



Ethers of glycerol and ethanol as bioadditives for biodiesel



Bianca P. Pinto^{a,c}, Jéssica T. de Lyra^a, Júlia A.C. Nascimento^b, Claudio J.A. Mota^{a,b,c,*}

^a Universidade Federal do Rio de Janeiro, Instituto de Química, Av Athos da Silveira Ramos 149, CT Bl A, Cidade Universitária, Rio de Janeiro 21941-909, Brazil

^b Universidade Federal do Rio de Janeiro, Escola de Química, Av Athos da Silveira Ramos 149, CT Bl E, Cidade Universitária, Rio de Janeiro 21941-909, Brazil

^c INCT Energia e Ambiente, UFRJ, 21941-909 Rio de Janeiro, Brazil

ARTICLE INFO

Article history:

Received 30 July 2015

Received in revised form 9 November 2015

Accepted 12 November 2015

Available online 25 November 2015

Keywords:

Biodiesel

Glycerol

Ethers

Oxygenated fuel additive

ABSTRACT

The production of biofuel has increased considerably over the last years. Glycerol, a by-product of biodiesel synthesis, accounts for about 10 wt% of the total mass balance in the transesterification process and has a limited range of applications. The acid-catalyzed etherification of glycerol with alcohols could be an attractive solution to address the excess of glycerol. This study is focused on the etherification of glycerol with ethanol over solid acid catalysts, such as zeolites, clays and sulfonic resins. All the catalysts produced mono, di and tri-glycerol-ethers that can be used as biodiesel fuel components. Higher conversion and selectivity to ethyl glyceryl ethers were obtained at 180 °C, ethanol/glycerol molar ratio of 3:1 and 4 h of reaction time, with Amberlyst-15 acid resin as catalyst. Under these reaction conditions, 96% of glycerol conversion and 80% selectivity to the ethyl ethers were observed. Laboratory tests using a blend containing 0.5–1.0 vol% of the ethyl glyceryl ethers in biodiesel showed reduction of pour and cloud points, indicating the potential of these ethers as bioadditives to fuels.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The first chemical industrial application of glycerol was developed by Alfred Nobel, who reported in 1860 the use of nitroglycerin to produce dynamite. Glycerol is a component of all natural fats and oils in the form of fatty acid esters, and an important intermediate in the metabolism of living organisms. It is the most important byproduct of the oleochemistry industry and it can also be produced through fermentation of sugars and chemical synthesis from propylene [1,2].

Glycerol is the main coproduct of biodiesel production by the transesterification of oils and fats with methanol [3]. For each 90 m³ of biodiesel produced from transesterification, approximately 10 m³ of glycerol are generated [4]. The world production of glycerol is rising significantly, leading to lower market prices, which makes glycerol a particularly attractive molecule for the synthesis of many products, such as surfactants [5,6], emulsifiers [7], solvents, humectants, lubricants and cosmetics [8]. A potential and promising application of glycerol derivatives is the automotive sector. Glycerol acetals [2,9–14] and glycerol ethers have been identified as valuable fuel additives.

Etherification of glycerol is one of the promising processes for the production of oxygenated fuel additives [15]. It can also be a good alternative for the glycerol produced from biodiesel [4,16]. Glycerol has three hydrophilic hydroxyl groups, that are responsible for its solubility in water and hygroscopic nature [17,18]. It also has a high viscosity and boiling point and it is miscible with polar substances and immiscible with hydrocarbons and other nonpolar substances. Therefore, it cannot be directly added to fuels, but must be transformed into other chemicals to reduce the polarity and viscosity.

The use of glycerol ethers can reduce the emissions, mainly particulate matters, carbon monoxide and carbonyl compounds in exhaust gases [19]. They can decrease the cloud point of diesel fuel when combined with biodiesel [20]. Appropriate ratio of glycerol ether, alcohol and gasoline could reduce the vapor pressure to the desired level and reduce fuel consumption [21]. The presence of glycerol ethers could help lowering the gel temperature of fuels, which leads to viscosity reduction. The presence of hydroxyl groups could also lower the NO_x emission [22].

