



The Synthesis of a CoMo/ γ -Al₂O₃ Catalyst and Its Use in the Hydrodesulfurization of High-Olefinated Fuel Components

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Abstract

Research Octane Number (RON) is a benchmark for the quality of fuel oil based on the octane value, which indicates the level of knocking or knocking produced by the fuel when combustion occurs in the vehicle engine. RON value is influenced by the composition of branched and aromatic carbon naphtha hydrocarbons. Ultra Low Sulfur Diesel (ULSD) is a type of fuel that has a sulfur content that can be overcome by the hydrotreating process. One of the hydrotreating processes is to remove sulfur, nitrogen, oxygen, and other metals, which is known as the hydrodesulfurization (HDS) process. The purpose of this study was to determine the temperature variation of the high-olefin racing fuel feed to produce a low sulfur content of 10 mg/L and a stable RON value of the feed with a minimum RON 95 value. Therefore, the catalyst used in this experiment is a catalyst containing the active metal cobalt (Co), namely a CoMo/ γ -Al₂O₃ catalyst with a concentration of 0.5 (% w/w), which has been characterized using a surface area analyzer (SAA), X-ray fluorescence (XRF), and X-ray diffraction (XRD). The catalyst activity tested in the microreactor effi PID with temperature variations of 250 °C, 260 °C, and 270 °C to reduce the amount of sulfur in the racing fuel feed. The products produced from the reactor tested for sulfur content using a total sulfur analyzer and then tested using GC-DHA (Gas Chromatography Detailed Hydrocarbon Analysis) to determine and analyze the RON values and the content of n-paraffin, isoparaffin, olefins, naphthene, and aromatics (PIONA) contained in the product. Synthesized CoMo/ γ -Al₂O₃ catalyst has a wide area of 175.49 m²/g, a pore diameter of 98.95 Å, and a pore volume of 0.52 cc/g. The active metal content of the CoMo/ γ -Al₂O₃ catalyst produced based on XRF analysis is 0.55 % w/w for CoO content and 7.82 % w/w for MoO₃ content. The CoMo/ γ -Al₂O₃ catalyst products can reduce the sulfur content produced to 31.33, 26.09, and 20.45 mg/L at various temperatures of 250 °C to 270 °C. These results were still below the Euro 5 standard, namely 10 mg/L at a concentration of 0.5 % w/w, and also did not obtain optimal temperature variations for the hydrodesulfurization process, resulting in a decreased RON value from the feed used.

Keywords: Co; Mo; γ -Al₂O₃; Catalyst; RON; hydrodesulfurization; High-olefinated fuel.

1. Introduction

The quality of available crude oil has decreased year on year, with sharp increases in sulfur and nitrogen content. The decline in crude oil was caused by an increase in impurities such as sulfur, nitrogen, oxygen, salt, and water in the crude oil content [1]. The atmosphere becomes critical in the presence of pollution containing high sulfur compounds in transportation fuels. This is the basis for this experiment.

Racing fuel, commonly known as gasoline, is used for high-speed vehicles. This product basically has a high-olefinated fuel component that is the result of a catalytic cracking process in which oil

is cracked without the aid of hydrogen gas. In petroleum, there are various kinds of hydrocarbon compounds, one of which is an organic compound containing sulfur. Sulfur oxide gases (SO_x) come from burning sulfur compounds, which causes the formation of acid rain. Sulfur oxide can damage the environment, have an impact on humans if inhaled, accumulate excessively in the organs of the body, and most importantly, cause death. Moreover, exhaust from vehicle exhausts, processing of toxic emissions, and corrosion in combustion engines [2].

The Indonesian government has set emission standards for motor vehicles as written in the Regulation of the Minister of Environment and Forestry of the Republic of Indonesia [3], which

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states that the minimum RON parameter is 91 and the maximum sulfur content is 50 mg/L. The Ministry of Energy and Mineral Resources of the Republic of Indonesia concerning Standards and Quality (Specifications) for Gasoline Fuel Oil with an Octane Number Value of 90 marketed domestically [4] states that the minimum octane number is 90 and the maximum sulfur content is 500 mg/L. In this experiment, the quality standard specifications used are in accordance with the emission standard specifications according to Euro 5 [5], which states that the minimum octane number is 95.

Research Octane Number (RON) is a benchmark for the quality of fuel oil based on the octane value, which indicates the level of knocking or knocking produced by the fuel when combustion occurs in the vehicle engine. The high octane number or RON value is influenced by the composition of branched and aromatic carbon naphtha hydrocarbons. The higher the composition of the aromatic and branched carbon naphtha hydrocarbons, the higher the RON value of the fuel, so as to improve the quality of the fuel. As a result, experiments to reduce sulfur levels are required in order to reduce the effects of SO_x compounds and obtain low sulfur diesel fuel. Ultra Low Sulfur Diesel (ULSD) is a type of fuel that has a sulfur content below 10 mg/L [6]. This can be overcome by the hydrotreating process. The hydrotreating process involves the use of hydrogen gas to remove impurities. One of the hydrotreating processes is to remove sulfur, nitrogen, oxygen, and other metals, which is known as the hydrodesulfurization (HDS) process.

