Synthesis of oxygenated compounds for fuel formulation: Etherification of glycerol with ethanol over sulfonic modified catalysts

Juan A. Melero[a,*], Gemma Vicente[b], Marta Paniagua[a], Gabriel Morales[a], Patricia Muñoz

[a]Department of Chemical and Environmental Technology, ESCET, Universidad Rey Juan Carlos, C/ Tulipán s/n, E-28933 Móstoles, Madrid, Spain.

[b]Department of Chemical and Energy Technology, ESCET, Universidad Rey Juan Carlos, C/ Tulipán s/n, E-28933 Móstoles, Madrid, Spain.

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*Corresponding author:

Juan A. Melero, Department of Chemical and Environmental Technology, ESCET, Universidad Rey Juan Carlos. C/ Tulipán s/n. E-28933 Móstoles, Madrid, Spain.

Tel.: [34] 91 488 73 99

Fax: [34] 91 488 70 68

e-mail: **juan.melero@urjc.es**

ABSTRACT

The present study is focused on the etherification of glycerol with anhydrous ethanol over arenesulfonic acid-functionalized mesostructured silicas to produce ethyl ethers of glycerol that can be used as gasoline or diesel fuel components. Within the studied range, the best conditions to maximize glycerol conversion and yield towards ethyl-glycerols are: T = 200ºC, ethanol/glycerol molar ratio = 15/1, and catalyst loading = 19 wt.%. Under these reaction conditions, 74% glycerol conversion and 42% yield to ethyl ethers have been achieved after 4 h of reaction but with a significant presence of glycerol by-products. In contrast, lower reaction temperatures (T=160ºC) and moderate catalyst loading (14 wt.%) in presence of a high ethanol concentration (ethanol/glycerol molar ratio = 15/1) are necessary to avoid the formation of glycerol by-products and maximize ethyl-glycerols selectivity. Interestingly, a close catalytic performance to that achieved using high purity glycerol has been obtained with low-grade water-containing glycerol.

Keywords: oxygenated compounds, glycerol, sulfonic, mesoporous silica.

1. Introduction

In recent years, the development of biodiesel production has generated a huge increase in the glycerol stock since its production is equivalent to 10 wt.% of the total produced biodiesel. Moreover, the new energy legislation implemented in Europe promotes the use of biofuels for transport purposes. Thus, traffic fuels should contain 10% of energy content produced from renewable sources by the end of 2020 [Directive 2009/28/EC]. In this context, the production of biodiesel in the European Union is expected to grow further in the next years. In fact, according to the European Biodiesel Board, biodiesel production in Europe increased by 16.6% in 2009 compared to 2008, reaching the amount of 9 Mt. This implies a side production of about 900.000 t of glycerol. This situation has produced a large surplus of glycerol causing important effects in the glycerol market. For instance, the price of refined glycerol was 1.35-1.75 $/kg in 2005, but with the onset of new glycerol from biodiesel production the prices dipped as low as 0.55 $/kg in 2007 [Knothe et al, 2010]. Hence, it is necessary to give an outlet for the increasing glycerol stock in order to ensure the economic viability of the biodiesel activity.

In the production of biodiesel, glycerol is obtained as crude glycerol after a liquid-liquid decanting or centrifugation step followed by a neutralization of the homogeneous catalyst, washing step and a distillation or flash separation in order to recover unreacted methanol for recycling purposes. This crude glycerol contains salts resulting from the neutralization step of the homogeneous catalyst (e.g., sodium methoxide), ash from caustic catalyst (e.g., sodium hydroxide) and water from the washing step. The process of glycerol refining separates glycerol from the different impurities by vacuum distillation and solid-liquid separation in order to produce a pharmaceutical-grade

glycerol (>99%). Also, an intermediate grade, with only water as impurity, may be produced (technical glycerol).

An important research is currently being performed in order to find new applications for this expected low-cost feedstock, converting glycerol to commodity chemicals with larger markets than traditional ones capable of absorbing a great part of the newly produced glycerol. Some of these strategies include selective reduction – hydrogenolysis to propylene glycol, dehydroxylation to 1,3-propanediol–, halogenation to obtain epichlorohydrin, dehydration to produce acrolein, acrylic acid or 3-hydroxypropionaldehyde, and selective oxidation [Pagliaro and Rossi, 2008]. Another appealing alternative is to transform glycerol into oxygenated compounds that could find use as fuel additives or components, improving the engine performance [Rahmat et al, 2010; Melero et al, 2010]. For instance, when such oxygenated glycerol derivatives are blended with biodiesel, the resulting fuel has lower viscosity and better cold properties [Noureddini, 2000]. In addition, the emission of solid particles, hydrocarbons and carbon monoxide are decreased [Kesling et al, 1994; Jaecker-Voirol et al, 2008]. With the purpose of manufacturing such fuel additives, different alternatives of catalytic transformation of glycerol have been studied: acetalisation with acetone [Clarkson et al, 2001; Umbarkara et al, 2009; Vicente et al, 2010], etherification with isobutylene [Serio et al, 2010; Frusteri et al, 2009; Klepacova et al, 2007; Melero et al, 2008], esterification with acetic acid [Galan et al, 2009; Balaraju et al, 2010; Melero at al, 2007], and transesterification with methyl acetate [Delgado, 2004; Zhou et al, 2008]. On the other hand, the etherification of glycerol with ethanol [Pariente et al, 2009] is a poorly studied and very interesting alternative. Ethanol is also a renewable compound, produced mainly by sugars fermentation, and commonly used as biofuel for gasoline engines. Furthermore, glycerol ethyl ethers could be incorporated as components in

diesel fuel, the leading fuel in Europe. Higher glycerol ethyl ethers (di- and tri-derivatives) have a large potential for diesel and biodiesel formulation because of their insolubility in water. Likewise, the water-soluble mono-ethyl ether is an interesting intermediate for the production of a variety of chemicals, such as dioxolanes, also suitable for diesel fuel blends [Green and Wuts, 1999] that can be readily obtained by reaction with a carbonyl group-containing substrate, under mild conditions [Hibbert and Timm, 1924]. The etherification of glycerol with ethanol proceeds in the presence of an acid catalyst. Pariente et al, 2009 analyzed the performance of different types of acidic heterogeneous catalysts, including sulfonic acid-functionalized resins, zeolites and sulfonic acid-grafted silicas. The best results were found at 200ºC by using grafted silica (68% glycerol conversion with a 75% selectivity to mono-ethyl ether and 25% selectivity to di-ethyl ether) and zeolites with intermediate aluminium content, Si/Al = 25 (57% glycerol conversion with 75% and 25% selectivity to mono- and di-ethyl ethers, respectively). More recently, Yuan et al, 2011 have reported the etherification of glycerol with ethanol over tungstophosphoric acid (HPW) to synthesize glycerol ethers. The SiO_2-supported HPW catalyst has a high initial activity (91% glycerol conversion with 68%, 23% and 9% selectivity to mono-, di- and tri-ethyl ethers, respectively) at 160 ºC and 20 h, but it undergoes a strong deactivation because of active sites leaching.

