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APPLICATION TRENDS OF GLYCEROL FROM BIODIESEL PRODUCTION

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ABSTRACT

Biodiesel has become in one of the most employed sustainable and renewable fuels in the XXI century, since can be produced from many vegetal oils or animal greases. Nevertheless, one of the highest inconvenient is that glycerol is produced as a by-product in around 10% in weight of biodiesel obtained. The consequence is that glycerol market has an overproduction which cannot be used in the chemical industry, promoting an environmental problem for its disposal. Nevertheless, in the lasts decades many researches have been conducted in order to give a value added to this biodiesel by-product through its use as raw material of multiple valuable chemical products as well as its use in energy alternatives. This paper makes a review of the concepts of biodiesel and glycerol as well as the new different chemical and biochemical alternatives of glycerol employment which can diminish the actual high cost of biodiesel production.

Keywords: Crude glycerol, biodiesel, biofuel, combustion, added-value

Introduction

Energetic crisis due to the high cost of fossil fuels which are subject to a high and accelerated demand, as well as the effects of air pollution produced by their consume, has promoted the search of alternative renewable energies (Yang et al.2012, Anithaaet al. 2016). According to estimations from the Organization of the Petroleum Exporting Countries (OPEC), the world demand of petroleum in 2015 was 92,978,600 daily barrels, the gasoline demand 24,611,600 daily barrels and diesel 6,837,000 daily barrels (OPEC, 2016). On the other hand, in comparison to 1990, the global emissions will be duplicated by 2035 (Mofijur et al., 2014); thus the development of alternative clean fuels is a global agenda.

One alternative for the accomplishment of fuel demand, in addition to mitigation of atmospheric emissions, is the use of biodiesel, since is a fuel with biogenic origin with different and less emissions than diesel (Bashaet al. 2009), since has high degradability, it is not toxic, has not sulfur content and the greenhouse gases and atmospheric pollutant emissions are lower decreasing consequently the air pollution (Delfort et al, 2008).

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2.Biodiesel

The US Environmental Protection Agency (EPA, 2014) defines biodiesel as an alternative fuel from virgin or used vegetal oil"; although animal origin greases can be employed to produce biodiesel fuel. Biodiesel is renewable and can be mixed with conventional diesel to obtain mixtures as B2 (2% biodiesel and 98% diesel; B20 (20% biodiesel) or any other proportion, but it can be used 100% (B100) without the modification of diesel engines. It can be colorless until a light yellow. As biodiesel is a high oxygenated biofuel, can be used in diesel engines improving combustion efficiency (Lin et al. 2006).

In 1990 have been identified 360 oil crops for biofuels, but only some are considered as a potential alternative for diesel engines. Most employed vegetal oils used for diesel manufacture are coconut, olive, sunflower, peanut, palm and jatropha(Lin et al. 2006, Bashaet al. 2009), with properties depending on the raw material used (Murugesanet al. 2009); althoughbiodiesel should have the specific properties of the biodiesel standard of European Community (EN-14214-03) and the USA ASTM D6751-03.

Biodiesel has high lubricant properties that extend the engines life, its cetane index is higher than the diesel one, high oxygen content provides greater efficiency than diesel combustion, and comes from renewable sources (Demirbas2009, Fontaraset al. 2010).

Chemically, biodiesel is equivalent to fatty acids methyl esters (FAME) or fatty acids ethyl esters (FAEE), from the transesterification reaction of fatty acids; FAME are the most employed kind of biodiesel, whereas FAEE have been produced only in pilot scale (Ravindra y Raman, 2015).

Among biodiesel disadvantages are the decrease of engine performance due to high viscosity and low volatility and cupper corrosion, as well as the increase of fuel consumption (around 5% depending of mixture) and the high volumes of produced glycerol as a by-product (Maricq 2011).

Biodiesel production is carried out through a transesterification process of grease and oils with high content of around 97% triglycerids (Demirbas 2009), with a final glycerol weight content of around 10% (Silva et al. 2010).

Figure 1 shows the transesterification reaction of animal fats or vegetable oils with an alcohol (usually methanol or ethanol) for the preparation of biodiesel which is a mix of alkyl esters of fatty acids. The transesterification is a sequence of three reversible reactions with or without the use of catalysts, where triglycerids are converted in diglycerids and finally in monoglycerdsandglycerol.