This hydrodesulfurization process usually uses a catalyst consisting of an alumina support impregnated with the active metals Co (cobalt) and Mo (molybdenum). The CoMo catalyst was chosen because the catalyst with the Co promoter has a tendency to take the path of direct desulfurization or hydrogenolysis, namely by first removing sulfur, followed by hydrogenation [7]. The finished catalyst will later be activated through sulfidation, namely by using a feed with a high sulfur content. During this process, the MoO_3 layer will turn into MoS_2 in the form of microcrystals, where a number of cobalt ions will bind and form the active core of CoMoS. The effect of the promoter on CoMoS will be seen from the hydrogen activity, which will help in the sulfur removal process [8].

Therefore, this experiment aims to determine the temperature variation of the high-olefin racing fuel feed to produce a low sulfur content of 10 mg/L and a stable RON value of the feed with a minimum RON 95 value [5]. Therefore, the catalyst used in this experiment is a catalyst containing the active metal cobalt (Co), namely a $\text{CoMo}/\gamma\text{-Al}_2\text{O}_3$

catalyst with a concentration of 0.5 (% w/w), which will be characterized using a surface area analyzer (SAA), X-ray fluorescence (XRF), and X-ray diffraction (XRD). Furthermore, its activity will be tested in the microreactor effi PID with temperature variations of 250 °C, 260 °C, and 270 °C to reduce the amount of sulfur in the racing fuel feed. The products produced from the reactor will be tested for sulfur content using a total sulfur analyzer and will also be tested using GC-DHA (Gas Chromatography Detailed Hydrocarbon Analysis) to determine and analyze the RON values and the content of n-paraffin, isoparaffin, olefins, naphthene, and aromatics (PIONA) contained in the product.

2. Experimental

2.1. Instruments

The tools used in this test consist of both main and supporting tools. The main tools consist of the Surface Area Analyzer (SAA), X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Furnace KSL-1100x, GC-DHA PIONA, and Microreactor effi PID. Supporting equipment consisting of a Mettler Toledo analytical balance, a set of glass tools, dropper pipettes, volumetric pipettes, and vials.

2.2. Materials

The materials used in this experiment are test materials and chemicals. The test material included $\gamma\text{-Al}_2\text{O}_3$ buffer (PT Pertamina, Indonesia), racing fuel feed (PT Pertamina, Indonesia), NH_4OH (25% purity Merck, Germany), powdered MoO_3 (Merck, Germany), and $\text{Co}(\text{NO}_3)_2$ (Merck, Germany). The chemicals consist of acetone ($\text{C}_3\text{H}_6\text{O}$) (Merck, Germany), doctor's test solution (Pb and NaOH), sulfur powder, nitrogen gas (Samator, Indonesia), and hydrogen gas (Samator, Indonesia).

2.3. Methods

This research method consists of 3 stages, namely the process of preparing the catalyst $\text{CoMo}/\gamma\text{-Al}_2\text{O}_3$ with a metal target of CoO of 0.5 (% w/w) and MoO_3 of 20 (% w/w), the characterization of the catalyst $\text{CoMo}/\gamma\text{-Al}_2\text{O}_3$, and the product characterization of the $\text{CoMo}/\gamma\text{-Al}_2\text{O}_3$ catalyst activity test results in the PID effi microreactor.

2.3.1. Process for Making Impregnation Solutions and Catalysts

The CoMo impregnation solution was prepared at a concentration of 0.5 (% v/v). This solution was prepared by dissolving 3.5 grams of cobalt nitrate and 25 grams of molybdenum trioxide

in a 25 percent v/v ammonia solution with a total volume of 50 mL. Before entering the impregnation stage, the water pick-up (WPU) is first calculated to determine the maximum volume of water that can be absorbed into the weight of the support using the equation:

$$WPU = \frac{W_t - W_o}{W_o}$$

Information :

W_t = Final weight of support after immersion process
 W_o = Initial weight of support before immersion process

Furthermore, the γ -Al₂O₃ buffer for which WPU was calculated is weighed at 30 grams and impregnated by soaking in 21 mL of the prepared impregnation solution. The impregnated support was then dried at 120°C for 1 hour to remove the water content in the catalyst and calcined at 450°C for 3 hours to remove contents in the sample that could evaporate, such as bound water (OH), free water (H₂O), and CO₂, with the goal of decomposing compounds in the form of salts or dihydrates into oxide forms and then forming a crystalline phase.

2.3.2. Test the Catalyst Surface Area, Pore Size, and Pore Volume Using SAA [9-11].

Surface Area Analyzer (SAA) is one of the main tools in material characterization, which requires a small amount of sample, usually around 0.1 to 0.01 gram. Analysis of surface area, pore diameter, and pore volume was carried out using the SAA 2400. The sample cell containing the filter was closed and weighed as an empty weight. The sample is placed in the tube up to 0.1 gram, which is recorded as the initial weight.

