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Solvent-Free Methods for Making Acetals Derived from Glycerol and Furfural and Their Use as a Biodiesel Fuel Component

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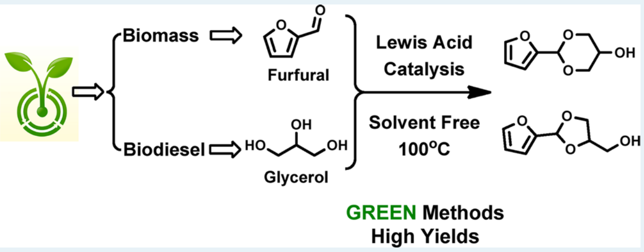
Supporting Information



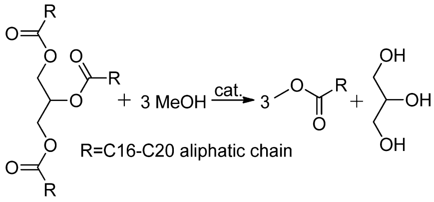
ABSTRACT: The increased production of biodiesel has resulted in the overproduction of glycerol. Many researchers have begun investigating new uses for glycerol, including its conversion to fuel additives. In this paper, glycerol has been reacted with furfural to yield the corresponding acetal. This condensation reaction is carried out under neat conditions with 5-fold excess of furfural, and a number of homogeneous Lewis acids and heterogeneous solid acids as catalysts. Reactions are routinely carried out at 100 °C, allowing for yields up to 90%. The addition of a dry stream of nitrogen gas purging the headspace was found to improve yields and allowed for a reduction in the excess amount of furfural. These reaction methods are applicable to crude glycerol, affording up to 80% yield with short reaction times. The isolated acetal products can be hydrogenated, and the free hydroxyl group can subsequently be acetylated. The resulting materials have been investigated as additives to biodiesel, aiming to improve the low temperature properties. While there was no benefit to the low temperature properties, we have no evidence that would preclude the use of these materials as biodiesel additives.

KEYWORDS: *furfural, glycerol, acetalization, Lewis acid, heterogeneous acid, biodiesel*

INTRODUCTION

Renewable fuels have become a focus of energy research because of a combination of global warming and an ever decreasing supply of fossil fuels.[1] As liquid fuels are currently a major necessity for nearly all forms of transportation, biodiesel stands out as one of the most practical solutions, at least in the short term.[2] Biodiesel is produced through the transesterification of vegetable oils or animal fats with an alcohol, generally methanol, yielding a methyl ester with combustion properties suitable for a diesel engine (Scheme 1).[3] Besides being a renewable fuel, biodiesel has several other benefits over petrodiesel, notably a decrease in harmful emissions, improved biodegradability, and lower toxicity.[4,5] Already, many parts of the world are pushing for increased biodiesel use, including Brazil, the European Union, United States, Canada, and China.[6,7] Expanded use of biodiesel, however, is hampered by two major drawbacks: (1) the large amount of glycerol byproduct yielded in the transesterification process greatly impacts profitability and the price to the consumer,[8] and (2) biodiesel exhibits poor low temperature properties.[9] Therefore, to further expand biodiesel use, it is necessary to address both these drawbacks.

Scheme 1. Transesterification of Triglycerides with Methanol, Yielding Fatty-Acid Methyl-Esters and Glycerol



When obtained directly from the biodiesel process, the crude glycerol is generally about 80−90% pure. Contaminants include soaps, salts, methanol, and water. Optimally, any chemical transformations with glycerol should utilize the crude grade to avoid expensive purification steps. Much interest has been placed on upgrading glycerol to more valuable chemicals, using methods such as selective oxidation, hydrogenolysis, dehydration, pyrolysis, esterification, etherification, carboxylation, and polymerization. These topics have been featured in several recent review articles.[10−12] Additionally, glycerol, with ∼52% of its mass being oxygen, has been targeted as a platform for deriving fuel additives for both gasoline and biodiesel, an appealing approach since it increases the overall yield of biofuels obtained from triglycerides.[13] Toward this end, several methods have been explored, including etherification,[14]

