



Full Length Article

Use of biobased crude glycerol, obtained biocatalytically, to obtain biofuel additives by catalytic acetalization of furfural using SAPO catalysts

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ABSTRACT

High-pure crude glycerol, obtained from the transesterification of coconut oil with ethanol using lipase enzyme-type as biocatalyst, has been used for the acetalization of furfural with several SAPO 5 and SAPO 34 catalysts. SAPOs were prepared using microwaves and conventional heating for comparison, and were characterized by X-ray diffraction, nitrogen physisorption, elemental analysis, thermogravimetry of adsorbed cyclohexylamine and scanning electron microscopy techniques. The use of microwaves allowed us the incorporation of slightly higher amounts of silicon into the aluminophosphate structure, and the preparation of the materials in much shorter preparation times, with the subsequent energy saving. Additionally, the SAPOs prepared with microwaves showed lower crystallinity but higher surface area than those prepared by conventional heating. Comparable catalytic results were obtained when these catalysts were tested for the acetalization of furfural with commercial or with the crude glycerol obtained by biocatalytic transesterification of coconut oil, leading to very high selectivity values to the desired mixture dioxane + dioxolane (93–100 %), which can be used as biofuel additives, for conversion values between 60 and 73 %, as determined by gas chromatography. This confirmed the high purity of the glycerol obtained by the biocatalytic process, as previously observed by ¹H NMR. SAPO 34 catalysts showed higher conversion than SAPO 5 catalysts due to their higher amount of more accessible Brønsted acid sites, related to their structure. Interestingly, catalysts prepared with microwaves resulted in slightly higher conversion values than those prepared by conventional heating. This can be explained by the incorporation of higher amounts of silicon in the framework, probably due to the higher homogeneity of the microwaves heating, which results in a higher amount of protons, as confirmed by TGA of adsorbed cyclohexylamine, responsible for the catalysis.

1. Introduction

Valorization strategies of wastes from agri-food processes must necessarily be intertwined with clean technological approaches and eco-industrial management within a sustainable biorefinery concept. Biorefineries might integrate processes developing cascade approaches, which often require the application of biotechnological and chemical processes in order to obtain high-added value products.

Glycerol (1, 2, 3-propanetriol) is obtained in significant amounts as by-product in a great variety of industrial processes, such as transesterification of triglycerides to produce fatty acid methyl esters, e.g. biodiesel (about 10% w/w) or through saponification processes [1]. Although glycerol has many applications in cosmetics, pharmaceuticals

and food products [2–3], it is necessary to develop new processes to transform this surplus into high-added value products [2,4–8].

For most of these applications, and independently of the origin (synthetic, animal or vegetable fat), crude glycerol should be refined to obtain glycerol with high purity degree [9,10]. Crude glycerol is initially produced in a raw form that contains water and other residues as impurities depending on the production process. It is usually treated and refined by filtration, adding chemical additives, by fractionated distillation in vacuum or using lower-energy intensive filtration by a series of ion exchanges in resins [11]. Another alternative is to develop cleaner processes to obtain more pure glycerol, for example, by applying enzymatic technologies.

Transesterification of triglycerides to obtain the corresponding

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esters, and crude glycerol as by-product, can be catalysed by acid or basic catalysts in addition to biocatalysts [12]. Lipase-catalysed biotransformation is one of the most popular and practical enzymatic technologies. Lipases (triacylglycerol acylhydrolases, EC 3.1.1.3) are enzymes that catalyse a broad spectrum of reactions [13], and consequently, they are used in a wide range of industrial processes, including food, chemical, pharmaceutical and detergent production [14]. One of the processes in which biocatalysts have been used is in the production of ethyl esters with applications in aromas and fragrances industries [15]. Unlike the conventional chemical routes, biocatalytic routes allow carrying out the transesterification reactions at more soft conditions (e. g. low temperatures), can have greater specificity and high selectivity, which prevent the formation of by-products [16], and can be immobilized on resins improving their handling. Furthermore, products separation and purification are much easier, resulting in a more environmentally friendly process [17].

One interesting option for the revalorization of the glycerol obtained as surplus byproduct is the synthesis of oxygenated compounds for their application as fuel additives. Hydroxyl groups of glycerol can react with a carbonyl group, yielding two isomeric acetals [18–21]. The acetalization of furfural with glycerol led to the formation of 1,3-dioxane (2-(furan-2-yl)-1,3-dioxane-5-ol) and 1,3-dioxolane (2-(furan-2-yl)-1,3-dioxolane-4-yl)methanol) (Scheme 1). These acetals have shown an improvement in the viscosity and cold properties of biodiesel, having reasonable oxidation stability and flash point. Moreover, when added to the diesel fuel, significant reduction of hydrocarbons, carbon monoxide and particulate matter emissions were observed [22].

Traditionally, Brønsted acids (H_2SO_4 , HCl, HF, H_3PO_4 , p-toluene-sulphonic acid) [23] and Lewis acids (AlCl_3 , ZnCl_2 , $\text{La}(\text{OTf})_3$, AgBF_4) [24] have been employed for acetalization reactions. To overcome corrosion, environmental and products separation and purification problems, heterogeneous catalysts, such as ion-exchange resins, zeolites, heteropolyacids, and promoted metal oxides, have been checked for the acetalization of glycerol with different carbonyl compounds. However, there are few references about the acetalization of glycerol with furfural [18,25–32].

Mallesham et al. achieved 51, 67 and 75 % of glycerol conversion values when using SnO_2 , WO_3/SnO_2 and $\text{MoO}_3/\text{SnO}_2$ catalysts under solvent free conditions at room temperature [26]. Konwar et al. reported high conversion of glycerol (≥ 93 %) using lignosulfonate-based macro/mesoporous solid catalysts for the acetalization of glycerol with acetone, furfural and methyl levulinate at 100 °C [27]. Then, several sulfonated montmorillonite MK-10 catalysts resulted in high conversion (62–68 %) and high selectivity to dioxane + dioxalane values (72–86%) at 40 °C for 2 h and montmorillonite modified with Zr exhibited 84 % of furfural conversion and 78 % of selectivity to dioxane + dioxalane at room temperature for 4 h [29–30]. More recently, Patel et al. designed a novel catalyst, TSA/nMCM-48 that showed high conversion (89 %) and high selectivity to dioxane (69 %) [31] and Appaturi et al. synthesized an aniline functionalized MCM-41 that resulted in high conversion (90 %) and high selectivity to dioxalane (78 %) for the acetalization of glycerol with furfural [32].

The main objective of this work is to compare the use of crude bio-based glycerol, obtained biocatalytically as byproduct from the transesterification reaction of coconut oil, versus commercial glycerol for the catalytic acetalization of furfural, using silicoaluminophosphate acid

catalysts (SAPO5 and SAPO34). SAPOs can be prepared by the isomorphous substitution of silica into a microporous aluminophosphate conferring negative charge to the framework, which is charge-balanced by protons, so they can be used as Brønsted acid catalysts [33–38]. In fact, Song et al. studied the acetalization of furfural with 1,2-propanediol using SAPO-34 catalysts leading high yield to furfural acetal (88.2%) [39]. Special attention will be also paid to study the effect of using microwaves vs conventional heating for the preparation of the SAPO catalysts. Microwaves, in addition to reduce the preparation temperatures or times, with the corresponding energy saving, can also modify the final properties of the solids [40–43].

