

Document downloaded from:

<http://hdl.handle.net/10251/121855>

This paper must be cited as:

Garcia-Ortiz, A.; Arias Carrascal, K.S.; Climent Olmedo, M.J.; Corma Canós, A.; Iborra Chornet, S. (2018). One-Pot Synthesis of Biomass-Derived Surfactants by Reacting Hydroxymethylfurfural, Glycerol, and Fatty Alcohols on Solid Acid Catalysts. *ChemSusChem*. 11(17):2870-2880. <https://doi.org/10.1002/cssc.201801132>



The final publication is available at

<http://doi.org/10.1002/cssc.201801132>

Copyright John Wiley & Sons

Additional Information

This is the peer reviewed version of the following article: A. Garcia-Ortiz, K. S. Arias, M. J. Climent, A. Corma, S. Iborra, *ChemSusChem* 2018, 11, 2870, which has been published in final form at <http://doi.org/10.1002/cssc.201801132>. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Self-Archiving.

ACCEPTED ARTICLE

**Biomass derived surfactant molecules by reacting
HMF, glycerol and fatty alcohols in one pot process with
heterogeneous acid catalysts of controlled polarity**

Andrea Garcia-Ortiz, Karen S. Arias, Maria J. Climent*, Avelino Corma*, Sara Iborra

Instituto de Tecnología Química (UPV-CSIC).

Universitat Politècnica de València

Avda dels Tarongers s/n, 46022, Valencia (Spain)

Fax: (+34) 963877809

E-mail: acorma@itq.upv.es

mjcliol@qim.upv.es

Abstract

A new type of biomass derived nonionic surfactants have been obtained by reacting hydroxymethylfurfural (HMF), glycerol and fatty alcohols. For instance, 5-(octyloxymethyl)furfural glyceryl acetal can be obtained in a one pot process by etherification of HMF with fatty alcohols followed by acetalization with glycerol. For a successful solid catalyst, acidity and polarity have to be optimized to improve conversion, selectivity and catalyst deactivation, owing to the different adsorption characteristics of the reactant molecules.

Accordingly Beta zeolite with a high Si/Al ratio and practically free of connectivity defects showed good results when dealing with these biomass derivatives that include a highly polar reactant such as glycerol.

The scope of the reaction is good and a variety of new stable surfactant molecules can be obtained that present HLB values in the range of 4.9 to 6.6 that are of interest for water in oil emulsions.

Keywords: surfactants molecules from HMF, hydrophobic solid acid catalysts, solid acid catalysts for biomass transformations, surfactants molecules from biomass.

Introduction

The growing interest for the preparation of non petroleum chemicals has increased the research effort on the transformation of nonfood lignocellulosic carbohydrates, the most abundant source of renewable carbon material,^[1] into chemicals. One way to valorize lignocellulosic biomass is through the conversion of platform molecules into high value compounds.^[2]

In this context, 5-hydroxymethylfurfural (HMF) is a platform molecule readily accessible from the acid catalyzed dehydration of hexoses (mainly fructose). Its chemical versatility makes HMF a suitable starting material for the production of a variety of high added value compounds.^[3]

Glycerol is another interesting platform molecule which production is linked to the biodiesel manufacture, and it is predicted a production of 36.9 million tons in the year 2020.^[4] Considering that one kilogram of glycerol is obtained per each ten kilograms of biodiesel produced,^[5] the increasing production of biodiesel has already provoked an overproduction of glycerol. This scenario has boosted researchers to develop new processes that valorize glycerol by converting it into fuel additives and chemicals, to ensure the sustainability of the biodiesel production.^[6]

Fatty alcohols constitute other abundant biomass building blocks that is expected to reach 3.3 million tons production by 2022.^[7] Today they are

obtained from petrochemical and oleochemicals feedstocks, but owing to the increasingly severe environmental policy, the production of fatty alcohols from conventional petroleum-based products is decreasing, while a huge growth in the market of oleochemicals is expected in the next years. Fatty alcohols from renewable sources are commercially produced by hydrogenation of fatty acids methyl esters of vegetable oils using copper-based catalysts.^[8]

With this scenario, we thought that an interesting route to valorize HMF, glycerol and fatty alcohols could be through its combination to produce new biobased surfactants.

Surfactants are commonly used as detergents and cleaners, although they have many applications in different fields of industry such as in pharmaceuticals, cosmetics, foods, agricultural, textile and even petrochemical processes. Currently surfactants are among the synthetic chemicals produced in larger volumes and an annual growth of 3-4% has been estimated.^[9] Although they have been produced (except soaps) using either petrochemicals or oleochemicals feedstock, classically petrochemical starting materials have been predominant. However, in the last decade, oleochemicals and a variety of other renewable products, as for instance carbohydrates, organic acids and amino acids, have been explored as feedstocks for surfactant.^[9]

The large interest in production and use of biobased surfactants lies on its renewable nature, the lower CO₂ footprint,^[10] their good biodegradability, and the fact that they can have physicochemical properties that are comparable, or even better, to the petrochemical derived surfactants. Since some surfactants derived from petrochemicals are characterized by its persistency in the

environment and potential toxicity, we believe that new opportunities for biomass derived biodegradable surfactants are being opened in the field of fracking to produce gas and liquid hydrocarbons.

The molecular structure of a surfactant molecule consists of a group that has low polarity (lipophilic part) and a group that has high polarity (hydrophilic part). These molecules generally known as amphiphilic molecules, form micelles and vesicular microaggregates whose properties depend on the composition and structure of the polar (*head*) groups and on the length and shape of the hydrophobic hydrocarbon counterpart (*tail*).

HMF exemplifies a bifunctional substrate suitable for the preparation of a plethora of furanic analogues that can be used as starting molecules for further chemical transformation, including its conversion into surfactants. Thus, anionic and non-ionic surfactants have been prepared from HMF and related structures. For instance 2,5-furandicarboxylic acid mono-n-decyl ester sodium salt (A),^[11] 5-alkoxymethyl- α -hydroxyfuranmethanesulfonic acid sodium salts (B)^[12] and aminoesters of HMF derivatives (C),^[13] (see Scheme 1), have been claimed as biodegradable surfactants.

Recently, we have reported that the combination of HMF and fatty alcohols through a one pot process using heterogeneous catalysts leads to a new class of biodegradable anionic surfactants (5-alkoxymethylfuroic acid sodium salts) (D, Scheme 1) with a surfactant capacity similar to the commercial alkyl benzene sulfonic acid sodium salts.^[14]

Following our ongoing interest on new environmental benign routes for transformation of HMF into surfactants, we present here the preparation of new

amphiphilic molecules with potential application as non-ionic surfactants, through the combination of three biomass derived chemicals such as HMF, glycerol and fatty alcohols. These new surfactants are expected to be biodegradable as they are produced from biodegradable synthons.

With this purpose, a one pot process has been studied which consists in the selective etherification of HMF with a fatty alcohol giving a 5-alkoxymethylfurfural intermediate which is subsequently acetalized with glycerol in the presence of a heterogeneous acid catalyst (Scheme 2). The reaction produces the cyclic acetals isomers (1,3-dioxolanes and 1,3-dioxanes) of the 5-alkoxymethylfurfural. The positive effect of the molecules of bearing cyclic acetal moieties on the surface active properties has been previously claimed.^[15]

Etherification and acetalization are typical Bronsted acid catalyzed reactions, and a wide variety of liquid and solid acids have been reported as catalysts for both acetalization and etherification. In the case of the acetalization of aldehydes and ketones with glycerol the cyclic acetals, 1,3-dioxolanes and 1,3-dioxanes (see Scheme 2), are obtained in different ratios depending on experimental conditions and catalyst.^[16]

On the other hand, when HMF is involved in etherification or acetalization reactions, the selectivity to the target compound can be strongly affected due to its high reactivity. The bifunctionality of HMF possessing an alcohol and an aldehyde functions can give, in the presence of an alcohol and an acid catalyst, etherified and at the same time acetalized derivatives. Moreover, in the presence of the water produced during these reactions, the HMF can also be hydrolyzed giving levulinic and formic acids, while strong Bronsted acids can

promote the HMF polymerization and formation of humins. Therefore, owing to the large variety of reaction that may occur, we aim to develop an acid catalyst able to promote the etherification of HMF with fatty alcohols, and that maintains activity for the subsequent reaction, i.e. the acetalization with glycerol, while avoiding the undesired competing reactions. We thought that structured aluminosilicates which offer the possibility to modulate acidity, polarity and pore dimensions could give us the opportunity to design an heterogeneous catalyst with optimized acidity, adsorption-desorption properties and reactant and product diffusion, able to promote with success both reactions in a one pot process. In this work, we will show that by optimizing catalyst and reaction conditions it is possible to couple etherification of HMF and acetalization of the alkoxyethylfurfural intermediate with glycerol to produce a new type of surfactant molecules (Scheme 2).

Results and Discussion

Recently, we reported that the two-dimensional (2D) ITQ-2 zeolite, prepared by delamination of a laminar precursor of MWW zeolite, was an excellent catalyst for performing the acetalization of HMF with glycerol giving the corresponding 1,3-dioxolane and 1,3-dioxanes useful as diol monomers.^[17] Therefore, we have firstly explored here the possibility to produce glyceryl acetals of 5-alkoxyethylfurfural (**2**) in one pot, by combining the acetalization step of HMF with glycerol followed by etherification of the free hydroxymethyl group with a fatty alcohol in the presence of ITQ-2 zeolite (Scheme 3). However, we considered that this reaction sequence could be problematic due to the inherent reactivity of acetals in the presence of water or alcohols that could lead to the

acetal hydrolysis or transacetalization reaction respectively. Nevertheless, the preparation of (2-(5-(octyloxymethyl)furan-2-yl)-1,3-dioxolan-4-yl)methanol (**2a**) and 2-(5-(octyloxymethyl)furan-2-yl)-1,3-dioxan-5-ol (**2b**) (denoted as 5-(octyloxymethylfurfural) glyceryl acetals, **2**), directly from HMF, glycerol and octanol according to Scheme 3, was attempted.

