Acetalisation of bio-glycerol with acetone to produce solketal over sulfonic mesostructured silicas†

Gemma Vicente,*[a] Juan A. Melero,[b] Gabriel Morales,[b] Marta Paniagua[b] and Eric Martín[b]

Received 13th November 2009, Accepted 19th February 2010
First published as an Advance Article on the web 22nd March 2010
DOI: 10.1039/b923681c

Downloaded by City College of New York on 24 November 2010
Published on 22 March 2010 on http://pubs.rsc.org | doi:10.1039/B923681C

Sulfonic acid-functionalized mesostructured silicas have demonstrated excellent catalytic behaviour in the acetalisation of glycerol with acetone to yield 2,2-dimethyl-1,3-dioxolane-4-methanol, also known as solketal. This molecule constitutes an excellent compound for the formulation of gasoline, diesel and biodiesel fuels. The activity achieved with arenesulfonic acid-functionalized silica is comparable to that displayed by Amberlyst-15. Optimal production of solketal over arenesulfonic acid mesostructured silica has been established for a reaction system consisting of three consecutive 2-step batches (30 min under reflux and an evaporation step under vacuum), and using a 6/1 acetone/glycerol molar ratio. The use of lower grades of glycerol, such as technical (purity of 91.6 wt%) and crude (85.8 wt%) glycerol, has also provided high conversions of glycerol over sulfonic acid-modified heterogeneous catalysts (84% and 81%, respectively). For refined and technical glycerol the catalysts have been reused, without any regeneration treatment, up to three times, keeping the high initial activity. However, the high sodium content in crude glycerol deactivates the sulfonic acid sites by cation exchange. This deactivation is readily reversed by simple acidification of the catalyst after reaction.

1. Introduction

Biodiesel constitutes a renewable fuel that is almost compatible with commercial diesel engines and has clear benefits relative to diesel fuel, including enhanced biodegradation, reduced toxicity and a lower emission profile.[1] In a recent European Union (EU) Directive (2009/28/EC), biodiesel is defined as a methyl ester produced from vegetable or animal oil, of diesel quality, to be used as biofuel. Methyl esters, usually referred to as fatty acid methyl esters (FAMEs), are products from the transesterification of vegetable oils and animal fats with methanol in the presence of an acid catalyst or a basic one.[2] In addition, the process yields an amount of glycerol which is equivalent to approximately 10 wt% of the total biodiesel produced. The glycerol obtained at this stage is called crude glycerol and it is about 80% pure, the main contaminants being soaps, salts, methanol and water. By further refinement, this glycerol turns into usable and profitable grades. Thus, technical glycerol (>90% pure) is obtained as an intermediate to high-purity glycerol (pharmaceutical-grade glycerol). It results essentially from a desalting process. Finally, pharmaceutical glycerol (>99.7% pure) is produced by additional purification through distillation.

In turn, the EU 2009/28/EC Directive establishes a 10% share of energy from renewable sources for transport in EU energy consumption by 2020. Conversely, another EU Directive (2003/96/EC) allows the Member States exemptions or reductions on excise duties so as to promote biofuels. As a consequence, and also taking into account the unstable petroleum prices, there is a growing interest in FAMEs as an alternative diesel fuel in Europe. That implies an increase in biodiesel manufacturing in the next few years, which also means a dramatic rise in the availability of its by-product (crude glycerol). In fact, the production of this biofuel has already increased significantly in the EU in recent years, reaching a production of 7.75 million tonnes in 2008.[3] Therefore, the value of glycerol has fallen as a result of its oversupply in the global market.

In this context, important research is currently being developed in order to find new applications for this cheap and off-grade glycerol from biodiesel plants. Some recent reviews have dealt with the related research into glycerol upgrading to be processed into valuable chemicals.[4–9] These strategies include selective oxidation to produce a range of products such as dihydroxyacetone, glyceraldehyde, glyceric acid, glycolic acid, hydroxypyruvic acid, mesoxalic acid, oxalic acid, and tartronic acid; reduction to obtain 1,3-propanediol and 1,2-propanediol; hydrogenolysis to obtain propylene glycol; dehydration to yield acrolein or 3-hydroxypropionaldehyde; halogenation to produce 1,3-dichloropropanol (intermediate in the epichlorohydrin synthesis); fermentation towards 1,3-propanediol; or polymerization to obtain polyglycerols and polyglycerol esters. Apart from these alternatives, the transformation of glycerol into fuel oxygenates is being explored by means of etherification with olefins or alcohols,[10–17] esterification with low molecular weight

---

[a]*Department of Chemical and Energy Technology, ESCET, Universidad Rey Juan Carlos, C/Tulipán s/n, 28933, Móstoles, Madrid, Spain. E-mail: gemma.vicente@urjc.es; Fax: +34 91 488 70 68; Tel: +34 91 488 85 31*
[b]*Department of Chemical and Environmental Technology, ESCET, Universidad Rey Juan Carlos, C/Tulipán s/n, 28933, Móstoles, Madrid, Spain*

† Electronic supplementary information (ESI) available: XRD patterns; nitrogen adsorption-desorption isotherms. See DOI: 10.1039/b923681c

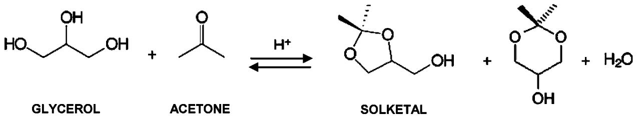
Downloaded by City College of New York on 24 November 2010
Published on 22 March 2010 on http://pubs.rsc.org | doi:10.1039/B923681C

acids,[18–21] transesterification using low molecular weight esters[18] and acetalisation with aldehydes or ketones.[18,22–27] This approach is a promising and economically viable alternative since it not only makes a profitable use of glycerol but also increases the yield of biofuel in the overall biodiesel production process, helping to meet the target for energy from renewable sources for transport in the EU Directive.