The tube is attached to the degasser port for the degassing process. The heating mantle is turned on, and the temperature is adjusted. Degassing was carried out for 1 hour at a temperature of 100 °C in a slow vacuum, the temperature was raised to 300 °C for 5 hours in a fast vacuum (following the applicable SOP). After the degassing process is complete, the tube is removed, the outside is cleaned first, and then it is weighed again after degassing.

The cooling container tube is filled with liquid nitrogen up to $\frac{3}{4}$ of its volume and then mounted on the SAA 2400 instrument. The degassing result tube that has been weighed is installed in the analysis port. SAA instruments are programmed according to available Standard Operation Procedures

(SOP). The sample is then flown with helium and nitrogen gas in a vacuum. After the tool has finished analyzing, the results can be seen automatically on the computer. The resulting data is in the form of surface area (m²/g), pore size (Å), and pore volume (cc/g).

2.3.3. Test the Catalyst Phase Using X-Ray Diffraction

X-ray diffraction is a method for identifying solid crystalline elements and characteristics of crystalline materials and can be used to determine the crystalline phase of a material. The CoMo/ γ -Al₂O₃ catalyst is pulverized first, and then the fine powder of the CoMo/ γ -Al₂O₃ catalyst is put into the sample holder. Then the sample is entered according to the number to be analyzed. The XRD analysis was carried out using Cu radiation at a voltage of 40 kV and a current of 25 mA with an angle range of 5-90°. The resulting diffraction will provide information about the crystal phase and dispersion, which can identify the active components in the catalyst.

2.3.4. Test the Components of the Catalyst Using X-Ray Fluorescence

The X-ray fluorescence is a method for identifying the elements that make up a material, the composition of a substance, and the concentration of the substance. That intensity will be proportional and will be read as the concentration of elements in the sample. The CoMo/ γ -Al₂O₃ catalyst is smoothed first, then the sample powder is put into a special aluminum container for testing XRF samples and compacted using a press until it solidifies. The sample is identified at the bottom of the container and wrapped with a plastic clip to prevent contamination. The samples were then placed in the XRF apparatus and analyzed for CoMo/ γ -Al₂O₃ catalyst levels using a quantitative analysis program at a voltage of 40 kV and a current of 45 mA.

2.3.5. Catalyst Activity Test

The activity of the CoMo/ γ -Al₂O₃ catalyst was tested, and the catalyst was activated using a PID effi microreactor. As much as 5 cc of catalyst was put into the microreactor and the reactor tube, and then a leak test was carried out to observe whether there was a leak in the reactor. If not, proceed with the process of activating the catalyst through the sulfidation

process by flowing H_2 gas and dimethyl disulfide solution (DMDS) in naphtha as feed, which will react to form H_2S gas that will be flowed into the catalyst compartment. This sulfidation process is useful for activating a catalyst that was initially inactive into an active form. The sulfidation process is said to be successful if a black precipitate forms in the doctor's test solution at the gas outlet and the amount of water in the reservoir continues to increase.

After the sulfidation process has been successfully carried out, the DMDS feed stream in the naphtha is stopped and replaced by the hydrotreating process. The hydrotreating process was carried out using racing fuel feed with a sulfur content of 212.290 mg/L. Then the reactor is ready to run with temperature variations of 250 °C, 260 °C, and 270 °C and a liquid-hour space velocity (LHSV) of 3.9 h⁻¹ at a pressure of 30 bar. At each temperature transfer, conditioning is carried out on the device for 4 hours, then product samples will be taken after a span of 8 hours that have been accommodated in bottles with the resulting product in liquid form, and the product will be analyzed for sulfur content and PIONA content with GC-DHA.

2.3.6. PIONA Content Test Using GC-DHA

In this study, GC-DHA was used quantitatively to measure the PIONA content in the product produced from the PID effi microreactor in liquid form. The liquid sample was prepared in a 1.5-mL vial, and the sample was put into a capillary tube that had been coated with the predetermined stationary phase. The sample is injected and then evaporated, and the vapor is carried by helium carrier gas to the column. The hydrocarbon components contained in the sample can then be separated based on the strength of their interactions with the stationary phase and the boiling point so that they reach the detector at different times. The resulting data are retention time, product area, and solvent.

2.3.7. Total Sulfur Analyzer Performance Evaluation of Sulfur Removal [12]

The product produced from the PID effi microreactor in liquid form will be analyzed for sulfur content using the Total Sulfur Analyzer (TSA) instrument. Sample and tool preparation is done by first turning on the tool, after which it is warmed up for 2 hours in order to raise the temperature to 1000

°C so that the instrument is stable. If the instrument has finished warming up, the first thing to do is inject a blank in the form of isooctane compounds. If the blank has been read, then enter the sample that has been prepared in a vial, which will be injected using a 25 μ L syringe into the TSA tool. Testing for each sample was carried out twice. Each sample test will last for 5 minutes, with the results of the analysis being the sulfur content in units of mg/L.