Taking into account previous results,^[17] the first step, i.e., the acetalization of HMF with glycerol, was carried out under previously optimized reaction conditions, using a mixture of HMF and glycerol (1:2 molar ratio) in the presence of ITQ-2 (20 wt%) at 82 °C, using a mixture of trifluorotoluene:acetonitrile (1:1 mL/mL) as solvent and a Dean-Stark to remove the water released during the reaction. After 3h, a mixture of the cyclic five membered ring acetal (2-(5-(hydroxymethyl)furan-2-yl)-1,3-dioxolan-4-yl)methanol (**1a**) and the six membered ring acetal (2-(5-(hydroxymethyl)furan-2-yl)-1,3-dioxan-5-ol) (**1b**) (Scheme 3), along with the two geometrical isomers (Z and E configurations) were obtained with a total yield of 97%. This mixture of isomers is formed as a consequence of the nucleophilic attack of a primary hydroxyl group of glycerol to the protonated carbonyl group of HMF forming the hemiacetal followed by the removal of a water molecule which leaves a carbocation intermediate. In the next step the nucleophilic attack of the secondary hydroxyl group of glycerol (1,2-addition) to the carbocation of HMF leads to 1,3-dioxolane (five member ring acetal). Meanwhile the attack of the other primary hydroxyl group of glycerol (1,3-addition) will give the 1,3-dioxane (six member ring acetal)(see Scheme 2). The four conformational isomers 1,3-dioxolane and 1,3-dioxane acetals, were identified by gas chromatography (CG) and ¹H-NMR spectroscopy. Here, we will refer to HMF glyceryl acetals (**1**) to

the mixture containing the four isomers. During the reaction when the yield of acetals **1** was 97% (99% selectivity), octanol (1 mmol) was added to the reaction mixture. However, after 24 h of reaction it was observed that the acetals **1** remained unreacted and the etherification process did not take place. This behaviour indicates that a strong deactivation of the catalyst during the first step could occur, probably due to the strong adsorption of the highly polar glycerol (which is in excess) on the catalyst surface.

To explore that possibility, HMF glyceryl acetals **1** (1mmol) were prepared, purified and reacted with n-octanol (1mmol) in the presence of fresh ITQ-2 under the same reaction conditions. In this case the etherification process was observed, however the selectivity to **2** was very low due to the formation of numerous byproducts. Thus, products coming from hydrolysis of the starting acetals, and subsequent hydrolysis of HMF giving octyllevulinate and octylformate, and ethers of HMF with glycerol were detected among others. Considering these results, the reaction strategy was modified and we explored the possibility to perform the one pot process but starting from the etherification between the hydroxymethyl group of HMF and n-octanol to give the corresponding ether (5-octyloxymethylfurfural (**3**)) as first step, followed by its acetalization reaction with glycerol (Scheme 3).

Acetalization of 5-(octyloxymethyl)furfural with glycerol

To optimize the one pot process in the new strategy the acetalization of 5-(octyloxymethyl)furfural (**3**) with glycerol in the presence of different structured aluminosilicates as solid acids catalysts was firstly studied. Microporous aluminosilicates with different pore topology such as tridirectional zeolites HBeta and USY, the delaminated ITQ-2 zeolite and a mesoporous

aluminosilicate (MCM-41) were selected as catalysts in a first approximation, and the main physico-chemical properties of the catalysts are summarized in Table 1.

When the acetalization of 5-(octyloxymethyl)furfural (**3**) with glycerol (molar ratio 1:2), was performed in the presence of HBeta (Si/Al=12) in acetonitrile as a solvent at 82 °C, 48 % yield of a mixture of (Z+E) isomers, 1,3-dioxolane (**2a**) and 1,3-dioxane (**2b**) at 95 % conversion was obtained after 8h reaction time. (Table 2). The low selectivity to the target compound was due to the strong polymerization process observed during the reaction, evidenced by the dark colour of the product and by the low molar balance (58 %) observed after reaction. Similar results were obtained when using the USY zeolite as catalyst. We thought that the rapid degradation of the reactants and/or products could be due to the high density of Bronsted acidity of the tridirectional zeolites used (see Table 1), which strongly promotes polymerization reactions. Indeed, when the acetalization of **3** was performed with an homogeneous strong Bronsted acid catalyst such as p-toluenesulfonic acid (1 wt%), the polymerization was the predominant process and compound **2** was not detected at all. However, when the reaction was performed using a weaker homogeneous Bronsted acid as formic acid (5 wt %), after 24h of reaction time the selectivity to **2** was 100 %, although the conversion of **3** was very low (only 40 %).

As was mentioned above, the advantage for using zeolites as acid catalysts is the possibility to tune and adjust its physicochemical properties to the requirements of a given reaction. Particularly, Beta zeolite is an industrial relevant catalyst with a variety of catalytic applications in biomass transformation, fine chemicals, petrochemistry, and environmental chemistry.^[18]

Its high applicability is due to the combination of an open crystalline structure, formed by three directional interconnected large pores along with the possibility to be synthesized with very different chemical compositions.

One way to decrease the Bronsted acidity of the Beta zeolite would be by partial exchange of protons with sodium cations.^[19] Thus, in order to check the effect of decreasing catalyst acidity on the reaction, a sample with a 0.49 wt% of Na content (0.49NaBeta(12)), that correspond to 16% of the H⁺ exchanged, was prepared and tested in the acetalization of 5-(octyloxymethyl)furfural with glycerol. As can be seen in Table 2, the decrease of Bronsted acidity of the Beta zeolite (see Table 1) has a positive impact on the selectivity to **2**, suppressing secondary reactions and polymerization, and achieving 100 % selectivity at 80 % conversion after 24h of reaction, with a molar balance higher than 95 %. However, from the kinetic results presented in Figure 1, it can be inferred that the catalyst deactivates during the reaction and deactivation can be due to the strong adsorption of reactants and/or products on the catalyst surface. To confirm that, after reaction, the solid was subjected to a Soxhlet extraction using ethanol as a solvent and the analysis of the liquid phase showed that glycerol (14.5 wt% respect the amount of solid) was the only extracted product. Besides, the termogravimetric analysis of the catalyst showed that 7.8 wt% of organic material remained adsorbed on the solid (0.49NaBeta(12)) after solid-liquid extraction.

From the results presented above, it is clear that besides acidity, adsorption and product diffusion properties of the catalyst have to be optimized to obtain high conversion and selectivity to the acetals **2**. The adsorption properties of a catalyst have special impact on activity, selectivity and catalyst decay,

particularly when reactants and/or products with different polarities are involved in the process. In our case, we have to consider that the acetalization reaction involves a highly hydrophilic reactant (glycerol) and a less hydrophilic compound 5-(octyloxymethyl)furfural, that have to diffuse through the pores and adsorb on the acid sites of the zeolite. Thus, we could expect that increasing the hydrophobic character of Beta zeolite, the 5-(octyloxymethyl)furfural could be preferentially adsorbed to glycerol, while a lower amount of glycerol may remain adsorbed. This should have an impact, not only on the reaction rate, but also on the rate of catalyst decay. One way to modify the adsorption properties of the catalyst will be by adjusting the polarity of the Beta zeolite. Changes in the zeolite polarity could be achieved by optimizing the framework Si/Al ratio. This parameter does not only determine the number of potential protons, and consequently the number and strength of acid sites, but it also defines the adsorption properties of the zeolite,^[14] in such way that the higher the framework Si/Al ratio, the less polar the zeolite will be. Moreover, another factor that can also have an impact on the polarity on the zeolite is the number of silanols (external and internal) present in the zeolite structure.

Thus, with the aim to determine the influence of the Si/Al ratio of the zeolite Beta on the activity and selectivity, samples of HBeta with Si/Al ratios of 25, 50, 100 and 200 were prepared in fluoride media. This type of synthesis produces almost defect free (silanols) Beta samples, and the resultant catalysts were tested for the acetalization reaction of **3** with glycerol.

The Bronsted acidity of these samples has been determined using *in situ* FTIR combined with the adsorption of pyridine and desorption at different temperatures (Table 3). The results presented in Table 3 show that the amount

of Bronsted acid sites, determined by the IR adsorption of the pyridinium band at 1554 cm^{-1} , continuously decreases when decreasing the bulk aluminum content. The amount of Lewis acid sites, determined by the IR adsorption band at 1455 cm^{-1} , was small in all samples due to the small amount of extra-framework Al (EFAL) formed during the two-steps activation of these samples.

Results from Figure 2 show that the catalytic activity (initial reaction rate of formation of acetals **2**) first increases when increasing Al/Si+Al ratio and reach a maximum at Al/Si+Al of 0.01 which correspond to a Si/Al ratio of 100, then the catalytic activity decrease in spite the fact that the number of the acid sites increases. These results can not be explained taking only into account the variation in the number of acid sites in the zeolite, but the adsorption properties of the catalyst also play an important role. Indeed, when the hydrophobicity of the catalyst is increased (lower Al/Si+Al molar ratio Figure 2), a preferential adsorption of the more hydrophobic 5-(octyloxymethyl)furfural and lower adsorption of the more polar glycerol should occur, favoring the acetalization reaction. Then, there is an optimum in the characteristics of the Beta zeolite that combines acidity and adsorption properties leading to a maximum in activity at a Si/Al around 100.

On the other hand, due to acetalization reaction does not require strong acid sites, it will be possible that silanol groups were contributing to the catalytic activity. To check this, the area of the IR band associated to silanols of BetaF zeolites were plotted versus initial reaction rate. From the results presented in Figure S1 one could conclude that silanol groups are already acid enough to carry out the acetalization reaction. To check that possibility, two new samples were prepared, i.e. pure silica ITQ-2 and pure silica MCM-41. In these samples

the amount of silanols were much larger than in the BetaF samples (see Figures S2 and S3. However, when activity in the acetalization reaction was tested it was very low for the samples with high concentration of silanol groups (25 and 30 % yield of acetal were obtained after 24h reaction time with pure silica ITQ-2 and MCM-41 respectively). These results indicate that the catalyst activity for the acetalization reaction can not be associated to the silanol groups. Thus we have associated the catalytic activity of the zeolite Beta to the presence of bridged Al containing hydroxyl groups.