Special interest is focused on the preparation of acetals and ketals of glycerol by acetalisation with an aldehyde or a ketone, respectively, in the presence of an acid catalyst. The most-used solid acids for the production of these glycerol derivates have been homogeneous catalysts (mainly *p*-toluenesulfonic acid),[18,23,26] ion-exchange organic resins[22,24,25,28] and acid zeolites.[25,27] Acetals and ketals of glycerol constitute an excellent component for the formulation of gasoline, diesel and biodiesel fuels. These oxygenated compounds, when incorporated into standard diesel fuel, have led to a decrease in particles, hydrocarbons, carbon monoxide and unregulated aldehyde emissions.[18,24] Likewise, these products can act as cold flow improvers for use in biodiesel, also reducing its viscosity.[18] This issue is of significant importance due to the growing demand for new additives specifically for biodiesel that are biodegradable, non-toxic and renewable. More recently, García *et al.*[26] confirmed that the addition of these compounds to biodiesel improved the viscosity and also met the established requirements for flash point and oxidation stability.

The main drawback of the glycerol acetalisation is the production of water, which has to be removed in order to hinder the reversibility of the reaction. The use of solvents such as benzene, toluene, petroleum ether or chloroform to increase the conversion of glycerol into acetals or ketals has been described.[25] However, this method is not very efficient in this reaction and presents environmental problems. In addition, Bruchmann *et al.*[23] have used aldehyde or ketone in excess, which is continuously removed by distillation during the reaction to favour the irreversibility of this reaction and increase the glycerol conversion. The level of liquid in the reactor was kept constant by continuously feeding dry aldehyde or ketone. Also, continuous processes for the formation of solketal employing heterogeneous catalysts, such as the commercial macroporous acid resins of the Amberlyst family, have been described by others authors.[24,25] More recently, da Silva *et al.*[27] reported the use of zeolite Beta with a Si/Al ratio of 16 as a catalyst for the acetalisation of glycerol. The hydrophobic character of this zeolite prevents the diffusion of the water into the pores, preserving the strength of the acid sites and impairing the reverse reaction.

In this work, the synthesis of solketal (2,2-dimethyl-1,3-dioxolan-4-methanol) from glycerol acetalisation with acetone (Scheme 1) was carried out, for the first time, over different sulfonic acid-modified mesostructured silicas. These materials, characterized by high surface areas, large uniform pores, high thermal stability, and the possibility of controlling the surface hydrophilic/hydrophobic balance as well as the strength and concentration of acid sites,[29] appear to be promising catalysts for the acid-catalyzed transformation of bulky molecules such as glycerol. Indeed, they have previously demonstrated an excellent catalytic behaviour in the transformation of glycerol into fuel components by means of etherification with isobutylene[17] and esterification with acetic acid.[19]



Scheme 1 Main reaction products in the glycerol acetalisation with acetone.

The catalytic performance of these sulfonic acid-modified mesostructured silicas has been benchmarked with other commercial acid catalysts. In addition, the process was developed and optimised by following the factorial design and response surface methodology. This technique is a powerful tool that involves many advantages that have been described in previous studies.[30] Finally, the effects of different glycerol grades ranging from crude glycerol to refined glycerol (pharmaceutical grade) were evaluated in this acetalisation reaction.

2. Experimental section

2.1. Catalysts preparation

Propylsulfonic acid-functionalized mesostructured silica (Pr-SBA-15) was synthesized following a previously reported procedure.[31] The molar composition of the mixture for 4 g of templating co-polymer was: 0.0369 tetraethylorthosilicate (TEOS, Sigma-Aldrich), 0.0041 mercaptopropyltrimethoxysilane (MPTMS, Sigma-Aldrich), 0.0369 H_2O_2, 0.24 HCl, and ≈6.67 H_2O.

Arenesulfonic acid-functionalized mesostructured silica (Ar-SBA-15) was obtained as described elsewhere.[31] In this case, the molar composition of the mixture for 4 g of co-polymer was: 0.0369 TEOS, 0.0041 chlorosulfonyl-phenyl ethyltrimethoxysilane (CSPTMS, ABCR), 0.24 HCl, and ≈6.67 H_2O. The amount of sulfur-containing precursor in both materials (MPTMS and CSPTMS) was established to be 10 mol% of total silicon species.

Hydrophobized arenesulfonic acid-functionalized mesostructured silica (Hydrophobized Ar-SBA-15) was synthesized in order to increase the surface hydrophobicity of the abovementioned catalyst. For this purpose, 1 g of dried arenesulfonic acid material was subjected to a silylation procedure of capping the free surface silanol groups (Si–OH) by reacting them with trimethylmethoxy silane (1 g) in dry toluene under reflux (12 h).

Other commercial catalysts used in this work were Nafion®-SiO_2 composite (SAC-13) with resin content in the range of 10–20 wt%, supplied by DuPont, and an ionic-exchange sulfonic acid-based macroporous resin, Amberlyst 15, supplied by Rohm and Haas. Both catalysts were ground to powder in order to minimize mass transfer limitations and thus avoid distortions in the catalytic results. Also, arenesulfonic and propylsulfonic-acid-functionalized non-ordered silicas, under the commercial names Silia*Bond*® Tosic Acid and Silia*Bond*® Propylsulfonic Acid, were acquired from Silicycle directly in powder form.

2.2. Catalyst characterization

In order to characterize textural properties of the synthesized catalyst, nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics TRISTAR 3000 system. The data was analyzed using the BJH model and

Downloaded by City College of New York on 24 November 2010
Published on 22 March 2010 on http://pubs.rsc.org | doi:10.1039/B923681C

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

	Textural Properties					Acid Properties		
						Acid capacity[e]/ meq g^{-1}		
Sample	d_{100}[a]/Å	Pore size[b]/Å	BET area/m^2 g^{-1}	Pore volume[c]/cm^3 g^{-1}	Wall thickness[d]/Å	Sulfur	H^+	Accessibility[f] (%)
Pr-SBA-15	104	81	721	1.44	39	0.95	0.94	99
Ar-SBA-15	108	92	712	1.03	32	1.05	1.06	100
Hydrophobized Ar-SBA-15	114	83	533	0.75	48	1.01	1.04	100

[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 $P/P_o = 0.975$ 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 meq of acid centers per g of catalyst (obtained either directly by titration or indirectly from sulfur content by elemental analysis). [f] Defined as the ratio between H^+ from acid–base titration and sulfur content from elemental analysis.

total pore volume was taken at $P/P_o = 0.975$ single point. Structural ordering was determined by X-ray powder diffraction (XRD) on a PHILIPS X'PERT diffractometer using Cu-Kα radiation. Cationic-exchange capacities corresponding to the sulfonic acid-modified mesostructured materials (acid capacity) were measured using 2M NaCl (aq.) as cationic-exchange agent. The resulting suspension was potentiometrically titrated at room temperature by dropwise addition of 0.01 M NaOH (aq). Sulfur and organic contents were determined by means of elemental analysis in a Vario EL III apparatus, and thermogravimetric analysis (SDT 2960 Simultaneous DSC-TGA, from TA Instruments).

