

Upgrading Oil Palm Empty Fruit Bunch Bio Oil via Catalytic Hydrodeoxygenation Using Nickel Impregnated Activated Carbon and Natural Zeolite Catalysts

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Abstract

Biomass is a promising alternative energy feedstock because of its cellulose, hemicellulose, and lignin content and its availability as an agricultural and plantation residue. Pyrolysis can convert biomass into bio-oil, a complex liquid containing oxygenated compounds such as ketones, acids, phenols, alcohols, aldehydes, and hydrocarbons. This study evaluates the upgrading of crude bio oil (CBO) derived from oil palm empty fruit bunches (EFB) using nickel-impregnated activated natural zeolite (ZAA/Ni) and nickel-impregnated activated carbon (AA/Ni) catalysts under hydrodeoxygenation (HDO) conditions. The physicochemical properties and available GCMS results were compared descriptively before and after upgrading. After correction of the compound classifications and recalculation from the listed GCMS peaks, the hydrocarbon peak-area totals were 20.59% for CBO, 20.36% for ZAA/Ni, and 26.66% for AA/Ni. The AA/Ni-treated bio oil showed an increase in higher heating value (HHV) from 39.13 to 40.27 MJ/kg. Because the original chromatograms and independent replicate measurements were unavailable for this revision, the GCMS results are interpreted as semi-quantitative, and the numerical differences are not presented as statistically significant. Overall, AA/Ni showed the more favorable combination of oxygen removal and HHV improvement under the tested conditions, although the increased viscosity indicates that further stabilization or fractionation would be required before considering diesel-equivalent applications.

Keywords

Biomass, Bio-Oil, Pyrolysis, Catalytic Cracking

Received: 17 July 2026, Accepted: 20 September 2026

<https://doi.org/10.26554/ijems.2026.10.4.380-389>

1. INTRODUCTION

Biomass is one of the most promising alternative energy feedstocks due to its high content of cellulose, hemicellulose, and lignin. Biomass is commonly derived from agricultural, forestry, and plantation waste residues. During the pyrolysis process, biomass undergoes thermal decomposition, resulting in the production of bio oil. However, bio-oil cannot be directly utilized as a fuel because it still contains significant amounts of nitrogen (N), oxygen (O), and sulfur (S). Pyrolysis-derived bio oil consists of a complex mixture of aliphatic, aromatic, and acidic compounds that influence its physical and chemical properties (Duan et al., 2016).

Bio oil contains various oxygenated compounds, including ketones, acids, phenols, alcohols, aldehydes, and hydrocarbons. These compounds are formed during the pyrolysis process through the decomposition of the major biomass constituents, namely cellulose, hemicellulose, and lignin, leading

to the generation of oxygenated products. Consequently, bio oil exhibits several undesirable characteristics, such as high oxygen content, elevated acidity, low calorific value, and poor storage stability. Therefore, upgrading processes are required to improve the quality of bio-oil, commonly through the use of catalysts.

Among the available upgrading technologies, catalytic cracking combined with hydrodeoxygenation (HDO) has attracted considerable attention. Hydrodeoxygenation removes oxygen from bio oil by converting oxygen containing compounds into water (H₂O), carbon monoxide (CO), and carbon dioxide (CO₂), while simultaneously promoting the cleavage of long hydrocarbon chains into lighter fractions. This process is typically carried out at temperatures above 450 °C and pressures exceeding 100 bar in the presence of hydrogen and suitable catalysts (Qu et al., 2021). Catalytic cracking further enhances the conversion by breaking large

organic molecules into smaller hydrocarbon compounds with improved fuel characteristics. Hydrocarbon chain cleavage can be achieved either through catalytic conversion in the presence of hydrogen or through non-catalytic thermal cracking at elevated temperatures. In this study, the upgrading process employed catalytic hydrodeoxygenation using hydrogen gas. The feedstock consisted of crude bio-oil (CBO) derived from oil palm empty fruit bunches (EFB), an abundant agricultural residue generated by the palm oil industry. Upgrading this bio oil is essential to produce a liquid fuel with properties closer to those of conventional petroleum-based fuels.

Although catalytic hydrodeoxygenation has been widely investigated for upgrading biomass-derived bio-oil, most studies have relied on expensive commercial or noble metal catalysts, limiting their large-scale implementation (Qu et al., 2021). Nickel based catalysts have emerged as a cost effective alternative; however, studies comparing nickel impregnated activated carbon and nickel impregnated natural zeolite for upgrading crude bio oil derived from oil palm empty fruit bunches remain limited. Furthermore, previous studies have primarily focused on deoxygenation efficiency or heating value improvement, while comprehensive evaluations linking physicochemical properties with the available GC/MS compositional output are still scarce. Therefore, this study addresses these gaps by evaluating two low cost nickel supported catalysts derived from natural materials within a circular economy framework to improve the quality of oil palm empty fruit bunch bio-oil. The scientific contribution of the present work is therefore not the introduction of Ni as a new active metal, but the experimental comparison of two low cost Ni impregnated supports derived from natural zeolite and palm oil empty fruit bunch waste under the same bio oil upgrading temperature, hydrogen pressure, reaction time, and catalyst to feed ratio. The study further links the observed changes in hydrocarbon peak area, oxygen content, sulfur content, viscosity, and heating value with previously measured physicochemical characteristics of the selected catalysts. This comparative linkage is particularly relevant for identifying a low-cost catalyst configuration for EFB derived crude bio oil within a waste valorization framework.

