Preparation of Ni Catalyst Supported on Green SiO2 for Green Diesel Production from Sludge Oil

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**Abstract**. The current dominance of food-based feedstocks in green diesel production has a detrimental impact on the food industry, resulting in an economic deficit. To address this challenge, alternative feedstocks, such as sludge from downstream processing of crude palm oil containing 36.5% oil, offer a promising solution. The sludge oil contains various chemical compounds, including biodiesel, triglycerides, free fatty acids, non-polar compounds, and some polar compounds, which can be converted into green diesel. Therefore, the objective of this study is to investigate the use of sludge oil from downstream processing of crude palm oil for green diesel production via catalytic hydrotreating, with a particular focus on the synthesis, properties, and performance of Ni/SiO catalysts. A response surface methodology (RSM) technique with a Box-Behnken experimental design (BBD) was employed to assess and optimize hydrocarbon yield, considering variables such as reaction temperature (250-300°C), reaction time (3-5 hours) and catalyst loading (3- 7g). The synthesis of silica (SiO2) with 91.8% purity and an amorphous phase was successfully achieved through rice husk ash's calcination and acid leaching processes, which was subsequently employed as a support for nickel (Ni) catalysts. A 7.44% weight Ni catalyst was successfully impregnated into SiO2. The hydrodeoxygenation (HDO) process was conducted under the following conditions: 275°C, 4 h, 5 g of catalyst, and 5 MPa H2 gas. The results indicated that 89.62% of the hydrocarbons produced were diesel-like hydrocarbons (C15-C18), with 16.81% being lighter hydrocarbons (C12-C14) through the HDO pathway. The results of the response surface methodology with Box–Behnken design (RSM- BBD) indicated that the interaction between reaction time and catalyst loading significantly influenced the reaction activity. The model predicted that the optimal conditions for hydrocarbon yield were a reaction temperature of 261°C, a reaction time of 3.67 h, and a catalyst loading of 4.86 g.

# INTRODUCTION

The utilization of fossil fuels is not conducive to long-term social progress due to their harmful effects on the ecology, environmental protection, and non-renewable nature [1]. As a direct consequence of the excessive extraction of fossil fuels, the accessibility of energy and the condition of surrounding ecosystems have reached a critical point of concern [2]. The mounting environmental impact of fossil fuel usage, coupled with governmental initiatives aimed at environmental protection, has increased interest in adopting environmentally friendly fuels. This interest is driven by the desire to reduce CO2 and other greenhouse gas emissions, thereby reducing the adverse impact on the environment [3]. Green diesel is a hydrocarbon that is environmentally friendly and has the potential to replace petroleum diesel.

Green diesel production can utilize a multitude of feedstocks, including vegetable oils, animal lipids, used cooking oil, microalgae, and lignocellulosic biomass. This latter material, consisting mainly of triglycerides, is particularly interesting due to its high carbon content. It is believed to be a promising attribute for biofuels, given its potential to reduce carbon footprint. The selection of a suitable feedstock depends upon several factors, including its availability, cost, and environmental impact. Renewable feedstocks, such as vegetable oils and microalgae, do not release greenhouse gases during combustion and represent more environmentally friendly alternatives to petroleum diesel.

Nevertheless, the cost of producing diesel from renewable sources is currently higher than the cost of producing diesel from petroleum. Despite the challenges above, the production of diesel from renewable feedstocks represents an attractive and potentially profitable technology with the potential to reduce greenhouse gas emissions and improve air quality [4]. Another potential and economically viable feedstock for producing environmentally friendly diesel fuel is industrial sludge derived from the crude palm oil processing industry. One advantage of this feedstock is that it does not impact the economy or food consumption but reduces pollution. Annually, Indonesia generates 67.8 million tons of waste, some of which originates from the industrial sector. A significant number of industries in Indonesia continue to grapple with the effective management of their waste. The majority of these companies' sewage treatment facilities generate approximately 183 tons of sludge per week. These industries reimburse a third party IDR 2,400 per kilogram to facilitate the disposal of the sludge, thereby preventing the accumulation of sludge within the industry. In addition to the issues above about the feedstock, this palm oil industry sludge represents an optimal feedstock for producing environmentally friendly green diesel through a hydrotreating process. The production of eco-friendly green diesel will reduce diesel demand and provide a solution to the sludge problem currently faced by the palm oil industry.

In comparison to pyrolysis, which is conducted at temperatures between 400 and 600 degrees Celsius, triglyceride hydrotreatment is a more effective process due to its higher carbon source utilization ratio [5]. Hydrotreatment converts triglycerides into green diesel with low oxygen content and high cold flow properties. Green diesel processes high cetane numbers (85-99), which are even higher than those of fossil diesel (45-55) [6].

The hydrotreatment process is comprised of three fundamental steps. The initial stage of the process is the hydrogenation of unsaturated triglycerides to form saturated triglycerides. The second stage follows the hydrogenolysis of the saturated triglycerides to produce fatty acids. The final step is the deoxygenation of intermediate fatty acids to form diesel-like hydrocarbons via three main pathways: decarbonylation (DCO), decarboxylation (DCO2), and hydrodeoxygenation (HDO) [7].

