Heterogeneous acid catalysts for biodiesel production: current status and future challenges

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The reduction of oil resources and the consequent increasing price of oil distillates as well as the environmental concerns of conventional fuels has renewed and increased interest on the preparation of biofuels from renewable resources. One of those interests is nowadays focused on biodiesel, which is usually prepared from crude and refined triglyceride containing raw materials, such as vegetable oils, animal fats and wastes—for instance waste cooking oil and yellow and brown grease. Since several commercial interests converge on this kind of feedstock, one of the priorities being crops for human food supply, the research efforts on biodiesel production are diverting towards the use of low quality triglyceride-containing raw materials. Nevertheless, all of these feedstocks feature high water and free fatty acids (FFAs) content, which strongly affects the behaviour of conventional homogeneous base catalysts. These catalysts are primarily NaOH and KOH, but also $NaOCH_3$ and $KOCH_3$ are employed—as solutions in methanol—mainly in large-scale production plants. In this context, an appropriate solid acid catalyst which could simultaneously carry out esterification of FFAs and transesterification of triglycerides would be of great interest for biodiesel production. Moreover, a heterogeneous acid catalyst could be easily incorporated into a packed bed continuous flow reactor, simplifying product separation and purification and reducing waste generation. The present review attempts to provide a wide overview on the possibility of heterogeneous acid catalysts for biodiesel production replacing the homogeneous conventional process. In this way, three aspects of solid acid catalysis for biodiesel production will be reviewed. The first section deals with the solid acid-catalyzed esterification of FFAs, the second topic relates to the transesterification of triglycerides, while the third deals with solid acid-catalyzed transformation of bioglycerol into oxygenated compounds for biodiesel formulation.

1. Introduction

An important European Union energy policy target is to double the share of renewable energy sources in gross inland energy consumption from 5.4% in 1997 to 12.0% by 2010—White Paper for Renewable Energy Sources, 1997. According to the White Paper, the energy from biomass should be 62% of the total renewable energy production and 7.5% of the primary energy in EU-15. Various legislative actions are in place to achieve this target. In the case of biofuels for transport, the Directive 2003/30/EC of the European Parliament and of the Council of May 8th 2003 on the promotion of the use of biofuels or other renewable fuels for transport, stated that by the end of the year 2010 member states should ensure a biofuel proportion of 5.75%, calculated on the basis of energy content, for all the fuels used for transport purposes.[1] The diesel and petrol demand in the EU in 2010 is expected to be around 324 Mtoe (million tons of oil equivalent), so that in order to comply with the above-mentioned directive the production of biofuels should increase up to 18.6 Mtoe. Moreover, the EU is already turned towards the future and the biofuels proportion could be increased up to 10% in 2020.

In order to attain these ambitious targets, innovative technologies and process integration are needed to produce biofuels in an energy efficient way, from a wider range of biomass resources and reducing operation costs. Nowadays, there is a huge range of technologies for the production of biofuels for transport from biomass.[2,3] Some of them are currently commercially used—*first generation biofuels*—but most of them have only been tested on pilot plant scale or even on bench scale, and therefore important advances in conversion technologies are still necessary—*second generation biofuels*. At the present time, we can consider two principle types of first generation biofuels: bioethanol and biodiesel. Bioethanol is mainly produced in Brazil and USA by means of the fermentation of sugar grains or starch, whereas biodiesel is commonly obtained by the transesterification, with methanol, of oleaginous plants, although it can also be generated from animal fats or waste cooking oils, WCO. Both technologies are widely commercialized but their production costs are rather high compared to petroleum-based fuels. Some improvements in the process could be carried out in order to obtain higher energy yields, better use of co-products, reduction of operational costs through simplified production schemes, and use of less-expensive and non-edible feedstocks.

Biodiesel is a mixture of different chemicals comprising fatty acid alkyl esters, FAAEs, as the main components, but also free fatty acids, FFA, or fatty acid monoglycerides can be found. The former are usually obtained by transesterification

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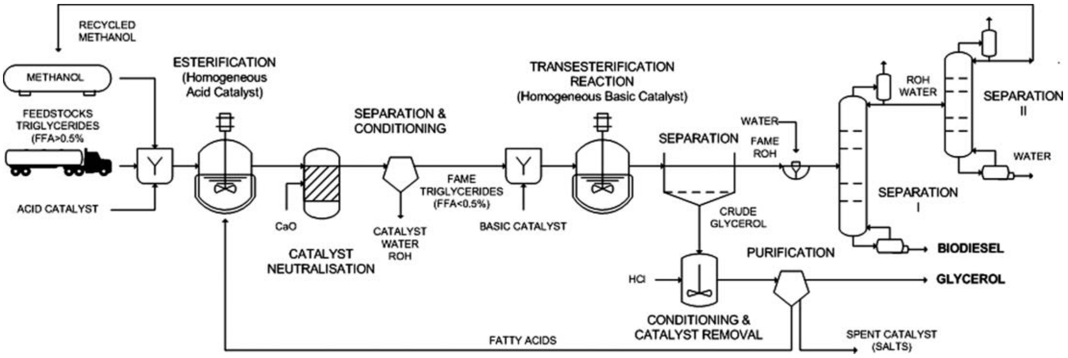


Fig. 1 Global flowchart of conventional process for the biodiesel production using homogeneous alkaline catalysts with a previous acid esterification step.

of triglycerides using short chain alcohols, mostly involving the use of methanol to lead to FAMEs, fatty acid methyl esters, or ethanol to lead to FAEEs, fatty acid ethyl esters, though other alcohols can be used. Conventional processes include the use of homogeneous alkaline catalysts—NaOH, KOH, NaOMe and KOMe—under mild temperatures (60–80 °C) and atmospheric pressure.[4] Fig. 1 illustrates a flow diagram for a typical base-catalyzed process for the production of biodiesel in which a previous esterification acid step has been included in order to reduce the free fatty acids content of the initial feedstock. There are two main factors that affect the cost of traditional biodiesel production: the cost of raw materials and the cost of processing (multiple steps), though the commercialization of resultant glycerol can share the production costs with biodiesel, improving the overall process profitability. In order to reduce the costs associated with feedstock, waste cooking oils, animal fats or non-edible oils could be used. However, the use of homogeneous alkaline catalysts in the transesterification of such fats and oils involves several troubles due to the presence of large amounts of free fatty acids (FFAs). Of course, alkaline catalysts can be used to process these raw materials, but a large consumption of catalyst as well as methanol is compulsory to achieve biodiesel of standard specifications. Thus, FFA concentration in the oil inlet stream is usually controlled below 0.5% (w/w), avoiding the formation of high soap concentrations as a consequence of the reaction of FFAs with the basic catalyst. The soap causes processing problems downstream in the product separation because of emulsion formation. Usually, this problem is overcome through a previous esterification step where FFAs are firstly esterified to FAMEs using a homogeneous acid catalyst, and then, once the acid homogeneous catalyst has been removed, transesterification of triglycerides is performed as usual by means of an alkaline catalyst (Fig. 1). Likewise, homogeneous acid catalysts (H_2SO_4, HCl, BF_3, H_3PO_4) have been proposed to promote simultaneous esterification of FFAs and transesterification of triglycerides in a single catalytic step, thus avoiding the pre-conditioning step when using low cost feedstock with high FFA content.[5] However, these catalysts are less active for transesterification than alkaline catalysts and therefore higher pressure and temperature, methanol to oil molar ratio and catalyst concentration are required to yield adequate transesterification reaction rates. Hence, despite its insensitivity to free fatty acids in the feedstock, acid-catalyzed transesterification has been largely ignored mainly due to its relatively slower reaction rate.

In addition, non-catalytic processes have been also described in literature with supercritical methanol to reduce the multiple steps of the homogeneous alkaline-catalyzed process.[6,7] In this case, the reaction takes place in a single homogeneous phase since the supercritical methanol is fully miscible with the vegetable oils. Moreover, the reaction rate is very high and the subsequent purification is much simpler than that of the conventional process. The supercritical route is also characterized by a high yield because of simultaneous transesterification of triglycerides and esterification of fatty acids. The main drawback is that the non-catalytic supercritical process requires very high temperatures (350–400 °C) and pressures (200–400 bar), and thus high operational costs are addressed.

Another important technological challenge in biodiesel production is the design of heterogeneous catalysts. The use of heterogeneous catalysts would result in simpler, cheaper separation processes, a reduced water effluent load as well as capital and energy costs. There would be fewer inputs and less waste, as no soap would be formed. Furthermore, catalyst would not have to be continuously added and would be easier to reuse. There would be no neutralization products, so a higher grade of glycerol could be obtained. In contrast, the main drawbacks are the high temperature and pressure, as well as the higher methanol to oil ratio needed for the transesterification reaction as compared with homogeneous systems.

The development of basic heterogeneous catalysts for biodiesel production has been widely described in the literature, including carbonates and hydrocarbonates of alkaline metals; alkaline metal oxides; alkaline metal hydroxides; anionic resins, basic zeolites, *etc.*[8,9] Some of these catalysts have shown a good catalytic performance even under reaction conditions similar to those used for the homogeneous catalysts. However, this kind of catalyst is still far from an industrial application, since its evaluation has only been carried out in stirred batch reactors, there being few studies on continuous processes using packed bed flow reactors. Currently, the unique heterogeneous commercial process is based on the Esterfip-H technology developed by the Institute Français du Petrole (IFP),[10–12] with a plant starting up in 2006 producing 160 000 t per year (France). In this continuous process, the transesterification reaction is promoted by a completely heterogeneous catalyst.

This catalyst consists of a mixed oxide of zinc and aluminium, which promotes the transesterification reaction without catalyst loss. The reaction is performed at higher temperature and pressure than homogeneous catalysis processes, with an excess of methanol. This excess is removed by vaporization and recycled to the head of the process to be mixed with fresh methanol. The desired chemical conversion, required to produce biodiesel at the European specifications, is reached after two successive stages of reaction and glycerol separation in order to shift the methanolysis equilibrium. The catalytic section includes two fixed bed reactors fed with vegetable oil and methanol at a given ratio. The purification section of methyl esters comprises finishing methanol vaporization under vacuum followed by final purification in an additional step to remove solubilized glycerol. Glycerol is directly produced with high purity levels, at least 98%, and free of salt contaminants. This aspect is very important from the economical point of view because it reduces the cost of obtaining high-grade glycerol, thus increasing the profitability of the process. Biodiesel yield is close to 100% and purity higher than 99%. Nevertheless, the raw material must have a FFAs content lower than 0.25% and water content lower than 1000 ppm.

Since acid catalysts can simultaneously carry out esterification of FFAs and transesterification of triglycerides, they could help in processing low-cost, low-quality feedstocks generally with high FFAs concentration, and thereby lowering overall production costs. Economical assessment of different biodiesel production processes using homogeneous alkali and acid catalysts, as well as heterogeneous acid catalysts and supercritical methods have been recently discussed in the literature.[13] The results indicate that heterogeneous acid-catalyzed process is clearly advantageous over the other studied processes, as it has the highest rate-of-return, lowest capital investment, and technically is a relatively simple process. Likewise, in particular reaction conditions the acid catalyst can promote the *in-situ* transformation of glycerol into oxygenated-derivatives of interest for the formulation of biodiesel.[5,11] However, few research studies dealing with transesterification reactions catalyzed by solid acids have been reported in the literature, while many papers are devoted to esterification reactions with solid acid catalysts—mainly acid resins.[5,14] Nevertheless, the commercial introduction of these catalysts still need important advances to impact in a positive way on the biodiesel synthesis technologies, as it can be concluded from the low amount of licensed processes in the patent literature. These improvements include aspects such as: increasing the stability of acid sites avoiding their leaching, increasing thermal stability, enhancement of mass transfer avoiding diffusional limitations, milder operation conditions by means of an adequate design of acid catalysts combining high activities and selectivities for transesterification reactions, as well as resistance to water impurities usually present in unrefined feedstocks. Thus far, it seems that an ideal acid solid catalyst should join the following characteristics:[5,15] interconnected system of large pores to minimize diffusional problems of molecules having long alkyl chains; moderate to high concentration of strong acid sites to promote the transesterification reaction with significant rates; high thermal stability of acid sites to minimize leaching effects and hydrophobic surface to promote the preferential adsorption of oily hydrophobic species on the catalyst surface and avoiding possible deactivation of catalytic sites by strong adsorption of polar compounds, especially water.

Thus, increasing awareness of the economical and environmental costs of traditional base-catalyzed chemical processes, as well as the growing interest of heterogeneous catalysis has created an opportunity for solid acid catalysts. In this review, we will describe in what way this opportunity is being addressed through the application of different heterogeneous acid catalysts for biodiesel production. Special attention will be paid to the strategies to tune the acid strength and to control the hydrophobic microenvironment of the acid sites and the subsequent improvements of the catalytic performance (activity and stability). Likewise, it is essential to make an efficient use of the glycerol, main co-product obtained in the biodiesel production process, wherein acid catalysts can also play an important role.[16] Finally, the intensification of the biodiesel production using heterogeneous acid catalysts will be discussed.

2. Biodiesel production through esterification of free fatty acids (FFAs)

One of the possibilities to reduce FFA content in the feedstock is to introduce an intermediate step in the biodiesel production process before the main reaction stage catalyzed by alkaline catalysts. This additional step is required for reducing the FFA content, typically to below 0.5%,[17] to ensure the good behaviour of the basic catalyst; otherwise those cannot lead to good yields towards biodiesel, or higher catalyst and alcohol loadings are required. One of the possibilities for this stage is the saponification of FFAs with NaOH solutions to lead soap formation[4,17] However, this method leads to partial consumption of the starting material and waste generation and, thus, other possibilities are preferred. An alternative is to pre-treat the FFA-containing feedstock through an esterification step with short-chain alcohols. In this way, the FFA content is also converted into biodiesel without waste generation. Usually this stage is driven in the presence of homogeneous acids as catalysts. Brønsted acids can catalyze the esterification of free fatty acids because of protonation of the acid group to give an oxonium ion which is readily attacked by an alcohol through an exchange reaction to give the corresponding ester after losing a proton (Fig. 2).

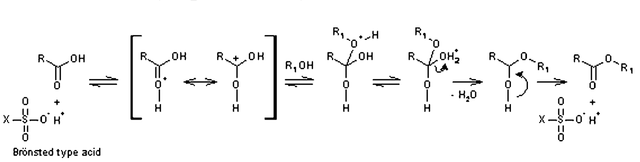


Fig. 2 Mechanism for esterification using Brønsted-type acid catalysts (sulfonic acids).

Sulfuric acid[18–20] and alkyl sulfonic compounds[21,22] are probably the most extended acid catalysts used for the esterification of free fatty acids. These acids show high acid strength and, unlike other mineral acids, can be found in high concentration, avoiding the addition of large amounts of water in the reaction media because of the use of diluted acids—for instance HCl 35 wt%. However, the use of these strong acids leads to biodiesel with high sulfur content which is out of specifications. For this reason and many others, such as the impossibility to reuse mineral acids, heterogeneous acid catalysts are preferred over homogeneous ones. In the literature, several kinds of heterogeneous acid catalysts can be found to catalyze the esterification of free fatty acids to biodiesel, but two types are mainly reported: sulfonic acid-functionalized solids—both ion-exchange organic resins and inorganic supports—and inorganic metal-oxide based superacids.

