

**Acid-catalyzed production of biodiesel over arenesulfonic SBA-15:
insights into the role of water in the reaction network**

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Published on:

Renewable Energy 75 (2015) 425-432

doi:10.1016/j.renene.2014.10.027

ABSTRACT

This work presents a systematic approach to understand the effect of the presence of water in highly acidic crude palm oil—typical conditions of low grade oleaginous feedstock- on the performance of arene-SO₃H-SBA-15 catalyst in the batch-production of biodiesel. The addition of small amounts of water (1 wt%) to the reaction medium led to a clear reduction of the observed yield to fatty acid methyl esters (FAME), being this decay usually attributed to the highly hydrophilic nature of arenesulfonic acid groups, and the associated difficulties of hydrophobic substrates to access these catalytic acid sites. However, the addition of larger amounts of water –up to 10 wt%– did not cause a proportional decay in the yield to FAME, but a higher production of free fatty acids (FFA). This is attributed to the promotion of acid-catalyzed hydrolysis of both starting triglycerides and formed FAME. The net result is not only a significant reduction of the final FAME yield, but also the appearance of high acid values, i.e. FFA contents, in the final biodiesel. Consequently, the overall process is simultaneously affected by transesterification, esterification and hydrolysis reactions, all of them catalyzed by Brønsted acid sites and dependent on the reaction conditions – temperature and water concentration– to different extents. Several strategies devoted to manage such behavior of sulfonic acid-modified SBA-15 catalysts in presence of water, aiming to maximize FAME yield while minimizing FFA content, have been explored: (1) minimization of the water content in the reacting media by pre-drying of feedstock and catalyst; (2) addition of molecular sieves to the reacting media as water scavengers, (3) hydrophobization of the catalyst surface to minimize the water uptake by the catalyst; and (4) use of a decreasing reaction temperature profile in order to first promote transesterification at high temperature and then reduce the temperature to keep at a minimum the hydrolysis of formed FAME. All these strategies resulted in an

improvement of the catalytic performance, especially the use of a decreasing temperature profile. The results showed by the latter strategy open new possibilities and reaction pathways in which readily available, low-grade, cheap oleaginous feedstock with high water and FFA contents can be efficiently converted into biodiesel.

Keywords: biodiesel; heterogeneous acid catalysis; sulfonic SBA-15; effect of water; esterification; transesterification; hydrolysis.

1. Introduction

Biodiesel (usually defined as fatty acid methyl esters, or FAME) can be conventionally prepared from a huge variety of lipid sources by transesterification of glycerides (mainly triglycerides) and esterification of free fatty acids (FFA) with short chain monoalcohols, usually methanol, using homogeneous alkaline catalysts (NaOH, KOH) at atmospheric pressure and mild temperatures (60-80°C) [Melero et al., 2009a]. One of the main disadvantages of this process is the high and unstable prices of the raw materials, as well as the overall processing costs. Conditioning steps of the feedstock to decrease the FFA content, below 0.5 wt%, and other impurities are usually required, especially when the starting material is not refined oil. In example, such conditioning stages are mandatory when using base catalysts in order to avoid their saponification leading to soap formation, which generates serious problems in the downstream separation of the produced biodiesel [Dorado et al., 2002; Leung et al., 2010]. On the other hand, upon reaction, the homogeneous alkaline catalysts must be removed from the products stream by acid-neutralization, thus generating salt wastes that finally contaminate the glycerol by-product, which seriously reduces the possibilities to market it. Additionally, the conventional base-catalyzed process is also quite sensitive to water content in the feedstock, a quite common feature of low-grade cheap oleaginous feedstock. Depending on the reaction conditions, water may cause the hydrolysis of triglycerides and methyl esters, leading to the formation of undesired FFAs [Atadashi et al., 2012], which negatively affects alkali-driven processes.

Currently, in order to avoid all the above mentioned troubles, conventional biodiesel production plants are practically obliged to use refined vegetable oils as feedstock, where FFA and water contents are strongly limited. Therefore, the costs associated to the acquisition of the feedstock (with increasing market prices) as well as

those attributed to the conditioning process clearly impact on the profitability of the process. This is motivating the development of new technologies for biodiesel production in order to get not only more profitable but also more environmentally sustainable processes. One of such possibilities is the use of new technologies devoted to the transformation of unrefined low-grade oleaginous feedstock, like waste oils and fats, into biodiesel. This alternative leads to 2nd generation biodiesel –not competing with food market– and as such is being promoted by several policies –Directives 2009/28/EC and 2009/30/EC from the European Union. However, such feedstocks (usually waste oils and fats) commonly contain a significant number of impurities including, among others, FFA and water [Iglesias & Morales, 2010]. Thus, they could not be processed by existing homogeneous base-catalyzed biodiesel processes, being necessary the use of alternative systems such as acid heterogeneous catalysts [Melero et al., 2009a; Sharma et al., 2011; Lee & Wilson, 2014]. These catalysts are of great interest in this field as they allow carrying out simultaneously the esterification of FFA and the transesterification of glycerides. This approach thus eliminates the necessity of FFA removal and makes possible the use of low-grade oils and fats as feedstock. However, the acid-catalyzed production of biodiesel can be compromised by the presence of significant amounts of water due to the strong interaction between acid sites and water molecules as well as the promotion of hydrolysis reactions –easily catalyzed by strong acid moieties.

In this context, many of the non-edible raw materials of potential application for the production of 2nd generation biodiesel display simultaneously relatively high FFA and water contents. This is the case, e.g., of rendered animal fats [Encinar et al., 2011] and sewage sludge [Kargbo, 2010], where a large portion of the fatty acid chains are in FFA form and water can represent up to 50 wt% of their total composition. The

application of solid acid catalysts for the production of biodiesel from such raw materials would require a careful control the effect of water on the hydrolysis-esterification-transesterification reaction network. Hence, the analysis of such effect appears to be crucial in order to find robust solid acid catalysts capable of processing low-grade feedstock for biodiesel production. So far a wide collection of heterogeneous acid catalysts has been tested for the non-conventional production of biodiesel [Melero et al., 2009a; Lee & Wilson, 2014]. Among them, organosulfonic acid-functionalized mesoporous silicas have shown high potential for this and other acid-catalyzed reactions [Melero et al., 2006]. In previous works, we have demonstrated that these catalysts show high activity and stability in the production of biodiesel not only from conventional edible refined oils, but also from FFA- and other impurities-containing sources such as non-refined oils, waste cooking oils and even low-grade animal fats [Melero et al., 2009b; Melero et al., 2010a; Melero et al., 2010b; Morales et al., 2011]. We have also previously assessed the interaction of the sulfonic acid sites in these catalysts with water in hydrophobic reaction media, through a detailed bidimensional solid-state NMR spectroscopic analysis that revealed their strong hydrophilic nature [Morales et al., 2008]. Thus, silica-grafted SO₃H groups tend to produce water-rich microenvironments around them, thereby potentially jeopardizing their catalytic performance in water sensitive reactions.