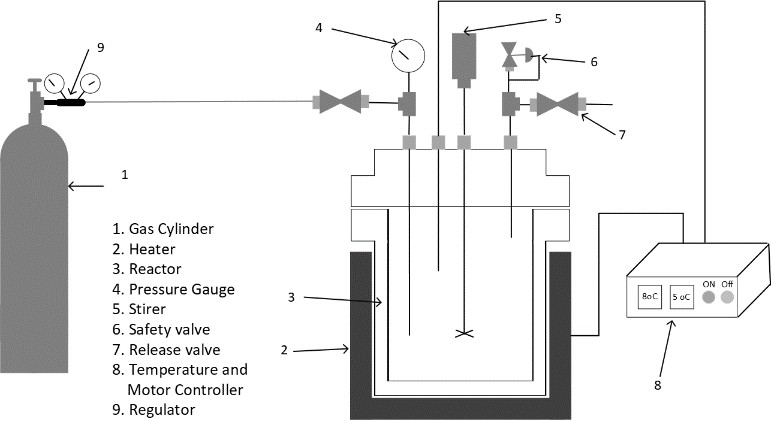
The efficacy of water treatment processes is contingent upon the selection of catalysts and the reaction conditions. It is noteworthy that two distinct categories of catalysts have attracted significant research attention for triglyceride hydrotreatment: noble metal catalysts, including palladium (Pd) and platinum (Pt), and transition metal catalysts, such as nickel (Ni) and molybdenum (Mo). Veriansyah et al. researched the efficacy of diverse catalysts, including NiMo, CoMo, Pd, Ni, Pt, and Ru, in influencing the hydroprocessing of soybean oil to produce renewable diesel [8]. Similarly, Silva et al. researched the synthesis of biokerosene and green diesel from macauba oil, utilizing palladium-on-carbon (Pd/C) catalysts [9]. Noteworthy contributions were also made by Coumans and Hensen in 2017, who investigated the hydrodeoxygenation of model compounds representative of vegetable oils using NiMo/Al2O3 sulfide catalysts [10]. Noble metal catalysts are distinguished by their high catalytic activity, yet their rarity renders them costly. Recently, researchers have introduced molybdenum catalysts into the hydrotreating process. For instance, Hollak and colleagues investigated the hydrodeoxygenation of oleic acid using a catalyst comprising tungsten carbide (W₂C) and molybdenum carbide (Mo2C) [11]. Similarly, Han et al. described a novel method for synthesizing carbon-supported molybdenum carbide (MoC) catalysts, which were subsequently evaluated for the hydrodeoxygenation of edible oils [12]. Bitter and Stellwagen researched using molybdenum and tungsten carbide catalysts to deoxygenate fatty acids [13]. Notably, the current catalysts for producing green diesel from palm oil industrial sludge necessitate using specific and costly precursor materials.

This research addresses the issue of catalyst cost by developing Ni/SiO₂ catalysts from commercial Ni and SiO₂ extracted from rice husks. Rice husk is a plentiful and sustainable raw material for catalyst production in Indonesia, the third largest rice-producing country in the world. Rice husk is a byproduct of rice milling, and Indonesia produces approximately 54 million tons of rice per year, resulting in 4.32 to 5.4 million tons of rice husk. Rice husk is primarily utilized as animal feed, though it can be employed for many other applications, including the production of catalysts. No research has been conducted using palm oil industrial sludge to produce green diesel using Ni/SiO catalysts derived from rice husks. This research will focus on reducing pollution and fossil fuel dependence by developing a sustainable and cost-effective catalyst to produce green diesel from palm oil industrial sludge and rice husk. Furthermore, response surface methodology (RSM) will be employed using the Box-Behnken experimental design (BBD) to optimize the hydrocarbon yield.

# EXPERIMENT

## Material

The raw materials employed comprise industrial sludge (solid waste) derived from PT Wilmar Nabati Gresik. These materials are stored at refrigeration temperature to maintain their properties. Furthermore, PT Benteng Api Technic kindly provided rice husk ash, n-hexane by PT Bratachem, distilled water, Ni(NO3)2.6H2O, HCl, N2 gas, and H2 gas were obtained from commercial sources. The experimental setup, illustrated in Figure 1, employs a cylindrical hydrothermal reactor with an outer material of SS-316 stainless steel. The reactor is equipped with essential components, including a thermocouple connected to a pressure controller and gauge, a stirrer with adjustable stirring speed, and a jacket heater. Moreover, various auxiliary equipment was employed to facilitate the research process, including a furnace, a tube furnace, and an oven.



**Image 1.** Schematic of the catalytic hydrotreatment setup.

## Green Silica Extraction

Green Silica (SiO2) was extracted from rice husk ash using the calcination method, **modifying** the operating conditions described by Della, Kühn, and Hotza in 2002 [15]. A furnace was utilized to calciner 58.5 grams of rice husk ash at a temperature of 800oC for two h**ours**. The resulting rice husk ash (RHA) was subsequently extracted from the furnace and cooled to room temperature. Subsequently, the RHA was pulverized using a household blender with the objective of reducing its size. Subsequently, the blended RHA was subjected to leaching with a solution of 10% 37% HCl in water at a volume-to-weight ratio 8:1. The leaching process was conducted at 80°C with 800 rpm stirring for 1.5 hours. Subsequently, the leached RHA was subjected to a second calcination process at 800°C for another two h**ours**. The final RHA was subjected to a ball milling at 500 rpm for 15 minutes, **forming** fine particles of SiO2. The chemical composition of the product was characterized using X-ray fluorescence analysis (XRF). At the same time, X-ray diffraction (XRD) and scanning electron microscopy (SEM) were employed to investigate the phase and morphology of the material. Furthermore, the surface area and pore dimensions of the SiO₂ were determined through Brunauer-Emmett-Teller (BET) analysis.