2. Experimental

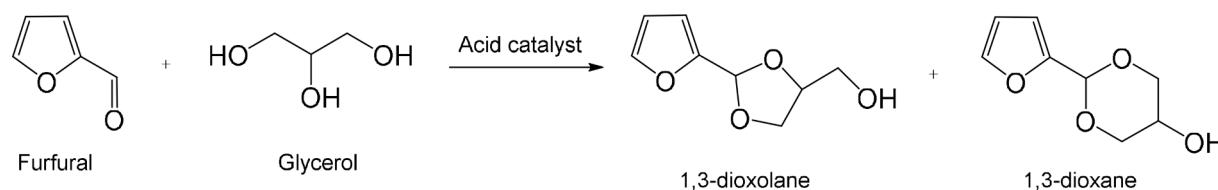
2.1. Preparation of biobased crude glycerol

Initially, the fatty acid profile of the coconut oil was analysed using an Agilent 6890 series gas chromatograph coupled to a flame ionization detector (FID). The results showed that coconut oil contained more than 90 % of saturated fatty acids (lauric acid (46.7 %), myristic acid (20.6 %), palmitic acid (9.2 %), caprylic acid (6.6 %), capric acid (5.1 %) and stearic acid (2.9 %)) and less than 10 % of unsaturated fatty acids (oleic acid (7.2 %) and linoleic acid (1.7 %)). Ethyl esters were prepared from coconut oil and ethanol (1:3) at 25 °C for 24 h in a solvent-free medium in presence of *Candida antarctica* lipase B immobilized on acrylic resin (Novozym® 435) (10 wt%, Novozym® 435/coconut oil). Considering that the water activity (a_w) is one of the most important factors affecting enzyme activity (water content may affect reaction rate, yield, enzyme stability and excess water favours hydrolysis over condensation reactions) all reactions were carried out after equilibrating the water activity of the biocatalysts to 0.54. For it, the biocatalyst was left at room temperature for at least 48 h in a closed container containing a saturated solution of $\text{Mg}(\text{NO}_3)_2$. This salt gives an $a_w = 0.54$ and was chosen because in a previous study it was observed that at this a_w Novozym® 435 achieving its highest activity in a transesterification reaction [16]. The water activity of the biocatalyst was measured using an Aqua Lab series 3TE from Decagon Devices Inc. (Pullman, WA, USA).

The reaction was scale-up from 2 mmol (1,37 g) to 2000 mmol (1370 g) of coconut oil and the stability of the immobilized lipase was evaluated for different cycles according to the filtration method. Three filtration methods were tested to separate the biocatalyst from the crude of reaction. The first method was performed applying positive pressure using a syringe. The second method was carried out by means of a vacuum system and finally the third method was performed using a nylon filter mesh (50 μm). The glycerol was separated from the ethyl esters by decantation and final centrifugation. The crude glycerol and the ethyl esters obtained in all reactions were analysed by ^1H NMR. Spectra were recorded with a MERCURYplus NMR Spectrometer Systems VARIAN 400 MHz magnet using deuterated chloroform (99.9 atom % D) for the ethyl esters and deuterated DMSO for glycerol as solvents.

2.2. Preparation of the heterogeneous catalysts

Two different microporous SAPOs, SAPO 5 and SAPO 34, were prepared following the method previously reported [44] but using microwaves in addition to conventional heating during crystallization for



Scheme 1. Catalytic acetalization of glycerol with furfural to obtain fuel additives.

comparison. The microwaves equipment was a Milestone ETHOS-TOUCH CONTROL with temperature control.

For the preparation of SAPO 5, appropriate amounts of aluminum isopropoxide (98 %, Aldrich), phosphoric acid (85 % in H₂O, Aldrich) and water were vigorously stirred. Next, triethylamine (TEA) (99 %, Acros) and more water were added and stirred for 1 h. Finally, silica sol (40 % in H₂O, Aldrich) was added and the mixture was stirred for 1.5 h to obtain a white gel with the molar composition 1.0 Al: 1.0P: 0.8 TEA: 50 H₂O: 0.15Si. This gel was submitted to hydrothermal treatment in a Teflon-lined stainless-steel autoclave at 180 °C for 24 h by conventional heating or in a Teflon autoclave at 180 °C for 2 h under microwaves. The resulting solids were washed by centrifugation (400 rpm, 5 min) with 3 × 50 mL of deionized water. Products were dried at 120 °C overnight, and calcined under an air flow (1 mL/s) at 550 °C for 16 h (samples S5C and S5MW crystallized by conventional heating and microwaves, respectively).

For the preparation of SAPO 34, appropriate amounts of aluminum isopropoxide (98 %, Acros) and tetraethyl ammonium hydroxide (TEAOH) (35 % in H₂O, Aldrich) were stirred for 1 h. Next, fumed silica (99.8 %, Aldrich) was added and stirred until homogeneous. Finally, deionized water and phosphoric acid (85 % in H₂O, Scharlau) were added and stirred for 2 h to obtain a white gel with the molar composition: 1.0 Al: 1.0P: 1 TEAOH: 65 H₂O: 0.15Si. This gel was heated in a Teflon-lined stainless-steel autoclave at 180 °C for 48 h by conventional heating or in a Teflon autoclave at 180 °C for 8 h under microwaves. The resulting solids were washed by centrifugation (400 rpm, 5 min) with 3 × 50 mL of deionized water. Products were dried at 120 °C overnight, and calcined under an air flow (1 mL/s) at 550 °C for 16 h (samples S34C and S34MW crystallized by conventional heating and microwaves, respectively). Three more S34 samples were prepared with the same procedure but heating the gel mixture under microwaves at 180 °C for 2, 4 and 6 h.

2.3. Characterization of the heterogeneous catalysts

Powder X-ray diffraction patterns of the calcined samples were obtained with a Siemens D5000 diffractometer using nickel-filtered CuK α radiation and detecting between 2 θ values of 5°–70°. Crystalline phases were identified using the Joint Committee on Powder Diffraction Standards (JCPDS) files (49–0659 SAPO 5, 47–0617 SAPO 34). TOPAS 6.0 software was used to fit the diffractograms using the Rietveld method and the crystal structure of each phase. The average crystallite size was calculated as a mean value from all the diffracted peaks once the instrumental contribution to the peak width was removed.

BET surface areas were calculated from the nitrogen adsorption isotherms at –196 °C using a Quantachrome Quadrasorb SI surface analyzer and a value of 0.164 nm² for the cross-section of the nitrogen molecule. Pore size distribution was predicted from the desorption wing of the isotherm by applying the BJH method.

Elemental analyses of the samples were obtained with a Philips PW-2400 sequential XRF analyzer with Phillips Super Q software. All measures were made in triplicate.

