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A Twitchell Reagent Revival: Biodiesel Generation from Low Cost Oils

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Abstract: The transesterification of triglycerides with short-chain alcohols, such as methanol, is the most used process for the obtention of biodiesel. This is a biphasic reaction which can occur both in polar and apolar phases. Using lipophilic sulphonic acids as catalysts, the transesterification reaction takes place primarily in the oil phase. Under these conditions, the reaction rates are considerably improved, with conversions up to 98% in 90 min at 80 °C and with 17.6% mol of catalyst. The most remarkable features of this process are that the catalytic efficiency is not affected by the presence in the oil of free fatty acids or small amounts of water, the transesterification takes place at low temperature (below the boiling point of methanol) and high conversions are reached within a short time. Therefore, low-cost feedstocks containing high levels of FFA (free fatty acids) and water can be used as raw material for biodiesel production. Finally, catalyst recovery by adsorption on a silica gel column was also tested.

Keywords: biodiesel; homogeneous acid catalysis; lipophilic sulphonic acids; transesterification; Twitchell reagents

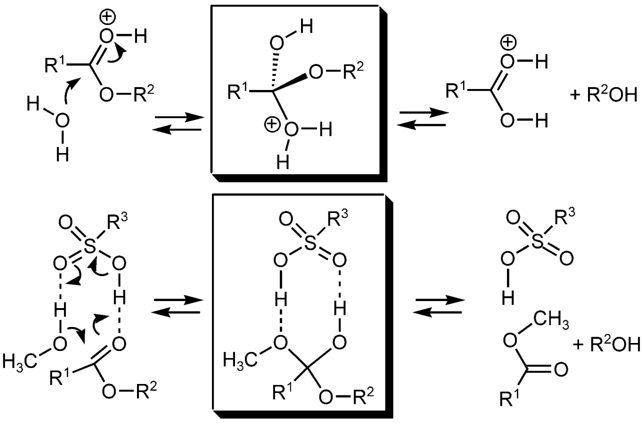
Introduction

Over the past years, biodiesel has gained importance as an alternative to fossil fuels due, among others, to environmental reasons.[1] To date, the best procedure for the transformation of triglycerides in biodiesel is the transesterification with short-chain alcohols to yield the corresponding esters and glycerine.[2]

The search for an ideal catalyst for this apparently simple transformation is, still, an ongoing work.[3] The most popular catalysts in use are alkaline metal hydroxides;[4] nevertheless, these reagents show the following disadvantages.[5] (i) The presence of free fatty acids in oils leads to non-practical procedures. (ii) The phase separation is complicated by the generation of emulsions. (iii) The presence of water in the alcohol increases the soap formation, yielding non-efficient processes. (iv) Additionally, an acidic reagent is necessary to neutralize the base, this leads to an increase in the biodiesel price. (v) Glycerine is obtained in the presence of salts, increasing the cost of glycerine purification, which is an important by-product for a cost-efficient procedure.

On the other hand, acid catalysts such as sulphuric acid or sulphonic acids do not show these pitfalls, but reactions are slow and large amounts of alcohol are necessary.[6] A comparison between transesterification and the traditional fat hydrolysis reactions can be useful to understand this low reactivity. The transformation of triglycerides into the corresponding fatty acids has been thoroughly studied until the 1950s; the preparation of soap and glycerine justified this work,[7] but the commercialization of detergents and the development of new procedures to obtain glycerine,[8] led to a fast decay in this research work. The conclusions reached in these studies can be summarized as follows.[9] (i) Triglyceride hydrolysis is a biphasic procedure due to the low solubility of oil and water. (ii) Esters which exhibit partial solubility in water, hydrolyse in the aqueous phase following the classic Ingold mechanism.[10] Kinetics show zero order in the esters, since ester concentration remains constant during the process due to solubilization from the apolar phase. (iii) Esters that are sparingly water soluble, such as triglycerides, prefer to react fast in the apolar phase, with only a minor contribution from the aqueous phase. Complex kinetics are obtained revealing an induction period, followed by a fast reaction in the fat, and finally a slow reaction due to consumption of the reagents. (iv) Hydrophilic acids, like hydrochloric or sulphuric acids, choose the water phase, and therefore are poor catalysts for triglyceride hydrolysis. On the other hand, long-chain sulphonic acids (Twitchell reagents)[11] are good catalysts for the reaction since they dissolve better in the triglyceride phase.

Triglyceride transesterification with methanol in the presence of an acid catalyst shows a remarkable resemblance to the previous hydrolysis. The water molecule is now substituted by the more lipophilic methanol, but the mutual solubility with the triglyceride is still small and the reaction is again a biphasic process. As in hydrolysis, the transformation of the triglyceride can take place in both polar and apolar phases. Hydrophilic catalysts, such as sulphuric acid, render reactions which are faster in the methanolic phase. This can be easily shown since the reaction rate is proportional to the methanol volume.[12] However, the small triglyceride concentration in the methanolic phase (1/300 mol/mol measured for sunflower seed oil) yields small reaction rates. The fact that the lack of solubility of the triglyceride is a main problem can be readily demonstrated by comparing the rate of transesterification with the esterification of fatty acids. Since fatty acids are soluble in methanol, they undergo esterification at a reasonable rate, and this reaction can be used in industrial processes for biodiesel preparation. Nevertheless, the transesterification of triglycerides is slow, and the resultant generation of water further reduces the solubility of the triglyceride in methanol, making transesterification even more difficult.



