

Synthesis, Characterization and Activity Test of Natural Zirconium Zeolite (Zr-ZA) Catalyst in The Esterification Reaction of Glycerol with Acetic Acid Anhydride

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Manuscript received: 26 September, 2022. Revision accepted: 05 October, 2022. Published: 17 October, 2022.

Abstract

Synthesis of Zr-ZA catalyst used as catalyst for esterification reaction of glycerol with acetic acid anhydrous has been done. Catalysts are characterized using an infrared spectrophotometer, X-ray diffraction, and measurement of surface acidity, while reaction products are characterized using a gas chromatography-mass spectrometer. Effect of catalyst acidity, reaction time and re-addition of acetic acid anhydrous studied by glycerol conversion and selectivity value of triacetin were yielded. Infra-red spectrophotometer and X-ray diffraction analysis of the catalyst showed that the synthesized catalyst was zirconium zeolite (Zr-ZA), while esterification analysis using a gas chromatography-mass spectrometer showed a triacetin product.

Keywords: Glycerol; Triacetin; Acetic Acid Anhydrous.

INTRODUCTION

For Muslims, the halal food is absolute, even if it contains only a trace of additives it would not be allowed. As a result, the production of halal-certified additives is critical, both in terms of sources and production processes; currently, many additives are obtained from non-halal sources and processes. For example, some Monoacetyl Glycerol (MAG), Diacetyl Glycerol (DAG), and Tri Acetyl Glycerol (TAG)/Triacetin are derived from the esterification of non-halal animal glycerol, such as pork (Gültekin, et al., 2020; Alzeer and Hadeed 2021).

Triacetin has many uses in both food and non-food applications. Triacetin can be used as an aroma ingredient in candy (confectionery), milk drinks, soft drinks, and chewing gum. As for non-food ingredients, triacetin can be used as a solvent in perfumes, printing inks, solvents for aromas, plasticizers for cellulose resins, polymers, co-polymers, and can even be used as a fuel additive to reduce knocking in car engines. In addition to Triacetyl Glycerol (TAG) and Triacetin, Monoacetyl Glycerol (MAG) and Diacetyl Glycerol (DAG) are formed during the esterification of glycerol with acetic acid (Nuryoto et al., 2010; Gama et al., 2019; yanti et al., 2019)

Glycerol derivatives such as monoacetyl glycerol (MAG), diacetyl glycerol (DAG), and triacetyl glycerol

(TAG)/triacetin can be used as alternative food additives (additives). Food additives are ingredients that are intentionally added to food to improve the appearance, texture, taste, and shelf life of the food. Food additives such as monoacetyl glycerol (MAG) and diacetyl glycerol (DAG) are used as thickening agents or emulsifiers. Meanwhile, Triacetyl Glycerol (TAG)/Triacetin is a solvent for other additives such as flavorings and dyes (Ogawa., et al.,1992; Fiume 2003; Jiang et al 2010)

Glycerol is a by-product of biodiesel from the transesterification process to obtain methyl esters. In 2010, it is estimated that glycerol production was around 1.2 million tons, of which more than half came from biodiesel production (Appleby, 2003).

As a by-product of the biodiesel industry, glycerol has not been processed much, so its selling value is still low. Therefore, it is necessary to process glycerol so that it can become a product with higher selling value and more benefits. One of them is by making glycerol derivatives through the esterification process. One of the glycerol esterification products is triacetin. (Ghoreishi., 2013; Setyaningsih et al., 2020; reddy, 2010)

The glycerol esterification reaction usually uses acetic acid. Silva et al. (2010) have conducted a study to compare the glycerol esterification reaction using acetic acid and anhydrous acetic acid. In the study described, under the same conditions, esterification of glycerol

using anhydrous acetic acid gave high selectivity to triacetin (100% at 80 minutes) compared to acetic acid (7% at 120 minutes).