Although hydrodeoxygenation has been extensively studied, several challenges remain, including high energy consumption, significant hydrogen demand, and reliance on expensive catalyst materials (Qu et al., 2021). Furthermore, studies investigating nickel supported natural catalysts for upgrading crude bio oil derived from oil palm empty fruit bunches remain relatively limited. Therefore, the novelty of this study lies in the application of circular economy principles through the utilization of natural resource and waste based catalysts specifically activated natural zeolite and activated carbon impregnated with nickel (Ni) metal for the upgrading process of crude bio-oil (CBO) derived from oil palm empty fruit bunches. Importantly, the catalyst characterization used to interpret the present catalytic

results was conducted as part of the same research program and is reported in the authors' dissertation (Yanti et al., 2019). Accordingly, the present manuscript treats those characterization results as previously obtained supporting data rather than as newly generated measurements.

Oil palm empty fruit bunches (EFB) are one of the largest lignocellulosic residues generated by the palm oil industry and are still underutilized despite their high energy potential. Converting EFB into bio oil through pyrolysis represents an attractive waste to energy strategy that supports the principles of circular economy by transforming agricultural waste into renewable fuels. However, crude bio oil contains a high concentration of oxygenated compounds that limit its direct application as transportation fuel. Therefore, upgrading through catalytic hydrodeoxygenation is required to improve its fuel properties. The novelty of this work lies in the integration of waste valorization of EFB with catalytic upgrading using low cost nickel supported activated carbon (AA/Ni) and activated natural zeolite (ZAA/Ni) catalysts. This approach not only enhances the hydrocarbon content and fuel quality of bio-oil but also provides a potentially lower cost pathway for converting palm oil waste into sustainable bioenergy. Therefore, this study evaluates the performance of nickel impregnated activated carbon and nickel impregnated activated natural zeolite as catalysts for bio oil upgrading.

2. EXPERIMENTAL SECTION

2.1 Materials

This study is a continuation of previous research specifically that of Yanti et al. (2019) which addressed the catalyst preparation process and identified the best performing catalysts as nickel impregnated zeolite (ZAA/Ni 3%) and nickel impregnated activated charcoal (AA/Ni 2%). The bio oil used in this study was crude bio oil (CBO) produced through the hydrothermal pyrolysis of oil palm empty fruit bunches (EFB). Two catalysts were evaluated for the upgrading process: nickel impregnated activated natural zeolite (ZAA/Ni, 3 wt.% Ni) and nickel impregnated activated carbon (AA/Ni, 2 wt.% Ni). The selected formulations were not intended to represent an equal Ni loading comparison. AA/Ni 2% and ZAA/Ni 3% were selected because the earlier catalyst study identified these formulations as the recommended catalysts for the subsequent bio-oil upgrading experiment. Thus, the comparison in the present study evaluates the practical performance of the two previously selected catalyst formulations, while the unequal Ni loading is recognized as a limitation when attributing performance differences solely to the support material.

The upgrading experiments were conducted using a catalytic cracking reactor equipped with a magnetic stirrer. Additional laboratory equipment included an analytical balance, sieve, separatory funnel, and Erlenmeyer flasks. The physicochemical properties of the bio oil were characterized using an Automatic Total Acid Number Tester for acidity

measurements and a capillary viscometer coupled with a Visco Clock for viscosity determination. Elemental composition, including carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S), was analyzed using a Vario EL Cube Elemental Analyzer. The chemical composition of the bio oil was determined by Gas Chromatography–Mass Spectrometry (GCMS, Agilent Technologies).

The catalyst characterization data above were obtained in the catalyst preparation stage of the same research program and are reported in [Yanti et al. \(2019\)](#). Brunauer Emmett Teller (BET) analysis showed a high surface area for both selected catalysts, with 974.44 m²/g for ZAA/Ni 3% and 835.819 m²/g for AA/Ni 2% (Table 1). The corresponding pore volumes were 0.99 and 0.870 cm³/g, while the average pore radii were 40.79 and 41.646 Å, respectively. X-ray diffraction (XRD) analysis showed crystallinity values of 53.80% for ZAA/Ni 3% and 44.46% for AA/Ni 2%. Scanning electron microscopy (SEM) observations also showed Ni-containing deposits on the catalyst surfaces, supporting successful impregnation. Fourier transform infrared spectroscopy (FTIR) analysis of the zeolite indicated structural changes associated with acid activation/dealumination. These previously obtained results are used here only to support interpretation of the catalytic performance; transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and quantitative Ni dispersion measurements were not available in the present dataset.

2.2 Methods

A total of 90 g of crude bio oil obtained from the hydrothermal pyrolysis of oil palm empty fruit bunches was used as the feedstock. The upgrading process was carried out separately using nickel-impregnated activated natural zeolite (ZAA/Ni, 3 wt.% Ni) and nickel impregnated activated carbon (AA/Ni, 2 wt.% Ni). Each catalyst was added at a loading of 4 wt.% relative to the bio oil feed before the mixture was transferred into the catalytic cracking reactor. The catalyst preparation procedure followed the previously reported wet impregnation method. Natural zeolite from Bayah was activated using 3 M HCl at 90 °C for 30 min, washed with distilled water until neutral pH, dried at 100–120 °C, and calcined at 500 °C for 60 min. Activated carbon was prepared from EFB derived char using H₃PO₄ activation followed by steam activation at 750 °C for 60 min. For Ni impregnation, Ni(NO₃)₂ · 6H₂O was added to the activated supports at nominal loadings of 1, 2, and 3 wt.%, followed by refluxing with stirring at 80 °C for 3 h, oven drying at 110 °C for 24 h, and calcination at 500 °C for 60 min ([Yanti et al., 2019](#)). The available experimental record does not document a separate post-impregnation H₂ reduction step; therefore, the catalysts are referred to throughout this manuscript as Ni-impregnated catalysts rather than assuming a quantitatively verified metallic Ni dispersion.

