Effect of water and lipophilic alcohols or amines on the 4-dodecylbenzenesulfonic acid-catalyzed esterifications, trans- esterifications, and amidations

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4-Dodecylbenzenesulfonic acid (DBSA) was employed in the esterification of oleic acid (OA) and the *trans*-esterification of oleic oil (OO) with 1-butanol as alcohol in the presence of various degrees of excess water. Under these conditions DBSA was found to be a highly active esterification catalyst regardless of excess water content, but was found to be a less effective for *trans*-esterification reactions. Lipophilic alcohols of differing straight and branched C3-6 chains were also tested on mixtures of OA/water (1:1) in DBSA-catalyzed esterifications; OO/water (1:1) in *trans*-esterifications; and OA/OO/water (1:1:1) in simultaneous esterifications and *trans*-esterifications. While longer straight chain alcohols generally gave a two-fold increase in yield of their corresponding alkyl oleates to 80%+, we observed a doubling from 30–50% to 60–95% of alkyl oleate yield for the OO/OA/water mixture. DBSA-catalyzed amidations of OO and methyl oleate emulsions in water were conducted with 1-butyl and 1-heptyl amine where it was found that the more lipophilic the ester moiety the higher the yield of alkyl amide.

Practical applications: The practical advantages of DBSA as catalyst are high conversions to the desired product along with its tolerance to high quantities of water, emulsified within the lipid material. A capacity to transform a range of substrates with varying lipophilic character in a range of condensation reactions. In addition, we demonstrate that esterification and *trans*-esterification reactions could be performed simultaneous and in the presence of high quantities of water. This is of direct interest to the transformation of waste sources of lipids that often contain a mixture of triglycerides and free fatty acids in various concentrations, emulsified with waste water. Furthermore, we demonstrate that all of the value-added products/co-products can be separated by an effective and industrially relevant methodology, including recovery of the DBSA catalyst as well as the water and water soluble co-products, such as glycerol.

Keywords: amidation / DBSA / esterification / lipophilic / *trans*-esterification

DOI: 10.1002/ejlt.201600483

1 Introduction

Performing catalytic dehydrative condensation reactions in the presence of water is a demanding challenge as the reaction is forced to go against Le Chatelier's Principle (Scheme 1) [1]. This is because by increasing the concentration of water in the reaction mixture the equilibrium constant is shifted in favor of the starting materials.

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Kobayashi et al. were the first in 2001 to demonstrate the use of 4-dodecylbenzenesulfonic acid (DBSA) to act as an acid catalyst in dehydrative esterifications of carboxylic acids using water as solvent [2, 3]. Their results were followed by other reports using similar catalysts capable of working in biphasic or emulsified media, which worked on a similar principle of creating an isolated hydrophobic environment in which the reagents would condense and the produced water molecule would be expulsed upon production [4–6]. Within this field surfactant (micellar) catalysts are of particular interest [7, 8] as due to their hydrophobic tail and hydrophilic head they are able to either: Form micelles that create isolated hydrophobic environments in which organic reagents can react within an aqueous media [2, 3, 9–12], or form reverse

$$[RCO_2H] + [R'OH] \rightleftharpoons [RCO_2R'] + [H_2O]$$

Scheme 1. Le chatelier's principle in relation to the reaction equilibrium when performing esterifications in water.

micelles that trap the water released from the condensation reaction in hydrophilic pockets, separate from the organic phase of the reaction mixture [13, 14]. In many of these cases, however, the catalytic dehydrative esterifications performed in water were conducted with long-chain hydrophobic carboxylic acids and long-chain, equally hydrophobic, alcohols [2–4]. In reports where short chain hydrophilic alcohols (methanol or ethanol) were used, the ester production is dramatically reduced [3, 15], except where the reactions are performed neat, and the surfactant catalysts act as a trap for the water produced from the reaction, without the need for an azotrope distillation apparatus [14].

