Valorisation of glycerol into biofuel additives over heterogeneous catalysts

J. Farinha, M. Caiado and J. E. Castanheiro
Centro de Quimica de Évora, Departamento de Quimica, Universidade de Évora, 7000-671 Évora, Portugal

Transesterification of glycerol with methyl acetate was carried out over resins, poly(vinyl alcohol) (PVA) and chitosan (CH) with sulfonic acid groups at 70°C. The products of glycerol transesterification are monoacetic, diacetic and triacetic. It was observed that the catalytic activity increases with the amount of sulfonic acid groups on materials. The CH material showed the highest catalytic activity of all catalysts. In order to study the catalytic stability of CH-SO3H, three consecutive batch runs with the same catalyst were carried out. The CH-SO3H catalyst can be recycled and reused with negligible loss in the activity, after third use.

Keywords: bio-additives, biodiesel, glycerol, heterogeneous catalysts

1. Introduction

Biodiesel contains fatty acid alkyl esters (usually methyl esters, FAME) derived from either the transesterification of triglycerides or the esterification of free fatty acids with low-molecular-weight alcohols in the presence of acid or base catalysts. Biodiesel can also be prepared through the esterification of the free fatty acids present in animal fats (e.g., lard or tallow) with methanol over acid catalysts [1]. Fig. 1 represents the transesterification reaction of triglycerides with alcohols. Glycerol can be converted into added value chemicals or materials by different catalytic processes involving reforming, oxidation, hydrogenolysis etherification and esterification [2, 3].

Another possibility to valorise the glycerol is into oxygenated additives for liquid fuels (Fig. 2). Different glycerol-based compounds such as glycerol ethers, acetyl glycerol and glycerol acetal have been identified as valuable replacement of fuel additive which depends on depleting sources, price uncertainty and growing environmental concern of petroleum feedstock [2].

The products of esterification reaction of glycerol are mono-acetyl esters (monoacetin), di-acetyl esters (diacetin) and triacetyl esters. The triacetin has application as fuel additive, while the monoacetin and diacetin can be used in cryogenics and as raw material for production of biodegradable polyesters [4]. This esterification was carried out over different heterogeneous catalysts, like resins, zeolite, heteropolyacids, catalysts with sulfonic acid groups. The esterification of glycerol with acetic acid was carried out over resin and zeolites (HY and HZSM-5) [4]. Amberlyst-35 was found to be an excellent catalyst. The optimal conditions were temperature of 105 °C and an acetic acid to glycerol molar ratio of 9:1 with 0.5 g catalyst. Esterification of glycerol with acetic acid was carried out over dodecamolybdoephosphoric acid encaged in the NaUSY zeolite [5], tungstophosphoric acid supported on silica [6], supported on activated carbon [7], supported on Cs-containing zirconia [8] and supported on niobic acid [9]. Sulfonic acid groups linked on mesostructured materials [10] (Melero et al., 2007), activated carbon (Starbon1-400-SO3H) [11] and activated carbon (AC) treated with sulfuric acid [12] were used as catalysts in the esterification of glycerol with acetic acid.
Oxygen additives for diesel fuel can be also obtained from glycerol by etherification of this alcohol. Mixtures of mono-, di-, and trialkyl glycerols are suitable for use as oxygenates in diesel fuels [2]. Etherification of glycerol with isobutene was studied with acidic ion exchange resin catalyst [13]. Strong acid ion exchange resins of Amberlyst type and two large-pore zeolites H-Y and H-Beta were used as catalysts in etherification of glycerol with isobutylene or tert-butyl alcohol [14]. The etherification of glycerol with isobutylene to yield tert-butylated derivates was carried out over sulfonic-acid-functionalized silicas [15]. The production of glycerol tert-butyl ethers (GTBEs) from etherification of glycerol with isobutene over Amberlyst 15 was studied by Serio et al. [16]. Etherification of glycerol with ethanol was studied using different types of heterogeneous catalysts (sulfonic resins, zeolites and grafted silicas) [17] and over arenesulfonic acid-functionalized mesostructured silicas [18].

The acetals can be used as oxygenated diesel additives [2]. Acetalisation of glycerol with aqueous formaldehyde and acetone was carried out over Amberlyst-15, K-10 montmorillonite, zeolites (ZSM-5 BETA and USY) and p-toluene-sulfonic acid [19]. The acetalisation of glycerol and formaldehyde was studied in the presence of Amberlyst-47 acidic ion exchange resin [20]. The acetalisation of glycerol with acetone was studied over sulfonic acid-functionalized mesostructured [21] and heteropolyacids immobilized in silica [22]. The acetalisation of glycerol with different aldehydes was carried out using Amberlyst-15 acid resin [23] and mesoporous MoO$_3$/SiO$_2$ [24] as catalyst. Acetalisation of glycerol with butanal was carried out over zeolites (USY, BEA and ZSM-5) as catalyst [25]. USY zeolites, with different Si/Al ratio, were used as catalyst.

