

# Solid Acid Catalysts for Biodiesel Production – Towards Sustainable Energy

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**Abstract:** The advantages of biodiesel as an alternative fuel and the problems involved in its manufacturing are outlined. The pros and cons of making biodiesel *via* fatty acid esterification using solid acid catalysts are examined. The main problem is finding a suitable catalyst that is active, selective, and stable under the process conditions. Various solid acids (zeolites, ion-exchange resins, and mixed metal oxides) are screened as catalysts in the esterification of do-

decanoic acid with 2-ethylhexanol, 1-propanol, and methanol at 130–180 °C. The most promising candidate is found to be sulphated zirconia. The catalyst's stability towards thermal decomposition and leaching is tested and the effects of the surface composition and structure on the catalytic activity are discussed.

**Keywords:** alternative fuels; esterification; green chemistry; heterogeneous catalysis; sulphated zirconia

## Introduction

Sustainable energy management has become a high priority for many countries. A large percentage of our global energy expenditure is for automotive purposes, making the implementation of sustainable automotive fuels an urgent issue worldwide.<sup>[1]</sup> Biodiesel is a renewable fuel comprised of monoalkyl esters of fatty acids. It can be manufactured from vegetable oils, animal fat, and even from recycled grease from the food industry.<sup>[2]</sup> Remarkably, it is the only alternative fuel currently available that has an overall positive life cycle energy balance – it yields as much as 3.2 units of fuel product energy for every unit of fossil energy consumed in its life cycle, compared to only 0.83 units for petroleum diesel.<sup>[3]</sup> Biodiesel contains no petroleum products, but it may be blended with conventional diesel to provide an alternative to the latter. A blend of 80% petroleum diesel and 20% biodiesel (known as B20) can be used in unmodified diesel engines (in fact, using B20 in buses and trucks reduces the black smoke emitted during acceleration<sup>[4]</sup>). Biodiesel can also be used in its pure form (B100), but this requires minor engine modifications to avoid maintenance problems.<sup>[5]</sup> Table 1 shows the average biodiesel emissions compared to conventional diesel.<sup>[3,6]</sup>

Interest in biodiesel as an alternative fuel has accelerated tremendously as a result of recent legislations that require a major reduction of vehicle emissions, as well as the increasing price of petroleum.<sup>[2,4,6,7]</sup> Biodiesel is now

**Table 1.** Average biodiesel emissions compared to conventional diesel.

| Emission type                           | B20   | B100   |
|-----------------------------------------|-------|--------|
| Total unburned hydrocarbons             | – 20% | – 67%  |
| CO                                      | – 12% | – 48%  |
| CO <sub>2</sub>                         | – 16% | – 79%  |
| Particulate matter                      | – 12% | – 47%  |
| NO <sub>x</sub>                         | + 2%  | + 10%  |
| SO <sub>x</sub>                         | – 20% | – 100% |
| Polycyclic aromatic hydrocarbons (PAHs) | – 13% | – 80%  |
| Nitrated PAHs                           | – 50% | – 90%  |

recognized as a “green fuel” that has several advantages over conventional diesel. It is safe, renewable, non-toxic, and biodegradable in water (*ca.* 98% biodegrades in just a few weeks).<sup>[2]</sup> It contains less sulphur compounds,<sup>[7]</sup> and has a high flash point (> 130 °C). Furthermore, it is almost neutral with regard to carbon dioxide emissions, and emits 80% fewer hydrocarbons and ~50% less particles. Finally, biodiesel production enjoys a positive social impact, by enhancing rural revitalisation.<sup>[3,6]</sup>

Current biodiesel manufacturing processes primarily employ transesterification of triglycerides with methanol using NaOH as a base catalyst.<sup>[8]</sup> This catalyst is corrosive to equipment and also reacts with free fatty acids to form unwanted soap by-products, requiring expensive separation. Another route to fatty esters, the main components of biodiesel, is batch esterification catalysed by

