

## Effect of Ni-Co Ratio on the ZSM-5 Catalyst Performance during Catalytic Hydrocracking of Palm Oil for Biofuel Production

I. Istadi<sup>1,2,\*</sup>, Teguh Riyanto<sup>2,3</sup>, Astrid Eka Permatasari<sup>1</sup>, and Daniella Cipta Dinara<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, Faculty of Engineering, Universitas Diponegoro  
Jl. Prof. Soedarto, SH, Tembalang, Semarang

<sup>2</sup>Laboratory of Plasma-Catalysis (R3.5), Center for Research and Services of Integrated Laboratory - Diponegoro  
University (CORES-DU), Universitas Diponegoro, Semarang, Central Java 50275, Indonesia.

<sup>3</sup>Industrial Chemical Engineering Technology, Vocational College, Universitas Diponegoro, Semarang, Central Java  
50275, Indonesia.

\*) Corresponding author: [istadi@che.undip.ac.id](mailto:istadi@che.undip.ac.id)

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### Abstract

*ZSM-5 catalysts are essential for the hydrocracking of palm oil into biofuel due to their unique structural and acidic properties. However, the challenge remains in optimizing the catalyst's composition to enhance product yield and selectivity while minimizing undesirable by-products. Their effectiveness can be further improved through modifications, making them a versatile and promising option for biofuel production from palm oil. Therefore, this study investigates Ni-Co/ZSM-5 catalyst with Ni-Co metal ratios of 1:0.5, 1:1, and 1:1.5 to examine their effects on the catalyst characteristics and performance in the hydrocracking process of palm oil into biofuel. The catalyst synthesis was carried out using the co-impregnation method with ultrasound assistance, followed by characterization using XRD and XRF. The hydrocracking process was conducted at a temperature of 450 °C and a Weight Hourly Space Velocity (WHSV) of 0.1 min<sup>-1</sup>, while the gas product was analyzed using GC and the liquid product was distilled. The XRF results showed that the actual Ni-Co ratio did not significantly differ from the designed ratio. Furthermore, the XRD analysis indicated the occurrence of crystal agglomeration at a 1:1.5 ratio due to the competition between the Ni and Co metal particles diffusing into zeolite pores, as well as the presence of dislocations and crystal defects. Differences in the catalyst characteristics resulted in the variations in yield, selectivity, and gas distribution in the hydrocracking process. The catalyst with a Ni-Co ratio of 1:1.5 exhibited the highest liquid product yield and biogasoline selectivity, but also produced a higher concentration of CO, CO<sub>2</sub>, and C<sub>2</sub> gases. It is associated with the breakdown of triglycerides into fatty acids, which subsequently fragment into shorter-chain biofuel components.*

**Keywords:** nickel; cobalt; ZSM-5; hydrocracking; palm oil; biofuels

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## INTRODUCTION

The increasing global population and industrialization have led to a surge in energy demand, particularly for fuel oil. This trend has raised concerns about the long-term sustainability of fossil fuel consumption and its detrimental effects on the environment. As fossil fuel reserves dwindle and climate change becomes an increasingly pressing issue, the need for alternative, renewable energy sources has become more urgent than ever. Biofuels, especially those derived from vegetable oils, have emerged as a promising solution to address these challenges.

Palm oil-based biofuels have garnered significant attention, particularly in Indonesia, where palm oil production is abundant. This renewable energy source offers several advantages over traditional fossil fuels. Biofuels are renewable, meaning they can be replenished within a human lifetime, unlike fossil fuels that take millions of years to form. Additionally, biofuels are generally more environmentally friendly, as they produce fewer greenhouse gas emissions during combustion compared to fossil fuels (Kurniawati *et al.*, 2022). The potential for biofuels to reduce overall carbon dioxide emissions and mitigate climate change makes them an attractive option for countries seeking to transition towards more sustainable energy sources. Furthermore, the development of a robust biofuel industry could provide economic benefits, including job creation and reduced dependence on imported fossil fuels.

The conversion of palm oil into biofuel can be done through cracking methods such as thermal cracking, pyrolysis, catalytic cracking, plasma-assisted catalytic cracking, and hydrocracking (Riyanto *et al.*, 2020, 2021). Hydrocracking is preferred as it produces high yields of biofuel, such as gasoline, by breaking down long-chain hydrocarbons (Hasanudin *et al.*, 2022). Hydrocracking reactions include decarboxylation, decarbonylation, and dehydrocarboxylation, which remove oxygen from triglycerides and produce hydrocarbon fuels. Catalysts play a crucial role in hydrocracking by reducing acid value and oxygen concentration, thereby improving biofuel quality (Febriansyar *et al.*, 2022).

ZSM-5 as a catalyst in the hydrocracking process can be impregnated with certain metals to increase its working function into a bifunctional catalyst due to the function of the impregnated metal and the carrier as a catalyst. The impregnation of Ni and Co with a certain ratio functions as a Lewis acid site and the active ZSM-5 acts as a Bronsted acid site (Sumari *et al.*, 2019). The part that can accept electron pairs is the Lewis acid site while the Bronsted acid site can donate protons (Riyanto *et al.*, 2021). The Lewis acid site in ZSM-5 functions in cracking branched chain reactants, carrying out cracking with dehydrogenation, and carrying out cracking and dehydrogenation to produce olefin compounds. In contrast to the Bronsted acid site in the ZSM-5

catalyst, it functions in cracking straight chain reactants, reducing coke in the cracking process, and converting cycloalkanes resulting from the Lewis acid site conversion in the dehydrogenation-aromatization process into aromatic compounds. As a result, the process at the Bronsted acid site reduces coke in the process, while the Lewis acid site produces more coke in the process due to dehydrogenation on the catalyst (Riyanto *et al.*, 2021).