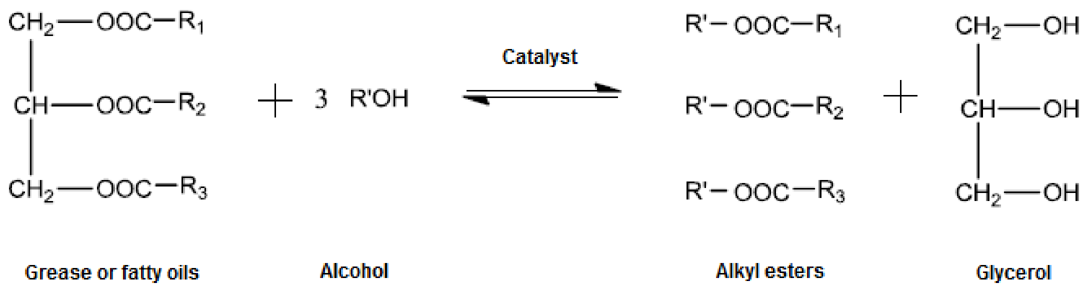

Figure 1. Transesterification reaction for biodiesel synthesis

3.Glycerol

Glycerol, also known as 1,2,3propanetriol, glycerin or glycerine (that it is normally applied to purified products with more than 95% glycerol) , is a colorless, odorless,viscous liquid obtained as a by-product of the oleo-chemical industrywith a syrupy-sweet taste. Glycerol was traditionally obtained as a by-product in the soap industry, fatty acids or esters production as well as by microbial fermentation, then, the volume of crude glycerol used to be relatively stable (Wang et al. 2001).

Glycerol is a tri-alcohol with two primary and one secondary hydroxyl groups with different possibilities of reaction, offering a great versatility as raw material. Glycerol is a flexible and stable substance due to the combination of hydrogen bonds and intermolecular solvation of hydroxyl hydrocarbons, it has low vapor pressure and low volatility due to its hygroscopic properties.

Pure glycerol is a very stable compound, not irritant, has a low grade of toxicity and it is compatible with many chemical products. For this reason it has many uses in pharmaceuticals, soaps, food, paints, cosmetic and personal hygiene among others. As aqueous glycerine solutions resist freezing it is commonly employed as antifreeze (Colin et al 2001); nevertheless, since 2003, when the biodiesel production began to increase, the production of glycerol as a by-product was duplicated; the market was flooding and the glycerol prices drop to the extent that glycerol could be dealt with as a waste product (Quispe et al, 2013). In the last years, the highest volume of commercial glycerol originates from biodiesel production (Ayoub and Abdullah 2012), inducing the closure of factories that use to synthetize glycerol from petrochemical process. Purification of crude glycerol is an expensive technique, then the research on applications of crude glycerol has been increased in the last decade and there are several commercial grades of glycerol depending of its grade of purification:

- Pure glycerol is a product with pharmaceutical quality that can be used in food, personal hygiene, cosmetics and other special applications. Should meet the requirements of the United States Pharmacopeia (USP) and the Food Chemicals Codex (FCC).

- Glycerine technical grade is a high purity product almost without impurities like methanol, soaps, salts or other substances.

- Crude glycerol is the by-product from the transesterification in the biodiesel production. The chemical composition is dependent of the raw material employed, the type of catalyst, process condition and transesterification efficiency. It has impurities from the manufacture process such as methanol, inorganic and organic salts, water, soap, and traces of glycerids(Hansen et al. 2010, Asad-ur-Rehmanet al. 2008). It can be refined until 99% (Wen 2012), but the cost is not feasible for small producers, then applications of this material is mandatory (Anithaet al. 2016).

One way to reduce production biodiesel costs is the glycerol transformation in value added products, for that reason the European Union has proposed “glycerol refineries” focus in industrially efficient process from glycerol to obtain high quality products with high economic value (GRAIL, 2014). Nowadays in the whole word many researches are in process to find new applications for refined and crude glycerol. These efforts can be classified according with its application, which will be analyzed in the next sections: the more extensive is related with synthetic routes where glycerol is used as building block or feedstock for chemical value-added products, the second is the use of glycerol as an energy source or as raw material to obtain energetic product (Quispe et al, 2013; Wang et al. 2013; Yuan et al. 2010; Xu et al. 2014).And finally other applications of raw glycerol, such as animal feedstuff will be discussed also (Yang et al., 2012).

