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The Processing of Glycerol with Acetone to Produce Solketal Using Amberlite IR 120 Na Catalyst: Comparison of solketal Production Using Gas Chromatography

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Abstract

Solketal is a chemical that can be made by combining glycerol with acetone. This compound can be used as a fuel oil additive to improve the cold flow properties of liquid transportation fuels, reduce specific emissions, aid in the reduction of gum formation (oil sap), increase oxidation stability, and increase the octane number by up to 2.5 points to accelerate the initiation process in motor fuel combustion. The addition of solketal, a bio-additive material in biodiesel, is expected to reduce emissions from diesel engines. Solketal can reduce glycerol waste created from biodiesel synthesis in addition to reducing resultant emissions because glycerol waste can be used as the primary raw material in the process manufacture of the solketal. The purpose of this research is to find out The catalytic process of glycerol and acetone using Amberlite IR 120 Na catalyst was traced using gas chromatography analysis. Solketal formation analysis using gas chromatography was used in this study. According to the results of gas chromatography analysis, the solketal produced without going through the distillation process has a purity of 23.54%, while the solketal produced after going through the distillation process has a purity of 38.94% when compared to the synthetic solketal produced by Sigma Aldrich, which has a purity of 95.67%. To manufacture solketal with a higher level of purity, the batch method was improved by adding a distillation process step to remove the water content and acetone that was still present in the sample.

Keywords: Solketal, glycerol, amberlite IR 120 Na, gas chromatography

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Introduction

Biodiesel is a viable alternative to traditional fuels (fossil fuels). Biodiesel can be produced using a variety of organic raw materials such as vegetable oil, animal fat, and plant seed oil, making it a more environmentally friendly fuel due to its non-toxic and biodegradable properties. Biodiesel (Ghanei et al., 2011). The use of biodiesel as a renewable fuel can reduce CO_2 emissions while not requiring extensive modifications to the diesel engine and can lower sulfur levels in the air (Chansorn et al., 2022).

In 2003, the biodiesel industry alone produced approximately 200,000 tonnes of crude glycerol, which increased exponentially to 2 million tonnes in 2012. A significant portion of this supply was surplus, posing a disposal problem because crude glycerol has little economic value and use due to the presence of inorganic salts and other impurities (Chol et al., 2018). In general, the biodiesel production process in Indonesia involves the transesterification of crude palm oil with the by-product of the transesterification process, namely glycerol, at a volumetric ratio of 1: 10, or 0.1 m^3 of glycerol in 1 m^3 of biodiesel (Shirani et al., 2014). If biodiesel production is increased, glycerol as a byproduct of the process can result in a large glycerol surplus. Its output is growing faster than its consumption (Cazumbá et al., 2022).

As a result, efforts must be made to use glycerol waste as a byproduct of biodiesel production. Glycerol is the main byproduct of acyl glyceride transesterification reactions in oils and fats. This reaction has been widely used in the production of biodiesel, which exhibits rapid development while producing a large amount of

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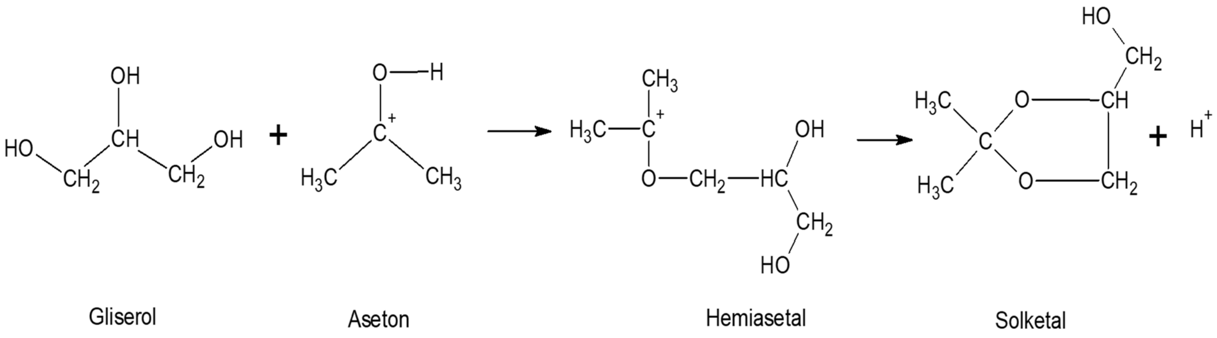