As early as 1999, we had demonstrated the ability of DBSA to act as a highly efficient catalyst for the partial esterification of oleic acid (OA) and glycerol [16, 17]. In light of this, and our recent development of a catalytic process for the recovery and transformation of slaughterhouse animal fatty wastewater sludge into fatty acid butyl esters (FABE) as potential biofuels, using 1-butanol as alcohol and DBSA as catalyst [18, 19], we were interested to further investigate the effect of hydrophilic substrates upon DBSA-catalyzed reactions in the presence of water. Recent reports in the literature have suggested that the fatty acid esters of short (C_{2-4}), straight or branched chain alcohols have potential as possible biofuels, exhibiting similar properties to those of fatty acid methyl esters (biodiesel) in engine tests [20, 21]. We present here our results on the effect of different concentrations of water upon the DBSA-catalyzed esterification and *trans*-esterification with 1-butanol. In addition, we have investigated the substrate scope of the DBSA catalyst by varying the lipophilic nature of the alcohols or amines employed. Most significantly, we have evaluated DBSA as a novel catalyst for simultaneous esterification and *trans*-esterification with lipophilic alcohols in the presence of excess water.

2 Materials and methods

OA was obtained from high oleic sunflower oil, generated from enzymatic hydrolysis by a method developed in our laboratories [22]. Oleic oil (OO) was purchased as high oleic sunflower oil (87.6% OA) from ITERG (Pessac, France). Unless otherwise stated all reagents and solvents were purchased from Sigma–Aldrich and used without further purification. Lewatit MP 500 was pre-conditioned via a method developed in our laboratories [23]. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance® 300 MHz instrument using tetramethylsilane (TMS) as an internal standard. Optical Microscopic images were recorded using a Nikon Eclipse E600 microscope fitted with a Nikon Digital Sight DS-Fi2 camera. All catalytic experiments and GC measurements were performed three times and the average reported, as is clearly stated in the methodology.

2.1 Quantitative determination of product distribution of samples by gas chromatography

All samples for GC analysis were prepared in the same manner: 10 mg of sample were taken up in 10 mL of cyclohexane, to which 100 μL of internal standard solution was added, (heptadecane – 10 mg in 1 mL cyclohexane). To 160 μL of this solution was added 40 μL of the silylating agent BSFTA and the sample was heated at 103°C for 3 min. For analysis 1 μL was injected directly onto the column. The samples were characterized on a Perkin Elmer Autosystem XL Instrument (Perkin Elmer, USA) fitted with a Restek Rtx-5 column (15 m × φ0.32 mm × 0.25 μm) using helium as carrier gas at 15 psi of pressure which was coupled to a flame ionization detector (FID). The injector temperature was set at 55°C for 30 s, and then ramped at 200°C per minute to 340°C. The oven temperature ramp was programmed to be 55°C for 0.5 min, rising by 45°C per minute until 80°C, then 10°C per minute up to 360°C where the temperature was held constant for 16 min. The temperature of the detector (FID) was set at 360°C. The product distributions were determined by their retention times, in comparison to those obtained with pure, purchased samples of the same product.

2.2 Catalytic procedures

2.2.1 Esterification of OA

OA (10 g) and the desired weight of water were added to a 50 mL round bottom flask. DBSA (10 mol% with respect to OA) was added followed by the alcohol of choice (2 eq.). The reaction mixture was heated at 80°C for 3 h, before cooling to room temperature, where the emulsified mixture was placed at 4°C overnight. The resulting biphasic mixture was transferred into a separating funnel, and the aqueous layer was recovered by decantation. Lewatit 500 MP (1 g) was added to the organic phase and stirred at room temperature for 1 h. Filtration followed by drying upon a rotary evaporator produced the product mixture for GC analysis.

2.2.2 *Trans*-esterification of OA

OA (5 g) and the desired weight of water were added to a 50 mL round bottomed flask. DBSA (5 mol% with respect to triolein) was added followed by the alcohol of choice (6 eq.). The reaction mixture was heated at 80°C for 6 h, before cooling to room temperature, where the emulsified mixture was placed at 4°C overnight. The resulting biphasic mixture was transferred into a separating funnel, and the aqueous layer was recovered by decantation. Lewatit 500 MP (0.5 g) was added to the

organic phase and stirred at room temperature for 1 h. Filtration followed by drying upon a rotary evaporator produced the product mixture for GC analysis.

