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# Green Acetylation of Solketal and Glycerol Formal by Heterogeneous Acid Catalysts to Form a Biodiesel Fuel Additive

Jennifer R. Dodson, Thays d C. M. Leite, Nathália S. Pontes, Bianca Peres Pinto, and Claudio J. A. Mota<sup>\*[a]</sup>

A glut of glycerol has formed from the increased production of biodiesel, with the potential to integrate the supply chain by using glycerol additives to improve biodiesel properties. Acetylated acetals show interesting cold flow and viscosity effects. Herein, a solventless heterogeneously catalyzed process for the acetylation of both solketal and glycerol formal to new products is demonstrated. The process is optimized by studying the effect of acetylating reagent (acetic acid and acetic anhydride), reagent molar ratios, and a variety of commercial solid acid catalysts (Amberlyst-15, zeolite Beta, K-10 Montmorillonite, and niobium phosphate) on the conversion and selectivities.

### Introduction

The transesterification of fats and oils to biodiesel produces approximately 10 wt% of glycerol as a byproduct.<sup>[11]</sup> With an increasing demand for biodiesel, especially in Europe and the Americas, there is the potential for glycerol to become an important feedstock for the chemical industry if sustainability concerns of biodiesel production are addressed. In Brazil, since 2010 it has been mandatory for diesel to be blended with 5% biodiesel. The use of crude glycerin from biodiesel production for traditional pharmaceutical and cosmetic uses is limited as a result of its low purity; approximately 20% is a mixture of water, unrecovered methanol, and dissolved salts from neutralization of the basic catalyst. The chemical transformation of glycerol into value-added products has therefore attracted a great deal of interest, with a variety of routes available.<sup>[1,2]</sup>

One opportunity is the production of biodiesel fuel additives, thereby enabling the whole supply chain to be integrated. Owing to solubility problems, polymerization, and its decomposition at high temperatures, glycerol cannot be added directly to the fuel. However, several studies have shown that glycerol-derived fuel additives can enhance the biodiesel fuel specifications, including the viscosity, cetane number, cloud point, oxidation stability, and emissions.<sup>[3,4]</sup> Glycerol acetals and ketals are of particular interest, with the former produced by the acid-catalyzed reaction of glycerol with aldehydes, and the latter by reaction with ketones. Upon reaction with ketone, the High conversions (72–95%) and selectivities (86–99%) to the desired products results from using acetic anhydride as the acetylation reagent and a 1:1 molar ratio with all catalysts. Overall, there is a complex interplay between the solid catalyst, reagent ratio, and acetylating agent on the conversion, selectivities, and byproducts formed. The variations are discussed and explained in terms of reactivity, thermodynamics, and reaction mechanisms. An alternative and efficient approach to the formation of 100% triacetin involves the ring-opening, acid-catalyzed acetylation from solketal or glycerol formal with excesses of acetic anhydride.

main ketal formed is a five-membered ring, whereas a mixture of five- and six-membered cyclic acetals are produced from reactions with aldehydes. These products may also have further applications as surfactants, flavorings, solvents, and plasticizers among others.<sup>[5,6]</sup>

We previously demonstrated that solketal (1), which is the product of the reaction of acetone with glycerol, improved the octane number and reduced gum formation upon addition to gasoline,<sup>[7]</sup> whereas glycerol acetals improved the cold flow properties,<sup>[3]</sup> although there were problems of solubility of glycerol formal in biodiesel. Recent work has demonstrated the synthesis of acetylated solketal as a potential additive for biodiesel, with improvement in the viscosity and cloud point of the biodiesel beyond that of the non-acetylated version.<sup>[8]</sup> However, optimization of the synthetic process was not performed: large amounts of solvent were used and, without the use of a heterogeneous catalyst, the workup procedures were intensive. Herein, we study the effect of various parameters, including acetylating reagent, reagent ratios, and a variety of solid acid catalysts, on the formation of acetylated solketal with this extended to glycerol formal; this demonstrates the potential for a greener, solvent-free, heterogeneous catalyzed process (Scheme 1). A complex relationship between the various factors is demonstrated.

