

Glycerol acetylation mediated by thermally hydrolysed biosolids-based material

Original

Glycerol acetylation mediated by thermally hydrolysed biosolids-based material / Bartoli, Mattia; Zhu, Chengyong; Chae, Michael; Bressler, David C.. - In: CATALYSTS. - ISSN 2073-4344. - ELETTRONICO. - 10:1(2020), p. 5.
[10.3390/catal10010005]

Availability:

This version is available at: 11583/2777315 since: 2020-01-08T16:00:51Z

Publisher:

MDPI

Published

DOI:10.3390/catal10010005

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

(Article begins on next page)

Article

Glycerol Acetylation Mediated by Thermally Hydrolysed Biosolids-Based Material

Mattia Bartoli, Chengyong Zhu, Michael Chae and David C. Bressler *

Department of Agricultural, Food and Nutritional Science, University of Alberta, 410 Ag/For Building, Edmonton, AB T6G 2P5, Canada; mattia.bartoli@polito.it (M.B.); chengyon@ualberta.ca (C.Z.); mchae@ualberta.ca (M.C.)

* Correspondence: dbressle@ualberta.ca; Tel.: +1-780-492-4986

Received: 15 November 2019; Accepted: 16 December 2019; Published: 18 December 2019

Abstract: Crude glycerol is the main by-product of many renewable diesel production platforms. However, the process of refining glycerol from this crude by-product stream is very expensive, and thus does not currently compete with alternative processes. The acetylation of glycerol provides an intriguing strategy to recover value-added products that are employable as fuel additives. In this work, the conversion of glycerol to acetyl derivatives was facilitated by a heterogeneous catalyst generated from the thermal hydrolysis of biosolids obtained from a municipal wastewater treatment facility. The reaction was studied using several conditions including temperature, catalyst loading, acetic acid:glycerol molar ratio, and reaction time. The data demonstrate the potential for using two distinct by-product streams to generate fuel additives that can help improve the process economics of renewable diesel production.

Keywords: biosolids; esterification; glycerol conversion; heterogeneous catalysis

1. Introduction

Biodiesel and renewable diesel commodities are one of the main driving forces of the green economy [1] as they decrease the emission of CO₂ compared to fossil fuels [2]. Currently, biodiesel production is mainly performed through transesterification of triglycerides using methyl or ethyl alcohols, which leads to the massive production of glycerol as a by-product [3]. Other technologies that are capable of generating renewable diesel, such as thermal conversion of lipids, also generate glycerol as a by-product [4–6]. The Organization for Economic Co-operation and Development of the Food and Agriculture Organization of the United Nations (OECD-FAO) reports that global biodiesel production will increase from 36 to 39 billion litres between 2017 and 2027 [7]. Since the amount of crude glycerol recovered as a by-product is roughly 10% of the biodiesel generated [8], annual global production of crude glycerol is anticipated to reach 3.9 billion litres by 2027. Currently, producing refined glycerol from crude by-product streams is far more expensive than traditional processes [9–11] even if glycerol itself has many uses [12], such as an additive for cosmetic [13,14] and pharmaceutical [15] industries and as cattle feed [16,17]. Nonetheless, glycerol is an attractive feedstock for several conversion procedures, including oxidation [18], hydrogenolysis [19], etherification [20], esterification [21,22], glycerol carbonate synthesis [23–25] and biological conversions [24]. In particular, glycerol acetyl derivatives have received increasing attention due to their wide applications in many fields, from polymer production to fuel additive manufacturing [26–30]. The glycerol acetylation process produces three different compounds, monoacetins, diacetins and triacetin, whose yields are affected by many process and chemical parameters [31,32]. Mixtures of diacetins and triacetin are valuable diesel or gasoline additives leading to enhanced cold resistance, improved viscosity and anti-knocking properties [33,34]. Similarly, monoacetins could be converted

to solketal derivatives that show the same properties of di- and triacetin, with low consumption of acetic acid required for their production [35]. Furthermore, acetins mixtures are used by the pharmaceutical industry as filming [36] and as dispersant agents [37] and as a solvent for hydrophobic molecules and essential oils [38,39].

Glycerol acetylation is generally performed under catalytic conditions using heterogeneous acidic catalysts (i.e., ion exchange resins [40,41], heteropolyacids [42], zeolites [43], clays [44], biochar [45]) as well as both acetic acid [46] and acetic anhydride [47]. Acetic anhydride is a very effective acetylation agent under mild conditions (room temperature with short reaction time) and leads to the chemoselective formation of triacetin with a high release of heat. Despite this, acetic acid is preferentially used for glycerol acetylation due to its lower cost and the strict regulations associated with acetic anhydride use [48]. The acetylation procedure carried out using acetic acid as the acylating agent leads to the formation of various acetyl esters of glycerol and generally requires higher temperatures and a high acetic acid/glycerol ratio [33]. Acetic acid consumption and product purification has been optimized using several continuous processes based on distillation as reported in many studies [49–52].

Recently, Bartoli et al. [23] described a novel catalyst derived from the solid residue recovered after the thermal hydrolysis of biosolids. Thermal hydrolysis of biosolids has been shown to dramatically improve settling rates, and thus offers a potential alternative to current disposal strategies that employ natural settling in large biosolids lagoons [53]. To help offset the high costs that would be associated with the thermal hydrolysis of biosolids at large-scale, valorisation of the metal-rich solid residues recovered from hydrolysates was explored. Bartoli et al. [23] demonstrated that this material functioned as an effective inter- and intramolecular esterification agent for the production of glycerol carbonate and glycidol through urea glycerolysis.

Following up on this study, the same biosolids-based catalyst was employed and evaluated for glycerol acetylation using acetic acid. The esterification reaction was studied under several conditions of reaction time, temperature, acetic acid/glycerol ratio, and catalyst loading. Here, we provide a proof-of-concept that our biosolids-based catalyst can facilitate conversion of glycerol to acetyl derivatives, which could potentially provide value to both renewable diesel producers, as well as wastewater treatment facilities.

2. Results

2.1. Preliminary Considerations Regarding Catalyst-Induced Reactivity and Composition

Glycerol acetylation proceeds through a well-known, multi-step mechanism (Figure 1). The first esterification reaction occurs using one of the hydroxylic functionalities bounded to either a terminal or internal carbon atom of glycerol. The acetylation of terminal groups is both statistically and chemically preferred due to less steric hindrance. As a consequence, the formation of 1-monoacetin is far more common than the formation of 2-monoacetin. The second acetylation occurs preferentially on the remaining terminal carbon of 1-monoacetin, again due to steric hindrance. According to Zhou et al. [54], the production of internal acetin is very slow and is the rate determining step in each acetylation reaction [31,55] causing a low yield of triacetin, 1,2-diacetin and 2-moacetin.

Catalysts currently used for glycerol acetylation are mainly solid acids, such as resins or inorganic salts [43], that promote a classical acid-mediated esterification. Nonetheless, Reddy et al. [56] reported the use of metal oxides as effective catalysts for glycerol acetylation. Considering the beneficial activity of metal oxides joined to acidic sites, the heterogeneous biosolids-based catalyst studied by Bartoli et al. [23] for the urea glycerolysis process is also a promising candidate for glycerol acetylation. The solid residue obtained through the thermal hydrolysis of biosolids showed very promising characteristics, such as a high concentration of acidic sites (up to 5.32 ± 0.03 mmol/g) and several transitional metals (Table 1), mainly as oxide derivatives [23], as shown by XRD analysis reported in Figure 2.

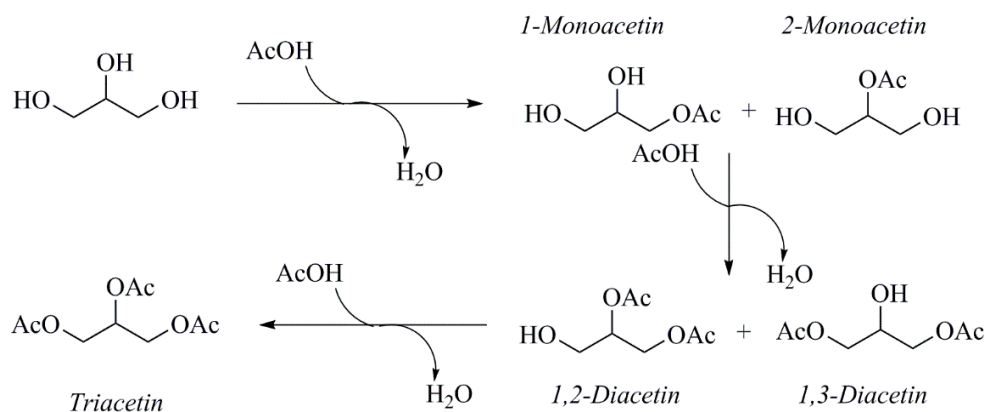


Figure 1. Esterification reaction pathways of glycerol to acetyl derivatives.

