We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

6,900
Open access books available

186,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS

BOOK CITATION INDEX

INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Chemical Conversion of Glycerol from Biodiesel into Products for Environmental and Technological Applications

Miguel Araujo Medeiros[1], Carla M. Macedo Leite[2]
and Rochel Montero Lago[2]
[1]Universidade Federal do Tocantins,
[2]Universidade Federal de Minas Gerais,
Brasil

1. Introduction

Currently, fossil fuels represent over 80% of energy consumption in the world. However, due to environmental and geopolitical issues the development of new energy sources is mandatory. For example, only the Middle East holds 63% of global reserves, which directly influences in the final price of fuel.

In developed nations there is a growing trend towards employing modern technologies and efficient bioenergy conversion using a range of biofuels, which are becoming cost competitive with fossil fuels (Puhan et al., 2005). In Brazil, this work is focused on the production of bioethanol and biodiesel.

There are discussions around the world on the feasibility of using renewable fuels, which may cause a much smaller impact to global warming, because the balance of CO_2 emissions decreases when using these fuels. (Demirbas, 2008)

In 1997 at a meeting in Kyoto, Japan, many of the developed nations agreed to limit their greenhouse gas emissions, relative to the levels emitted in 1990. In this occasion Brazil established social and environmental policies to collaborate with those global goals (Puhan et al., 2005). An example is the biodiesel program which in 2008 implemented the use of B2 (2% biodiesel into conventional diesel). In other countries, like Germany, it is possible to supply only with B100 biodiesel (100% biodiesel).

1.1 Biodiesel

Biodiesel, a renewable biofuel produced from biomass, is biodegradable and does not cause significant contamination with emissions containing sulfur or aromatics. Biodiesel, is an viable alternative for compression-ignition engines (Puhan et al., 2005), in total or partial substitution of fossil diesel (Chiang, 2007).

The use of biodiesel as fuel should occupy a prominent place in the world, with a market that is booming because of its enormous contribution to the environment, such as qualitative and quantitative reduction of environmental pollution (Ferrari et al., 2005). Furthermore, this fuel is a strategic source of renewable energy to replace petroleum products.

Biodiesel is fuel produced mainly by transesterification of vegetable oils, but can also be obtained by the reaction of animal fat (Pinto et al. 2005; Puhan et al., 2005; Chiang, 2007)

soybean (Costa Neto & Rossi, 2000), Cotton (Pinto et al., 2005; Puhan et al., 2005), castor bean (Pinto et al., 2005), canola (Pinto et al., 2005; Catharino et al., 2007; Kocak et al., 2007; Puhan et al., 2005), palm (Pinto et al., 2005; Catharino et al., 2007; Puhan et al., 2005), sunflower (Pinto et al., 2005; Catharino et al., 2007; Puhan et al., 2005; Costa Neto & Rossi, 2000), peanut and babassu.

Synthesis of biodiesel can be accomplished by using acid, basic (Costa Neto & Rossi, 2000; Puhan et al., 2005; Chiang, 2007; Pinto et al., 2005) or enzymes (Talukder et al., 2007; Schuchardt, 1990) catalysts or even in supercritical methanol (Puhan et al., 2005).

1.2 Biodiesel production

Transesterification (Figure 1) is the reaction of triglycerides with an alcohol to form esters and glycerol (Chiang et al., 2007; Georgogianni et al., 2007; Krishna et al., 2007; Wu et al., 2007; Talukder et al., 2007; Aparício et al., 2007; Zuhair, 2005; Vicente et al., 2005; Medeiros et al., 2008; Stern & Hillion, 1990; Freedman et al., 1984; Encinar et al, 2002; Vicente et al., 2006; Bunyakiat et al., 2006; Karinen & Krause, 2006). This process decreases the viscosity of the oil and transforms the large, branched molecular structure of bio-oils into smaller molecules, of type required in regular diesel engines.
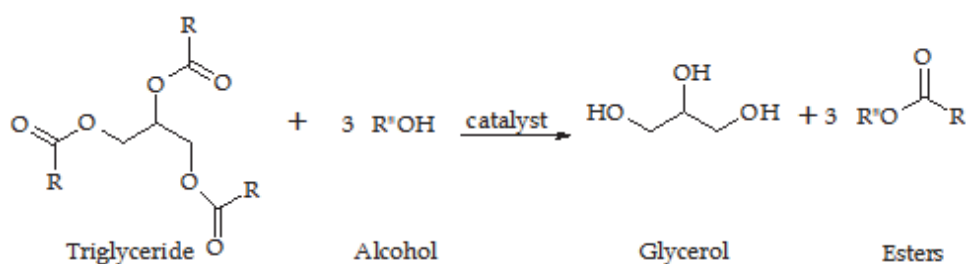

Fig. 1. Synthesis of biodiesel by transesterification of triglyceride.

In the transesterification for biodiesel production, a large amount of glycerol as a byproduct (about 10% compared to the mass of ester produced) (Puhan et al., 2005; Medeiros et al., 2010) is produced. The separation step of glycerol can be accomplished by decanting, in which the lower phase has the glycerol, the catalyst of the process (usually homogeneous and high polar character), alcohol and oil residue without reacting (crude glycerol, Figure 2, a). The biodiesel separates from the upper stage, almost pure.

The transesterification using methanol is the most used process around the world (Chiang, 2007) offering several advantages, such as: (i) small volume of alcohol recovery, (ii) lower cost of alcohol compared to ethanol (not in Brazil) and (iii) shorter reaction times (Pinto et al., 2005). The use of ethanol proves more advantageous, when considering its lower toxicity.
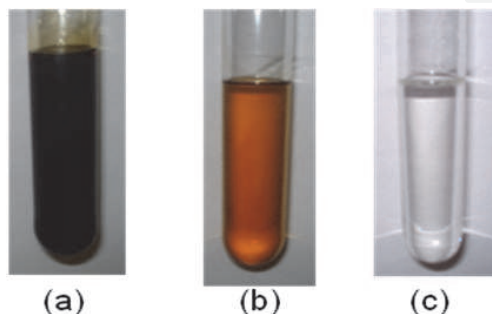

Fig. 2. (a) crude glycerol, (b) pre-purified glycerol, (c) glycerol purified.

1.3 Use of the glycerol

The investigation of new uses for glycerol is critical for the success of the biodiesel program, especially in relation to the crude glycerol, which has few direct uses and market value marginalized. Currently, the demand for purified glycerol PA for the pharmaceuticals, food additives, personal care (Puhan et al., 2005), industry is supplied by the petrochemical industry.

The biodiesel production will produce a large increase in, the amount of glycerol in the market, causing a decrease in the prices significantly, in the world. In the European Union, for example, the price of glycerol, in 1995 was € 1500 t^{-1} and reduced to 330 € t^{-1} in 2006 (Puhan et al., 2005). In Brazil, in 2005 the price of glycerol reached € 1270 t^{-1}, but already in 2007 the price dropped to 720 € t^{-1}. And in regions close to the price of biodiesel plants did not exceed € 300 t^{-1}, in 2010.

Different routes have been investigated to transform this glycerol to new products and new applications. Some of these processes are listed in Table 1.

Process	Conditions	Products	Ref.
Polymerization	T = 210-230°C; reduced pressure (~0,3atm); 0,5-1,5% NaOH.	Cyclic polymers.	(Blytas & Frank, 1993)
Pyrolise	T = 650°C.	CO; acetaldehyde; acrolein.	(Chiang, 2007)
steam reforming	T = 200-250°C; 1% cat. Níquel-Raney (Ni-Sn).	50-70% H_2; 30-40% CO; 2-11% of alkanes.	(Stein et al., 1983)
Esterification	T = 200-240°C; 0,1-0,3% NaOH; t =0,5 h; 100% methanol.	Carbohydrates and esters.	(Noureddini & Medikonduru, 1997)
Oxidation	T = 50°C; Pd/C (5-8% of Pd), t = 8h; pH = 5-11.	Dihydroxyacetone.	(Garcia et al., 1995)
Etherization	T = 90°C; 1-7,5% amberlist 15; t = 2-3h.	70% of 3-tert-butoxi-1,2-propanodiol (*mono ether*). 87% of mono ether.	(Klepácová et al., 2003, 2006)
Oligomerization	T = 260°C; 2% $Mg_{25}Al_{20}$ (cat.); t = 8h.	65% of diglycerol; 20% of triglycerol and 15% of tetraglycerol.	(Barrault et al., 2004)

Table 1. Conversion of glycerol to different products.