### Results

The effect of three variables on the acetylation of **1** and glycerol formal (**3**) were studied: the acetylating reagent, the molar ratio of ketal or acetal to the acetylating agent, and the effect

<sup>[</sup>a] Dr. J. R. Dodson, T. d. C. M. Leite, N. S. Pontes, Dr. B. Peres Pinto, Prof. C. J. A. Mota Institute of Chemistry, Federal University of Rio de Janeiro Cidade Universitária—Rio de Janeiro, 21941-909 (Brazil) E-mail: cmota@iq.ufrj.br



Scheme 1. a) Synthesis of solketal (1) from glycerol and acetone, and subsequent acetylation to form ketal 2. b) Synthesis of acetals 3a and 3b from glycerol and formaldehyde (9), and subsequent acetylation to form acetals 4a and 4b.

of using different solid acid catalysts. For the formation of **2**, the catalysts tested were niobium phosphate, Amberlyst-15, K-10 Montmorillonite, and zeolite Beta, whereas, for **4**, niobium phosphate and Amberlyst-15 were tested because these catalysts showed the largest variations in conversions and selectivities.

The results show that high conversions and good selectivities to the acetylated products were achieved under solventless conditions and by using solid acid catalysts (Figure 1). However, variations were observed between different catalysts, reagents, and reagent ratios. Blank reactions were also studied in the absence of the solid acid catalysts for comparison purposes. These showed lower and slower rates of conversions (Figures 1 and 2).

Due to the nature of the ketal and acetal reagents, in the case of the acetylation of **1**, only the five-membered ring product was observed, whereas for **3** a mixture of five- and sixmembered ring products were formed (Scheme 1). Almost identical trends for the effect of reagent, reagent molar ratios, and catalyst were observed for both the ketal and acetal. Under almost all reaction conditions, triacetin (**8**) and small quantities of mono- (**5**) and diacetin were formed; this was also observed by García et al. in the acetylation of **1** in triethylamine.<sup>[8]</sup>

#### Effect of the acetylating reagent

Across all catalysts, acetic anhydride displayed a more rapid reaction and higher conversion than acetic acid as an acetylating reagent, without the need for an excess amount (Figure 2).

The reactions with acetic anhydride were complete within 2 h, and generally reached maximum conversion (90–100%) within 5 min (Figure 2a). Only niobium phosphate displayed slower reaction rates, and a lower conversion with a 1:1 molar ratio, although the selectivity to the desired product was generally higher than that of the other catalysts.

In contrast, the use of acetic acid resulted in slower reactions and lower conversions with much greater variation between the catalysts (Figure 2b). Of the four catalysts, Amberlyst-15 achieved the highest conversions for the acetylation of both **1** and **3** with acetic acid, reaching 56% with a 1:1 molar ratio and 86% with a 1:3 molar ratio for **1**. K-10 montmorillonite, zeolite Beta, and niobium phosphate were all poor catalysts for the reaction with conversions of only 17–47% after 2 h. However, only traces of **8** were formed, in contrast to the reactions with acetic anhydride.

The only striking difference between the use of **3** and **1** was the selectivity to the desired products when acetic acid was



**Figure 1.** a) Conversion and b) selectivity to the acetylated products of ketal 1 or acetal 3 by using different catalysts and molar ratios by using either acetic acid after 2 h or acetic anhydride after 1 h of reaction.

