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Shift of Multiple Incompatible Equilibriums by a Combination of Heterogeneous Catalysis and Membranes

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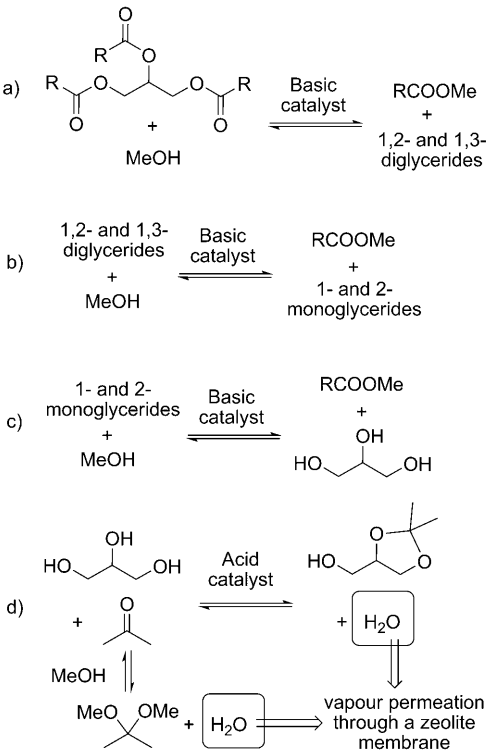
Dedicated to Professor Pelayo Camps on the occasion of his 65th birthday

Many organic reactions are equilibriums, in which a large excess of one reagent is required to shift them to completion. One example of industrial interest is biodiesel production by the base-catalyzed transesterification of triglycerides.[1] This reaction consists of a sequence of three equilibriums (Scheme 1a–c) with low equilibrium constants,[2] which makes it necessary to use a large excess of methanol. One alternative would be the use of the modern technology of membrane systems[3] to eliminate the concomitant product from the reaction mixture, in this case glycerol. However, to the best of our knowledge, the separation of glycerol in an excess of methanol would not be possible with any type of membrane. Given the very high efficiency of some membranes to eliminate water[4] they have been used in reactions, such as esterification,[5] in which water is the concomitant product. Therefore a possible way to use membranes in biodiesel production could be by the addition of another equilibrium reaction to the series and, thereby, transforming glycerol into a new, valuable product with water as the only byproduct.

Solketal (2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane) is a simple glycerol derivative with multiple applications.[6] Similar to the transesterification reaction, the acetalization equilibrium for the formation of solketal (Scheme 1d) is also disfavored, and the use of an excess of acetone is needed. The combination of both types of reaction would require the simultaneous presence of a base and an acid in the reaction medium. The concept of sequential reactions involving mutually destructive reagents, the so-called "wolf and lamb" reactions,[7] was demonstrated with the use of polymer-supported reagents, that otherwise would react rapidly with each other in solution. In fact, site isolation is also one of the paradigms of heterogeneous catalysis and it has been proposed as the basis for the separation of mutually destructive catalysts, such as acids and bases. The combination of



Scheme 1. Integrated process of biodiesel and solketal production.

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two heterogeneous catalysts in the same reactor allows one-pot, multistep synthetic routes to be performed, by the isolation of reaction sites in the particles of the two solids.[8] The same effect has been reproduced in solution by using star polymers with highly branched, non-interpenetrating catalytic cores.[9] This methodology should constitute a powerful tool in applied chemistry, allowing extremely complex chemical transformations to take place in a cleaner and more efficient one-pot process.

An integrated biodiesel–solketal process (Scheme 1) would consist of three heterogeneous base-catalyzed transesterifications ("wolf" reactions), and one heterogeneous acid-catalyzed acetalization[10] ("lamb" reaction) promoted by the removal of water through a membrane.[11] In this way, not only would glycerol be directly converted into a valuable and easily distillable product (b.p. 188 °C vs. b.p. of glycerol 182 °C/20 mmHg), but this second equilibrium, shifted by the membrane, should also shift the first equilibrium, improving the yield of the transesterification reaction and hence the global efficiency of the process. Herein, we demonstrate the feasibility of this type of integrated process.

