



Ultrasound-assisted acetylation of glycerol for triacetin production over green catalyst: A liquid biofuel candidate



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ABSTRACT

Upgrading of crude glycerol to high value-added chemical products is an attractive process in biomass conversion and biorefinery industry. In this work, production of triacetin (TAG) from direct conversion of glycerol with acetic acid over SO₃H-glycerol-carbon catalyst assisted with ultrasound was investigated for the first time. The catalyst was synthesized from glycerol via in-situ carbonization and sulfonation. The significant factors for TAG production obtained from 2^k factorial design were in the order of reaction temperature > ultrasonic power > reaction time. The TAG selectivity (100%) was successfully achieved in mild conditions. Kinetic studies indicated that ultrasound-assisted acetylation reaction followed first-order reaction while an activation energy of 51.08 kJ/mol was obtained. For comparison between as-synthesized catalyst with various commercial solid acid catalysts, the glycerol conversion turnover rate toward TAG was considerably highest on SO₃H-glycerol-carbon with the rates exhibited in the order of SO₃H-glycerol-carbon > Amberlyst-35 > H-USY > SiO₂-Tosic acid > Al₂O₃. The SO₃H-glycerol-carbon also exhibited excellent reusability for 10 consecutive cycles without any decreasing in glycerol conversion and TAG selectivity after regeneration process was carried out. The obtained results indicated that the contribution of catalyst acidity with ultrasonic power was responsible for determining TAG selectivity.

1. Introduction

In the past few years, the total energy consumption in the world has been significantly expanding. The mostly predominant resources for world energy supply are fossil fuels including crude oil and coal [1,2]. However, due to the limitation of existed fossil fuels with a few amount, investigating alternative source is a popular option to solve this problem. Biodiesel can be considered as the most promising eco-friendly biofuel due to its high cetane number, renewability, biodegradability, low emissions of carbon monoxide and sulfur dioxide [3,4]. Up to date, the demand of biodiesel production via transesterification of vegetable oils with methanol in the presence of alkali catalysts has attracted significant attention in recent years [5]. Unavoidably, a large amount of crude glycerol was also produced as a by-product in chemical industry with an approximate portion equivalent to 10 wt% of the total biodiesel produced. Meanwhile, the direct application of excess glycerol in industry might be not suitable due to its impurities including soap,

methanol and water, leading to increasing of waste product in environment. Moreover, high cost for purification of glycerol is required in order to meet industrial grade (98% purity) [6,7]. Therefore, it is necessary to find new ways for effective utilization of glycerol.

Recently, the chemical conversion of glycerol into high value-added chemical products via different reaction routes such as esterification, acetylation, dehydration and hydrogenolysis [8]. Among them, acetylation of glycerol with acetic acid into glycerol-esters (monoacetin (MAG), diacetin (DAG), and triacetin (TAG)) is more attractive. Preferably, TAG has been reported as the most attractive acetin due to its wide applications as building blocks of polyester and cryogenics, cosmetic and bio-fuel additives [9,10]. In general, the glycerol acetylation can be easily catalyzed by homogeneously acidic catalysts such as H₂SO₄, H₃PO₄, HCl, *p*-toluenesulfonic acid and/or acidic ionic liquids [11,12]. It is reported that the acidity of the catalyst is the key toward the selective formation of the favored DAG and TAG products. However, in an industrial process, the high corrosion to equipment, high

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toxicity to environmental and recycling difficulty of these homogeneously acidic catalysts always exist [13–15]. From this point of view, the heterogeneous acid catalysts can be preferentially considered and applied since their environmental friendly. Many heterogeneous acid catalysts such as zeolites, Amberlyst-15, sulfated zirconia and sulfonic mesostructured silica showed good activity for catalyzing glycerol acetylation [16–19]. Zhou et al. [20] found that glycerol conversion (97%) and a high total yield of DAG + TAG (90%) catalyzed by over amberlyst-15 could be achieved after 120 min. Chamack et al. [21] found that zirconium-modified mesoporous silica exhibited high selectivity (> 90%) for total DAG and TAG production. Kim et al. [22] also reported that Brønsted acid strength of sulfonic acid functionalized PrSO₃H-SBA-15 and Amberlyst-15 was important key for acetylation reaction. However, low selectivity and stability for TAG production as well as high production cost hinder their applications. As such, novel green heterogeneous catalysts with low cost and high activity as well as high stability should be developed and process enhancement should be considered.

In this study, glycerol acetylation with ultrasound assistance was investigated. The application of ultrasound may offer advantages, since the cavitation effect by it can create intense turbulence and liquid circulation at micro scale which could decrease the mass transfer resistance in the presence of heterogeneous catalysts, resulting in faster reaction rate and higher product yield [23,24]. Moreover, glycerol was also applied as a feedstock for preparing SO₃H-glycerol-carbon catalyst via *in-situ* carbonization and sulfonation processes. The physical and chemical properties of as-prepared catalyst were investigated. In order to minimize the error occurring the effect of each factor and their interaction based on TAG selectivity, 2^k factorial design was applied in this work as well. The optimization for glycerol acetylation was systematically investigated with various parameters such as reaction temperature, reaction time, ultrasonic power and ultrasonic duty cycle. Kinetic constant and activation energy for the acetylation reaction were determined at optimum operating conditions. The performance of as-synthesized catalyst based on glycerol conversion turnover rate and selectivity toward TAG product were extensively compared with various commercial solid acid catalysts such as Amberlyst-35, SiO₂-Tosic acid, H-USY and Al₂O₃. Moreover, the reusability of catalyst was also evaluated for 10 cycles under optimum conditions. To the best of our knowledge, there is no information available concerning in this study, especially for improving the selectivity of TAG by ultrasonic system. It is expected that this system can be applied for efficient conversion of crude glycerol into high value-added chemical products in practical process.

