [3] MEIRA, M.; QUINTELLA, C. M.; FERRER, T. M.; SILVA, H. R. G.; GUIMARÃES, A. K.; SANTOS; M. A. Identification of adulteration of bioduel by addition of residual oil instead of biodiesel to the diesel by total spectrofluorimetry and principal component analysis. Química Nova, 2011, 34, 4.
- [4] JOSHI, H.; MOSER, B. R.; TOLER, J.; WALKER, T. Preparation and fuel properties of mixtures of soybean oil methyl and ethyl esters. Biomass and Bioenergy, 2010, 34.
- [5] SUAREZ, P. A. Z.; MOSER, B. R.; SHARMA, B. K.; ERHAN, S. Z. Comparing the lubricity of biofuels obtained from pyrolysis and alcoholysis of soybean oil and their blends with petroleum diesel. Fuel, 2009, 88, 6.
- [6] FARIA, R. C. M.; REZENDE, M. J. C.; REZENDE, C. M.; PINTO, A. C. Development and validation of a methodology FOR analysis of biodiesel: diesel blends using gas chromatography-mass spectrometry. Química Nova, 2007, 30, 8.

- [7] KNOTHE, G.; STEIDLEY, K. R. Lubricity of components of biodiesel and petrodiesel. The origin of biodiesel lubricity. Energy Fuels, 2005, 19, 3.
- [8] COSTA NETO, P. R.; ROSSI, L. F. S.; ZAGONEL, G. F.; RAMOS, L. P. Biofuel production alternative to diesel oil through the soybean oil used transesterification in frying. Química Nova, 2000, 23, 4.
- [9] BRAILE, P. M.; CAVALCANTI, J. E. W. A. Industrial Wastewater Treatment Handbook. São Paulo: CETESB, 1993. 764p.
- [10] MENEGHETTI, S. P.; MENEGHETTI, M. R.; BRITO, Y. C. A Transesterification, some applications and biodiesel production. Revista Virtual de Química, 2013, 5, 1.
- [11] FERRARI, R. A.; SOUZA, W. L. Evaluation of oxidation stability of sunflower oil biodiesel with antioxidants. Química Nova, 2006, 32, 1.
- [12] AZEVEDO, D. M. P.; LIMA, E. F. O Agronegócio da mamona no Brasil. Brasília, 2004.
- [13] COSTA, V. L.; KOVALESKI, J. L.; ANDRADE JUNIOR, P. P.; COSTA, D. L.; MORSCHEL, E. L. Transferência de tecnologia na produção de biodiesel: alternativa para inclusão social e desenvolvimento regional no estado do Paraná. Revista Brasileira de Gestão e Desenvolvimento Regional, 2013, 9, 1.
- [14] SOUSA, R. A.; RIBEIRO, C. Study of an electrochemical method to sunflower oil to biodiesel conversion assessment. Química Nova, 2012, 35, 1.
- [15] CORDEIRO, C. S.; RAMOS, L. P. Biodiesel in South America; Knothe, G.; Krahl, J.; Gerpen, J. V., eds.; AOCS Press: Llinois, 2010.
- [16] HOMIAK, J. A. Produção de biodiesel utilizando microalgas. Revista de Saúde e Biologia, 2014, 9, 2.
- [17] HASS, M. J.; MC. ALOON, A. J.; YEE, W. J.; FOGLIA, T. A. Renewable hydrogen and carbon nanotubes from biodiesel waste glycerol. Bioresource Technology, 2006, 97, 671.
- [18] MIAO, X.; WU, Q. Biodiesel production from heterotrophic microalgal oil. Bioresource Technology, 2006, 97, 841.
- [19] ANTOLIN, G.; TINAUT, F. V.; BRICENO, Y.; CASTAÑO, V.; PEREZ, C.; RAMIREZ, A. I. Optimisation of iodiesel production bysunflower oil transesterification. Bioresource Technology, 2002, 83, 111.
- [20] SCHUCHARDT, U.; RIBEIRO, M. The petrochemical industry in the next century: how to replace oil. Química Nova, 2001, 24, 2.
