Jurnal Teknologi, Vol. 25, No. 2, Agustus, 2025, 123-128

The Catalytic Performance of Vanadium–Nickel Supported on Zeolite for the Conversion of Crude Palm Oil into Short-Chain Hydrocarbons

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Abstract

Article history:
Received: 28-05-2025
Accepted: 22-06-2025
Published: 27-07-2025

The increasing global demand for fossil fuels, alongside declining domestic oil production, has intensified interest in renewable energy sources. Among Indonesia's abundant biomass options, crude palm oil (CPO) is a promising candidate for biofuel production due to its high triglyceride content and chemical similarity to petroleum. This study explores the catalytic cracking of CPO using a vanadium–nickel catalyst supported on natural zeolite, aiming to evaluate its physicochemical properties and catalytic performance in converting CPO into short-chain hydrocarbons for potential use as biogasoline. The catalyst was synthesized via wet impregnation of natural zeolite with ammonium metavanadate and nickel nitrate hexahydrate, followed by calcination. Characterization using Thermogravimetric Analysis (TGA), X-Ray Diffraction (XRD), and Scanning Electron Microscopy (SEM) confirmed good thermal stability, crystallinity, and surface morphology. Catalytic cracking was performed at elevated temperatures under atmospheric pressure. The liquid products were analyzed using Gas Chromatography-Mass Spectrometry (GC-MS). The results showed that the catalyst successfully facilitated the breakdown of triglycerides, producing mainly medium-chain fatty acids. Pentadecanoic acid ($C_{15}H_{30}O_2$) was identified as the dominant compound, indicating partial cracking of CPO. However, the product composition still contained oxygenated species, suggesting incomplete deoxygenation. Consequently, the resulting mixture does not yet meet biogasoline specifications. These findings highlight the potential of vanadium–nickel/zeolite catalysts in biofuel conversion processes, while also emphasizing the need for further catalyst optimization or additional processing stages to achieve complete transformation into fuel-grade hydrocarbons.

***Keywords**:*
catalytic;
crude palm oil;
performance;
short chain hydrocarbons;
vanadium-nickel;
zeolite.

1. Introduction

Climate change and the growing global demand for energy have driven a worldwide push for sustainable and environmentally friendly alternatives to fossil fuels. Biofuels, derived from renewable resources such as crude palm oil (CPO), have emerged as a promising solution due to their renewability, biodegradability, and potential to reduce greenhouse gas emissions[1, 2].

Crude palm oil, a triglyceride-rich vegetable oil, is particularly attractive as a biofuel feedstock. Triglycerides in CPO consist of long-chain fatty acids bound to a glycerol backbone, making them suitable precursors for hydrocarbon production through thermal and catalytic cracking processes[3]. In addition to triglycerides, CPO contains carotenoids, sterols, and phospholipids, which may influence product quality during conversion[4].

Indonesia and Malaysia, the world's largest producers of palm oil, generate millions of tons of CPO annually, offering a stable and abundant feedstock for biofuel production. Utilizing CPO as a renewable fuel not only helps reduce petroleum dependency but also adds value to agricultural by-products, contributing to energy security and rural development in tropical regions[5, 6].

One of the most promising methods for converting CPO into fuel-grade hydrocarbons is catalytic cracking. This process involves the thermal decomposition of large organic molecules into smaller, more volatile compounds in the presence of a catalyst. While traditionally used in petroleum refining to produce gasoline, catalytic cracking has been successfully adapted for processing vegetable oils, including CPO, to produce light hydrocarbons such as alkanes, alkenes, and aromatics[7, 8].

The efficiency of catalytic cracking relies heavily on the properties of the catalyst used. Zeolites, especially natural zeolites and synthetic variants like HZSM-5 and HY, are widely applied due to their porous structure, high thermal stability, and strong acidity, which promote selective breaking of carbon–carbon bonds[9, 10]. Natural zeolites, in particular, offer economic and ecological advantages, as they are widely available and can be modified through acid activation to enhance surface area and catalytic activity[10, 11].

