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REVIEW OF THE MAJOR ENERGY ALTERNATIVES TO THE USE OF GLYCEROL AS WASTE IN THE BIODIESEL PRODUCTION IN BRAZIL AND WORLDWIDE

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Abstract. *The growing shortage of fossil fuels and the consequent rise in oil prices indicate the need to obtain new alternative fuels from renewable resources. Biodiesel stands out as being derived from renewable sources and offer environmental advantages; its policy is based on the use of biomass as a consolidation of a new energy option. Moreover, the automotive market has shown great interest in its production, and its high cost, the main obstacle to commercialization of the product. The recovery of by-products, especially glycerol, generated in the transesterification process has been the alternative most favorable to minimize production costs and thus make biodiesel more competitive in the market. In this scenario, it becomes imperative to find alternative economic use and co-processing applications of glycerol to reduce the cost of biodiesel production chain. The present article will present the possible energy alternatives for disposal of by-products generated in the production of biodiesel, especially glycerol, and the current costs of the market of glycerol, national and global market.*

Keywords: *biodiesel, glycerol, by-products, costs.*

1. INTRODUCTION

With increasing oil prices, the biodiesel is becoming more atractive due to its environmental benefits and its renewable sources. The automotive market has demonstrated the interest in its production, however, the hight cost, compensated, in many coutries, by means of legislation, regulatory frameworks or tax exemption subsidies, is one of the many obstacles for the trade.

One key factor for the economic viability of this biofuel production is that there are the byproducts generated in the very own biodiesel production chain, the main ones being: glycerin, lecithin, bran and oilseed cake, excess alcohol and catalyst. Glycerine, for example, is a substance appreciated by the industries of plastics, lubricants, cosmetics, pharmaceuticals, explosives, and in most cases, the sale of this byproduct can cover operating costs of a biodiesel production plant (KNOTHE *et al*., 2006). However, it is observed saturation of the market for this substance, which encourages the pursue of new uses to promote marketing both the glycerin and other byproducts.

Most industrialized countries governments have incentives to research alternative fuels, in order to achieve energetic independence. In Germany and France, for instance, the biodiesel has been extensively utilized to avail the exceeding canola oil for its production. In addition, they already used glycerol for the soap production and the production of explosives in wartime. Metzger (2007) concluded that it is possible to use the thermal energy from the glycerol by its combustion. According to Rahmat *et al.* (2010), glycerol-based additives are excellent when used in diesel, biodiesel and gasoline.

In Brazil, production and marketing have important advantages due to the large availability of raw materials and the continued growth of the vegetable oil industry and ethanol (OLIVEIRA *et al*. 2006; OISTI, 2007). Its current ethanol production capacity has been the focus of interest of other countries.

The introduction of biodiesel in the Brazilian energy matrix is given by law 11.097/2005, which provides for the authorization of the mixture of biodiesel on a commercial scale on the proportion of 2% for 98% diesel fuel, becoming mandatory in 2008 (CIVIL HOUSE OF THE PRESIDENCY OF THE REPUBLIC, 2005). Currently, following the pattern of this scale, the ratio is 5% (B5) biodiesel and 95% diesel fuel. Therefore, biodiesel production in Brazil has increased and the amount of glycerin (byproduct) generated is growing, and the search for new solutions to their use will be of fundamental importance (FRIENDRICH, 2004; BIODIESELBRASIL, 2007). The increase in biodiesel production can only be economically feasible if new applications and markets are found, for example, for the glycerol produced. Thus, the need for research on the production and uses of glycerol derivatives (CARDOSO *et al*., 2007).

Glycerol is the main by-product generated in the production of biodiesel, but also are generated bran, oil cake, excess alcohol and catalyst. Such residues require destination economically and ecologically viable, so there is a need to study the potential of turning them into value-added products. The combustion of glycerol is an interesting option for utilization of this residue, where it can leverage its thermal energy for other purposes, even with the help of some auxiliary fuels such as

LPG (liquefied petroleum gas) or natural gas in order to improve emissions of particulate matter, considered the villain in the glycerol combustion. One option is the use of this energy is in the very process of biodiesel production for electricity generation, steam or for heating purposes. This option, could certainly add value to the worldwide biodiesel production.

In Brazil, there is not enough material in the scientific literature or studies evaluating the products generated in the production of biodiesel and the potential benefits, both economic and environmental, of their use. As studies are insufficient regarding the use of by-products in order to enable the biodiesel production chain, it is essential to carry out a detailed research on this subject.

2. METHODOLOGY

A literature review was conducted on the theoretical basis of the subject for possible uses and disposal of by-products generated in the production of biodiesel, the Brazilian and world energy markets. Texts were searched and scientific articles were indexed during the review that gave grants to obtain information about the current data production and characterization of products generated in biodiesel production, use and marketing of residues and energy market of glycerol (glycerol combustion).

From the survey for state of the art, we identified the provision and disposal of by-products generated in the production of biodiesel, and traced the perspective of the energy market these major by-products.

3. RESULTS

3.1. Theme related concepts

3.1.1. Biodiesel

Biodiesel is a biofuel used to replace conventional diesel, and aims to reduce the emission of greenhouse gases from combustion in diesel engines and power as a strategic reserve against future scarcity, depletion and / or dispute in the main international oil reserves, fulfilling the same role that ethanol, in Brazil in the 1970s and 1980s (CORONADO, 2010). Biodiesel may be produced by a wide variety of materials including most vegetable oils and animal fats (tallow) as well as vegetable oils for disposal (e.g. oil from fried food).

