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Submission date: 10-Apr-2023 06:51PM (UTC+0700)

Submission ID: 2060488069

File name: IJISRT22MAR972.pdf (347.54K)

Word count: 3549

Character count: 19214

Implementation of a New Wetland Material for the Production of the Additive Triacetin Using Biodiesel By-Products

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Abstract:- One of the by-products of the biodiesel industry is crude glycerol. Crude glycerol with the esterification process assisted by the use of heterogeneous catalysts can produce triacetin. Projected biodiesel production until 2030 will reach 50 billion liters. The impact on the amount of by-product produced also continues to increase so it needs to be optimized in further processes. The research aimed at producing triacetin using biodiesel industry products as a source of glycerol and determine various ratios of glycerol volume during the esterification process and the use of catalysts based on wetland biomass waste from Marabahan orange peel. The method started from the preparation of materials, extraction and synthesis of catalysts, purification of crude glycerol and the esterification process. The results of which were then carried out a GC-MS test to determine the selectivity of triacetin. The highest glycerol conversion was obtained in a treatment using a reactant volume ratio of 1:12 with a heterogeneous catalyst of SiO₂ derived from orange peel biomass. The conversion value obtained was 97.41% with 100% triacetin selectivity. Wetland potential such as biomass from orange peel which is used as heterogeneous catalyst can be recommended in the esterification process to obtain high conversion values.

Keywords:- Esterification Process, GC-MS, Glycerol Conversion, SiO₂, Triacetin Selectivity.

I. INTRODUCTION

Global biodiesel production is projected to increase to 59 billion L in 2030. Biodiesel production in Indonesia is projected to increase to 9.7 billion L in 2030 [1]. Biodiesel is a promising renewable energy. When its production increases, so does the production of the main by-product, namely crude glycerol [2]. Biodiesel production will produce about 10% (w/w) glycerol as the main by-product. In other words, for every 100 pound of biodiesel produced, about 10 pounds of crude glycerol is produced [3]. Effective utilization of crude glycerol will contribute to the viability of biodiesel.

The glycerol derivative product is acetin which is obtained by reaction of glycerol with acetic acid (or carboxylic acid), acetic anhydride, or by transesterification of triglyceride or glycerol with methyl acetate. There are three types of acetin depending on the number of hydroxyl group substituted from the glycerol atom with an acetyl or acyl group. Hence, the reaction is referred to as acetylation. Acetins include

monoacetin (monoacetyl glycerol), diacetin (diacetyl glycerol) and triacetin (triacyl glycerol). All types of acetin have wide applications [4].

Some of the glycerol derivative products which can be used in industry includes emulsifiers, plasticizers and additives. Additive is widely used in the coating and paint industries. In the manufacturing industry, additive used for octane boosters to reduce engine knocking is known as Tri Acetyl Glycerol or triacetin [5]. In general, the process of triacetin production uses a homogeneous catalyst. The disadvantage is that homogeneous catalysts are difficult to separate and purify the product besides being able to cause corrosion on industrial equipment and having a toxic impact on the environment [6]. Homogeneous catalysts can be replaced with environmentally friendly heterogeneous catalysts because they are made from biomass and are easily separated from the reaction products and can be reused [7].

The source of biomass has the potential as a new material, namely the procurement of basic materials for making heterogeneous catalysts to replace commercial catalysts to meet industrial needs. Biomass is a term for all organic material derived from plants (including algae, trees and plants). Biomass is produced by green plants which convert sunlight into plant material through the process of photosynthesis. Biomass resources can be thought as organic matter where the energy of sunlight is stored in chemical bonds [8].

