



Selective formation of triacetin by glycerol acetylation using acidic ion-exchange resins as catalyst and toluene as an entrainer



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ABSTRACT

Esterification of glycerol with acetic acid in the presence of toluene as an entrainer was performed over acidic Amberlyst ion-exchange resins in a batch reactor. Toluene continuously removed the reaction water, thus the chemical equilibrium was effectively shifted; the selectivity for the most desired product triacetin was dramatically increased. The influence of reaction conditions such as reaction time, acetic acid: glycerol molar ratio and catalyst amount were investigated. More than 95% selectivity to triacetin at complete glycerol conversion was obtained. The ion-exchange resin catalysts were reusable in subsequent runs, but due to some deactivation the triacetin yields deteriorated.

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1. Introduction

In recent years, biodiesel has gained significant attention as a renewable transportation fuel. Presently, biodiesel is produced by transesterification of triglycerides with methanol to produce methyl esters of long chain fatty acids (FAMES) with glycerol as a by-product. Global production of biodiesel market is estimated to reach 36.9 million metric tons in 2020, which will give approximately 3.7 million metric tons of crude glycerol [1,2]. The rapid increase in the biodiesel production has resulted in an increased amount of low value crude glycerol available in the market. Pure glycerol has many commercial and industrial uses such as cosmetics, soap and medicines, but the uptake capacity of related markets is rather low [3,4]. Chemical valorization of low value glycerol to other valuable chemicals can be done by using several catalytic processes, such as the selective oxidation to glyceric acid or hydroxyacetone [5], dehydration to acrolein [6], hydrogenation to 1,2- or 1,3-propanediol [7], etherification to alkyl ethers [8], condensation to dimers or oligomers [9], and many others (e.g. [10,11]).

In addition, glycerol esterification with acetic acid (acetylation) leads to useful glycerol acetates like monoacetyl glycerol (MAG, monoacetin), diacetyl glycerol (DAG, diacetin) and triacetyl

glycerol (TAG, triacetin) as shown in Fig. 1. Mono- and diacetin exist in two different isomers. MAG and DAG have applications in food industry, cryogenics and as biodegradable polymers, while DAG and TAG may act as additive in various fuels and TAG is mainly used as humectant [11–13].

To perform the glycerol acetylation, it is necessary to use strong acid catalysts. Generally, this reaction is performed using homogeneous catalysts such as sulfuric acid, hydrofluoric acid or p-toluene sulfonic acid [14]. However, these strong acids are not convenient to use as they are hazardous, corrosive and difficult to remove from the reaction mixture. Therefore, it is desired to replace these mineral or organic acids by solid acid catalysts. Successful glycerol acetylation has been reported using several solid acid catalysts such as sulfated mesoporous silica [15], sulfated zirconia [16,17], sulfated activated carbon [18], double SO₃H-functionalized ionic liquids [19], magnesium fluorides [20], supported heteropolyacids [21,22], and ion-exchange resins like Amberlyst-15 or Amberlyst-36 [23,24] using in general batch reactor set-ups, but the reported triacetin yields were rather low. In most cases, they showed accumulated selectivities for DAG and TAG of around 80–90% at complete glycerol conversion. Recently, Zhu et al. reported that silicotungstic acid supported on ZrO₂ gave 32.3% selectivity for TAG at high acetic acid to glycerol molar ratio (10:1) at 120 °C in 4 h [22]. However, maximum selectivity for TAG achieved was 44.5% using Amberlyst-15 and an acetic acid to glycerol molar ratio of 9:1 at 110 °C within 4.5 h [23].

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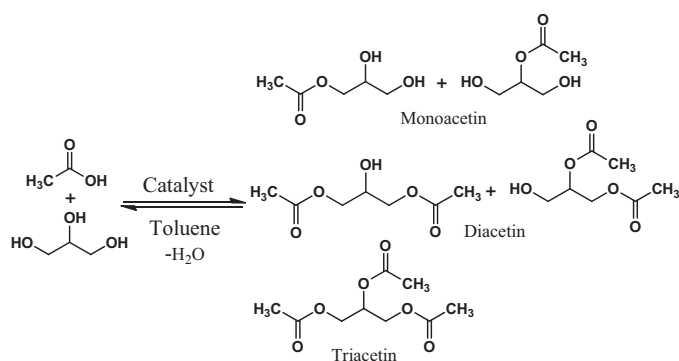


Fig. 1. Reaction scheme of glycerol acetylation.

In case of glycerol esterification with acetic anhydride (molar ratio 1:4) over H-Beta, Amberlyst-15 and niobium phosphate at 60 °C over 2 h, the selectivity for triacetin rises to 100%. But acetic anhydride is much more expensive than acetic acid as well as hazardous to health, hence it is not economically and environmentally acceptable [25,26]. Amberlyst-15 was also used, giving 100% selectivity for TAG with 41% yield at an extremely high molar ratio of acetic acid to glycerol (24:1) and very high pressure (200 bar) [27]. However, such extreme conditions are not attractive for an application in industry. Hasabnis and Mahajani carried out a continuous reactive distillation process for glycerol esterification over Amberlyst-15 with acetic acid using ethylene dichloride as an entrainer. In this process, selectivity to TAG was 39.8% [28] with complete conversion of glycerol.