The definition of biodiesel in Brazil, according to the National Agency of Petroleum, Natural Gas and Biofuels (ANP) is as follows: "Fuel consisting of fatty acid alkyl esters of derived from vegetable oils or animal fats, designated B100 complying with ANP Technical Regulation No. 4/2004." According to the American standard definition of biodiesel and in accordance with American Society for Testing and Materials (ASTM): "Mono-alkyl esters of long chain fatty acids derived from renewable lipid, such as: vegetable oils or animal fats, which are used in compression ignition (diesel) engines or boilers. " The American standard for the production of Biodiesel is ASTM D6751 (2006) and is the European standard UNE-EN 14214 (2003).

In the biodiesel production process by-products are generated in their own supply chain, among which we can mention: glycerin, lecithin, bran and oilseed cake, excess alcohol and catalyst.

3.1.2. Raw Materials for biodiesel

The suitable raw materials for biodiesel production from lipids may have any animal or vegetable origin, being the most typical for this purpose the refined vegetable oils. There are more than 350 identified oilseed crops, of which only soybeans, palm, sunflower, safflower, cottonseed, canola, peanut, and are considered as potential alternative fuels for use in diesel engines (GOERING *et al*, 1982; PRYOR *et al*, 1982).

The potential for oil extraction of each type of oilseed varies greatly and the supply coupled with the ease of cultivation is usually the determining factor for choice. Table 1 has the main features of some oilseed crops.

TABLE 1. Characteristics of some oilseeds (adapted from CHIARANDA *et al.,* 2005).

Oilseed	Oil Content (%)	Harvest time (month)	Yield (Oil Tonnes/hectare)
Palm	20,0	12	3,0 - 6,0
Babassu	66,0	12	0,1 - 0,3
Sunflower	38,0 - 48,0	3	0,5 - 1,9
Canola	40,0 - 48,0	3	0,5 - 0,9
Castor	43,0 - 45,0	3	0,5 - 0,9
Soybeans	17,0	3	0,2 - 0,4
Cotton	15,0	3	0,1 - 0,2

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In the United States is usually processed soybean oil and animal fats (JEWET, 2003); palm oil predominates in tropical countries (SII *et al*., 1995) (MASJUKI SAPUAN, 1995) and rapeseed oil and sunflower predominate on the European continent (HAROLD, 1997), whereas in the case of India and Southeast Asia, the tree jathrofa is used as an important source of biodiesel production (DERMIRBAS, 2007).

The federal government created the National Program for Production and Use of Biodiesel in 2004, which initially established as mandatory, the 2% blend of biodiesel in diesel oil from July 2008 and 4% from July 2009. On October 26, 2009, the National Council for Energy Policy increased to 5% blend of biodiesel to diesel, from 1 January 2010. The continuous increase in the share of biodiesel demonstrates, in a way, the success of the program and the experience Brazil accumulated in the production and use of biofuels on a large scale.

From the beginning of the program, soybean oil constitutes the major raw material for biodiesel production. In April 2011 accounted for 83.8% of biodiesel, followed by bovine fat (13.7%), cottonseed oil (0.7%) and other sources (1.8%). The wide domain of technological processes of production, processing and use of soy products, fruits of decades of investment in science and technology and the entrepreneurship in the sector, together with the high intrinsic nutritional value of soy products, explain, at least in part the absolute dominance of this oilseed in Brazil (UDOP, 2010).

Figure 1 below highlights the raw materials most used for biodiesel production in Brazil from 2005 to 2011.

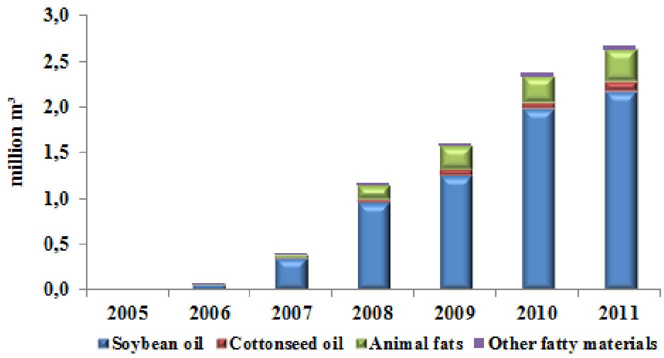

FIGURE 1. Main raw materials used in Brazil for biodiesel production (ANP, 2012).

According to information from the ANP, the data from animal fat include beef fat, chicken fat and pork fat, and other fatty materials represent oil palm oil, peanut oil, forage radish, sunflower oil, castor oil, sesame oil, used frying oil, and other fatty materials.

We can observe in the figure above, even soy being an oilseed crop with low oil content this is responsible for the largest share of biodiesel in the country, this is due to its ease of cultivation coupled with its short harvest time, so almost 80 % of all extracted oil for biodiesel production in Brazil comes from it.