Sulfonic acid-functionalized mesostructured materials have demonstrated an excellent catalytic behaviour in the transformation of glycerol into oxygenated compounds for fuel formulation [Vicente et al, 2010; Melero et al, 2008; Melero et al, 2007]. In the particular case of the etherification of glycerol with isobutylene, the activity and selectivity of the silica-supported sulfonic acid catalysts have been shown to be comparable or even superior to other conventional acid catalysts (Amberlyst 15, CT-275 and Nafion®-silica composite SAC-13) [Melero et al, 2008]. Herein, we have

deeply studied the etherification of glycerol with anhydrous ethanol over these sulfonic acid mesostructured silicas in a wide range of reaction conditions. A multivariate analysis has been used to assess the conditions (temperature, ethanol/glycerol molar ratio and catalyst loading) that yield the best catalytic results in terms of glycerol conversion and yield or selectivity towards the glycerol ethyl-ethers, while minimizing the formation of other non-desired compounds coming from the dehydration of glycerol –acrolein, acetol, formaldehyde, etc. Also, the catalytic performance of the sulfonic acid-modified mesostructured silica has been benchmarked with other commercial acid catalysts. The effect of using different glycerol grades, ranging from crude glycerol to refined glycerol (pharmaceutical grade), has also been evaluated, as well as the reusability of the catalyst.

2. Materials and methods

2.1 Catalyst preparation

Arenesulfonic acid-functionalized mesostructured silica (Ar-SBA-15) was synthesized following a previously reported procedure [Melero et al, 2002]. Molar composition of the synthesis mixture for 4 g of templating co-polymer was: 0.0369 TEOS; 0.0041 chlorosulfonyl-phenylethyltrimethoxy-silane (CSPTMS, ABCR); 0.24 HCl; ≈ 6.67 H_2O. The amount in synthesis of sulfur precursor (CSPTMS) is established at 10% of total silicon moles, optimum value to simultaneously achieve high mesoscopic ordering and organic incorporation degree.

Other commercial catalysts used in this work were cationic-exchange sulfonic acid-based macroporous resin, Amberlyst 70, supplied by Rohm and Haas; and a microporous material, zeolite ammonium beta with a SiO_2/Al_2O_3 mole ratio of 25 (CP814E), provided by Zeolyst International and calcined at 500 ºC to obtain the acid

form. These catalysts were ground to powder in order to minimize mass transfer limitations and thus avoid distortions in the comparison of the catalytic performance.

2.2 Catalyst characterization

Textural properties have been evaluated by means of nitrogen adsorption and desorption isotherm at 77 K using a Micromeritics TRISTAR 3000 system. Data was analyzed using the BJH model and pore volume was taken at P/Po= 0.975 as single point. Structural characterization was completed by X-ray powder diffraction (XRD) performed on a PHILIPS X`PERT diffractometer using Cu Kα radiation. XRD data was recorded from 0.6 to 5º (2θ) using a 0.02º step resolution. Acid capacity was measured through the determination of cationic-exchange capacity using aqueous sodium chloride (2 M) exchanging agent. Released protons were then potentiometrically titrated [Melero et al, 2002; Margolese et al, 2000]. Sulfur content was assessed by means of Elemental Analysis (HCNS) in a Vario EL III apparatus. Table 1 summarizes the most relevant physicochemical properties for the arenesulfonic acid-modified mesostructured silica. Data from XRD and N_2 adsorption isotherm evidences high mesoscopic ordering and high surface area along with narrow pore size distribution around 10 nm (size enough to avoid the steric constraints imposed by pore size when relatively bulky substrates such as glycerol derivatives are considered).

Additionally, some characterization data corresponding to the commercial acid heterogeneous catalysts used in this study with the purpose of comparison is summarized in Table 1. In this case, the characterization is provided by the suppliers (Rohm & Haas for the Amberlyst-70 resin and Zeolyst International for the zeolite ammonium beta CP814E).

2.3 Reaction procedure

Crude-, technical- and pharmaceutical-grade glycerol used in the present work were kindly provided by Acciona Biocombustibles, from the biodiesel production plant in Caparroso (Navarra, Spain). The rest of the reagents used in the experiments and sample analysis, absolute ethanol (99.9%), 3-ethoxy-1,2-propanediol (98%) and 1,4-butanediol (99%), were acquired from Sigma-Aldrich.

Scheme 1 is a representation of the etherification of glycerol with ethanol, showing the main etherification products: mono-ethylglycerols (MEG), di-ethylglycerols (DEG), and tri-ethylglycerol (TEG). Note that MEG and DEG can include several isomers depending upon the etherification position within the glycerol molecule. Hence, the terms MEG and DEG include all the possible mono- and di-ethylethers, respectively.

Simultaneously to glycerol etherification, the excess of ethanol can autoreact producing diethylether (DEE) as by-product (Scheme 2). Another side reaction detected is the glycerol dehydration to yield acrolein (Scheme 2). The extent of these undesired side reactions strongly depends on the reaction conditions, being especially favoured at high temperature and catalyst loading as below discussed.

Catalytic runs were carried out in liquid phase with a stirred stainless-steel 50 ml autoclave under autogenous pressure. Reaction temperature, ranging from 160 to 200 ºC, was controlled using a thermocouple immersed in the reaction mixture. Experimental range of 5/1-15/1 ethanol/glycerol molar ratio and 5-25 wt.% catalyst loading, based on glycerol mass, was used. Reaction products were analyzed by gas chromatography (Varian 3900 chromatograph) using a CP-WAX 52 CB column (30 m x 0.25 mm, DF = 0.25) and a flame ionization detector (FID). Reaction products detected and identified by GC included ethylglycerols (EGs) and, under certain reaction conditions, diethylether (DEE) and acrolein, coming from the side reactions. These non-

desired by-products coming from side reactions of glycerol, together with other non-identified possible products (e.g. polyglycerols), are herein considered under the designation *others* for the discussion of the results. Catalytic results are shown either in terms of absolute conversion of glycerol or in terms of selectivity and/or yield towards the desired ethyl-ethers. The quantification of the products was performed by GC using commercial MEG and pharmaceutical glycerol for calibration. In the case of DEG and TEG, non-commercially available, response factors were extrapolated from that of MEG assuming similar behaviour. Selectivity to *others* has been calculated as the difference to 100%.

3. Results and discussion

3.1. Optimization of the reaction conditions

This part of the work deals with the optimization of the reaction conditions to reach a high conversion of glycerol and a high yield to ethers using arenesulfonic acid-functionalized mesostructured silica, Ar-SBA-15, as catalyst. The optimization was achieved by means of an Experimental Design Methodology [Box et al, 1978], studying the influences of the most significant reaction variables. In this sense, chosen factors were reaction temperature, T, ethanol to glycerol molar ratio, MR, and catalyst loading, C. A 3^3 factorial experimental design (three different levels for each factor) was carried out. The central point experiment was repeated three times in order to determine the variability of the results and assess the experimental error. Selected responses were glycerol conversion, X_G, selectivity towards the different products, S_{MEG}, S_{DEG}, S_{TEG}, and S_{Others}, and the global yield to ethers, Y_{Ethers}. The higher ethyl-ethers, DEG and TEG, can be used directly as oxygenated components for diesel or biodiesel formulation, whereas MEG ethers should not be used for this purpose due to its relative

solubility in water and it must be necessary transformed into dioxolanes which are revealed to be excellent blends, being compatible with the diesel fuel and featuring a high oxygen molar content [Pariente et al, 2009].

Selection of the levels was based on results obtained in previous studies [Pariente et al, 2009], considering the constraints imposed by the available experimental set-up and limit operating conditions of the different materials used. The lower and upper levels of the experimental factors were: 160-200 ºC for the temperature, 5/1-15/1 for the ethanol to glycerol molar ratio, and 5-25% for the catalyst loading (based on glycerol weight). The standard experimental matrix for the design is shown in Table 2.