One of the heterogeneous catalysts having been developed is mesoporous silica. In current developments, the natural potential which can be used as raw material for heterogeneous catalysts is agricultural biomass waste such as orange peel (*Citrus Suhuiensis*). According to the Central Statistics Agency of South Kalimantan Province, the annual production of citrus plants in 2020 is 1,770,748 quintals [9], the famous citrus plant in South Kalimantan itself comes from Barito Kuala Regency as a leading commodity in South Kalimantan Province [10] having high value in economy but has not been properly managed due to the lack of knowledge and technology, especially in rural areas, so it tends to be neglected [11]. It is necessary to provide innovations, one of which is as a heterogeneous catalyst being able to support the esterification process.

The research objectives were to produce triacetin using by-products from the biodiesel industry as a source of glycerol and to implement new materials from wetland commodities

namely orange peel waste as ² supporting catalyst in the esterification reaction process based on the advantages of terogenous catalysts which could be easily separated from the reaction products and the ability to be reused.

II. RESEARCH METHODHS

A. Material Preparation

The source of the catalyst material used in this study was peel waste. The famous citrus plant in South Kalimantan itself came from Barito Kuala Regency as a leading commodity in South Kalimantan Province. The first steps were selecting orange peel waste which was free from pests and washing using running water, then drying under the sun until the water content was 5%. The sample was ground and sieved using an 80 mesh sieve. The refined sample then went through a furnace process to produce fine ash from the calcination, the furnace process was carried out for 4 hours at a temperature of 800°C. Again, the calcined ash was sifted with an 80 mesh sieve to obtain a uniform size.

B. Catalyst Extraction and Synthesis

The calcined ash was then refluxed using 3M NaOH solution for 12 hours at temperature of 90°C, stirring speed of 300 rpm and the ratio between sample and NaOH solution was 1: 4 (w/v). The results of the extraction using the reflux method were then separated between the residue and the filtrate using filter paper. The filtrate obtained was then dripped with 1M HCl little by little until a white precipitate was formed ¹², reached a neutral pH (6.5 – 7). The resulting precipitate was washed using distilled water to a neutral pH and dried using an oven at 80°C for 5 hours to form serogel. The serogel was then pulverized and calcined at 700°C for 3 hours to obtain crystalline silica.

C. Crude Glycerol Purification

In this study, the sample for crude glycerol came from the biodiesel industry located in Kotabaru, South Kalimantan. Crude glycerol was diluted using distilled water in a ratio of 2: 3 (v/v). The bleaching process on crude glycerol used activated carbon as much as 5% of the total sample volume. The crude glycerol solution was then stirred for 30 minutes and allowed to stand for 24 hours, the adsorption process was carried out 3 times to produce clear colored glycerol, then an evaporation process was carried out at 100°C for 4 hours to evaporate the water content in crude glycerol to obtain glycerol with a high concentration of glycerol.

D. Esterification Process

Glycerol with a certain volume was heated at a temperature of 115°C ± 1°C in a three-neck flask, separately also heated acetic acid at a temperature of 115°C ± 1°C in an Erlenmeyer. When it had reached a temperature of 115°C ± 1°C acetic acid and heterogeneous catalyst from orange peel were added into the three-neck flask and time was recorded as the start of the reaction. The esterification process lasted for 180 minutes with a stirrer speed of 1000 rpm and the ratio of the volume of glycerol: acetic acid was 1: 12 (mole ratio equal to 0.03: 0.4) and with heterogeneous catalysts from orange peel waste, every 60 minute the sample was taken for glycerol

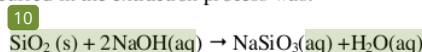
conversion analysis using the acid-base titration method. The filtrate from the esterification process was then separated using filter paper and tested using GC-MS Type GCMS QP2010 Plus, Shimadzu.

III. RESULTS AND DISCUSSION

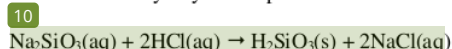
A. Results of Extraction and Synthesis of Catalysts from Biomass Sources

The raw material for making heterogeneous catalysts from a new material source for wetland commodities, namely orange peel waste, after the initial preparation carried out, was extracted using NaOH and synthesized using HCl. The yield for heterogeneous catalysts with the source of the catalyst material from orange peel was 0.12%.

