

Glycerol Acetylation: Effect of Graphene Oxide Catalyst Mass Percentage on Glycerol Conversion and Acetin Selectivity

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ARTICLE INFO

Article history

Received March 06, 2023

Revised July 18, 2023

Accepted July 18, 2023

Keywords

Acetin

Acetylation

Conversion

Glycerol

Graphene oxide

ABSTRACT

Glycerol, a byproduct of the transesterification reaction, has a wide range of applications. Acetylation is a promising method for converting surplus glycerol into mono-, di-, and tri-acetin, which is used in the cosmetic, pharmaceutical, polymer, and fuel additive sectors. The contribution of this paper is to report the mass effect of a catalyst applied to the glycerol acetylation reaction mixture using a graphene oxide catalyst on the conversion and selectivity of acetine. The kind of catalyst and reaction conditions influence glycerol conversion and acetylation selectivity. Acetylation of glycerol was performed in this study by reacting acetic acid and glycerol with a graphene oxide catalyst produced using the Hummers method. The amount of graphene oxide catalyst (3%, 5%, and 7%) in the reaction mixture was adjusted to see how it affected glycerol conversion and reaction product selectivity. Other variables, such as the glycerol: acetic acid mole ratio of 1:9, reaction temperature of 120 °C, stirring speed of 1000 rpm, and reaction time of 120 minutes, were held constant. Glycerol conversion improves with increasing catalyst mass in the reaction mixture, with the highest conversion (92.1%) achieved when employing a 7% catalyst mass, with its selectivity to monoacetin, diacetin, and triacetin being 70.2%, 4.2%, and 25.6%, respectively. The efficiency of acetylated glycerol conversion is improved by increasing the catalyst's mass.

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1. Introduction

Currently, energy sources rely mainly on fossil fuels. Because these non-renewable fossil energy sources are depleting daily, initiatives such as identifying renewable energy sources and enhancing power plant efficiency are required to avoid a global energy crisis [1]. Biodiesel is one type of sustainable energy. Biodiesel has emerged as one of the alternatives for replacing fossil fuels [2]. The transesterification reaction of triglycerides with alcohol and an alkaline catalyst produces biodiesel. Glycerol is created as a by-product of biodiesel manufacturing, accounting for 10% of the total produced [3]. The abundance of glycerol must be engineered into value-added goods [4]. Glycerol acetylation is performed by adding acetic acid, resulting in monoacetin, diacetin, and triacetin, which can provide advantages and have a higher economic value [5].

Monoacetin and diacetin can be used to make biodegradable polyester [6]. In addition to these applications, monoacetin can be employed in fat synthesis. Diacetin can be utilized as a plasticizer, food, an intermediary in the fat structure system, and a blooming agent for cocoa butter [7]. Diacetin and triacetin have more economic worth than monoacetin due to their abilities as gasoline additives

to raise octane numbers and viscosity, and triacetin can also be utilized as a flavor enhancer, emulsifier, plasticizer, and additives in coating and paint [8], [9], [4].

The production of acetin is a lengthy reaction; even triacetin formation might take more than 4 hours [9]. The acetylation process can be sped up by utilizing a suitable acid catalyst. Despite their high catalytic activity, homogeneous catalysts like sulfuric acid are corrosive, poisonous, and challenging to remove from the product [10]. To overcome the limitations of homogeneous catalysts, heterogeneous catalysts such as Amberlyst-15 [10], Amberlyst-35 [11], Indion 225 Na [12], and polymer-based-catalyst [12] have been widely employed in glycerol acetylation. Carbon-based acid catalysts are another explored type because they are easy to prepare, hydrophobic, regenerable, and have strong acid sites [13]. Furthermore, carbon is derived from nature, is abundantly available, can be regenerated, and has a large catalyst surface area that is stable and high in activity [14], [15]. Sulfonated activated carbon [14], [15], [16], and carbon-supported yttrium oxide [17] are examples of carbon-based catalysts that have been produced. Because of its high conversion in a short time under moderate reaction conditions, graphene oxide produced from graphite has also been described as an excellent catalyst for the acetylation of alcohols and phenols, in addition to being inexpensive, not excessively acidic and toxic, and environmentally benign [18]. Graphene oxide nanoribbons formed of multi-walled carbon nanotubes (MWCNT) have a very wide surface area, which speeds up the process of ion adsorption and diffusion onto the catalyst's surface [19].