Table 1. The concentration of the main metal species in the solid heterogeneous catalyst acquired through the thermal hydrolysis of biosolids.

Catalyst	Concentration (mg/g)									Ref.
	Cr	Fe	Mn	Sr	Al	Cu	Zn	Pb	Ti	
Initial	0.4 ±	26.5 ±	0.58 ±	0.4 ±	26.9 ±	0.7 ±	1.1 ±	0.1 ±	3.2 ±	[23]
	0.2	1.3	0.03	0.1	1.3	0.1	0.1	0.1	0.2	
After 5 reactions	0.4 ±	28.7 ±	0.36 ±	0.4 ±	25.2 ±	0.2 ±	0.7 ±	0.2 ±	0.1 ±	Current study
	0.2	1.7	0.02	0.1	1.6	0.01	0.1	0.1	0.1	

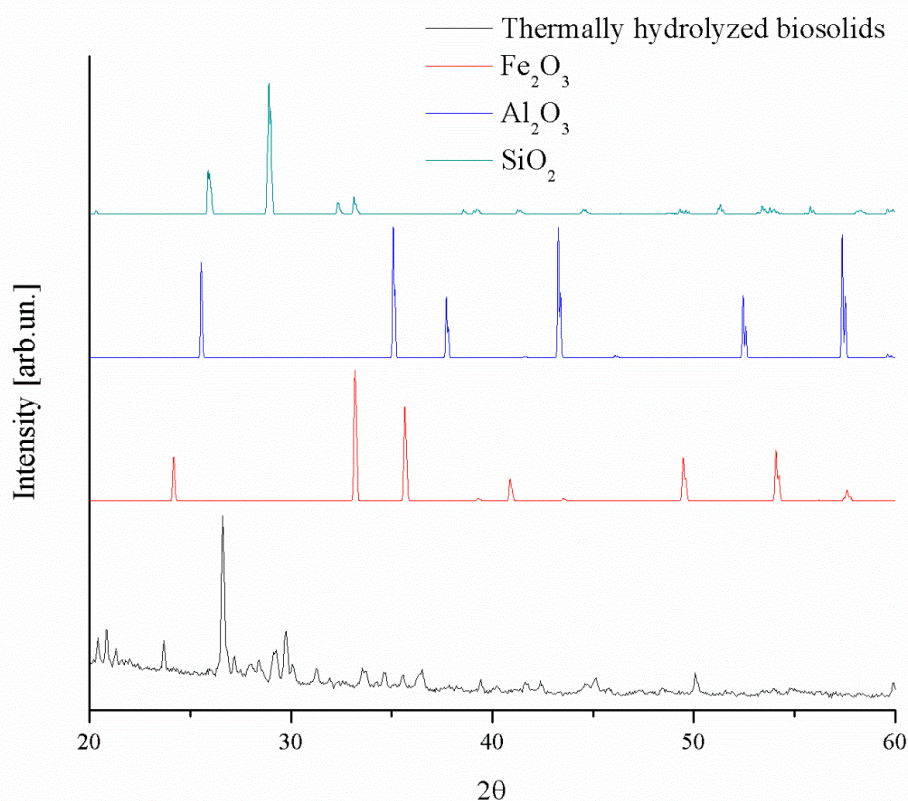


Figure 2. XRD pattern of thermally hydrolysed biosolids-based material in the range from 20 2θ to 60 2θ compared with pure phases of Fe₂O₃, Al₂O₃ and SiO₂ [57].

Due to the very complex composition of thermally hydrolysed biosolids-based material, XRD analysis can provide only qualitative data. The XRD pattern of thermally hydrolysed biosolids-based

material using QualX software (IC-CNR, Bari, Italy) and the RRUFFTM Project database for pure materials showed the presence of silicon oxide, iron oxide and aluminum oxide (quality match of 94%, 89% and 79%, respectively) as amorphous or mixed phase materials. The additional peaks in the spectrum were reasonable due to residual oxides, halides, phosphate metals and organic residues that compose the complex mixture of biosolids-based catalysts.

Since the early years of 19th century, it has been known that metals and their oxides could improve the performance of catalysts during the esterification reactions [58]. Consequently, the metals mixture recovered from thermally-hydrolysed biosolids could potentially be used as a catalyst without further purification procedures.

2.2. Influence of Temperature on Glycerol Acetylation Conversion Rate and Selectivity

The influence of the reaction temperature on glycerol acetylation was investigated during a 4 h period using four different temperatures (60 °C, 80 °C, 100 °C, 120 °C) and a fixed catalyst/glycerol weight ratio (4 wt%) and acetic acid/glycerol molar ratio (6:1) as reported in Figure 3. According to two-way ANOVA tests, the temperature and reaction time both had significant relevance ($p < 0.05$) on the conversion values. At a temperature of 60 °C, conversions were generally low reaching a maximum of $32.1 \pm 1.6\%$ after 4 h. When the reaction temperature was increased to 80 °C, the conversion slightly increased to $41.1 \pm 2.1\%$ after 4 h, but at the 1 h or 2 h time points, there were no significant differences compared with the corresponding time points at 60 °C. After 1 h at 100 °C, the conversion value observed ($8.9 \pm 0.7\%$) was not statistically different from the 1 h reactions conducted at both 60 °C and 80 °C. However, an increase in reaction time at 100 °C led to improved conversion values, reaching a maximum of $63.2 \pm 1.5\%$ after 4 h. Furthermore, significantly higher conversion was achieved at all time points at 120 °C, reaching $27.7 \pm 1.2\%$ and $78.4 \pm 0.2\%$ after 1 h and 4 h, respectively.

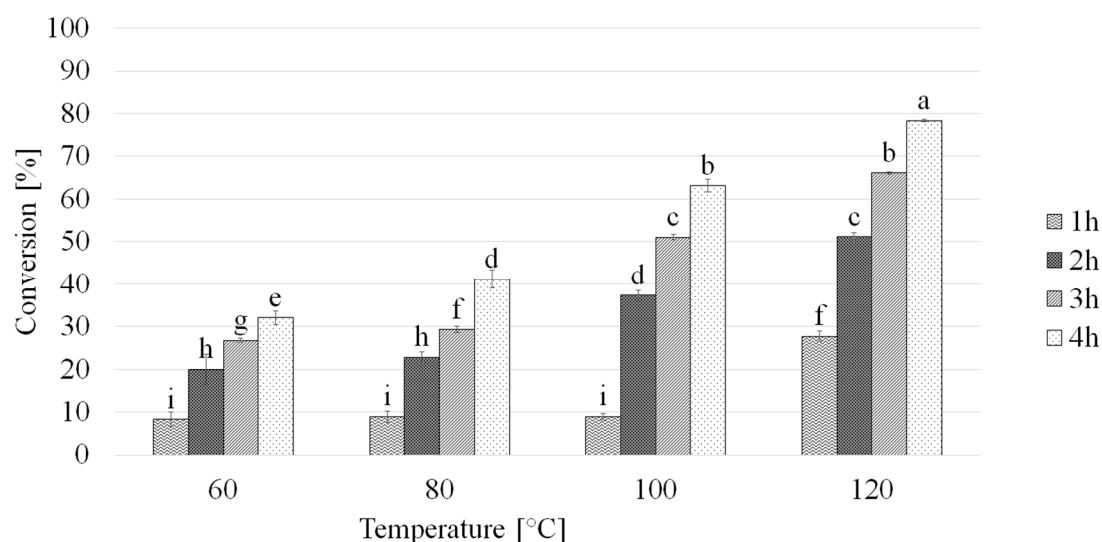


Figure 3. The effect of temperature on the conversion of glycerol to acetyl derivatives catalysed by the biosolids-based catalyst. Reactions were carried out using a catalyst:glycerol ratio of 4% (w/w), and a 6:1 molar ratio of acetic acid:glycerol. The conversion values were examined using four different temperatures: 60 °C, 80 °C, 100 °C and 120 °C. The averages \pm standard deviations shown were calculated using values from three experiments. Data annotated with different letters are significantly different (at a 95% confidence level).

