

Acid-catalyzed etherification of bio-glycerol and isobutylene over sulfonic mesostructured silicas

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ABSTRACT

Sulfonic-acid functionalized mesostructured silicas have demonstrated an excellent catalytic behavior in the etherification of glycerol with isobutylene to yield *tert*-butylated derivatives. Di-*tert*-butylglycerols (DTBG) and tri-*tert*-butylglycerol (TTBG) have shown to be valuable fuel additives leading to decreases in the emission of particulate matter, hydrocarbons, carbon monoxide and unregulated aldehydes. Likewise, said ethers can also act as cold flow improvers for use in biodiesel, reducing also its viscosity. The activities and selectivities achieved over sulfonic acid-functionalized mesostructured silicas are comparable or even superior to those displayed by widely-used macroporous commercial acid resins. Under optimized reaction conditions, these mesostructured catalysts yield a complete glycerol conversion with a combined selectivity towards DTBG and TTBG up to ca. 90%. Furthermore, no formation of undesirable isobutylene oligomers is observed. The acid strength of the sulfonic acid sites has also been found to be an important factor affecting the catalytic performance of these materials.

Keywords: sulfonic, isobutylene, glycerol, tertiary butyl ethers, mesoporous, fuel additives.

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1. Introduction

Mono-alkyl esters of fatty acids (biodiesel) obtained from transesterified vegetable oils or animal fats are an attractive and environmentally friendly alternative to petrodiesel fuel. Biodiesel is biodegradable, renewable and non-toxic, and exhibits improved lubricity, higher flash point, reduction of most exhaust emissions, close heat combustion and viscosity, and similar or even superior cetane number in comparison to diesel [1]. Glycerol is the main by-product of the transesterification process, whose production is equivalent to approximately 10 wt. % of the total produced biodiesel.

Production of biodiesel in the European Union has grown exponentially in the last years. According to the *European Biodiesel Board*, the production in EU was 5 MTm in 2006 with a fast and sharp annual increase of ca. 28 % from year 2000. Moreover, the Directive 2003/30/EC of the European Union has stated that by the end of the year 2010 member states should ensure a biofuels proportion of 5.75 %, calculated on the basis of energy content, for all the petrol fuels used for transport purposes [2]. That implies an increase in the biodiesel manufacturing up to 10 MTm for the year 2010, which means ca. 1 MTm per year of glycerol. With this expected increased production of biodiesel, a glut of glycerol will be created which will reduce the glycerol market prices. In this context, an important research is currently starting in order to find new applications for this expected low-cost feedstock [3-4]. These strategies include selective oxidation, hydrogenolysis to obtain propylene glycol, dehydration to yield acrolein, fermentation towards 1,3-propanediol, synthesis of epichlorohydrin, or even reforming towards syngas [3]. Apart of these alternatives, the transformation of glycerol into fuel oxygenates by means of etherification [5-9] and esterification reactions [10-11] is being explored. This approach is a promising and economically viable alternative since not

only makes a good use of the glycerine by-product but also increases the yield to biofuel in the overall biodiesel production process.

Special interest is focused on the preparation of alkyl ethers of glycerol by etherification with isobutylene [6-9]. Isobutylene reacts with glycerol in presence of acid catalysts to yield a mixture of mono-, di-, and tri-*tert*-butyl glycerol ethers (MTBG, DTBG, and TTBG, respectively). Higher ethers (DTBG and TTBG) are excellent additives with a large potential for diesel and biodiesel formulation. These oxygenated compounds, when incorporated into standard diesel fuel, have lead to a decreasing in particles, hydrocarbons, carbon monoxide and unregulated aldehydes emissions [12]. Likewise, these ethers can act as cold flow improvers for use in biodiesel, reducing also its viscosity [7]. This issue is of significant importance due to the growing demand of new additives specifically for biodiesel that are biodegradable, non-toxic and renewable. In addition, these derivates can also be used as octane boosters for gasoline, as an alternative to commercial trialkylethers (MTBE and ETBE) [13].

This reaction has been usually performed over sulfonic resins [14-16] and homogenous acid catalysts (mainly *p*-toluenesulfonic) [16]. Usually, low surface areas and lack of thermal stability are the major drawbacks of sulfonic resins. On the other hand, the use of conventional homogenous acid catalysts must be avoided to comply with the increasingly strict environmental regulations. The incorporation of organosulfonic groups over mesostructured silicas have generated effective solid acid catalysts with enhanced catalytic properties as compared with conventional homogeneous and heterogeneous acid catalysts [17]. Moreover, these type of silica materials functionalized with organosulfonic acid groups have been used previously for the conversion of biorenewable molecules [18-21], showing better catalytic

performances than the commercial sulfonated resins. These highly surface materials, with large interconnected mesopores and high accessibility of strong Brönsted acid sites might be suitable candidates for this etherification reaction.

Within the scope of this work, the etherification of glycerol with isobutylene has been studied over different sulfonic acid-modified mesostructured silicas. A multivariate analysis has been used to assess the conditions (isobutylene/glycerol molar ratio and temperature) that yield the best catalytic results in terms of glycerol conversion and selectivity towards the di- and tri-derivates, while minimizing the formation of the mono-derivate compound (MTBG) and the extension of the isobutylene dimerization. MTBG has relatively high water solubility and thus is not suitable as diesel-blending agent, whereas isobutylene oligomers could lead to the formation of undesirable deposits in the motor during the combustion. Finally, the catalytic performance of these sulfonic acid-modified mesostructured silicas has been benchmarked with other commercial acid catalysts.