In this study, 90 g of crude bio-oil (CBO) derived from

the hydrothermal pyrolysis of oil palm empty fruit bunches was processed using ZAA/Ni 3% and AA/Ni 2% catalysts at 450 °C for 60 min with an initial hydrogen pressure of 15 bar. These conditions enabled simultaneous hydrogenation, cracking, hydrocracking, and deoxygenation reactions. The use of Ni based catalysts is relevant to the hydrodeoxygenation (HDO) mechanism because the metal phase facilitates hydrogenation, while the acidic characteristics of the support material assist in dehydration, deoxygenation, and C–O bond cleavage. Therefore, the bifunctional nature of the catalyst is a key factor determining the effectiveness of bio-oil upgrading ([Qu et al., 2021](#); [Carrasco Díaz et al., 2024](#)). The reactor was first evacuated to remove trapped air before H₂ charging. Hydrogen was introduced to an initial pressure of 15 bar. The reactor was then heated to 450 °C, held for 60 min, and subsequently cooled in an ice-water bath immediately after the reaction. The dissertation records the final pressure at reaction temperature as approximately 125 bar. The available record does not specify the reactor volume, heating rate, or stirring speed; these parameters therefore cannot be reported retrospectively without introducing unsupported information.

The available experimental record does not include a direct measurement of hydrogen consumption; therefore, hydrogen demand is not quantified in this study. The reactor was heated to 450 °C and maintained at this temperature for 60 min. The available experimental record reports a final pressure of approximately 125 bar at reaction temperature.

After the reaction was completed, the reactor was immediately cooled in an ice water bath to rapidly terminate the reaction and prevent further thermal degradation. The upgraded bio-oil (UBO) was then collected for subsequent characterization. The physicochemical properties of the upgraded bio oil were evaluated by measuring pH, viscosity, and elemental composition, including carbon, hydrogen, oxygen, nitrogen, and sulfur contents. The chemical composition was further analyzed using Gas Chromatography Mass Spectrometry (GCMS). Because the original GCMS chromatogram files for the crude bio-oil (CBO), ZAA/Ni treated bio oil, and AA/Ni-treated bio oil were not available in the dataset retained for the present manuscript, representative chromatograms cannot be provided. Accordingly, the GCMS interpretation is restricted to the compound identities and relative peak area percentages available from the original GCMS output, and no retention-time or chromatogram-based interpretation is presented beyond what can be verified from that output.

The research data were analyzed using a descriptive quantitative approach. The physicochemical characteristics of crude bio-oil (CBO) and upgraded bio oil (UBO) including pH, viscosity, elemental composition, higher heating value (HHV), lower heating value (LHV), and compound profiles from GCMS analysis were compared descriptively to evaluate the effect of the hydrodeoxygenation process using AA/Ni and ZAA/Ni catalysts. Because the available up-

Table 1. Previously Reported Catalyst Characterization

Catalyst	Ni Loading	BET Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)	Average Pore Radius (Å)	Crystallinity (%)
ZAA/Ni	3 wt.%	974.44	0.99	40.79	53.80
AA/Ni	2 wt.%	835.819	0.870	41.646	44.46

grading dataset contains single reported values rather than independent replicate measurements for the AA/Ni and ZAA/Ni upgrading runs, standard deviations and inferential significance tests (e.g., ANOVA) cannot be calculated retrospectively without the underlying replicate observations. The present study therefore uses descriptive comparison and explicitly avoids interpreting numerical differences as statistically significant. Replication and uncertainty analysis are identified as priorities for future experimental validation.

3. RESULTS AND DISCUSSION

3.1 Yield of Upgraded Bio Oil

The upgrading process produced high bio oil yields for both catalyst systems, with recovery values of 96.81% for the AA/Ni catalyst and 96.09% for the ZAA/Ni catalyst (Figure 2). These results indicate that the catalytic hydrodeoxygenation process was highly efficient in preserving the liquid product during upgrading. The high product recovery can largely be attributed to the tightly sealed reactor system, which minimized the loss of liquid products throughout the reaction. The slight reduction in yield is mainly associated with unavoidable handling losses during product collection, as a small amount of bio oil remained inside the reactor after the experiment. In addition, a fraction of the feedstock was converted into gaseous products, including CO₂, CO, H₂, and CH₄, which were released during reactor depressurization following the high temperature, high-pressure upgrading process. The reported 96.81% and 96.09% values represent liquid-product recovery and should not be interpreted as a complete process mass balance. The available dataset does not contain measured masses of gas and coke/solid products. The manuscript therefore reports liquid recovery only and recognizes the absence of a complete liquid gas solid mass balance as a limitation of the study.

3.2 Physicochemical Properties of Upgraded Bio Oil

The physicochemical properties of crude bio-oil (CBO) and upgraded bio oil (UBO) are summarized in Table 2. Following the upgrading process, the pH of the bio oil decreased from 6.56 in the crude sample to 5.54 and 5.40 after treatment with the ZAA/Ni and AA/Ni catalysts, respectively. Although both upgraded products remained slightly acidic, their pH values were close to those commonly reported for diesel fuel.