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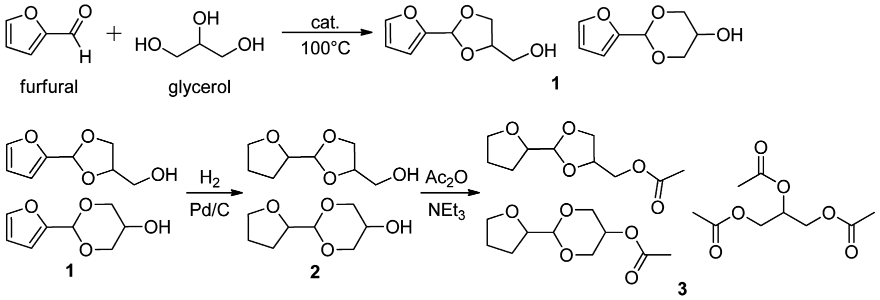
Scheme 2. Condensation of Furfural and Glycerol to Yield 1 as a Mixture of Dioxolane and Dioxane, Which May Be Hydrogenated to Give 2 and Then Acetylated to 3



esterification,[15] and acetalization.[16] For example, solketal, prepared from the condensation of acetone and glycerol, has been investigated as an additive in gasoline and biodiesel.[16,17]

Another group of materials which has received heavy attention in recent years are the biomass derived furans, furfural and hydroxymethylfurfural.[17,18] These compounds are prepared through the dehydration of sugar residues and are being regarded as suitable platform chemicals for replacing numerous petroleum based products. In addition to several industrial applications, furfural has received consideration as a substrate for the production of biofuels.[19] For example, Dumesic has published reports regarding the catalytic production of gasoline and diesel range alkanes starting from furan precursors.[20,21] The acetalization of glycerol with furfural has also been previously realized; however in all examples, the synthesis has been carried out in refluxing organic solvent with a water separation apparatus.[22,23] The products, furyl-1,3-dioxacyclanes, have been noted for their significant potential as synthetic platforms as well as practical applications.[24]

Herein, we report on the acetalization of glycerol with furfural under neat or pseudoneat conditions, employing simple Lewis acid salts or acidic solids as catalysts and simple reaction methods designed to increase yields. Additionally, we have examined postsynthetic modifications of the acetal products, mainly hydrogenation and acetylation (Scheme 2), and have investigated the applicability of these novel compounds as fuel additives to biodiesel. The applicability of our reaction methods to crude glycerol is demonstrated.

■ EXPERIMENTAL SECTION

Materials. Furfural was purchased from Sigma and was freshly distilled under reduced pressure and stored under an atmosphere of nitrogen prior to use. Pharmaceutical grade glycerol (>99%) was obtained from Sigma and used as received. All Lewis acid catalysts were used as received, and were supplied by Acros, Aldrich, Strem, or Alfa Aesar. The MCM-41 aluminosilicate, $(SiO_2)_{0.9875}(Al_2O_3)_{0.0125}\cdot xH_2O$, was purchased from Sigma and used as received (Al ≈ 3%, pore volume = 1.0 cm^3/g, pore size = 2.5−3 nm, BET spec. surface area = 940−1000 m^2/g). Anthracene, used as an internal standard in several experiments, was purchased from Sigma. 5% palladium on activated carbon (Pd/C) was purchased from Strem and was activated prior to use by first heating under flowing air at 110 °C for 1 h, then heating under flowing hydrogen at 250 °C for 1 h, and cooling under flowing hydrogen. Crude glycerol was obtained from Integrity Biofuels and used as received.

Lewis Acid Catalyzed Condensation of Furfural and Glycerol. In a typical reaction, furfural (1.92 g, 20 mmol) and glycerol (0.37 g, 4 mmol) were combined in a round-bottom flask, fitted with a reflux condenser, and heated to 100 °C with magnetic stirring. The catalyst (0.04−0.4 mmol, for salts, or 1−10 wt % for solid acids) was then added. In some cases, anthracene was added as an internal standard at approximately 10 mol % with respect to glycerol. Samples were withdrawn and dissolved in deuterated chloroform for analysis by NMR. To obtain isolated yields, the reaction was run as described above for an allotted period of time, and then the reaction vessel was placed under vacuum to remove water and excess furfural. The residue was dissolved in ether and filtered to yield a pink solution and often a black solid. After removal of the solvent under reduced pressure, the oil was passed through a silica gel column using a mixture of hexanes and ether (1:1) as eluent. Fractions containing the condensation products were combined, and the solvent removed under reduced pressure. Alternatively, for larger scale reactions, fractional vacuum distillation can be employed to isolate products. In this case, after filtration of the dissolved reaction mixture, the solvent was removed. Excess furfural was then distilled off under vacuum, after which the temperature was increased and the acetal products were distilled. In all cases, the products were obtained as a mixture of (2-(furan-2-yl)-1,3-dioxolan-4-yl)methanol and 2-(furan-2-yl)-1,3-dioxan-5-ol, each with a Z and E isomer, in approximately 7:3 ratio, respectively. Henceforth, this mixture of acetal products will be referred to as **1**.