2.2.3 Simultaneous esterification of OA and *trans*-esterification of OO

OA (5 g), OO (5 g), and water (5 g) were added to a 50 mL round bottomed flask. DBSA (10 mol% with respect to OA, +5 mol% with respect to OO) was added followed by the alcohol of choice (2 eq. with respect to the total number of FFA chains present). The reaction mixture was heated at 80°C for 6 h, before cooling to room temperature, where the emulsified mixture was placed at 4°C overnight. The resulting biphasic mixture was transferred into a separating funnel, and the aqueous layer was recovered by decantation. At this stage a sample of the organic phase was taken for quantitative analysis of the product mixture by GC analysis. Pure alkyl oleate was isolated by adding Lewatit 500 MP (1 g) to the organic phase and stirred at room temperature for 3 h. Filtration followed by drying upon a rotary evaporator produced the pure alkyl oleate: 1-butyl oleate (5.61 g, 48%); 1-pentyl oleate (10.2 g, 84%); and 1-hexyl oleate (9.4 g, 74%).

3 Results and discussion

3.1 Catalytic esterification of OA

3.1.1 Effect of water

Similarly, to that of Kobayashi, [2, 3] we evaluated the effect of water upon the DBSA-catalyzed esterification of Oleic Acid (OA) at a catalyst loading of 10 mol% and 1-butanol as alcohol. We created emulsions of OA and water based upon a percentage weight of water with respect to OA (Table 1). Without DBSA as catalyst (Table 1, entry 1) no esterification reaction occurred suggesting that the acidity of the OA is not sufficient enough to auto-catalyze the esterification. In the absence of water, DBSA is an extremely active catalyst for the esterification of OA to 1-butyl oleate without the need for the removal of water produced (Table 1, entry 2). Increasing incrementally the water content of the reaction mixture had only a negligible effect upon the conversion of OA to 1-butyl oleate (Table 1, entries 3–6). Importantly, and with respect to a sustainable system, the emulsified reaction mixture can be easily broken at low temperature (4°C), resulting in well-defined organic and aqueous layers. The water can be recovered for further use by decantation, while the organic phase can be treated with a basic resin [24], to remove the DBSA, and subsequently dried to produce pure butyl oleate. Our results are of industrial importance as the current catalyst technologies employ acid-resin catalysts that are poisoned by the presence of water [25]. A DBSA-catalyzed process, on the other hand, would be capable of esterifying free fatty acids (FFA) and hydrophilic alcohols even in the presence of large amounts of water. The advantage being that DBSA not only acts as an acid catalyst but also an emulsifying agent that organizes the reaction mixture in such a way that defined hydrophobic pockets of reactivity can be created within the emulsified milieu, a phenomenon already noted by our research team [16, 17] and Kobayashi [2, 3].

Table 1. Effect of H_2O content on butyl oleate yield in DBSA catalyzed esterification and *trans*-esterification[a]

Entry	wt% H_2O	Butyl oleate yield from OA (%)[b]	Butyl oleate yield from OO (%)[b]
1[c]	0	8	4
2	0	97	98
3	30	93	32
4	50	93	42
5	70	92	29
6	100	91	31

[a]Experimental conditions: 10 g of OA/5 g of OO, 2 eq. 1-butanol, 10 mol% DBSA, 80°C for 3 h (for OA), or 5 mol% DBSA, 80°C for 6 h (for OO).
[b]Determined quantitatively by GC.
[c]Without DBSA catalyst.

3.1.2 Effect of alcohol

We wished to see if there was a correlation between the lipophilic nature of the alcohol and it's reactivity in the DBSA catalyzed esterification reaction (Table 2). To this end we evaluated the alcohols with respect to the logarithm of their partition coefficient.[1] All experiments were performed on a model system of a 1:1 mixture of OA and water. Excluding methanol and ethanol, which have already been extensively reported on [26–31]. 1-(or *n*-) propanol produced the corresponding 1-propyl oleate in 84% yield. Surprisingly, 2-(or *i*-) propanol gave a 33% yield of 2-propyl oleate under the same reaction conditions. This phenomenon was equally observed with the straight and branched isomers of butanol with 1-butanol giving 91% of 1-butyl oleate while 2-butanol gave only 39% of 2-butyl oleate.[2] Similar observations have already been reported and suggest that the differences are due to the steric influence of the alcohol upon its propensity to react with the carboxylic acid [32, 33]. Thus, the more

[1] The authors note that the LogP value is not an exact measure of a compound's lipophilicity, but is highly representative when compared in a series.