In the available literature, the glycerol acetylation suffers from limited selectivity to triacetin, as the reaction remains in equilibrium in the presence of water. In order to increase the selectivity to the most desired product triacetin, it seems that a promising route would be the removal of water as stoichiometric reaction product. This measure would shift the equilibrium towards the product side, i.e. triacetin. However, the only way to remove water via azeotropic distillation would be the addition of an external component, referred to as an entrainer. Some results are already known but the selectivity to triacetin is still low [cf. 28].

In the present work, the catalytic performance of acidic ion-exchange resins Amberlyst-15 and Amberlyst-70 for glycerol acetylation was evaluated with the main target to reach highest TAG yield. In order to shift the chemical equilibrium to the side of the products, favorably to TAG, toluene was used as an entrainer to permanently remove the stoichiometric by-product water by azeotropic distillation. The effects of reaction time, acetic acid: glycerol molar ratio and catalyst amount were investigated. Fresh and spent materials were analyzed by means of CHS analysis.

2. Experimental

2.1. Materials

Commercial ion-exchange resin Amberlyst-70 (A70, moisture holding capacity 51–59%, Dow Chemicals) and Amberlyst-15

(A15, dry, Aldrich) were used. A70 was rested for 24 h at room temperature in the fume hood to remove moisture. Glycerol of high purity (>99%, Alfa Aesar), acetic acid (Aldrich) and toluene (Applichem) were used as reactants and entrainer, respectively. Furthermore, trimethylchlorosilane and hexamethyl disilazane (Aldrich), dodecane (TCI Europe), hexadecane (Aldrich) and pyridine (ACROS) were used for analytical purposes. Table 1 presents a short overview on the physical properties of A70 and A15.

2.2. Catalyst test procedure

Glycerol acetylation was performed in a three-necked 250 ml glass flask at atmospheric pressure. The flask was equipped with a fractionating Vigreux column, a modified Dean-Stark apparatus equipped with thermometer to measure the temperature of the boiling azeotropic mixture, a reflux condenser, a magnetic stirrer (1200 rpm) and a glass tube with thermocouple inside the flask to monitor the temperature of the reaction mixture (Fig. 2). The flask was heated using an oil bath (150 °C, TI1), and the temperature fluctuation measured inside the flask was less than ±1 K (TI2). In a typical experiment, 10 g of glycerol (0.108 mol) and 39.16 g of acetic acid (0.652 mol) representing an acetic acid to glycerol ratio of 6: 1, 60 g of toluene (0.652 mol) and 1 g of dodecane (internal standard to evaluate liquid volume change) were introduced into the reactor, followed by heating till the reaction mixture had the desired temperature. Then 500 mg of catalyst was added to the reaction mixture. Samples of 100 µl volume were taken periodically. In addition, a blank test in absence of a catalyst was carried out under similar reaction conditions. Moreover, a stop-experiment was conducted by removal of catalyst from a regular experiment after a defined reaction time, addition of fresh glycerol-acetic acid feed and continuation of the run with the same reaction conditions as before.

For proper GC analysis we had to reduce the polarity of the compounds to be analyzed and therefore, the OH groups of unconverted glycerol, MAG and DAG were silylated in a common procedure before gas chromatographic analysis by using hexamethyl disilazane and trimethylchlorosilane with pyridine as solvent. In addition, hexadecane was always used as an internal standard for the GC analysis (this means that two internal standards were used to cover the complete analysis procedure). Thereby prepared product samples were kept at 70 °C in a drying oven for 45 min and then analyzed using a gas chromatograph (HP 5890 series II) equipped with a CP-Sil 13 CB column (25 m × 0.32 mm). The temperature program was as follows: 50 °C for 1 min hold, heating at 20 K/min to 310 °C, 2 min hold at 310 °C. The educts glycerol and acetic acid as well as the silylated products MAG, DAG and TAG were clearly eluted. For DAG, two isomers were detected in the chromatograms, but separation was incomplete and individual quantification was impossible. Quantification of all reactants was carried out using specific response factors determined from GC analysis of authentic compounds in calibration mixtures of known composition. Diglycerol tetraacetate (DGTA) was identified by using an authentic sample prepared from linear diglycerol and acetic anhydride; product identification was carried out using a GC-MS combination (HP G1800 C, GCD Series II). The relative error of

Table 1
Properties of the used Amberlyst catalysts.^a

Catalyst	Acidity (eq./kg)	Cross-linkage (%)	Particle size (mm)	Surface area (m ² /g)	Average pore diameter (nm)	Thermal stability (°C)
Amberlyst-15	4.7	20	0.297–0.841	53	30	120
Amberlyst-70	2.55 2.80 ^b	n.a.	0.500	36	22	190

^aData taken from supplier and from data reported in [35].

