Esterification of Acetin Production from By-Products of Biodiesel Industry Using Heterogeneous Catalysts Based on Wetland Commodities

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ABSTRACT

The peculiarities of wetland commodities are unique and can produce new materials which function as catalysts. The objective was to determine the best catalyst components, crystalline properties, pore size, catalyst morphology, and selectivity in producing acetin. The research started with sampling, sorting, purification, extraction, catalyst synthesis, characterization, and determining the molar ratio between glycerol sourced from biodiesel industry by-products and CH_3COOH. Determination of catalyst components by XRF spectrometry, crystallinity by XRD, pore size by Brunauer-Emmett-Teller, and morphology of the resulting catalyst used SEM/EDS. Selectivity of the target compound in the form of acetin, either monoacetin, diacetin, or triacetin, used GC-MS. The catalyst of orange peels obtained silica 29.201% and alumina 4.115%, pineapple leaves obtained silica 34.072% and alumina 0.074%, and sugar palm peels obtained silica 40.017% and alumina 0.953%. The diffractogram results showed that all heterogeneous catalysts had sharp-narrow peaks, meaning the crystallinity of the sample was high according to the typical peak of SiO_2. The pore size of the orange peel catalyst was 4.328 nm with a surface area of 263.475 $m^2\,g^{-1}$, the pineapple leaf catalyst was 4.850 nm and 35.983 $m^2\,g^{-1}$, and the sugar palm peel catalyst was 5.658 nm and 10.884 $m^2\,g^{-1}$. The results of the morphological test of orange peels were composed of a very heterogeneous dense porous structure; pineapple leaves were amorphous, while sugar palm peels were composed of small, irregular pores. All the

resulting heterogeneous catalysts met the characteristics of standard SiO_2 silica catalysts. The best acetin selectivity result is a 1:9 molar ratio.

Keywords: Acetin, biodiesel, catalyst, esterification, selectivity

INTRODUCTION

Most of the processes done by developing countries in manufacturing industry activities involve homogeneous and heterogeneous catalysts, reaching 80% (Hermann et al., 2016; Bravo-Suárez et al., 2013). Along with technology and innovation development to reduce environmental degradation, agricultural biomass sources have potential as new basic materials for heterogeneous catalysts in replacing commercial catalysts to meet industrial needs, including biodiesel, biogas, bioethanol, and biosorbents to remove heavy metals in water (Heryani & Yanti, 2020). In recent years, agricultural waste has been considered and has proven to be an excellent source of solid catalysts and catalyst supports (Sharma et al., 2012; Sadh et al., 2018; Khan et al., 2021). Sources of biomass come from the agro-industry, which is categorized into two types, namely agricultural waste and industrial waste. Agricultural waste as field residue is in the form of the waste left in the field, such as stems, leaf stems, and seed pods. Process waste after harvesting is residue up to the point where the crop is converted into another valuable resource. These remains consist of leaf straw, stems, husks, bagasse, the bark of stem shells, and roots. Meanwhile, industrial waste can be generated from food processing plants, such as potato chips, juice, candy, and fruit industries, producing large organic residue every year (Sadh et al., 2018).

Agricultural waste material has been identified to contain high levels of potassium produced as a by-product of the combustion of agricultural biomass waste. It is a potential source of alkali, which can be used as an alternative to inorganic alkalis such as KOH and NaOH. Research shows that the high catalytic potential of this waste ash can be attributed to the high content of metal oxides, especially potassium and other metals such as calcium, sodium, and magnesium, which are important sources of alkali production (Betiku & Ajala, 2014; Abdullah et al., 2017b; Etim et al., 2020). Potassium derived from agricultural waste is chemically pure and poses no threat to its development and use (Khan et al., 2021). However, millions of tons of this waste biomass are found in various world regions. Therefore, proper waste management is needed for optimal utilization, especially in reducing environmental pollution and will reduce pollution. Various sources of agricultural waste which have been studied are plantain peels (Betiku & Ajala, 2014; Onoji et al., 2016), banana peels (Betiku et al., 2016; Gohain et al., 2017), orange peels (Lathiya et al., 2018), cocoa pod husks (Syamsiro et al., 2012; Betiku et al., 2017; Campos-Vega et al., 2018; Ofori-Boateng & Lee, 2013), coconut shell (Endut et al., 2017), rubber seed shell (Onoji et al., 2016), oil palm trunk (Zulkefli et al., 2017) and rice husk (Chen et al., 2015).

Agricultural waste has not been used, especially in rural areas, due to the lack of knowledge and technology (Marshall & Farahbakhsh, 2013). The utilization of pineapple, sugar palm, and orange plants so far has only been limited to fruit, while the leaves or peels of each plant have not been widely used. According to the Food and Agriculture Organization, citrus production, which dominates the global fruit market, reaches 68 million tons, with orange peel waste accounting for 44% of the weight of citrus fruits (Widmer et al., 2010). Then the pineapple, whose leaves are only removed by burning or left to rot (Yusof et al., 2015). Waste from pineapple plants is rich in lignocellulosic materials, especially the pineapple leaves. Many studies show that pineapple leaves are rich in insoluble fiber-rich fractions, wherein cellulose generally accounts for 20%–25% of dry weight (Huang et al., 2011). Similarly, pineapple leaf fiber has a high content of lignin and cellulose, most of which are in the crystalline structure and hemicellulose (6%-19%). The remainder consists of lignin (4%–15%), wax (4%), and ash (1%–5%) (Huang et al., 2011; Hemalatha & Anbuselvi, 2013). Meanwhile, orange waste has 2.34% ash content, 42.7% carbon, 6.4% hydrogen, 1% nitrogen, and 47.6% oxygen. Furthermore, the pectin content is 35.3%, hemicellulose is 16.6%, cellulose is 17.1%, and the remaining 28.7% is lignin, protein and dissolved sugars, and some fats (Alvarez et al., 2018). The chemical composition of sugar palm peels is fiber consisting of 43.88% cellulose, 33.24% lignin, 7.24% hemicellulose, 51.12% holocellulose, 1.01% ash, and 8.36% moisture content (Ilyas et al., 2019). The three commodities above have biomass waste which can be processed to produce new or smart materials, apart from the fact that their availability is continuous and does not depend on the season.

