



Acetylation of glycerol to biofuel additives over sulfated activated carbon catalyst

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ABSTRACT

Oxygenated fuel additives can be produced by acetylation of glycerol. A 91% glycerol conversion with a selectivity of 38%, 28% and 34% for mono-, di- and triacetyl glyceride, respectively, was achieved at 120 °C and 3 h of reaction time in the presence of a catalyst derived from activated carbon (AC) treated with sulfuric acid at 85 °C for 4 h to introduce acidic functionalities to its surface. The unique catalytic activity of the catalyst, AC-SA5, was attributed to the presence of sulfur containing functional groups on the AC surface, which enhanced the surface interaction between the glycerol molecule and acyl group of the acetic acid. The catalyst was reused in up to four consecutive batch runs and no significant decline of its initial activity was observed. The conversion and selectivity variation during the acetylation is attributed to the reaction time, reaction temperature, catalyst loading and glycerol to acetic acid molar ratio.

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1. Introduction

Fatty acids alkyl esters (biodiesel) production has attracted significant attention in recent years (Leung et al., 2010; Hasheminejad et al., 2011; Lee et al., 2011; Olutoye and Hameed, 2011a,b). This eco-friendly biofuel is becoming a competitive alternate to petrodiesel fuel since it is renewable, biodegradable, reduces exhausts, has superior ignition properties and a high cetane number in comparison to petrodiesel (Juan et al., 2011).

Biodiesel is generally synthesized via the transesterification reaction of triglycerides (vegetable oils or animal fats) with low molecular weight alcohol (methanol or ethanol) in the presence of alkali-based catalysts (Corma et al., 2007; Behr et al., 2008). This process ensures the conversion of raw triglycerides into fatty acids methyl/ethyl esters (FAMES/FAEEs), but generates glycerol as a by-product with an approximate portion equivalent to 10 wt.% of the total biodiesel produced. The uses of this glycerol are currently limited due to such issues as contamination with toxic methanol, and therefore additional venues for this raw chemical are being sought (Yuan et al., 2010; Pagliaro et al., 2007; Behr et al., 2008). The chemical transformation of glycerol into high value oxygenated fuel additives is a possibility (Hasheminejad et al., 2011) and can be achieved by etherification (Calcens et al., 2002; Klepáčová et al., 2007; Frusteri et al., 2009) or acetylation (Ferreira et al., 2009; Balaraju et al., 2010; Reddy et al., 2010).

Mono-, di- and triacetyl glycerides (MAG, DAG and TAG) are the main products from the acetylation of glycerol with acetic acid and/

or acetic anhydride (Liao et al., 2009; Silva et al., 2010; Ferreira et al., 2011). These acetylated esters (also known as mono-, di- and triacetin) have shown a versatile industrial applications ranging from cryogenics to fuel additives. MAG and DAG can be used as building blocks of polyester and cryogenics, and triacetylated esters can be added to cosmetics as moisturizers to diesel fuel as effective fuel additives (Rahmat et al., 2010; Smith et al., 2010).

Glycerol acetylation has been carried out using different heterogeneous acid catalysts such as Amberlyst-15, zirconia, niobic acid, HPAs and zeolites (Jagadeeswarai et al., 2010; Silva et al., 2010; Balaraju et al., 2010; Reddy et al., 2010; Ferreira et al., 2011). When Amberlyst-15 acid resin was used as a catalyst, a selectivity of 54% and 13% toward DAG and TAG, respectively was achieved (Gonçalves et al., 2008). Sulfated zirconia catalysts were considerably less active (Dosuna-Rodríguez et al., 2011). In the presence of niobic acid-supported tungstophosphoric acid (TPA) catalyst, a relatively high selectivity of 57% and 20% toward the formation of DAG and TAG, respectively was recorded (Balaraju et al., 2010). Dodecatungstophosphoric acid immobilized into a silica matrix as a heterogeneous catalyst achieved selectivity of 62% and 3% for DAG and TAG, respectively (Ferreira et al., 2009). However, some of these catalysts cannot be applied industrially. Some silicates are difficult to functionalize, HPAs are soluble in polar media, zeolites have low surface area and thermal stability, and some materials are too expensive (Freese et al., 1999; Kuang et al., 2003; Melero et al., 2007).