3.1.3. Glycerol

Glycerol is the main by-product generated in the production of biodiesel, estimated the generation of 100 kg of glycerol in processing each cubic meter of biofuel (PARENTE, 2003). The official chemical name of glycerol, according to the International Union of Pure and Applied Chemistry (IUPAC), 1,2,3-propanetriol is an organic compound belonging to the family of alcohol. Presents itself naturally in combined forms, such as glycerides and in all the animal and vegetable fatty oils, and is recovered as a co-product when these oils or fats are: transesterified with methanol (or other alcohol) to produce methyl (alkyl) esters, hydrolyzed or saponified to produce fatty acids in soap manufacturing process. Several levels of glycerin are commercially available, which differ in their content of glycerol, color, odor and traces of impurity (KNOTHE *et al.,* 2006; TACONI, 2007). The term "glycerol" applies only to the pure chemical compound 1,2,3-propanetriol whereas the term "glycerol" is often applied to the commercial product purified content exceeding 95% glycerol. In its raw form it has low added value due to containing residues of methanol, sodium hydroxide, fatty acids, salts, sulfur and other contaminants (BARBOSA, 2009).

3.1.4. Byproducts

The main products generated in the production of biodiesel that can be used in animal feed are: cake, if the oil extraction is done by pressing (physical extraction), or bran, when the material is subjected to solvent extraction (chemical extraction) after the process of physical extraction (BOMFIM *et al*., 2007). According to Oliveira *et al*. (2010a), oil cakes derived from the production of biodiesel have a potential use in ruminant feed, given the considerable concentrations of protein and lipids, which characterize them as food protein and/or energy, and they can still be destined for organic fertilizer. Also, the cakes also contain fibers and different residual oil percentages, demanding different extraction techniques. The castor bean bran is a co-product of biodiesel with higher protein content, with approximately 37% crude

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protein, and can replace soybean meal. Other waste as babassu meal, cotton, palm oil and soy can be used in animal feed without preprocessing (ABDALLA *et al*., 2008).

3.1.5. Excess Alcohol

Short chain alcohols such as methanol, ethanol and butanol, are often used as reactants. The use of the type of alcohol depends on the cost and performance which can give the process (ENCINAR *et al*., 2007). Other alcohols used in the manufacture of biodiesel are propanol, butanol and amyl alcohol (KNOTHE *et al*., 2006).

The excess alcohol is due to the common practice of adding more alcohol, and a catalyst which is stoichiometrically required to reduce the reaction time in transesterification process for production of biodiesel. While the alcohol recovery for reuse is generally effective, it makes more expensive the purification (i.e., water removal from the catalyst, salt and other impurities) of the crude glycerol generated (METZGER, 2007).

3.1.6. Catalyst

From the kinetic point of view, the transesterification can be conducted in processes catalyzed by acids, enzymes or bases. The basic catalysis is arguably the most used worldwide (OLIVEIRA, 2005).

The catalysts used in the basic catalysis, the alkali metal hydroxides (sodium hydroxide, NaOH and potassium hydroxide, KOH) and metal alkoxides (sodium metilatos, also called sodium methoxides) ($NaOCH_3$) and potassium metilatos (also called methoxides potassium) ($KOCH_3$) both (hydroxides and alkali metal alkoxides) are known as "alkaline catalysts." They can be used also other alkoxides such as ethoxides, butoxides and propóxidos (CORONADO, 2010).

The acids used in the transesterification process include sulfuric acid, sulfonic acid, phosphoric acid or hydrochloric among others. Of these, sulfuric acid is the most commonly used (OLIVEIRA, 2005). The use of basic catalysts allows to obtain reaction rates almost 4,000 times higher than those obtained with the same amount of catalysts in acid (MA & HANNA, 1999).

The transesterification of triglycerides with an alcohol in the presence of an intracellular or extracellular lipase has been used to produce biodiesel, whereas the majority of published studies have used commercial preparations of lipases in pseudo-homogeneous reaction system and also in immobilized form (RANGANATHAN *et al.,* 2007; JEGANNATHAN *et al*., 2008). The use of free enzymes results in technical difficulties, and it is practically impossible to recover and reuse them, which increases the economic costs of the process, and promotes product contamination with residual enzyme activity (AL-ZUHAIR, 2007; JEGANNATHAN *et al.,* 2008). These difficulties can be overcome by the use of these enzymes in their immobilized form, allowing the reuse of biocatalyst several times, reducing costs while still improving the quality of the product (KINAST & TYSON, 2003; HASS *et al*., 2006).

3.2. Production and characterization of by-products generated in the biodiesel production

3.2.1. Glycerol

Glycerol was discovered by Swedish researcher Scheele in 1779 (HAJÉK & SKOPAL, 2009; KNOTHE *et al*., 2006), during the process of saponification of olive oil, which generated a residue containing a sweet tasting substance (HARTSHORNE, 1865). The official chemical name of the substance, according to the International Union of Pure and Applied Chemistry (IUPAC), 1,2,3-propanetriol is an organic compound belonging to the family of alcohol. It is present naturally in combined forms, such as glycerides in all animal and vegetable fatty oils, and is recovered as a by-product when these oils or fats are transesterified with methanol (or other alcohol) to produce methyl (alkyl) esters, hydrolyzed in the production of fatty acids or saponified in the manufacturing process of soap. Its molecular structure is presented in Figure 2 which follows below.

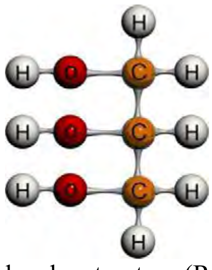

Figura 1. Glycerol molecular structure (RAHMAT *et al.,* 2010).

Table 2 shows the main physical-chemical properties of the glycerol, these features are evidenced below.

