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Research article

Study of glycerol etherification with ethanol in fixed bed reactor under high pressure

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ABSTRACT

The aim of this work was to optimize the reaction parameters for the glycerol etherification with ethanol in a fixed bed pressurized reactor using Amberlyst 15 as a catalyst. A three factor central composite design was proposed to study the effect of reaction temperature (180–250 °C), ethanol/glycerol molar ratio (4–20/1) and amount of catalyst (0–0.80 g) over the glycerol conversion and yield of ethers. Analysis of variance (ANOVA) was used to evaluate the significance of the independent variables and their interactions. The correlations between reaction parameters and response variables were made by regression models. Among the variables screened, the reaction temperature and catalyst amount were statistically significant in glycerol conversion and ethers yield. The optimum levels of the parameters on yield of ethers were: temperature (238 °C), ethanol/glycerol molar ratio (16/1) and catalyst amount (0.61 g). Experimental verification of the predicted optimum conditions for yield of ethers gave the unprecedented response of 56%. These results indicated that the models were capable in describing the actual experimental data. Therefore, a process using a fixed bed high-pressure reactor has the potential to be used in glycerol transformation into ethers.

1. Introduction

Biodiesel is an excellent alternative to fossil fuels because it can be produced from renewable sources, such as soybean oil, and helps to reduce emissions of toxic gases. Moreover, biodiesel has similar chemical properties of diesel fuel, such as lubricity, high flash point and viscosity [1,2]. The transesterification of vegetable oils is the predominantly used route to produce this biofuel but it forms glycerol as the main byproduct, which express approximately 10% of the total synthesized biodiesel [3,4]. To find a destination for this large glycerol production represents a huge challenge in the biodiesel process economy.

The physical and chemical characteristics of glycerol make it a valuable material which offers great opportunities for chemical conversion into high value-added products [5]. Among the various transformation reactions that glycerol may suffer, as acetalization, dehydration, oxidation and esterification, those capable of producing additives to fuels, such as etherification, have been of interest to researchers [6,7]. These additives can act as cold flow improvers, viscosity reducers in biodiesel and also as octane impellers for gasoline [8,9]. Moreover, glyceryl ethers and their derivatives are interesting molecules in many applications, such as cosmetics, polymers, food and pharmaceutical industries [10,11].

The glycerol etherification can occur with or without reagents in the reaction medium and this characteristic results in the formation of chemically different products. The production of polyglycerols occurs when glycerol combines with one or more identical molecules and can generate linear, cyclic or branched diglycerols, or even larger molecules (triglycerols, tetraglycerols, etc.) [11,12]. The transformation of glycerol into ethers can also occur by reaction with alkenes or with primary or secondary alcohols in the presence of acid catalysts [13]. The etherification reaction of glycerol with ethanol has been poorly reported in the current literature, although ethanol is a renewable compound easily produced by the fermentation of biomass and commonly used as bioadditive in gasoline.

Melero et al. [14] analyzed the performance of a mesostructure silica to produce ethyl ethers of glycerol with ethanol. At 200 °C and 4 h of reaction conditions, glycerol conversion and yield to ethers reached

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maximum values of 74% and 42%, respectively, but with a significant amount of byproducts. Pinto et al. [15] studied the etherification of glycerol with ethanol in a batch reactor over zeolites, clays and sulfonic resins as catalysts. Among the samples tested, Amberlyst 15 presented the highest conversion (96%) and selectivity to ethyl glyceryl ethers (80%) obtained at 180 °C, ethanol/glycerol molar ratio of 3:1 and 4 h of reaction time. Yuan and coworkers [16] observed that several acid solids, such as H-ZSM5, H-β, tungstophosphoric acid (HPW) and H_2SO_4 are capable to produce ethers from glycerol and HPW exhibited the highest activity, with a 97.1% of glycerol conversion at 160 °C and 20 h. Pariente et al. [1] studied the etherification of glycerol with ethanol in batch reactor under mild reaction conditions (pressure between 0.6 and 2.1 MPa), showing a positive influence of pressure and temperature variation in terms of product selectivity. The best compromise has been found using beta zeolite (Si/Al 25 and 12.5) and Amberlyst catalyst family. Our group has investigated glycerol etherification with ethanol in continuous reactor and the optimum values for glycerol conversion and yield to ethers was 91% and 13%, respectively, even with a residence time about 60 s in both cases [17].

In a reaction performed under pressure, the mass transfer problems among the catalyst and the reactants are minimized and there is an increase in contact between the reactants. Thereby, in this work, a fixed bed reactor was selected to evaluate glycerol etherification with ethanol under high pressure. The catalytic performances of Amberlyst 15 and beta zeolite were benchmarked and the best result in terms of yield to ethers was selected to a deeper investigation. A design of experiments was chosen to assess the effects of temperature, ethanol/glycerol molar ratio and catalyst amount and their interactions on the glycerol conversion and yield of ethers. In addition, the response variables were optimized using a canonical analysis.

