Valorization of crude glycerin from biodiesel production by acetalization

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**ABSTRACT**

Biodiesel, produced by alcoholysis of fats, is viewed as a feasible substitute of fossil diesel. From economical point of view, biodiesel cannot compete with fossil diesel since raw materials and the production process are expensive. To improve biodiesel viability, the glycerin coproduced (10% w/w) must be valorized. Glycerin acetalization, with ketones or aldehydes, is among the several routes referred in the literature to produced high value chemicals from glycerin. It is a condensation reaction that produces 1,3-dioxolanes and 1,3-dioxanes, used as fuel additives, surfactants, flavorings and solvents. Crude glycerin (<82% w/w), from a local biodiesel industry, was reacted with acetone and butanone over commercial montmorillonite catalysts (K10 and K30) and over acid activated (H₂SO₄) carbon catalyst derived from crude glycerin. Pro-analysis and water containing (87%) were used as reference. The reaction carried out at reflux temperature of the used ketone showed, always, high selectivity towards the 5 members ring product being the carbon catalyst the most active. Crude glycerin had a negative effect on the catalytic performances mainly due to the high MONG content. Only activated carbon was effective for crude glycerin acetalization. The observed differences between the tested acid catalysts can be related with higher adsorption of MONG by montmorillonite. The presence of solvents studied with ethanol and n-hexane showed an almost null effect in the tested conditions.

1. Introduction

In the last few decades, world energy consumption has increased significantly. The depletion of fossil fuels and their environmental impacts have led to a development of biofuels production, the most viable alternative to oil. The rapid growth of biodiesel industry resulted in oversupply of glycerin, its major by-product (10% w/w). To ensure the economic viability of biodiesel production, it is urgent to develop value added products to consume the excessive glycerol [1,2, 3].

Nowadays, biodiesel is obtained by the transesterification of vegetable oils or animal fat with methanol in the presence of a basic homogeneous catalyst, according to the European and American specifications: EN14214 and ASTM6751 [4, 5]. It is a renewable, non-toxic and biodegradable mixture of FAME (fatty acid methyl esters) that has almost the same properties of diesel fuel [6].

Glycerol is synthetized from fats and oil by three different processes: hydrolysis, saponification and transesterification [5, 7]. However, biodiesel industry was responsible for about 68% of glycerine produced worldwide in 2015. Glycerin production by transesterification is expected to grow about 6,8% by 2022 [8, 9].

Glycerin traditional applications which dominate glycerol demand are personal care, pharmaceuticals, foods, and healthcare products [8]. As mentioned before, new value added-products have been suggested in
literature to consume the excessive glycerol, for instance, the production of: hydrogen, 1,2-propanediol and 1,3-propanediol, acrolein, dihydroxyacetone (DHA), gliceric acid (GA) and mesoxalic acid (MA), epichlorohydrin (ECH), glycerol ethers, glycerol esters, glycerol carbonate and glycerol ketals and acetalts [5]. These last products are 1,3-dioxolanes (five membered ring) and 1,3-dioxanes (six membered ring), produced by the acetalization reaction of glycerol with aldehydes or ketones in the presence of an acid catalyst. The acetalization of glycerol is a condensation reaction, resulting in the production of one molecule of water per molecule of glycerol [6]. When glycerin’s condensation is performed with a ketone, mostly five membered ring compounds are obtained. However, the selectivity of acetals depends on the reaction conditions [10]. Glycerin’s acetalts and ketals are used as fuel additives in gasoline, diesel and biodiesel, depending on the carbonyl compound used. Their application on fuels can improve many properties such as pour point, freezing point, flash point, viscosity, octane ratio, among others [11-14]. Glycerol ketals and acetals have applications also as surfactants, flavorings and solvents [11].

Recently, heterogeneous catalysts have received special attention due to their many advantages over homogeneous catalysts, mainly their reusability, easy separation from the product and less environmental impact [15]. Modified montmorillonite clays and carbon-based materials are non-toxic, non-corrosive, economical and recyclable. These catalysts have high mechanical stability and their specific surface area can be controlled [16, 17]. Besides, montmorillonite have strong acidity and are mined all over the planet [16]. Activated carbons are also obtained from renewable materials such as waste materials and sugars [17]. Modified montmorillonite clays and activated carbons from crude glycerin were used in the acetalization of glycerol with acetone and 2-butanol.

\[ \text{Figure 1: Acetalization of glycerol with acetone [18].} \]

2. Experimental

2.1. Glycerin characterization

The three types of glycerin available were analysed using a thermogravimetric system (model TG-DTA/DSC Labsys) equipped with an alumina crucible. The thermogravimetric analysis was performed in the presence of air and using a heating rate of 20°C/minute. The mass loss curve (TG) and the first derivative of the mass loss curve (DTG) were obtained for each glycerin to determine its composition.