A limitation on the use of fat acid methyl esters, the biodiesel, in many engines is the cloud point. For petroleum-derived diesel fuels, the cloud point is around –16 °C, but for biodiesel the cloud point can be around 0 °C. The addition of ethers, such as glycerol ethers, decrease the cloud point of diesel fuels [23].

A number of studies on the preparation of glycerol ethers, using different catalytic systems, have been reported. Klepáčová and

* Corresponding author at: Universidade Federal do Rio de Janeiro, Instituto de Química, Av Athos da Silveira Ramos 149, CT Bl A, Cidade Universitária, Rio de Janeiro 21941-909, Brazil.

E-mail address: cmota@iq.ufrj.br (C.J.A. Mota).

collaborators studied the etherification of glycerol with isobutene or tert-butanol over Amberlyst resins and zeolites H-Y and H-Beta [24]. They reported that zeolites H-Y and H-Beta provided lower selectivity than ion-exchange resins; in addition, water formation, in the case of using tert-butyl alcohol (TBA) as reagent, has an inhibition effect on glycerol etherification. The highest yield with Amberlyst-15 and Amberlyst-35 (88%) were obtained at 60 °C when isobutene was used as the etherification agent.

Karinen and Krause reported that the tert-butyl glyceryl ethers obtained have octane number suitable for gasoline component [25]. Mota and collaborators reported the etherification of glycerol with benzyl alcohol using heterogeneous acid catalysts [26]. Jérôme and collaborators studied the direct etherification of glycerol with alkyl alcohols, olefins and dibenzyl ethers catalyzed by acid-functionalized silica, allowing the first catalytic access to valuable monoalkyl glycerol ethers [1].

Pariente and collaborators reported different types of acidic heterogeneous catalysts, including sulfonic resins, zeolites and grafted silicas for the synthesis of mono-ethers of glycerol using ethanol. With the Amberlyst resin, monoethyl glyceryl ethers were selectively produced up to a glycerol conversion of 40% at a temperature of 160 °C. The best results were found at 200 °C, using grafted silica (68% glycerol conversion with a 75% selectivity to mono and 25% selectivity to di-ethyl ether). Silicon-rich zeolites (Si/Al = 25) also presented good activities, with glycerol conversion of 57% and selectivity of 75% and 25% to mono and di-ethyl glyceryl ethers, respectively [27].

Yuan and collaborators have reported the etherification of glycerol with bioethanol over tungstophosphoric acid (HPW) to synthesize glycerol ethers. Bulk HPW and SiO₂-supported HPW catalysts exhibited the highest activity among the tested catalysts, with 97% of glycerol conversion at 160 °C, ethanol/glycerol molar ratio of 6:1 and 20 h. The selectivity to mono ether (62%) decreased with the increased conversion of glycerol, whereas the selectivity toward di (28%) and tri ether (10%) increased [28].

Frusteri and collaborators investigated the heterogeneous catalytic etherification of glycerol with tert-butyl alcohol in the presence of solid acid catalysts. An increase in reaction temperature favors the formation of di-substituted ethers. Steric hindrance and water prevent the formation of the tri-substituted ether. Water removal was necessary to achieve higher yields of the ethers [29]. The etherification with tertiary alcohols occurs through a S_N1-type reaction, involving the formation of a tertiary carbocation. On the other hand, for ethanol and other primary alcohols, the mechanism is typically a S_N2 reaction, involving the nucleophilic attack of glycerol, to the protonated ethanol, with concomitant loss of water.

Melero and collaborators studied the best conditions to maximize glycerol conversion. At 200 °C, ethanol/glycerol molar ratio of 15:1 and catalyst loading of 19 wt%, they obtained 74% of glycerol conversion and 42% yield to ethyl ethers after 4 h of reaction [30].

Frusteri and collaborators produced ethers of glycerol through the reaction with isobutene over spherical silica supported Hyflon as catalysts. They obtained yields to di and tri-ethers higher than that obtained with Amberlyst-15 commercial catalyst. Engine tests, using a blend containing 10 vol% of the glycerol ether mixture, confirmed the positive role as additives to reduce emissions of particulates and unburned hydrocarbons, with significant improvement of diesel combustion efficiency [31].