Metal impregnation on the ZSM-5 catalyst to produce biofuels via hydrocracking process has been widely carried out. The impregnation aims to increase the selectivity of the resulting hydrocarbon products. Hydrocracking with the ZSM-5 catalyst with metal impregnation in a certain ratio has been proven to produce biofuel. According to Al-Muttaqii *et al.* (2019), the hydrocracking process of coconut oil with the HZSM-5 catalyst with Ni-Fe impregnation produced n-paraffine of 39.24%. Meanwhile, Mirzayanti *et al.* (2017) reported that the hydrocracking process of kapok seed oil with the Zn-Mo/HZSM-5 catalyst produced 35.51 area% of n-paraffins and the highest content for gas oil-range alkanes was 17.24 area% at 400 °C. In addition, Istadi *et al.* (2023) reported the simultaneous cracking-deoxygenation process of palm oil using Ni-Co catalyst on ZSM-5 resulted in a triglyceride conversion of 76.5%. Nickel in the catalyst has the main function of increasing the activity of the catalyst and promotes the deoxygenation of palm oil into liquid fuel. Cobalt can reduce the formation of coke produced by Ni metal on the ZSM-5 catalyst, which excessive amount of coke on the catalyst will reduce the activity of the ZSM-5 and can reduce the occurrence of carbon deposition (Estephane *et al.*, 2015; Istadi *et al.*, 2023).

In the previous studies, the incorporation of Ni and Co on ZSM-5 catalyst for hydrocracking process of palm oil into biogasoline has good performance because of the properties of Ni-Co which can increase the acidity of the catalyst and reduce the basicity of the catalyst. However, the effect of Co metal on the Ni/ZSM-5 catalyst is still unclear. Therefore, further research was conducted on the impregnation of Ni-Co metal on ZSM-5 in the hydrocracking process to process palm oil into biofuel in the form of gasoline. In this study, the effect of Co metal on the properties of the Ni-Co/ZSM-5 catalyst was studied to determine its effect on the crystallite sizes and its performance in converting palm oil into gasoline.

## MATERIALS AND METHODS

### Materials

The zeolite utilized in this research was commercial ZSM-5 (CBV 8014), sourced from Zeolyst International. Nickel (II) nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and Cobalt (II) nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) as precursors were obtained from Merck. The feedstock used in the hydrocracking process to evaluate the catalyst performance was palm oil. Nitrogen ( $\text{N}_2$ ) (UHP) gas was used as the flushing

agent for the hydrocracking apparatus prior to the hydrocracking process, while hydrogen ( $H_2$ ) (UHP) gas was employed during the hydrocracking reaction.

### Catalysts Synthesis

The synthesis of the NiO-CoO/ZSM-5 catalyst was carried out using the co-impregnation method, assisted by ultrasound stirring. Nickel ( $Ni(NO_3)_2 \cdot 6H_2O$ ) and cobalt ( $Co(NO_3)_2 \cdot 6H_2O$ ) precursor metals were dissolved in ethanol with a total volume of 200 mL. Subsequently, Ni and Co were dispersed onto the surface of 20 grams of ZSM-5 with the aid of ultrasound. The Ni content impregnated with the Ni-Co catalyst was fixed at 10% wt., while the Co content was varied at 5%, 10%, and 15% wt. The ultrasonic generator operated at a power of 400 W, and the ultrasonic wave radiation was applied for 1 hour. The resulting material was then dried at 100°C for 18 h before being calcined at 550°C for 4 h (Istadi et al., 2023). Finally, the catalyst was shaped into pellets and crushed with a size range of 1 – 1.18 mm.

### Catalysts characterization methods

X-Ray Diffraction (XRD) analysis was used to identify crystalline materials, such as crystal structure and crystal phase. The XRD analysis was performed using an XRD analyzer (SHIMADZU XRD-700) with Cu-K $\alpha$  radiation ( $\lambda = 1.504056 \text{ \AA}$ ), operated at 30 mA and 30 kV. The powdered sample was scanned within a  $2\theta$  range of 5° to 90° at a scanning speed of 2°/minute, with the data were recorded at every 0.02°. The resulting diffractogram was compared with data from the Joint Committee on Powder Diffraction Standards (JCPDS) to determine the crystalline compounds and crystal phases present in the catalyst. Meanwhile, X-ray Fluorescence (XRF) analysis was used to determine the composition and concentration of solid components in the analyzed catalyst material.

The XRF analysis was performed using Rigaku Supermini200.

### Catalysts Performance Test

A carefully prepared 5 grams of catalyst was filled into the fixed-bed cracking reactor (Figure 1) and fixed using glass wool layers on both ends for catalytic cracking test. Prior to pumping of palm oil into the fixed-bed catalytic reactor, all equipment was flushed by flowing UHP Nitrogen Gas ( $N_2$ ) at 100  $cm^3/min$  at 350°C to remove residual oxygen in the system before the reaction commenced. The reactor temperature was maintained at 450°C. Palm oil, used as the feedstock, was introduced into the reactor using a peristaltic pump at a weight hourly space velocity (WHSV) of 0.1  $min^{-1}$ , calculated by Equation (1).

$$WHSV \text{ (} min^{-1} \text{)} = \frac{v \times \rho_{oil}}{m_{cat}} \quad (1)$$

where  $v$  represents volumetric flowrate of palm oil (ml/min),  $\rho_{oil}$  represents the palm oil density (g/ml), and  $m_{cat}$  represents the catalyst amount (g)

The gaseous phase products formed during the reaction were directed to a condenser, where they were condensed, while a portion was collected in a sampling bag for gas chromatography (GC) analysis. The liquid biofuel product obtained from the cracking process was collected for further analysis. For analytical purposes, biofuel samples were withdrawn within the first 2 h after the system reached steady-state conditions, assuming steady-state was achieved within 30 min.