2.2. Preparation of the catalysts

Carbon-based catalysts were prepared by mixing crude glycerine with sulphuric acid using a molar ratio of 1:4. The mixture was stirred continuously and heated to 100°C, promoting carbonization and sulphonation in one step. After carbonization, catalysts were filtered, washed and dried at 60°C.

2.3. Catalysts characterization

Montmorillonite catalysts and carbons were analysed by X-ray diffraction (XRD), SEM-EDS and thermogravimetry. The diffraction analysis
was performed on a Bruker D8 Advance Powder Diffractometer equipped with a secondary monochromator, under Cu Kα radiation and using a Bragg Brentano geometry. SEM-EDS analysis was carried out using a JEOL SEM (model 7001F) equipped with a tungsten Field Emission Gun with Schottky emission. SEM was also equipped with secondary and backscattered detectors and an Energy Dispersive Spectroscopy (EDS) X-ray detector.

2.4. Catalytic experiments
The acetalization catalytic experiments were carried out in a 500 mL three necked round bottom reactor equipped with a condenser and a magnetic stirrer. Reactants, solvents and catalysts (w_{cat}/w_{glyc}=10\%) relative to glycerol) were added to the reactor, stirred and heated to ketone reflux temperature, under atmospheric pressure. When reflux temperature was reached, samples were taken periodically (T_{reflux} = 58°C for acetone and 80°C for butanone). Glycerol conversion and selectivity of reaction products were determined by Gas Chromatography analysis. A system equipped with a fused silica capillary column and a flame ionization detector (FID) was used (model Varian CP 3800).

3. Results and Discussion
3.1. Glycerin characterization
The DTG curves obtained showed the presence of water and glycerol in all types of glycerin and the presence of MONG (matter organic non-glycerol) in crude glycerin. The loss of weight relative to water (and other volatile compounds like methanol) is visible near its boiling point (100°C) and occurred due to vaporization. The loss of weight visible near 290°C is also relative to glycerol vaporization. Below that temperature, a mass loss relative to MONG is visible in crude glycerin DTG curve. Finally, a mass variation relative to partial burning of glycerol can be visible near 300°C. For crude glycerin, this combustion may be relative to a mixture of glycerol and salts from biodiesel production [19]. It is known that crude glycerin may contain many impurities such as salt, soap, methanol, water, ashes, polyols, FAME (free acids methyl esters), FFA (free fatty acids), FAE (free acids esters) and others MONG [5].

![DTG curves obtained for glycerin.](image)

The mass variations visible in DTG curves allowed to determine glycerin composition (table 1).

### Table 1: Glycerin composition assessed by TG analysis.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>(99.6%)</th>
<th>(87%)</th>
<th>crude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.2</td>
<td>13.7</td>
<td>7.2</td>
</tr>
<tr>
<td>Glycerol</td>
<td>98.8</td>
<td>86.3</td>
<td>71.3 – 75.6</td>
</tr>
<tr>
<td>MONG</td>
<td>-----------</td>
<td>-------</td>
<td>17.1</td>
</tr>
<tr>
<td>Salts*</td>
<td>-----------</td>
<td>-------</td>
<td>0 – 4.3</td>
</tr>
</tbody>
</table>

*mainly Na

3.2. Catalysts characterization
3.2.1. XRD
The XRD patterns of K10 and K30 showed the
disaggregation of montmorillonite sheets due to acid treatment and match with the diffraction pattern of mica (phengite), which is typical of collapsed 2:1 phyllosilicates. The peaks relative to montmorillonite and impurities, such as quartz and feldspar (albite), were also identified. This structural behaviour is more evident in K10 than in K30. The results showed also a pattern typical of amorphous phases between 21° and 27° 2θ [20].

In XRD pattern of activated carbon, two weak diffraction peaks at 2θ equal to 20° and 40° were identified, which can be attributed to typical planes of the amorphous carbon consisting of polycyclic aromatic carbon sheets [21].

