Jurnal Akta Kimia Indonesia

INDONESIA CHIMICA ACTA

PAPER

View Article Online

View Journal View Issue

Cite this: *Indo. Chim. Acta.*, 2021, **14**, 1.

Esterification Reaction of Glycerol to The Derivatives Catalyzed by Amberlyst 36

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Received Date:
2nd February 2021
Accepted Date:
27th June 2021

Keywords:
acetic acid;
amberlyst 36;
esterification reaction;
glycerol;
triacetin.

DOI: http://dx.doi.org/
10.20956/ica.v14i1.12837.

Abstract. Several studies reported the use of acid catalysts of esterification of glycerol to acetin derivatives and amberlysts are no exception. However, among these strong sulfuric acid catalysts, amberlyst 36 is still rarely used and hence challenging to investigate. This study aimed to determine the yield and the selectivity of the esterification reaction of glycerol into acetine derivatives using a 5% of solid catalyst amberlyst 36 at a temperature of 90°C in a reflux system. The conversion value resulting from the reaction was 80.74%, with a selectivity value of 6.8% for triacetin. FTIR and GC-MS data support the monoacetin and triacetin structures. The findings indicate that the simple method and easily obtained catalyst can produce a high yield of acetin derivatives. This method is still possibly optimized to perform maximum yield with high selectivity.

Introduction

Biodiesel production globally increases continuously, with expected production volume reaching 41. 4 billion liters in 2025 (OECD/FAO, 2016). This high-volume projected production will produce an abundance of glycerol by-products. Glycerol can be converted into derivative products, such as ester derivatives that are more economically valuable (Kong, Aroua, & Daud, 2016). These ester derivatives from glycerol are widely used in the pharmaceutical, food, and polymer industry (Barauskas, Misiunas, Gunnarsson, Tiberg, & Johnsson, 2006; Macierzanka & Szeląg, 2004; Zhang et al., 2017).

Conversion of glycerol to ester derivatives by esterification reactions are generally acid-catalyzed (Handayani, Marsudi, Nasikin, & Sudibandriyo, 2006; Kong, Aroua, & Wan Daud, 2015; Mostafa, Maher, & Abdelmoez, 2013). Some of the homogeneous acids that are commonly used include sulfuric acid and p-toluene sulfonic acid, which are corrosive. Therefore, the use of solid catalysts is recommended, such as amberlyst ion exchange resin. Besides being non-corrosive, amberlyst resin is also easily regenerated and separated from the reaction product.

Several studies reported the use of amberlyst, such as amberlyst 35 and 15 that resulted in conversion values of 7.5% and 10% at 120 °C and 90 °C (Klepáčová, Mravec, Kaszonyi, & Bajus, 2007). Besides, 80% of the yield was obtained from the esterification of glycerol catalyzed by Aquivinon and amberlyst 15 (Kong et al., 2015)

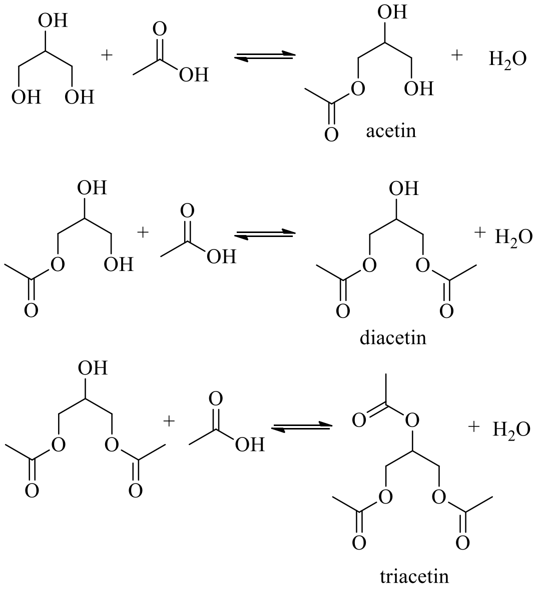

Figure1. Esterificattion reaction of glycerol to acetin products.

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Amberlyst 36 performed higher result in converting palmitic acid and oleic acid's to acetine products, namely; 91% and 86%. However, the reaction run for 8 hours and reached the maximum yield in quite high temperature, 120°C (de Aguiar et al., 2017). Amberlyst 36 performed optimal catalysis of glycerol at a temperature of 80 °C with a ratio of acetic acid to glycerol of 1: 3. By these conditions, the exergetic efficiency reached a value of 25,38% (Aghbashlo, Tabatabaei, Rastegari, & Ghaziaskar, 2018). Other methods include the use of microwave radiation (Rajabi & Saidi, 2005) and catalysis of the complex Salen cobalt (II) complex with SiO2 (Rajabi, 2009). The conversion rate for both methods reached 99-100%.