Hydrogenation of 1. Hydrogenation reactions were performed using a Parr series 5000 multiple reactor system. For a typical reaction, 200−300 mg of **1** was added to a glass liner and dissolved in 20 mL of ether. 10w/w% of 5% Pd/C was then added, along with a glass coated stir bar. The reaction vessel was assembled and briefly purged with hydrogen gas before being pressurized to 2.76 MPa of hydrogen. The mixture was then stirred at 600 rpm for 6 h at 22 °C. Afterward, the catalyst was removed by gravity filtration and washed with ether. The resulting product mixture, **2**, was then analyzed by gas chromatography. Aliquots were removed, and the solvent was evaporated for analysis by NMR and MS.

Alternatively, larger scale reactions may be done under nearly neat conditions, using a minimal amount of ether to facilitate the complete transfer of **1** to the hydrogenation reactor. Under these conditions, the product mixture is identical as that described above. However, because of the nature of the reactor, it was necessary to recharge the hydrogen pressure several times before the hydrogenation was complete.

Acetylation of 2. Acetylation of the free hydroxyl group was performed by combining **2** with two equivalents each of acetic anhydride and triethylamine. After stirring for 4 h, the mixture was dissolved in ethyl acetate and washed with saturated sodium bicarbonate, water, and brine. The ethyl acetate fraction was then dried over magnesium sulfate, and, after filtration, the solvent was removed under reduced pressure. The obtained mixture, **3**, was a combination of acetylated acetals and triacetin in approximately a 4:1 ratio.

Determination of Crude Glycerol. To determine the concentration of glycerol in the crude glycerol, a sodium periodate assay was performed according to the established method.[25] Briefly, a sample of glycerol (ca. 0.2 g) was dissolved in 50 mL of water. To this, 50 mL of sodium periodate TS (12 mL 0.1 N H_2SO_4 and 6 g of $NaIO_4$ dissolved to make 100 mL solution). The solution was swirled to mix, stoppered, and left in the dark for 30 min. Excess sodium periodate was then quenched by adding 10 mL of ethylene glycol/water (1:1), swirled to mix, and left for 20 min. To this, 100 mL of water was added, and the mixture was titrated with a standardized NaOH solution (approximately 0.1 M), using phenolphthalein as an indicator. A blank was performed for correction. In this manner, the amount of glycerol in the original sample was determined. This method was found to have a tolerance of ±2% by testing pharmaceutical grade glycerol (>99%).

Product Analysis. NMR analysis was performed on either a Bruker ARX-400 instrument outfitted with a 5 mm QNP probe or a Varian Inova-300 instrument with a 5 mm 4-nucleus probe. Gas chromatography was performed using an Agilent Technologies 6890N instrument. GC/MS was done using an Agilent 5975C GC/MS for both EI and CI.

NMR yields are calculated by integration of the product versus a known quantity of internal standard (anthracene). The moles of product are determined by the following equation:

$$\text{mol}_{\text{prod}} = \text{mol}_{\text{std}} \cdot (\text{Integral}_{\text{prod}}/\text{Integral}_{\text{std}}) \cdot (N_{\text{std}}/N_{\text{prod}}) \tag{1}$$

where N is the number of nuclei for the relevant signal. The yield is then determined by the following formula:

$$\text{yield}_{\text{prod}}(\%) = (\text{mol}_{\text{prod}}/\text{mol}_{\text{glycerol}}) \cdot 100\% \tag{2}$$

where the $\text{mol}_{\text{glycerol}}$ is the initial amount of glycerol in the reaction mixture. In this way, we obtain accurate and reproducible yields which correlate well with the isolated yields that we obtain.

Fuel Analysis. Biodiesel samples were analyzed for cloud point, density, and flash point. Cloud point was determined by gradually cooling the sample and observing the temperature at which crystallization begins. The density was obtained by recording the mass of 1 cm^3 of sample. The flash point was determined using a Petro-test PM-4 closed-cup flash point tester, using the standard ASTM D93 method.