2.1 Esterification of free fatty acids with sulfonic acid-based heterogeneous catalysts

Ion exchange sulfonic-functionalized organic resins have been reported to display excellent catalytic activity in esterification reactions[23,24] for small organic acids, and the studies carried out on their catalytic activity in this kind of reaction have been extended to the treatment of free fatty acids. A pioneering work, in which sulfonic-functionalized resins were employed as esterification catalysts for biodiesel production, was first reported by Santacesaria *et al.*[25] These authors reported the kinetics of the esterification of a synthetic mixture of an acidity-free oil with high contents of oleic acid (~50% by wt) using a polystyrene-divinylbenzene-based resin showing an acid content of 3.6 meq g^{-1}. The catalytic assays were carried out under mild temperature conditions using methanol to oleic acid molar ratios of 8 to 10 and 2.5% by wt of catalyst. The evolution of the composition of the reaction media was assessed by means of direct titration of the acidity, so that only esterification reaction, but not transesterification of triglycerides, was monitored. The sulfonic acid resin resulted to be a very active catalyst under the reaction conditions, reaching 80% conversion of free fatty acids at 85 °C after two hours. The authors also found a fairly good correlation between the experimental data and a pseudo-homogeneous second-order kinetic model. Though ion exchange resins do not show high values for textural properties—pore size, surface area, pore volume—no mass transfer limitations were detected, probably because the resin swells in the organic reaction media and small pores become macropores making most of the acid functionalities accessible[26,27] However, no recycling catalytic tests were described so that no data about the reutilisation of these materials was given.

Papayannakos *et al.*[28] reported a similar study on the esterification of the saponificable content of a real oil refinery by-product containing almost 40 wt%. FFAs. In this case, a stronger acid resin was used as catalyst, showing an acid sites content of 5.2 meq g^{-1}. In this case too, the evolution of the reaction media was monitored by titration of the acid content so that only esterification of FFAs was evaluated. Several parameters of a homogeneous second-order kinetic model were calculated from the correlation of experimental data, in a similar way to that previously reported by Santacesaria, though the energy of activation and pre-exponential factor calculated for the direct and reverse reactions differ in both works. Papayannakos *et al.*[28] also studied the resistance of the catalysts against deactivation through a series of reutilization runs. The authors found that, after the first run, the catalytic activity of the resin remained unchanged—even after eight consecutive recycling tests—but no reasons for the activity decay during the first assay were given.

Sulfonic polystyrene-divinylbenzene resins were also applied as catalysts in the esterification of free fatty acids by Wu *et al.*[29] in the same way as already described for the works reported by Santacesaria and Papayannakos, but with an extended experimental field. In this case, soybean oil was hydrolyzed with enzymes to give the feedstock which was used in the esterification assays showing almost only free fatty acids in its composition. In other words, the content of the raw material in triglycerides was almost completely transformed by enzymatic hydrolysis. In this work, the experimental runs where conducted in very wide ranges of catalyst loading and methanol to fatty acids molar ratio, though the temperature was only varied in 20 °C. Again, a pseudo-homogeneous kinetic model was applied for the determination of the kinetic parameters through the correlation of the experimental data. Wu *et al.* reported similar activation energy for the forward reaction to that reported by Santacesaria and lower to that reported by Papannayakos, whereas the activation energy calculated for the forward reaction resulted to be negative. Table 1 depicts the main properties of the sulfonic acid resins described in these works, the kinetic model used for fitting the experimental data and the activation energies calculated for the forward reaction kinetic constant and the equilibrium constant.

Differences related to activation energies for the forward and backward reactions have been ascribed to the use of different catalysts. More specifically these differences can be due to

Table 1 Kinetic models and parameters proposed for the esterification of free fatty acids with methanol in the presence of sulfonic-functionalized PS-DVB resins

Ref.	Catalyst/sulfonic resin	Kinetic model	Activation energy Fw; Eq/kJ mol^{-1} [a]
[25]	Relite CFS Particle size: 0.3–1.2 mm [H] = 3.6 meq g^{-1}	$r = k x_a x_{OH} C_{cat}\left(1-\frac{1}{K_{eq}}\frac{x_e x_w}{x_a x_{OH}}\right)$	Fw = 58.5; Eq = 11.2
[28]	Purolite CT-275 Particle size: 0.7–0.9 mm [H] = 5.2 meq g^{-1}	$r = k_{fw} C_a C_{OH} - k_{bw} C_e C_w$	Fw = 70.3; Eq = 32.4
[29]	Dowex monosphere 88 Particle size: 0.5–0.6 mm [H] = 4.5 meq g^{-1}	$r = k_{fw} C_{a0}\left[(1-x)(\theta-x)-\frac{x^2}{K_{eq}}\right]$	Fw = 59.4; Eq = 77.7

[a] Fw: forward reaction; Eq: equilibrium.

different properties of the organic resins, mainly related to the swelling behaviour in the reaction media and to the particle size used for the catalyst. Thus, Wu *et al.* found negative activation energy for the backward reaction in the study they performed, indicating that the hydrolysis of the fatty acid esters is controlled by mass transfer. On the other hand, Santacesaria *et al.*[25] determined, through the comparison of two reaction assays carried out in the presence of the same catalyst but with two different particle sizes, that there were no mass transfer restrictions under the tested reaction conditions. Bearing in mind the same organic nature of the sulfonic acid-functionalized resin matrix, polystyrene–divinylbenzene, it can be assumed that the adsorption and desorption processes are rather similar in all of the catalysts for each chemical present in the esterification–hydrolysis equilibria. Therefore, the differences found in the mass transfer transport for all these catalysts should be due to the different swelling behaviour in the reaction media but not to the adsorption–desorption processes. Thus, Purolite CT-275 used by Papayannakos[28] does not largely swell in polar solvents such as methanol, according to the manufacturer, and probably that is the cause for the lower catalytic activity and higher activation energy found for the forward reaction with this catalyst. Also the larger mean particle size of this catalyst could be another parameter affecting the mass transfer.

R. Talukder *et al.*[30] have reported a study focused on the comparison of the catalytic activities shown by a sulfonic-functionalized PS-DVD resin, Amberlyst 15, and a heterogenized enzyme, Novozym 435, in the esterification of palm fatty acid distillate containing more than 90% FFAs by wt. The reaction was monitored by both HPLC analysis and acid titration. In this case no kinetic study was performed, but the influence of different reaction parameters on the catalytic performance of both catalysts was studied. Thus, the catalytic activity of the polystyrene-based resin was improved insofar as the amount of methanol and temperature were increased in contrast to that found for the enzyme, which suffered a poisoning effect for high methanol loadings. 30 wt% of catalyst, referred to the FFA content, was determined to be the optimal amount of Amberlyst 15, but only small amounts of enzyme were required to achieve similar yields towards biodiesel in two hours (~92%), indicating a superior catalytic behaviour of the enzyme with regards the heterogeneous sulfonic acid-based resin. The influence of the reaction solvent was also studied, with the result that the more hydrophobic nature of the solvent the higher catalytic activity found for the resin. This is in fairly good agreement with the above mentioned conclusions about the strong dependency of the catalytic performance of this kind of resin on the swelling behaviour in the reaction media. Thus, these resins show a more pronounced swelling effect in the presence of non-polar solvents, increasing the amount of catalytic sites readily accessible by the reaction substrates. In the same sense, the presence of water in the reaction media did not lead to a strong decay of catalytic activity of the sulfonic catalyst, probably because the organic nature of the PS-DVB matrix hinders the access of water to the inner sulfonic groups to catalyze the backward reaction. In contrast, Novozym 435 displayed a stronger dependency with the water content in the conversion of free fatty acids, being lower when higher loadings of water were used. With regards to the stability of the catalysts, none of them evidenced catalyst poisoning, being reusable for at least 15 reaction cycles without noticeable activity decay.

Hoelderich *et al.*[31] have recently reported a complete study on the behaviour of different PS-DVB-based sulfonic acid-containing resins in the preesterification treatment of different oils and fats showing high FFA content. Commercially and non-commercially available strong acidic resins were used for comparison purposes. In general all the resins displayed good performance in the esterification of FFA in waste cooking oil and in the esterification of stearic acid in sunflower oil—almost 100% conversion after 6 h under optimized conditions—but also deactivation was also detected in consecutive recycling tests. The activity decay was, unlike in the previously described works, attributed to ion exchange with alkaline cations. These cations are specially plentiful in waste cooking oils because of the use of salt. Recycling tests carried out with desalted raw materials led to a much better catalytic performance of the strongly acid cation exchange resins since more than 80% of the initial catalytic activity was preserved after five consecutive reaction runs and also the materials could be easily regenerated with hydrochloric acid. These results indicate the catalytic activity of these materials is conditioned by the content of mineral salts in the starting raw material.

Caetano *et al.*[32] have also reported the behaviour of a sulfonic acid-containing resin, this time based on poly(vinyl alcohol),PVA, prepared by crosslinking the same with sulfosuccinic acid. The resultant material display a much better catalytic behaviour than PS-DVB-based resins, such as D50W8 and D50W2, in the esterification of palmitic acid with methanol, showing almost total conversion of the fatty acid after only few hours. Besides, the same authors reported the esterification of FFA in lard with methanol displaying also good catalytic activity. Recycling tests and comparison with PS-DVB resins revealed a much better resistance against deactivation of these PVA resins probably as consequence of a better swelling behaviour of these materials in methanol.

Recently, Goodwin *et al.*[33] reported another study about the use of sulfonic acid-containing catalysts on the esterification of free fatty acids with methanol. The catalyst consisted of sulfonated carbons previously obtained by pyrolization of sugars in nitrogen atmosphere. These materials displayed lower TOF values but greater substrate conversion than Amberlyst-15, used for comparison purposes, in the esterification of acetic acid. This was because of the higher acid concentration incorporated on the carbon support than in the resin, increasing the overall activity but decreasing the intrinsic catalytic activity per acid site because not all the sulfonic acid groups were accessible in the carbon. These catalysts were also investigated with other model compounds for biodiesel production, such as caprylic acid, but much lower catalytic activity was obtained. Nevertheless, a different trend in the activity of the carbon-based catalyst after several recycling tests was determined. Thus, for esterification of acetic acid, the activity was reduced cycle after cycle, suggesting sulfur leaching—the authors have estimated that 75–80% of the initial acid centres are stable after 5 recycling tests—whereas the esterification of caprylic acid reached higher yields on each reutilization assay. This different trend was ascribed to the swelling effect of the carbon matrix by adsorption of the fatty acid, indicating that the activity of this catalyst, as it is the case for sulfonic-functionalized organic resins, is determined by the swelling of the catalysts by chemicals present in the reaction.

Shanks *et al.*[34] have reported another study on the use of sulfonic acid-based catalyst in the esterification of free fatty acids. In this case the catalyst was not a resin but a silica-based mesostructured material, SBA-15, functionalized with propyl sulfonic groups covalently bound onto the inner surface of the mesopores system. This catalyst shows, as an advantage over the sulfonic resins and analogues, that its textural properties are fixed and non-dependent on the swelling behaviour because of the rigidity of the silica matrix. Beef tallow with approximately 7 wt% FFA concentration was used as feedstock in order to condition it for the transesterification step using alkaline catalysts. The objective was to reduce the acidity below 0.5 wt%. Catalytic assays revealed a strong catalytic loss when reusing the SBA-15-based catalyst, which was also found for a Nafion NR50 resin used for comparison purposes. This poisoning effect was ascribed to the adsorption of polar impurities coming from the beef tallow which caused pore blocking. Other possibilities, such as the poisoning by formed water, were discarded since no poisoning effect was observed when esterifying palmitic acid in soybean oil. The purification of the feedstock fat was carried out by treatment with activated charcoal and silica to adsorb impurities but, although lower, catalytic activity reduction was still observed. In order to avoid or partially reduce the deactivation phenomena, modification of the acid-functionalized mesoporous silica was carried out. Thus, simultaneous functionalization of the mesoporous silica was carried out with both the sulfonic acid groups and alkyl chains in order to provide hydrophobicity to the surface of the catalyst. Both the purification of the feedstock and the modification of the silica-based material lead to almost negligible catalyst deactivation. Besides, despite the catalytic activity being enhanced, the initial objective was not achieved, since the final reaction media showed a FFA content rather close to the target value, though higher than 0.5 wt%.

In the patent literature, few examples on the use of sulfonic acid functionalized solids in FFA esterification with short chain alcohols can be found. Thus, Morgan[35] has reported the use of a sulfonic acid resin in the production of biodiesel fuel from the treatment of FFA and FFA-containing raw materials in a reactive distillation column. The described apparatus consists of a distillation column in which the structured packing is formed by a sulfonic acid-functionalized resin, though no data about the behaviour of such system was provided. More recently, Prabhavathi Devi *et al.*[36] have patented the synthesis and use of a carbonaceous sulfonic acid-functionalized material, prepared from glycerol and sulfuric acid as starting compounds. The resultant material displays high acid loading and surface area and it allows for reaching more than 99.5% conversion in the esterification of different sources of free fatty acids at 60 °C in only 4 hours.

2.2 Esterification of free fatty acids with inorganic heterogeneous acid catalysts

In the literature, several examples of acid-catalyzed reactions can be found using inorganic solid acids. Among all the described applications, esterification reactions have been widely studied,[37–39] but the use of these inorganic heterogeneous acid catalysts in the esterification of free fatty acids have not been so widely reported. Some of the most important examples of these materials are the superacid solids[40]—materials showing stronger acidity than sulfuric acid. There are several ways to produce superacid solids but probably the most studied catalytic systems are sulfated and mixed metal oxides. These materials display heterogeneous acid centres, being some of them Lewis-type acid sites. These acid centres are, like Brønsted-type acids, able to catalyze esterification reactions. In this case the mechanism is slightly different since direct coordination of the fatty acid to the acid metal site is required. Fig. 3 displays a general mechanism for esterification reactions using a Lewis-type acid catalyst.

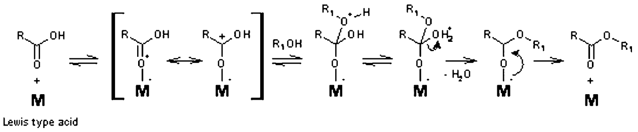


Fig. 3 Mechanism for esterification using Lewis-type acid catalysts.

One of the first examples of the use of inorganic acid materials in biodiesel production was carried out by Prasad *et al.*,[41] who reported the use of tungstated zirconia—a mixed oxides-based material showing superacid properties—in the esterification of palmitic acid with methanol at atmospheric pressure and refluxing conditions. The evolution of the reaction mixture was monitored by acid titration. Different preparation methods—impregnation and co-precipitation—were used for comparison purposes. Regardless the preparation method, it was found that the best catalytic activity was achieved for amorphous WO_3 domains dispersed on tetragonal crystalline zirconia and moderate tungsten loadings, though optimal values were different depending on the preparation method—5 wt% of tungsten for impregnation and 15 wt% for co-precipitation. The catalytic activity found for these materials was rather low, compared to that found for homogeneous sulfuric acid, and high catalyst loadings were required to achieve good yields towards the fatty acid methyl ester—up to 75% by weight of catalyst referred to substrate was needed to obtain 95% acid conversion after 1 hour. No reutilisation runs were performed in order to determine the reusability of the catalyst.