In South Kalimantan, the well-known waste of pineapple leaves is from the Tamban Pineapple Varieties, sugar palms growing well on land near swamps, have sap, sugar palm fruit, and sugar palm peels which can be used as new materials. Marabahan Oranges or Madang Oranges, also known in Malaysia and Saudi Arabia, compete with Bali Oranges for their sweet taste. Remnants are fully utilized before they are converted into other valuable resources. One of them is unconventional catalysts as a viable alternative to chemical catalysts, and it has received considerable attention because it comes from biogenic/ biomass waste sources. It is renewable, non-toxic, biodegradable, easy and safe to develop, non-corrosive, does not produce used water, is abundantly available and can be recovered and reused (Güleç et al., 2019; Chakraborty et al., 2016). Heterogeneous catalysts derived from biomass materials (sugarcane bagasse, wood ash, *Lemna perpusilla Torrey*, palm kernel shell, banana peduncle, Enterolobium cyclocarpum pod husk, kola nut pod husk, and tucuma peels) is effective and very efficient in biodiesel production. Transesterification can catalyze oil with a high Free Fatty Acid (FFA) content of up to 3% or more and can operate under mild conditions with a short residence time. The final product is pure and does not cause any difficulties during the separation and purification process. There has

been a great increase in the discovery of new biomass materials with effective catalytic power, but most of them have not been studied. It is, therefore, necessary to develop a database of biomass waste materials with the effective catalytic potential to exploit waste biomass sources for the development of heterogeneous catalysis for biodiesel synthesis (Sharma et al., 2012; Chouhan & Sarma, 2013; Abdullah et al., 2017a; Balajii & Niju, 2019; Falowo et al., 2019; Betiku et al., 2019; Mendonça et al., 2019; Etim et al., 2020).

Biodiesel is a potential option among existing biofuel production technologies. It has renewable nature, low toxicity, and environmental impact if it is compared to petroleum-based diesel (Daud et al., 2015). The biodiesel process is a production to process Refined Bleached Deodorized Palm Oil (RBDPO) into Fatty Acid Methyl Ester (biodiesel). There are several benefits of biodiesel for the environment, such as reducing CO_2 emissions, particulates, and unburned hydrocarbons. These benefits make it promising (Mahmudul et al., 2017). However, industrial developments, especially in South Kalimantan, have generated waste of fatty matter and crude glycerol, which amounts to 10% of the daily biodiesel production capacity of 1100 metric tons (mt).

Crude glycerol is a by-product of the biodiesel industry, which has begun to develop in research in recent years. It is triggered by the development of the search for alternative energy to meet energy needs in the future. The increasing target for biodiesel production from year to year will also increase the crude glycerol produced as a by-product (Monteiro et al., 2018; Chong et al., 2020). The source of glycerol comes from crude glycerol from the biodiesel industry waste, which is previously purified. Crude glycerol can be used as a starting material to produce valuable products such as mono, di and triacylglycerols and through the esterification process.

It is estimated that in 2027 the annual production of crude glycerol globally will reach 3.9 billion liters (Ciriminna et al., 2014; Ardi et al., 2015). One solution for converting glycerol into acetin derivative products is the esterification of glycerol with acetic acid using a catalyst to obtain monoacetin, diacetin, and triacetin (Rastegari & Ghaziaskar, 2015; Oliverio et al., 2016; Nda-Umar et al., 2019). The group of acetin compounds such as monoacetin (MAG), diacetin (DAG), and triacetin (TAG) are compounds that are widely needed in the industry. Monoacetin and diacetin have applications in the food industry, cryogenics for biodegradable polymers, and solvents (Kale et al., 2015; Gorji & Ghaziaskar, 2016). In addition, diacetin and triacetin can act as additives in various fuels to reduce engine knocking, namely the ability to increase engine performance, octane rating, and are used as an additive for biodiesel (Malaika & Kozłowski, 2019; Herrada-Vidales et al., 2020; Tasuna et al., 2021).

Several researchers have carried out the use of solid catalysts in the production of acetin due to the ease in the product purification process, including ion exchange resins (Dosuna-Rodríguez & Gaigneaux, 2012; Mufrodi et al., 2018; Caballero et al., 2019), heteropoly acids, HPAs (Ferreira et al., 2011; de Abreu Dessimoni et al., 2018), clays

(Dill et al., 2019; Yanti et al., 2019). The target is to reduce the import of chemicals, especially new materials such as catalysts, by replacing the source of materials based on wetland biomass which is very potential in South Kalimantan. From an eco-friendly point of view, functionalized clay and activated carbon (Sulphonated Hydrothermal Carbon (SHTC)) have been used in glycerol acetylation reactions to synthesize glycerol esters (mono, di, and triacetin) (Ferreira et al., 2011; Khayoon & Hameed, 2011; de la Calle et al., 2015). Studies that have been conducted (Ferreira et al., 2011; Khayoon & Hameed, 2011) using carboxylic acid reported that sulfonated carbon obtained by mild hydrothermal carbonization of D-glucose achieved a combined selectivity of DAG of 74% and TAG of 64% at 120°C with a reaction time of 3 hours.

Optimizing the by-product and waste industry must become industrial supporting materials and pioneering materials for future hopes (Kemenristekdikti RIRN 2017-2045, 2017). Therefore, the opportunity to be upgraded into applied research with Micro and Small Enterprises and then into development research for commercialization in partnership with the industry has a very big opportunity. The study aims to obtain the best catalyst of the three types of wetland biomass by using catalyst characterization tests, including catalyst components using X-Ray Fluorescence spectrometry (XRF), crystallinity using X-ray Diffraction (XRD), pore size using Brunauer-Emmett-Teller (BET), and morphology of the resulting catalyst using Scanning Electron Microscopy- Energy Dispersive X-Ray (SEM-EDX). Furthermore, testing the performance of heterogeneous catalysts produced to produce acetin (monoacetin, diacetin, and triacetin) used glycerol as a by-product of the biodiesel industry purification.