^bDetermined by titration with KOH.

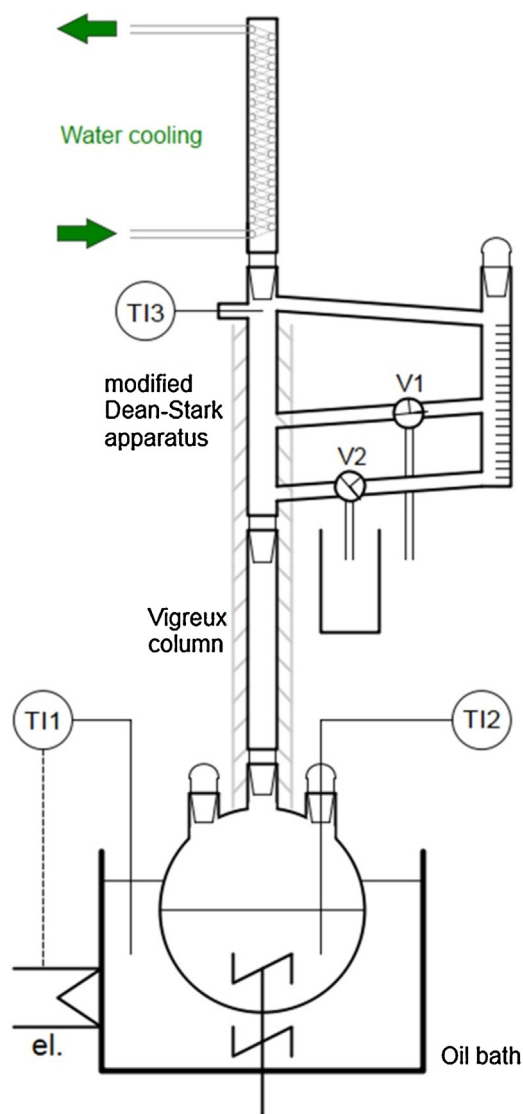


Fig. 2. Scheme of reaction setup.

the GC analysis procedure was below 1%. All reported conversion data refer to glycerol.

2.3. Solid characterization

Carbon, hydrogen and sulfur contents of the catalysts were analyzed quantitatively before and after reaction by elementary analysis performed on a TruSpec CHNS Micro analyser (Leco). The same apparatus was used for sulfur analysis of the product solutions.

3. Results and discussion

3.1. Glycerol esterification with water removal

Glycerol acetylation is a consecutive reaction with stepwise formation of MAG, DAG and TAG and their respective isomers, where every step is controlled by chemical equilibrium. Therefore, the theoretical maximum selectivity for TAG as calculated over all steps is rather low. The equilibrium can be shifted towards the products either by using one reactant in excess or by removing one of the products during the reaction. Thus, continuous removal of water helps to shift the chemical equilibrium towards the desired

Table 2

Performance of Amberlyst catalysts in glycerol acetylation using toluene as an entrainer.^a

Catalyst	Reaction time (h)	Conversion (%)	Selectivity (%)		
			MAG	DAG	TAG
Blank test	4	52.2	84.6	15.4	0
Amberlyst-15	4	100	1.5	54.2	44.3
Amberlyst-70	4	100	2.5	51.7	45.8
Amberlyst-70 ^b	4	97.0	30.4	60.3	9.3

^aGlycerol = 10 g, acetic acid = 39.16 g, toluene 60 g, catalyst = 0.5 g, 105 °C.

^bExperiment without removal of water.

products. Furthermore, an excess of acetic acid also helps to increase triacetin yield, as the glycerol then becomes the limiting compound and can be converted completely within one batch. When the reaction was performed in the absence of a catalyst (blank test) under the described reaction conditions over 4 h, the conversion of glycerol was already above 50% and MAG was the major product with a selectivity of 85%. Only a small amount of DAG with a selectivity of 15% was detected (Table 2). This behavior is probably due to the presence of acetic acid and points to a homogeneously driven acid catalysis. Fig. 3 depicts glycerol conversion and product selectivities of the blank test over reaction time. It becomes clear that the selectivity to MAG as primary product drops with time and selectivity to DAG as consecutively formed product increases. TAG formation could not be observed. In contrast, the use of A15 and A70 gave complete conversion of glycerol after 4 h with selectivity for TAG of 44.3% and 45.8%, respectively (see Table 2).