Rothenberg *et al.*[42] also reported a similar study about the comparison of several solid acids in the esterification of lauric acid with 2-ethylhexanol as model compounds for biodiesel production. This work consists of a screening study for determining which catalyst shows the higher catalytic activity and stability to be applied in a continuous process. These authors compared zeolites, sulfonic acid-containing resins and metal oxides. With regards to the zeolites, H-ZSM-5, Y and Beta materials were assayed. All of them displayed poor catalytic activity—only 5% substrate conversion was achieved over that obtained in the non-catalyzed assay—because of the hindered access of substrates to the acid catalytic sites present inside the porous structure. Thus, the reaction occurs only on the external surface, which is impractical for an industrial process. Amberlyst 15 and Nafion NR50 were also applied as catalysts to the same reaction, finding that the resins suffered some deactivation, as already described,[28] after only 2.0 and 4.5 hours respectively. This behaviour makes sulfonic-functionalized resins unsuitable to be used as catalysts in a continuous FFA esterification process. Sulfated zirconia was used as representative of the metal oxides family. This material showed a very high activity and selectivity towards the ester when reacting the fatty acid with a large variety of alcohols. The catalyst showed increasing activity when smaller alcohols were used, probably because of lower mass transfer limitations. In the same way, lower alcohol to fatty acid molar ratios were required to achieve higher ester yields. The stability of sulfate groups on the surface of the zirconia-based catalyst was also studied—leaching of sulfate groups is always suspected, especially when polar substances and water are present in the reaction media. The authors reported that, from the analysis of the reaction media and used catalyst, no leaching of sulfated groups occurred concluding that there was a high potential of sulfated zirconia to be used as an industrial catalyst in biodiesel production. The same authors have reported the use of sulfated zirconia, titania and stannia in the same esterification reactions, but the former was still the most active.[43,44] Nevertheless, several troubles, such as the large amount of catalyst required to achieve proper substrate conversions, make the applicability of sulfated zirconia for biodiesel production at industrial scale difficult. For this reason, Rothenberg and co-workers have proposed coupling the esterification reaction with water removal in order to displace the esterification–hydrolysis equilibrium by catalytic reactive distillation.[43,44] Conceptual design and simulations support the feasibility of this operation mode for industrial biodiesel production.

Meunier *et al.*[45] reported a study focused on the esterification of a synthetic mixture of palmitic acid in sunflower oil with methanol, in order to reproduce the conditions for a feedstock to be treated to produce an acidity-free oil to be further transesterified in presence of alkali catalyst. In a similar way to that reported by Rothenberg, these authors compared as catalyst a pure inorganic solid, sulfated zirconia, and a hybrid organic–inorganic material containing perfluorosulfonic acid groups, Nafion SAC-13, for the previously mentioned reaction. Prior to the catalytic assays, the catalysts were fine powdered and sulfated zirconia was pre-activated by calcination at various temperatures—temperatures above 500 °C were enough to achieve good catalytic properties. Sulfated zirconia displayed high catalytic activity in batch reactions, even higher than that corresponding to the hybrid SAC-13 material which displayed more than 50% of palmitic acid conversion after only 7 minutes– the highest TOF reported for an esterification catalyst up to that point. Nevertheless, the reutilization runs revealed a dramatic activity decay for sulfated zirconia during the two first recycling tests. Thus, the activity of sulfated zirconia was reduced down to a third of its initial catalytic activity, which was fairly well correlated with the leaching of sulfate groups, measured by direct analysis of the used catalysts. This different behaviour found for sulfated zirconia in the works of Rothenberg and Meunier could be due to different preparation procedures. In the case of the catalyst reported by Meunier, this is a home-made sulfated zirconia, whereas Meunier reported the catalytic assays using a commercial material. Since no preparation conditions have been given for the latter, no comparison can be made on this matter. With regards to the hybrid material SAC-13, this catalyst showed a much higher stability than the pure inorganic material and the consecutive recycling runs only led to a slight decrease of the catalytic activity, which was ascribed to pore blocking by hydrophobic products entangled within the polymer matrix. Due to its better stability, SAC-13 was also assayed in a fixed bed reactor but, after 30 hours in the reaction stream, a slowdown in reaction rate was observed. Several causes were given for this loss of catalytic activity including the catalyst poisoning by water adsorption and ester entanglement which could cause pore blocking.

Another example in which sulfated zirconia was also used as catalyst for esterification of free fatty acids has been reported by Mou and co-workers.[46] This time, the sulfated zirconia active phase was dispersed on a mesostructured silica matrix—SBA-15 type material—looking for higher interfacial surface area and pore volume than conventional zirconia-based materials and, thus, a higher number of active catalytic sites readily accessible to reactants. In this case, the synthesis was performed in a single step through the direct-synthesis by the co-condensation pathway, taking advantage of the stabilizing effect of sulfate ions in the synthesis of SBA-15 mesostructure and tuning the yield towards tetragonal zirconia, which is a requirement for the good catalytic performance of these materials. The catalysts displayed good textural and structural properties typical of SBA-15 type materials and an extremely high density of acid sites, comparable to that found for the sulfonated carbons above mentioned.[33] Anhydrous methanol was used as alcohol for the esterification of lauric and palmitic acids, used as reference substrates. In both cases, the supported sulfated zirconia displayed more than twice the activity obtained for unsupported sulfated zirconia. Also, the presence of water in the reaction mixture was studied, revealing almost negligible effect on the catalyst activity for supported zirconia, whereas the activity of the unsupported catalyst was reduced by almost 20%. This work demonstrated the high activity of sulfated zirconia when its textural properties are improved by supporting on high surface silicas, though no reutilization tests were reported in order to prove the real heterogeneous nature of the catalyst.

Lee and co-workers[47] have also reported another example about the use of pure inorganic materials as acid catalysts for the esterification of free fatty acids present in used vegetable oils, WCO, with methanol. In this case, several inorganic materials were assayed, including supported heteropolyacids, sulfated zirconia, alumina and silica and tungstated zirconia. All these materials showed high acid strength and they were used in a batch reactor for the esterification tests—20 wt% of catalyst to WCO was used. The evolution of the composition of the reaction mixture was followed by acid titration with KOH standard solution. Sulfated and tungstated zirconias were the most active catalysts among the tested materials but, since sulfated zirconia is known to suffer leaching of sulfate groups in presence of polar solvents such as methanol, only tungstated zirconia was used, this time in pellet form, in a fixed bed reactor under continuous operation conditions with a residence time equal to that used for the discontinuous reactor. The catalyst showed a lower catalytic performance in the fixed-bed reactor than in batch conditions, probably as a consequence of mass transfer limitations. On the other hand, stability of the catalyst was ensured by developing the reaction for 140 hours. Only a small decrease of catalytic activity was detected, being ascribed to partial leaching of tungsten which was accompanied by decreasing of the surface acidity. Nevertheless, the initial catalytic activity was almost obtained by catalyst regeneration through air-recalcination.

A different type of metal oxides mixture as acid catalyst for esterification of free fatty acids can be found in the works reported by Guo *et al.*[48] and Kozhevnikov *et al.*[49] These authors have independently reported the use of polyoxometalates supported on different supports materials. Different oxides were used as solid supports, including SiO_2 and Ta_2O_5. Polyoxometalates are known to show high catalytic activity in esterification reactions but also high solubility in organic solvents though, when supported, the system becomes highly stable. The catalysts were used in the esterification of lauric acid with ethanol and esterification of hexanoic acid with methanol. Silica supported polyoxometalates showed higher catalytic activity than the material prepared with tantalum oxide as solid support, but the acid groups easily leach from silica, in contrast to that found for the material prepared from Ta_2O_5. Optimization of the reaction conditions allowed to achieve total conversion of the substrate after only 2 hours of reaction using the tantalum based catalyst—7.4 g of lauric acid, 50 mg of catalyst, methanol to oil ratio of 9.0 and refluxing conditions. Reutilization tests evidenced great catalytic activity decay but not acid sites leaching. However, the catalysts were easily regenerated by washing in methanol and hexane, indicating that the observed reduction of catalytic activity was due to poisoning caused by adsorption of chemicals on the catalytic centres.

Finally, regarding the patent literature, there are scarce examples about the use of pure inorganic acid solids in the esterification of free fatty acids to produce biodiesel. As an example, the patent from Gomes Aranda *et al.*[50] can be cited, who reported the use of niobic acid, among other mineral acids, as catalysts for biodiesel production from FFA-containing raw materials, previously prepared by enzymatic hydrolysis of vegetable oils. These authors have reported conversions for soybean derived FFA in the range from 85 to 95% after reacting at 200 °C during 1 hour in methanol (methanol to oil of 1.5 to 4).

From the previous works it can be concluded that heterogeneous acid catalysts—both Brønsted-type such as sulfonic acid-containing materials or Lewis-type catalysts like mixed and sulfated oxides—are able to drive the esterification of free fatty acids with short chain alcohols to produce biodiesel. These materials can be effectively used as catalysts in a previous stage for conditioning the FFA-containing oils to be further treated with alkaline catalysts. Nevertheless, some remarks should be considered: though sulfonic-containing materials display higher catalytic activity than any other solid acid catalyst, and thus lower amounts of catalysts are required, they suffer several poisoning effects, mainly coming from polar compounds, limiting their use in continuous operation conditions. Besides, some regeneration strategies, such as calcinations, cannot be used due to their organic nature. These deactivation processes can be partially avoided and even removed by proper surface hydrophobization. With regards to the inorganic materials, sulfated zirconia display high catalytic activity which is, under certain conditions, similar to that showed by homogeneous sulfuric acid. Nevertheless, sulfate groups easily leach from the catalyst because of hydrolysis or alcoholysis with the esterifying methanol, thus making the heterogeneous nature of the catalytic activity of these materials subject to some controversy. On the contrary, tungstated zirconia displays a very high stability, compared with sulfated zirconia, though this catalyst shows lower catalytic activity than the previously mentioned ones. Nevertheless, some immobilization strategies, like the use of high-surface silicas as supports, can be used in order to achieve better specific catalytic activities. Table 2 summarizes the main results reported in biodiesel production through the esterification of free fatty acids with short chain alcohols using heterogeneous solid-acid catalysts.

3. Biodiesel production through transesterification of triglycerides

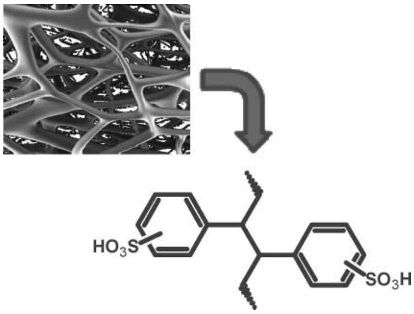
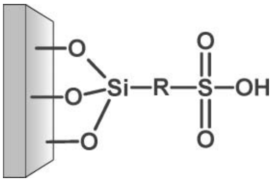
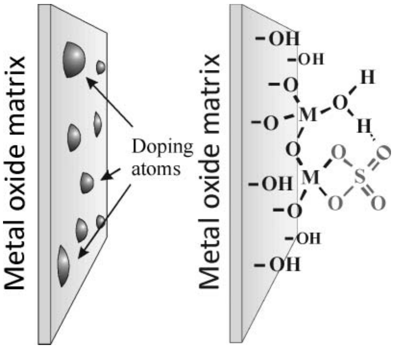
Since esterification and transesterification reactions share a common molecular mechanism, acid catalysts showing activity in the former usually drive the latter. In fact, even the free fatty acid in oils are able to catalyze not only their esterification with short chain alcohols but also the transesterification of the accompanying triglycerides.[51] Thus, most of the acid catalysts presented above have also been reported to be used for biodiesel production in transesterification of vegetable oils with short chain alcohols. In this way, if the alkaline catalysts for the transesterification stage are changed by acid catalysts, the initial stage for FFAs removal from feedstock vegetable oil is not needed anymore, reducing the complexity of the biodiesel production process. However, it must be noted that these acid catalysts are known to show a much lower catalytic activity in transesterification reactions, compared with alkaline catalysts, and this lack of activity is usually compensated by operating at higher temperatures. Nevertheless, several recent studies have proved the technical feasibility and the environmental and economical benefits of biodiesel production *via* heterogeneous acid-catalyzed transesterification.[13,52] As in the case of the catalysts for esterification of FFA, most of the reported acid catalysts can be classified in two main groups: inorganic and organically-functionalized catalysts.

3.1. Transesterification of triglycerides with inorganic acid catalysts

Inorganic catalysts for transesterification of vegetable oils with short chain alcohols reported up to now comprise sulfated and mixed metal oxides and supported polyanions as well as other less reported acid catalysts such as zeolites, heterogenized metal cyanides and many others.

Sulfated metal oxides show superacid properties powered by the interaction between sulfate groups and the metal oxide centres. These catalysts are known to show both Brønsted and Lewis acid sites. The good performance in esterification reactions, as well as in several transesterification assays carried out on short chain esters, has prompted authors to study the catalytic activity of these materials also in the transesterification of triglyceride-containing feedstocks for biodiesel production. Thus, several authors have reported a large variety of investigations on the use of sulfated zirconia in the transesterification of different

Table 2 Heterogeneous acid catalysts used in the esterification of free fatty acids, FFAs, with short chain alcohols for biodiesel production