## Catalyst preparation

Ni/SiO₂ catalysts were prepared using the impregnation method with modified operating conditions, as described by Chen (2015) [16]. A solution of 37.29 grams of Ni(NO₃)₂·6H₂O in 250 milliliters of deionized water was heated until Ni(NO₃)₂·6H₂O was fully dissolved. Subsequently, 100 g of green silica (SiO2) was added and stirred (300 rpm) for 12 h at 110°C. The solid product was then dried at 110°C for 24 hours. Subsequently, the dried solid product was crushed and sieved through a 325-mesh sieve. Subsequently, the sieve product was transferred to a tube furnace. The product was subjected to calcination in the presence of nitrogen gas at 500°C for two hours. Subsequently, the gas was switched to hydrogen, and the temperature was increased to 500°C for two more hours. Subsequently, the tube furnace was permitted to cool to ambient temperature.

## Catalyst characterization

X-ray diffraction (XRD), a technique that employs X-rays to analyze the crystal structure of materials, was employed to ascertain the phase identity of the catalyst. The Brunauer-Emmett-Teller (BET) method was employed to determine the specific surface area of the catalyst. The specific surface area is defined as the total surface area of a material, expressed in units of area per unit mass. This is an important parameter for catalysts, as a high surface area provides more sites for catalytic reactions. Scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX) was employed to analyze the catalyst morphology, elemental distribution, and crystallization. Scanning electron microscopy (SEM) is a method of viewing very small surface details using an electron beam. Energy-dispersive X-ray spectroscopy (EDX) is a technique that can be employed to ascertain the composition of a given sample. Fourier transform infrared spectroscopy (FTIR) is employed to identify the chemical bonds present in the catalyst. Fourier transform infrared spectroscopy (FTIR) is a technique that measures the absorption of a sample by infrared radiation. The absorption spectrum of the sample can be employed to ascertain the nature of the functional groups present.

## Green Diesel Production

A hydrothermal reactor constructed from SS-316 stainless steel was employed to generate green diesel. The hydrothermal reactor was filled with 100 mL of sludge oil (sludge oil was extracted from sludge using the maceration method) and 5 g of Ni/SiO₂ catalyst. Subsequently, hydrogen gas was introduced into the reactor solution, increasing the pressure to 5 MPa. The reactor was heated to 275°C and maintained at this temperature for four hours. The mixture was subjected to mechanical stirring at a constant speed of 500 rpm throughout the reaction to achieve thorough homogeneity.

For quantification purposes, liquid samples were diluted with n-hexane and analyzed using Shimadzu GC/MS gas chromatography (2010 model). The external standard technique employed a capillary HP-5MS column (30 m x 320 μm x 0.25 μm). The GC/MS operating parameters included an oven program that commenced at 60°C for two minutes, increased by 10°C/min to 160°C and was maintained for five minutes, then increased by 10°C/min to 240°C and was maintained for five minutes, and finally increased by 10°C/min to 300°C and was maintained for 14 minutes, with an injection temperature of 270°C. Equation (1) can be employed to calculate feedstock conversion from GC/MS analysis.

Conversion = 𝐶𝐻𝐶×100%

𝐶𝑇𝑂𝐿

CHC is the hydrocarbon content, and CTOL is the total compound.

(1)

The ratio of hydrodeoxygenation to decarboxylation and decarbonylation (HDO/(DCO2 + DCO)) was found with Equation (2).

HDO/(DCO2 + DCO) ratio = 𝐶16+𝐶18 × 100% (2)

𝐶15+𝐶17

The proportional compositions of hexadecane, octadecane, pentadecane, and heptadecane are denoted as C16, C18

, C15 , and C17, respectively.

The cracking ratio is evaluated by Equation (3).

Crack Ratio = 𝐶𝐻𝐶−𝐶15−𝐶16−𝐶17−𝐶18 × 100% (3)

𝐶𝑇𝑂𝐿

Where total hydrocarbons, pentadecane, hexadecane, heptadecane, octadecane, and total compounds in the liquid product are denoted by CHC, C15, C16, C17, C18, and CTOL.

## Experimental design

A Box-Behnken experimental design with three variables was used to examine the response pattern and identify the optimal combination of variables. The effects of reaction temperature (A, in °C), reaction time (B, in hours), and

catalyst loading (C, in grams) at three different levels are summarized in Table 1. A total of 15 experiments were conducted and analyzed using Minitab 18 software.

**Table 1.** Input variables and experimental levels for Box-Behnken on hydrocarbon yields

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Variables** | **Symbol** | **Level** | | |
| -1 | 0 | 1 |
| Reaction Temperature (0 C) | A | 250 | 275 | 300 |
| Reaction time (hour) | B | 3 | 4 | 5 |
| Catalyst Loading (g) | C | 3 | 5 | 7 |