It is known that the synthesis of zeolites in fluoride, instead of OH^- media, produces samples with lower amount of connectivity defects or internal silanol groups and, consequently, materials with lower polarity are produced. Then, in order to see the effect of the presence of defects on the catalyst surface on the catalytic activity, we synthesized a sample in OH^- media (BetaOH(114)) with a similar Si/Al ratio (114), i.e., similar amount of protons than the Beta prepared in fluoride media (Si/Al =100)(see Table 3). IR spectra in the OH stretching region for the BetaF(100) and BetaOH(114) samples are presented in Figure 3. As can be observed the band at 3745 cm^{-1} which correspond to external silanol groups, and internal silanols that appears as a broad band ($3550\text{--}3700\text{ cm}^{-1}$)^[20] are considerably higher for the BetaOH(114), which confirm the higher hydrophilic character of this sample. In the results presented in Table 2 (entry 8) one can observe that when the acetalization was carried in the presence of BetaOH(114) the rate of formation of acetals **2** decreases twofold with respect to the more hydrophobic Beta sample (BetaF(100)), though both samples have a similar framework Si/Al ratio and acidity. Furthermore, the BetaOH(114) catalyst is less selective and deactivates faster than BetaF(100), giving 78%

conversion at 10 h and no further increase is observed with time (see Figure 4). Then it appears that the presence of defects has a strong impact on activity, selectivity and catalyst decay. This behavior could be attributed to a strong adsorption of the more polar products (glycerol and water) and confinement effects which favors subsequent reactions and blockage of the pores of the tridirectional Beta zeolite. This result strongly contrasts with those obtained with the more hydrophobic BetaF(100) zeolite, practically free of connectivity defects, where 96% conversion (100% selectivity) was achieved in 10 h reaction time.

To study the possible deactivation of the BetaF(100) sample, after reaction, the solid was submitted to a solid-liquid extraction with a Soxhlet apparatus using ethanol as a solvent and it was then reacted in a second cycle. The results showed that with the used catalyst only a 60 % conversion (100% selectivity to **2**) was achieved after 10 h, indicating that deactivation of the catalyst occurs during the reaction. In fact, the amount of organic extracted by Soxhlet after the first run was 12.3 wt%, (composed by 90 % glycerol and 10 % of **2**). Moreover, the thermogravimetric analysis of the used catalyst after Soxhlet extraction, showed that 10 wt% of organic material (with respect the amount of catalyst) still remains on the catalyst. Since, the micropore volume of BetaF(100) after reaction is almost half of the initial, while the crystallinity of the zeolite remains practically the same, it can be said that catalyst deactivation occurs by pore blockage, from the products remaining occluded in the pores. However, the calcination of the catalyst at 540 °C restored the initial catalytic activity.

At this point we have showed that a beta zeolite sample that combines adequate acidity and adsorption properties displays very good performance in

the acetalization of 5-(octyloxymethyl)furfural. However the catalyst deactivates during the reaction due to the adsorption of organic material inside the pores of the zeolite. Therefore, it is possible that a catalyst with better diffusion of reactants and products would be more adequate to perform this reaction. Thus, we selected a two-dimensional delaminated zeolite (ITQ-2) with large external surface area (Table 1). Nevertheless, we are aware, that the large concentration of silanols on the surface of ITQ-2 could have an impact on selectivity and catalyst decay (see Figure 3).

When the acetalization of 5-(octyloxymethyl)furfural (**3**) with glycerol in the presence of ITQ-2, is followed with time (Figure 4), we can see that the catalyst performs well, achieving 91 % conversion while maintains excellent selectivity (100 %), showing the benefit of the open structure of ITQ-2. However, from the shape of the curve it appears that conversion does not get 100% but the reaction stops at 89% conversion. This observation indicates that the catalyst, as expected, also deactivates with time (Figure 5). Indeed, after reaction the solid was submitted to a solid-liquid extraction with a Soxhlet apparatus using ethanol as a solvent, and the analysis of the organic phase showed that 10.5 wt% (respect the amount of solid catalyst) of organic material, composed by glycerol as the only product, was retained on the solid. The TG analysis showed that 13 wt% of organic material remains on the ITQ-2 after extraction, which is higher than the remaining on BetaF(100) zeolite (10 wt%).

These results indicates that for this reaction, despite a possible benefit of a catalysts with easy diffusion of reactants and products the presence of defects and adsorption characteristics can have an important influence on the evolution of conversion with reaction time. To confirm that, we selected a mesoporous

aluminosilicate MCM-41 catalyst, with weak acidity, as measured by pyridine adsorption-desorption, large pore diameter (3.2 nm) for easier product diffusion, but it has a higher concentration of silanol groups on its surface than ITQ-2, (see Figure 3).

The results presented in Table 2 and Figure 6 show that this catalyst performs the reaction less efficiently than ITQ-2 achieving only 70% conversion after 10 h reaction time, indicating a higher rate of deactivation than ITQ-2 though with an excellent selectivity (100%). Moreover, when the used MCM-41 catalyst was subsequently submitted to a continuous solid-liquid extraction with a Soxhlet equipment using ethanol as a solvent, 18.4 wt% of organic (only glycerol) was recovered being this amount about twofold higher than with ITQ-2 (10.5 wt %). Meanwhile, the thermogravimetric analysis of the MCM-41, showed that 9.5 wt % of organic material was retained on MCM-41 after extraction.

These results allow concluding that for the process here studied, acidity, and different adsorption properties of the catalyst are determining activity, selectivity and catalyst decay. In the case of ITQ-2 and MCM-41 catalysts with weak acidity, as measured by adsorption desorption of pyridine, and where, an easy diffusion of reactants and products can be expected, the catalyst decay is due to the adsorption of polar compounds (glycerol and water), as well as other heavier not soluble products, while in the tridirectional zeolites, free of connectivity defects (BetaF(100)), catalyst deactivation is also due to the adsorption of organic material mainly inside the pores, blocking channels for diffusion and active sites.

Synthesis of 5-(octyloxymethyl)furfural glyceryl acetals in one pot process

In a previous work^[14] the etherification of HMF with fatty alcohols was studied using aluminosilicates as acid catalysts. We found that highly hydrophobic defect-free HBeta zeolites with Si/Al ratios higher than 25 were excellent acid catalysts to perform the selective etherification of HMF with fatty alcohols, avoiding the competitive self-etherification of HMF. Taking this into account and from the results presented above, the hydrophobic BetaF(100) zeolite could be a promising catalyst to prepare the target products, (5-(alkyloxymethyl)furfural glyceryl acetals) formed by the etherification between HMF and the fatty alcohol, followed by its acetalization with glycerol in a single vessel and with the same catalyst (Scheme 3).

Thus, etherification reaction (first step) was carried out using an equimolar mixture of HMF and n-octanol (1:1) at 100 °C in absence of solvent. After 2 h reaction time, 97% yield of ether **3** was obtained. Then, the reaction temperature was decreased at 82 °C and 2 mmol of glycerol, dissolved in 5 ml of acetonitrile, were added to the reactor affording 80% conversion with 99 % selectivity to the target 5-(octyloxymethyl)furfural glyceryl acetals (**2**) (entry 1, Table 4). The long time required to achieve an acceptable yield of **2** is indicative that deactivation of the catalyst probably occurs already during the first step of the reaction. Then, to overcome this problem, and to achieve high yield of **2** while reducing the reaction time, the one pot process was performed by adding the same amount of BetaF(100) catalyst (40wt%) in two times, 20wt% in the first step (etherification reaction) and 20wt% of fresh catalyst in the acetalization step (entry 2, Table 4). Under these conditions, the total yield of 5-

(octyloxymethyl)furfural glyceryl acetals **2** in the one pot reaction was 87% with 99% selectivity in 24h reaction time.

Since ITQ-2 showed good performance in terms of yield and selectivity to **2** during the second step, we have also carried out the one pot process with ITQ-2. However, in order to achieve acceptable conversion during the first and second steps, a 60 wt% of catalyst and long reaction times were required (entry 3, Table 4) showing that BetaF(100) zeolite is a more adequate catalyst for the one-pot process.

Finally, the reusability of the BetaF(100) catalyst after the one pot reaction was studied. Thus, after the reaction, the solid was submitted to calcination in air at 540 °C before each reuse and the activity and selectivity was practically maintained during three consecutive cycles (see Figure 6 and Figure S4).

Substrate scope

Since it is known that the biodegradability of surfactants is related to length and branching of the hydrocarbon chain,^[21] the one pot process was extended to other linear aliphatic alcohols such as decanol, dodecanol and hexadecanol to obtain the corresponding 5-(alkyloxymethyl)furfural glyceryl acetals using BetaF(Si/Al=100). The results, summarized in Table 5, show that the length of the carbon chain of the fatty alcohol affects particularly to the yield of the second step that decreases when increasing the chain length. This behavior can be related with the increase in size of reactants and products with the corresponding geometrical and diffusion constrains in the zeolite pore.