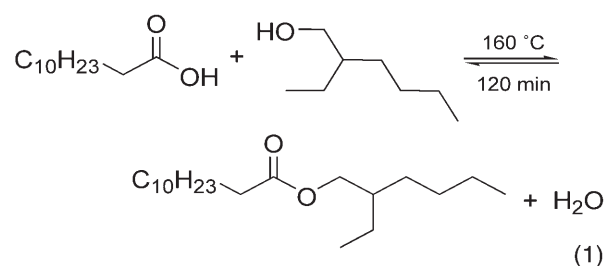
homogeneous sulphuric acid. This is followed by a distillation process for water removal, recycling of excess alcohol and ester purification. The problem with this process is the discontinuous operation mode that also involves a costly separation of homogeneous catalyst.<sup>[9,10]</sup>

During the last decade many industrial processes shifted towards using solid acid catalysts.<sup>[11,12]</sup> In contrast to liquid acids that possess well-defined acid properties, solid acids may contain a variety of acid sites.<sup>[13]</sup> Generally they are categorised by their Brønsted or Lewis acidity, the strength and number of sites, and the textural properties of the support (porosity and surface area). Recently, one of us proposed a continuous process for fatty esters production, based on catalytic reactive distillation.<sup>[14,15]</sup> The non-ideal nature of the mixtures, however, leads often to phase segregation, and the aqueous phase may easily cause deactivation of the solid acid catalyst, so a water-tolerant catalyst is required.<sup>[16]</sup> To solve these problems, we are investigating solid acid catalysts for fatty acids esterification. In this paper, we report the results of a screening of catalyst candidates and discuss the possible applications to biodiesel production.

## Results and Discussion

On the large scale of automotive fuel applications, a good esterification catalyst must fulfil several conditions that may not seem so crucial in the laboratory. First, the catalyst should be very active and selective, as by-products other than water are likely to render the process uneconomical. Second, it should be water-tolerant and stable at relatively high temperatures. Finally, it should be an inexpensive material that is also readily available on an industrial scale. Bearing the above conditions in mind, we envisaged a strong Brønsted acid with increased hydrophobicity, which is stable at temperatures up to 200–250 °C (hydrophobic surfaces are preferable for conducting organic reactions in water, because water covers the surface of the solid acids and prevents the adsorption of organic materials). For the first set of experiments, we chose to screen four solid acid families: zeolites, mixed metal oxides, composite materials and carbon-based polysulphonic acids. All these catalysts were benchmarked against H<sub>2</sub>SO<sub>4</sub>, as the reference homogeneous catalyst.

In a typical reaction, equivalent amounts of dodecanoic (lauric) acid (**1**) and 2-ethylhexanol (**2**) were reacted at 160 °C in the presence of 1 wt % solid acid catalyst, to give 2-ethylhexanol dodecanoate (**3**) [Eq. (1)]. Reaction progress was monitored by GC. Time-resolved profiles were then measured for both catalysed and non-catalysed reactions, at various temperatures exceeding 100 °C (below 100 °C, at normal pressure and equimolar ratio of reactants, the liquids separate before equilibrium conversion is reached). The following results are divided according to the type of catalyst families: zeolites,



composite materials, carbons-based solid acids and mixed metal oxides (in particular, sulphated zirconia).

In the figures that follow, the conversion is defined as:  $X [\%] = 100 \times [\text{Acid}]_{\text{final}} / [\text{Acid}]_{\text{initial}}$ , and the amount of catalyst used is normalised, i.e.,  $W_{\text{cat}} [\%] = M_{\text{cat}} / (M_{\text{acid}} + M_{\text{alcohol}})$ .