Table 1 summarizes the most relevant physicochemical properties for the sulfonic acid-modified mesostructured materials. Data from XRD and nitrogen 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 the pore size when relatively bulky substrates such as glycerol derivatives are considered). All the materials, prepared through a co-condensation technique, display high incorporation yields for the sulfonic acid moieties. It must be noted that the mesostructure of the hydrophobized Ar-SBA-15 was not modified by the silylation procedure, although the incorporation of trimethylsilyl species on the silica mesopores produces an increase of the apparent wall thickness accompanied by a slight decrease in pore volume and BET surface area.

Additionally, some characterization data corresponding to the commercial sulfonic acid-based catalysts 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 resin, DuPont for SAC-13 nanocomposite, and Sylicycle for the functionalized silicas).

2.3. Reaction procedure

Crude, technical and pharmaceutical grade glycerols 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 analyses, acetone (99.93% purity), solketal (98% purity) and 1,4-butanediol (99% purity), were purchased from Sigma-Aldrich.

Scheme 1 is a representation of the acetalisation of glycerol with acetone. This reaction yields the five- and the six-membered ring isomers, whose relative formation depends on the acetalisation position within the glycerol molecule. In this case, the five-membered ring compound, solketal, is obtained in a ratio of 99 : 1,[5] and thus will be the only product considered. In addition, water is a by-product of the reaction. Other secondary products (*e.g.* polyglycerols) were not detected.

As previously stated, it is important to note that the present reaction possesses an unfavourable equilibrium constant. Taking this into account, to reach high conversions of glycerol it is necessary to shift the equilibrium towards the formation of solketal, feeding acetone in excess or continuously removing the water generated during the reaction.[23] For this reason, the reaction was carried out following a two-step batch mode of operation. In the first step, the reaction mixture (glycerol, acetone and the catalyst) was stirred under reflux in a 100 mL round-bottom flask fitted with a water-cooled condenser (refluxing stage). Agitation was fixed at 500 rpm using a magnetic stirrer, and the reaction temperature was achieved using a thermally controlled water bath at 70 °C. Then, in a second step, the water produced during the reaction along with the excess of acetone was removed by extraction under vacuum keeping the flask at 70 °C. For the study of this reaction system, the number of two-step batches has

Table 2 Physicochemical properties corresponding to commercial sulfonic acid-based catalysts[a]

Catalyst	Acid capacity/meq H^+ g^{-1}	BET area/m^2 g^{-1}	Pore size/Å	Pore volume/cm^3 g^{-1}	Max. Op. T/°C
Amberlyst-15	≥4.80	53	300	—	120
Silia*Bond*® Propylsulfonic Acid	1.04	301[b]	20–200[b]	0.44	>200
Silia*Bond*® Tosic Acid	0.78	279[b]	20–200[b]	0.38	>200
Nafion® SAC-13	0.12	>200	>100	—	200

[a] Properties provided by the suppliers. [b] Experimentally determined by N_2 adsorption-desorption isotherm at 77 K.

View Online

Downloaded by City College of New York on 24 November 2010
Published on 22 March 2010 on http://pubs.rsc.org | doi:10.1039/B923681C

been considered as an additional reaction variable. Thus, every batch consisted of a certain reaction time under reflux followed by vacuum extraction, and the addition of fresh acetone to start a new cycle. Typically, weight composition of the reaction mixture was 5 g of glycerol, from 6.3 g to 18.9 g of acetone (which also played the role of solvent), which means from a 2/1 to 6/1 acetone/glycerol molar ratio, and a constant catalyst loading of 0.25 g (5 wt% based on glycerol).

Reaction samples were analyzed by GC (Varian 3900 chromatograph) using a CP-WAX 52 CB column (30 m × 0.25 mm, DF = 0.25) and a flame ionization detector (FID). Catalytic results are shown in terms of absolute conversion of glycerol. Solketal was the only reaction product detected by GC. The GC-quantified amount of this compound matches with the reacted glycerol, indicating that no other secondary products are being obtained in significant amounts.

3. Results and discussion

3.1. Screening of catalysts

First of all, a screening of different sulfonic acid-modified solids as catalysts was performed. This comparative study was focused on the analysis of catalytic properties such as acid site strength and concentration, surface hydrophobicity, and porous structure, and their effect on the catalytic conversion of glycerol into solketal. For all the catalysts, reaction conditions were fixed as follows: single batch (reaction time 30 min), bath temperature 70 °C (under reflux), acetone/glycerol molar ratio 6/1 and pharmaceutical grade glycerol.

Fig. 1 shows the conversion of glycerol achieved by each catalyst. Three groups of catalysts are shown: arenesulfonic acid-functionalized silicas, propylsulfonic acid-functionalized silicas, and sulfonic acid-modified commercial catalysts. The highest conversion (85.1%) was obtained over the sulfonic acid resin Amberlyst-15, despite its poor structural properties and low surface area. Acid site concentration—almost 5 meq H^+ g^{-1} in this catalyst—appears to be the most influential factor affecting the progression of the reaction. Also, sulfonic acid-functionalized silicas display high conversion rates, especially those comprised of arenesulfonic acid catalytic sites, which provide higher activities than the corresponding propylsulfonic silicas (*e.g.*, 82.5% for Ar-SBA-15 *vs.* 79.0% Pr-SBA-15). Thus, the higher acid strength of the phenylsulfonic acid moiety relative to that of the alkylsulfonic acid site[29] can also be considered a beneficial factor for the development of the catalytic process. Importantly, arenesulfonic acid-modified mesostructured SBA-15 resulted in a glycerol conversion very close to that achieved by the resin Amberlyst-15, even with a much lower acid site concentration.