![XRD pattern of K10.](image1)

![XRD pattern of K30.](image2)
3.2.2. SEM-EDS

The images of montmorillonite obtained by SEM-EDS showed that K30 has bigger and more irregular grains than K10. As seen in XRD analysis, the elemental analysis confirmed that K30’s structure was more affected by acid treatment than K10, exhibiting a higher Si/Al ratio.

![SEM images of K10 and K30 (400x)](image)

Figure 5: SEM images of K10 and K30 (400x).

Table 2: Si/Al ratios obtained by elemental analysis.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>K10</td>
<td>3.6</td>
</tr>
<tr>
<td>K30</td>
<td>4.1</td>
</tr>
</tbody>
</table>

The SEM-EDS analysis performed with the activated carbon catalyst confirmed the incorporation of sulphur on the surface of the carbon during the activation treatment. As expected, carbon, oxygen and sulphur were detected by EDS.

![SEM micrograph and elemental composition by EDS of activated carbon (400x)](image)

Figure 6: SEM micrograph and elemental composition by EDS of activated carbon (400x).

3.2.3. Thermogravimetric analysis

For catalytic tests performed using crude glycerin with glycerol conversions below 50%, it was impossible to analyse post reaction catalysts by SEM-EDS. The catalysts form colloidal mixtures with crude glycerin that may damage the equipment. Though, K10 and K30 samples with 43% and 0% of glycerol conversion, respectively, were analysed by thermogravimetry. The analysed catalysts were recovered from catalytic tests 24 and 25.

DTG curves similar to the one obtained for crude glycerin were obtained, showing only the presence of glycerol and crude glycerin impurities. The mass loss observed near 290°C corresponds to glycerol vaporization in the K30 sample. On the other hand, a similar mass loss is observed before 290 °C in the DTG curve of K10 sample, which may be explained by vaporization of the mixture glycerol/solketal. The catalysts represent 40% w/w of the total mass of the samples, corresponding to the final residue.

![DTG curve obtained for K10 and K30 samples](image)

Figure 7: DTG curve obtained for K10 and K30 samples.

3.3. Catalytic experiments

Glycerin acetalization using acetone was performed with three types of glycerin. 2-Butanone was tested only in the presence of pure glycerin (99.6%). Some catalytic tests were performed without a catalyst (table 2, tests 1, 4, 7, 10, 13 e 16). A glycerol conversion of 0% was obtained, showing the importance of using catalysts in this reaction. Mostly 1,3-dioxolanes (5 MR) were produced in all tests, as
expected in acetalization with ketones.

Table 3: Reaction conditions (where molar ratio is the ketone/glycerin ratio).