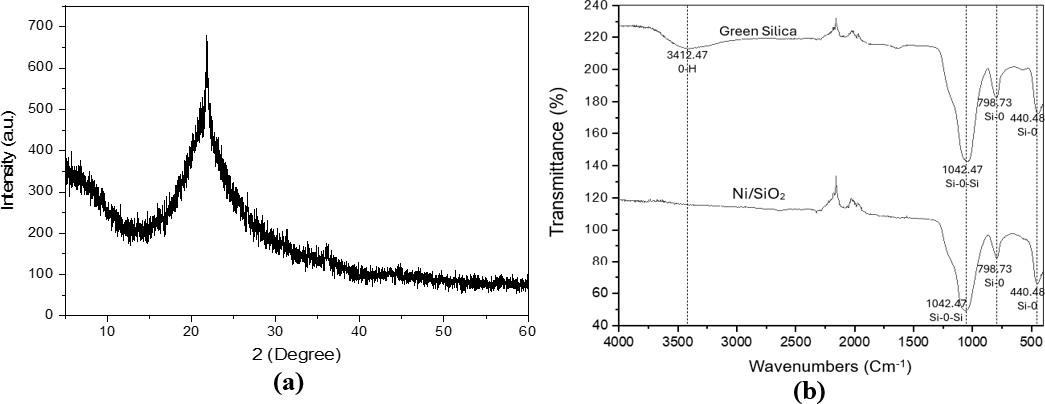
# RESULTS AND DISCUSSION

## SiO2 Characterization

The RHA samples were subjected to a two-hour calcination at 800°C and an acid-leaching process at 80°C for an hour and a half, followed by another two-hour calcination at 800°C. The multi-stage method removes elemental carbon and other unwanted components from the RHA, thereby increasing the percentage of green silica. Table 2 presents the extracted green silica content, which is 91.8%, slightly lower than the results reported by Della et al. (SiO2 94.95%) [15]. In addition to silica, Table 2 indicates the presence of several other elements, including potassium (K), calcium (Ca), iron (Fe), copper (Cu), manganese (Mn), and zinc (Zn). These compositional variations may be attributed to several factors, including the material's geographical origin, the year it was harvested, the methodology employed in the sample preparation process, and the analytical methodology used [15].

**Table 2**. Chemical composition of RHA and green silica (SiO).2

|  |  |  |
| --- | --- | --- |
| **Compound** | **RHA (%)** | **Green Silica (%)** |
| Al O23 | - | 0.4 |
| SiO2 | 82.15 | 91.8 |
| P O25 | 1.8 | 0.985 |
| SO3 | 0.15 | - |
| K O2 | 7.165 | 3.21 |
| CaO | 2.08 | 0.875 |
| TiO2 | 0.046 | 0.035 |
| Cr O23 | 0.7615 | 0.265 |
| MnO | 0.864 | 0.3985 |
| Fe O23 | 4.51 | 1.75 |
| NiO | 0.17 | 0.0575 |
| CuO | 0.16 | 0.096 |
| ZnO | 0.025 | 0.01 |
| Rb O2 | 0.0185 | - |
| BaO | - | 0.02 |
| Re O27 | 0.04 | 0.045 |
| OsO4 | 0.0095 | - |

The calcination temperature and time are crucial factors that influence whether green silica retains its amorphous state (as observed in rice husk ash) or undergoes crystallization. Notwithstanding the relatively elevated calcination temperature and duration employed in this investigation, the green silica configuration within the ash predominantly preserves its amorphous nature. Figure 2a illustrates the results of the X-ray diffraction (XRD) analysis, which revealed the presence of a peak at approximately 22°. This peak indicates an initial crystallization process that results in the formation of a poorly structured cristobalite phase. Notably, the absence of significant peaks across the scanning range (10° to 80°) indicates that the sample has a well-defined crystal structure. X-ray diffraction analysis revealed the presence of a distinctive amorphous component in the green silica sample, indicating the absence of an organized crystalline phase. This observation is consistent with the preferred calcination temperature below 700 °C. It is possible that higher temperatures may cause the amorphous green silica to become crystalline. Furthermore, studies have demonstrated that reheating RHA at elevated temperatures for an extended period can facilitate the crystallization of green silica [15]. This phenomenon was not observed throughout the calcination process employed in this study. The green silica structure of the RHA treated in this study remained amorphous.

**Image 2.** (a) XRD spectra of green silica (b) FTIR spectra of green silica and Ni/SiO .2

**Table 3.** Textural properties of SiO2 and Ni/SiO2

|  |  |  |  |
| --- | --- | --- | --- |
| **Sample** | **surface area (m²/g)** | **pore volume (cm³/g)** | **average pore diameter (nm)** |
| SiO2 | 6.6 | 0.01550 | 6.3938 |
| Ni/SiO2 | 6.537 | 0.00851 | 26.061 |

Fourier transform infrared (FTIR) spectroscopy characterized the green silica sample. The resulting spectrum is depicted in Figure 2b. The band at 3412.47 cm-1 indicates the hydroxyl group's stretching vibration (O-H). The band at 1042.47 cm-1 indicates asymmetric stretching vibrations of the Si-O-Si bond. The band at 798.73 cm-1 corresponds to symmetric vibrations of the Si-O bond. Finally, the band at 440.48 cm-1 indicates the bending of the Si-O bond in the siloxane group. [17] The characteristic bands observed in the green silica synthesized for this study are similar to those found in commercially available silica. The BET method (Table 3) indicates that silicon dioxide (SiO2) has a surface area of 6.6 m²/g, a pore volume of 0.01550 cm³/g, and an average pore diameter of 6.3938 nm (Table 3). This surface area is considerably lower than that of rice husk ash (RHA), which is reported to be between 100 and 150 m²/g (18). This reduction in surface area is likely attributable to the heating process employed to prepare the SiO2. Higher temperatures and longer heating times may result in particle agglomeration, which could subsequently reduce the overall porosity. [19][15]. It is also important to note that the surface area of RHA can be affected by the fineness of the soil, with studies reporting values ranging from 10.857 m²/g to 17.463 m²/g [20]. The RHA samples exhibit a diverse range of appearances, predominantly black with scattered gray particles (Figure 3a). This color is a consequence of the presence of carbonaceous material at various stages of combustion, which is a result of the rice husk combustion process. Following the heating and grinding stages of the activation process, the resulting green silica undergoes a reduction in particle size. It shifts towards a uniform gray color (Figure 3b). This transformation is associated with eliminating carbonaceous material, which produces a more refined and dynamic silica product.