Acetic anhydride as an acylating reagent can achieve 100% selectivity for TAG either through acetylation followed by esterification with the acid resin Amberlyst-35 as a catalyst in the presence of a high excess of carboxylic acid (Liao et al., 2009) or by direct

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acetylation with acetic anhydride with K-10 montmorillonite as catalyst (Frusteri et al., 2009). In both cases, the formation of DAG was not occurred, due to the forced reactions toward the formation of TAG.

In this study, we describe the functionalizing of activated carbon (AC) with sulfur containing groups via hydrothermal treatment with sulfuric acid to prepare a suitable catalyst for the acetylation of glycerol with acetic acid. To obtain maximum conversion and selectivity, different reaction parameters such as reaction temperature, reaction time, glycerol to acetic acid molar ratio and catalyst loading were studied.

2. Methods

2.1. Materials

Anhydrous glycerol of high purity (>99%) and sulfuric acid (95–98%) were obtained from R&M Chemicals, Ltd., Malaysia. Glacial acetic acid (100%), ethanol and nitric acid ($\approx 65\%$) were purchased from Merck, Malaysia. Phosphoric acid (85 wt.%) and sodium hydroxide (>98 wt.%) were supplied by Sigma–Aldrich. Hydrochloric acid ($\approx 37\%$) from Mallinckrodt was used. Activated carbon (particle size: 10–900 μm) was purchased from Galcon carbon corporation, USA. All the received chemicals were used without any further purification.

2.2. Acidic treatment of AC

Functionalized AC samples were prepared via hydrothermal treatment with solutions of sulfuric acid. Initially, AC was sieved and particles 500–710 μm in size were selected for further study. The surface chemistry of AC was modified by treating 10 g of AC with different acidic solutions in a high-pressure stainless steel reactor. Phosphoric acid treatment was carried out by heating AC in the presence of 200 ml of 5 M acid solution to 120 °C at a heating rate equal to 5 °C min^{-1} and stirring at 530 rpm for 24 h. AC surface oxidation with nitric acid was conducted by boiling AC in 200 ml of 5 M nitric acid solution for 4 h under reflux. Sulfuric acid treatments were carried out with 200 ml of 0.1, 1, 3, 5 and 7 mol L^{-1} of sulfuric acid, and the resulting samples were designated as AC-SAX (where X = 0.1, 1, 3 and 5 M sulfuric acid) under vigorously stirring in a Teflon lined autoclave reactor at 85 °C for 4 h. All the samples were filtered, repeatedly washed with deionized warm water until neutrality of the rinse water, and dried in an oven at 120 °C for 6 h.

2.3. Catalyst characterization

The surface areas and textural characteristics of the prepared catalysts were determined using the Brunauer Emmett Teller (BET) method. The data were acquired on Micromeritics ASAP 2020 adsorption analyzer (Micromeritics instruments corporation, USA) at -197 °C.

The surface chemistry for the prepared catalysts characterized with respect to sulfuric acid groups on the surface, determined by Fourier transform infrared spectroscopy (FTIR), the concentration of acidic sites as evaluated by the neutralization titration method (Gomes et al., 2008), and the amount of sulfur presented on the catalyst surface before and after acetylation as determined by an Elemental Analyzer Perkin–Elmer 2400 system (series II, CHNS/O analyzer).

2.4. Reaction procedure

The catalytic activity was identified by means of glycerol conversion to acetylated products (MAG, DAG and TAG) and the

selectivity of these products. The path of such reaction involves the conversion of glycerol to MAG, whereas DAG and TAG products will be formed through consecutive acetylation reactions (Gonçalves et al., 2008). This mechanism showed that a product with low MAG content will be of high DAG and/or TAG content (based on high glycerol conversion) and *vice-versa*.

