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Acetylation of glycerol catalyzed by different solid acids

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Abstract

This work describes the acetylation of glycerol with acetic acid catalyzed by different solid acids. Reactions were carried out in batch mode under reflux. The kinetics of glycerol transformation and selectivity to the products, notably mono, di and triacetyl esters, were determined within 30 min of reaction time to observe the primary products. The results showed that the acid exchange resin, Amberlyst-15, was the most active catalyst, achieving 97% conversion in this period, followed by K-10 montmorillonite, niobic acid, HZSM-5 and HUSY. The selectivity varied for each catalyst and conversion degree, but the yield of di and triacetylated products increased with increasing conversion and reaction time. In all cases, the formation of α-hydroxy-acetone (acetol) was observed and associated with the glycerol dehydration. The poor performance of the zeolites might be related to diffusion problems of the acetylated esters inside the cavities.

Keywords: Acid catalysis; Glycerol; Biodiesel; Esterification

1. Introduction

The growing concern about the global heating is one of the main issues at the beginning of this century, motivating discussions on renewable energy sources, which have a lower impact on the CO_2 emissions. The modern society is still very dependent on fossil fuels, like petroleum and natural gas, but all over the world the viability of using renewable fuels is gaining increased importance. Among these new energy sources the biodiesel [1,2] appears as one of the most promising and feasible at short term. Its production and use has been stimulated in many countries, especially in Europe. Biodiesel is generally produced by transesterification of vegetable oils with methanol or ethanol, under base catalysis conditions [3]. In Brazil, the Federal Government has launched a national program for the production and use of biodiesel, establishing a mandatory mixture of 2% in the normal diesel oil in 2008, the so-called B2, and 5% in 2013 (the B5). These actions will place Brazil in the vanguard of the use of renewable fuels, as the bioethanol is being used for decades, to replace gasoline.

From the chemical point of view, the most traditional route to biodiesel production involves transesterification of vegetable oils, which are triglycerides, fatty acid esters of glycerol. Under base catalyst conditions [3], or even acid catalysis [4], in the presence of methanol, there occurs formation of three methyl esters of fatty acid molecules, which are the biodiesel themselves, releasing glycerol as by-product (Scheme 1).

For each 90 m^3 of biodiesel produced from transesterification of vegetable oils, approximately 10 m^3 of glycerol are generated. The estimated glycerol production from biodiesel upon the introduction of B2 in Brazil in 2008 is 80,000 tonne/year, for a present consumption of glycerol in the Brazilian market of around 30,000–40,000 tonne/year. The forecast is even worse for 2013, when the B5 will be mandatory, and the glycerol production from biodiesel will reach the amount of 150,000 tonne/year. These scenarios indicate that the commercial feasibility of the biodiesel program is directly linked with the commercial use of the glycerol. In Europe, with the increasing use of biodiesel, the glycerol prices are lowering and many plants that produce glycerol from petrochemical raw materials are closing, indicating that such a situation is global and deserves special attention. The main application of glycerol is in cosmetics, soaps and medicines [5]. With the introduction of large volumes of glycerol coming from biodiesel production, it is imperious to find new applications for this chemical, otherwise the economic feasibility of the biodiesel as a renewable fuel is jeopardized.

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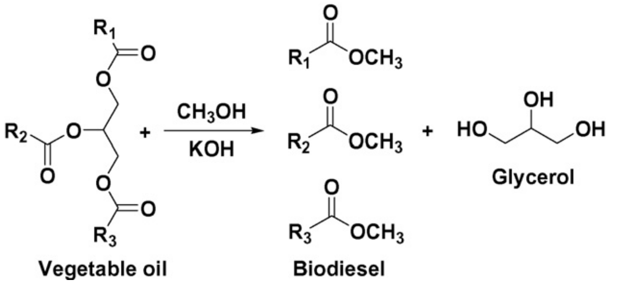
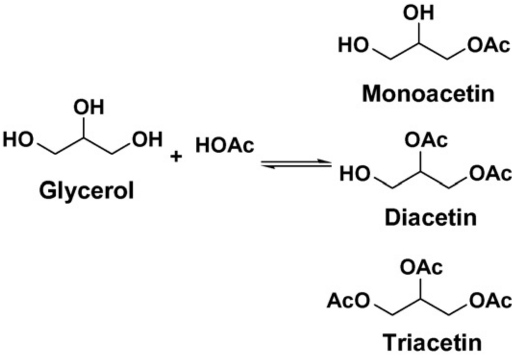