To determine the product yield obtained from the hydrocracking process from palm oil, Equation (2) was employed.

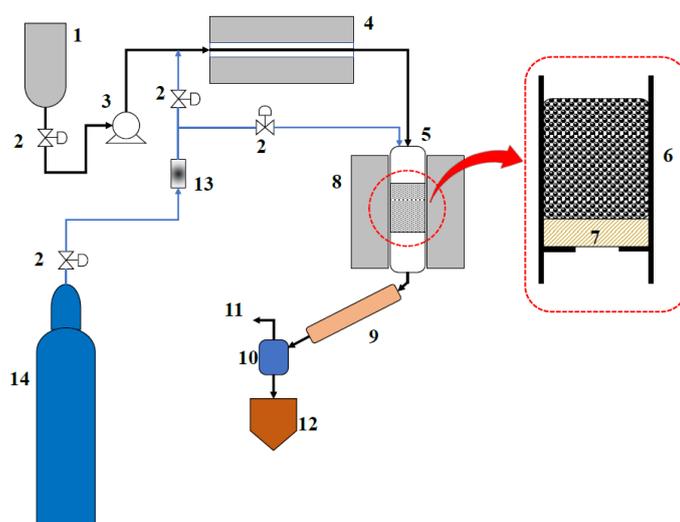


Figure 1. Schematic diagram of experimental set up of the continuous catalytic cracking process : (1) Palm oil feedstock tank, (2) Gate valve, (3) Peristaltic pump, (4) Preheater, (5) Reactor tube, (6) Catalyst packing , (7) Glass wool, (8) Electric heating furnace as reactor heater, (9) Condenser, (10) Gas-liquid separator, (11) Gas by product, (12) Liquid fuels product, (13) Gas flowmeter, (14) Nitrogen (UHP) gas tank

$$\text{Yield (\%)} = \frac{m_i}{m_{feed}} \times 100\% \quad (2)$$

In this equation, *Yield (%)* represents the yield of liquid, coke, or the gas product,  $m_i$  represents the mass of liquid, coke, or the gas product,  $m_{feed}$  represents mass of the palm oil used as the feedstock of the process. Meanwhile, the fraction of gasoline, kerosene, and diesel were determined using batch distillation process. The produced liquid biofuels were distilled within the temperature ranges of 25-205 °C for gasoline, 205-310 °C for kerosene, and 310-370 °C for diesel fraction (Istadi et al., 2020).

$$\text{Selectivity (\%)} = \frac{m_i}{m_{liquid\ product}} \times 100\% \quad (3)$$

In this equation, selectivity (%) represents selectivity of gasoline, kerosene, or diesel product,  $m_i$  represents the mass of gasoline, kerosene, or diesel product, while  $m_{liquid\ product}$  represents mass of the total of liquid product produced.

Gas Chromatography (GC) analysis was used to analyze the composition of gases produced from the hydrocracking of palm oil into biofuel. The produced gas was collected using a gas sampling bag and then analyzed using gas chromatography equipped with a Thermal Conductivity Detector (TCD) and a Flame Ionization Detector (FID). The FID functions as a detector for hydrocarbon gas compositions in the sample, while the TCD detects non-hydrocarbon gases such as N<sub>2</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>. Argon is used as the carrier gas in this analysis. The columns used in this GC system are HayeSep Porapak Q and Molecular Sieve.

## RESULTS AND DISCUSSION

### Catalysts Characterizations

#### *Composition of the impregnated metals on catalysts*

Metal composition on the catalyst's active surfaces is a critical factor in determining the catalytic performance. The atomic arrangement of metal atoms on the catalyst's active surfaces, including steps and low-coordination sites, significantly influences its activity and selectivity (Somorjai and Park, 2007; Hendriksen *et al.*, 2010). For these reasons, the metal composition on catalysts should be determined. Table 1 presents the metal composition on the 1Ni-0.5Co/ZSM-5, 1Ni-1Co/ZSM-5, and 1Ni-1.5Co/ZSM-5 catalysts. In addition, the XRF spectra of the catalysts are presented in Figure 2. The peaks

corresponding to Ni and Co elements are clearly visible in them, indicating a higher concentration of Ni and Co in the catalyst composition. This observation aligns with the intended catalyst formulation, where Ni and Co serve as the primary active components for the hydrocracking of palm oil into biofuel.

The XRF analysis of the 1Ni-0.5Co/ZSM-5, 1Ni-1Co/ZSM-5, and 1Ni-1.5Co/ZSM-5 catalysts reveals important insights into their surface composition. The ZSM-5 support is confirmed to be a mixture of silica (SiO<sub>2</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>) structures, which is consistent with the typical composition of zeolite materials (Hamid *et al.*, 2020). The close agreement between the actual and designed Ni/Co ratios in these catalysts demonstrates the precision of the catalyst synthesis method employed. The consistency between the designed and actual Ni/Co ratios is particularly significant for catalytic applications. The results suggest that the metal loading process was highly controlled, allowing for the formation of catalysts with their intended specific metal compositions. This level of control is crucial for studying the effects of different metal ratios on catalytic performance and for optimizing catalyst formulations. However, the presented values in Table 1 were obtained from single measurements, and duplication or triplication was not conducted for these particular experiments; therefore, standard deviations are not available. Furthermore, the presence of both nickel and cobalt in the ZSM-5 support develops the potential for the synergistic effects between the two metals, which could lead to the enhanced catalytic performance in palm oil cracking process. The ability to accurately control the metal composition on the catalyst surface provides a solid foundation for investigating the structure-activity relationships and developing more efficient catalysts for palm oil cracking process.