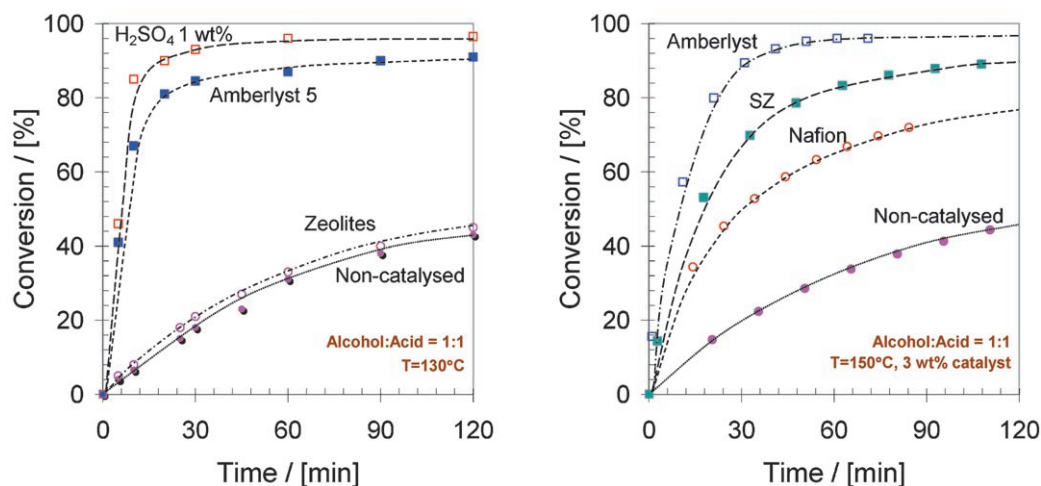
### Catalysis using Zeolites and Ion-Exchange Resins

Figure 1 shows the degree of conversion vs. time for different catalyst types. We tested three types of zeolites: H-ZSM-5, Y and Beta. The zeolites showed only a small increase of conversion (1–4%), compared to the non-catalysed reaction (Figure 1, *left*). This is in agreement with previous findings,<sup>[16]</sup> suggesting that the reaction may be suppressed by the limited diffusion of the bulky reactant into the zeolite pores. The catalysis probably takes place only on the external surface. Zeolites contain silicon, aluminium and oxygen in their framework, and cations, water and/or other molecules within their pores. The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio can be used to control the acid strength and hydrophobicity of the zeolites.<sup>[17]</sup> While acid strength increases at lower SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, hydrophobicity increases at higher SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios. This means a trade-off is required for optimal performance.<sup>[16]</sup>

Note that the maximum achievable conversion in the case of esterification is limited by the chemical equilibrium.

We then tested two representatives of the main classes of ion-exchange organic resins: Amberlyst-15, a styrene-based sulphonic acid and Nafion-NR50, a copolymer of tetrafluoroethene and perfluoro-2-(fluorosulphonylethoxy)propyl vinyl ether.<sup>[18–20]</sup> Both catalysts showed high initial activity (Figure 1, *right*). However, the Amberlyst catalyst deactivated after 2 h, and the Nafion after 4.5 h, making them unsuitable for continuous industrial processes, where a long catalyst lifetime is essential.

Carbon-based solid acid catalysts were only recently reported as promising esterification catalysts.<sup>[21]</sup> These compounds are allegedly easily prepared by heating aromatics such as naphthalene in concentrated sulphuric acid under nitrogen at 473–573 K. The excess sulphuric acid is then removed by vacuum distillation, resulting in a black solid. This solid was reported to be insoluble in



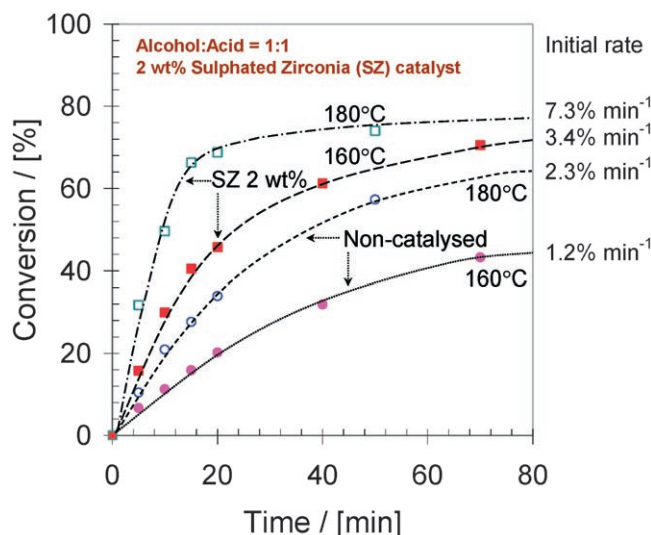
**Figure 1.** Esterification of dodecanoic acid with 2-ethylhexanol: (left) reactions at 130 °C using homogeneous and heterogeneous acid catalysts; (right) reactions at 150 °C, in the presence of Amberlyst, sulphated zirconia (SZ) and Nafion, 3 wt %. The conversion is defined as:  $X [\%] = 100 \times [\text{Acid}]_{\text{final}} / [\text{Acid}]_{\text{initial}}$ , and the amount of catalyst used is normalised, i.e.,  $W_{\text{cat}} [\%] = M_{\text{cat}} / (M_{\text{acid}} + M_{\text{alcohol}})$ .