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TABLE 2. Physical-chemical properties of the glycerol (at 20.1°C) (GUPTA & KUMAR, 2012)

Molecular Weight	92,09	**Viscosity**	1499 c.p. a 20 °C
Melting Point	18,17 °C	**Specific Heat**	2,42 J/gm a 26 °C
Boiling Point (760mm Hg)	290 °C	**Heat of vaporization**	21060 cal/mole a 55 °C
Density (20 °C)	1,261 g/cm³		18170 cal/mole a 195 °C
Vapor Pressure	0,0025mm Hg a 50 °C	**Heat of formation**	159,6 Kcal/gm mole
	0,195mm Hg a 100 °C	**Heat of combustion**	1662 Kj/mole = 18,05 Mj/kg
	4,3mm Hg a 150 °C	**Heat of Fusion**	18,3 Kj/mole
	46mm Hg a 200 °C	**Thermo-Conductivity**	0,29 w/°K
Refractive index	1,474	**Flash point**	177 °C
Surface tension	63,4 dyne/cm a 20 °C	**Fire Point**	204 °C
Compressibility	2,1 x 10 MPa		

Glycerol is known as nontoxic, allowed as a feed additive, used in medicine and as a substance labelled "GRAS" ("Generally Regarded as Safe" - generally recognized as safe) by the Federal Drug Administration and the U.S. Food (FDA) (MORRISON, 1994). Glycerol is also used in the food and beverage industry as a food additive due to its stabilizing, humectant, antioxidant and emulsifier properties. In the pharmaceutical industry is used in ointments, syrups, anesthetics, toothpaste and cosmetics in general. It can also be used as lubricant for food processing machines, dynamite manufacturing, and as softener for fibers in the textile industry. In the chemical industry is widely used in the production of products for cleaning and for the synthesis of resins and esters. It is also considered as a cryoprotective agent for microorganisms, because it allows the formation of ice crystals in the cell, while maintaining stability and vitality of the cell wall during the freezing process for its preservation. In Brazil, the use of glycerol in food products is ensured by Resolution No. 386 of August 5, 1999 (ANVISA, 1999).

3.2.2. Oilseed cake

The cakes are residues from the extraction of oil from the seeds of oilseed plants. There are many co-product of biodiesel, distributed throughout Brazil including cake and meal that can be rationally utilized for feeding ruminant animals, but in some cases require a prior process of detoxification or deallergination for its use in animal feed and this can encumber the final price of the product (CIGB, 2010).

Table 3 presents a compilation of dry matter, crude protein, crude fiber and ether extract some cakes obtained as co-product in the production of biodiesel.

Table 3. Chemical composition of the major oilseed cakes generated as byproducts of biodiesel. Adapted from SOUZA (1979), BRINGEL (2009), ARAÚJO *et al.* (2011) e OLIVEIRA *et al.* (2010a).

Composition (%)	Castor	Cotton	Palm	Sunflower	Turnip Forrage	Jathropa
Dry Matter	91,5	92,3	91,9	91,9	91,1	91,6
Raw Protein	42,5	46,1	14,0	23,8	38,8	25,4
Fibers	20,0	11,4	40,0	32,5	11,4	43,2
Lipids	4,2	4,6	10,8	12,1	14,5	24,2

From the results shown in table 3, and from several authors, we can consider the protein content of these pastries relatively high (35%), ranging from 14 to 46%, suggesting the use as a protein source for the animals (JARDIM, 1976) . The fat (ether extract) also varies considerably (4-24%) which may be another benefit to ruminants, whereas the inclusion of oil in the diet can help mitigate enteric methane (GRAINGER, 2008). The fiber content is relatively low (25%) confirming the lable to these cakes as concentrated food (MORRISON, 1966) and rich in nutrients, with minimum estimated 63% total digestible nutrients according to Kearl (1982).

3.2.3. Bran

The bran and oil cakes are the main source of protein used in animal feed and bears the interest of the zootechnical comunity worldwide. According to surveys of the American Soybean (SOY STATS, 2010), soybean meal accounted for 69% of global consumption of meal protein in 2008, followed by canola meal (12%), cotton (7%) and sunflower (4 %). Canola meal is especially important in Europe and Canada.

The values of major nutritional composition bran obtained as a co-product during the biodiesel production are presented in Table 4.

Table 1. Chemical composition of the main bran obtained in generating biodiesel.
Adapted from SANTOS *et al.* (2010), CARVALHO *et al*. (2005), GARCIA *et al*. (2004), NCPA (2002), ADERIBIGBE *et al*. (1997) and OLIVEIRA *et al.* (2010b)

Composition (%)	Cotton	Jathropa	Sunflower	Palm	Castor	Turnip Forrage
Dry Matter	89,1	93,3	90,9	93,0	88,1	91,3
Raw Protein	47,6	58,0	31,4	17,5	37,3	42,1
Lipids	2,2	1,2	1,1	2,5	3,1	3,5
Raw Fiber	11,2	6,8	28,5	46,0	46,5	7,4

As shown above, these food items have variations in their nutrient content, demonstrating the need for prior review of this product before the inclusion in the diets.

3.2.4. Fatty Acids

The fatty acids correspond to unreacted vegetable oil with the catalyst during alcoholysis and represent about 4.4% of the oil used in processing. These fatty acids can be obtained in the form of washed and dried fatty acid or fatty acid purified by distillation, which have different prices and markets (OLIVEIRA, 2005).

According to Rocha *et al*. (2008), the biodiesel is produced from vegetable oils via transesterification of homogeneous basic catalysis providing methyl or ethyl esters of fatty acids. The composition of the samples of biodiesel produced and analyzed by Rocha *et al*. (2008) are presented in Table 5.