Table 1 can be summarized in Scheme 1, which shows some reactions that originate from glycerol.

Oxidation products of glycerol, for example, can be used in cosmetics and pharmaceuticals intermediates (Davis et al., 2000; Pachauri & He, 2006; Krishna et al., 2007) and even suntan lotion (Kimura, 1993).
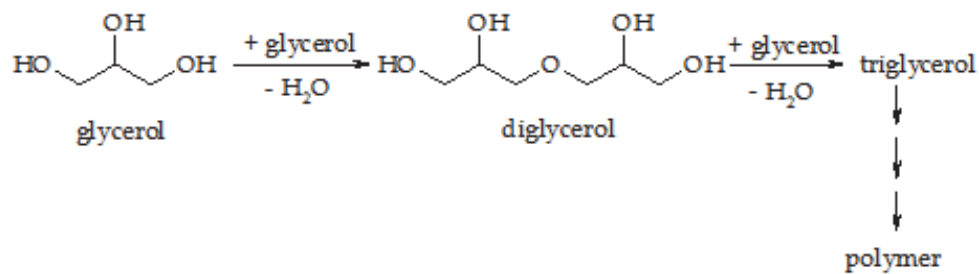
The products of oligomerization of glycerol can be used as additives for cosmetics and foods, the raw material for resins and foams (Shenoy , 2006; Lemke, 2003; Werpy, 2004; Pagliaro & Rossi, 2008), lubricants (Pagliaro & Rossi, 2008), cement additives (retains moisture) and are synthetic intermediates and possible substitutes of polyols, e.g. polyvinyl alcohol, in some applications (Werpy, 2004; Pagliaro & Rossi, 2008; Medeiros et al., 2008).
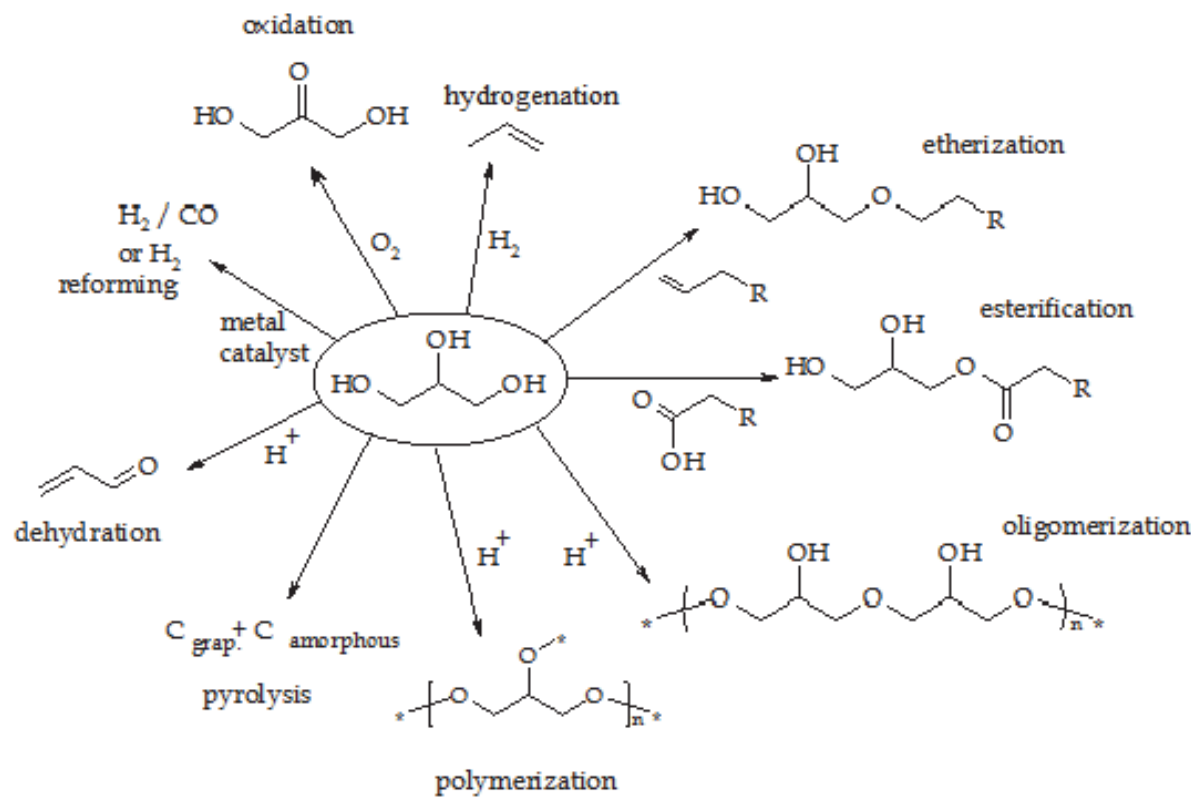
Scheme 1.

It is noteworthy that many of the applications mentioned for the glycerol require high degree of purity, which for glycerol derived from biodiesel requires several stages of treatment, increasing its cost. The main impurities in the glycerol from biodiesel is methanol or ethanol, water, inorganic salts and catalyst residues, free fatty acids, unreacted mono, di and triglycerides and various other matter organic non-glycerol (MONG) (Pagliaro & Rossi, 2008). Thus, it is necessary to develop new routes for the consumption of glycerol from biodiesel.

In this chapter, will be treated the transformation of glycerol based on production of ethers from condensation of two (or more) glycerol's molecules. One of the mechanisms Favorable for the formation of ethers is by alcohol protonation (ROH_2^+), followed by condensation of other alcohol and water loss. The condensation reaction of glycerol (Scheme 2), is usually catalyzed by acids or bases producing small polymers called oligomers and water. Along the text will be described the oligomers, polymers and carbons obtained from polyglycerol and its applications.

Scheme 2.

2. Oligomers

Oligomerization of glycerol (Scheme 2) is an alternative to the use of byproduct of biodiesel, because their products have wide application. For a better understanding of oligomerization (and polymerization), was accompanied through ESI-MS (Electrospray Ionization Mass Spectrometry in the positive ion mode) a typical reaction of oligomerization - glycerol PA catalyzed by 1% H_2SO_4 at 280°C/2h, in reflux.

Analysis of the sample (2h) is shown in Figure 3. The presence of an intense ion of m/z 93 (protonated glycerol = [glycerol + H]$^+$) is clearly noticeable indicating the subsistence of glycerol in the reaction medium even after 2 h reaction.
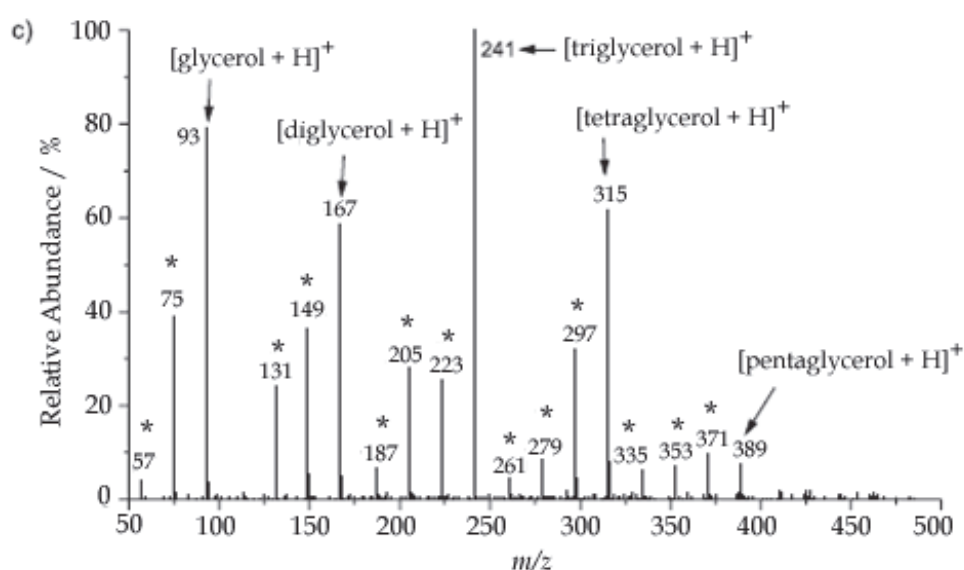

Fig. 3. ESI(+)-MS of the acid-catalyzed oligomerization of glycerol conducted in aqueous medium at 280 °C, 2 h. The ions marked with an asterisk (*) refer to dehydration products.