Surfactant properties of 5-(alkyloxymethyl)furfural glyceryl acetals

One way to determine the potential application of a surfactant is by estimating the ratio between the hydrophilic to hydrophobic moiety of the molecule, which is expressed as the Hydrophilic-Lipophilic Balance (HLB). This numerical value is useful to predict the surfactant properties that may be expected from an amphiphilic molecule. The HLB scale ranges from 0 to 20. In the range of 3.5 to 6.0, surfactants are more suitable for use in W/O (water in oil) emulsions, while surfactants with HLB values in the 8 to 18 range are most commonly used in O/W (oil in water) emulsions.^[22] Thus, HLB values of the new compounds were determined according to the method proposed by Griffin^[22] and the calculated HLB value ranges from 4.9 to 6.6 (see Table 5), indicating that these molecules could have applications as humectants, and emulsifiers of water in oil emulsions. For instance, the 5-(octyloxymethyl)furfural glyceryl acetals (entry 1, Table 5) have a HLB of 6.6 which is similar to the estimated for the Sorbitan monopalmitate (Span 40), a commonly non-ionic surfactant used as dispersant in paintings inks, and stabilizer and emulsifying agent for oil field and in pharmaceuticals.

On the other hand, since some acetals can be easily hydrolyzed in the presence of water, we have also studied the stability of the new molecules in water. To do that, a mixture of 5-(octyloxymethyl)furfural glyceryl acetals and water (30mg/1mL) was maintained under stirring at room temperature during 50 hours. After this time, the solution was extracted with dichloromethane and analyzed by GC and GC-MS. The results showed that the compound remained unchanged indicating the good stability of the new non-ionic surfactant in presence of water and oxygen during the time of experiment.

Finally, the thermal stability was determined by means of the thermogravimetric analysis of the 5-(octyloxymethyl)furfural glyceryl acetals. The results showed that the compound present high thermal stability, and requires temperatures higher to 200 °C to decompose (see Fig S5).

Conclusions

New biomass derived compounds with nonionic surfactant properties have been obtained by reacting HMF, glycerol and fatty alcohols. The new surfactants have been synthesized in good yields through a one pot process that combines etherification of HMF with fatty alcohols as first step, leading to 5-(alcoxymethyl)furfural which is subsequently acetalized with glycerol in the same pot and with the same catalyst. Optimization of the second step, i.e. acetalization with glycerol showed that tridirectional zeolites with high density of Bronsted sites are not adequate for this transformation, leading to low mass balances. Reactions performed in presence of a sodium exchanged beta zeolite, and with beta zeolite with different Si/Al ratios (i.e. with different acidity and polarity), evidenced that acidity and adsorption properties are important parameters controlling catalytic activity, selectivity and catalyst decay. The study showed that a beta zeolite free of connectivity defects and with a Si/Al ratio of 100 (BetaF(100)) combines the proper acidity and adsorption properties to obtain good performance in terms of yield, selectivity and deactivation rate.

Moreover, it has been showed that the presence of connectivity defects (silanol groups) promotes the preferential adsorption of glycerol, being this the main cause of deactivation of catalysts such the 2D zeolite ITQ-2 and the mesoporous aluminosilicate MCM-41.

The BetaF(100) catalyst has been applied with good success in the one pot process for the synthesis of a variety of surfactant molecules with different hydrophobic moiety by changing the nature of the fatty alcohol. The surfactant compounds with HLB values in the range of 4.9 to 6.6 and good thermal and water stability, can be useful for industrial applications as W/O emulsifiers.

Experimental Section

Reactants

Glycerol ($\geq 99\%$), n-octanol ($\geq 99\%$), and acetonitrile ($\geq 99.9\%$) were purchased from Sigma-Aldrich and 5-hydroxymethyl-2-furfural (HMF) ($\geq 99\%$) was purchased from Carbosynth.

Catalysts preparation and characterization

HBeta(12) (CP811) and USY(12) (CBV 720) were purchased from PQ Zeolites B. V. and, before use, the catalysts were calcined at 580 °C for 3 h. The following catalysts were prepared: Na-exchanged Beta zeolite (0.49NaBeta(12)), where the number indicates the wt% of sodium content were prepared by impregnating the commercial HBeta zeolite (Si/Al =12) with 2 mL of an aqueous solution of sodium acetate (11mg/mL) followed by drying at 100 °C overnight and then calcination at 580 °C for three hours. The Na content of the sample was determined by chemical analysis (Varian 715-ES ICP-optical emission spectrometer) after dissolving the solids in a HNO₃/HF solution.

BetaF samples were synthesized in fluoride aqueous solution (to obtain a zeolite with a low concentration of defects and, therefore, with high hydrophobicity) following the method described in literature. ^[23] The sample BetaOH(114) was synthesized in hydroxyl media following the method reported

in literature.^[24] The MCM-41(Si/Al = 15) sample was prepared according the described method,^[25] and the two-dimensional zeolite ITQ-2 (Si/Al = 15) was prepared by expansion and subsequent exfoliation of the corresponding laminar precursors of the MWW structure by following the literature.^[26] Before use, all the catalysts were calcined at 540 °C for 3h.

Both silanol groups and Bronsted and Lewis acidity of the samples were monitored by infrared spectroscopy. IR spectra were recorded at room temperature by using a Nicolet 750 spectrophotometer using self-supported wafers of 10 mg cm⁻². The calcined samples were outgased overnight at 400 °C under vacuum (10⁻⁹ to 10⁻¹⁰ bar). Then, pyridine was adsorbed on the catalysts at room temperature up to saturation and desorbed at different temperatures (150, 250, and 350°C). After each desorption the spectra were recorded at room temperature. In Figures S6 and S7 are presented the IR of pyridine titration of the different catalysts. The acidity of the catalysts was measured as $\mu\text{mol pyridine/gram catalyst}$ at different temperatures, calculated using extinction coefficients reported by C.A. Emeis.^[27] All spectra were normalized to weight (10 mg) and then the area of the IR band of silanol groups of each sample was referenced to the sample with the lowest IR intensity of the silanol groups.

Surface area measurements were carried out with a Micrometrics ASAP 2000 apparatus following the BET procedure by means of nitrogen adsorption at 77 K. Thermogravimetric analyses (TGA) were performed with a Netzsch STA 409 EP thermal analyzer with about 20 mg of sample and a heating rate of 10°C min⁻¹ in air flow. The physicochemical characteristics of the different samples studied are presented in Table 1.

For ESI–HRMS (electro-spray ionization–high resolution mass spectrometry) analysis the samples were diluted in acetonitrile and analyzed by means of a Waters ACQUITY XevoQ ToF spectrometer (Waters Corp.) through direct infusion of the liquid sample in an ESI interface. The ESI source was operated in positive ionization mode with the capillary voltage at 1.5 kV. The temperature of the source and desolvation was set at 100 °C and 400 °C, respectively. The cone and desolvation gas flows were 100 and 800 Lh⁻¹, respectively. All data collected in centroid mode were acquired by using the Masslynx software (Waters Corp.). Leucine-enkephalin was used as the lock mass generating an [M+H]⁺ ion (m/z=556.2771) at a concentration of 2 ngmL⁻¹ and flow rate of 50 mLmin⁻¹ to ensure accuracy during the MS analysis.

¹H, ¹³C and distortion less enhancement by polarization transfer (DEPT) NMR spectra were recorded by using a Bruker Avance 300 (¹H 300 MHz, ¹³C 75 MHz) in CDCl₃. The chemical shifts are given in ppm and the *J* values are given in Hz. Abbreviations were defined as follows: s=singlet, d=doublet, t=triplet, m=multiplet.

Reaction procedure

Acetalization of 5-(octyloxymethyl)furfural with glycerol.

In a typical reaction, the acid catalyst (40mg) was activated in a two-neck round-bottom flask of 10mL by heating the solid at 200 °C under vacuum for 2h. Then, a mixture of 5-(octyloxymethyl)furfural (**3**) (0.42mmol) and glycerol (0.84mmol) in 2mL of acetonitrile was added into the reactor. The mixture was heated at 82 °C using a system equipped with a silicone bath, magnetic stirrer,

Dean-stark system and condenser. The reaction was followed taking samples at regular periods that were analyzed by gas chromatography using a flame ionization detector and a capillary column (HP5, 30 m x 0.25 mm x 0.25 mm), using nonane as external standard. GC analysis conditions: initial temperature 100 °C (1min), rate 20 °/min up to 280 °C. Injector temperature 280 °C, detector temperature 300 °C, N₂ flow of 1mL/min.

To avoid the control by external diffusion the acetalization was carried under different stirring speed (300, 600, 1000, 1400 rpm). It was found that working at stirring speeds between 1000 and 1200 rpm there is not influence on the initial reaction rates. Thus, all the experiments were carried out at 1000 rpm.

When the reaction was finished, the catalyst was filtered off and the mixture was analyzed by GC-MS chromatography. GC-MS analyses were performed with an Agilent 6890N equipped with the same column as for GC. Purification of the final product was carried out by flash chromatography using mixtures of hexane/ethyl acetate as eluent.

The products were characterized by ¹H, ¹³C NMR spectroscopy. The molar ratio between (2-(5-(octyloxymethyl)furan-2-yl)-1,3-dioxolan-4-yl)methanol (**2a**) and 2-(5-(octyloxymethyl)furan-2-yl)-1,3-dioxan-5-ol (**2b**) was determined by ¹H-NMR using the singlet signals at 6.02-5.87 for (E)-(Z)-dioxolan ring and 5.58-5.47 for (E)-(Z)-dioxan ring.^[28]

One pot two steps process

First, the acid catalyst (50mg) was activated in a two-neck round-bottom flask of 10mL by heating the solid at 200 °C under vacuum for 2h. Preheated mixture of HMF (1 mmol) and n-octanol (1 mmol) at 100 °C was added into the reactor. The mixture was heated at 100 °C using a system equipped with a silicone

bath, magnetic stirrer, Dean-Stark system and condenser. The reaction was followed taking samples at regular periods that were analyzed by gas chromatography using a flame ionization detector and a capillary column (HP5, 30 m x 0.25 μ m x 0.25 mm) and using nonane as external standard. When the conversion to 5-(octyloxymethyl)furfural was maximal, glycerol (2mmol) in acetonitrile (5mL) were added via syringe and the temperature was decreased to 83 °C. The progress of the reaction was followed by taking samples at regular periods that were analyzed by gas chromatography using a flame ionization detector (FID) and a capillary column (HP5, 30 m x 0.25 μ m x 0.25 mm), performing first a microextraction to remove the glycerol. Finally, when the reaction finished the catalyst was remove by filtration and the crude was analyzed by GC and GC-MS. Purification of the final product was carried out by flash chromatography using mixtures of hexane/ethyl acetate as eluent.