MATERIALS AND METHODS

Materials

The raw material for biomass waste comes from sugar palm peels, Tamban pineapple leaves, and Madang orange peels located in wetlands or swamps. Furthermore, crude glycerol was a by-product of industrial biodiesel sourced from the palm oil agro-industry in Kotabaru Regency, South Kalimantan. The materials used include active carbon, CH_3COOH, H_2SO_4, NaOH, $NaIO_4$, KOH, $C_2H_6O_2$, C_2H_5OH, HCl, bromthymol blue (BTP), and phenolphthalein indicator, had a pre-analysis degree. Meanwhile, all heterogeneous catalysts were sourced from orange peels, pineapple leaves, and sugar palm peels.

Preparation of Catalyst Source Material

The stage of providing catalyst material began with taking it at the source and sorting it to ensure it was not mixed with other materials or biomass. Furthermore, washing, drying, and drying in the sun are done until the water content is 10% (Moni et al., 2016). Furthermore, the samples were mashed with a porcelain mortar and pestle and sieved using an 80 mesh

sieve. The refined sample was then put into the NaberthErm brand furnace from Germany for the calcination process. The furnace process was carried out for 4 hours at a temperature of 800°C at a heating rate of 15°C min^{-1} and below a nitrogen flow rate of 150 ml min^{-1} for an inert atmosphere. Furthermore, the charcoal was pulverized to 200 mesh by sifting using an ASTM sieve measuring 200 mesh until a uniform size was obtained (Ogungbenro et al., 2018; Yanti et al., 2019).

Synthesis of Wetland Biomass-Based Heterogeneous Catalyst

Sources of biomass that had gone through the preparation stage and calcined were extracted using 3M NaOH solution in a ratio of 1:4 (w/t) from the weight of the biomass used. It referred to previous research done by Heryani and Yanti (2020), which had produced silica (SiO_2) from the hydrolysis process with the addition of NaOH under alkaline conditions so that the concentration of NaOH set to 3M could dissolve silica in biomass and produced a gel-shaped solid. The leaching process was then carried out at 90°C for 12 hours, at a speed of 300 rpm, using a magnetic stirrer. Furthermore, the extracted filtrate and residue were separated with filter paper. The filtrate was then added with 1M HCl drop by drop until the pH reached neutral (pH 7), and a white precipitate was formed. The precipitate obtained was then washed with distilled water and baked in an oven at a temperature of 110°C for 6 hours for the drying process to form dry silica gel. The dry silica gel was then ground into powder. Its final calcination was carried out at 700°C for 3 hours to obtain a heterogeneous catalyst (silica) at a heating rate of 15°C min^{-1} and below a nitrogen flow rate of 150 ml min^{-1} for an inert atmosphere (Ogungbenro et al., 2018; Yanti et al., 2019).

Glycerol Crude Refining

The distillation process was carried out among by-products of glycerol from the biodiesel industry and added with distilled water in a ratio of 2: 3 (v/v). Furthermore, 5% (v/v) activated carbon was added after washing. The sample mixture and activated carbon were stirred for 30 minutes, then allowed to stand for 24 hours. After 24 hours, the sample was filtered using filter paper. Next, the sample was put into a rotary evaporator set at a vacuum pressure and a temperature of 60°C. To increase the purity of glycerol, the bottom product of the rotary evaporator was distilled for 4 hours. Then the physical properties were analyzed, including glycerol content, water content, ash content, and density or density (Tan et al., 2013; Domingos et al., 2019).

Characterization of Wetland Biomass-Based Heterogeneous Catalyst Synthesis

The characterization of the synthesis of heterogeneous biomass-based catalysts could be carried out using the X-Ray Fluorescence (XRF) method with the PANalytical Epsilon 3 apparatus, which was used to determine the composition of the elements in the sample.

The instrument was equipped with a Benchtop tube under a dispersive X-ray fluorescence spectrometer. Then, characterization using the X-Ray Diffraction (XRD) method was carried out with a Shimadzu XRD 7000 apparatus. The XRD pattern was measured at 30 mA and 40 kV under Cu-Kα radiation conditions at k = 1.54. The diffraction pattern was observed at an angle of 2θ from 10 to 90◦ with a step time of 0.5 s. The data obtained were then processed using match software (Match Copyright 2003–2016 Crystal Impact, Bonn, Germany-Phase Analysis Report) to find the peak intensity component. Furthermore, the Brunauer Emmett–Teller (BET) method was used to estimate the sample's surface area. Characterization was carried out using the ChemBET PULSAR Quantachrome apparatus using the Nitrogen adsorption-desorption method at 195.8°C (77.35 K). The samples were degassed at 300°C (573.15 K) for 5 hours under vacuum (6.58×10^{-5} 1Torr^1) before adsorption. Finally, to determine the surface structure (morphology) and catalyst components using Scanning Electron Microscopy-Energy Dispersive of X-ray Spectroscopy (SEM-EDX) with the Hitachi SEM S-4700 tool (Buchori et al., 2020; Yanti et al., 2019)

Production of Acetin Additive

There were three types of acetin produced in this research: monoacetin, diacetin, and triacetin. The production principle started from glycerol material derived from the crude glycerol biodiesel industry. First, glycerol with a certain volume was put into a three-neck flask, then heated to a temperature close to 100°C. Second, the acetic acid with a certain volume was heated to a temperature of 100°C in an Erlenmeyer. Third, the acetic acid was put into a three-neck flask, then heated to maintain the temperature while the magnetic stirrer continued to run; the stirring speed was constant at 600 rpm. Next, put the heterogeneous catalyst as much as 3% by weight of glycerol; the reaction process ran at a temperature of 115°C for 180 minutes. Finally, the solution resulting from acetic acid and glycerol reaction with a biomass-based silica catalyst was analyzed using Gas Chromatography-Mass Spectrometry (GC-MS) from the Shimadzu (GCMS QP2010 Plus). The column oven temperature is set to 100.0°C, with the split mode injection temperature of 250.00°C. The flow control mode linear velocity is set to 107.2 kPa pressure, the total flow of 433.8 mL min-1, column flow of 1.43 mL min-1, the linear velocity of 44.5 cm sec-1, purge flow of 3.0 mL min-1, a split ratio of 300.0 and injection volume of 1 microliter. The mixture of compounds containing glycerol, acetic acid, monoacetin, diacetin, and triacetin could be easily separated in gas chromatography so that GC identified all compounds.