According to two-way ANOVA tests ($p < 0.05$), selectivity was also affected by both temperature and reaction time (Table 2). At 60 °C, the use of a catalyst derived from thermally hydrolysed biosolids led to selective formation of monoacetins within the first 3 h of the reaction. However,

diacetins were detected in appreciable amounts ($11.4 \pm 0.9\%$) after 4 h. Although the selectivity for the monoacetins at $60\text{ }^{\circ}\text{C}$ was quite high, the overall yields (calculated as the product of selectivity and conversion) were quite low reaching a maximum of around 28% after 4 h. At $80\text{ }^{\circ}\text{C}$, selectivity for monoacetins was still extremely high ($95.7 \pm 0.6\%$) after 1 h, decreasing to $87.5 \pm 1.0\%$ after 4 h. At the same time, diacetins conversion increased from 3.6 ± 0.1 after 1 h to $11.3 \pm 0.6\%$ after 4 h. Moreover, traces of triacetin were detected in appreciable amounts after 4 h ($1.2 \pm 0.4\%$). A further increase in temperature to $100\text{ }^{\circ}\text{C}$ dramatically reduced monoacetins selectivity to $53.3 \pm 0.7\%$ after 4 h, while the occurrence of diacetins reached $41.3 \pm 0.4\%$. Under these conditions, triacetin was also detected at $5.4 \pm 0.8\%$. After 4 h at $120\text{ }^{\circ}\text{C}$, the selectivity of monoacetins ($45.5 \pm 1.4\%$) and diacetins ($46.6 \pm 1.5\%$) were statistically similar ($p < 0.05$), while the selectivity for triacetin increased to $6.6 \pm 0.8\%$. Generally, increments in diacetin and triacetin conversion were observed as a result of both increasing temperature, as well as longer reaction times.

Table 2. Effect of the temperature on the selectivity during glycerol acetylation catalysed by a biosolids-based catalyst. Reactions were carried out using a catalyst/glycerol ratio of 4% (*w/w*), and a molar ratio of acetic acid:glycerol of 6:1.

T [h]	T [°C]	Conversion ^a (%)	Selectivity ^b (%)		
			Monoacetins	Diacetins	Triacetin
1	60	8.3 ± 1.7	>99	Not detected	Not detected
2		20.0 ± 3.4	>99	Not detected	Not detected
3		26.8 ± 0.5	>99	Not detected	Not detected
4		32.1 ± 1.6	88.4 ± 0.8	11.4 ± 0.9	Not detected
1	80	8.9 ± 1.3	95.7 ± 0.6	3.6 ± 0.3	0.7 ± 0.2
2		22.8 ± 1.2	93.7 ± 0.5	6.1 ± 0.5	0.5 ± 0.2
3		29.3 ± 0.8	91.0 ± 0.7	8.6 ± 0.4	0.5 ± 0.3
4		41.1 ± 2.5	87.5 ± 1.0	11.3 ± 0.6	1.2 ± 0.4
1	100	8.9 ± 0.7	86.6 ± 0.7	12.5 ± 0.2	0.8 ± 0.2
2		37.3 ± 1.2	73.9 ± 0.3	25.3 ± 0.6	0.9 ± 0.3
3		51.1 ± 0.7	62.7 ± 0.9	33.5 ± 0.3	3.8 ± 0.9
4		63.2 ± 1.5	53.3 ± 0.7	41.3 ± 0.4	5.4 ± 0.8
1	120	27.7 ± 1.2	70.9 ± 1.9	23.9 ± 2.0	1.5 ± 0.1
2		51.1 ± 1.1	64.7 ± 0.5	33.1 ± 1.7	2.0 ± 0.7
3		66.1 ± 0.3	54.2 ± 1.4	40.8 ± 3.0	4.6 ± 0.1
4		78.4 ± 0.2	45.5 ± 1.4	46.6 ± 1.5	6.6 ± 0.8

^a Conversion: $100 \times ((\text{initial mass of glycerol} - \text{final mass of glycerol}) / (\text{initial mass of glycerol}))$;

^b Selectivity: $100 \times (\text{area of product}_i / \sum_i \text{area product}_i)$.

2.3. Influence of the Acetic Acid:Glycerol Ratio on Glycerol Acetylation Conversion Rate and Selectivity

The influence of the molar ratio of acetic acid and glycerol on glycerol acetylation using a biosolids-based catalyst was investigated using four different acetic acid:glycerol molar ratios (9:1, 6:1, 3:1 and 1:1) at $120\text{ }^{\circ}\text{C}$, and a catalyst/glycerol weight ratio of 4% as shown in Figure 4. According to two-way ANOVA tests, both reaction time and acetic acid/glycerol ratio had a significant impact on conversion. Despite this, there were no statistically differences ($p < 0.05$) in conversion after 1 h between the various acid:glycerol molar ratios tested, with an average conversion value around 27%. Using an acetic acid:glycerol molar ratio of 1:1, a slight increase in conversion from $26.0 \pm 1.2\%$ after 1 h to $40.8 \pm 0.5\%$ after 4 h was observed. A greater increase in conversion was observed using an acetic acid:glycerol ratio of 3:1, reaching $73.1 \pm 0.7\%$ after 4 h. Further increments in the acetic acid:glycerol molar ratio (6:1 and 9:1) led to increases in conversion of $78.4 \pm 0.2\%$ and $85.8 \pm 1.2\%$ after 4 h, respectively.

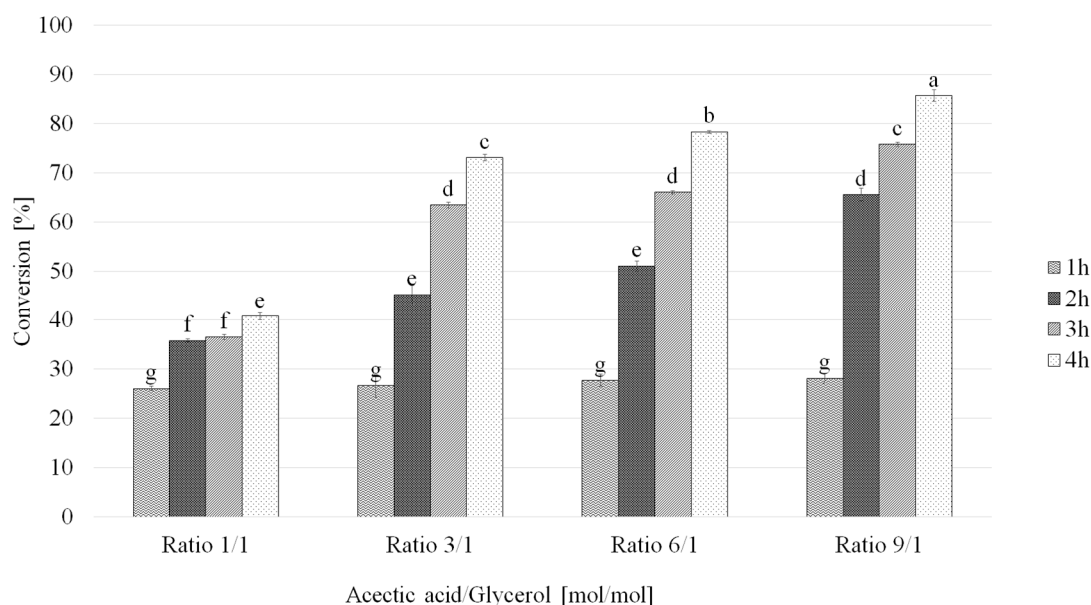


Figure 4. Effect of the acetic acid:glycerol molar ratio on the conversion of glycerol to acetyl derivatives catalysed by a biosolids-based catalyst. For the reactions shown above, the catalyst/glycerol ratio was maintained at 4 wt%, with a reaction temperature of 120 °C. To determine the relationship between conversion and the acetic acid:glycerol ratios, four molar ratios were employed: 9:1, 6:1, 3:1 and 1:1. The errors bars represent the standard deviations from the averages calculated from triplicate experiments. Data annotated with different letters are significantly different (at a confidence level of 95%).