To further enhance catalytic performance, transition metals such as nickel (Ni) and vanadium (V) are often impregnated into zeolite matrices. Nickel is known for its hydrogenation activity, promoting the saturation of double bonds and enhancing fuel stability. Vanadium, on the other hand, facilitates decarboxylation and dehydrogenation reactions, crucial for cleaving the ester bonds in triglycerides and reducing oxygen content in the resulting fuel[12-14]. The synergy between these two metals has been demonstrated to improve both cracking efficiency and hydrocarbon selectivity[15, 16].

Recent studies have explored various metal-zeolite systems for CPO conversion. For example, Ni/HY and NiCo/HY catalysts have shown enhanced activity in converting palm oil into gasoline-range hydrocarbons, with yields up to 40% and significant selectivity toward C5–C12 fractions[14]. Other works have used natural zeolites impregnated with ZnO, PbO, or MoO_3, achieving high thermal stability and favorable product profiles in the bio-oil obtained [17].

However, challenges such as catalyst deactivation (due to coke formation), cost-effectiveness, and the need for process optimization remain barriers to commercial adoption. Consequently, research continues to focus on catalyst development, reaction mechanism elucidation, and scale-up feasibility.

This study investigates the catalytic performance of vanadium–nickel supported on natural zeolite for the conversion of CPO into short-chain hydrocarbons. The objective is to evaluate how the incorporation of V and Ni influences catalyst activity, product selectivity, and the potential of this system as a sustainable route for biofuel production.

2. Methods

2.1 Pre-treatment and Catalyst Preparation

The initial washing of the zeolite was carried out using distilled water three times to remove surface impurities. After washing, the zeolite was dried in an oven at 105°C for three hours. Subsequently, the zeolite was activated by immersion in a 1 M HCl solution for 24 hours. After acid treatment, the zeolite was rinsed thoroughly until a neutral pH was achieved, then dried in an oven at 120°C for four hours. The dried zeolite was ground using a grinding mill and sieved to pass through a 120-mesh screen. The final zeolite product was labeled as NZ.

For the catalyst impregnation process, the first step involved preparing vanadium and nickel solutions with the following concentration variations of Vanadium 0.25 M, Nickel 0 M; Vanadium 0.25 M, Nickel 0.15 M; Vanadium 0.25 M, Nickel 0.25 M; Vanadium 0.15 M, Nickel 0.25 M; and Vanadium 0 M, Nickel 0.25 M.

Then, 50 g of NZ was added to each solution and stirred at 25°C for six hours. The mixture was then filtered and dried in an oven at 115°C for six hours. The dried catalyst powder was subsequently calcined at 500°C for four hours.

2.2 Catalytic Cracking Reaction

The second stage involved the catalytic reaction process. At this stage, the pre-activated catalyst was reacted with crude palm oil. A total of 100 mL of CPO was placed in a reaction flask, and 1 g of catalyst was added. The reaction was conducted for two hours. The resulting products were transferred into a distillation flask to separate the formed compounds. The reaction products were then analyzed using Gas Chromatography-Mass Spectrometry (GC-MS) to identify the compounds formed during the reaction.

3. Results and Discussion

3.1 Catalyst Characterization

The catalyst preparation began with the use of natural zeolite as the supporting material, followed by an activation process involving impregnation with vanadium and nickel precursors. The impregnated materials were subjected to thermogravimetric analysis (TGA) to examine their thermal stability and determine appropriate calcination conditions.

3.1.1 Thermal Stability Analysis (TGA)

The thermogravimetric analysis (TGA) plot in the Figure 1 illustrates the thermal stability of various zeolite-based catalysts supported with different loadings of vanadium (V) and nickel (Ni), labeled as ZV0Ni25, ZV15Ni25, ZV25Ni25, ZV25Ni15, and ZV25Ni0. As the temperature increases from 0 °C to 600 °C, all samples exhibit a gradual weight loss, which is indicative of material decomposition, desorption of physically adsorbed species, or structural degradation. Among the samples, ZV0Ni25 shows the highest weight loss across the temperature range, implying the lowest thermal stability. In contrast, ZV25Ni0 displays the least weight loss, indicating the highest thermal resistance.