To accelerate the acetylation of glycerol so that the conversion is maximized, factors that affect the reaction, such as the ratio of reactants, temperature, catalyst, and agitation during the reaction, must be considered in addition to the type of catalyst. Increasing the acetic acid to glycerol mole ratio increases the glycerol conversion rate and acetate selectivity [20], [21]. Temperature increases increase glycerol conversion and acetin selectivity [22], [23]. It was reported that stirring speed also influences the conversion of glycerol [24] because stirring speed determines molecular diffusivity [25]. The mass factor of the catalyst introduced to the reaction mixture influences glycerol conversion [26].

The contribution of this paper is to report the mass effect of a catalyst applied to the glycerol acetylation reaction mixture using a graphene oxide catalyst on the conversion and selectivity of acetine. Graphene oxide catalyst was chosen as a carbon-based catalyst due to its advantages, including high electron mobility, large surface area, and high electrochemical activity [27], [28].

2. Research Methodology

2.1. Materials

The material used in this research is a multi-wall Wall Carbon Nano Tube (MWCNT) from Jiangsu XFNANO Materials China. Other ingredients are H₂SO₄ (98% purity Mallinckrodt), HCl (37% purity Mallinckrodt), KMnO₄ (VWR Life Science), H₃PO₄ (85% purity Merck, Germany), NaNO₃ (Merck, Germany), Glycerol (85% purity Merck, Germany), CH₃COOH (>99.5% purity Merck, Germany), chloroform (99.4% purity Merck, Germany), HIO₄ (99% purity Merck, Germany), H₂O₂ (50% purity Merck, Germany), KI (99.5% purity Merck, Germany), Na₂S₂O₃ (99% purity Merck, Germany), K₂Cr₂O₇ (99.9% purity Merck, Germany) and C₂H₆O (99.5% purity Ajax Finechem).

2.2. Procedures

1) Catalyst Preparation

Three grams of carbon were added to a mixture of 360 mL of H₃PO₄ and 40 mL of H₂SO₄. A total of 18 g of KMnO₄ was progressively added to the mix to oxidize carbon at a temperature below 20 °C. The mixture was then stirred for 12 hours and elevated to 50 °C. Due to the exothermic nature of the reaction, 400 mL of distilled water and 3 milliliters of 30% H₂O₂ were added slowly to the solution in an ice bath. The solution was stirred for two hours, filtered through a vacuum filter, and rinsed twice with 200 mL of distilled water, 200 mL of 30% HCl, and 200 mL of ethanol. The precipitate was dried overnight at ambient temperature (30 °C) in a vacuum oven.

2) Catalyst Characteristics

Catalyst characterization was tested using the BET method to determine the surface area of the catalyst using a Quantachrome Novatouch 4LX with an adsorbate in the form of nitrogen at a temperature of 77.35 K. The samples tested included carbon without preparation and with preparation. In addition, an XRD test was carried out to determine the crystal structure of the graphene oxide

catalyst using the MD10 Minidiffractometer at an angle of 10-70° with an exposure time of 1000 sec. The FTIR method was also carried out to analyze the functional groups contained in the catalyst using the Shimadzu IR Spirit tool with a wavelength of 400-4000 cm⁻¹.