Therefore, within the scope of this work, we give a step forward in this line of research, aiming to explore the effect of water in the acid-catalyzed production of biodiesel from a low-grade feedstock such as highly acidic crude palm oil. A further object of the present research is to provide and evaluate potential strategies for improving the performance of the catalyst in this system.

2. Materials and methods

2.1. Materials

Crude palm oil (Gran Velada, see Table 1 for properties) and methanol (ACS grade, Aldrich) were used as feedstock for fatty acid methyl esters (FAME) production without previous purification. Tetraethylorthosilicate (TEOS, 98%, Aldrich) and 2-(4-chlorosulfonylphenyl)-ethyltrimethoxy silane (CSPTMS, 50% in methylene chloride, ABCR) were used as silica and arenesulfonic acid groups precursors, respectively. Pluronic P123 (PEO₂₀-PPO₇₀-PEO₂₀, Aldrich), a tri-block copolymer surfactant, was used as structure-directing agent. Trimethyltrimethoxysilane (TMS, Aldrich) was used for the surface hydrophobization of the catalyst.

2.2. Synthesis of the arenesulfonic acid-functionalized SBA-15 catalyst

Arenesulfonic acid-functionalized SBA-15 silica (Arene-SO₃H-SBA-15) with 10% sulfonic-acid molar loading (based on Si) was prepared through a previously described co-condensation method using TEOS and CSPTMS [Melero et al., 2002]. Briefly, Pluronic P123 (4 g) was dissolved at room temperature in 1.9 M aqueous hydrochloric acid (125 mL), the solution was then heated up to 40°C, TEOS (7.67 g) was added under vigorous stirring, and the resultant solution was allowed to pre-hydrolyze for 45 min. Afterwards, sulfur precursor CSPTMS was added dropwise (2.67 g) and the solution was stirred at 40°C for 20 h and then statically aged at 110°C for 24 h. The material was recovered by filtration, and surfactant removal was accomplished by double ethanol-washing under reflux. Silanized arenesulfonic-acid functionalized SBA-15 silica was prepared as follows: 2 g of arene-SO₃H-SBA-15 were suspended in 300 mL of dry toluene. TMS was added at 1:1 catalyst:TMS mass ratio. The mixture

was placed in an oil-heated bath at 110°C under nitrogen for 12h. Thereafter, the solid was filtrated and washed thoroughly with fresh toluene. The resultant solid was finally dried at 80°C for 12h.

2.3. Catalyst characterization

The textural properties of the arene-SO₃H-SBA-15 catalyst were determined from N₂ adsorption-desorption isotherm at 77 K using a Micromeritics TRISTAR 3000 unit. Surface area was calculated from the adsorption branch of the isotherm using B.E.T. method, whereas pore size distribution was estimated by the B.J.H. method using the K.J.S. correction. Total pore volume was assumed to be that recorded at $p/p_0 = 0.985$. Structural properties were further assessed by means of X-ray powder diffraction (XRD) on a Philips X'Pert diffractometer using the Cu K α line in the 2θ angle range of 0.6-5.0° with a step size of 0.02°. Concentration and accessibility of the sulfonic acid groups incorporated to the mesostructured material were calculated through a combination of the sulfur content, as determined by elemental analysis using an Elemental Vario El III unit, and the acid capacity (H⁺ loading), as determined by acid-base titration. Such titration was carried out potentiometrically using 2M NaCl as cationic-exchange agent and a dropwise addition of 0.01M NaOH as titration agent. Table 2 summarizes the most relevant physicochemical properties of the synthesized arene-SO₃H-SBA-15 catalyst. Combined data from XRD and N₂ adsorption isotherm evidences high mesoscopic ordering and high surface area (over 700 m²/g), accompanied by a narrow distribution of pore sizes centered at 8 nm (large enough to minimize the steric hindrances occurring when relatively bulky substrates such as fatty acids and glycerides are processed). Likewise, the high wall thickness (~4 nm) should provide the material with good hydrothermal stability. On the other hand, the high yield

of organic incorporation leads to an acid capacity over 1 meq H⁺/g (theoretical synthesis value, 1.17 meq/g), with practically total accessibility of available sulfonic groups.

Table 2 also includes the characterization of the hydrophobized arene-SO₃H-SBA-15 catalyst, indicating a partial loss of textural properties –surface area and pore volume– as a consequence of the post-grafting of hydrophobic trimethyl species.

2.4. Catalytic experiments

The experiments were carried out in a 25 mL stainless-steel batch reactor (Autoclave Engineers) equipped with mechanical stirrer, temperature controller and pressure transducer. In a typical assay, oil (5 g), methanol (30 MeOH:oil molar ratio) and catalyst (8 wt% based on oil) were placed inside the reactor vessel. The system was tightly closed and the temperature (160°C) and stirring rate (2000 rpm) set up. These reaction conditions were previously optimized in a preceding work on the methyl ester production using the same catalyst [Melero et al., 2010b]. The reaction was allowed to proceed and the reactor was cooled down using an iced water bath. Collection of reaction products and catalyst was performed using acetone (25 mL) as solvent in order to ensure a complete recovery of all the reactants and products. The resultant solution was then filtered using a nylon membrane to recover the catalyst. The acetone and the residual methanol were removed by rotary evaporation under vacuum. The molar yield of the transformation of fatty acid alkyl chains (comprising both FFA and glycerides) into fatty acid methyl esters (FAME) was measured from crude reaction samples without any further purification using ¹H NMR analysis in a Varian Mercury Plus 400 unit in a similar way to that described by Whalen et al (2008). The acid value in the final product, indicative of the free fatty acids content, was determined by volumetric

titration according to the UNE-EN 14104:2003 standard (using a Metrohm 905 Titrando potentiometric titrator).

3. Results and discussion

In our previous work, arene-SO₃H-SBA-15 catalyst showed high activity in the simultaneous esterification of FFA and transesterification of triglycerides to yield FAME using low-grade oils and fats as feedstock [Morales et al., 2011]. Nevertheless, these low-grade raw materials usually contain high amount of water producing a negative effect on FAME yield. Therefore, the first aim of the present work was to study the effect of water content in the crude oil feedstock on the catalytic behavior of arene-SO₃H-SBA-15 for the production of FAME under previously optimized reaction conditions: 160 °C, 30:1 methanol to oil molar ratio, 8 wt% catalyst loading, and 2000 rpm stirring rate [Melero et al., 2010b].