Acid catalyst	Catalyst features	Reaction conditions[a]	FFA conversion	Ref.	Comments
Ion exchange resins. Styrene-divinyl benzene. 	Relite CFS 3.6 meq H^+ g^{-1}	Oleic acid (50 wt%) + soybean oil + methanol. MR = 10.7. *t* = 3 h. *T* = 85 °C. Cat = 2.5 wt%	85%	[25]	Powdered catalyst
	Purolite CT-275 5.2 meq H^+ g^{-1}	Vegetable high acid oil (38.1 wt%) + methanol. MR = 6.6. *t* = 3 h. *T* = 90°C. Cat = 2 wt%	76%	[28]	
	Dowex monosphere 88 4.5 meq H^+ g^{-1}	Enzymatically hydrolysed soybean oil (~100%) + methanol. MR = 10. *t* = 0.5 h. *T* = 60 °C. Cat = 3.6 wt%	57%	[29]	Used in bead form
	Amberlyst 15 4.7 meq H^+ g^{-1}	Palm Fatty Acid distillate (97 wt%) + methanol. MR = 20. *t* = 6 h. *T* = 60 °C. Cat = 30 wt%	>95%	[30]	
	EBD-100 5.4 meq H^+ g^{-1}	Stearic acid (10 wt%) + rapeseed oil + methanol. MR = 20. *t* = 6 h. *T* = 60°C. Cat = 1 wt%	>98%	[31]	Easily regenerated
	Amberlyst 15 4.7 meq H^+ g^{-1}	Dodecanoic acid + 2-ethyl hexanol. MR = 1. *t* = 2 h. *T* = 150 °C. Cat = 3 wt%	96%	[42]	
	Nafion-NR50 0.8 meq H^+ g^{-1}	Dodecanoic acid + 2-ethyl hexanol MR. = 1. *t* = 2 h. *T* = 150 °C. Cat= 3 wt%	74%		
	Poly(vinyl alcohol) sulfosuccinic acid	FFA in lard + methanol. MR = unknown. *t* = 90 h. *T* = 60 °C. Cat = 10 wt%	60%	[32]	Highly stable after first run
Sulfonated solids 	Sulfonated carbon 0.6 meq H^+ g^{-1}	Caprylic acid + methanol. MR = 2. *t* = 1 h. *T* = 60 °C. Cat = 2.5 wt%	~20%	[33]	Prepared from sugar/starch
	Sulfonated carbon 1.6 meq H^+ g^{-1}	Soybean oil fatty acids (70%) + methanol. MR = 10. *t* = 6 h. *T* = 60°C. Cat = 14 wt%	99.5%	[36]	Prepared from glycerol
	Sulfonated SBA-15 0.9 meq H^+ g^{-1}	Flotation beef tallow (7%) + methanol. MR = 20. *t* = 2 h. *T* = 120 °C. Cat = 10 wt%	>95%	[34]	Strong deactivation
	SAC-13 0.1 meq H^+ g^{-1}	Palmitic acid (10 wt%) + sunflower oil + methanol. MR = 30. *t* = 3 h. *T* = 60 °C. Cat = 40 wt%	43%	[45]	Highly stable
Metal oxides 	Tungstated zirconia 1.0 meq H^+ g^{-1}	Palmitic acid + methanol. MR = 200. *t* = 6 h. *T* = 60°C. Cat = 75 wt%	>95%	[41]	Tetragonal ZrO_2 and amorphous WO_3 is required
	Tungstated zirconia. Uknown acid loading	Oleic acid (4 wt%) + methanol (fixed bed). MR = 20. *T* = 75 °C. Residence time = 1 h	65%	[47]	
	Sulfated zirconia 1.2 meq H^+ g^{-1}	Dodecanoic acid + 2-ethyl hexanol. MR = 1. *t* = 2 h. *T* = 150 °C. Cat = 3 wt%	88%	[42]	
	Sulfated zirconia 0.7 meq H^+ g^{-1}	Dodecanoic acid + 2-ethyl hexanol. MR = 5. *t* = 2 h. *T* = 160 °C. Cat = 3 wt%	68%	[43]	No data about deactivation behavior
		Dodecanoic acid + 2-ethyl hexanol. MR = 3. *t* = 2 h. *T* = 140 °C. Cat = 3 wt%	84%	[44]	
	Sulfated zirconia 0.6 meq H^+ g^{-1}	Palmitic acid + methanol. MR = 30. *t* = 25 min. *T* = 60 °C. Cat = 40 wt%	~90%	[45]	Sulfur leaching – deactivation
	Sulfated zirconia on SBA-15 1.3 meq H^+ g^{-1}	Palmitic acid + methanol. MR = 80. *t* = 6 h. *T* = 68 °C. Cat = 2 wt%	89.2%	[46]	No data about deactivation behavior
		Lauric acid + methanol. MR = 62.5. *t* = 6 h. *T* = 68 °C. Cat = 2 wt%	87.4%		
Suported heteropolyacids	Cs-heteropolyacid	Oleic acid (4 wt%) + methanol. MR = unknown. *t* = 1 h. *T* = 60 °C. Cat = 25 wt%	75%	[47]	
	$H_3PW_{12}O_{40}/Ta_2O_5$	Lauric acid + ethanol. MR= 3. *t* = 3 h. *T* = 78 °C. Cat = 3 wt%	70%	[48]	

[a] MR = Molar ratio methanol to FFA. *t* = Reaction time. *T* = Reaction temperature. Cat = Catalyst loading referred to FFA.

vegetable oils, containing variable amounts of free fatty acids, with short chain alcohols.[53–57]

Kitiyanan *et al.*[53] reported the use of sulfated zirconia and stannia in the transesterification of crude palm kernel and coconut oils with methanol. These catalysts displayed catalytic activity in this reaction at 200 °C but also deactivation after the first run, a fact which was ascribed to both sulfate leaching and catalytic sites poisoning, but no indications about poisons were reported. Schuchardt *et al.*[54] who reported a novel preparation method, consisting on the calcination of a fine grounded mixture of $ZrOCl_2{\cdot}8H_2O$ and $(NH_4)_2SO_4$, proved that the preparation method displays a dramatic effect on the catalytic activity of these materials. Whereas conventional sulfated zirconia (SZ) displays a very low catalytic activity for the methanolysis of soybean oil, the novel material led to very high conversions of soybean oil even though no crystalline phases were detected by XRD—the tetragonal phase has been ascribed to be essential to achieve high acidity on this kind of material. Nevertheless, though no crystalline phases were detected, small crystallites could be present, which is consistent with the high surface area value achieved for this material. The high catalytic activity found for this sulfated zirconia-based material—99.8% substrate conversion after reacting for only one hour using methanol to oil molar ratio of 20, 150 °C and 5 wt% of catalyst—was attributed to a much higher concentration of acid sites and higher surface area compared to conventional SZ. However, recycling tests revealed activity decay, run after run, for the sulfated zirconia—59% substrate conversion in the first reutilization run and 30% in the second—which was ascribed to a continuous leaching of sulfate groups into the reaction mixture. The same conclusion was extracted from the studies carried out by Goodwin *et al.*[55] when using similar materials in the transesterification of tricaprylin with ethanol—used as a model substrate for transesterification of vegetable oils. These authors used commercial sulfated zirconia and compared it with other superacid catalysts, such as tungstated zirconia and titania-zirconia mixed oxides. All the samples displayed catalytic activity in the transesterification reaction, though sulfated zirconia exerts a much larger catalytic effect than that achieved with the rest of catalysts. In contrast with the results achieved by these authors, Xiao and co-workers[57] have recently reported very high stability of sulfate groups supported onto the surface of crystalline zirconia. In a similar study to those discussed already, these authors used sulfated zirconia as catalysts for the transesterification of waste cooking oil, yellow grease, with methanol. The analysis of the remaining sulfur content onto the used catalysts evidenced negligible loss of catalytic sites and, on this basis, the authors concluded no leaching of sulfate groups occurred during the transformation of WCO into biodiesel. Nevertheless, Goodwing *et al.*[55,58] reported a method in which the leaching of sulfate groups was undoubtedly assessed; treating the sulfated zirconia with the short chain alcohol to be used in the transesterification reaction. The washing solution was titrated with bases, evidencing the presence of acid species which were able to catalyze both esterification and transesterification reactions in a similar way to that found for sulfuric acid. In fact, the same substrate conversion was obtained when transesterifying tricaprylin in presence of a fresh sulfated zirconia catalyst and when using the washing methanol solution in absence of the zirconia-based material. This result evidenced the truly homogeneous nature of the catalytic activity of sulfated zirconia in transesterification reactions, since the active sites easily leach in alcoholic solutions.

Another superacidic sulfated metal oxide used in transesterification of vegetable oils is sulfated titania. Though less active than sulfated zirconia in transesterification of vegetable oils,[59] its activity can be increased when increasing the surface area of the catalyst in a similar way to that previously described for zirconia.[46] Another example of this surface extension is the silica-supported sulfated titania reported by Wang *et al.*[60] This catalyst has been prepared by impregnation of silica with titanium isopropoxide and consequent calcination, followed by impregnation with sulfuric acid and re-calcination. The so-prepared material displayed improved textural properties compared with conventional sulfated titania. This material was used in the simultaneous esterification and transesterification of an oleic acid-refined cotton seed oil mixture with methanol. Several operation variables were studied, such as the FFA content, the reaction temperature, the catalyst concentration and the methanol to oil molar ratio. In every case, high catalytic activity was achieved and, under the optimized reaction conditions—50 wt% FFA, 200 °C, 3 wt% catalyst loading and 9 : 1 methanol to oil—a yield over 90% of methyl esters was achieved. With regards to the stability of the catalyst, up to four consecutive reutilization runs were carried out, finding very small catalytic activity decay, though no analyses of reaction media or catalyst were performed for leached sulfate groups. Nevertheless, the satisfactory recycling tests reveal a higher stability of this sulfated catalyst with regards to sulfated zirconia. Several possibilities can be ascribed to this difference, such as the stronger interaction between titania and the sulfate groups, or the presence of silica as stabilizating agent. Bearing in mind the high stability of the catalyst, the authors applied the same to a continuous biodiesel production plant—10 000 tons per year capacity—comprising three serial catalytic reactors, a gas–liquid separator, and two consecutive distillation columns for methanol removal and biodiesel purification, respectively. The obtained biodiesel showed properties consistent with the ASTM D 6751–02 and DIN EN 14214 standards, though no data about catalyst life under the operation conditions was given.

Taking into account the low stability of sulfated metal oxides in alcoholic solutions, some authors have reported the use of different non-sulfated superacid materials. This is the case of tungstated zirconia, which has recently attracted much attention due to its high stability and acid properties. Goodwin *et al.* have reported several studies on the catalytic activity of these materials in the transesterification of several feedstocks like triacetin[61] or tricaprylin[55,56]—used as model compounds. Several variables on the preparation of tungstated catalysts were studied. Thus, calcination temperature not only affects the amount of crystalline phases on the material but also to the amount of accessible tungstenium sites and thus to the final acidity of the catalyst. The optimal calcination temperature was determined to be 800 °C, which resulted in the most acidic catalyst with the higher catalytic activity in the transesterification of triacetin with methanol. These authors proved that the presence of tungstenium species helped to stabilize the tetragonal phase of zirconia, since no transition between tetragonal and monoclinic phases was detected even at such a high temperature as 900 °C. Also, through the use of a selective Brønsted acid sites poison, 2,6-di-*tert*-butylpyridine, the authors extracted an interesting conclusion, only the Brønsted acid sites present in the material were really responsible for the transesterification catalytic activity of the material, with the Lewis-type acid centres having just marginal activity. This result is rather interesting, since several Lewis acid-type catalysts have proved to be highly active in transesterification reactions, though when using different metal species such as Zn, Fe or Mo.[62–64] Nevertheless, the comparison of tungstated zirconia-based catalysts with sulfated zirconia and mixed titania-zirconia oxides revealed a much lower catalytic activity for the metal oxides mixtures than sulfated zirconia—less than 20% of the yield of SZ towards methyl caprylate was achieved for the mixtures. In contrast, these mixtures of oxides were easily regenerated by air calcination after reaction, entirely recovering the initial catalytic activity, even after four consecutive recycling runs, indicating that the catalytic activity decay in this case is caused by acid sites coverage rather than by leaching of catalytic species.[56] This good performance of mixed metal oxides as transesterification catalysts has allowed their application to a continuous flow operation mode. Thus, Furuta *et al.*[65,66] have reported several works focused on the study of the catalytic performance of different metal oxide mixtures in the catalytic transesterification of soybean oil in a fixed bed reactor. The comparison between Al-doped tungstated zirconia and sulfated zirconia and stannia[65] reported interesting results, since the former appeared as the most active catalyst among the three of them. This result indicated that the interaction of aluminium centres with tungstenium and zirconium species boosts the catalytic activity of these materials. Also, this catalyst displayed a very good stability, being slightly deactivated for long reaction time on stream. The same authors have reported similar catalytic studies for titania–zirconia and alumina–zirconia mixed oxides,[66] finding catalytic activities as high as over tungstated zirconia. In fact, all these materials were compared with zirconia-based catalysts impregnated with potassium hydroxide—a basic catalyst—but this one, though highly active, was easily deactivated because of leaching of potassium species, evidencing the great advantages of using mixed metal oxides-based catalysts.

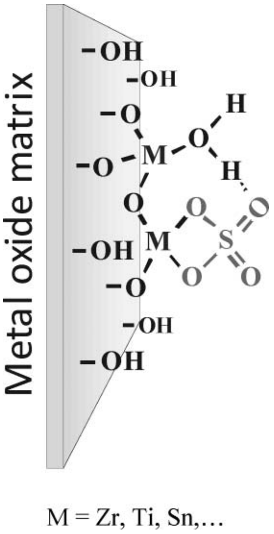
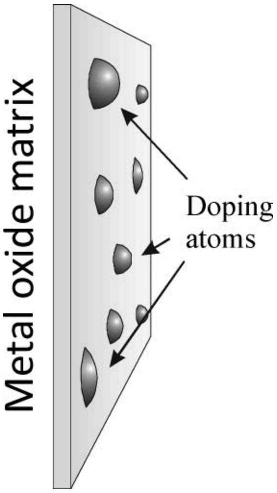
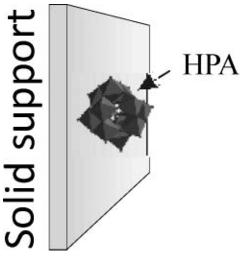
Another important group of strongly acid heterogeneous catalysts used in biodiesel production through transesterification of triglycerides is that formed by supported heteropolyacids. Though lower than that found for sulfated metal oxides or mixed oxides, these polyanions show high acidity and thus they have been widely used in many different types of catalytic applications. One of those applications is the production of biodiesel[67–70] through esterification and transesterification of triglycerides. Dalai *et al.*[67] reported the immobilization of Keggin-type heteropolyacids (HPA) on different supports such as hydrous zirconia, silica, alumina and activated carbon. All these materials displayed high catalytic activity in the transesterification of canola oil containing 10% of FFA, though the catalyst prepared from the hydrous zirconia support led to the best catalytic performance. This catalyst was selected for a deeper study in which several operation variables were investigated. Thus, it was concluded that the catalytic activity is highly dependent on the reaction temperature, but less sensitive to the oil to methanol molar ratio or the FFA content, in contrast with other acid catalysts. Reutilization runs revealed a very high stability of the HPA polyanion supported on the hydrous zirconia but no results relative to deactivation of the acid sites by water adsorption were given.

Wang and co-workers[68,69] have also reported different studies on the catalytic activity of several solid heteropolyacids in the transesterification of both crude and waste oils. These HPAs showed similar catalytic activity to that found for sulfuric acid and optimal reaction temperature conditions were as low as 65 °C. In contrast, these catalysts were easily deactivated in the presence of small quantities of water—1 wt% of water in the feedstock was enough to reduce the catalytic activity to negligible values. This result explains the activity decay found for the catalysts in consecutive recycling runs when FFAs were present in the feedstock, since their esterification produces water molecules which act as a poison for the catalyst.

More recently, Clark *et al.*[70] have reported another catalyst based on tungstenium Keggin-type heteropolyacid supported on mesostructured tantalum oxide. Ta_2O_5 was selected as solid support because of the strong affinity between tantalum and tungstenium, reducing the possibilities of active species leaching. Besides, tantalum oxide shows acid properties which can also play an important role in the transesterification reaction. This catalyst showed moderate catalytic activity in the transesterification of tripalmitin both in the absence and presence of FFA, and it was easily poisoned by adsorption of different species over the acid sites, though it was also easily regenerated by washing. In this context, Guo *et al.*[71] took a step forward in the development of these catalysts, reporting the synthesis of similar catalysts, though instead of pure tantalum pentoxide, a mixture of Ta_2O_5 and SiO_2 was employed as solid support for the immobilization of $H_3PW_{12}O_{40}$ (tungstophosphoric acid, TPA), through the preparation of hybrid organic inorganic materials. In this work, the functionalization of tantalum oxide-silica supported TPA with organic groups is described. In this way, the hydrophobic/hydrophilic balance can be tuned to enhance the catalytic activity and reusability of the catalyst. These materials displayed good catalytic activity in the simultaneous esterification/transesterification of FFA-containing soybean oil. Improved catalytic stability in consecutive recycling catalytic tests was observed for the hydrophobized catalyts when compared with the materials reported by Clark,[70] because the adsorption of polar compounds is reduced limiting the deactivation phenomena.