Glycerol derivatives are made from the esterification process between glycerol and acetic acid with the help of a catalyst. In previous research using a homogeneous catalyst as done by Widayat et al. (2013), they used a sulfuric acid catalyst because it is superior in its hygroscopic properties, which can absorb water, for the esterification reaction goes towards the product. However, the use of homogeneous catalysts has disadvantage that the catalyst is difficult to separate from the product after the reaction because it is in one phase (Dewajani., et al., 2019)

The use of heterogeneous catalysts is an alternative in the glycerol esterification reaction. Zirconium is widely used in catalytic processes as a support and a promoter in catalysts (Tanabe and Yamaguchi., 1994; Teterycz et al., 2003). Zirconium is also an important metal because of the possibility of strong bond polarization between SiO₂ and Zr⁴⁺ (Beck et al., 1992). In addition, zirconium has a low surface area (usually 50 m² g⁻¹) (Nawrocki, J. et al., 1993).

For this reason, this research would focus on the synthesis of glycerol derivatives, namely triacetin, using heterogeneous zirconium catalysts immersed in natural zeolites. Then proceed with the optimization of reaction conditions and the analysis of halal results through food critical point tests.

METHODS

Natural Zirconium Zeolite Catalyst Synthesis

Zeolite pretreatment

The first stage was natural zeolite obtained from Klaten, Central Java, was pulverized to form a powder with a size of 100 mesh, then washed with distilled water and heated at a temperature of 120°C for 1 hour.

Activation of Natural Zeolite

80 grams of natural zeolite were soaked with 100 mL of 1% HF solution in a plastic container, then washed and dried in an oven for 1 hour at 120 °C. Then soaked again in 100 mL of HCl 2M for 30 minutes and washed again

with distilled water until the Cl ions disappear. Then dried again in the oven.

Making Natural Zirconium Zeolite Catalyst by the Impregnation Method

The natural zeolite obtained was impregnated with zirconium metal with concentrations of Zr 0%, 1%, 2%, 3%, 5% and immersed in ZrOCl₂·8H₂O solution while stirring with a magnetic stirrer, then washed with distilled water and calcined for 4 hours at 400°C.

Synthesis of Glycerol Derivatives

This step was carried out by heating glycerol and anhydrous acetic acid separately until it reaches 80 °C. Both are reacted in a three-neck flask after reaching 80 °C, and a zirconium zeolite catalyst was added. The combined solution was then heated to 115 °C and stirred with a magnetic stirrer at 1000 rpm for 4 hours.

DISCUSSION

Catalyst Characterization

Characterization using FT-IR

Characterization using FT-IR is shown in Figure 1. Infrared analysis was carried out to determine the active group in the zeolite solid. Hendayana (1994) stated that infrared spectroscopy is used to determine the structure, which is important information about the functional groups of a molecule. Infrared spectra analysis is grouped into 2 parts, namely wave numbers 4000–1250 cm⁻¹ and 1250-350 cm⁻¹. Observations with an infrared spectrophotometer showed specific peaks. Generally, there is no significant difference in absorption in the infrared spectrum of activated natural zeolite (ZA) and zirconium-impregnated natural zeolite (ZA-Zr). In the spectrum, it can be seen that there are peaks at the same wave number, namely 3448.72 cm⁻¹ which indicates OH absorption. At absorption wave numbers 2360.87cm⁻¹ and 2368.59 cm⁻¹, it shows the stretching vibration of Si-OH. The absorption is sharply widening in the wavenumber region. Internal and external zeolites interwoven are shown at an absorption of about 1000 – 1250 (cm⁻¹)