Scanning electron microscopy (SEM) were performed on a scanning electron microscope, JEOL JSM6400, operating at accelerating voltage of 20 kV and work distances of 10 mm, and magnifications of 8,000x.

Thermogravimetric analysis (TGA) of adsorbed cyclohexylamine (CHA) was carried out using a Mettler Toledo TGA 2 to determine acidity of the materials following the method previously applied for clays, zeolites and mesoporous materials [45–47]. This method involves thermogravimetric analysis following adsorption of the base on the catalysts and determines the number of acid sites, which are accessible and sufficiently strong to interact with the base after heat treatment at 250 °C. Firstly, the samples were left in a solution of cyclohexylamine at room temperature overnight. Then, the samples were heated at 80 °C for 4 h in order to eliminate excess of cyclohexylamine and for a further 2 h at 250 °C to remove the physisorbed CHA. Finally, the samples were

analysed using the TGA from 50 °C to 800 °C at 10 °C/min under N₂. Acidity values were calculated from the weight loss observed between 250 °C and 450 °C.

2.4. Catalytic activity

The catalytic tests were made in a batch reactor (50 mL amber three necked round bottom flask) with commercial glycerol (ACS reagent greater than 99.5 %, Sigma Aldrich) or crude glycerol (1 g), and furfural (99 %, Sigma–Aldrich) in a ratio 1:1, at 150 °C for 45 min, using 5 wt% of catalyst and bubbling a N₂ flow (1 mL/s) during reaction to avoid the formation of byproducts, mainly due to furfural degradation. Reaction products were analysed using a gas chromatograph (Shimadzu GC2010A) with FID detector equipped with a TRB-WAX column. Calibration lines were applied to calculate glycerol conversion and selectivity to the reaction products using butanol as internal standard.

In order to study the stability of the best catalyst, it was washed with ethanol, recovered by centrifugation and reused three times at the same reaction conditions.

3. Results and discussion

3.1. Preparation of biobased crude glycerol

The transesterification of coconut oil with ethanol catalysed by *Candida antarctica* lipase B (Novozym® 435) in a solvent-free system was performed in order to produce ethyl esters, mainly ethyl laurate, which is used as aroma in food and cosmetic industry. The interest in biotechnologically produced aroma compounds has risen in the past few decades, since this approach is considered a sustainable way to supply natural additives for the industrial processes. Additionally, the implementation of these bioprocesses may use by-products of the agri-food industry as alternative raw materials, which is advantageous in terms of both ecological and economical sustainability [48]. In this process, besides of producing the corresponding esters, glycerol was obtained as byproduct. There are different ways to produce glycerol depending on the process and starting material used. It can be obtained by propylene synthesis via several pathways, by both hydrolysis or transesterification of vegetable oil and fats. Nonetheless, glycerol production can be also carried out by fermentation with yeast such as *Saccharomyces cerevisiae*, *Candida* sp., bacteria such as *Bacillus subtilis* and algae such as *Dunaliella tertiolecta* [49]. The transesterification process applied in this work to the synthesis of the ethyl esters allowed us to recover a high purity glycerol.

Novozym® 435 showed high catalytic activity for the transesterification reaction when 2 (1.37 g) and 20 mmol (13.7 g) of coconut oil were used. In these cases, the yield of the ethyl esters was more than 90 % in the first cycle and the catalytic activity remained around 80 %

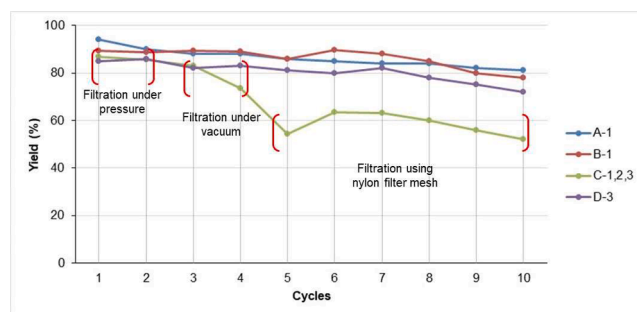


Fig. 1. Transesterification reaction at different coconut oil concentrations (A: 2 mmol; B: 20 mmol; C: 200 mmol; D: 2000 mmol) during various cycles and the effect of the filtration method (1: filtration under pressure; 2: filtration under vacuum; 3: filtration using nylon filter mesh) in the enzymatic activity of the biocatalyst.

until the tenth cycle (Fig. 1 (A-1 and B-1)). Here, after each cycle the biocatalyst was separated from reaction crude by a pressure system using a syringe.

A wide variety of vegetable oils and biocatalysts have been used to obtain ethyl esters through transesterification reactions. Costa-Silva et al. reported high ethyl esters yields (97 %) from coconut oil using *Cercospora kikuchii* lipase covalently immobilized onto a chitin derived support. After five reuse cycles the ester content remained above 96.5 %, however, they used a molar ratio oil to ethanol (1:12) higher than that used in this study (1:3) [50]. Furthermore, Novozym® 435 lipase has been used to obtain ethyl esters by transesterification of different vegetable oils, including residual oils. In this sense, fatty acid ethyl esters had been produced from waste cooking oil using Novozym® 435 in a solvent-free system with a total ester content of 77.2 and 89.5 % produced after 10 and 24 h, respectively [51]. In the same way residual oil from babassu (*Orbignya* sp.) was used in the enzymatic esterification for biodiesel production. The conversion into ethyl esters was 96.8 % and it was found that after 10 consecutive cycles of esterification under optimal conditions (1:18 M ratio (FFAs/alcohol)), Novozym® 435 showed a maximum loss of activity of 5.8 % [52]. These results are in concordance with the results obtained in our study.

When the reaction was performed using 200 mmol (137 g) of coconut oil the yield of the ethyl esters remained over 80 % until the third cycle (Fig. 1 (C-1, 2, 3)). However, after the third cycle the lipase was separated from the reaction crude using a vacuum system and the biocatalyst showed a decrease in the enzymatic activity in the following cycles (fourth and fifth cycle). Perhaps, the applied vacuum was too high and produced a lixiviation of the enzyme from the support and a consequent loss of the activity and recyclability as when mechanical agitation was used [53]. Despite this, after the fifth cycle the reaction crude was filtered by means of a nylon filter mesh and in the next cycle the enzymatic activity was improved around 10 %, increasing from 54 up to 63%. Here, the filtration method allowed the extraction of the maximum quantity of glycerol produced in the transesterification reaction and this enabled remain the yield over 50 % until the tenth cycle. Various factors can determine the reaction rate and yield of these biocatalyzed reactions. Among them, selection of organic solvent, optimization of molar substrate ratio, temperature, water activity, pH of the enzyme's micro-environment and the highest permissible glycerol concentration in the reaction products (the so called sub-parameters) [54].

Taking into account that the nylon filter mesh allowed to perform the filtration process in an easy way, we decided to carry out the transesterification reaction in a higher scale. For that, 2000 mmol (1370 g) of coconut oil was used and the reaction was performed during ten cycles (Fig. 1 (D-3)). The maximum yield of ethyl esters was achieved in the first (85 %) and second cycle (86 %), and the reaction yield stayed over 70 % until the tenth cycle. In this process, once the reaction crude was filtered, the glycerol was separated from the crude by means of decantation followed by centrifugation. The amount of high pure glycerol obtained was around 6 wt% (with respect to the weight of coconut oil).