[2] The authors have deliberately chosen not to study the *tert*-butanol isomer as our interest lies in potential biofuels, and the price of *t*-butanol remains too high to be considered. The price of the *n*- and *i*-isomers, however, is predicted to dramatically reduce due to their use as bio-additives in petrol, see Bio-butanol: The game changer. An emerging biofuel and biochemical. Informa Economics. 05–2013. http://www.informaecon.com/MCSBiobutanol2013.asp

Table 2. Esterification of OA with ROH[a]

Entry	Alcohol (ROH)	LogP of ROH	Alkyl oleate yield (%)[b]
1	$(CH_3)_2CH_2OH$	0.26	33
2	$CH_3CH_2CH_2OH$	0.34	84
3	$(CH_3)_2CH_2CH_2OH$	0.61	39
4	$CH_3(CH_2)_2CH_2OH$	0.88	91
5	$CH_3(CH_2)_3CH_2OH$	1.6	86
6	$CH_3(CH_2)_4CH_2OH$	2.0	92

[a]Experimental conditions: 10 g OA, 10 g H_2O, 2 eq. ROH, 10 mol% DBSA, 80°C for 3 h.
[b]Determined quantitatively by GC.

sterically hindered the alcohol (i.e., the branched isomers), the more encumbered it is to react, and subsequently lower conversions to esters are found Scheme 2.

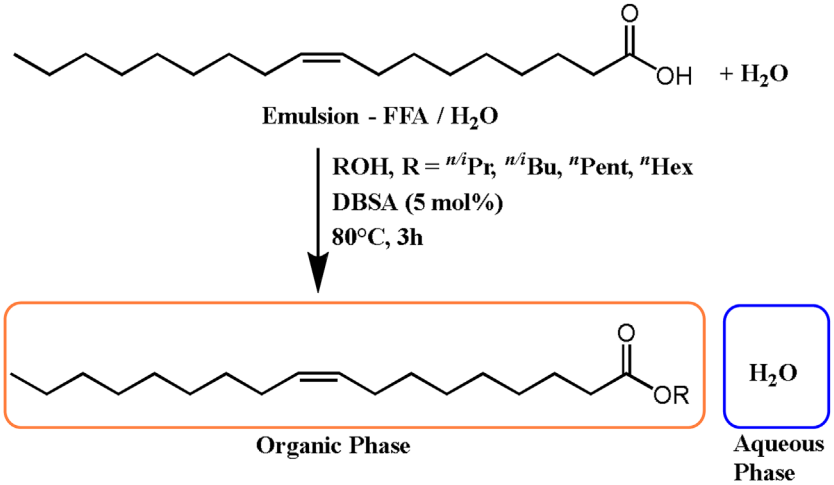
The straight chain alcohols of 1-pentanol and 1-hexanol gave ester conversions of 86 and 92%, respectively (Table 2, entries 5 and 6). Comparison of the straight chain alcohols and their reactivity to give the corresponding ester suggests that the lipophilic nature of the short (C_{3-6}), straight chain alcohols has a negligible effect upon its reactivity in the DBSA catalyzed esterification of OA (Fig. 1). For example, 1-propanol and 1-hexanol gave comparable conversions to their corresponding alkyl esters despite 1-propanol being freely miscible with water and 1-hexanol being very poorly soluble (Table 2, entries 2 and 6). Therefore, the steric encumbrance of the alcohol is the determining factor of the DBSA catalyzed esterification of OA in water, rather than the lipophilic nature. This suggests that the contact between the reagents (acid and alcohol) is sufficiently good enough in the emulsified reaction mixture to allow high conversions to esters.