many solvents (water, methanol, ethanol, benzene, and hexane). The last parts of the synthesis consist of grinding the solid and washing it repeatedly in boiling water. When attempting to perform this last part of the synthesis the resulting black solid was always soluble in water, much to our frustration. Despite repeated efforts, we could not obtain an insoluble compound as reported in the literature.<sup>[21]</sup>

### Catalysis using Metal Oxides

We chose sulphated zirconia as a representative of the metal oxides family, after an initial screening of various metal oxides. Zirconia can be modified with sulphate ions to form a highly acidic or superacidic catalyst, depending on the treatment conditions.<sup>[22–26]</sup> This type of catalyst is well known in the industry for a variety of processes.<sup>[27–30]</sup> We found that sulphated zirconia showed high activity and selectivity for the esterification of fatty acids with a variety of alcohols ranging from 2-ethylhexanol to methanol. Figure 2 shows the reaction profiles for fatty acid conversion in time, at temperatures of 160 °C and 180 °C, for the catalysed and non-catalysed systems. The initial rate of the catalysed reaction is about three times higher compared to that of the non-catalysed reaction (after 20 min, the conversion of the catalysed reaction was double that of the non-catalysed one).

Seeing these promising results with 2-ethylhexanol, we tested the applicability of sulphated zirconia also for 1-propanol and methanol (Figures 3 and 4). As shown in Figure 3, in the absence of a catalyst, high acid conversion can be achieved only above 180 °C. The increase of conversion with the temperature is

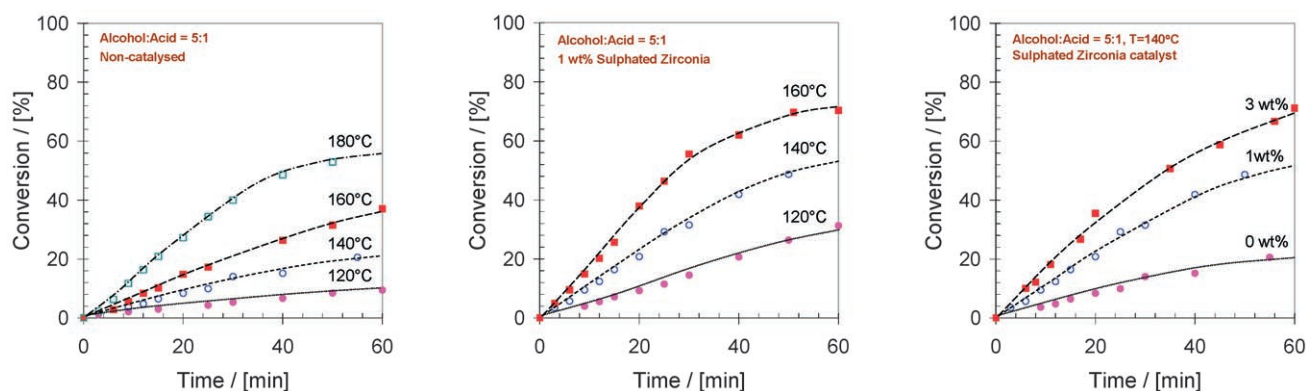


**Figure 2.** Esterification of dodecanoic acid (1) with 2-ethylhexanol (2): activity comparison at 160 °C and 180 °C using 2 wt % sulphated zirconia catalyst. The initial rates are given as the percentage of conversion per min over the first 20 min.