Figure 1 Solketal formation process

waste glycerol (million tons per year). Many advanced processes, such as distillation, sequential extraction/purification, and ion exchange techniques (Raman et al., 2019), involving various types of analytical tools, have been developed to convert waste glycerol into a high-quality product. Biodiesel was one of the first alternatives considered for use as a biofuel. It is made from vegetable oils or animal fats as a mixture of ethyl and methyl esters of fatty acids (FAEE or FAME) via a transesterification reaction with a mono-alcohol, usually methanol, in the presence of an alkali catalyst. This biofuel has some inherent advantages over fossil fuels, such as low toxicity and being biodegradable, renewable, and biocompatible (Hidalgo-Carrillo et al., 2021).

Since the beginning of biodiesel production, glycerol, a byproduct, has gained market share in comparison to other drugs. Many studies use glycerol by-products (Türck et al., 2022), one option is to convert glycerol into acetals, ethers, and esters, which have demonstrated potential for use as oxygenated fuel additives (Cazumbá et al., 2022; Rifani et al., 2016). Examples of promising approaches include the catalytic reaction of glycerol isopropylphene or solketal with acetone (Figure. 1) (Türck et al., 2022).

Solketal, a derivative of Fatty Acid Glycerol Ester (FAGE) that contains formaldehyde-based acetal, is an excellent fuel additive (Türck et al., 2022). Solketal is created by catalyzing glycerol with acetone. Solketal and its isomer (2,2 dimethyl-1,3-dioxan-5-ol), which is thermodynamically less stable than the solketal molecule due to the presence of a methyl group in the axial position of the six-membered ring, are the reaction products. There is a short carbon chain in solketal, and its structural features are expected to increase the cetane number value and reduce particulate emissions (Manjunathan et al., 2015; Türck et al., 2022) because it reduces particulate emission and improves both the flow properties and the oxidation stability of liquid fuels (Aguado-deblas et al., 2022) and It is of high quality and improves the flash point and viscosity of the fuel, resulting in better engine performance (Sharma et al., 2022). The solketal formation process can be carried out with the help of a catalyst, which has a relatively high conversion value when compared to without a catalyst.

Therefore, there is a need for further research on the process of solketal formation through a catalyzation reaction with the help of certain catalysts and the process of analyzing solketal content using analytical instruments.

The most popular methods for fuel forensics are one-dimensional gas chromatography (GC) with flame ionization (FID) or mass spectrometry (MS) detection; they have been widely used because they can provide fundamental information for major components. However, when it comes to minor compounds, they may not provide enough resolution (Bai et al., 2018).

In this study, the catalytic process of glycerol and acetone using Amberlite IR 120 Na catalyst was traced using gas chromatography analysis.

Methods

The material used in this study, Glycerol ($C_2H_5(OH)_3$) purchased from PT. Brataco (Indonesia), Acetone ($(CH_3)_2CO$) from *Merck (Germany)*, and Amberlite IR 120 Na Catalyst purchased from PT. Brataco & manufactured by Rohm and Haas (USA), Chloroform from *Merck (Germany)*, Sodium thiosulfate solute, Periodic acid solute 0.1 N, Potassium iodide solute 10%, Starch Solute 1%, Potassium dichromate from *Merck (Germany)*, hydrochloric acid (37% purity) from *Merck (Germany)* and Aquadest by genera labora (Indonesia).

Catalyzation glycerol with acetone using amberlite IR 120 Na

The process of catalyzation glycerol as a by-product of biodiesel with acetone using an Ambelite IR 120 Na catalyst (**Figure. 5**) was carried out with a series of batch reactors consisting of a 500 mL three-neck flask connected to a mercury stirrer and a stirrer motor, and equipped with a reverse cooler and a thermometer to measure the internal temperature. solution. The heating process is carried out in a water bath. The catalyzation procedure begins by introducing glycerol and acetone into a three-neck flask as a reactor with a mole ratio of 1:3.