Comparing the results obtained with the three arenesulfonic acid-modified silicas, the best performance was achieved by the sample Ar-SBA-15. However, the same material after surface hydrophobization—hydrophobized Ar-SBA-15—did not result in an improved glycerol conversion but instead in a slight decrease. The synthesis of this modified sample was directed to displace the reaction equilibrium by affecting the local concentration of water molecules inside the mesopores, in an attempt to improve the overall glycerol conversion. The lower conversion obtained using this catalyst compared to the parent material can be ascribed to a combination of two factors. Firstly, the passivation process reduces the available surface area from 739 to 533 m^2 g^{-1}, and secondly the hydrophobization of the mesopores may also affect the local concentration of other polar molecules aside from water (dielectric constant, $\varepsilon_0 = 80.0$), such as acetone and glycerol (dielectric constants, 20.7 and 42.5, respectively). Hence, the use of hydrophobic catalysts in this reaction is not a valid approach. Likewise, the arenesulfonic acid-functionalized non-ordered silica—Tosic acid-SiO_2—gave a significantly lower glycerol conversion likely because of its reduced surface area as a consequence of its non-structured nature. The same trend is observed for the propylsulfonic acid-functionalized non-ordered silica—Pr-SO_3H-SiO_2. This fact justifies the use of mesostructured silicas over non-ordered silicas. Surprisingly, comparing both commercial silicas, and in contrast to the previously discussed results for SBA-15 materials, the propylsulfonic one gave a higher glycerol conversion despite the lower acid strength of its acid sites. The lower acid capacity of the Tosic acid-SiO_2 sample, 0.78 *vs.* 1.04 meq H^+ g^{-1}, could be the reason behind this discrepancy, and would also confirm that the acid site concentration is the most influential parameter.

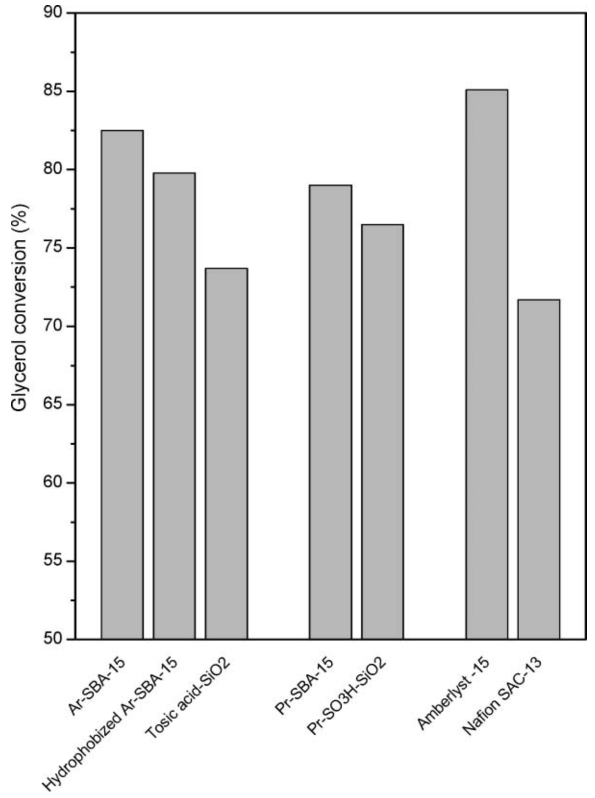


Fig. 1 Screening of sulfonic acid-modified catalysts for the acetalisation of glycerol with acetone. Reaction conditions: t_r 30 min, bath temperature 70 °C (under reflux), acetone/glycerol molar ratio 6/1, catalyst 5 wt% based on glycerol, pharmaceutical grade glycerol.

The low conversion obtained using the composite Nafion-SAC-13 must also be noted. The low acid capacity of this catalyst is considered the main cause of this result. A further effect to be taken into account is the perfluorinated nature of its sulfonic acid sites, which makes it the catalyst with the highest acid strength and hence the most hydrophilic material.

Downloaded by City College of New York on 24 November 2010
Published on 22 March 2010 on http://pubs.rsc.org | doi:10.1039/B923681C

The high affinity between perfluorosulfonic acid moieties and water molecules could produce a relatively high local water concentration around the catalytic acid sites, thus creating an unfavourable microenvironment from the point of view of reaction equilibrium. This would indicate that an excessive acid strength would be as undesirable as a low acid strength.

3.2. Optimization of the reaction conditions

Preliminary kinetic experiments were carried out to determine the evolution of the glycerol conversion with the reaction time for the acetalisation of pharmaceutical glycerol with acetone over arenesulfonic acid-functionalized mesostructured silica (Ar-SBA-15) since this catalyst has demonstrated an excellent catalytic behaviour in this reaction. All the catalytic tests were performed under the same reaction conditions, increasing the refluxing time. Fig. 2 shows that glycerol conversion reaches a constant value (80%) after only 15–30 min, indicating that the reaction achieves the equilibrium state. Therefore, higher refluxing times are not necessary since glycerol conversion keeps constant.

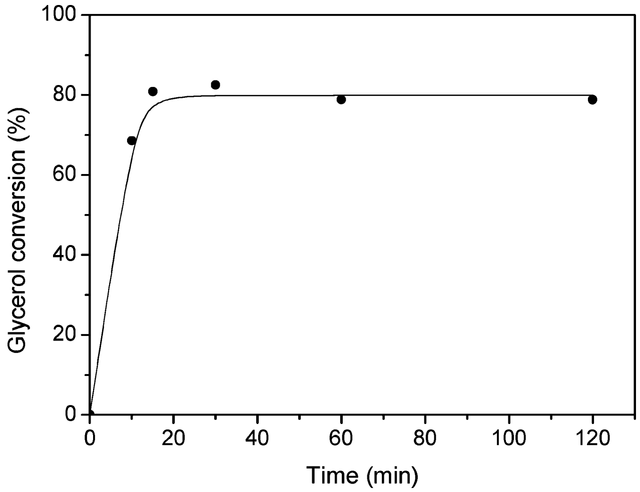


Fig. 2 Evolution of glycerol conversion with the refluxing time over arenesulfonic acid-modified mesostructured silica (Ar-SBA-15). Reaction conditions: bath temperature 70 °C (under reflux), acetone/glycerol molar ratio 6/1, catalyst 5 wt% based on glycerol (0.25 g), pharmaceutical grade glycerol.