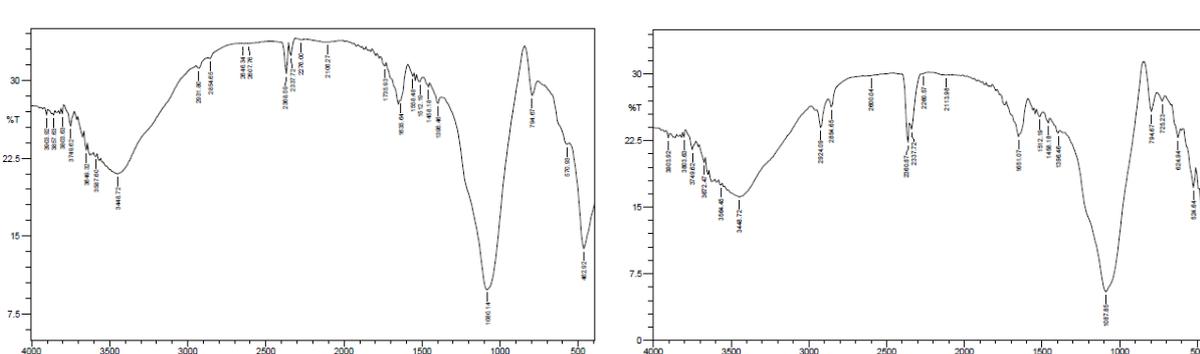


Figure 1. Infrared spectrophotometer results of activated natural zeolite (ZA) and zirconium-impregnated natural zeolite (ZA-Zr).

which indicates the presence of O-Si-O and O-Al-O asymmetric stretching vibrations of the alumina silicate framework. The absorption area 770-803 (cm^{-1}) is the fingerprint region of the zeolite, which shows the presence of O-Si-O and O-Al-O vibrations. The spectra show the absorption of O-Si-O and O-Al-O asymmetric stretching vibrations in the 1087.85 cm^{-1} and 1080.14 cm^{-1} regions and the O-Si-O and O-Al-O symmetric stretching vibrations in the 794 regions. 67 cm^{-1} . The Si-O and Al-O buckling vibrational regions are shown in the absorption regions of 447.49 cm^{-1} and 462.92 cm^{-1}

In the wave number table of 1660 cm^{-1} to 1620 cm^{-1} , there is a reduction in intensity from 1651.07 cm^{-1} to 1635.64 cm^{-1} which indicates that there is a release of

water molecules bound to the zeolite physically. The loss of absorption proves that the zeolite is cleaner than impurities, so the pores are getting bigger. The increase in intensity at wave numbers 500 cm^{-1} - 420 cm^{-1} indicates that there are more silanol groups in the zeolite framework. This shows that there is a reduction in Al-O bonds in the zeolite framework when HCl is added. The width of the peak indicates the increasing number of silanol groups until the crystallinity decreases. where the Si-O bond is stronger than the Al-O bond, resulting in a higher wave number used to vibrate. This is also supported by the increase in intensity at wave numbers 2385 cm^{-1} - 2363 cm^{-1} which indicates the presence of more silanol groups in the zeolite framework.

Table 1. Zeolite FTIR Spectrum Interpretation.

Spectral Interval (cm^{-1})	Wave Number (cm^{-1})		Functional group interpretation	
	Natural Zeolite	Active Zeolite		Zeolite-Zr 5%
3620 - 3420		3448,72	3448,72	Stretching vibration -OH
2385 - 2363		2360,87	2368,59	Stretching vibration Si-OH
1660 - 1620		1651,07	1635,64	Bending vibration H ₂ O
1213 - 1000		1087,85	1080,14	Asymmetric stretching vibration O-Si-O and O-Al-O
803 - 770		794,67	794,67	Symmetric stretching vibration O-Si-O and O-Al-O
500 - 420		447,49	462,92	Bending vibration Si-O and Al-O

Characterization using XRD

The results of the crystallinity test using XRD can be seen in Figure 2. The crystallinity characterization of zeolite was carried out qualitatively using XRD. The X-ray diffractograms of the ZA/Zr-0 and ZA/Zr-5 samples provide information about the type of mineral and the degree of crystallinity of the structural components that make up the sample. The type of mineral that composes the sample is indicated by the area of peak appearance (2θ), while the level of crystallinity of the component structure is indicated by the high and low peak intensity. The mineral diffractogram from the XRD results is matched its 2θ value with JCPDS data (Joint Committee on Powder Diffraction Standards) so that the type of mineral in the sample will be known. The diffractogram of the zeolite test results using XRD can be seen in Figure 2. The diffractogram pattern of ZA/Zr-0 and ZA/Zr-5 in Figure 2 looks almost the same. There are certain peaks that experience a change in intensity and a shift in the value of 2θ . Changes in intensity there is an

increase and there is a decrease depending on the crystal structure, the position of atoms in the unit cell, and thermal vibrations. However, the crystal structure of ZA did not change much because it was stable when activated. It is as shown in the table.