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**Figure 2.** Kinetics of the acetylation of 1 at 60 °C by using four different solid acid catalysts, or none, and different acetylating agents at a molar ratio of 1:3: a) acetic anhydride and b) acetic acid.

used as the acetylating agent. In general, across the reactions high selectivities to the desired products 2, 4a, and 4b were observed. However, when acetic acid was used as the acetylating agent for 3, a range of byproducts were observed. These included glycerol, 5, and four peaks with the most intense signals at m/z 71, 87, 117, and 147. These were identified as glycerol ethers (6), and were identical to those observed during the hydrolysis of 3.<sup>[9]</sup> However, in contrast to the reactions with acetic anhydride, 8 was not identified. The selectivity of these byproducts combined ranged from 50 to 80% during the reaction, based on the quantity of product formed. Observations indicate that the concentrations of glycerol and 6 increase in selectivity in parallel at the beginning of the reaction followed by a shift in the selectivity towards the desired acetylated products and 5 as the reaction proceeded (Figure 3). Both Amberlyst-15 and niobium phosphate show the same trends in product distribution, but with a slower rate for the lower molar ratio reactions and when using niobium phosphate. In contrast, the reaction of 1 with acetic acid formed the product (2) in high selectivity with minor, but increasing, levels of 5 and glycerol and traces of 8 with longer reaction times. The 6 were not observed.



**Figure 3.** Conversion and product distribution from the reaction of **3** and acetic acid at a molar ratio of 1:3 with Amberlyst-15. The selectivities of the **5**, **6**, and glycerol are qualitative.

#### Effect of the acetal/acetylating reagent molar ratio

In general, the use of a higher molar ratio of acetylating reagent resulted in a higher total conversion (Figure 1). In all of the reactions with acetic anhydride, the conversion reached 96–100% after 2 h of reaction with a 1:3 molar ratio of acetal/ acetylating reagent. The improvement was particularly noticeable for niobium phosphate, although the rate of conversion was still slower than that for the other catalysts. Generally, small increases in conversion were also observed for a higher molar ratio with acetic acid; Amberlyst-15 showed a much larger increase in conversion with a higher molar ratio.

Particularly striking is the impact of the molar ratio on the increased selectivity to 8 when using acetic anhydride, especially with Amberlyst-15 as a catalyst (Figure 4). With no excess of anhydride, the selectivity to the desired products was high: 83% for the ketal (2) and 92% for the acetals (4a, 4b) combined. However, when an excess of acetic anhydride was present, following an initial rapid conversion to the desired products, almost complete conversion to 8 occurred with a concurrent reduction in the concentration of the product (Figure 4b and c). This was especially rapid and complete in the case of the reaction of 3 with acetic anhydride in the presence of Amberlyst-15, for which the selectivity from acetal to 8 occurred over 5 min. All of the other catalysts showed an increase in the selectivity to 8 with excess acetic anhydride. However, the extent of the conversion of acetal or ketal product to 8 was not as rapid or as extensive with K10 Montmorollinite, zeolite Beta, or niobium phosphate (Figure 4a). In the case of niobium phosphate for the acetylation of the acetal (3), no byproducts were formed at a molar ratio of either 1:1 or 1:3. Very little 5 or diacetin was observed for any of the samples.

### Discussion

### Effect of the acetylating reagent on conversion and selectivity

The much more effective acetylation of the acetal and ketal with acetic anhydride versus acetic acid was not unexpected. It

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**Figure 4.** Increase in selectivity to **8** with higher molar ratios of acetic anhydride: a) Selectivity to **8** at different reagent molar ratios for all catalysts after 120 min of reaction. Variation in the selectivity to **8** and acetylated products for b) **1** and c) **3** at a reagent molar ratio of 1:1 (unfilled markers) or 1:3 (filled markers) with Amberlyst-15 and acetic anhydride.

is well known that acetic anhydride is a better acetylating agent, as observed for the acetylation of glycerol among other alcohols.<sup>[4,10]</sup> This has been suggested to be because the for-

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mation of **8** is endothermic in the case of acetic acid, whereas it is exothermic when acetic anhydride is used; this accounts for the lower conversions and requirement for greater excesses of reagent for acetic acid than that with acetic anhydride.<sup>[10]</sup> Furthermore, in acetylation reactions for glycerol, a similar trend for the solid acid catalysts was observed as those for the ketal and acetal in this study; niobium phosphate was much less active at 60 °C than Amberlyst-15, zeolite Beta, or K-10 Montmorillonite.<sup>[10]</sup> In addition, Amberlyst-15 showed a higher selectivity to **8** than the other catalysts with acetic acid, that is, greater acetylation correlating with this study.<sup>[10]</sup>