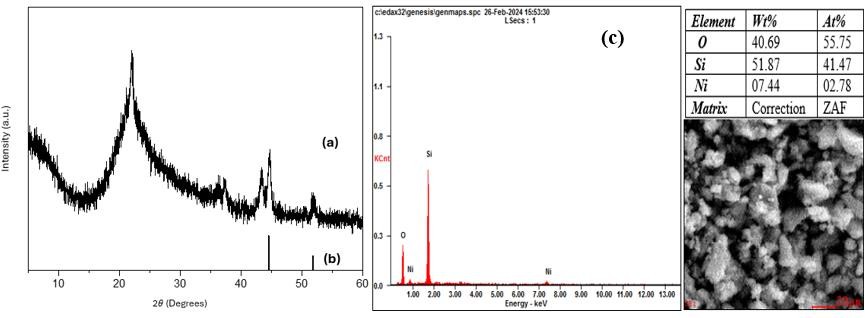
**Image 3.** (a) Rice husk ash (a) green silica (SiO

## Catalyst Characterization

The catalyst was synthesized via a wet impregnation approach. Subsequently, the samples were subjected to a drying process in an oven for 24 hours. Subsequently, the samples were pulverized to achieve a more homogeneous particle size distribution. The resulting catalyst was placed into a tube furnace for calcination under a nitrogen flow of 500°C for two hours. Subsequently, the calcined material was subjected to a reduction step, exposing it to hydrogen gas at a temperature of 500°C for two hours. The objective of this research is to develop a 7% Ni/SiO₂ catalyst. This research was inspired by Peng's (2012, 2013) work, which investigated the impact of nickel loading on n-C selectivity using ZrO₂ as a support material. In 2012, the findings demonstrated an increase in the selectivity of n-C17 from 90% to 96% when the nickel content was elevated from 5% to 10%. However, the results of the 2013 study indicated a contrasting trend, with the selectivity of n-C17 decreasing from 90% to 85% for the same nickel loading variation [21][22] .

Figure 2b presents the Fourier Transform Infrared Spectroscopy (FTIR) spectrum of the synthesized catalyst (Ni/SiO₂). The catalyst spectrum is comparable to that of the SiO₂ buffer, indicating minimal structural alteration during the catalyst preparation process. Notably, most characteristic bands associated with SiO₂ were retained in the catalyst spectrum. Notably, the absence of the O-H stretching band is a noteworthy observation. Furthermore, the bands potentially caused by the catalyst, observed at 1042.47 cm-1, 798.73 cm-1, and 440.48 cm-1, appear less intense than those observed in the SiO2 reference spectrum. This reduction in peak intensity can be attributed to nickel sintering during catalyst manufacturing, as previously reported in reference [23]. The FTIR results confirmed the presence of nickel. However, given the minimal quantity of Ni deposited, it was not feasible to discern the specific form of Ni via FTIR analysis. Table 3 presents the Brunauer-Emmett-Teller (BET) analysis results, demonstrating a reduction in surface area, pore volume, and average pore diameter for Ni/SiO₂ compared to pure SiO₂. These observations can be attributed to the precipitation-precipitation of Ni particles within the pores of the silica support, which leads to partial blockage and a reduction in accessible surface area and porosity [24].

Figure 4a presents the synthesized catalyst's X-ray diffraction (XRD) pattern for the 2θ range from 5° to 60°. The diffraction pattern exhibits well-defined peaks at 44.79° and 51.8°, which can be attributed to metallic nickel (Ni). These peaks correspond to the Ni crystal planes, identified using the Joint Committee on Powder Diffraction Standards (JCPDS) file No. 04-850 (Figure 4b). The observed lattice constants, calculated from the peaks above, are 2.02321 Å and 1.76406 Å, which closely agree with the Ni standard values reported in the JCPDS database. This close agreement indicates the catalyst's successful formation of the Ni phase. Furthermore, the presence of diffraction peaks with relatively narrow widths indicates the presence of Ni nanoparticles in the catalyst. [25] Chen also observed similar results in his research [16].



**Image 4**. (a) XRD spectra of 7% Ni/SiO catalyst2 (b) JCPDS file no. 04-850 (c) Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX) analysis of 7% Ni/SiO catalyst.2

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were employed to investigate the morphology and elemental composition of the synthesized catalyst (Figure 4c). As illustrated in the SEM image, the distribution of the particles is irregular. The EDX spectra exhibited characteristic peaks at 0.9 keV and 7.5 keV, thereby confirming the presence of nickel. The quantitative EDX analysis revealed that the predominant elements were silicon (Si), oxygen (O), and nickel (Ni), with respective weight percentages of 51.87%, 40.69%, and 7.44%. The results are in accordance with the expected composition of the 7% Ni/SiO₂ catalyst, indicating the successful impregnation of nickel nanoparticles on the silica support.

## Hydrocarbon production and statistical analysis

A preliminary selection process was employed to identify the optimal conditions for producing green diesel from sludge oil using a Ni/SiO₂ catalyst. The selected conditions were a reaction temperature of 275°C, a reaction time of 4 hours, and a catalyst loading of 5 g. The experimental results, as analyzed by GC/MS, demonstrated a total hydrocarbon yield of 98.63%, consisting of 83.16% diesel-like hydrocarbons (C15-C18), 16.81% lighter hydrocarbons (C12-C14), and a cracking ratio of 0.15. To ascertain the efficacy of the catalyst, a control reaction was conducted under identical conditions in the absence of the catalyst, resulting in the production of 70.18% hydrocarbons, including 75.26% diesel-like hydrocarbons (C15-C18), 15.26% lighter hydrocarbons (C12-C14), and 9.48% hydrocarbons (C20-C24). The HDO/(DCO2 + DCO) ratio was employed to assess the level of HDO and the prevalence of the DCO2 + DCO pathway. Boda et al. proposed that the adsorption characteristics on the catalyst surface result in disparate pathways, given that metal sites exhibit distinctive preferences for adsorbing functional groups. [26] With Ni/SiO₂, the ratio is 1.78, indicating a preference for the HDO pathway over DCO₂ + DCO.

