

Article

Green-Synthesized Nanoflower FeNi Catalysts for Low-Temperature Pyrolysis of Waste Lubricating Oil into High-Quality Diesel-Like Fuel

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Abstract

The growing accumulation of waste lubricating oil presents serious environmental issues, calling for sustainable management solutions. This research discusses the creation of FeNi/TiO₂ nanocatalysts that were synthesized through an eco-friendly method utilizing grape seed extract (GSE) as a natural reducing agent for the catalytic pyrolysis of waste lubricating oil. The nanocatalyst was produced using the microemulsion technique and refined via Response Surface Methodology (RSM) to optimize its catalytic performance. Pyrolysis was carried out at 400 °C, leading to a significant conversion of waste oil into valuable fuel. The FeNi/TiO₂ nanocatalyst exhibited exceptional capabilities in facilitating the breakdown of heavy hydrocarbons into lighter fuel fractions while reducing unwanted byproducts. GC-MS analysis demonstrated the prevalence of C₆–C₂₀ hydrocarbons in the pyrolysis oil, underscoring its potential as a high-quality alternative fuel similar to traditional diesel. This study aids in the progress of environmentally sustainable waste-to-energy technologies, offering a promising pathway for effective fuel production and hazardous waste management.

Keywords: FeNi/TiO₂; nanoflower; nanocatalyst; catalytic pyrolysis; green synthesis; grape seed extract



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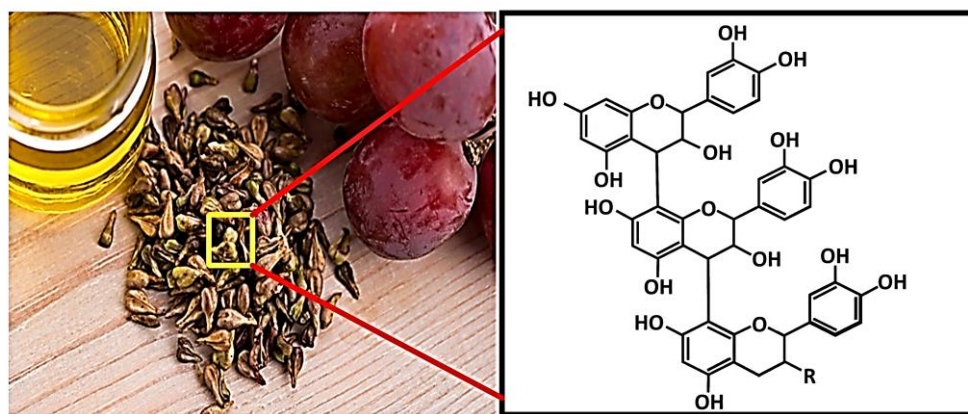
1. Introduction

The accumulation of waste lubricating oil represents a growing environmental concern due to its classification as Hazardous and Toxic Materials. If improperly disposed of, it can contaminate soil and water, threaten aquatic ecosystems, and pose serious health risks to humans [1]. As global industrialization and vehicle use expand, the volume of used oil increases, underscoring the need for effective and sustainable waste management strategies. One promising approach to managing this hazardous waste is its conversion into value-added products such as liquid fuels through catalytic pyrolysis. Pyrolysis is an efficient thermochemical technique for the recycling of lubricating oil waste that converts waste oil into valuable fuel in the absence of oxygen. This process provides a practical solution for waste management, while generating alternative fuels under reduced environmental

impact and enhanced energy efficiency. This thermochemical process not only reduces the environmental burden but also provides an alternative energy source. However, pyrolysis efficiency and fuel quality are significantly influenced by the chosen catalyst [2]. Recent studies have highlighted the potential of bimetallic catalysts, especially FeNi-based systems, to enhance pyrolysis performance. FeNi/TiO₂ nanocatalysts offer several advantages: they accelerate the breakdown of long-chain hydrocarbons into lighter, more combustible fuel fractions, reduce the formation of undesirable byproducts, and enable reactions at lower temperature [3]. The synergy between Fe and Ni improves hydrogenation activity [4,5], while TiO₂ provides thermal stability and dispersion support [6]. Fe contributes to the cleavage of C–C bonds in long-chain hydrocarbons, while Ni facilitates hydrogenation and dehydrogenation reactions. This synergy significantly improves the conversion of heavy hydrocarbons into lighter fuel fractions.

In this work, the FeNi/TiO₂ nanocatalysts are synthesized via a green method using grape seed extract (GSE) as a natural reducing and stabilizing agent. The bioactive compounds in GSE, particularly oligomeric proanthocyanidins (OPC), facilitate the formation of metal nanoparticles and prevent their agglomeration. This environmentally friendly synthesis approach aligns with the Sustainable Development Goals [7]. The microemulsion technique was selected for the environmentally friendly synthesis of FeNi/TiO₂ nanocatalysts, because it can generate nanoparticles that are evenly sized and well dispersed. Microemulsions are one phase systems made up of water, oil, surfactant, and co-surfactant, which create a stable solution at the nanoscale. When synthesizing nanocatalysts, microemulsions provide a uniform reaction environment, improving nucleation efficiency and promoting controlled particle growth [8,9]. Natural reducing agents like mangosteen peel or grape seed extract were utilized to reduce Fe and Ni metal ions to their corresponding nanoparticles; these are eco-friendly options that also enhance the stability of the nanoparticles. Furthermore, a commercial TiO₂ modification with a high surface area was used as the support material to boost catalytic performance and extend the lifespan of the catalyst during the pyrolysis process. This method is anticipated to yield an FeNi/TiO₂ nanocatalyst with optimal morphology and exceptional catalytic characteristics. The uniform particle structure and well-distributed deposition on the TiO₂ surface will enhance the interactions between the catalyst and substrate, speeding up the pyrolysis reaction and increasing the conversion yield of waste lubricating oil producing a high-quality fuel. Additionally, this green synthesis method has benefits in terms of sustainability and energy efficiency, making it a promising option for more environmentally friendly industrial applications.

The synthesis of nanoparticles utilizing natural reducing agents is a quickly evolving technique due to its ecological and cost-effective benefits. GSE is one of the commonly used reducing agents in nanoparticle synthesis. This extract is abundant in bioactive substances such as polyphenols (Figure 1), flavonoids, and tannins, which not only have reducing properties but also serve as stabilizers [10,11]. These bio-based compounds support the conversion of metal ions into metal nanoparticles, while preventing nanoparticle agglomeration during the synthesis phase. This approach avoids the use of toxic chemicals and also utilizes natural waste, making it a more sustainable choice [12]. Nanoparticles generated with GSE as the reducing agent offer numerous advantages, including uniform particle size, remarkable stability, and significant catalytic efficacy [13]. Characterization techniques reveal that the nanoparticles obtained exhibit ideal optical and structural properties for various applications, including photocatalysis and pyrolysis. Additionally, using GSE as a natural reducing agent adds value to the synthesis process, as it is readily available and can be sourced from agricultural byproducts, thereby promoting the idea of a circular economy.



Oligomeric Proanthocyanidin (OPC)

Figure 1. Chemical structure of an oligomeric proanthocyanidin (OPC) unit, a key bioactive compound in grape seed extract responsible for reducing metal ions during green synthesis.

Research shows that grape seeds are abundant in a bioflavonoid recognized for its antioxidant properties, particularly oligomeric proanthocyanidin (OPC) [14]. The OPC present in grape seeds has antioxidant efficacy that surpasses vitamin C by 20 times and vitamins E by 50 times [15]. This impressive potency is due to the aromatic structure of OPC (Figure 2), which enables it to generate a greater number of free radicals [16]. The process of generating Fe and Ni nanoparticles using GSE as the reducing agent involves the transformation of Fe^{2+} and Ni^{2+} ions into metallic Fe^0 and Ni^0 atoms (Figure 2). The OPC acts as a reducing agent by transferring electrons from the phenolic groups to the metal ions.