Nafion NR-50 was chosen as the acid catalyst, and 1,5,7-triazabicyclo[4.4.0]dec-5-ene bound to polystyrene (TBD–PS) as the basic catalyst. In a first approach, the methanol/oil molar ratio was set to 30:1 and the acetone/glycerol molar ratio to 20:1, based on the theoretical amount of glycerol obtained at total conversion of oil. The reaction in the presence of only an acid catalyst does not proceed at all under mild conditions, whereas the presence of only a basic catalyst produces high yields of fatty acid methyl esters (FAME), but not solketal, thus, demonstrating the need for both catalysts. The presence of both solvents, methanol and acetone, from the beginning of the reaction is detrimental to the kinetics of FAME formation, since 2,2-dimethoxypropane (up to 5.5% yield) and aldol condensation products (diacetone alcohol and mesityl oxide, up to 1.8% yield) are obtained as a result of the acetalization of acetone with methanol in the presence of the acid catalyst and aldol self-condensation of acetone in the presence of the basic catalyst, respectively. A more efficient method is to add acetone when the transesterification equilibrium is reached, leading to an 80% yield of methyl esters and 77% yield of solketal (calculated with respect to the maximum theoretical amount) at the equilibrium point (Figure 1a). Interestingly, the amount of di- and monoglycerides obtained is very low,[12] resulting in a parallel increase of both FAME and solketal yields. This effect had already been observed in the case of transesterification with sodium methoxide.[13] The use of a membrane should then be effective even at low oil conversion, due to the presence of a significant amount of glycerol from the beginning of the reaction.

One zeolite A membrane,[11] grown on the external surface of a cylindrical α-alumina support, was used to selectively remove water from the reaction mixture. Selectivity tests were carried out by pervaporation, by using a mixture of water and an organic solvent, 10:90 (w/w) at 110 °C. Under such conditions a water flux of 150 $g\,h^{-1}\,m^{-2}$ and sep-

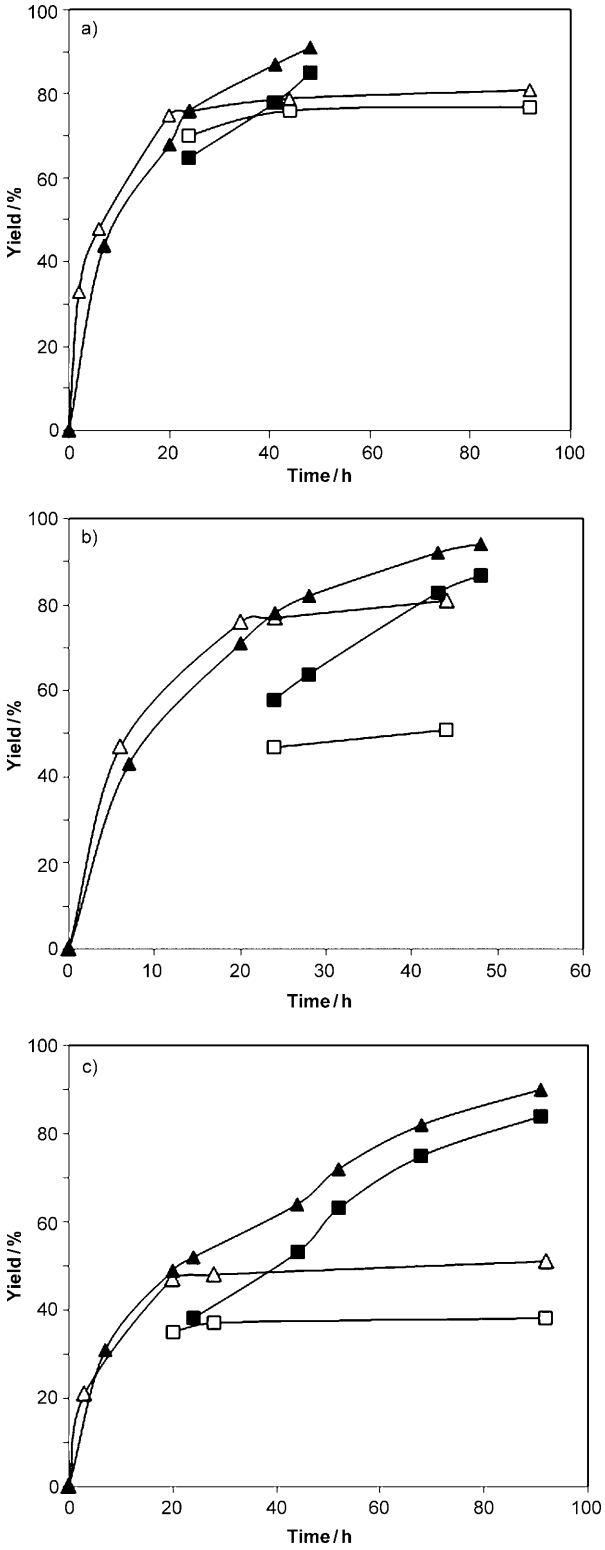

Figure 1. Yields of fatty acid methyl esters (triangles) and solketal (squares) with (filled symbols) and without (empty symbols) membrane. Reaction conditions: a) methanol/oil 30:1; acetone/glycerol 20:1; b) methanol/oil 30:1; acetone/glycerol 5:1; c) methanol/oil 15:1; acetone/glycerol 5:1. In all cases the addition of acetone occurred and pumping began after 20 h.