The product was characterized by ^1H , ^{13}C NMR spectroscopy. Spectra are showed in Supporting Information (Figure S3).

For catalyst reuse, the catalyst was collected after the reaction by vacuum filtration, and it was calcined at 540 °C in air flow during 3h under air flow and used in subsequent cycles.

Spectral data

(2-(5-(octyloxymethyl)furan-2-yl)-1,3-dioxolan-4-yl)methanol (**2a**) and 2-(5-(octyloxymethyl)furan-2-yl)-1,3-dioxan-5-ol (**2b**) (molar ratio 70:30): ^1H NMR (300 MHz, CDCl_3) δ 6.42 (t, J = 2.8 Hz, 2H), 6.38 (t, J = 3.3 Hz, 2H), 6.27 (dd, J = 7.1, 3.5 Hz, 5H), 6.02 (s, 1.5H), 5.87 (s, 1.5H), 5.58 (s, 0.5H), 5.47 (s, 1H), 4.41 (s, 10H), 4.31 – 3.95 (m, 12H), 3.88 – 3.50 (m, 14H), 3.48 – 3.40 (m, 10H),

2.03 (s, 2H), 1.55 (dd, $J = 12.7, 5.9$ Hz, 12H), 1.38 – 1.15 (m, 37H), 0.86 (t, $J = 6.7$ Hz, 15H); ^{13}C NMR (75 MHz, CDCl_3) δ 153.17 (2C), 152.98 (C), 152.43 (C), 150.97 (2C), 150.22 (C), 150.02 (C), 109.94 (CH), 109.46 (CH), 109.36 (CH), 109.32 (2CH), 109.20 (CH), 108.45 (CH), 108.34 (CH), 98.19 (CH), 98.05 (CH), 96.27 (CH), 95.40 (CH), 76.36 (2CH), 72.09 (CH_2), 71.34 (2CH_2), 70.64 (2CH_2), 70.56 (2CH_2), 70.52 (CH_2), 66.68 (CH), 66.35 (CH), 64.74 (2CH_2), 64.68 (CH_2), 63.88 (CH_2), 62.95 (CH_2), 62.46 (CH_2), 61.11 (CH_2), 60.36 (CH_2), 31.75 (4CH_2), 29.54 (2CH_2), 29.35 (2CH_2), 29.18 (4CH_2), 26.02 (2CH_2), 22.58 (4CH_2), 14.13 (CH_3), 14.02 (3CH_3). UPLC-MS [M^+ ; calculated for $\text{C}_{17}\text{H}_{28}\text{O}_5$: 312.1937] found m/z 335.18 [$\text{M}^+ + \text{Na}^+$]

(2-(5-(decyloxy)methyl)furan-2-yl)-1,3-dioxolan-4-yl)methanol, and 2-(5-(decyloxymethyl)furan-2-yl)-1,3-dioxan-5-ol (molar ratio 60:40): ^1H NMR (300 MHz, CDCl_3) δ 6.43 (t, $J = 3.0$ Hz, 2H), 6.38 (t, $J = 3.4$ Hz, 2H), 6.27 (dd, $J = 7.2, 3.5$ Hz, 5H), 6.02 (s, 1.5H), 5.88 (s, 1.5H), 5.59 (s, 1H), 5.47 (s, 1H), 4.41 (d, $J = 1.1$ Hz, 10H), 4.31 – 4.01 (m, 14H), 3.86 – 3.50 (m, 10H), 3.47 – 3.40 (m, 10H), 2.19 (s, 1H), 2.03 (s, 5H), 1.55 (dd, $J = 12.8, 6.1$ Hz, 10H), 1.25 (s, 60H), 0.87 (t, $J = 6.6$ Hz, 15H), ^{13}C NMR (75 MHz, CDCl_3) δ 153.21 (C), 153.01 (C), 152.48 (C), 152.46 (C), 150.97 (C), 150.23 (C), 150.23 (C), 149.99 (C), 109.94 (CH), 109.45 (2CH), 109.35 (CH), 109.32 (CH), 109.21 (CH), 108.48 (CH), 108.35 (CH), 98.21 (CH), 98.08 (CH), 96.30 (CH), 95.41 (CH), 76.37 (2CH), 72.11 (2CH_2), 71.32 (2CH_2), 70.66 (CH_2), 70.58 (CH_2), 70.54 (CH_2), 66.69 (CH_2), 66.35 (CH_2), 64.76 (2CH_2), 64.70 (2CH_2), 63.90 (CH_2), 62.97 (CH_2), 62.49 (CH_2), 61.18 (CH_2), 60.36 (CH_2), 31.85 (6CH_2), 29.56 (4CH_2), 29.54 (6CH_2), 29.51 (4CH_2), 29.41 (4CH_2), 29.27 (4CH_2), 26.04 (4CH_2), 22.63

(6CH₂), 20.98 (2CH₂), 14.14 (CH₃), 14.05 (3CH₃). UPLC-MS [M⁺; calculated for C₁₉H₃₂O₅ : 340.2249] found m/z 363.2147 [M⁺+Na⁺]

(2-(5-(dodecyloxymethyl)furan-2-yl)-1,3-dioxolan-4-yl)methanol, and 2-(5-(dodecyloxymethyl)furan-2-yl)-1,3-dioxan-5-ol (molar ratio 73:27): ¹H NMR (300 MHz, CDCl₃) δ 6.41 (t, *J* = 3.0 Hz, 3H), 6.36 (t, *J* = 3.0 Hz, 3H), 6.25 (q, *J* = 3.5 Hz, 5H), 6.00 (s, 2H), 5.85 (s, 2H), 5.57 (s, 0.5H), 5.44 (s, 1H), 4.40 (s, 11H), 4.25 – 3.96 (m, 13H), 3.70 (m, 14H), 3.43 (ddd, *J* = 8.5, 6.5, 2.9 Hz, 12H), 2.01 (s, 3H), 1.54 (dd, *J* = 12.6, 6.0 Hz, 20H), 1.23 (s, 90H), 0.85 (t, *J* = 6.6 Hz, 17H), ¹³C NMR (75 MHz, CDCl₃) δ 153.05 (C), 152.88 (C), 152.33 (C), 150.96 (C), 150.24 (C), 150.05 (C), 109.86 (2CH), 109.41 (CH), 109.33 (2CH), 109.28 (2CH), 109.14 (2CH), 108.35 (CH), 108.31 (CH), 98.13 (2CH), 97.98 (2CH), 96.19 (CH), 95.37 (CH), 76.35 (2CH), 72.02 (2CH), 71.38 (2CH), 70.60 (2CH), 70.52 (2CH), 70.47 (2CH), 66.66 (3CH), 66.34 (2CH), 64.68 (3CH), 64.62 (CH), 63.79 (CH), 62.85 (2CH), 62.36 (2CH), 60.91 (CH), 60.33 (CH), 31.81 (6CH₂), 29.55 (6CH₂), 29.53 (6CH₂), 29.48 (10CH₂), 29.35 (6CH₂), 29.24 (6CH₂), 25.97 (4CH₂), 22.57 (6CH₂), 14.06 (CH₃), 13.99 (3CH₃). UPLC-MS [M⁺; calculated for C₂₁H₃₆O₅ : 368.2574] found m/z 391.2460 [M⁺+Na⁺] UPLC-MS [M⁺; calculated for C₂₁H₃₆O₅ : 368.2574] found m/z 369.2653 [M⁺+H⁺].

(2-(5-(hexadecyloxymethyl)furan-2-yl)-1,3-dioxolan-4-yl)methanol, and 2-(5-(hexadecyloxymethyl)furan-2-yl)-1,3-dioxan-5-ol, (molar ratio 62:38): ¹H NMR (300 MHz, CDCl₃) δ 6.42 (t, *J* = 2.8 Hz, 2H), 6.38 (t, *J* = 3.2 Hz, 3H), 6.27 (dd, *J* = 7.0, 3.5 Hz, 5H), 6.02 (s, 1.6H), 5.87 (s, 1.4H), 5.58 (s, 1H), 5.46 (s, 1H), 4.41 (s, 10H), 4.08 (m, 12H), 3.92 – 3.49 (m, 13H), 3.48 – 3.39 (m, 10H), 2.03 (s,

4H), 1.55 (d, $J = 6.6$ Hz, 12H), 1.24 (s, 128H), 0.87 (t, $J = 6.6$ Hz, 15H), ^{13}C NMR (75 MHz, CDCl_3) δ 153.16 (C), 152.96 (C), 152.42 (C), 150.97 (C), 150.25 (C), 150.02 (C), 109.92 (CH), 109.44 (2CH), 109.34 (2CH), 109.30 (2CH), 109.19 (2CH), 108.43 (CH), 108.33 (CH), 98.18 (CH), 98.04 (CH), 96.26 (CH), 95.40 (CH), 76.36 (2CH), 72.08 (2CH), 71.35 (2CH), 70.64 (2CH), 70.56 (2CH), 66.68 (2CH), 66.34 (2CH), 64.74 (2CH), 64.67 (CH), 63.81 (CH), 62.93 (2CH), 62.44 (3CH), 61.07 (CH), 60.35 (CH), 31.87 (8CH₂), 29.63 (20CH₂), 29.54 (10CH₂), 29.41 (8CH₂), 29.30 (8CH₂), 26.02 (8CH₂), 22.62 (8CH₂), 14.12 (CH₃), 14.04 (3CH₃). UPLC-MS [M⁺; calculated for C₂₁H₃₆O₅ : 368.2574] found m/z 369.2641 [M⁺+H⁺] UPLC- MS [M⁺; calculated for C₂₁H₃₆O₅ : 368.2574] found m/z 391.2460 [M⁺+Na⁺]