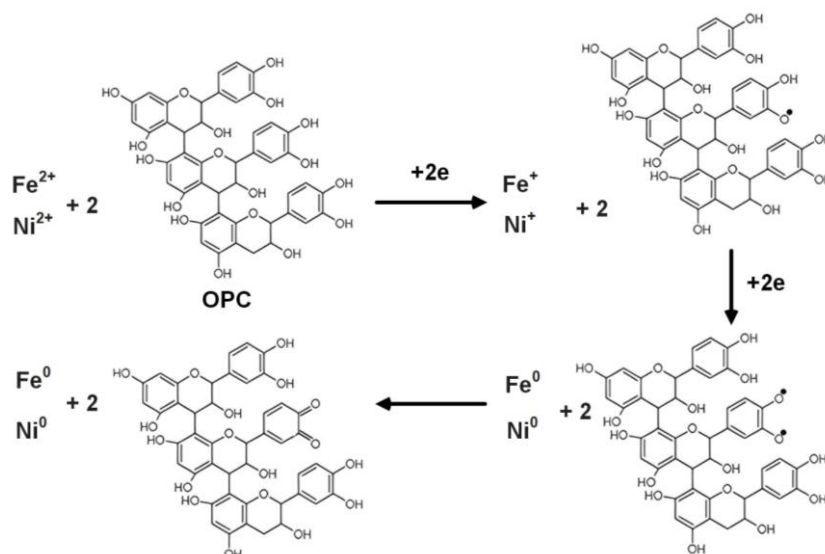


Figure 2. Proposed reduction mechanism for the formation of Fe and Ni nanoparticles with OPC.

The properties of FeNi/TiO₂ nanocatalysts are influenced by various synthesis parameters that have a direct impact on morphology, particle size, and catalytic efficacy. The parameters also define the amount of nanocatalyst that can be produced under certain conditions (catalyst yield). If synthesis parameters such as precursor concentration are not optimized, it can lead to an uneven distribution of FeNi in TiO₂, which ultimately affects the quality of the catalyst [17]. Moreover, the reducing agent plays a vital role in the synthesis process, and proanthocyanidins found in GSE act as natural reducing agents that promote the formation of metal nanoparticles [18]. But, using excessive amounts results in the production of larger particles, which subsequently decreases the available active surface

area and lowers catalytic efficiency [19]. The ratio of Fe to Ni within the TiO_2 matrix is a vital element affecting catalytic performance. An optimized Fe/Ni ratio improves catalyst yield while ensuring enhanced catalytic performance [20].

Proper handling of used lubricating oil is critical because it contains hazardous materials like heavy metals and intricate organic compounds. To reduce these harmful impacts, it is important to treat used lubricating oil to eliminate or lessen its toxic elements prior to disposal or possible reuse [21,22]. Developing effective treatment approaches not only reduces environmental harm but also lessens reliance on new oil production, preserves natural resources, and promotes sustainable waste management practices. Additionally, reusing spent lubricating oil, whether as an energy source or as a foundational material for reprocessed lubricants, adheres to circular economy concepts and greatly diminishes its ecological impact [21,23].

The study aims to evaluate the catalytic performance of FeNi/ TiO_2 nanocatalysts in the pyrolysis of used lubricating oil. Particular focus is on the impact of catalyst composition on fuel yield, density, calorific value, and viscosity. By optimizing catalyst formulation and reaction parameters, this research contributes to the development of efficient, low-emission, and sustainable technologies for converting hazardous waste into high-quality fuel. To achieve an efficient optimization process, this study employs Response Surface Methodology (RSM) with a Central Composite Design (CCD) approach. This statistical experimental design allows for the modeling of the complex interactions between critical synthesis parameters and the prediction of optimal conditions for maximizing both catalyst performance and fuel quality.

2. Materials and Methods

2.1. Materials

The green synthesis of FeNi/ TiO_2 nanocatalysts was carried out using the microemulsion method. Nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 99.9%, Sigma-Aldrich, St. Louis, MO, USA) and iron chloride hexahydrate ($\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$, 99.9%, Sigma-Aldrich) were used as metal precursors. GSE (Raab Vitalfood GmbH, Rohrbach, Germany) was used as the reducing agent. The microemulsion solution was formulated using Triton X-100 (99%, Carl-Roth, Karlsruhe, Germany) as the surfactant, 1-pentanol (99%, Sigma-Aldrich) as the co-surfactant, cyclohexane (99.8%, Sigma-Aldrich) as the oil phase, and distilled water. CristalActiv- TiO_2 (PC-500, Tronox, Stamford, CT, USA) was used as the support material for the nanocatalyst. The FeNi nanocatalyst deposited on the TiO_2 surface was purified using acetone (99.9%, Carl-Roth, Karlsruhe, Germany) to remove residual impurities.

2.1.1. Synthesis of the FeNi/ TiO_2 Nanocatalyst

To synthesize FeNi nanoparticles, two microemulsions were prepared with the following specifications: 6.945 g of Triton X-100, 6.945 g of 1-pentanol, 33.35 g of the oil phase, and 2.737 g of the aqueous phase. The required amounts of Fe and Ni salts were dissolved in the aqueous phase of microemulsion one ($\mu\text{E}1$), while GSE was dissolved in the aqueous phase of microemulsion two ($\mu\text{E}2$). The GSE solution was prepared by adding the GSE powder to water and stirring the suspension for one hour at 70 °C to extract the active compounds. The solid residues were removed using centrifugation.

The reactor was filled with $\mu\text{E}1$, and $\mu\text{E}2$ was added using a micro-pump at a flow rate of 0.2 mL/s. The thermostat was maintained at 25 °C, and the mixture was stirred at 700 rpm. After a certain nanoparticle formation time, the deposition process was initiated by adding a predetermined quantity of TiO_2 as the support material to the mixture and increasing the temperature to 55 °C. After the deposition was finished (usually 1 h), the solution was withdrawn from the reactor and centrifuged to isolate the FeNi/ TiO_2

nanocatalyst. The resulting nanocatalyst was washed three times with acetone and then calcined at 350 °C for 2 h. The schematic of the microemulsion reactor setup used for the synthesis of NPs is illustrated in Figure 3.

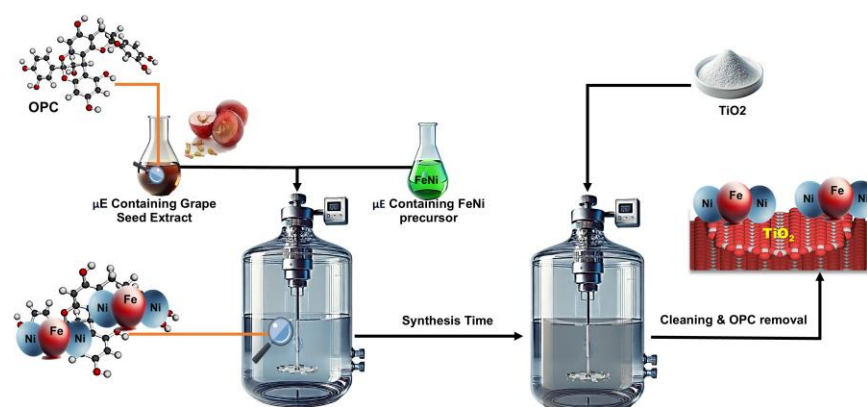


Figure 3. Scheme of the synthesis process of FeNi/TiO₂ nanocatalysts using grape seed extract (GSE) as the reducing agent.