2. Experimental Section

2.1 Catalysts preparation

Propylsulfonic-acid functionalized mesostructured silica (Pr-SBA-15) was synthesized following a previously reported procedure [22]. Molar composition of the synthesis mixture for 4 g of templating block-copolymer (Pluronic 123, $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, BASF) was: 0.0369 tetraethylorthosilicate (TEOS, Aldrich); 0.0041 mercapto-propyltrimethoxysilane (MPTMS, Aldrich); 0.0369 H_2O_2 ; 0.24 HCl; $\approx 6.67 \text{ H}_2\text{O}$. **Arenesulfonic-acid functionalized mesostructured silica** (Ar-SBA-15) was synthesised as described elsewhere [23]. For this catalyst, the molar composition of the

synthesis mixture for 4 g of copolymer was as follows: 0.0369 TEOS: 0.0041 chlorosulfonyl-phenylethyltrimethoxy-silane (CSPTMS, Gelest): 0.24 HCl: \approx 6.67 H₂O. In both cases, the amounts of sulfur precursors (MPTMS and CSPTMS) have been selected to provide 10 % of total silicon moles. These two sulfonic acid-modified mesostructured silicas provide different acid strengths, as introduced by the different molecular environments of the sulfonic acid sites (Pr-SBA-15 < Ar-SBA-15).

Commercial acid catalysts: Nafion®-SiO₂ composite (SAC-13) with resin content in the range of 10-20 wt. % was supplied by Sigma-Aldrich. Acidic macroporous resins Amberlyst 15 and Amberlyst 36 (Rohm and Haas), and Purolite CT-275 (Purolite) were also tested in the present work.

2.2 Catalysts characterization

Textural properties of sulfonic acid-modified mesostructured silicas have been evaluated by means of nitrogen adsorption and desorption isotherm at 77 K using a Micromeritics TRISTAR 3000 system. Data were analyzed using the BJH model and pore volume was taken at P/P₀= 0.975 single point. Structural characterization was completed by X-ray powder diffraction (XRD) patterns, which were acquired on a PHILIPS X'PERT diffractometer using Cu K α radiation. Data were recorded from 0.6 to 5° (2 θ) using a 0.02° step resolution. Acid capacity was measured through the determination of cation-exchange capacities using aqueous sodium chloride (2 M) solutions as cationic-exchange agent. Released protons were then potentiometrically titrated [22-23]. Sulfur contents were assessed by means of Elemental Analysis (HCNS) in a Vario EL III apparatus, in combination with the information obtained from thermogravimetric analyses (SDT 2960 Simultaneous DSC-TGA, from TA Instruments).

Table 1 summarizes the most relevant physicochemical properties for the two sulfonic acid-modified mesostructured silicas. Data from XRD and N₂ adsorption isotherms evidence high mesoscopic ordering and high surface areas along with narrow pore size distributions around 8-9 nm (size enough to avoid the steric constraints imposed by pore size when relatively bulky substrates such as glycerol derivatives are considered). For both samples, prepared by co-condensation of the different silanes, high incorporation yields for the sulfonic-acid moieties (over 90%) are observed. Likewise, for Pr-SBA-15, complete oxidation of the precursor thiol groups into sulfonic moieties can be deduced from actual sulfur content and acid capacity by titration.

Table 1. Physicochemical, textural and acidity-related properties for sulfonic-acid-modified mesostructured silicas.

Sample	Textural Properties					Acid Properties		
	d_{100} ^a (Å)	Pore size ^b (Å)	BET area (m ² /g)	Pore volume ^c (cm ³ /g)	Wall thick. ^d (Å)	Acid capacity ^e (meq/g)		Organic incorp. ^f (%)
						Sulfur	H ⁺	
Pr-SBA-15	111	82	666	1.19	32	1.17	1.21	91
Ar-SBA-15	103	80	720	1.03	26	1.20	1.24	99

^a d (100) spacing, measured from small-angle X-ray diffraction.

^b Mean pore size (D_p) from adsorption branch applying the BJH model.

^c The pore volume (V_p) was taken at $P/P_0 = 0.975$ single point.

^d Average pore wall thickness calculated by a_o -pore size ($a_o = 2 d(100) / \sqrt{3}$).

^e Acid capacities defined as milliequivalents of acid centers per gram of catalyst, obtained either directly by titration (meq H⁺/g) or indirectly from sulfur content by elemental analysis (meq S/g).

^f Organic incorporation estimated from actual sulfur content and maximum theoretical content.

Additionally, some characterization data corresponding to the commercial sulfonic acid-based resins used in this study with the purpose of comparison is summarized in Table 2. In this case, the characterization is provided by the suppliers (Rohm & Haas for the Amberlyst resins, Purolite for the CT-275 and DuPont for SAC-13 nanocomposite).