Based on table 2 in the ZA/Zr-0 and ZA/Zr-5 diffractograms there are many peaks of interpretation of mordenite character zeolite, this proves that the ZA/Zr catalyst has been dealuminated after activation using 2M HCl. With the decrease in the composition of Al cations, the Si/Al ratio in natural zeolite changed from previously clinoptilolite with the molecular formula $[\text{Na}_{1.84}\text{K}_{1.76}\text{Mg}_{0.2}\text{Ca}_{1.24}(\text{H}_2\text{O})_{21.36}] [\text{Si}_{29.84}\text{Al}_{16.16}\text{O}_{72}]$ to mordenite with the molecular formula $\text{Na}_8(\text{H}_2\text{O})_{24} [\text{Si}_{40}\text{Al}_8\text{O}_{96}]$ here the Si/Al ratio increases. The results of the XRD diffractogram show that Zr metal has been successfully distributed in active natural zeolite, which is indicated by the presence of peaks at $2\theta = 22.09$ and at $2\theta = 35.55$.

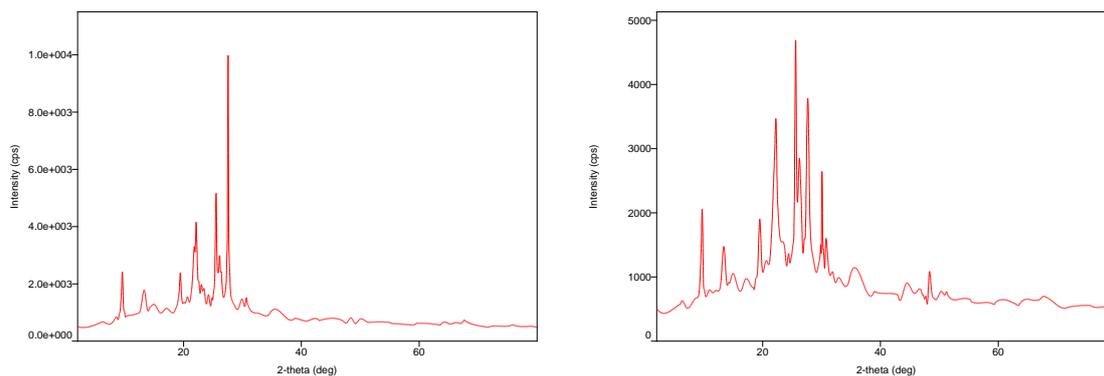


Figure 2. Diffractogram Data of activated natural zeolite (ZA) and zirconium-impregnated natural zeolite (ZA-Zr).

Table 2. Interpretation of diffraction peaks at ZA/Zr-0 and ZA/Zr-5.

2θ JCPDS	2θ ZA/Zr-0	Interpretation
9,77	9,78	Mordenite
13,41	13,39	Mordenite
19,58	19,58	Mordenite
21,24	22,238	Mordenite
25,62	25,603	Mordenite
26,25	26,25	Clinoptilolite
27,60	27,64	Clinoptilolite
30,068	30,069	Clinoptilolite
30,828	30,83	Mordenite
35,65	35,66	Mordenite
48,21	48,34	Mordenite
2θ JCPDS	2θ ZA/Zr-5	Interpretation
13,41	13,33	Mordenite
19,36	19,47	Clinoptilolite
21,79	21,84	Mordenite
22,05	22,09	Zr
25,56	25,51	Mordenite
26,10	26,13	Mordenite
27,54	27,54	Mordenite
35,53	35,55	Zr

Acidity Test for zirconium-impregnated natural zeolite (ZA-Zr) Catalyst

Zeolite acidity can be measured gravimetrically using the ammonia adsorption method. Zr metal impregnation treatment on zeolite is expected to increase the acidity of the zeolite. This increase in acidity is due to the exchange of the Zr⁴⁺ group with the H⁺ group found in the active zeolite.