2. Methods

2.1. Catalysts and chemicals

The solid acid catalysts used in this work were the macroreticular sulfonic resins Amberlyst 15 supplied by Dow Chemical Company, dried at 110 °C for 1 h, and beta zeolite synthesized in laboratory. The methodology followed to prepare beta zeolite sample (Si/Al = 12.5) was described in detail previously in U.S. Patent of Wadlinger and collaborators [18]. This catalyst was prepared from a solution composed of $25SiO_2$:$1.0Al_2O_3$:$1.5Na_2O$:4.5TEAOH:$240H_2O$. Sodium aluminate was added to a solution composed of TEAOH and deionized water and the mixture was stirred for 10 min. After the addition of colloidal silica (Ludox HS40, Sigma Aldrich) and subsequent agitation for 30 min the resulting suspension was kept for 10 days at 150 °C. Afterward, the obtained solid was recovered by filtration, dried at 100 °C for one night and calcined at 540 °C for 8 h. Finally, the ion exchange was carried out using NH_4Cl followed by calcination at 550 °C for 8 h.

The reactants were glycerol and ethanol (purity 99.5%) provided by Synth. Analytical standards for GC analysis were supplied by Sigma-Aldrich.

2.2. Catalyst characterization

All physicochemical properties of Amberlyst 15 were provided by the supplier. Acid sites were determined by Temperature-programmed desorption (TPD) of NH_3 using a Quantachrome Chembet 3000 instrument. The catalyst sample was initially activated at 300 °C for 1 h under flowing nitrogen gas (20 mL/min) to clean the surface of the catalyst. After this treatment, the sample was exposed to a NH_3 flow at 100 °C for 30 min. The sample was then flushed with N_2 for 2 h to drive off physisorbed NH_3. Finally, the TPD of the catalyst was then carried out in N_2 (20 mL/min), in a temperature range of 100–700 °C and with a ramp of 10 °C/min.

Table 1
Studied range of each factor in actual and coded form.

	Levels				
	−α	−1	0	+1	+α
(X_T) Temperature (°C)	180	190	215	240	250
($X_{M.R.}$) Molar ratio	4:1	6:1	12:1	18:1	20:1
($X_{C.A.}$) Catalyst amount (g)	0	0.12	0.40	0.68	0.80

Table 2
Physicochemical properties for the catalysts.

Catalyst	Acid capacity (mmol/g)	Surface area (m^2/g)	Pore volume (cm^3/g)		Pore size (Å)	
			Meso	Micro	Meso	Micro
Amberlyst 15	4.70[a]	53[a]	0.40[a]	–	300[a]	–
Beta zeolite	0.29	434	0.05	0.15	15	6

[a] Provided by the supplier.

Surface area and pore volume were determined by the nitrogen adsorption/desorption isotherms at −196.15 °C performed in a Quantachrome Nova 1200 instrument. The isotherms were elaborated according to the Brunauer−Emmett−Teller (BET) method. Pore size distributions were calculated using the t-method and the Barrett−Joyner−Halenda (BJH) used for micropores and mesopores, respectively.

Structural characterization was completed by powder X-ray diffraction patterns of the beta zeolite sample which were obtained with a Rigaku Miniflex II Powder X-ray diffractometer using nickel-filtered Cu Kα radiation. The patterns were recorded with an account time of 3 s/step and 2θ range of 2° to 50°.

2.3. Reaction procedure

The experiments were carried out in a continuous pressurized flow reactor system whose details were given in our recently published work [17]. The etherification reactions were carried out in a 316-stainless steel tubular reactor (ID: 6.8 mm, OD = 3/8″ and length: 30 cm) placed in a furnace. The reactor was loaded with catalyst (0 up to 0.8 g) with glass wool as bed supporter. The values of residence time (W/F) in this study were between 0 and 27 g of catalyst·min/g of glycerol. The feed was a mixture of ethanol and glycerol at a specific molar ratio (varying from 4:1 to 20:1). In a typical run, the feed containing the reagents were well mixed and pumped into the reactor with a high-pressure liquid pump (Lab Alliance series III) adjusted to a flow rate of 0.40 mL/min. After the system was filled, the back-pressure regulator was closed to the desired position (in this case until the pressure gauge reached 8.5 MPa). The heating ramp used to reach the desired reaction temperature was 10 °C/min. When temperatures were stabilized under the desired conditions and after waiting at least twice the time required to fill the entire reaction system, 10 mL of sample were collected and subjected to analysis.

Amberlyst 15 and beta zeolite were submitted to tests in the temperature range of 150–250 °C at an ethanol/glycerol molar ratio of 10:1 and catalyst amount of 0.4 g to identify which catalyst was most effective in converting glycerol to ethers. To obtain lower and upper limits, preliminary experiments were performed. The catalyst that presented the best performance was well studied using a design of experiments methodology and a canonical analysis.

2.4. Analysis

Reaction products and remaining glycerol, as well as glycerol present in the starting substrate, were analyzed and quantified on a