The trend suggests that increasing vanadium content enhances the thermal stability of the catalyst, while increasing nickel content appears to decrease it. For instance, when vanadium content is held constant at 25% (ZV25), reducing nickel from 25% (ZV25Ni25) to 0% (ZV25Ni0) significantly reduces the weight loss, confirming nickel's destabilizing effect. Conversely, increasing vanadium from 0% (ZV0Ni25) to 25% (ZV25Ni25) while maintaining a constant nickel content improves thermal stability. This behavior may be attributed to the strong metal–support interaction and thermal resistance conferred by vanadium species, whereas nickel may promote the formation of less stable phases or enhance decomposition of volatile components. Overall, the TGA results suggest that vanadium contributes positively to catalyst stability under thermal conditions, whereas excessive nickel loading may compromise it. These findings are valuable for optimizing catalyst formulations intended for high-temperature applications, such as in catalytic cracking, hydroprocessing, or bio-oil upgrading.

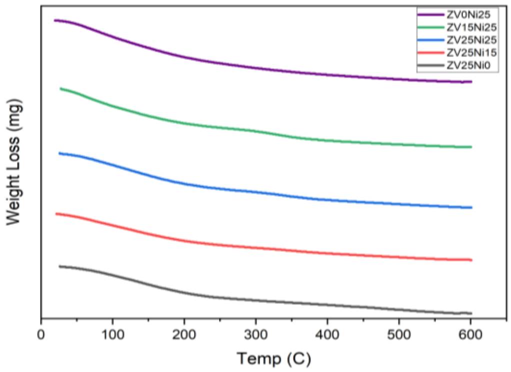


Figure 1. TGA curve of samples preparation

The TGA curve shows three primary stages of weight loss. The first stage, occurring up to 110°C, corresponds to the removal of physically adsorbed water. This is typical for zeolite-based catalysts due to their high surface area and porous nature. The second stage of degradation between 110°C and 300°C likely corresponds to the decomposition of residual nitrate and ammonium groups from the metal precursors. The final stage, occurring between 400°C and 600°C, may be attributed to structural rearrangements or the crystallization of metal oxides, confirming the thermal decomposition of the impregnated metals.

Based on the TGA results, the catalyst was calcined at 600°C for 2 hours to ensure the removal of residual components and to promote the formation of catalytically active metal oxide species.

3.1.2 Crystallographic Analysis (XRD)

The X-ray diffraction analysis was used to identify the crystalline phases present in the catalyst after calcination. As shown in Figure 2, all catalyst samples exhibited characteristic peaks at 2θ ≈ 27°, which are consistent with the incorporation of vanadium oxides into the zeolite matrix. The retention of the zeolite crystalline structure and the similarity in peak positions across different vanadium–nickel ratios suggest that the impregnation did not significantly disrupt the zeolite framework. The appearance of new or enhanced peaks corresponding to vanadium species also confirms successful dispersion of active metals into the support. This behavior aligns with previous findings that vanadium oxides can be stabilized within zeolitic pores while retaining catalytic activity.

The X-ray diffraction (XRD) patterns as shown in the Figure 2 provide insight into the crystallographic structure and phase composition of zeolite-based catalysts with varying vanadium (V) and nickel (Ni) contents: ZV0Ni25, ZV25Ni25, ZV25Ni0, and the parent zeolite. The baseline sample (Zeolit) displays sharp and well-defined diffraction peaks between 2θ = 10° to 35°, which are characteristic of a crystalline zeolite framework. These peaks confirm the presence of ordered microporous structures typically found in crystalline aluminosilicates. However, after the incorporation of metals, especially in the ZV0Ni25 and ZV25Ni25 samples, the intensity of the diffraction peaks diminishes and broadens, suggesting a partial loss of crystallinity. This decrease in intensity can be attributed to the disruption of the zeolite lattice due to the insertion of metal species and possibly due to ion exchange or surface dispersion of metal oxides.