RESULTS AND DISCUSSIONS

Characterization of Heterogeneous Catalyst Extract Yield

X-Ray Spectroscopy (XRF) showed that the highest Si element content was from sugar palm peels at 40.017%, followed by Si element content from pineapple leaves at 34.072%

and Si element content from orange peels at 29.201%. It showed that the calcination process at 700°C in the catalyst extract of SiO_2 sugar palm peel was able to remove dissolved impurities to increase the crystallinity of high-purity SiO_2. In addition, according to Ilyas et al. (2019), components contained in sugar palm peel, namely cellulose, lignin, hemicellulose, holocellulose, were a constituent of fiber in a plant. Furthermore, the highest Al content based on XRF results from orange peels was at 4.115%, followed by the content of Al elements from sugar palm peels at 0.953%, and the catalyst extract from pineapple leaves at 0.074%, as could be seen in Figure 1.
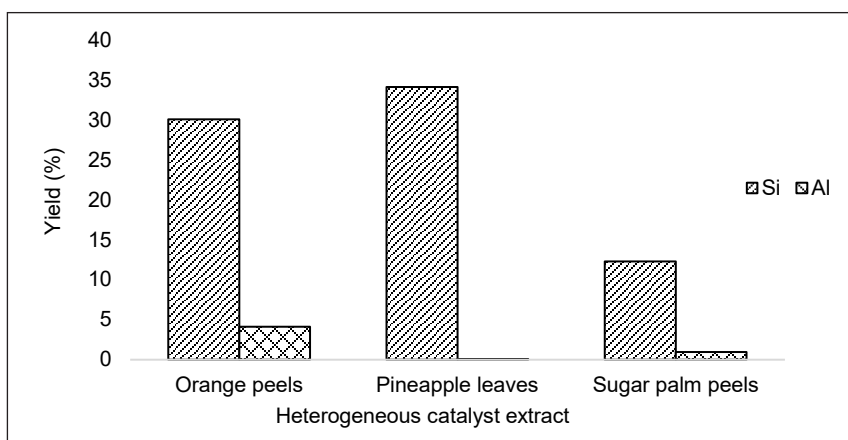

Figure 1. Yield of wetland biomass-based heterogeneous catalyst extract

From Figure 1, it could be seen that the silica produced from the extraction of wetland commodity sources contained Si elements having a high level of purity and was an element that made up SiO_2 in plants. The results of previous research showed that the content of Si elements from calcined pineapple leaves was 34.131%, orange peels were 30.102%, and sugar palm peels were 12.281% (Heryani & Yanti, 2020). NaOH concentration, leaching process, and temperature would affect the Si/Al content in silica sources obtained from wetland-based plants. The higher the Si/Al ratio, the lower the crystallinity was. It was known that citrus Si/AL is 7.10%., Pineapple Si/AL was 460.43%, sugar palm rind Si/AL was 41.99%, and the catalyst was amorphous when the Si/AL ratio was 75%. After adding acid, a clear glassy $[Si(OH)_4]$ hydrogel was formed in the gelling stage. It was then dried at 110°C to a constant weight. Drying was carried out to remove the water content in the sample by evaporating water from its surface, obtaining dry silica gel by removing the liquid present in the gel's pores, and obtaining a white silica powder.

Characterization of Wetland Biomass-Based Heterogeneous Catalyst Synthesis

The characterization using X-ray diffraction (XRD) determined the crystallinity of the heterogeneous catalyst synthesis material based on wetland biomass produced. The

material's crystallinity could be observed from the peak intensity generated on the diffractogram. The results of the X-ray diffraction pattern using a long angle of 2θ were between 10° and 90°. The hump formed from the X-ray diffraction pattern showed that all synthesis of heterogeneous catalysts based on wetland biomass was a combination of amorphous and crystalline. Peaks that were clearly visible, high, sharp, and had high intensity indicated an increasingly regular crystal arrangement so that it had a high level of crystallinity. Then, if the material had low regularity (amorphous), the peak intensity appearing on the diffractogram looked low, less clear, and wide.

The hump indicated that the amorphous structure was sloping and wide. In the synthesis of sugar palm peel catalyst extract, the highest amorphous structure was at 2θ at 10.17°, while the highest amorphous structure in the synthesis of orange peel catalyst extract was at 2θ at 10.27°, and the highest amorphous structure in the synthesis of pineapple leaf catalyst extract was at 2θ at 10.09°. It showed that when the sample was calcined at a temperature of 700°C with a holding time of 3 hours, a change began to occur, namely the appearance of crystal peaks. The amorphous structure had enough energy to transform into a crystalline structure, as shown in Figure 2. These broad peaks indicated that the heterogeneous catalyst synthesis material based on wetland biomass had a crystalline structure, meaning an orderly arrangement of particles.

From that Figure 2, it was obtained data in the form of distance among planes, intensity, and angle (2θ), which was then matched with data on the JCPDS (Joint Committee for Powder Diffraction) X-ray diffraction pattern. It was done so that the compounds contained in the sample could be identified, as presented in Table 1.
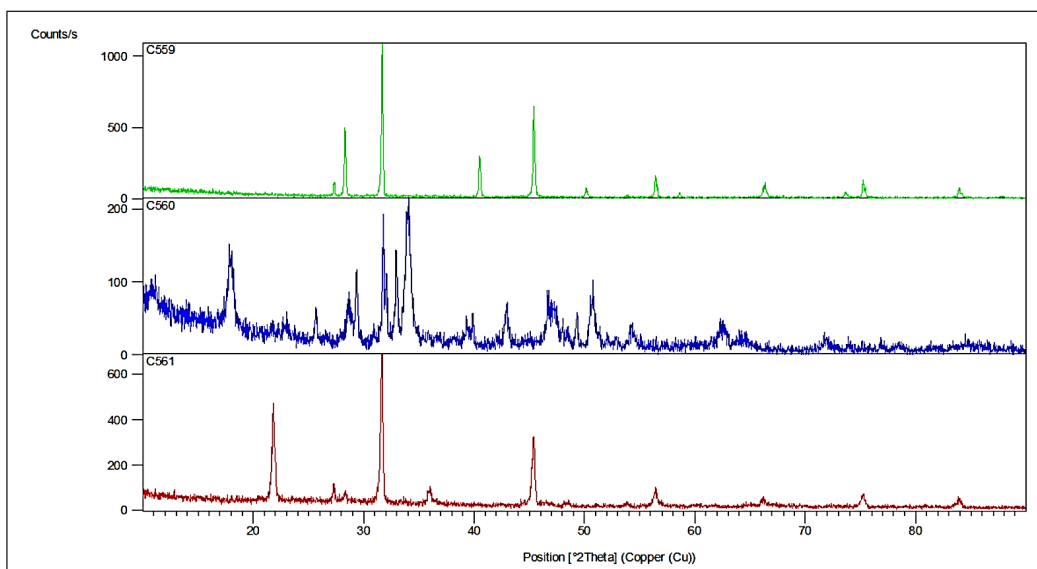