3.1. Effect of water content on the catalytic activity

In order to study the effect of the presence of water in the starting oil on the catalytic activity of the arene-SO₃H-SBA-15 catalyst, the following experiments were carried out: an increasing amount of water –1, 5, and 10 wt%– was added to the reaction mixture, directly mixed with the methanol. As a reference for the significance of such values, it must be noted that the expected combined humidity accompanying the raw materials (oil and methanol) together with the water formed *in situ* as by-product of the esterification of FFA, accounts for approximately 0.5 wt%. Therefore, the assayed range of water contents corresponds to water-rich systems. Catalyst was then added and the reaction was allowed to proceed under the above-mentioned optimized reaction conditions. After predetermined reaction times, up to 8h, and the corresponding

processing of the resultant products, FAME yields were assessed. Fig. 1A and B show the results for water-doped experiments along with a water-free control experiment (0 wt% added water). The addition of 1 wt% of water to the reaction medium causes a slight loss of catalytic activity. The underlying cause for this behavior is the hydrophilic nature of the arenesulfonic acid active sites, which tends to produce water-rich microenvironments around them [Morales et al., 2008], shifting the equilibria of the esterification/hydrolysis reactions and eventually reducing the formation of FAME. However, for 5 wt% of water content, an improvement in the catalytic activity at short times (0.5-1 h, Fig. 1B) is observed. This can be attributed to a boosting effect in the hydrolysis of the starting triglycerides and subsequent catalytic esterification of formed FFA [Olutoye & Hameed, 2011]. However, higher water content (10 wt%) reduces the catalytic activity at short times (0.5-1 h, Fig. 1B) because although high water content promotes the hydrolysis of triglycerides simultaneously hinders the esterification of FFA and transesterification of triglycerides. On the other hand, at the longer reaction time (8h), where the chemical equilibrium must have almost been reached, the presence of water in the reaction media slightly decreases the yield to FAME, though such a decrease appears not to be affected by the amount of water used in these experiments.

In order to complete the analysis of the influence of water content on the catalytic activity of arene-SO₃H-SBA-15, FFA content was also assessed by an indirect measurement method, through the determination of the acid content (mg KOH/g) present in the reaction media as determined by acid-base titration (Fig. 2). Importantly, the crude palm oil used for the study presents 22 mg KOH/g starting acid value (Table 1), thus corresponding to 0 min reaction time. The results depicted in Fig. 2 evidence a strong decrease of the acidity at short reaction times (up to 1h) due to the rapid esterification of FFA with methanol to produce FAME. This effect is more pronounced

with none or small amounts of water (0-1 wt%) added to the reaction media because esterification versus hydrolysis reaction is favored. Nevertheless, insofar as the water content is increased (5-10 wt%), the reduction in the acid value (i.e. FFA content) is not so marked. This can be explained both in terms of a promotion of the hydrolysis of triglycerides and an impairment of the esterification of FFA (due to the above-mentioned equilibrium limitations and/or because water can limit the mass transfer of fatty molecules into the catalytic acid sites). On the other hand, for longer reaction times, the results clearly reveal a gradual increase in FFA content in the reaction media as a result of the sustained hydrolysis of FAME molecules previously formed via transesterification. Such hydrolysis process is mediated by the Brønsted sulfonic acid sites of the catalyst in the presence of water-rich environments.

To confirm the strong effect of water content on the catalytic acid sites, used arene-SO₃H-SBA-15 catalyst was further characterized to determine the remaining acid capacity after catalytic tests. Thus, after each reaction (8h), the catalyst was recovered and double-washed with methanol and *n*-hexane in order to remove both polar and non-polar residual compounds. The results, included in Table 3, show a steady loss of acid capacity with increasing water content. This phenomenon might be attributed to the partial leaching of the most labile arenesulfonic acid groups from the silica surface under hydrothermal conditions [Melero et al., 2002], although some neutralization effect from the presence of alkaline and alkaline earth metals in the crude palm oil (Table 1) should not be discarded (especially in light of the result for the non-water-doped experiment). Therefore, a high concentration of water affects not only the catalytic performance but also the stability of the active centers of this catalyst.

3.2. Improvement of the catalytic behavior

One of the main advantages of using heterogeneous acid catalysts, such as arene-SO₃H-SBA-15, for the production of biodiesel is their capability for simultaneously esterify FFAs and transesterify triglycerides. On the contrary, as shown before, a major drawback of such acid catalysts in this context is their capability for catalyzing the hydrolysis of FAME into free fatty acids when significant amounts of water appear in the reaction medium. Regarding this issue, here we include a study of different strategies focused on how to improve the catalytic performance of arene-SO₃H-SBA-15, aiming to increase the yield to FAME from crude palm oil while keeping as low as possible the formation of FFAs. The study has been performed using a real non-refined oil showing high acidity (21.45 mgKOH·g⁻¹, approximately corresponding to 10 wt% FFA, Table 1).

3.2.1. Minimization of water content

The obvious approach in order to reduce the above-discussed deactivating effect on arene-SO₃H-SBA-15 catalyst due to high water content into the reaction mixture is associated to the reduction of said water content. In this way, two strategies have been assessed. Strategy 1 consisted of minimizing the presence of water by previously drying crude palm oil at 100°C and the catalyst at 80°C under vacuum (70 mbar) for 12 h. On the other hand, a second approach –Strategy 2– consisted of the *in situ* removal of water molecules from the reaction media as they are generated upon esterification of FFA. This has been achieved by the addition of dehydrating molecular sieve (zeolite 4A) at 10/1 catalyst/zeolite mass ratio. The zeolite was previously activated in an oven at 180°C and 110 mbar for 12 h. Fig. 3 shows the evolution of yield towards FAME with reaction time over arene-SO₃H-SBA-15 catalyst using both strategies. The results reveal

that a controlled drying of catalyst and oil (Strategy 1) leads to a significant ~5% increase in the final yield to FAME, verifying that the presence of water molecules actually has a contribution in the lowering of the activity. It must be noted, however, that this approach does not prevent the detrimental effect of the in situ generated water – from the esterification of FFAs. Therefore, a step ahead was taken by removing the water from the reaction media by means of the addition of molecular sieve (Strategy 2). As shown in Fig. 3, this alternative is highly efficient, since it resulted in the highest FAME yield (90% yield to FAME after just 1 hour). Thus, the water generated during the esterification of FFA seems to be more relevant in the catalytic process than that accompanying the catalyst and the oil feedstock, probably because the water molecules emerging from the esterification of FFA are in close proximity with the catalytic acid sites and readily interact with them. Fig. 4 shows the FFA content, as indirectly determined through the acid value of the reaction products, of both strategies and different reaction times. As shown, the resultant acidities are much lower than that achieved in the reaction without any improving strategy, especially for longer reaction times when the hydrolysis of FAME becomes more important (the reaction media is mainly comprised of FAME after 1h, as shown in Fig. 3). These results further evidence the modulating effect of water on the yield to FAME as a consequence of the hydrolysis of FAME, and how simple water-removing strategies can partially compensate for it. Nevertheless, it must be noted that the acid values of the final products obtained by both strategies still remain high.