A remarkable presence of an ion of m/z 167 is also noticed in Figure 3. This corresponds to the protonated form of diglycerol, i.e. [(glycerol)$_2$ – H_2O], formed under these reaction conditions via the condensation of two molecules of glycerol and loss of water. This condensation can occur via the primary or secondary hydroxyl groups at the glycerol molecule to yield linear (α, α -diglycerol) and branched (α, β -diglycerol; β, β -diglycerol) isomers, as displayed in Scheme 3.
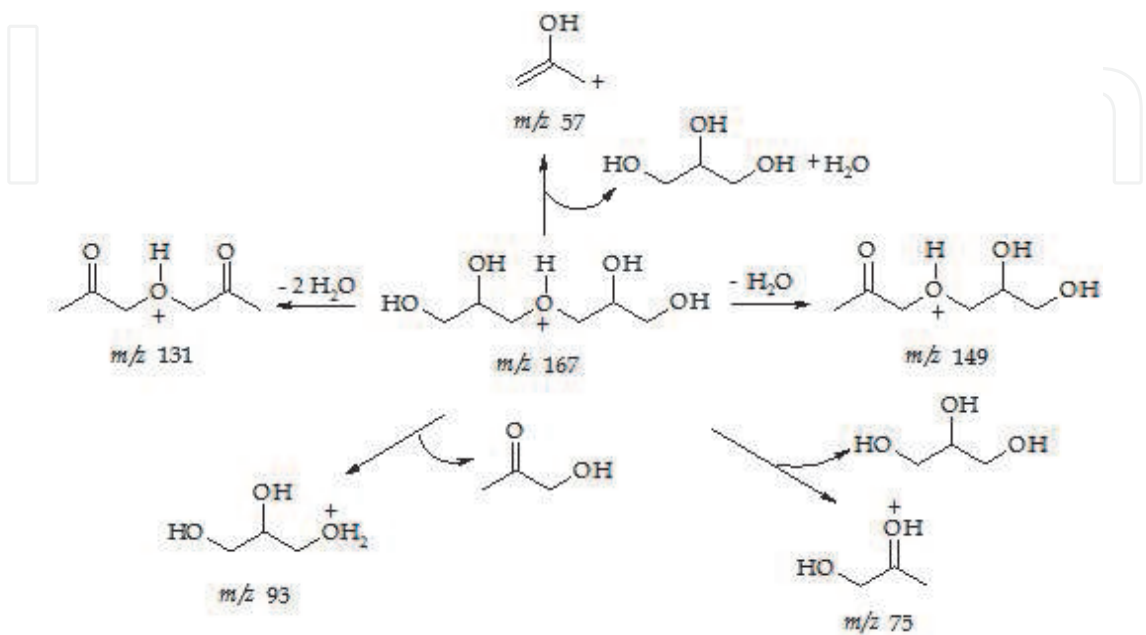

α,α–diglycerol   α,β–diglycerol   β,β–diglycerol
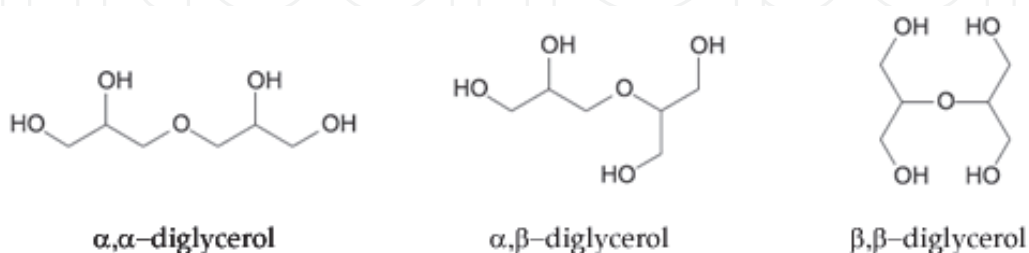
Scheme 3.

Across of the fragmentation of the ion of m/z 167 are yield mainly product ions from losses of one or two molecules of water (m/z 149 and 131, respectively) besides to other product

ions, such as [glycerol + H]$^+$ (m/z 93), [glycerol – H_2O + H]$^+$ (m/z 75), and [glycerol – 2 H_2O + H]$^+$ (m/z 57). To illustrate the formation of such fragments, the dissociation pathways for protonated α, α-diglycerol are shown in Scheme 4.

In the Table 2, are showed ions ascribed to be the protonated forms of products formed by successive dehydrations of di, tri, tetra and pentaglycerol.
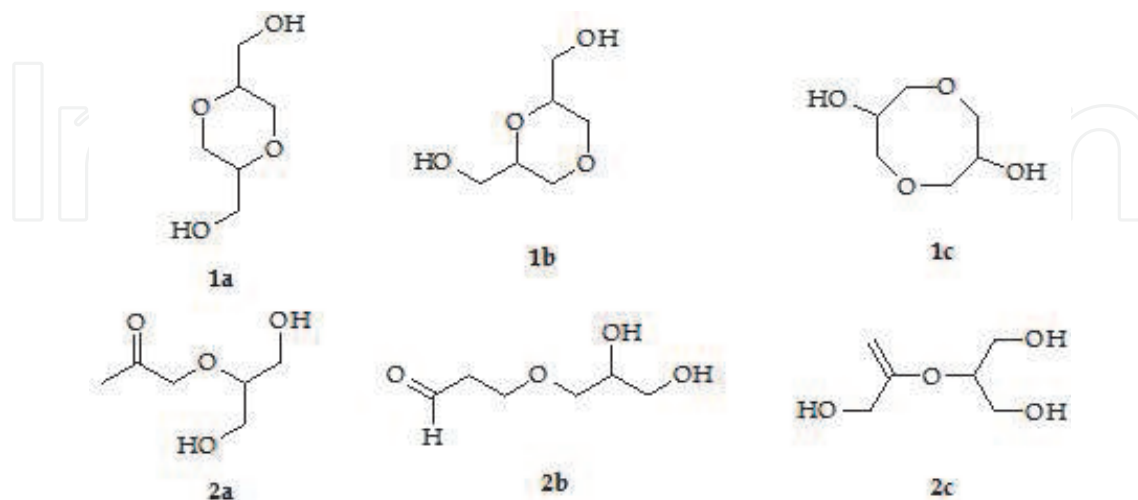

Scheme 4.