<table>
<thead>
<tr>
<th>Test</th>
<th>Glycerin</th>
<th>Time (hours)</th>
<th>Catalyst 10%wt</th>
<th>Molar ratio</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>99.6%</td>
<td>2</td>
<td>K10</td>
<td>1.5</td>
<td>----------</td>
</tr>
<tr>
<td>2*</td>
<td>99.6%</td>
<td>2</td>
<td>K30</td>
<td>1.5</td>
<td>Ethanol</td>
</tr>
<tr>
<td>3</td>
<td>87%</td>
<td>2</td>
<td>K10</td>
<td>1.5</td>
<td>----------</td>
</tr>
<tr>
<td>4</td>
<td>Crude</td>
<td>2</td>
<td>K10</td>
<td>1.5</td>
<td>Ethanol</td>
</tr>
<tr>
<td>5</td>
<td>Crude</td>
<td>2</td>
<td>K30</td>
<td>1.5</td>
<td>Ethanol</td>
</tr>
<tr>
<td>6</td>
<td>Crude</td>
<td>2</td>
<td>K10</td>
<td>1.5</td>
<td>Ethanol</td>
</tr>
<tr>
<td>7*</td>
<td>99.6%</td>
<td>2</td>
<td>K10</td>
<td>1.5</td>
<td>Ethanol</td>
</tr>
<tr>
<td>8*</td>
<td>99.6%</td>
<td>2</td>
<td>K30</td>
<td>1.5</td>
<td>Ethanol</td>
</tr>
<tr>
<td>9*</td>
<td>Crude</td>
<td>2</td>
<td>K10</td>
<td>1.5</td>
<td>Ethanol</td>
</tr>
<tr>
<td>10*</td>
<td>Crude</td>
<td>2</td>
<td>K30</td>
<td>1.5</td>
<td>Ethanol</td>
</tr>
<tr>
<td>11*</td>
<td>Crude</td>
<td>2</td>
<td>K10</td>
<td>1.5</td>
<td>Ethanol</td>
</tr>
<tr>
<td>12*</td>
<td>Crude</td>
<td>2</td>
<td>K30</td>
<td>1.5</td>
<td>Ethanol</td>
</tr>
<tr>
<td>13</td>
<td>Crude</td>
<td>2</td>
<td>K10</td>
<td>1.5</td>
<td>Ethanol</td>
</tr>
<tr>
<td>14</td>
<td>Crude</td>
<td>2</td>
<td>K30</td>
<td>1.5</td>
<td>Ethanol</td>
</tr>
<tr>
<td>15</td>
<td>Crude</td>
<td>2</td>
<td>K10</td>
<td>1.5</td>
<td>Ethanol</td>
</tr>
<tr>
<td>16</td>
<td>Crude</td>
<td>2</td>
<td>K30</td>
<td>1.5</td>
<td>Ethanol</td>
</tr>
<tr>
<td>17</td>
<td>Crude</td>
<td>2</td>
<td>K10</td>
<td>1.5</td>
<td>Ethanol</td>
</tr>
<tr>
<td>18</td>
<td>Crude</td>
<td>2</td>
<td>K30</td>
<td>1.5</td>
<td>Ethanol</td>
</tr>
<tr>
<td>19</td>
<td>Crude</td>
<td>6</td>
<td>H2SO4</td>
<td>4.5</td>
<td>n-Hexane</td>
</tr>
<tr>
<td>20</td>
<td>Crude</td>
<td>6</td>
<td>K10</td>
<td>4.5</td>
<td>n-Hexane</td>
</tr>
<tr>
<td>21</td>
<td>Crude</td>
<td>6</td>
<td>K30</td>
<td>4.5</td>
<td>n-Hexane</td>
</tr>
<tr>
<td>22</td>
<td>Crude</td>
<td>6</td>
<td>Activated carbon</td>
<td>4.5</td>
<td>n-Hexane</td>
</tr>
<tr>
<td>23</td>
<td>Crude</td>
<td>6</td>
<td>Activated carbon</td>
<td>4.5</td>
<td>n-Hexane</td>
</tr>
<tr>
<td>24</td>
<td>Crude</td>
<td>6</td>
<td>Activated carbon</td>
<td>4.5</td>
<td>n-Hexane</td>
</tr>
<tr>
<td>25</td>
<td>Crude</td>
<td>6</td>
<td>Activated carbon</td>
<td>4.5</td>
<td>n-Hexane</td>
</tr>
<tr>
<td>26</td>
<td>Crude</td>
<td>6</td>
<td>Activated carbon</td>
<td>4.5</td>
<td>n-Hexane</td>
</tr>
<tr>
<td>27</td>
<td>Crude</td>
<td>6</td>
<td>Activated carbon</td>
<td>4.5</td>
<td>n-Hexane</td>
</tr>
<tr>
<td>28</td>
<td>Crude</td>
<td>6</td>
<td>Activated carbon</td>
<td>4.5</td>
<td>n-Hexane</td>
</tr>
<tr>
<td>29</td>
<td>Crude</td>
<td>6</td>
<td>Activated carbon</td>
<td>4.5</td>
<td>n-Hexane</td>
</tr>
</tbody>
</table>

* Test performed using 2-butanoine.
** Test performed using a smaller amount of catalyst (4% wcat/ wglyc).
*** Test performed using recycled catalyst from test 27.

3.3.1. Catalytic experiments: K10 and K30

- Pure glycerin (99.6%)

Ethanol was tested as solvent to improve glycerin solubility in acetone and to maintain the homogeneity of the mixture. The reaction between acetone and ethanol to produce hemiketals or ketal is not favourable under the experimental conditions used [18]. However, glycerin conversion is lower in the presence of ethanol, as showed in figure 3. On the other hand, chromatograms obtained for these tests didn’t show any ketal or hemiketal produced by the reaction between acetone and ethanol.

Montmorillonite clay K10 had the best performance, with a glycerol conversion of 86%. K30 is more acidic, has higher specific area and porosity than K10, but K10 seems to be more hydrophobic. Water is a by-product of acetalization reaction and its adsorption on K30’s acid sites may reduce K30’s activity. Glycerol conversion has increased during time in these tests, reaching a maximum at the end of the reaction (figure 10). Catalytic tests using 2-butanoine showed a similar performance for both catalysts, K10 and K30, and a glycerol conversion of 80% was obtained (figure 9). Besides, the presence of ethanol as a solvent didn’t have a significant influence on the results. On these tests, the reverse reaction of glycerin acetalization was observed, due to the accumulation of water in
the reaction medium.