#### *Crystal structure and crystallite phase of the catalysts*

As discussed previously, metal composition on catalyst surfaces is crucial in determining catalytic performance. Interestingly, the metal composition is not always static during catalytic reactions. Exposure to reactants can cause new structures to form on the catalyst surface, which may dramatically influence the reaction by acting as the catalytically active phase or by poisoning it (Hendriksen *et al.*, 2010). Therefore, the crystal structure or crystal phase of the metals should be determined.

Table 1. The composition of the impregnated metals on catalysts by XRF analysis

| Catalysts       | Metal Composition |      |      |      | Si/Al Ratio | Ni/Co Ratio |        |
|-----------------|-------------------|------|------|------|-------------|-------------|--------|
|                 | Si                | Al   | Ni   | Co   |             | Design      | Actual |
| 1Ni-0.5Co/ZSM-5 | 0.613             | 24.5 | 6.90 | 3.56 | 0.025       | 2           | 1.94   |
| 1Ni-1Co/ZSM-5   | 0.574             | 24.7 | 6.72 | 6.89 | 0.023       | 1           | 0.98   |
| 1Ni-1.5Co/ZSM-5 | 0.725             | 29.1 | 6.14 | 6.14 | 0.025       | 0.667       | 0.658  |

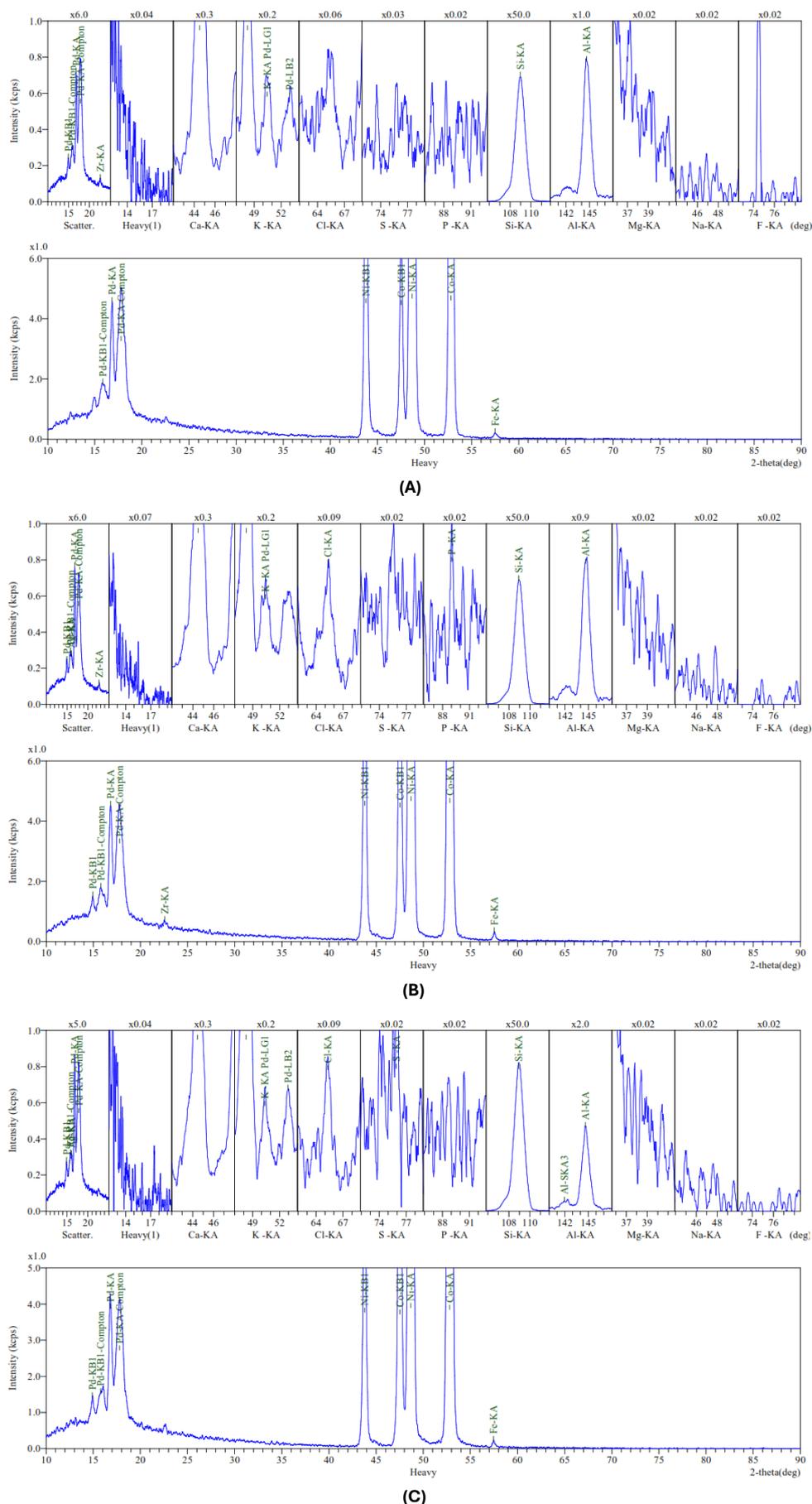


Figure 2. XRF spectra of the catalysts (1Ni-0.5Co/ZSM-5, 1Ni-1Co/ZSM-5, and 1Ni-1.5Co/ZSM-5)