Another advantage of our catalytic procedure is the mild conditions employed. Under harsher reaction conditions it has been shown that when using an unsaturated FFA, such as OA, isomerisation, and cyclization can occur producing the lactone [34], and/or butyoxylation of the double bond by the excess butanol [35]. ^1H and ^{13}C NMR analysis of our esters revealed that no cyclization or butyoxylation of the double bond in OA occurred under the employed reaction conditions (see ESI Figs. S1 and S2).

3.2 Catalytic *trans*-esterification of OO

3.2.1 Effect of water

DBSA has already been reported to be an effective catalyst for the *trans*-esterification of triglycerides at a catalyst loading of 5 mol%, but was shown to be significantly inhibited by 5 vol% of added water [36]. Reports to date, however, have yet to study the ability of DBSA as catalyst in the presence of equal quantities of water to triglycerides. Thus, as with OA, we tested the water tolerance of DBSA as catalyst in the *trans*-esterification of OO, as representative example of a triglyceride (Table 1). Similarly to OA, the reaction does not proceed in the absence of the DBSA catalyst (Table 1, entry 1). The *trans*-esterification of OO by DBSA takes 6 h to arrive at 98% conversion at a catalyst loading of 5 mol%, similar to that already reported by Cuellar et al. [36] (Table 1, entry 2). In addition, the catalysis is severely affected by the addition of water to the reaction mixture. Even at 30 wt% of water the yield of 1-butyl oleate decreases to 32%, in comparison to 98% with no added water. Interestingly, the yield of 1-butyl oleate does not continue to decrease upon further addition of water (entries 3–6), and appears to stabilize around 30–40% conversion. This suggests that while the DBSA catalyst is tolerant to the water produced from the dehydrative *trans*-esterification of OO, if additional water is added, the rate of the *trans*-esterification is greatly diminished, but this effect is unique and independent to



Scheme 2. Esterification of oleic acid emulsified in water.

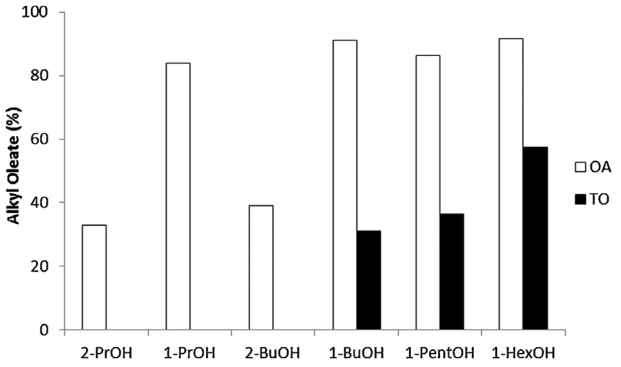


Figure 1. Esterification of OA and *trans*-esterification of OO with ROH (see Tables 2 and 3).

the amount of water added. Upon analysis of the break-down of the components of the reaction mixture after 6 h, we noticed that the amount of partial or complete hydrolysis of the OO remains relatively small (see ESI Table S1). The amounts of diglycerides (DG), monoglycerides (MG), and OA are relatively low suggesting that neither partial, nor complete hydrolysis of the OO occurs to a large degree. Thus, we concluded that the predominant pathway for formation of the butyl oleate is via the DBSA catalyzed *trans*-esterification of OO, and not the hydrolysis of the OO, by the excess water in the emulsified reaction mixture, and then esterification of the resulting OA to 1-butyl oleate.

3.2.2 Effect of alcohol

All reactions were performed on 1:1 mixtures of OO and water (Table 3 and Scheme 3). In the absence of any alcohol no hydrolysis of the OO to OA is observed (Table 3, entry 0). This result confirms that the reaction proceeds via a *trans*-esterification process and not by hydrolysis followed by esterification.