■ RESULTS AND DISCUSSION

Lewis Acid Catalyzed Condensation of Furfural and Glycerol. Previously, we have reported on the condensation of furfural and glycerol to form a mixture of furyl-1,3-dioxacyclanes, consisting of both 1,3-dioxolanes and 1,3-dioxanes, using a cationic rhenium oxazoline complex as a catalyst.[26] These products, **1**, have been described in the literature previously, having been formed using Brønsted acid catalysts.[22] Now we report on the use of simple and affordable Lewis acids to perform this reaction in the absence of an additional solvent. Because of the unfavorable equilibrium constant, we have found that a 5-fold excess of furfural is required to drive the reaction to products at 100 °C; however, under certain conditions, the excess of furfural may be significantly lowered. At room temperature the reaction mixture is not homogeneous, as glycerol and furfural are not miscible. Often, the Lewis acid salt is insoluble as well. Upon heating, the mixture becomes homogeneous. Generally, we observe a series of color changes as the reaction progresses; first going from colorless to a light brown/yellow, then to a dark pink, and finally the mixture will often become black, indicative of furfural loss through resin formation, resulting in polyfurfural; this transition to a black solution is often accompanied by the formation of a solid dark residue. The acetal products themselves (**1**) are pale yellow. The appearance of the dark color and solid residue is explained by the polymerization of furfural, causing the discoloration through an increase in conjugation. However, the origin of the pink color observed in the course of these reactions is not obvious, and is currently attributed to an acetal byproduct. While the structure of these byproduct(s) has not been discerned, NMR and MS data suggest that they are derivatives of the main acetal product **1** (see Supporting Information for additional details).

Table 1 shows the results for the various Lewis acids investigated. All salts exhibited comparable performance within a narrow range. Moderate yields of 60–80% were obtained within 30 min; yields increased with extended times as shown for $ZnCl_2$, reaching 90% yield after 2 h. These reactions were done on a small scale of 2–3 mL total volume in a closed system fitted with a reflux condenser. We note here that at these scales, the buildup of water in the reaction mixture is not very significant, because the reaction is carried out at 100 °C and there is sufficient surface area in the headspace for the water to condense on without reentering the reaction medium. Larger reaction volumes caused a decrease in the reaction yields as water becomes more prevalent. Anthracene was used as an internal standard because it gives a clear and defined peak in the NMR, and it is unreactive under our reaction conditions.

Table 1. Results for Several Lewis Acid Catalysts for the Reaction of Glycerol with Furfural[a]

entry	Lewis acid	concentration (mol %)	*t* (min)	% yield of **1**, NMR (isolated)
1	$ZnCl_2$	1	30	75
2	$ZnCl_2$	1	120	90 (89)
3	$CuCl_2$	1	30	55
4	$Cu(OTf)_2$	1	5	75 (67)
5	$AlCl_3$	10	30	70
6	$NiCl_2$	1	30	80
7	Ag(OTf)	1	30	60
8	$AgBF_4$	3	30	62

[a] All reactions were performed at 100 °C and at a reaction volume less than 3 mL. Anthracene was used as an internal standard for NMR analysis.

The general trend observed for these reactions is a fast initial period that accounts for most of the product followed by a slow phase in which product formation continues until the maximum yield is obtained. With respect to the ratio of acetal products formed (see Scheme 2), all the catalysts give similar selectivity; a mixture of approximately 70% dioxolane and 30% dioxane is obtained. Mechanistically, the Lewis acid catalyzed reaction is analogous to the traditional Brønsted acid catalyzed acetalization, and considering the elevated temperature, one would expect to preferentially form a higher portion of the kinetically favored product (dioxolane) rather than the thermodynamically favored product (dioxane). The main noticeable difference between catalysts, other than activity, is in the extent of furfural resinification, causing the accumulation of highly colored material. For example, $Cu(OTf)_2$ begins generating black material within several minutes of adding the catalyst, and the reaction mixture eventually solidifies to a gel. $ZnCl_2$, on the other hand, will remain a pink solution, even after several hours of heating.

Of the homogeneous Lewis acids studied, two stood out as candidates for further study: $Cu(OTf)_2$ for its high initial rate and $ZnCl_2$ for its high yields and significantly diminished side reactions. To examine the reaction further, the condensation products were isolated for both $Cu(OTf)_2$ and $ZnCl_2$. Silica gel columns were done to purify and isolate the condensation products, using a 1:1 mixture of hexanes/diethyl ether as eluent. From this, it is evident that a greater amount of byproducts was formed from the $Cu(OTf)_2$ catalyzed reaction than from the $ZnCl_2$ reaction. Additionally, the use of $Cu(OTf)_2$ results in a significant amount of insoluble black material, while $ZnCl_2$ results in virtually no insoluble products. The isolated yields obtained from these experiments also support the idea that $ZnCl_2$ is a superior catalyst, with an isolated yield of 89%, versus 67% for $Cu(OTf)_2$. These factors have led us to conclude that $ZnCl_2$ is the catalyst of choice for this reaction from the pool of Lewis acids examined herein.