4.New trends for glycerol applications

Traditionally, glycerol has been raw material for the generation of many chemical compounds with important applications in the pharmaceutical, cosmetic (including personal hygiene products) and food industries (since glycerol is not toxic, and easily digested), representing those industries more than 70% of its use (Figure 2); but also is used in bacterial additives, plasticizers, lubricants, antifreezes, alkyl resins, polymers, adhesives, including in the tobacco production as a solvent to avoid desiccation and control the fire when it is burned, as well as in the synthesis of other chemical products; more than 1500 applications of glycerol have been reported, but only few of them require significant amounts (Ott, Bicker an Vogel 2006; Gong et al. 2009, 2010;Durgapal et al. 2014, Anithaet al. 2016).

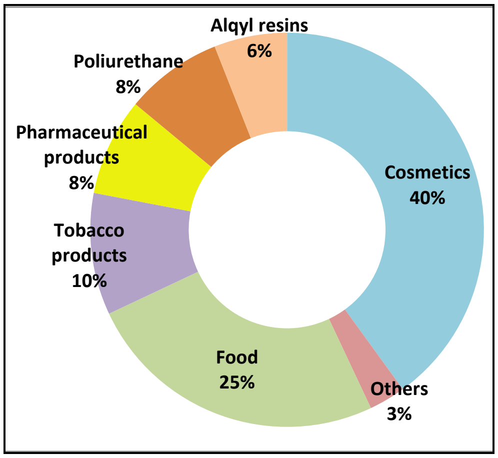

Figure 2. Traditional applications of glycerol

4.1 Glycerol as precursor for the synthesis of chemical products of high value added.

The use of glycerol as feedstock for chemical value added products has grown in the last decades since has begun to offer great cost-benefices that could valorize the use of glycerol. These applications can be divided in two types according to the catalytic via to obtain the valorized products, which can be through chemical conversion, or through biological conversion.

4.1.1 Glycerol applications for added-value products with chemically selective catalysis.

The big challenge, for most of glycerol applications related with chemical process, is the development of low cost catalysts, since those who can reach high selectivity are based in gold, palladium and platinum, which in addition to be expensive, they require low oxygen pressures to reduce their trend to deactivation (Kwon et al., 2011).The application of glycerol for the production of chemically catalyzed products can be revised based on the type of chemical reaction: carboxilation, cyclization, dehydration, etherification, esterification and transesterification, oxidation, gasification, hydrogenolisis, pyrolisis and reforming; the characteristics and use of these products are described briefly in Table 2.

4.1.2 Glycerol applications for added-value products through biological conversions.

Several technologies for the employment of glycerol have been development using microorganism for transformation of crude glycerol to valuable products described in Table 3.

