



Full Length Article

Synthesis of oxygenated fuel additives via glycerol esterification with acetic acid over bio-derived carbon catalyst



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ABSTRACT

Glycerol derived from biodiesel (BD) production is oversupplied and requires urgent utilization. Hence, crude bio-derived glycerol was utilized as a carbon precursor for heterogeneous solid acid catalyst synthesis via partial sulphonation and carbonization in a single step. The as-synthesized catalyst was utilized to catalyze glycerol acetylation reaction with acetic acid to produce oxygenated fuel additives (diacetin and triacetin) and monoacetin. Under reaction conditions of 110 °C, glycerol-to-acetic acid molar ratio of 3, 2 wt% catalyst dose, and 3 h reaction time, 88% combined DAG and TAG selectivity was attained with a corresponding glycerol conversion of 99%. The high surface acid sites density of the catalyst primarily contributed to its enhanced catalytic performance. The catalyst displayed sufficient heterogeneity and robustness in polar reaction media despite high hydrophilic acid sites density. Hence, it was reused in seven cycles of the experiment without experiencing significant deactivation.

1. Introduction

Awareness on biodiesel (BD) contribution to CO₂ emission reduction as an alternative energy source has led to increased demand and production of this type of diesel. Glycerol is a byproduct of BD synthesis and it constitutes about 10 wt% of the total produced BD weight. In this case, BD-derived glycerol is surplus and combined with presence of impurities, such as soap, methanol, and water, which poses serious limitations during refining, its market value is reduced compared with refined glycerol [1]. Thus, techniques to add more value to low-cost glycerol directly will boost the BD industries. Current research focus on ways to utilize crude glycerol is predominantly on upgrading to fine chemicals, identifying that over a thousand chemical products can be synthesized from glycerol [2,3]. Upgrading pathways such as low temperature steam reforming of glycerol over various Sn loaded Pt/C catalysts and non-catalytic conversion of glycerol to syngas at intermediate temperatures have been employed to upgrade glycerol. Also, hydrogen and ethanol production from glycerol over bacteria's and acetylation of glycerol over solid acid catalysts have been explored by researchers to synthesize renewable fuel or fuel additives [4–7].

The acetylation of glycerol using acylation agents has been receiving research attention for its valuable ester compounds notably monoacetin (MAG), diacetin (DAG), and triacetin (TAG). The acetyl esters can also be synthesized from the thermodynamically resisted glycerolysis of free fatty acids (FFA) to reduce the fatty acid content of

oils used in biodiesel production, before alkaline transesterification [8]. These acetylated esters (mono, di, and triacetin) have vast potential applications as detailed out in our earlier review [9,10]. Particularly, the DAG and TAG products have been established as oxygenated fuels additives that can enhance the cold flow properties of conventional diesel fuel, increase cetane number, and reduce noxious gas emission. They could lead to possible attainment of 100% atom efficiency in diesel engines by blending TAG with fatty acid methyl ester, FAME; since the physicochemical properties of TAG blended FAME are similar to biodiesel fuel [11].

Acylation agents such as acetic acid (AcOH) and acetic anhydride are required to produce esters of mono, di, and triacetin. Glycerol acetylation with AcOH is thermodynamically resistant and proceeds via consecutive three-step reaction from MAG to TAG. However, the use of acetic acid as acylation agent is preferred over acetic anhydride because the acetic anhydride reaction regime is highly exothermic with negative Gibbs free energy, whereas, glycerol acetylation with AcOH has positive Gibbs free energy [12]. Moreover, acetic anhydride is a potential substance for narcotic production and enlisted as contraband in many countries, even for laboratory use. The three-step reaction from MAG to TAG releases one molecule of water in each step, the reaction is reversible, and equilibrium controlled. The selectivity to TAG is considerably slower compared to MAG and DAG, possibly because of the reaction polar medium [13]. To positively shift the reversible equilibrium reaction towards higher TAG and DAG selectivity, several

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techniques have been adopted. Approaches such as an increase in temperature, increase in glycerol/AcOH molar ratio, the use of catalytic material, continuous removal of in situ formed water molecules during the reaction or combination of these can promote high selectivity towards TAG and DAG [14–16].

From the viewpoint of sustainable technology, heterogeneous catalyst such as Amberlyst-15 resin, mixed oxide catalysts [17], sulphonic acid functionalized zeolite support [18], K-montmorillonite, silica functionalized acids [19,20], WO₃ functionalized polypyrrole [21] and heteropoly acids, HPAs [22], have been utilized in acetylation reaction. When zirconia supported heteropoly acid was used, TAG and DAG selectivity attained 62.8% and 29.9%, respectively at 120 °C and 4 h reaction time [15]. Also, yttrium functionalized SBA-3 achieved 55% TAG and 34% DAG at a reaction temperature and time of 110 °C and 2.5 h, respectively [23]. Goncalves et al. [24], in their conducted studies using different solid acid catalysts reported that while, amberlyst-15 resins and K-10 montmorillonite-catalyzed the glycerol acetylation reaction to combined DAG and TAG of 67% and 54%, respectively. Meanwhile, HZSM-5 and HUSY achieved 10% and 14%, respectively of combined DAG and TAG after 30 min reaction time. The HZSM-5 and HUSY poor selectivity to DAG and TAG were attributed to narrow pore channel that poses diffusion limitation. Furthermore, application potentials of many acetylation catalysts are seriously limited. For instance, amberlyst-15 is thermally unstable at 120 °C and can be threatened by the co-produced water during the acetylation reaction because of its high hydrophilicity while, HPAs hydrolyses in polar media. Some materials used for the catalyst synthesis are expensive and functionalizing some silica to enhance its performance is challenging. Hence, catalyst active site thermal stability, acid strength as well as textural properties are vital to achieving high DAG and TAG selectivity.