The percentage of SiO₂ yield of orange peel extract was in the small category. This could be caused by NaOH not being maximally able to penetrate cell walls in orange peels. Silica was found in the cell wall matrix, especially in the epidermal wall, and in the lumen of some types of epidermal cells [12]. The extraction process using NaOH could cause silica solubility where Na₂SiO₃ was produced. Silica was easily dissolved in alkaline conditions but it would form a precipitate in neutral or acidic conditions [13]. The reaction which occurred in the extraction process was:



The resulting filtrate, namely sodium silicate (Na₂SiO₃), was used in the catalyst synthesis process using the sol-gel method by adding HCl little by little to form a white precipitate (pH 6.5 – 7). pH 7 was the optimum concentration to obtain silicic acid deposits, at a pH of less than 7 there were fewer deposits, this happened because at that pH conditions the formed precipitate dissolved again. The precipitate obtained at pH of more than 7 was also small because at that pH condition the HCl solution used to react with sodium chloride was only slightly so that the exchange between Na⁺ and H⁺ ions was so small [14]. The addition of HCl solution into the filtrate or sodium silicate solution caused the exchange of Na⁺ ions with H⁺ to produce a gel-shaped solid which eventually separated particles from silica bound to water molecules, namely silica hydrosol or silicic acid (H₂SiO₃) [14]. The reaction which occurred in the catalyst synthesis process was:



B. Results of Glycerol Crude Purification

The raw material for crude glycerol was purified using activated carbon but previously added aquades with a ratio of 2:3 (v/v), the addition of distilled water aimed at facilitating the adsorption process because crude glycerol had a fairly high viscosity [15]. The addition of activated carbon aimed at removing compounds such as water content, methanol and other compounds contained in crude glycerol, this was because the length of the adsorption process caused the adsorbent and impurity compounds to interact, as a result the adsorbed impurities became more so that the resulting density became greater [16].



Fig 1. Color Comparison between (a) Crude glycerol and (b) Glycerol Purification

This purification process produced glycerol with a density of $1,257 \text{ gm}^{-1}$ which was higher than the density of crude glycerol of $1,224 \text{ gm}^{-1}$. In addition, activated carbon could absorb impurities contained in glycerol so that it could increase the density value of glycerol [17]. It could be seen that the color of the glycerol changed from reddish yellow to clear yellowish. This was caused by the adsorption process using activated carbon. Activated carbon was a bleaching agent which could adsorb color on glycerol [18]. This was because the adsorption process using activated carbon could separate glycerol from

various impurities, including beta carotene dyes, MONG (matter organic non glycerin) and other compounds [19].

C. Results of Esterification Process

The glycerol conversion was analyzed using the acid-base titration method, the end point of the titration was indicated by the change of the solution to pink. In this study, in the esterification process of triacetin formation, purified glycerol was used with a ratio of glycerol: acetic acid reactant volume of 1:12 and 3% SiO_2 catalyst from orange peel.