The production of acetal from glycerol using an arene-SO_3H-functionalized mesostructured silica (Ar-SBA-15) as the catalyst was developed and optimized by following factorial design and response surface methodology.[32] In order to shift the equilibrium towards higher production of solketal, improving in this way the glycerol conversion, a two-step batch operation methodology as described in the experimental section was used. The experimental design applied to this study was a full 3^2 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 error. The selected response was the glycerol conversion, X_G, since the main objective was to achieve, if possible, a complete conversion of glycerol. Selection of the factors was based on the results obtained in preliminary studies and on the fact that the equilibrium has to be driven towards the production of solketal using a large excess of acetone or by removing the water produced from reaction media. As a result, the chosen factors were the number of 2-step batches and the molar ratio of acetone to glycerol, MR. The lower and upper numbers of 2-step batches were 1 and 3 and the levels of MR were 2/1 and 6/1. 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 randomly to minimize errors due to possible systematic trends in the variables. Table 3 also shows the experimental results obtained for the glycerol conversion.

Table 3 Experiment matrix and experiment results for the acetalisation of pharmaceutical glycerol with acetone over arenesulfonic acid-modified mesostructured silica (Ar-SBA-15) [catalyst/glycerol weight ratio = 5%; T = 70 °C; t_r = 30 min before each water removal]

Run Number	B	MR	I_B	I_{MR}	X_G (%)
1	3	6/1	+1	+1	89.5
2	3	2/1	+1	-1	61.8
3	1	6/1	-1	+1	82.5
4	1	2/1	-1	-1	54.3
5	2	4/1	0	0	80.7
6	2	4/1	0	0	78.0
7	2	4/1	0	0	75.5
9	2	6/1	0	+1	86.7
10	3	4/1	+1	0	85.4
11	2	2/1	0	-1	59.2
12	1	3/1	-1	0	73.5

B, number of 2-step batches; MR, acetone/glycerol molar ratio; I, coded value; X_G, conversion of glycerol.

Table 4 Predictive equations obtained by design of experiments

Statistical model $X_G = 78.55 + 4.4I_B + 13.9I_{MR} + 0.17I_B{}^2 - 6.33\,I_{MR}{}^2 - 0.12\,I_BI_{MR}$	$r^2 = 0.983$	(1)
Technological model $X_G = 16.9 + 3.84B + 19.76MR + 0.198B^2 - 1.588MR^2 - 0.0575B \times MR$	$r^2 = 0.983$	(2)

B, number of 2-step batches; MR, acetone/glycerol molar ratio; I, coded value; X_G, conversion of glycerol.

From the matrix generated by the experimental data and assuming a second-order polynomial model, equations 1 and 2 were obtained by multiple regression analysis (Table 4). The statistical model is obtained from coded levels giving the real influence of each variable on the process, whereas the technological model is obtained from the real values of the variables. Consequently, the influence of variables on the response is discussed using the statistical model shown in eqn (1) (Table 4).

Statistical analysis of the studied experimental range identifies the acetone : glycerol molar ratio (I_{MR}) as the most important factor in the glycerol conversion response. The second factor in importance is the number of batches (I_B) followed by the quadratic effect of the molar ratio ($I_{MR}{}^2$). The first two have a positive effect on the glycerol conversion: an increase in the molar ratio and the number of batches produces an increase in the conversion of glycerol. But the enhancement of this

Published on 22 March 2010 on http://pubs.rsc.org | doi:10.1039/B923681C
Downloaded by City College of New York on 24 November 2010

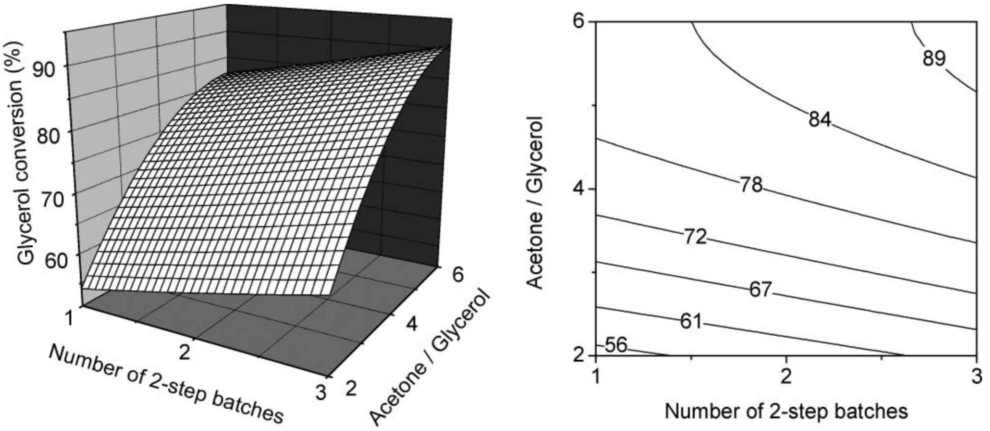


Fig. 3 Response surface and contour plots for glycerol conversion over the catalyst Ar-SBA-15 predicted by the model.

response by I_{MR} is three times that of I_B. The quadratic effect of the molar ratio has a significant negative influence on the glycerol conversion. This, in turn, indicates that the increase in this operating variable does not produce a constant rise in the glycerol conversion, because the curvature effect is significant at high molar ratios. In addition, the rest of the coefficients, the quadratic effects of the number of batches ($I_B{}^2$) and the number of two step batches-molar ratio interaction ($I_B - I_{MR}$), have no significant influence on the glycerol conversion since their absolute values are smaller than the corresponding main effects.