Table 2. Percentage composition of fatty acids in samples of biodiesel from vegetable oils analyzed (ROCHA *et al*., 2008)

Fatty Acids	Babassu	Castor	Soy	Palm
C8:0	4,8±0,5	nd	nd	nd
C10:0	5,0±0,7	nd	nd	nd
C12:0	41,6±0,1	nd	nd	0,8±0,1
C14:0	17,9±0,9	nd	nd	1,5±0,1
C15:0	9,4±0,8	1,6±0,1	9,6±0,6	60,3±1,0
C18:2	3,2±0,3	6,6±0,8	51,1±2,0	19,0±0,9
C18:1	13,3±1,7	5,9±1,0	34,9±2,0	8,6±0,5
C18:0	4,9±0,7	1,2±0,1	4,4±0,6	9,8±0,2
C18:1OH	nd	84,6±2,3	nd	nd
nd – Not Detected				

The samples obtained from vegetable oils of soybean oil and palm oil showed similar composition, differing only in hexadecanoic fatty acid content(C16: 0), 9,12-octadecadienoic acid (C18: 2), 9-octadecenoic acid (C18: 1) and octadecanoic (C18: 0), while palm oil also presents other two that are minority components in the mixture, dodecanoic acids (C12: 0) and tetradecanoic (C14: 0). In biodiesel obtained from soybean oil fatty acid is the major 9,12-octadecadienoic acid (51.1%), while this acid in palm oil composed only 19.0% of the biodiesel. In palm oil biodiesel , on the other hand, hexadecanoic acid (60.3%) is the majority, while the biodiesel obtained from soybean this acid alone reaches 9.6%.

The analysis of fatty acids in babassu oil showed that the major constituent is the dodecanoic (C12: 0), with contents of 41.6%, followed by tetradecanoic (C14: 0) with 17.9% and 9 -octadecenoic acid (C18: 1), 13.3%. Only in this oil were also observed octanoic acids (C8: 0) and decanoic (C10: 0). The castor oil has as a major component (84.6%) of the fatty acid 12-hydroxy-9-octadecenoic acid (C18: 1), known as ricinoleic acid.

The differentiation of these biodiesel oil samples can be performed by identifying its major components since, as noted, babassu biodiesel is characterized by having the dodecanoic acid (C12: 0) as the major component in addition to the acids C8: 0 and C10: 0, which are not found in the other samples. Castor biodiesel can be identified to be the only one to present the ricinoleic acid as its major constituent. The samples of soybean oil and palm oil biodiesel, despite having the same fatty acids in their composition, can be differentiated by the intensities of all components which differ significantly.

3.3. Possible uses and marketing of these residues

Nowadays glycerol has been widely used as raw material in food and beverages, chemicals research, laboratory use and pharmaceutical applications (DUANE & KATHERINE, 2007). The variety of fields for glycerol applications are suggested in Table 6, where they are transformed by chemical reactions or biological agents (RAHMAT *et al*., 2010).

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Tabela 3. Glycerol uses (RAHMAT *et al.*, 2010).

Product	Reaction	Use
1,3-Propanediol	- Fermentation of glycerol by Klepsiella pneumoniae. - Selective dehydroxylation glycerol.	Use as monomer in the synthesis of various polyesters such as polytrimethylene terephthalate (PTT) and polyethylene terephthalate PET)
Propylene glycol	Hydrogenolysis of glycerol.	Mainly applied to unsaturated polyester, antifreeze and additives for liquid detergent
Docosahexaenoic acid (DHA)	Crude glycerol with cultured microalgae.	Omega-3 polyunsaturated fatty important (v-3 PUFA) with clinically established therapeutic capabilities against cardiovascular disease, cancer, schizophrenia and Alzheimer's disease, another essential nutrient during early human development.
Glycerol carbonate	Glycerol with CO_2.	Prominent role as the monomer, can be used for the synthesis of new functional polymers which may have interesting new applications.
Dichloropropanol (DCP)	Glycerol heteropolyacid. Catalyzed reaction of glycerol with hydrochloric acid for acetic acid as acid catalyst.	Chemical inputs to organic compounds, monomers and reagents for the production of plastics.
Butanol	Fermentation of glycerol by Clostridium pasteuriunum.	Biofuel potential that could be used for gas / oil without changes in engine design as a solvent for the chemical and textile process, organic synthesis and chemical intermediate, as well as coating applications.

The use of bacterial transformation of glycerol was also clearly demonstrated for the production of dihydroxyacetone for cosmetic applications (GATGENS *et al.*, 2007), succinic acid (SONG & LEE, 2006) and citric acid (IMANDI *et al.,* 2007) to food and pharmaceutical industries, polihidroxiacanoate for medical and agricultural (SOLAIMAN *et al*., 2006), as well as other products for basic chemical applications. In addition to the biological, chemical transformation another approach is to convert glycerol to more valuable products, which include selective oxidation, hydrogenolysis, dehydration, acetylation, carboxylation, decomposition dehydroxylation, selective oligomerization and so on. The transformation of glycerol into fuel oxygenates by etherification (NOUREDDINI, 2001; BRADIN, 1996) and methods of esterification (JALINSKI, 2006; DELGADO, 2003) are among the chemical reactions that attract the interest of research since they are economically beneficial.