3. Result and Discussion

3.1. Results of Catalyst Surface Analysis using SAA

Measurement analysis of surface area, pore volume, and pore diameter was performed using the SAA 2400 instrument. This tool specifically functions to determine the surface area of the material, the pore distribution of the material, and the adsorption isotherm of a gas on a material [13]. Brunaur-Emmet-Teller created this technique, known as the BET Method, which operates on the idea of isothermic adsorption and desorption of nitrogen gas (N_2) by solid samples under conditions of liquid nitrogen temperature as a monolayer [14]. With the BET method, which is based on the isothermal adsorption and desorption of nitrogen gas (N_2) by solid samples that are directly proportional to the surface area, the greater the volume of nitrogen gas adsorbed, the greater the surface area. The results of the analysis using a surface area analyzer are shown in Table 1.

Table 1. Result of The Catalyst Analysis using SAA

Sample	Wide Area (m ² /g)	Pore Diameter (Å)	Pore Volume (cc/g)
γ -Al ₂ O ₃	231.08	100.43	0.58
CoMo/ γ -Al ₂ O ₃	175.49	98.95	0.52
Specification	140-300	50-200	0.4-1.0

The surface area of the catalyst will affect its activity. The more wider surface area of a catalyst, the more the active phase is spread, so that it will increase the activity of the catalyst and increase product activity [15]. Table 1 shows a comparison between γ -Al₂O₃ and CoMo/ γ -Al₂O₃ which resulted in a significant conversion reduction of 24% for surface area, 1.5% for pore diameter, and 10.3% for pore volume. This is possible because the active metal impregnated into the γ -Al₂O₃ support reduces

the SAA analysis produced by the catalyst. According to Hensley et al.'s [16] specifications, a good surface area for the catalyst used for the hydrodesulfurization process is 140–300 m²/g, the pore diameter is 50–200 Å, and the pore volume is 0.4–1.0 cc/g. Based on Table 1 and the results of the analysis using the SAA instrument, the CoMo/ γ -Al₂O₃ catalyst produced meets specifications because it has a surface area of 175.49 m²/g, a pore diameter of 98.95 Å and a pore volume of 0.52 cc/g.

3.2. Result of X-ray Diffraction Analysis

The X-ray diffraction (XRD) is an instrument used to analyze crystalline solids such as ceramics, metals, electronic materials, geological materials, organics, and polymers. The crystal size of the active core compound and the buffer in the catalyst samples

formed can also be calculated using XRD analysis [16]. The principle of the test is that there are 3 components, namely the detector, sample, and X-ray. When X-rays are fired, the scattering electrons will hit the surface of the crystal so that the crystal plane will refract X-rays that have a wavelength equal to the distance between the lattices in the crystal. The refracted light will be captured by the detector and then interpreted as a diffraction peak. The more crystal fields contained in the sample, the stronger the resulting intensity of refraction [17]. The sample tested in this study was a CoMo/ γ -Al₂O₃ catalyst with a visible crystalline phase. This analysis was tested using an XRD instrument. The catalyst diffraction pattern is shown in Figure 1.

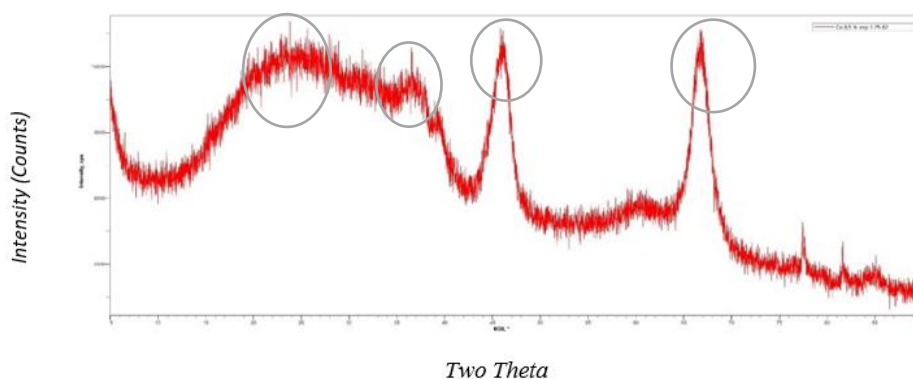


Figure 1. Results of CoMo/ γ -Al₂O₃ Catalyst Diffraction Patterns

The characterization of crystal properties using an X-ray diffractometer is intended to identify the phase of a catalyst and determine the crystalline properties, or crystallinity, of the catalyst. The more peaks and peaks a catalyst has after being analyzed using XRD, the more crystalline the compound is [18]. The crystallinity of the CoMo/ γ -Al₂O₃ catalyst was examined using an XRD instrument to see the peaks of the Mo metal dispersion. According to Abboudi et al. [19], the specific peaks of MoO₃ metal dispersions at 2θ are around 23°, 25°, and 27° (marked with yellow circles in Figure 1). In general, the main peak of γ -Al₂O₃ is at the diffraction angle (2θ) at 35–50° and 60–70° [20].