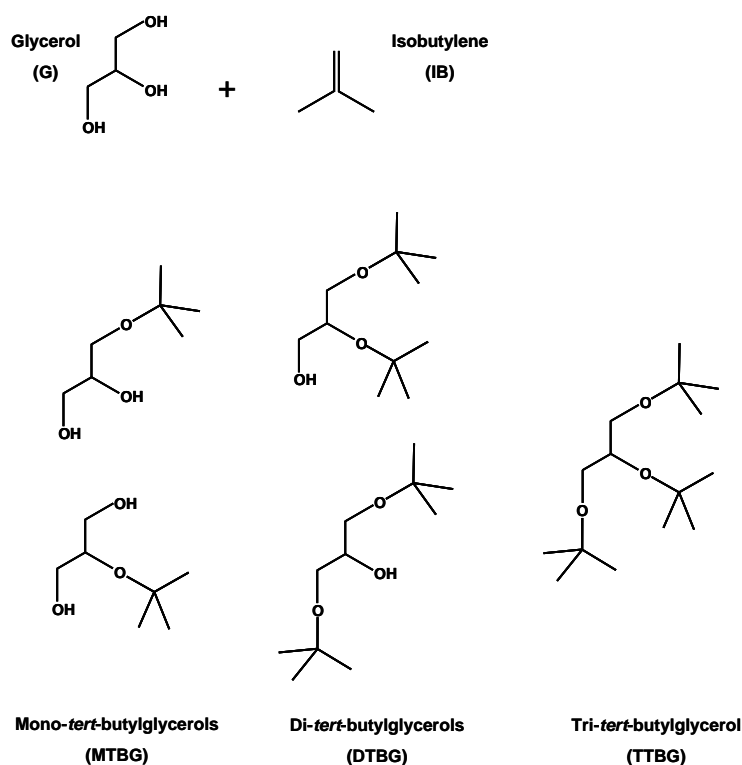
Table 2. Physicochemical properties for commercial SO₃H-based resins^a.

Catalyst	Acid capacity (meq H ⁺ /g)	BET area (m ² /g)	Pore volume (cm ³ /g)	Pore Size (Å)	Temp. limit (°C)
Amberlyst-15	≥4.70	53	0.4	300	120
Amberlyst-36	≥5.40	33	0.2	240	150
CT-275	≥5.20	20-40	0.4-0.6	400-700	145
SAC-13	0.12	>200	0.6	>100	200

^a Properties provided by the suppliers.

2.3 Reaction procedure

Scheme 1 is a representation of the etherification of glycerol with isobutylene, showing the main etherification products: mono-*tert*-butylglycerols (MTBG), di-*tert*-butylglycerols (DTBG), and tri-*tert*-butylglycerol (TTBG). Note that MTBG and DTBG can include several isomers depending upon the etherification position within the glycerol molecule. Hence, herein the terms MTBG and DTBG are intended to embrace all the possible mono- and di-*tert*-butyl-ethers, respectively. Being undesired the presence of MTBG in the final product, reaction conditions must be established with the purpose of maximizing the production of the di- and tri-derivatives.



Scheme 1. Main reaction products in the glycerol etherification with isobutylene.

Etherification experiments were performed in liquid phase at temperatures ranging from 60 to 90 °C in a stainless steel stirred autoclave (150 mL) equipped with a temperature controller and a pressure gauge, operating under autogenous pressure. Liquid phase pressurized isobutylene was injected into the reactor at the beginning of the reaction using nitrogen at 8 bar as pushing agent. Stirring was fixed for all the experiments at 1000 rpm to avoid external diffusional limitations. In order to monitor the reaction progress, reaction time was set at 1 and/or 4 hours. Typically, the composition of the reaction mixture was: 10 g of glycerol, Isobutylene/Glycerol (IB/G) molar ratio (MR) ranging from 2/1 to 4/1; and constant catalyst loading of 5 wt. % (referred to glycerol mass). Reaction samples were analyzed by GC (Varian 3900 chromatograph) using a CP-WAX 52 CB column (30m x 0.25 mm, DF=0.25) and a FID detector. Reaction products detected by GC included glycerol ethers and in certain cases di-isobutylenes (DIB), coming from the acid-catalyzed dimerization of isobutylene but

tert-butanol was not detected. The olefin dimerization is an undesired side reaction that depends upon the reaction conditions (especially favored at high temperatures and times when using over-stoichiometric amounts of IB). The unique products coming from glycerol are *tert*-butylated derivatives. Catalytic results are shown either in terms of absolute conversion of glycerol or in terms of weight products distributions or selectivities of glycerol toward *tert*-butylated derivatives. Selectivities and weight products distributions were obtained by GC using commercial MTBG to obtain a response factor that was extrapolated to DTBG and TTBG, non-commercially available.

3. Results and Discussion

3.1. Design of experiments

In this part of the work, the production of alkyl ethers of glycerol using a propyl-SO₃H-functionalized mesostructured silica (Pr-SBA-15) as a catalyst was developed and optimized by following factorial design and response surface methodology [24]. The experimental design applied to this study was a full 3² design (two factors each one at three levels). The central point experiment was repeated three times in order to determine the variability of the results and to assess the experimental errors. The responses selected were the glycerol conversion, X_G , and the selectivities towards the different ether derivatives, S_{MTBG} , S_{DTBG} and S_{TTBG} . The production of isobutylene oligomers was not considered in the optimization, because the isobutylene oligomerization was negligible using Pr-SBA-15 as a catalyst. In this sense, the optimisation was carried out to achieve high conversions of glycerol and high selectivities to DTBG and TTBG. The MTBG derivatives cannot be used as diesel additives since they are relatively soluble in water. Selection of the factors was based on

the operating conditions that have a significant influence on the glycerol etherification. As a result, the factors chosen were temperature, T , and the molar ratio of isobutylene to glycerol, MR . Selection of the levels was based on results obtained in previous studies [14-15], considering the constraints imposed by the experimental installation and the working conditions of all reactants and products. The lower and upper temperature levels were 60 and 90 °C, respectively. The levels of the IB/G molar ratio were 2/1 and 4/1 (upper levels were not considered since this olefin has a high demand in refinery for the preparation of trialkylethers and alkylates and it is not supposed to be so available). Thus, the standard experimental matrix for the design is shown in Table 3. Columns 4 and 5 represent the 0 and ± 1 encoded factor levels on a dimensionless scale, whereas columns 2 and 3 represent the factor levels on a natural scale. Experiments were run at random to minimize errors due to possible systematic trends in the variables. Table 3 also shows the results of the glycerol conversion and the selectivities towards MTBG, DTBG and TTBG after 4 hours of reaction.

