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Technological monitoring of the potential of glycerol as raw material to obtain chemical inputs

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ABSTRACT: *The literature has reported advances in the development of new technologies for the production of chemical inputs from different sources of biomass. Among the compounds derived from these sources, the surplus glycerol of biodiesel production is a target of continuous commercial interest. Its use in higher value-added products has been the subject of a study of the valorization of the biodiesel production chain. The objective of this paper is to evaluate the potential application of glycerol as a chemical platform for the production of biobased products. The evaluation of the state of the art and the analysis of the scenario consisted of consulting the patent database of SciFinder and WIPO and database Science Direct. The obtained data suggest that the implantation of technologies of conversion of glycerol into new products is viable in Brazil, and would stimulate the substitution of some imports, generating foreign exchange savings and a greater economic activity. In the environmental scope, this approach is aligned with the principles of circular economy and green chemistry, mainly promoting the reduction of greenhouse gas emissions and waste.*

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I. INTRODUCTION

The world's climate situation and the commitments made since COP21 and reinforced and amended at COP22 and COP23 require a low-carbon world to contain the temperature rise and consequently damage to health, agriculture and transport and trade.

At the macro level some actions have opened spaces for optimizing the use of biomass to supply energy and products, such as: 1) The Fourth UN Assembly for the Environment, whose theme was "Innovative Solutions for Environmental Challenges and Consumption and Sustainable Production",held in March 2019 in Nairobi, Kenya. In this event, ministers from more than 170 countries proposed a change acceleration plan for the development of sustainable models applying science and innovation, in order to make the use of natural resources more efficient, reduce the use of disposable plastic and promote low carbon economies; 2) the Green Bank Design Summit , held in Paris in March 2019, aimed at facilitating the establishment of green investment banks (GIBs) and other green financial institutions in emerging markets, through continued collaboration by Green Banks already existing in some countries of the OECD (Organization for Economic Co-operation and Development). REFERENCES?

Parallel to the above actions due to the depletion of fossil raw materials and concerns about the environment, considerable progress has been made in recent years in the development and diffusion of new technologies for obtaining new products from biomass , mainly biofuels.

Over the last ten years, world biofuel production has increased considerably and continues to expand. Considering the base year of 2017, there was a 4% increase in its production, driven mainly by Argentina, Brazil and Spain. In the Brazilian scenario, this increase is evidenced by the production of 4.29 million cubic meters of biodiesel, about three and a half times higher than in 2007. Approximately 41% of this volume comes from the southern region.

Glycerol is the main co-product generated in biodiesel production. Also called glycerin, it corresponds to 10% of the total volume of biodiesel produced (ANITHA et al., 2016). Its production prospects in the Brazilian market are very promising: In 2017 422 thousand tons were produced and the projection for the market in 2024 suggests a co-production with biodiesel of 1.1 million tons. This estimate is based on an industry with a technological structure in a government that encourages the increase of the addition of biodiesel to diesel sold in the country (in 2024 the percentage of biodiesel added to diesel will be 15%), on the availability of raw material (mainly bovine fat and soybean) and the commitment established at COP21 to reduce carbon dioxide emissions (PEITER et al., 2016).

II. TRADITIONAL APPLICATIONS OF GLYCEROL

Due to characteristics such as non-toxicity and absence of color and odor, glycerol has a wide application in the pharmaceutical, cosmetic, tobacco and food industries, which use derivatives of glycerol in the form of esters, polyglycerol and resins (PEITER et al. 2016).