The purpose of this work is to study the production of ethyl glyceryl ethers from the acid-catalyzed reaction of glycerol with ethanol, to obtain bioadditives with high oxygen content (Scheme 1) that could improve fuel properties. Ethanol is a renewable compound, produced mainly from the fermentation of sugars and commonly used as bioadditive in gasoline. The combination of

glycerol and ethanol to form ethers may lead to a fuel additive 100% derived from renewable sources. This work also aims to study these ethers as bioadditives to improve fuel properties, by testing blends of the ethers with biodiesel.

2. Material and methods

Glycerol and ethanol were analytical grades. The K-10 Montmorillonite and Amberlyst-15 acid resin were obtained from Sigma-Aldrich. Zeolites H-ZSM-5 and H-Beta were purchased from Zeolyst. Tallow biodiesel was kindly provided by Instituto Virtual Internacional de Mudanças Globais (Ivig), Coppe UFRJ. The soybean biodiesel was prepared in the laboratory by traditional transesterification with sodium hydroxide and methanol.

The acid strength distribution of the catalysts was measured by temperature-programmed desorption (TPD) of *n*-butylamine, using a thermo gravimetric equipment. About 25 mg of the catalyst were initially pretreated in a straight glass reactor, under flowing helium (40 mL min⁻¹), at the temperatures shown in Table 1. The temperature was then set to 150 °C and the flow of helium (10 mL min⁻¹) was driven to a saturator containing *n*-butylamine at room temperature. The flow of the amine was passed over the catalyst for 10 min. Then, the excess of the amine was desorbed by passing a flow of helium (20 mL min⁻¹) over the catalyst bed for an additional 20 min period. The solid was then carefully placed in the thermo gravimetric equipment (Shimadzu TGA-51) and the TPD profile was taken following the weight loss up to 450 °C, under flowing nitrogen gas.

Surface area was determined by nitrogen adsorption/desorption isotherms using a Micromeritics Tristar 2000 equipment. Before analysis, all the samples were outgassed at 300 °C under vacuum for 24 h. The areas were calculated according to the BET equation.

The catalysts were pre-treated for 30 min (Table 1), just previously to the reaction. The number of acid sites was kept constant (1.5 mmol), varying the amount of catalyst loaded. After cooling to room temperature 10 g (109 mmol) of glycerol and the appropriate molar amount of ethanol were introduced in a 100 mL Parr reactor loaded with the catalyst. The system was previously purged with N₂ to remove the air, and the experiments were performed under inert atmosphere, with glycerol:ethanol molar ratio varying from 1:3 to 1:6. The reaction was conducted at 180 °C and kept at this temperature for 4 or 8 h under autogenic pressure (5–30 bar). At the end, the system was cooled down to room temperature, the catalyst separated by filtration and the liquid phase analyzed by gas chromatograph (Agilent 6850) coupled to a mass quadrupole spectrometer (Agilent 5973), operating in electron impact ionization (70 eV), using a methyl-phenyl-silicone column. Analyses were carried out with the temperature program increasing from 80 to 220 °C (with a slope of 10 °C/min). Blank experiments, without adding catalyst, were also carried out for comparison purposes.

The glycerol ethers were also produced at higher scale, using a 2 L autoclave. No separation of the MEG, DEG and TEG was attempted in this case.

The glycerol ether mixtures were blended with soybean and palm biodiesel in 0.5 and 1 vol%. The mixtures were subjected to tests of cloud point (ASTM D 2500) [32] and pour point (ASTM D 97) [33].

3. Results and discussion

The main physical and chemical properties of the catalysts are reported in Table 1. The areas varies from 54 to 564 m² g⁻¹. Zeolite Beta showed the highest BET area, but its acidity was 1.4 mmol g⁻¹. On the other hand, the Amberlyst-15 acid resin catalyst showed

Download English Version:

<https://daneshyari.com/en/article/205474>

Download Persian Version:

<https://daneshyari.com/article/205474>

[Daneshyari.com](https://daneshyari.com)