Scheme 1. Biodiesel production from the transesterification of vegetable oil.

Glycerol is a triol and up to its three hydroxyl groups can be functionalized. Recently, Karinen and Krause reported [6] the etherification of glycerol with isobutene, over acid exchange resin catalyst. These *tert*-butyl glycerol derivatives might be used as fuel additives [7]. They can also be obtained by etherification of glycerol with *tert*-butanol over acid exchange resin [8] or zeolite catalysts [9]. Dumesic and coworkers reported [10] on the low-temperature reforming of glycerol, to produce syngas. They showed that Pt supported on CeO_2/ZrO_2 is efficient to convert glycerol at 350 °C. Hydrogenolysis of glycerol over bifunctional catalytic systems yields 1,2- and 1,3-propanediol as the main products [11–13]. Acetylation of glycerol can also be a good alternative for the glycerol produced from biodiesel. The mono, di and triacetyl esters have great industrial applications. The triacetylated derivative is known as triacetin, and has applications going from cosmetics to fuel additive [14–17]. The mono and diacetylated esters are also known as mono and diacetin, and have applications in cryogenics and as raw material for production of biodegradable polyesters [18,19]. Moreover, the production of acetylated glycerol derivatives might be of potential interest to find applications for the excess of glycerol produced from biodiesel. In this work, we studied the production of mono, di and triacetin in the acetylation of glycerol with acetic acid catalyzed by different solid acids (Scheme 2).



Scheme 2. Acetylation of glycerol with acetic acid.

2. Experimental

2.1. Materials

The glycerol and acetic acid used were of analytical grade. The Amberlyst-15 acid resin was obtained from Room and Hass, whereas the K-10 montmorillonite was purchased from Fluka. Niobic acid was supplied by CBMM and the zeolites HZSM-5 and HUSY by Petrobras. Except for Amberlyst-15, whose acidity was informed in the specifications supplied by the manufacturer, the total acidity of the other catalysts was measured by adsorption of *n*-butylamine at 150 °C. Table 1 shows some characterization data and the total acidity of the catalysts.

2.2. Acidity measurements

The acid strength distribution of the catalysts, except Amberlyst-15, which does not have great thermal stability, was measured by temperature-programed desorption (TPD) of *n*-butylamine, using a thermo gravimetric equipment to follow the weight loss. About 25 mg of the catalyst were initially pretreated in a straight glass reactor, under flowing helium (40 ml/min), to the temperatures stated in Table 1. The temperature was then set to 150°C and the flow of helium (10 ml/min) was driven to a saturator containing *n*-butylamine at room temperature for a period of 10 min. The excess of the amine was desorbed, by passing a flow of helium (20 ml/min) over the catalyst bed during 20 min. The solid was then carefully placed in the thermo gravimetric equipment, Shimadzu TGA-51, and the TPD profile was taken following the weight loss up to 450 °C, under flowing nitrogen gas.