aration factors of 250 for water/acetone and 450 for water/ethanol mixtures were obtained. Under the reaction conditions, water was removed by vapor permeation in a system depicted in Figure 2, without contact between the membrane and the reaction mixture to prevent any damage to the membrane by contact with the stirred particles of both catalysts. A clear membrane effect was observed with a large excess of methanol and acetone, reaching yields of 91% for FAME and 85% for solketal (Figure 1a), with a water permeation result of 7.9 $g\,h^{-1}\,m^{-2}$ after 48 h. The selectivity for water versus acetone and methanol was very high as evidenced by the high molar fraction of water that permeated (0.77–0.82) in spite of the very low molar fraction in the reaction medium (<0.034, the maximum value at total conversion with a low excess of organic solvent). As a side effect, the final yield of 2,2-dimethoxypropane was increased to 5.9%, but the yield of the aldol condensation products was reduced to 0.7%.

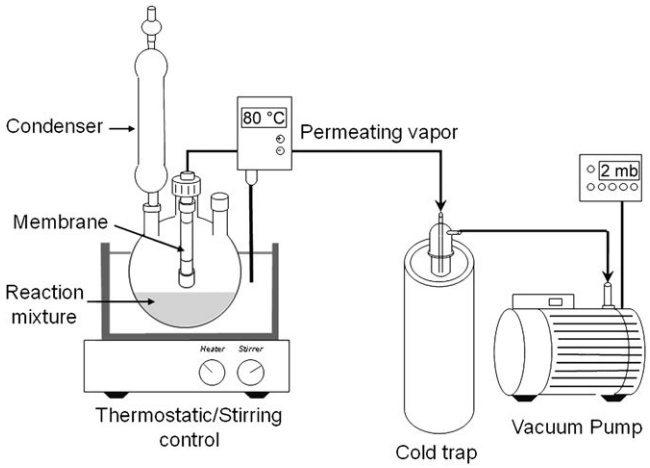

Figure 2. Experimental system for the combined incompatible equilibriums and membrane system ("wolf and lamb" system).

However, the most interesting feature of this strategy is the possibility of reducing the excess of reagents needed. In fact, because the membrane shifts the last equilibrium, it should be straightforward to lower the excess of acetone used. Therefore, in the subsequent test the excess was reduced from 20/1 to 5/1. In contrast to the system without a membrane, in which only a 51% yield of solketal is obtained together with 81% of FAME, the use of a membrane results in a 94% yield of FAME and an 87% yield of solketal (Figure 1b). The water permeation under such conditions is the same as before (8.0 $g\,h^{-1}\,m^{-2}$) and the separation factor remained the same.

Taking into account that the main products of transesterification are glycerol and FAME, instead of di- and monoglycerides, it should be possible to shift the first three equilibriums, even at low triglyceride conversion, with a lower excess of methanol. In fact, in the absence of a membrane, a reduction of the methanol/oil ratio to 15:1 and the acetone/glycerol ratio to 5:1 leads to only a 50% yield of FAME and a 38% yield of solketal, whereas the use of a membrane increases those yields up to values close to those obtained with a larger excess of solvents, that is, a 90% yield of FAME and an 84% yield of solketal (Figure 1c). An additional advantage of the use of less methanol and acetone is that the amount of byproducts formed is also reduced to one third, resulting in a cleaner, integrated procedure. Moreover, the reduction in volume of the reaction mixture enabled a scale-up of the system, with the same membrane obtaining the same results. In fact, the system would be amenable to a further increase in scale, since the membrane is working far below its maximum water flux capacity.

These results demonstrate the possibility of combining two heterogeneous catalysts to promote "wolf and lamb" reactions, with the use of membranes to shift the sequential equilibriums, even in complex systems. The coupling of a final equilibrium, the concomitant product of which is water, can expand the applicability of any type of hydrophilic membrane, including zeolitic ones.

Experimental Section

The experimental system is represented in Figure 2. A mixture of sunflower oil (16 g), Nafion NR-50 (160 mg), TBD–PS (880 mg), 4-ethylanisole (internal standard), and methanol (28 mL; methanol/oil 30:1) was stirred and heated under reflux for 20 h. Acetone (26 mL; theoretical acetone/glycerol 20:1) was added and subsequently the permeate was collected in a liquid-nitrogen-cooled glass condenser, while a vacuum pump was used to maintain the vacuum level (2 mbar). The reaction mixture was monitored and the permeate was analyzed by GC.

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