- [21] İLKILIÇ, C.; ÇILĞIN, E.; AYDIN, H. Terebinth oil for biodiesel production and its diesel engine application. Journal of the Energy Institute, 2014, 1.
- [22] GATEAU, P.; GUIBET, J. C.; HILLION, G.; STERN, R. Rev. L'Institut Français du Pétrole, 1985, 40, 509.
- [23] ROPKINS, K.; QUINN, R.; BEEBE, J.; LI, H.; DAHAMC, B.; TATE, J.; BELL, M.; ANDREWS, G. Real-world comparison of probe vehicle emissions and fuelconsumption using diesel and 5% biodiesel (B5) blend. Science of the Total Environment, 2007, 267.
- [24] RAMOS, L. P.; SILVA, F. R.; MANGRICH, A. S.; CORDEIRO, C. S. Biodiesel production technologies. Revista Virtual de Química, 2011, 3, 5.
- [25] ROSA, H. A.; CHAVES, L. I.; SECCO, D.; REOLON, C. B.; WAZILEWSKI, W. T.; VELOSO, G. Avaliação das emissões de monóxido de carbono (CO) em um motor-gerador ciclo diesel utilizando diesel e biodiesel. Acta Iguazu, 2012, 1, 1
- [26] MMA- Ministério do Meio Ambiente. Biodiversidade Fauna. Available in: <a href="http://www.mma.gov.br/biodiversidade/biodiversidade-brasileira">http://www.mma.gov.br/biodiversidade/biodiversidade-brasileira</a>> Accessed at November 26th, 2014.
- [27] CRUCIBLE GROUP. Gente, plantas y patentes. Impactos de la propiedad intelectual sobre la biodiversidad, el comercio y las sociedades rurales, 1995, 4.
- [28] MOTA, C. J. A.; PESTANA, C. F. M. Co-product of biodiesel production. Revista Virtual de Química, 2011, 3, 5.

- [29] PAULA, A. J. A.; KRÜGEL, M.; MIRANDA, J. P.; ROSSI, L. F. S.; COSTA NETO, P. R. Use of clays for purification of biodiesel. Química Nova, 2011, 34, 1.
- [30] GAMA, P. E.; GIL, R. A. S. S.; LACHTER, E. R. Biodiesel production by in situ transesterification of sunflower seeds by homogeneous and heterogeneous catalysis. Química Nova, 2010, 33, 9.
- [31] BRASIL. Ministério da Ciência e Tecnologia. Plano Nacional de Agroenergia. Brasília, 2005. 120p.
- [32] ANP Agência Nacional de Petróleo, Gás Natural e Biocombustíveis. Dados estatísticos mensais. Vendas, pelas distribuidoras, dos derivados combustíveis de petróleo (metros cúbicos). Available in: <a href="http://www.anp.gov.br/?pg=64555">http://www.anp.gov.br/?pg=64555</a>> Accessed at March 28th, 2008.
- [33] ANP Agência Nacional de Petróleo, Gás Natural e Biocombustíveis. Dados estatísticos mensais. Vendas, pelas distribuidoras, dos derivados combustíveis de petróleo (metros cúbicos). Available in: <a href="http://www.anp.gov.br/?pg=64555">http://www.anp.gov.br/?pg=64555</a>> Accessed at March 14th, 2014.
- [34] MELO, W. C.; DA SILVA, D. B.; PEREIRA JR., N.; SANTA-ANNA L. M. M.; DOS SANTOS, A. S. Produção de etanol a partir de torta de mamona (*Ricinus communis* L.) e avaliação da letalidade da torta hidrolisada para camundongos. Química Nova, 2008, 31, 1104.
- [35] LÔBO, I. P.; FERREIRA, S. L. C.; CRUZ, R. S. Biodiesel: quality parameters and analytical methods. Química Nova, 2009, 32, 1596.
- [36] BURTON, R.; FAN, X.; AUSTIC, G. Evaluation of two-step reaction and enzyme catalysis approaches for biodiesel production from spent coffee grounds. International Journal of Green Energy, 2010, 7, 5.