Scheme 1. Proposed mechanisms – showing tetrahedral intermediates– for the classic ester hydrolysis (*top*) and transesterification in an apolar phase (*bottom*).

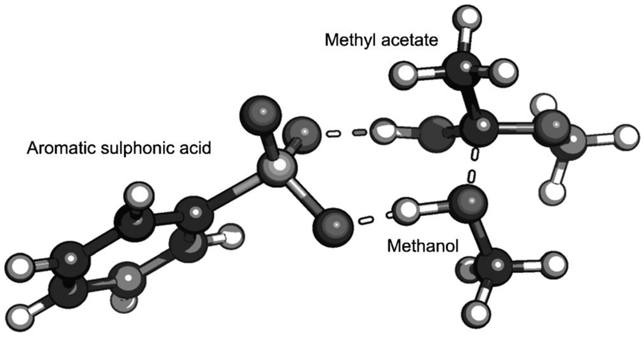


Figure 1. Transition state of the reaction of methanol with methyl acetate catalysed by phenylsulphonic acid (B3LYP/6-31G**).

As in fat hydrolysis, a good alternative may be to promote the reaction in the apolar triglyceride phase, since the methanol molar concentration in this phase is, by far, larger (1/0.4 mol/mol measured in refined sunflower seed oil) than the triglyceride concentration in the polar phase. Recent calculations related to lactone polymerizations suggest a possible mechanism for this transformation in the apolar phase (Scheme 1).[13]

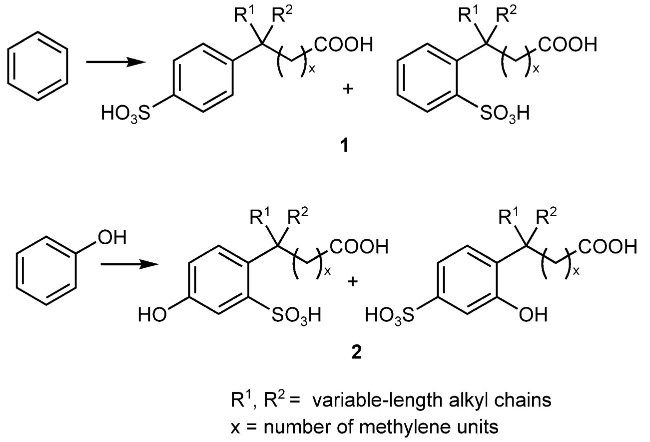
Our own calculations reveal that a similar mechanism is also operative in the transesterification of acyclic esters (Figure 1).

To make use of this alternative, the acid catalyst should preferentially dissolve in the triglyceride phase, therefore a Twitchell reagent could be a good choice.[11] The use of such a lipophilic acid catalyst may offer some interesting advantages in the biodiesel preparation. (i) The presence of large amounts of free fatty acids may be of little effect in the transesterification reaction, because they do not interfere with the acid catalyst. (ii) The existence of small amounts of water (from fatty acid esterification or from a low quality methanol, or a wet fat), which will remain in the methanolic phase, should not strongly influence the reaction kinetics in the apolar phase. (iii) Since methanol will be saturating the triglyceride phase, its total amount will not affect the reaction rate, and therefore its amount can be kept at a minimum. (iv) Glycerine can thus be obtained in the absence of salts and its purification becomes an easy process.

Results and Discussion

Twitchell Reagents

Twitchell reagents have been prepared from several different sources. Although the initial Twitchell re-



Scheme 2. Proposed structures for the Twitchell reagents **1** and **2**, prepared from benzene or phenol, respectively.

ports[11] utilized oleic acid, an aromatic hydrocarbon (benzene or naphthalene) and sulphuric acid, later procedures broadened the scope of the reaction making use of different aromatic rings (xylenes, phenol),[14] or changing the oleic acid for triglycerides, petroleum derivatives or butanol.[15] These reagents were commercialized under several different names such as Pfeilring, Neokontakt, Idrapid and Divuslon, but nowadays they cannot be purchased any more.

Therefore, to test the efficiency of these lipophilic acid catalysts in the biodiesel preparation, we have synthesized two Twitchell reagents, **1** and **2**, starting from olive oil (due to its high content in oleic acid), benzene or phenol and sulphuric acid. An excess of the aromatic compounds was used to prevent dialkylation of these rings. But even in this case, Twitchell reagents turn out to be complex mixtures of compounds, due to rearrangement of the oleic acid alkyl chains and different substitution patterns in the aromatic rings. Nevertheless, the aromatic portions of both Twitchell reagents **1** and **2** can be easily recognized in the ^{1}H NMR spectra (see Supporting Information), and are in agreement with the structures shown in Scheme 2.

Catalytic Activity of Twitchell Reagents

The catalytic properties of reagents **1** and **2** were tested in the transesterification of commercial sunflower seed oil, and compared with those of sulphuric acid. In a typical reaction, methanol (6 mmol) and triglyceride (1 mmol) were reacted at 60 °C and in the presence of 1 wt% sulphuric acid or the same molar amounts of Twitchell reagents **1** and **2**. The conversion of the transesterification reaction was determined by ^{1}H NMR spectroscopy (see Supporting Information).