In Fig. 3, the technological model (equation 2, Table 4) is represented as a response surface and contour plots for predicted values of glycerol conversion over the experimental range studied. It clearly shows an enhanced conversion of glycerol at high acetone/glycerol molar ratios and with a high number of batches. Thus, the optimal values are the highest molar ratio (6/1) and the highest number of 2-step batches (3). At these operating conditions, the glycerol conversion predicted by the non-linear model is 90.6%.

Finally, the arithmetical average and the standard deviation of the response were calculated from the central point replicas: glycerol conversion 78% ± 2.6%. The standard deviation was lower than 5%. Therefore, the experimental error corresponding to the results shown in Table 4 is not excessively significant which indicates that the models accurately represent the influence of acetone/glycerol molar ratio and number of 2-step batches on glycerol conversion over the experimental range studied. Likewise, Fig. 4 shows the relationship between experimental and predicted values. As can be observed, values calculated with the predictive equation are very close to those obtained experimentally, indicating again the high accuracy of the obtained models.

In view of the results from the experimental design, where a constant value of glycerol conversion was not reached, an extension of the experimental design was made. In order to improve the glycerol conversion response, some additional reactions were carried out increasing the acetone/glycerol molar ratio up to 8/1 and 10/1 and the number of 2-step batches up to 4 and 5. Fig. 5 confirms the conclusion obtained from the experimental design since the most influential factor on the reaction of the glycerol acetalisation is the acetone/glycerol molar ratio. In this sense, a large excess of acetone can drive the equilibrium towards the production of solketal, but the amount of acetone needed for doing so is too high to be practically and economically effective. On the other hand, the increase in the number of 2-step batches leads only to a slight increase of the glycerol conversion which becomes almost constant over 3 consecutive 2-step batches.

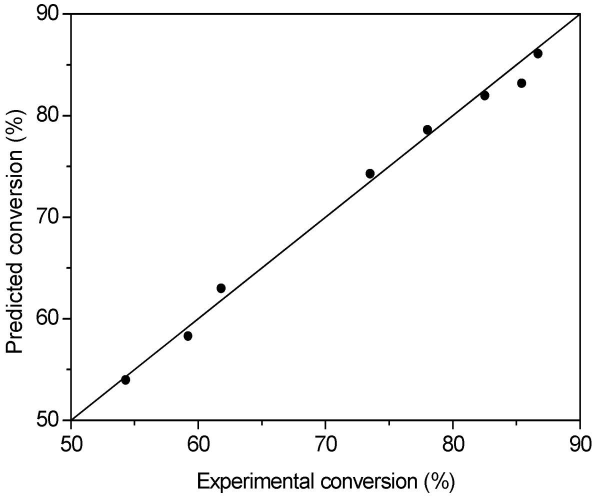


Fig. 4 Accuracy of the predicted data relative to the experimental data for the conversion of glycerol (catalyst: Ar-SBA-15).

3.3. Applicability to different grades of glycerol and catalyst reusability

Another purpose of the present work was to evaluate the possibility of using low-grade glycerol for the reaction of acetalisation with acetone. Specifically, crude and technical grades have been tested. Table 5 includes mass composition of the different grades of glycerol considered in this work. The presence of salts and/or water adversely affects the catalytic performance. As discussed above, the presence of water in the medium imposes a thermodynamic barrier, limiting the reaction. Likewise, sodium cations can deactivate sulfonic acid-modified materials by simple cationic-exchange of the catalytic protons in the sulfonic acid moieties.

This journal is © The Royal Society of Chemistry 2010

Downloaded by City College of New York on 24 November 2010
Published on 22 March 2010 on http://pubs.rsc.org | doi:10.1039/B923681C

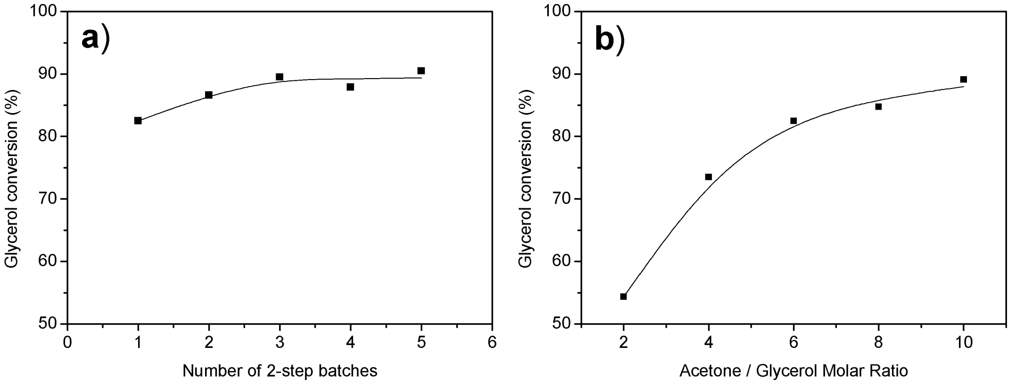


Fig. 5 Extension of the design experiment. Reaction conditions: catalyst Ar-SBA-15, bath temperature 70 °C (under reflux), catalyst 5 wt% based on glycerol, $t_r = 30$ min before each water removal. (a) Acetone : glycerol molar ratio 6/1 (b) Number of consecutive 2-step batches: 1.

Table 5 Composition of the different grades of glycerol evaluated (wt%)

			Ash (%)		
Glycerol grade	Purity (%)	Water (%)	NaCl	Others	MONG (%)
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

Others: non-NaCl inorganic compounds; MONG: matter (organic) non-glycerol; n.d., not detected.

Fig. 6 shows the glycerol conversions achieved with the different grades of glycerol in a blank reaction—no catalyst added—and with Amberlyst-15 and Ar-SBA-15 as the most active catalysts in this reaction. Reaction conditions were those above optimized in the experimental design, an acetone/glycerol molar ratio of 6/1 and 3 two-step batches of 30 min.