Based on the experimental results shown in Figure 1, the catalyst crystal phase analysis shows very significant peaks between the angle ranges 35–40°, 45–47°, and 65–69° (marked with green circles in Figure 1), which indicates the presence of γ -Al₂O₃ compounds in the catalyst tested. In this experiment,

γ -Al₂O₃ was used as a buffer because it has a high melting point and can withstand temperatures of up to 750 °C. The support is a solid phase where the active metal is spread, which aims to place the active metal in it so that it is perfectly dispersed. The results from the peak XRD instrument for metal content (MoO₃ and CoO) were not visible because the phases used were different from the support, namely the solid phase and the liquid phase. Therefore, the impregnation solution absorbed by the support is perfectly dispersed, and no agglomeration forms on the synthesized CoMo/ γ -Al₂O₃ catalyst. In addition, the absence of visible Co and MoO₃ metal peaks could be due to the fact that the active metal components have spread evenly into the support pores during the impregnation process, so this catalyst is good for use in the hydrodesulfurization process. However, if a catalyst agglomeration forms, the performance of the catalyst will suffer because the active components are not evenly distributed in

the pores of the catalyst, making it difficult to sulfide.

3.3. Result of X-ray Fluorescence Analysis

The X-ray fluorescence (XRF) is an instrument used to identify and determine the concentration of an element or an element contained in a sample. The working principle of XRF analysis is based on the collision of atoms on the surface of the sample with X-rays. If the primary X-ray excitation occurs from the X-ray tube or radioactive source and hits the sample, the X-rays can be absorbed or scattered by the material. The process by which x-rays are absorbed by atoms by transferring their energy to electrons in deeper shells is called the photoelectric effect. During this process, if the primary x-rays have enough energy, electrons will move from the inner shells to create vacancies. This vacancy results in an unstable state of the atom. When the atom returns to a stable state, electrons from the outer shell move to the deeper shells, and this process produces a certain amount of x-ray energy [21]. The results of the qualitative analysis are shown by the spectral peaks, which represent the types of elements according to their characteristic X-ray energy, while the results of the quantitative analysis are obtained by comparing the intensity of the sample with the standard. In the quantitative analysis, the factors that influence the analysis include the material matrix, vacuum conditions, and the concentration of elements in the material [22].

The XRF instrument was used to determine the metal content of the CoMo/ γ -Al₂O₃ catalyst. The metal content of molybdenum (Mo) and cobalt (Co) affects the activity of the catalyst for the process of removing sulfur, nitrogen, oxygen, or other metals (hydrotreating). Table 2 shows the active metal content of the CoMo/ γ -Al₂O₃ catalyst.

Table 2. Active Metal Content of The CoMo/ γ -Al₂O₃ Catalyst

Sample	CoO Level (% w/w)	MoO ₃ Level (% w/w)
Target	0.50	20.00
CoMo Catalyst	0.55	7.82

The results of the research and analysis in Table 2 show that the catalyst CoMo/ γ -Al₂O₃ has

metal contents of MoO₃ and CoO of 7.82 % w/w and 0.55 % w/w, respectively. These results exceeded the levels of the targeted catalyst, namely the CoMo/ γ -Al₂O₃ catalyst with a concentration of 0.5 % w/w CoO. This happens because the CoO metal impregnation solution that enters the support is perfectly dispersed. Meanwhile, the MoO₃ level produces a level that is quite far from the predetermined concentration, which is 7.82 % w/w MoO₃ from the target concentration, which is 20 % w/w. The amount of metal that enters the support is influenced by the support itself, one of which is the calculation of water pick-up (WPU), or where the ability of the support to absorb water can be calculated and can also be seen from the results of reading the SAA instrument, which can determine the surface area, pore volume, and pore diameter of the buffer. Supports that have a large pore volume can absorb more active metal solutions. Besides that, when the active metal is absorbed into the support, there is competition between CoO and MoO₃ metals, which results in the effectiveness of one of the metals being lower.

3.4. Analysis of Catalyst Performance in Removing Sulfur Compounds

To produce Ultra Low Sulfur Diesel (ULSD), the HDS reaction was carried out in this experiment using a PID microreactor, which produced a liquid product that was further characterized using a Total Sulfur Analyzer (TSA). The working principle of this instrument is that the sample is injected into the instrument and will enter the furnace room. In that room, the sulfur present in the sample will be oxidized with O₂ so that it will form SO₂, which will enter the detector and calculate the electrical signal [23]. This experiment was carried out using a hydrodesulfurization process to produce a feed with a low sulfur content, namely racing fuel with an initial sulfur content of 212.29 mg/L. The product resulting from the hydrodesulfurization process was analyzed using a Total Sulfur Analyzer (TSA). The Conversion value and the sulfur content of the products are calculated and presented in Figure 2.