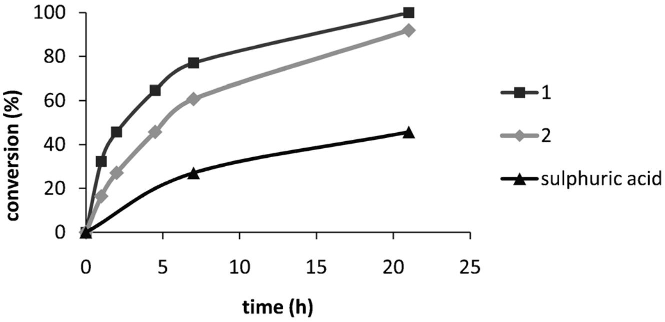


Figure 2. Sunflower seed oil transesterification with 1 wt% sulphuric acid and the same molar amounts of Twitchell reagents **1** and **2**. The molar ratio methanol to triglyceride was kept at 6/1 and the temperature at 60 °C.

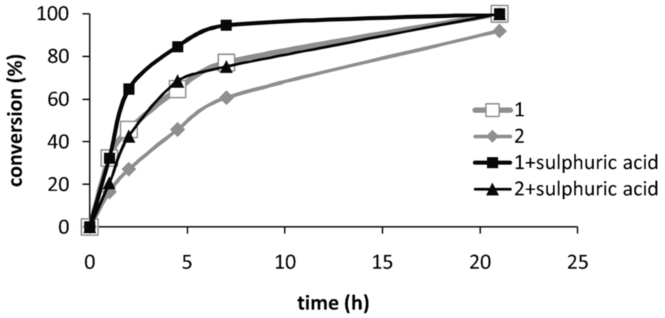


Figure 3. Sunflower seed oil transesterification with Twitchell reagents **1** and **2**, in the presence and absence of 1 wt% sulphuric acid. The molar ratio methanol to triglyceride was kept at 6/1 and the temperature at 60 °C.

Results are shown in Figure 2. The hydrophilic sulphuric acid showed a very small catalytic activity, while the catalyst **1** derived from benzene provided the best results. The phenolic group in catalyst **2**, which increases the hydrophilicity, yielded slower reaction rates.

It is well established that one of the reasons for a loss of catalytic activity of Twitchell reagents in fat hydrolysis reactions is their partition between water and the oil phase; as much as 45% of the catalyst can remain in the water phase.[14] If an unfavourable partition constant reduces the reaction rate, a simple way to improve the catalytic properties of Twitchell reagents is to add a small amount of sulphuric acid to the water phase. The presence of this strong acid decreases the dissociation of sulphonic acid, raising the Twitchell reagent concentration in the apolar phase.[14a,16]

Partition between methanol and the triglyceride can be even less favourable than with water, therefore we tested the effect of added sulphuric acid to the reaction. As shown in Figure 3, the catalytic properties of both Twitchell reagents **1** and **2** improved in the presence of 1 wt% sulphuric acid, when tested under the previous conditions.

The use of sulphuric acid as a co-catalyst has, however, several drawbacks. (i) Sulphuric acid is a sulphonating and dehydrating compound which can transform glycerine into acrolein.[17] (ii) Separation of the sulphuric acid from the polar phase will increase the cost of the transesterification process. (iii) Sulphuric acid is a corrosive reagent to the equipment.

Since the major role of sulphuric acid is only to improve the partition constant of the catalyst towards the apolar phase, it should not be necessary in the presence of a highly lipophilic catalyst with a more favourable partition coefficient to the triglyceride phase.

Lipophilic Sulphonic Acids

To test this hypothesis catalyst **3** was prepared using a known procedure (Figure 4).[18] Since it lacks the hydrophilic carboxylic group, it should be more lipophilic than the previous Twitchell reagents **1** and **2** (Figure 5).

Catalyst **3** was tested under the same previous conditions, showing improved results with respect to the Twitchell reagents **1** and **2**, in both the presence and absence of sulphuric acid.

To confirm the relevance of the catalyst lipophilicity, the partition constant between sunflower seed oil and methanol was studied by ^{1}H NMR. Integration of the catalyst signals in deuterated methanol, before and after partition with the oily phase, allowed the determination of the constant. As shown in Table 1 (entry 1), catalyst **3** still prefers the methanolic phase, and therefore more lipophilic catalysts could improve the catalytic results.

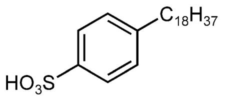


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Figure 4. Structure of catalyst **3**.

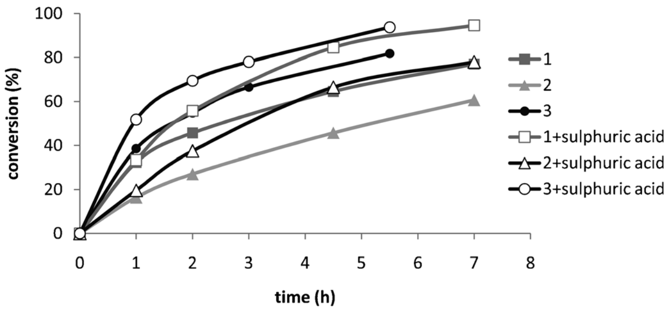


Figure 5. Sunflower seed oil transesterification with Twitchell reagents **1** and **2** and catalyst **3**, in the presence and absence of 1 wt% sulphuric acid. The molar ratio methanol to triglyceride was kept at 6/1 and the temperature at 60 °C.