The reduction in pH may be attributed to the characteristics of the catalyst supports. Activated natural zeolite was prepared by acid activation using hydrochloric acid

(HCl), while activated carbon was chemically activated with phosphoric acid (H₃PO₄). Residual acidic species remaining on the catalyst surfaces after preparation may have contributed to the acidity of the upgraded bio-oil. In addition, the ash content present in activated carbon has been reported to influence the acidity of bio-oil, which is consistent with the findings of Duan et al. (2016). A significant

Table 2. Physicochemical Characteristics of Upgraded Bio-Oil

Parameter	CBO	ZAA/Ni 3%	AA/Ni 2%
pH	6.56	5.54	5.40
Viscosity (cP)	9.33	22.96	41.32
Carbon (%)	75.67	78.00	79.03
Hydrogen (%)	9.81	9.02	9.78
Nitrogen (%)	1.77	2.20	2.45
Total sulfur (%)	0.66	0.49	0.08
Oxygen (%)	13.09	11.39	9.00
HHV (MJ/kg)	39.13	38.81	40.27
LHV (MJ/kg)	36.99	36.84	38.13

ZAA/Ni : nickel-impregnated activated natural zeolite
AA/Ni : nickel-impregnated activated carbon
LHV : Lower heating value

increase in viscosity was observed after upgrading. The viscosity increased from 9.33 cP in crude bio-oil to 22.96 cP and 41.32 cP following treatment with the ZAA/Ni and AA/Ni catalysts, respectively. This increase is likely associated with polymerization reactions involving phenolic and acidic compounds during the upgrading process. Furthermore, heating the bio-oil to 450 °C reduced its moisture content, resulting in a more concentrated liquid phase with higher viscosity. Similar observations have been reported by Cheng et al. (2017), who linked viscosity changes to hydrodeoxygenation, deoxygenation, and decarbonylation reactions occurring during catalytic upgrading. The increase in viscosity should therefore be interpreted as a trade-off rather than evidence that every fuel property improved simultaneously. Hydrodeoxygenation can remove oxygenated species and increase energy density, while the simultaneous cracking, condensation/polymerization, loss of volatile components, and concentration of the remaining liquid phase can increase viscosity. In the present dataset, the viscosity increase was especially pronounced for AA/Ni (from 9.33 to 41.32 cP), despite its favorable reduction in oxygen and increase in HHV. Thus, the AA/Ni product should be re-

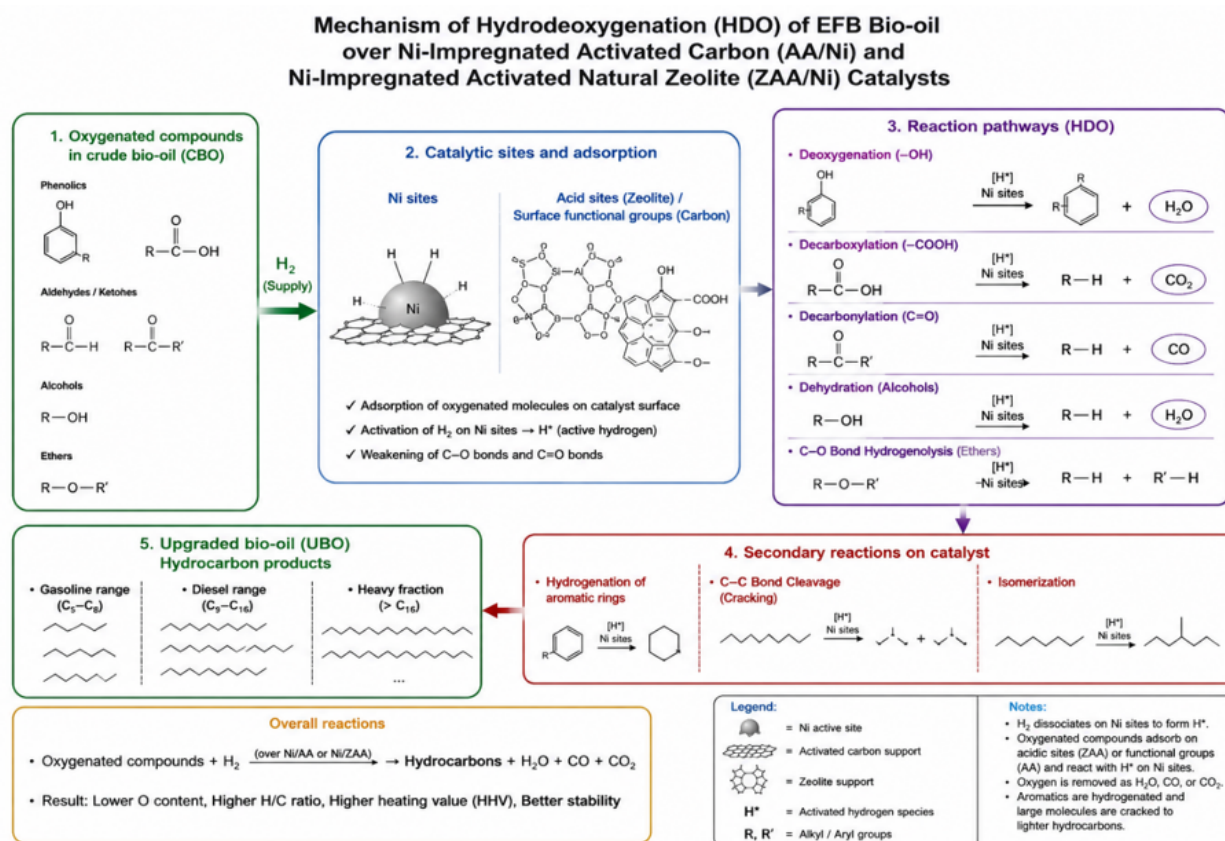


Figure 1. Schematic Representation of Possible Hydrodeoxygenation Pathways over Ni-Impregnated Catalysts