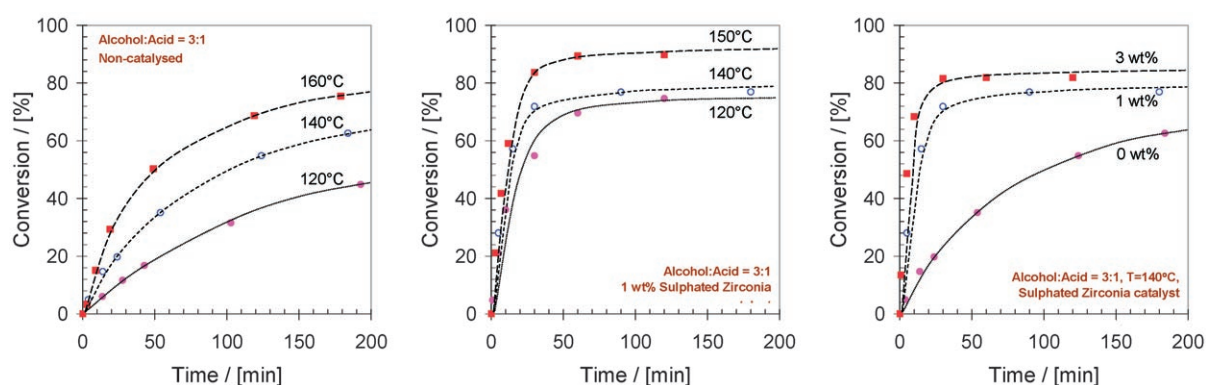
much higher in the case of the catalysed reaction. Moreover, high conversions can be reached even at 140 °C (results not shown), providing that an increased amount of catalyst is used.

In a separate set of experiments, we tested the catalyst reusability and robustness. In five consecutive runs, with no treatment between the runs, the activity dropped to 90% of the original value, and remained constant thereafter. Re-calcination of this (slightly) deactivated catalyst restored it to the original activity.

Figure 4 shows the reaction profiles for the esterification of dodecanoic acid with methanol. As expected, the



**Figure 3.** Esterification of dodecanoic acid with propanol, using an alcohol:acid ratio of 5:1 and sulphated zirconia as catalyst; (left) non-catalysed reaction at 120°C, 140°C, 160°C and 180°C; (centre) 1 wt % catalyst at 120°C, 140°C and 160°C; (right) uncatalysed, 1 wt % catalyst and 3 wt % catalyst at 140°C.



**Figure 4.** Esterification of dodecanoic acid with methanol, using an alcohol:acid ratio of 3:1 and sulphated zirconia as catalyst; (left) non-catalysed reaction at 120°C, 140°C, and 160°C; (centre) 1 wt % catalyst at 120°C, 140°C and 150°C; (right) uncatalysed, 1 wt % and 3 wt % catalyst at 140°C.

fatty acid conversion increases at higher amounts of catalyst and higher temperatures. Comparing the reactions with the three alcohols, one sees that the esterification of dodecanoic acid with methanol takes place at higher rates compared to propanol or 2-ethylhexanol. This can be explained by the relative sizes of the alcohols.

### Testing for Leaching of Sulphonic Groups

In the case of sulphated zirconia, we also tested the catalyst to see if sulphonic groups are leaching into the reaction mixture. This is important, because water can, in principle, capture sulphonic groups from the surface and hydrolyse them to give homogeneous  $\text{H}_2\text{SO}_4$  (if you mix sulphated zirconia in water, the pH of the suspension decreases quickly, as water accumulates on hydrophilic acidic sites and sulphate groups are hydrolysed). The presence of sulphate ions in solution was checked with  $\text{BaCl}_2$  and KOH titration. Following reaction at 403 K and catalyst recovery, the resulting mixture was washed with water for the extraction of sulphate ions. No sul-

phate ions were found. Control experiments showed that when an aqueous suspension of sulphated zirconia was shaken at 25°C sulphate ions did leach out. From these tests we can conclude that sulphated zirconia is not deactivated by leaching of sulphate groups when a small amount of water is present in the organic phase, but is easily hydrolysed in an aqueous phase.<sup>[14]</sup>