Experiments were run randomly to minimize errors due to possible systematic trends in the variables. Table 2 also shows the results of the glycerol conversion, the selectivity to MEG, DEG, TEG, and other non-identified products, and the yield to EGs (Y_{Ethers}). The non-identified products, denoted in the table as *others*, likely come from the dehydration of glycerol to yield acrolein, acetol, formaldehyde, etc. as well as from the condensation of glycerol. These reactions are especially promoted in the presence of an acid catalyst at relatively high temperatures [Pathak et al, 2010; Márquez-Alvarez et al, 2004].

From the matrix generated by the experimental data and assuming a second-order polynomial model, equations 1-6 were obtained by multiple regression analysis (Table 3). The statistical model was obtained from encoded levels giving the real influence of each variable on the process, and the technological model was obtained from the real values. Consequently, the influence of the variables on the responses is discussed using the statistical models shown in Equations 1 to 3 (Table 3).

Statistical analysis of the studied experimental range identifies the ethanol/glycerol molar ratio as the most important factor in the glycerol conversion response (Eq. (1)).

The second more influential factor is the temperature followed by the catalyst loading and the temperature-molar ratio interaction. The ethanol/glycerol molar ratio has a negative effect on the glycerol conversion which means that an increase in the molar ratio produce a decrease in the conversion of glycerol. Under low molar ratio, secondary reactions contribute to a high consumption of glycerol and do not favour the etherification process. In contrast, an increase in the catalyst loading or temperature produces an increase in the conversion of glycerol, but the enhancement of this response with the temperature is more significant at high values of molar ratio. The corresponding decrease with the molar ratio is also more substantial at low values of the temperature. In addition, the quadratic effect of temperature and molar ratio has a significant negative influence on the glycerol conversion, which indicates that the increase in these variables does not produce a constant rise in the glycerol conversion due to curvature effects. Thus, from the point of view of the glycerol conversion, the optimal values are 190 ºC, 7/1 molar ratio and 25 wt.% of catalyst loading. However, under these conditions a lot of non-desired compounds coming from side reactions are also formed.

Since the ethylglycerols (MEG, DEG and TEG) are the desired products, it is interesting to analyze the influence of each factor on the selectivity and yield to these ethers. According to Eq. (2), the molar ratio is the most significant factor in the selectivity to ethers, having an overall positive effect on this response. The temperature has also a very significant influence on this response, though negative. In this sense, the highest selectivities to ethers were obtained working under moderate conditions, which limits the extent of side reactions, the optimum reaction conditions being the lowest temperature (160 ºC), and the highest molar ratio (15/1) and a catalyst loading of 14 wt.%. At these reaction conditions the catalytic results were: X_G = 19%, S_{Ethers} = 100%

and Y_{Ethers} = 19%. On the other hand, the most significant factor on the yield towards the glycerol ethyl-ethers through the interpretation of Eq. (3) is the molar ratio-temperature interaction with a positive effect. At high values of molar ratio, the response increases slightly with the temperature, following the opposite trend at low molar ratios and in a more accentuated manner. This is attributed to the fact that the extent of glycerol etherification reaction enhances when the amount of ethanol present in the medium is increased. However, the above-mentioned side reactions are especially promoted at low ethanol/glycerol molar ratio, leading to the formation of higher amounts of *others* and consequently reducing the Y_{Ethers}. The following factor in importance for the yield to ethers is the quadratic effect of molar ratio, also showing a negative effect. This means that the curvature effect is significant and the response does not increase linearly. Hence, the optimal operating conditions for maximizing the yield to ethers are high temperature (200 ºC), molar ratio (15/1), and catalyst loading (19 wt.%). At these reaction conditions, the model gives an optimal yield to ethers of 40% with a glycerol conversion of 74%, which implies a non-desired yield to others of 34%.

Finally, the arithmetical averages and the standard deviations of all the responses were calculated for the central point experiments: glycerol conversion (89% ± 2.9%), selectivity to ethers (39% ± 2.5%) and yield to ethers (35% ± 2.5%). Obtained standard deviations are low enough to consider that experimental error is not very significant.

Figures 1, 2 and 3 show the response surfaces for glycerol conversion and yield to ethers predicted by the above technological models (equations 4-6, Table 3). In Figure 1, the temperature and the ethanol/glycerol molar ratio are represented for a fixed catalyst loading. A gradual increase in the catalyst loading leads to higher glycerol conversion and yield to ethers (the response surfaces are shifted upwards, especially in the region of low temperature). The yield trend shows the behaviour above discussed

with the statistical equations: higher ethanol concentration leads to an enhancement of etherification with the temperature, whereas the opposite occurs, and in larger extent, under low ethanol to glycerol molar ratio.

In Figure 2, the temperature and the catalyst loading are represented for a fixed ethanol/glycerol molar ratio. From the point of view of glycerol conversion, the highest results are obtained in the region of high temperature and catalyst loading, and especially at the lowest values of molar ratio, where undesired side-reactions become more relevant contributing to a fast consumption of the glycerol present. Concerning the yield to ethers, due to the interactions among factors above-discussed this response shows a strong curvature effect. Thus, this response decreases with the temperature and catalyst loading at low molar ratios, since glycerol side-reactions are promoted. In contrast, at the highest ethanol to glycerol molar ratio, an enhancement of the yield to ethers is observed at the highest temperature and catalyst loading. Therefore, a large ethanol concentration in the reaction medium promotes the etherification reactions of glycerol minimizing side reactions.

Figure 3 includes the representation of the response surfaces corresponding to molar ratio vs. catalyst loading at a fixed temperature. As shown, glycerol conversion clearly increases with the temperature, as both the etherification with ethanol and the side-reactions are simultaneously favoured. On the other hand, yield to ethers shows a changing behaviour with the molar ratio at the three different levels of temperature due to a strong interaction which leads to curvature effects on the model, as explained previously.

3.2. Comparative study among sulfonic acid-modified mesostructured silica and commercial acid heterogeneous catalysts in the etherification of glycerol with ethanol.

In order to compare the catalytic performance of the synthesized mesostructured catalyst with other acid solid catalysts, a commercial sulfonic acid-modified solid and a zeolite were used. An effect of the type of catalyst on the reaction is expected, not only due to acid sites strength and concentration but also to porosity or pore volume limitations on the catalytic conversion of glycerol into ethyl-ethers. Selected reaction conditions for the screening correspond to the optimal conditions obtained in terms of maximizing yield to ethyl-ethers from the above-discussed design of experiments (200 ºC, ethanol/glycerol 15/1 and constant acid sites loading of 0.2 mmol H^+/g glycerol equivalent to 19 wt.% Ar-SBA-15 loading based on glycerol). The reaction time was fixed in 4 hours.

Figure 4 shows the conversion of glycerol and the yield and selectivity to ethers achieved by each catalyst at the selected reaction conditions. Three catalysts are shown: sulfonic acid-functionalized mesostructured silica (Ar-SBA-15), synthesized as shown in the experimental section, sulfonic acid-modified commercial resin (Amberlyst-70), and a microporous catalyst (zeolite beta). This zeolite has been reported as an efficient catalyst for this reaction, by Pariente et al, 2009 although under different reaction conditions.