2.1.2. The Pyrolysis Process of Waste Lubricating Oil into Fuel Oil

Pyrolysis converts waste lubricating oil into valuable fuel in an oxygen-free environment. For the reaction, 30 g of waste lubricating oil and 0.5 g of the FeNi/TiO₂ nanocatalyst were placed in the pyrolysis reactor. To prevent undesired oxidation reactions, pyrolysis was carried out in nitrogen (N₂) atmosphere. The reaction temperature was controlled using a thermocouple. Pyrolysis was performed at about 400 °C to initiate the cracking of long-chained hydrocarbons into smaller fragments, which results in the generation of a pyrolysis gas.

The whole experiment took four hours, including a heating stage, a reaction phase lasting three hours from the moment the first product droplet was collected, and a cooling phase of 45 min before the reactor was opened for cleaning. A water-cooled circulating system was employed to condense the pyrolysis gas, and subsequently, the final product was weighed to determine the exact yield. The application of the FeNi/TiO₂ nanocatalyst significantly enhances the process efficiency by lowering the required reaction temperature and improving the quality of the resulting fuel. A scheme of the pyrolysis process is shown in Figure 4.

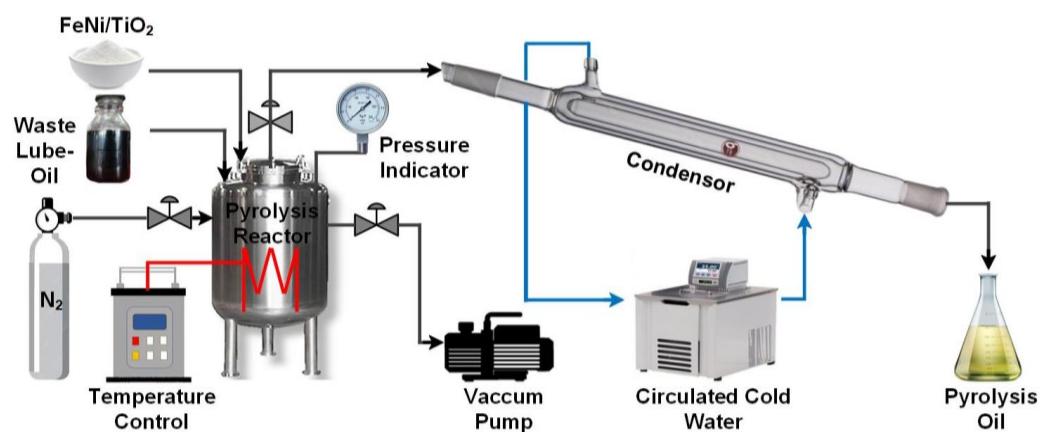


Figure 4. Schematic illustration of the pyrolysis process.

3. Results

3.1. Analysis of Key Factors Affecting Pyrolysis Oil Quality from Factorial Design

The synthesis of nanocatalysts for the pyrolysis of waste used oil is affected by various factors that have a direct impact on the quality of the resulting oil. These factors are crucial in influencing conversion efficiency, physicochemical characteristics, and the energy content of pyrolysis oil. Figure 5 shows the Pareto chart obtained from our factorial design analysis, which identifies the key factors significantly affecting the pyrolysis oil yield and quality. It also highlights several key factors that notably affect important oil quality indicators, such as yield percentage, calorific value, density, and viscosity. It is vital to identify and optimize these significant parameters to improve the pyrolysis process for producing high-quality oil. Figure 5a emphasizes the strong relationship between the reducing agent (B) and the support material (C) in determining the yield of oil. This insight highlights the necessity of selecting the right type and concentration of both components to enhance the synthesis of nanocatalysts and their catalytic efficiency. Figure 5b reveals that the support material (C) and the duration of the reaction (D) are essential in establishing the calorific value of the produced oil [24,25]. An optimized support material guarantees catalyst stability while an appropriate reaction time allows for complete decomposition, resulting in smaller hydrocarbons with elevated energy content [26].

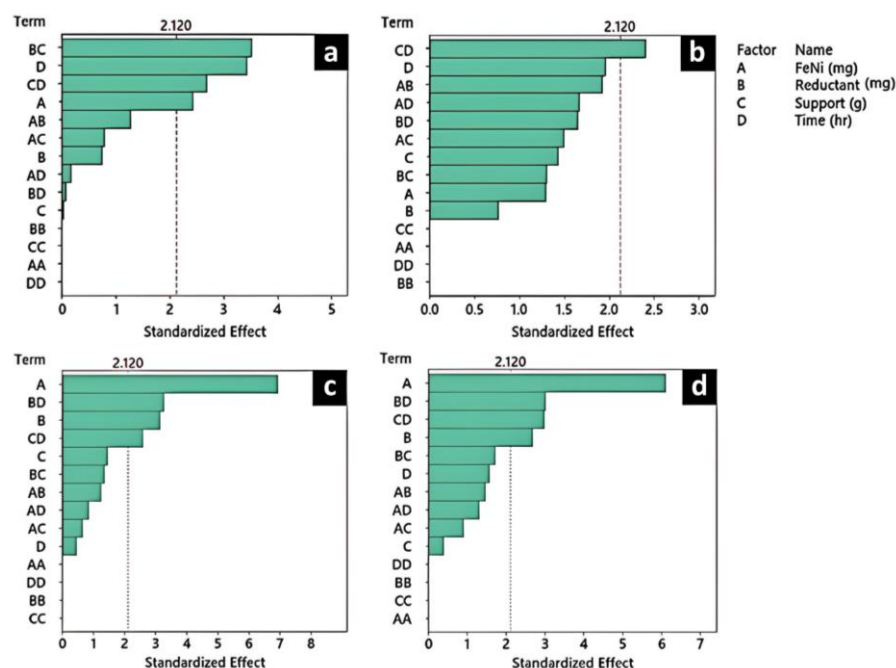


Figure 5. Pareto charts showing the standardized effects of synthesis factors (A: FeNi amount, B: GSE amount, C: TiO₂ support amount, D: reaction time) on the properties of the resulting pyrolysis oil: (a) yield, (b) calorific value, (c) density, and (d) viscosity.

Figure 5c shows that the FeNi content in the catalyst (A) significantly influences the quality of pyrolysis oil, especially the oil density [27]. Increased FeNi concentrations heighten the proportion of heavier fractions, causing a rise in density, whereas lower concentrations impede the effective breakdown of larger molecules. Likewise, Figure 5d indicates that the FeNi content (A) is the primary factor affecting viscosity. Increasing FeNi content in the catalyst lowers the viscosity of pyrolysis oil by enhancing hydrocarbon chain cracking and promoting hydrogenation reactions. This reduces heavy compounds and oxygenates, leading to lighter, more stable oil [28]. A well-optimized catalyst facilitates the conversion of complex hydrocarbons into lighter fractions, decreasing viscosity and

enhancing the oil's potential for fuel applications. In contrast, a poorly performing catalyst results in a more viscous product, restricting its usability.

Figure 6 shows the visual appearance of the pyrolysis oil products from our experimental runs, demonstrating the variation in quality based on different synthesis parameters. Figure 6 depicts the conversion of used lubricating oil via the catalytic pyrolysis process, resulting in pyrolysis oil with enhanced properties and potential as a renewable fuel alternative. Prior to the pyrolysis, the waste oil is dark black, signifying the presence of impurities and the breakdown of complex compounds. Following the process, the resulting pyrolysis oil displays color variations from light yellow to brown, which indicate differences in the composition of lighter and heavier fractions, influenced by experimental conditions. These variations are affected by factors like the quantity of FeNi catalyst, reductant, support material, and duration of the reaction. This finding shows that by fine-tuning the pyrolysis parameters, it is possible to produce higher-quality oil, thereby creating a valuable opportunity to convert waste into cleaner and more advantageous energy sources.