The conversion value resulting from amberlyst catalysis was found to be below the performance of other solid catalysts. However, it is still widely used because it is more available and economical than other solid acid catalysts. This study aims to determine the conversion value and selectivity of glycerol's esterification reaction to acetine derivative products through the amberlyst 36 catalyst.

Experimental

Materials and Method

Materials used in this study consisted of glycerol, amberlyst resin, acetic acid, and talc were purchased from Merck.

Glycerol Purification Materials and Process

Glycerol was purified by mixing it with talc 1% (w/w). The mixture was stirred for 30 minutes and then filtered by using filter paper.

Synthesis of Esther Derivatives

Pure glycerol was then reacted with acetic acid at the ratio of 1: 7 mol equivalent in a three-neck flask. A 5% of amberlyst 36 by weight of glycerol was added to the mixture as a catalyst. The mixture was then refluxed for 4 hours at 90oC. After the reaction was ended, the product mixture was then filtered using filter paper. Water was removed by heating to 105^{o}C. The conversion value of glycerol to acetine was calculated from the percentage by weight of acetine with glycerol. GCMS and FTIR analysis were performed using GC-MS Agilent GC Tipe 7890 A MS Tipe 5975 and FTIR Prestige-21 Shimadzu.

Result and Discussion

Characterization of Glycerol

The glycerol raw material was first purified using talc to remove residual impurities. The impurities commonly found in crude glycerol were free fatty acids in the form of soap and inorganic salts (Yong, Ooi, Dzulkefly, Wan Yunus, & Hazimah, 2001) . The characteristics of glycerol before and after purification can be seen in Table 1.

Table 1. Physical characteristic comparison between crude glycerol, purified glycerol and pure glycerol.

Physical Characteristics	Glycerol before Purification	Glycerol after Purification	Pure Glycerol (Miner & Dalton, 1953)
Density (g/ml)	1.19	1.2	1.26
Viscosity (cP)	159.81	166.51	350
Color	Clear	Clear	Clear

The density of glycerol before and after purification did not change significantly. This value was slightly below the density value of pure glycerol, which was 1.261 g/cm3. The glycerol viscosity value was also below the pure viscosity value, which was 350 dyn.s/cm3. This value showed that the purity of the glycerol was between 70 and 85% (Miner & Dalton, 1953). This moderate level of purity will decrease the yield (Sari, Hambali, Suryani, & Permadi, 2017).

Glycerol Esterification

The glycerol esterification reaction was carried out with a ratio of glycerol and acetic acid reagent of 1: 7 at a temperature of 90 °C with a 5% amberlyst 36 catalyst. The yield obtained was 80.74%. This yield was higher than previous studies using sulfuric acid catalysts (Widayat, Roesyadi, & Rachimoellah, 2012), acetic acid (Nuryoto, Sulistyo, Sri Rahayu, & Sutijan, 2010), amberlyst 35 and 15, (Klepáčová, Mravec, Kaszonyi, & Bajus, 2007).

The esterification reaction was a selective reversible reaction (See Figure 1) Several factors that influence the esterification reaction yield include the glycerol purity, glycerol acetic acid molar ratio (Medina et al., 1999), catalyst concentration, temperature (Kong et al., 2015) and reaction time.

The glycerol purity used in this reaction was 70-85%. This impurity may cause a low glycerol conversion to triacetin (Martín, Ruiz, García, Feng, & Mateos, 2019). To cope with the use of a low level of glycerol purity, the mole ratio of glycerol to catalyst and reaction temperature can be optimized to obtain a high yield product (Mufrodi, Rochmadi, Sutijan, & Budiman, 2014).

When the reaction runs selectively, the glycerol esterification reaction's conversion rate is strongly influenced by the acid's active site (Kong et al., 2016). In this study, the acid is used as glacial acetic acid. One of the advantages of using acetic acid was that it was more widely available than other reagents such as acetic acid anhydride and vegetable oil-derived acids. However, the reaction with acetic acid requires a longer reaction time. In this procedure, reflux lasts for 4 hours. Therefore, a catalyst supporting the increase in yield is needed in the 4 hours reaction time.

The catalyst used was amberlyst 36. The effective conversion was obtained from the catalytic sites of the resin. It is also influenced by the hydrophobicity and catalyst pore volume. With a conversion value of 80.74, it can be said that the catalyst has worked significantly to reduce the activation energy so that the reactive intermediates can react to produce the acetin products. In 4 hours and 90°C, amberlyst 36 catalytic reactions work relatively more efficiently than the previous study (de Aguiar et al., 2017). It proves that the reaction time and temperature are also influential factors.

Triacetin Characteristics

Esterification product was a mixture of mono-, di- and triacetin, residual glycerol, residual catalyst, and water. The product obtained from the esterification process is then purified and tested for density, viscosity, and solubility values in water, ethanol, and acetone. A comparison of the characteristics of acetin products with standard triacetin can be seen in Table 2.