2.3. Esterification reactions

A round bottom flask was initially loaded with a certain amount of the solid acid catalyst. The weight of the materials

Table 1
Characterization of the catalysts

Catalyst	Area (m^2/g)	Si/Al molar ratio	Acidity (mmol base/g)[a]	Catalyst loading[b] (g)	Activation temperature[c] (°C)
Amberlyst-15	50	–	4.2[d]	0.47	150
K-10	240	6.6	0.5	4.0	150
Niobic Acid	187	–	0.3	6.3	300
HZSM-5	374	28	1.2	1.6	300
HUSY	566	2.6[e] (4.5)[f]	1.9	1.1	300

[a] Measured from *n*-butylamine adsorption at 150 °C.
[b] To achieve 2 mmol of acid sites in each experiments.
[c] Rate = 10 °C/min; time in activation temperature = 2 h.
[d] Informed by the supplier.
[e] Global Si/Al.
[f] Framework Si/Al.

varied in order to keep the same total acidity (2 mmol) in all the experiments (Table 1). The flask was then transferred to an oven and the catalyst was activated for 2 h according to the temperature profile shown in Table 1. After cooling the system to the room temperature, in an empty glass box kept under vacuum, 2.0 g (21.7 mmol) of glycerol and 5.0 ml (65.1 mmol) of acetic acid were added to the flask containing the pre-activated catalyst. The system was stirred with a magnetic bar and kept under reflux. Samples of the reaction medium were removed at 5 min time interval, for analysis by gas chromatography coupled to a mass quadrupole spectrometer, operating in electron impact ionization (70 eV).

3. Results and discussion

Figs. 1–4 show the conversion and selectivity results for the acetylation of glycerol over the different solid acid catalysts. Table 2 presents the conversion and selectivity to the products at 30 min of reaction time. It can be seen that Amberlyst-15 acid resin presents the highest conversion among all solid acid catalysts tested, also showing the highest selectivity to di and triacetin. After 30 min of reaction time the glycerol conversion was 97%, with a selectivity of 54% to diacetin, 31% to monoacetin and 13% to triacetin. It is interesting to notice that the glycerol conversion is around 90% even after 10 min of reaction time, indicating the high activity of the acid resin catalyst for esterification. This also explains the highest selectivity to diacetin and triacetin, because they are formed through consecutive esterification reactions. In fact, acid exchange resins are effective catalysts for esterification [20,21]. For instance, in the esterification of acetic acid with butanol, Amberlyst-15 was more active than HUSY, HZSM-5 and niobic acid catalysts [22], in agreement with the present results. It is worth mentioning that we were not able to separate or identify the two different mono and diacetylated products, formed by reaction on the primary and secondary hydroxyl group of glycerol. The reaction shown in Scheme 2 is only a pictorial representation and does not imply selectivity for one particular hydroxyl group in any catalyst studied.

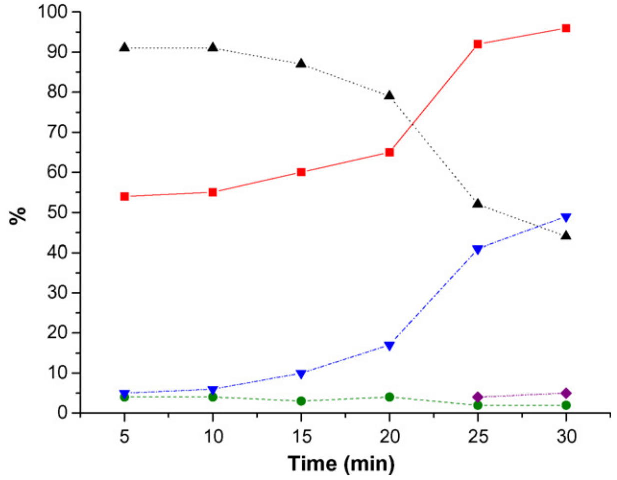


Fig. 2. Kinetics of esterification of the glycerol with acetic acid, catalyzed by the clay K-10 montmorillonite. (■) Conversion; (▲) selectivity to the monoacetin; (▼) selectivity to the diacetin; (◆) selectivity to the triacetin; (●) selectivity to the α-hydroxy-acetone. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

The K-10 clay presented a conversion of 96% after 30 min of reaction time, but the selectivity to di and triacetin was lower when compared with Amberlyst-15, being 49% and 5%, respectively. The monoacetin was produced with 44% selectivity, indicating that a second and third acetylation of glycerol is slower in K-10 montmorillonite than in Amberlyst-15. In fact, Fig. 2 shows that glycerol conversion achieves 90% only after 25 min of reaction time, when triacetin begins to appear among the products. This result contrasts with the data obtained for Amberlyst-15, which showed 90% conversion after 10 min (Fig. 1), indicative of a more active catalyst.