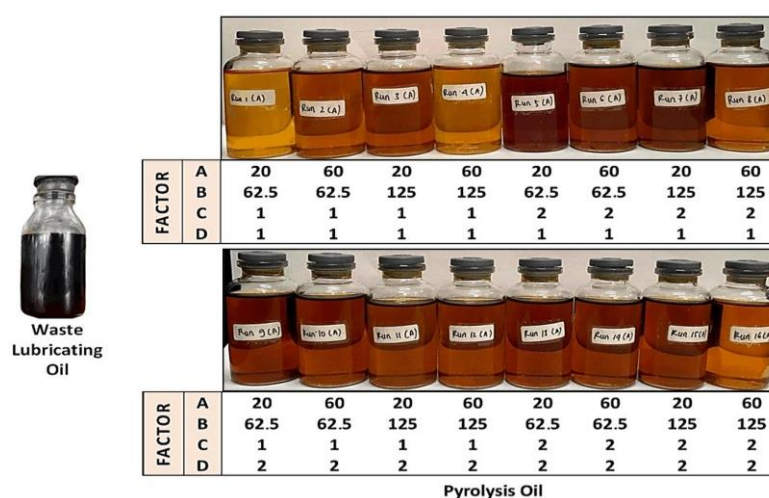


Figure 6. Colors of pyrolysis oil products obtained under various experimental conditions according to the factorial design: A: FeNi amount, B: GSE amount, C: TiO₂ support amount, and D: reaction time.

3.2. The Determination of Optimal Factor Values for Optimization Is Based on Contour Plot Analysis

Figure 7 shows contour plots that demonstrate how interactions between different factors affect the percentage of oil yield in the catalytic pyrolysis process. The contour plots in Figure 7, derived from our RSM analysis, illustrate the interaction effects between key synthesis parameters on the oil yield. There are six subplots, each illustrating the relationship between two critical experimental factors: the FeNi composition of the nanocatalyst, the quantity of reductant used, the type and quantity of support, and the duration of the reaction. In each subplot, the horizontal and vertical axes represent the two variables being analyzed, while the color gradient in the plot reflects the distribution of oil yield values based on the provided legend. The identified color patterns indicate that specific combinations of variables greatly enhance the oil yield, while other combinations lead to a decreased yield. This underscores the intricate interactions among experimental factors that impact the efficiency of catalytic pyrolysis.

The examination of color patterns in these contour plots offers valuable insights into how changes in FeNi content, reductant quantity, amount of support, and reaction duration influence the conversion efficiency of waste oil into fuel. In the subplot discussing FeNi and reductant, it is clear that increasing the FeNi amount up to a certain limit boosts the oil yield, especially when paired with an adequate quantity of reductant. However, too much

FeNi or reductant can lead to decreased catalytic efficiency due to saturation issues or poor synergy. Another subplot that looks at the reaction time and support demonstrates that choosing the correct amount of support material and fine-tuning reaction time enhances the pyrolysis efficiency. Less support material may undermine catalyst stability, whereas extended reaction times can result in undesirable degradation of the products. By grasping these interaction dynamics, the ideal experimental conditions can be identified to maximize oil yield, ultimately improving both the efficiency and sustainability of catalytic pyrolysis for transforming waste into high-quality fuel.

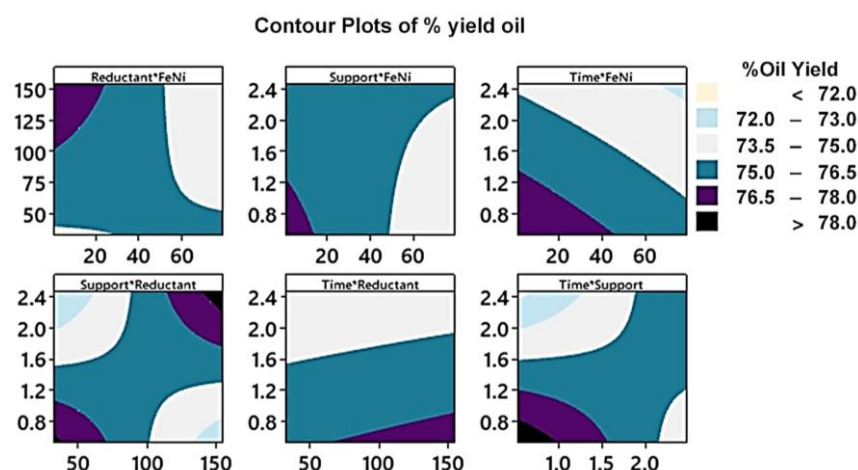


Figure 7. Contour plots illustrating the interaction effects between pairs of synthesis factors on the yield of pyrolysis oil. The factors are: A (FeNi amount), B (GSE amount), C (TiO₂ support amount), and D (reaction time).

3.3. Optimization of the Green FeNi/TiO₂ Synthesis Process to Enhance Efficiency and Effectiveness in the Pyrolysis of Waste Lubricating Oil

The Central Composite Design (CCD) method is applied to enhance the pyrolysis process of waste lubricating oil because it can investigate intricate relationships between various operational factors and the desired results. This technique, which is part of Response Surface Methodology (RSM), allows for a comprehensive examination of both direct impacts and interactions between variables that notably affect the outcomes. By utilizing this method, the research seeks to determine the optimal conditions for maximizing oil yield, calorific value, density, and viscosity, thereby ensuring the production of high-quality pyrolysis products.

In this study, several crucial factors to optimize FeNi properties were identified and examined, including the concentration of FeNi, the quantity of natural reductant, the amount of TiO₂ support material, and the synthesis time. FeNi is the catalyst that speeds up the pyrolysis process, and variations in its concentration affect the rate of decomposition of complex hydrocarbons found in waste oil. GSE, which is abundant in polyphenols, acts as a natural reducing agent that facilitates the formation of uniformly dispersed FeNi nanoparticles.

The optimization using CCD was conducted with 31 data sets. This process was designed to identify the most effective parameter composition to maximize the desired outcomes, such as calorific value, standard-compliant density, optimal viscosity, and high oil yield. Each data set used in this statistical modeling (RSM analysis) provides insights into the interaction of factors. The RSM analysis results indicate the parameters that can be applied to the pyrolysis process, as shown in Table 1.

Table 1. Simulation-based experimental results from the Central Composite Design (CCD).