In the pharmaceutical industry, glycerol is found in the formulation of cough syrups, expectorants, ointments, creams, antibiotics, antiseptics and plasticizers for drug capsules. As a humectant, it integrates the chemical composition of cosmetics and moisturizing products such as shampoos and hair conditioners, hair tonics, lotions, sunscreens, after sun lotions, gels, shaving lotions, deodorants and make-up (PAGLIARO et al. , 2007; SINGHABHANDHU and TEZUKA, 2010 apud PEITER et al., 2016). In the food industry, it is used as a thickener of sauces and humectant in the manufacture of candies, soft drinks and sweets. It is also applied in the textile industry, usually in the manufacture of paints and resins. In the fabric industry, it is used in the adjustment and softening of yarns and fabrics, and in the lubrication of fiber processing (KNOTHE et al., 2006; SINGHABHANDHU and TEZUKA, 2010 apud PEITER et al., 2016). In the processing of tobacco industry products, glycerol acts as a humectant, preventing the product from drying out (MOTA et al., 2009; SINGHABHANDHU and TEZUKA, 2010 apud PEITER et al., 2016).

In Brazil there is no specific legislation for the disposal of glycerol. The two possible forms are dumping into rivers and burning. However, both forms cause serious environmental problems, because the waste generated has high biochemical oxygen demand (BOD) and burning releases carcinogenic compounds, such as acrolein. Some industries use glycerol in energy production, but a significant number of companies store this product without providing a specific destination (PEITER et al., 2016).

III. POTENTIAL ALTERNATIVES FOR THE USE OF GLYCEROL

In 2010, the US Department of Energy identified glycerol as a promising platform for obtaining chemical inputs as there is technology in progress adaptable for the production of different products; the products obtained can replace those obtained by petrochemicals; the technology allows to obtain volumes in industrial scale and that can be sold; glycerol is a chemical platform for a biorefinery; and bioproducts are accepted and recognized in the market (BOZEEL and PETERSON, 2010).

According to Market Research, global consumption of 6 million tons of glycerol in 2024 is estimated. This estimate is in line with national and regional policies, new technologies developed, the need to reduce carbon dioxide emissions and make the economy more circular.

Improving the sustainability of the biodiesel production chain is associated with the conversion of glycerol into products of high economic value. The new applications of glycerol contribute to minimize the environmental impacts generated by its disposal and/or accumulation (YAZDANI and GONZALEZ, 2007). In this context, the development of glycerol valorization technologies has been fundamental for the continuity and expansion of the biodiesel production chain (PEITER et al., 2016).

This co-product can be converted into chemical fuels and intermediates of industrial value both by chemical synthesis and by biotechnological conversion. Among the chemical inputs, polyurethanes, acrolein, propene, formic acid, synthesis gas, epichlorohydrin, 1,3-propanediol - an important intermediary in the manufacture of polymers - and additives for similar fuels to ETBE (ethyl tert - butyl ether) . Using biotechnology, acetic acid, succinic acid, butyric acid, lactic acid, 2,3-butanediol, ethanol and synthesis gas (ANITHA et al., 2016) can be obtained depending on the microorganism used in the process.

Adding value to glycerol by converting it into inputs for the chemical industry has been presented as an alternative to direct export, minimizing the use of fossil raw material and concomitantly leveraging the biodiesel production chain.

As the basis of the development of new technologies involves the encouragement of scientific and technological research, the purpose of this work is to conduct a technological prospecting study to identify the derivatives of glycerol and the respective processes of obtaining it with greater potential of industrial application.

IV. METHODOLOGY

Because it is the insertion of technologies into different industrial sectors, the evaluation of the profile of publications is of great relevance to understand the state of the art.