2. Experimental

2.1. Synthesis of SO₃H-glycerol-carbon catalyst

In-situ hydrothermal carbonization and sulfonation were applied for synthesis of SO₃H-glycerol-carbon catalyst [25]. In brief, a certain mixture of glycerol (≥99.5%, Sigma-Aldrich) with conc. H₂SO₄ (98%, Merck) was added into autoclave and heated at 150 °C for 24 h. Here, the mass ratio of H₂SO₄ to glycerol (3–1) was applied in this synthesis which obtained from our preliminary study based on highest acidity on catalyst. Thereafter, the SO₃H-glycerol-carbon catalyst (black precipitate) was filtered, washed for several times with distilled water and ethanol (96%, Merck) to remove excess sulfate ions and finally dried in vacuum oven at 110 °C for 12 h. For glycerol-carbon, it was synthesized using the same process as above mentioned without adding conc. H₂SO₄.

2.2. Catalyst characterization

N₂ sorption isotherms were measured at liquid nitrogen temperature of –196 °C using a Quantachrome Autosorb 1 gas adsorption/

desorption analyzer. The catalyst was pretreated at 150 °C for 6 h before measurement in order to remove out moisture and some impurities within the catalyst structure. The surface area of catalyst was measured by N₂ adsorption over a relative pressure range (P/P₀) of 0.03–0.28 using 11-point Brunauer–Emmett–Teller (BET) analysis equation. Pore volume and pore size of catalyst were measured from N₂ desorption curves using the Barrett–Joyner–Hallenda (BJH) analysis. The morphology of catalyst with the existence and the distribution of sulfonic group on catalyst were observed by a scanning electron microscope (SEM S-4800; Hitachi) equipped with energy dispersive spectroscopy (EDS). Here, the catalyst was dried in vacuum oven at first and then dispersed on carbon tape supported on stub. The acidity of catalyst were evaluated by NH₃-Temperature-programmed desorption (NH₃-TPD) using a BET-CAT catalyst analyzer (BEL, Japan) equipped with a thermal conductivity detector (TCD). The catalyst was preheated under He flow at 150 °C for 6 h. For NH₃ adsorption process, the mixing gas of NH₃ with He was flowed to catalyst at ambient temperature for 1 h with a flow rate of 50 ml/min. Then, NH₃ desorption was performed from 50 to 350 °C with a heating rate of 5 °C/min under He flow (50 ml/min). Thermal decomposition range of sulfonic group on catalyst was determined using a Thermogravimetric analyzer (Mettler Toledo TGA/SDTA 851). The catalyst was heated from 100 to 550 °C with heating rate (5 °C/min) under N₂ flow (50 ml/min). The existence of each functional group on the catalyst surface was proved by Fourier transform infrared spectrometry (FT-IR) using a PerkinElmer Spectrum 100 FT-IR spectrometer. Total acidity of catalyst was determined using acid-base back titration method [26]. Typically, 0.2 g of sample with an aqueous solution of NaOH (30 ml, 0.1 M) were mixed and stirred at temperature of 50 °C for 1 h with a speed of 150 rpm. After centrifugal separation, the supernatant solution was titrated by an aqueous solution of HCl (0.01 M) using phenolphthalein as an indicator.

2.3. Catalytic activity test and product analysis

The catalytic conversion of glycerol into acetylated products (MAG, DAG and TAG) was performed in a three-neck round bottom flask equipped with a reflux condenser and an ultrasonic horn as well as a thermocouple. A schematic diagram of the experimental setup was presented elsewhere [27]. In each batch, the stirring speed and the frequency of the ultrasonic probe were fixed at 650 rpm and 40 kHz, respectively. 5 g of glycerol, 0.25 g of catalyst and a certain amount of acetic acid (a molar ratio of acetic acid to glycerol = 8:1) were loaded into reactor. Then, reaction was conducted at different temperatures (60–120 °C), times (30–210 min), ultrasonic powers (40–100 W) and ultrasonic duty cycles (20–80%) in an oil bath. After finishing reaction, the mixture product was cooled in an ice-bath. During this step, in order to test the reusability of catalyst, glycerol acetylation were also carried out using an optimum condition for 10 cycles with the same catalyst. In each reuse cycle, the spent catalyst was separated from liquid product by centrifugation, washed for several times with ethanol to remove the adsorbed by-products prior to reuse in the next run, and then dried at 110 °C for 12 h. Thereafter, the washed spent catalyst was regenerated by soaking with conc. H₂SO₄ [28]. Moreover, the regenerated catalyst was also compared with the spent catalyst without regeneration using the responses of glycerol conversion and TAG selectivity. The liquid product was analyzed by gas chromatography (GC, Agilent 7820A) equipped with a flame ionization detector (FID) and a capillary column (ZB5-HT, 30 m × 0.25 mm × 0.25 μm). MAG, DAG and TAG were purchased from Alfa Aesar and used as the standard samples. The glycerol conversion and the product selectivity were quantified using external standard method and calculated using the following Eqs. (1) and (2):

$$\text{Glycerol conversion (\%)} = \frac{\text{Mole percentage of glycerol reacted}}{\text{Mole percentage of initial glycerol}} \quad (1)$$

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