With the glycerol market currently saturated, arises the need to create technologies to add value to the product, alternatives that have demand equal to the supply of glycerol, and large-scale applications to prevent the exportation of such substance that is currently inexpensive.

Among the studies that have been done to discover new uses for glycerol, glycerol conversion to green propene is present. Propene, a resin obtained from petroleum, is one of the main raw materials for the petrochemical industry. It is used in the manufacture of polypropylene, a plastic widely used in automotive parts, household appliances and packaging for food and cleaning products. According to Professor Claudio Mota, Institute of Chemistry, UFRJ, although there was, at that time, references in the scientific literature of the transformation of glycerol to propene, his group was able to develop a catalyst and an efficient process, which ended up generating a patent for the university and a private industry, Quattor petrochemical, purchased it two years ago by Braskem (REVISTA PESQUISA FAPESP, 2012).

In addition to such conversion, there´s also been focus of studies the conversion of glycerol to ethanol and hydrogen. At the Federal University of Rio Grande do Sul (UFRGS), a group of scientists developed a line of research where they want to produce, in addition to 1,3-propanediol, also through biotechnology, ethanol and hydrogen from glycerol from biodiesel. According to chemical engineer Marco Antônio Ayub, Professor of the Institute of Science and Food Technology from UFRGS, the first stage of the research has been completed, it was the identification of biological agents to metabolize residual glycerol. The second stage is in progress and is the completion of the physiology study of bacteria of the genus *Klebsiella pneumoniae.* The next step is work and operation optimization of bioreactors with the cultivation of microorganisms. Ayub gives account that prototype bioreactors designed and built by a group of scientists are already undergoing preliminary testing and points out that the process proved to be technically feasible, with strains and converting glycerol without any pretreatment to remove impurities and good rates production (REVISTA PESQUISA FAPESP, 2012).

Another focus would be energy production from glycerol, which is a very promising field for research, due to its non-toxicity, extremely low vapor pressure, low flammability characteristics and high energy density (ARECHEDERRA & MINTEER, 2009). Recent studies show the possibility of using crude glycerol for the production of synthesis gas by steam reforming (DOU *et al*., 2008; ADHIKARI *et al*., 2008), the production of hydrogen by fermentation (SABOURIN-PROVOST & HALLENBECK, 2009) and production of energy through fuel cells and biofuels (ASHFIELD & RAGSDALE, 2008; ARECHEDERRA & MINTEER, 2009).

The use of glycerol as a fuel for generating electricity and heat in the cogeneration system operating in the steam cycle may be an alternative to meet the energy requirements of the production process of biodiesel (ALBARELLI *et al*., 2011). Chemical engineer Juliana Albarelli State University of Campinas (Unicamp), in its feasibility study of the use of glycerol

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as a fuel to produce electricity and steam in a cogeneration system, aims to use the energy generated by the residual glycerol produced by biodiesel to reduce manufacturing costs and bring financial benefit to the company. According to Juliana, with the aid of software programming, energy and economic analysis, it was possible to verify that only 50% of the electricity generated would be required to supply the biodiesel production process, there remaining 50% surplus that could be sold to the local community or dealership for the region, generating an additional source of income for the company (REVISTA PESQUISA FAPESP, 2012).

The group of Professor Carlos Mota, Institute of Chemistry, Federal University of Rio de Janeiro, works on producing Bio additives from glycerol. One additive developed by the group improves the flow of biodiesel, mainly produced from beef tallow, which is subject of freezing when exposed to temperatures below 15 ° C. The team also developed a bioadditive with antioxidant properties with potential to be used in various industrial applications such as: food preservation or blended in biodiesel made from soybeans, which requires an antioxidant to not undergo chemical degradation when in contact with air. According to the researcher, many of these oxidants are imported and expensive and producing them from a renewable source such as glycerol from biodiesel, is not just an environmental advantage, but also an important economic gain for the country (REVISTA PESQUISA FAPESP, 2012).

3.4. Glycerol Energy Market (Glycerol Combustion)

The combustion of glycerol can be an essential factor for the development of new processes for biodiesel production that require large thermal inputs and also generate as waste glycerol. It has been said that the combustion of glycerol "would be an elegant solution, if it worked well enough" (JOURNEY TO FOREVER, 2012). The heating of the reactants can significantly increase the speed of the transesterification reaction, and so any biodiesel plant becomes necessary to use a significant amount of thermal energy. The burning of glycerol for process heating would offset the energy costs, eliminating transport costs (plants could burn glycerol in their own site), and act as an efficient way of disposal. However, the difficulty of burning glycerol prevented this from becoming the solution chosen by the biodiesel industry (VAN GERPEN, 2004).

Glycerol is much more difficult to burn than conventional hydrocarbon fuels. Even glycerol containing significant energy, its energy density is much lower than conventional hydrocarbon fuels possess. One kilogram of glycerol contains about 16 MJ of chemical energy in comparison with kerosene, which is 42.8 MJ / kg or gasoline 44.4 MJ / kg. Glycerol is also highly viscous liquid at room temperature, with a kinematic viscosity of 450 centistokes as compared to water, which has a kinematic viscosity of 1 centistoke. Kerosene has a kinematic viscosity of 2.71 centistokes and gasoline is from 0.46 to 0.88 centistokes depending on the degree. It should be noted that the residual glycerol from biodiesel production may contain a little alcohol, which will reduce its viscosity, however, many biodiesel producers prefer to retrieve this alcohol for future reuse of the glycerol (METZGER, 2007).