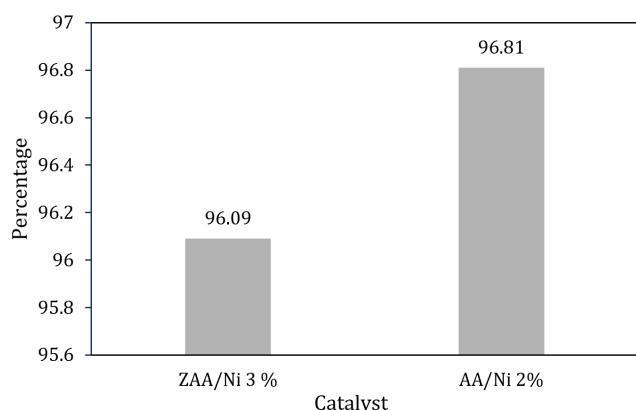


Figure 2. Liquid-Product Recovery of Upgraded Bio Oil

garded as chemically upgraded in terms of oxygen removal and energy density, but not as a finished diesel equivalent fuel without further stabilization or fractionation.

Elemental analysis revealed noticeable changes in the chemical composition of the upgraded bio-oil. Carbon content increased from 75.67% in the crude bio oil to 78.00% and 79.03% after upgrading with ZAA/Ni and AA/Ni, re-

spectively. At the same time, oxygen content decreased from 13.09% to 11.39% and 9.00%. These results indicate that both catalysts effectively promoted deoxygenation, with the AA/Ni catalyst showing superior performance. To quantify the effect, oxygen-removal efficiency (ORE) was calculated as $ORE = [(O-CBO - O-UBO)/O-CBO] \times 100$. Using the measured oxygen contents of 13.09% for CBO, 11.39% for ZAA/Ni, and 9.00% for AA/Ni, the calculated ORE values are 12.99% for ZAA/Ni and 31.25% for AA/Ni. These values provide a quantitative basis for the conclusion that AA/Ni produced stronger net oxygen removal under the tested conditions.

Sulfur content also decreased substantially after upgrading, particularly with the AA/Ni catalyst, where the sulfur concentration declined from 0.66% to only 0.08%. Lower sulfur levels are advantageous because they reduce pollutant emissions and improve the environmental performance of the resulting fuel. On the same basis, sulfur decreased by approximately 25.76% with ZAA/Ni and 87.88% with AA/Ni relative to CBO. However, the available GCMS table does not identify sulfur-containing compounds before and after upgrading, so a compound-specific sulfur removal mechanism cannot be established from the present data. The sulfur decrease is therefore interpreted as an observed elemental change rather than as direct evidence for a specific

hydrodesulfurization pathway.

The heating value of the bio-oil was also influenced by catalyst type. Treatment with the AA/Ni catalyst increased the higher heating value (HHV) from 39.13 MJ/kg to 40.27 MJ/kg, whereas the ZAA/Ni catalyst resulted in a slightly lower HHV of 38.81 MJ/kg. Similarly, the lower heating value (LHV) increased to 38.13 MJ/kg for the AA/Ni-treated bio oil. The improvement in heating value is closely related to the increase in carbon content and the reduction in oxygen content achieved during hydrodeoxygenation. Oxygenated functional groups lower the energy density of bio oil; therefore, their removal through deoxygenation enhances the fuel's calorific value (Qu et al., 2021). At the operating temperature of 450 °C, hydrogen-assisted catalytic reactions promoted oxygen removal through hydrodeoxygenation, decarbonylation, and decarboxylation pathways, producing H₂O, CO, and CO₂ while enriching the hydrocarbon fraction of the bio oil.

These findings are consistent with previous studies. Cheng et al. (2017) reported an HHV of 40.59 MJ/kg using a 5% Ni/AC catalyst, while (Shakya et al., 2018) obtained an HHV of 35.2 MJ/kg using a Ni/C catalyst. The improved HHV observed in the present study is also supported by the reduction in oxygenated compounds, particularly organic acids and phenolic compounds, which contributed to a higher energy density and improved fuel quality. The comparison should nevertheless be interpreted cautiously because catalyst loading, feedstock, reactor configuration, and operating conditions differ among studies. In particular, the present AA/Ni product has improved HHV but substantially increased viscosity; therefore, the upgraded bio-oil should not be claimed to meet a complete commercial diesel specification based on HHV alone. A full fuel-standard assessment would require additional properties and standardized test methods that were not included in the available dataset.