As expected, reactions performed without catalyst resulted in substantially reduced glycerol conversions as compared to those performed with acid solid catalysts. Furthermore, the result of the blank reaction for pharmaceutical glycerol notably differs from those with technical and crude glycerols (below 10% conversion even in the optimized reaction conditions). This is a clear indication of the negative effect of the presence of water on the reaction progress. Nevertheless, in the presence of Amberlyst-15 or Ar-SBA-15, high activities are obtained even for the low-purity glycerol grades. The observed trend is similar for both catalysts, with only a minimal decrease in conversion when treating technical and crude glycerols relative to pharmaceutical glycerol. This behaviour can be partly attributed to the efficient water removal under vacuum between consecutive batches, which would minimize the detrimental effect of the presence of water in the reaction medium as well as the presence of a catalytic system. Concerning the presence of sodium cations, surprisingly it does not seem to have a strong impact on the catalytic performance. However, a certain degree of Na$^+$/H$^+$ cationic-exchange can be expected to occur so that part of the actual catalytic effect would likely come from homogeneous released protons. If that is the case, then the heterogeneous

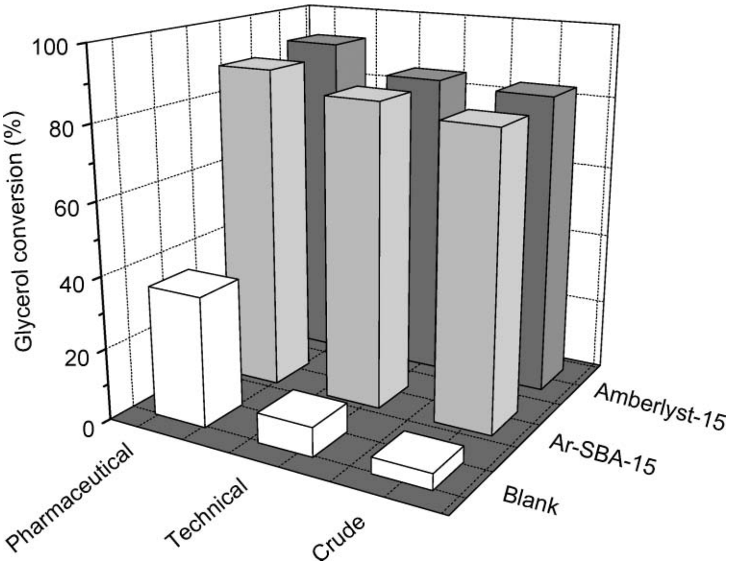


Fig. 6 Influence of the glycerol grade. Reaction conditions: t_r 30 min before each water removal, 3 consecutive 2-steps batches, bath temperature 70 °C (under reflux), acetone/glycerol molar ratio 6/1, catalyst 5 wt% based on glycerol.

Downloaded by City College of New York on 24 November 2010
Published on 22 March 2010 on http://pubs.rsc.org | doi:10.1039/B923681C

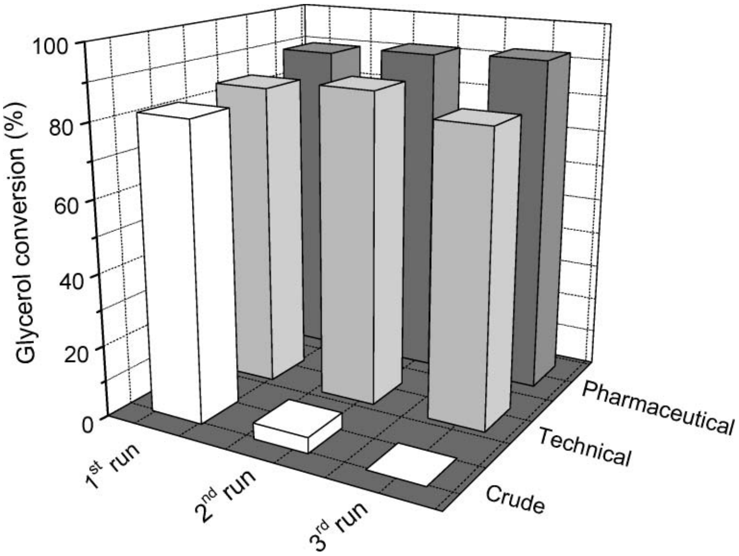


Fig. 7 Direct reutilization of catalyst Ar-SBA-15 for the different grades of glycerol. Reaction conditions: every run consists of 3 two-step batches of 30 min, bath temperature 70 °C (under reflux), acetone/glycerol molar ratio 6/1, catalyst 5 wt% based on glycerol.

catalysts would be transformed into the corresponding sodium forms, and hence they would be deactivated.

In order to confirm this hypothesis, a reutilization test using Ar-SBA-15 as the catalyst in three consecutive reaction cycles for each glycerol grade under the optimized reaction conditions was performed. The reuse procedure was kept as simple as possible, without washing or regenerating the catalyst, just separation by centrifugation and overnight drying at 90 °C before being use again. Fig. 7 illustrates the experimental results of this study in terms of glycerol conversion. The high activity observed initially for technical and pharmaceutical glycerols is maintained after 3 runs, indicating that no deactivation is produced. This is consistent with the very low sodium content of these two types of glycerol, which will not lead to a relevant cation-exchange deactivation effect. However, in the case of crude glycerol, an important catalytic deactivation is observed already in the second run, as glycerol conversion dramatically drops to values close to zero. The high sodium content of crude glycerol is considered the main factor responsible for this situation, very likely through an almost complete cation exchange of the arenesulfonic protons by sodium ions during the first reaction cycle.

An attempt to recover the activity of the catalyst Ar-SBA-15 after use with crude glycerol was made using the following procedure: separation of the solid by centrifugation, ethanol washing under reflux for 2 h, acidification with 2M HCl (aq.) for 30 min to produce the reverse cation exchange, washing with deionised water until neutral pH, and drying overnight at 90 °C. After this regeneration treatment, the Ar-SBA-15 catalyst was evaluated again in reaction with crude glycerol and using the same reaction conditions shown in Fig. 7. Resultant glycerol conversion was 77%, *i.e.* an almost complete recovery of the initial activity. This confirms that the catalyst deactivation is due to a Na^+/H^+ cationic-exchange, which can be readily reversed by means of the above regeneration procedure.