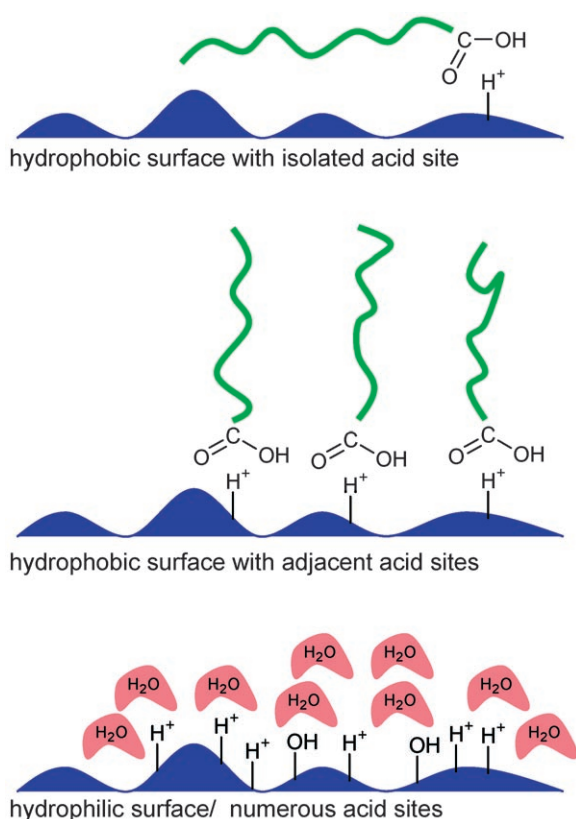
### Product Selectivity and Side Reactions

Typically, the alcohol-to-acid ratio inside an industrial reactive distillation unit may vary over several orders of magnitude.<sup>[14,15]</sup> Especially for stages where an excess of alcohol is present, the use of an acid catalyst may lead to side reactions such as ether formation or alcohol dehydration. For all of the catalysts described here, we assessed the selectivity by testing the formation of side products in a suspension of, e.g., sulphated zirconia in pure 2-ethylhexanol under reflux for 24 h. No ethers or dehydration products were detected by GC analysis.



### The Influence of Surface Hydrophobicity

Although the reaction mechanism for the heterogeneous acid-catalysed esterification was shown to be in principle similar to the homogeneously catalysed one,<sup>[31]</sup> there is an important difference that concerns the relationship between the surface hydrophobicity and the catalyst's activity. This is especially true for dodecanoic acid and 2-ethylhexanol, that are both very lipophilic compounds. One can envisage three possible cases. First, if there is but one isolated Brønsted acid site, surrounded by a hydrophobic environment, it is likely that the hydrophobic 'tail' of the acid would be adsorbed parallel to the hydrophobic surface (Figure 5, *top*). Second, if there are a few acid sites in the vicinity, the fatty acid molecules could adsorb perpendicular to the surface, with the tails forming a local hydrophobic environment. Finally, in the case of a very acidic and/or hydrophilic material (many adjacent acid sites and/or hydroxy groups), the by-product water from the esterification would adsorb on the surface, and the catalyst would lose its activ-



**Figure 5.** Cartoon of the influence of the surface hydrophobicity on the catalytic activity; (*top*) adsorption of a fatty acid on a hydrophobic catalyst surface with an isolated acid site; (*middle*) adsorption of three fatty acid molecules on adjacent acid sites, with the tails forming a local hydrophobic environment; (*bottom*) formation of water layer on hydrophilic acid catalyst.

ity (the water layer would prevent the access of dodecanoic acid and 2-ethylhexanol to the catalyst, Figure 5, *bottom*).

The potential phase separation into an aqueous and an organic phase has important catalytic implications. Homogeneous acid catalysts transfer preferentially to the aqueous phase, where they lose their effectiveness. Some heterogeneous catalysts may be similarly inhibited by water sorption, if they have too many hydrophilic acid sites. In fatty acid esterification, it is usually the alcohol, rather than the acid, that mixes better with water. Accordingly, when there is an excess of alcohol, the reaction mixture remains monophasic until equilibrium conversion is reached. In these cases, e.g., when using a 3:1 methanol:dodecanoic acid ratio, no catalyst deactivation was observed.