Perhaps the greatest difficulty in burning glycerol is its high autoignition temperature. Glycerol has an autoignition temperature of 370 ° C, compared with gasoline of 280 ° C and 210 ° C with kerosene (DIPPR, 2005). Whereas a standard fuel such as kerosene can be ignited with a single spark and hold a flame in ambient air, glycerol under the same conditions will not light. Patzer (2007) and Striugas (2008) also reported that they encountered difficulties in the direct use of glycerol as fuel, according to which were attributed to high viscosity, density and high ignition temperature compared to other liquid fuels. Another factor that should be taken into consideration are the toxic emissions caused by the combustion of biodiesel, particularly acrolein. Acrolein is a product of thermal decomposition of glycerol, toxic at very low concentrations, about 2 ppm. Some studies suggest risks to human health with only 0.09 ppm (EPA, 2003). However, acrolein and becomes increasingly unstable when higher temperatures and highly flammable. Thus, it is conceivable that efficient combustion can of consuming any acrolein the glycerol produced before the combustion gas to evade the environment (EPA, 2003).

The previous work on combustion are exempt from comparisons because there is a significant difference between the types of glycerol and combustion systems used in these experiments. Such circumstances can´t be easily avoided, granted the different processes used for biodiesel production and the differences that are determinant to the physico-chemical properties, and consequently to the use as fuel, of the glycerol produced (MATURANA, 2010).

Some examples of burners used in experiments already carried out can be checked below in Figure 3, Figure 4 and Figure 5.

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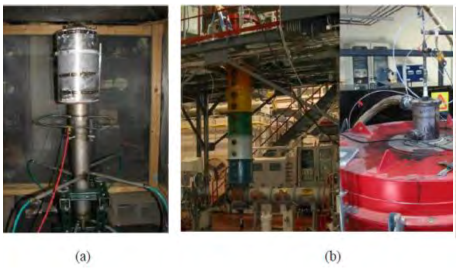

Figura 2. Burner used by BOHON *et al.*, 2010: a) 7kW, b) 82kW

Figura 3. Burner used by METZGER, 2007.

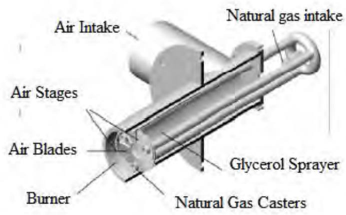

Figura 4. Burner used by STRIUGAS *et al.*, 2008.

According to the study by Maturana (2010), the energetic utilization of glycerol by direct combustion is technically, environmentally and economically feasible provided the adoption of the necessary controls to prevent or reduce to acceptable limits the emission of particles. Energy production by direct combustion of glycerol was 61% cheaper than diesel in similar conditions and techniques. According to Maturana (2010), proper combustion of glycerol as an alternative means of collection and utilization of energy, contributes to reducing the greenhouse effect. The actual recovery of energy was 4.96 kW per kg of glycerol. Although the result is very significant and interesting, there is need for more complete economic analysis on the subject.

3.5. Identification of the disposal and destination of by-products

In 2011 the production of glycerol reached about 260 tons merely as a byproduct of biodiesel, volume nearly eight times higher than the demand, estimated at about 40 tons (BIODIESELBRASIL, 2012). The traditional markets of the substance, popularly known as glycerin - term used to refer to the product in the commerce, with purity above 95% - are the cosmetics, medicine, food and chemical industries.

Figure 6 shows the percentage utilization of glycerol in the Brazilian industry sector. The cosmetics, food and beverages are the most use glycerol in their processes.

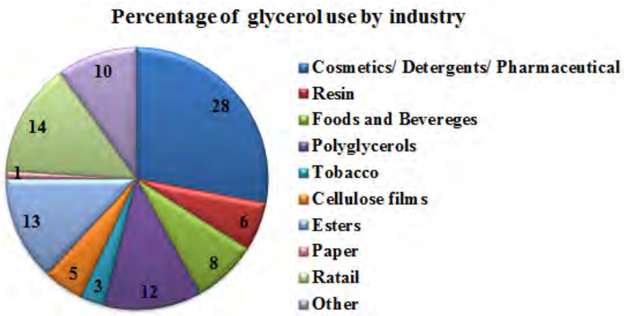

Figura 5. Major Brazilian industrial sectors that consume glycerol (adapted from MOTA, 2009).

According to Umpierre and Machado (2012), the current annual production of glycerol has already reached approximately 250 thousand tons. This production far exceeds demand and absorption capacity of the current markets, which is mainly based on the use of glycerol for cosmetics and food products, in addition to resale for direct consumption. Also, the volume of surplus glycerol definitely limits its long-term storage due to sufficiently high microbial degradation rates. Therefore, glycerol is a product already increasingly abundant and which must be converted industrially by catalytic new routes and lower environmental impact when compared to traditional routes.

Much of glycerol generated in biodiesel plants in Brazil is burned in furnaces and boilers to generate heat energy in industrial units, the same as in biofuel production, and potteries, steel etc. According to Expedito José de Sá Parente Junior, a member of the technical committee of Aprobio, this activity can be considered environmentally friendly, because the glycerol replacing firewood and fossil fuels such as fuel oil and coal. According to him, major producers of biodiesel, as Oleoplan, Rio Grande do Sul, also export their surplus glycerol to other countries, where the substance is used as raw material in traditional markets. Parente said that burning the product to generate heat and export to China are the two main destinations of glycerol from biodiesel production in Brazil. (REVISTA PESQUISA FAPESP, 2012).