A high-pressure Teflon lined stainless steel reactor (200 cm^3) equipped with magnetic stirrer was used to perform the acetylation reaction. In a typical experiment, the reactor was charged with 20 g of anhydrous glycerol and 39.12–130.4 g of acetic acid taken (total volume not exceeding 150 cm^3) and 0.8 g of catalyst was added. The reactor was heated to the desired reaction temperature (60–135 °C) for 1–5 h. After each run the used catalyst was removed by filtration and thoroughly washed with deionized water followed by washing with ethanol (5–20 wt.% H_2SO_4). The catalytic activity of AC was assessed under the same operating conditions.

2.5. Analysis of products

Samples were collected at different intervals (0–5 h) and qualitatively analyzed using a GC/MS Perkin Elmer system (Clarus 600 gas chromatography attached to a Clarus 600T mass spectrometer) equipped with a DB-5 column. Samples were quantitatively analyzed with a gas chromatograph (GC; Shimadzu 2010 plus chromatograph, Japan) equipped with a flame ionization detector (FID). A ZB5-HT (30 m \times 0.25 mm \times 0.25 μm) GC capillary column was used. The analysis followed the internal standard technique. Samples were prepared by mixing 500 μl of product with 20 μl of ethanol (GC grade) as internal standard. About 0.2 μl of the sample was then injected into the column. The column temperature was set initially at 60 °C (2 min) followed by an initial ramp of 10 °C/min to 260 °C and then at 30 °C min^{-1} to 300 °C. The FID and injection temperatures were fixed at 350 °C and 250 °C, respectively. The carrier gas rate was 38.3 ml/min with split ratio of 20.

3. Results and discussion

3.1. Catalysts characterization

BET surface area, pore volume (V_p) and mesoporous surface area (S_{MES}) of the virgin AC and catalysts are summarized in Table 1. The results revealed that sulfuric acid treatment did not influence the surface characteristics of virgin AC material to a great extent compared to other acids. Treatment with 5 M sulfuric acid solution resulted in a slight change in the surface area (<5%) compared to nitric acid treatment (16.4%). This reduction in surface area can be explained by the introduction of sulfur-containing groups. Such sulfur moieties (sulfones, sulfides, sulfoxides, and sulfur atoms) may lead to active sites occlusion inside the pores and on the surface of AC. A relatively high temperature was required for the hydrothermal treatment of AC material with sulfuric acid solution in order to obtain uniform surface activation and to increase the number of accessible active sites.

Table 1

Textural and surface chemistry characteristics of activated carbon samples prepared by various acid treatments.

Catalyst	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{MES} ($\text{m}^2 \text{g}^{-1}$)	V_p ($\text{cm}^3 \text{g}^{-1}$)	Acidity ($\pm 10 \mu\text{mol/g}$)
AC	780	220	0.52	480
AC-PA ^a	761	216	0.47	570
AC-NA ^a	652	265	0.36	1080
AC-SA5	742	208	0.47	890

^a Activated carbon samples were treated with 5 M of above acids solutions.

The acidity is also illustrated in Table 1. The acid functionalities of the untreated AC material were relatively high (480 $\mu\text{mol/g}$). Virgin AC samples treated with 5 M nitric acid solution possessed an extremely high number of acid sites indicated by a surface acidity of 1080 $\mu\text{mol/g}$. Samples with moderate acidity (570 $\mu\text{mol/g}$) were produced when AC material was treated with 5 M phosphoric acid, whereas the treatment with 5 M sulfuric acid solution resulted in a material (AC-SA5) with stronger acidic functionalities (890 $\mu\text{mol/g}$). This sulfonated acidic character of treated AC material achieved the highest catalytic activity during the acetylation of glycerol with acetic acid.

The diffuse reflectance FT-IR spectrum (data not shown) showed absorbance at 1065 cm^{-1} (sulfuric acid groups) (Liang et al., 2010), but also indicated decomposition of some of the virgin functional groups such as C–H (indicated by weak absorbance at 2926 cm^{-1}) (Mohamed et al., 2006) in response to the reaction with sulfuric acid (Liang et al., 2010) and aliphatic nitro compounds C–N as indicated by decreased peak intensity at 1378 cm^{-1} after treatment. Primary amines (N–H) groups increased as observed at 1642 cm^{-1} (Terzyk, 2003).