Factor				Response			
FeNi in Precursor (mg)	Natural Reductant (mg)	TiO ₂ Support (g)	Reaction Time (h)	Oil Yield. (%)	Calorific Value (cal/g)	Density (kg/L)	Viscosity (cP)
(A)	(B)	(C)	(D)				
40	93.8	1.5	0.5	76.7	11,040	1.297	780
60	62.5	1.0	2.0	73.9	11,047	1.619	780
40	93.8	1.5	1.5	75.4	11,113	1.501	781
20	62.5	2.0	1.0	76.0	11,061	1.213	776
60	62.5	2.0	2.0	75.7	11,662	1.012	768
40	32.8	1.5	1.5	75.0	11,142	1.153	771
20	62.5	1.0	1.0	76.8	11,064	0.818	761
1	93.8	1.5	1.5	76.3	11,065	0.705	760
40	93.8	1.5	1.5	75.3	11,113	1.501	781
40	93.8	1.5	1.5	75.3	11,113	1.501	781
40	93.8	1.5	1.5	75.3	11,113	1.501	781
20	125.0	2.0	1.0	76.5	11,094	1.183	773
60	62.5	1.0	1.0	77.1	11,071	1.432	779
60	125.0	2.0	1.0	75.5	11,021	1.667	790
40	154.7	1.5	1.5	75.7	11,085	1.850	790
20	62.5	2.0	2.0	72.2	11,009	1.132	769
20	125.0	1.0	2.0	74.0	11,080	1.238	776
40	93.8	2.5	1.5	75.3	11,167	1.451	785
60	125.0	1.0	1.0	76.0	11,143	1.313	778
40	93.8	1.5	2.5	74.0	11,187	1.706	782
40	93.8	1.5	1.5	75.3	11,113	1.501	781
40	93.8	1.5	1.5	75.3	11,113	1.501	781
79	93.8	1.5	1.5	74.4	11,162	2.298	802
60	125.0	1.0	2.0	71.8	11,043	3.671	815
40	93.8	0.5	1.5	75.3	11,060	1.552	776
40	93.8	1.5	1.5	75.3	11,113	1.501	781
60	62.5	2.0	1.0	73.4	11,013	2.386	810
20	125.0	2.0	2.0	77.8	11,160	1.032	767
60	125.0	2.0	2.0	75.6	11,108	2.178	811
20	125.0	1.0	1.0	76.9	11,140	1.161	775
20	62.5	1.0	2.0	76.4	11,100	0.968	765

3.4. Optimization and Validation

Revising catalytic pyrolysis parameters is essential for maximizing oil production and improving fuel quality. This research assesses critical factors such as the amount of FeNi precursor, concentration of reductant, mass of support, and duration of the reaction. The results show that increasing the FeNi quantity typically causes a decline in oil yield beyond a certain optimal point, likely due to catalyst agglomeration that restricts the active surface area available. On the other hand, a greater concentration of the reductant improves FeNi dispersion, which enhances the catalytic performance. The mass of the support is also vital for maintaining catalyst distribution and ensuring effective interaction with the feed molecules. Further refinement of the reaction duration indicates that excessively long times can result in secondary cracking, which increases the gas production and decreases the yield of liquid oil.

Additionally, the intricate interplay among these factors indicates that achieving an optimal equilibrium between the quantity of FeNi and the level of reductant is vital for enhancing catalyst effectiveness. A suboptimal combination of these parameters could lead

to ineffective conversion processes and oil properties that stray from standard fuel specifications. Thus, employing a methodical strategy to identify the best operating conditions is essential for increasing the pyrolysis efficiency and ensuring the sustainable treatment of waste lubricating oil. Figure 8 depicts how the amount of FeNi precursor and the concentration of reductant affect the oil yield during the catalytic pyrolysis process. This figure underscores the considerable impact these two factors have on oil production. An in-depth examination through the subsequent contour diagram offers greater understanding of how FeNi quantity and reductant concentration interact in relation to key aspects of the catalytic pyrolysis process, such as density, viscosity, calorific value, and oil yield.

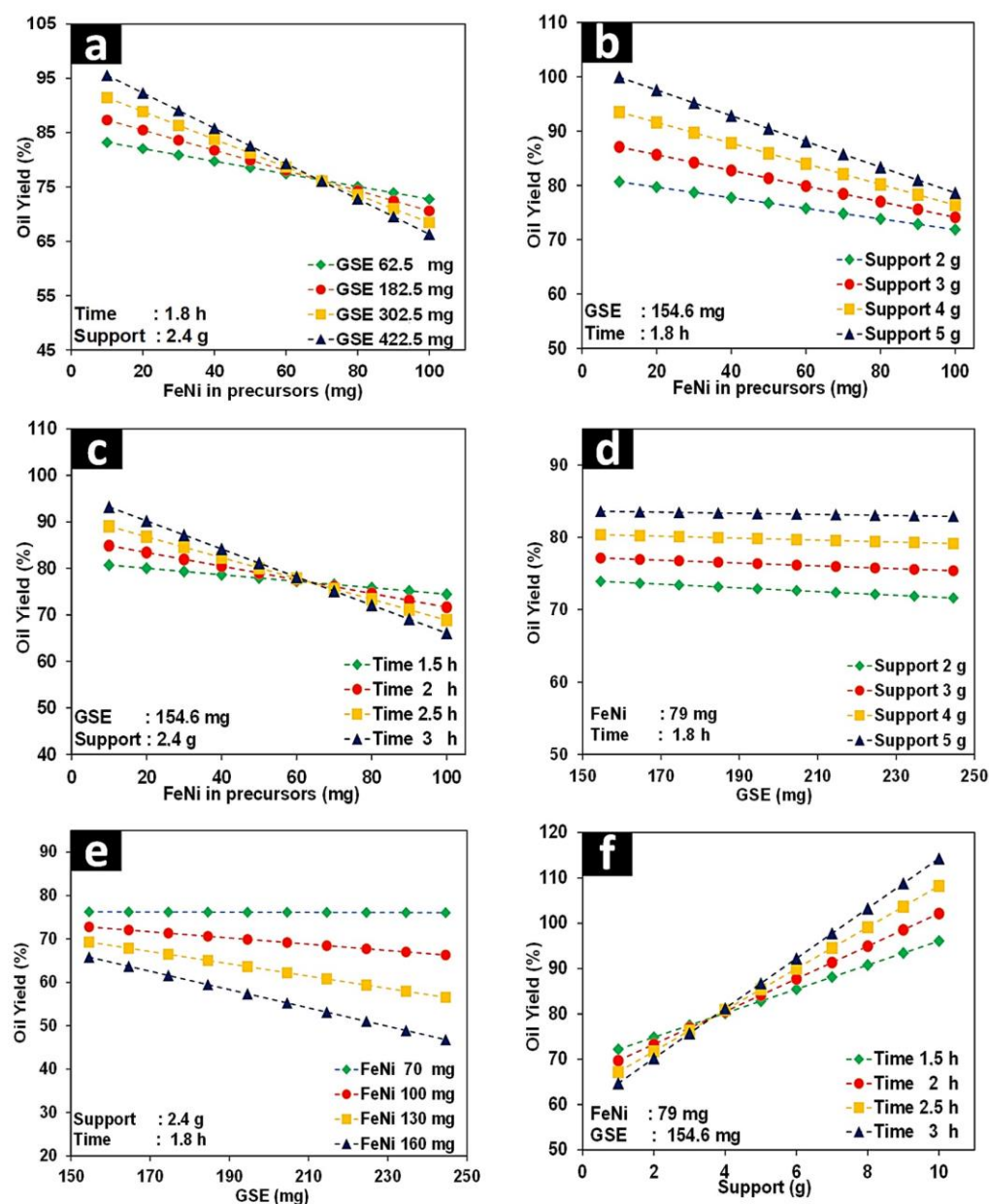


Figure 8. Interaction plots for pyrolysis oil yield, showing the effect of varying one factor while holding others constant: (a) FeNi and GSE; (b) FeNi and support; (c) FeNi and time; (d) GSE and support; (e) GSE and time; (f) support and time.

Figure 9 displays the overlay contour plot that shows how the concentration of reductant (Red. Conc.) and the amount of FeNi affect several crucial parameters in the catalytic pyrolysis of waste lubricating oil, which include density, viscosity, calorific value, and oil

yield. In this graph, the mass of support and reaction time are maintained at constant values (2.4 g and 1.8 h). The horizontal axis signifies the quantity of FeNi (mg), while the vertical axis represents the reductant concentration (mg/L). Various colored lines illustrate the trends in density (blue line), viscosity (red line), calorific value (green line), and oil yield (purple line). The graph reveals that an increase in the quantity of FeNi typically results in a reduction in both the density and viscosity of the pyrolysis oil, suggesting that the resulting oil has properties more similar to those of conventional fuels. Additionally, the calorific value exhibits a slight increase with a rise in FeNi, indicating an enhancement in the energy content of the pyrolysis oil. The oil yield demonstrates an optimal trend under particular conditions, highlighted by an orange circle that marks the optimal point reached at around 80 mg FeNi and 150 mg/L of reductant concentration. These observations imply that there are optimal conditions for the use of FeNi and reductant to improve the quality and efficiency of the pyrolysis oil conversion process. By grasping the interactions among these variables, the catalytic pyrolysis process can be fine-tuned to generate high-quality fuel. Further improvements through experimental methods and kinetic modeling can be pursued to deepen the understanding of the key mechanisms and enhance the sustainability of the treatment process for waste lubricating oil.

