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Batch reactor coupled with water permselective membrane: Study of glycerol etherification reaction with butanol

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HIGHLIGHTS

- Novel batch reactor coupled with water-permselective membrane.
- Use of solid acid catalysts.
- Shifting of reaction equilibrium by water removal with membrane.
- Production of ethers from glycerol and butanol.

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ABSTRACT

Etherification of glycerol with (*bio*)butanol was investigated in order to obtain glycerol ethers usable as oxygenated additives for diesel fuel. Experiments were carried out using a batch reactor assisted by a tubular water-permselective membrane. A-15 resin was used as solid acid catalyst at a reaction temperature ranging from 70 to 160 °C in view of maximizing the glycerol conversion. The water formed during the reaction was continuously removed by recirculation the gas phase through the membrane and this allowed to enhance reactions kinetics reaching both a total glycerol conversion and the formation of *poly*-substituted ethers not obtainable without the membrane. The alcohol dehydration and self-etherification of glycerol or alkyl alcohols give rise to the formation of several side products at moment hardly to identify.

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1. Introduction

In recent years, the development of biodiesel production in Europe was implemented by energy legislation which promotes the use of biofuels for transport purpose. Since glycerol represents about the 10 wt.% of byproduct of transesterification process, a huge increase in the glycerol stock has been generated, causing important effects in the glycerol market [1–4]. Hence, although the glycerol has many commercial applications in cosmetic and pharmaceutical industries, the development of new efficient ways of converting it to added-value products is necessary in order to ensure the eco-sustainability of the global process of biomass transportation [5].

The combustion of glycerol “as it is” would represent a desirable solution but, unfortunately, because of its detrimental physical and

chemical properties, raw glycerol is hardly usable in conventional energy production plants. Considering its highly functionalized nature, glycerol can readily be oxidized, reduced, halogenated, etherified and esterified to obtain alternative commodity chemicals. On this account, etherification of glycerol represents an important approach, as it will directly affords compounds that can be used as fuel additives, intermediates in the pharmaceutical industry, agrochemicals or non-ionic surfactants [1]. More specifically, when oxygenated glycerol derivatives, like *tert*-butyl glyceryl ethers (TBGEs), are blended with biodiesel, benefits in terms of environmental compliance and efficiency of diesel engines are gained: particularly, engine performance, like cold properties, are improved, whereas fuel viscosity and contaminant emissions of fumes and PM, hydrocarbons, CO and aldehydes emissions are reduced [6]. However, several catalytic and technological aspects must be still considered in order to develop an economically feasible process of glycerol conversion. Generally the isobutylene (IB), produced by steam cracking of high boiling petroleum fractions or mixture of saturate hydrocarbons, is used for the etherification reaction

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[7–9]. However, its use is conditioned by its high cost, its low solubility in glycerol and the formation of *di*-enes and *poly*-oligomers by oligomerization reaction that affect the alkylate yields and catalyst stability [7,9–10]. These compounds could lead to the formation of undesirable deposits during combustion in the diesel engine, therefore they must be removed from the ethers mixture before its use as additive. The use of a liquid reagent instead of gaseous IB could be favourable since it can act both as reactant and solvent allowing to overcome the technological problems arising from the need to operate with solvents to dissolve glycerol or the need to use pressure to keep IB in the liquid phase [11–15]. On this account, to date, the catalytic etherification of glycerol has been studied starting from *tert*-butyl alcohol (TBA), which is a *by*-product of polypropylene production. TGBEs are obtained in three consecutive reversible reactions which lead to the formation of *mono*-, *di*- and *tri*-substituted compounds. Nevertheless the use of different alcohols such as *bio*-ethanol or *bio*-butanol, which are renewable reactants [16], could represent a further interesting alternative route to valorise biodiesel derived glycerol thus leading to the production of a completely biomass-derived product. For example, *n*-butanol is a potential product from biomass fermentation on a large scale [17]. The *di*- and *tri*-*poly*-butyl substituted ethers (DBGs and TBG) could have a large potential for diesel and biodiesel formulation because of their solubility in such fuels. Likewise, the amphiphilic *mono*-butyl glyceryl ethers (MBG) could be used as green solvent for catalysis [18] or as precursor for surfactants synthesis [19]. In fact, the etherification of glycerol with *n*-butanol to the selective synthesis of MBG represents another active area of research of academic and industrial relevance. Anyhow, glycerol etherification reaction in presence of linear alcohols is not widely studied since it is thermodynamically much more difficult than in presence of *tert*-butyl alcohol. In addition, in presence of an alcohol, water is formed as *by*-product with consequent negative effects on catalytic activity and selectivity [13–15]. The water formed in each step in fact competes with reactants on the active site adsorption, preventing the total glycerol conversion and the formation of desired *poly*-substituted ethers [19].