Acknowledgements

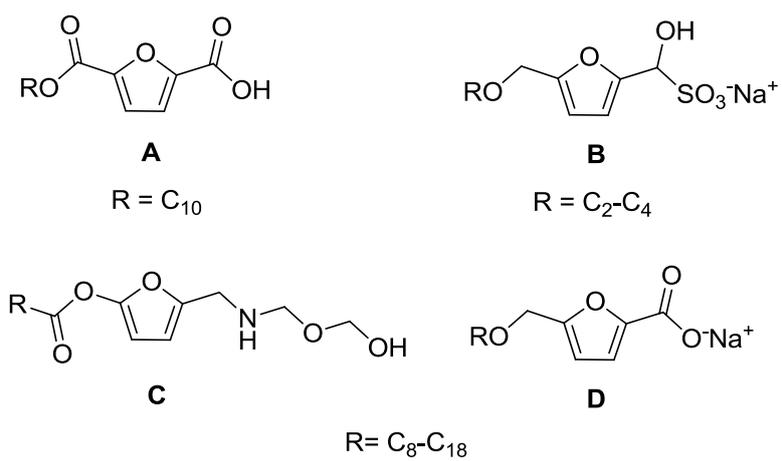
Authors acknowledge financial support from MICINN Project CTQ-2015-67592-P, and Program Severo Ochoa (SEV-2016-0683). AGO thanks Severo Ochoa Program for predoctoral fellowships.

References

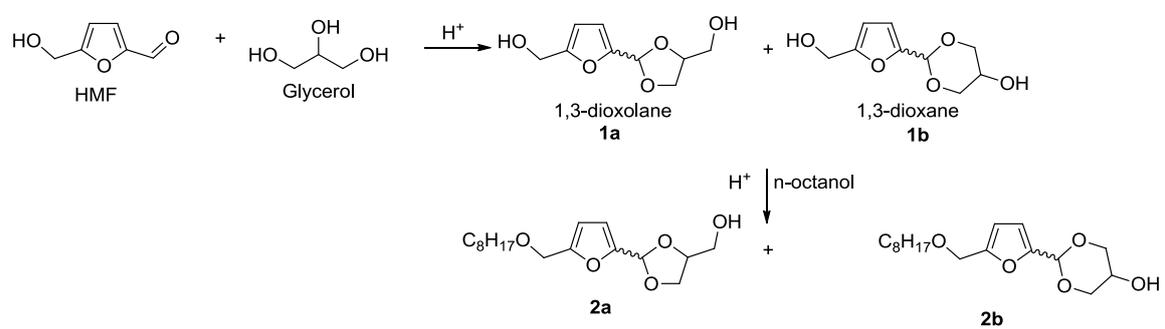
- [1] a) A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, 107,2 411–2502; b) M. Besson, P. Gallezot, C. Pinel, *Chem. Rev.* **2014**, 114,1827–1870.
- [2] a) M. J. Climent, A. Corma, S. Iborra, *Green Chem.* 2011, 13, 520-540; b) J. Verduyckt, D.E. De Vos, *Chem. Commun.* 2017, 53, 5682-5693.
- [3] a) R.J. van Putten, J. C. van der Waal, E de Jong, C. B. Rasrendra, H. J. Heeres and J. G. de Vries, *Chem. Rev.* **2013**, 113, 1499–1597; b) B. Xiao,

- M.Zheng, X. Li,, J. Pang, R. Sun, H. Wang, X. Pang, A. Wang, X. Wang, T. Zhang, *Green Chem.* **2016**, 18, 2175-2184.
- [4] B. Katryniok, S. Paul, F. Dumeignil, *ACS Catal.* **2013**, 3, 1819-1834
- [5] M. Ayoub, A. Z. Abdullah, *Renew. Sustain. Energy Rev.* **2012**,16, 2671-2686
- [6] a) C. Zhou, J. N. Beltramini, Y. Fan, G. Lu, *Chem. Soc. Rev.* **2008**, 37, 527-549; b) P.S. Kong, M.K. Aroua, W. M. A. W Daud, *Renew. Sustain Energy Rev.* **2016**, 63, 533-555; c) D. Sun, Y. Yamada, S. Sato, W. Ueda ,*Green Chem.* **2017**, 19, 3186-3213.
- [7] A. Colin, Higher alcohols 2025. Houston Associates report, **2013**.
- [8] S. Deepak, A.K. Thakur, *J. Am. Oil Chem. Soc.* **2016**, 93, 1575–1593.
- [9] P. Foley, A. Kermanshahi, E.S. Beach, J.B. Zimmerman, *Chem. Soc. Rev.* **2012**. 41, 1499-1518
- [10] M. Patel, G.A. Reinhardt, G. Zemanek, *Fett/Lipid* **1999**, 101, 314-320.
- [11] D.S. Van Es, S. Marinkovic, X. Oduber, B. Estrine, *J. Surfact. Deterg.* **2013**, 16, 147-154.
- [12] G.A. Kraus, J.J. Lee, *J. Surfact. Deterg.* **2013**, 16, 317-320.
- [13] K. Stensrud, L. Wicklund, WO 2016/028845 (2016).
- [14] K.A. Arias, M. J. Climent, A.Corma, S. Iborra, *ChemSusChem*, **2014**, 7, 210-220.
- [15] A. Masuyama, D. Ono, A. Yamamoto, T. Kida, Y. Nakatsuji, T. Takeda, *J. Jpn. Oil Chem. Soc.* **1995**, 44, 446-450.
- [16] A. R. Trifoi, P. S. Agachi, T. Pap, *Renew. Sustain. Energy Rev.* **2016**, 62, 804-814 and references cited herein.
- [17] K. S. Arias, A. Garcia-Ortiz, M. J. Climent, A. Corma, S. Iborra, *ACS Sustain. Chem. Eng.* **2018**, 6, 4239-4245.

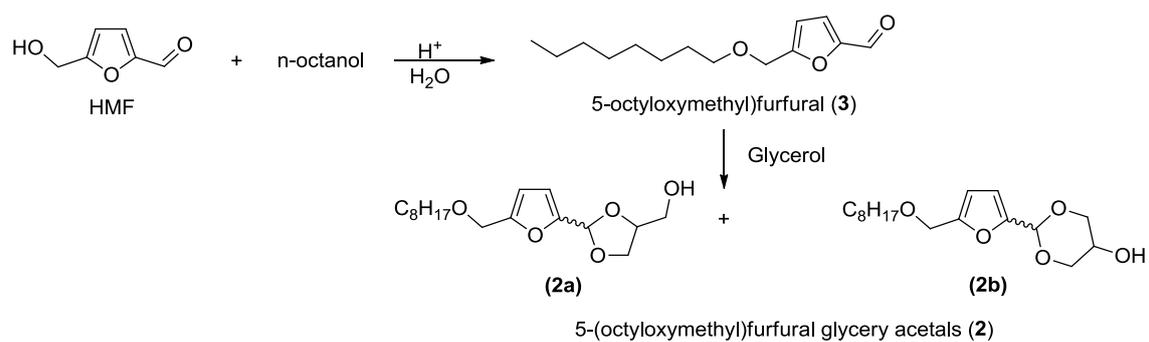
- [18] a) J. C. Van Der Waal, H. Van Bekkum, H., Special Publication - Royal Society of Chemistry **2001**, 266, 27-37; b) H. Kobayashi, H. Yokoyama, B. Feng, A. Fukuoka, Green Chem. **2015**, 17, 2732-2735; c) P. Che, F. Lu, X. Si, H. Ma, X. Nie, J. Xu, Green Chem. **2018**, 20, 634-640.
- [19] K. S. Arias, Saud I. Al-Resayes, M. J Climent, A. Corma, S. Iborra, *ChemSusChem* **2013**, 6, 123-131.
- [20] M. A. Cambor, A. Corma, H. Garcia, V. Semmer-Herledan, and S. Valencia, *J. Catal.* **1998**, 177, 267–272
- [21] M. Perez Garcia, L.I. Romero Garcia, J. M. Quiroga Alonso, D. Sales Marquez, *Chem. Biochem. Eng.* **1996**, 10, 75-78.
- [22] W.C. Griffin, *J. Soc. Cosmetic Chem.*, **1954**, 249-256.
- [23] S. Valencia, M.A. Cambor, A. Corma, SP 9600625 (1996).
- [24] M.A. Cambor, A. Corma, S. Valencia, *Micro. Mesoporous Mater.* **1998**, 25 59–74.
- [25] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S Beck, *Nature*, **1992**, 359, 710-712.
- [26] A. Corma, V. Fornes, S. Pergher, T. L. Maesen, J. Buglass, *Nature*, **1998**, 396, 353-356).
- [27] C.A. Emeis, *J. Catal.* **1993**.141, 347-354.
- [28] B. Mallesham, P. Sudarsanam, G. Raju, B. M. Reddy, *Green Chem.* **2013**,15, 478–489.



Scheme 1. Structure of different surfactants derived from HMF



Scheme 2. One pot two steps process (acetalization followed by etherification) for preparation of 5-(octyloxymethylfurfural) glyceryl acetals, **2**.