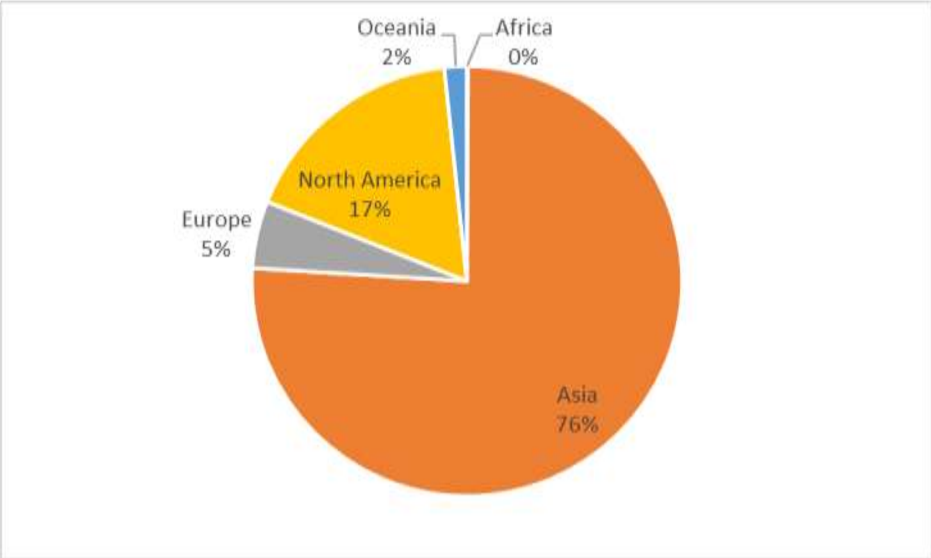
Patent search for new derivatives of glycerol has been conducted on the SciFinder and WIPO patent databases. In SciFinder, the search strategy consisted of using the term glycerol raw material and then glycerol in process in the research topic field. In WIPO, the term glycerol in the process was used in the cover page field. In both databases, the temporal restriction comprised the years from 2008 to 2017.

Database Science Direct was consulted to evaluate the technological trends regarding products obtained from glycerol in the period from 2013 to 2018. For this purpose, the term products from glycerol was used in the title, abstract and keywords fields.

V. RESULTS AND DISCUSSION

We found 2,136 documents on the SciFinder database and 2,939 on the WIPO database. These numbers are high due to the registration of the same patent with different agencies. The data collected show that China is the main patent applicant on both databases.

The WIPO database showed that China is the leader of patent publications using glycerol as raw material (Figure I).



Source: Prepared from WIPO data (2017).

Figure 1: Percentage of patents published per continent from 2008 to 2017

As searched in the WIPO database, Table 1 shows the main products obtained from glycerol and patented by twelve companies operating in various segments of the chemical industry.

Table 1. Main derivatives of glycerol patented by leading companies in different industrial segments

COUNTRY	COMPANY	NUMBER OF PATENTS	DERIVATIVES OF GLYCEROL	OBSERVATIONS / CHARACTERISTICS
France	Adisseo	8	Acrolein	No project using glycerol was found on the company's website
France	Arkema	68	Acrylic acid and acrolein	The company's website states that the project is based on the replacement of propylene of petrochemical origin and is under development
United States	Archer Daniels Midland Company	16	Propanediol	The company has a production plant of 100 thousand tons per year of propanediol from glycerol. It also produces glycerol used in the plant
Germany	Basf	46	propanediol, sirinol, polyurethane and glycerol carbonate polymers	No project implemented using glycerol was found on the company's website
France	Metabolic Explorer	16	Propanediol and butyric acid through biotechnological processes	The company is developing studies to build a 1,3-propanediol plant using biotechnology in France

Netherlands	DSM	19	Alcohol and citric acid using biotechnological processes	It has a tendency on its website to use bio-based raw materials, but no project implemented using glycerol was found
Malaysia	Emery Oleochemicals	7	polyglycerols	The company has biolubricant factories, green additives for polymers, biopolies and green solutions for agriculture. The company's website does not indicate which Bio Raw Materials are used in the various processes
United States	Nalco	24	Polyol	No project using glycerol was found on the company's website
Netherlands	Purac	16	propionic acid and derivatives using biotechnological processes	The company's website does not indicate whether the patented products are obtained from glycerol
Brazil	Rhodia	7	dioxolane	The company has been investing in the production of sustainable solvents from glycerin at the Paulínia Industrial Complex (SP) to meet the demand of the paint and varnish, cleaners and aromatizers industry.
Belgium	Solvay	85	propanediol and dichloropropanol	It has a production plant of 100 thousand tons of epichlorohydrin from glycerol, which replaces propene in the initial chain

Table 2 shows the processes for obtaining and applying the derivatives of glycerol. These data were collected on WIPO patent database and database Science Direct. Table 3 is derived from Table 2 and shows the number of documents pertaining to major derivatives of glycerol.