3.3 GCMS Analysis

The chemical composition of the crude and upgraded bio oils was evaluated using gas chromatography mass spectrometry (GCMS), and the identified compounds and relative peak-area percentages retained from the original GCMS output are summarized in Table 3. The original GCMS chromatogram files for the CBO, ZAA/Ni treated bio oil, and AA/Ni treated bio oil were not available in the dataset retained for this revision. Therefore, representative chromatograms cannot be provided and have not been reconstructed from the peak area table. Compound identification is treated as semi quantitative and is discussed only on the basis of the retained GCMS output. The available dataset does not contain the original library matching scores or individual retention times; these parameters therefore cannot be independently verified. Accordingly, the reported peak-area percentages are used only to describe relative compositional differences and are not interpreted as absolute concentrations.

The retained GCMS summary was rechecked against the individual peak area values in Table 3. The previously reported hydrocarbon totals (20.59% for CBO, 20.36% for ZAA/Ni, and 26.66% for AA/Ni) were not fully consistent with the listed compounds. In particular, the sum of the compounds placed under the former hydrocarbon heading for AA/Ni is 24.42%, not 26.66%. The table was therefore reclassified and recalculated. Benzene, toluene, and naphthalene are treated as hydrocarbons; phenol, cresols, benzofurans, and related oxygenated aromatics are treated as oxygenated aromatic compounds; pyridine, amines, nitrile, amide, and indolizine-related entries are treated as nitrogen-containing compounds; and pentadecanone is treated as a ketone rather than a hydrocarbon. On this corrected basis, the listed hydrocarbon peak areas are 20.59% for CBO, 20.36% for ZAA/Ni, and 26.66% for AA/Ni. The corrected values are calculated directly from the entries retained in Table 3; they are not absolute concentrations because the original chromatograms, library matching scores, and raw files were unavailable.

The activated carbon-based catalyst (AA/Ni) yielded the highest corrected hydrocarbon peak area (26.66%), compared with 20.36% for ZAA/Ni and 20.59% for CBO. When considered together with the available physicochemical data, the observed difference may be related to differences in pore accessibility, support structure, and the nature of the support Ni interface. ZAA/Ni 3% had the larger BET surface area (974.44 m²/g) than AA/Ni 2% (835.819 m²/g), indicating that surface area alone does not explain the observed difference. AA/Ni had a slightly larger average pore radius (41.646 Å) versus 40.79 Å), together with differences in the porous carbon framework and the catalyst-specific XRD/SEM features reported during the earlier characterization stage. Because quantitative Ni dispersion and acidity measurements are unavailable, these factors are presented as evidence-supported interpretations rather than definitive explanations of the catalytic mechanism.

1. Porosity and mesopore structure (macromolecule transport): the available pore-size data suggest that differences in pore accessibility may have influenced the interaction of relatively large phenolic and aromatic molecules with catalyst surfaces. AA/Ni had a slightly larger average pore radius (41.646 Å) than ZAA/Ni (40.79 Å), and its carbonaceous porous framework may provide different transport characteristics from the activated natural zeolite. Such differences could facilitate access of medium-to-large reactant molecules to accessible catalytic regions and influence product diffusion. However, the present study does not include pore-size-distribution measurements under reaction conditions or direct transport experiments; therefore, the proposed role of pore accessibility should be regarded as a plausible interpretation rather than a demonstrated diffusion mechanism (Gong et al., 2019).

2. Possible effects of Ni incorporation and pore-blocking behavior: incorporation of Ni species may alter pore ac-

Table 3. GC-MS Analysis Results for Crude and Upgraded Bio-Oils

Compound / Chemical Class	CBO Peak Area (%)	ZAA/Ni 3% Peak Area (%)	AA/Ni 2% Peak Area (%)
Hydrocarbons			
Hexane	1.37	-	-
Heptane	-	-	4.04
Nonane	1.95	3.23	4.28
Naphthalene	0.99	-	-
Decane	-	-	1.89
Undecane	0.88	-	3.04
Dodecane	-	-	1.89
Tridecane	1.59	-	2.1
Tetradecane	2.27	2.13	4.74
Pentadecane	0.62	2.13	1.14
Hexadecane	1.84	3.23	-
Heptadecane	0.76	1.56	-
Octadecane	0.43	1.33	1.3
Tricosane	0.85	-	-
Toluene	-	2.26	0.31
Benzene	7.04	4.49	1.93
Corrected Hydrocarbon Subtotal			
Oxygenated Aromatic / Phenolic Compounds			
Phenol	28.59	18.27	23.38
Benzofuran	-	1.26	1.66
p-Cresol	-	1.99	1.99
m-Ethyl-Phenol	2.3	3.3	-
Dimethylbenzofuran	-	0.82	-
2-Methyl-6-propylphenol	-	0.74	-
1-Naphthalenol	-	-	0.28
5,7-Dimethyl-1-indanol	-	0.16	-
Cortol	-	0.78	-
2,2-Dimethyl-5-methoxyindan	-	0.45	-
Carbolic Acid (Phenol; Separate Reported Library Entry)	12.34	-	-
Oxygenated Aromatic / Phenolic Subtotal			
Carboxylic Acids			
Dodecanoic Acid	-	0.55	3.64
Hexadecanoic Acid	0.82	0.05	0.61
Tetradecanoic Acid	-	0.17	-
Acetic Acid	0.39	-	2.86
Octadecanoic Acid	0.14	-	-
Carboxylic-Acid Subtotal			
Nitrogen-Containing Compounds			
Pyridine	1.87	3.5	0.82
2,4-Dimethylbenzenamine	-	0.43	-
Villalstonin	-	1.31	-
Indolizine	-	1.14	-
Dodecanenitrile	-	-	1.2
N-Methyldodecanamide	-	-	0.79
Nitrogen-Containing Subtotal			
Carbonyl / Ester Compounds			
Pentadecanone	1.26	-	-