Primary Oligomers (m/z of the protonated forms)	Dehydration Products (m/z of the protonated forms)
diglycerol (167)	[diglycerol – H_2O] (149)
	[diglycerol – 2 H_2O] (131)
triglycerol (241)	[triglycerol – H_2O] (223)
	[triglycerol – 2 H_2O] (205)
	[triglycerol – 3 H_2O] (187)
tetraglycerol (315)	[tetraglycerol – H_2O] (297)
	[tetraglycerol – 2 H_2O] (279)
	[tetraglycerol – 3 H_2O] (261)
pentaglycerol (389)	[pentaglycerol –H_2O] (371)
	[pentaglycerol – 2 H_2O] (353)
	[pentaglycerol – 3 H_2O] (335)

Table 2. Primary products (diglycerol, triglycerol, tetraglycerol and pentaglycerol) and their dehydration products formed upon acid-catalyzed oligomerization of glycerol at 280°C. All these products were observed as their protonated forms in the ESI(+)-MS (Fig. 3).

These findings thus indicate that under acidic medium and heating, olygomers can easily lose one or two molecules of water to form a myriad of isomeric products. Scheme 5 shows, for instance, products possibly formed as a result of the mono-dehydration of diglycerol,

such as the cyclic species **1a-c** (their formation have been reported by Barrault and coworkers (Barrault et al., 2004, 2005) that submitted glycerol to similar reaction conditions than those employed herein) besides the acyclic carbonyl compounds **2a-b** and the alkene **2c**.

Scheme 5.

All the products resulting from the mono-dehydration of diglycerol, including the ones shown in Scheme 3 (**1a-c** and **2a-c**), possess the same chemical formula ($C_6H_{12}O_4$) and bear similar functional groups (especially hydroxyl substituents). Hence, these protonated molecules lose mainly water and other small molecules, being unfeasible the unambiguous characterization of a particular product based exclusively on your fragmentation profile.
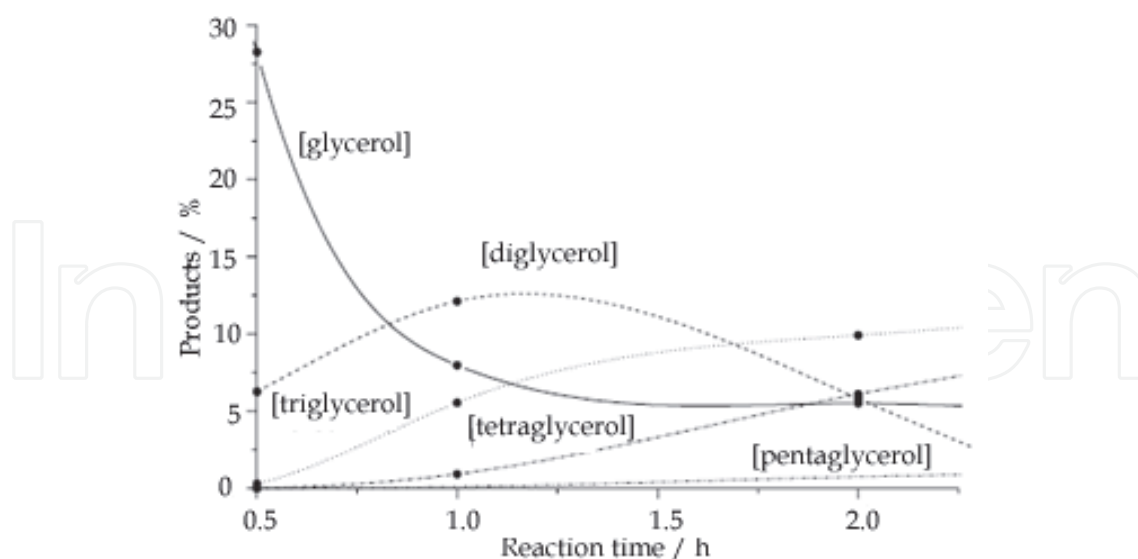

Fig. 4. Fractions of the ions of m/z 167, 241, 315, and 389 as a function of reaction time. Each fraction was calculated as the quotient ratio between the absolute intensity of one of such ions and the sum of the absolute intensities of the whole set of ions.

In Figure 4, the fraction of the ions of m/z 93, 167, 241, 315 and 389 (protonated glycerol, di, tri, tetra and pentaglycerol, respsctively), given as a quotient ratio between the absolute

intensity of one of such ions and the sum of the absolute intensities of the whole set of ions, are plotted against the reaction time. These results show that after 2 h reaction more than 90% of glycerol is consumed. Furthermore, during the first 30 min a relatively high concentration of diglycerol is formed. At longer reaction times, however, its concentration decreases whereas the amount of the heavier oligomers (tri, tetra and pentaglycerol) concomitantly increases. The result shows that glycerol is continuously converted into the heavier oligomeric compounds.

3. Polymerization of glycerol

In open system, the polycondensation (condensation of many molecules to create larger molecules - polymers) that the glycerol suffers in the presence of H_2SO_4 at 150 ° C, is a type of polymerization in which mingle the three stages: initiation, propagation and termination, which are characteristic of polymerization reactions (Mano & Mendes, 1999). The condensation polymerization, when employ monomers (molecules susceptible to undergo polymerization) with more than two functional groups (glycerol has three OH groups), tends to form crosslinked or branched polymers (structures with crosslinks between chains). In this case, the polymerization is complex because it is formed gel (polymer molecular weight too large), in the same setting of the sol (the fraction that remains soluble and can be extracted from the middle). As the sol will turn into gel, the mixture becomes increasingly viscous until elastic consistency, and finally rigid. In this transformation of glycerol in hard polymer, the catalyst concentration has an important role. An example of the participation of the catalyst in the polymerization of glycerol is shown in Figure 5, in which the viscosities of solution reaction is monitored by 60 minutes, with different concentrations of catalyst (0.5, 1, 3 and 5 mol%) .
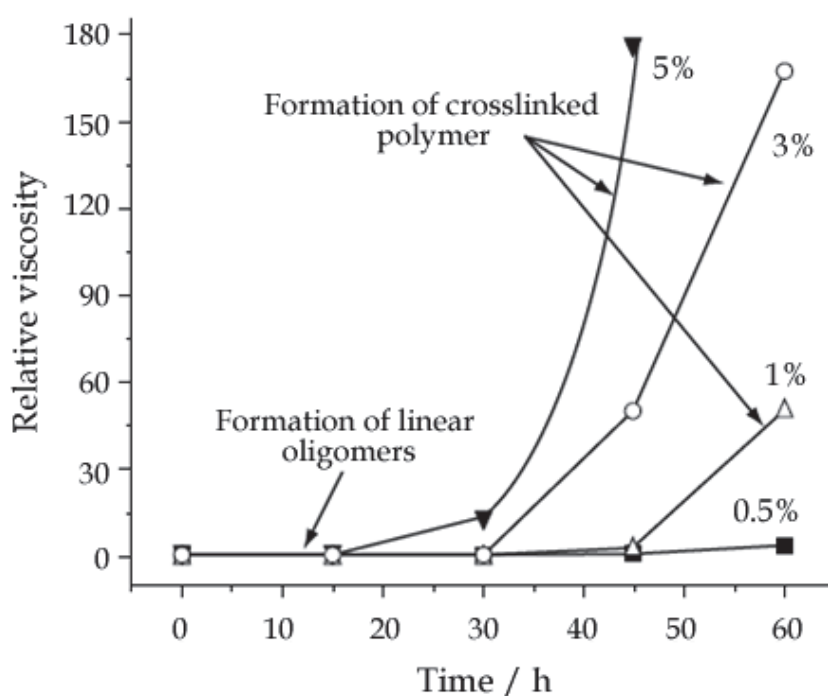

Fig. 5. Variation of relative viscosity of the solution for the polymerization of glycerol, with 0.5,1, 3 and 5 mol% H_2SO_4 (viscosity values are relative to the glycerol).