As shown in Table 2, the density and viscosity are slightly below the standard triacetin. The value indicates that the triacetin product has been formed. However, it was still mixed mainly with the monoacetin. Solubility in water, ethanol and acetone are quite similar.

Table 2. Characteristics comparison between the acetin product and standard triacetin (Lide, 2009).

Physical Characteristics	Triacetin Product	Standard Triacetin
Density (g/cm3)	1.143	1,155
Viscosity (cP)	19.72	23
Solubility in:		
Water	Slightly soluble	Slightly soluble*
96% of ethanol	Dissolved	Dissolved
Acetone	Dissolved	Dissolved

The reaction's selectivity to produce triacetin was influenced by the temperature of the reaction (Mufrodi et al., 2014). The higher the reaction temperature, the higher the triacetin selectivity is. Increasing the temperature also encourages the equilibrium of the reaction towards the formation of reactants. Thus, it is obvious that increasing the temperature and removing the product from the reactor will possibly increase the result.

Functional Group Identification

The esterification product was identified using an FTIR device to determine the esterification product mixture's functional groups. The identification results can be seen in Table 3.

Table 3. FTIR Spectrum Data of Esterification Product

Triacetin Products		Standard Triacetin (Marwan, et.al., 2019)		Stretch Vibration Type
Wavenumber (cm^{-1})	Intensity	Wavenumber (cm^{-1})	Intensity	
3434.14	*b*	3100-3400	*b*	-O-H
2956.25	*m*	2934	*m*	C-H (*sp*^{3})
1380.80	*m*	1388.07	*m*	C-H
1725.95	*s*	1702.42	*s*	C=O
1260.57 1048.55	*s*	1240.84 1039.90	*s*	C-O

The FTIR analysis results showed that there were similarities between the spectrum pattern of triacetin products with previous research (Marwan et al., 2019; Setyaningsih et al., 2019). The typical absorption at wavenumbers 1725 cm-1 and 1260.57-1048.55 cm-1 indicated a vibration of -C = O and -C-O bond strains. Despite its width, the absorption band of the –OH stretch intensity decreased, which proved a reduction in the hydroxyl group after converting glycerol to its ester derivatives, either in the form of mono-, di- or triacetin.

Antioxidant Activity of Edible Film

Further identification was conducted using chromatogram and fragmentation data from the GC-MS instrument. This data also serves to determine the selectivity of the reaction. Table 4. Data on the selectivity of the components resulting from the glycerol esterification reaction based on the broad spectrum area of the GC-MS.

Table 4. GC-MS Data of the Product of Glycerol Esterification

Peak No	Compound	RT	Area (%)	Similarity
2	Monoacetin	12,224	33,93	78
5	Monoacetin	12,655	3,29	83
10	Triacetin	13,183	6,87	90

The GC-MS data suggest that three peaks are close together. The peak with the highest RT value was confirmed to be triacetin with a level of 6.87%. The remainder was a monoacetin product that appeared in two peaks at a lower RT value. Triacetin appears higher because it is more nonpolar than monoacetin so that it will stay longer in the column.

The result showed a low selectivity of triacetin products against monoacetin, namely 6.9%, from 93.1%. Slightly higher results can be seen in previous studies. With the same catalyst, Amberlyst 36 glycerol was reacted with acetic acid for 25 hours resulting in conversion values and selectivity of mono-, di- and triacetin of 100%, 43%, 44%, and 13% (Rastegari, S. Ghaziaskar, & Yalpani, 2015). The finding suggests that the reaction, which lasts longer, results in higher triacetin selectivity but is not economically viable in production. The use of other catalysts such as the zirconia-silica mixture for 4 hours of reaction resulted in a glycerol conversion value of 80% with selectivity values of 94% for mono and diacetin, which is greater than triacetin (Kong et al., 2016). Broader results were shown by the use of catalysts with HZSM-a/ MCM-41 micro-pores with more optimal glycerol conversion values and triacetin selectivity of 100% and 91% (Liu et al., 2019). It showed that in addition to the general reaction conditions such as temperature, reaction time, catalyst and glycerol ratio, the catalyst and acid ratio and the pore size of the catalyst also significantly affect the conversion value and selectivity of the triacetin product.

Conclusion

Acetins were successfully synthesized from glycerol and acetic acid with glycerol and acetic acid at a 1: 7 ratio for 4 hours at 90ºC using 5% amberlyst 36 catalyst. The glycerol conversion value was 80.74%. Triacetin selectivity was 6.87%. This value is potentially increased through the optimization of reaction conditions that will be the focus of future research.

Conflict of Interest

Authors declare that there is no conflict of interest.

Acknowledgement

We would like to extend our sincere thanks to Rani Maharani for comments from the early drafts that greatly improved the final one. We also especially thank to Nuraini and Awaluddin Iwan Perdana for the tehcnical help and providing the FTIR and GCMS data.

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