Both sulfonic acid-based catalysts used in the etherification of glycerol gave a similar glycerol conversion. However, higher yield to ethers was reached over the sulfonic acid-functionalized mesostructured silica, Ar-SBA-15. Moreover, it is important to point out that the mesostructured catalyst Ar-SBA-15 displays the lowest production of non-desired by-products with a selectivity to others around 40% (S_{Ethers} = 60%). These results confirm that the adequate textural properties of an open porous accessible structure and the higher specific surface characteristic of the mesostructured catalyst, as compared with the low surface area resin, lead to a best catalytic activity and

production of desired products. On the other hand, the low conversion and yield to EGs obtained using zeolite beta contrast with previously reported results [Pariente et al, 2009]. The diffusion limitations through the microporous network are considered the main cause of the low performance of this commercial catalyst. Moreover, beta zeolite seems to catalyze preferably the glycerol side reactions since the selectivity to *others* is 100%.

3.3. Applicability to different grades of glycerol

Another purpose of the present work was to evaluate the possibility of using low-grade glycerol for the reaction of etherification with ethanol. Table 4 shows the composition of the different grades of glycerol –crude, technical and pharmaceutical– tested in this work. The presence of salts and/or water in the reaction medium could adversely affect the catalytic performance. Thus, the presence of water may affect the reaction equilibrium, limiting its extent. Likewise, sodium cations from salts can deactivate acid materials by simple cationic-exchange of the catalytic protons. As in the screening of catalyst, optimal reaction conditions for maximizing yield to EGs from the design of experiments have been used (200 ºC, ethanol/glycerol 15/1 and catalyst/glycerol 19 wt.%).

Table 5 shows the glycerol conversion, the yield to EGs and the selectivity to these ethers achieved with the different grades of glycerol. Reactions performed with crude glycerol resulted in no conversion of glycerol. This behaviour is attributed to the presence of sodium cations in the medium which have a strong impact on the catalytic performance due to a Na^+/H^+ cationic-exchange. In this case, the heterogeneous catalyst is transformed into the corresponding sodium form, and hence it is deactivated. On the other hand, the observed trend for technical-grade glycerol is similar to that of

pharmaceutical glycerol, with only minimal decreases in conversion and yield to ethers, the presence of water being the main cause of this fact. The presence of water in the reaction medium affects the product distribution since this fact could modify the equilibrium composition of the reaction mixture.

3.4. Reusability of the catalyst

An analysis of reusability was performed on the catalyst Ar-SBA-15 in order to evaluate catalyst life. Table 6 depicts the results of three consecutive catalytic runs performed reusing the catalyst under both sets of optimal reaction conditions obtained from the experimental design, one for maximizing Y_{Ethers} (Case A) and the other for maximizing S_{Ethers} (and thereby minimizing S_{Others}) (Case B), at a fixed reaction time of 4 hours and using pharmaceutical glycerol. After each reaction, catalyst was recovered by filtration, mild double-washed in ethanol and hexane at room temperature (in order to remove both polar and non-polar adsorbed compounds), and air-dried before the reuse. The results are shown in Table 6.

Under the reaction conditions of case A, an important deactivation is observed already in the second run, as glycerol conversion drops to values close to zero. The production of relevant amounts of by-products, as a consequence of the high temperature used in this case, is considered the main factor responsible for this activity decrease. The mild double-washing treatment is not enough to remove strongly adsorbed organic compounds that deactivate the acid sites by poisoning. On the other hand, analyzing the results shown in case B, no loss of activity is observed either in terms of glycerol conversion or yield to EGs even after 3 consecutive runs. The milder temperature used in this case avoids the formation of secondary compounds and thus the catalyst is not deactivated by poisoning.

In order to evaluate the feasibility of catalyst regeneration, a more stringent regeneration treatment was performed with the aim of recovering the initial activity of the catalyst Ar-SBA-15. The procedure was as follows: separation of the solid by filtration, ethanol and hexane washing under reflux for 2 h each, acidification with 1.9 M HCl (aq.) for 30 min, washing with deionised water until neutral pH, and overnight drying at 90 ºC. After this regeneration treatment, Ar-SBA-15 catalyst was evaluated again in reaction at the same reaction conditions. When applying the regeneration treatment, Ar-SBA-15 catalyst recovers or even slightly increases its initial catalytic activity. This indicates that the deposition of deactivating by-products can be reversed by means of the proposed regeneration treatment. The observed increase of the activity with regards to the fresh catalyst might be attributed to a modification of the strength of the acid sites due to the catalyst contact with the acid solution during the regeneration. Also, a better surfactant removal, which increases the number of accessible sulfonic acid sites in the material, could lead to an improvement in its catalytic performance.

4. Conclusions

The catalytic results show a great interaction among temperature, ethanol to glycerol molar ratio and catalyst loading. Under low ethanol concentration, secondary reactions of glycerol are clearly enhanced as temperature and catalyst loading increases. In contrast, the gradual increase of ethanol concentration, promotes the glycerol etherification reactions towards ethyl-glycerols being beneficial the increasing of both temperature and catalyst amount. Nevertheless, moderate reaction conditions are necessary to avoid the formation of glycerol by-products and maximize ethyl-glycerols selectivity. Moreover, the catalytic performance of arenesulfonic silica is quite

outstanding as compared with commercial catalysts and even with the use of technical grade glycerol.

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References

Balaraju M., Nikhitha P., Jagadeeswaraiah K., Srilatha K., Sai Prasad P. S., Lingaiah N., 2010. Acetylation of glycerol to synthesize bioadditives over niobic acid supported tungstophosphoric acid catalysts. Fuel Process. Technol. 91, 249–253.

Box G. E. P., Hunter W. G., Hunter J. S., 1978. Statistics for Experimenters. Wiley, New York.

Clarkson J. S., Walker A. J., Wood M. A., 2001. Continuous Reactor Technology for Ketal Formation: An Improved Synthesis of Solketal. Org. Process Res. Dev. 5, 630-635.

Delgado J., 2004. Procedimiento para producir combustibles biodiésel con propiedades mejoradas a baja temperatura. ES 2201894.

Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009.

Frusteri, F., Arena, F., Bonura, G., Cannilla, C., Spadaro, L., Di Blasi, O., 2009. Catalytic etherification of glycerol by *tert*-butyl alcohol to produce oxygenated additives for diesel fuel. Appl. Catal. A-Gen. 367, 77-83.

Galan M. I., Bonet J., Sire R., Reneaume J. M., Ples A. E., 2009. From residual to useful oil: Revalorization of glycerine from the biodiesel synthesis. Bioresour. Technol. 100, 3775–3778.

Green T. W. and Wuts P. G. M., 1999. Protective Groups in Organic Synthesis, Wiley-Interscience, New York, 308-322.

Hibbert H. and Timm J. A., 1924. Studies on the reactions relating to carbohydrates and polysaccharides x. Synthesis and relative stability of cyclic acetals from 1,2- and 1,3-glycols. J. Amer. Chem. Soc. 46, 1283.

Jaecker-Voirol A., Durand I., Hillion G., Delfort B., Montagne X., 2008. Glycerin for New Biodiesel Formulation. Oil Gas Sci. Technol. 63, 395-404.

Kesling S., Karas L. J., Liotta F. J., 1994. Diesel fuel containing glycerol ether additive. US 5308365.

Klepacova K., Mravec D., Kaszonyi A., Bajus M., 2007. Etherification of glycerol and ethylene glycol by isobutylene. Appl. Catal. A-Gen. 328, 1–13.