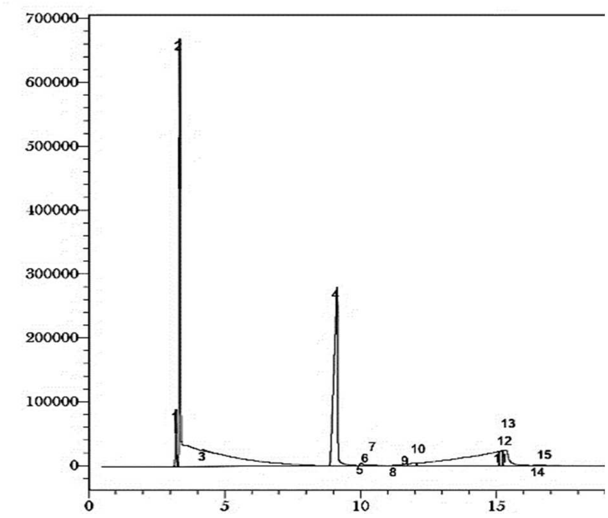

Figure 2. Solketal chromatogram without separation process

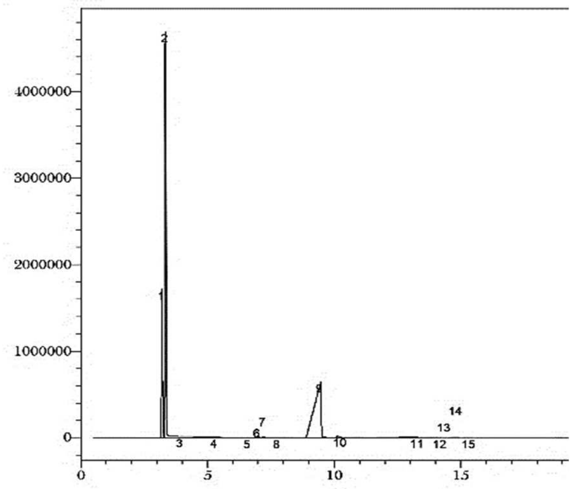

Figure 3. Solketal chromatogram with separation process

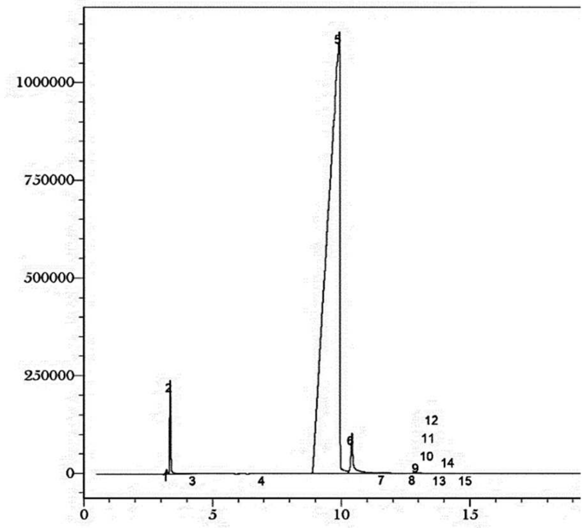

Figure 4. Standard solketal chromatogram (Sigma Aldrich 96%)

Furthermore, the stirrer motor was run with a rotating speed of 500 rpm and the water bath was turned on by setting the reaction temperature to 50 °C and the catalyst was 5% of the glycerol mass of 4.06 grams. When the two reactants have reached the desired homogeneity and reaction temperature, then the time is calculated as the initial reaction time (t=0), the reaction lasts for 90 minutes.