Compound / Chemical Class	CBO Peak Area (%)	ZAA/Ni 3% Peak Area (%)	AA/Ni 2% Peak Area (%)
Ethyltetramethylcyclopentadiene Ethanone	-	1.33	-
Picolinyl 2-Octadecenoate	-	0.12	-
Diacetate	-	-	0.42
Cyclic Tetra(3,5-Dimethyl-4-Oxyben) Carbonyl / Ester Subtotal	-	-	0.56

cessibility and the availability of catalytic sites within a porous support. Previous studies have reported that metal incorporation into zeolitic materials can modify pore accessibility and may cause partial pore blockage depending on preparation conditions. In the present study, however, quantitative Ni dispersion measurements and post impregnation microscopic characterization capable of resolving Ni particle size and dispersion were not available. Therefore, it cannot be established directly whether differences in Ni dispersion or pore blocking caused the observed performance difference. The porous carbon framework and the available pore radius data may have contributed to differences in reactant accessibility and product transport, but this interpretation remains tentative (Zhang et al., 2018; Srifa et al., 2018).

3. Possible effects of adsorption and desorption of aromatic compounds: the carbonaceous structure of activated carbon may provide favorable interactions with aromatic and phenolic compounds and may influence their adsorption and accessibility to Ni-containing regions. Such interactions could facilitate contact between oxygenated aromatic molecules and catalytically active regions. Following hydrogenation and oxygen removal, changes in molecular polarity could also influence product desorption. Nevertheless, adsorption capacities, surface-interaction strengths, and adsorption kinetics were not directly measured in the present study. Therefore, the proposed adsorption reaction desorption sequence should be considered a plausible interpretation of the observed product distribution rather than a directly demonstrated mechanism.

The increase in hydrocarbon content is consistent with the possible contribution of hydrodeoxygenation and catalytic cracking reactions, which may promote C–O bond cleavage and formation of hydrocarbon products. Similar observations were reported by Zhang et al. (2018), who identified a larger number of hydrocarbon compounds following catalytic upgrading at elevated pyrolysis temperatures. A noticeable reduction in aromatic compounds was also observed after upgrading. The total aromatic peak area decreased from 37.50% in the crude bio-oil to 35.89% after treatment with the ZAA/Ni catalyst and further declined to 28.10% with the AA/Ni catalyst. This reduction is consistent with possible conversion of oxygen-containing aromatic compounds through hydrogenation, deoxygenation, and related secondary reactions (Sun and Wang, 2014).

Phenol, which was the dominant aromatic compound in

the crude bio oil, decreased from 28.59% to 23.38% following treatment with the AA/Ni catalyst and to 18.27% with the ZAA/Ni catalyst. Since phenolic compounds are mainly derived from lignin decomposition during pyrolysis, their reduction is consistent with upgrading involving removal or transformation of oxygen-containing functional groups. Compared with the study by Idris et al. (2020), which reported phenol-rich bio-oil containing up to 42.95% phenolic compounds, the present study demonstrates a more effective reduction in phenolic content.

Elemental analysis further supports these findings. The oxygen content decreased from 13.09% in the crude bio-oil to 9.00% after upgrading with the AA/Ni catalyst and to 11.39% with the ZAA/Ni catalyst. The greater reduction obtained with AA/Ni indicates stronger net oxygen removal under the tested conditions. Ni-containing sites may contribute to hydrogenation and oxygen removal reactions, while activated carbon may influence reactant accessibility through its porous structure. However, the present study does not provide direct evidence to assign the observed oxygen removal to specific Ni active sites, Ni dispersion, or a particular elementary reaction pathway (Muangsuwan et al., 2021; Hadi et al., 2025).

The corrected classification also changes the interpretation of the oxygenated and acidic compounds. The listed oxygenated aromatic/phenolic peak areas sum to 43.23% for CBO, 27.77% for ZAA/Ni, and 27.31% for AA/Ni, indicating a lower reported oxygenated-aromatic fraction after upgrading. Phenol, the dominant reported oxygenated aromatic compound, decreased from 28.59% in CBO to 18.27% with ZAA/Ni and 23.38% with AA/Ni. In contrast, the explicitly identified carboxylic acid peaks sum to 1.35% for CBO, 0.77% for ZAA/Ni, and 7.11% for AA/Ni. Therefore, the present GCMS data do not support a generalized decrease in carboxylic-acid peak area, and no acid-removal conclusion is drawn from these semi-quantitative peak areas. The decrease in elemental oxygen remains an independent observation from elemental analysis. Mechanistically, oxygen removal may involve hydrogenation, C–O bond cleavage, decarboxylation, decarbonylation, and related reactions, but the present GCMS and elemental data provide product level evidence only and cannot distinguish among individual elementary pathways. In addition, quantitative Ni dispersion, catalyst acidity, surface speciation, and in situ characterization were not available. Accordingly, the mechanism

Table 4. Comparison with Selected Published Catalysts.