From the above presented works it can be concluded that there is a whole library of different acid catalysts which can effectively be used for transesterification of triglycerides. Table 3 lists the main advances reported on this matter dealing with purely inorganic acid catalytsts useful for biodiesel production from triglyceride-containing raw materials. Among the most cited materials, sulfated metal oxides, though highly active, have been revealed to be poorly resistant to hydrolysis and alcoholysis of sulfate groups, which causes the irreversible deactivation of these materials. In contrast, different metal oxide mixtures showing superacid properties can be used as alternative catalysts. These materials show, most of the time and under most reaction conditions, lower catalytic activity than their sulfated analogues. Nevertheless, these catalysts are highly stable against poisoning or deactivation and, if this occurs, easy to regenerate

Table 3 Main examples on the use of heterogeneous inorganic acid catalysts in biodiesel production

Inorganic acid catalysts		Preparation method	Reaction conditions[a]	Yield towards FAAE	Ref.	Comments
Sulfated metal oxides; M = Zr, Ti, Sn,... 	Sulfated zirconia	$ZrO_2 + H_2SO_4$.	Crude palm kernel oil (FFA= 1.05%) and methanol. MR= 6. $t = 2$ h. $T = 200$ °C. Cat = 3 wt%	96 wt%	[53]	Strong deactivation
			Coconut oil (FFA= 2.25%) and methanol. MR = 6. $t = 2$ h. $T = 200$°C. Cat = 3 wt.%	88 wt%		
		$ZrOCl_2{\cdot}8H_2O$ + $(NH_4)_2SO_4$.	Soybean oil (FFA= 0.09 wt.%) and methanol. MR= 20. $t = 2$ h. $T = 150$ °C. Cat = 5 wt%	>99 mol%	[54]	Sulfate leaching
		Commercial catalyst	Tricaprylin and ethanol. MR = 6. $t = 8$ h. $T = 75$°C. Cat = 5 wt.%	10 mol%	[55]	
			Tricaprylin and methanol. MR = 12. $t = 2$ h. $T = 120$ °C. Cat = 5 wt%	84 wt%	[58]	
			Tricaprylin and ethanol. MR = 12. $t = 2$ h. $T = 120$°C. Cat = 5 wt%	45 wt%		
			Tricaprylin and butanol. MR= 12. $t = 2$ h. $T = 120$ °C. Cat = 5 wt%	37 wt%		
		Zirconium hydroxide + H_2SO_4.	Waste cooking oil and methanol. MR = 9. $t = 3$ h. $T = 120$ °C. Cat = 3 wt%	94 wt%	[57]	Apparently stable
	Sulfated titania	$Ti(OiPr)_4$ + $H_2SO_4 + HNO_3$ + iPrOH.	Soybean oil and methanol. MR = 6. $t = 1$ h. $T = 120$ °C. Cat = 1 mol%	40 wt%	[59]	No recycling tests carried out
			Castor oil and methanol. MR = 6. $t = 1$ h. $T = 120$°C. Cat = 1 mol%	25 wt%		
		$SiO_2 + Ti(OiPr)_4$ + H_2SO_4.	Oleic acid + refined cotton seed oil and methanol. MR = 9. $t = 6$ h. $T = 200$ °C. Cat = 3 wt%	88 wt%	[60]	Highly stable
	Sulfated stannia	Meta stannic acid + H_2SO_4.	Soybean oil and methanol (fixed bed). MR = 40. $T = 200$ °C. Flux = 0.75 g oil g^{-1} cat h^{-1}	10 wt%	[65]	
Mixed metal oxides 	Tungstated zirconia	Commercial catalyst	Tricaprylin and ethanol. MR = 12. $t = 8$ h. $T = 120$°C. Cat = 5 wt%	22 wt%	[55]	Highly stable
		Hydrated zirconia + $(NH_4)_6H_2W_{12}O_{40}$.	Soybean oil and methanol (fixed bed). MR = 40. $T = 200$ °C. Flux = 0.75 g oil g^{-1} cat h^{-1}	>90 wt%	[65]	Stable after 100 hours on stream
			Soybean oil and methanol (fixed bed). MR = 40. $T = 250$ °C. Flux = 0.75 g oil g^{-1} cat h^{-1}	>90 wt%	[66]	
		Hydrous zirconia + WO_3.	Waste cooking oil (FFA 15%) and methanol. MR = 6. $t = 10$ h. $T = 200$ °C. Cat = 3 wt%	67 wt%	[63]	Highly stable
	Zirconia MoO_3	Hydrous zirconia + MoO_3.	Waste cooking oil (FFA 15%) and methanol. MR = 6. $t = 10$ h. $T = 200$ °C. Cat = 3 wt%	71 wt%		
	Zirconia titania	Commercial catalyst	Soybean oil and methanol (fixed bed). MR = 40. $T = 250$ °C. Flux = 0.75 g oil g^{-1} cat h^{-1}	>95 wt%	[66]	Stable after 100 hours on stream
	Zirconia alumina	Commercial catalyst	Soybean oil and methanol (fixed bed). MR = 40. $T = 250$ °C. Flux = 0.75 g oil g^{-1} cat h^{-1}	>97 wt%		
Supported heteropolyacids 	TPA ($H_3PW_{12}O_{40}$)	$H_3PW_{12}O_{40}$ + hydrous ZrO_2	Canola oil (FFA 10%) and methanol. MR = 6. $t = 10$ h. $T = 200$ °C. Cat = 3 wt%	77 wt%	[67]	Highly stable. Good reusability
		$H_3PW_{12}O_{40}{\cdot}6H_2O$	Waste frying oil (FFA 15.65%) and methanol. MR = 70. $t = 14$ h. $T = 65$ °C. Cat = 1 wt%	87 wt%	[69]	Activity decay in recycling tests
		$H_3PW_{12}O_{40}$ + tantalum pentoxide	Soybean oil (FFA 20%) and methanol. MR = 90. $t = 24$ h. $T = 65$ °C. Cat = 1 wt%	75.8 wt%	[70]	Easily regenerated by washing and calcination
			Tripalmitin and methanol MR= 90. $t = 6$ h. $T = 65$°C. Cat = 2 wt%	51.4 wt%		
		$H_3PW_{12}O_{40}$ + Met/Ph + tantalum pentoxide	Soybean oil (myristic acid 20 wt%) and methanol MR = 90. $t = 24$ h. $T = 65$ °C. Cat = 2 wt%	~80 wt%	[71]	Stable after six recycling runs
	HPA	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	Eruca sativa oil (FFA 3.65%) and methanol. MR = 5.3. $t = 1$ h. $T = 65$ °C. Cat = 2 wt%	>96 wt%	[68]	

[a] MR = Molar ratio methanol to oil. t = Reaction time. T = Reaction temperature. Cat = Catalyst loading.

through a simple calcination step. In the same sense, supported heteropolyacids are also an alternative to previously described catalysts, but still some efforts have to be focused on their development since they are easily deactivated in presence of small quantities of water.

3.2. Transesterification of triglycerides with organically-functionalized acid catalysts

The use of sulfonic acid-based heterogeneous catalysts has also been proposed as an alternative in the transesterification of vegetable oils. The objective is to overcome several troubles related to leaching of the active species, thermal stability and low surface area, that might occur when using other heterogeneous acid catalysts such as sulfated metal oxides, zeolites, or heteropolyacids. The activity of this family of catalysts is based on the presence of sulfonic acid sites, which can be considered as the heterogeneous counterpart of sulfuric acid. Indeed, sulfuric acid has been previously evaluated and optimized as a homogeneous catalyst in the synthesis of biodiesel,[72,73] leading to high conversions using a variety of sources of triglycerides. Alcohols used in the sulfuric acid-catalyzed transesterification have included methanol, ethanol, propanol, butanol and amyl alcohol, and most of the authors conclude that the process achieves greater and faster conversions at high alcohol concentrations. Recently, Wahlen *et al.*[74] have studied the synthesis of biodiesel from mixed feedstocks, which include significant quantities of free fatty acids, and longer chain alcohols such as *n*-butanol using a sulfuric acid-catalyzed method. They utilized a microwave-heated reaction to accelerate the reaction with a sulfuric acid loading of 3% (w/w) relative to oil, where biodiesel yields greater than 98% were achieved in less than 40 minutes. Key properties of the resulting butyl-diesel were determined, showing comparable cetane and viscosity values to the corresponding methyl esters, but significantly improving the pour point, thus making the butyl esters better choices for cold weather locations.

In view of the excellent performance of the sulfuric acid in the acid-catalysed transesterification reaction, some attempts have been made on its heterogenisation to overcome the traditional drawbacks of homogeneous catalytic systems, such as equipment corrosion and difficult separation from the products. Furthermore, acid-contaminated glycerol has little value in today's market and is increasingly becoming a disposal issue.[75] On the other hand, the use of heterogeneous acid catalysts will most likely experience a longer time, a higher reaction temperature, and a higher methanol/oil molar ratio compared with the homogeneous-catalyzed reaction because of the obvious mass and heat transfer hindrances. All these issues must be dealt with for an adequate sulfuric acid heterogeneous counterpart to be found.

One of the approaches followed in this line is the direct impregnation of sulfuric acid over wooden activated carbon, reaching H_2SO_4 loadings that range from 40 to 60 wt%.[76] With castor oil and methanol as the feedstock, Yuan *et al.* used a microwave radiation-assisted reactor that exhibits a notable enhanced effect for transesterification compared with conventional heating methods, thus partially palliating the detrimental properties of heterogeneous systems. In this way, at a temperature of 338 K, with a 12 : 1 molar ratio of methanol to castor oil, 50 wt% loading of H_2SO_4 on activated carbon, and 5 wt% of catalyst relative to oil, after only 60 minutes the yield to FAME was 94%, compared to only 70% after 180 min using conventional heating.

Likewise, given the variety of sulfonic acid ionic-exchange resins commonly used as heterogeneous acid catalysts and their good performance in FFAs esterification, it is not surprising that several attempts have also been made to prepare biodiesel through transesterification with such polymeric catalysts. For example, de Rezende *et al.*[77,78] have prepared different polymer supports based on styrene and divinylbenzene which were conveniently functionalised with sulfonic acid moieties through a sulfonation process with H_2SO_4 to perform the transesterification of soybean and coconut oils with methanol. Similar materials were reported by César-Oliverira *et al.* though in this case starting from linear polystyrene and using a similar sulfonation procedure.[79] These authors have compared the activity of these synthesised sulfonic resins with that of commercial references such as Amberlyst-15 and Amberlyst-35. De Rezende, reported that in order to obtain an appropriate triglyceride conversion at the low temperature achieved under methanol reflux (approximately 65 °C) it is necessary to use high methanol to oil ratios—from 50 : 1 to 300 : 1—and high catalyst loadings—between 50 and 25% w/w relative to oil. Under these conditions, the obtained yield to FAME reaches a maximum value over 90% using a sulfonated poly(DVB) ion-exchange resin that presented a surface area of 442 m^2 g^{-1} and an acid capacity of 3.4 meq_{H^+} g^{-1} (see Table 4). Higher divinylbenzene contents in the prepared resins produce an increased porosity that leads to higher yields to methyl esters. In contrast, the swelling behaviour of the resin is reduced, but probably the high concentration of methanol used in the transesterification step does not allow the swelling properties of the resin to exert its influence on the catalytic activity.

Alcohol-based resins such as poly(vinyl alcohol) polymer cross-linked with sulfosuccinic acid have also been evaluated as acid catalyst for the transesterification of soybean oil with methanol at 60 °C and atmospheric pressure.[80] In this case, the authors carried out the reactions using the catalyst as pellets and as a membrane in a membrane reactor. The concentration profiles of methyl esters observed with these catalysts in the form of pellets showed a pronounced initial induction period. When the experiments were carried out in a membrane reactor this behavior was not observed. The authors proposed that this feature suggests that glycerol is successfully removed from the reaction mixture and is not accumulated in the membrane. In the same work, commercial resins and/or membranes such as Nafion—perfluorinated-based ion-exchange resins—and Dowex 50 × 2 and 50 × 4 were benchmarked, leading to lower activities than the poly(vinyl alcohol) polymers. This fact was attributed to its higher swelling properties. To better understand solid acid catalyst performance, a fundamental transesterification kinetic study was carried out using triacetin, the simplest triglyceride, and methanol on Nafion catalysts. In particular, López *et al.*[81] investigated the kinetics of Nafion SAC-13-silica-supported Nafion and Nafion NR50-unsupported Nafion, in comparison with the kinetics of H_2SO_4. The initial reaction rate was found to be greatly affected by the extent of swelling of the resin, where a greater effect was observed for Nafion NR50 than for the

Table 4 Main examples on the use of heterogeneous organically-functionalized acid catalysts in transesterification reactions

Sulfonic acid-based catalysts	Material and preparation method	Examples of reaction conditions [a]	Yield towards FAAE	Ref.	Comments
Sulfonated activated-carbons	Wooden activated carbon impregnated in aq. H_2SO_4. 40–60 wt% final loading of H_2SO_4	Castor oil (acid value 2 mg KOH) + oleic acid and methanol/ethanol. MR = 12. Microwave radiation. t = 60 min. Cat = 5 wt%	94%	[76]	High reaction rate. No recycling tests reported.
	Sulfonation of incompletely carbonized carbohydrates (starch, cellulose, D-glucose and sucrose) with H_2SO_4 >96%	Waste cooking oil (FFA = 27.8 wt%) and methanol. MR= 20. t = 8 h. T = 80 °C. Cat = 10 wt%	92%	[84]	Excellent operational stability
Sulfonic acid ionic-exchange resins	Poly(DVB) resin sulfonated with H_2SO_4 95–97% (1h at 90°C)	Babaçu coconut oil and methanol. MR = 150. t = 8 h. T = 65 °C (reflux). Cat = 25 wt%	99 mol%	[78]	Mild reaction conditions are necessary to avoid degradation of catalyst
		Soybean oil and methanol. MR= 300. t = 8 h. T= 65 °C (reflux). Cat = 50 wt%	97 mol%		
	Amberlyst-15 (Rohm & Haas)	Babaçu coconut oil and methanol. MR = 300. t = 8 h. T = 65 °C (reflux).	74 mol%		
		Soybean oil and methanol. MR = 150. t = 8 h. T = 65 °C (reflux). Cat = 25 wt%	56 mol%		
		Sunflower oil and methanol. MR = 6. T = 60 °C	0.7 mol%	[5]	
		Ethyl propionate and methanol. MR = 20. t = 6h. T = 60 °C. Cat = 1 wt%	21.6 mol%	[49]	
		Ethyl hexanoate and methanol. MR = 20. t = 6h. T = 60 °C. Cat = 1 wt%	7.8 mol%		
	Amberlyst-35 (Rohm & Haas)	Babaçu coconut oil and methanol. MR= 150. t = 8 h. T = 65 °C (reflux). Cat = 25 wt%	87 mol%	[78]	Mild reaction conditions are necessary to avoid degradation of catalyst
		Soybean oil and methanol. MR = 150. t = 8 h. T = 65 °C (reflux). Cat = 25 wt%	30 mol%		
	Nafion SAC-13 (Nafion-silica composite)	Triacetin and methanol. MR = 6. t = 2 h. T = 60 °C. Cat = 2 wt%	8%	[55]	No leaching of resin. Reusability checked for 3 cycles.
Sulfonic acid-modified mesostructured silica	Propyl-SO_3H-SBA-15 Surfactant-templated synthesis *via* co-condensation and in-situ oxidation of thiol groups	Refined soybean oil and methanol. MR = 10. t = 8 h. T = 180 °C. Cat = 6 wt%	95.9 wt%	[87]	High activity and stability at high temperature. Slight decrease of activity in reutilization test.
		Crude soybean oil (FFA = 0.96) and methanol. MR = 10. t = 8 h. T = 180 °C. Cat = 6 wt%	93.1 wt%		
		Refined palm oil and methanol. MR = 10. t = 8 h. T = 180 °C. Cat = 6 wt%	95.4 wt%		
		Crude palm oil (FFA = 5.6 wt%) and methanol. MR = 10. t = 8 h. T = 180 °C. Cat = 6 wt%	98.4 wt%		

[a] MR = Molar ratio methanol to oil. t = Reaction time. T = Reaction temperature. Cat = Catalyst loading.

highly dispersed Nafion SAC-13. Both the reaction orders for triacetin and methanol and the apparent activation energy for the conversion of triacetin to diacetin were comparable to those of sulfuric acid. These results suggest that the reaction catalyzed by the ion-exchange resin can be considered to follow a similar mechanism to that of the homogeneous catalyzed one, where the reaction of protonated triglyceride (on the catalyst surface) with methanol is the rate-limiting step. When considering larger triglycerides, such as those in profitable feedstocks for biodiesel production, a decrease in reaction rate is expected, but the reaction rates of small triglycerides are directly related to those of much larger triglycerides.