From the matrix generated by the experimental data and assuming a second-order polynomial model, equations 1-10 were obtained by multiple regression analysis (Table 4). The statistical model is obtained from encoded levels giving the real influence of each variable on the process and the technological model is obtained from the real values of the variables. Consequently, the influence of variables on the responses is discussed using the statistical models shown in Equations 1 to 5.

Table 3. Experiment matrix and experiment results for the etherification of glycerol with isobutylene over propylsulfonic acid-modified mesostructured silica, Pr-SBA-15 [Catalyst/Glycerol weight ratio = 5%; Reaction time = 4 hours].

Run Number	T (°C)	MR	I _T	I _{MR}	X _G (%)	S _{MTBG} (%)	S _{DTBG} (%)	S _{TTBG} (%)
1	90	4:1	+1	+1	97	16	62	22
2	90	2:1	+1	-1	61	51	45	4
3	60	4:1	-1	+1	69	61	38	1
4	60	2:1	-1	-1	61	81	19	0
5	75	3:1	0	0	86	12	66	20
6	75	3:1	0	0	87	13	66	21
7	75	3:1	0	0	84	21	65	14
8	75	3:1	0	0	85	20	64	16
9	75	4:1	0	+1	90	14	59	27
10	90	3:1	+1	0	88	30	58	12
11	75	2:1	0	-1	72	36	56	8
12	60	3:1	-1	0	73	70	30	0

Note: T, temperature; MR, isobutylene/glycerol molar ratio; I, coded value; X_G, conversion of glycerol; S, selectivities towards the different products (MTBG, DTBG, and TTBG).

Table 4. Predictive equations obtained by design of experiments.

Statistical models		
$X_G = 86.16 + 10.33 I_{MR} + 7.17 I_T - 6.50 I_{MR}^2 + 7.00 I_{MR}I_T - 7.00 I_T^2$	(r ² =0.986)	(1)
$S_{MTBG} = 17.54 - 12.83 I_{MR} - 19.17 I_T + 5.37 I_{MR}^2 - 3.75 I_{MR}I_T + 30.37 I_T^2$	(r ² =0.984)	(2)
$S_{DTBG} = 64.46 + 6.50 I_{MR} + 13.00 I_T - 5.37 I_{MR}^2 - 18.87 I_T^2$	(r ² =0.965)	(3)
$S_{TTBG} = 17.58 + 6.33 I_{MR} + 6.17 I_T + 4.25 I_{MR}I_T - 11.25 I_T^2$	(r ² =0.935)	(4)
$S_{DTBG+TTBG} = 82.04 + 12.83 I_{MR} + 19.17 I_T - 5.12 I_{MR}^2 + 3.75 I_{MR}I_T - 30.12 I_T^2$	(r ² =0.987)	(5)
Technological models		
$X_G = -109.17 + 14.33 MR + 3.74 T - 6.50 MR^2 + 0.47 MR T - 0.03 T^2$	(r ² =0.986)	(6)
$S_{MTBG} = 903.37 - 26.33 MR - 20.78 T + 5.37 MR^2 - 0.25 MR T + 0.13 T^2$	(r ² =0.984)	(7)
$S_{DTBG} = -547.79 + 41.25 MR + 13.55 T - 5.37 MR^2 - 0.08 T^2$	(r ² =0.965)	(8)
$S_{TTBG} = -247.50 - 16.42 MR + 7.06 T + 0.28 MR T - 0.05 T^2$	(r ² =0.935)	(9)
$S_{DTBG+TTBG} = -795.29 + 24.83 MR + 20.31 T - 5.12 MR^2 + 0.25 MR T - 0.13 T^2$	(r ² =0.987)	(10)

Note: T, temperature; MR, isobutylene/glycerol molar ratio; I, coded value; X_G, conversion of glycerol; S, selectivities towards the different products (MTBG, DTBG, and TTBG). The models include only the significant terms.

Statistical analysis of the studied experimental range identifies the isobutylene/glycerol molar ratio as the most important factor in the glycerol conversion response. The second factor in importance is temperature followed by the molar ratio-temperature interaction. All of them have a positive effect on the glycerol conversion.

An increase in the molar ratio and the temperature produces an increase in the conversion of glycerol, but the enhancement of this response with temperature is more significant at high values of the molar ratio factor and the corresponding improvement with the molar ratio is also more substantial at high values of temperature. In addition, the quadratic effects of both variables have a significant negative influence on the glycerol conversion. However, their absolute values are smaller than their corresponding main effects. This, in turn, indicates that the increase in the operating variables does not produce a constant rise in the glycerol conversion, because the curvature effect is significant at high values of these variables. Figure 1 clearly shows an enhanced conversion of glycerol at high temperatures and IB/G molar ratios. Thus, from the point of view of glycerol conversion, the optimal values are the highest molar ratio (4/1) and temperature (90 °C). At these operating conditions, the glycerol conversion predicted by the non-linear model (Equations 1 or 6) is 97.2 %.