In particular, the ZV25Ni25 sample shows more pronounced peak broadening compared to ZV25Ni0, indicating that the addition of nickel may further disturb the crystal framework or result in amorphous phase formation. Additionally, the appearance of small broad humps in the higher 2θ region (>40°) could imply the formation of poorly crystalline or highly dispersed metal oxides on the zeolite surface. The retention of some peak positions across all samples suggests that the fundamental zeolite structure is partially preserved, although metal impregnation has a clear impact on its crystallinity. Overall, the XRD analysis indicates that vanadium and especially nickel incorporation affects the structural integrity of the zeolite, which could influence the textural and catalytic properties of the materials in subsequent applications.

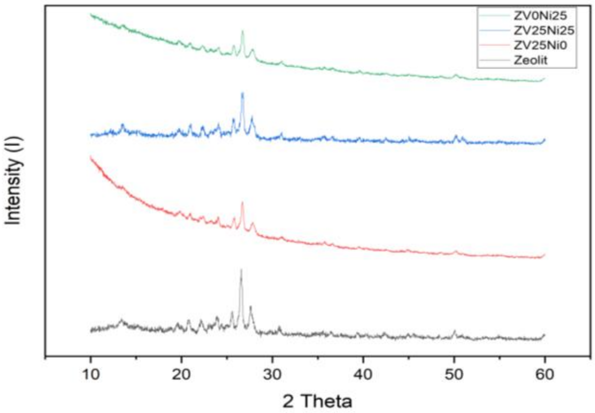


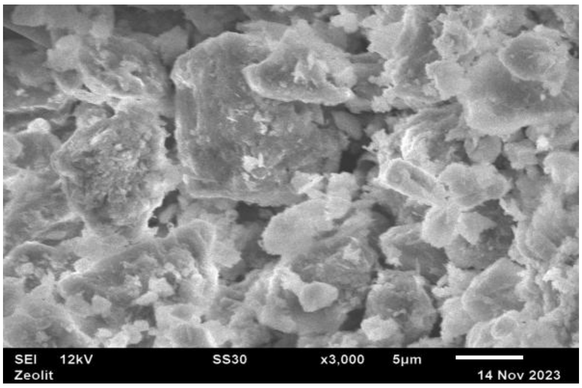
Figure 2. XRD patterns at various activator concentrations

3.1.3 *Morphological Observation (SEM)*

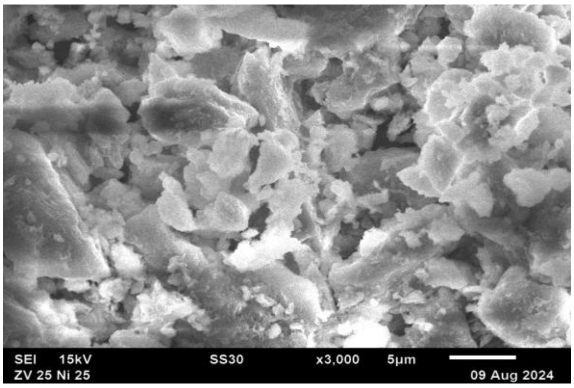
SEM micrographs (Figure 3a and 3b) reveal that the surface morphology of natural zeolite remains relatively unchanged after metal impregnation. Although some agglomeration is observed on the surface of the impregnated sample, the zeolite's porous texture and granular structure are preserved. This indicates that metal loading was well-distributed without causing significant pore blockage, an important factor for catalytic performance.

A comparative analysis of Figure 3a and Figure 3b, which depict the SEM micrographs of natural zeolite and the metal-loaded catalyst ZV25Ni25 respectively, reveals distinct morphological differences resulting from the incorporation of vanadium and nickel. In Figure 3a, the natural zeolite displays a highly porous, crystalline structure with irregularly shaped particles, sharp edges, and open voids between the particles—characteristics that reflect its high surface area and well-preserved microporous framework. In contrast, Figure 3b shows a denser and more compact structure in the ZV25Ni25 catalyst, with smoother surfaces, more agglomerated particles, and a noticeable reduction in visible porosity. The once-clear crystalline boundaries observed in the raw zeolite are less pronounced in the metal-loaded sample, indicating that the impregnation process and possible thermal treatment have partially coated or disrupted the zeolite's surface structure.