Recently, a new strategy for preparing novel sulfonic acid carbon-based solids has been developed by Hara's research group:[82] sulfonation of incompletely carbonized carbohydrates such as starch, cellulose, D-glucose and sucrose. The incomplete carbonization of the carbohydrates leads to a rigid carbon material consisting of small polycyclic aromatic carbon sheets in a 3D sp^3-bonded structure. Sulfonation of such carbon material has been demonstrated to afford a highly stable and physically robust solid with a high density of active sulfonic sites. Among other uses, such carbohydrate-derived acid catalysts have been successfully applied to biodiesel production from higher fatty acids and especially waste oils with high acid values by simultaneous esterification and transesterification reactions.[83,84] Variables such as starting material, carbonization temperature and time, and sulfonation temperature and time for catalyst preparation all had significant impact on the catalytic and textural properties of the prepared solid acids. In this way, using WCO with an acid value of 27.8 wt% FFAs, under the optimized reaction conditions, that is, temperature, 80 °C, methanol to oil molar ratio, 20 : 1, catalyst loading, 10 wt% relative to oil, and over the most effective starch-derived sulfonic acid catalyst, a methyl ester yield of about 92% after 8 h was obtained. Furthermore, the starch-derived solid acid manifested a very excellent operational stability. The same authors have adopted a new strategy for the preparation of carbon/SBA-15 high-surface area composites bearing sulfonic acid groups through the sulfonation of amorphous carbon deposited in the mesopores of the SBA-15 material.[85] Under different carbon loadings, they synthesized composite materials with BET surface areas ranging from 700 to 1000 m^2 g^{-1} and SO_3H densities from 0.1 to 0.4 mmol g^{-1}. Although these materials have not been assessed in transesterification reactions to yield biodiesel, the enhancement of surface area and the hydrophobic character of the silica SBA-15 support might have a significant relevance in this particular type of reaction. A further alternative in the context of sulfonic acid-based heterogeneous catalysts is the incorporation of organosulfonic groups over mesostructured silicas, which have led to effective solid acid catalysts with enhanced catalytic properties as compared with conventional homogeneous and heterogeneous acid catalysts.[86] These materials, featured by large uniform pores, high thermal stability due to its silica support and the possibility to control their hydrophobicity and concentration of acid sites through organic functionalization, apparently pool the ideal properties for an acid solid catalyst to be employed in transesterification for the production of biodiesel.[5] Melero *et al.*[87] have recently reported the transesterification of refined and crude vegetable oils over a propyl-sulfonic acid-modified mesostructured SBA-15 silica catalyst. This catalyst produced a FAME purity over 95 wt% for oil conversions close to 100% under the best reaction conditions selected by an experimental design methodology (temperature, 180 °C, methanol to oil molar ratio, 10, and catalyst loading 6 wt% referred to oil). Interestingly, high methanol concentrations led to a detrimental effect on the catalyst activity in the range of studied reaction parameters. Regardless of the presence of free fatty acids, the propyl-SO_3H-modified mesostructured silica catalyst showed high activities towards the simultaneous esterification of FFAs and transesterification of triglycerides. This was demonstrated by the use of crude palm oil containing 5.6 wt% FFAs as substrate, where a biodiesel with purity in FAMEs as high as 98.4% was obtained. In this way, these sulfonated mesostructured materials are shown as promising catalysts for the acid-catalyzed preparation of biodiesel, but some aspects related to the tuning of the adsorption properties, *i.e.* hydrophobicity of the silica surface, and the enhancement of the catalyst's reusability need to be addressed in future work. Also, less harsh reaction conditions must be optimized in order to make the process costly-effective and improve the catalyst operational stability.

Although not strictly a heterogeneous sulfonic acid-based approach, it is interesting to mention also the use of sulfonic-based Brønsted acidic ionic liquids.[88] The group of Wu has performed the transesterification of cottonseed oil with methanol to biodiesel with various acidic ionic liquids with an alkane SO_3H group. The interest on these ionic liquids lays on their catalytic activity which is near that of concentrated sulfuric acid, and contrary to H_2SO_4 they are presented as environmentally friendly catalysts that posses negligible vapour pressure, excellent chemical and thermal stability, potential recoverability and ease of separation.[89] Among all the ionic liquids evaluated for transesterification of oil, 1-(4-sulfonic acid) butylpyridinium hydrogen sulfate exhibited the best catalytic performance, which is ascribed to its strong Brønsted acidity. Using this ionic liquid-based catalyst, a high yield of fatty acid methyl esters of 92% was obtained after 5 h at 180 °C with a methanol to oil molar ratio of 12 : 1.

In summary, organically-functionalized heterogeneous acid catalysts are highly active for transesterification of triglycerides, showing catalytic performances even superior to those displayed by the above-discussed heterogeneous inorganic acid catalysts. Table 4 lists the main results described within the articles previously presented. The enhanced activity of these sulfonic acid-functionalized materials allows milder reaction conditions to be used while maintaining an appropriate reaction rate for transesterification process. On the other hand, when poisoned or deactivated, they are more difficult to regenerate due to their organic nature, which makes the use of thermal treatments such as calcination impossible. Thus, still important research efforts must be done in their stabilization and regeneration.

4. Acid-catalyzed transformation of glycerol mediated by heterogeneous catalysts

Glycerol is the major co-product in the production of biodiesel through transesterification of glycerides (oils and fats); its production estimated as equivalent to approximately 10 wt% of the total biodiesel production. Therefore, considering the expected growth of biodiesel market in the near future, the accompanying increase in glycerol production will shortly create a glut which most likely will dramatically reduce glycerol market prices. Currently, glycerol has over two thousand different applications in as distinct fields as cosmetics, pharmaceuticals, food and drinks, tobacco, paper, inks and printing, production of resins (phtalic and maleic alkyl resins) and cross-linked polyesters, and as a hydraulic agent. Likewise, polyglycerols have a wide range of applications as emulsifiers, and technical esters of glycerol with fatty acids are used as synthetic lubricants.[90] In this scene, world-wide demand for glycerol was approximately 0.2 Mt in 2007, and is forecasted to grow by 2.2% per year, driven mainly by personal care and food industries.[91] However, if the objectives of the European Union directives for either 2010 or 2020 are achieved, the production of glycerol will result in 1 Mt.[92] The above-mentioned traditional markets for glycerol will not be able to absorb such a production of glycerol, leading to large surplus thereof. To date glycerol is too expensive to be used as a fuel but, as the biodiesel production increases, its availability could exceed the demand for traditional use and hence its price will decrease making it a cost-effective raw material for the preparation of fuels. The price of glycerol has already fallen by more than 50% over the past ten years.[91,93] In this context, an extensive research effort is currently being applied by the scientific community in order to find new applications for such expected low-cost feedstock. An interesting option being explored is the conversion of glycerol into fuel which, due to its biomass origin, could be referred to as biofuel. This approach is a promising and economically viable alternative since not only makes a good use of the glycerol by-product but also increases the yield to biofuel in the overall biodiesel production process.

On the other hand, due to its low solubility in hydrocarbons, glycerol cannot be blended directly to fuels. Furthermore, it presents high viscosity, and decomposition, polymerization and consequential engine problems can be expected at engine-operating temperatures. Although glycerol can be directly burnt as heating fuel,[94,95] it could be more advantageously processed into more valuable fuel components following different approaches.[16,96] Such strategies include selective oxidation, hydrogenolysis to obtain propylene glycol, dehydration to yield acrolein, fermentation towards 1,3-propanediol, synthesis of epichlorohydrin, or even reforming towards syngas.[16,97] Apart from these alternatives, the transformation of glycerol into liquid fuel additives using different heterogeneous acid catalysts has also been explored. Fig. 4 depicts a schematic diagram with the most interesting alternatives in this area, including the chemical transformation of glycerol with different organic reactants such as olefins, alcohols, carboxylic acids, esters, and ketones, with the purpose of manufacturing biodiesel additives.

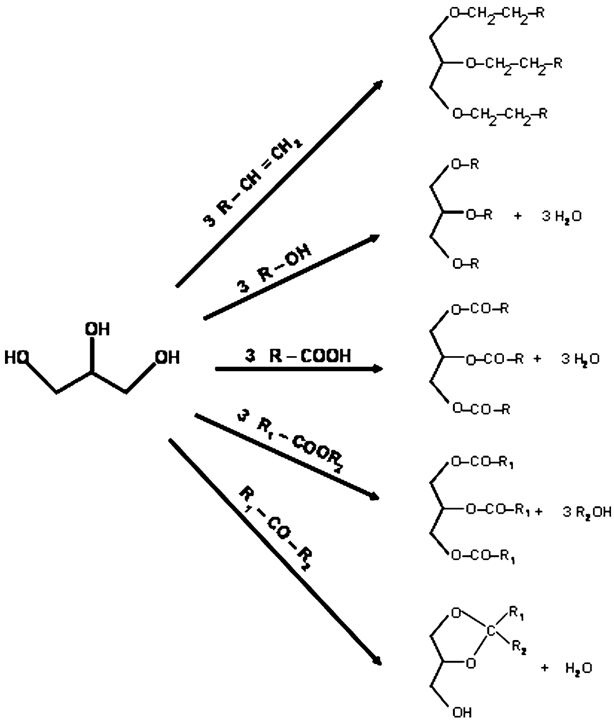


Fig. 4 Different pathways to obtain potential fuel additives from glycerol.

4.1. Ethers derived from glycerol

One alternative is to etherify glycerol with either alcohols or alkenes and produce branched oxygenated components, which could have suitable properties blended with liquid fuels. Special interest is focused on the preparation of alkyl ethers of glycerol by etherification with isobutylene. Isobutylene reacts with glycerol in the presence of acid catalysts to yield a mixture of mono-, di-, and tri-*tert*-butyl glycerol ethers (MTBG, DTBG, and TTBG, respectively)[98,99] (Fig. 5). Higher glycerol ethers—di- and tri-ethers—due to their solubility in diesel fuel could be similar to the current commercial oxygenate additives (MTBE, ETBE, TAME applied in gasoline)[100] used as oxygenates in diesel fuel, biodiesel or their mixture.[101–104] Di-*tert*-butylglycerols (DTBG) and tri-*tert*-butylglycerol (TTBG) have been shown to be valuable fuel additives leading to decreases in the emission of particulate matter, hydrocarbons, carbon monoxide and unregulated aldehydes in the exhaust gases.[101,105] In addition, said ethers can also act as cold flow improvers for use in biodiesel, reducing also its viscosity.[106,107] Octane numbers of 112–128 blending research octane number (BRON) and 91–99 blending motor octane number (BMON) have been reported for an ether product mixture.[108] These numbers are very suitable for gasoline components. The BRON was observed to be higher for mixtures where monoethers were the main product and lower for mixtures containing more substituted ethers. In contrast, mono-*tert*-butylglycerol (MTBG) has relatively high water solubility making it not suitable as a diesel-blending agent. Jamróz *et al.*[109] have recently published a complete characterization study of these *tert*-butyl ethers of glycerine by means of several spectroscopic techniques, *i.e.* MS, NMR, IR and Raman.

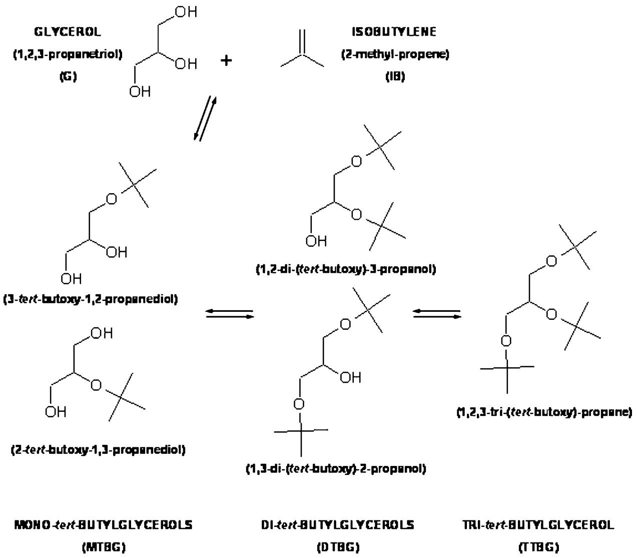


Fig. 5 Main reaction products in the glycerol etherification with isobutylene.

This reaction has been usually performed over sulfonic resins and homogeneous acid catalysts (mainly *p*-toluenesulfonic). Behr and Obendorf[110] studied homogeneous and heterogeneous catalysts for glycerol etherification. The best results among heterogeneous catalysts were achieved over commercial strong acid ion-exchange resin Amberlyst 15 and the best one from homogeneous catalysts was *p*-toluenesulfonic acid which was investigated more thoroughly. The authors studied the kinetics of *tert*-butylation of glycerol without solvent using the following conditions: 2 wt% *p*-toluenesulfonic acid, pressure 2 MPa, temperature in the range 70–90 °C, molar ratio isobutylene/glycerol = 1 : 1 and 2 : 1). Klepácočá *et al.*[111–113] extended this investigation by an intensive study of the catalytic activity and selectivity of ion-exchange resins of Amberlyst type—Amberlyst 15 and 35—and the large-pore zeolites—H-Y and H-Beta—on *tert*-butylation of glycerol with isobutylene. They studied the influence of the main reaction parameters; including the swelling of commercial macroreticular resins—Amberlyst 15, 35, 36 and 39—and resins with gel structure—Amberlyst 31 and 119. The authors carried out the reactions in the temperature range of 50–90 °C at autogenous pressure in the presence of different solvents (dioxane, dimethyl sulfoxide and sulfolane). The highest conversion of glycerol was reported for H-Beta zeolite, but the formation of the most-interesting TTBG was sterically hindered over this microporous catalyst. The highest amount of di- and tri-ethers was formed over Amberlyst 35. A comparative homogeneous catalytic system, *p*-toluenesulfonic acid, provided satisfactory results only when sulfolane was used as solvent. The authors claim an essential role of the solvent because it affects the homogenization of reaction mixture. A kinetic model for the whole complex system of involved etherification reactions has also been proposed.[113] However, authors reported that the side reaction of isobutylene dimerisation occurs over Amberlyst-type catalysts, especially at higher temperatures. The formation of di-isobutenes—C_8 alkenes—is undesired as it consumes olefin feedstock and produces by-products that could be problematic when blended into liquid fuels, as isobutylene oligomers could lead to the formation of undesirable deposits in the motor during the combustion. However, it must also be pointed out that if the glycerol ethers are to be used in gasoline, C_8 alkenes would be a very valuable gasoline component,[114] since the main formed C_8 isomers are 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene, which have high octane numbers—RON 100, MON 89. Karinen and Krause[115] also studied the effect of the reaction conditions on the etherification of glycerol with isobutylene in the liquid phase with an acidic ion-exchange resin (Amberlyst 35). In their work, conditions for optimal selectivity towards ethers were established to be isobutylene/glycerol molar ratio 3 and temperature 80 °C, finding the same C_8 alkenes as the main products in the side reaction of isobutylene oligomerisation.