4. Conclusions

Sulfonic acid-functionalized mesostructured silicas have demonstrated an excellent catalytic behaviour in the acetalisation of bio-glycerol and acetone to produce solketal as a fuel component. The activities achieved in the acetalisation of this glycerol using sulfonic acid-functionalized mesostructured silicas, especially those comprised of arenesulfonic acid-catalytic sites, are comparable to those displayed by the widely used macroporous commercial acid resin (Amberlyst-15). The acid capacity of the catalysts is the most significant factor affecting the catalytic performance of this reaction. The acid strength of the catalytic sites has also proved to be an influential parameter. However, the use of hydrophobized catalysts (*e.g.* hydrophobized arene- and propyl-sulfonic mesostructured materials) in the acetalisation of glycerol with acetone is not an adequate approach, because these modified catalysts have a lower available surface area and the hydrophobized mesopores limit the access of highly polar glycerol and acetone molecules. The experimental design model carried out for different levels of two-step batch number and acetone to glycerol molar ratio with the arenesulfonic acid-modified mesostructure catalyst has shown that it is necessary to use the highest molar ratio (6/1) and the highest number of two-step batches (3) in order to maximize the conversion of pharmaceutical grade glycerol. The glycerol conversions obtained using crude and technical grade glycerols are similar to those achieved using the high purity pharmaceutical grade glycerol in the presence of arenesulfonic acid-modified mesostructured silica and the macroporous sulfonic acid resin as catalysts. These activities are maintained after three reaction cycles using pharmaceutical and technical grade glycerols, in which both catalysts are reutilized without an intermediate purification stage, indicating that these catalysts are not deactivated. However, using crude glycerol, both catalysts need to be regenerated in order to achieve high glycerol conversions.

This journal is © The Royal Society of Chemistry 2010

View Online

Downloaded by City College of New York on 24 November 2010
Published on 22 March 2010 on http://pubs.rsc.org | doi:10.1039/B923681C

Acknowledgements

The financial support from the "Ministerio de Ciencia e Innovación" through the project CTQ2008-01396 and CENIT Program (2006) through a research project entitled "Proyecto de innovación para el impulso del biodiésel en España" (PiIBE) are gratefully acknowledged.

References

1 G. Vicente, M. Martínez and J. Aracil, *Bioresour. Technol.*, 2004, **92**, 297–305.
2 B. Freedman, E. H. Pryde and T. L. Mounts, *J. Am. Oil Chem. Soc.*, 1984, **61**, 1638–43.
3 European Biodiesel Board, http://www.ebb-eu.org/index.php.
4 M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi and C. Della Pina, *Angew. Chem., Int. Ed.*, 2007, **46**, 4434–40.
5 C. Zhou, J. N. Beltramini, Y. Fana and G. Q. Lu, *Chem. Soc. Rev.*, 2008, **37**, 527–549.
6 Y. Zheng, X. Chen and Y. Shen, *Chem. Rev.*, 2008, **108**, 5253–5277.
7 A. Behr, J. Eilting, K. Irawadi, J. Leschinski and F. Lindner, *Green Chem.*, 2008, **10**, 13–30.
8 Y. Gu, A. Azzouzi, Y. Pouilloux, F. Jérôme and J. Barrault, *Green Chem.*, 2008, **10**, 164.
9 A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411.
10 V. P. Gupta, *U.S. Patent* 5 476 971 to ARCO Chem. Technology, L.P, 1995.
11 D. S. Bradin, *U.S. Patent* 5 578 090, BRI, 1996.
12 H. Noureddini, *U.S. Patent* 6 015 440, 2000.
13 H. Noureddini, *U.S. Patent* 6 174 501, 2001.
14 A. Behr and L. Obendorf, *Eng. Life Sci.*, 2002, **2**, 185–189.
15 K. Klepacova, D. Mravec, A. Kaszonyi and M. Bajus, *Appl. Catal., A*, 2007, **328**, 1–13.
16 R. S. Karinen and A. O. I. Krause, *Appl. Catal., A*, 2006, **306**, 128–133.
17 J. A. Melero, G. Vicente, G. Morales, M. Paniagua, J. M. Moreno, R. Roldán, A. Ezquerro and C. Pérez, *Appl. Catal., A*, 2008, **346**, 44–51.
18 J. Delgado, *Spanish Patent* 1 331 260, 2002.
19 J. A. Melero, R. van Grieken, G. Morales and M. Paniagua, *Energy Fuels*, 2007, **21**, 1782–1791.
20 M. I. Galan, J. Bonet, R. Sire, J. M. Reneume and A. E. Pleçu, *Bioresour. Technol.*, 2009, **100**, 3775–3778.
21 X. Liao, Y. Zhu, S. G. Wang and Y. Li, *Fuel Process. Technol.*, 2009, **90**, 988–993.
22 H. Gerard, D. Bruno, D. Isabelle, *WO Patent* 093 015 A1, 2005.
23 B. Bruchmann, K. Häberle, H. Gruner, M. Hirn, *U.S. Patent* 5 917 059, 1999.
24 B. Delfort, I. Durand, A. Jaecker, T. Lacome, X. Montagne, F. Paille, *U.S. Patent* 0 163 949, 2003.
25 J. Deutsch, A. Martin and H. Lieske, *J. Catal.*, 2007, **245**, 428–435.
26 E. García, M. Laca, E. Pérez, Á. Garrido and J. Peinado, *Energy Fuels*, 2008, **22**, 4274–4280.
27 C. X. Da Silva, V. L. Gonçalves and C. J. Mota, *Green Chem.*, 2009, **11**, 38–41.
28 R. Wessendorf, *Petrochem.*, 1995, **48**, 138–143.
29 J. A. Melero, R. van Grieken and G. Morales, *Chem. Rev.*, 2006, **106**, 3790–3812.
30 G. Vicente, M. Martínez and J. Aracil, *Bioresour. Technol.*, 2007, **98**, 1724–33.
31 R. van Grieken, J. A. Melero and G. Morales, *Appl. Catal., A*, 2005, **289**, 143–152.
32 G. E. P. Box, W. G. Hunter and J. S. Hunter, *Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building*, Wiley, New York, 1978.