It is well known that the acid strength of the catalyst has a significant influence on the catalytic activity and selectivity. Theoretically, we can assume a Fischer esterification mechanism operating in this process [24]. First addition of proton (for example from Amberlyst catalysts) to the carbonyl oxygen takes place which generates positive charge on the carbonyl carbon, facilitating nucleophilic attack of hydroxyl group from glycerol to produce MAG (in consecutive steps DAG and TAG) with water as a by-product (Fig. 4). In the present work, toluene is used as an entrainer to remove the formed water by azeotropic distillation which ultimately shifts the equilibrium towards the product side. Toluene forms an azeotropic mixture with water at 84 °C as well as with acetic acid at 104 °C [29], hence, two azeotropic mixtures may form that clearly determine the boiling point of the mixture during glycerol acetylation due to their proportions. At the beginning of the run, the mixture

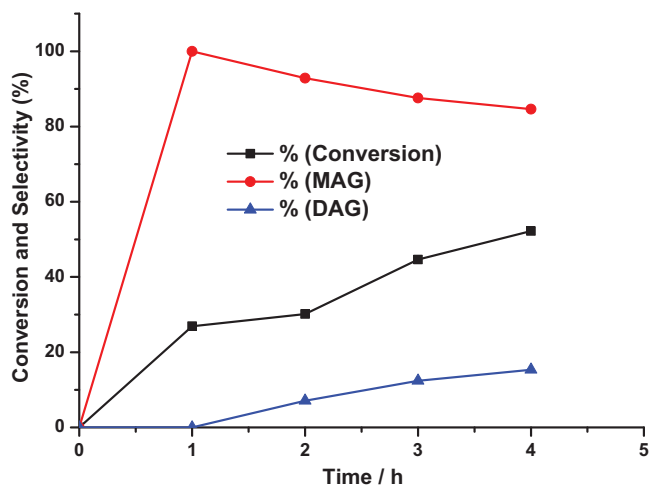


Fig. 3. Conversion of glycerol and selectivities to products in a blank test (glycerol = 10 g, acetic acid = 39.16 g, molar ratio acetic acid: glycerol = 6:1, toluene = 60 g, T = 105 °C).

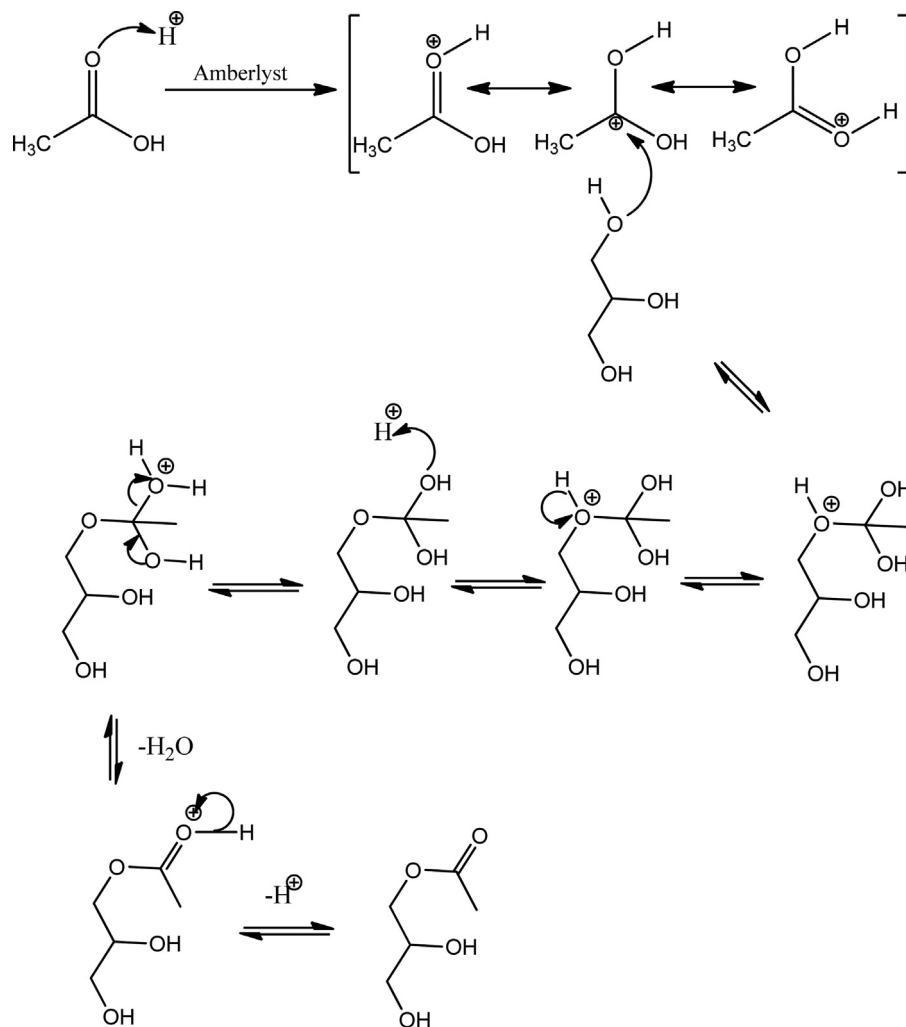


Fig. 4. Fischer esterification mechanism of glycerol with acetic acid to MAG.

started to boil at 100°C and the rate of reaction was fast. As the reaction proceeded, temperature of the mixture increased as measured on top of the column (Fig. 2, T13). For the longest time, temperature remained at 105°C . The final temperature of 110°C (boiling point of toluene) was reached after a large fraction of acetic acid had been consumed. Depending on reaction progress and the extent of water formation, the reaction mixture might also lose acetic acid, which has to be avoided.