The crystal structure of the synthesized Ni-Co/ZSM-5 catalysts was investigated using XRD analysis. Diffraction patterns were recorded over  $2\theta$  ranges of  $5-90^\circ$ . Figure 2 presents the diffraction patterns of Ni-Co/ZSM-5 catalysts with Ni-Co ratios of 1:0.5, 1:1, and 1:1.5. As tabulated in Figure 2, all catalysts exhibit the characteristic MFI structure, indicated by the presence of intense diffraction peaks at  $2\theta = 23.1^\circ$ ,  $23.24^\circ$ ,  $23.76^\circ$ ,  $23.97^\circ$ , and  $24.46^\circ$ , corresponding to the (501), (051), (151), (303), and (133) planes (COD reference code: 1540267), respectively. Additionally, NiO diffraction peaks appear at  $2\theta = 37.26^\circ$ ,  $43.28^\circ$ , and  $62.84^\circ$ , corresponding to the (111), (002), and (022) planes (COD reference code: 1010381), while CoO diffraction is identified at  $2\theta = 36.77^\circ$  (113) (COD reference code: 1538531). For the Ni-Co/ZSM-5 catalyst with a Ni-Co ratio of 1:1, similar diffraction peaks are observed at  $2\theta = 23.12^\circ$ ,  $23.34^\circ$ ,  $23.76^\circ$ ,  $23.9^\circ$ , and  $24.48^\circ$ , confirming the MFI structure. NiO diffraction peaks appear at  $37.29^\circ$  and  $43.32^\circ$  (COD reference code: 1010093), while CoO diffraction is observed at  $36.74^\circ$  (COD reference code: 1526734). The presence of the characteristic MFI structure in all catalysts, confirmed by the quintet peaks at  $2\theta = 23-25.5^\circ$ , suggests that the primary crystal structure remains consistent across different Ni-Co compositions.

The crystallite phases and sizes of Ni-Co/ZSM-5 catalysts with varying Ni-Co ratios (1:0.5, 1:1, and 1:1.5) exhibit distinct characteristics. The catalysts consist of MFI-phase ZSM-5, bunsenite-phase NiO, and spinel-phase CoO. The crystallite sizes of NiO and CoO vary significantly across the different Ni-Co ratios, with the largest sizes observed in the 1:1.5 ratio for both metal oxides. The crystallite sizes of NiO in the Ni-Co ratios of 1:0.5, 1:1, and 1:1.5 are 30.76 nm,

28.40 nm, and 169.29 nm, respectively. In addition, the crystallite sizes of CoO in the Ni-Co ratios of 1:0.5, 1:1, and 1:1.5 are 25.93 nm, 26.96 nm, and 42.72 nm, respectively. This variation in crystallite size is attributed to the competition between the Ni and Co metal particles as they diffuse into the zeolite pores. In particular, the Ni-Co/ZSM-5 catalyst, with sizes of 169.29 nm and 42.72 nm, respectively, appear larger than those in the Ni-Co/ZSM-5 catalysts with Ni-Co ratios of 1:0.5 and 1:1.

The Ni-Co/ZSM-5 catalyst with a Ni:Co ratio of 1:1.5 demonstrates unique behaviour due to the excess of Co relative to Ni. In this case, the competition between Ni and Co particles leads to pore blockage, which impedes the free diffusion of a significant amount of Co into the zeolite pores. Furthermore, while Co ions have a strong ability to form crystal nuclei, their growth is limited by dislocations and crystal defects. These imperfections hinder the growth of crystal nuclei, even in the presence of a higher Co ratio (Saab *et al.*, 2020). This phenomenon describes the observed differences in crystallite sizes and highlights the complex interplay between metal ratios, particle diffusion, and crystal growth in the Ni-Co/ZSM-5 catalyst system.

#### The Effect of Ni-Co Ratio in Ni-Co/ZSM-5 Catalyst on the Products Yield

Hydrocracking is a vital catalytic process in the petroleum industry, transforming heavy oil fractions and residues into more valuable lighter fractions. This process involves the breaking down of large hydrocarbon molecules into smaller ones under high pressure and temperature conditions in the presence of a catalyst.

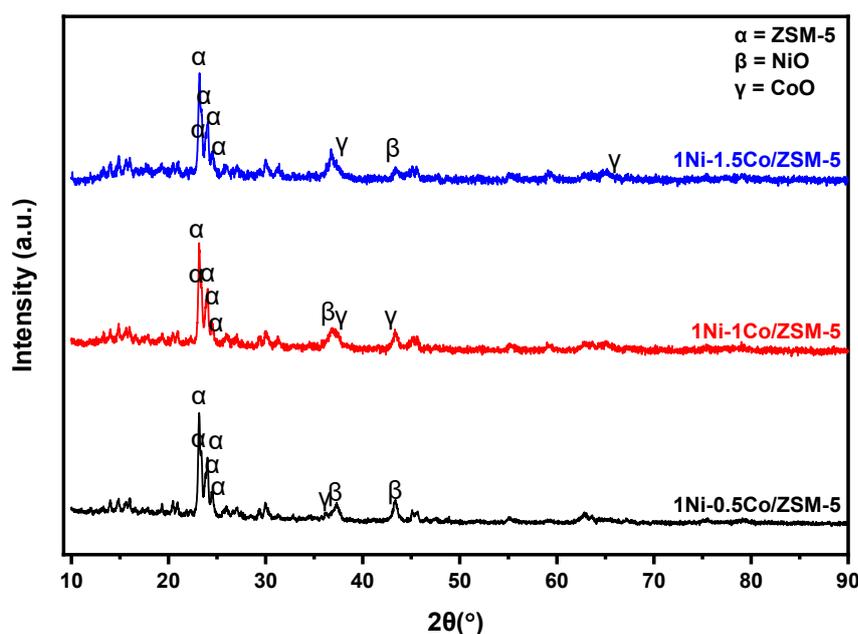


Figure 3. X-ray diffraction (XRD) patterns of Ni-Co/ZSM-5 catalysts with varying metal ratios