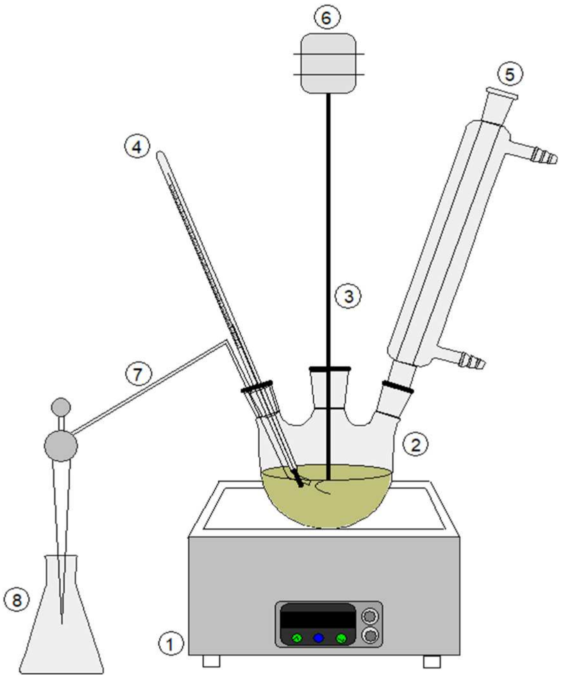

Figure 5. Series of ketalization Glycerol with acetone

Description:

1. Waterbath
2. three-neck flask
3. mercury stirrer
4. Thermometer
5. Reverse Cooler
6. Stirring motor
7. Sampler
8. Sample Holder

Solketal distillation

The distillation process is included in a series of solketal synthesis processes to remove more or less of the water and acetone content found in solketal products that have previously been catalyzation. This procedure is carried out with the help of a Rounded Bottom Flask, a return cooler with L and T connectors, a 250 mL Erlenmeyer as a distillate reservoir, a mercury thermometer as a temperature gauge in the system, statives, and clamps. In this series of tools, asbestos is used to keep the heat generated in the system contained. In addition, to produce a purer solketal. A heating mantle is used as a heat source during the distillation process. The distillation process is carried out by adjusting the temperature in the system which reaches 80 °C for 2 hours.

Solketal analysis using GC-FID

Gas chromatography was used to analyze solketals. The concentration of solketal in the synthesized sample was determined using an Agilent 7890B GC equipped with a flame ionization detector (FID). The concentration of solketal was determined under the following conditions: Capillary column DB-5MS, internal diameter 0.250 mm, column length 30 meters with 0.25 m liquid film, helium gas as a carrier gas, injection volume 0.5 L, injector temperature 70 °C, and total operating time 15 minutes.

Results and Discussion

Gas chromatography is one method for determining the composition of the glycerol and acetone catalysis reaction using an Amberlite IR 120 Na catalyst. The basic principle of gas chromatographic separation is based on differences in the affinity of each substance's surface vapor components (Anggraini et al., 2013). This separation works by separating a mixture into components based on the interaction of the mobile phase and the stationary phase. The stationary phase can be a solid or liquid, while the mobile phase is a stable gas. This method can only be used to separate volatile samples (Darmapatni et al., 2016).

Before being used as a bio-additive in biodiesel fuel, the solketal synthesized from glycerol and acetone was analyzed using gas chromatography to determine the concentration contained in the reaction product between glycerol and acetone using Amberlite IR 120 Na as a catalyst previously. Also, whether the solketal was formed as a result of the glycerol and acetone catalysis reaction using the Amberlite IR 120 Na catalyst.

The standard analysis of solketal obtained from Sigma Aldrich with a purity of 96% is intended to be used as a reference to prove whether or not solketal is formed by the catalytic reaction of glycerol and acetone using the Amberlite IR 120 Na catalyst. According to the results of the GC analysis, there are 15 peaks, with three peaks dominating, namely peaks 2.5 and 6, as shown in **Figure 4**, which shows the chromatogram curve with the peak data formed in the GC analysis. The chromatogram results and peak data from the solketal standard show that the solketal peak appears on the 5th peak with a retention time of 9.93 minutes and an area of 36963618 and the concentration of solketal reaches 95.67%. This is by the solketal purity data previously listed by Sigma Aldrich.

The analysis of the synthesized solketal was performed at a temperature of 50 °C without any separation (simple distillation) to determine the significant differences that occurred between the analysis of solketal formation before the separation method was performed using a simple distillation apparatus, As shown in **Figure 2**. According to the results of the GC analysis, there are 10 peaks, with the major peaks being the 1, 2, 4, and 11 peaks. Based on the chromatogram and peak data acquired, it can be seen that the solketal peak emerges at peak 4 with a retention time of 9.14 minutes, an area of 2661355, and a concentration of synthetic solketal which only reaches 23.54%.