Table 1. Partition constants between methanol and sunflower seed oil calculated by integration of ^{1}H NMR signals.

Entry	Catalyst	Partition constant
1	**3**	9/1
2	**4**	1/1
3	**4**	6/4[a]
4	**5**	2/98[b]

[a] MeOD with 10% v/v D_2O.

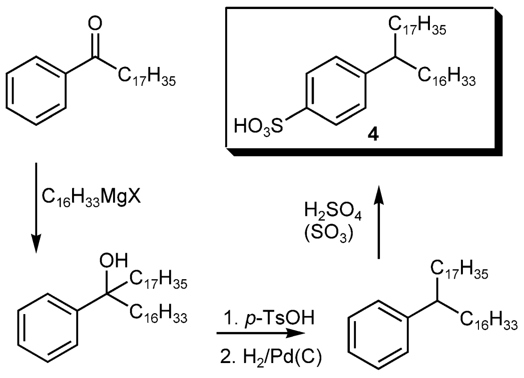
[b] Estimated.

A new catalyst, **4**, comprising an aliphatic 34-carbon atom chain, was designed and synthesized (Scheme 3).

Catalyst **4** showed a suitable partition constant (Table 1, entry 2) with similar affinity for both phases methanol and oil. Taking into account the small methanol volume under the reaction conditions, most of the catalyst should stay in the oil. The catalytic properties of this lipophilic catalyst **4** are displayed in Figure 6. In agreement with its enhanced partition constant, compound **4** shows a higher catalytic activity and the effect of the addition of sulphuric acid is less pronounced than in the previous catalysts.

Finally, an even more lipophilic catalyst **5** was prepared starting from isophthalic acid dimethyl ester as shown in Scheme 4.

Catalyst **5** turned out to be a crystalline compound with a low solubility in methanol but with a favourable partition constant in the triglyceride (Table 1, entry 4). Accordingly, this new catalyst **5** further increased the reaction rate with respect to catalyst **4**, affording similar results to those obtained when catalyst **4** was combined with sulphuric acid. Moreover, the addition of sulphuric acid to catalyst **5** led to no im-



Scheme 3. Synthesis of catalyst **4**.

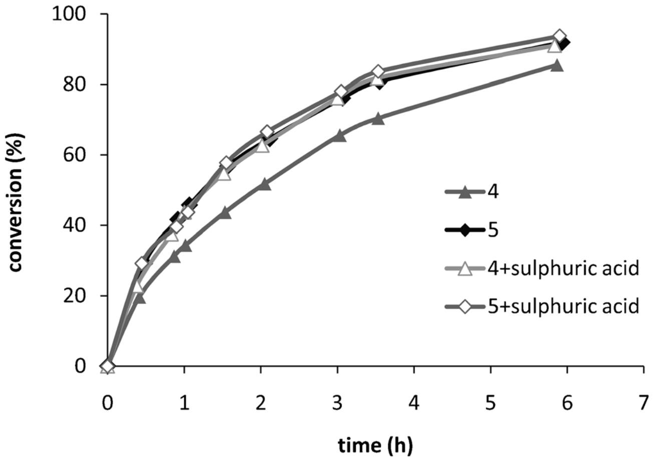
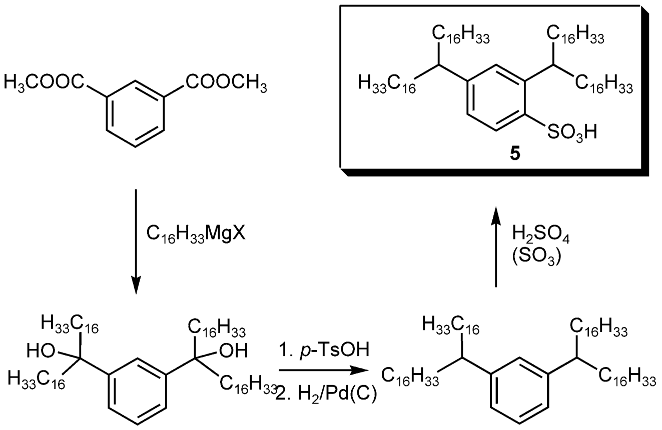


Figure 6. Sunflower seed oil transesterification with catalysts **4** and **5**, in the presence and absence of 1 wt% sulphuric acid. The molar ratio methanol to triglyceride was kept at 6/1 and the temperature at 60 °C.



Scheme 4. Synthesis of catalyst **5**.

provement, which may indicate that no further reaction rate increase will be achieved by increasing the lipophilicity of the catalyst.

Since catalysts **4** and **5** showed the best performance, both of them were selected to study the influence of different factors in the transesterification reaction.

Influence of the Free Fatty Acids Content of Oil

As already pointed out, the presence of free fatty acids (FFA) makes the conventional alkaline transesterification inappropriate.[19] However, this inconvenience could be overcome by using acid catalysts like **4** and **5**. The effect of FFA content in the reaction rate was investigated.