This densification and particle clustering in ZV25Ni25 suggest a decrease in surface area and pore accessibility, which may affect its catalytic performance by limiting the exposure of active sites. Therefore, the comparison highlights how metal loading significantly alters the textural and morphological properties of the zeolite, transforming it from a highly porous support into a more compact catalyst material.



(a)



(b)

Figure 3. Scanning electron micrographs of a) natural zeolite and b) ZV25Ni25 catalyst

3.2 Product Analysis

The product obtained after catalytic cracking of crude palm oil (CPO) was analyzed using Gas Chromatography–Mass Spectrometry (GC-MS). As shown in Figure 4 and summarized in Table 1, two major fatty acids were detected: tetradecanoic acid (7.93%) and pentadecanoic acid (92.07%).

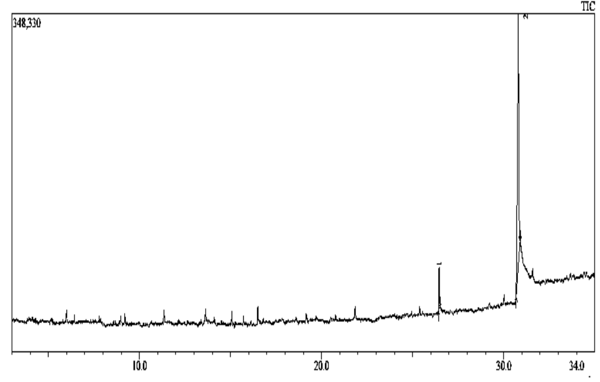


Figure 4. GC-MS chromatogram of the product

The dominance of pentadecanoic acid ($C_{15}H_{30}O_2$) in the product spectrum indicates effective cleavage of triglyceride molecules into medium-chain fatty acids. This demonstrates that the vanadium–nickel catalyst played a critical role in breaking the ester bonds and C–C bonds in triglyceride chains, which typically have a general formula of $C_{35}H_{98}O_6$. Such conversions are in line with the goals of biofuel production, which aims to yield shorter-chain hydrocarbons compatible with fuel standards.

Vanadium's oxidative properties facilitated decarboxylation and dehydrogenation reactions, promoting the formation of fatty acids and light hydrocarbons. while nickel likely contributed to hydrogenation steps, enhancing the stability of the produced hydrocarbons.

Furthermore, the high selectivity toward pentadecanoic acid suggests that the catalyst formulation favored the production of linear saturated fatty acids, which are precursors to green diesel components. This is consistent with previous studies where V–Ni supported catalysts exhibited high activity and selectivity in converting CPO into biofuels.

Table 1. Compounds detected in the product

No.	Area %	Compound Name
1	7.93	Tetradecanoic acid (CAS: Myristic acid)
2	92.07	Pentadecanoic acid (CAS: Pentadecylic acid)

4. Conclusion

The characterization of the vanadium–nickel supported zeolite catalyst revealed that the thermal, structural, and morphological properties are well-suited for catalytic cracking applications. TGA analysis confirmed the thermal stability of the material, with calcination at 600°C leading to optimal activation. XRD analysis validated the incorporation of metal species without compromising the crystallinity of zeolite. SEM micrographs showed that the physical morphology of the zeolite support remained largely intact post-impregnation.

GC-MS analysis demonstrated that the catalyst was effective in transforming crude palm oil into medium-chain fatty acids, particularly pentadecanoic acid, confirming the successful breakdown of triglycerides into shorter hydrocarbons. The combined catalytic functions of vanadium and nickel proved to be synergistic, enhancing both cracking and hydrogenation processes. These results underscore the potential of vanadium–nickel supported on zeolite as a promising bifunctional catalyst for sustainable biofuel production.

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