The formation of glycerol, 5, and 6 during the reactions of 3 and acetic acid can be explained by the formation of water from the reaction of acetic acid and the acetals, which are not removed from the reaction medium under the conditions used (Scheme 2). Water present can result in acid-catalyzed hydrolysis of both the initial acetals and the acetylated products; this accounts for the formation of glycerol and 5, respectively. Byproduct 6 will result from the reaction of free glycerol with the initial acetal; these compounds have also been observed during the hydrolysis of **3**, but not **1**, as described previously.<sup>[9]</sup> It appears that 6 formed favorably during the initial period of the reaction, but was gradually converted into the acetylated product; this indicates that the latter is thermodynamically favored, especially with excess acetic acid. With Amberlyst-15, a higher product/ether ratio is observed after 2 h than that with niobium phosphate; this is presumably due to the general lower reactivity of the latter catalyst. Monoacetin (5) could form from either the reaction of acetic acid and glycerol or the ring-opening hydrolysis of the acetylated acetal; this accounts for the increasing selectivity to 5 with reaction time as greater quantities of products 4a and 4b are formed (Scheme 2). As mentioned previously, the lack of formation of 8 under these reaction conditions can be attributed to the low reactivity of acetic acid for the acetylation of glycerol.<sup>[10]</sup> Interestingly, byproduct 6 was not observed during the acetylation of 1 with acetic acid. We attribute this to the faster reaction of 1, leading to rapid formation of the more stable final acetylated product. Indeed, during the hydrolysis of 1, no 6 or other byproducts were observed, in contrast to that of **3**.<sup>[9]</sup>

#### Formation of triacetin (8)

The conversion of **2**, **4a**, and **4b** quantitatively into **8** with Amberlyst-15 and, to a lesser degree, with zeolite Beta and K-10 Montmorillonite with an excess of acetic anhydride was unexpected. Ring-opening hydrolysis could occur if some of the acetic acid formed from the initial reaction of acetic anhydride also reacted to form water. However, the high reactivity of acetic anhydride; the lack of **5** or diacetin observed in the reaction mixtures, particularly at a 1:1 molar ratio of reagents; and the variation between the different catalysts suggests that an alternative mechanism may be in operation. Ethers are well known as protecting groups, and therefore, cleavage reactions are extremely important; cyclic ethers such as tetrahydrofuran (THF) have been widely studied. These are known to be cleaved by mixtures of acetic anhydride with concentrated sul-



Scheme 2. Reaction scheme showing possible routes for the formation of monoacetin (5), glycerol, and glycerol ether 6 byproducts observed during the reaction of 3 with acetic acid.

furic acid or with Lewis acids such as ZnCl<sub>2</sub>, FeCl<sub>3</sub>, and MgBr<sub>2</sub> resulting in ring opening and the formation of 1,4-diacetoxybutane.[11-13] Recently solid heteropolyacids, such as 12-tungstophosphoric acid and also sulfamic acid (NH<sub>2</sub>SO<sub>3</sub>H), have shown to be effective for this reaction.<sup>[14,15]</sup> In these studies, acetic anhydride was shown to be vital for ring cleavage to occur; a small concentration of acetic acid was necessary to prevent nucleophilic attack of THF at the acetylated THF oxocations. Little work has been done on dioxanes or dioxolanes; however, solid heteropolyacids catalysts were tested on the cleavage of 1,4-dioxane, with a conversion of 2% for the heteropolyacid and 86% for sulfamic acid to 1,2-diacetoxyethane.<sup>[14,15]</sup> This suggests that a similar mechanism to ether cleavage could explain the formation of 8 through nucleophilic attack of 2, 4a, or 4b on the acylium cation (7) formed from acetic anhydride (Scheme 3). Typically, the product of ether ring-cleavage reactions results in acyl group addition at the oxygen atom and acetate addition at the  $\alpha$  carbon; however, further reaction could occur to form 8 and formaldehyde (9; or