Figure 7 shows the influence of 5, 10, 20%, w/w of stearic acid added to the sunflower seed oil. Even high free fatty acid contents have little influence on the reaction rate, despite the generation of a certain amount of water due to the esterification of the free carboxylic acids.

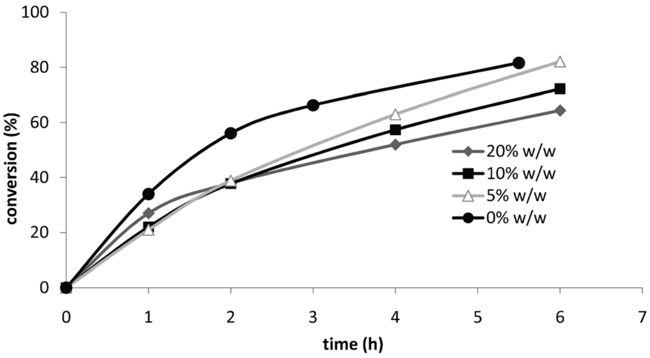


Figure 7. Sunflower seed oil transesterification with catalyst **4**, in the presence of oil containing 5, 10, 20% (w/w) of stearic acid. The molar ratio methanol to triglyceride was kept at 6/1 and the temperature at 60 °C (FAME integral was used to measure the conversion).

Influence of the Water Content

The presence of water in the reaction mixture slightly reduces the yield and the reaction rate. This effect has been studied for catalysts **4** and **5** with 5, 10, 20% (v/v) water in the methanol phase (see Supporting Information). These results can be explained due to a change in the partition constant between the methanol and triglyceride phases. In the presence of water, the partition constant for catalyst **4** increases from 1/1 to 6/4 (Table 1, entries 2 and 3) which now favours the methanolic phase. Since a smaller amount of the catalyst is now present in the oily phase, a lower reaction rate is expected. On the other hand, this effect is smaller in the case of the more lipophilic catalyst **5**, which prefers the oily phase, and therefore a smaller effect from water is expected (Figure 8). Since these catalysts are not water soluble, the effect of water in the partition constant is somehow surprising, but it can be explained due to the basicity of the water molecule which probably favours the ionization of the sulphonic acid in the methanolic phase, at least if a relatively small of water is used. In any case, the effect of water in this reaction is relatively small.

Influence of the Methanol/Triglyceride Molar Ratio

The effect of a very small excess of methanol was also analysed with catalyst **4**. Working with a molar ratio methanol to triglyceride of only 3.5/1, rendered reactions which are faster at the beginning. This fact is in agreement with a larger amount of the catalyst in the

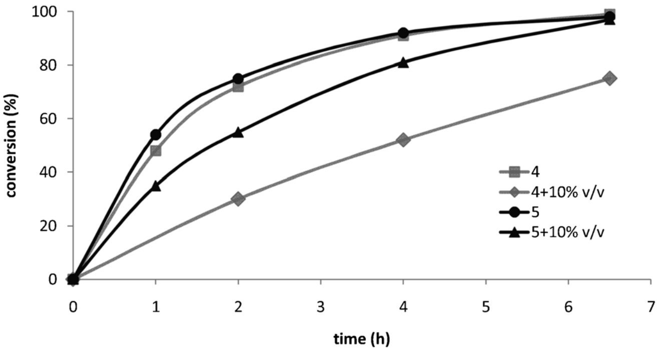


Figure 8. Sunflower seed oil transesterification with catalysts **4** and **5**, in the presence of methanol containing 0, 10% (v/v) of water. The molar ratio methanol to triglyceride was kept at 6/1 and the temperature at 60 °C.

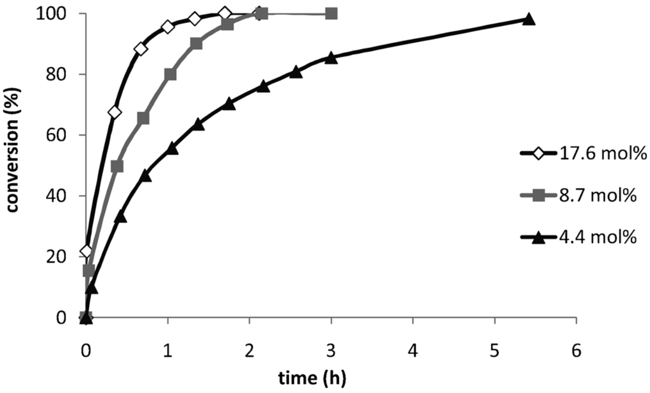


Figure 10. Jatropha seed oil transesterification with 4.40, 8.70 and 17.60 mol% catalyst **5**. The molar ratio methanol to triglyceride was kept at 6/1 and the temperature at 80 °C.