Usually, low surface areas and lack of thermal stability are the major drawbacks of acid-based sulfonic resins, but the use of conventional homogeneous acid catalysts, such as the *p*-toluenesulfonic acid, must be avoided to comply with the increasingly strict environmental regulations. As discussed in previous sections of this review, the incorporation of organosulfonic groups over mesostructured silicas has generated effective solid acid catalysts,[86] which have been shown to also be suitable candidates for the present etherification reaction.[116] Melero *et al.* have analyzed the etherification of glycerol with isobutylene over different sulfonic acid-modified mesostructured silicas in comparison with sulfonic acid resins (Amberlyst- and Nafion-type). A multivariate analysis was used to assess the reaction conditions that yield the best catalytic results in terms of glycerol conversion (100% as determined by GC) and selectivity towards the di- and tri-derivatives (combined selectivity towards DTBG and TTBG up to 92%), while minimizing the formation of the mono-derivative compound (MTBG). Optimal conditions were established to be isobutylene/glycerol molar ratio 4/1 and temperature of 75 °C. Comparison with different commercial sulfonic resins—Amberlyst 15, Amberlyst 36, CT-275, and Nafion–silica composite SAC-13—evidenced the high activity and selectivity of this catalyst. Table 5 shows a summary including the most relevant results reported in this work for the *tert*-butylation of glycerol, as well as some data extracted and calculated from the literature for comparison purposes. Catalyst Ar-SO_3H-SBA-15 (arene–sulfonic acid-modified SBA-15 silica) gives the highest production of DTBG and TTBG. In terms of selectivity towards di- and tri-ethers, a value of 92% is obtained over Ar-SO_3H-SBA-15 after 4 h

Table 5 Comparison of the catalytic performance of several acid catalysts reported in literature for the etherification of glycerol with isobutylene[a]

		Reaction conditions						Distribution of products (wt%)				
Catalyst	Reference	IB/GOH/ mol mol^{-1}	T/°C	Time /h	Catalyst (wt%)	Stirring/ rpm	X_G (%)	MTBG	DTBG	TTBG	DIB	$S_{DTBG+TTBG}$ (%)
Amberlyst-15Dry	[112]	4/1	60	8	7.5	1200	100	8.5	59.6	21.2	10.9	86.6
	[112]	4/1	90	8	7.5	1200	95.6	16.2	68.4	20.3	15.4	75.9
Amberlyst-35Dry	[112]	4/1	60	8	7.5	1200	100	7.6	59.3	29.8	3.4	88.7
	[112]	4/1	90	8	7.5	1200	80.1	27.9	56.0	8.1	16.1	49.5
H-Y	[112]	4/1	90	8	7.5	1200	100	16.2	57.3	14.3	12.3	75.4
H-Beta	[112]	4/1	90	8	7.5	1200	18.0	14.6	34.5	0	51.0	63.2
$H_3PW_{12}O_{40}$ (HPA)	[110]	2/1	90	5	2	700	79	—	41	—	1	—
Amberlyst-15	[110]	2/1	90	5	2	700	45	—	47	—	2	—
p-Toluenesulf. acid	[110]	2/1	90	5	2	700	89	—	34	—	0	—
Amberlyst-35Wet	[115]	4/1	80	7	—	1300	—	2	46	41	11	96
Pr-SO_3H-SBA-15	[116]	4/1	75	4	5	1000	90	9	56	35	0	86
Ar-SO_3H-SBA-15	[116]	4/1	75	4	5	1000	100	5	54	41	0	92
Amberlyst-15Dry	[116]	4/1	75	4	5	1000	99	6	51	28	15	90
Amberlyts-36Dry	[116]	4/1	75	4	5	1000	96	6	51	32	11	89
CT-275	[116]	4/1	75	4	5	1000	100	8	55	30	7	87
Nafion SAC-13	[116]	4/1	75	4	5	1000	–[b]	—	—	—	—	—

[a] IB/GOH: isobutene/glycerol molar ratio. X_G: glycerol conversion. $S_{DTBG+TTBG}$: selectivity to di- and tri-ethers calculated with respect to glycerol. When not directly available, weight distribution of products was deduced from published data. [b] System with two phases, indicating low glycerol conversion (below 50%), not possible to be accurately quantified.

(77% after 1 h). In contrast to macroporous commercial sulfonic acid resins, no presence of oligomerisation products is detected over this silica-based catalyst. Therefore, the use of a silica matrix reduces the process of isobutylene oligomerisation, adding an important benefit to the final products, since isobutylene oligomers must be removed from the fuel additive before use. The acid strength of the sulfonic acid sites was also found to be a crucial factor affecting the catalytic performance of these materials, with an optimized acid strength among the tested materials such as that in arene-sulfonic acid moieties being needed for this particular reaction.

An alternative approach to produce *tert*-butylated derivates is the direct etherification of glycerol with *tert*-butyl alcohol (TBA) using strong acid catalysts. Klepácočá *et al.*[112,117] also reported the etherification of glycerol with *tert*-butanol over sulfonic acid resins. The optimal reaction temperature was reported to be 75 °C on catalyst A-35 (more acidic)—glycerol conversion 87.8%—and on A-15—glycerol conversion 68.4%. Glycerol conversion and ethers yield increased when using high (TBA)/(G) molar ratios; the stoichiometric ratio was clearly insufficient to achieve good results. Water present in the reaction system, either from the wet catalyst or as reaction product, was observed to have an inhibition effect on glycerol *tert*-butylation. On the wet catalyst (approximately 54% water) conversion was lower than on the dry form of the same catalyst (amount of water $\leq$ 3%); with the degree of cross-linking of the sulfonic resin also being an important factor since it influences the porosity of the polymer after swelling. Nevertheless, best etherification results were obtained with isobutylene and not with *tert*-butyl alcohol as etherifying agent, especially when higher ethers are to be obtained. See Table 6 for an example of data on typical product distributions obtained when using *tert*-butanol as etherifying agent, remarking the presence of undesired H_2O and DIB and the limited production of DTBG and TTBG.

R. Luque *et al.*[118] have evaluated a new family of mesoporous carbonaceous materials derived from renewable bioresources denoted as Starbon® in several glycerol acid-catalysed transformations, including the etherification with *tert*-butyl alcohol. Starbon® acids had previously been proved to show excellent activities and selectivities in different acid catalysed reactions including the esterification of various organic acids in water.[119,120] Etherification reactions were carried out in a microwave-irradiated tube under continuous stirring for short time periods. Reaction conditions used for *tert*-butyl alcohol were as follows: catalyst Starbon® acid 0.1 g, glycerol : *tert*-butyl alcohol 1 : 3 ratio, microwave 300 W, 100–120 °C, 15 min. Under these conditions the authors reported glycerol conversion of 66% with almost unique selectivities to MTBG (over 99%). Nevertheless, they demonstrated the utility and versatility of Starbon® acids in several other etherification reactions of glycerol with different alcohols, which might also be considered as alternative oxygenated derivatives for fuel additives.

4.2. Esters derived from glycerol

Glycerol esters can be prepared by esterification of glycerol with carboxylic acids as well as by transesterification with their methyl esters. They have many industrial applications, ranging from the food industry to cosmetics or pharmaceuticals. Here, we describe the preparation of glycerol esters with interesting properties as fuel additives. Yadav and Mehta[121] reviewed several synthetic routes for obtaining organic esters, with the direct esterification of carboxylic acids with alcohols in the presence of acid catalysts being the most-used methodology, taking into account equilibrium limitations controlling the reaction course. The scientific literature contains a growing amount of reports on the use of heterogeneous acid catalysts for a wide range of esterification reactions, aiming to substitute their homogeneous counterparts. The most-used solid acids for the production of esters as in the previous sections have been ion-exchange organic resins such as those under the trade name Amberlyst,[122] zeolites,[123] and silica-supported heteropolyacids[124] Nevertheless, they have been shown to exhibit some limitations in applicability for catalyzing certain esterification reactions due to either low thermal stability (resins), mass transfer resistance (zeolites),[125] or loss of active acid sites due to high solubility in a polar medium (heteropolyacids).[124] Moreover, the presence of water can seriously affect the catalytic behavior of these solid acid catalysts due to their highly hygroscopic nature,[126] with the practice of removing product water from reaction media as the reaction proceeds being common. In the case of esterification of glycerol for production of bio-additives for petrol fuels, the most interesting reaction is the acetylation with acetic acid, generally described in Fig. 6.

The industrial production of acetylglycerols is known since decades ago, and all of them have several applications in chemical industry. Already in 1983 Bremus *et al.*[127] invented a two-step process for the continuous production of triacetylglycerol (TAG, also called triacetin) using a mixture of acetic acid and acetic anhydride to achieve almost complete conversion of glycerol to triacetin using a homogeneous acid catalyst, the *p*-toluenesulfonic acid. More recently, diacetylglycerols, DAG,

Table 6 Comparison of two ion-exchange resins, A-15 (Dry) and A-35 (Dry) at 60 °C and 90 °C for glycerol etherification by *tert*-butyl alcohol (TBA).[a] From reference 117

		Distribution of products/mass%									
Catalyst	T/°C	G	MTBG	DTBG	TTBG	DIB	TBA	H_2O	X_G (%)	S_{di+tri} (%)	Y_{di+tri} (%)
A-15 (Dry)	60	5.0	24.4	7.7	0.1	0.1	58.3	4.4	79.0	18.7	14.8
	90	11.8	13.7	7.3	0.3	0.2	63.8	3.0	50.2	28.5	14.3
A-35 (Dry)	60	4.6	27.7	7.0	0.1	0	57.3	3.3	86.0	15.6	13.4
	90	7.4	19.8	8.5	0.3	0.2	59.8	4.0	68.6	24.2	16.6

[a] Reaction conditions: 7.5 mass% of catalyst (in G), n(TBA)/n(G) mole ratio = 4 : 1, reaction time = 8 h. X_G = glycerol conversion. S_{di+tri} = selectivity to di- and tri-ethers. Y_{di+tri} = yield of di- and tri-ethers.

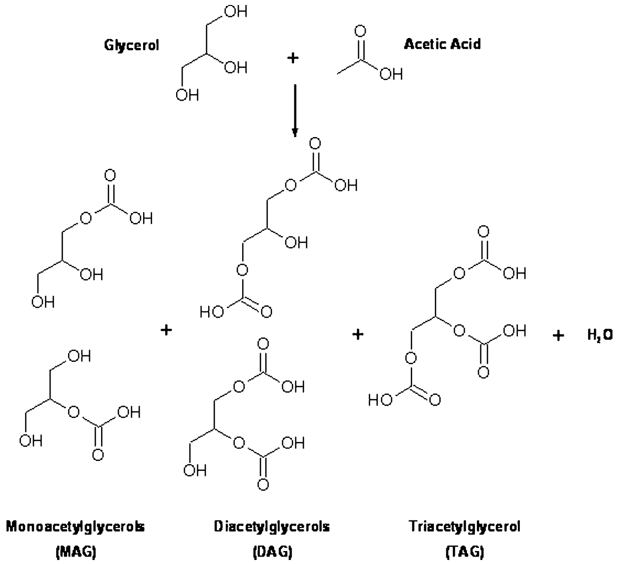


Fig. 6 Reaction of esterification of glycerol with acetic acid.

and triacetylglycerol, TAG, have been claimed to be valuable petrol fuel additives leading to either enhanced cold properties when blended with diesel-fuel,[128] or anti-knocking properties when added to gasoline.[108] Table 7 shows data revealing the improvement in cold properties in biodiesel (comprising fatty acid methyl esters from rapeseed oil) when mixed with small amounts of triacetin. Likewise, triacetin has also been used as antiknock additive for gasoline (see Table 8).

The group of Mota *et al.*[129] investigated the acetylation of glycerol with acetic acid catalyzed by different solid acids. In this work, the kinetics of glycerol transformation and selectivity towards the products, notably mono, di- and triacetyl esters, were determined within 30 min of reaction time to observe the primary products. The results showed that the acid exchange resin, Amberlyst 15, was the most active catalyst, achieving 97% conversion of glycerol in this period, followed by K-10 montmorillonite, niobic acid, HZSM-5 and HUSY. The selectivity varied for each catalyst and conversion degree, but the yield of di- and triacetylated products increased with increasing conversion and reaction time. In all cases, the formation of α-hydroxyacetone (acetol) was observed, and was established to be associated with a glycerol dehydration originated in the presence of strong acid sites. The poor performance observed over zeolites was attributed to diffusion hindrances of the acetylated esters inside the micropores. Likewise, the group of Clark at the University of York also tested their Starbon® acid catalysts in the glycerol esterification with acetic acid under microwave irradiation to selectively give MAG, DAG or TAG under conditions of quantitative conversion of glycerol.[118] Thus, a maximum selectivity of *ca.* 60–75% was obtained separately for mono-, di- or the triacetylglycerol depending on the reaction conditions, *i.e.* microwave power, temperature, catalyst loading, and glycerol : acetic acid ratio. Briefly, low glycerol : acetic acid ratios were most favourable for the preparation of MAG, as was the use of short times of reaction and low microwave power. On the other hand, longer reaction times combined with an increase in the amount of catalyst at maximum microwave power improved selectivities to triacetin. They also compared the activity of various catalysts in this esterification reaction under microwave irradiation, such as H_2SO_4 and sulfated zirconia. Under the same reaction conditions, the Starbon® acid was found to be the most active and selective catalyst.

As in the above-mentioned case of glycerol *tert*-butylation, the group of Melero *et al.* at the Universidad Rey Juan Carlos demonstrated the excellent catalytic behavior of sulfonic acid-functionalized mesostructured materials in the acetylation of glycerol with acetic acid to yield acetylated compounds with interesting properties as bio-additives for petroleum fuels.[130] The activity and selectivity of these silica-supported sulfonic catalysts have been shown to be comparable or even superior to other conventional acid catalysts (H_2SO_4, Amberlyst 15, and Nafion®-silica composite SAC-13). The authors used an experimental design methodology for different levels of temperature and acetic

Table 7 Cold properties improvement when mixing triacetylglycerol with biodiesel (data from reference 128)

Parameter	Biodiesel [a]	Biodiesel + 1% of triacetin	Biodiesel + 5% of triacetin	Biodiesel + 10% of triacetin
Density/g cm^{-3}	0.8592	0.8615	0.8689	0.8806
M.p.[b]/°C	−7	−16	−16	−17
Viscosity at −10 °C/cSt	—	—	931.2	453.9

[a] Fatty acid methyl esters from rapeseed oil. [b] Melting point of the mixture.

Table 8 Triacetylgycerol properties as fuel additive (data from reference 108)

		Solubility in fuels		
Density/g cm^{-3}	Boiling pt./°C	Gasoline	Diesel	FAME
1.10	259	+	+	+

Engine Test					
MON [a]		RON [b]		CN [c]	
Gasoline	10% Mix	Gasoline	10% Mix	Diesel	10% Mix
85.3	88.0	97.0	98.3	50.5	45

[a] Motor octane number. [b] Research octane number. [c] Cetane number.