3.2.2. Surface hydrophobization of arene-SO₃H-SBA-15 catalyst

Another studied strategy in order to reduce the detrimental effect of water on the production of biodiesel from crude palm oil using arene-SO₃H-SBA-15 is the

hydrophobization of the catalyst surface, seeking to reduce the inherent water affinity of sulfonic acid groups by modifying their microenvironments with hydrophobic organosilica species. In a previous work [Melero et al., 2010b], we showed that this strategy can significantly improve the catalytic performance of this type of catalyst in water-mediated reactions. The surface hydrophobization was accomplished through a silanization procedure by reacting free surface silanol groups on the catalyst surface with trimethylmethoxysilane in toluene under reflux (typical grafting procedure). Table 2 includes the physicochemical properties of the hydrophobized arene-SO₃H-SBA-15 catalyst, evidencing that the material keeps acceptable textural properties after the grafting step. Fig. 5 shows the kinetic curves for FAME yield over the hydrophobized catalyst corresponding to catalytic runs with 0 and 1 wt% added water. The parent catalyst (non-hydrophobized) is also included as reference. As shown, the hydrophobized catalyst provided significantly higher FAME yields in the absence of added water, indicating an increased water tolerance against the *in situ* produced water, giving 88% FAME yield after 8h vs. 82% over the parent catalyst. Furthermore, such water resistance is not altered by the addition of 1wt% water to the reaction medium, in contrast with the strong loss of activity observed for the non-hydrophobized catalyst. Table 4 includes the acid values of the final product after 8h for both catalysts and for 0 wt% and 1wt% added water. For the hydrophobized catalyst, a decrease in the acid value is clearly observed, especially for the 1wt% water-doped experiments. This effect is directly related to the lower degree of hydrolysis of FAME into FAA as a consequence of the more hydrophobic environment of the acid sites [Lien et al., 2010]. However, with this strategy the acid value of the final product is again too high for a biodiesel sample.

3.2.3. Decreasing reaction temperature profile

Aiming to simultaneously maximize the FAME yield and reduce the FFA content in the final product, the major drawback of the arene-sulfonic acid functionalized SBA-15 catalysts with regards to their activity in biodiesel production, an alternative reaction process with a decreasing temperature profile in two steps is envisioned: a first step at high temperature (160-180°C) to promote the transesterification of triglycerides to methyl esters, as well as the hydrolysis of triglycerides to FFA [Ngaosuwan et al., 2009]; followed by a second step under milder temperature conditions (80-100°C) targeting to enhance the esterification of FFA vs. the hydrolysis of the formed FAME [Brahmkhatri & Patel, 2011]. Fig. 6 shows the FAME yields obtained with the proposed two-step reaction process under previously optimized conditions (30:1 methanol:oil molar ratio, 8 wt% catalyst loading, 2000 rpm stirring rate) for different combinations of high temperature (T_1)-low temperature (T_2). Thus, the first reaction step was carried out at 140, 160 and 180°C for 2h, while the second stage was performed at 80, 100 and 120°C for an additional 2h reaction period. Temperature change was forced with the help of a water-ice bath in order to minimize the transition period. A control experiment without temperature variation (last column, 160-160) has also been included. Likewise, the acid content of the resultant products is represented in Fig. 6 (right axis). Importantly, regardless of the selected combination of temperatures, the use of a decreasing temperature profile results in a dramatic reduction in the acid value –and hence in FFA content– from more than 20 mg KOH/g in the control experiment to values below 5 mg KOH/g. Regarding the temperature of the first step (T_1), the results reveal an increasing trend in the yield to FAME as the temperature increases from 140°C to 180°C. Thus, when using a T_1 of 180°C, over 95% FAME yield can be achieved. However, as expected, the acid value of the final product depends

more significantly on the temperature of the second step (T_2). In this case, the lower temperatures (80-100°C) are more efficient for the optimization of the esterification-hydrolysis reactions, reaching acid values below 1 mg KOH/g. In conclusion, the best results can be considered those reached by the system 160-100°C, leading to 96% FAME yield and 0.4 mg KOH/g acid value.

3.3. Proposed reaction scheme

From the above experimental results, a reaction scheme is proposed for the production of FAME over arene-SO₃H-SBA-15 catalyst (Fig. 7). Briefly, fatty acid methyl esters are produced not only by means of transesterification of triglycerides (4), (5) and (6); but also by the hydrolysis of triglycerides (1) –in the presence of water molecules– followed by the esterification of formed FFA (2) and (3). The relative rate of such transformations is influenced by reaction conditions (mainly temperature and water content). As shown before, reaction conditions for maximizing the yield to FAME while minimizing the presence of FFA are those based on a decreasing reaction temperature profile, where high temperature is used in a first stage to promote reactions (1), (4), (5) and (6), while a reaction temperature below 100°C is fixed in a later stage for boosting the esterification of FFA (2) and (3), and consequently hindering the hydrolysis of methyl esters. Furthermore, this particular catalytic behavior of the arene-SO₃H-SBA-15 catalyst leads to an increase in FAME production for moderate water contents (1-5 wt%) as a result of the enhancing of the hydrolysis of triglycerides into FFA and glycerol (1). On the other hand, an excessive amount of water molecules starts to adversely affect the transesterification (due to strong interaction with the catalytic SO₃H sites) and esterification (due to reaction equilibrium shift) reactions.

4. Conclusions

Arene-SO₃H-SBA-15 is shown as a remarkable heterogeneous acid catalyst for FAME production from highly acidic crude palm oil, showing high FAME yields even in the presence of water content as high as 5 wt%. However, this catalyst also promotes the appearance of high FFA contents in the final biodiesel as a consequence of hydrolysis reactions. Although the addition of relatively small amounts of water can improve the overall yield to FAME, due to hydrolysis of triglycerides producing FFA that can subsequently undergo esterification, higher amounts of water result in reduced FAME yields due to strong interaction with the catalytic sites and equilibrium shift towards the hydrolysis. Taking this into account, several strategies have been proposed to improve the catalytic performance: (1) previous drying of feedstock and catalyst; (2) addition of dehydrating molecular sieves, (3) catalyst surface hydrophobization; and (4) use of a decreasing reaction temperature profile. All these strategies resulted in clear improvements of the catalytic performance, mainly in terms of FAME yield. Importantly, the use of a decreasing temperature profile, in order to promote first the transesterification at high temperature and then the esterification of FFA at low temperature, led additionally to a strong reduction of the final FFA content. Thus, a catalytic system operated 2h at 160°C followed by 2h at 100°C resulted in 96% FAME yield and 0.4 mg KOH/g acid value.

Acknowledgements

The financial supports from the Spanish Science and Innovation Ministry through the project CTQ2008-01396 and from the Regional Government of Madrid through the project S2009-ENE1743 are gratefully acknowledged. The Spanish government is kindly acknowledged by the award of a FPI grant to RSV.