The elemental sulfur content in the virgin AC was 0.49%, but 2.88% after hydrothermal treatment of AC-SA5. After the fourth reuse the sulfur content decreased slightly from 2.88% to 2.74% (about 4.8% reduction of sulfur).

3.2. Catalytic acetylation of glycerol

When the performance of H_3PO_4 , HCL, HNO_3 and H_2SO_4 as homogeneous catalysts was evaluated, H_2SO_4 showed the highest glycerol conversion (Table 2). The superior activity of H_2SO_4 during the acetylation is related to the role of protons and SO_4^{2-} anions in the enhancement of the catalytic performance (Gomes et al., 2010; Dosuna-Rodríguez et al., 2011).

The AC-SA5 catalyst presented the highest conversion of glycerol with minimal selectivity towards MAG among the prepared catalysts (Fig. 1), and a catalyst preparation obtained with 5 M sulfuric acid solution at 120 °C after 3 h of the reaction achieved the highest glycerol conversion of 91% with a selectivity of 38%, 28% and 34% to MAG, DAG and TAG, respectively (Fig. 2). Treatments with H_2SO_4 solutions of >5 M resulted in damaged surface

Table 2

Homogenous catalytic activity using different conventional acids. Reaction conditions: $T = 120^\circ\text{C}$, molar ratio of glycerol to acetic acid = 1:8, time = 5 h.

Acid glycerol	Conversion (%)
H_3PO_4	57
HCL	49
HNO_3	61
H_2SO_4	96
Blank	22

structures of the AC (indicated by particle discoloring) and low catalytic activity. The highest catalytic activity (expressed by glycerol conversion and selectivity toward DAG and TAG) of AC-SA5 catalyst is attributable to its high acidity (890 $\mu\text{mol/g}$), as determined by neutralization titration, and to the presence of SO_4^{2-} anions which enhanced surface interactions between the acylium moiety of the acetic acid with the OH^- anion of glycerol. The fact that AC-NA possessed the highest surface acidity of 1080 $\mu\text{mol/g}$, but did not exhibit the best catalytic performance suggests that the nature of the acidic group is also important. Sulfur-containing acidic groups have also been shown to be better performers by other researchers (Gomes et al., 2010; Dosuna-Rodríguez et al., 2011).

The results obtained using AC-SA5 catalyst (selectivity of 28% and 34% to DAG and TAG, respectively) are better than those employing sulfated zirconia as catalyst (Dosuna-Rodríguez et al., 2011) which had achieved 98% and 2% selectivity toward MAG and DAG, respectively with no TAG formed. A low TAG content of 3% was observed when silica matrix supported tungstophosphoric acid catalyst was applied (Ferreira et al., 2009), and a maximum selectivity of 57% and 20% toward the formation of both DAG and TAG, respectively, was achieved using a catalyst prepared by supporting tungstophosphoric acid on niobic acid (Balaraju et al., 2010). Commercial Amberlyst-15 acid resin catalyzed the acetylation of 97% of the glycerol with acetic acid with a selectivity of 31%, 54% and 13% toward MAG, DAG and TAG, respectively (Gonçalves et al., 2008). Conversion of 100% of the glycerol with selectivity of 53%, 40% and 7% to MAG, DAG and TAG, respectively,