Solid Acid Catalyzed Condensation. A number of solid acids were also utilized as catalysts for this reaction, as seen in Table 2. These include the hexagonally structured mesoporous aluminosilica MCM-41 (Al = 3%) and Montmorillonite K-10 clay. For each of these, around an 80% yield was achieved, comparable to many of the Lewis acids described above, though a slightly longer reaction time was necessary. The product distribution is the same as with the homogeneous Lewis acids, approximately a 7:3 ratio of dioxolane to dioxane. Curiously, an amorphous aluminosilicate material, DAVICAT SIAL 3113 (13% alumina), showed no improvement over the uncatalyzed reaction. The use of solid acids is beneficial since it simplifies the reaction separation and the catalyst can be easily recovered and reused in another batch of reactions. Additionally, use of a heterogeneous catalyst adds the prospect of potentially having a catalyst that is tolerant to water. While neither of the active catalysts here shows any tolerance to water (no products are observed when water is intentionally added to the reaction mixture), a select few catalysts have been noted in the literature as being water tolerant.[27]

Table 2. Catalytic Results for Several Solid Acid Catalysts[a]

entry	solid acid	% yield of **1**, NMR (isolated)
1	aluminosilicate MCM-41	80 (84)
2	montmorillonite K-10	79
3	davicat SIAL-3113	20

[a] All reactions were performed at 100 °C and at a small scale of less than 3 mL total volume and a catalyst loading of 10 wt % with respect to glycerol. Reaction times were all 2 h.

We tested the reusability of the mesoporous aluminosilica MCM-41 through a series of reactions. This was done by running the reaction for 2 h, after which time a small sample was removed for NMR analysis. The remaining reaction volume was dissolved with ethyl ether, and the catalyst was removed via vacuum filtration. The catalyst was then washed with ethyl ether and allowed to dry for several minutes. A fresh batch of furfural and glycerol was prepared, and the recovered catalyst was added. The same catalyst sample was used in a series of three reactions, and there was no evident loss of activity (Figure 1). The observed yields, however, were lower than previously observed because of the larger scale of the reaction and the increased product inhibition caused by the buildup of water, as mentioned in the previous section. As a follow up, a sample of the recovered catalyst was used in a fourth reaction of a smaller scale, and as expected, a higher yield was obtained. As it was reused, the MCM-41 material, initially a pristine white, took on a gray color; however, as evident by our experimental data, this did not hinder its catalytic activity.

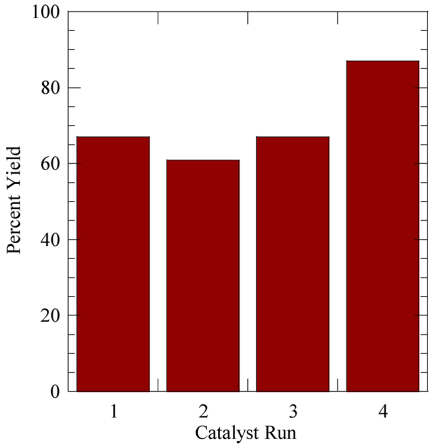


Figure 1. Reusability of the aluminosilicate MCM-41 catalyst. All runs done at 100 °C for 2 h with a 5:1 ratio of furfural to glycerol and approximately 10% w/w MCM-41. Runs 1−3 had a reaction volume of 2.5 mL, while run 4 had a reaction volume of 1.25 mL, thus affording a higher yield.

As noted earlier, we have noticed as a general trend for all catalysts that as the scale of the reaction increases, the yields drop. We attribute this to the buildup of water in the reaction mixture as the reaction proceeds, which shifts the equilibrium back toward reactants. Traditionally, with acid catalyzed reactions of this type, this problem is dealt with by using a Dean−Stark apparatus to remove water from the solvent. This, however, is impractical for our purpose. In a recent report on the acetalization of glycerol with acetone using sulfonic acid functionalized mesostructured silicas under pseudo-neat conditions (using a 6-fold excess of acetone), this issue was dealt with by removing all of the acetone and water byproduct under reduced pressure, and adding in a fresh quantity of dry acetone and continuing to run the reaction. After several of these cycles, yields were improved from around 80% to over 90%.[28] Again, for our case, it would be cumbersome to remove all the furfural in each cycle, because of the lower volatility of furfural. However, based off this methodology, we devised a simple and straightforward method for improving reaction yields. After heating the reactants together to 100 °C, the catalyst MCM-41 was added, and the reaction was allowed to proceed as usual for 10 min. After this, a continuous stream of dry nitrogen was blown over the reaction while maintaining the reaction temperature at 100 °C, effectively purging the headspace of any volatiles. A diagram of the reaction setup is provided in the Supporting Information. After 30 min of nitrogen flow, the yields were improved from 60 to 70% to nearly 90% (Figure 2).