The aim of this work is to study the conversion of glycerol into biofuel additives in the presence of heterogeneous catalysts. The transesterification of glycerol with methyl acetate was studied over catalysts with sulfonic acid groups.
2. Experimental

2.1 Preparation of catalyst

All other reagents and solvents were analytical reagent grade purchased from Sigma–Aldrich and used without further purification. Chitosan was purchased from Sigma–Aldrich, USA.

The chitosan with sulfonic acid groups were prepared according to Xiang et al. [26]. A mixed solution of H$_2$SO$_4$ (95 wt%, 40 ml) and HCISO$_3$ (98 wt%, 20 ml) was thoroughly stirred and previously cooled to 4 °C. Then, 1 g of chitosan was added into the mixing solution, followed with stirring for 60 min at 25 °C. The product was precipitated by pouring and washing the reaction mixture into 250 ml of cold diethyl ether.

PVA (poly(vinyl alcohol)) with sulfonic acid groups was prepared according to Rhim et al. [27]. 3.0 g of PVA (MERCK, average molecular weight: 72000) was dissolved in water at 90°C, during 6 h. After that, an appropriate amount (2.68 mL) of sulfosuccinic acid was added to PVA solutions, which were vigorously stirred at room temperature for 24 h. The homogeneous solutions were poured and cast on a Teflon plate. The cast polymers were allowed to dry at 60°C during 24 h. The dried PVA matrix was heated at 120°C, during 2 h.

In this work were also used three commercial acid resins: Dowex 50X8 (R1), Dowex 50X4 (R2) and Dowex 50X2 (R3).

2.2 Catalyst characterisation

Acid capacity was measured via the determination of cation-exchange capacities. The ion capacities of the sulfonic acid groups in the functionalised chitosan were quantified using 0.1 M NaCl (aq) as the ion-exchange agent. One hundred milligrams of the sample was added to 15 ml of the salt solution, and the mixture was shaken for 24 h at room temperature. Thereafter, the solution was titrated via the dropwise addition of 0.025 M NaOH (aq).

The FTIR spectra were recorded in a Bio-Rad FTS 155 instrument.

The sulphur content was determined on a CHNS Elemental Analyser 1112 series instrument from Thermo Finnigan.

Scanning electron microscopy (SEM-FIB) was performed on a Zeiss Auriga scanning electron microscope operated at 2 kV.

2.3 Catalytic experiment

The catalytic experiments were performed in a stirred batch reactor at 70 °C. In a typical experiment, the reactor was loaded with 30 mL of methyl acetate, 1 g of glycerol and 0.07 g of catalyst that contained sulfonic acid groups.

The stability tests of the CH-SO$_3$H were carried out by three consecutive experiments, at the same reaction conditions. Between the catalytic experiments, the catalyst was separated from the reaction mixture by centrifugation, washed with water and dried at 80 °C overnight.

Undecane was used as the internal standard.

Samples were periodically collected and analysed via GC on a Hewlett Packard instrument equipped with a 15 m × 0.53 mm HP-5 column.

3. Results and Discussion

3.1 Catalyst characterisation

Fig. 3 shows the FTIR spectra of PVA and PVA with sulfonic acid group catalyst (PVA-SO$_3$H). In PVA-SO$_3$H spectra, the absorption band at 1730-1735 cm$^{-1}$ was observed, which is usually assigned to the ester group (-CO-O-), suggesting that the crosslinking with SSA was succeeded. The absorption band at 1037 cm$^{-1}$, which is associated with sulfonic acid groups, appears in the PVA-SO$_3$H spectra but not in the spectra of PVA, indicating the formation of sulfonic acid groups by SSA introduction [27].
Fig. 3 FT-IR spectra of catalysts: (A) PVA; (B) PVA with sulfonic acid groups.

Fig. 4 shows the FTIR spectra of chitosan (Fig. 4A) and chitosan with sulfonic acid groups (Fig. 4B). The absorption band at 1255 cm\(^{-1}\) in the spectrum of CT4, which does not appear in the spectrum of CT, indicates the presence of a sulfonic acid group introduced by chlorosulfonic acid. Additionally, the band at 808 cm\(^{-1}\), which can be attributed to the C-O-S group, indicates that the sulfonic acid groups were grafted onto chitosan. The peak at 1543 cm\(^{-1}\) is assigned to the specific absorbance of N-H bonds in NH\(^3\)+ groups [26]. All of the results demonstrated that the sulfonic groups were successfully grafted on chitosan pynarose rings.