Table 2. Synthesis of chemical products of high value added

Glycerine carbonate (GC)	GC is an excellent solvent for cosmetics and medicines; it is used also as solvent in the sugar industry in the saccharification of lignocellulosics fractions to fermentable sugars and can be utilized as source of new polymeric materials. GC has been synthetized from glycerol and dimethylcarbonate without solvents catalyzed by K_2CO_3 at 70°C (Zhang et al., 2013; Esteban, J, 2014).
Solketal	Solketal is used in the synthesis of glycerides by ester bond formation and can be utilized by blending with gasoline or biodiesel as an additive. It is produced from the reaction between glycerol and ketone (Garcia et al., 2014).
Acrolein	This compound is a synthetic intermediary of other chemical substances such as 1,3propanediol, acrylic acid esters, superabsorbent polymers, detergents, and methionine. It has been used in residual water treatments. Watanabe et al. (2007) synthetized acrolein from dehydration of glycerol and hot compressed water; Yan et al. (2009) produced acrolein from glycerol through dehydration in gaseous phase. Both studies showed that low concentrations of glycerol increase selectivity, avoiding polymerization. A recent option has been the use of tungsten oxide supported on ZrO_2, SiO_2 and Al_2O_3 in fixed beds with glycerol obtaining around 60% yields (Chai et al., 2014)
ESTERIFICATION **Glycerids**	Glycerol esters have applications as emulsifiers in food, cosmetic and pharmaceuticals products, as well as biodegradable surfactants (Gottlieb al., 1994). Monoglycerids (MG) and diglycerids (DG) are obtained by triglycerids hydrolysis, glycerol transesterification with fatty acids methylesters or by fatty acids; glycerine acetates, which are valuable fuel additives, can be produced from glycerol with acetic acid, although purity of products depends of reaction conditions and kind of used catalysts (Zhou et al., 2008). Catalysts used in these reactions are mostly metal oxides or supported salts on mesoporous materials with or without functionalization with organosulfonic groups. (Bancquart et al., 2001; Barrault et al., 2004; Perez-Pariente et al., 2003); cinnamateglycerids have been prepared also by Homogeneous catalytic esterification of glycerol with cinnamic and methoxycinnamic acids (Molineroet al., 2014).
ETHERIFICATION **GTBE**	Selective etherification o glycerol can yield valuable fuels. Glycerol ethers are applied as oxygenated solvents or biodegradable fuel additives. Glycerol tertiary butyl ether (GTBE) is used in reformulation of diesel and biodiesel mixtures, increasing the octane number and decreasing particles emissions, hydrocarbons, carbon monoxide and aldehydes after combustion (Liota et al., 2003). GTBE is obtained from glycerol and isobutene catalyzed with acid resins or mesoestructurated sulfonic silica (Melero et al., 2008), whereas glycerol alkyl ethers are synthetized from glycerol and alkenes (Behr et al., 2008).
HYDROGENOLYSIS **1,2 Propanediol**	The 1.2 PD is an additive in nutritional products (colorant solvents and flavorings). Used also in the formulation of antifreezes and lubricants and as humectant of tobacco (Kenar, 2007). Synthesis from hydrogenation of glycerol is performed with Cu catalysts supported on ZnO and Al_2O_3 at 200°C and 60 bar (Wang and Liu, 2014) or with Cu catalyst supported on SiO_2 at 240°C and 80 bar (Vasiliadou et al., 2014).
HYDROGENOLYSIS **1,3 Propanediol**	1,3 PD is used as antifreeze, and for production of aliphatic polyesters as PTT which is used to obtain adhesives, coatings, wood paintings and moldings (Yazdani and González 2007). 1,3 PD is carried out with ruthenium and rhenium catalysts, although the synthesis is not very selective. (Ma and He, 2009).
OXIDATION **Dihydroxiacetone (DHA)**	DHA is used in cosmetic industry as a tanning substance, for wine preservation and as fungicide, as a monomer for biomaterial production and for production of hydroxipiruvic acid that is a precursor of pharmaceutical products. (Pagliaro and Rossi, 2008). DHS can be obtained through electro catalytic oxidation of glycerol (Ciriminna et al. 2006).
OXIDATION **Glyceraldehide**	Gliceraldehide is an intermediary for carboxylic acids production, such as glyceric, tartronic, and mesoxalic acids (Stockel, 2007).
OXIDATION **Glyceric, tartronic and mexosalic acids**	Glyceric acid in intermediate in the biosynthesis of some aminoacids. Tartronia and mexosalicacides are used as emulsifiers and for dermatologic and mesoxalic acids illness. Mexosalic acid can be used as intermediate for the synthesis of other chemical and polymers, and is a valuable chelating agent. (Stockel, 2007)
POLIMERIZATION **Oligoglycerols**	Glycerol polymers named also oligoglycerols are used as emulsifiers and surfactants. They have been obtained using homogenous basic catalysts such as Na_2CO_3 with high conversions of glycerol (Charles et al, 2003), or using metals supported on MCM-41.

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Table 3.Chemicals produced by biological conversions