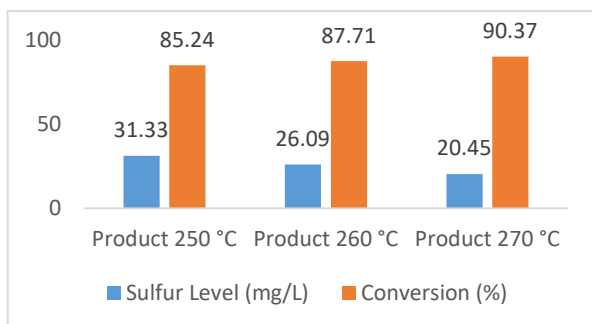


Figure 2. Conversion Value and Sulfur Content based on Temperature Variations

Based on the graph that has been presented, it can be seen that the sulfur content decreased significantly before and after the catalyst was operated into the reactor, with a resulting conversion of 90.37%. From the results of reading the sulfur content of the TSA tool, it shows that the higher the temperature during operation, the greater the decrease in sulfur content will be. This shows that temperature affects the reaction; the higher the temperature, the faster the reaction will take place. Arrhenius' law states that an increase in temperature causes an increase in energy, so that the kinetic energy of the molecules will increase. As a result, the reacting molecules become more active, allowing the collision to take place [24]. Performance test temperatures of 250 °C to 270 °C showed a good reduction in sulfur content and exceeded that of the feed used. However, these results do not fit the 5-euro standard that has been set, which is below 10 mg/L [5]. This means that the catalyst does not work optimally in the hydrodesulfurization process.

Basically, the CoMo catalyst plays an important role in the hydrodesulfurization process. The Co promoter has a tendency to take the hydrodesulfurization pathway first and then be replaced by the hydrogenation process [7]. However, in this experiment, there was an inhibition of the hydrodesulfurization process because the feed used contained a lot of olefins and the acidity of the buffer was more dominant, which caused the formation of cyclic and aromatic bonds. So the CoMo catalyst takes the hydrogenation path first and then enters the hydrodesulfurization process, which causes the sulfur content produced by the catalyst not to decrease significantly. CoMo catalysts with feeds that are rich in olefin content cannot work optimally in the sulfur removal process.

3.5. PIONA Analysis on Products

Chromatography is a separation method based on the distribution of analytes in the stationary and mobile phases. In this experiment, GC-DHA was used quantitatively to measure the PIONA content in the feed and the resulting product. The principle used by this instrument is that the sample is introduced into a gas chromatograph equipped with an open-tube capillary column that is coated with a specified stationary phase. Samples in the form of gas or vapor are injected and then carried by helium carrier gas to the column, where the hydrocarbon components present in the sample are separated based on their interaction strengths with the stationary phase in the column and based on their boiling points so that the sample components will reach the detector at different times. Based on this research, the PIONA data reading results were obtained from the products that had been tested in the reactor which can be seen in Figure 3 below.

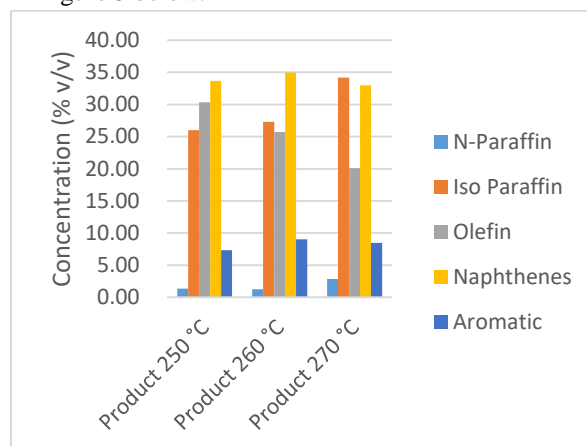


Figure 3. The PIONA Analysis Result using GC-DHA

The results read from the GC-DHA instrument were in percent volume units obtained for 2 variables, with the independent variable being temperature and the dependent variable being PIONA data (n-paraffin, iso-paraffin, olefin, naphthenes, and aromatics). Based on these data, it can be seen that a very significant decrease occurred in the olefin content and a very significant increase occurred in the naphthene content. In the Euro 5 standard specifications [5], the maximum olefin content is 10 (% v/v), and the aromatic content is 35 (% v/v). Therefore, the results of the analysis of the GC-DHA test for the content of olefins did not meet the Euro 5 standard specifications, while the analysis of the results of the aromatic content met the Euro 5

standard specifications in all operating conditions (Table 3).

Table 3. The PIONA Analysis Result using GC-DHA

Product	N-Paraffin (% v/v)	Iso Paraffin (% v/v)	Olefin (% v/v)	Naphthenes (% v/v)	Aromatic (% v/v)
Feed	3,32	24,19	60,68	7,69	3,38
250 °C	1,37	26,00	30,34	33,67	7,34
260 °C	1,27	27,31	25,69	34,98	9,05
270 °C	2,83	34,16	20,07	32,98	8,47

The feed used in this reactor test experiment is racing fuel, which is made by a catalytic cracking process in which oil is cracked without the aid of hydrogen gas. Therefore, the olefin content in the feed has a high level. In addition, the feed used has been stored for 2 years, so the RON (research octane number) value in the bait has also decreased dramatically. Hydrodesulfurization is how cobalt-active metal-based catalysts work. This hydrodesulfurization reaction undergoes two kinds of reactions, namely direct hydrodesulfurization and hydrogenation. The hydrogenation process is the addition of hydrogen to the double bonds of the oil's carbon chain so as to reduce the unsaturation in the oil. In the hydrogenation reaction, there is a change in the double bond to be bonded with hydrogen gas. The reaction produced by the CoMo catalyst with the olefin content in the feed is as follows (Figure 4.):