**Table 4**. Experimental designs generated by RSM-BBD and corresponding responses for hydrocarbon yields.

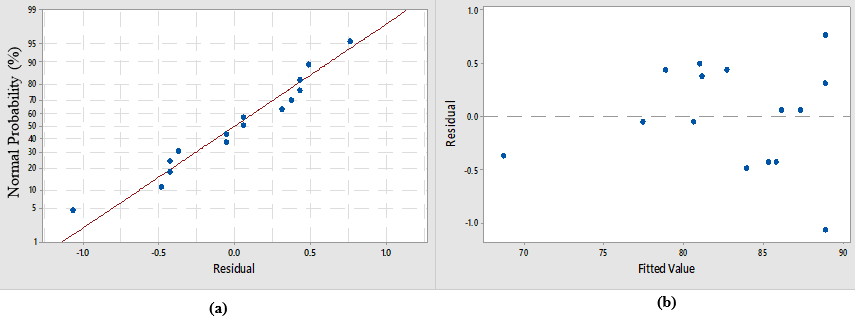
|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Run** | **A: Reaction temperature (oC)** | **B: Reaction time (hours)** | **C:**  **Catalyst Loading** | **Hydrocarbon yield (%)** | **C15 -C18 (%)** | **C12 -C14 (%)** |
| 1 | 250 | 3 | 5 | 87.33 | 83.63 | 16.37 |
| 2 | 300 | 3 | 5 | 86.15 | 81.59 | 18.41 |
| 3 | 250 | 5 | 5 | 80.52 | 82.39 | 17.61 |
| 4 | 300 | 5 | 5 | 77.35 | 81.89 | 18.11 |
| 5 | 250 | 4 | 3 | 85.34 | 82.94 | 17.06 |
| 6 | 300 | 4 | 3 | 84.84 | 83.95 | 16.05 |
| 7 | 250 | 4 | 7 | 83.11 | 80.39 | 19.61 |
| 8 | 300 | 4 | 7 | 79.26 | 83.24 | 16.24 |

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Run** | **A: Reaction temperature (oC)** | **B: Reaction time (hours)** | **C:**  **Catalyst Loading** | **Hydrocarbon yield (%)** | **C15 -C18 (%)** | **C12 -C14 (%)** |
| 9 | 275 | 3 | 3 | 81.5 | 81.88 | 18.12 |
| 10 | 275 | 5 | 3 | 81.47 | 82.68 | 17.32 |
| 11 | 275 | 3 | 7 | 83.42 | 82.48 | 17.52 |
| 12 | 275 | 5 | 7 | 68.3 | 81.07 | 18.93 |
| 13 | 275 | 4 | 5 | 87.79 | 84.18 | 15.81 |
| 14 | 275 | 4 | 5 | 89.17 | 83.03 | 16.97 |
| 15 | 275 | 4 | 5 | 89.62 | 83.19 | 16.81 |

An optimization study was conducted using the RSM-BBD approach, and the responses of each experiment are presented in Table 4. The ANOVA analysis of the quadratic model of the response surface in Table 5 indicates that the F value of 68.85 is highly significant. There is a 0% chance that an F value of this magnitude could occur due to error. In this model, the parameters A, B, C, B², C², and BC affect hydrocarbons' yield significantly. The analysis of variance (ANOVA) of the regression model demonstrated a coefficient of determination (R²) of 0.9920, indicating that the model explained 99.2% of the variability in the response, thereby demonstrating strong predictive power. The adjusted coefficient of determination (adjusted R²) was 97.76%, further reinforcing the significance of the model. The F value of 0.55 indicates that the discrepancy is not a significant contributor to the pure error (1.819). A residual analysis was conducted to assess the adequacy of the model. This involved using a normal probability plot of the residuals (Figure 5a) and a plot of the residuals versus the fitted values (Figure 5b). The normal probability plot indicates that the residuals are distributed normally along a straight line, suggesting that the errors are not statistically significant. Furthermore, the residuals are randomly distributed across the upper limit in relation to the predicted reaction, which indicates that the model accurately estimates the relationship between the variables [27].

**Table 5.** ANOVA analysis of the response surface mode and each model term.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Source** | **df** | **Sum of squares** | **Mean square** | **F value** | **p-value** |
| Model | 9 | 411.974 | 45.775 | 68.85 | 0 |
| A: Reaction Temperature | 1 | 9.461 | 9.461 | 14.23 | 0.013 |
| B: Reaction Time | 1 | 118.272 | 118.272 | 177.89 | 0 |
| C: Catalyst Loading | 1 | 45.41 | 45.41 | 68.3 | 0 |
| A2 | 1 | 0.01 | 2.239 | 3.37 | 0.126 |
| B2 | 1 | 87.855 | 101.527 | 152.71 | 0 |
| C2 | 1 | 90.242 | 90.242 | 135.73 | 0 |
| AB | 1 | 0.99 | 0.99 | 1.49 | 0.277 |
| Ac | 1 | 2.806 | 2.806 | 4.22 | 0.095 |
| SM | 1 | 56.927 | 56.927 | 85.62 | 0 |
| Error | 5 | 3.324 | 0.665 |  |  |
| Lack of fit | 3 | 1.506 | 0.502 | 0.55 | 0.695 |
| Pure Error | 2 | 1.819 | 0.909 |  |  |
| Total | 14 | 415.298 |  | Adjusted R2 | 97.76% |
| Standard deviation | 0.815383 |  |  | R2 Prediction | 93.21% |
| R2 | 99.20% |  | Sufficient precision | | 28.1822 |