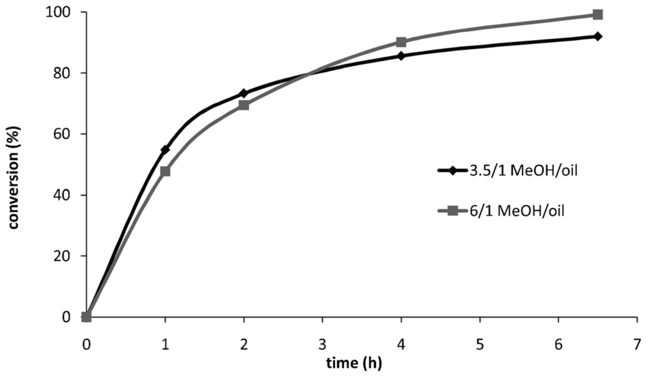


Figure 9. Sunflower seed oil transesterification with catalyst **4** and molar ratios methanol to triglyceride of 3.5/1 and 6/1.The temperature was kept at 60 °C.

apolar phase. Nevertheless, as the reaction proceeds and most of the methanol is consumed, the reaction rate is reduced (Figure 9).

Influence of the Catalyst Amount

The amount of catalyst was also tested as depicted in Figure 10. Within the range of concentrations studied, the reaction rate increased linearly with the catalyst concentration. This is interesting since it is well known that in hydrolysis reactions with Twitchell reagents, there is a saturation effect when the catalyst is around 1% w/w.[16]

The molar ratio methanol to triglyceride was kept at 6/1 and the temperature at 80 °C.

Influence of the Temperature

Higher temperatures also provide better reaction rates, yielding short reaction times. Working at 80 °C with catalyst **5**, the reaction is practically finished after only 90 min (Figure 10).

It is also possible to work at room temperature with longer reaction times. Catalyst **5**, due to its low solubility led to non-practical procedures, however, large conversions after 3 days were obtained with catalyst **3** (78%) and **4** (97%).

Jatropha Oil as Biofuel Source

To illustrate that indeed these catalysts are promising in the preparation of biodiesel from low cost raw materials, jatropha oil was used. As can be seen in Figure 11, the results found in this case are quite similar to those reported for the sunflower seed oil previously studied.

Catalyst Recovery

In biodiesel production technologies the recovery of the catalyst can be an important factor due to the fol-

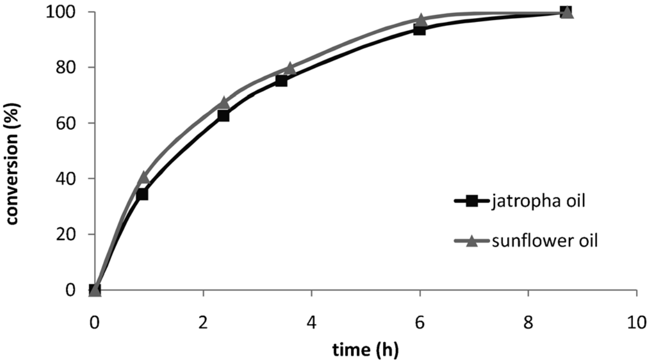


Figure 11. Jatropha oil and sunflower seed oil transesterification catalysed by compound **5**. The molar ratio methanol to triglyceride was kept at 6/1 and the temperature at 60 °C.

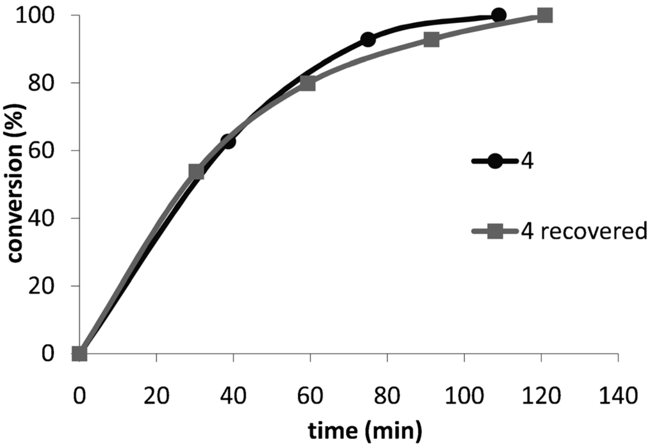


Figure 12. Sunflower seed oil transesterification catalysed by 18.5 ol% of compound **4** and catalyst **4** recovered. The molar ratio methanol to triglyceride was kept at 6/1 and the temperature at 80 °C.

lowing reasons. (i) Sulphonic acid catalyst is corrosive and may damage the fuel deposit or the engine. (ii) A maximum amount of sulphur has been established in the diesel contents.[20] (iii) The content of acid in biodiesel (acid number) has been stipulated to a maximum value of 0.50 mg KOH per g biodiesel.[21] (iv) The cost of the catalyst makes its recovery important for a cost-efficient procedure.

Separation of catalyst **4** from the biodiesel was achieved by adsorption of the catalyst on a silica gel column. Once the reaction was finished, the glycerine was separated from the crude biodiesel through decantation. Methanol was distilled from the biodiesel phase and the remaining liquid was passed through a short silica gel column The highly polar sulphonic acid protonated the basic stationary phase groups, and stayed in the adsorbent, while the fatty acid methyl esters were eluted from the column. Ten grams of silica per gram of catalyst were enough to provide a clean catalyst separation. FAMEs can be eluted with petroleum ether from the column, but in this case, the solvent has to be distilled before biodiesel commercialization. Alternatively, since biodiesel is sold as a blend with diesel fuel, this last compound can be used to elute the biodiesel yielding directly the desired commercial fuel. Finally, elution with methanol allowed recovery of the catalyst, which showed the same activity as the initial catalyst **4** (Figure 12).