DEHYDRATION **3-HPA**	3-Hydroxipropionaldehyde is precursor of acrylic acid and 1,3 PD. It is produced with bacteria such as *Klebsiella. Citrobacter, Enterobacter o Clostridium* with yields of 85% (Pagliaro and Rossi, 2008).
ESTERIFICATION **Glycerolesters**	Monoglycerids and polyglycerol esters have been applied as emulsifiers in for food, pharmaceutical, and cosmetic products. Glycerol has been esterificated with enzymatic catalysts, to phenylalcanoictriglycerids using Vovozym 435 (Chang y Wu, 2007).
FERMENTATION **Hydrogen**	Ethanol is a feedstock for many chemical reactions and it used in almost all kind of industries as solvent. It has an important medical use and is the base of alcoholic beverages. It can be produced by fermentation of glycerol using *Pachysolentannophilus* (CBS4044), *K. pneumoniae* (GEM167) y *E. coli.* (Baek et al. 2011, Fakas et al. 2009, Yazdani and Gonzalez 2008). It has been reported also the production of high yield of ethanol from crude glycerol using *K.pneumoniae* mutant strain and nonpathogenic *Kluyveracryocrescens* S26 (Choi et al, 2011; Oh et al., 2011).
FERMENTATION **1,2 PD**	1,2Propanodiol is an additive in nutritional products (colorant solvents and flavorings). Used also in the formulation of antifreezes and lubricants and as humectant of tobacco (Kenar, 2007). Microbiological transformations of glycerol have been performed with *Escherichia coli o Thermoanaerobacteriumthermosaccharolyticum* (Altaras et al., 2001).
FERMENTATION **1,3 PD**	1,3 Propanodiol is produced mainly through biological fermentation of glycerol by microorganisms such as *Citrobacterfreundii,Klebsiellaoxytoca and Lactobacillus reuteri*(Anand et al., 2011); Jiang et al. 2014, Durgapal et al., 2014, Jolly et al., 2014; Przystałowska et al., 2015)
FERMENTATION **Ethanol**	Ethanol is a feedstock for many chemical reactions and it used in almost all kind of industries as solvent. It has an important medical use and is the base of alcoholic beverages. It can be produced by fermentation of glycerol using *Pachysolentannophilus* (CBS4044), *K. pneumoniae* (GEM167) y *E. coli.* (Baek et al. 2011, Fakas et al. 2009, Yazdani and Gonzalez 2008).
FERMENTATION **Butanol**	Butanol production has importance since has better characteristics as an alternative fuel in comparison of ethanol. Some strains that have had good results are *C. pasteurianum* DSMZ 525 and *Clostridium acetobutylicum* KF158795 (Yadav et al. 2014).
OXIDATION **DHA**	Dihydroxiacetone (DHA) is used in the cosmetic industry as a tanning and fungicidal. It has been produced through fermentation using*Schizochytriumlimacinum* on raw glycerol, detecting that to avoid a negative impact in the DHA production, methanol and soap methanol should be evaporated with an autoclave and soap should be precipitate with pH adjusting. Pyle et al. (2008)
Lacticacid	Lactic acid is used in food, cosmetic and pharmaceuticals industries, as well as in agriculture (Datta and Henry 2006). Hong et al. (2009) studied the AC-521 strain derived from *Escherichia coli* for the production of lactic acid from glycerol with 90% yield.
Propionicacid	This acid is a universal conservative with many applications in the production of solvents, pesticides, thermoplastics and pharmaceutical products (Bertleff et al. 2005). Propionbacterias are used for propionate or propanoate ion from glycerol and some researches concludes promising production of propanoic acid from glycerol (Ohtake et al. 2011).
POLIMERIZATION **Citricacid**	This acid is applied as food additive, flavoring, conservative in drinks and nutriments; is an additive in cosmetic and pharmaceutical products. It is produced from glycerol fermentation, and has been reported that crude glycerol can be used instead pure glycerol with some species of *Y. lipolytica*with similar results (Imandi et al. 2007, Rymowicz et al. 2009).
POLIMERIZATION **Fattyacids**	The production of some unsaturated fatty acids, such as Docosahexaenoic acid (DHA) acid, Eicosahenoic Acid (EPA) and gamma linolenic Acid (GLA), an omega 6 fatty acid, has an important role in cancer, Alzheimer and other cardiovascular illness treatment. DHA was produced from glycerol with the algae *Schizochytriumlimacinum* SR21 (Chi et al. 2007); EPA has been produced from glycerol with the fungi Pythium irregular (Athalye et al. 2009), whereas GLA can be obtained using *T. elegans, Cunninghamellaechinulata* and *Mortierellaisabellina* strains.
POLIMERIZATION **Biopolymers**	Other biopolymers of industrial importance such as acrylates, polyhydroxialkanoates (PHA) and polyhydroxibutirates (PHB), can be produced with glycerol as a carbon source through *Bacillus sp., Pseudomonas sp.* and *Burkholderiacepacia* ATCC (Ashby et al., 2004).