Table 3. Catalyst Acidity.

Catalyst	Acidity (mmol/gram)
ZA/Zr-0	4,52
ZA/Zr-5	5,88
ZA/Zr-10	6,79

From the results of the ammonia adsorption analysis, it was found that the total acidity contained in the zeolite increased with the increase in the amount of Zr metal impregnation into the active zeolite (Table 3). This is due to the interaction between the NH₃ base and the acid in the zeolite. H⁺ is a bronsted acid, which will form NH₄⁺ ions when it interacts with NH₃. The presence of Zr metal is possible to cause an increase in the acidity of the catalyst because Zr metal has a (d) orbital that is not fully filled so it effectively accepts electron pairs from the adsorbate base. The contribution of the number of acid sites of Zr metal is a Lewis acid site (Comelli et al., 2006). The presence of a large number of active sites, increases the adsorption power of the reactants.

Analysis of Glycerol Acetylation Results

The product of glycerol esterification reaction with acetic acid anhydride using zirconium-impregnated natural zeolite (ZA-Zr) as catalyst was analyzed qualitatively using an infrared spectrophotometer. This analysis is intended to determine the presence of esters (triacetin or mono acetin and diacetin) in the esterification reaction product. The results of the infrared spectra can be seen in Figure 3.

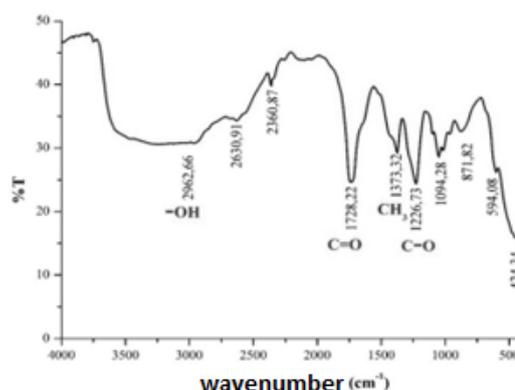


Figure 3. Infrared spectra of glycerol esterification reaction with acetic acid anhydride using zirconium-impregnated natural zeolite (ZA-Zr) as catalyst.

The infrared spectra show a strong absorption at a wave number of 1728.22 cm⁻¹, a strong absorption at a wave number of 1226.73 cm⁻¹, and a medium absorption at 1373.32 cm⁻¹, where the absorptions successively indicate the presence of vibrations from

groups C=O, C-O (from the ester), and CH₃. The presence of these three functional groups corresponds to the product resulting from the glycerol esterification reaction, which is in the form of an ester. with a reaction like Figure 4 (Silva et al., 2010).

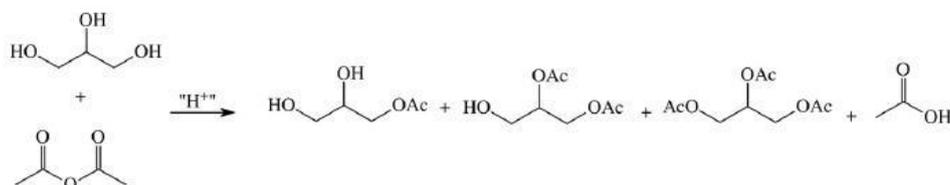


Figure 4. Reaction of glycerol esterification with acetic acid anhydride using acid catalyst and with the proposed reaction mechanism, namely:

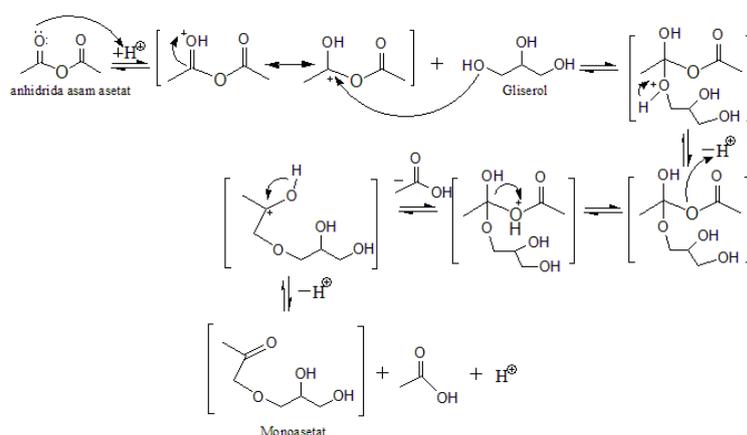


Figure 5 The mechanism of the esterification reaction for the formation of monoacetate/monoacetin.

The reaction mechanism in the figure continues until all the hydroxy groups in glycerol are replaced by acetate groups and triacetin is formed. For one triacetin compound, it takes three compounds of acetic acid or acetic acid anhydride to react with glycerol.

The spectrum of the hydroxy group (–OH) also appears in the infrared spectra of the product, which is in the form of a wide absorption at wave numbers of

2962.66 cm⁻¹ to 3600 cm⁻¹, which indicates the presence of vibrations from the hydroxy group (O-H) (Sastrohamidjojo, 2007). The hydroxy group can come from acetic acid as a by-product, or from glycerol and (excess) acetic acid anhydride that have not reacted. The results of the complete interpretation of infrared spectra data are presented in Table 4 below:

Table 4. Interpretation results of infrared spectral data of glycerol esterification products.

Wavenumber (cm ⁻¹)		Functional group
Research result	Reference spectra (Sastrohamidjojo, 2007)	
1728,22 (strong absorption)	1600-1820 (strong absorption)	C=O
1226,73 (strong absorption)	1000-1300 (strong absorption)	C-O (of ester)
1373,32 (medium absorption)	±1375 (medium absorption)	-CH ₃
2962,66-3600 (widen)	2400-3400 (widen)	-OH

From the FT-IR data, it can be seen that glycerol has undergone an esterification reaction and has been converted into an ester, namely monoacetin, diacetin, and triacetin. The FT-IR test performed on the product was not sufficient to detect the presence of triacetin. Therefore, it is necessary to carry out further tests using

a gas chromatography instrument (Gas Chromatography/GC) which is connected to a mass spectrometer (Mass Spectrometer/MS). With this instrument triacetate compounds can be identified and the percentage can be calculated in the resulting product. The results of the analysis with GC-MS in the form of

two data, namely the chromatogram derived from the results of the GC analysis and the mass spectra from the results of the MS analysis. Chromatogram analysis was based on the level of similarity or Similarity Index (SI) between the retention time (tR) obtained and the

retention time (tR) from the library search report (Wiley7Nist05.L). The chromatogram results of the esterification reaction products are presented in Figure 6.