**Image 5.** (a) Normal probability plot of hydrocarbon yield residuals (b) plot of hydrocarbon yield residuals vs. matched values

## Influence of variables on hydrocarbon yield

An optimization study was conducted using the Box-Behnken design to maximize the yield of hydrocarbons from oil sludge. This entailed examining the effects of three distinct combinations of variables. Two-dimensional (2D) contour plots and three-dimensional (3D) response surface plots were employed to illustrate the influence of the three parameters on the hydrocarbon yield. To illustrate the optimal hydrocarbon yields under varying conditions, plots were constructed for reaction time and reaction temperature, catalyst loading and reaction time, and catalyst loading and reaction temperature. Figure 6a-b illustrates the interaction between reaction temperature (A) and reaction time (B) on the hydrocarbon yield using a 3D response surface plot and a 2D contour plot, with a constant catalyst loading of 5 g. It can be observed that an increase in reaction temperature and a reduction in reaction time have a beneficial effect on the reaction. It can be observed that the hydrocarbon yield does not increase with an extension of the reaction time in the process.

Conversely, the rapid increase in reaction activity is largely attributable to the elevated reaction temperature [28]. Furthermore, elevated temperatures can facilitate cracking events by inducing the cleavage of C-C bonds, resulting in the formation of shorter hydrocarbon chains [29]. The results from the Box-Behnken design indicate that a reaction temperature of 250-298°C, a catalyst loading of 5 g, and a reaction period of 3.1-4.2 hours are optimal for achieving hydrocarbon yields exceeding 88%.

Figures 6c and 6d illustrate the 3D response plots and 2D contour plots, respectively, for the interaction of reaction time (B) and catalyst loading (C) on hydrocarbon yield, with the temperature set to 275°C. The results demonstrate that the maximum hydrocarbon yield exceeds 85% when the catalyst loading is within the range of 3.9 to 6.7 grams and the reaction time is between 3.5 and 4.6 hours. Nevertheless, an increase in the catalyst loading and reaction time reduced the hydrocarbon yield. This finding is consistent with the negative interaction of BC in Equation (4), which indicates that increasing both parameters simultaneously will reduce hydrocarbon yield. The reduction in hydrocarbon yield with increasing reaction time is attributed to unfavorable side reactions, such as over- cracking into lighter fractions that become gaseous instead of liquid hydrocarbons. In addition, an extended reaction time results in the catalyst's deactivation due to coke deposition, which reduces the reaction activity [30].

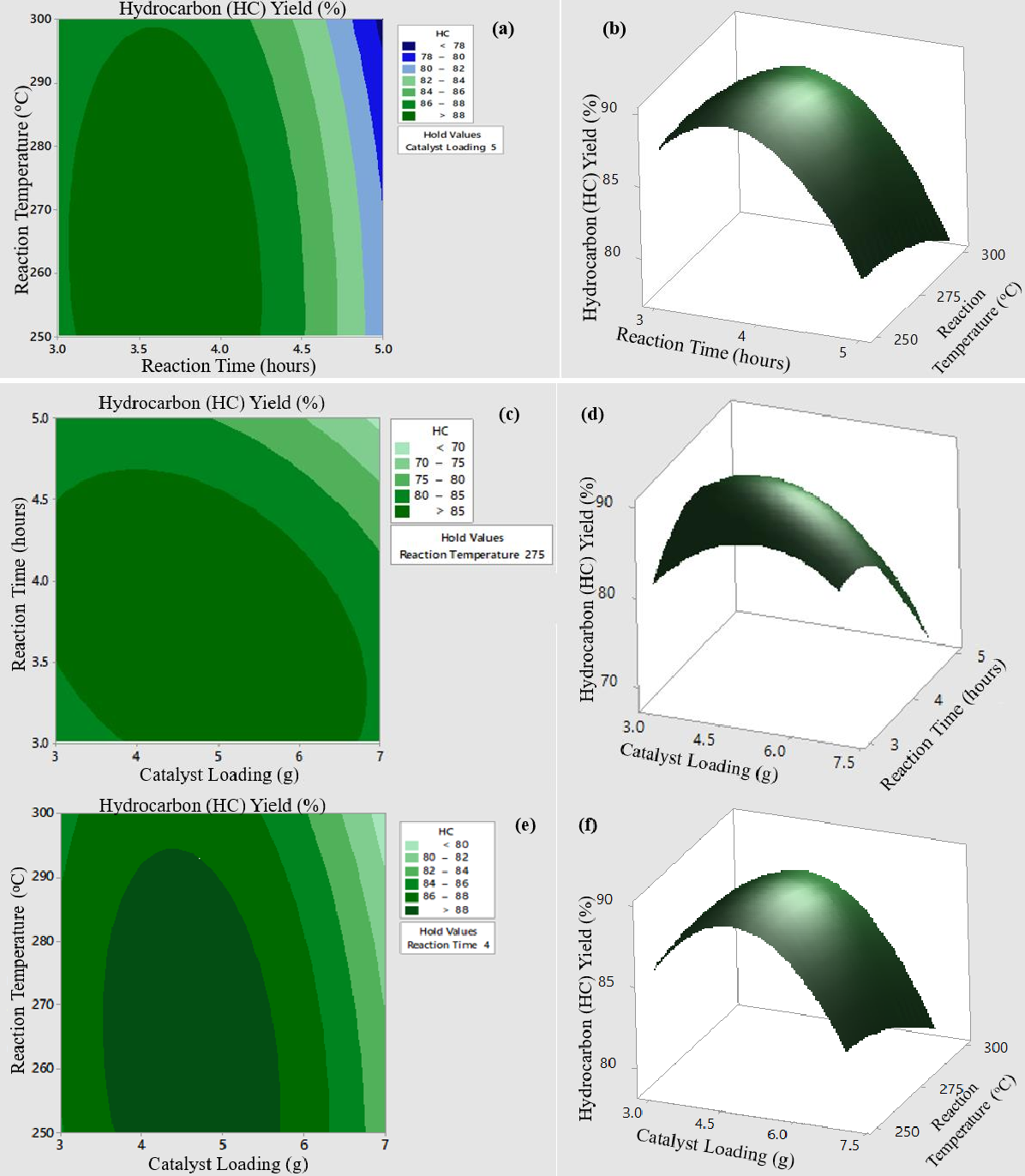
Hydrocarbon yield = -169.5 + 0.805 A + 53.01 B + 23.32 C – 0.001246 A2 – 5.244 B2

