



## 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 SO<sub>3</sub>H-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 ZrO<sub>2</sub> 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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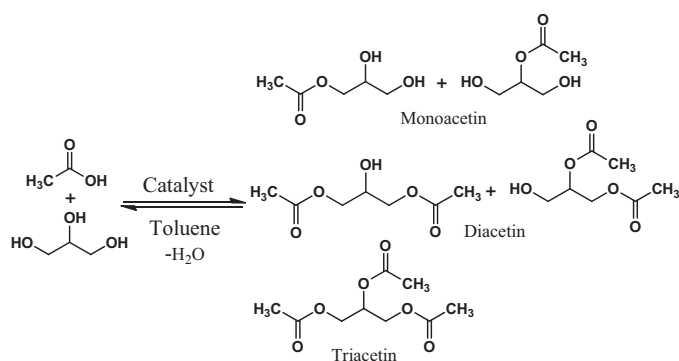


Fig. 1. Reaction scheme of glycerol acetylation.

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.<sup>a</sup>

Catalyst	Acidity (eq./kg)	Cross-linkage (%)	Particle size (mm)	Surface area (m <sup>2</sup> /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 <sup>b</sup>	n.a.	0.500	36	22	190

<sup>a</sup>Data taken from supplier and from data reported in [35].

<sup>b</sup>Determined by titration with KOH.

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