- [37] GERPEN, J. V. Biodiesel processing and production. Fuel Processing Technology, 2005, 86, 1097.
- [38] SOBOLEV, E. P.; CHURSHUKOV, E. S.; ROZHKOV, I. V.; RUBINSHTEIN, I. A. Corrosivity of sulfur-bearing diesel fuels. Chemistry and Technology of Fuels and Oils, 1966, 2, 648.
- [39] ANASTOPOULOS, G.; LOIS, E.; KARONIS, D.; KALLIGEROS, S.; ZANNIKOS, F. Impact of oxygen and nitrogen compounds on the lubrication properties of low sulfur diesel fuels. Energy, 2005, 30, 415.
- [40] PARASCHIVESCU, M. C.; ALLEY, E. G.; FRENCH,W. T.; HERNANDEZ, R.; ARMBRUST, K. Determination of methanol in biodiesel by headspace solid phase microextraction. Bioresources Technology, 2008, 99.
- [41] HOEKMAN, S. K.; BROCH, A.; ROBBINS, C.; CENICEROS, E.; NATARAJAN, M. Review of biodiesel composition, properties, and specifications. Renewable and Sustainable Energy Reviews, 2012, 16, 143.
- [42] ATABANI, A. E.; MAHLIA, T. M. I.; MASJUKI, H. H.; BADRUDDIN, I. A.; YUSSOF, H. W.; CHONG, W. T.; LEE, K. T. A comparative evaluation of physical and chemical properties of biodiesel synthesized from edible and non-edible oils and studyon the effect of biodiesel blending. Energy, 2013, 58, 296.
- [43] AL-WIDYAN, M. I.; TASHTOUSH, G.; ABU-QUDAIS, M. Utilization of ethyl ester of waste vegetable oils as fuel in diesel engines. Fuel Process Technology, 2002, 76, 91.
- [44] MONYEM, A.; GERPEN, V. J. H. The effect of biodiesel oxidation on engine performance and emissions. Biomass & Bioenergy, 2001, 20, 317.
- [45] AGARWAL, A. K.; DAS, L. M. Biodiesel Development and characterization for use as a fuel in compression ignition engines. Journal of Engineering for Gas Turbines and Power, 2001, 123, 440.
- [46] CORRÊA, I. M.; MAZIERO, J. V. G.; ÚNGARO, M. R.; BERNARDI, J. A.; STORINO, M. Desempenho de motor diesel com misturas de biodiesel de óleo de girassol. Ciências Agrotécnicas, 2008, 32, 3.
- [47] ANP Agência Nacional de Petróleo, Gás Natural e Biocombustíveis. Superintendência de pesquisa e

- desenvolvimento Produção nacional de biodiesel puro B100, 2015. Available in: <a href="http://www.anp.gov.br/">http://www.anp.gov.br/</a>. Accessed at March 10th, 2015.
- [48] DORADO, M. P.; BALLESTEROS, E.; LÓPEZ, F. J.; MITTELBACH, M. Optimizacio of alkali-catalyzed transesterifition of *Brassica carinata* oil for biodiesel production. Energy Fuels, 2004, 18, 77.
- [49] GAZZONI, D. L. P. Agroenergia, o futuro que vem aí. Cultivar, 2005, 7, 44.
- [50] USDA United States Department of Agriculture. The oil seeds Group. World markets and trade 2001-2011. Washington: USDA, 2013. Available in: <a href="http://www.fas.usda.gov/oilseeds/circular/2011/May/oilseeds.pd">http://www.fas.usda.gov/oilseeds/circular/2011/May/oilseeds.pd</a> f>. Accessed at May 13th, 2014.
- [51] MC Mudanças Climáticas. Brasil e os Biocombustíveis. Available in: <a href="http://www.mudancasclimaticas.andi.org.br/content/brasil-e-os-biocombustiveis?page=0,0">http://www.mudancasclimaticas.andi.org.br/content/brasil-e-os-biocombustiveis?page=0,0</a> Accessed at November 28th, 2014.