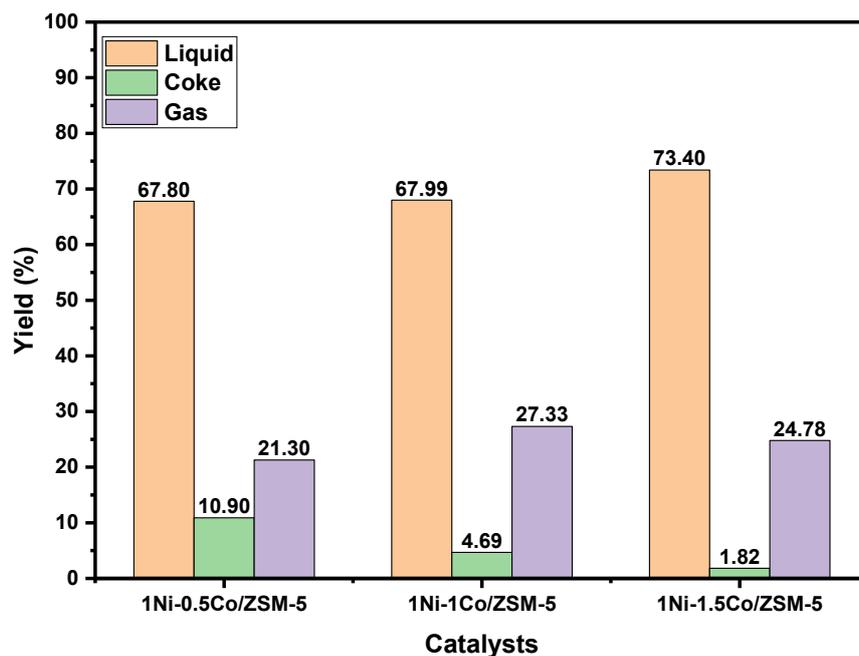


Figure 4. The products distribution of palm oil hydrocracking process using Ni-Co/ZSM-5 catalysts

The resulting products, including gasoline, kerosene, and diesel, are then separated based on their boiling points through a distillation process. The efficiency of this process is crucial for maximizing the yield of desirable products while minimizing the formation of undesirable by-products. In this study, the synthesized catalysts were used to convert palm oil into hydrocarbons through a cracking process. Figure 4 presents the distribution of products obtained from the hydrocracking of palm oil using Ni-Co/ZSM-5 catalysts with varying metal ratios

As seen in Figure 3, the research indicates that increasing the cobalt content in these catalysts leads to enhanced biofuel yield and reduced coke formation. Coke, a carbonaceous deposit that forms on the catalyst surface, is a significant concern in hydrocracking as it can deactivate the catalyst and decrease overall efficiency. The presence of cobalt in the catalyst plays a crucial role in minimizing coke deposition, thereby maintaining catalytic activity and improving biofuel production efficiency. Excessive coke formation is influenced by the excessive activity of Ni metal on the catalyst, which triggers the dehydrogenation reaction, leading to coke deposition that blocks the catalyst pores and reduces product selectivity. Additionally, incomplete reactions during the cracking process also contribute to increasing coke production (Li *et al.*, 2023). This finding highlights the importance of optimizing catalyst composition to achieve better performance and higher yields in hydrocracking processes (Saab *et al.*, 2020; Istadi *et al.*, 2023). Kaewtrakulchai *et al.* (2020) reported that cobalt phosphide (CoP) nanoparticles supported on porous carbon derived from palm male flowers have demonstrated effectiveness in producing green diesel

and bio-jet fuel fractions. It's also reported that the presence of Co on catalyst could reduce the coke formation.

These studies also suggest that the improved performance of Ni-Co/ZSM-5 catalysts with higher cobalt content may be attributed to the synergistic effect between nickel and cobalt, which enhances the catalyst's ability to crack larger hydrocarbon molecules. Furthermore, the increase in cobalt content appears to modify the acidity of the ZSM-5 zeolite support, potentially leading to a more favorable distribution of active sites on the catalyst surface. The data indicates that a higher Co content in the Ni-Co/ZSM-5 catalyst leads to an increase in the biofuel yield while simultaneously reducing the coke formation during the hydrocracking process, this effect occurs because Co plays a crucial role in minimizing coke deposition, which can otherwise degrade the catalyst's performance and reduce biofuel production efficiency (Istadi *et al.*, 2023). Therefore, increasing the amount of Co impregnated into the catalyst enhances biofuel yield by mitigating coke formation and maintaining catalytic activity.

#### The Effect of Ni-Co Ratio in Ni-Co/ZSM-5 Catalyst on the Products Selectivity

The hydrocracking of palm oil yields hydrocarbons with varied carbon chain lengths, categorized into gasoline, kerosene, and diesel fractions. Gasoline consists of C<sub>5</sub>-C<sub>11</sub> hydrocarbons, kerosene consists of C<sub>12</sub>-C<sub>14</sub> hydrocarbons, and diesel contains C<sub>15</sub>-C<sub>22</sub> hydrocarbons (Siregar *et al.*, 2023). However, for broader more technical application purposes, the fraction of gasoline, kerosene, and diesel were determined using a batch distillation process.