Table 9 Cold properties improvement when mixing glycerol formal with biodiesel (data from reference 128)

Parameter	Biodiesel [a]	Biodiesel + 0.5% of glycerol formal	Biodiesel + 1% of glycerol formal	Biodiesel + 5% of glycerol formal
Density/g cm^{-3}	0.8592	0.8620	0.8631	0.8711
M.p.[b]/°C	−7	−16	−21	−21
Viscosity at −10 °C/cSt	—	—	548.2	343.3

[a] Fatty acid methyl esters from rapeseed oil. [b] Melting point of the mixture.

acid : glycerol ratios which showed that it is necessary to use high acetic acid excesses in order to push the equilibrium to maximize simultaneously the conversion of glycerol and the selectivity towards the most valuable (from a fuel-additive point of view) DAG and TAG derivatives. Within the range of study, optimal conditions were found to be 125 °C and acetic acid : glycerol molar ratio of 9 : 1. Under these conditions glycerol conversions over 90% and combined selectivities towards di- and tri-acetylglycerol over 85% were achieved after 4 hours of reaction over sulfonic acid-modified SBA-15. Additionally, catalyst reusability was confirmed for at least three consecutive runs. The acid strength of the catalytic sites was also shown to be a determinant parameter in the catalytic performance. The use of stronger acid centers, such as those in arene-sulfonic acid- and fluorosulfonic acid-modified mesostructured materials, provides improved kinetic results both in glycerol conversion and selectivity towards the desired products.

4.3. Acetals and ketals derived from glycerol

Various acetals and ketals derived from glycerol can be used as ignition accelerators and antiknock additives in combustion engines either based on petrochemical fuel like diesel and Otto fuel or bio-fuels. They can be added up to 10 vol% of the fuel,[131–133] and the main advantages claimed are the reduction of particle emissions and the improvement of cold-properties.

Acetals or ketals can be formed by reaction of glycerol with various aldehydes or ketones yielding five- or six-membered cycles (Fig. 7). In the acetalisation reaction, the five- and six-ring compounds are usually formed in a ratio of 50 : 50, but there are some examples that do favour one of the forms, *e.g.* the reaction of glycerol with acetone where a ratio of the five-membered to the six-membered ring of 99 : 1 is obtained, whereas when using formaldehyde as reagent a ratio of 22 : 78 is found.[97] To perform this reaction a catalyst is needed, which is mostly a solid acid catalyst. For example, the resin Amberlyst 15 has been reported to catalyze the acetalisation of glycerol with various aldehydes or ketones,[134] *e.g.* butanal or acrolein at temperatures below 70 °C leading to high selectivities. Within the same family of catalysts, Amberlyst 36 has also been shown to be active in the reaction of glycerol with formaldehyde to give glycerol formal at $T = 50–110$ °C with a yield of 77%. The glycerol formal has several uses, such as disinfectant or solvent for medical or cosmetic applications, but its utilisation as fuel additive has also been studied.[128] Table 9 shows the reported cold-improvement effects of this glycerol formal when mixed with biodiesel, especially the melting point and the viscosity at low temperature. However, no information about other interesting cold-properties such as the cloud point or the cold filter plugging point (CFPP) is available. Recently, Mota *et al.*[135] have reported the acid-catalyzed reaction of glycerol with aqueous formaldehyde and acetone in the absence of solvent over heterogeneous catalysts. Authors reported that zeolites with moderate aluminium content and large pore size such as beta zeolite promote the acetalisation of glycerol with outstanding activities as compared with other conventional acid catalysts, medium-pore size zeolites and Amberlyst-15. This catalytic behaviour was attributed to its hydrophobic zeolitic environment (high-silica zeolite with moderate acid content) that prevents the diffusion of the water molecules towards the inner of the pores. In the same way, the water formed upon the acetalisation is expelled off from the pores. Both facts preserve the integrity and strength of the acid sites, while minimizing the reverse reaction.

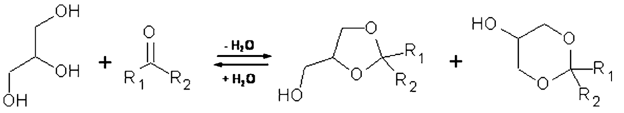


Fig. 7 Reaction scheme of glycerol with aldehydes or ketones.

More recently, a new glycerol-derived acetal, (2,2-dimethyl-1,3-dioxolan-4-yl) methyl acetate, has been reported as a new oxygenated biodiesel additive.[136] The authors claim that this acetal not only improves biodiesel viscosity but also meets the requirements established by diesel and biodiesel fuels by the European and American Standards (EN 14214 and ASTM D6751, respectively) for other important parameters, such as flash point and oxidation stability. This glycerol acetal is obtained through a two-step strategy using an acid homogeneous catalyst (*p*-toluenesulfonic acid) in a first step, and subsequently reacting the obtained product with acetic anhydride in the presence of triethylamine in a second step. In our opinion, the first acid-catalysed step could also be conveniently carried out over a heterogeneous acid catalyst.

4.4. Assessment of oxygenated derivatives synthesized from glycerol as biodiesel additives

The assessment of these kinds of oxygenated compounds as biodiesel additives has been poorly described in literature. In this context, an interesting work has been recently published by Delfort *et al.*,[137] in which different oxygenates derived from glycerol, such as acetals, ethers and carbonates, have been synthesized and evaluated as blending components for diesel fuel. Their potential in terms of pollutant emissions have been evaluated with different engine technologies. Blends with 5% by volume of glycerol derivatives reduced particulate matter emissions by 15% to 25% without a significant increasing in NO_x emissions. Although all the compounds showed a good behaviour in terms of pollutant emissions, the authors

Table 10 Preparation and composition of glycerol derivatives evaluated in mixtures with soybean biodiesel (see Table 11)

Sample	Synthesis	Composition (wt%)[a]
GE (glycerol *tert*-butyl ethers)	Isobutylene + glycerol. Reaction conditions: isobutylene/glycerol molar ratio 4/1, 75 °C, 4 hours, 5 wt% catalyst (arene-SO_3H-SBA-15) referred to glycerol.[116]	MTBG: 5%, DTBG: 54%, TTBG: 41%, DIB: 0%
AC (solketal)	Acetone + glycerol. Commercially available from Sigma.	Solketal (2,2-dimethyl-1,3-dioxolan-4-yl)methanol, 98%.
TR (triacetin)	Acetic acid or anhydride + glycerol. Commercially available from Sigma.	Triacetin (tri-acetyl-glycerol), 99.5%.
GA (glycerol acetates)	Acetic acid + glycerol. Reaction conditions: acetic acid/glycerol molar ratio 9/1, 125 °C, 4 hours, 4 wt% catalyst (arene-SO_3H-SBA-15) referred to glycerol.[130]	MAG: 15%, DAG: 48%, TAG: 37%

[a] Either determined experimentally by gas chromatography or provided by the commercial supplier. Nomenclature: MTBG: mono-*tert*-butyl-glycerol; DTBG: di-*tert*-butyl-glycerol; TTBG: tri-*tert*-butyl-glycerol; DIB: di-isobutene; MAG: mono-acetyl-glycerol; DAG: di-acetyl-glycerol; TAG: tri-acetyl-glycerol or triacetin.

Table 11 Effect of glycerol-derived compounds addition to soybean biodiesel B100 fuel properties. Preparation of mixtures: 100 g biodiesel + 10 g of additive

Parameter *Standard*	Specifications[a]	B100[b]	B100 + 10% GE	B100 + 10% AC	B100 + 10% TR	B100 + 10% GA
Density at 20 °C/g cm^{-3} *EN ISO 12185*	850–900	881	881	895	899	900
Viscosity at 40 °C/mm^2 s^{-1} *EN ISO 3104*	3.50–5.00	4.12	4.05	4.07	4.14	4.30
CFPP [c]/°C *DIN EN 116*	Max. 0 °C (summer)	1	0	0	0	0
Iodine number (g/100g) *EN 14111*	Max. 140	128	117	118	116	116
Heating value/cal g^{-1} *UNE 51123*	—	9518	9404	9187	9050	9058
Flash point/°C *ISO 3679*	Min. 120	167	116	109	161	154
Oxidation stability/h *EN 14112*	Min. 6	6.9	6.9	3.8	5.88	3.3

[a] Upper and lower limits specified by the corresponding standard for biodiesel fuels. [b] Fatty acid methyl esters from soybean oil. [c] Cold filter plugging point.

concluded that the glycerol *tert*-butyl ether is the best cost-efficient alternative. However, there is still a need for determining the influence of these compounds on the quality parameters standardized for biodiesel, such as those included in the EN 14214 standard for Europe.

On the basis of our previous experience in the field, we have prepared several of the above-mentioned glycerol derivatives using sulfonic acid-modified mesostructured catalysts to be tested as biodiesel additives. The results presented herein form part of a larger study being currently performed and not yet published. Table 10 shows the glycerol derivatives used for this study, their composition, and the method followed for their preparation.

These additives have been blended with a B100 biodiesel from soybean oil in the following proportion: 100 g of biodiesel + 10 g of glycerol-derived additive. The mixtures have been analyzed for their properties as fuels, considering parameters such as density, viscosity, cold filter plugging point (CFPP), iodine number, heating value, flash point and oxidation stability. Each parameter has been obtained following procedures established by applicable standards. Table 11 summarizes the values of the measured parameters for the pure biodiesel and the mixtures with the different additives. Density generally increases with the addition of glycerol-derived compounds reaching a maximum of 900 g cm^{-3} (upper limit of the specification for biodiesel in the standard EN ISO 3675). This is consistent with these additives being denser than biodiesel. Viscosity at 40 °C is modified downwards by the ethers and the acetal, which would be especially useful when mixed with biodiesel coming from more viscous oils, such as palm oil. On the other hand, triacetin and the mixture of glycerol acetates increase the viscosity measured at 40 °C, although keeping the value within the specified limits. This observation seems to contradict the values previously reported[128] where mixtures of rapeseed biodiesel and triacetin gave lowered viscosities as measured at −10 °C. Only small changes are observed in the CFPP, an important parameter to evaluate the cold properties of the mixtures. Nevertheless, all the additives tested tend to lower the value of CFPP, improving the usability of the final fuel. Iodine number consistently decreases with the addition of glycerol-based additives regardless of the type of additive, since these molecules have no double bonds in the chemical structure and thus are not iodine-reactive. Similarly, the reduction in the heating value can be attributed to the molecular formula of the additives, as they present relatively high oxygen contents. In this aspect, the additive that appears to be more interesting is the mixture of glycerol ethers (GE) since the heating value remains close to that measured for B100 fuel. Likewise, the oxidation stability is not affected by the glycerol ethers but it is affected by the acetal or the mixture of esters due to the high content of free hydroxyl groups.[136] The flash point of the final mixture is also affected by the addition of these oxygenated compounds. In all the cases, a reduction of this parameter is observed; being more pronounced for the more volatile additives, *i.e.* glycerol ethers, which is slightly below the lower limit of the specification ISO 3679. Mixtures with the glycerol acetal give the lowest flash point, whereas the

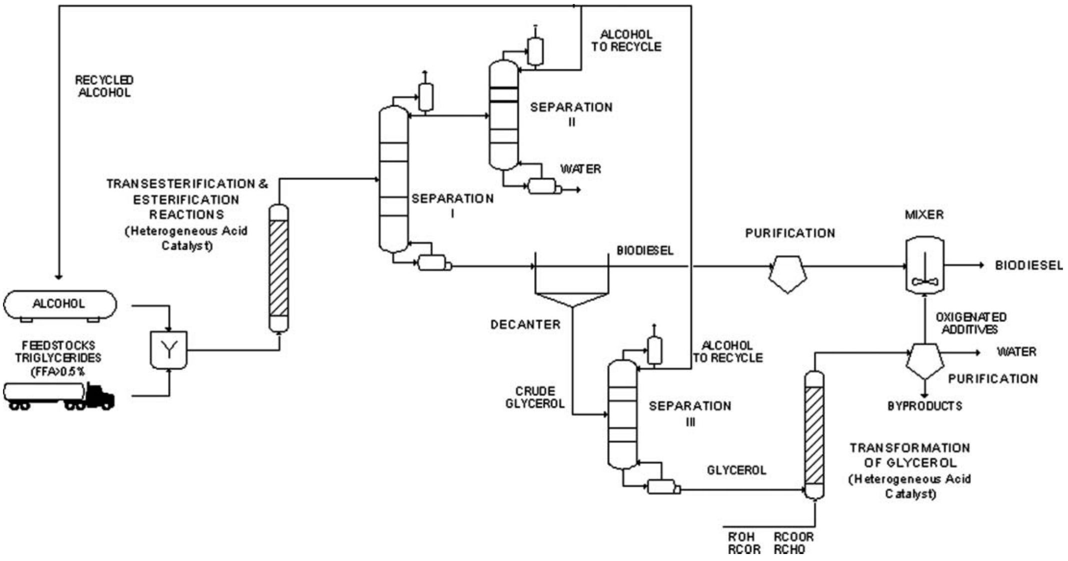


Fig. 8 Integrated process for biodiesel production over heterogeneous acid catalysts.

acetates—triacetin or the mixture of acetates—only introduce a slight reduction in this safety-relevant parameter.

Considering globally all this data, it can be said that these glycerol-based additives are adequate to be used as fuel-additives for biodiesel—fatty acid methyl esters—with the glycerol ethers obtained by *tert*-butylation of glycerol with isobutylene over sulfonic acid-modified SBA-15 being especially interesting, as they improve some properties without adversely affecting the rest.

5. Challenges and future outlook

As described in the present review, the use of heterogeneous acid catalysts for biodiesel production is an emerging field of research which has been gradually growing during the last years. A great variety of acid solids have been reported for this particular reaction but some aspects must be solved in order to impact in a positive way on the biodiesel technologies. The main challenges are related with the stability of acid sites and the control of surface properties to favour the diffusion of oily feedstock towards the acid sites and to promote the expelling off of the polar compounds (glycerol and water, *etc.*) from the catalyst framework.

It is likely that intensification of biodiesel production using heterogeneous acid catalysts will ultimately improve overall energy and economic efficiency. This kind of catalyst can be easily incorporated into a packed bed continuous flow reactor and would allow diversification of feedstock, easy separation of catalyst from the reaction medium avoiding the neutralization step necessary when using alkaline homogeneous catalysts, a higher grade of glycerol (salt-free) and hence a reduction of the purification costs, and in particular conditions even the glycerol transformation during the esterification and transesterification reactions might be promoted. This integrated process would minimize the production cost (low-cost feedstock and simplified downstream process with fewer steps), provide a better use of the glycerol (transformation into oxygenated additives with interesting properties for biodiesel formulation), and also minimize waste effluents. A possible scheme of this integrated process using heterogeneous acid catalysts is depicted in Fig. 8.

Hence, it is vital that efficient acid catalysts are discovered in the future. Heterogeneous catalysts, and in particular solid acid catalysts, which have been the backbone of the petrochemical and refining industry, will most likely play a key role in the transition to the so-called "*second generation*" biodiesel. Of particular significance is the integration of biodiesel production using heterogeneous acid catalysts based on three essential issues: diversification of feedstocks, packed-bed continuous processes and transformation of glycerol by-product into biofuels for transport. We honestly think that further research in developing heterogeneous acid-catalyzed processes for biodiesel production is warranted.

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