- **Commercial glycerin (87%)**

To confirm the influence of water in the reaction, commercial glycerin with 87% of purity was used in the presence of K10 and K30 (figure 11).

The influence of water on reaction equilibrium was confirmed, as shown in figure 10. Despite the difference between the performances of K10 and K30 in the reaction with acetone and glycerin (99.6%), the performance of both catalysts was similar when glycerin (87%) was used, reaching a maximum conversion of glycerol of 79%.

- **Crude glycerin**

Catalytic experiments with crude glycerin were performed in similar conditions of the catalytic tests where acetone and pure glycerin were used, with K10 or K30 as catalyst, in the presence or absence of ethanol (tests 13-18). Despite of the positive results obtained for pure glycerin, glycerol conversion obtained with crude glycerin was 0% in these tests. These results were obtained because of the interaction of crude glycerin impurities with the reaction mixture and catalysts acid sites. So, it was necessary to optimize the reaction conditions: reaction time and molar ratio acetone/glycerin were increased. Other solvent was also tested, n-hexane, because it is known that it may improve glycerol conversion in acetalization with acetone [22]. As obtained in the experiments with pure glycerin, K10 had the best performance reaching a maximum glycerol conversion of 43% at the end of the reaction. Glycerol conversion was 27% after 1h of reaction and 0% after 2 and 4 hours. Glycerol conversion remained equal to 0% with K30. Figure 13 summarizes the best results obtained with the 3 types of glycerin tested.
3.3.3. Catalytic experiments: Activated carbon
Activated carbon from crude glycerin was tested in the optimized conditions of clays catalytic experiments: n-hexane as solvent, molar ratio acetone/glycerin=4,5, 58°C and 10% (w<sub>catalyst</sub>/w<sub>glycerin</sub>) of catalyst. However, carbon-based catalyst showed a better performance in acetalization of glycerol than montmorillonite clays, reaching high conversions in less time of reaction (figure 13). Thus, it was possible to confirm that crude glycerin’s impurities have no affinity with activated carbon acid sites as observed with K10 and K30. Although the reverse reaction of acetalization was observed in tests 26 and 27 due to the presence of water, maximum glycerol conversions were obtained at the end of the reaction with crude glycerin.

Test 28 was performed to optimize the quantity of catalyst used. However, glycerol conversion remained approximately equal to 30% since the 2nd hour of reaction. The maximum glycerol conversion reached in each test and the corresponding time of reaction can be observed in table 4.

3.3.4. Catalytic experiments (homogeneous catalysis with H$_2$SO$_4$
Sulphuric acid was used as a reference. It is known that H$_2$SO$_4$ is one of the homogeneous catalysts tested in literature for glycerin’s acetalization with ketones, reaching a yield of 80% [13]. Catalytic tests with sulphuric acid were performed in the presence of pure and crude glycerin. In tests 23 and 22, the reverse reaction of acetalization was observed,
reaching glycerol conversions of 89% and 43%, respectively. In addition to the presence of water that may be responsible for these results, the equilibrium may have been influenced by the presence of an unexpected by-product. This product gave an orange colour to the reaction mixture and wasn’t detected by GC analysis. Thus, it has certainly a high molecular weight and it may be organic.

3.3.5. Best results obtained for crude glycerin valorization

![Figure 15: Best results obtained in catalytic tests using acetone and crude glycerin (reaction temperature = 58°C)](image)

4. Conclusions

Glycerin acetalization is possible only in the presence of an acid catalyst in the conditions tested. Butanone can be used as reactant, but acetone is cheaper and allows to obtain similar results. The presence of solvents did not influence the results in the conditions tested. Montmorillonite clays and activated carbon from crude glycerin can be used for glycerin acetalization and have many advantages: they are obtained from renewable materials and can be recycled and easily separated from the product. The adsorption of glycerin impurities (water and MONG) on montmorillonite acid sites lead to a decrease of glycerol conversion, which was not observed with activated carbons. Thus, a simple, efficient and ecofriendly process had been demonstrated for crude glycerin valorization.

5. References


[8] Glycerol Market Size By Application (Personal Care, Polyether Polyol Applications,