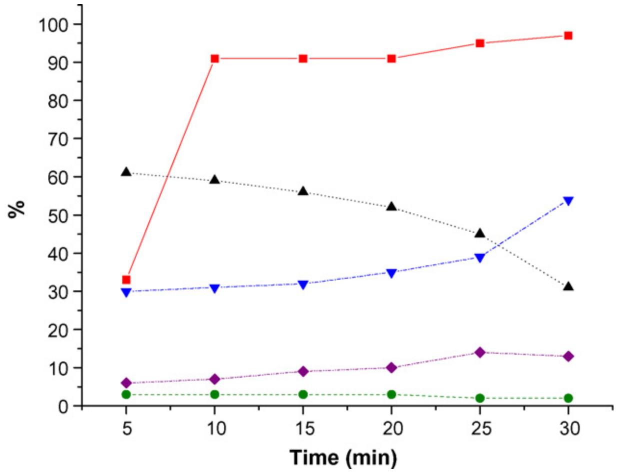


Fig. 1. Kinetics of esterification of the glycerol with acetic acid, catalyzed by the resin Amberlyst-15. (■) Conversion; (▲) selectivity to the monoacetin; (▼) selectivity to the diacetin; (◆) selectivity to the triacetin; (●) selectivity to the α-hydroxy-acetone. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

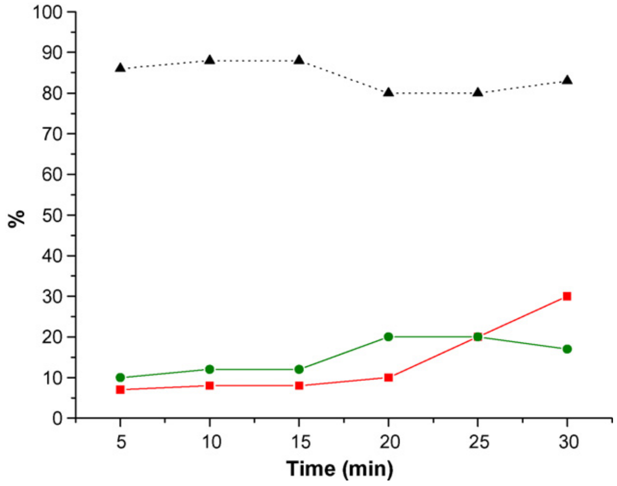


Fig. 3. Kinetics of esterification of the glycerol with acetic acid, catalyzed by the niobic acid. (■) Conversion; (▲) selectivity to the monoacetin; (●) selectivity to the α-hydroxy-acetone. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