The rapid glycerol conversion and high selectivity to TAG is attributed to the acidity of the catalysts as well as removal of water (kinetic and thermodynamic effects). To confirm this, a reference experiment was carried out with A70 catalyst without removal of water (simple reflux operation) while still using toluene as a part of the reaction mixture under the same conditions as described above. Indeed we found an almost complete conversion of glycerol (97.9%) after 10 h and high selectivity to DAG (58.1%) but low selectivity to MAG and TAG (23.6% and 18.3%, respectively), proving that in the presence of water the selectivity to TAG remains low. Table 2 contains some data taken after 4 h for comparison clearly showing that TAG is formed only in minor amount.

3.2. Reaction progress monitoring

It is important to note that the mixture containing glycerol, acetic acid and toluene is biphasic at room temperature. However, good homogenization of the mixture at the initial stage of the runs

was achieved at a stirring speed of 1200 rpm. As the temperature increases up to 100°C , the mixture became truly homogenous.

The reaction was monitored for 24 h with both the catalysts A15 and A70 under identical conditions to study the change in the product distribution with time under continuous water removal (Fig. 5). As expected in a consecutive reaction network, an increase in TAG selectivity was observed together with a decrease in MAG and DAG selectivities with progressive reaction time. A rapid glycerol conversion on both the catalysts was recognized in the first 2 h of the reaction; both of the graphs look very similar. Main products are MAG (that will be efficiently converted to DAG) and DAG in the beginning. After 10 h, the selectivity to TAG reached 83.9% and 87.6% and after 24 h, it increased to 94.1% and 95.3% using A15 and A70, respectively. At the end, the procedure using toluene as entrainer successfully provided more or less quantitative yields of the desired TAG.

Surprisingly, the quite different solid properties of A15 and A70 did not lead to significantly different performance in esterification. This was confirmed by repeating experiments. As surface area and total number of acid sites are higher for A15, one has to conclude that the acid sites on A70 must be much stronger to achieve same activity.

Moreover, one has to take into account that the polymer resins might swell during reaction, i.e. by contact with polar solvents and reactants, respectively, consequently changing the accessibility of the acidic sites (e.g. [30,31]). Another point is also the size of the

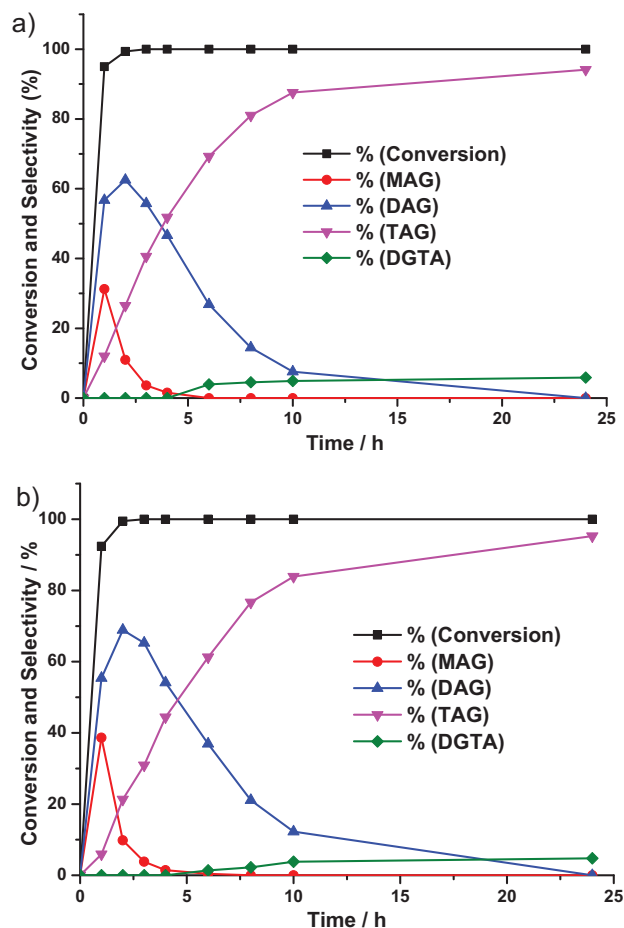


Fig. 5. Conversion of glycerol and selectivities to products over (a) Amberlyst-70 (A70) and (b) Amberlyst-15 (A15) during 24 h of reaction (glycerol = 10 g, acetic acid = 39.16 g, molar ratio acetic acid: glycerol = 6:1, toluene = 60 g, catalyst = 0.5 g, $T = 105^\circ\text{C}$).

reactants that might influence the molecular traffic inside such swelling resins. In addition, catalyst reactivity can be strongly influenced by non-polar interactions, for example by toluene [32]. As a consequence, not only acid properties influence catalytic performance but also accessibility to acid centers is an important issue.