The data shows that both the straight and branched isomers of propanol are unreactive, possibly due to their free solubility in water (Table 3, entries 1 and 2). 2-Butanol is also unreactive, while the straight chain isomer 1-butanol gives a 31% conversion to the 1-butyl oleate (Table 3, entries 3 and 4). The straight chain isomers of pentanol and hexanol give 37 and 57% conversions to the corresponding esters, respectively, suggesting that the longer the carbon chain of the alcohol, or, an alcohol with a LogP value greater than 0.8, the more reactive it is to the *trans*-esterification process (Fig. 1). With the exception of 2-butanol, we postulate that the reactivity of the alcohol in the DBSA catalyzed *trans*-esterification of a 1:1 OO/water mixture is tied specifically to the alcohol's solubility in water. Thus, we propose that the higher the solubility of the alcohol in water, the lower conversion to ester observed, due to the alcohol's tendency to remain within the droplets of water within the emulsified reaction mixture. This effect would dramatically reduce the contact between the OO (in the organic phase of the emulsion) and the alcohol, and reduce the chance of the *trans*-esterification reaction occurring (see ESI Fig. S1). In the case of 2-butanol, it is lipophilicity could be the major attributing factor, but as we have shown with the esterification of OA, the steric encumbrance of the branched isomer versus the straight chain isomer, could equally be a determining factor in the lack of reactivity observed with 2-butanol compared to 1-butanol.

Table 3. DBSA catalyzed *trans*-esterification[a]

Entry	Alcohol ROH	LogP of ROH	Alkyl oleate (%)[b]
0	None	–	0
1	$(CH_3)_2CH_2OH$	0.26	0
2	$CH_3CH_2CH_2OH$	0.34	0
3	$(CH_3)_2CH_2CH_2OH$	0.61	0
4	$CH_3(CH_2)_2CH_2OH$	0.88	31
5	$CH_3(CH_2)_3CH_2OH$	1.6	37
6	$CH_3(CH_2)_4CH_2OH$	2.0	57

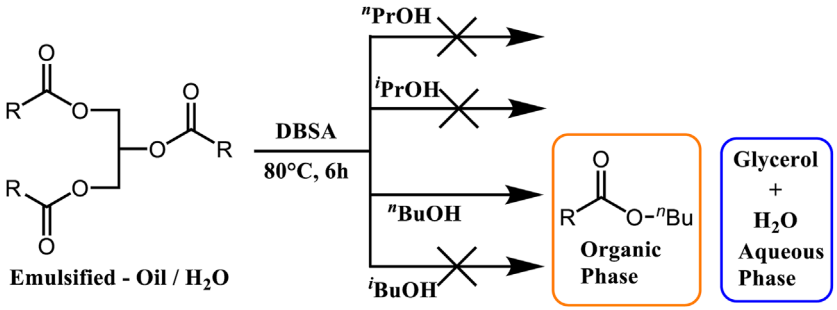
[a]Experimental conditions: 5 g OO, 5 g H_2O, 6 eq. ROH, 5 mol% DBSA, 80°C for 6 h.

[b]Determined quantitatively by GC.

3.3 Catalytic amidations of esters

Fatty amides (FAs) are important industrial compounds and have a plethora of uses in industrial applications from: Coatings; lubricants; printing; etc. In addition, recent reports have suggested that it could be feasible to consider FAs as a potential biodiesel [37–39]. Commonly, the amidation of a triglyceride is base-catalyzed, and to the best of knowledge there are neither reports in the literature of the DBSA catalyzed amidation of oils, nor reports of the amidation being performed in water. All reactions were performed on a 1:1 mixture of OA/OO and water. Initial attempts to achieve the DBSA catalyzed amidation of OA with 1-butylamine or 1-heptylamine were unsuccessful due to the formation of the ammonium salt and no further reactivity. This is a commonly reported phenomenon in the case of the direct reaction between carboxylic acids and amines [40].

The DBSA-catalyzed amidation of esters with 1-butylamine and 1-heptylamine, on the other hand, successfully gave the corresponding amides in modest yields. OO gave higher conversions to the corresponding alkyl amide the more lipophilic the amine used, a correlation we have already observed in this work. Methyl oleate, however, gave a slighter higher conversion to the amide with the shorter chain butylamine than with heptylamine. The difference in reactivity between the two esters is presumable due to their differences in lipophilicity. OO exhibits a partition coefficient three times higher than that of methyl oleate. Therefore, once mixed as an emulsion in water and



Scheme 3. *Trans*-esterification of OO emulsified in water.