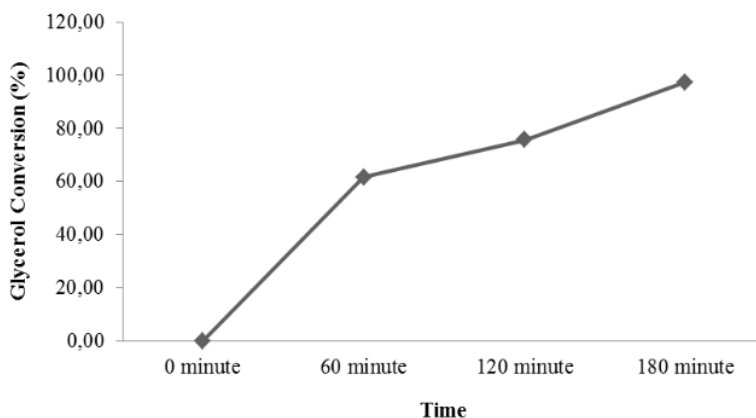


Figure 2. Conversion of glycerol for each change in reaction time

From Fig. 2, it could be seen that the conversion of glycerol had increased with increasing reaction time, this was because the longer the reaction time, the greater the conversion of glycerol due to the greater opportunity for the reagents to collide with each other [20]. Another factor affecting the conversion of glycerol was the ratio of reactants. To produce more products, the reaction equilibrium had to be shifted to the right or towards the products and one way being able to be done was to add reactants so that an excess reaction occurred [22] stoichiometrically every 1 mole of glycerol required 3 moles of acetic acid, so when the ratio of acetic acid was increased, it would result in the conversion of glycerol produced to be high. The conversion of glycerol from purification with reactants ratio of 1:12 increased with the addition of time, from glycerol conversion of 61.69% at 60 minutes to 97.41% at 180 minutes.

The results of GC-MS analysis on a product with a reactant ratio of glycerol:acetic acid 1:12, silica catalyst from orange peel 3% triacetin compound was formed at peak 7 with a retention time of 13.232, while neither monoacetin nor diacetin was formed. The area (%) of triacetin at peak 7 was 60.54%.

Based on the GC-MS analysis, the triacetin formation reaction was able to produce triacetin with a selectivity of 100%. Reaction time could increase the selectivity to triacetin which decreased the selectivity of diacetin and monoacetin [22]. This was due to the acetylation of monoacetin and diacetin to produce triacetin products [23].

Table 1. Glycerol conversion and triacetin selectivity from multiple sources

Catalyst	Ratio reactants	Time; temperature	Glycerol Conversion (%)	Triacetin Selectivity (%)	Reference
SiO ₂ orange peel 3 wt%	1 : 12	180 minute; 115°C	97.41	100	Research
CsPWA 7 wt%	1 : 10	120 minute; 85°C	98.2	16	[24]
Glycerol-based carbon 2 wt%	1 : 3	180 minute; 110°C	99	88 (combined DAG, TAG)	[25]
Resin-Amberlyst	1 : 10	240 minute; 120°C	100%	32.9%	[26]

Table 1 showed that the factor affecting the conversion of glycerol was not only time of reaction. Other factors could be the percentage of catalyst, the ratio of reactants, temperature and type of catalyst. The effect of the source of the catalyst material was measured based on the ability of the catalyst to convert glycerol and the ability to obtain selectivity values for triacetin in the esterification reaction. The use of new material sources from wetland commodities as a catalyst in the esterification process made it possible to determine the conversion value of glycerol and the selectivity of the resulting triacetin.

From Table 1 it could be seen that silica catalyst from orange peel produced higher selectivity of triacetin. This result was in line with the study of mesoporous silica nanoparticles (SiO₂) which stated that SiO₂ orange peel extract had a larger surface area [11]. Catalysts having a larger surface area had more contact area with reactant molecules so that it could produce greater glycerol conversion and greater catalyst activity [27].

IV. CONCLUSION

The new material for wetland biomass based on Marabahan orange producing SiO₂ catalyst can be implemented in the esterification process for the production of acetin, especially triacetin. The esterification process is able to produce conversions reaching 97.41% with selectivity reaching 100%. The highest glycerol conversion and triacetin selectivity are found in the 1:12 reactant volume ratio treatment. The recommendation given is that the waste potential of wetland commodities is very potential in producing new materials which can be useful as heterogeneous catalysts. In addition, the by-product of palm oil agroindustry is very possible to be developed with purification technology into a source of glycerol to produce additives such as triacetin.

ACKNOWLEDGMENT

We would like to thank the Ministry of Education and Culture, Research and Technology, Directorate of Resources, for the funding provided through the National Competitive Basic Research with SK KPA of the Directorate of Resources No. 1867/E4/AK.04/2021, dated on the 07th of June 2021.

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