Figure 2. X-ray diffraction pattern of silica synthesized from wetland biomass-based heterogeneous catalyst extract

Table 1
Diffractogram peaks for the synthesis of wetland biomass-based heterogeneous catalysts

Silica Source	Peak of Difactogram			Information
	2θ	2θ	2θ	
SiO_2 standard	26,640°	45,793°	50,139°	JCPDS No. 46-1045
SiO_2 orange peel extract	25,664°	46,715°	50,727°	Research
SiO_2 pineapple leaf extract	27,302°	45,410°	53,861°	Research
SiO_2 sugar palm peel extract	28.331°	45.421°	50,183°	Research

From Table 1, the diffractogram showed that all the results of the wetland biomass-based synthesis of heterogeneous catalyst extracts identified the quartz SiO_2 form with a sharp peak typical of silicon oxide (SiO_2). Similar XRD resulted in the catalysts of orange peels and sugar palm peels because they had close Si/Al ratios. It was following the XRD standard for the structure of silicon oxide (SiO_2) JCPDS card No. 46-1045 in the ICDD database. The wetland biomass-based synthesis of silica catalyst extract, whose process ended with calcination at a temperature of 700°C, was able to form a fairly high intensity of the crystalline and reduce the amorphous form. The results of previous research conducted by Heryani and Yanti, 2020 were also following the XRD standard for the structure of silicon oxide (SiO_2) JCPDS card No. 46-1045 at 2θ in the range of 25.917°-45.660° at a temperature of 700°C that the product had a crystallinity which met the standard of silicon oxide (SiO_2).

Furthermore, the pore size measurement of the catalyst of the wetland biomass-based synthesis obtained from the adsorption isotherm describes the type of adsorption of the solid produced using the Brunauer Emmett Teller (BET) method. The pore size of the material was classified into three according to its range: the microporous (<2 nm), mesoporous (2–50 nm), and macropore (>50 nm) areas. The pore size of the catalyst of the synthesis of orange peel extract was 4.328 nm, that of pineapple leaf extract was 4.850 nm, and that of sugar palm peel extract was 5.658 nm. The organic matter content of large sugar palm peels reached 69.59%, with the calcination process reaching a temperature of 700°C, causing the loss of these components to open the previously closed pores due to the complex composition. It was higher than orange peels and pineapple leaves. It was in line with research (Trisunaryanti et al., 2018) which successfully synthesized mesoporous silica with a pore size diameter of 3.43 nm. It showed that the final leaching and calcination process at 700°C for 3 hours was able to open the pores of the catalyst surface so that water evaporation occurred on the porous catalyst surface. Pore size without calcination ranged from 0.04 nm to 0.05 nm. The reaction for the formation of biomass-based silica through the calcination process was as follows:

Compounds C, H, and Si + O_2 → CO_2 + H_2O +SiO_2
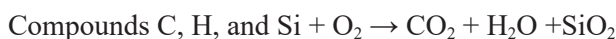
According to ALOthman (2012), this reaction produced silica in the form of a solid such as a gel. The gel-shaped solid was then heated to remove the water content on the silica surface and pulverized to obtain white silica powder. It was for various applications such as gas and liquid separation, optical coatings, protective films, membranes, and catalysis.

Furthermore, the Brunauer Emmett–Teller (BET) results showed that silica synthesized catalyst of orange peels had a surface area of 263.475 m^2 g^{-1}. This result was in line with research (Zhang et al., 2010), showing that SBET nano-silica catalyst synthesized surface area was 120 to 288 m^2 g^{-1}. The surface area of the catalyst of the synthesis of silica from sugar palm peels was 10.884 m^2 g^{-1}, and that from pineapple leaves was 35.983 m^2 g^{-1}. This result was in line with the silica catalyst research done by Putra et al. (2017), which had a surface area of 39.7 m^2 g^{-1}. Silica nanoparticles took an important role in scientific research due to their easy preparation methodology and wide use in various applications. The results of XRF analysis showed the presence of different ratios of Si and Al. The ratio of Si and Al on the orange peel catalyst of 7.10% gave a sharper and narrower XRD diffractogram meaning that the surface area of SiO_2 was much larger than the other two catalysts. This phenomenon meant that there was high sample crystallinity. It showed that the catalyst produced from biomass waste had the potential as a supporting catalyst in the production process.

The characterization of the synthesis of wetland biomass-based heterogeneous catalysts on orange peels, sugar palm, and pineapple leaves using *Scanning Electron Microscopy-Energy Dispersive X-Ray* to determine the morphology and elemental content can be seen in Figure 3.