References

1. Atadashi, I.M., Aroua, M.K., Abdul Aziz, A.R., Sulaiman, N.M.N., 2012. The effects of water on biodiesel production and refining technologies: A review. *Renew. Sust. Energ. Rev.* 16, 3456–3470.
2. Brahmkhatri, V., Patel, A. 2011. Biodiesel production by esterification of free fatty acids over 12-Tungstophosphoric acid anchored to MCM-41. *Ind. Eng. Chem. Research.* 50, 6620–6628.
3. Dorado, M.P., Ballesteros, E., Almeida, J.A., Schellert, C., Lohrlein, H.P., Krause, R., 2002. An alkali-catalyzed transesterification process for high free fatty acid waste oils. *Trans ASAE* 45, 525–529.
4. Encinar, J.M., Sánchez, N., Martínez, G., García, L., 2011. Study of biodiesel production from animal fats with high free fatty acid content. *Bioresour. Technol.* 102, 10907–10914.
5. Iglesias, J., Morales, G., 2012. Biodiesel from waste oils and fats: methods and catalysis, in Luque, R., Melero, J.A. (Eds.), *Advances in biodiesel preparation. Second generation processes and technologies.* Woodhead Publishers Ltd., Cambridge, pp. 154–178.
6. Kargbo, D.M., 2010. Biodiesel production from municipal sewage sludges. *Energ. Fuel.* 24, 2791–2794.
7. Lee, A.F., Wilson, K., 2014. Recent developments in heterogeneous catalysis for the sustainable production of biodiesel. *Catal. Today*, *in press*
<http://dx.doi.org/10.1016/j.cattod.2014.03.072>.
8. Leung, D.Y.C., Wu, X., Leung, M.K.H., 2010. A review on biodiesel production using catalyzed transesterification. *Appl. Energy* 87, 1083–1095.

9. Lien, Y-S., Hsieh, L-S., Wu, J.C.S., 2010. Biodiesel synthesis by simultaneous esterification and transesterification using oleophilic acid catalyst. *Ind. Eng. Chem. Res.* 49, 2118–2121.
10. Melero, J.A., Bautista, L.F., Iglesias, J., Morales, G., Sánchez-Vázquez, R., Suárez, I., 2010b. Biodiesel production over arenesulfonic acid-modified mesostructured catalysts: optimization of reaction parameters using response surface methodology. *Top. Catal.* 53, 795–804.
11. Melero, J.A., Bautista, L.F., Morales, G., Iglesias, J., Briones, D., 2009b. Biodiesel Production with Heterogeneous Sulfonic Acid-Functionalized Mesostructured Catalysts. *Energy Fuels* 23, 539–547.
12. Melero, J.A., Bautista, L.F., Morales, G., Iglesias, J., Sánchez-Vázquez, R., 2010a. Biodiesel production from crude palm oil using sulfonic acid-modified mesostructured catalysts. *Chem. Eng. J.* 161, 323–331.
13. Melero, J.A., Iglesias, J., Morales, G. 2009a. Heterogeneous acid catalysts for biodiesel production: current status and future challenges. *Green Chem.* 11, 1285–1308.
14. Melero, J.A., Stucky, G.D., van Grieken, R., Morales, G., 2002. Direct syntheses of ordered SBA-15 mesoporous materials containing sulfonic acid groups. *J. Mater. Chem.* 12, 1664–1670.
15. Melero, J.A., van Grieken, R., Morales, G., 2006. Advances in the synthesis and catalytic applications of organosulfonic-functionalized mesostructured materials. *Chem. Rev.* 106, 3790–3812.
16. Morales, G., Athens, G., Chmelka, B.F., van Grieken, R., Melero, J.A., 2008. Aqueous-sensitive reaction sites in sulfonic acid-functionalized mesoporous silicas. *J. Catal.* 254, 205–217.

17. Morales, G., Bautista, L.F., Melero, J.A., Iglesias, J., Sánchez-Vázquez, R, 2011. Low-grade oil and fats: Effect of several impurities on biodiesel production over sulfonic acid heterogeneous catalysts. *Bioresour. Technol.* 102, 9571–9578.
18. Ngaosuwan, K., Lotero, E., Suwannakarn, K., Goodwin, J.G., Prasertham, P. 2009. Hydrolysis of triglycerides using solid acid catalysts. *Ind. Eng. Chem. Research.* 48, 4757–4767.
19. Olutoye, M., Hameed, B.H., 2011. Synthesis of fatty acid methyl ester from used vegetable cooking oil by solid reusable $Mg_{1-x}Zn_{1+x}O_2$ catalyst. *Bioresour. Technol.* 102, 3819–3826.
20. Sharma, Y.C., Singh, B., Korstad, J., Roberts, O., 2011. Advancements in solid acid catalysts for ecofriendly and economically viable synthesis of biodiesel. *Biofuels, Bioproducts and Biorefining* 5, 69–92.
21. Wahlen, B.D., Barney, B.M., Seefeldt, L.C., 2008. Synthesis of Biodiesel from Mixed Feedstocks and Longer Chain Alcohols Using an Acid-Catalyzed Method. *Energ. Fuel* 22, 4223–4228.

Table 1. Properties of crude palm oil used as feedstock for FAME production.

Property	Analysis Method	Value
Acid value (mg _{KOH} /g)	UNE-EN ISO 660:2000	21.45
Metals (mg/kg)	ASTM D5185-05	
Na		15.7
K		n.d.
Mg		4.9
Ca		5.3
Phosphorous (mg/kg)	ASTM D5185-05	13.1
Fatty acid profile(wt%)	UNE-EN ISO 5508:1996 and UNE-EN ISO 5509:2000	
Myristic acid (14:0)		0.8
Palmitic acid (16:0)		43.3
Palmitoleic acid (16:1)		0.0
Stearic acid (18:0)		5.2
Oleic acid (18:1)		39.7
Linoleic acid (18:2)		10.5
Linolenic acid (18:3)		0.4
Water (mg/kg)	UNE-EN ISO 12937:2001	687
Unsaponifiables (wt%)	Method reported by Plank and Lorbeer, 1994	2.5

n.d.: not detected (below detection limit).

Table 2. Physicochemical properties of the arenesulfonic acid-modified mesostructured SBA-15 silicas.