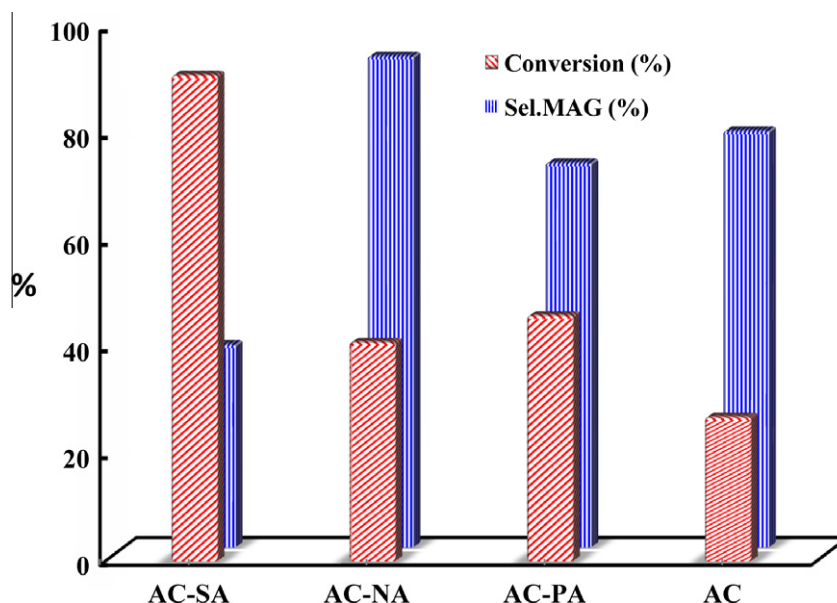


Fig. 1. Conversion (%) and selectivity to MAG (%) of heterogeneous catalysts prepared by hydrothermal treatment of AC with different Brønsted acids. AC-SA, AC-NA, AC-PA refers to sulfuric acid, nitric acid and phosphoric acid treated AC, respectively.

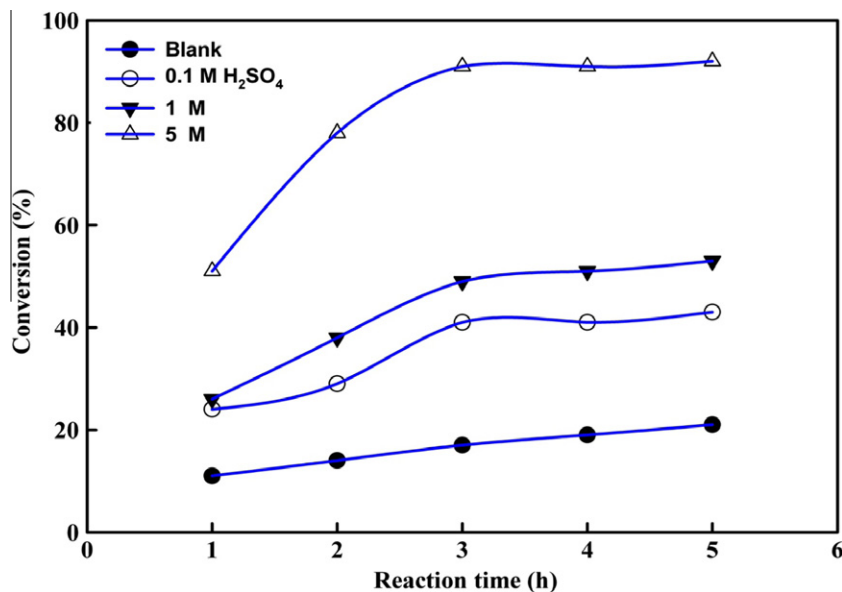


Fig. 2. Conversion (%) profiles of sulfuric acid treated AC catalysts during acetylation of glycerol with acetic acid. Reaction conditions: catalyst loading: 0.8 g; reaction temperature: 120 °C; molar ratio of glycerol/acetic acid: 1:8.

was observed using MoO_x/TiO₂–ZrO₂ catalyst (Reddy et al., 2010). None of these studies achieved TAG contents of more than 30% using a low cost process. The results of this work may lead to improved economics of biodiesel production since DAG and TAG are more valuable and can be used to improve the performance of biodiesel.

3.2.1. Effect of catalyst loading

Fig. 3 shows the glycerol conversion and product selectivities. Conversion increased with increased amounts of catalyst up to a catalyst load of 0.8 g at a level at which saturation appears to have been reached. The selectivity toward DAG and TAG increased linearly with the number of available active sites.