In the case of zeolites, the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio represents a trade-off between the hydrophobic character of a zeolite and its acidity. The zeolite must be hydrophobic in order to avoid the absorption of the water by-product that will lead to deactivation. However, if the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio is too high, the zeolite may lose its acidic properties. At low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, water is easily absorbed to the surface, blocking the access of the fatty acid. By increasing the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, 'reaction pockets' are created inside a hydrophobic environment. The fatty acid can then absorb to acid sites on the hydrophobic surface and react further (water molecules are unlikely to be absorbed on sites surrounded by hydrophobic areas). The literature reports that high-silica zeolites were efficient catalysts for esterifying AcOH with EtOH, but showed a decreased activity for 2-BuOH.<sup>[16]</sup> Accordingly, no significant differences were observed in our case for the various  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios, probably because the reactants are too large to fit in the pores.

The ion-exchange resin Nafion is non-porous, and Amberlyst has large pores. The hydrophobicity in this case is governed by the polymer chain, and the polymer backbone itself is likely to have a high affinity towards the tails of the fatty acid and alcohol. Moreover, the sulphonic acid groups grafted on the chain are strong acids compared to the hydroxy groups on zeolites or metal oxides. All these make the resins good esterification catalyst candidates, but they fail on the thermal stability tests.

Of the mixed oxides family, sulphated zirconia is shown to be a good catalyst with high thermal stability and strong acid sites. It has large pores that improve the diffusion of the fatty acid molecules. It does not leach under the reaction conditions (although it *does* leach in water) and does not give rise to side reactions such as etherification or dehydration. This makes sulphated zirconia an interesting candidate for catalytic biodiesel production.

## Conclusion

The systematic study of initial reaction rates and detailed conversion profiles under controlled process conditions (temperature, pressure, and composition) is a suitable method for comparing solid acid catalyst candidates for fatty acid esterification. Catalysts with small pores (microporous), such as zeolites, are not suitable for biodiesel manufacture because of the diffusion limitations of the large fatty acid molecules. Ion-exchange resins are active strong acids, but have a low thermal stability. This is problematic as the reaction must be carried out at high temperatures. Sulphated zirconia, on the other hand, is found to be a good candidate as it is active, selective, and stable under the process conditions. The hydrophobicity of the catalyst surface and the density of the acid sites are of paramount importance in determining the catalyst's activity and selectivity.

## Experimental Section

### Materials and Instrumentation

Reactions were performed using a system of six parallel reactors (Omni-Reacto Station 6100) as well as a higher pressure autoclave. These are batch reactors of 100 mL, equipped with magnetic stirrers, heating/cooling and partial/total reflux system. GC analysis was performed using an InterScience GC-8000 gas chromatograph with a 100% dimethylpolysiloxane capillary column (DB-1, 30 m  $\times$  0.21 mm). GC conditions: isotherm at 40 °C (2 min), ramp at 20 °C min<sup>-1</sup> to 200 °C, isotherm at 200 °C (4 min). The injector and detector temperatures were set at 240 °C. The helium flow rate was 1.9 cm<sup>3</sup> min<sup>-1</sup>. Characterisation of sulphated zirconia was performed by atomic emission spectroscopy with inductively coupled plasma atomisation (ICP-AES) on a CE Instruments Sorptomatic 1990. NH<sub>3</sub>-TPD was used for the characterisation of acidic site distribution. Sulphated zirconia (0.3 g) was heated up to 600 °C using He (30 mL min<sup>-1</sup>) to remove adsorbed components. Then, the sample was cooled at room temperature and saturated for 2 h with 100 mL min<sup>-1</sup> of 8200 ppm NH<sub>3</sub> in He as carrier gas. Subsequently, the system was flushed with He at a flow rate of 30 mL min<sup>-1</sup> for 2 h. The temperature was ramped up to 600 °C at a rate of 10 °C min<sup>-1</sup>. A thermal conductivity detector (TCD) was used to measure the desorption profile of NH<sub>3</sub>. Unless noted otherwise, chemicals were purchased from commercial firms and were used as received. Double distilled water was used in all experiments.