Scheme 3. One pot two steps process (etherification followed by acetalization) for preparation of 5-(octyloxymethylfurfural) glyceryl acetals, **2**

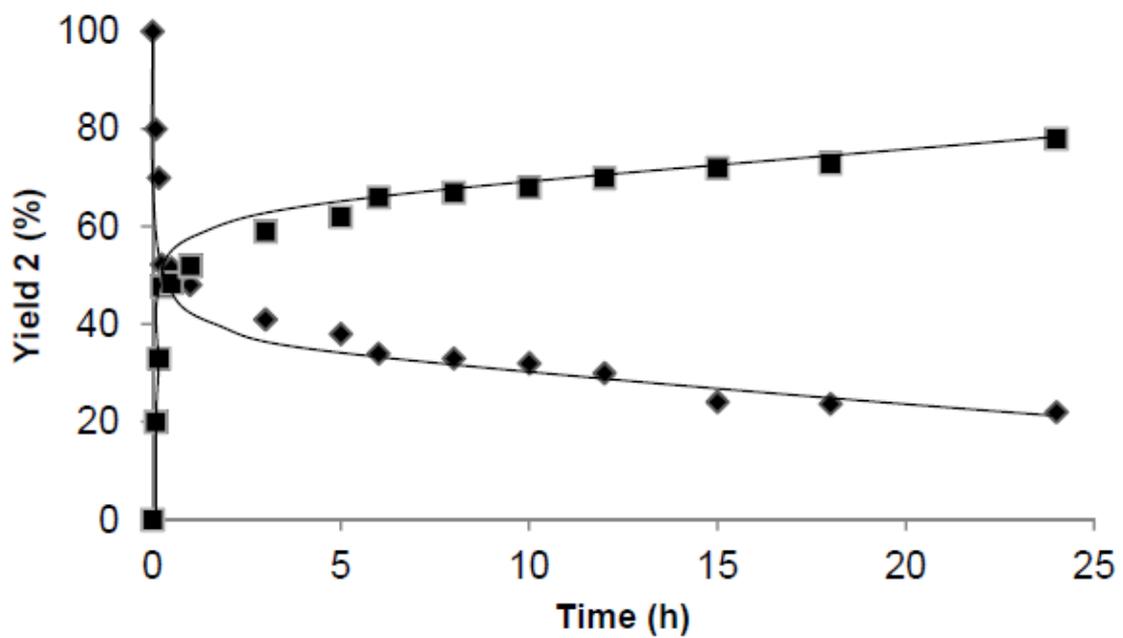


Figure 1. Kinetic curve of acetalization of 5-(octyloxymethyl)furfural with glycerol in the presence of 0.49NaBeta (12). 5-(octyloxymethyl)furfural (♦), acetals **2** (■)

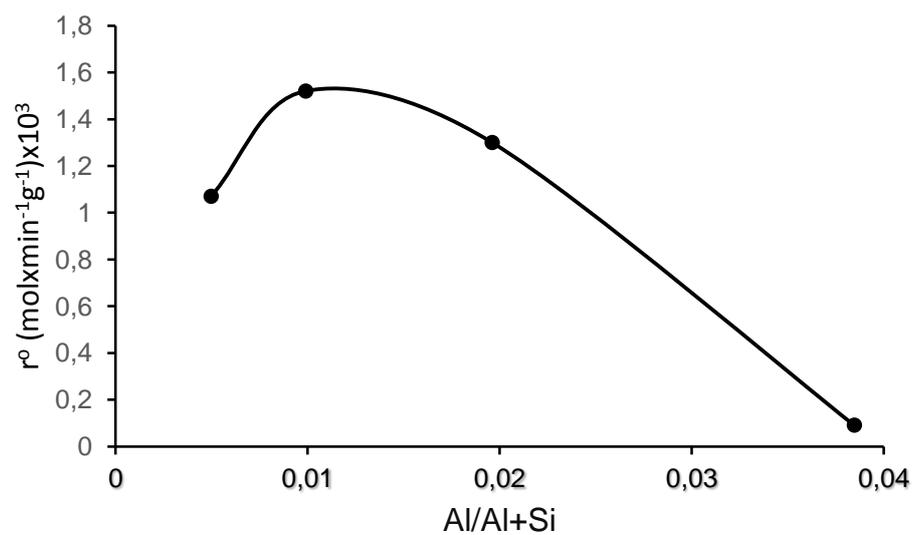


Figure 2. Initial reaction rate of formation of acetals **2** in function of Al/Al+Si ratio of different Beta zeolites synthesized in fluoride media

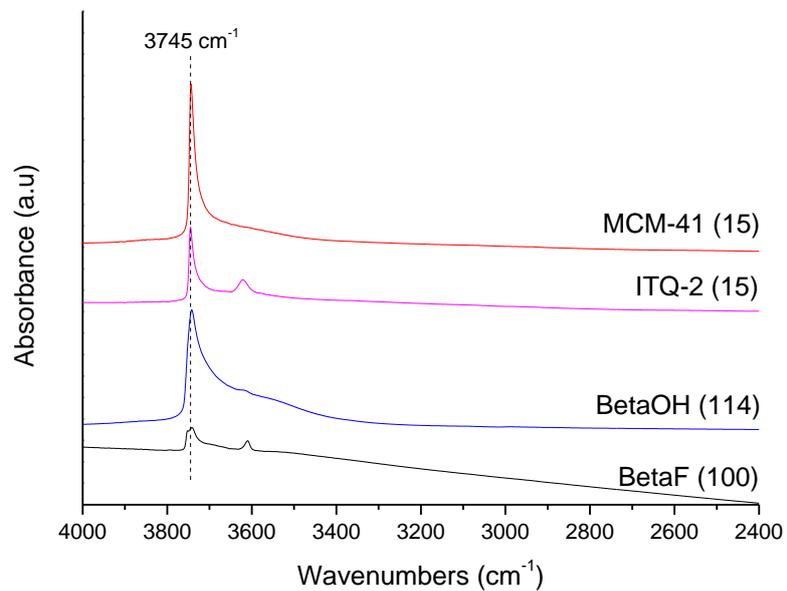


Figure 3. IR spectra in the OH stretching region for BetaF (Si/Al=100), BetaOH (Si/Al=114), ITQ-2 (15) and MCM-41(15) catalysts.

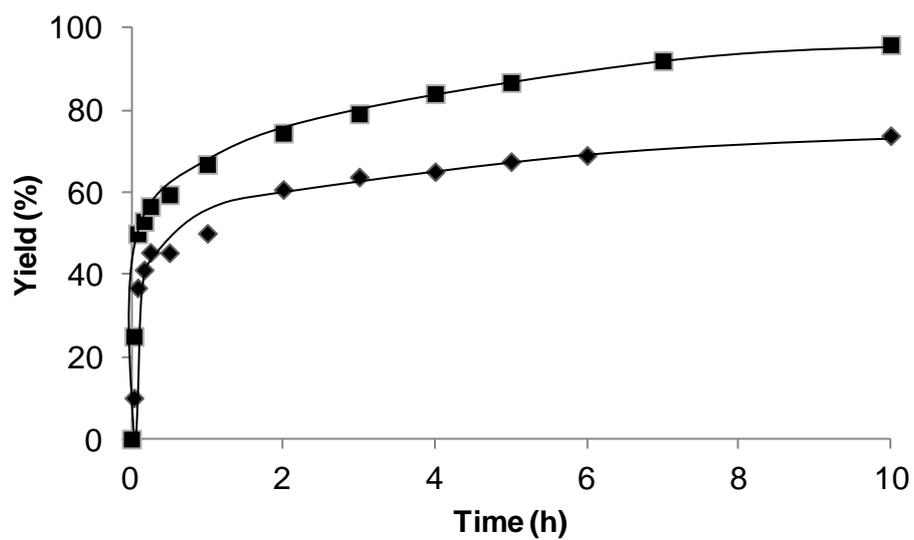


Figure 4. Kinetic curve of acetalization of 5-(octyloxymethyl)furfural with glycerol using BetaF(100) (■) and BetaOH (114) (◆).

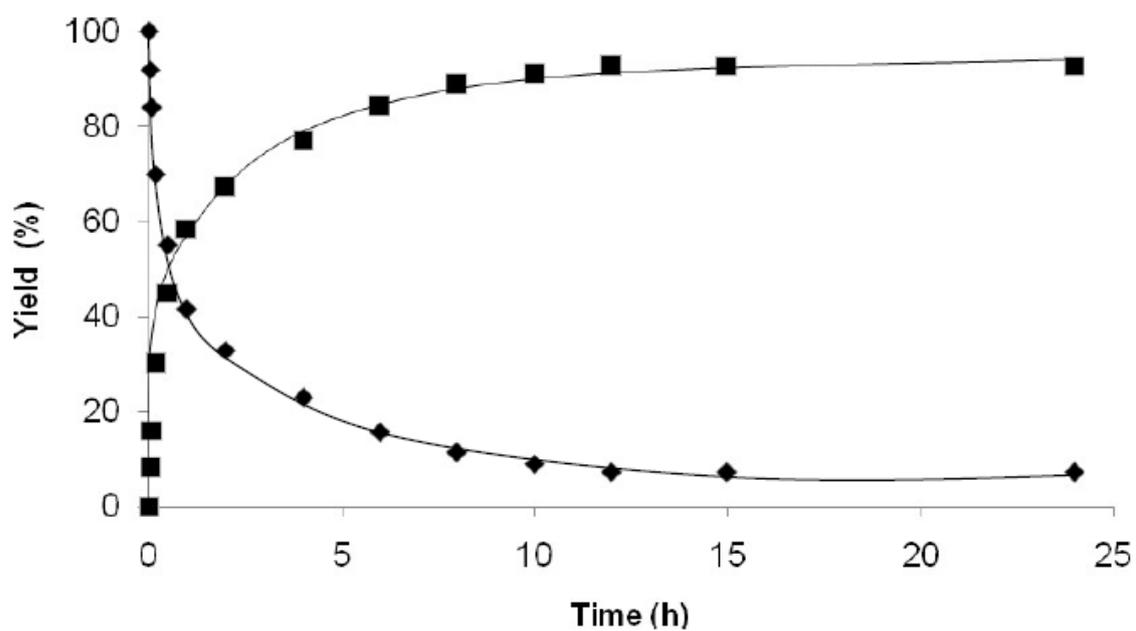


Figure 5. Kinetic curve of acetalization of 5-(octyloxymethyl)furfural with glycerol using ITQ-2 zeolite. 5-(octyloxymethyl)furfural (♦), acetals 2 (■)