The curves shown in Figure 4 indicate a significant increase in viscosity of the solution, by varying the mole percentage of catalyst of 0.5-5%. However, this increase is gradual, as it rises the concentration of H_2SO_4. It is interesting to note that the system promoted by 5 mol% of catalyst is very active, because it took only 45 minutes to produce a solid polymer (unable to measure the viscosity, since the material solidified, Figure 5), whereas in other systems it took at least 120 minutes.
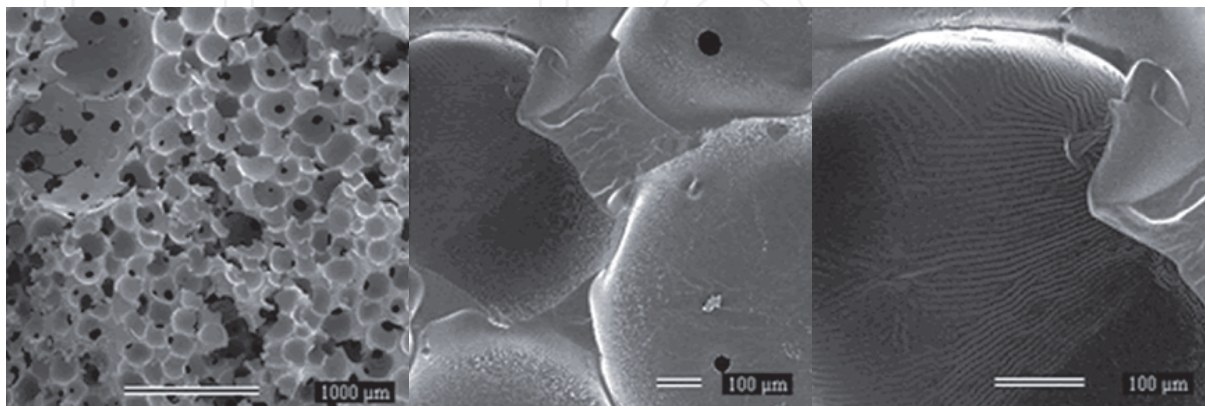

Fig. 6. Images of scanning electron microscopy (SEM) of polyglicerol with 5 mol% of H_2SO_4, after 45 min of reaction.

The system promoted by 0.5, 1 and 3 mol% H_2SO_4 show similar viscosity curves (Figure 4) but with varying slopes (the higher the catalyst concentration, greater the slope of the viscosity). With the increase of H_2SO_4 concentration (0.5-3%) is expected larger number of simultaneous condensation, therefore, the selectivity of the catalyst to reactive hydroxyl groups of glycerol decreases, leading to complex structures, which offer increased viscosity of the solution (in 60 minutes: system promoted by 0.5 mol% → relative viscosity of 4,1%; 1 mol% → relative viscosity of 51 e 3 mol% → relative viscosity of 169 times that of glycerol.

In the first 15 minutes of reaction, the viscosity of the medium practically does not change. It is believed that during this period, is occurring the formation of linear oligomers and products of dehydration. However, as the polymerization reaction progresses, the ethers formed formed become larger and more complex, mainly due to the formation of branches and some bonds between parallel chains of oligomers and/or polymers. And this is the increase size and complexity of structures of the ethers formed which increased the solution viscosity, reaching 169 times the viscosity of glycerol in just 60 minutes (system promoted by 3 mol% H_2SO_4), because the move of the structures is becoming increasingly difficult.

To confirm the nature (thermoplastic or thermosetting) polymeric material formed by polymerization of glycerol, are carried out two separate tests: heating in the direct flame of a Bunsen burner, to ensure that it is malleable (suffers fusion) or undergo thermal decomposition, and washing the polymer in solvents with different polarities (hexane, THF and ethanol). The results of these tests showed that all the polymers (0.5, 1, 3 and 5 mol% H_2SO_4) are thermosets, because not suffers fusion, but rather, thermal decomposition and did not dissolve in any solvent tested.

The polyglycerol may be used as a substitute for thermosetting phenolic resins, used in home utensils as well as controlled release fertilizers.

4. High surface area carbons

The thermosetting polymers have the property that thermally decomposes, producing carbon in quantities that can vary with the degree of crosslinking of the polymer. As previously discussed, the degree of crosslinking (polymerization in all directions, linking parallel chains of the polymer) is influenced by the concentration of the catalyst. Hence, a polymer obtained with 5 mol% H_2SO_4 is more reticulated and produces more carbon than a polymer with only 1 mol% catalyst.

The thermal decomposition of polyglycerol (obtained with 5 mol% H_2SO_4) yields 16% of carbon (relative to initial mass of polymer), which has extremely low surface area ($2\ m^2g^{-1}$). For environmental applications, are typically used carbonaceous materials with high surface area. Thus, it was necessary to increase the surface area of carbons derived from polyglycerol, performing physical activation (850°C) with a flow of CO_2 by 3, 5, 10, 15 and 18 h (Figure 7).
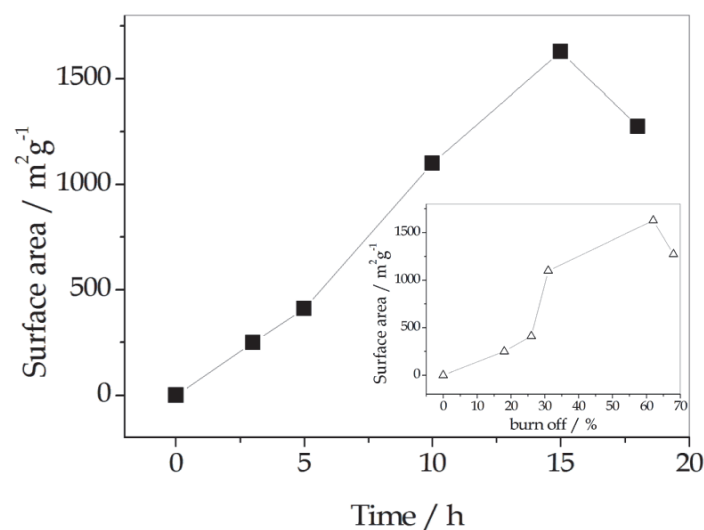

Fig. 7. Surface area of carbons derived from polyglycerol. Detail: surface area as a function of burn off.
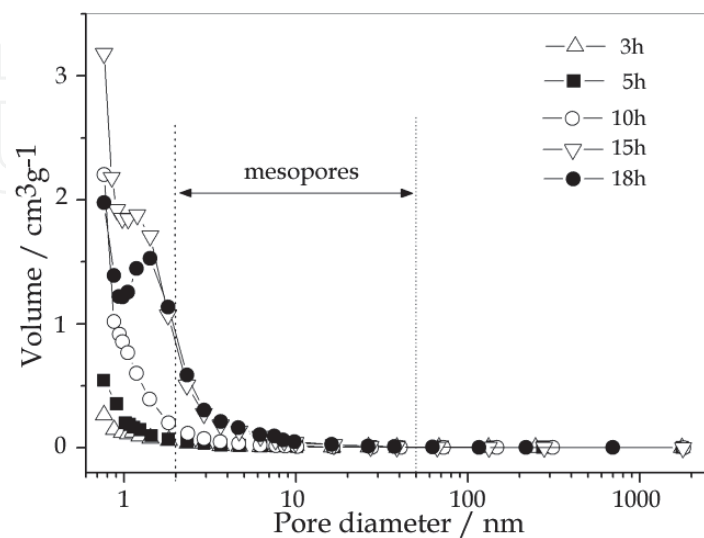

Fig. 8. Distribution of pores in activated carbonaceous material for 3, 5, 10, 15 and 18 h.

The Figure 7 shows a gradual increase in surface area of carbonaceous material up to 1830 m2 g-1, 15 h of activation. After that time, the surface area begins to decrease, reaching a value of 1275 m2 g-1 at 18 h. A similar behavior, but not linear is observed for the surface area as a function of burn off (mass loss of carbon during activation) (detail of Figure 7). The analysis of distribution of pores indicates that the materials are essentially microporous (internal diameter of less than 2 nm) (Figure 8).

As the surface area of carbonaceous material derived from polyglycerol increased with activation time by 15 hours, tests were made to adsorb organic contaminants (methylene blue) during the activation process (0, 3, 5, 10 and 15 h). The results of these tests are shown in Figure 9.