Figure 3 shows the shape and size of the solids of the synthesis of wetland biomass-based heterogeneous catalysts at a magnification of 10000x. The morphology of the orange peel catalyst synthesis showed the presence of large lumps, but it had pores on the surface. The pineapple leaf catalyst synthesis results showed that the morphology of the solid surface filled with the pores was very dense, relatively small. The synthesis results of the
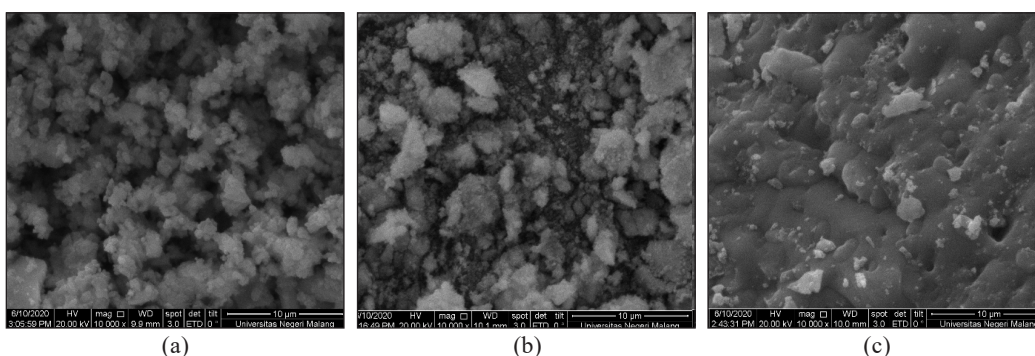

| (a) | (b) | (c) |

Figure 3. SEM morphology of catalyst solids of (a) orange peels, (b) pineapple leaves, and (c) sugar palm peels

sugar palm peel catalyst showed that the surface morphology of the solids was irregular, denser, and perforated on the surface. In addition, it showed that the silica particles were not evenly distributed; some formed small particles, and some formed uneven lumps. In line with the research results conducted (Heryani & Yanti, 2020), the SiO_2 catalyst of

orange peel extract was composed of a very heterogeneous dense porous structure. The SiO_2 catalyst of pineapple leaf extract was composed of round lumps, and the SiO_2 catalyst of sugar palm peel extract was composed of small pores orderly.

The solid morphological results of the catalyst using SEM supported the diffractogram data in the International Center for Diffraction Data database. The catalysts synthesized from extracts of orange peels, pineapple leaves, and sugar palm peels had peaks already representing the SiO_2 diffractogram with high crystallinity. In the SiO_2 catalyst of orange peel extract and the pineapple leaf extract, there was an increase in fiber crystallinity caused by the removal of non-cellulose fiber compounds (lignin and hemicellulose) by chemical treatment and calcination. The process caused the SiO_2 catalyst of sugar palm peel extract, pineapple leaf extract, and orange peel extract to crystallize more with open pores so that the surface area increased.

Then in the analysis of the Energy Dispersive X-Ray test, the results of the content contained in the wetland biomass-based catalyst solids in Figure 4 showed that the composition of the orange peel element was O by 28.86%, Na by 21.83%, Al by 05.46%, Cl of 40.66% and K of 11.19%. The elemental composition of pineapple leaves was 38.44% O, 17.46% Na, 10.97% Al, 17.50% Cl, and 15.62% Si. Meanwhile,
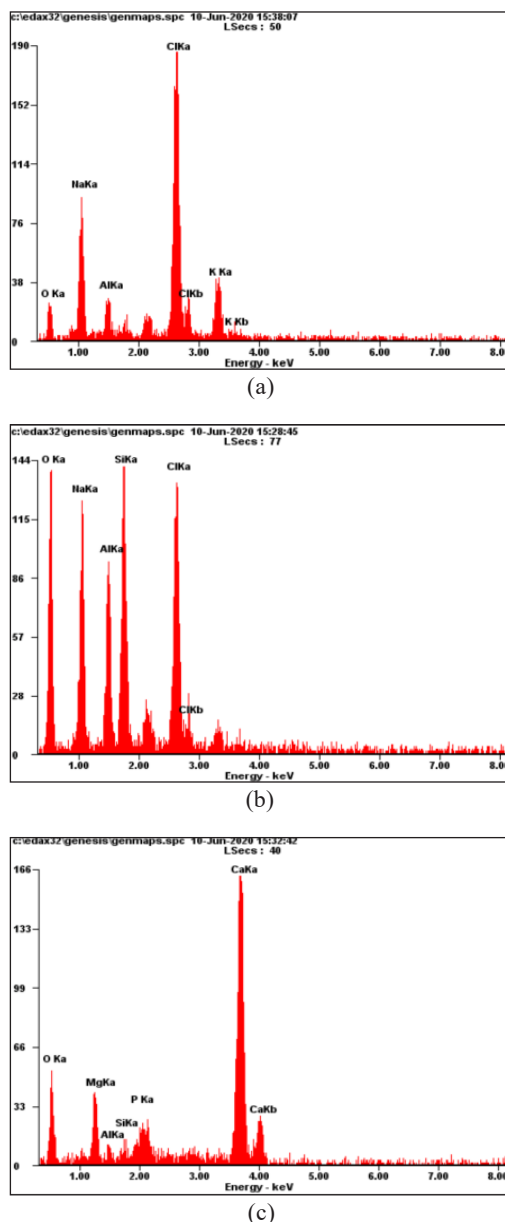

Figure 4. EDX elemental composition of solid catalysts of (a) orange peels, (b) pineapple leaves, and (c) sugar palm peels

the composition of the sugar palm peel elements was O by 43.36%, Mg by 0.816%, Al by 01.39%, Si by 01.17%, P by 03.70%, and Ca by 42.22%. It showed that the ratio of Si and AL indicated a high crystallinity process. It could increase the percentage of silica purity due to the increasing number of impurities in the form of volatile compounds released, and organic compounds can be degraded by heat. In addition, it meant that the catalyst had a high selectivity. The elements contained in the wetland biomass-based catalyst solids were micro and macronutrients which were very important for the growth process and productivity of a plant.

Analysis of Acetin Products from Glycerol Esterification Results By-Products from the Biodiesel Industry with Acetic Acid

Glycerol Crude Refining. The crude glycerol used came from the by-product of the biodiesel industry in South Kalimantan. Before being used as a raw material to manufacture acetin products, the impurities of crude glycerol needed to be removed using activated carbon and purified using the evaporation method to remove water, methanol, and residual acid. After purification, the yield obtained was 57.5% glycerol, while 42.5% impurities such as water, residual methanol, catalysts, and others were lost. Therefore, the area was 57.5%, whereas the selectivity of triacetin was 100% when it was calculated. The total area produced was only 57.5% because, in the esterification process, the main product was triacetin. However, there were also by-products in the form of water and residual acetic acid.