in the presence of DBSA catalyst, the more lipophilic ester would possess a greater probability of contact with the amine and thus a greater degree of reactivity. The amidation reactions appear to be unaffected by the excess water present, producing higher conversions to the product amide than the corresponding alcohol does to ester when comparing the same carbon chain (C_4) (Table 3, entry 4 cf Table 4, entries 1 and 3). This is presumably due to the amine moiety on 1-butylamine being a stronger nucleophile than the corresponding alcohol moiety of 1-butanol. Also, and in agreement with our results for the alcohols, the longer the carbon chain of the amine the higher the amide product yield, due to greater solubility of the amine in the organic phase, and a higher probability of contact with the ester. Our investigations here constitute the first examples of DBSA as a viable catalyst for amidation reactions in the presence of water.

3.4 Simultaneous catalytic esterification and *trans*-esterification

Catalysts capable of simultaneous *trans*-esterification and esterification remain an active area of research [41–44]. To the best of our knowledge, however, there are no reports of a catalyst capable of simultaneous *trans*-esterification and esterification in the presence of equal amounts of water to reagents. To this end we tested DBSA as catalyst for the simultaneous esterification of OA and the *trans*-esterification of OO in the presence of an equal weight of water.

Without DBSA catalyst being added (Table 5, entry 1) trace amounts of 1-butyl oleate are observed, suggesting that OA is not a sufficiently strong enough acid to auto-catalyze it's esterification with 1-butanol, nor initiate the *trans*-esterification of OO. Upon analysis of the reaction mixture at the end of the reaction, we also observed that only trace amounts of the OO have been hydrolyzed to OA. This correlates with our observations for the catalysis of OO alone, suggesting that hydrolysis of the OO to OA is not the predominant mechanism of the reaction (see ESI, Table S3), rather that the DBSA catalyst acts as a *trans*-esterification catalyst and an esterification catalyst, simultaneously. Therefore with DBSA as catalyst we observed a dramatic increase in the conversion rate to 1-butyl oleate upon a mixture of OA and OO compared to OO alone. After only 3 h a 60% conversion rate is observed, while after 6 h the yield of 1-butyl oleate is 89% (Table 4, entries 2 and 3). This compares to a 1-butyl oleate yield of only 31% (Table 3, entry 4) for the *trans*-esterification of OO alone in water. We postulate that the addition of the OA to the reaction mixture

Table 4. DBSA catalyzed amidations[a]

Entry	Ester (LogP)	Amine (LogP)	Alkyl amide yield (%)[b]
1	Oleic oil (18.10)	$CH_3(CH_2)_2CH_2NH$ (1.45)	63
2	Oleic oil (18.10)	$CH_3(CH_2)_5CH_2NH$ (2.62)	83
3	Methyl oleate (6.20)	$CH_3(CH_2)_2CH_2NH$ (1.45)	66
4	Methyl oleate (6.20)	$CH_3(CH_2)_5CH_2NH$ (2.62)	56

[a]Experimental conditions: 5 g ester, 5 g H_2O, 6 eq. amine, 5 mol% DBSA, 80°C for 6 h.

[b]Determined quantitatively by GC.

Table 5. DBSA catalyzed simultaneous esterification and *trans*-esterification[a]

Entry	Alcohol (ROH)	LogP of ROH	Alkyl oleate yield (%)[b]
1[c]	$CH_3(CH_2)_2CH_2OH$	0.88	2
2[d]	$CH_3(CH_2)_2CH_2OH$	0.88	61
3	$CH_3(CH_2)_2CH_2OH$	0.88	89
4	$CH_3(CH_2)_3CH_2OH$	1.6	76
5	$CH_3(CH_2)_5CH_2OH$	2.0	95

[a]Experimental conditions (see ESI): OA:OO:H_2O (1:1:1), DBSA, 80°C for 6 h.