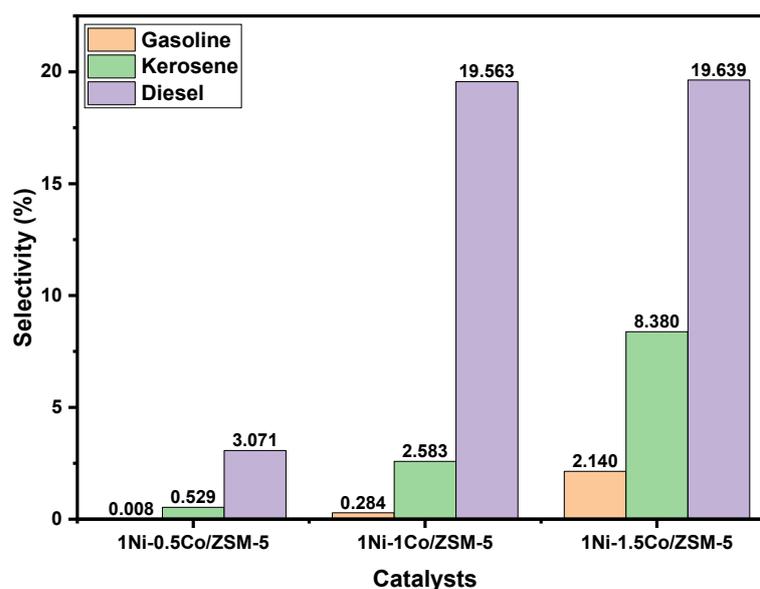


Figure 5. The effect of catalysts type on biofuels selectivity

The resulting liquid biofuels were distilled within the temperature ranges of 25-205 °C for gasoline, 205-310 °C for kerosene, and 310-370 °C for diesel fraction (Istadi *et al.*, 2020). In this study, the influence of Ni-Co ratios (1:0.5, 1:1, and 1:1.5) on product selectivity was investigated using ZSM-5 as the catalyst support. The distribution of biofuel products obtained from the hydrocracking process of palm oil is displayed in Figure 4. The Figure 4 illustrates that the increase of Co content in the Ni-Co/ZSM-5 catalyst enhances the selectivity of biofuels fractions. Although all catalysts exhibit the ability to produce gasoline, kerosene, and diesel; the Ni-Co/ZSM-5 1:1.5 catalyst demonstrates the highest biogasoline selectivity at 2.14%.

The impregnated Co in the Ni-Co/ZSM-5 catalyst plays a crucial role in reducing the coke formation during the hydrocracking palm oil into gasoline. Excessive coke deposition negatively impacts the catalyst's selectivity toward gasoline production (Saviola *et al.*, 2024). As previously discussed, the amount of coke decreases as the Co content on the surface of catalyst increases. Interestingly, as shown in Figure 4, a higher Co content on the catalyst correlates with an increased gasoline selectivity, reinforcing the role of Co in minimizing the coke formation and enhancing overall catalyst performance. Basically, an excessive coke formation is influenced by the excessive activity of Ni metal on the catalyst, which triggers the dehydrogenation reaction, leading to coke deposition that blocks the catalyst pores and reduces product selectivity. Additionally, incomplete reactions during the cracking process also contribute to increasing coke production (Li *et al.*, 2023). Based on the data in Figure 4, a higher Co metal content impregnated into the Ni-Co/ZSM-5 catalyst enhances the selectivity

towards gasoline products. This study is also in agreement with the previous studies. According to Trisunaryanti *et al.* (2020), cobalt metal often has a good propensity for starting cracking reaction. In addition, Istadi *et al.* (2021) also reported that the combination of Ni and Co metals on HY zeolite catalyst could increase the catalyst performance by decreasing the coke formation because of the presence of Co metal.

#### The Effect of Ni-Co Ratio in Ni-Co/ZSM-5 Catalyst on the Gaseous Products

Gas products from palm oil hydrocracking process using Ni-Co/ZSM-5 catalysts were analyzed using gas chromatography with series detectors, Thermal Conductivity Detector (TCD) and Flame Ionization Detector (FID). The non-condensable gases were detected using TCD, while the hydrocarbon products were detected using FID. The gas distribution is shown in Figure 6. The results of GC analysis indicate the presence of CO, CO<sub>2</sub>, and hydrocarbon products, such as ethylene, acetylene, ethane, propylene, propane, C<sub>4</sub>, C<sub>5</sub>, C<sub>6</sub>, methane, and H<sub>2</sub>O, suggesting that multiple reaction mechanisms occur during the hydrocracking process, including decarboxylation (-CO<sub>2</sub>), decarbonylation (-CO), and hydrodeoxygenation (-H<sub>2</sub>O). Decarboxylation involves the removal carbon dioxide, commonly used for the elimination of carboxylic acids, producing CO<sub>2</sub> as a byproduct (Nguyen *et al.*, 2024). Meanwhile, decarbonylation removes a carbonyl group (C=O) from a molecule, releasing CO and generating hydrocarbons with an odd number of carbon atoms with H<sub>2</sub>O as byproduct (Peng *et al.*, 2019). Meanwhile, hydrodeoxygenation results in hydrocarbons formation with H<sub>2</sub>O as a byproduct (Nguyen *et al.*, 2024).