Sample	Textural Properties					Acid capacity ^e	
	d_{100} ^a (Å)	Pore size ^b (Å)	BET area (m ² /g)	Pore vol. ^c (cm ³ /g)	Wall thick. ^d (Å)	Sulfur (meq/g)	H ⁺ (meq/g)
Arene-SO₃H-SBA15	108	92	712	1.03	32	1.2	1.2
Hydrophobized arene-SO₃H-SBA15	114	83	533	0.75	48	1.0	1.0

^a $d(100)$ spacing, measured from small-angle X-ray diffraction. ^b Mean pore size (D_p) from adsorption branch applying the BJH model. ^c Total pore volume (V_p) was taken at $P/P_0 = 0.975$ single point. ^d Average pore wall thickness calculated by a_o -pore size ($a_o = 2 d(100) / \sqrt{3}$). ^e Acid capacity defined as meq of acid centers per g of catalyst (obtained either directly by titration or indirectly from sulfur content by elemental analysis).

Table 3. Acid capacity of the double-washed catalyst with methanol and *n*-hexane after 8h of reaction with different amounts of water in the reaction medium (0, 1, 5, and 10 wt%). Reaction conditions: crude palm oil; 160°C; 30:1 methanol:oil molar ratio; 8 wt% catalyst loading; 2000 rpm stirring rate.

Arene-SO₃H-SBA-15	Acid Capacity (meq H⁺/g)
Fresh	1.1
0 wt% water	1.0
1 wt% water	0.9
5 wt% water	0.9
10 wt% water	0.8

Table 4. Acid values of the reaction product after 8h for hydrophobized and non-hydrophobized arene-SO₃H-SBA-15 catalysts with 0% and 1wt% added water. Reaction conditions: crude palm oil; 160°C; 30:1 methanol:oil molar ratio; 8 wt% catalyst loading; 2000 rpm stirring rate.

Catalyst, added water	Acid value (mg KOH/g)
Arene-SO ₃ H-SBA-15, 0% water	24.0
Arene-SO ₃ H-SBA-15, 1% water	27.3
Hydrophobized arene-SO ₃ H-SBA-15, 0% water	21.0
Hydrophobized arene-SO ₃ H-SBA-15, 1% water	21.0

Figure captions

Figure 1. Evolution of yield to FAME from crude palm oil over arene-SO₃H-SBA-15 catalyst with different amounts of water in the reaction medium (0, 1, 5, and 10 wt%). Reaction conditions: 160°C; 30:1 methanol:oil molar ratio; 8 wt% catalyst loading; 2000 rpm stirring rate.

Figure 2. Acid content (mgKOH/g) in the production of FAME from crude palm oil over arene-SO₃H-SBA-15 catalyst with several amounts of water in the reaction medium (0, 1, 5, and 10 wt%). Reaction conditions: 160°C; 30:1 methanol:oil molar ratio; 8 wt% catalyst loading; 2000 rpm stirring rate.

Figure 3. Evolution of yield to FAME from crude palm oil over arene-SO₃H-SBA-15 catalyst with the different strategies. Strategy 1: pre-drying of catalyst and oil. Strategy 2: addition of molecular sieve. Reaction conditions: 160°C; 30:1 methanol:oil molar ratio; 8 wt% catalyst loading; 2000 rpm stirring rate.

Figure 4. Acid content (mgKOH/g) in the production of FAME from crude palm oil over arene-SO₃H-SBA-15 catalyst with the different strategies. Strategy 1: pre-drying of catalyst and oil. Strategy 2: addition of molecular sieve. Reaction conditions: 160°C; 30:1 methanol:oil molar ratio; 8 wt% catalyst loading; 2000 rpm stirring rate.

Figure 5. Yield to FAME from crude palm oil over arene-SO₃H-SBA-15 and hydrophobized-arene-SO₃H-SBA-15 catalysts. Effect of the addition of 1 wt% water. Reaction conditions: 2h; 160°C; 30:1 methanol:oil molar ratio; 8 wt% catalyst loading; 2000 rpm stirring rate.

Figure 6. Yield to FAME from crude palm oil over arene-SO₃H-SBA-15 using a decreasing temperature profile. Reaction conditions: 2h at temperature T₁ followed by 2h at temperature T₂; 30:1 methanol:oil molar ratio; 8 wt% catalyst loading; 2000 rpm stirring rate.

Figure 7. Simplified reaction network for the production of fatty acid methyl esters from highly acidic crude palm oil over arene-SO₃H-SBA-15 catalyst.