Knothe G., Krahl J., Gerpen J. V., 2010. The Biodiesel Handbook, second ed., AOCS Press, Illinois.

Margolese D., Melero J. A., Christiansen S. C., Chmelka B. F., Stucky G. D., 2000. Direct syntheses of ordered SBA-15 mesoporous silica containing sulfonic acid groups. Chem. Mater. 12, 2448.

Márquez-Alvarez C., Sastre E., Pérez-Pariente J., 2004. Solid catalysts for the synthesis of fatty esters of glycerol, polyglycerols and sorbitol from renewable resources. Top. Catal. 27, 105-117.

Melero J. A., Stucky G. D., van Grieken R., Morales G., 2002. Direct syntheses of ordered SBA-15 mesoporous materials containing arenesulfonic acid groups. J. Mater. Chem. 12, 1664.

Melero J. A., Grieken R. van, Morales G., Paniagua M., 2007. Acidic mesoporous silica for the acetylation of glycerol: Synthesis of bioadditives to petrol fuel. Energy Fuels 21, 1782-1791.

Melero J. A., Vicente G., Morales G., Paniagua M., Moreno J. M., Roldán R., Ezquerro A., Pérez C., 2008. Acid-catalyzed etherification of bio-glycerol and isobutylene over sulfonic mesostructured silicas**.** Appl. Catal. A-Gen. 346, 44-51.

Melero J. A., Vicente G., Morales G., Paniagua M., Bustamante J., 2010. Oxygenated compounds derived from glycerol for biodiesel formulation: Influence on EN 14214 quality parameters. Fuel 89, 2011–2018.

Noureddini H., 2000. Process for producing biodiesel fuel with reduced viscosity and a cloud point below 32 ºF. US 6015440.

Pagliaro M. and Rossi M., 2008. The future of glycerol: new usages for a versatile raw material, RSC Publishing, Cambridge.

Pariente S., Tanchoux N., Fajula F., 2009. Etherification of glycerol with ethanol over acid catalysts. Green Chem. 11, 1256–1261.

Pathak K., Reddy K. M., Bakhshi N. N., Dalai A. K., 2010. Catalytic conversion of glycerol to value added liquid products. Appl. Catal. A-Gen. 372, 224-238.

Rahmat N., Abdullah A. Z., Mohamed A. R., 2010. Recent progress on innovative and potential technologies for glycerol transformation into fuel additives: A critical review. Renew. Sust. Energ. Rev. 14, 987–1000.

Serio M. D., Casale L., Tesser R., Santacesaria E., 2010. New Process for the Production of Glycerol tert-Butyl Ether. Energy Fuels 24 (9), 4668–4672.

Umbarkara S. B., Kotbagia T. V., Biradara A. V., Pasrichab R., Chanalea J., Dongarea M. K., Mamedec A-S, Lancelot C., Payenc E., 2009. Acetalization of glycerol

using mesoporous MoO3/SiO2 solid acid catalyst. J. Mol. Catal. A-Chem. 310, 150–158.

Vicente G., Melero J. A., Morales G., Paniagua M., Martín E., 2010. Acetalisation of bioglycerol with acetone to produce solketal over sulfonic mesostructured silicas, Green Chem. 12, 899-907.

Yuan Z., Xia S., Chen P., Hou Z., Zheng X., 2011. Etherification of Biodiesel-Based Glycerol with Bioethanol over Tungstophosphoric Acid To Synthesize Glyceryl Ethers. Energy Fuels 25, 3186-3191.

Zhou C. H., Beltramini J. N., Fana Y. X., Lu G. Q., 2008. Chemoselective catalytic conversión of glycerol as a biorenewable source to valuable commodity chemicals. Chem. Soc. Rev. 37, 527–549.

Figure captions

Fig. 1. Response surfaces for glycerol conversion and yield to ethers predicted by the models for the three different levels of catalyst loading (Ar-SBA-15).

Fig.2. Response surfaces for glycerol conversion and yield to ethers predicted by the models for the three different ethanol/glycerol molar ratios.

Fig. 3. Response surfaces for glycerol conversion and yield to ethers predicted by the models for the three different temperatures.

Fig. 4. Screening of solid acid catalysts for the etherification of glycerol with ethanol. Reaction conditions: reaction time 4 h, temperature 200 ºC, ethanol/glycerol molar ratio 15/1, constant acid sites loading 0.2 mmol H^+/g glycerol.