¹H NMR spectra of the pure commercial glycerol and crude glycerol are shown in Fig. 2. The signals that appeared at around 4.5 ppm can be attributed to the OH groups, a doublet due to the OH coupled to CH and a triplet due to the 2 OH groups attached to CH₂. The signals observed at around 3.3 ppm can be assigned to the protons of the groups CH₂ and CH of glycerol in addition to CH₂ due to some ethanol present in the samples from the transesterification reaction as confirmed by the singlet observed at 3.5 ppm that could be attributed to the OH of ethanol together with water. The signal at 2.5 ppm is due to the DMSO solvent. Finally, the triplet observed at around 1.05 ppm can be identified as the protons of the CH₃ group coupled to the CH₂ of ethanol. From this result, we can conclude that the crude glycerol had enough purity to be used in the reaction since only some impurities of ethanol (up to 6% w/w), and water (up to 17% w/w) were observed by ¹H NMR.

It is important to remark that in the biodiesel process, glycerol is usually generated at the rate of one mole of glycerol for every three moles of synthesized methyl esters; approximately 10% of the total product by mass [55]. However, the crude glycerol generated during the transesterification process by conventional chemistry leading to biodiesel contains impurities such as methanol, water, inorganic salts (catalyst residue), free fatty acids, unreacted mono-, di- and triglycerides, methyl esters and a variety of other organic materials, depending on the biodiesel process [56]. In this case, the use of a biocatalytic process allowed obtaining a glycerol with better quality and by means of "green" process, so we can consider the glycerol as "natural".

3.2. Characterization of heterogeneous catalysts

XRD patterns of the samples S5 and S5MW were identified as SAPO 5 (Fig. 3). No other crystalline phases were observed. S5MW, prepared

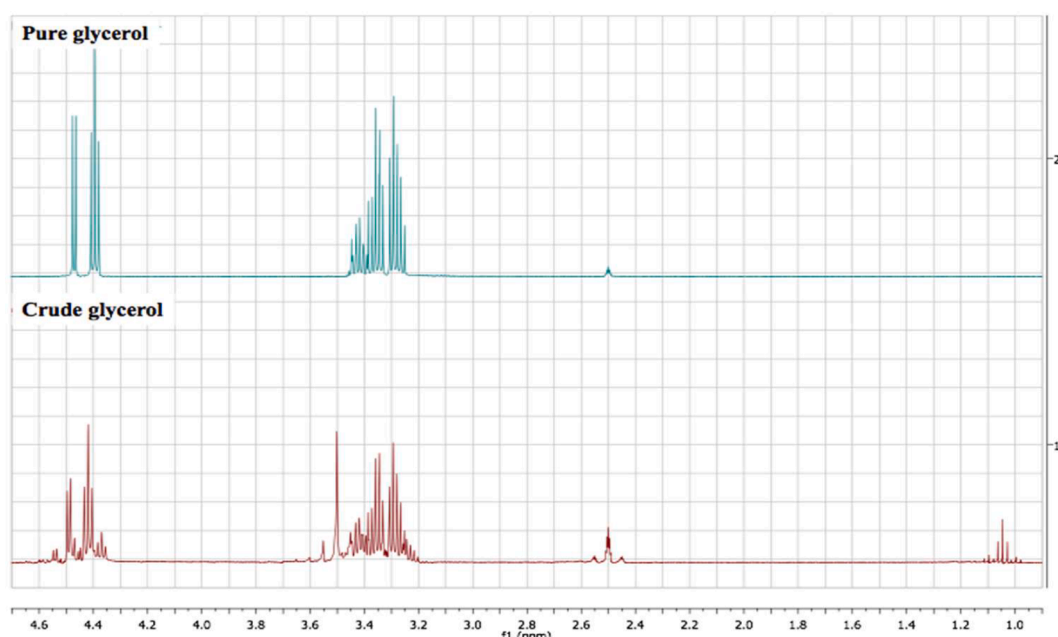


Fig. 2. ¹H NMR spectra of pure glycerol and the crude glycerol obtained biocatalytically from the transesterification of coconut oil with ethanol.

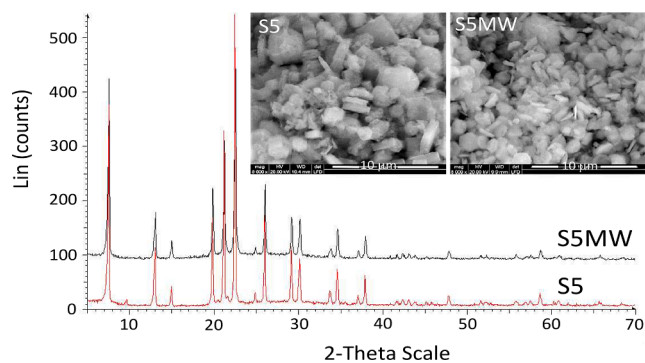


Fig. 3. XRD patterns and SEM images of catalysts S5.

under microwaves, showed slightly lower crystallinity than S5, which was synthesized by conventional heating. The considerably shorter time used for preparing the sample under microwaves (2 h) can justify this fact. The micrographies of these samples, obtained by SEM, confirmed the presence of the typical hexagonal SAPO 5 crystals for both samples with lower size for S5MW. This can be related to the lower crystallinity of this sample, as observed by XRD. Thus, the crystallite size, calculated by the Scherrer equation, of S5 was higher than that of S5MW (Table 1).

For SAPO 34 samples (Fig. 4), the XRD pattern of the sample prepared with microwaves showed in addition to the SAPO 34 phase a couple of minor peaks, marked on the figure with asterisk, which were identified as AlPO-5. In Fig. 5 it is possible to observe the evolution of the crystalline phases at lower microwaves heating time. After heating 2 h under microwaves the sample had very low crystallinity and only few peaks of AlPO-5 were observed, at 4 h crystalline AlPO-5 was obtained, and it is from 6 h of microwaves heating that the peaks corresponding to SAPO 34 phase were observed. Longer heating times did not increase the purity of the SAPO 34 phase, so, at the conditions used, some minor amount of AlPO-5 remained in the sample. It is important to remark the considerably lower heating time (8 h) used to obtain the S34MW compared to the 48 h of conventional heating used to prepare sample S34. The micrographies of these samples obtained by SEM (Fig. 4) confirmed the presence of the typical cubical SAPO 34 crystals for both samples with lower size for S34MW, due to its lower crystallinity. Thus, the crystallite size of S34MW was lower than that of S34 (Table 1).

Chemical analysis of the samples confirmed the incorporation of small amounts of silicon in all samples, interestingly, slightly higher for the SAPOs prepared under microwaves (Table 1). This could be explained by the higher homogeneous heating achieved with microwaves [57], which should favour the substitution of phosphorus or aluminium by silicon.