Fig. 1

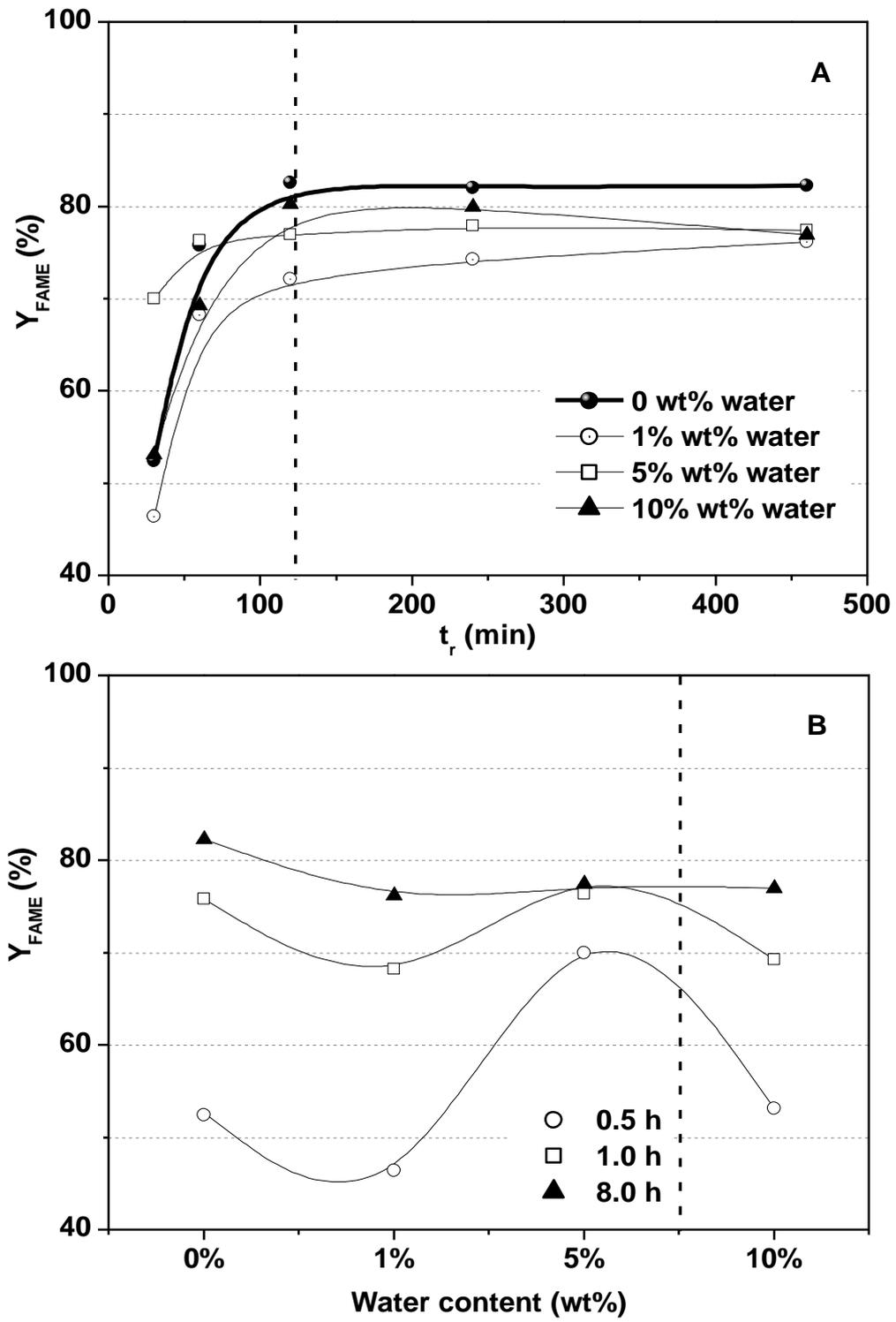


Fig. 2

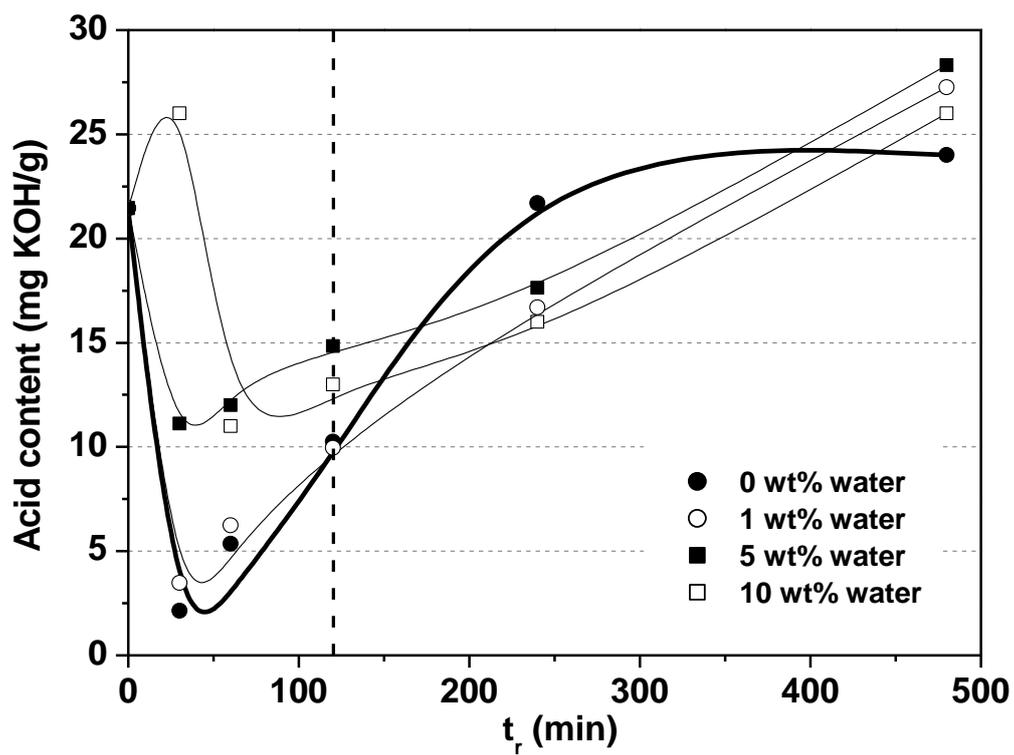


Fig. 3

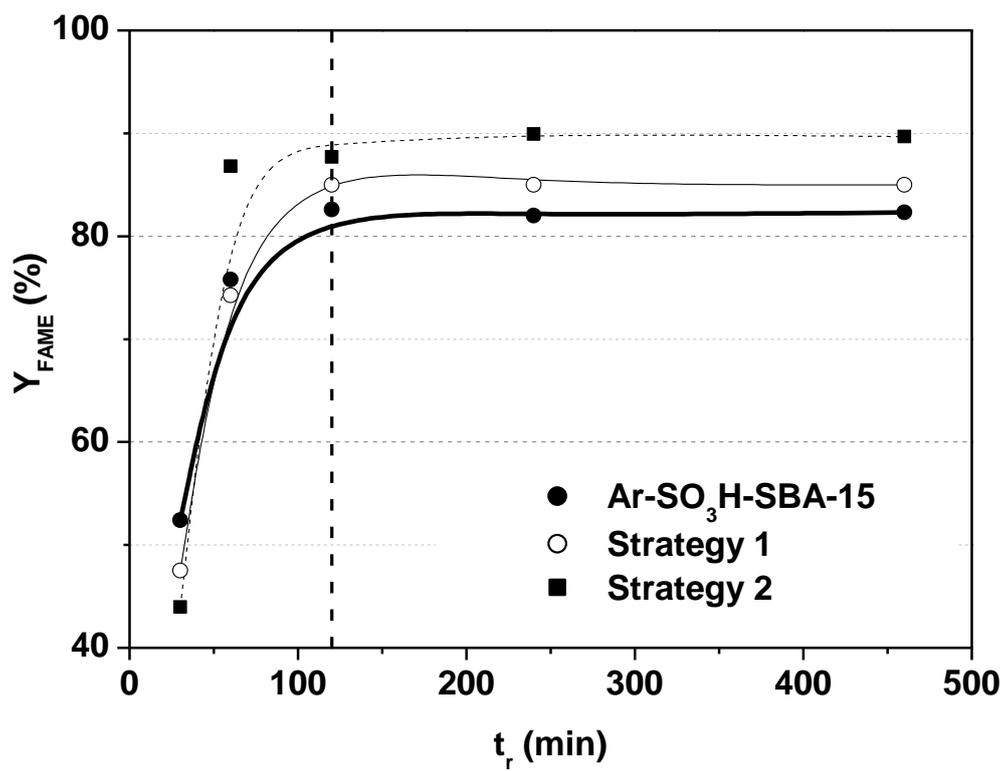