3.2.2. Effect of molar ratio of glycerol to acetic acid

Glycerol conversion increased linearly with the molar ratio of glycerol/acetic acid up to the ratio of 1:8 (Table 3). An excess of carboxylic acid utilized in acetylation reactions might shorten the time required to reach reaction equilibrium (Pagliaro et al., 2007) and provide more acetylating agent which undertakes the formation of DAG and TAG through further acetylation reactions. These data correlates with those already reported (Balaraju et al., 2010; Ferreira et al., 2009).

3.2.3. Effect of reaction time

Fig. 4 shows the influence of reaction time on the conversion and selectivity during the acetylation of glycerol with acetic acid.

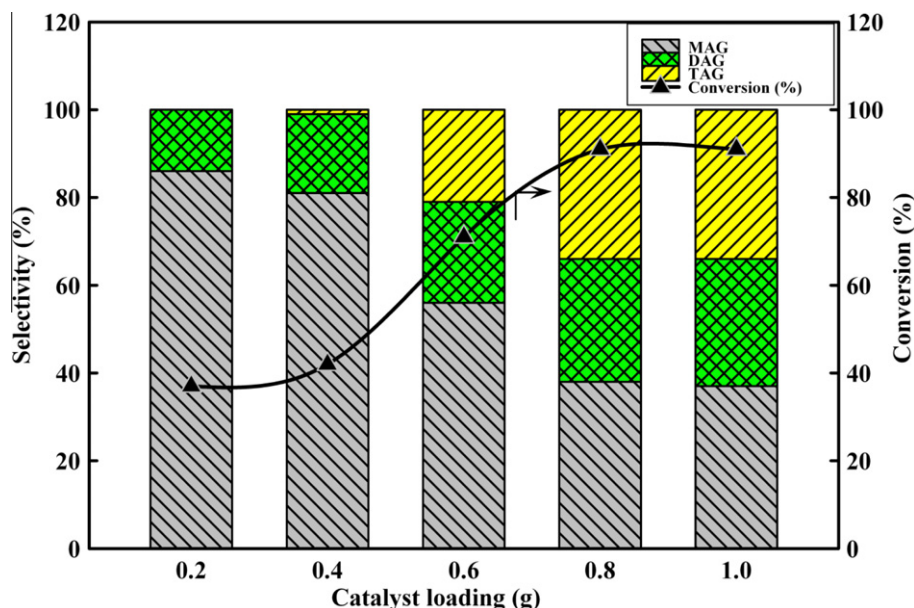


Fig. 3. Conversion (%) and selectivity (%) of catalyst loading during acetylation of glycerol with acetic acid over AC-SA5 catalyst. Reaction conditions: reaction time: 3 h; reaction temperature: 120 °C; molar ratio of glycerol/acetic acid: 1:8.

Table 3

Influence of molar ratio of glycerol to acetic acid on glycerol conversion and products selectivity over AC-SA5 catalyst acetylation. Reaction conditions: $T = 120\text{ }^{\circ}\text{C}$; catalyst weight = 0.8 g.

Glycerol: acetic acid	Conversion ^a (%)	Selectivity ^a (%)		
		MAG	DAG	TAG
1:05	72	44	35	21
1:06	72	41	34	25
1:07	78	38	31	31
1:08	91	38	28	34
1:09	91	38	28	34
1:10	92	37	29	34

^a Values recorded after 3 h.

The conversion reached about 70% within 1 h and its maximum value of 91% after 3 h. The selectivity for MAG was high at the start of the reaction; as the reaction proceeds, the formation of DAG and TAG increased at the expense of MAG. This behavior can be explained by the ionic attack of a hydroxyl group of glycerol on the carbonyl group of acetic acid and the formation of an acylium ion intermediate (Freese et al., 1999). The rate of formation of acylium ions on the catalyst surface represents the fastest and determining step during the acetylation reaction (Lilja et al., 2005). The acid site–acetic acid complex could facilitate the approach of glycerol molecules rather than that of other acetic acid molecules and this complex could be susceptible to multiple nucleophilic attacks of the hydroxyl groups of glycerol. The formation of MAG is the second reaction step and is energetically less favorable than the additional acetylations due to higher stability of the intermediate formed (Silva et al., 2010).