To investigate the catalyst performance at lower global reaction rates while removing the formed water, additional experiments were carried out with a lower catalyst load of 50 mg. As expected, the initial glycerol conversion is lower and complete glycerol conversion was not reached within 10 h. However, even at lower conversion far away from equilibrium there was no significant difference between A15 and A70. Regarding the fact that the reaction mixture was homogeneous and the mesoporous nature of the catalysts, the impact of external or internal mass transfer should be negligible.

As the reaction proceeded (i.e. after 4 h), a new by-product, diglycerol tetraacetate (DGTA), was observed. Oligomerization of glycerol is well known to run at slightly higher temperatures in the presence of strong acid catalyst [9]. As we never observed any peak for diglycerol (oligomerized product) in the GC analyses, it is most likely that DGTA is formed by MAG and/or DAG oligomerization after partial esterification. The product distribution points at the competition of two reactions, esterification and etherification, both forming water and being controlled by equilibrium. We analyzed the water content of the reaction mixtures after 2 h by Karl Fischer-titration, and the water concentration was

Table 3

Results of reusability tests for glycerol acetylation in the presence of toluene as an entrainer over Amberlyst-70 (A70) and Amberlyst-15 (A15).^a

Catalyst	X(glycerol)	S(MAG)	S(DAG)	S(TAG)	S(DGTA)
A70-1st run	100	0	9.4	85.4	5.2
A70-2nd run	100	0.5	30.4	64.8	4.3
A70-3rd run	100	1.7	39.9	54.7	3.8
A15-1st run	100	0	12.3	83.9	3.8
A15-2nd run	100	1.7	59.9	38.4	0

^aGlycerol = 10 g, acetic acid = 39.16 g, molar ratio acetic acid: glycerol = 6:1, toluene = 60 g, catalyst = 0.5 g, $T = 105^\circ\text{C}$, $t = 10$ h.

below 0.05%, which is almost negligible. According to the reaction sequence in experiments at ca. 100°C , first a significant amount of MAG and water formed via esterification. In contrast, the parallel formation of dimers is not observed. On the other side, two separate experiments in our lab at 140°C in absence of water proved that DAG reacts much faster towards DGTA than glycerol to its dimers (kinetic control). However, the formation of DGTA is only significant when DAG is available at high concentration level (cf. Fig. 5), i.e. it looks that DGTA is a consecutive product of DAG. However, in runs without water removal at high glycerol conversion, DGTA reacts partly back to less substituted acetins. This might explain why this compound has not been reported for conventional experiments.

To the best of our knowledge, we are first to report the formation of DGTA under these conditions (glycerol = 10 g, acetic acid = 39.16 g, molar ratio acetic acid: glycerol = 6:1, toluene = 60 g, catalyst = 0.5 g, $T = 100$ – 110°C). However, DGTA has applications in cosmetics and can act as food additive [33] and is also used in the preparation of filter materials [34].

3.3. Catalyst stability, reusability and homogeneous catalysis test

The catalysts were separated by filtration after stopping the runs after 10 h and used for repeated runs with fresh reactant solution. For both the catalysts, glycerol conversion was retained at 100% in subsequent runs. However, the high initial TAG selectivity was not reproduced for both the catalysts. There was a considerable decrease in TAG selectivity to 54.7% (after 3rd run for A70) and to 38.4% (after 2nd run for A15), indicating a catalyst deactivation under reaction conditions (Table 3). It was also observed that already after the 1st run A15 started to break down into fine particles; this may be due to its lower thermal stability (120°C) though the reaction was run below the temperature limit or due to mechanical reasons.

In contrast, the observed extent of catalyst swelling is comparatively small. We observed in past experiments that Amberlysts that were used as catalysts for glycerol etherification at higher temperature around 140°C showed extreme swelling (by 1000% and more). It is known that swelling of such materials is remarkable mostly in the case of polar media (water, glycerol, acetic acid). Dumesic and co-workers [35] reported that high water amounts caused severe swelling of such polymers, coming along with catalyst deactivation. This is obviously suppressed in our water-free system and another remarkable benefit of toluene, which lowers the overall polarity of the reaction mixture.

Besides mechanical breakdown and swelling, the deactivation of both the catalysts may also be due to leaching of sulfonic acid groups and/or deposition of carbonaceous compounds on the catalyst surface. To check this, the proportions of carbon, hydrogen and sulfur in fresh and spent catalysts were analyzed (Table 4). The sulfur content in the catalysts dropped slightly probably due to the hydrolysis of some sulfonic groups of the polymer support by water traces [36] or the insufficient thermal stabilities. In particular, the sulfur content of the catalysts decreased from 14.0 to 10.7 wt%

Table 4
Elemental analysis of fresh and spent Amberlyst-15 (A15) and Amberlyst-70 (A70) catalysts.