Nitrogen adsorption–desorption isotherms of S5, S5M, S34 and S34M were classified as type I (Fig. 6), corresponding to microporous materials, according to the Brunauer, Deming, Deming and Teller classification [58], as expected. Interestingly, the isotherms of the samples prepared under microwaves exhibited additional capillary condensation at partial pressures greater than 0.90 due to the filling of textural mesopores. The high surface areas obtained for these SAPOs, in the range 250–500 m²/g (Table 1), and the average pore diameter, micropore and pore volume values (Table 1) are typical for these materials [33,44]. The

Table 1

Characterization of the SAPO samples.

Samples	Crystallite size (XRD) (nm) ^a	Al (wt %) (XRF)	P (wt %) (XRF)	Si (wt %) (XRF)	BET area (m ² /g)	Average pore diameter (Å)	Pore volume (cc/g)	Micropore volume (cc/g)	Acidity (mEq CHA/g) (TGA) ^b
S5	125.4 ± 5.9	19.1	21.3	2.5	239	37.7	0.10	0.09	0.152
S5MW	73.8 ± 2.4	19.3	21.2	2.7	306	41.2	0.13	0.09	0.169
S34	82.0 ± 8.8	19.5	21.6	2.2	418	52.4	0.26	0.25	0.250
S34MW	34.5 ± 2.4	19.9	20.6	2.8	489	55.6	0.28	0.24	0.262

^a Calculated by using the Scherrer equation; ^b calculated from cyclohexylamine (CHA) desorbed between 250 and 450 °C by TGA.

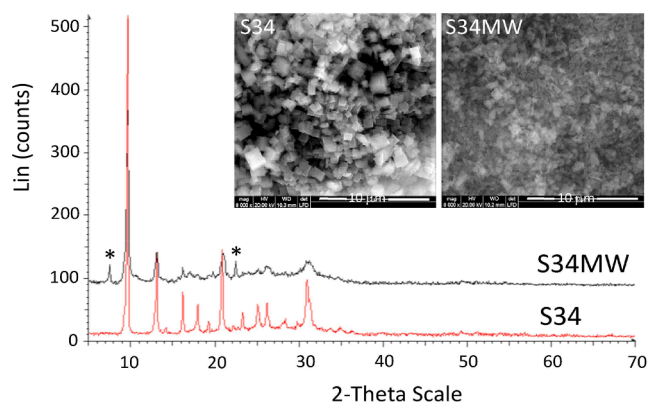


Fig. 4. XRD patterns and SEM images of catalysts S34. * AlPO-5 minor phase.

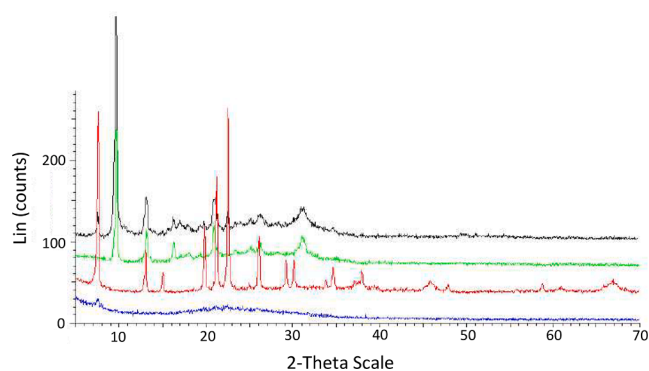


Fig. 5. XRD patterns of samples S34 prepared at different microwaves heating time: 2 h (blue), 4 h (red), 6 h (green) and 8 h (black).

use of microwaves for the synthesis led to materials with higher surface area. This can be related to the lower crystallinity detected for the microwaved samples by XRD (Figs. 2 and 3) together with the presence of textural mesoporosity, as observed by N₂ physisorption (Fig. 6). Differences in surface and porosity properties when using microwaves instead of conventional heating have been previously reported for the preparation of materials [41–43].

The bridging Si-OH-Al groups in the SAPOs materials, are responsible for the Brønsted acidity. It is well known that SAPO 5 has lower and weaker strength of the Brønsted acid sites than SAPO 34 [56,59]. Table 1 shows the amount of Brønsted acid sites for the SAPO samples obtained from TGA of adsorbed cyclohexylamine. SAPO-5 samples had lower amount of Brønsted acid sites than SAPO-34 samples. The structure of SAPO-5 possesses one-dimensional 12-ring channels (diameter 7.4 Å) linked to one another via 4- and 6-rings. SAPO 34 is an analogue of chabazite; it has nearly spherical cages linked throughout the structure by 8-ring windows (diameter ca 4.0 Å) [33]. Thus, the lower acidity of SAPO 5 has been related to the inaccessibility of the hydroxiles in 6-rings channels in contrast to the three dimensional channel structure of the SAPO-34, which provides accessibility to the internal protons, thereby leading a higher fraction of available active sites for catalysis

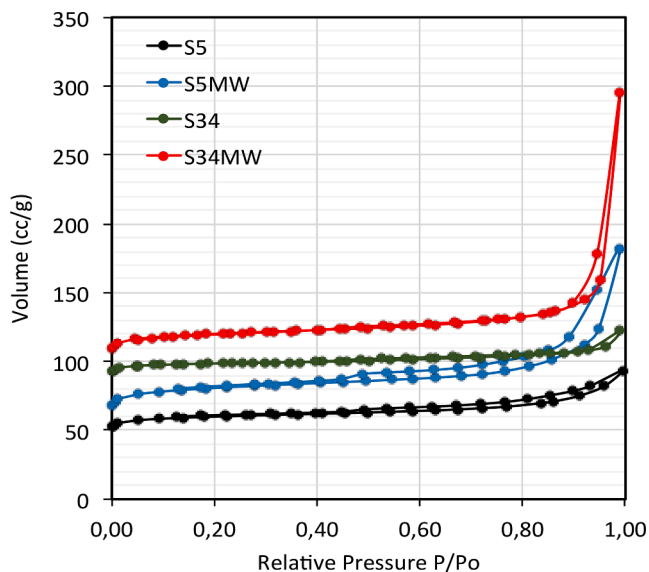


Fig. 6. N_2 adsorption-desorption isotherms for the SAPO samples.

[33,59]. Interestingly, the SAPOs obtained with microwaves showed higher amount of Brønsted acid sites than those prepared by conventional heating (Table 1). This can be explained by the higher Si content observed for these samples by XRF.

3.3. Catalytic activity

Fig. 7 shows the catalytic results obtained for the four catalysts when using commercial glycerol (Fig. 7A), and when using the crude glycerol obtained biocatalytically from the transesterification of the coconut oil (Fig. 7B).