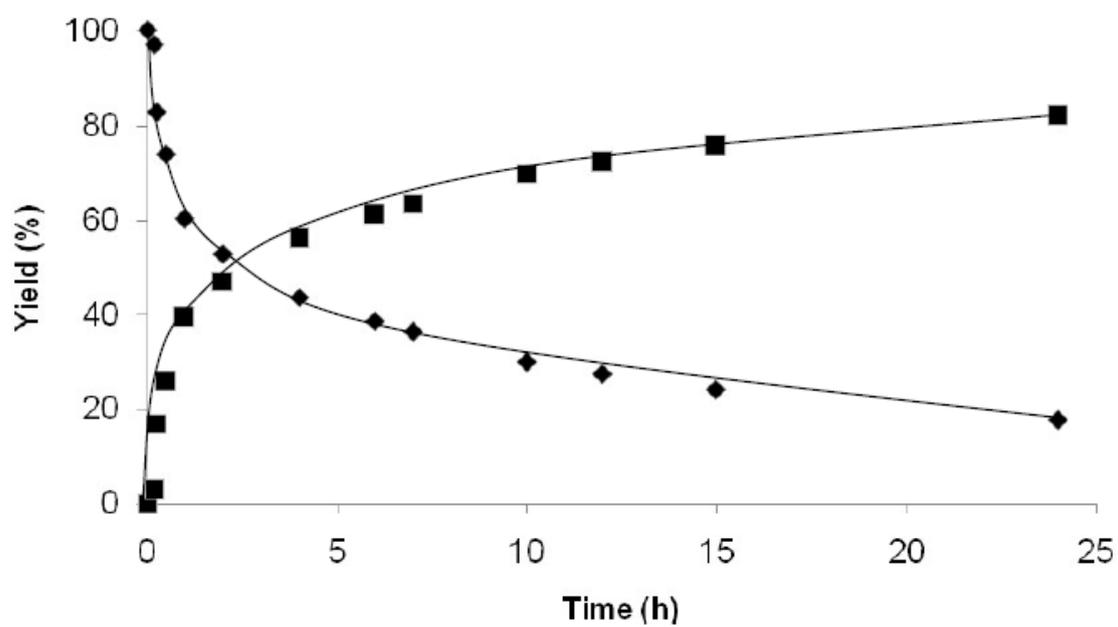


Figure 6. Kinetic curve of acetalization of 5-(octyloxymethyl)furfural with glycerol using MCM-41 catalyst. 5-(octyloxymethyl)furfural (◆), acetals 2 (■)

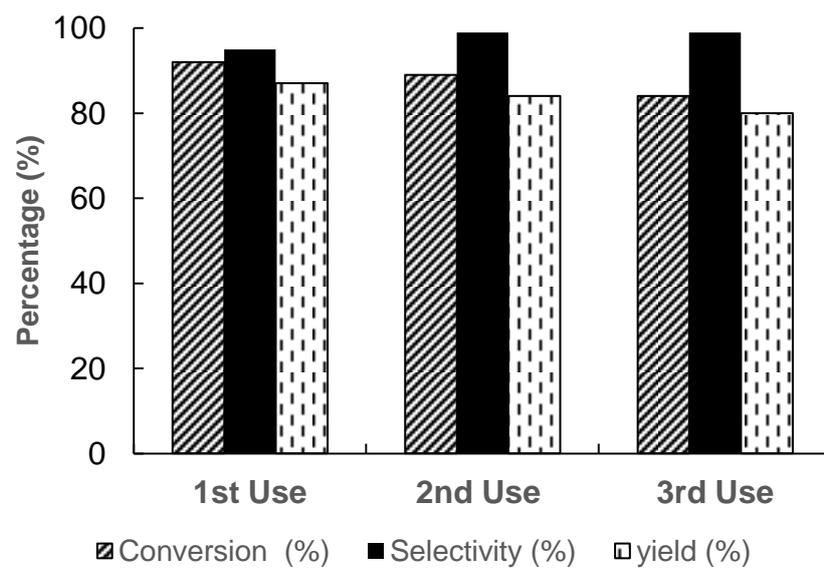


Figure 7. Results of reusability of the BetaF(100) zeolite in the one pot process after 24h reaction time

Table 1. Physicochemical properties of the catalysts

Catalyst (Si/Al)	BET (m ² /g)	Micr. vol. (cm ³ /g)	250°C		350°C	
			B	L	B	L
HBeta(12)	581	0.18	244	209	105	108
USY(12)	603	0.27	277	48	172	37
ITQ-2(15)	745	0.26	155	67	67	48
MCM-41(15)	898	-	21	171	17	127
0.49NaBeta(12)	556	0.17	147	101	96	96
MCM-41(Si)	1190	-	-	-	-	-
ITQ-2(Si)	511	0.24	-	-	-	-

The acidity of the catalysts was measured as μmol pyridine/gram catalyst at different temperatures, calculated using extinction coefficients reported in Ref [27]. B: Bronsted sites; L: Lewis sites

Table 2. Acetalization of 5-(octyloxymethyl)furfural with glycerol in presence of different catalysts.^[a]

Entry	Catalyst (Si/Al)	r^o ^[b]	time (h)	Conv. 3 (%)	Yield (%) / 2b:2a	Select. 2 (%)
1	HBeta(12)	1.0	6	85	49 / 36:64	50
			8	95	48 / 36:64	
2	USY(12)	3.9	6	85	53 / 38:62	62
			10	90	56 / 40:60	
3	0.49NaBeta(12)	0.16	6	66	66 / 34:66	100
			10	68	68 / 35:65	
4	BetaF(25)	0.091	6	50	50 / 41:59	100
			10	53	53 / 40:60	
5	BetaF(50)	1.30	6	65	65 / 42:58	100
			10	69	69 / 42:58	
6	BetaF(100)	1.52	6	90	90 / 43:57	100
			10	96	96 / 42:58	
7	BetaF(200)	1.07	6	73	73 / 40:60	100
			10	82	82 / 42:58	
8	BetaOH(114)	0.73	6	74	69 / 37:63	93
			10	78	73 / 39:61	
9	ITQ-2(15)	0.80	6	84	84 / 40:60	100
			10	91	91 / 40:60	
10	MCM-4(15)	0.28	6	59	59 / 34:66	100
			10	70	70 / 34:66	

[a] Reaction conditions: glycerol/5-(octyloxymethyl)furfural = 2, catalyst (40mg, 40 wt% with respect to **3**), 2mL acetonitrile, at 82°C. [b] r^o ($[\text{mol min}^{-1} \text{g}^{-1}]10^3$) initial reaction rates calculated at conversion below 20 %.

Table 3. Physicochemical characteristics of hydrophobic Beta zeolites

Catalyst (Si/Al)	BET (m ² /g)	Micr. vol. (cm ³ /g)	250°C		350°C	
			B	L	B	L
BetaF(25)	469	0.21	185	108	55	78
BetaF(50)	413	0.19	122	45	50	37
BetaF(100)	413	0.17	84	52	38	26
BetaF(200)	453	0.21	66	7	33	6
BetaOH(114)	370	0.16	72	16	38	9

Acidity of the catalysts was measured as μmol pyridine/gram catalyst at different temperatures, calculated using extinction coefficients reported in Ref. [27]. B: Bronsted sites; L: Lewis sites

Table 4. Synthesis of 5-(octyloxymethyl)furfural glyceryl acetals (**2**) in one pot two steps process (etherification-acetalization) ^[a]

Entry	Firts Step					Second Step					
	Catal. (Si/Al)	t (h)	Conv. HMF (%)	Yield 3 (%)	Selec. 3 (%)	t (h)	Conv. 3 (%)	Yield 2 (%)	Select. 2 (%)/ 2b:2a	Total Yield 2 (%)	TON
1	BetaF (100)	2	99	97	98	46	80	79	99 / 34:66	77	94.47
2 ^[b]	BetaF (100)	2	98	94	96	24	94	93	99 / 38:62	87	106.74
3 ^[c]	ITQ-2 (15)	3	98	93	95	45	85	84	99 / 36:64	80	10.58

[a] Reaction conditions: first step, HMF(1mmol), *n*-octanol (1mmol), 100°C ; 40 wt % catalyst with respect to HMF; second step, glycerol (2mmol) dissolved in 5mL acetonitrile, 82°C. [b] The reaction was carried out by adding the catalyst in twice [c]:60 wt% of catalyst respect to HMF. TON is calculated as mmol of product obtained per mmol of protons.

Table 5: One Pot two steps process employing different alcohols to prepare the 5-(alkyloxymethyl) furfural glyceryl acetals

Entry	Alcohol	First Step ^[a]				Second Step ^[b]				HLB	TON	
		t (h)	Conv. HMF (%)	Yield ether (%)	Selec ether (%)	t (h)	Conv (%)	Yield (%)	Selec (%)			Total Yield (%)
1	C ₈ H ₁₇ OH	2	98	94	96	5	87	86	99	87	6,6	106.74
						10	89	88	99			
						22	94	93	99			
2	C ₁₀ H ₂₂ OH	3	96	94	98	5	56	56	100	80	6,1	98.16
						10	74	74	100			
						21	85	85	100			
3	C ₁₂ H ₂₅ OH	3	88	85	96	5	45	45	100	73	5,6	89.57
						10	52	52	100			
						20	61	61	100			
						45	85	85	100			
4 ^[c]	C ₁₆ H ₃₃ OH	3	95	91	95	5	31	31	100	62	4,9	50.32
						10	40	40	100			
						20	48	48	100			
						45	68	68	100			

[a] HMF (1mmol), fatty alcohol (1 mmol), BetaF(100), 20 wt % (25mg) 100°C. [b] glycerol (2mmol), acetonitrile (5mL), BetaF(100), 20 wt % (25mg) at 82°C. [c] 40 wt % BetaF(100) (50mg) for each step. TON is calculated as mmol of product obtained per mmol of protons