Scheme 3. Proposed mechanism for the formation of 8 during the reaction of 3 and acetic anhydride

acetone from 1). The slower conversion to **8** for the ketal system may be due to steric hindrance for this final step. If the molar ratio is only 1:1, little diacetin is formed; this indicates that acetylation of the alcohol is more favorable than that of ring-opening acetylation. The presence of a strong Brønsted acid is necessary for the formation of the acylium ion, and this could explain the variation in the trend for different solid acid catalysts used in this study.

In terms of the catalytic activity, the trends for the catalysts in this study mirror those observed for the acetylation of glycerol with acetic acid and acetic anhydride; niobium phosphate displays a lower catalytic activity, whereas Amberlyst-15 is distin-

guished by its significantly increased acetylating activity compared with those of K-10 Montmorillonite and zeolite Beta with acetic acid.<sup>[10]</sup> The acid-catalyzed reaction of glycerol with acetone to form **1** also shows a catalytic activity trend in the order of Amberlyst-15 > zeolite Beta > K-10 Montmorillonite.<sup>[5]</sup>

There are huge challenges in the measurement of the acid strength of solid acids, with little agreement on a preferred method and variations in the acid strengths and its relationship with catalytic activity observed.<sup>[16–18]</sup> The presence of metals, cations, and confinement effects can all make Brønsted acid quantification difficult. A recent study on the free energy relationship with acidic strength of solid acid catalysts showed that the acid strength varied in the order Amberlyst-15 > zeo-lite Beta > niobic acid > K-10 Montmorillonite, whereas *n*-butyl-amine thermodesorption showed strong/weak acidity ratios in the order of zeolite Beta > K-10 Montmorillonite > niobic acid.<sup>[18,19]</sup> Amberlyst-15 could not be measured by this method due to its low thermal stability. Niobium phosphate is expected to have a higher acid strength than that of niobic acid from

 $NH_3$  adsorption studies;<sup>[20]</sup> however, this technique measures both Lewis and Brønsted acid sites, which may not both be catalytically active.<sup>[16]</sup> Overall, these acid strength trends agree with the catalytic activities observed in this study and the other studies highlighted above. However, they do not account for the much lower activity of niobium phosphate in general or the much higher activity of Amberlyst-15 for the conversion of the acetylated product to **8**. This

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may be due to the effect of the reaction solution on the catalytic activity. For instance, the activity of niobium phosphate reduces dramatically in polar solvents,<sup>[20]</sup> whereas anion stabilizing solvents, such as CF<sub>3</sub>COOH, have been shown to dramatically increase the acidic strength of Nafion, which is a sulfonated solid acid, and its ability to protonate hydrocarbons by the formation of strong hydrogen bonds by CF<sub>3</sub>COOH with the anion of the acidic site.<sup>[17]</sup> It can be postulated that the remarkable conversion of the acetylated products **2**, and **4** to **8** in the presence of Amberlyst-15, and the much higher conversion in the presence of acetic acid with the same catalyst, could be due to a similar anion-stabilizing effect upon interaction with CH<sub>3</sub>COOH formed in situ from acetylation by acetic anhydride.

Further work is needed to understand the detailed mechanistic process and the specific influence of the solution on the catalytic activities of the solid acids. Nevertheless, alongside the formation of the acetylated acetals, the observations in this study could open up an alternative route to the selective formation of **8** from glycerol, which has a range of applications from cosmetics to fuel additives,<sup>[4]</sup> through the initial formation of an acetal followed by ring opening with acetic anhydride in the presence of Amberlyst-15. In the case of **3**, 100% selectivity to **8** was observed; the reaction was more rapid and involved a lower ratio of acetic anhydride than that for the equivalent conversion and selectivity directly from glycerol.<sup>[10]</sup> Byproduct **9** formed should be recyclable. It would be interesting to test whether the same product could be formed with a lower excess of acetic anhydride.