Table 2. Main processes for obtaining and applying derivatives of glycerol

		Application (* for fuels)							
Final Product	**Process**	**Additive (*)**	**Cosmetics**	**Food**	**Drug**	**Chemical platform**	**Resin**	**Polymer**	**Other**
1,2-propanediol	hydrogenolysis		X	X	X		X	X	X
1,3-Propanediol	fermentation						X	X	

citric acid	fermentation		X	X	X			X	
glyceric acid	oxidation				X			X	X
glycolic acid	oxidation		X	X	X	X			X
glycolic acid	fermentation		X	X	X	X			X
Hydroxypyruvic acid	oxidation				X				
mesoxalic acid	oxidation				X				
oxalic acid	fermentation							X	X
propionic acid	fermentation			X					
succinic acid	fermentation			X		X		X	X
tartronic acid	oxidation with catalysts								X
Acrolein	Dehydration				X	X		X	
Butanediol	fermentation					X		X	
Butanol	fermentation					X		X	

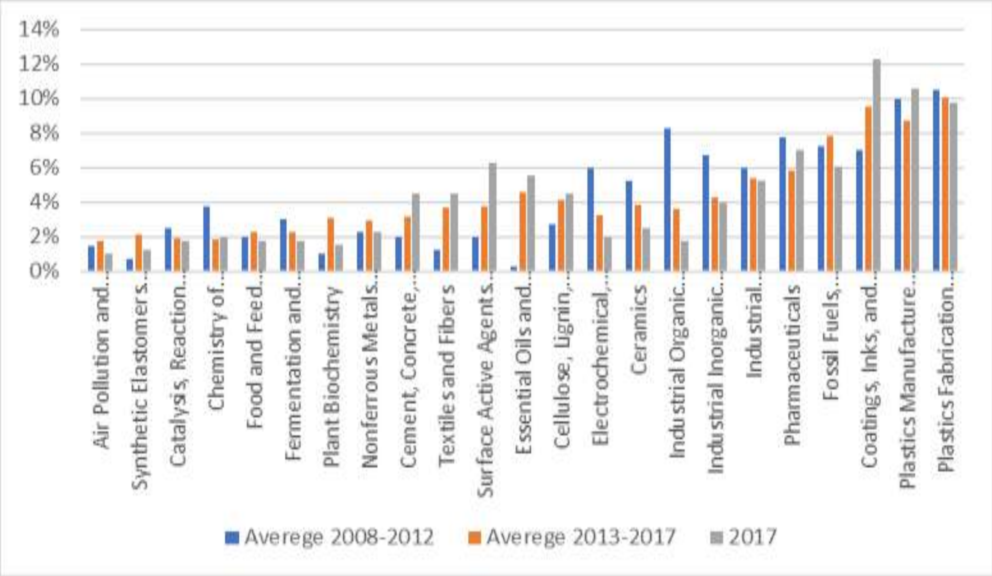
glycerol carbonate	glycerolysis					X		X	X
glycerol carbonate	transesterification					X		X	X
glycerol carbonate	carboxylation					X		X	X
acetals	acetylation	X							X
Dihydroxy acetone	fermentation		X					X	
dioxolane	acetylation				X				X
epichlorohydrin .	chlorination with HCl						X	X	X
glycerol tertiary butyl ether (GTBE)	etherification with isobutylene	X							X
Glyceraldehyde .	oxidation				X				
Hydrogen	Steam reforming								X
Glycerol monostearate	esterification		X						X
Polyester	Condensation polymer							X	
Polyhydroxyalkanoate . butyrate	fermentation				X				X

Polyglycerol .	esterification		X		X	X		X	X
Polyol	esterification or etherification						X	X	
glycerol triacetate (TAG)	esterification	X							X

Table 3. Quantification of major derivatives of glycerol from WIPO and Science Direct databases