Selectivity (Table 3) was also affected by both temperature and acetic acid:glycerol molar ratio according to two-way ANOVA outputs ($p < 0.05$). Considering a reaction time of 1 h, the biosolids-based catalyst showed a monoacetins selectivity of $74.3 \pm 3.2\%$ using an acetic acid:glycerol molar ratio of 1:1. A decrease in monoacetins selectivity to around 70% was observed using molar ratios of acetic acid:glycerol of 3:1 and 6:1. A further increment in acetic acid:glycerol ratio (9:1) led to a monoacetins selectivity of $80.4 \pm 3.8\%$. Monoacetins selectivity generally decreased with reaction time down to $43.8 \pm 2.0\%$ using an acetic acid:glycerol molar ratio of 1:1 after 4 h. A similar trend was observed for all other ratios tested. Conversely, diacetins selectivity increased with increasing acetic acid:glycerol molar ratios. Considering yields instead of the selectivity values, it is very clear that the acetic acid:glycerol molar ratio had a remarkable impact. Using acetic acid:glycerol at a molar ratio of 1:1, the yields of monoacetins and diacetins were $17.9 \pm 1.0\%$ and $20.0 \pm 1.4\%$ after 4 h, respectively. Increasing the acetic acid:glycerol molar ratio to 9:1 led to increased monoacetins and diacetins yields of $40.2 \pm 2.4\%$ and $41.5 \pm 0.8\%$, respectively.

Table 3. Effect of the acetic acid:glycerol molar ratio on the selectivity during glycerol acetylation catalysed by a biosolids-based catalyst. For the reactions, the catalyst/glycerol weight ratio was maintained at 4 wt% and the reaction temperature used was 120 °C.

T [h]	Acetic Acid: Glycerol (mol/mol)	Conversion ^a (%)	Selectivity ^b (%)		
			Monoacetins	Diacetins	Triacetin
1	1	26.0 ± 0.5	74.3 ± 3.2	24.5 ± 1.8	1.2 ± 0.3
2		35.8 ± 0.3	59.7 ± 2.6	34.6 ± 1.1	4.1 ± 0.9
3		36.5 ± 0.5	51.7 ± 0.9	42.5 ± 2.6	5.5 ± 0.5
4		40.8 ± 0.7	43.8 ± 2.0	49.0 ± 2.8	6.3 ± 0.1
1	3	26.6 ± 0.3	70.9 ± 1.9	23.9 ± 2.0	1.5 ± 0.1
2		45.3 ± 1.9	64.7 ± 0.5	33.1 ± 1.7	2.0 ± 0.7
3		63.5 ± 0.6	54.2 ± 1.4	40.8 ± 3.0	4.6 ± 0.1
4		73.1 ± 0.7	45.5 ± 1.4	46.6 ± 1.5	6.6 ± 0.8
1	6	27.7 ± 0.7	70.9 ± 1.9	23.9 ± 2.0	1.5 ± 0.1

2		51.1 ± 1.1	64.7 ± 0.5	33.1 ± 1.7	2.0 ± 0.7
3		66.1 ± 0.3	54.2 ± 1.4	40.8 ± 3.0	4.6 ± 0.1
4		78.4 ± 0.2	45.5 ± 1.4	46.6 ± 1.5	6.6 ± 0.8
1	9	28.1 ± 0.9	80.4 ± 3.8	17.0 ± 0.5	0.9 ± 0.1
2		65.6 ± 1.2	62.1 ± 2.6	34.2 ± 1.5	2.4 ± 0.4
3		75.9 ± 0.5	49.7 ± 2.1	44.1 ± 0.7	3.9 ± 0.3
4		85.8 ± 1.2	46.9 ± 2.0	48.4 ± 0.3	6.3 ± 0.4

^a Conversion: $100 \times ((\text{initial mass of glycerol} - \text{final mass of glycerol})/(\text{initial mass of glycerol}))$;

^b Selectivity: $100 \times (\text{area of product}_i / \sum_i \text{area product}_i)$.

2.4. Influence of Catalyst Loading on Glycerol Acetylation Conversion Rate and Selectivity

The effect of catalyst loading on acetylation of glycerol was studied using five different catalyst/glycerol weight ratios (0 wt%, 2 wt%, 4 wt%, 8 wt%, 16 wt%). The reactions were carried out for 4 h at 120 °C, with an acetic acid:glycerol molar ratio of 6:1 as shown in Figure 5. Two-way ANOVA testing ($p < 0.05$) confirmed that both catalyst loading and reaction time affected the conversion during acetylation of glycerol. The uncatalysed reaction in which no biosolids-based catalyst was employed proceeded very slowly, reaching a conversion of only $3.6 \pm 0.4\%$ after 1 h and $65.7 \pm 0.4\%$ after 4 h. Using the same conditions, a catalyst loading of 2 wt% substantially improved conversion, reaching $22.6 \pm 0.7\%$ after 1 h and $72.2 \pm 1.5\%$ after 4 h. Further increments in catalyst loading induced significant increases in conversion, achieving $90.8 \pm 2.3\%$ after 4 h using a catalyst loading of 16 wt%. The effect of catalyst was particularly evident after 1h. In this experiment, a catalyst loading of 2–8% promoted conversions of ~22–27% while a catalyst loading of 16 wt% resulted in a conversion of $54.9 \pm 1.1\%$.

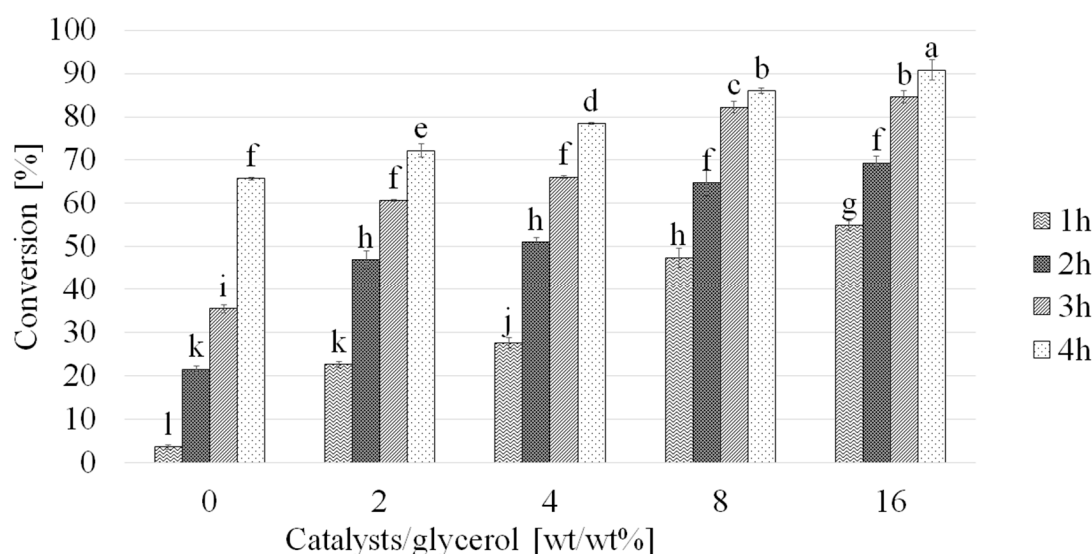


Figure 5. The effect of the catalyst loading on the conversion of glycerol to acetyl derivatives. Reactions were performed at 120 °C, with a 6:1 molar ratio (acetic acid:glycerol). For these experiments, different catalyst/glycerol weight ratios (0 wt%, 2 wt%, 4 wt%, 8 wt%, 16 wt%) were examined, using a biosolids-based catalyst. The data reported represent averages ± standard deviations of triplicate experiments. Values that are annotated with different letters are statistically different at a 95% confidence level.

The selectivity achieved during glycerol acetylation was also affected by catalyst loading and reaction time. According to the data shown in Table 4, the trends observed with regards to the selectivity of monoacetins and diacetins were comparable with other experiments. In general, a simultaneous increase in diacetins and a decrease in monoacetins was observed with increasing reaction time and catalyst loading. Triacetin selectivity followed the same trend as diacetins, albeit at much lower levels, with the exception of the experiments without the use of catalyst where no

triacetin was detected. This suggests that a catalyst is necessary in order to promote the third esterification reaction, which is associated with a very low kinetic rate due to the high steric hindrance of diacetins. Thus, the catalyst obtained through thermal hydrolysis of biosolids positively affected the esterification of the internal hydroxylic functionality that is characterized by a reaction ΔG higher than terminal groups [32].

Table 4. The effect of catalyst loading on selectivity during glycerol acetylation catalysed by the biosolids-based catalyst. Reactions were performed at 120 °C, with a 6:1 molar ratio of acetic acid:glycerol.