3.2.4. Effect of reaction temperature

The temperature was a dominant factor affecting glycerol conversion and product selectivity (Table 4). A substantial increase in conversion from 27% to 91% occurred when the reaction temperature increased from 60 to 120 °C and the combined selectivity for DAG and TAG was 62% at 120 °C after 3 h. The consecutive acetylation reactions are highly endothermic

Table 4

Effect of temperature on the conversion and selectivity during the acetylation of glycerol with acetic acid over AC-SA5 catalyst. Reaction conditions: molar ratio of glycerol to acetic acid = 1:8, catalyst loading = 0.8 g.

Temperature (°C)	Conversion ^a (%)	Selectivity ^a (%) ± (0.6%)			
		MAG	DAG	TAG	Others
60	27	77	5	0	18
75	46	69	17	5	9
90	59	62	24	11	3
105	81	45	27	28	0
120	91	38	28	34	0
135	91	37	29	34	0

^a Conversion of glycerol and selectivity after 3 h.

mic (Gonçalves et al., 2008) with temperature dependent selectivity, which explains the formation of mainly MAG at low temperatures (around 60 °C) after 3 h. However, the observation that AC-SA5 catalyst presented the highest selectivity toward DAG and TAG among the tested catalysts indicates that their formation is governed by the acid strength of the catalyst surface. It is possible that the acetylation occurs at the terminal or central hydroxyl group during the first acetylation, which would lead to the formation of MAG isomers (1, acetyl mono-glyceride or 2, acetyl mono-glyceride). The elevated temperatures enhanced the formation of higher glycerol acetates (DAG and TAG) due to the protonation of the remaining hydroxyl groups of glycerol molecule by steric factors and/or interaction with the active sites on the catalyst surface. The higher temperatures utilized the endothermic subsequent acetylations to form DAG and TAG.

3.3. Catalyst reusability and stability

The stability of the AC-SA5 catalyst was examined by recycling it through four successive runs (Fig. 5). A slight decrease in conversion and marginal change in selectivity was observed after the fourth run. These changes are probably due to either mass transfer limitations or deactivation of some of acid sites. The vulnerability of active sites is attributable to different deactivation factors that

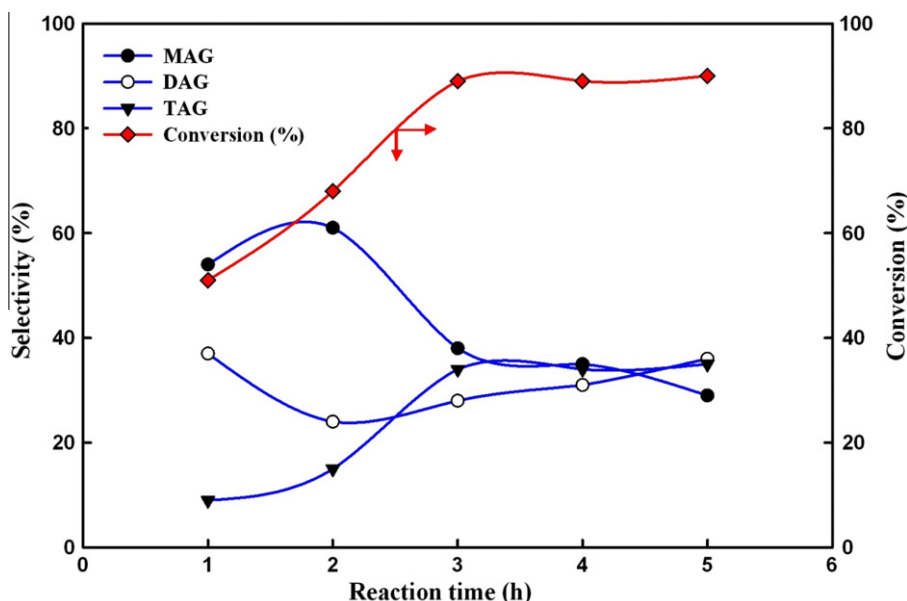


Fig. 4. Effect of reaction time during the acetylation of glycerol with acetic acid over AC-SA5 catalyst. Reaction conditions: catalyst loading: 0.8 g; reaction temperature: 120 °C; molar ratio of glycerol/acetic acid: 1:8.