Fig. 1

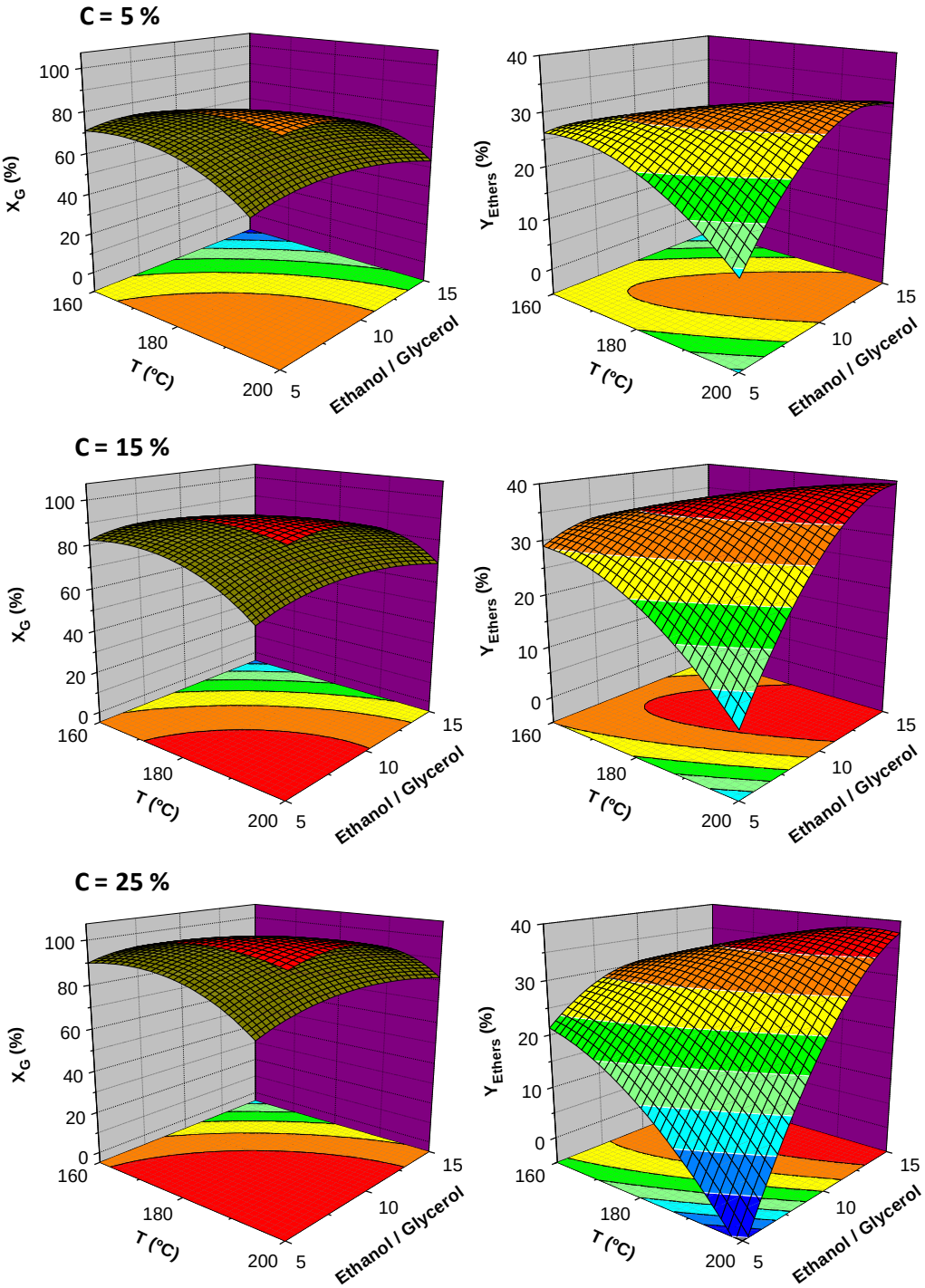

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Fig. 1

Fig. 2

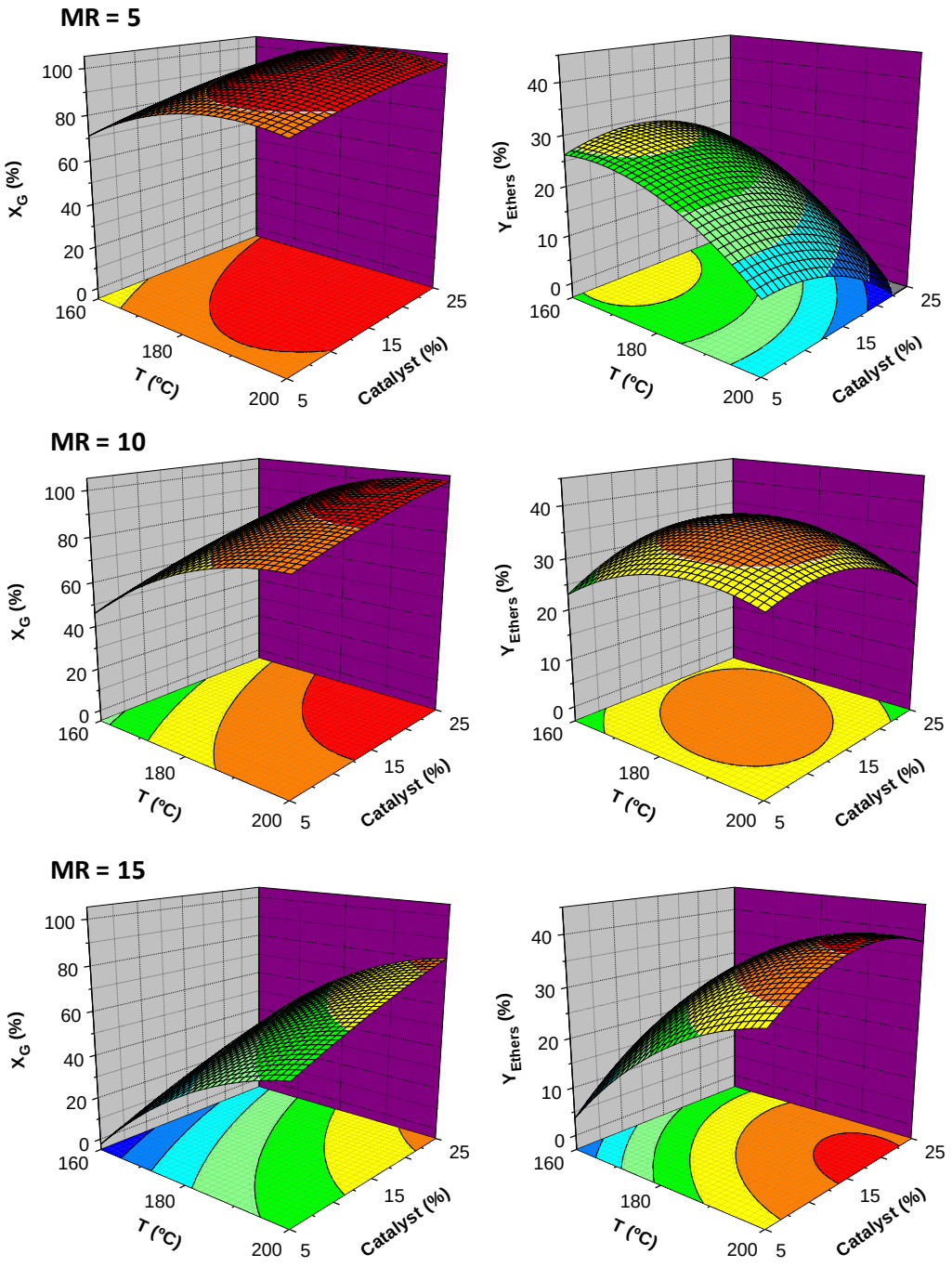


Fig. 2. Response surfaces for glycerol conversion and yield to ethers predicted by the models for the three different ethanol/glycerol molar ratios.

Fig. 3

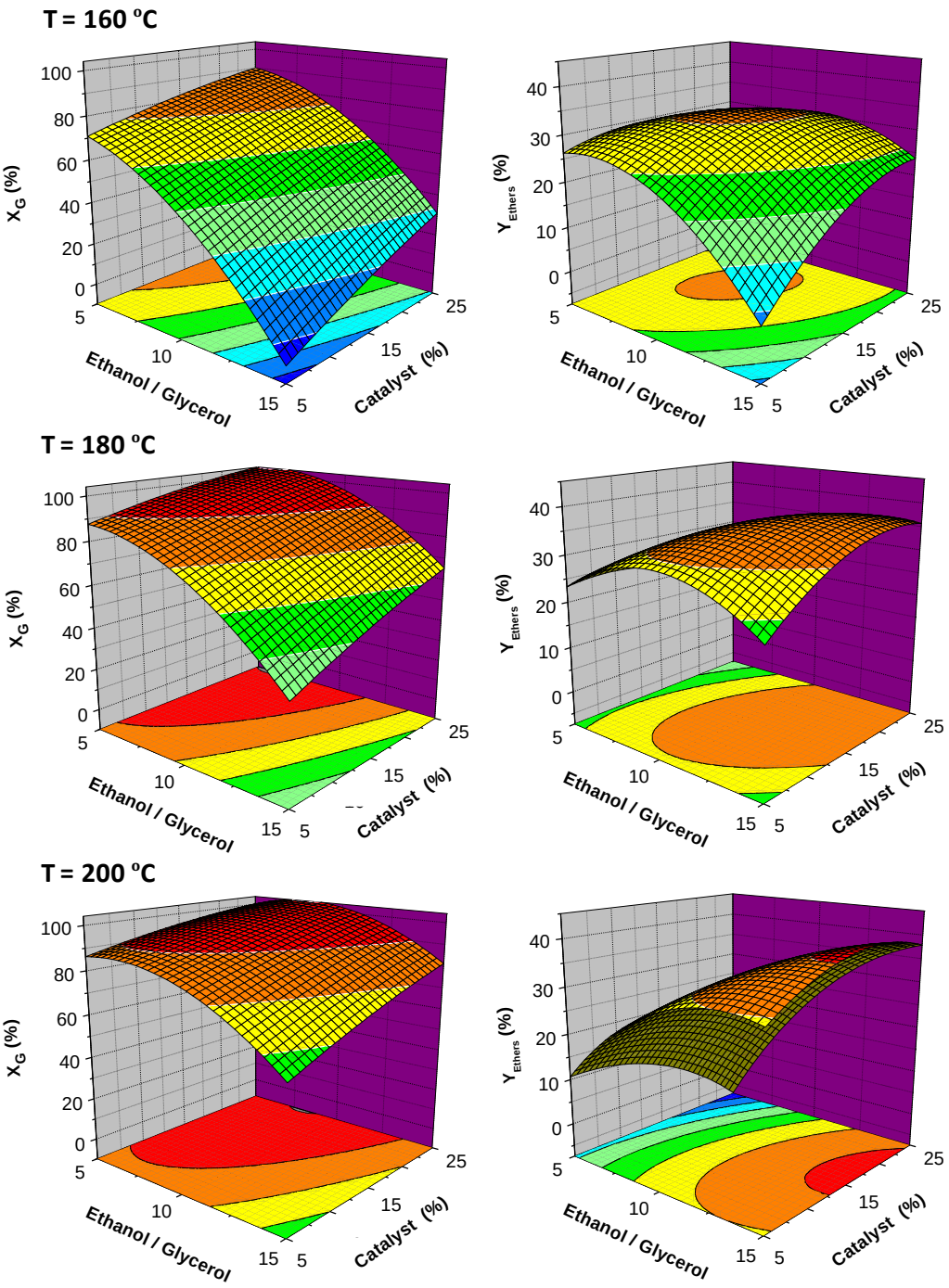
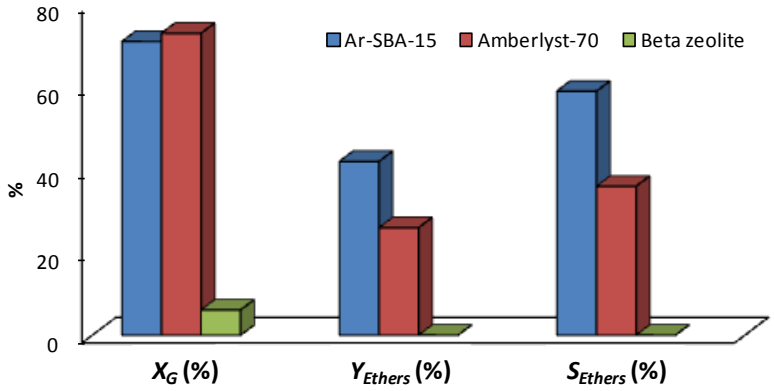