It is evident the relationship between the activation time of the carbonaceous material (surface area) and the adsorption of organic contaminant. During the activation process of the carbonaceous material, there was a gradual increase of its surface area, which is intimately related to the growth of its adsorption capacity. The sample of the material that was activated for 15 hours showed better results in the removal of organic contaminant (in 20 minutes, the removal of contaminant was 90%, while others samples took at least 60 minutes to obtain the same results).

5. Vermiculite composites/activated carbon

In order to facilitate the application of carbonaceous material in environmental problems, was produced a composite based in vermiculite clay and activated carbon, derived from the polyglycerol. This composite was designed, considering (i) some properties of the expanded vermiculite clay (Figure 10), which has low cost and ability to float in water, (ii) large adsorption capacity of Activated carbon derived from polyglycerol and (iii) facility removal of the composite in case of water application, requiring only one net.
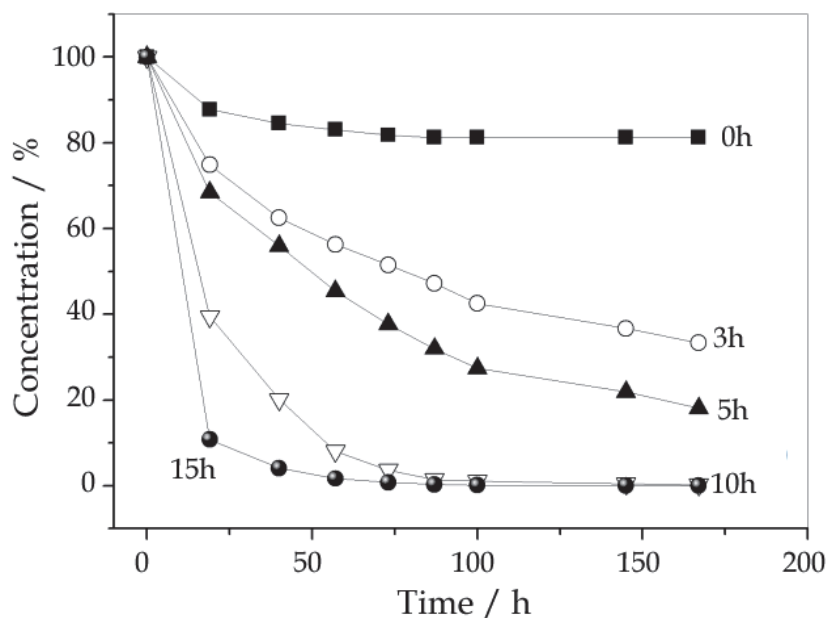

Fig. 9. Adsorption of methylene blue by carbonaceous material derived from the polyglycerol at different activation times (0, 3, 5, 10 and 15 h).

Fig. 10. (a) Sample vermiculite *in natura*; (b) Sample expanded vermiculite.

The composite vermiculite/carbon is prepared the same way that the pure carbon, except that the clay expanded vermiculite (EV) is added before the initial stage of polymerization of glycerol, which will occur on the surface of clay.

The best condition for prepare of the composite (GVE4), which has carbon content of 25% (compared to the mass of the composite) is 3 mol% H_2SO_4 and 580°C/3h and ratio (by mass) glycerol/VE = 4. This condition was obtained after tests with different reaction conditions. The images of scanning electron microscopy (SEM) for pure EV and composite (GVE4) showed significant differences in their surfaces (Figure 11).
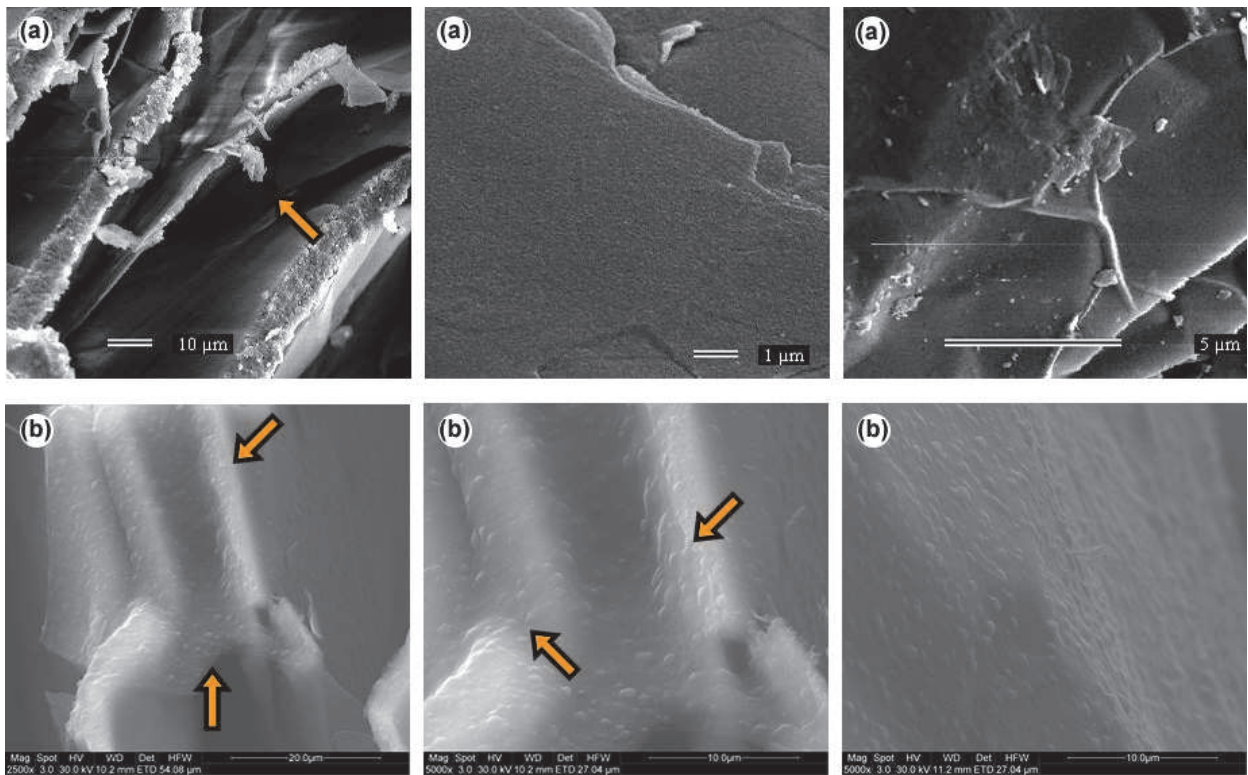
Fig. 11. SEM images of: (a) EV; (b) GVE4.

The SEM images for pure EV (Figure 11 (a)) show regular flat surfaces with an interlamellar space between 10-100 μm with some fragments attached to the edges (arrow). Figure 11 (b) shows large amounts of regular deposits on the EV layers with materials connecting some layers.

To obtain a good adsorbent material, the composite GVE4 was submitted to physical activation with CO_2 for periods of 0.5 (GVE4CA0.5); 1 (GVE4CA1), 2 (GVE4CA2) and 4 hours (GVE4CA4). Table 3 shows the surface area and burn off the composite GVE4, activated at different times.

To observe the data presented in Table 3 and Figure 12, perceives a linear increase in surface area, depending on the activation time, until the limit value of 835 m^2g^{-1} (2h of activation), when the value of surface area begins to decrease to 143 m^2g^{-1}, 4h of activation. A similar performance is observed for the surface area as a function of burn off (detail of Figure 12).