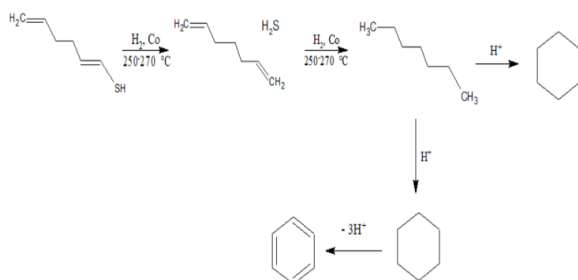


Figure 4. The Reaction of CoMo Catalyst with Olefin

Based on the reaction mechanism, it can be seen that the CoMo catalyst carries out the hydrodesulfurization process through the direct hydrodesulfurization stage so that the olefin content contained in the feed binds sulfur directly, and then in the presence of hydrogen gas and a cobalt metal catalyst at a temperature of 250–270 °C, the reaction will produce released H₂S and olefin. Furthermore,

the olefin will react again with hydrogen gas and a metal catalyst at a temperature of 250–270 °C, which will release the double bond because the double bond is a weak bond and can be easily released to produce an alkane or paraffinic compound. This is evidenced by the results of the analysis of the compound content in the product and feed, where it was found that the olefin compound (O₂₈) in the feed was high, at around 11.84 % v/v. However, the product content produced does not contain olefin (O₂₈), which has been replaced by the formation of 2,3-dimethylpentane, which increases with every increase in temperature in the product produced.

The resulting reaction is an unfinished reaction mechanism, meaning that the process of removing sulfur is hampered because the catalyst used is cobalt, which prioritizes the hydrogenolysis reaction, namely the reaction of carbon-carbon single bonds experiencing breakdown by hydrogen gas. In this process, the reaction proceeds with two kinds of reactions directly, namely the removal of the high olefin content and also the process of removing sulfur. However, because the active metal used in this experiment is cobalt, which prioritizes hydrogenolysis reactions over hydrogenation reactions (Ni), when these two reactions occur simultaneously, the active metal cobalt with a concentration of 0.5 % w/w is less strong at resolving olefins and sulfur simultaneously.

Furthermore, during the process of forming naphthenes, this alkane compound reacts with an acidic support. Because the chemical nature of γ -Al₂O₃ is identified with an acidic center, this acidic buffer has a significant influence. The types of acid centers that appear on the surface of the supports are Lewis and Bronsted acids. This Lewis acid is required in the hydrodesulfurization process because it acts as an electron acceptor, allowing the sulfur group to be withdrawn, whereas Bronsted acid breaks the double bond during the hydrodearomatization process [25].

Table 4. Differences in The Conversion of Product Content

Research	Olefin Conversion (%)	Sulfur Conversion (%)	Naphthene Conversion (%)	Aromatic Conversion (%)
Our Research	66.92	90.37	330.17	150.59
Istanto's Research [27]	90.21	100.00	151.10	195.56

Anazia's research [26] stated, it is feared that too high a buffer acidity will tend to produce a cracking reaction and will lead to a breaking reaction so that it can direct the reaction towards the formation of aromatics, making it less appropriate for the hydrodesulfurization process because it will reduce conversion. Based on the experiments that have been mentioned, the high acidity of the buffer tends to direct the reaction towards the formation of aromatics, as can be seen in the reaction mechanism that has been shown. Alkane compounds will react with the acidity of the buffer, which will produce naphthenes and aromatic bonds. Two reactions occur in the formation of naphthenes, namely when the alkanes meet with acids from the support and when the alkanes form aromatic compounds, which initially produce naphthenes compounds first, and then these naphthenes compounds will be dehydrogenated to form aromatic compounds. This is also strengthened by the content of converted naphthenes and aromatics in the product that can be seen in table 4.

Based on the results of the analysis (Table 4), the content of olefins decreased from the feed with a conversion of 66.92% and the sulfur content decreased with a conversion of 90.37%. This conversion is very different, which means that the active metal cobalt is difficult to convert in feeds with high olefin compounds. While the content of naphthenes decreased with a conversion of 330.17% and aromatic compounds with a conversion of 150.59%. Based on these results, it is clear that the conversion of naphthenes compounds is two times greater than that of aromatic compounds. Based on the data and reaction mechanism that have been mentioned (Figure 4), it can be seen that the metal content present in the catalyst is unable to balance the acid content present in the support, so that the metal content, which should react to form alkane bonds (paraffin) and hydrodesulfurization, is hampered by the acidity of the catalyst. The dominant buffer dominates the reaction. Based on the reaction mechanism, it can also be seen that the reaction is not complete in terms of removing olefin and sulfur content.