The analysis of the synthesized solketal at 50 °C in the presence of a separation process (simple distillation) is intended to determine the significant difference between the analysis of solketal formation after the separation method using a simple distillation tool and the analysis of solketal formation after the separation method using a simple distillation tool. As shown in **Figure 3**, the chromatogram and peak solketal data from the separation procedure are shown first. The GC analysis revealed 15 peaks, with three dominating peaks, notably the 1, 2, and 9 peaks. As seen in **Figure 3** Based on the chromatogram and peak data acquired, the solketal peak can be seen at peak 9 with a retention duration of 9.47 seconds, with an area of 12546793 and a concentration of synthetic solketal reaching 38.94%.

From the overall analysis results obtained, the solketal peak appears at ± 9 minutes. This is following the results of the analysis on the standard solketal (Sigma Aldrich), where the solketal peak is found at 9.93 minutes with a concentration of 95.67 %. Likewise, for the results of the solketal analysis without the separation process and the results of the solketal with the previous separation process, the peaks of solketal were found at 9.14 and 9.47 minutes, and with their respective concentrations of 23.54% and 38.94%. From the concentration data obtained, it can be seen that there is a significant difference between solketal without the separation process and solketal with the separation process first. This proves that it is very important to do the separation process first to increase the concentration of the solketal present, and to minimize the possibility of other compounds contained in the glycerol-acetone catalyzation reaction.

Other substances contained in the glycerol-acetone catalyzation reaction, such as the leftover glycerol and acetone that were not evaporated in the earlier distillation procedure, could account for the existence of other dominant peaks in the solketal analysis data. The analysis of solketal without separation, which is then mixed with standard solketal, shows that solketal is formed in the catalytic reaction of glycerol and acetone with the help of Ambelite IR 120 Na catalyst. In the findings of this investigation, the solketal peak came at 9.58 minutes with a rather substantial concentration increase, namely 48.38%.

Several factors contributed to the increase in the percentage of soketal in this study, including the choice of the desired target product's method or reaction route. When glycerol is catalyzed with formaldehyde, the percentage of solketal and acetal products produced is 30%: 70%, whereas when acetone is used, the percentage of solketal and acetal products produced is 95%, 5% (Manjunathan et al.,

2015) The right catalyst can also speed up the process of forming solketal in the system, making it more efficient because the process of forming solketal compounds does not take long. Furthermore, the separation process using simple distillation is very beneficial in increasing the existing solketal content, as evidenced by the increase in solketal content before and after the separation process using simple distillation.

Many previous studies have discussed the synthesis of solketals via this reaction route, including work by Li et al. (2019) and Ilgen et al. (2017). Each of these studies employed a different catalyst, specifically zirconium phosphate and amberlyst - 46. The glycerol conversion rate for the zirconium phosphate catalyst was 98.6% (optimum temperature 50 °C), while the yield for the amberlyst - 46 catalyst was 84% with the optimum reaction conditions of 1% catalyst, 60 °C, and 30 minutes of reaction time. Both studies used the same reaction method, which was acetone. The two studies, however, did not conduct any additional analysis of the number of solkets formed. As a result, the concentration of the solketal formed using the same reaction route and different catalysts was determined in this study.

The glycerol content of solketal can help maximize biodiesel performance when used as a bio-additive for fuel oil such as biodiesel (Manjunathan et al., 2015). Whereas biodiesel is an environmentally friendly solution to the dwindling availability of fossil fuels.

Solketal can improve the cold flow properties of liquid transportation fuels, reduce specific emissions, aid in gum formation (oil sap), increase oxidation stability, and increase the octane number by up to 2.5 points to speed up the initiation process in motor fuel combustion. (Manjunathan et al., 2015).

Conclusions

To manufacture solketal with a higher level of purity, the batch method was improved by adding a distillation process step to remove the water content and acetone that was still present in the sample. This is seen by the rise in solketal yield from 23.54% to 38.94%.

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