3) Glycerol Acetylation Reaction Process

Glycerol 9.6 mL and acetic acid 56.6 mL were reacted at 120 °C for 120 minutes with stirring at 1000 rpm in a series of acetin production apparatus; 3 necks flasks equipped with reflux and different mass quantities of catalyst (3%, 5%, and 7%). When the reaction was complete, the catalyst was separated by filtering to stop the reaction, followed by catalyst rinsing with distilled water and ethanol [2]. During the reaction, one gram of sample was collected at regular intervals. The sample was subsequently diluted with 100 mL of distilled water. The sample solution was mixed with 50 mL chloroform in a 500 mL measuring flask. The sample was then mixed with 100 mL of deionized water. After 45 seconds of mixing, distilled water was added, and the solution was again agitated until homogenous. The answer was then allowed to stand until the chloroform and aqueous layers were completely separated. Fifty milliliters of the aqueous solution was taken, put in a 250 mL Erlenmeyer containing 2 mL of periodic acid solution, and shaken slowly. The mixture is then left to rest for 30 minutes. Then, 2 mL of potassium iodide solution was added, the mixture was gently agitated, and it was left in the dark for 1 minute. The sample is titrated with a previously standardized sodium thiosulphate solution until the brown color of the iodine nearly disappears. Then, 2 mL of a starch indicator was added, and the titration was repeated until the blue color disappeared [31]. The following equation can be used to determine the glycerol conversion factor:

$$\text{Conversion} = \frac{2.302 (B-C)N}{\left(\frac{a-b}{900}\right)} \times 100\% \quad (1)$$

B = titration volume of Na₂S₂O₃ for blank solution (mL)

C = titration volume of Na₂S₂O₃ for sample solution (mL)

N = normality of Na₂S₂O₃ solution (N)

a = initial sample weight (g)

b = weight of sample dilution (g)

4) Acetin Selectivity

Acetin selectivity testing was carried out by testing Gas Chromatography Mass Spectrometry (GC-MS) using a Shimadzu QP 2010 tool with an Rtx-5MS column with a thickness of 0.25 μm, length of 30 m, inside diameter of 0.25 mm and temperature 330 °C which is helpful in determining the composition of acetin in the product.

3. Results and Discussion

3.1. Catalyst Characteristics

1) BET Analysis

The specific surface area was determined using BET analysis and multilayer nitrogen adsorption, which was measured as a function of relative pressure and covered the solid outer area and the pore area. Using adsorption and desorption techniques, barrett-Joyner-Halenda (BJH) analysis was used to determine the pore area and specific pore volume. This technique is also used to characterize the pore size distribution. The results of the MWCNT BET test and the GO catalyst made are presented in Table 1.

Table 1. Surface Properties of MWCNT and GO Catalyst

Character	Catalyst	
	MWCNT	GO
Surface area (m ² /g)	255.9510	8.1829
Pore volume (cm ³ /g)	0.6571	0.0037
Pore size (nm)	5.1342	0.9062

The surface area of the GO catalyst decreased significantly, from 255.951 m²/g to 8.1829 m²/g, as well as the volume and pore size. Protonation of carbon bonds that are too strong due to the oxidation

process can cause the collapse of the pore walls, causing agglomeration and reduction of the pore volume. Other research mentions that the effect of temperature that exceeds the optimum limit it will form clumps (agglomeration) on the surface of the catalyst, thereby reducing the surface area of the catalyst [29]. In addition, the downward trend in surface area may be due to clogging of the pores by the active non-porous species that form [30].

2) XRD Analysis

The XRD diffractogram determines a sample's crystallographic information, such as atom arrangement, crystal structure, lattice parameters, and orientation. XRD diffractograms of the MWCNT and GO catalyst are displayed in Fig. 1, and the d-spacing for the MWCNT and GO catalyst at crystallographic planes (002) and (100) are listed in Table 2. Two peaks of MWCNT are formed, which at 2θ are around 25° and 42° . From this pattern, it is determined that the change in the pattern of the MWCNT angle shifted to the left from a value of 25.498° to 22.644° in the GO angle pattern and similarly, from a value of 42.482° to 41.503° , which indicates a change in the material's crystallinity properties of MWCNT is reduced [31]. The introduction of various functional groups during the oxidation process of MWCNT results in a rise in the distance between the layers, which goes from 3.4905 for MWCNT to 3.9237 for GO. This is the cause of the increase in the distance between the layers [32]. The fact that the resulting GO diffractogram tends to spread points to the fact that GO has a more amorphous crystal structure. The widening of the d-spacing in GO can also be attributed to the incorporation of H_2O molecules and oxygen group molecules [31].