All catalysts were active for the acetalization of furfural with commercial glycerol (Fig. 7A). There are not significant differences between the activity results of S5 and S34 catalysts. Dioxane or dioxalane were the main reaction products for all of them, with very high selectivity values to the mixture (98–100 %). No other reaction products were detected by gas chromatography, although the very small percentage

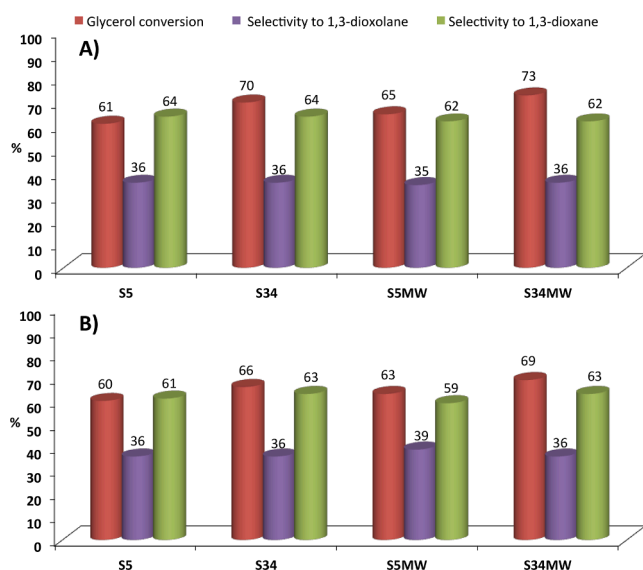


Fig. 7. Catalytic activity of the SAPO catalysts for the acetalization of furfural with A) commercial glycerol, and B) crude glycerol obtained from the biocatalytic transesterification of coconut oil. Reaction conditions: furfural: glycerol ratio 1:1, 150 °C, 45 min, 5 wt% catalyst, bubbling a N_2 flow (1 mL/s).

needed to arrive to 100 % of selectivity in some catalysts should be due to the formation of some condensation products. The main product was 1,3-dioxane, probably due to the higher thermodynamic stability of the 6-membered ring. The higher conversion values of S34 catalysts with respect to the S5 ones could be related to the higher Brønsted acidity of the former, as previously reported for other reactions [33,59]. Interestingly, the catalysts prepared with microwaves showed slightly higher conversion than those prepared by conventional heating. This could be attributed to the higher substitution of the silicon in the aluminophosphate structure for the catalysts prepared with microwaves (Table 1). This involves the presence of higher amount of protons compensating the negative charge of the framework [33].

When these catalysts were tested at the same reaction conditions using the crude glycerol obtained from the biocatalytic transesterification of coconut oil (Fig. 7B), the results were comparable to those obtained with commercial glycerol, with slight lower conversion of glycerol but similar high selectivity to the mixture dioxane + dioxalane (97–100 %).

The best catalyst, S34MW, was reused three times at the conditions specified in the experimental section. A loss of conversion less than 7 % was observed while selectivity to the desired products maintained. In addition, XRD pattern of the reused catalyst did not show significant differences with respect to that taken for the fresh catalyst (Fig. 8). Therefore, this catalyst showed good stability for this reaction.

4. Conclusions

High-pure crude glycerol has been obtained from the transesterification of coconut oil using lipase enzyme-type as biocatalyst. SAPOs prepared by microwaves showed lower crystallinity but higher surface area, slightly higher silicon incorporation and higher amount of acid sites than those prepared by conventional heating, in addition to be obtained at much shorter preparation times. The catalytic results of the SAPO catalysts for the acetalization of furfural were comparable when using commercial glycerol or crude glycerol with high selectivity values to the mixture dioxane + dioxalane. The catalysts prepared with microwaves showed slightly higher conversion values, which can be related to the higher amount of acid sites due to the higher content of silicon on these samples.

CRediT authorship contribution statement

Federico Guerrero-Ruiz: Investigation, Visualization, Writing – original draft. **Edinson Yara-Varón:** Investigation, Visualization, Writing – original draft. **María Dolores González:** Conceptualization, Validation, Writing – original draft. **Mercè Torres:** Conceptualization, Resources, Supervision. **Pilar Salagre:** Conceptualization, Resources, Supervision. **Ramon Canela-Garayoa:** Conceptualization, Resources, Validation, Supervision. **Yolanda Cesteros:** Conceptualization, Resources, Supervision, Writing – original draft, Writing – review &

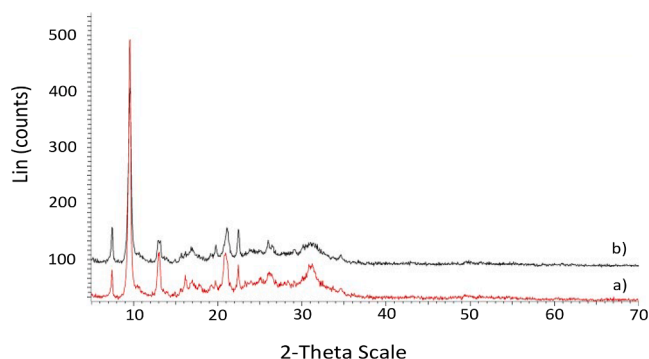


Fig. 8. XRD of the a) fresh and b) used S34MW catalyst.

editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Quispe CAG, Coronado CJR, Carvalho Jr JA. Glycerol: Production, consumption, prices, characterization and new Trends in combustion. *Renew Sustain Energy Rev* 2013;27:475–93. <https://doi.org/10.1016/j.rser.2013.06.017>.
- Pagliaro M, Ciriminna R, Kimura H, Rossi M, DellaPina C. From Glycerol to Value-Added Products. *Angew Chem Int Ed* 2007;46(24):4434–40.
- D'Aquino R, Ondrey G. Outlets for glycerine. *Chem Engineering* 2007;114(9):31–7.
- Behr A, Eilting J, Irawadi K, Leschinski J, Lindner F. Improved utilisation of renewable resources: New important derivatives of glycerol. *Green Chem* 2008;10:13–30. <https://doi.org/10.1039/B710561D>.
- Barrault J, Jerome F. Design of new solid catalysts for the selective conversion of glycerol. *Eur J Lipid Sci Technol* 2008;110:825–30. <https://doi.org/10.1002/ejlt.200800061>.
- Pagliaro M, Ciriminna R, Kimura H, Rossi M, Della PC. Recent advances in the conversion of bioglycerol into value-added products. *Eur J Lipid Sci Technol* 2009;111:788–99. <https://doi.org/10.1002/ejlt.200800210>.
- Rahmat N, Abdullah AZ, Mohamed AR. Recent progress on innovative and potential technologies for glycerol transformation into fuel additives: A critical review. *Renew Sustain Energy Rev* 2010;14:987–1000. <https://doi.org/10.1016/j.rser.2009.11.010>.
- Guerrero-Pérez MO, Rosas JM, Bedia J, Rodríguez-Mirasol J, Cordero T. Recent Patents on Chemical Engineering 2009;2:11.
- Choi WJ. Glycerol-based biorefinery for fuels and chemicals. *Recent Patents Biotechnol* 2008;2(3):173–80.
- Bizzari S, Blagoev M, Mori H. Glycerin, Chemical Economics Handbook—SRI Consulting, Jun2012, (<http://www.ihc.com/products/chemical/planning/ceh/glycerin.aspx?pu=1&rd=chemihs>) (accessed 20May2013).
- Marchetti JM, Miguel VU, Errazu AF. Possible methods for biodiesel production. *Renew Sustain Energy Rev* 2007;11:1300–11. <https://doi.org/10.1016/j.rser.2005.08.006>.
- Aguilera-Oviedo J, Yara-Varón E, Torres M, Canela-Garayoa R, Balcells M. Sustainable Synthesis of Omega-3 Fatty Acid Ethyl Esters from Monkfish Liver Oil. *Catalysts* 2021;11:100. <https://doi.org/10.3390/catal11010100>.
- Busto E, Gotor-Fernandez V, Gotor V. Hydrolases: catalytically promiscuous enzymes for non-conventional reactions in organic synthesis. *Chem Soc Rev* 2010;39:4504–23. <https://doi.org/10.1039/C003811C>.
- Solarte C, Yara-Varón E, Eras J, Torres M, Balcells M, Canela-Garayoa R. Lipase activity and enantioselectivity of whole cells from a wild-type *Aspergillus flavus* strain. *J Mol Catal B Enzym* 2014;100:78–83. <https://doi.org/10.1016/j.molcatb.2013.12.005>.
- Fernandes MLM, Krieger N, Baron AM, Zamora PP, Ramos LP, Mitchell DA. Hydrolysis and synthesis reactions catalysed by *Thermomyces lanuginosa* lipase in the AOT/Isooctane reversed micellar system. *J Mol Catal B Enzym* 2004;30:43–9. <https://doi.org/10.1016/j.molcatb.2004.03.004>.
- Yara-Varón E, Eras J, Torres M, Balcells M, Villorquina G, Canela-Garayoa R. Biocatalytic preparation of dichloropropyl acrylates. Application to the synthesis of poly(dichloropropyl acrylates). *J Mol Catal B Enzym* 2013;92:7–13. <https://doi.org/10.1016/j.molcatb.2013.03.005>.
- Costa e Silva W, Freitas L, Oliveira PC, de Castro HF. Continuous enzymatic biodiesel production from coconut oil in two-stage packed-bed reactor incorporating an extracting column to remove glycerol formed as by-product. *Bioprocess Biosyst Eng* 2016;39(10):1611–7.
- Wegenhart BL, Liu S, Thom M, Stanley D, Abu-Omar MM. Solvent-free methods for making acetals derived from glycerol and furfural and their use as a biodiesel fuel component. *ACS Catal* 2012;2:2524–30. <https://doi.org/10.1021/cs300562e>.
- Zhou R, Jiang Y, Zhao H, Ye B, Wang L, Hou Z. Synthesis of solketal from glycerol over modified SiO₂ supported p-phenolsulfonic acid catalyst. *Fuel* 2021;291. <https://doi.org/10.1016/j.fuel.2021.120207>.
- da Silva MJ, Teixeira MG, Chaves DM, Siqueira L. An efficient process to synthesize solketal from glycerol over tin (II) silicotungstate catalyst. *Fuel* 2020;281:118724. <https://doi.org/10.1016/j.fuel.2020.118724>.
- Gonçalves M, Rodrigues R, Galhardo TS, Carvalho WA. Highly selective acetalization of glycerol with acetone to solketal over acidic carbon-based catalysts from biodiesel waste. *Fuel* 2016;181:46–54. <https://doi.org/10.1016/j.fuel.2016.04.083>.
- Delfort B, Durand I, Jaecker A, Lacombe T, Montagne X, Paille F. Diesel fuel compounds containing glycerol acetals. US Patent 6890364, 2005.
- Umbarkar SB, Kotbagi TV, Biradar AV, Pasricha R, Chanalea J, Dongare MK, et al. Chemical Acetalization of glycerol using mesoporous MoO₃/SiO₂ solid acid catalyst. *J Mol Catal A* 2009;310:150–8. <https://doi.org/10.1016/j.molcata.2009.06.010>.
- Ruiz VR, Vely A, Santos LL, Leyva-Pérez A, Sabater MJ, Iborra S, et al. Gold catalysts and solid catalysts for biomass transformations: Valorization of glycerol and glycerol-water mixtures through formation of cyclic acetals. *J Catal* 2010;271:351–7. <https://doi.org/10.1016/j.jcat.2010.02.023>.
- Climent MJ, Corma A, Iborra S. Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels. *Green Chem* 2014;16:516–47. <https://doi.org/10.1039/C3GC41492B>.
- Mallesham B, Sudarsanam P, Raju G, Reddy BM. Design of highly efficient Mo and W-promoted SnO₂ solid acids for heterogeneous catalysis: acetalization of bioglycerol. *Green Chem* 2013;15:478–89. <https://doi.org/10.1039/C2GC36152C>.
- Konwar LJ, Samikannu A, Mäki-Arvela P, Bostrom D, Mikkola J-P. Lignosulfonate-based macro/mesoporous solid protonic acids for acetalization of glycerol to bio-additives. *Appl Catal B: Environ* 2018;220:314–23. <https://doi.org/10.1016/j.apcatb.2017.08.061>.
- Trifoi AR, Agachi PS, Pap T. Glycerol acetals and ketals as possible diesel additives. A review of their synthesis protocols. *Renew Sustain Energy Rev* 2016;62:804–14. <https://doi.org/10.1016/j.rser.2016.05.013>.
- Gutiérrez-Acebo E, Guerrero-Ruiz F, Centenero M, Martínez JS, Salagre P, Cesteros Y. Effect of using microwaves for catalysts preparation on the catalytic acetalization of glycerol with furfural to obtain fuel additives. *Open Chem* 2018;386–92. <https://doi.org/10.1515/chem-2018-0047>.
- Patil A, Shinde S, Kamble S, Rode CV. Two-step sequence of acetalization and hydrogenation for synthesis of diesel fuel additives from furfural and diols. *Energy Fuels* 2019;33:7466–72. <https://doi.org/10.1021/acs.energyfuels.9b01640>.
- Patel A, Pithadia D. Low temperature synthesis of bio-fuel additives via valorisation of glycerol with benzaldehyde as well as furfural over a novel sustainable catalysts, 12-tungstosilicic acid anchored to ordered cubic nano-porous MCM-48. *Appl Catal A: Gen* 2020;602:117729. <https://doi.org/10.1016/j.apcata.2020.117729>.
- Appaturi JN, Ramalingam RJ, Al-Lohedan HA, Khoerunnisa F, Ling TC, Ng EP. Selective synthesis of dioxolane biofuel additive via acetalization of glycerol and furfural enhanced by MCM-41 aniline bifunctional catalyst. *Fuel* 2021;288:119573. <https://doi.org/10.1016/j.fuel.2020.119573>.
- Chen J, Wright PA, Natarajan S, Thomas JM. Understanding the Brønsted acidity of SAPO-5, SAPO-17, SAPO-18 and SAPO-34 and their catalytic performance for methanol conversion to hydrocarbons. *Stud Surf Sci Catal* 1994;84:1731–8. [https://doi.org/10.1016/S0167-2991\(08\)63726-X](https://doi.org/10.1016/S0167-2991(08)63726-X).
- Erichsen MW, Svelle S, Olsbye U. The influence of catalyst acid strength on the methanol to hydrocarbons (MTH) reaction. *Catal Today* 2013;215:216–23. <https://doi.org/10.1016/j.cattod.2013.03.017>.
- Hajfarajollah H, Askari S, Halladj R. Effects of micro and nano-sized SAPO-34 and SAPO-5 catalysts on the conversion of methanol to light olefins. *React Kinet Mech Cat* 2014;111:723–36. <https://doi.org/10.1007/s11444-013-0650-6>.
- Potter ME, Cholerton ME, Kezina J, Bounds R, Carravetta M, Manzoli M, et al. Role of isolated acid sites and influence of pore diameter in the low-temperature dehydration of ethanol. *ACS Catal* 2014;4:4161–9. <https://doi.org/10.1021/cs501092b>.
- Bakhtiar SH, Ali S, Dong Y, Wang X, Yuan F, Li Z, et al. Selective synthesis of the SAPO-5 and SAPO-34 mixed phases by controlling Si/Al ratio and their excellent catalytic methanol to olefins performance. *J Porous Mater* 2018;25:1455–61. <https://doi.org/10.1007/s10934-018-0558-7>.
- Zhang L, Xi G, Chen Z, Qi Z, Wang X. Enhanced formation of 5-HMF from glucose using a highly selective and stable SAPO-34 catalyst. *Chem Eng J* 2017;307:877–83. <https://doi.org/10.1016/j.cej.2016.09.003>.
- Song H, Jin F, Liu Q, Liu H. Zeolite-catalyzed acetalization reaction of furfural with alcohol under solvent-free conditions. *Mol Catal* 2021;513:111752. <https://doi.org/10.1016/j.mcat.2021.111752>.
- Gebretsadik FB, Mance D, Baldus M, Salagre P, Cesteros Y. Microwave synthesis of delaminated acid saponites using quaternary ammonium salt or polymer as template. Study of pH influence. *Appl Clay Sci* 2015;114:20–30. <https://doi.org/10.1016/j.clay.2013.10.027>.
- Granados-Reyes J, Salagre P, Cesteros Y. Effect of microwaves, ultrasounds and interlayer anion on the hydrocalumites synthesis. *Micropor Mesopor Mater* 2014;199:117–24. <https://doi.org/10.1016/j.micromeso.2014.08.004>.
- Sánchez T, Salagre P, Cesteros Y. Ultrasounds and microwave-assisted synthesis of mesoporous hectorites. *Micropor Mesopor Mater* 2013;171:24–34. <https://doi.org/10.1016/j.micromeso.2013.01.001>.
- Bergadà O, Vicente I, Salagre P, Cesteros Y, Medina F, Sueiras JE. Microwave effect during aging on the porosity and basic properties of hydrocalumites. *Micropor Mesopor Mater* 2007;101:363–73. <https://doi.org/10.1016/j.micromeso.2006.11.033>.
- Newland SH, Sinkler W, Mezza T, Bare SR, Carravetta M, Haies IM, et al. Expanding beyond the Micropore: Active-Site Engineering in Hierarchical Architectures for Beckmann Rearrangement. *ACS Catal* 2015;5:6587–93. <https://doi.org/10.1021/acscatal.5b01595>.
- Breen C. Thermogravimetric and infrared study of the desorption of butylamine, cyclohexylamine and pyridine from Ni- and Co-exchanged montmorillonite. *Clay Miner* 1991;26:487–96. <https://doi.org/10.1180/claymin.1991.026.4.04>.