### Conclusions

This work demonstrated the effective acetylation of glycerol acetal and ketal under a solventless, heterogeneously catalyzed system. Higher selectivities and conversions to the desired products were obtained by using acetic anhydride as the ace-tylation reagent and a 1:1 molar ratio of the reagents with Amberlyst-15, zeolite Beta, and K-10 Montmorillonite; these were all effective catalysts. There is a complex interplay between the solid catalyst, reagent ratio, and acetylating agent on the conversion, selectivities, and byproducts formed. An alternative approach to the highly selective formation of **8** was found through the ring-opening, acid-catalyzed acetylation from **1** or **3** with higher molar ratios of acetic anhydride in the presence of Amberlyst-15. Further tests on the use of the acetylated products as additives to biodiesel will be performed.

# **Experimental Section**

Amberlyst-15 was purchased from Room and Hass, K-10 Montmorillonite was from Fluka, niobium phosphate was supplied by CBMM (Brazil), and zeolite Beta was obtained from Zeolyst. The other reagents used were analytical grade and purchased from Sigma–Aldrich.

Ketal 1 and acetals 3a and 3b were synthesized by using a modified procedure reported by da Silva et al.<sup>[5]</sup> The reactions were performed under batch conditions. Typically, glycerol (500 g, 5.4 mol) was stirred with acetone or a 37% aqueous solution of formalde-

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hyde (5.4 mol) and Amberlyst-15 (50 g) at 70  $^\circ\text{C}.$  Before use, the reagents were purified by vacuum distillation.

To study the acetylation of the ketal and acetal, typically the distilled reagent (75 mmol) was added to a round-bottomed flask along with either acetic anhydride or acetic acid (1:3 or 1:1 molar ratio) and the catalyst (1.5 mmol acid sites). The mixture was heated in an oil bath at 60 °C for 2 h. Four different catalysts were used in this study with varying acidic properties (Table 1). Prior to each reaction, an activation procedure was used to remove water and impurities (Table 1).

Table 1. Characterization data and pretreatment temperature of the cata- lysts.		
Catalyst	Pretreatment temperature [°C] <sup>[a]</sup>	Acidity $[mmol g^{-1}]^{[b]}$
Amberlyst-15	120	4.7 <sup>[c]</sup>
K-10 Montmorillon- ite	150	0.6
zeolite Beta	300	1.4
niobium phosphate	90	0.3
[a] Rate = 10 °C min <sup>-1</sup> . Time in activation temperature = 1 h. [b] Measured by <i>n</i> -butylamine adsorption at 150 °C. <sup>[21]</sup> [c] Informed by the producer (Rohm and Haas).		

Samples (50  $\mu$ L) were removed at intervals over 2 h to analyze the products formed. The final product generally contained a mixture of **8** and the acetylated acetal or ketal. As observed by García et al., it was not possible to separate **8** by vacuum distillation or solvents, including water, ethanol, methanol, acetone, dichloromethane, ethyl acetate, chloroform, heptane, toluene, and hexane.<sup>[8]</sup>

Characterization of samples: The conversion and selectivity of the reactions were followed by GC by using an Agilent Model 6850 instrument. Prior to injection, aliquots (50  $\mu$ L) of the reaction solution were added to dichloromethane (1 mL) and immediately filtered. An Agilent HP-5 capillary column (30 m×0.25 mm) with a 0.25  $\mu$ m methyl silicone stationary phase was used with helium as a carrier gas. Aliquots (0.2  $\mu$ L) were injected and a heating program was used to heat from 70 to 200 °C at 10 °C min<sup>-1</sup>. The separated compounds were identified by mass spectrometry on a quadrupole mass spectrometer, Model 5973 Network Agilent, with impact ionization of electrons at 70 eV. The reagents, acetylated products, and **8** were quantified. Monacetin (**5**), glycerol, and **6** were identified by GC-MS.

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**Keywords:** acetylation • glycerol • heterogeneous catalysis • reaction mechanisms • waste prevention

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