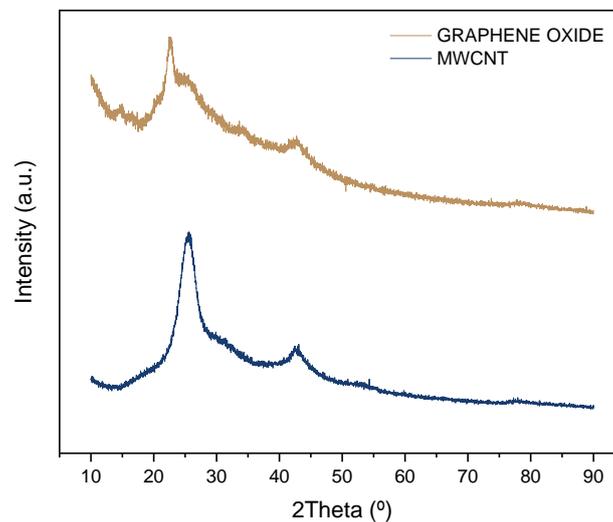


Fig. 1. XRD Patterns of MWCNT and GO Catalyst

Table 2. 2θ and d-spacing of MWCNT and GO Catalyst

Catalyst	(002)		(100)	
	2θ	d-spacing	2θ	d-spacing
MWCNT	25.498°	3.4905 Å	42.482°	2.1262 Å
GO	22.644°	3.9237 Å	41.503°	2.1741 Å

3) FTIR Analysis

FTIR spectroscopy can identify the functional groups present in a compound. Different chemical bonds and groups have characteristic absorption frequencies in the infrared region. The functional group GO and MWCNT were analyzed by FTIR spectroscopy in the transmittance mode over the wavenumber range $500\text{--}4000\text{ cm}^{-1}$ (Fig. 2). The GO shows the broad absorption band was obtained at $3500\text{--}3000\text{ cm}^{-1}$ corresponding to the stretching vibration of hydroxyl groups (-OH) which overlaps with C-H stretching vibrations. The band around 1700 cm^{-1} is assigned to C=O stretching vibrations of carbonyl/carboxylic groups attached to the cyclic ring, while the band around 1560 cm^{-1} is assigned to C=C of the aromatic compound. Epoxy group (C-O-C) stretching vibrations are found at 1030 cm^{-1} .

¹. These peaks do not appear in the spectrum of MWCNT, indicating that the oxidation steps have introduced strong oxygen-containing functional groups in GO.

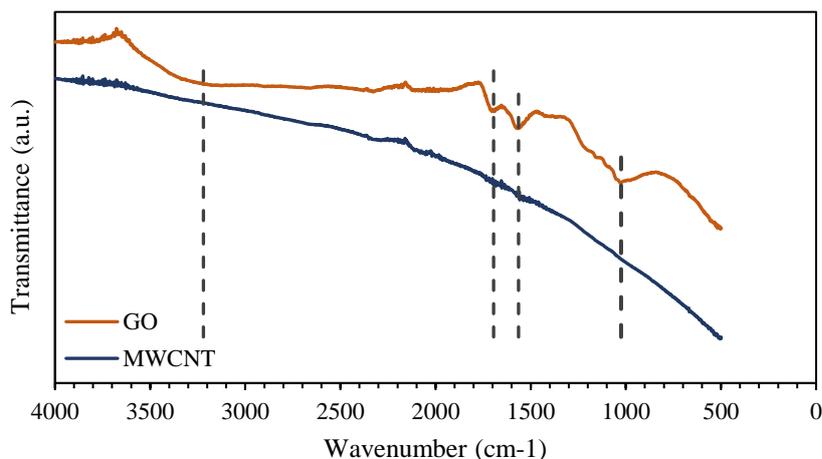


Fig. 2. FTIR Spectra of MWCNT and GO Catalyst

3.2. Glycerol Conversion and Acetone Selectivity

Iodometric titration was used to determine the amount of leftover glycerol after completing the conversion process. Indirect titration with iodine-iodide is beneficial for identifying chemicals with a higher oxidation potential than substances that are oxidizing agents. Titration with a sodium thiosulfate solution is performed by first reducing the sample with potassium iodide to create iodine [33]. The addition of chloroform serves as a solvent, while the addition of potassium iodide liberates iodine, as indicated by the yellow coloration of the sample. At this point, the subsequent reaction takes place:



Before titration with sodium thiosulfate, starch is added to the solution. At this stage, the following reactions take place [34]:



In iodometric titrations, starch is employed to identify the end point of the titration, which can be marked on the color change from blue to colorless. This color change can be seen as the iodine concentration reaching its maximum. The addition of a starch indicator solution just before the endpoint of the titration because the formation of iod-amylose, which has a complicated blue color and makes it difficult to titrate with sodium thiosulfate, can occur if a starch indicator solution is applied at the beginning of the titration. This can be avoided by adding the starch indicator solution just before the endpoint of the titration [35].

Fig. 3 depicts the determination of glycerol conversion as a function of time and the quantity of catalyst for glycerol conversion. The results indicated that the conversion of glycerol increased as the amount of catalyst in the reaction mixture increased. Similar trends were reported by other studies regarding the effect of catalyst mass on conversion [36]. In the first 10 minutes, the reaction proceeded with a very steep inclination; in the subsequent minutes, the reaction continued, though at a slower rate than in the first 10 minutes. The performance of the 3% catalyst mass was the lowest, while the performance of the 5% and 7% catalyst masses was nearly identical. This is because the mass of the catalyst is proportional to the quantity of available active phase. Increasing the mass of the catalyst increases the amount of active phase capable of facilitating the protonation of acetic acid. Still, excessive addition does not accelerate the rate of the reaction [37]. The addition of five percent by mass of the catalyst to the reaction mixture has provided an active phase sufficient to facilitate the reaction of glycerol and acetic acid, so the addition of seven percent does not significantly impact the reaction's conversion. The highest conversion was obtained at 7% catalyst mass with a conversion value of 92.08 percent, the lowest conversion was obtained at 3% catalyst mass with a conversion value of 59.88 percent, and 5% catalyst mass with a conversion value of 89.8 percent. While Costa et

al. reported that glycerol acetylation was conducted for 120 minutes at 120°C using H-ZSM-5 catalyst, the glycerol: acetic acid ratio was 1:3, and 5% catalyst mass yielded an 87% conversion [5].

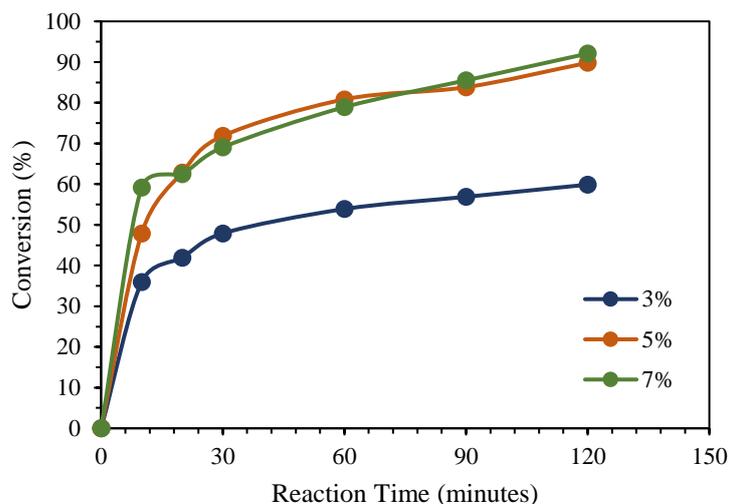


Fig. 3. Glycerol Conversion Over GO Catalyst by Varying Catalyst Mass and Reaction Time

GC-MS analyzed the end product of glycerol acetylation to determine the selectivity of acetin. In the context of acetin production, selectivity refers to the degree to which a specific product (monoacetin, diacetin, or triacetin) is selectively formed in the reaction process. Acetin refers to a group of esters derived from glycerol and acetic acid, including monoacetin (glycerol monoacetate), diacetin (glycerol diacetate), and triacetin (glycerol triacetate). The composition of acetin obtained with various catalyst masses is presented in Fig. 4.