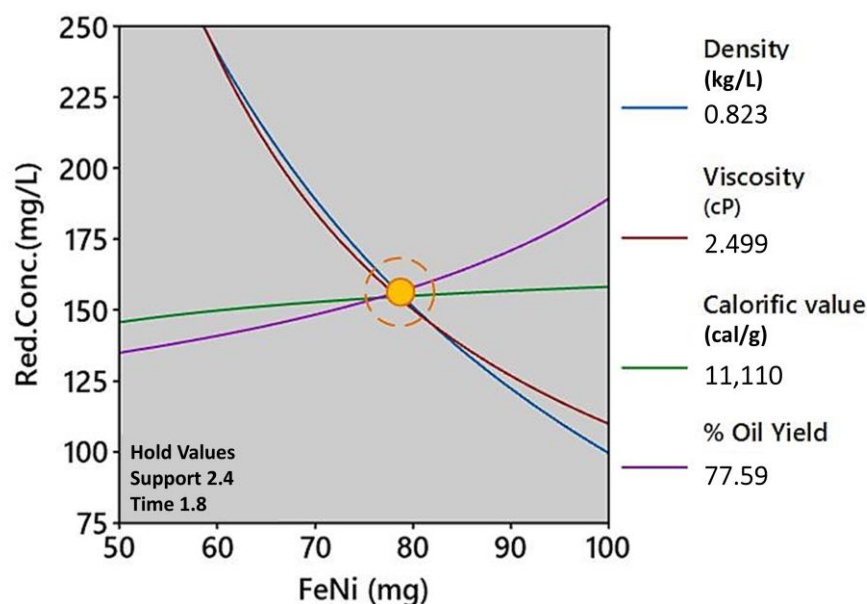


Figure 9. Overlay contour plot for multiple responses (oil yield, calorific value, density, viscosity) as functions of FeNi quantity and GSE concentration. The plot was generated with TiO₂ support mass and reaction point held constant at 2.4 g and 1.8 h, respectively. The yellow circle indicates the optimal predicted point.

Among the numerous valorization methods, pyrolysis has become one of the most effective techniques for transforming used lubricating oil into valuable products. This thermochemical decomposition process breaks down high-molecular-weight hydrocarbons into lower-molecular-weight fractions, improving their suitability for fuel applications [29]. As shown in Table 2, the hydrocarbon makeup of used lubricating oil mainly consists of heavy hydrocarbons in the C₂₁–C₄₀ range, which represent 46.430% of the total content prior to pyrolysis. However, after the pyrolysis process, this fraction is notably reduced to 19.164%, illustrating the breakdown of long-chain hydrocarbons into lighter compounds. At the same time, the percentage of hydrocarbons in the C₇–C₁₇ range increases, with C₇ rising from 1.790% to 6.532%, alongside the appearance of previously unrecognized fractions such as C₁₄, C₁₅, C₁₇, and C₁₉. These changes in composition suggest that

pyrolysis effectively converts heavy hydrocarbons into shorter-chain compounds with improved fuel characteristics. This transformation is further depicted in Figure 10, which illustrates the alteration in hydrocarbon distribution before and after pyrolysis.

Table 2. Hydrocarbon composition before [30] and after optimized pyrolysis.

Compounds	Composition of Pyrolysis Oil	
	Before (%) [30]	After (%)
C5	0	0.282
C6	0	2.911
C7	1.790	6.532
C8	7.440	8.826
C9	12.330	10.454
C10	12.520	9.967
C11	9.390	7.504
C12	2.830	4.911
C13	1.340	3.011
C14	0	4.570
C15	0.960	3.996
C17	0	4.588
C18	1.150	0
C19	0.000	6.464
C20	3.820	6.818
C21–40	46.430	19.164

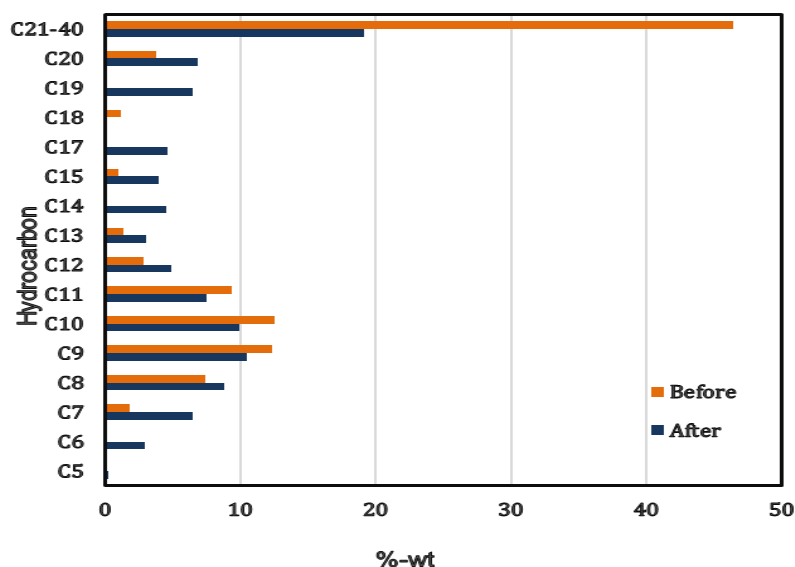


Figure 10. Comparison of hydrocarbon chain length distributions in waste lubricating oil before pyrolysis and after catalytic pyrolysis using the optimized FeNi/TiO₂-GSE nanocatalyst at 400 °C.

The validation outcome indicates that the oil yield obtained for the optimized parameters is 76.07%, which is slightly below the earlier optimization figure of 77.59% (Figure 9). This difference may stem from modifications made to other parameters, including viscosity, density, and calorific value, all of which were fine-tuned to satisfy stricter fuel quality requirements. The optimized FeNi/TiO₂ nanocatalyst was characterized by Atomic Absorption Spectroscopy (AAS) to determine the FeNi loading. Validating both oil yield and catalyst yield enhances our understanding of the FeNi/TiO₂ nanocatalyst's efficiency in the pyrolysis process. Evaluating the calorific value, density, and viscosity is crucial for assessing the quality of pyrolysis oil. These characteristics not only indicate the physical and

thermal properties of the oil but also influence its viability as an alternative fuel. Density is a critical factor that impacts the fuel's transportability and behavior, while viscosity affects the ease of fuel flow through the engine's injection system. The calorific value, in contrast, helps to ascertain the energy output from the combustion of the fuel. The nanoflower-shaped FeNi/TiO₂ catalyst contributes to the overall enhancement of the pyrolysis process. Its high surface area and porous configuration, as observed in SEM images, allow greater accessibility of reactant molecules to active sites, thus accelerating hydrocarbon conversion and improving fuel properties. According to the validation findings, the resulting pyrolysis oil has a calorific value of 11,016 cal/g, a density of 829.4 kg/m³, and a viscosity of 2.2715 cP, as detailed in Table 3.

Table 3. Average and validation results of pyrolysis process.