Based on the chemical properties analysis carried out on the purified crude glycerol and glycerol, it was known that the water content of crude glycerol before purification was 13.52%, and crude glycerol purified was 2.33%. The evaporation process influenced the decrease during purification. According to Wu et al. (2020), the decrease in water content was due to some of the water absorbed by the adsorbent (activated carbon). For the ash content, the ash content of crude glycerol before purification was 4.54% and crude glycerol purified was 4.35%. It showed that the low inorganic compounds in the form of metal and mineral remnants contained therein. In terms of color, the crude glycerol turns from reddish yellow to yellowish clear after purification. It was caused by the adsorption process using activated carbon. According to Babayemi et al. (2021), activated carbon was a bleaching agent that could adsorb color on glycerol. The activated carbon adsorption process could separate glycerol from various impurities, including beta carotene dyes, MONG (non-glycerin organic matter), and other compounds.

Furthermore, it was known that the pH of crude glycerol was 3.9 and the purified crude glycerol obtained was a pH of 3.7. For crude glycerol before purification, it was known that the glycerol content was 32.23%, and the glycerol content of the purified crude glycerol was 99.5%. Then, the density of crude glycerol, having not gone through the purification stage of 1.255 g ml^{-1}, looked lower than the density of crude glycerol after purification of 1.265

g ml^{-1}. However, it followed the pro analysis glycerol standard, which was 1.260 g ml^{-1}, due to other compounds present in crude glycerol before purification, such as methanol, catalyst, water, gum, and others affecting its density. In this study, glycerol from crude glycerol, a by-product of the biodiesel industry, which had been purified, was used as a raw material to manufacture acetin products.

Testing the Performance of Heterogeneous Catalysts on Acetin Products

The products resulting from the esterification of glycerol and acetic acid with a heterogeneous catalyst based on biomass waste were analyzed using Gas Chromatography-Mass Spectrometry GC-MS. This treatment used variations in moles of reactants, namely the formulation of moles of reactants 1:7, 1:8, 1:9, 1:10, 1:12 with a heterogeneous catalyst ratio of 3% by weight of glycerol. A ratio of 12 acetic acids could produce a glycerol conversion of 100% with a selectivity of 99.9% (Souza et al., 2017) and 75% glycerol conversion with 91% selectivity (Chamack et al., 2018).

According to the attached journal, in general, it could be said that there was no significant difference between 3% and 5% catalyst concentrations; thus, it could be
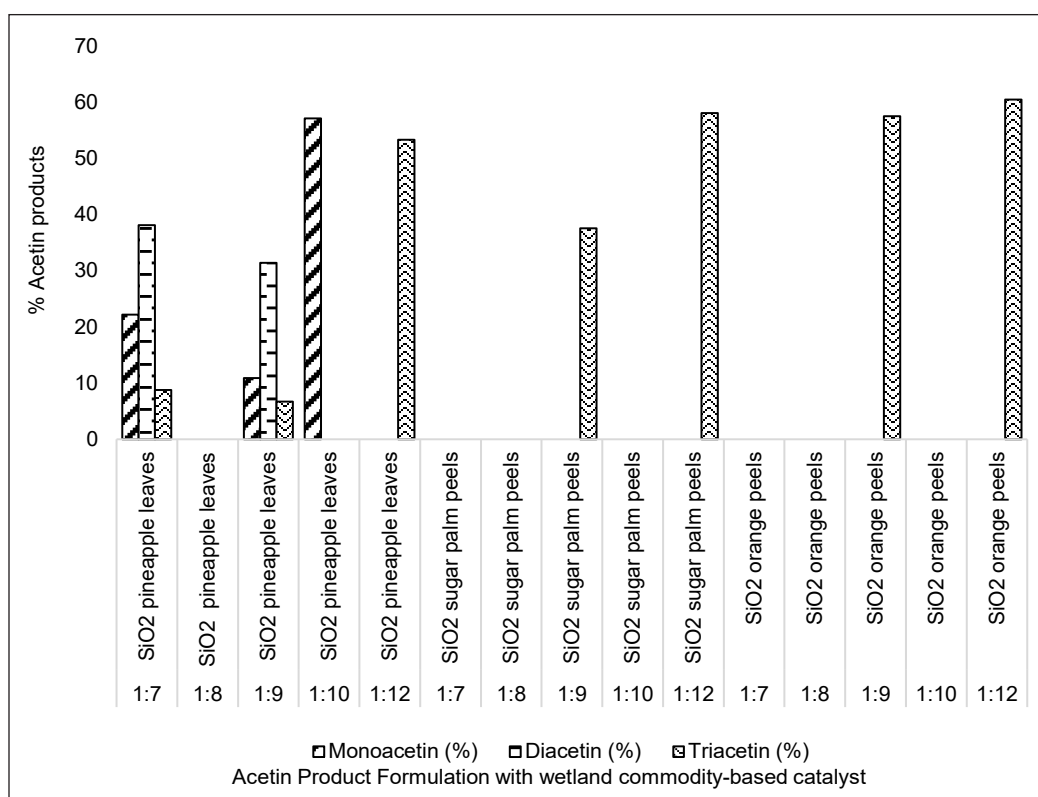

Figure 5. The products of the esterification of glycerol and acetic acid with heterogeneous catalysts based on biomass waste

concluded that 3% catalyst concentration was the optimum concentration. The products obtained were monoacetin, diacetin, and triacetin, presented in Figure 5.

From Figure 5, the results of the GC-MS analysis of acetin products showed at a temperature of 115°C with a mole ratio of glycerol reagent with acetic acid 1:7; 1:8; 1:9; 1:10; and 1:12 resulted in different compositions of monoacetin, diacetin and triacetin formed in the esterification reaction, some of which were formed but some were not. This condition was because heterogeneous catalysts involved several reaction steps on the catalyst surface, such as external and internal diffusion, the adsorption of molecules, surface reactions, desorption, internal diffusion away from the catalyst surface, and external diffusion. Therefore, variations in the molar ratio and catalyst concentration of 3% were used, referring to the preliminary study using the same glycerol source as the esterification process. It was in line with Arsyad et al. (2015) research.