The formation of monoacetin, diacetin, and triacetin from glycerol acetylation is an established fact. With a 3% catalyst mass, the resultant acetin has a monoacetin selectivity of 58.0%, a diacetin selectivity of 22.6%, and triacetin selectivity of 19.4%. A 5% catalyst mass yields 47.4% monoacetin, 29.4% diacetin, and 23.2% triacetin, while a 7% catalyst mass yields 70.2% monoacetin, 4.2% diacetin, and 25.6% triacetin. The findings of the experiments indicate that the catalyst mass influences the acetin's final composition. In contrast to mono- and diacetyl, the amount of triacetin in the reaction mixture increased as the catalyst mass increased from 5% to 7%. Since the conversion from diacetin to triacetin occurs more quickly than from monoacetin to diacetin, the yield of diacetin increases when the catalyst mass is decreased to 5% from 7%. Glycerol acetylation with a 3% catalyst mass, 120 minutes of reaction time, and 110 °C was reported by Khayoon et al. to produce 29.2% monoacetin, 30.5% diacetin, and 40.3% triacetin [38].

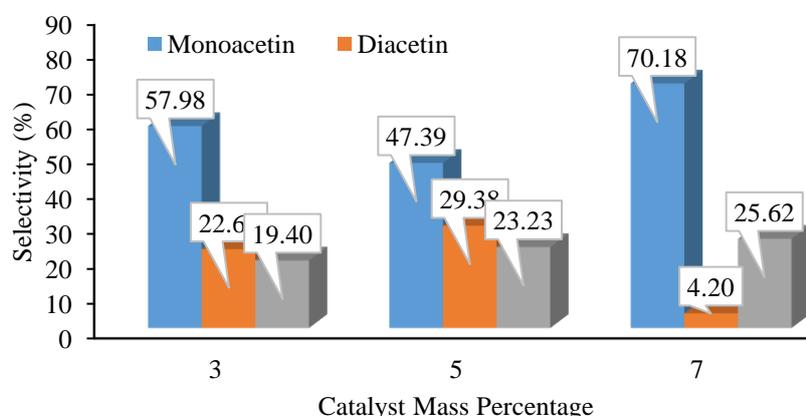


Fig. 4. Acetin Selectivity by Varying Catalyst Mass

4. Conclusion

A graphene oxide catalyst has been prepared and tested for its physical properties and activity on glycerol acetylation. The XRD diffractograms identified the MWCNT angle pattern changing to the left, going from 2θ of 25.498° to 22.644° in the GO angle pattern; the GO angle pattern also changed from 2θ of 42.482° to 41.503° , and the distance between layers increased from 3.4905 in the MWCNT to 3.9237 in the GO. The GO catalyst had a surface area of $8.1829 \text{ m}^2/\text{g}$. The FTIR analysis also revealed the presence of a number of functional groups in the GO catalyst, including C=O, C=C, C-O-C, O-H, and C-H, identifying successful oxidation of MWCNT. The conversion and selectivity of a reaction are influenced by the amount of catalyst present in the reaction mixture. The efficiency of acetylated glycerol conversion is improved by increasing the catalyst's mass. With a 7% catalyst mass, the highest glycerol conversion (92.08%) was achieved. At the same time, mono-, di-, and triacetin selectivity were 70.2%, 4.2%, and 25.6%, respectively.

Acknowledgement

The authors appreciate the financial support received from the Universitas Muhammadiyah Surakarta for providing the *RKD Akselerasi* grant (No. 145.6/A.3-III/LRI/VII/2022).

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