- 1.236 C2 – 0.0199 AB – 0.01675 AC – 1.886 BC (4)

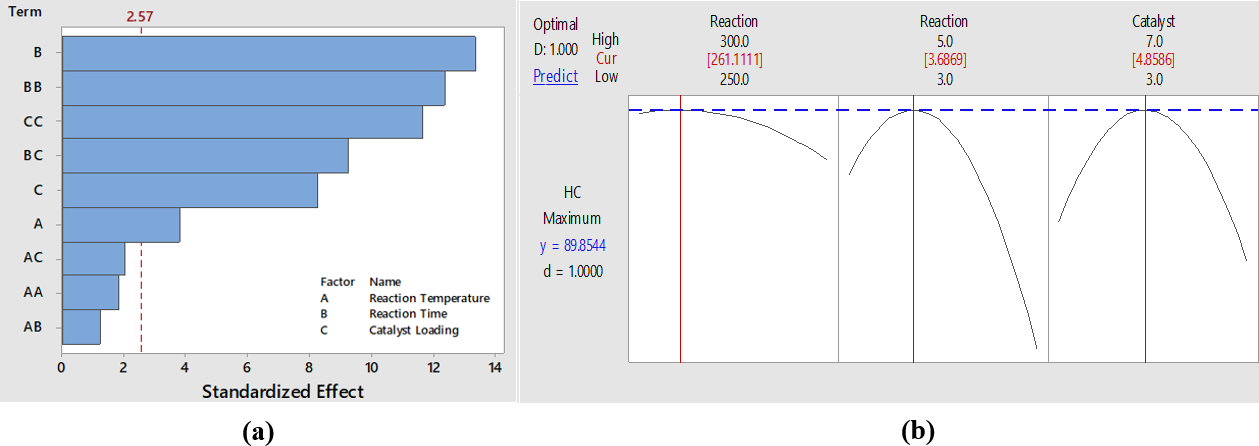
Figures 6e-f illustrate the effects of reaction temperature (A) and catalyst loading (C) on hydrocarbon yield, with a constant reaction time of 4 hours, as depicted in 3D response surface plots and 2D contour plots. The results demonstrate a positive correlation between hydrocarbon yield and catalyst loading, with an optimal range of 3.7 to

5.8 g at elevated temperatures. However, the hydrocarbon yield decreased when the catalyst loading exceeded 6 g and the temperature exceeded 295°C. While an increased catalyst loading should provide more active sites for the reaction, this may result in mass transfer constraints between the oil and catalyst, limiting mixing and reducing the reaction rate. Furthermore, excess active sites can give rise to side reactions, such as polymerization, at elevated

temperatures, resulting in coke production and catalyst deactivation [31]. The 2D contour plot indicates that the maximum hydrocarbon yield (88%) was achieved with a catalyst load of 4.5 g and a reaction temperature of 295°C over four hours.



**Image 6.** 2D contour plots and 3D response surface plots for (a-b) interaction of reaction temperature (A) and reaction time (B) (c-d) interaction of reaction time (B) and catalyst loading (C) (e-f) reaction temperature (A) and catalyst loading (C).



**Image 7**. (a) Standard effect chart (b) optimal operating conditions.

The results demonstrate that the interaction between reaction time (B) and catalyst loading (C) is more pronounced than the interaction between reaction temperature (A) and catalyst loading (C) and between reaction temperature (A) and reaction time (B). This is evident from the 3D surface curvature in Figures 6b, d, and f, which is also corroborated by Figure 7a. Furthermore, it was determined that the optimal set of parameters for the reaction was 261°C, 3.67 h, and 4.86 g of catalyst loading (Figure 7b).

# CONCLUSIONS

This research successfully produced a 7% Ni/SiO**2** catalyst using a commercial nickel source and 91.8% SiO**2** from rice husk ash. Furthermore, the research employed the RSM-Box-Behnken experimental method to investigate the influence of various parameters on the hydrocarbon yield from sludge oil. The model identified reaction time and catalyst loading as the most influential variables affecting the reactivity of the process. The results demonstrated a hydrocarbon yield of 98.63%, comprising 83.16% diesel-like hydrocarbons (C**15**-C**18**) and 16.81% lighter hydrocarbons (C**12**-C**14**), under conditions of 275°C, 4 h, 5 g catalyst loading, and 5 MPa H**2** gas. This reaction is conducive to a high HDO pathway. RSM-Box-Behnken analysis indicated that the optimal conditions for the reaction were a temperature of 261°C, a reaction time of 3.67 h, and a catalyst loading of 4.86 g.

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