- [52] IPEA. Instituto de Pesquisa Econômica Aplicada. Ipeadata, 2014.
- [53] EPE- EMPRESA DE PESQUISA ENERGÉTICA. Informe Técnico Análise da geração das usinas a biomassa 2008 2011. Available in: <a href="http://epe.gov.br/geracao/Documents/Estudos\_23/EPE\_DEE\_IT\_059\_2012.pdf">http://epe.gov.br/geracao/Documents/Estudos\_23/EPE\_DEE\_IT\_059\_2012.pdf</a>: Accessed at January 25th, 2013.
- [54] EUROBSERVER. Make your own request of indicators. Available in: <a href="http://www.eurobserv-er.org">ttp://www.eurobserv-er.org</a> Accessed at March 20th, 2013.
- [55] EUROBSERVER. Demanda de biodiesel na União Europeia recuou em 2013. Available in: < http://www.biodieselbr.com/noticias/inter/ue/demanda-biodieselue-recuou-2013-210714.htm> Accessed at December 12th, 2014.
- [56] AGROANALYSIS O crescimento da indústria global. Available in: <ttp://www.agroanalysis.com.br/materia\_detalhe.php?idMateria= 1659> Accessed at February 2th, 2014.
- [57] SILVA, J. A. Avaliação do Programa Nacional de Produção e Uso do Biodiesel no Brasil – PNPB, 2013.
- [58] GOMES, S.; GAUER, M. A.; SCHIRMER, W. N.; SOUZA, S. N. M. Análise da concentração mássica de materiais particulados provenientes da combustão de diesel e biodiesel. Revista do Setor de Ciências Agrárias e Ambientais, 2013, 9, 2.
- [59] PUHAN, S.; VEDARAMAN, N.; RAM, B. V. B.; SANKARNARAYANAN, G.; JEYCHANDRAN, K. Mahua oil (*Madhuca indica* seed oil) methyl ester as biodiese-preparation and emission characteristics. Biomass and Bioenergy, 2005, 28, 87
- [60] TURRIO-BALDASSARRI, L.; BATTISTELLI, C. L.; CONTI, L.; CREBELLI, R.; DE BERARDIS, B.; IAMICELI, A. L.; GAMBINO, M.; IANNACCONE, S. Emission comparison of urban bus engine fueled with diesel oil and 'biodiesel' blend. Science of the Total Environment, 2004, 147, 327.
- [61] EUROPEAN COMMISSION. Statistical pocketbook 2011. Available in: <a href="http://ec.europa.eu/transport/publications/statistics/pocketbook-2011\_en.htm">http://ec.europa.eu/transport/publications/statistics/pocketbook-2011\_en.htm</a>> Accessed at January 23th, 2011.
- [62] FORE, S. T.; LAZARUS, W.; PORTER, P.; JORDAN, N. Economics of small-scale on-farm use of canola and soybean for biodiesel and straight vegetable oil biofuels. Biomass and Bioenergy, 2011, 35, 193.
- [63] CNT Confederação Nacional do transporte. Os impactos da má qualidade do óleo diesel brasileiro. Brasília, 2012. 28 p.
- [64] DAUD, N. M.; ABDULLAH, S. R. S.; HASAN, H. A.; YAAKOB, Z. Production of biodiesel and its wastewater treatment technologies: A review. Process Safety and Environmental Protection, 2015, 94, 487.
- [65] WBCSD World Business Council for Sustainable Development
  -Eco-Efficency learning module. Available in:
  <HTTP://www.wbcsd.org/DocRoot/MRdaDUNiWNU4NZ1Ww9
  eM/ee\_module.pdf> Accessed at October 10th, 2014.

- [66] PARK, J. B. K.; CRAGGS, R. J.; SHILTON, A. N. Wastewater treatment high rate algal ponds for biofuel production. Bioresource Technology, 2011, 102, 35.