Quality	Average Results	Optimization Results	Validation	Standard of Premi-um Diesel [31]
Oil yield (%)	73.3	77.6	76.0	-
Caloric value (cal/g)	11,041	11,110	11,016	>10,500
Density (Kg/L)	815.4	825	829.4	815–880
Viscosity (cP)	3.7	2.5	2.2	2.0–5.0

Although there are small differences between the validation outcomes and the previously achieved optimization values, they arise from modifications in calorific value, density, viscosity, and oil yield. Despite these minor differences, the resulting values are within an acceptable range for fuel applications. Nevertheless, the values overall remain within the characteristic range of commercially available diesel fuel. The goal of the optimization process is to improve the quality of pyrolysis oil so that it aligns with market diesel fuel standards. Therefore, the optimization strategy shows that employing FeNi/TiO₂ nanocatalysts, which were synthesized using a colloidal approach combined with GSE as a green reductant, helps to enhance the characteristics of the pyrolysis oil.

The SEM images (Figure 11) illustrate the structure of FeNi nanoflower and FeNi/TiO₂ nanocatalysts utilized in the pyrolysis process. The FeNi nanoflower configuration, shown in Figure 11A,B, features a large surface area that facilitates more effective interactions between the catalyst and the reactants. In contrast, Figure 11C,D reveal the coarse and porous nature of FeNi/TiO₂, which improves thermal stability. Employing FeNi/TiO₂ in the pyrolysis of waste lubricant oil has been shown to effectively lower reaction temperatures, enhance the conversion of waste oil into fuel fractions, and decrease the formation of carbon residues. The FeNi nanoflower design promotes quicker and more selective decomposition processes, leading to cleaner and higher-quality fuel outputs. Furthermore, the addition of TiO₂ aids in minimizing the generation of undesired compounds and boosts catalytic activity. Consequently, these nanocatalysts exhibit remarkable efficacy in enhancing reaction efficiency, reducing operational temperatures, and yielding high-quality fuel products. The average size of the FeNi nanoparticles, as seen in the SEM images (Figure 11), is estimated to be in the range of 30 to 70 nm. This small and consistent particle size boosts catalytic efficiency by increasing surface area and providing more active sites. The nanoscale characteristics of the catalyst facilitate effective thermal breakdown of long-chain hydrocarbons during pyrolysis, resulting in a greater oil yield and enhanced fuel quality. These attributes account for the transformation of heavy hydrocarbons into lighter C6–C20 fractions.

Figure 12 is a comparative analysis of the pyrolysis yield obtained using different catalysts. Notably, the prepared FeNi/TiO₂ nanocatalyst achieves the highest pyrolysis yield, approaching 80% under optimal conditions. Even under non-optimal conditions,

this catalyst maintains a relatively high yield. A comparable study conducted by Parapat et al. [32] on the pyrolysis of waste lubricating oil explored the use of FeNi/TiO₂ nanocatalysts in combination with mangosteen peel extract (MPE) as a natural reductant. Their results indicated an oil yield of 54.11%, a density of 799 kg/m³, and a calorific value of 10,957 cal/g, further reinforcing the potential of FeNi/TiO₂-based nanocatalysts for waste oil valorization. Moreover, the FeNi/TiO₂ nanocatalyst with MPE exhibits a significant improvement in pyrolysis yield compared to zeolite or non-catalytic methods, with its optimal conditions yielding superior results compared to suboptimal scenarios. While zeolite as a catalyst produces a lower yield than FeNi/TiO₂-based nanocatalysts, it still outperforms non-catalytic pyrolysis, which records the lowest yield. These findings underscore the remarkable advantages of FeNi/TiO₂ nanocatalysts synthesized with natural reductants, particularly in enhancing pyrolysis efficiency over conventional catalysts such as zeolite. This enhancement can be attributed to the superior catalytic performance of FeNi, synergistically supported by TiO₂, which ensures better stability and uniform dispersion of active metal sites throughout the pyrolysis process. Therefore, the optimization of FeNi/TiO₂ nanocatalysts presents a highly promising approach for the production of high-quality liquid fuel from waste oil, paving the way for more sustainable and efficient waste-to-energy conversion technologies [32].

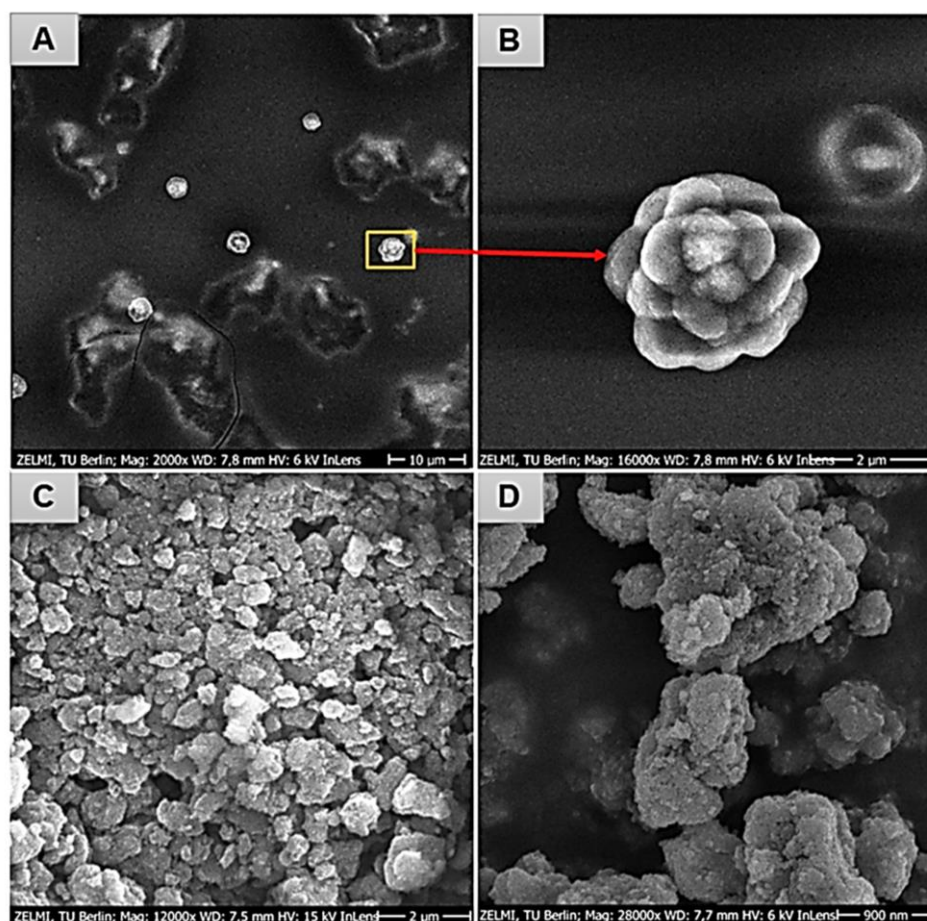


Figure 11. SEM images of FeNi nanoflowers and FeNi/TiO₂ at different magnifications. (A) FeNi nanoflowers at 2000× magnification, showing initial formation and dispersion. (B) A single FeNi nanoparticle flower at 16,000× magnification, revealing its distinct petal-like morphology, indicating a self-assembled growth mechanism. (C) FeNi/TiO₂ at 28,000× magnification, displaying a porous and agglomerated structure that enhances catalytic performance. (D) FeNi/TiO₂ at 12,000× magnification, highlighting the homogeneous distribution of FeNi within the TiO₂ matrix.

