



Glycerol oligomers production by etherification using calcined eggshell as catalyst

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ABSTRACT

The growing expansion of biodiesel industries led to an increasing formation of by-products as glycerol, which can be considered as building block molecule to high-added value products. The use of natural materials, formed by calcium carbonate, has recently become an interesting approach to the development of inexpensive and widely available basic catalysts. In this work, the use of eggshell waste as catalytic precursor was evaluated in the glycerol etherification reaction to obtain glycerol oligomers. Both raw and calcined eggshell were characterized by XRD, FTIR, N₂ adsorption-desorption at –196 °C, particle size analysis, SEM, CO₂-TPD and TG/DTG. For comparative purposes, commercial CaO was also tested. The solids were tested as-received and calcined in the reaction. Several parameters as catalyst loading, reaction temperature, reaction time and the leaching of calcium to the reaction medium were evaluated. The optimal reaction conditions for the calcined eggshell were catalyst loading of 2 wt.%, temperature of 220 °C and reaction time of 24 h, promoting 85% glycerol conversion and oligomers yielding of 43% (Di- and Triglycerol). The material tested shows leaching; however, taking account its low cost and good basic properties, calcined eggshell can be considered as promising catalyst for glycerol oligomerization.

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1. Introduction

In the context of the biodiesel market, glycerol plays a very important role, since about one kilogram of glycerin is obtained for every ten kilograms of biodiesel [1]. In Brazil, for example, glycerol production has already reached about 250 thousand tons/year. Far exceeding demand and the absorption capacity of the current markets mainly based on the consumption of glycerol for cosmetics and food products [2].

The presence of three OH– groups, attached to each of the three carbon atoms of glycerol, turns it in a potential candidate for a wide variety of chemical reactions. Factors such as low price and high availability makes glycerol an attractive starting material to obtain high-added value products. This fact leads glycerol to become a major chemical platform for future biorefineries [1,3].

Traditionally, glycerol plays a role in producing various types of polymers, such as polyglycerol esters, some of which are

commercially available. The esters, with great potential for use in the synthesis of polymeric materials, can be obtained by glycerol oligomers esterification with carboxylic acids. Treatment of glycerol with basic or acidic catalysts and temperatures of 200 °C can lead to a mixture of diglycerol, triglycerol and higher oligomers. In general, the primary hydroxyl group is more reactive functional group to obtain dimers as main product. Together these dimers, other products can be obtained by the condensation of condensation between primary-secondary hydroxyls or secondary-secondary hydroxyls leading to a variety of products [2,4,5]. Polyglycerols with a low degree of condensation (di- and/or triglycerol) are products with high interest to be used as starting material for a range of products from emulsifiers in the food and cosmetic industries to polymeric materials. These products are attractive due to their good biodegradability, high thermal stability and transparency [2,6].

Different strategies have been explored for the selection of suitable catalysts for glycerol oligomerization, both homogeneous and heterogeneous catalyst with basic or acidic properties. Richter et al. [6] have evaluated the glycerol etherification using CsHCO₃ by a homogeneous process in a batch reactor at 260 °C. Their studies

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have pointed that high selectivity of linear diglycerols was achieved at low glycerol conversion, after 8 h of reaction. Ruppert et al. [7] evaluated the glycerol etherification in presence of alkaline earth metal oxides. These data were compared with a homogenous process, using Na_2CO_3 as catalyst. The reactions were carried out at 220°C under air flow. The best selectivity values for di- and triglycerol (>90% at 60% conversion) were obtained over CaO, SrO, and BaO catalysts. Another series of experiments, different types of CaO materials were prepared. Stabilities studies performed pointed to increasing amounts of Ca from the catalyst leached to the liquid phase with reaction time.

Pouilloux et al. [8] have carried out glycerol etherification at 260°C using mesoporous silica (MCM-41 and SBA-15) impregnated with cesium species as active phase. Both materials present similar glycerol conversion (74% Cs/MCM-41 and 72% for Cs/SBA-15) and diglycerol selectivities of 81% and 79%, respectively. However, the catalyst supported on SBA-15 showed to be more stable and recyclable, maintaining the selectivity after several cycles. Ayoub et al. [9] have evaluated the performance of a zeolite Y catalyst modified with lithium. Reaction was carried out at 240°C for 8 h. The activity of Li-ZeY in terms of polyglycerol yield (71%) was higher than that of homogeneous LiOH under the same catalytic conditions and similar glycerol conversions were reached.

Another group of materials that has been widely studied as a catalyst for glycerol etherification is the mixed oxides derived from lamellar double hydroxides. Garcia-Sancho et al. [10] have investigated the use of MgAl mixed oxides as basic catalysts for the etherification of glycerol, also evaluating the routes of synthesis of precursors by coprecipitation and urea hydrolysis. The catalysts were active in the reactions at 220°C . The highest conversion (about 51%) was found for the catalyst prepared by coprecipitation using NaOH/ Na_2CO_3 as precipitating agent, full selectivity to diglycerols was only reached for low conversion values. Gholami et al. [11] have carried out glycerol etherification at 250°C using mixed metal oxide catalysts $\text{Ca}_{1.6}\text{Al}_{0.4}\text{La}_{0.6}\text{O}_3$ obtaining a glycerol conversion of 96% and diglycerol yield of 52%. Pérez-Barrado et al. [12] have studied the influence of acid-base properties of calcined lamellar double hydroxides of MgAl and CaAl in the catalytic etherification of glycerol at 235°C . Less acid catalysts led to lower conversion, 24% for MgAl and 40% for CaAl, respectively, but higher selectivity to di- and triglycerol that of highly acid ones.