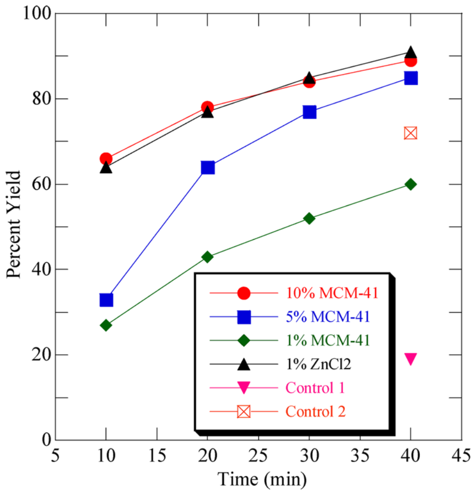


Figure 2. Improvement of yields by continuous stream of nitrogen gas flow over the reaction mixture. Reactions were done at 100 °C with a 5:1 ratio of furfural to glycerol, and the stream of nitrogen gas was started after the first 10 min. Control 1: No catalyst was added to the reaction mixture while the nitrogen stream was used. Control 2: 5% w/w MCM-41 in the absence of the nitrogen flow.

This method of continuous nitrogen flow was tested for 10%, 5%, and 1% w/w MCM-41 catalyst. As expected, the higher catalyst loading results in higher yields in the given time, though between 10% and 5%, the final yields are essentially identical. The 1% catalyst loading was noticeably slower. In addition, we tested this continuous nitrogen flow method for the zinc chloride homogeneous catalyst as well and observed increased yields. After 40 min reaction time, 91% yield of **1** was observed, which is up from 70 to 80% for a closed system at a similar scale and time.

While there is a small loss of both furfural and glycerol from the reaction while the stream of dry nitrogen gas is passed over it, the effect is minimal, and the overall benefit outweighs any negative drawbacks. The volatiles lost because of the nitrogen stream may be collected by either passing the gas through a tube that is cooled in a dry ice bath, or by simply directing the gas flow into a small Erlenmeyer flask. By doing this, we have collected a liquid which separates into two layers, one primarily composed of furfural and the other being glycerol and water. While the loss of glycerol and furfural from the reaction may ultimately have an impact on the yield, both chemicals could be recycled. Furthermore, neither the condensation products nor the internal standard were removed by the nitrogen flow, meaning that accurate yields were obtained.

A control reaction was done mimicking the normal reaction conditions for the continuous flow method, without the addition of a catalyst. A sample was removed after 30 min of the nitrogen flow, revealing a 19% yield. A second control experiment was done using 5% MCM-41 catalyst and no nitrogen flow. In this case, the yield after 40 min of total reaction time was 72%. These controls highlight the importance of both the catalyst material and the nitrogen flow; in the absence of one, the yield is severely impacted.

With this new methodology, two applications were pursued. First, whether the reaction can be achieved using crude glycerol generated from biodiesel production, and second, whether the reaction can be conducted under truly neat conditions, stoichiometric furfural and glycerol. A sodium periodate assay was used to determine the glycerol content in crude glycerol samples obtained from Integrity Biofuels. The glycerol content of our crude samples was found to be 87% by weight. This value was used to calculate the amounts of furfural and catalyst needed. Our efforts were focused on using the MCM-41 aluminosilicate catalyst under the optimal conditions described above (100 °C with a stream of nitrogen gas purging the headspace). Significant differences between the crude and the pharmaceutical glycerol samples were noted instantly by mere observation. The MCM-41 catalyst clumped up in the reactions with crude glycerol, whereas with the pharmaceutical glycerol, the MCM-41 catalyst retained its fine powder state. This is indicative that the MCM-41 was acting as an absorbent to remove water from the reaction mixture with crude glycerol.

Results for the reactions done with the crude glycerol are summarized in Table 3. At 100 °C, significant yields were not observed until the catalyst loading reached 10 wt %. By increasing the temperature to 125 °C, improved yields were observed with 5 wt % catalyst loading. However, during the course of these reactions, the reaction mixture showed little to no change for a period of time, then rapidly changed color and began accumulating black material. Two hypotheses are put forward to rationalize this observation: (1) some component of the crude glycerol is acting as a secondary catalyst and (2) both the MCM-41 and the N_2 flow are removing water from the reaction mixture. The reaction proceeds only when sufficient water has been removed.