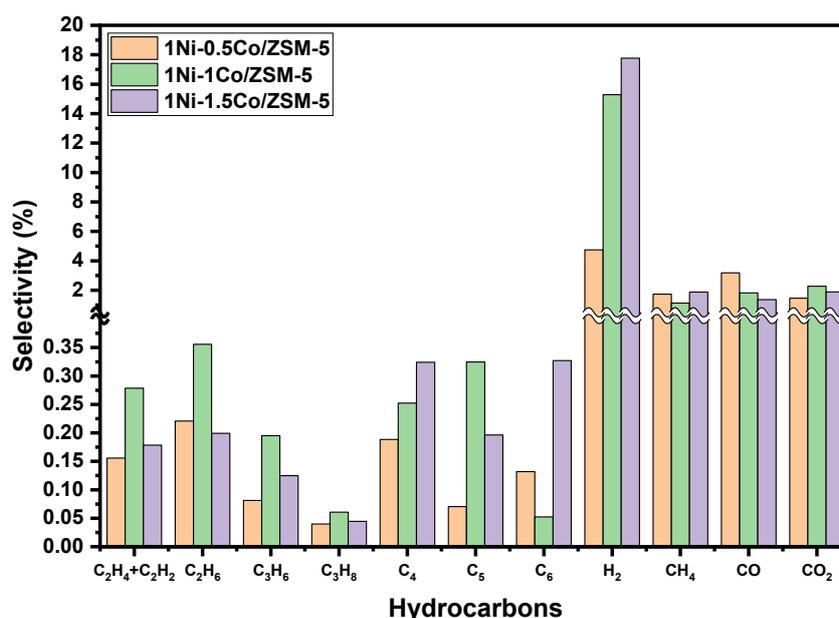
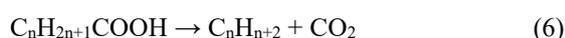
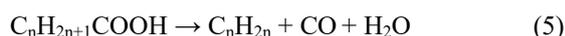


Figure 6. GC analysis results of gas product for Ni-Co/ZSM-5 catalysts with ratios of 1:0.5, 1:1, and 1:1.5

Therefore, the presence of CO<sub>2</sub>, CO, and H<sub>2</sub>O in the gas product proved that decarboxylation, decarbonylation, and hydrodeoxygenation reactions were occurring during the palm oil cracking process. The production of CO and CO<sub>2</sub> during palm oil cracking process involves several complex reactions. CO formation is primarily attributed to two main pathways: decarbonylation and hydrodeoxygenation. In the decarbonylation reaction (Eq. 4), carbonyl groups present in the fatty acid compounds are cleaved, resulting in the release of CO molecules. Hydrodeoxygenation (Eq. 5) is another significant route for CO production, where fatty acid compounds are removed through reaction with hydrogen, yielding CO as a byproduct. CO<sub>2</sub> generation, on the other hand, is primarily associated with the decarboxylation reaction (Eq. 6). This process involves the removal of carboxyl groups (-COOH) from the fatty acid compounds, leading to the formation of CO<sub>2</sub>. Decarboxylation can occur spontaneously at high temperatures or can be catalyzed by specific catalysts.



As seen in Figure 5, the presence of Co on catalysts' surface increases both hydrocarbons and CO<sub>2</sub> selectivity in the gas product. It indicates that the Co metal not only has a good propensity for initiating cracking reaction but also has a good performance in decarboxylation reaction. Co-based catalysts have been shown to improve the C(sp<sup>2</sup>)-O cleavage via the

direct deoxygenation pathway (Bui *et al.*, 2011; Crawford *et al.*, 2019). However, the CO<sub>2</sub> selectivity decreased when the Ni:Co ratio was 1:1.5. It is due to the higher crystallite size of Co of the catalyst's surface. As discussed previously, the crystallite size of Co metal on 1Ni-1.5Co/ZSM-5 catalyst has the largest size. A large crystallite size decreases the metal surface area; therefore, the reaction activity decreases due to reduced contact area.

The analysis also reveals that the composition of C<sub>4</sub> and C<sub>6</sub> gases is predominantly produced using the 1Ni-1.5Co/ZSM-5 catalyst due to the higher concentration of Co, which plays a significant role in chain growth, leading to longer carbon chains (Ghogia *et al.*, 2021), whereas C<sub>2</sub>, C<sub>3</sub>, and C<sub>5</sub> gases are more abundant with 1Ni-1Co/ZSM-5, attributed to the balanced concentrations of Ni and Co, where Ni promotes the formation of C<sub>2</sub> and C<sub>3</sub> carbon chains, while the balanced Co concentration results in less chain growth compared to 1Ni-1.5Co/ZSM-5, facilitating more C<sub>5</sub> formation (Ghogia *et al.*, 2021).

## CONCLUSION

The impregnation of Ni-Co on the ZSM-5 catalyst with ratios of 1:0.5, 1:1, and 1:1.5 exhibits different catalytic characteristics. XRF analysis shows that the actual Ni/Co ratio in the catalysts is consistent with the designed ratio, while XRD analysis indicates variations in crystal size due to competition between Ni and Co particles diffusing into the zeolite pores. Although Co has good nucleation ability, crystal growth is limited by dislocations and defects. In the palm oil hydrocracking test, the Ni-Co/ZSM-5 1:1.5 catalyst produced the highest liquid yield and biogasoline selectivity. However, the dominant gas

products are CO, CO<sub>2</sub>, and C<sub>2</sub> as the results of triglycerides conversion into fatty acids, which are then further broken down into C<sub>2</sub> and C<sub>15</sub>, indicating that the selectivity towards gasoline remains low. Excessive coke formation is caused by the high activity of Ni metal on the catalyst, which triggers dehydrogenation reactions, leading to pore blockage and reduced product selectivity, while incomplete cracking reactions further contribute to coke production.

### CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. Funder of research: World Class Research Universitas Diponegoro (WCRU-A) contract number: 118-22/UN7.6.1/PP/2021 (I. Istadi).

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