BASE / NUMBER OF DOCUMENTS	DERIVATIVES OF GLYCEROL	CHARACTERISTICS
WIPO: 91 SCIENCE DIRECT: 389	Acrolein	This product is a very important chemical platform as it is a precursor of acrylic acid. Currently several companies are conducting research so that the economic cost thereof is compatible with the use of petrochemistry.
WIPO: 16 SCIENCE DIRECT: 76	ketals: soketal and 1,3-dioxolane	Samoilov et al. (2016) argue that when this product is added to gasoline (including bioethanol-gasoline fuel), there is an increase in octane number of the fuel and reduction of gum formation. In diesel and biodiesel or in mixtures thereof, ketals reduce emissions of nitrogen oxides, carbon monoxide and soot, and improve cold flow properties, but decrease oxidation stability
WIPO: 97 SCIENCE DIRECT: 62	dichloropropanol epichlorohydrin	Solvay commercially produces these products from glycerol. Most articles address future process improvements
WIPO: 7 SCIENCE DIRECT: 22	glycerol tertiary butyl ether (GTBE)	The Dutch company GTBE Company NV holds virtually all patent applications. This product is used as a diesel additive and reduces particulate emissions to the atmosphere. Samoilov et al. (2016) indicate that the addition of GTBE and STBE (solketal tert-butyl ether) to biodiesel can reduce NOx emissions
WIPO: 68 SCIENCE DIRECT: 17	polyols	Kong et al. (2016) state that the reaction to obtain polyols stands out by controlling the size of the polyol and, consequently, of the polyglycerol. Application thereof is related to size and shape. The development of this bio-product mainly produces biopolyurethanes. This segment is expected to grow at a rate of 9% per year
WIPO: 18 SCIENCE DIRECT: 94	1,2-propanediol	The new research focuses on the optimization of the hydrogenolysis process and the production of 1,2-propanediol via fermentation
WIPO: 48 SCIENCE DIRECT: 42	glycerol triacetate	Many researches emphasize the bioadditive function. Cornejo et al. (2017) recommend that this additive be subjected to several tests to standardize its behavior and limit addition in different fuel mixtures

Figure 2 shows that the highest percentage of glycerol conversion patents is concentrated in the segments of plastics, coatings, fuel additives, pharmaceuticals and industrial carbohydrates. In addition to these patents presenting new methods, some are related to optimization of existing processes. Figure 2 also identifies segments where the application of glycerol is growing such as surface active agents and detergent, essential oils and cosmetics. Therefore, glycerol is a less polluting $_{C3}$ platform that can meet the consumption demands from various segments.



Source: Prepared from data taken from Scifinder Database

Figure 2: Percentage of patents per segment

VI. FINAL REMARKS

Whereas: 1) the report published by the Intergovernmental Panel on Climate Change (IPCC) of the UN in November 2018, stating that there is an urgent need to contain global warming and de-carbonize global industries until 2050, and that to maintain the possibility of limiting global warming to 1.5 degrees, global emissions of greenhouse gases need to fall 55% by 2030; 2) the result of the fourth Assembly of the UN which concluded that innovative solutions aligned with sustainable productions are required to meet world consumption and environmental challenges; 3) In 2030, the population of Brazil should be 206 million (information from IPEA (Institute of Applied Economic ResearchOctober 2018) and world population will be 8.5 billion (UN 2015 information); 4) the number of patents using glycerol as raw material (C3 platform) grew at rates exceeding 30% in the last 10 years; 5) that there are already technologies in commercial production; 6)Brazil has a potential to produce 18% of the world demand of glycerol in 2024, it can be concluded that with technological development policies and economic incentives for the development and deployment worldwide and nationwide of the use of glycerol as raw material, possibly the following scenario may be established: i) the world industry using glycerol for biobased products can grow, as this is an environmental necessity ii) Brazil can play an important role as glycerol supplier, processed locally, and expand the base of biobased products to meet the demands of national and international consumers. IV)The biorefineries producing biodiesel and glycerol can produce other products with higher value added

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