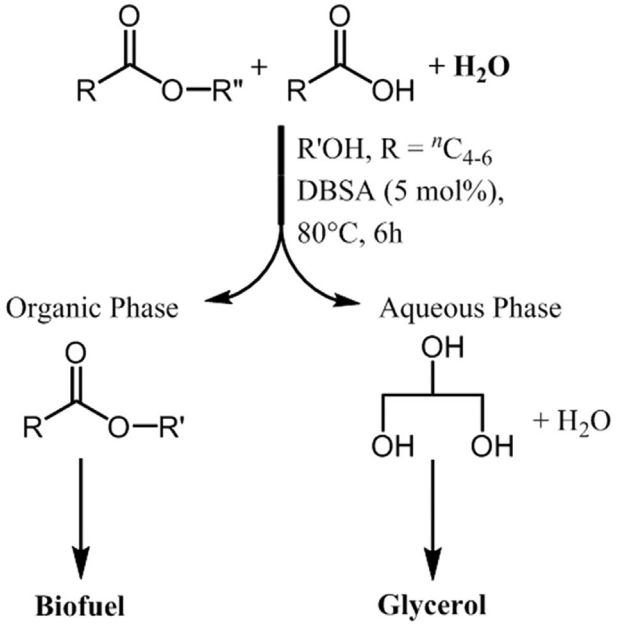
[b]Determined quantitatively by GC.

[c]Without DBSA catalyst.

[d]Three hours reaction time.

enhances the activity of the DBSA catalyst by increasing the acidic nature of the emulsified reaction mixture, especially in the organic phase, and an enhancement of the reaction rate and higher conversions to the 1-butyl oleate were observed. The same enhancement of the catalysis is observed for 1-pentanol (37–76%) and 1-hexanol (57–95%) in the simultaneous catalysis compared to the *trans*-esterifications performed alone.

In addition, the significant advantage of our system is the ability to recover and separate all of the potentially value-added products contained in the emulsified raw materials and, considering environmental factors, the water itself. We have thus developed a protocol in which the starting material emulsion is converted "in situ" by the DBSA catalyst and chosen alcohol, into the respective carboxylic esters under mild conditions. At the end of the reaction, in the case of 1-hexanol, the reaction mixture can be decanted at low temperature (4°C) into the organic and aqueous phases. After decantation the aqueous phase was distilled to produce pure water for recycling and the highly valued commercial product glycerol isolated in modest yield (44%). The organic phase was treated with a solid basic resin to recover the DBSA catalyst, as well as to absorb the remaining trace FFAs, that after drying gave the pure 1-hexyl oleate in high yield (74%) (see ESI). (The DBSA can then be recovered off the resin by treatment with a basic solution of methanol). Thus, our work-up does not require the use of additional solvents or prolonged treatments in order to obtain each commercially valued product (Scheme 4).



Scheme 4. Protocol for conversion and recovery of value-added products from emulsified raw material.

4 Conclusions

In conclusion, we have demonstrated that DBSA is an extremely effective polyvalent catalyst for either the acid-catalyzed: Esterifications; *trans*-esterifications; or amidations with substrates of varying lipophilicity in the presence of water. Adding excess water to the reaction mixtures has a negligible effect on the esterification reactions, regardless of the excess amount added. Excess water added to the *trans*-esterification reactions, on the other hand, causes a significant decrease in the conversion rate to alkyl esters (30–40%). This rate decrease in conversion shows no observed correlation with the total concentration of water in the reaction mixture. The lipophilic nature of the alcohol employed in the *trans*-esterification DBSA-catalyzed reactions in water is a critical factor in determining the conversion rate to ester. The higher the LogP value of the alcohol (above 0.8) the higher the conversion to the corresponding alkyl ester. A similar effect is observed for the DBSA-catalyzed amidations where we have demonstrated that the greater lipophilic character of either the ester or alcohol substrates employed causes a higher conversion to alkyl amide. For DBSA-catalyzed esterifications in water the lipophilic nature of the alcohol is negligible and the conversion rate to esters is determined by the steric encumbrance of the alcohol employed. Simultaneous DBSA-catalyzed esterification and *trans*-esterification in the presence of water is reported here for the first time. In addition, we have demonstrated an environmentally favorable post-treatment process in which all of the value added products generated via the tranformation are isolated without the need for the use of costly solvents or co-reagents.

The authors would like to thank the region of Midi-Pyrenees for funding through the project Metholva; DAER-RECH No. 12051396.

The authors have declared no conflict of interest.

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