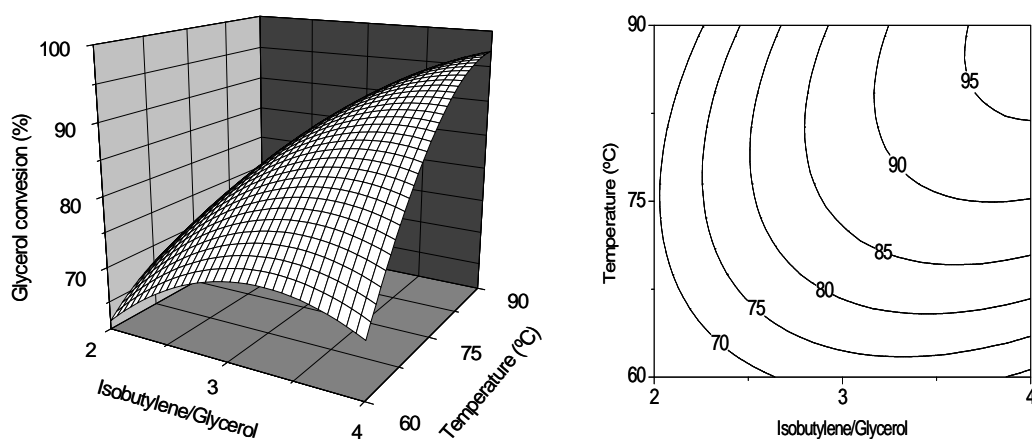


Figure 1. Response surface and contour plots of glycerol conversion. Catalyst: Pr-SBA-15. [Catalyst/Glycerol = 5 wt. %; Reaction time = 4 hours].

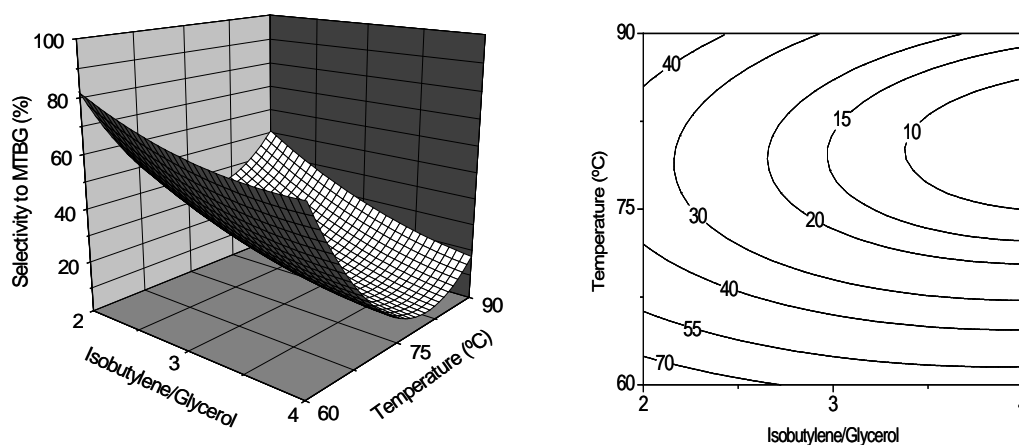


Figure 2. Response surface and contour plots of selectivity towards MTBG. Catalyst: Pr-SBA-15. [Catalyst/Glycerol = 5 wt. %; Reaction time = 4 hours].

Since the higher ethers (DTBG and TTBG) are the most suitable products for use as diesel additives, the optimum conditions for the product selectivities are those which result in the lowest selectivity to the MTBG derivative. According to Equation 2 and Figure 2, the temperature is the most significant factor in the selectivity towards MTBG, having an overall negative effect on this response. However, the quadratic effect of temperature has a very significant positive influence on this selectivity. As a consequence, the selectivity towards MTBG passes through a minimum as a function of temperature at any value of the isobutylene/glycerol molar ratio. This means that the dealkylation of higher ethers (DTBG, TTBG) with the formation of MTBG and isobutylene proceeds as a back reaction at high temperatures, although the reaction rate rises with the temperature. In addition, the selectivity to MTBG decreased with the isobutylene/glycerol molar ratio, because the conversion of glycerol enhances in line with this operating condition, favoring the production of the di- and tri-substituted derivatives. In this sense, the lowest selectivities to MTBG were obtained at temperatures between 75 and 85 °C with the highest IB/G ratio (4/1).

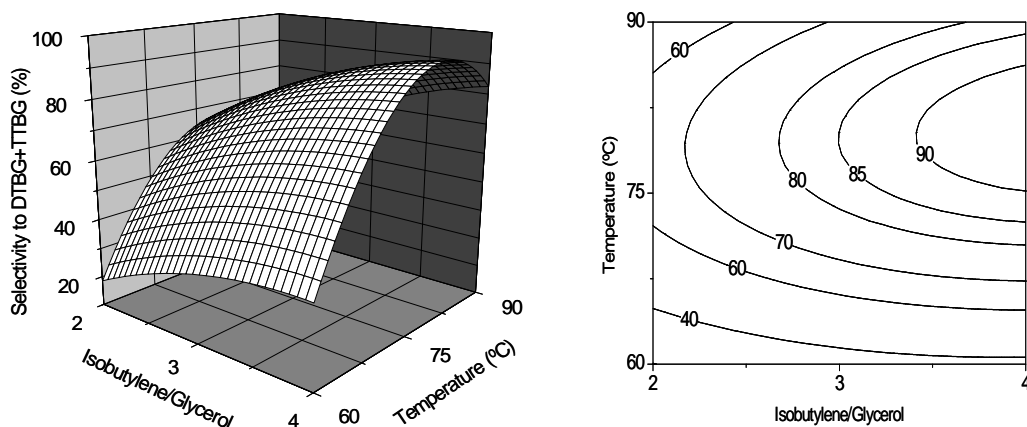


Figure 3. Response surface and contour plots for selectivity towards DTBG and TTBG. Catalyst: Pr-SBA-15. [Catalyst/Glycerol = 5 wt. %; Reaction time = 4 hours].