In this work, the attention has been focused at exploring the feasibility of using *n*-butyl alcohol (BUT) as *O*-alkylating agent for glycerol oxygenated additives production. Moreover, a permselective membrane coupled with the batch reactor has been proposed in the attempt of overcoming equilibrium limits arising from the water formation and improving *poly*-ethers productivity.

2. Materials and methods

2.1. Catalysts

A15 (dry) acid ion-exchange catalyst from Rohm and Haas was used as catalyst. Catalyst is a macro reticular styrene–divinylbenzene resin with sulfonic acid functionality characterized by an ion-exchange capacity of 4.7 meqH⁺/g_{cat}, a porosity value of 0.40 cm³/g (PV) and SA_{BET} of 45 m²/g. It has been employed in spherical form with a particle size of 400 μm. Anhydrous glycerol and butanol supplied by Sigma Aldrich were used as reactants.

2.2. Catalyst testing

The etherification reaction was carried out in a 300 cm³ stainless steel “jacketed batch” reactor under a stirring frequency of 1200 min⁻¹. Pressure was autogenous and R_{But/Gly} maintained 4–8 mol/mol. The temperature was ranged from 70 to 160 °C and the catalyst/glycerol weight ratio from 7.5 to 10 wt.%. At the end of the reaction, the reactor was cooled to room temperature. The liquid phase was analysed *offline* by using a gas chromatograph HP6890N, provided with a capillary column HP Innowax (1, 30 m;

i.d., 0.53 mm; film thickness, 1.0 μm) and an automatic sampler to obtain data with an accuracy of ±1%, from an average of five independent measurements. Commercial solutions of *mono-tert*-butylethers compounds and *mono*-butylethers were used as standard references for GC analysis to obtain the corresponding response factors: the response factors of *di*- and *tri*-ethers were deduced. The liquid phase was analyzed also by GC–MS Agilent 5975C equipped with a capillary column DB-Waxter (1, 30 m; *i.d.*, 0.25 mm; film thickness, 0.25 μm).

Conversion of glycerol and product selectivity were calculated based on the following formulae:

$$\text{Glycerol conversion } X_{\text{gly}}(\%) = \left[\frac{\sum n_p}{\sum n_p + n_G} \right] \times 100$$

$$\text{Product selectivity } S_p(\%) = \left(\frac{n_p}{\sum n_p} \right) \times 100$$

$$\text{Yield to DBGs and TBG } Y_{D-T}(\%) = \left[\frac{(n_{1,3-DBG} + n_{1,2-DBG} + n_{TBG})}{n_{G,in}} \right] \times 100$$

where *P* indicates *mono*-butylethers, *di*-butylethers, *tri*-butylether, *mono-tert*-butylethers and “extra” compounds.

2.3. Batch reactor coupled with membrane

In order to continuously remove the water formed during the reaction, the gas phase was recirculated through a water permselective membrane (HybSi), supplied by Pervatech BV. The Scheme 1 shows the process flow diagram including the batch reactor coupled with the membrane. To avoid the gas phase condensation, the recirculation loop was maintained at the same reaction temperature and the permeate membrane side was kept under vacuum (approximately 10 mbar) to favour the water removal. The recirculation flow of gas stream was realized by using a gas-pump provided with a variable potentiometer. The Scheme 2 represents the PVM-035 module which contains the HybSi membrane whereas in Fig. 1 the photo of the experimental setup which includes the electrical module is shown.

The main information regarding the membrane characteristics as furnished by Pervatech BV are reported in Table 1: HybSi membrane has hydrophilic properties and it consists of a gamma alumina tubular membrane coated with organic polymer. It can operate at a maximum temperature and pressure of 150 °C and 10 bar respectively. The permeability to pure H₂O at 105 °C was 19.66 l/m² bar.

3. Results and discussion

The reaction pattern considered when *tert*-butylation of glycerol is carried out in presence of an *O*-alkylating agent, such as isobutylene (IB), or *tert*-butyl alcohol (TBA) [7–15] is shown in Scheme 3.

As previously said, in case TBA is used, a mole of water forms for each mole of ether. Potentially, also during the etherification of glycerol with butanol, water should form along with two *mono*-butylglycerol ethers (1-MBG and 2-MBG), two *di*-butylglycerol ethers (1,3-DBG and 1,2-DBG) and a *tri*-butylglycerol ether (TBG), according to the reactions reported in Scheme 4.

In Table 2, a comparison among results in the etherification reaction catalyzed by the acid resin A-15, obtained by employing IB or an alcohol (TBA and BUT) is reported. It can be observed that, at 70 °C, by employing an amount of catalyst of 7.5 wt.% in respect to the glycerol, after 6 h of reaction, with IB, the glycerol totally converts [9] whereas, by using TBA, the glycerol conversion does not reach the 80% [20]. In the latter case, even the cumulative selectivity towards *di*- and *tri-tert*-butylethers (S_{D-T}) is much lower (28.3%) than the value obtained with IB (91.7%) and the 1-*mono*-

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