Fig. 3. Response surfaces for glycerol conversion and yield to ethers predicted by the models for the three different temperatures.

Fig. 4



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Schemes captions

Scheme 1. Reaction of etherification of glycerol with ethanol.

Scheme 2. Side reactions: A) Diethylether formation via ethanol auto-etherification; B) Glycerol dehydration to yield acrolein.

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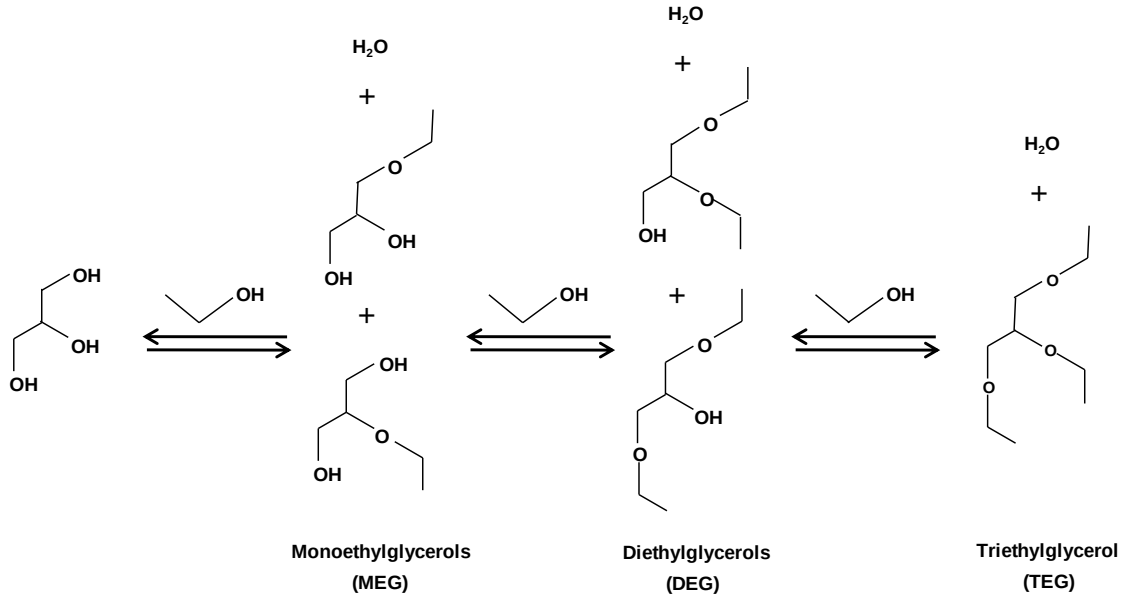

Scheme 1. Reaction of etherification of glycerol with ethanol.

Scheme 2.

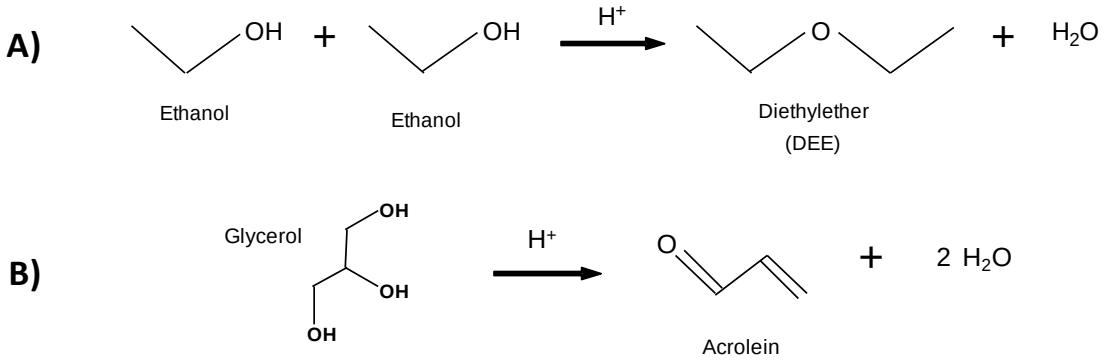

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Table 1. Physicochemical properties for arenesulfonic acid-modified mesostructured silica and commercial acid heterogeneous catalysts[a].

Sample	d_{100} [b] (Å)	Pore size [c] (Å)	BET area (m^2/g)	Pore volume [d] (cm^3/g)	Wall thick [e] (Å)	Acid capacity [f] (meq H^+/g)
Ar-SBA-15	123	104	741	0.97	38	0.92
Amberlyst-70	-	220	36	-	-	2.55
CP814E	-	(7.6 x 6.4); (5.5 x 6.5)	680	-	-	12.5[b]

[a] Properties provided by the suppliers.
[b] *d* (100) spacing, measured from small-angle X-ray diffraction.
[c] Mean pore size (D_p) from adsorption branch applying the BJH model.
[d] The pore volume (V_p) was taken at P/P_o= 0.975 as single point.
[e] Average pore wall thickness calculated by a_o-pore size ($a_o=2d(100)/\sqrt{3}$) assuming hexagonal symmetry.
[f] Acid capacities defined as meq of H^+ per gram of catalyst, obtained by titration.
[g] Si/Al molar ratio.