On the other hand, it is interesting to study the effect of operating conditions on the selectivity towards the sum of DTBG and TTBG derivatives. Thus, Equation 5 and 10 in Table 4 represent statistical and technological models for the combined selectivity to DTBG and TTBG, respectively. The technological model (Equation 10) is represented in Figure 3 as a response surface and contour plots for predicted values of this response over the experimental range studied. According to this Figure and Equation 5 (Table 4), the combined selectivity to DTBG and TTBG followed the opposite tendency to the selectivity towards MTBG, increasing consequently with the amount of isobutylene and reaching maximum values as a function of temperature before decreasing at the highest temperatures. Hence, the optimal operating conditions in terms of selectivities are the highest IB/G molar ratio (4/1) and temperatures between 75 and 85 °C, although the optimum cost-effective temperature would be the lowest one (75 °C). The selectivity to DTBG and TTBG predicted by the non-linear models is 89.8 % at a 4/1 molar ratio and 75 °C. At these operating conditions, the corresponding selectivities to MTBG, DTBG and TTBG were 10.1, 65.6 and 24.2 %, respectively.

Finally, the arithmetical averages and the standard deviations of all the responses were calculated for the central point experiments: glycerol conversion ($85 \% \pm 1.3 \%$), selectivity to MTBG ($16.5 \% \pm 4.7 \%$), selectivity to DTBG ($65.3 \% \pm 1 \%$) and selectivity to TTBG ($17.8 \% \pm 3.3 \%$). All the standard deviations were lower than 5 %. Therefore, the experimental errors corresponding to the results in Table 3 are not excessively significant. In addition, Figure 4 illustrates a graph of the residual distribution, defined as the difference between calculated and observed values for the glycerol conversion and the combined selectivity to DTBG and TTBG. In both cases, the fit is good because the residual distribution does not follow a trend with regard to the predicted variables. All the residuals are smaller than 3 % for glycerol conversion and smaller than 6 % for the selectivity to the higher ethers, which indicates that the models accurately represent the influence of both responses over the experimental range studied.

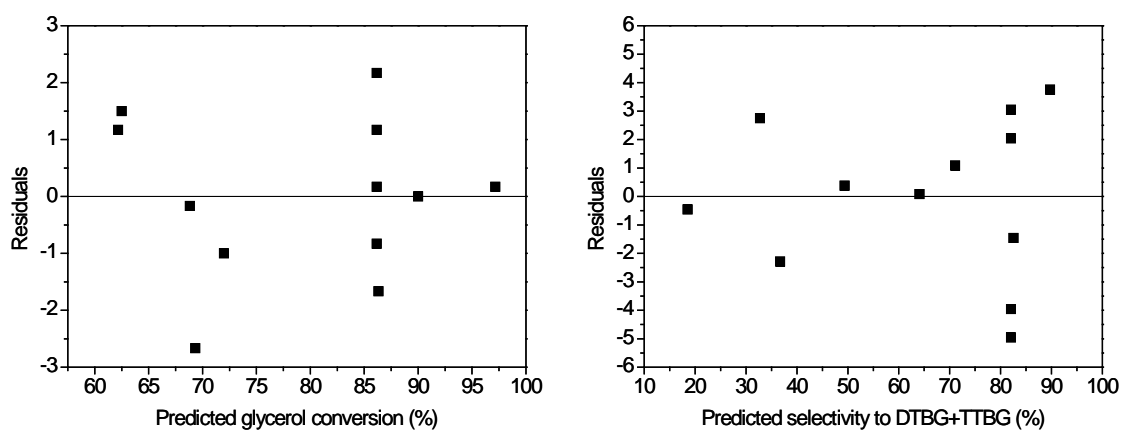


Figure 4. Residual plots of glycerol conversion and selectivity towards DTBG and TTBG.

3.2. Comparative study of sulfonic acid-modified mesostructured silicas in the etherification of glycerol with isobutylene

The feasibility of tuning the acid strength of the sulfonic-acid groups incorporated within mesostructured SBA-15-type silicas by close attachment of different moieties has led before to improvements in the catalytic activity in several acid-catalyzed reactions [17]. Taking this into account, the catalytic performance of propylsulfonic acid-modified SBA-15 has been compared with that of arene-sulfonic acid-modified SBA-15 in the *tert*-butylation of glycerol, using the optimized reaction conditions selected in the experimental design: intermediate temperature (75°C) and IB:G molar ratio (4/1). The results of glycerol *tert*-butylation with isobutylene catalysed by these two sulfonic acid-functionalized mesostructured silicas after different reaction times (1 and 4 h) are shown in Table 5.

Table 5. Comparison of sulfonic acid-functionalized mesostructured silicas for the etherification of glycerol with isobutylene.

Catalyst	Reaction time (h)	X_G (%)	Distribution of products (wt.%)				$S_{DTBG+TTBG}$ (%)
			MTBG	DTBG	TTBG	DIB	
Pr-SBA-15	1	65	68	30	2	0	24
Ar-SBA-15	1	84	16	72	12	0	77
Pr-SBA-15	4	90	9	56	35	0	86
Ar-SBA-15	4	100	5	54	41	0	92

Reaction conditions: 5.0 wt. % of catalyst referred to G, IB/G molar ratio = 4/1, temperature = 75°C. X_G : glycerol conversion. $S_{DTBG+TTBG}$: selectivity to di- and tri-ethers calculated as moles of glycerol reacted to form DTBG and TTBG referred to total moles of reacted glycerol.