Sample	Burn off/ %	Surface Area / m^2g^{-1}
GVE4CA0	0	9
GVE4CA0.5	23,4	387
GVE4CA1	44,2	648
GVE4CA2	58,0	835
GVE4CA4	73,0	146

Table 3. Data for surface area GVE4CA0, GVE4CA0.5, GVE4CA1, GVE4CA2 and GVE4CA4, obtained by BET method.
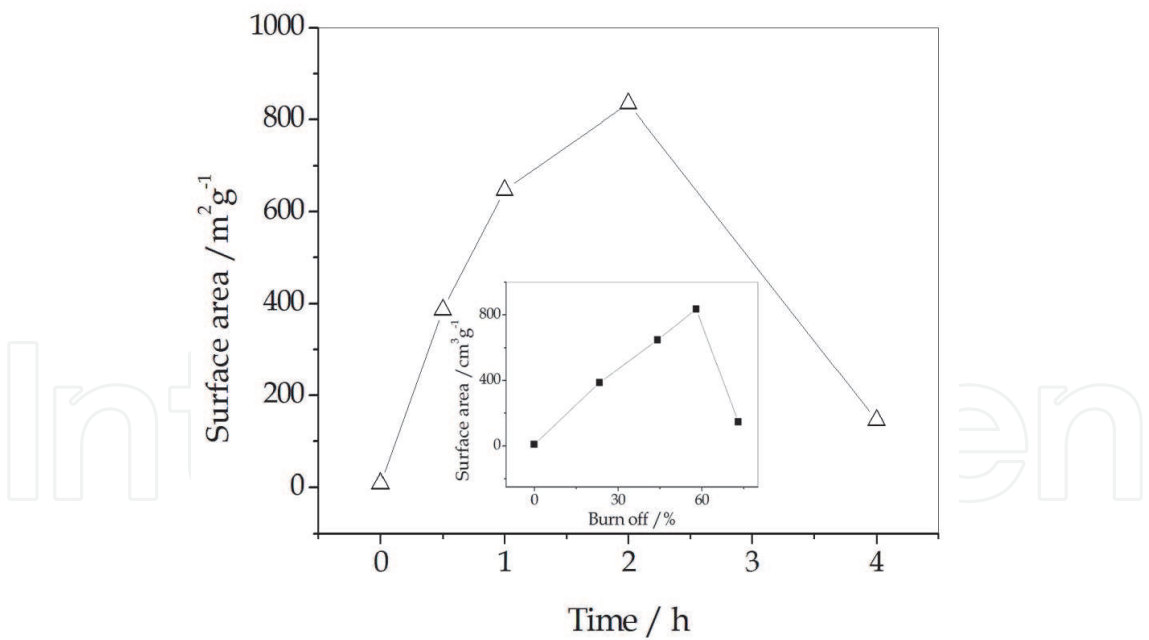

Fig. 12. Surface area of the activated composites. Detail: surface area as a function of burn off.

SEM images presented in Figure 13 show how the carbon deposits on the surface of the composites was changed during activation. After the first hour of activation, the amount of material deposits on the surface of the composite is significantly lower when compared to the composite without activation (Figure 11 (b)), because of the oxidizing action of CO2,

850°C/1h. SEM images show that 2 h of activation are sufficient to make large part of the surface of the EV is exposed, reducing the carbonaceous deposits, although the surface area is the largest obtained (835 m²g⁻¹). But it's after 4 h of activation that the composite loses most part of the carbon deposits and therefore reduces the surface area to only 146 m²g⁻¹.
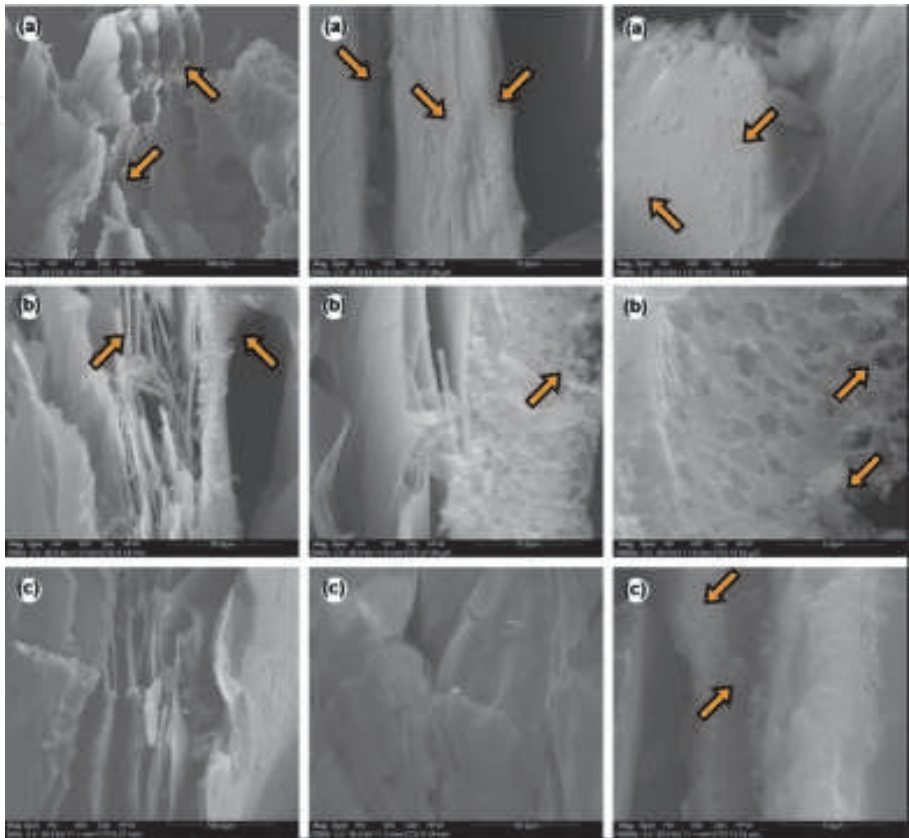

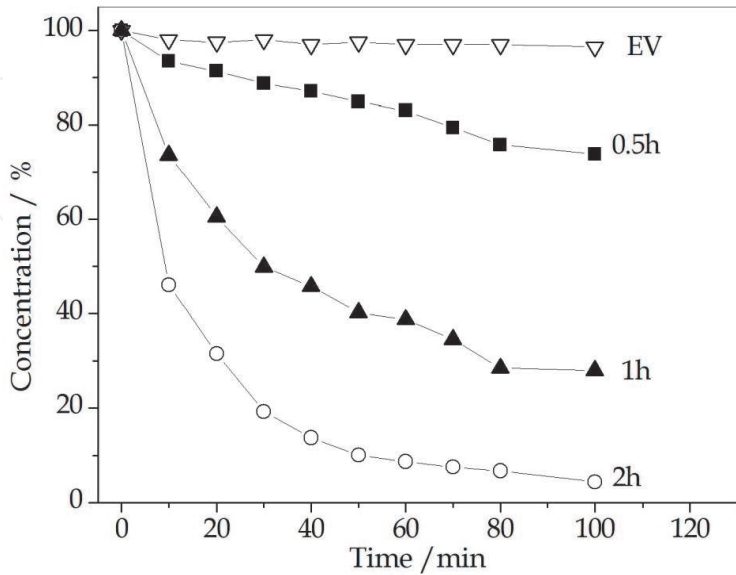Fig. 13. SEM images of GVE4, actived by: (a) 1h; (b) 2h and (c) 4h.

Fig. 14. Adsoption of methilene blue by EV and composites actived by 0.5, 1 and 2h.

After the activation process of the composite GVE4, samples of 0.5, 1 and 2h of activation were tested as adsorbents for organic contaminants (methylene blue) (figure 14).

It is possible notice that the EV practically no adsorbs or reacts with the contaminant during all the test period. The composite GVE4CA2 adsorbs 90% of the dye in only 60 minutes, tending to 100% until the end of the test (100 min). It is also notable, the action of the composite GVE4CA1, which absorbs more than 50% of the dye in the first 30 minutes of testing, tending to an equilibrium around 70% of contaminants adsorbed to the end of the test. Already the composite GVE4CA0.5, has unsatisfactory result, with only 20% of adsorbing dye after 100 minutes of testing.