4.2 Applications of glycerol for energy.

4.2.1 Glycerol application as fuel additives

Glycerol can be transformed in molecules containing branched oxygen, especially in alcohols and ethers that can be used as fuel additives (gasoline, diesel and biodiesel). Additives improve fuels properties such as: increase of octane number, decrease of turbidity point, viscosity decrease, and decrease of emitted particles (Melero et al. 2010, Rahmat et al. 2010). Other additives to increase octane number are the glycerol tertiary butyl ethers (GTBE or TTBG), prepared through the reaction of glycerol and isobutylene in the presence of MCM-41 or Amberlyt resins in the of a dioxane co-solvent (PCT/IB2016/050444; Boerakker et al. 2008; Xiao et al. 2011).

4.2.2 Application of glycerol as fuel and for fuel production.

Although calorific level of glycerol is moderate, varying from 18.6 to 20.5 J/kg depending from the raw material use, it has been explored its use as fuel in industrial process, since it could be combined with other biomass fuel or could be used as furnace fuel for production of heat and electricity (Epp, 2008).Pyrolysis and gasification are promising methods that transform or descompose glycerol in methanol, carbon monoxide, hydrogen, formaldehyde, alcohol, acetaldehyde, among others (Buhler et al. 2002). Several studies have shown that syngas (synthesis gas) is produced through a gasification process (Yoon et al. 2010, Skoulou et al. 2013), which has a good performance internal combustion engines (Wei et al. 2011).Anaerobic digestion of glycerol with biomass is a potential application for biogas generation, mainly methane. Since glycerol has a great biodegradability y deoxygenated environments, it is possible a significant methane yield in digestion processes (Yang et al. 2008; Siles et al. 2009), for instance Panpong et al. (2014) produced 5.8 m3 of CH4m-3in the anaerobic digestion of seafood treatment water using 1% of glycerol.

Hydrogen (H2) is considered a new fuel for energy and energy carrier which can be used for transport. Production of H2 from glycerol has gained attention since one mol of glycerol can yield up to seven mols of H2 (Chen et al. 2011). Some methods of H2 production from glycerol are: partial oxidation, autothermic reforming,supercritic reforming and vapor reforming (Adhikari et al. 2009, Pairojpiriyakul et al. 2013). Gasification with CO2 removal has been effective with high efficiency (Dou et al. 2014). **Hydrogen can be obtained also from crude** glycerol with bacterium Rhodopseudomonaspalustris through photofermentative conversion (Sabourin et al., 2009).

4.2.3 Applications of glycerol for fuel cells.

Glycerol is not toxic, flammable, or volatile, and due to its high energy density (6.26 kWh L-1), has been used in energy applications, such as alcohol energy cells since the production methods and storage are easy. In addition, many oxygenated derivatives, like glycerates, hydroxipiruvates, mesoxalic and tartrosalic acids, which are expensive and difficult to synthetize trough other catalytic or biologic process(Gallezot 1997, Ilie et al. 2011).

4.2.4 Animals feedstuff.

As crude glycerol contains carbohydrates, it can be used as nutritional supplement for ruminants and no ruminants animals; crude glycerol has been added from 5% to 15% dry matter of the diet and due to the high prices of corn, has gained attention (Donkin et al. 2009). Nevertheless more studies should be performed since crude glycerol can contain dangerous impurities like potassium and methanol residues(Yang et al. 2012).

4.2.5 Glycerol in the wastewater treatment.

The use of low load of crude glycerol (up to 1.35 % v/v) can improve the municipal wastewater treatment, increasing the elimination of chemical oxygen demand and volatiles solids, additionally biogas production and methane yield (Razaviarani and Buchanan 2015; Silvestre et al. 2015). The use of glycerol as carbon source for denitrification in water treatment plants improve the efficiency for nitrates elimination (Bodík et al. 2009, Chen et al. 2013); denitrification based in biomass on suspended phase showed that glycerol kinetic was three times greater that the methanol one (Lu and Chandran 2010). Additionally, glycerol can be used also as co-substrate in the sludge anaerobic digestion (Nartker et al. 2014;Bernat et al. 2015).

Conclusions.

The growing world production of biodiesel, as an alternative renewable energy source has had an important growth, causing an overproduction of glycerol since it is a by-product in the transesterifaction reaction to obtain that fuel and provoking the drop of this compound.

This paper presented that chemical and biological conversions of glycerol and crude glycerol can produce a great variety for creation of value added products with promising developments, suggesting that future biodiesel plants could be biodiesel refineries which **will help to decrease** the biodiesel prices, taking advantage of the many technological possibilities of glycerol transformations.

Nevertheless many challenges have to be faced to develop technically and economically viable processes, especially for the use of crude glycerol.

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