Catalyst / Study	Feed or Model System	Reaction Information Reported in the Present Reference Set	Hydrocarbon / Product Indicator	HHV Indicator
Fe-Co/SiO ₂ (Cheng et al., 2017)	Pyrolysis bio-oil	HDO; conditions differ from present study	48.53% hydrocarbon reported	40.59 MJ/kg
Ni/C (Shakya et al., 2018)	HTL bio oil from <i>Nannochloropsis</i>	Catalytic upgrading; conditions differ	Not reported in present manuscript text	35.2 MJ/kg
NiAl ₂ O ₄ spinel-type (Srifa et al., 2018)	Palm oil	Deoxygenation; 573 K; 5 MPa; conditions differ	94.3% product yield	Not reported
NiMo/Al ₂ O ₃ and CoMo/Al ₂ O ₃ (Muangsuwan et al., 2021)	EFB derived light bio-oil	Catalytic HDO; conditions differ	Not reported in present manuscript text	Not reported
ZAA/Ni 3% (present study)	EFB crude bio-oil	450 °C; initial H ₂ pressure of 15 bar; 60 min; final pressure ≈125 bar	20.36% peak area	38.81 MJ/kg
AA/Ni 2% (present study)	EFB crude bio-oil	450 °C; initial H ₂ pressure of 15 bar; 60 min; final pressure ≈125 bar	26.66% peak area	40.27 MJ/kg

presented in Figure 1 should be regarded as a plausible mechanistic interpretation consistent with the observed product changes, rather than definitive experimental evidence of the underlying reaction mechanism.

The corrected hydrocarbon peak area was highest for AA/Ni (26.66%) and was accompanied by the appearance of several aliphatic hydrocarbons such as nonane, undecane, tridecane, and tetradecane. These compounds fall within the carbon number range commonly associated with diesel fuels, suggesting that the upgraded bio oil may have greater relevance for liquid-fuel applications. The presence of tetradecane (4.74%), nonane (4.28%), undecane (3.04%), and tridecane (2.10%) in the AA/Ni-treated bio oil is consistent with the formation of fuel-range hydrocarbons. Although the corrected hydrocarbon peak area obtained in this study remained lower than the 48.53% reported by Cheng et al. (2017), the results indicate that nickel-supported activated carbon improved the measured hydrocarbon profile under the tested conditions. The simultaneous reduction of elemental oxygen and increase in the corrected hydrocarbon fraction are consistent with catalytic upgrading, although the available data do not by themselves establish the individual reaction pathways responsible.

The chemical composition analysis in this study is currently limited to a semi quantitative approach based on the relative peak area percentage normalization method derived from GCMS data. Although relative peak area percentages provide an initial overview of shifts and relative abundances

across compound groups (such as hydrocarbons, aromatics, and acids), this method has limitations as it does not account for the varying mass spectrometer detector response factors associated with individual compounds. Consequently, relative peak area percentages do not fully reflect the absolute mass concentrations (mass per sample volume or weight) of the identified chemical components (Negahdar et al., 2016). Additional limitations relevant to interpretation include the absence of catalyst-reuse experiments, post-reaction catalyst characterization, measured gas composition, coke quantification, complete carbon recovery, and independent replicate upgrading runs. These limitations prevent definitive conclusions regarding long-term catalyst stability, complete carbon fate, and statistical significance. Nevertheless, the available results are sufficient to establish a comparative performance trend between the two selected catalyst formulations under the tested conditions. A comparison of the results of this study with selected published catalysts is summarized in Table 4.

As shown in Table 4, the AA/Ni 2% catalyst produced a corrected hydrocarbon peak area of 24.42% and an HHV of 40.27 MJ/kg, compared with 13.61% and 38.81 MJ/kg for ZAA/Ni 3%, respectively. The hydrocarbon fraction obtained with AA/Ni was slightly higher than the 22.44% reported by Cheng et al. (2017), although its HHV was slightly lower (40.27 versus 40.59 MJ/kg). Shakya et al. (2018) reported a lower HHV of 35.2 MJ/kg using Ni/C for upgrading *Nannochloropsis*-derived bio-oil. However, differ-

ences in feedstock, catalyst, and reaction conditions prevent direct performance comparison. These results demonstrate that the present Ni-impregnated catalysts can generate upgraded bio oil with characteristics comparable to those reported in previous catalytic upgrading studies.

4. CONCLUSIONS

This study showed that catalytic hydrodeoxygenation changed the measured physicochemical and chemical characteristics of crude bio oil derived from oil palm empty fruit bunches (EFB). Both nickel impregnated activated carbon (AA/Ni) and nickel impregnated activated natural zeolite (ZAA/Ni) were associated with lower oxygen content and changes in the reported GCMS compound distribution. Among the two selected catalyst formulations, AA/Ni showed the more favorable reported performance under the tested conditions. It had the highest corrected hydrocarbon peak area (26.66%), reduced oxygen content from 13.09% to 9.00%, and increased HHV from 39.13 to 40.27 MJ/kg. The corrected GCMS output indicates a lower reported oxygenated aromatic fraction after upgrading, whereas the listed carboxylic acid peak areas do not show a consistent decrease. Hydrogen consumption was not directly measured and is therefore not quantified. These conclusions are limited to the selected formulations and single reported upgrading runs; the study does not establish statistical significance, catalyst durability, complete carbon balance, or compliance with a complete commercial fuel specification. The observed product changes are consistent with possible contributions from hydrogenation, deoxygenation, cracking, and related reactions, but the available dataset does not provide direct in situ evidence for specific active sites or elementary reaction mechanisms.

5. ACKNOWLEDGEMENT

The authors would like to express their sincere gratitude to Universitas Lancang Kuning for institutional support. The authors also gratefully acknowledge the Laboratory of the Center for Research and Development of Forest Products for providing laboratory facilities and technical assistance during the analysis.

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