The highest conversions of glycerol (X_G) have been obtained with the arenesulfonic acid-modified sample (Ar-SBA-15). Indeed, after only 4 hours of reaction the conversion of glycerol over this catalyst achieved a value of 100%, being the conversion within the first hour as high as 84%. Likewise, as shown in the experimental design, the relatively weak propyl-SO₃H active sites in Pr-SBA-15 provided a X_G of 90% after 4

hours. However, when considering this catalyst within the first hour of reaction the conversion remained much lower (65%). Since both mesostructured catalysts have similar textural properties, the differences in their catalytic performances are attributed to the lower acid strength of propyl-SO₃H sites in comparison to that of arene-SO₃H moieties. In a recent publication, we have shown that the most active acid catalyst in the acetylation of glycerol with acetic acid is the one characterized by the highest acid strength, i.e. the arene-SO₃H-functionalized one [25]. This indicates a clear improvement in the present catalytic process when using acid sites with higher acid strength.

The distribution of products presented in Table 5 (as wt. %), considering the di- and tri-ethers of glycerol as the most-desired products, shows that the catalyst Ar-SBA-15 gives the highest productions of DTBG and TTBG. In terms of selectivity towards di- and tri-ethers, a value of 92% is obtained over Ar-SBA-15 after 4 hours (77% after 1 h). Likewise, the amount of non-desired MTBG decreases up to 5 wt. % after 4 hours of reaction. Furthermore, no presence of oligomerization products (DIB) is detected even after 4 hours of reaction over Ar-SBA-15 or Pr-SBA-15 catalysts. This indicates that the use of a silica matrix avoids/reduces the process of isobutylene oligomerization, in contrast to sulfonic acid resins previously reported for the *tert*-butylation of glycerol [26]. This is an important benefit because isobutylene oligomers might lead to the formation of undesirable deposits in the motor during the combustion, and therefore they would have to be removed from the fuel additive before use, increasing the economic costs. In conclusion, Ar-SBA-15 has been demonstrated as an excellent catalyst for the etherification of glycerol with isobutylene.

Catalyst life has also been evaluated for Ar-SBA-15. Figure 5 depicts the results of four consecutive catalytic runs performed reusing the catalyst under the optimal reaction conditions selected in the experimental design. After each catalytic run, recovering of the catalyst was performed by filtration, mild-washing in ethanol and acetone at room temperature and air-drying. As concluded from Figure 5, no significant loss of catalytic activity or selectivity is observed after 4 hours of reaction in successive catalytic runs.

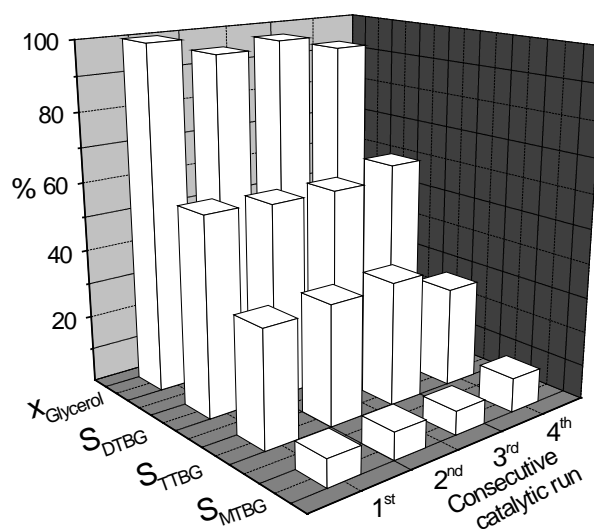


Figure 5. Reuse of catalyst: conversion of glycerol and selectivity towards MTBG, DTBG and TTBG after 4 hours of reaction in four consecutive catalytic runs reusing catalyst Ar-SBA-15. Temperature 75°C; IB/G molar ration 4/1, catalyst 5 wt. % referred to glycerol.

3.3. Comparative study among sulfonic acid-modified mesostructured silicas and commercial sulfonic resins in the etherification of glycerol with isobutylene.

Another purpose of the present work is to benchmark the catalytic performance of the mesostructured silicas with that of sulfonic macroporous resins, commercially available and conventionally used in acid-catalyzed processes. Thus, activity and selectivity of the arenesulfonic acid-modified SBA-15 sample (Ar-SBA-15, Table 1), have been compared with those provided by several sulfonic-acid resins such as Amberlyst 15 (A-15), Amberlyst 36 (A-36), and CT-275, and by perfluorosulfonic-acid resin supported on silica (Nafion® SAC-13). These acid resins are industrially used in several acid-catalyzed processes such as the production of ethyl *tert*-butyl ether (ETBE) for gasoline formulation. Likewise, they have been previously reported as active catalysts in the derivatization of glycerol to obtain fuel additives. Thus, they have been shown to be active and selective in the acetylation of glycerol [25] and in the *tert*-butylation of glycerol with isobutylene [14-16, 26]. Table 2 summarizes the main physicochemical properties of these acid commercial catalysts, as provided by the corresponding suppliers. Each catalytic test was run in the optimized reaction conditions within the evaluated range (temperature 75°C, and IB:G molar ratio 4:1), and using a constant mass of catalyst (5 wt. % referred to glycerol).

Table 6. Comparison of sulfonic acid-based mesostructured and commercial catalysts for the etherification of glycerol with isobutylene.

Catalyst	Reaction time (h)	X_G (%)	Distribution of products (wt.%)				$S_{DTBG+TTBG}$ (%)
			MTBG	DTBG	TTBG	DIB	
Ar-SBA-15	1	84	16	72	12	0 (0.0) ^b	77
A-15	1	95	3	54	37	6 (5.9) ^b	94
A-36	1	98	8	68	20	4 (3.7) ^b	88
CT-275	1	89	3	69	25	3 (2.6) ^b	95
SAC-13	1	- ^a	-	-	-	-	-
Ar-SBA-15	4	100	5	54	41	0 (0.0) ^b	92
A-15	4	99	6	51	28	15 (16.6) ^b	90
A-36	4	96	6	51	32	11 (11.4) ^b	89
CT-275	4	100	8	55	30	7 (7.1) ^b	87
SAC-13	4	- ^a	-	-	-	-	-

Reaction conditions: 5.0 wt.% of catalyst referred to G, IB/G molar ratio = 4/1, temperature = 75°C. X_G : glycerol conversion. $S_{DTBG+TTBG}$: selectivity to di- and tri-ethers calculated as moles of glycerol reacted to form DTBG and TTBG referred to total moles of reacted glycerol.