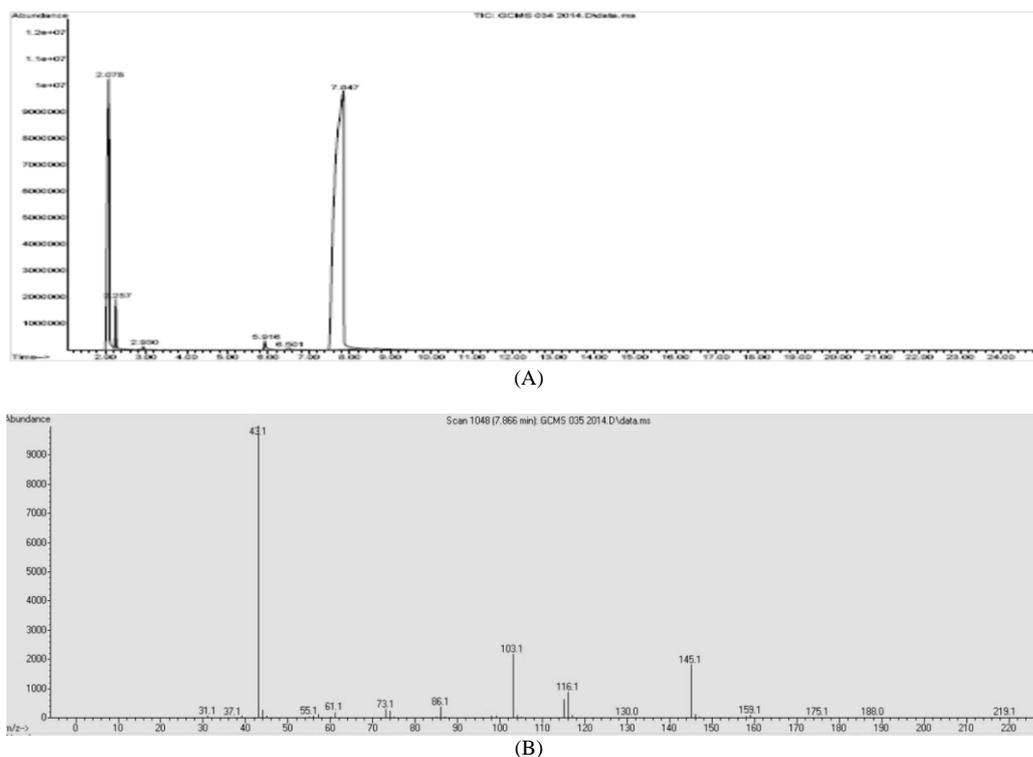


Figure 6. Chromatogram of esterification reaction products (A), mass spectrometry triacetin spectra (B).

In the chromatogram, the triacetin peak is located at the retention time (tR) 7.863 minutes, according to the library search report (Wiley7Nist05.L) on GC. The complete chromatogram analysis is presented in Table 4.

Table 5. Results of chromatogram analysis and results of glycerol esterification reactions.

No	Retention time (minutes)	Compound	SI (%) (Wiley7Nist05.L)
1	2,075	Acetic Acid	91
2	2,930	Acetic Acid anhydride	64
3	6,527	diacetin	83
4	7,863	Triacetin	90

The results of the chromatogram regarding the presence of Triacerin can be seen in (Figure 8 (A)), while the mass spectrometer data can be seen in (Figure 8 (B)). From these data we can know the relative

molecular mass of a compound and the fragmentation of the compound. The mass spectrometer data of the triacetin compound present at the retention time of 7.866 is presented in Figure 7. The figure shows that the molecular mass/charge (m/e) of the compound is 219.1 m/e. (Widayat et al, 2013).

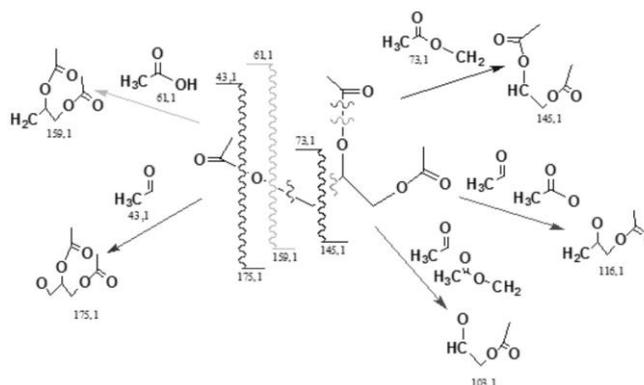


Figure 7. Fragmentation of Triacetin.

CONCLUSION

Zirconium-impregnated natural zeolite (ZA-Zr) catalyst has been successfully synthesized were indicated by diffractogram of X ray diffraction analysis. Zr metal impregnation treatment on zeolite was increase the acidity of the zeolite into 6,79 mmol/gram for ZA/Zr-10 catalyst. The results of the analysis of the esterification product base on Infrared spectra and mass spectrometry chromatogram showed the presence of triacetin products.

Acknowledgments: LPPM UIN Sunan Kalijaga for funding assistance for this research in the 2017 beginner research program.

Competing Interests: There was no conflict of interest in this study.

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