In the case of environmentally friendly and “green chemistry” standpoint, functionalized clay, and activated carbon (Sulphonated Hydrothermal Carbon (SHTC)) has been utilized in glycerol acetylation reaction to synthesize glycerol esters (mono, di, and triacetin) [22,25–27]. Carlos et al. [25], in their study using carboxylic acid, reported that sulphonated carbon obtained via mild hydrothermal carbonization of D-glucose, achieved good selectivity towards TAG and MAG. Also, commercial activated carbon impregnated with HAP and sulfuric acid attained combined DAG and TAG selectivity of 74% and 64%, respectively at 120 °C and 3 h reaction time [22,26]. Elsewhere, BD synthesis from FFA-containing Karanja oil in a single step via simultaneous esterification and transesterification using methanol was achieved over glycerol based carbon catalyst [28]. Their reaction revealed that the formed mono, di, and triglyceride during the reaction could be utilized in situ to produce 100% BD over the reaction time (1–5 h). The stability of these catalysts is key to their commercialization. The various activated carbon or functionalized carbon used in the acetylation reaction displayed considerable resistance to leaching due to the strong bond interaction created between the carbon and the functional moieties. Hence, the reaction could undergo four cycles of reuse with a negligible decrease in catalytic activity.

In this work, biodiesel derived glycerol was utilized as carbon precursor to synthesize glycerol-based carbon catalyst. The catalyst was subsequently utilized in glycerol acetylation with AcOH to produce MAG, DAG, and TAG. The influence of reaction parameters was investigated and surface basicity and textural properties of the catalyst was correlated with the catalytic activity. The stability of the catalyst against leaching of active sites was also probed.

2. Materials and methods

2.1. Materials

Crude glycerol (80 wt% purity, density = 1.23 as provided by the company) was supplied by a local company in Malaysia. Acetic acid (100%), anhydrous glycerol (> 99%), hexane (99%), concentrated

H₂SO₄ (95–97% assay) and HCl (37 wt%) were of analytical grade from Merck & Co.

2.2. Catalyst preparation

The synthesis of the solid acid glycerol-based catalyst was adopted from Ref. [29], with slight modification. Typically, a mixture of concentrated sulfuric acid (15 wt% relative to glycerol weight) and 10 g of glycerol was stirred for 10 min in a 100 ml flask. Then the mixture was transferred to reactor and temperature was increased to 150 °C for 1 h, to facilitate carbonization (dehydrating agent), sulphonation and eventual aromatic polycyclic carbon formation. After the foaming ceased, the temperature was increased to 200 °C under nitrogen flow (150 ml/min) for 1 h. Nitrogen gas was introduced to facilitate evaporation of unwanted materials and support any new pore formation. The product was cooled to room temperature and the foam was crushed to increase the surface contact area, followed by washing with distilled water until neutral pH as visibly observed using pH paper. Thereafter, the sample was dried at 110 °C for 2 h to remove moisture and a glycerol-based carbon catalyst, GBCC (49.4% yield) was obtained.

2.3. Catalyst characterization

The elemental compositions of the catalysts and the surface micrographs were obtained using energy-dispersive spectroscopy (EDS; FE-SEM ZEISS SUPRA 35VP) and scanning electron microscope techniques, respectively. The surface acid site density and acid strength of the catalyst were determined via NH₃-temperature-programmed desorption, NH₃-TPD (Micromeritics AutochemII 2920 chemisorption analyzer). The samples (25 mg) was purged, to remove impurities, with helium at a flow of 30 ml/min from ambient temperature to 150 °C for 1 h. Then the catalyst was cooled to 40 °C, and 15% NH₃ gas was absorbed by the sample for 1 h at a flow rate of 30 ml/min. The desorption of NH₃ was carried out under helium flow from 40 to 800 °C and the online gas chromatography equipped with a thermal conductivity detector was used to monitor the desorbed NH₃.

The Brunauer–Emmet–Teller (BET) technique was utilized to determine the catalyst specific surface area. Autosorb I (Quantachrome Corporation, USA) using Nitrogen at 77 K was used to obtain the adsorption–desorption isotherms. The pore size distribution, as well as the pore diameter, were calculated using Barrett–Joyner–Halenda, BJH technique. Perkin Elmer Spectrum GX, Fourier transform infrared spectrometer (FTIR) was used to analyze the surface functional groups over a range of 4000 cm⁻¹ to 400 cm⁻¹ using the KBr pelleting method.

2.4. Glycerol acetylation with acetic acid

The catalyst activity was determined based on glycerol conversion to acetylated esters (MAG, DAG, and TAG) and the selectivity to MAG, DAG, and TAG. In a typical batch experiment, a mixture 10 g of glycerol, 6.52–58.69 g AcOH and 1–4 wt% catalyst dosage (relative to glycerol weight), was stirred in a 250 ml glass reactor equipped with PID temperature controller and magnetic stirrer, at a temperature range of 100–120 °C for 1–5 h. All the reaction was conducted without reflux to aid evaporation of in situ water except the reaction conducted at 120 °C as acetic acid boils at 118 °C. After acetylation reaction, the catalyst was recovered by centrifuge and washed severally with distilled water and hexane (50 ml per wash) to remove organic impurities. Then it was dried in the oven at 100 °C for 2 h and reused in successive acetylation reaction cycles adopting same regeneration method for each reuse. Leaching of the active sites, (-SO₃H) after reusability studies was determined using EDX analysis.

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