Catalysts	Element fractions		
	C (wt%)	H (wt%)	S (wt%)
A15-fresh	41.5	5.7	14.0
A15-2nd run	44.4	5.7	10.7
A70-fresh	36.8	4.3	8.2
A70-3rd run	41.9	5.2	6.6

(1 mmol) in case of A15 (after 2nd run) and from 8.2 to 6.6 wt% (0.5 mmol) in case of A70 (after 3rd run). In addition, some titration tests with fresh and spent (used for 4 h in a regular test) A70 were carried out showing a solid acidity loss in the same order of magnitude. The overall acidity of A70 changed from 2.80 to 2.52 mmol/g. Consequently, some sulfur was also found in the liquid products. However, it seems to be unlikely that the leached sulfur species might act as homogeneous catalyst as some stop-experiments have proven (see below). The difference in A15 to A70 sulfur losses is most likely due to the higher bond strength between the polymer and the sulfonic groups in A70 because this resin is chlorinated which increases the strength of the acid sites and stability [37] (cf. Table 1). In addition, chlorine analysis of the liquid product sample from the reaction mixture by potentiometric titration showed that there was no leaching of chlorine.

The possible contribution of homogeneous catalysis was checked in a first separate stop-experiment under typical conditions where A70 catalyst was removed from the reaction mixture after 2 h. At that point, the selectivities to MAG, DAG and TAG were 14%, 63% and 23%, respectively, at complete conversion of glycerol. After additional 8 h of reaction without any catalyst, the selectivities to MAG, DAG and TAG did not significantly change, i.e. a selectivity distribution of MAG: DAG: TAG = 10%: 62%: 28% was obtained. This proves that leached sulfur species are not able to catalyze the consecutive reaction toward TAG. Moreover, a second stop-experiment was carried out under the typical conditions by removal of the catalyst after 4 h and addition of fresh reaction mixture. The reaction was continued for further 4 h under the same conditions and we observed a slowly increasing glycerol conversion and similar behavior of product selectivities (Fig. 6). Thus, the slope of the conversion and the selectivity curves look very similar to those obtained in the blank test (cf. Fig. 3). From these experiments,

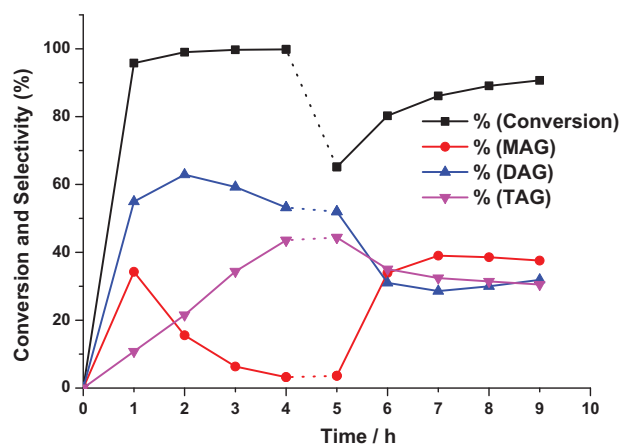


Fig. 6. Conversion of glycerol and selectivities to products over 0.5 g Amberlyst-70 (A70) in a stop-experiment (reaction conditions as in Fig. 5; catalyst was removed after 4 h and the run was continued for further 4 h without catalyst; the dotted lines mark the time span for catalyst removal and addition of fresh feed (glycerol = 5 g, acetic acid = 19.56 g)).

Table 5
Influence of catalyst amount and feed composition on glycerol acetylation in the presence of toluene as an entrainer using Amberlyst-70 (A70).^a

Catalyst	X(glycerol)	S(MAG)	S(DAG)	S(TAG)	S(DGTA)
3 wt%, 6:1	100	0.6	32.3	62.8	4.2
7 wt%, 6:1	100	0	0	95.7	4.3
5 wt%, 4:1	100	1.4	53.6	39.6	5.4
5 wt%, 6:1	100	0	9.4	85.4	5.2
5 wt%, 8:1	100	0	0	96.8	3.2

^aGlycerol = 10 g, acetic acid = 26.10–52.21 g, molar ratio acetic acid:glycerol = 4–8:1, catalyst amount = 0.3–0.7 g, toluene = 60 g, $T = 105^\circ\text{C}$, $t = 10\text{ h}$.

it can be concluded that the leached sulfur does not influence the reaction in a homogeneously catalyzed way. A similar experiment was conducted by Dosuna-Rodríguez and Gaigneaux showing the same feature that the leached species does not result in catalytic homogeneous reaction [38].