Fig. 4

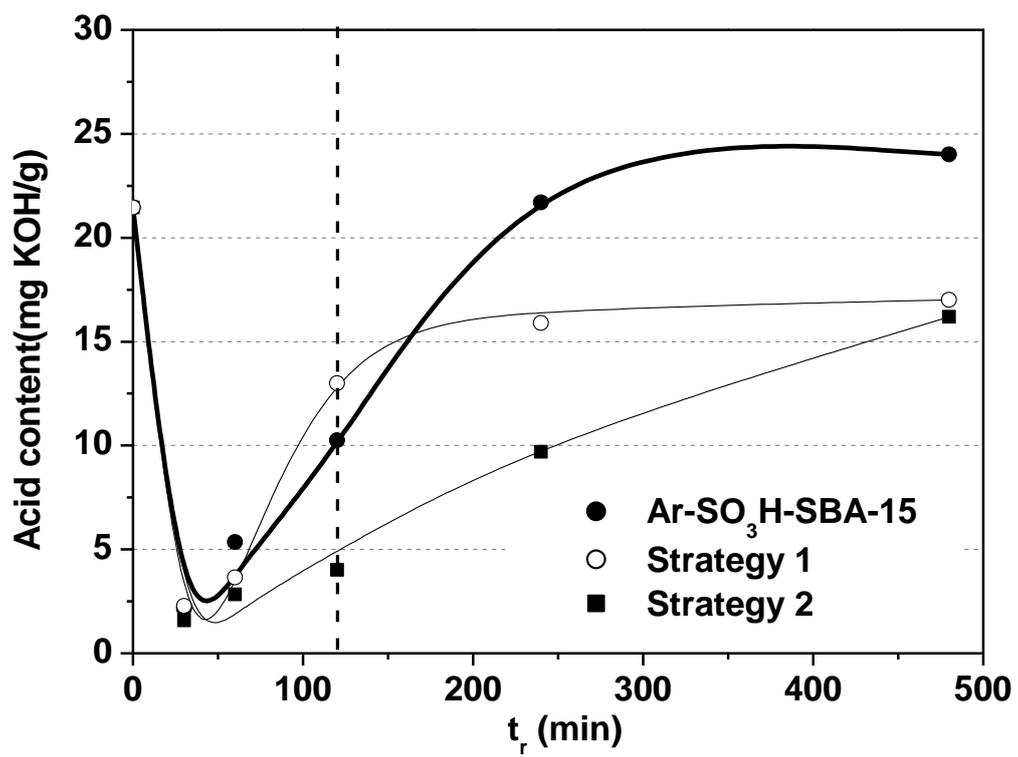


Fig. 5

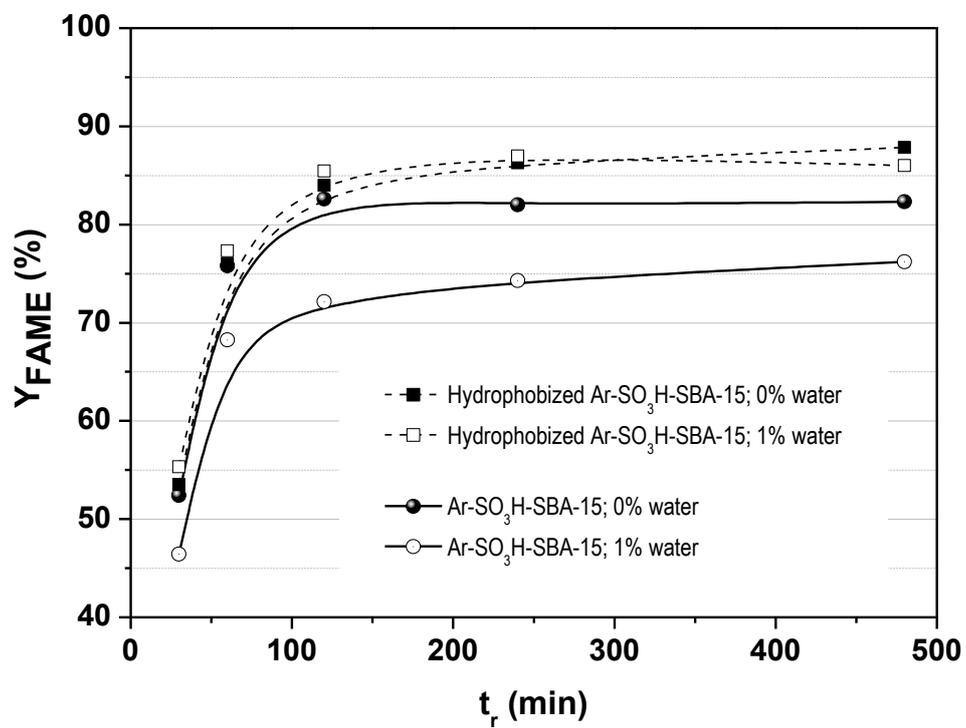


Fig. 6

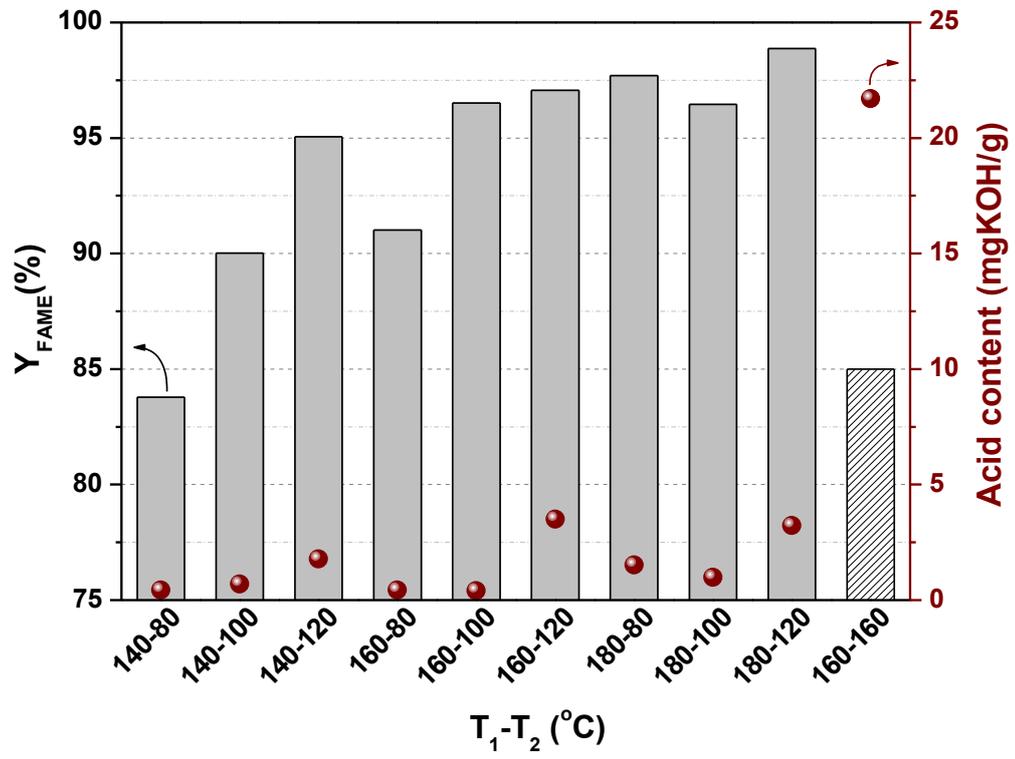


Fig. 7