T [h]	Catalyst [wt%]	Conversion ^a (%)	Selectivity ^b (%)		
			Monoacetins	Diacetins	Triacetin
1	0	3.6 ± 0.4	65.2 ± 2.6	34.5 ± 2.6	Not detected
2		21.5 ± 0.9	56.6 ± 1.2	42.9 ± 2.8	Not detected
3		35.5 ± 0.9	49.0 ± 3.7	52.3 ± 1.9	Not detected
4		65.7 ± 0.4	44.4 ± 1.0	55.8 ± 2.6	Not detected
1	2	22.6 ± 0.3	74.3 ± 3.2	24.5 ± 3.0	1.2 ± 0.3
2		47.0 ± 2.0	59.7 ± 2.6	34.6 ± 1.5	4.1 ± 0.9
3		60.7 ± 0.3	51.7 ± 0.9	42.5 ± 1.8	5.5 ± 0.5
4		72.2 ± 1.5	43.8 ± 2.0	49.0 ± 1.1	6.3 ± 0.1
1	4	27.7 ± 1.2	70.9 ± 1.9	23.9 ± 2.0	1.5 ± 0.1
2		51.1 ± 1.1	64.7 ± 0.5	33.1 ± 1.7	2.0 ± 0.7
3		66.1 ± 0.3	54.2 ± 1.4	40.8 ± 3.0	4.6 ± 0.1
4		78.4 ± 0.2	45.5 ± 1.4	46.6 ± 1.5	6.6 ± 0.8
1	8	47.5 ± 2.2	78.6 ± 2.2	20.3 ± 2.3	1.0 ± 0.3
2		64.8 ± 3.1	65.2 ± 2.5	33.0 ± 1.9	2.5 ± 0.4
3		82.2 ± 1.3	54.1 ± 1.2	41.4 ± 1.1	4.6 ± 0.4
4		86.0 ± 0.5	46.1 ± 1.3	47.2 ± 0.3	6.8 ± 0.7
1	16	54.9 ± 1.1	80.4 ± 3.8	17.0 ± 0.5	0.9 ± 0.1
2		69.3 ± 1.6	62.1 ± 2.6	34.2 ± 1.5	2.4 ± 0.4
3		84.6 ± 1.3	49.7 ± 2.1	44.1 ± 0.7	3.9 ± 0.3
4		90.8 ± 2.3	46.9 ± 2.0	48.4 ± 0.3	6.3 ± 0.4

^a Conversion: $100 \times ((\text{initial mass of glycerol} - \text{final mass of glycerol}) / (\text{initial mass of glycerol}))$;

^b Selectivity: $100 \times (\text{area of product}_i / \sum_i \text{area product}_i)$.

2.5. Influence of Catalyst Recycling on Glycerol Acetylation Conversion Rate and Selectivity

To assess reusability of the catalyst generated through thermal hydrolysis of biosolids, the same catalyst sample was used for five consecutive reactions. The reactions were performed at a catalyst loading of 4 wt%, an acetic acid:glycerol molar ratio of 6:1, and at 120 °C for 4 h (Figure 6). According to a one-way ANOVA test, there were no significant differences ($p < 0.05$) in the conversion values assessed during the five catalytic runs with average values $\sim 78\%$. Furthermore, comparable selectivity was also observed in the reaction products from the five catalytic runs (Table 5). Considering the metals concentrations assessed after the fifth catalytic run (Table 1), it reasonable to assume that the catalytic activity of thermally hydrolysed biosolids-based materials during glycerol acetylation was exploited by both metals and acidic sites. Acid sites remained untouched after the fifth catalytic runs with a concentration of 5.28 ± 0.05 mmol/g while key metals (Fe, Al) did not show any leaching. According to these observations, acetylation of glycerol was promoted by acidic sites, such as hydroxylic functionalities (mainly on silica as reported by Bartoli et al. [23]) and metal centres that can act as Lewis acids [59].

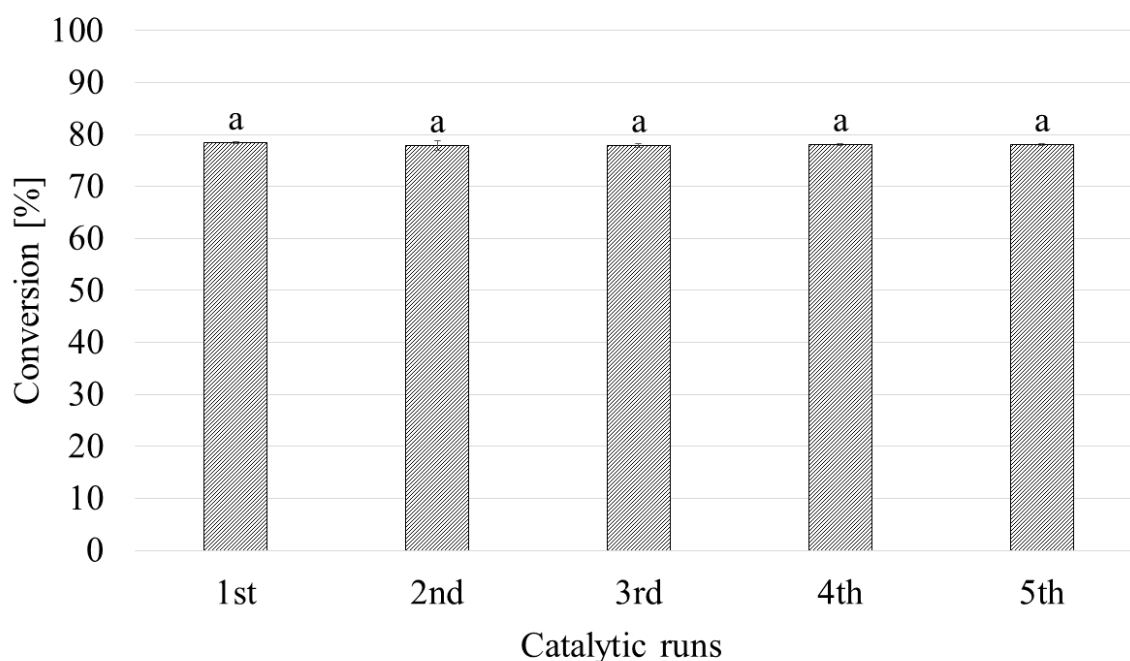


Figure 6. Conversion performance using recycled biosolids-based catalyst. The reactions were performed using a catalyst/glycerol ratio of 4 wt%, a temperature of 120 °C, an acetic acid:glycerol molar ratio of 6. These reactions were performed for 4 h. The values shown represent the average \pm standard deviations of three independent experiments. Data annotated with different letters are significantly different (at a confidence level of 95%).

Table 5. Selectivity observed in glycerol acetylation reactions using recycled biosolids-based catalysts. Reactions were performed with a catalyst loading of 4 wt%, an acetic acid:glycerol molar ratio of 2:1, and at 120 °C for 4 h.

Catalytic Run	Conversion ^a (%)	Selectivity ^b (%)		
		Monoacetins	Diacetins	Triacetin
1st	78.4 \pm 0.2	45.5 \pm 1.4	46.6 \pm 1.5	6.6 \pm 0.8
2nd	77.9 \pm 0.9	44.9 \pm 0.5	45.9 \pm 1.1	6.3 \pm 0.6
3rd	77.9 \pm 0.4	44.6 \pm 0.3	46.3 \pm 1.3	6.7 \pm 0.4
4th	78.1 \pm 0.2	46.6 \pm 0.8	45.8 \pm 0.8	6.0 \pm 0.9
5th	78.1 \pm 0.3	42.0 \pm 0.7	46.2 \pm 1.1	6.9 \pm 0.5

^a Conversion: $100 \times ((\text{initial mass of glycerol} - \text{final mass of glycerol}) / (\text{initial mass of glycerol}))$;

^b Selectivity: $100 \times (\text{area of product}_i / \sum_i \text{area product}_i)$.

2.6. Considerations on Catalytic Performance of Thermally Hydrolysed Biosolids and Available Catalysts

The catalytic performance of the biosolids-based catalyst is not as high as other reported materials, such as superacid resins. Dosuna-Rodríguez et al. [40] compared several acidic resins reaching a maximum conversion of up to 95% after 200 min with a selectivity for monoacetins and diacetins of up to 81% and 5%, respectively, using 0.8 wt% of Dowex-2[®]. Similar and even better results were achieved only using a high loading of thermally hydrolysed biosolids catalyst (from 8 wt% to 16 wt%). Other acid catalyst such as ionic liquids outperformed the biosolids-based catalyst, reaching conversions of up to 99% and selectivity for triacetin up to 47% [60]. Furthermore, nanostructured sulphated zirconia led to higher yields of triacetin (up to 40%) with low catalyst loading [61]. A similar behaviour was also observed using acidic zeolites as reported by many authors [62–64]. Nonetheless, thermally-hydrolysed biosolids catalyst operates at lower temperature compared with heteropolyacidic catalytic systems reaching the same performances [65]. Furthermore, as the biosolids-based catalyst is generated from a negative value material, the cost of this catalyst may offer significant advantages in commercial applications.