Table 3. Results of Reactions Utilizing Crude Glycerol[a]

entry	temperature (°C)	w/w% MCM-41	N_2-flow time (min)	% yield of **1**
1	100	10	20	80
2	100	5	50	27
3	100	1	20	<1
4	125	5	10	78
5	125	1	30	10

[a] All reactions were performed using a 5:1 ratio of furfural to glycerol, based on a glycerol content of 87% in the crude material. Reactants were stirred at temperature for 10 min prior to starting the nitrogen flow.

To test our hypothesis that a component of the crude glycerol is acting as a catalyst for the reaction, we ran condensation reactions with crude glycerol and furfural without an additional catalyst. Little to no yield was observed, even after an additional hour of continual nitrogen flow. Additionally, reactions run in the presence of either sodium sulfate or 3 Å molecular sieves also afforded little to no product. These results lead to the conclusion that the MCM-41 material is vital for the reaction. A recent study has investigated the impact of methanol, water, and NaCl on the catalytic acetalization of glycerol with acetone using the solid acids Amberlyst-15 and zeolite H-Beta.[29] All three materials have a deleterious effect on the catalytic conversion, and the effect was even more significant when two or more contaminants were combined. The presence of water has a dual effect of both inhibiting the forward acetalization reaction in addition to decreasing the strength of the acid sites. The addition of NaCl along with water causes the neutralization of acid sites through cation exchange, with the water aiding the transport of the salt into the pores. And while the cation exchange would release HCl into the reaction medium, HCl was ruled out as a catalyst for this reaction through a control experiment with concentrated HCl.

However, one might argue that the presence of a significant amount of water (inevitable when using concentrated HCl) would severely inhibit the reaction because of both the unfavorable equilibrium constant and the poor acid strength. So in a system such as ours, where water is being constantly removed from the reaction medium, the liberation of HCl would seem to explain the sudden reaction which we observe, as well as explain why the crude glycerol leads to the accumulation of furfural resins while the pure glycerol does not, since the furfural degradation pathways are known to be driven by both acid and heat.[30] In fact, when we add concentrated HCl to a hot solution of glycerol and furfural, the mixture instantly turns black and in a few minutes turns to a solid block of furfural resin. So, this collection of evidence seems to indicate a variety of factors governing the reactivity of crude glycerol with furfural, using the MCM-41 catalyst and the N_2-flow method. First, the slow cation exchange, releasing HCl into the solution, and second, the removal of water via the nitrogen flow until the mixture is sufficiently dry enough for the reaction to progress.

Our second goal was to decrease the amount of furfural included in the reaction mixture. Indeed, using our new methodology, we were able to significantly reduce the amount of furfural used in the reaction while maintaining good yields, as shown in Table 4. 25% molar excess of furfural, 4 w/w% MCM-41 catalyst, and an hour of N_2 flow gave an isolated yield of 68%. In a similar fashion, an 85% yield was achieved with only 2:1 furfural:glycerol molar ratio. This yield is comparable to that previously obtained with a 5-fold excess of furfural. With this knowledge, we were able to use a 50% molar excess of furfural to successfully scale up the reaction to volumes over 100 mL while maintaining an isolated yield of >80%.

Table 4. Survey of Reaction Conditions Aimed to Improve Yields while Decreasing the Excess of Furfural[a]

entry	molar ratio furfural:glycerol	total reaction vol. (mL)	cat. w/w%	N_2 flow time (h)	% isolated yield of **1**
1	1.25:1	12	4	1	68
2	2:1	15	4	1	85
3	1.5:1	40	2	1	65
4	1.5:1	110	2	1.5	48
5	1.5:1	110	2	3	76
6	1.5:1	116	2	4	82

[a] Reactions were performed at 100 °C with the aluminosilicate MCM-41 as catalyst.

Hydrogenation of 1. The furan ring of the condensation products can be hydrogenated using 5% Pd/C under mild conditions of 2.76 MPa hydrogen at 22 °C. The resulting product, **2**, is a complex mixture of tetrahydrofuryl-1,3-dioxacyclanes; the addition of another chiral center adds several isomeric forms. Analysis of the product mixture by GC/MS and NMR verifies that the furan ring was successfully hydrogenated while the rest of the molecule was left intact. NMR analysis of **2** shows several doublets from 4.3 to 5.0 ppm for the alpha proton. The furyl-1,3-dioxacyclanes, on the other hand, show 4 singlets from 5.5 to 6.1 ppm for the alpha proton.