6. Conclusions

Glycerol is a very versatile chemical species which can produce different materials to distinct applications. In this chapter, we discussed some possibilities for the glycerol that boost its use in the production of polymers and adsorbents for organic contaminants.

Study of oligomerization of glycerol, by ESI-MS, is an important step in understanding how the molecules of glycerol were initially organized to enable the formation of thermosetting polymers and, later, special carbonaceous materials.

The preparation of carbonaceous materials from glycerol, for environmental applications is a way to consume an important portion of glycerol introduced in the market from the production of biodiesel.

7. Acknowledgements

8. References

Aparício, C., Guignon, B., Rodriguez-Antón, L.M., Sanz, P.D. *J. Agric. Food Chem.*, 55, 7394-7398, 2007

Barrault, J., Clacens, Y., Pouilloux, Y. *Topics in Catalysis*, 27, 137-142, 2004.

Barrault, J., Jerome, F., Pouilloux, Y. *Lipid Technol.*, 17, 131-135, 2005.

Blytas, G.C., Frank, H. US Pat. US5401860, 1993 – atribuída à Shell Oil Company.

Bunyakiat, K., Makmee, S., Sawangkaew, R., Ngamprasertsith, S. *Energy Fuels*, 20, 812-817, 2006.

Catharino, R.R., Milagre, H.M.S., Saraiva, S.A., Garcia, C.M., Schuchardt, U., Eberlin, M.N., Augusti, R., Pereira, R.C.L., Guimarães, M.J.R., de Sá, G.F., Caxeiro, J.M.R., Souza, V. *Energy Fuels*, 21, 3698-3701, 2007.

Chiang, W. H. *Biodiesel – Sebrae*, 2007

Costa Neto, P.R., Rossi, L.F.S. *Quím. Nova*, 23 (4), 531-537, 2000.

Davis, W. R., Tomsho, J., Nikam, S., Cook, E. M., Somand, D., Peliska, J. A. *Biochemistry*, 39, 14279–14291, 2000.

Dorado, M.P., Ballesteros, E., Mittelbach, M., López, F.J. *Energy Fuels*, 18, 1457-1462, 2004.

Encinar, J.M., Gozález, J.F., Rodrigues, J.J., Tejedor, A. *Energy Fuels*, 18, 443-450, 2002.

Ferrari, R.A., Oliveira. V.S., Scabio, A. *Quim. Nova*, 28, 19-23, 2005.

Freedman, B., Pryde, E.H., Mounts, T.L. *J. Am. Oil Chem. Soc.*, 61, 1638, 1984.

Garcia, R., Besson, M., Gallezot, P. *Applied Catalysis A: Gen.*, 127, 165-176, 1995.

Georgogianni, K.G., Kontominas, M.G., Tegou, E., Avlonitis, D, Gergis, V. *Energy Fuels*, 21, 3023-3027, 2007.

Huber, G.W., Shabaker, J. W., Dumesic, J. A. *Science* 300(5628), 2075-2077, 2003.

Karinen, R.S., Krause, A.O.I. *Appl. Cat. A: Gen.*, 306, 128-133, 2006.

Kimura, H., *Appl.Catal. A: Gen.,* 105 (2), 147-158, 1993.

Klepácová, K., Miravec, D., Hájeková, E., Bajus, M. *Petroleum and Coal,* 45, 54-57, 2003.

Klepácová, K., Miravec, E., Bajus, M. *Chem. Pap.*, 60(3), 224,230, 2006.

Kocak, M.S., Ileri, E., Utlu, Z. *Energy Fuels*, 21, 3622-3626, 2007.

Krishna, C.R., Thomassen, K., Brown, C., Butcher, T.A., Anjom, M., Mahajant, D. *Ind. Eng. Chem. Res.*, 46, 8846-8851, 2007.

Lemke, D.W. US Patent US 6620904 (2003).

Mano, E. B.; Mendes, L. C.; *Introdução a Polímeros*, Blücher: São Paulo, 1999.

Medeiros, M.A., Oliveira, L.C.A., Gonçalves, M., Araújo, M.H., Lago, R.M. *Estudo por ESI-MS das reações de oligomerização catalítica do glicerol,* abstract XXI SICAT, Málaga, 2008.

Medeiros, M.A.; Oliveira, D.L.; Sansiviero, M.T.C.; Araujo, M.H. ; Lago, R.M. ; *J. Chem. Technol. Biotechnol*. 2010, 85, 447.

Noureddini, H., Medikonduru, V. *J. Am. Oil Chem. Soc.,* 74(4), 419-425, 1997.

Ott, L., Bicker, M., Vogel, H. *Green Chem.*, 8, 214-221, 2006.

Pachauri, N.; He, B. *Encontro Anual da American Society Biological and Agricultural Engineering*, 2006, *Paper Number: 066223.*

Pagliaro, M., Rossi, M. *The Future of Glycerol* – New uses of a versatile raw material, RSC Publishing: Cambridge, 2008.

Pinto, A.C., Guarieiro, L.L.N., Rezende, M.J.C., Ribeiro, N.M., Torres, E.A., Lopes, W.A., Pereira, P.A.P., Andrade, J.B. *J. Braz. Chem. Soc.*, 16, 1313-1330, 2005.

Puhan, S., Vedaraman, N., Rambrahaman, B.V., Nagarajan, G. 2005. Mahua (*Madhuca indica*) seed oil: a source of renewable energy in India. J Sci Ind Res 64:890−896.

Schuchardt, U., Sercheli, R., Vargas, R.M. *J.Braz. Chem. Soc.*, 9, 199-210, 1998.

Shenoy, M. A., Sabnis, A., D'Melo, D. J., *Pigment & Resin Technology*, 35, 326–333, 2006.

Stein, Y.S., Antal, M. J. J., Jones, M. *J. Anal. and Appl. Pyrolysis,* 4(4), 283-296, 1983.

Stern, R., Hillion, G. Eur. Pat. EP356317, 1990.

Talukder, M.M.R., Beatrice, K.L.M., Sond, O.P., Wu, S.P.J.C., Won, C.J., Chow, Y. *Energy Fuels*, 21, 2007.

Vicente, G., Martinez, M., Aracil, J. *Energy Fuels*, 20, 394-398, 2006.

Vicente, G., Martinez, M., Aracil, J., Estaban, A. *Ind. Eng. Chem. Res.*, 44, 5447-5454, 2005.

Werpy, T., Petersen, G. *Top Value Added Chemicals From biomass,* U.S. Department of Energy. Oak Ridge, Richland, 2004.

Wu, H., Fu, Q., Giles, R., Bartle, J. *Energy Fuels*, 21, 2007.

Zuhair, S.A., *Biotechnol. Prog.*, 21, 1442-1448, 2005.
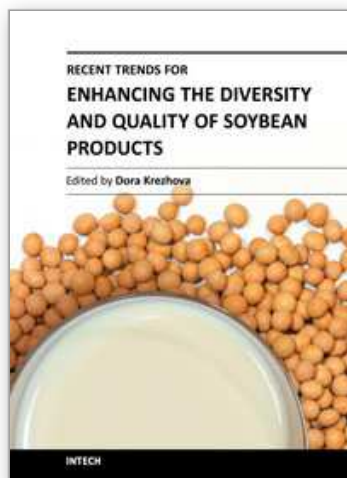
Recent Trends for Enhancing the Diversity and Quality of Soybean Products

Edited by Prof. Dora Krezhova

ISBN 978-953-307-533-4

Hard cover, 536 pages

Publisher InTech

Published online 28, October, 2011

Published in print edition October, 2011

This book presents new aspects and technologies for the applicability of soybean and soybean products in industry (human food, livestock feed, oil and biodiesel production, textile, medicine) as well as for future uses of some soybean sub-products. The contributions are organized in two sections considering soybean in aspects of food, nutrition and health and modern processing technologies. Each of the sections covers a wide range of topics. The authors are from many countries all over the world and this clearly shows that the soybean research and applications are of global significance.

INTECH

open science | open minds