3. Materials and Methods

3.1. Materials

Tetrahydrofuran (HPLC grade, >99.9%) and methyl nonadecanoate (used as internal standard for gas chromatography) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Acetic acid (>98%) and glycerol (98%) were purchased from Fisher Chemical (Fair Lawn, NJ, USA). Gases (Air, N₂, H₂, He) were purchased from Praxair (Praxair Inc., Edmonton, AB, Canada). The biosolids-based catalyst was obtained through thermal hydrolysis (121 °C, 1 h, >15 psi) of digested biosolids (~3.5% dry solids; pH ≈ 9) as previously described [23,53]. The solid material was collected through centrifugation, then dried at 105 °C to constant weight in a drying oven. The dried solids were then ground with a mortar and pestle, and then passed through a 200 mesh nylon cloth. The material passing through the filter was used as the biosolid-based catalyst.

3.2. Methods

3.2.1. Catalytic acetylation of glycerol

Glycerol (5 g) was placed into a one neck balloon with acetic acid (acetic acid:glycerol molar ratios of 9:1, 6:1, 3:1, and 1:1) and the biosolids-based catalyst (catalyst/glycerol weight ratio of 16 wt%, 8 wt%, 4 wt%, 2 wt%, and 0 wt%), which was then connected to a condenser. The reaction mixtures were stirred and heated at different temperatures (60 °C, 80 °C, 100 °C and 120 °C), with sampling every hour for a total of 4 h. After, the reaction mixture was cooled to room temperature and the catalyst was recovered through centrifugation (7155× g for 10 min), washed with acetone (5 mL three times), dried overnight at 105 °C, and then analysed as described below. Each test was replicated three times.

3.2.2. Sample analysis

The reaction mixture was analysed as previously reported [23]. Briefly, 100 µL of the crude reaction mixture were diluted with 900 µL of tetrahydrofuran and 10 mg of methyl nonadecanoate were added as the internal standard. The solution was analysed using a gas chromatograph (6890N, Agilent Technologies, Fort Worth, TX, USA) equipped with an autosampler (Agilent 7683 series; Agilent Technologies, Fort Worth, TX, USA), a flame ionization detector (FID) and a mass spectrometer (Agilent 5975B inert XL EI/CI MSD; Agilent Technologies, Fort Worth, TX, USA) used for the quantification and identification of each peaks, respectively. Analyses were carried out by injecting 1 µL of the samples into a DB-5 column (100 m × 250 µm × 0.25 µm; Agilent Technologies, Fort Worth, TX) according to the methodology described previously [66]. Analysis were carried out using helium as the carrier gas (flow rate of 1 mL/min), an injector temperature of 310 °C and FID temperature of 320 °C, respectively. The starting oven temperature was set at 35 °C, which was held for 0.1 min, increased to 280 °C at 10 °C/min, and then held for 5.4 min to reach a total time of 30 min. Mass spectrometry outputs were analysed and matched to those of the National Institute of Standards and Testing (NIST) mass spectral library. The concentration of unreacted glycerol was evaluated using a five point calibration curve ($m = 0.185 \pm 0.02$; $R^2 = 0.994$) established through the use of methyl nonadecanoate as the internal standard.

Analysis of the main inorganics in the catalyst was performed using a Thermo iCAP 6000 series Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES; Thermo Fisher Scientific, Madison, WI, USA) at the Natural Resources Analytical Laboratory (Department of Chemistry, University of Alberta). 50 mg of each sample were digested dissolved in 5 mL of trace-metal grade HNO₃ and further diluted with Milli-Q water to 25 mL. An internal standard solution containing Yttrium is used to correct for matrix effects in each sample. Final analyte values are reported after this correction factor has been applied. Analyses were carried out before and after the five catalytic runs. Analysis of acid residual groups on the surface of the catalyst was carried out according to methodology reported by Bartoli et al. [23], which was based on a modified Boehm's test [67].

XRD analysis was carried out using a D8 Discover X-ray diffractometer (Bruker, Madison, WI, USA) employing Cu Ka ($k = 1.5418 \text{ \AA}$) radiation. Diffractograms were acquired in the 2θ range from 10.0° to 90.0° , applying a step size of 0.50° . Inorganic species were detected using freeware software QualX software. Only species with a quality match of 80% or higher were reported.

3.2.3. Statistical analysis

One-way and two-way ANOVA tests and *t*-tests with a significance level of 0.05 ($p < 0.05$) were carried out using Excel™ software (Microsoft Corp., Redmond, WA, USA) and the “Data analysis” tool. Statistical analysis was performed using triplicate data, with the means and standard deviations reported.

Five grams (5 g) was placed into a one neck balloon with acetic acid (acetic acid:glycerol molar ratios of 9:1, 6:1, 3:1, and 1:1) and the biosolids-based catalyst (catalyst/glycerol weight ratio of 16 wt%, 8 wt%, 4 wt%, 2 wt% and 0 wt%), which was then connected to a condenser. The reaction mixtures were stirred and heated at different temperatures (60°C , 80°C , 100°C and 120°C), with sampling every hour for a total of 4 h. After, the reaction mixture was cooled to room temperature and the catalyst was recovered through centrifugation ($7155\times g$ for 10 min), washed with acetone (5 mL three times), dried overnight at 105°C , and then analysed as described below. Each test was replicated three times.

4. Conclusions

In this work, the effectiveness of a heterogeneous catalyst obtained from thermally hydrolysed biosolids in promoting glycerol acetylation was demonstrated. Glycerol conversion was studied using various temperatures, acetic acid:glycerol molar ratios, catalyst loading and reaction times. The results highlight the ability of the biosolids-based catalyst to promote a rapid conversion of glycerol to a mixture of monoacetins, diacetins, and triacetin. The maximum conversion obtained was $90.8 \pm 2.3\%$ after 4 h at 120°C using a catalyst loading of 16 wt% and an acetic acid:glycerol molar ratio of 6:1. Furthermore, under the same conditions, an extremely high selectivity of monoacetins were achieved after only 1 h. Considering the catalytic activity and negative cost of the material recovered from biosolids, a waste stream from wastewater management processes, catalysts recovered from thermally hydrolysed biosolids is a promising tool for the glycerol acetylation process.

Author Contributions: Conceptualization: M.B. and D.C.B.; methodology: M.B.; formal analysis: M.B.; investigation: M.B. and C.Z.; data curation: M.B.; writing—original draft preparation: M.B.; writing—review and editing: M.C. and D.C.B.; supervision: D.C.B.; project administration: M.C. and D.C.B.; funding acquisition: M.C. and D.C.B. All authors have read and agreed to the published version of the manuscript.

Funding: The work described in this research was achieved through generous financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) (grant number RGPIN 298352-20130, Mitacs Canada (grant number MI MA IT05367), BioFuelNet Canada (grant number NCEBFNC 6F), and our collaborators from Forge Hydrocarbons Inc. who also hosted Mattia Bartoli and Chengyong Zhu as interns.

Acknowledgments: The work described in this manuscript was supported by BioFuelNet Canada (grant number NCEBFNC 6F), Mitacs Canada (grant number MI MA IT05367), and the Natural Sciences and Engineering Research Council of Canada (NSERC) (grant numbers RGPIN 298352-2013 and RGPIN-2019-04184). The authors wish to thank Forge Hydrocarbons Inc. who hosted Mattia Bartoli and Chengyong Zhu as Mitacs Interns. The authors are also thankful for the support provided throughout the project by the Natural Resources Analytical Laboratory (Chemistry Department, University of Alberta), NanoFab Centre (University of Alberta), the City of Edmonton, EPCOR Water Services Inc., and Suez.

Conflicts of Interest: The funders had no role in the design of the study, in the collection, analyses, or interpretation of data, or in the writing of the manuscript. Forge Hydrocarbons Inc. reviewed the manuscript prior to submission strictly to ensure that there was no release of confidential information.