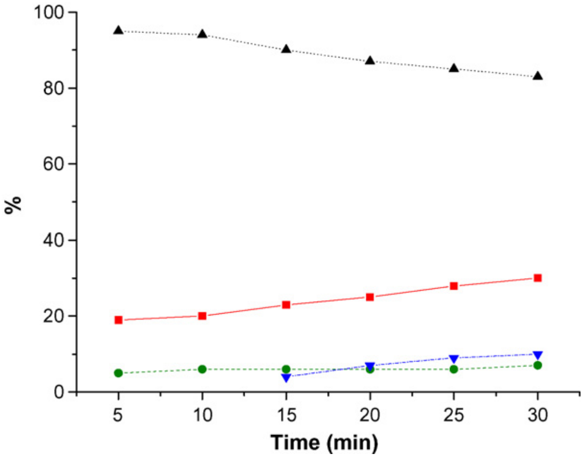


Fig. 4. Kinetics of esterification of the glycerol with acetic acid, catalyzed by zeolite HZSM-5. (■) Conversion; (▲) selectivity to the monoacetin; (▼) selectivity to the diacetin; (●) selectivity to the α-hydroxy-acetone. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Niobic acid presented a glycerol conversion of 30% after 30 min of reaction time, with a selectivity of 83% to the monoacetin. Within this period the other acetylated products, diacetin and triacetin, were not detected in the reaction products. Therefore, niobic acid is a high selective catalyst for producing monoacetin free from di and triacetin within the first 30 min of reaction. Fig. 3 shows the kinetic results, highlighting that only monoacetin is produced. The other observed product was the α-hydroxy-acetone (acetol), which will be discussed later. This result was somewhat surprising, since niobic acid is an effective catalyst for esterification [23]. It is possible that the activation temperature plays a major role in the activity of niobic acid, although the temperature used in this study (Table 1) is within the range of maximum acid strength for niobic acid [24].

The HZSM-5 zeolite presented a conversion of 30% after 30 min of reaction time. The main product formed was the monoacetin with a selectivity of 83%. The diacetin was also produced, but with a selectivity of 10%. Fig. 4 shows the kinetic data. HUSY was the catalyst that presented the worst performance among the catalysts tested. The conversion was around 14% after 30 min of reaction, with a selectivity of 79% to monoacetin and 14% for the diacetin. The kinetic data are shown in Fig. 5.

Table 2
Conversion and selectivity to the products of the esterification of glycerol with acetic acid after 30 min of reaction time

Catalyst	Conversion[a] (%)	Selectivity (%)			
		Monoacetin	Diacetin	Triacetin	Acetol[b]
Amberlyst-15	97	31	54	13	2
K-10	96	44	49	5	2
Niobic Acid	30	83	–	–	17
HZSM-5	30	83	10	–	7
HUSY	14	79	14	–	7

[a] Glycerol conversion.
[b] α-Hydroxy-acetone.

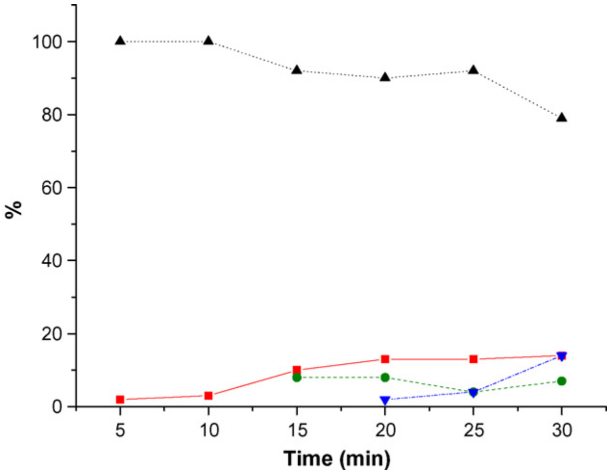


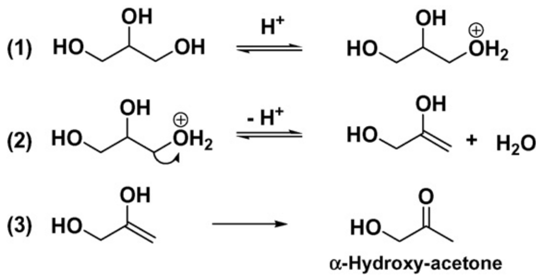
Fig. 5. Kinetics of esterification of the glycerol with acetic acid, catalyzed by zeolite HUSY. (■) Conversion; (▲) selectivity to the monoacetin; (▼) selectivity to the diacetin; (●) selectivity to the α-hydroxy-acetone. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