- [67] CROWNIRON. Usinas investem para tornar produção mais limpa 2013. Available in: <a href="http://www.crowniron.com.br/736/usinas-investem-para-tornar">http://www.crowniron.com.br/736/usinas-investem-para-tornar</a> producao-mais-limpa/ Accessed at April 23th, 2015.
- [68] MMA/CNMA. Ministério do Meio Ambiente e Conselho Nacional do Meio Ambiente. Condições, parâmetros, padrões e diretrizes para gestão do lançamento de efluentes em corpos de água receptores.
  - Resolução nº 430, 2011.
- [69] CHAVALPARIT, O.; ONGWANDEE, M. Optimizing electrocoagulation process for the treatment of biodiesel waste-water using response surface methodology. Journal of Environmental Sciences, 2009, 21, 1491.
- [70] YANG, T.; QIAO, B.; LI, G.; YANG, Q. Improving performance of dynamic membrane assisted by electrocoagulation for treatment of oily wastewater: Effect of electrolytic conditions. Desalination, 2015, 363, 134.
- [71] SANTOS, A. M. M. Tratamento de efluentes de biodiesel pelo processo combinado de coagulação-floculação e fenton. 2014. 95 f. Dissertação (Mestrado em Saneamento e Recursos Hídricos) -Universidade Federal de Minas Gerais, Belo Horizonte, 2014.
- [72] NGUYEN, T.; DO, L.; SABATINI, D. A. Biodiesel production via peanut oil extraction using diesel-based reverse-micellar microemulsions, Fuel, 2010, 89, 9.
- [73] MUTHUKUMARAN, N; SARAVANAN, C. G.; YADAV, S. P. R.; VALLINAYAGAM, R.; ROBERTS, S. W. L. Synthesis of cracked *Calophyllum inophyllum* oil using fly ash catalyst for diesel engine application. Fuel, 2015, 155, 68.
- [74] VIÊGAS, C. V.; HACHEMI, I.; FREITAS, S. P.; MÄKI-ARVELA, P.; AHO, A.; HEMMING, J.; SMEDS, A.; HEINMAA, I.; FONTES, F. B.; PEREIRA, D. C. S.; KUMAR, N.; ARANDA, D. A. G.; MURZIN, D. Y. A route to produce renewable diesel from algae: synthesis and characterization of biodiesel via in situ transesterification of *Chlorella alga* and its catalytic deoxygenation to renewable diesel. Fuel, 2015, 144, 155.
- [75] LIN, Y-C.; CHEN, S-C.; CHEN, C-E.; YANG, P-M.; JHANG, S-R. Rapid Jatropha-biodiesel production assisted by a microwave system and a sodium amide catalyst. Fuel, 2014, 135, 435.
- [76] NGAMPRASERTSITH, S.; LAETOHEEM, C; SAWANGKEAW, R. Continuous production of biodiesel in supercritical ethanol: a comparative study between refined and used palm olein oils as feedstocks. Journal of the Brazilian Chemical Society, 2014, 25, 9.
- [77] LI, X.; HE, X-Y.; LI, Z-L.; WANG, Y-D.; WANG, C. Y.; SHI, H.; WANG, F. Enzymatic production of biodiesel from *Pistacia chinensis bge* seed oil using immobilized lipase. Fuel, **2012**, 92, 89.
- [78] SUAREZ, P. A. Z.; MOSER, B. R.; SHARMA, B. K.; ERHAN, S. Z. Comparing the lubricity of biofuels obtained from pyrolysis and alcoholysis of soybean oil and their blends with petroleum diesel. Fuel, 2009, 88, 1143.
- [79] FERNANDES, P. S. R.; BORGES, L. E. P.; DE CARVALHO, C. E. G.; DE SOUZA, R. O. M. A. Microwave assisted biodiesel production from trap grease. Journal of the Brazilian Chemical Society, 2014, 25, 1730.
- [80] BRANCO, L. G. B. Biocombustíveis: vantagens e desafios. Revista Eletrônica de Energia, 2013, 3, 1.
- [81] MOTA, C. J. A.; PESTANA, C. F. M. Co-produtos da produção de biodiesel. Revista Virtual de Química, 2011, 3, 416.