When compared to research by Istanto [27] using a NiMo/ γ -Al₂O₃ catalyst with the same reactor dimensions and catalyst mass, the conversion of the CoMo catalyst was lower than that of the NiMo catalyst. This low conversion occurs due to the shorter residence time required to complete reactions such as hydrodesulfurization and olefin decontamination. This is because the activity of catalysts with the active metal cobalt is disrupted due to the presence of high levels of olefins. The residence time of a catalyst is required for a reaction process in the reactor volume used at a certain

temperature. So that the longer the residence time of a catalyst in the reactor, the more perfect the resulting reaction will be. The ability of the active metal, cobalt, is inferior to the acid present in the support, meaning that the number of moles of acid present in the support is higher than the number of moles of cobalt. This is also strengthened in the voltaic series produced by the element Co, where, compared to Ni, the Co element is more negative, so when it meets hydrogen gas (+), the cobalt bonds will bind hydrogen gas strongly.

In the research by Istanto [27], which states that the active metal nickel is better than the active metal cobalt in the hydrogenation process, the same feed and using the catalyst NiMo/ γ -Al₂O₃ managed to significantly reduce the levels of olefins and sulfur by conversion, which can be seen in Table 3. The olefin content is 90.21% and the sulfur content conversion is 100.00%. This reinforces the fact that the active metal cobalt is not good at the hydrogenation process and is not appropriate if you have to carry out two reactions simultaneously, namely removing olefins and sulfur. However, for the NiMo/ γ -Al₂O₃ catalyst, the reaction has almost the same conversion difference, so the NiMo/ γ -Al₂O₃ catalyst can carry out two reactions at once. The conversion of naphthenes content in the NiMo/ γ -Al₂O₃ catalyst was 151.10%, while the conversion of aromatic content was 195.56%. This results in a reaction mechanism that runs perfectly, the conversion of the naphthenes content which is lower than the aromatic content makes it possible that this reaction occurs where a portion of the naphthenes content has undergone a dehydrogenation process to become aromatic.

Aromatic compounds are good hydrocarbon compounds with increasing octane numbers. Therefore, if the fuel mixture contains aromatic compounds, the fuel will have a high octane rating [28]. However, in this experiment, the results read by the GC-DHA instrument are shown in Table 5.

Table 5. RON Value Analysis Results

Product	RON Value
Feed	86.980
Product 250 °C	81.279
Product 260 °C	80.466
Product 270 °C	79.546

The Regulation of the Minister of Environment and Health of the Republic of Indonesia states that the minimum RON value is 91, and the Decree of the Ministry of Energy and Mineral Resources states that the minimum RON value is 90 [3-4]. High aromatic compounds can produce good RON values [28]. The emission standard specifications according to Euro 5 state that the minimum RON value is 95 [5], so that you can see the RON value read from the GC-DHA instrument in Table 5, stating that the resulting RON value has decreased from the initial feed and does not meet emission standard specifications. Euro 5 [5] and the Decree of the Government of the Republic of Indonesia [3-4]. This happens because the content of olefin compounds in the feed decreases significantly at each temperature variation and will affect the RON value contained in the resulting product. The content will decrease because the olefin content is directly proportional to the RON value. The product's aromatic content has increased, but the amount of aromatics is two times lower than the amount of naphthene compounds, so the RON value obtained will also decrease.

It has been stated that high aromatic compounds can produce good RON values, but reduced olefin compounds are the reason for the decreased RON value in the resulting product. This is corroborated because the active metal, cobalt, has a lower activation energy in the hydrogenation process than catalysts based on nickel metal [29]. The reaction rate constant of the active metal cobalt is 0.30×10^{-4} m³/mol. This was demonstrated by the findings of the Lylykangas study [29], which found that after 30 hours of hydrogenation, 80% of the Ni metal-based catalyst remained active, whereas only 55% of the active compound remained in the Co-based catalyst. This shows that the cobalt-based catalyst is not good for the hydrogenation process. However, in this experiment, the feed used was rich in olefin content, causing the CoMo catalyst to be inhibited in the hydrodesulfurization process.

4. Conclusion

From this study, it can be concluded that the synthesized CoMo/ γ -Al₂O₃ catalyst has a wide area of 175.49 m²/g, a pore diameter of 98.95 Å, and a pore volume of 0.52 cc/g. The active metal content of the CoMo/ γ -Al₂O₃ catalyst produced based on XRF analysis is 0.55 % w/w for CoO content and 7.82 %

w/w for MoO₃ content. CoMo/ γ -Al₂O₃ catalyst products can reduce the sulfur content produced to 31.33, 26.09, and 20.45 mg/L at various temperatures of 250 °C to 270 °C. These results were still below the Euro 5 standard, namely 10 mg/L at a concentration of 0.5 % w/w, and also did not obtain optimal temperature variations for the hydrodesulfurization process, resulting in a decreased RON value from the feed used. Although a CoMo/ γ -Al₂O₃ catalyst containing 0.5 mol (w/w) cobalt metal cannot balance the acidity of the support, the resulting reaction mechanism is more dominant in producing side reactions in the form of olefin cyclization, increasing the naphthenes content in the product.

5. Conflict of Interest

There are no conflicts to declare.

6. Acknowledgment

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