In Brazil, in the present days, the price of crude glycerol varies from 200 to 400 U.S. $ / ton, the value of blond glycerin (glycerol partially treated to remove impurities) 600 to 800 U.S. $ / tonne (MELO, 2010). From glycerol which can not be sold in the market, a small part of this product is utilized in new applications, but the higher amount may be contributing only to generate an environmental liability in growing time (MATURANA, 2010).

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Figure 7 shows the evolution of prices of glycerol in Europe, United States, China and South America in 2010.

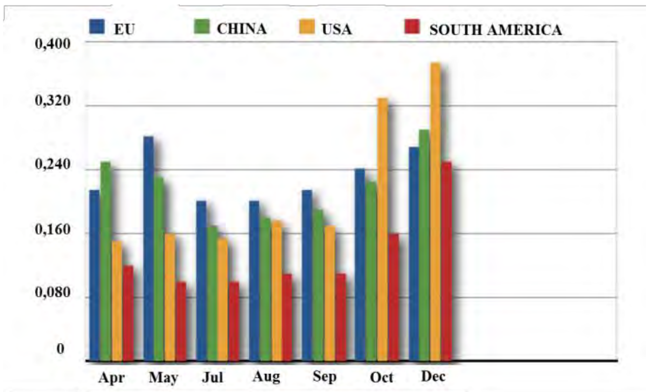

Figura 6. Glycerol price evolution in Europe, United States, China and South America in 2010 (MATURANA, 2010).

This information presented above corroborates the evident effect of the increase in the biodiesel production and the price of glycerol. Probably this turbulence helps to explain some anomalies in the international market, for example, the fact that the United States are both importers and exporters of crude and refined glycerol, and today some industrial glycerol producers are being closed, but other producers who wish to seize the new uses of glycerol have been initiated very enthusiastically (PAGLIARO; ROSSI, 2010).

Oilseed cakes are used primarily as organic fertilizer, power generation and feed. Considering the feed as the link between the production of biodiesel and livestock, the use of this by-product in ruminant feeding aims to increase productivity and generate lower emissions of greenhouse gases by animals, generating carbon credits and answering the interest of the private sector (ABDALLA *et al.,* 2008). The castor bean has predominant use as organic fertilizer, as it is a rich compost and nitrogened, efficient recovery for depleted lands and acts as nematodes controller. From castor meal, you can get significantly higher value if used as animal food, taking advantage of the high protein content. However, for this purpose, there is a need of bran detoxification due to the presence of toxic and allergenic elements in its composition (BIODIESELBRASIL, 2012).

Considering the wide range of biodiesel co-products with potential to be used in the diet of ruminants, studies are being developed in order to identify and evaluate the chemical composition and nutritional value of various biodiesel co-products that can be rationally explored in ruminant feed, and also to check the use of these co-products as fertilizers, due to their toxicity in animal diets, either by chemical or extraction process, it might impede their use in animal feed (CARNEIRO, 2013).

3.6. Perspectives of the Brazilian energy market for the major products generated

Several studies have addressed the identification of possible uses for crude glycerol from biodiesel chain. These studies are mainly focused on: generating different chemicals, such as 1,2-propanediol, 1,3-propanediol, and docosahexaenoic acid polymers, hydrogen production, development of fuel cells for automotive fuels and additives production ethanol or methanol. However, there are other potential uses that considerable potential to be adopted in the short term as part of a scene transition, as animal feed, the co-gasification, waste treatment, among others. In the medium and long term these alternatives must be replaced with alternatives that can provide products with higher added value and lower environmental impacts (LEONETI *et al*., 2012).

The possibility of using glycerol as fuel to generate energy through direct combustion or gasification becomes a real option, depending on the development of appropriate technology to succeed (MATURANA, 2010). In addition to the studies described previously in this paper, there are some patents or patent applications whose object has some relation to combustion of glycerol, however, there are still no specific patents in Brazil on this issue (MATURANA, 2010).

4. CONCLUSION

With the study regarding the uses, disposal and marketing of products generated in the production of biodiesel, one can see that actually the market's main by-product, glycerol, is saturated and there is a need to find new applications for the substance. Currently the applicability of glycerol is based on the use as raw material in food and beverages, chemicals for research, laboratory use and pharmaceutical and cosmetic applications, which present products with low added value and end up not making biodiesel production more feasible. With the saturation of the market arises the need to create technologies to add value to the product, alternatives that have demand equal to the supply of glycerol and large-scale applications to prevent the exportation of such substance that is currently inexpensive.

Some new trends in the market for glycerol are: the conversion of glycerol to propene, ethanol/methanol and hydrogen, biogas, energy production and Bio Additives. Also, the strategy of aerating and burn this byproduct for energy processes is able to offset the costs of traditional fuels, reducing emissions of greenhouse gases and eliminating a byproduct that is increasing year by year and which the disposal is becoming a liabillity. The other by-products, cake and meal, despite having proper applications on the market today, especially in the diet of ruminants and as fertilizer, and not being in surplus conditions, highlight the importance of further studies for their purposes, especially about the toxins present in his compositions.

Moreover, the prospects of the energy market in Brazil of these major by-products are positive, but there are still many controversies fueled by the lack of studies of glycerol combustion, which currently presents itself as one of the best alternatives to avoid glycerol becoming an environmental passive in time.

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