References

1. Gasparatos, A.; Doll, C.N.H.; Esteban, M.; Ahmed, A.; Olang, T.A. Renewable Energy And Biodiversity: Implications For Transitioning To A Green Economy. *Renew. Sustain. Energy Rev.* **2017**, *70*, 161–184.
2. Mahmudul, H.; Hagos, F.; Mamat, R.; Adam, A.A.; Ishak, W.; Alenezi, R. Production, Characterization And Performance Of Biodiesel As An Alternative Fuel In Diesel Engines—A Review. *Renew. Sustain. Energy Rev.* **2017**, *72*, 497–509.
3. Mardhiah, H.H.; Ong, H.C.; Masjuki, H.; Lim, S.; Lee, H. A Review On Latest Developments And Future Prospects Of Heterogeneous Catalyst In Biodiesel Production From Non-Edible Oils. *Renew. Sustain. Energy Rev.* **2017**, *67*, 1225–1236.
4. Espinosa-Gonzalez, I.; Parashar, A.; Chae, M.; Bressler, D.C. Cultivation Of Oleaginous Yeast Using Aqueous Fractions Derived From Hydrothermal Pretreatments Of Biomass. *Bioresour. Technol.* **2014**, *170*, 413–420.
5. Asomaning, J.; Mussone, P.; Bressler, D.C. Two-Stage Thermal Conversion Of Inedible Lipid Feedstocks To Renewable Chemicals And Fuels. *Bioresour. Technol.* **2014**, *158*, 55–62.
6. Espinosa-Gonzalez, I.; Asomaning, J.; Mussone, P.; Bressler, D.C. Two-Step Thermal Conversion Of Oleaginous Microalgae Into Renewable Hydrocarbons. *Bioresour. Technol.* **2014**, *158*, 91–97.
7. OCED. *OECD-FAO Agricultural Outlook 2018–2027*; OECD Publishing: Paris, France, 2018.
8. Monteiro, M.R.; Kugelmeier, C.L.; Pinheiro, R.S.; Batalha, M.O.; Da Silva César, A. Glycerol From Biodiesel Production: Technological Paths For Sustainability. *Renew. Sustain. Energy Rev.* **2018**, *88*, 109–122.
9. França, R.G.; Souza, P.A.; Lima, E.R.; Costa, A.L. An Extended Techno-Economic Analysis Of The Utilization Of Glycerol As An Alternative Feedstock For Methanol Production. *Clean Technol. Environ. Policy* **2017**, *19*, 1855–1865.
10. Ardi, M.S.; Aroua, M.K.; Hashim, N.A. Progress, Prospect And Challenges In Glycerol Purification Process: A Review. *Renew. Sustain. Energy Rev.* **2015**, *42*, 1164–1173.
11. Ciriminna, R.; Pina, C.D.; Rossi, M.; Pagliaro, M. Understanding The Glycerol Market. *Eur. J. Lipid Sci. Technol.* **2014**, *116*, 1432–1439.
12. Bartoli, M.; Rosi, L.; Frediani, M. Introductory Chapter: A Brief Insight About Glycerol. In *Glycerine Production And Transformation—An Innovative Platform For Sustainable Biorefinery And Energy*; Intechopen: London, UK, 2019.
13. Dunphy, P.J.; Meyers, A.J.; Rigg, R.T. Cosmetic Water-In-Oil Emulsion Lipstick Comprising A Phospholipid And Glycerol Fatty Acid Esters Emulsifying System. U.S. Patent 5,085,856, 2 April 1992.
14. Suh, Y.; Kil, D.; Chung, K.; Abdullayev, E.; Lvov, Y.; Mongayt, D. Natural Nanocontainer For The Controlled Delivery Of Glycerol As A Moisturizing Agent. *J. Nanosci. Nanotechnol.* **2011**, *11*, 661–665.
15. Tamarkin, D.; Besonov, A. Glycerol Ethers Vehicle And Pharmaceutical Compositions Thereof. U.S. Patent 20090130029A1, 21 May 2009.
16. Van Cleef, E.H.C.B.; Ezequiel, J.M.B.; D'aura, A.P.; Fávoro, V.R.; Sancanari, J.B.D. Crude Glycerin In Diets For Feedlot Nellore Cattle. *Rev. Bras. Zootec.* **2014**, *43*, 86–91.
17. Meale, S.; Chaves, A.; Ding, S.; Bush, R.; Mcallister, T. Effects Of Crude Glycerin Supplementation On Wool Production, Feeding Behavior, And Body Condition Of Merino Ewes. *J. Anim. Sci.* **2013**, *91*, 878–885.
18. Razali, N.; Abdullah, A.Z. Production Of Lactic Acid From Glycerol Via Chemical Conversion Using Solid Catalyst: A Review. *Appl. Catal. A Gen.* **2017**, *543*, 234–246.
19. Oberhauser, W.; Evangelisti, C.; Jumde, R.P.; Psaro, R.; Vizza, F.; Bevilacqua, M.; Filippi, J.; Machado, B.F.; Serp, P. Platinum On Carbonaceous Supports For Glycerol Hydrogenolysis: Support Effect. *J. Catal.* **2015**, *325*, 111–117.
20. Magar, S.; Kamble, S.; Mohanraj, G.T.; Jana, S.K.; Rode, C. Solid-Acid-Catalyzed Etherification Of Glycerol To Potential Fuel Additives. *Energy Fuels* **2017**, *31*, 12272–12277.
21. Shukla, K.; Srivastava, V.C. Synthesis Of Organic Carbonates From Alcoholysis Of Urea: A Review. *Catal. Rev.* **2017**, *59*, 1–43.
22. Oliverio, M.; Costanzo, P.; Nardi, M.; Calandrucchio, C.; Salerno, R.; Procopio, A. Tunable Microwave-Assisted Method For The Solvent-Free And Catalyst-Free Peracetylation Of Natural Products. *Beilstein J. Org. Chem.* **2016**, *12*, 2222–2233.
23. Bartoli, M.; Zhu, C.; Chae, M.; Bressler, D. Value-Added Products From Urea Glycerolysis Using A Heterogeneous Biosolids-Based Catalyst. *Catalysts* **2018**, *8*, 373.