Apart from this, some carbon deposition on the catalyst surface was also observed. The Amberlysts themselves are carbonaceous materials, however, the fraction of carbon in the solid samples increased from 41.6 to 44.3% in case of A15 (after 2nd run) and from 36.9 to 41.9% in case of A70 (after 3rd run). This relative increase outnumbers the theoretical increase of carbon content related to sulfur loss and clearly indicates surface deposits. The adsorbed carbonaceous material may be in the form of esters, oligomers or polymers which probably block the acid sites on the catalyst surface. Similar phenomenon was also observed by Cara et al. for xylan (hemicellulose) hydrolysis using A70 as catalyst [39].

3.4. Influence of reaction conditions

As the catalyst A70 showed best efficiency for glycerol esterification with 100% glycerol conversion and almost 94% selectivity for TAG after 24 h, further parameters like catalyst: glycerol ratio and acetic acid: glycerol molar ratio were varied, and the results are shown in Table 5. During these tests, the conversion of glycerol was always complete though changing the named ratios.

When the catalyst amount was gradually increased from 3 wt% to 7 wt% (i.e. 0.3 g, 0.5 g and 0.7 g) with respect to weight of glycerol (acetic acid: glycerol = 6:1), a significant increase in TAG selectivity was observed. With 3 wt% of catalyst, TAG selectivity was 62.8% which increased to 95.6% with 7 wt% catalyst loading after 10 h.

Similarly, the raise of the acetic acid: glycerol molar ratio from 4:1 to 8:1 increased the TAG selectivity from 40% to ca. 97% (using 5 wt% of catalyst related to weight of glycerol). Setting the acetic acid: glycerol molar ratio to 8:1 with 5 wt% of catalyst, a selectivity of 96.8% TAG was obtained together with 3.2% DGTA.

Previously, many solid acid catalysts including resins and supported heteropolyacids have been used for the acetylation of glycerol with almost 100% glycerol conversion. However, maximum selectivity to TAG achieved was 44.5% by using A15 with an acetic acid to glycerol molar ratio of 9:1 [23]. The use of either a zeolite catalyst and acetic anhydride or ion-exchange resins like A15 and high reaction pressure showed 100% selectivity for TAG, but such processes are not economically and industrially applicable [25–27]. Continuous reactive distillation using A15 as a catalyst and ethylene dichloride as an entrainer showed 39.8% selectivity to TAG only [28]. Obviously, the efficiency of using ethylene dichloride as an entrainer to remove enough water is rather low and thus, higher selectivity to TAG could not be seen [28]. In the present work using toluene as an entrainer we could reach more than 80% selectivity to TAG with complete conversion of glycerol after 10 h compared to literature data. Toluene as an entrainer is very efficient as its azeotropic mixture contains up to 20% of water.

The use of acetic acid in excess is beneficial for the target reaction in several ways: the feed composition is adapted to favor formation of target product triacetin and it is beneficial to use excess acetic acid to increase reaction rate and final conversion of glycerol and to shift the chemical equilibrium towards TAG. An excess of acetic acid also shifts the selectivity clearly towards esterification and not etherification as competing reaction. The remaining acetic acid can be easily recycled (even when mixed with toluene). Another aspect with regard to reaction engineering is the fact that acetic acid lowers the viscosity of the mixture and eases the handling (less stirring energy required). Literature data and own experiments give strong hints on the extreme swelling of Amberlysts with alcohols (in particular glycerol) which seems to be less pronounced in the presence of an excess of acetic acid.

4. Conclusions

Glycerol acetylation was studied in the presence of toluene as an entrainer over acidic ion-exchange resins Amberlyst-15 and Amberlyst-70. Both the catalysts, A15 and A70 showed best performance with selectivity to triacetin of more than 95% at complete conversion of glycerol. This could be explained in terms of both the strong Brønsted acid sites of these catalysts and the use of toluene as an entrainer to remove the formed water. In comparison to the strong impact of these two features, the intrinsic differences in catalyst properties were clearly outnumbered by the beneficial effect of water removal.

In addition, a possible inhibiting effect of water on the used catalysts (swelling) and/or the entire reaction system (equilibrium limitation) might be suppressed. A70 showed better performance in reusability due to its high thermal stability and higher strength of acid sites compared to A15, though its total number of acid sites and specific surface area were lower. In addition, polymer resins might swell in the presence of polar solvents and/or reactants leading to swelling and consequently, influencing the accessibility of acidic sites that might also influence catalytic behavior.

The formation of the new by-product diglycerol tetraacetate was observed, potentially formed by dimerization of diacetin. This by-product was only observed at low water content and high glycerol conversion, which can be explained first by the reaction rates of esterification and etherification (kinetic control) and the chemical equilibrium (thermodynamic control). Some catalyst deactivation was seen in repetition tests, probably due to some loss of sulfur from the resins and/or deposition of carbonaceous products on the catalyst surface. This study demonstrates the advantages of a water-free, acid catalyzed process with an excess of acetic acid in glycerol acetylation. The process uses thermodynamic and kinetic effects in optimum way to produce triacetin in much higher yields compared to state-of-art.

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