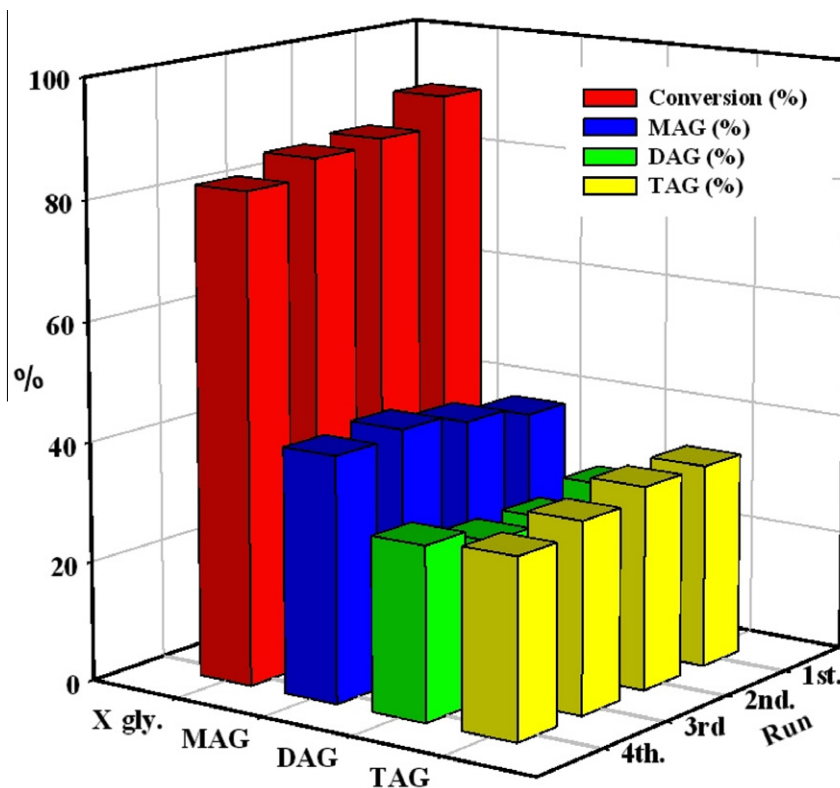


Fig. 5. Reusability test performed for the AC-SA5 catalyst in the acetylation of glycerol with acetic acid. Reaction conditions for each run: catalyst loading: 0.8 g; reaction time: 3 h; reaction temperature: 120 °C; molar ratio of glycerol/acetic acid: 1:8. MAG: monoacetyl glyceride; DAG: diacetyl glyceride; TAG: triacetyl glyceride; X_{gly} : glycerol conversion (%).

coincide with the change of fraction of unblocked sites. In some cases, when the process is accompanied by carbon formation, it will first block the fine pores, and this may lead to the stepwise termination of the contribution of the sites located inside them (Dosuna-Rodríguez et al., 2011; Kumbilieva et al., 2011).

4. Conclusions

The AC-SA5 catalyst exhibited predominant catalytic activity achieving glycerol conversion of 91% and a combined selectivity of 62% to both TAG and DAG. The best reaction conditions for the AC-SA5 catalyst are found to be 1:8 glycerol to acetic acid molar ratio, 120 °C reaction temperature and 0.8 g catalyst loading. Industrially, the developed findings may result in ameliorating the jeopardize economy of biodiesel production process. It was observed that the evolution of glycerol conversion and selectivity toward the preferred products (DAG and TAG) is governed by the combination of two groups of factors; density of Brønsted acid sites and the mass transfer rate in the mesoporous channels of activated carbon. It was observed the AC-SA5 catalyst presented good stability in its catalytic activity when reused in up to four consecutive batch runs.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.biortech.2011.07.035](https://doi.org/10.1016/j.biortech.2011.07.035).

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