Table 2. Experiment matrix and experimental results for the etherification of pharmaceutical glycerol with ethanol over arenesulfonic acid-modified mesostructured silica (Ar-SBA-15) [Reaction time = 4 h].

Run	T (ºC) (X)	MR (Y)	C (%) (Z)	I_T	I_{MR}	I_C	X_G (%)	Selectivity (%)				Y_{Ethers} (%)
								MEG	*DEG*	*TEG*	*Others*	
1	180	10	15	0	0	0	86	17	18	2	63	32
2	160	5	25	-1	-1	+1	93	16	9	1	74	24
3	180	5	5	0	-1	-1	87	16	5	0	79	18
4	180	15	15	0	+1	0	42	74	14	0	12	37
5	200	10	15	+1	0	0	86	12	15	3	70	26
6	180	10	15	0	0	0	88	17	22	3	58	37
7	160	5	5	-1	-1	-1	71	27	10	0	62	27
8	200	15	25	+1	+1	+1	84	35	9	0	56	37
9	160	15	5	-1	+1	-1	7	100	0	0	0	7
10	160	10	15	-1	0	0	65	44	12	1	44	37
11	160	10	5	-1	0	-1	35	55	4	0	41	20
12	180	15	5	0	+1	-1	41	43	3	0	54	19
13	200	15	15	+1	+1	0	73	54	14	0	32	49
14	180	10	5	0	0	-1	69	46	9	0	45	38
15	160	15	25	-1	+1	+1	19	88	12	0	0	19
16	180	5	25	0	-1	+1	99	4	3	0	93	7
17	200	15	5	+1	+1	-1	43	50	3	0	47	23
18	160	5	15	-1	-1	0	85	24	7	0	70	25
19	200	5	15	+1	-1	0	100	1	1	0	97	3
20	200	5	25	+1	-1	+1	99	0	0	0	100	0
21	200	10	5	+1	0	-1	92	22	15	1	62	35
22	200	10	25	+1	0	+1	99	5	9	3	83	17
23	160	15	15	-1	+1	0	14	100	0	0	0	14
24	180	10	25	0	0	+1	96	16	14	2	68	30
25	160	10	25	-1	0	+1	77	36	8	0	56	34
26	180	15	25	0	+1	+1	76	41	12	0	47	40
27	180	10	15	0	0	0	92	27	11	1	61	36
28	180	5	15	0	-1	0	95	19	9	1	71	27
29	200	5	5	+1	-1	-1	87	13	2	0	85	13

Note: T, temperature; MR, ethanol/glycerol molar ratio; C, catalyst loading (wt.% based on glycerol); I, coded value; X_G, conversion of glycerol; Y_{Ethers}, combined yield to MEG, DEG and TEG. Columns 2, 3 and 4 represent the factor levels on a natural scale whereas columns 5, 6 and 7 represent the 0 and ±1 encoded factor levels on a dimensionless scale.

Table 3. Predictive equations obtained by design of experiments.

	Statistical models		
X_G =	$86.49 + 16.50\ I_T - 23.17\ I_{MR} + 11.67\ I_C - 9.28\ I_T^2 + 10.25\ I_T\ I_{MR} - 1.33\ I_T\ I_C - 11.61\ I_{MR}^2 + 3.50\ I_{MR}\ I_C - 1.78\ I_C^2$	(r=0.975)	(1)
S_{Ethers} =	$41.95 - 15.83\ I_T + 26.83\ I_{MR} - 5.67\ I_C + 5.04\ I_T^2 - 4.92\ I_T\ I_{MR} - 1.50\ I_T\ I_C + 5.04\ I_{MR}^2 + 3.25\ I_{MR}\ I_C - 7.12\ I_C^2$	(r=0.956)	(2)
Y_{Ethers} =	$36.49 - 0.22\ I_T + 5.61\ I_{MR} + 0.44\ I_C - 4.78\ I_T^2 + 10.75\ I_T\ I_{MR} - 3.33\ I_T\ I_C - 8.28\ I_{MR}^2 + 6.17\ I_{MR}\ I_C - 5.11\ I_C^2$	(r=0.920)	(3)
	Technological models		
X_G =	$-648.172 + 8.11257\ T - 14.3376\ MR + 2.17829\ C - 0.0227657\ T^2 + 0.100383\ T\ MR - 0.0065625\ T\ C - 0.47085\ MR^2 + 0.0717167\ MR\ C - 0.0178626\ C^2$	(r=0.975)	(4)
S_{Ethers} =	$446.975 - 4.6611\ T + 9.16087\ MR + 2.31501\ C + 0.0124307\ T^2 - 0.0493\ T\ MR - 0.00757083\ T\ C + 0.205358\ MR^2 + 0.06525\ MR\ C - 0.0722106\ C^2$	(r=0.956)	(5)
Y_{Ethers} =	$-244.265 + 3.54577\ T - 13.493\ MR + 3.28363\ C - 0.0121849\ T^2 + 0.1067\ T\ MR - 0.01625\ T\ C - 0.322958\ MR^2 + 0.12485\ MR\ C - 0.0517561\ C^2$	(r=0.920)	(6)

Note: T, temperature; MR, ethanol/glycerol molar ratio; C, catalyst loading; I, coded value; X_G, conversion of glycerol; S_{Ethers}, combined selectivity to MEG, DEG and TEG; Y_{Ethers}, combined yield to MEG, DEG and TEG. The models include only the significant terms.

Table 4. Composition of the different grades of glycerol evaluated.[a]

Glycerol grade	Purity (wt.%)	Water (wt.%)	Ash (wt.%)		MONG [c] (wt.%)
			NaCl	Others [b]	
Pharmaceutical	99.9	0.1	< 0.001	n.d	n.d
Technical	91.6	6.2	< 0.001	0.2	2
Crude	85.8	8.0	5.2	0.94	0.06

[a] Analytical data provided by the supplier, Acciona Biocombustibles, Spain (Methods according to standards BS5711). [b] Others, inorganic compounds excluding NaCl. [c] MONG, Matter (Organic) Non-Glycerol; n.d., not detected.

Table 5. Influence of glycerol grade in the etherification with ethanol over Ar-SBA-15.

Glycerol grade	X_G **(%)**	Y_{Ethers} **(%)**	S_{Ethers} **(%)**
Pharmaceutical	71	42	59
Technical	72	37	51
Crude	0	0	0

Reaction conditions: 200 ºC temperature, 15/1 ethanol/glycerol molar ratio, 19 wt.% catalyst loading based on glycerol, 4 h reaction time.

Table 6. Reutilization and regeneration of catalyst Ar-SBA-15.

RUN	Case A			Case B		
	X_G (%)	Y_{Ethers} (%)	S_{Others} (%)	X_G (%)	Y_{Ethers} (%)	S_{Others} (%)
1	71	42	41	19	19	0
2	3	3	0	13	13	0
3	-	-	-	18	18	0
Regenerated	93	55	41	23	23	0

Pharmaceutical glycerol. (A) Reaction conditions for maximizing the yield to EGs, 200 ºC temperature, 15/1 ethanol/glycerol molar ratio, 19 wt.% catalyst based on glycerol, 4 h reaction time; and (B) reaction conditions for maximizing the selectivity to ethers, 160 ºC temperature, 15/1 ethanol/glycerol molar ratio, 14 wt.% catalyst based on glycerol, 4 h reaction time.