^a System with two phases, indicating low glycerol conversion (below 50%), not possible to be accurately quantified. ^b In brackets, percent of the initial IB that oligomerises.

Considering the conversion of glycerol (X_G), after 1 hour each commercial catalyst (except SAC-13) gave higher conversion than the mesostructured material, reaching values close to 100% (A-36). This evidences the high catalytic activity of these polymeric materials, mainly attributed to their extremely high sulfonic acid sites loading (Table 2). Nevertheless, after 4 h of reaction Ar-SBA-15 shows 100% of glycerol conversion, similar to that of Amberlyst-type catalysts. Therefore, despite its lower acid capacity (i.e., lower number of sulfonic acid sites per gram of catalyst), Ar-SBA-15 appears to be an excellent and competitive catalyst for the *tert*-butylation of glycerol. Nanocomposite Nafion-based SAC-13 gave poor activities even after 4 hours of reaction, leading to biphasic systems with low glycerol conversion. This result is surprising, since due to the presence of electron-withdrawing fluorine atoms close to the sulfonic acid moieties in the Nafion resin, the acid strength of this catalyst is even

higher than that of Ar-SBA-15. Indeed, the measure of the chemical shift of adsorbed triethyl phosphine oxide by ^{31}P MAS NMR spectroscopy on this material provides a signal at 88 ppm [27], indicating the presence of strong acid sites. Increasing values of said chemical shift indicate increasing acid strength [28]. Similar ^{31}P NMR measurements have been previously reported for the samples Pr-SBA-15, Ar-SBA-15 and A-15, providing chemical shifts of 71.1, 75.5, and 86.0, respectively [23]. All these values are lower than that for SAC-13, revealing lower acid strengths. Then, the low activity of SAC-13 in the *tert*-butylation of glycerol might be attributed to its limited acid capacity, 0.12 meq H^+ /g (Table 2), which would hinder the availability of active sites for the acid catalysis to proceed.

Table 6 also shows the distribution of products obtained with each catalyst. It is important to note that under the optimized reaction conditions the sulfonic acid resins produce di-isobutylenes (DIB), the non-desired byproducts which can be problematic when formulated with fuels. Furthermore, the amount of DIB produced over the three sulfonic acid-based resins (A-15, A-36 and CT-275) increases with time up to values of 15 wt. %. Once the glycerol has been almost completely converted (X_G close to 100%), these polymeric catalysts seem to be able to further dimerize the remaining isobutylene to produce the corresponding DIB. This is consistent with values reported previously where reaction times of 8 hours have been considered and larger amounts of DIB have been obtained [26]. In contrast, sulfonic acid-modified mesostructured silica Ar-SBA-15 produced no DIB, as determined by GC, even after 4 hours of reaction. In conclusion, polymeric (polystyrene-type) environment for the SO_3H sites favors the dimerization of isobutylene in a greater extent than the silica environment of Ar-SBA-15. Another important issue when preparing this kind of diesel additives is to reduce the amount of MTBG due to its relatively high solubility in water. From this point of view,

after 1 h of reaction the commercial resins provide lower amounts of MTBG than the Ar-SBA-15 material. Thus, the amount of MTBG reaches a minimum of 3 wt. % for the CT-275 and A-15 after 1 h. However at this point the X_G measured is still relatively low (89 % and 95%, respectively), being this parameter even more important than the amount of MTBG. When considering a reaction time of 4 hours, MTBG content is kept as low as 5 wt. % over Ar-SBA-15, which is in the order of that shown by sulfonic resins. The combination of 100% glycerol conversion, with very low formation of mono-substituted derivative (MTBG) and no formation of undesired di-isobutylenes makes Ar-SBA-15 a particularly interesting catalyst for this etherification reaction.

4. Conclusions

Sulfonic acid-functionalized mesostructured silicas have demonstrated an excellent catalytic behavior in the etherification of glycerol with isobutylene to yield *tert*-butylated compounds. Their activity and selectivity towards valuable products for fuel bio-additives (DTBG and TTBG) have shown to be comparable or even superior to those of macroporous sulfonic acid resins. The experimental design model carried out for different levels of temperature and isobutylene to glycerol molar ratios has shown that is necessary to use high isobutylene excesses in order to simultaneously maximize the conversion of glycerol and the selectivity towards the most valuable di- and tri-*tert*-butylated derivatives. Likewise, in order to attain optimal glycerol conversion as well as high yields towards DTBG and TTBG, is advantageous to work with moderate temperatures. Within the studied range, optimal conditions have been found to be 75°C and isobutylene to glycerol molar ratio of 4/1. Using these reaction conditions, glycerol conversions up to 100% and combined selectivities towards di- and tri-*tert*-butylglycerol over 92% were achieved after 4 hours of reaction over arenesulfonic-acid-

modified SBA-15 without isobutylene oligomerization. The acid strength of the catalytic sites has also been shown to be an influential parameter in the catalytic performance. The use of moderately strong acid centers, such as those located in arenesulfonic-acid modified mesostructured silicas, provides improved results both in glycerol conversion and selectivity towards the desired products.

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