The mole formulation of reactants at 1:7 and 1:9 with heterogeneous catalyst SiO_2 derived from pineapple leaf extract resulted in acetin with the composition of monoacetin, diacetin, and triacetin in the esterification reaction. The presence of Si and AL with a ratio of 1.42 indicated the crystallinity of the X-Ray Diffraction test, which aimed at characterizing the crystal structure, crystal size of a solid material. An increase in crystallinity could be seen from the peak formed by sharp and narrow X-ray diffraction, which showed the high crystallinity of the sample. Each crystal gave a specific pattern so that the peaks' position in the diffractogram indicated the presence of a particular compound. The good selectivity of pineapple leaves was shown by the results of XRF analysis on the characterization of components, especially the difference between Si and Al ratios of 1.42. It showed the high crystallinity of the sample and meaning each crystal gave a special pattern at the peak position indicating the presence of the target compound, namely acetin.

At a mole ratio of 1:10, reactants with a heterogeneous catalyst SiO_2 pineapple leaf extract formed the highest monoacetin composition of 57.14% at Mass Spectrometry Peak 8 with a retention time of 4.86 minutes. It was due to the difference in temperature of the monoacetin production process.

Furthermore, the composition of diacetin formed at the ratio of moles of reactants to moles of 1:7 with heterogeneous catalyst SiO_2 pineapple leaf extract was highest at 38.16% at Mass Spectrometry Peak 6 with a retention time of 8.23 minutes. Then for the composition of triacetin formed at the ratio of moles of reactants to moles of reactants 1:12 with a heterogeneous catalyst SiO_2 orange peel extract, the highest was 60.54% at Mass Spectrometry Peak 26 with a retention time of 13.232 minutes, which could be seen in Figure 6. Selectivity was a measure of the catalyst in accelerating the reaction in forming a product. In this study, the difference in the molar ratio used in producing acetin was a determining factor for selectivity.
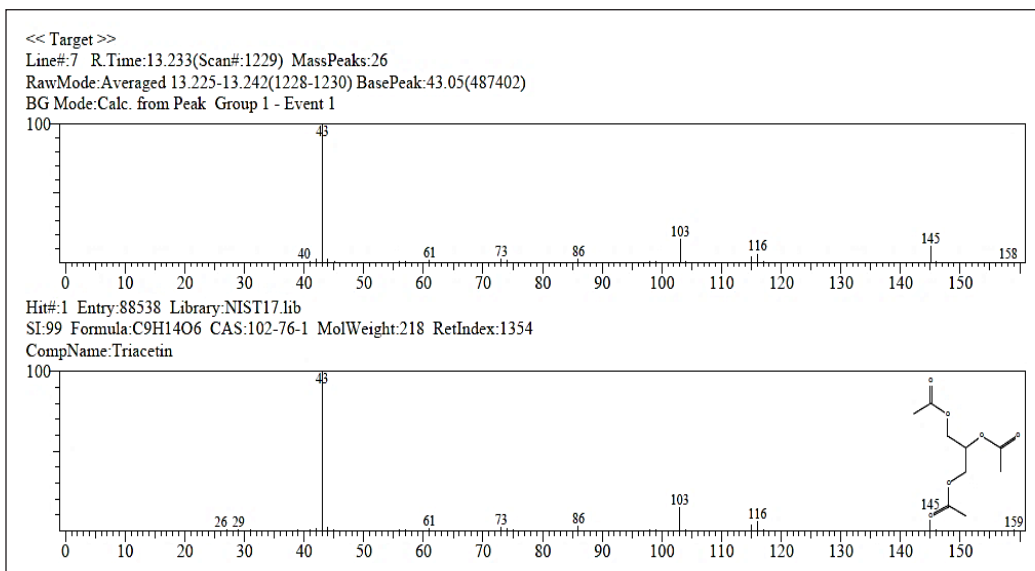
```
<< Target >>
Line#:7   R.Time:13.233(Scan#:1229)  MassPeaks:26
RawMode:Averaged 13.225-13.242(1228-1230) BasePeak:43.05(487402)
BG Mode:Calc. from Peak  Group 1 - Event 1
```

```
Hit#:1  Entry:88538  Library:NIST17.lib
SI:99  Formula:C9H14O6  CAS:102-76-1  MolWeight:218  RetIndex:1354
CompName:Triacetin
```

Figure 6. Results of GC-MS analysis of Acetin products

CONCLUSION

The study results show that the three types of catalysts originating from wetland biomass, namely Madang Orange peels, Tamban pineapple leaves, and sugar palm peels, are heterogeneous catalysts that can produce acetin from biodiesel industry products in the esterification process. The results of XRF analysis were on orange peels obtained silica 29.201% and alumina 4.115%, pineapple leaves obtained silica 34.072% and alumina 0.074%, and sugar palm peels obtained silica 40.017% and alumina 0.953%. The diffractogram from XRD analysis showed that all heterogeneous catalysts had sharp and narrow peaks, meaning that the crystallinity of the sample was high according to the typical peak of silicon oxide (SiO_2). The results of the BET analysis showed that the pore size of the catalysts of orange peels was 4.328 nm with a surface area of 263.475 m^2 g^{-1}, pineapple leaves had a pore size of 4.850 nm, and a surface area of 35.983 m^2 g^{-1} and sugar palm peels was 5.658 nm with a surface area of 10.884 m^2 g^{-1}. Morphological tests using SEM-EDX found that the catalyst of orange peels was composed of a very heterogeneous dense porous structure, that of pineapple leaves was amorphous. In contrast, sugar palm peels were composed of small, irregular pores. All the resulting heterogeneous catalysts met the characteristics of standard SiO_2 silica catalysts. The ratio used in the esterification process for acetin production was 1:7; 1:8; 1:9; 1:10; and 1:12. The molar ratio which gave the best acetin product selectivity was 1:9. In fulfillment in the industry, acetin can be used for the food and non-food industries.

ACKNOWLEDGEMENTS

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