24. Amaral, P.F.F.; Ferreira, T.F.; Fontes, G.C.; Coelho, M.A.Z. Glycerol Valorization: New Biotechnological Routes. *Food Bioprod. Process.* **2009**, *87*, 179–186.
25. Costanzo, P.; Calandrucchio, C.; Di Gioia, M.L.; Nardi, M.; Oliverio, M.; Procopio, A. First Multicomponent Reaction Exploiting Glycerol Carbonate Synthesis. *J. Clean. Prod.* **2018**, *202*, 504–509.
26. Mufrodi, Z.; Rochmadi, R.; Sutijan, S.; Budiman, A. Synthesis Acetylation Of Glycerol Using Batch Reactor And Continuous Reactive Distillation Column. *Eng. J.* **2014**, *18*, 29–40.
27. Rastegari, H.; Ghaziaskar, H.S. From Glycerol As The By-Product Of Biodiesel Production To Value-Added Monoacetin By Continuous And Selective Esterification In Acetic Acid. *J. Ind. Eng. Chem.* **2015**, *21*, 856–861.
28. Odibi, C.; Babaie, M.; Zare, A.; Nabi, M.N.; Bodisco, T.A.; Brown, R.J. Exergy Analysis Of A Diesel Engine With Waste Cooking Biodiesel And Triacetin. *Energy Convers. Manag.* **2019**, *198*. doi:10.1016/j.enconman.2019.111912.
29. Nda-Umar, U.I.; Ramli, I.; Taufiq-Yap, Y.H.; Muhamad, E.N. An Overview Of Recent Research In The Conversion Of Glycerol Into Biofuels, Fuel Additives And Other Bio-Based Chemicals. *Catalysts* **2019**, *9*, 15.
30. Gama, N.; Santos, R.; Godinho, B.; Silva, R.; Ferreira, A. Triacetin As A Secondary Pvc Plasticizer. *J. Polym. Environ.* **2019**, *27*, 1294–1301.
31. Okoye, P.; Abdullah, A.; Hameed, B. A Review On Recent Developments And Progress In The Kinetics And Deactivation Of Catalytic Acetylation Of Glycerol—A Byproduct Of Biodiesel. *Renew. Sustain. Energy Rev.* **2017**, *74*, 387–401.
32. Liao, X.; Zhu, Y.; Wang, S.-G.; Chen, H.; Li, Y. Theoretical Elucidation Of Acetylating Glycerol With Acetic Acid And Acetic Anhydride. *Appl. Catal. B Environ.* **2010**, *94*, 64–70.
33. Melero, J.A.; Van Grieken, R.; Morales, G.; Paniagua, M. Acidic Mesoporous Silica For The Acetylation Of Glycerol: Synthesis Of Bioadditives To Petrol Fuel. *Energy Fuels* **2007**, *21*, 1782–1791.
34. Herrada-Vidales, J.A.; García-González, J.M.; Martínez-Palou, R.; Guzmán-Pantoja, J. Integral Process For Obtaining Acetins From Crude Glycerol and Their Effect on the Octane Index. *Chem. Eng. Commun.* **2019**, *207*, 1–11.
35. Gorji, Y.M.; Ghaziaskar, H.S. Optimization Of Solketalacetin Synthesis As A Green Fuel Additive From Ketalization Of Monoacetin With Acetone. *Ind. Eng. Chem. Res.* **2016**, *55*, 6904–6910.
36. Lachman, L.; Drubulis, A. Factors Influencing The Properties of Films Used for Tablet Coating I. Effects of Plasticizers on the Water Vapor Transmission Of Cellulose Acetate Phthalate Films. *J. Pharm. Sci.* **1964**, *53*, 639–643.
37. Weber, F. Pharmaceutical Composition. U.S. Patent US7074412B2, 11 Jul. 2006.
38. Knowles, M.; Pridgen, H.S. Solvents For Fat And Oil Antioxidants. U.S. Patent 2944908A, 12 July 1960.
39. Deline, G.D. Homogeneous, Free-Flowing Liquid Black Pepper Oleoresin Composition. European Patent 0137082A1, 11 October 1983.
40. Dosuna-Rodríguez, I.; Gaigneaux, E.M. Glycerol Acetylation Catalysed By Ion Exchange Resins. *Catal. Today* **2012**, *195*, 14–21.
41. Caballero, K.V.; Guerrero-Amaya, H.; Baldovino-Medrano, V.G. Revisiting Glycerol Esterification With Acetic Acid Over Amberlyst-35 Via Statistically Designed Experiments: Overcoming Transport Limitations. *Chem. Eng. Sci.* **2019**. doi:10.1016/J.Ces.2019.06.003.
42. De Abreu Dessimoni, A.L.; De Oliveira Pereira, L.; Penido, E.S.; Lima Abreu Veiga, T.R.; De Barros Fernandes, R.V.; Teixeira, M.L.; Bonésio, M.D.R.; Bianchi, M.L. Characterization Of Catalysts For Glycerol Ester Production With Various Acetylating Agents. *Anal. Lett.* **2017**. doi:1080/00032719.2017.1385620.
43. Gonçalves, V.L.C.; Pinto, B.P.; Silva, J.C.; Mota, C.J.A. Acetylation Of Glycerol Catalyzed By Different Solid Acids. *Catal. Today* **2008**, *133–135*, 673–677.
44. Dill, L.P.; Kochevka, D.M.; Melinski, A.; Wypych, F.; Cordeiro, C.S. Microwave-Irradiated Acetylation Of Glycerol Catalyzed By Acid Activated Clays. *React. Kinet. Mech. Catal.* **2019**, *127*, 1–14.
45. Okoye, P.; Abdullah, A.; Hameed, B. Synthesis Of Oxygenated Fuel Additives Via Glycerol Esterification With Acetic Acid Over Bio-Derived Carbon Catalyst. *Fuel* **2017**, *209*, 538–544.
46. Okoye, P.U.; Hameed, B.H. Review On Recent Progress In Catalytic Carboxylation And Acetylation Of Glycerol As A Byproduct Of Biodiesel Production. *Renew. Sustain. Energy Rev.* **2016**, *53*, 558–574.
47. Silva, L.N.; Gonçalves, V.L.C.; Mota, C.J.A. Catalytic Acetylation Of Glycerol With Acetic Anhydride. *Catal. Commun.* **2010**, *11*, 1036–1039.
48. Cunningham, J.K.; Liu, L.-M.; Callaghan, R.C. Essential (“Precursor”) Chemical Control For Heroin: Impact Of Acetic Anhydride Regulation On Us Heroin Availability. *Drug Alcohol Depend.* **2013**, *133*, 520–528.

49. Len, C.; Luque, R. Continuous Flow Transformations Of Glycerol To Valuable Products: An Overview. *Sustain. Chem. Process.* **2014**, *2*, 1.
50. Mufrodi, Z.; Budiman, A. Continuous Process Of Reactive Distillation To Produce Bio-Additive Triacetin From Glycerol. *Mod. Appl. Sci.* **2013**, *7*, 70.
51. Costa, I.C.; Itabaiana, I., Jr.; Flores, M.C.; Lourenço, A.C.; Leite, S.G.; De, M.E.; Miranda, L.S.; Leal, I.C.; De Souza, R.O. Biocatalyzed Acetins Production Under Continuous-Flow Conditions: Valorization Of Glycerol Derived From Biodiesel Industry. *J. Flow Chem.* **2013**, *3*, 41–45.
52. Varma, R.S.; Len, C. Glycerol Valorization Under Continuous Flow Conditions-Recent Advances. *Curr. Opin. Green Sustain. Chem.* **2018**, *15*, 83–90.
53. Chae, M.; Xia, L.; Zhu, C.; Bressler, D.C. Accelerating Settling Rates Of Biosolids Lagoons Through Thermal Hydrolysis. *J. Environ. Manag.* **2018**, *220*, 227–232.
54. Zhou, L.; Nguyen, T.-H.; Adesina, A.A. The Acetylation Of Glycerol Over Amberlyst-15: Kinetic And Product Distribution. *Fuel Process. Technol.* **2012**, *104*, 310–318.
55. Patel, A.; Singh, S. A Green And Sustainable Approach For Esterification Of Glycerol Using 12-Tungstophosphoric Acid Anchored To Different Supports: Kinetics And Effect Of Support. *Fuel* **2014**, *118*, 358–364.
56. Reddy, P.S.; Sudarsanam, P.; Raju, G.; Reddy, B.M. Selective Acetylation Of Glycerol Over Ceo₂-M And So₄²⁻/Ceo₂-M (M= Zro₂ And Al₂O₃) Catalysts For Synthesis Of Bioadditives. *J. Ind. Eng. Chem.* **2012**, *18*, 648–654.
57. Arizona, U.O. Rruff™ Project. Available online: [Http://Rruff.info/](http://Rruff.info/) (accessed on 21 October 2019).
58. Jaeger, A.O.; Selden Co, Assignee. Catalytic Esterification. U.S. Patent 1,819,818, 18 August 1931.
59. Greenwood, N.N.; Earnshaw, A. *Chemistry of the Elements*; Elsevier: Amsterdam, The Netherlands, 2012.
60. Keogh, J.; Tiwari, M.S.; Manyar, H. Esterification Of Glycerol With Acetic Acid Using Nitrogen-Based Brønsted-Acidic Ionic Liquids. *Ind. Eng. Chem. Res.* **2019**, *58*, 17235–17243.
61. Testa, M.L.; La Parola, V.; Mesrar, F.; Ouanji, F.; Kacimi, M.; Ziyad, M.; Liotta, L.F. Use Of Zirconium Phosphate-Sulphate As Acid Catalyst For Synthesis Of Glycerol-Based Fuel Additives. *Catalysts* **2019**, *9*, 148.
62. Liu, J.; Wang, Z.; Sun, Y.; Jian, R.; Jian, P.; Wang, D. Selective Synthesis Of Triacetin From Glycerol Catalyzed By Hzsm-5/Mcm-41 Micro/Mesoporous Molecular Sieve. *Chin. J. Chem. Eng.* **2019**, *27*, 1073–1078.
63. Bandyopadhyay, M.; Tsunoji, N.; Bandyopadhyay, R.; Sano, T. Comparison Of Sulfonic Acid Loaded Mesoporous Silica In Transesterification Of Triacetin. *React. Kinet. Mech. Catal.* **2019**, *126*, 167–179.
64. Marwan, M.; Indarti, E.; Darmadi, D.; Rinaldi, W.; Hamzah, D.; Rinaldi, T. Production Of Triacetin By Microwave Assisted Esterification Of Glycerol Using Activated Natural Zeolite. *Bull. Chem. React. Eng. Catal.* **2019**, *14*, 672.
65. Huang, M.-Y.; Han, X.-X.; Hung, C.-T.; Lin, J.-C.; Wu, P.-H.; Wu, J.-C.; Liu, S.-B. Heteropolyacid-Based Ionic Liquids As Efficient Homogeneous Catalysts For Acetylation Of Glycerol. *J. Catal.* **2014**, *320*, 42–51.
66. Omidghane M., Jenab E., Chae M., Bressler D.C. Production of renewable hydrocarbons by thermal cracking of oleic acid in the presence of water. *Energ. Fuel.* **2017**, *31*(9), 9446-9454.
67. Boehm, H. Acidic And Basic Properties Of Hydroxylated Metal Oxide Surfaces. *Discuss. Faraday Soc.* **1971**, *52*, 264–275.