### Procedure for Acid-Catalyzed Esterification

Dodecanoic (lauric) acid (**1**; 20.0 g, 0.10 mol) and 2-ethylhexanol (**2**; 15.64 mL, 13.00 g, 0.1 mol) were reacted at 160 °C in the presence of 1 wt % solid acid catalyst, to give 2-ethylhexanol dodecanoate (**3**). The catalytic activity was measured as the difference between the reaction rate in the presence of catalyst and that of the thermal (non-catalysed) reaction, using the same initial composition and temperature. The particle size

of the catalyst was 0.05 mm. The kinetics of dodecanoic acid esterification with different alcohols were studied at 60 °C, 100 °C, 140 °C, 160 °C, and 180 °C. The catalyst concentration in the reaction mixture was varied from 0 to 5 wt %. The initial reactant molar ratio used was varied from alcohol:dodecanoic acid = 1:1 up to 5:1.

### Preparation of Sulphated Zirconia Catalyst

This is a modification of the two-step synthesis procedure.<sup>[22]</sup> ZrOCl<sub>2</sub>·8 H<sub>2</sub>O (50 g) was dissolved in water (500 mL), followed by precipitation of zirconium hydroxide at pH = 9 using a 25 wt % NH<sub>3</sub> solution. The resulting Zr(OH)<sub>4</sub> was washed with water (3  $\times$  500 mL) to remove the chloride salts [Cl<sup>-</sup> ions were determined with 0.5 N AgNO<sub>3</sub>]. In the second step, Zr(OH)<sub>4</sub> was dried for 16 h at 120 °C, impregnated with 1 N H<sub>2</sub>SO<sub>4</sub> (15 mL H<sub>2</sub>SO<sub>4</sub> per 1 g Zr(OH)<sub>4</sub>), and calcined in air for 3 h at 650 °C.

### Catalyst Characterisation

The textural properties were determined from the nitrogen adsorption isotherm determined after degassing at 200 °C under vacuum at 5–10 mbar. The surface area was calculated using the BET equation and the pore volume was determined at a relative pressure of 0.98. The pore size was calculated using the Barrett–Joyner–Halenda (BJH) method. The most important results are given in Table 2. In principle, the specific surface area depends on the calcination temperature. Values are in very good agreement with literature data.<sup>[32,33]</sup>

**Table 2.** Sulphated zirconia (SZ) catalyst characterisation.

| Parameter                                               | Value |
|---------------------------------------------------------|-------|
| Surface area (m <sup>2</sup> g <sup>-1</sup> )          | 118   |
| Specific pore volume (cm <sup>3</sup> g <sup>-1</sup> ) | 0.099 |
| Average pore size (nm)                                  | 3.0   |
| S/SZ (wt %)                                             | 2.5   |
| Zr/SZ (wt %)                                            | 69.4  |
| O/SZ (wt %)                                             | 28.1  |
| Acidity by NH <sub>3</sub> -TPD (μeq g <sup>-1</sup> )  | 282   |
| Acidity by titration (μeq g <sup>-1</sup> )             | 1150  |

### Procedure for Testing Catalyst Leaching

The catalyst leaching was studied in an organic and an aqueous phase. First, a sample of fresh sulphated zirconia catalyst (0.33 g) was stirred with H<sub>2</sub>O (50 mL) while measuring the development of the pH in time. After 24 h, the acidity was measured by titration with KOH (0.002 N). The suspension was then filtered and treated with a BaCl<sub>2</sub> solution to test for SO<sub>4</sub><sup>2-</sup> ions. In a second experiment, the catalyst was added to an equimolar mixture of reactants. After 3 h at 140 °C, the catalyst was recovered from the reaction mixture, dried at 120 °C and finally stirred in 50 mL H<sub>2</sub>O. The pH was measured and the suspension titrated with a diluted solution of KOH after 24 h. Sulphate ions in the suspension were determined qualitatively with BaCl<sub>2</sub> (at 140 °C the reaction mixture does not split into two liq-

uid phases, because the water evaporates). In a third experiment, the same procedure was repeated at 100 °C when the reaction mixture segregates and a separate aqueous phase is formed.

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