Acid Content in the Biodiesel

Although crude biodiesel phase reacted strongly with methyl orange, after adsorption on silica gel, this reaction completely disappeared, showing no mineral or sulphonic acids in the biodiesel.

Determination of the acid content in biodiesel was performed following the procedure described in UNE-EN 14104,[22] affording an acid number of 0.16 mg KOH/g, a value that complies with the requirements of both ASTM D 6751 and EN 14214. On the other hand, the acid number for the triglyceride source, the jatropha oil, proved to be 5.33–5.86 mg KOH/g.

Conclusions

Lipophilic sulphonic acids such as **4** and **5**, have proven to be an alternative for biodiesel manufacture. Because triglyceride transesterification with methanol is a biphasic reaction which can take place in both phases, lipophilic sulphonic acids will strongly catalyse this reaction in the oil phase since their partition constant favours the triglyceride phase. This allows one to work at temperatures below the boiling point of methanol and in reasonable reaction times.

A correlation between the partition constant and the catalytic efficiency is also observed.

When sulphuric acid is used as co-catalyst, only those sulphonic acids with more favourable partition into the polar phase improve their catalytic properties; on the other hand, addition of sulphuric acid has no influence on reaction rates when more lipophilic sulphonic acids are used.

Under these reaction conditions, neither free fatty acids nor small amounts of water change significantly the reaction rates; nevertheless, large amounts of water reduce the reaction rate in the case of the less lipophilic catalysts.

Although most of the experiments have been carried out with refined sunflower seed oil, low cost raw materials as jatropha oil show under these conditions the same behaviour.

Increasing the temperature (from 60 °C to 80 °C) and the amount of the catalyst speed up the reaction rates.

Catalyst recovery can be accomplished by adsorption of the crude FAMEs on silica; elution with methanol allows one to get a mixture of the catalysts, monoglycerides, diglycerides and the fatty acid methyl esters, which can be used as catalyst for the next batch.

Finally, the acid content in the obtained biodiesel is further below the limit of 0.5 mg g $^{-1}$ stipulated by the ASTM D 6751 and EN 14214 although the triglyceride source presents a high FFA content.

Experimental Section

Materials and Instrumentation

IR spectra were recorded with a Nicolet IR100. ^{1}H and ^{13}C NMR spectra were recorded at room temperature with Bruker model WP-200-SY, Varian model Mercury VS 2000, or Bruker Advance DRX spectrometers in deuterated chloroform (unless otherwise stated). J values are reported in Hertz and chemical shifts in ppm with the solvent signal as internal standard. Mass spectra were recorded on a Bruker ultraflex III spectrometer. Melting points were determined using a Leica Galen III microscope. Analytical thin layer chromatography was performed using pre-coated aluminium-backed plates and visualized by UV. For column chromatography silica gel (70–200 μm) was used.

Reagents were purchased and used without further purification unless otherwise noted. Refined sunflower seed oil was purchased from Aceites Coosur, S. A., Vilches (Jaén, Spain). Jatropha oil was gently provided by Miguel Cobo (Biotel).

General Procedure for the Transesterification Reaction

Methanol (0.67 mL, 16.68 mmol) and triglyceride (2.5 g, 2.78 mmol) were reacted in the presence of catalyst in a glass tube equipped with a screw cap with septum and magnetic stirring. The temperature of the sample was kept constant with a thermostat bath. The progress of the reaction was monitored by ^{1}H NMR analysis of aliquots. The initial biphasic reaction may turn homogeneous (15 min at 80 °C). Close to the end of the reaction, glycerine decantation provides a biphasic reaction mixture again (45 min at 80 °C). The conversion was measured by integration of the glycerine triglyceride signals or from the methyl ester signal of the fatty acids (see Supporting Information).

Determination of Partition Constant

A reference ^{1}H NMR spectrum of the catalyst **3** (20 mg, 48.7 μmol) in deuteromethanol (0.5 mL) was taken, and the signals of the catalyst were integrated against the solvent methyl protons. After extraction with the triglyceride (1.0 mL), a new ^{1}H NMR spectrum was run and integrated yielding the new catalyst concentration in the methanolic phase, from which the partition constant was calculated.

For catalysts **4** and **5** the procedure was similar, only changing the volume of triglyceride from 1.0 mL to 0.5 mL.

Recovery of the Catalyst

In a typical transesterification experiment [triglyceride (16.0 g) and catalyst **4** (1.0 g)], glycerine and methanol were removed by decantation and distillation, respectively. Crude biodiesel (17.0 g) was dissolved in petroleum ether or diesel fuel (32 mL). This solution was allowed to pass through a silica gel column (10.0 g) and eluted with petroleum ether or diesel fuel (32 mL) to yield FAME (14 g). Finally, methanol (32 mL) was added to the column affording a mixture of catalyst (0.9 g), FAME (1.4 g), diglycerides and monoglycerides (0.7 g), which were used in the next batch after methanol distillation.