Acetylation of 2. In consideration of observations made by Garcia et al in which acetylation of the free hydroxyl group of solketal yields a more attractive biodiesel additive,[16] a similar transformation on products **2** was carried out. **2** was reacted with acetic anhydride in triethylamine, yielding **3**, a mixture of tetrahydrofuryl-1,3-dioxacyclane acetates and triacetin. By NMR, an approximate molar ratio of acetal to triacetin was determined to be 4:1. Because of the complexity of this mixture, it is challenging to determine the exact ratio; however, it is clear that the amount of acetal present is multiple times that of triacetin. Since triacetin itself has been studied for use as a biodiesel additive with little to no ill-effects,[15] the presence of triacetin in this mixture is not detrimental to the viability of its use as a biodiesel additive.

Effect of 2 and 3 as Biodiesel Additives. To examine the viability of our products as additives to biodiesel, we blended the materials with B100 prepared from soybean oil. Blends of **2** were prepared in 1 and 5 wt %, while blends of **3** were prepared in 1, 5, and 10 wt %. The poor solubility of **2** in biodiesel prevented the preparation of a 10 wt % sample. **3** showed no problems with solubility, suggesting that it may be better suited as a fuel component. To get a basic understanding of the properties of our fuel blends, we measured the cloud point, density, and flash point of all our samples, results shown in Table 5. The cloud point serves as a good indicator for the fuel's performance at low temperature.

Table 5. Results of Fuel Analysis for Blends of Materials 2 and 3 in Biodiesel Obtained from Soybean Oil

sample	flash point, °C	cloud point, °C	density, g/cm^3
B100	126	0.9	0.895
1% **2**	140	1.2	0.899
5% **2**	148	0.7	0.907
1% **3**	150	1.0	0.905
5% **3**	140	0.0	0.909
10% **3**	144	0.1	0.920
2	140−148	n/a	1.220
3		n/a	1.191

The cloud point is measured by gradually lowering the temperature and observing the point at which crystals begin to form. From our tests, we can surmise that compounds **2** and **3** may be blended with biodiesel at low levels and have no adverse effects to the fuels low temperature properties. While statistically insignificant, we did observe a slight drop in the cloud point for blends of **3**. However, this effect may be due to the presence of triacetin in the sample, which has been reported to improve low temperature properties of biodiesel.[31] Additionally, compound **1** was tested as a cloud point suppressant in biodiesel, and again, the results for this material indicated that there was no effect.

We observed little to no impact on the density. As expected, because of the density of the additives being much larger than that of the biodiesel, there was some slight increase in the density of the blends. However, this increase is insignificant except for in the higher (10%) blending levels.

Finally, the flash points were determined according to the ASTM D93 specifications. The results indicate that the presence of these materials in the biodiesel do not significantly alter the flash point of the fuel.

We have demonstrated that the condensation of furfural and glycerol to acetals and their subsequent hydrogenation can be performed easily and economically. However the final step, the acetylation, requires several chemicals and may not be feasible on large scale. While this step does greatly improve the solubility of the additive in the biodiesel, based on our data collected so far, **3** does not offer significant advantages over **2**. Therefore, the final acetylation step may be omitted, still yielding a viable biodiesel additive while maintaining an economic and chemically efficient process.

■ CONCLUSIONS

Cyclic acetals have been prepared from the condensation of furfural and glycerol using neat conditions at moderate temperatures with a variety of homogeneous Lewis acid catalysts and heterogeneous solid acids. The introduction of N_2 flow over the reaction circumvented water inhibition and enabled high yields of acetal under nearly stoichiometric furfural to glycerol molar ratio at scales of >100 mL. The ideal Lewis acid catalyst was found to be $ZnCl_2$ because of the minimization of byproducts from furfural resinification; however, the aluminosilicate MCM-41 gives nearly the same yields and therefore should be considered the superior catalyst because of its heterogeneous nature. Additionally, we have found that our reaction methods and catalysts can be applied to crude glycerol while maintaining decent yields. These synthetic methods may be applied to other substrates and reactions provided that they retain a low volatility.

The isolated condensation products are easily hydrogenated under mild conditions, followed by acetylation of the free hydroxyl group. The resulting mixtures were tested as additives in biodiesel and were found to have no ill-effects based on the data collected. The described catalytic processes enable the recycling and use of a byproduct of biodiesel production, glycerol, in combination with biomass derived material, furfural, as a fuel component up to 10 wt % of the biofuel.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra, MS data, and GC traces for compounds **1**−**3**, along with additional details regarding the byproduct of the condensation reaction and the experimental setup. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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