The use of natural materials, formed by magnesium and calcium carbonate as a raw material has recently become an interesting approach to the development of inexpensive and widely available precursor to obtain basic catalysts. Among such materials, it is included eggshells wastes [13,14]. The eggshell is a rich source of carbonate based minerals, used as the basis for product development in the cosmetics industry, food supplements, bioceramics bases, fertilizers, bone and dental implants and as antitartar agent in toothpastes [15]. The high content of CaCO_3 that contains the eggshell leads to this material can be used as precursor to obtain heterogeneous catalysts [16].

In this study, eggshell waste was used as catalytic precursor for the glycerol etherification in the absence of solvent. It has been evaluated the influence of catalyst loading, temperature and reaction time. Finally, catalyst stability was also investigated taking account the leaching of the calcium species estimated from ICP analyses.

2. Experimental section

2.1. Catalysts preparation

The eggshell wastes were domestically collected. The catalyst preparation consisted on washing the material several times with warm water. Then it was dried in an oven at 100°C for 2 h, and

then named NE (natural eggshell). After crushing, the raw eggshell powder was calcined in muffle furnace at 900°C for 2 h to decompose the organic matter and carbonate species into oxide species. This sample was named CE. A scheme of the catalyst preparation is showed in Fig. 1.

2.2. Catalyst characterization

In order to study materials composition, X-ray fluorescence (X ZSXMini II Rigaku) was used. The crystalline structure of the materials before and after the thermal process was evaluated by X-ray diffraction (XRD) (D/max-b, Rigaku) and thereby assess whether there was modification of its phases after the thermal treatment.

FTIR was used to monitor functional group transformation during the thermal process (IR-PRESTIGE 21 SHIMADZU FTIR). Samples were analyzed in range of $400\text{--}4000\text{ cm}^{-1}$, with spectral resolution 8 cm^{-1} .

The textural analyses of catalysts were performed with ASAP 2420 equipment (Micrometrics). The nitrogen adsorption-desorption measurements were carried out at -196°C with a sample previously treated at 90°C for 2 h with N_2 .

Pore diameter and pore volume were determined from the adsorption branch of the isotherms by the Barrett–Joyner–Hallenda (BJH) method. The surface area was determined according to the Brunauer–Elmnett–Teller (BET) method (S_{BET}).

The particle size distribution of the materials was determined with a laser particle size analyzer (Malvern), using water as solvent.

The morphology of the samples was observed by scanning electron microscope (SEM), INSPECT S50 V (FEI Company).

The basicity of the catalysts was studied by temperature-programmed desorption of CO_2 , where approximately 100 mg of sample was pretreated in helium flow (60 ml min^{-1}) at 800°C for 30 min ($10^\circ\text{C min}^{-1}$). The reaction temperature was lowered to 100°C and pure CO_2 stream (60 ml min^{-1}) was subsequently introduced into the reactor for 30 min. The reaction of CO_2 -TPD was conducted between 100 and 800°C helium flow ($10^\circ\text{C min}^{-1}$ and 30 ml min^{-1}) and the amount of CO_2 evolved was analyzed using a quadrupole mass spectrometer (Balzer 02 GSB 200) equipped with a Faraday detector (0–200 U) that monitored the weight of CO_2 (44 U) during the experiment.

Thermogravimetric analysis/differential thermal analysis (TG/DTG) was carried out on a STA 449 F3–JUPITER/NETZSCH analyzer operating under the following conditions: flow of N_2 of 10 ml min^{-1} ; heating rate of $40^\circ\text{C min}^{-1}$; temperature range of $40\text{--}1000^\circ\text{C}$.

2.3. Catalytic studies

The glycerol reactions were carried out in batch reactor (Parr model), under nitrogen flow, using 100 g of glycerol. On preliminary tests it was investigated the effects of CE presence (without or 2 wt.%) and also a test with commercial CaO used directly as received. All tests were evaluated after 6 h reaction time at 245°C . Then, it was studied the effect of temperature (200, 220 and 245°C , after 24 h) and catalyst loading (0.5, 1, 2 wt.%, 24 h) with CE catalyst.

Kinetic reaction was accomplished and monitored at the times of 1, 2, 3, 4, 5, 6 and 24 h. Sampling occurred through a tube inserted into the middle of the reaction medium and a valve allowed the withdrawal of aliquots during the reaction without opening the reactor.

2.4. Products characterization

Product analysis was measured using gas chromatography with a flame ionization detector GC-FID (Agilent) after silylation with BSTFA [17], the adapted methodology consisted on dissolving an

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