- [46] Mokaya R, Jones W, Moreno S, Poncet G. n-heptane hydroconversion over aluminosilicate mesoporous molecular sieves. *Catal Lett* 1997;49:87–94. <https://doi.org/10.1023/A:1019084617120>.
- [47] González MD, Cesteros Y, Salagre P. Establishing the role of Brønsted acidity and porosity for the catalytic etherification of glycerol with tert-butanol by modifying zeolites *Appl. Catal A: Gen* 2013;450:178–88. <https://doi.org/10.1016/j.apcata.2012.10.028>.
- [48] Nicolau Paulino B, Sales A, Felipe L, Pastore GM, Molina G, Lemos BJ. Recent advances in the microbial and enzymatic production of aroma compounds. *Curr Opin Food Sci* 2021;37:98–106. <https://doi.org/10.1016/j.cofs.2020.09.010>.
- [49] Bagnato G, Iulianelli A, Sanna A, Basile A. Glycerol Production and Transformation: A Critical Review with Particular Emphasis on Glycerol Reforming Reaction for Producing Hydrogen in Conventional and Membrane Reactors. *Membranes* 2017;7:17. <https://doi.org/10.3390/membranes7020017>.
- [50] Costa-Silva TA, Carvalho AKF, Souza CRF, De Castro HF, Said S, Oliveira WP. Enzymatic Transesterification of Coconut Oil Using Chitosan-Immobilized Lipase Produced by Fluidized-Bed System. *Energy Fuels* 2017;31:12209–16. <https://doi.org/10.1021/acs.energyfuels.7b02033>.
- [51] Kochepka DM, Dill LP, Couto GH, Krieger N, Ramos LP. Production of Fatty Acid Ethyl Esters from Waste Cooking Oil Using Novozym 435 in a Solvent-Free System. *Energy Fuels* 2015;29:8074–81. <https://doi.org/10.1021/acs.energyfuels.5b02116>.
- [52] Moreira KS, Moura Júnior LS, Monteiro RRC, de Oliveira ALB, Valle CP, Freire TM, et al. Optimization of the Production of Enzymatic Biodiesel from Residual Babassu Oil (*Orbignya* sp.) via RSM. *Catalysts* 2020;10:414. <https://doi.org/10.3390/catal10040414>.
- [53] Itabaiana I, de Mariz e Miranda LS, de Souza ROMA. Towards a continuous flow environment for lipase-catalyzed reactions. *J Mol Catal B Enzym* 2013;85-86:1–9.
- [54] Luna C, Luna D, Bautista FM, Estevez R, Calero J, Posadillo A, et al. *Molecules* 2017;22:2025. <https://doi.org/10.3390/molecules22112025>.
- [55] Solarte C, Escribà M, Eras J, Villorbina G, Canela R, Balcells M. From Symmetric Glycerol Derivatives to Dissymmetric Chlorohydrins. *Molecules* 2011;16:2065–74. <https://doi.org/10.3390/molecules16032065>.
- [56] Choi WJ. Glycerol-based biorefinery for fuels and chemicals. *Recent Pat. Biotechnol* 2008:173–80. <https://doi.org/10.2174/187220808786241006>.
- [57] Kingston HM, Haswell SJ. *Microwave-enhanced chemistry: fundamentals, sample preparation and applications*. Washington DC: American Chemical Society; 1997.
- [58] De Boer JH. *The Structure and Properties of Porous Materials*. London: Butterworth; 1958.
- [59] Potter ME, Cholerton ME, Kezina J, Bounds R, Carravetta M, Manzoli M, et al. Role of Isolated Acid Sites and Influence of Pore Diameter in the Low-Temperature Dehydration of Ethanol. *ACS Catal* 2014;4:4161–9. <https://doi.org/10.1021/cs501092b>.