Fig. 4 FT-IR spectra of catalysts: (A) Chitosan; (B) chitosan with sulfonic acid groups.

Fig. 5 (A and B) show the surface SEM micrographs for chitosan (CH) and chitosan with sulfonic acid, respectively. The pure chitosan exhibits a void-free dense structure (Fig. 5A). The catalyst exhibits voids and cracks in its structure, which can improve the reactants access to the active sites [26].

Fig. 5 (A and B) show the surface SEM micrographs for chitosan (CH) and chitosan with sulfonic acid, respectively.
The characteristics of catalysts are shown in Table 1. The acid capacities, obtained by acid–base titration and those obtained by elemental analysis were similar.

Table 1 Characterization of sulfonated catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Acid capacities</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Titration\textsuperscript{a}</td>
</tr>
<tr>
<td>PVA-SO$_3$H</td>
<td>4.0</td>
</tr>
<tr>
<td>CH-SO$_3$H</td>
<td>4.5</td>
</tr>
<tr>
<td>R1</td>
<td>4.2</td>
</tr>
<tr>
<td>R2</td>
<td>4.4</td>
</tr>
<tr>
<td>R3</td>
<td>5.0</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Amount of Brönsted acid sites was determined by acid-base titration (mmol/g)

\textsuperscript{b}Sulphur molar content determined by elemental analysis (mmol/g)

3.2 Catalytic experiments

The products of transesterification of glycerol with methyl acetate over catalysts with sulfonic acid groups were monoacetin, diacetin and triacetin. Fig. 6 compares the initial catalytic activities of catalyst in the transesterification of glycerol with methyl aceate, calculated from the maximum slopes of the glycerol kinetic curves. For resin catalysts, it was observed that catalytic activity increased with the amount of sulfonic acid groups. A similar behaviour was also observed with PVA-SO$_3$H and CH-SO$_3$H. However, the catalytic activity of resins is smaller than the catalytic activity of PVA and chitosan with sulfonic acid groups, despite of sulfonic acid amount of the catalysts to be similar (Table 1). This behaviour can be explained due to the hydrophilic/hydrophobic balance of catalysts. The PVA and CH catalysts have got -OH groups on the structure, become, probably, these catalysts with more affinity to the glycerol than the resins one.
Table 2 shows the glycerol conversion and the selectivity to the products obtained by the transesterification of glycerol with methyl acetate over catalysts with sulfonic acid groups, after 6 h of the reaction. It can be seen that the sample CH-SO$_3$H exhibits the highest conversion. After 6 h of reaction, the glycerol conversion was 35%, with a selectivity of 60% to monoacetin, 35% to diacetin and 5% to triacetin. The low selectivity to diacetin can be explained due to the diacetin and the triacetin products to be formed through consecutive transesterification reactions.

Table 2 Conversion and selectivity to products of the transesterification of glycerol with methyl acetate over catalysts with sulfonic acid groups.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Monoacetin</td>
<td>Diacetin</td>
</tr>
<tr>
<td>R1</td>
<td>13</td>
<td>79</td>
</tr>
<tr>
<td>R2</td>
<td>15</td>
<td>75</td>
</tr>
<tr>
<td>R3</td>
<td>19</td>
<td>70</td>
</tr>
<tr>
<td>PVA-SO$_3$H</td>
<td>25</td>
<td>67</td>
</tr>
<tr>
<td>CH-SO$_3$H</td>
<td>35</td>
<td>60</td>
</tr>
</tbody>
</table>

$^a$Glycerol conversion after 6 h of reaction.

In order to study the catalytic stability, the CH-SO$_3$H catalyst was reused. Consecutive batch runs with the same catalyst sample and in the same reaction conditions were carried out. Fig. 7 shows the initial catalytic activity of the CH-SO$_3$H. It is observed a slight decrease of the catalytic activity from the first to the third run. These results can be explained due to a small leaching of sulfonic acid groups.
Fig. 7 Transesterification of glycerol with methyl acetate over CH with sulfonic acid groups. Stability studies of CH catalyst. Initial activities taken as the maximum observed reaction rate, calculated from the maximum slope of the glycerol kinetic curve.

4. Conclusion

The transesterification of glycerol with methyl acetate was carried out over catalysts with sulfonic acid groups at 70ºC. It was observed that the catalytic activity increases with the sulfonic acid amount. CH-SO_3H shows the highest catalytic activity of all catalysts. In order to study the catalytic stability of CH-SO_3H, three consecutive batch runs with the same catalyst were carried out. It was observed similar values of the catalytic activity.

Acknowledgements This work was carried out with support from the Project PTDC/CTM-POL/114579/2009.

References