The results cannot be explained by the acidity of the materials, because the TPD of *n*-butylamine indicated that the zeolites have higher acid strength than the amorphous materials. Table 3 shows the results of acid site distribution (medium and strong), obtained from the TPD experiments, as well as the temperature of the maximum weight loss derivative, which gives an indication of the average strength of the acid sites in the 350–450 °C temperature range. If one uses the temperature of the maximum weight loss derivative as a measure of the average acid strength of the materials, one will see that K-10 is the weakest solid acid tested, although the catalytic activity for esterification of glycerol is higher, when compared with zeolites and niobic acid. It is possible that the low conversion and selectivity to the di and triacetylated products, observed for the zeolites, might be partly explained in terms of diffusion problems. It is evident that di and triacetin are space demanding and their formation and diffusion inside the zeolite pores would be difficult, explaining the poor selectivity to these products on the zeolite catalysts. These problems are not present in K-10, and might explain the better performance of this catalyst for the esterification of glycerol.

However, one would expect that diffusion problems would be worse on ZSM-5, as the pore system is narrower than the pore system of USY zeolite. On the other hand, the water

Table 3
Acidic properties of the solid acid catalysts obtained through thermodesorption of *n*-butylamine

Catalyst	Medium acid sites, mmol g^{-1} (150–350 °C)	Strong acid sites, mmol g^{-1} (350–450 °C)	Temperature of the maximum weight loss derivative (°C)
K-10	0.3	0.2	352
Niobic Acid	0.22	0.1	370
HZSM-5	0.41	0.83	386
HUSY	0.76	1.12	397



Scheme 3. Mechanistic pathway to the formation of α- hydroxy-acetone upon glycerol dehydration over acidic catalysts.

formed upon esterification may be more harmful to the acid sites of HUSY, affecting their activity to catalyze the reaction. As HZSM-5 has a higher Si/Al ratio than HUSY, it is more hydrophobic, allowing the exit of the water molecules from the channels and probably preserving the acidity of the sites. The same situation does not occur inside the HUSY, which is highly hydrophilic and the presence of water may affect the strength of the acid sites. In fact, zeolite Y was less active than HZSM-5, presenting higher activation energy, in the esterification of benzyl alcohol with acetic acid [25], supporting the present results.

For all the catalysts studied, the formation of α-hydroxy-acetone (acetol) was observed and it might have originated from the dehydration of the glycerol. Table 2 shows the selectivity to this product for each catalyst studied. It is interesting to notice that Amberlyst-15 acid resin presented the lowest selectivity, whereas niobic acid was the most selective catalyst to this product, followed by the zeolites. Dehydration (Scheme 3) is supposed to be endothermic, which can explain the low selectivity observed, due to the relatively low temperature (around 110 °C) used in this study. However, the indication that zeolites and niobic acid show the highest selectivity to this product among the catalysts tested suggests that its formation is, in some way, related with the acid strength of the catalyst, although the different range of conversions does not allow a more conclusive discussion. It is interesting to notice that dehydration preferentially occurs in the terminal hydroxyl group and not in the central hydroxyl, which would lead to acrolein. It is possible that in solution or on the surface of the catalyst, protonation of the terminal hydroxyl is favored by steric factors and solvation or interaction with the catalyst surface. The α-hydroxy-acetone (acetol) can be an important intermediate in a new technological route for propylene glycol production from glycerol.

4. Conclusions

The acetylation of glycerol with acetic acid was studied over different solid acid catalysts. The Amberlyst-15 acid resin presented the best performance, with the highest conversion and selectivity to di and triacetylated products, after 30 min of reaction time. Zeolites HZSM-5 and HUSY presented the worst performance, probably due to diffusion and acid site deactivation problems. In all cases there was formation of α-hydroxy-acetone, originated from glycerol dehydration. Formation of this product might be associated with the presence of strong acid sites on the catalyst surface.

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