Materials

4-(Tetratriacontan-17-yl)benzenesulphonic acid (4): A solution of 1-phenyloctadecan-1-one[18] (26.5 g, 77 mmol) in diethyl ether (100 mL) was added dropwise to a Grignard reagent prepared from a mixture of 1-iodohexadecane (2.0 g, 5.7 mmol) and 1-chlorohexadecane (27.6 g, 106 mmol) with magnesium turnings (7.5 g) and a small crystal of iodine in ether (80 mL). After the addition, the reaction was stirred at room temperature for 12 h. Then the mixture was poured onto ice and acidified with 2 M hydrochloric acid. The aqueous phase was discarded, the organic layer dried over Na_2SO_4 and the solvent evaporated to dryness. The residue was purified by column chromatography on silica gel with dichloromethane as the eluent, yielding the corresponding alcohol, 17-phenyltetratriacontan-17-ol, as a white solid; yield: 37.4 g (85%).

The above alcohol (13.7 g, 24 mmol) and a catalytic amount of p-toluenesulphonic acid (162 mg, 0.94 mmol) were refluxed in toluene (280 mL) until no further water appeared. The mixture was washed with aqueous $NaHCO_3$ and the toluene was evaporated under reduced pressure. The crude residue was purified by column chromatography with hexane as eluent to afford the dehydrated compound; yield: 11.0 g (83%).

This unsaturated compound (11.0 g, 19.9 mmol) was dissolved in ethanol (40 mL) and hydrogenated (4 bar) in the presence of Pd/C (5%) (450 mg) at room temperature. After 12 h the catalyst was filtered and the solvent was removed. Silica gel percolation with hexane furnished the expected saturated hydrocarbon, tetratriacontan-17-ylbenzene; yield: 9.40 g (85%).

Finally, fuming sulphuric acid (20% SO_3, 6.8 g) was added to a solution of tetratriacontan-17-ylbenzene (9.40 g, 17 mmol) in dry CH_2Cl_2 (100 mL). After stirring for 5 min, ^{1}H NMR analysis of an aliquota revealed that the reaction had finished. Ice was then added to the reaction mixture and the layers were separated. The organic layer was dried over cellulose and the solvent removed under reduced pressure to afford the desired compound **4**, as a white solid; yield: 10.5 g (98%); mp 33–35 °C. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.74$ (d, $J = 8.0$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 2.50 (m, 1H), 1.50 (m, 4H), 1.25 (br s, 58H), 0.88 (t, $J = 6.6$ Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 151.1$, 138.7, 128.2, 126.3, 46.3, 36.9, 32.2, 30.0, 29.8, 29.6, 27.8, 22.9, 14.3; IR (film): $\nu = 3409$, 2916, 2851, 1735, 1469, 1378, 1150, 1041, 1002 cm^{-1}; HR-MS: $m/z = 679.5065$, calcd. for $C_{40}H_{73}Na_2O_3S$ $[M-H+Na]+Na^+$: 679.5070.

2,4-Di(tritriacontan-17-yl)benzenesulphonic acid (5): A solution of dimethyl isophthalate (3.9 g, 20.2 mmol) in diethyl ether (30 mL) was added dropwise to a Grignard reagent prepared from a mixture of 1-iodohexadecane (2.1 g, 6 mmol) and 1-chlorohexadecane (28.4 g, 109 mmol) with magnesium turnings (8.0 g) and a small crystal of iodine in ether (80 mL). After the addition, the resulting mixture was allowed to react at room temperature for 12 h. The reaction mixture was worked up in the same way as for the preparation of catalyst **4**, yielding the corresponding diol, 17,17′-(1,3-phenylene)ditritriacontan-17-ol, yield: 19.0 g (89%). The diol (17.0 g, 16.5 mmol) was dehydrated with p-toluensulphonic acid in refluxing toluene following the same procedure as described previously, affording the unsaturated hydrocarbon; yield: 16.0 g (96%). Hydrogenation of this compound (7.0 g, 7.0 mmol) was carried out in THF (40 mL) under 4 bar of hydrogen pressure at 40 °C with Pd/C (5%) (500 mg) in 12 h. The catalyst was removed by filtration, the solvent evaporated and the residue purified by percolation through silica gel (hexane as eluent) to yield the saturated hydrocarbon, 1,3-di(tritriacontan-17-yl)benzene; yield: 6.1 g (86%). The sulphonation of this compound (6.1 g, 6 mmol) was carried out under the same conditions previously described for catalyst **4**, to afford the expected compound as a white solid; yield: 6.2 g (96%); mp 79–80 °C. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.85$ (d, $J = 8.4$ Hz, 2H), 7.14 (s, 1H), 7.00 (d, $J = 8.4$ Hz, 2H), 2.51 (m, 2H), 1.60 (m, 8H), 1.25 (br s, 112H), 0.88 (t, $J = 6.4$ Hz, 12H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 151.8$, 146.5, 135.7, 128.2, 127.7, 124.9, 50.9, 46.2, 40.6, 37.1, 36.9, 32.2, 30.4, 30.0, 29.9, 29.6, 27.8, 27.6, 22.9, 14.3; IR (film): $\nu = 3403$, 2916, 2365, 1599, 1456, 1378, 1314, 1164, 1074, 1002, 892, 710 cm^{-1}; HR-MS: $m/z = 1128.0108$, calcd. for $C_{72}H_{138}O_3S$ $[M-H+Na]+Na^+$: 1128.0078.

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