The qualitative assessment of the optimized pyrolysis oil was performed using Gas Chromatography-Mass Spectrometry (GC-MS) to identify and quantify the hydrocarbon compounds found in the pyrolysis oil sample. This assessment is crucial for evaluating the quality of the produced pyrolysis oil, as the hydrocarbon composition profile plays a significant role in determining the fuel's physical properties and performance [33]. The results from the GC-MS analysis, shown in Table 4, indicate that the pyrolysis liquid product is made up of different types of hydrocarbons, such as alkanes, alkenes, aromatics, and aliphatics. Based on 49 identified compounds, the main hydrocarbon composition comprises 62.48% alkanes (paraffins), 20.61% alkenes (olefins), 1.78% aromatics, and 15.13% aliphatics. Regarding the composition of carbon atoms, hydrocarbons with C5–C11 chains represent 31.47%, hydrocarbons in the C12–C25 range account for 62.70%, and those with over C25 carbon atoms make up only 5.82%. The significant proportion of short- to medium-chain hydrocarbons suggests that the optimized pyrolysis process utilizing the FeNi/TiO₂ catalyst effectively promotes the breakdown of heavier compounds into lighter products. The FeNi/TiO₂ catalyst, with its innovative nanomaterial design, boasts an extensive surface area that maximizes interactions, significantly enhancing the efficiency of converting waste oil into high-quality diesel fuel [32].

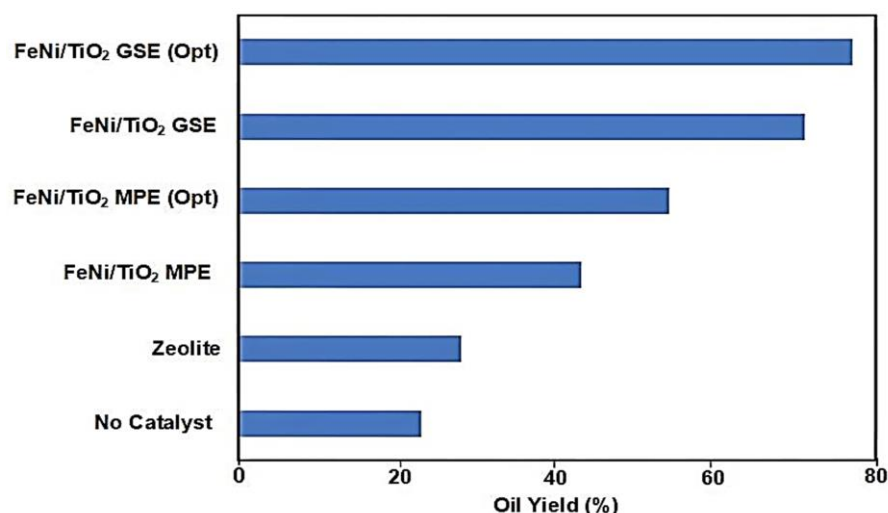


Figure 12. Comparison of pyrolysis oil yields achieved using different catalysts: optimized FeNi/TiO₂-GSE (this study), FeNi/TiO₂-MPE [34], natural zeolite, and a thermal (non-catalytic) process at 650 °C [32].

Figure 13 shows a comparative GC-MS chromatogram of pyrolysis oil from waste lubricating oil and pyrolysis oil obtained using optimized FeNi/TiO₂. In Figure 13a, the chromatogram of raw waste lubricating oil exhibits a dominance of heavy hydrocarbon compounds with long retention times, particularly in the 40–48 min range, indicating the presence of high-molecular-weight species such as polycyclic aromatics and asphaltenes [34]. In contrast, Figure 13b shows the chromatogram of pyrolysis oil obtained with the FeNi/TiO₂ nanocatalyst, where sharp peaks are distributed within the 2–30 min range, signifying the prevalence of lighter hydrocarbons such as paraffins, olefins, and simple aromatics. This shift demonstrates the catalytic effectiveness of FeNi/TiO₂ in breaking C–C and C–H bonds through hydrocracking and dehydrogenation mechanisms, thereby converting heavy fractions into lighter compounds with higher calorific value and characteristics comparable to commercial fuel fractions such as gasoline and diesel.

Table 4. Hydrocarbon composition and cetane number (CN) of the optimized pyrolysis oil based on GC-MS results.

Peak Number	Retention Time	Compound Name	wt%	CN *	CN *. wt%
1	1.654	1-Butanol. 3-methyl-	0.282	18.0	0.1
2	1.946	Cyclohexane	0.356	20.0	0.2
3	1.985	Hexane	2.236	50.0	0.3
4	2.329	Cyclopentene. 1-methyl-	0.319	15.0	0.1
5	2.634	Cyclopentane. 1,2-dimethyl-. trans-	1.168	24.0	0.6
6	2.715	Heptane	2.690	56.0	0.8
7	2.768	1,3-Pentadiene. 2,4-dimethyl-	1.366	15.0	0.1
8	3.003	Cyclohexane. methyl-	1.309	20.0	0.1
9	4.121	Octane	1.182	60.0	1.3
10	3.974	1-Octene	1.533	40.0	1.1
11	3.895	1-Heptene. 2-methyl-	0.788	27.0	0.4
12	3.765	Cyclohexane. 1,3-dimethyl-. cis-	0.465	30.5	0.3
13	3.540	Hexane. 3-ethyl-4-methyl-	0.779	18.9	0.3
14	9.840	1-Hexanol. 2-ethyl-	0.514	23.5	0.2
15	2.410	Hexane. 3,4-dimethyl-	0.565	18.9	0.2
16	5.936	1-Octene. 2-methyl-	2.131	50.0	0.9
17	5.227	5-Methyloctene-1	1.938	30.0	0.5
18	6.283	Nonane	3.780	74.0	2.1
19	6.079	1-Nonene	1.605	51.0	1.3
20	8.548	2-Methyl-1-nonene	1.056	49.1	0.8
21	8.729	1-Decene	1.919	60.0	1.7
22	7.713	1-Octene. 2,6-dimethyl-	0.766	49.0	0.5
23	5.588	Benzene. (3,3-dimethylbutyl)-	1.175	15.0	0.3
24	5.415	1-Iodo-2-methylnonane	4.234	30.0	1.0
25	3.425	1-Octene. 3,7-dimethyl-	0.817	48.0	0.6
26	7.630	3-Undecene. 6-methyl-	1.968	66.0	0.8
27	8.964	Undecane	2.312	83.0	2.5
28	10.937	Decane. 3-methyl-	0.797	79.0	0.8
29	11.584	1-Undecanol	1.427	53.2	1.5
30	14.714	Dodecane	2.712	74.0	2.4
31	11.393	1-Undecene. 2-methyl-	1.883	56.8	0.6
32	13.636	Undecane. 2-methyl-	1.172	60.0	0.8
33	14.460	1-Dodecanol	1.144	63.6	1.5
34	17.479	Tridecane	3.011	91.0	3.0
35	19.874	1-Tetradecanol	1.300	80.8	1.0
36	20.110	Tetradecane	3.271	96.0	3.2
37	22.595	Pentadecane	3.996	95.0	3.6
38	24.949	Heptadecane	4.588	89.0	3.4
39	27.179	Nonadecane	5.721	90.0	3.9
40	27.293	Pentadecane. 2,6,10,14-tetramethyl-	3.743	90.0	3.2
41	21.626	Hexadecane. 2,6,10,14-tetramethyl-	2.833	50.0	1.0
42	33.249	Eicosane	3.985	100.0	2.9
43	29.298	Heneicosane	4.253	92.0	3.3
44	31.321	Docosane	5.400	93.0	3.3
45	3.662	Oxalic acid. hexadecyl isohexyl ester	3.886	30.0	1.2
46	36.854	Tetracosane	1.805	70.0	1.6
47	35.095	Hexacosane	3.820	96.0	3.1
Total					64.3

* Encyclopedia of Liquid Fuels [35].

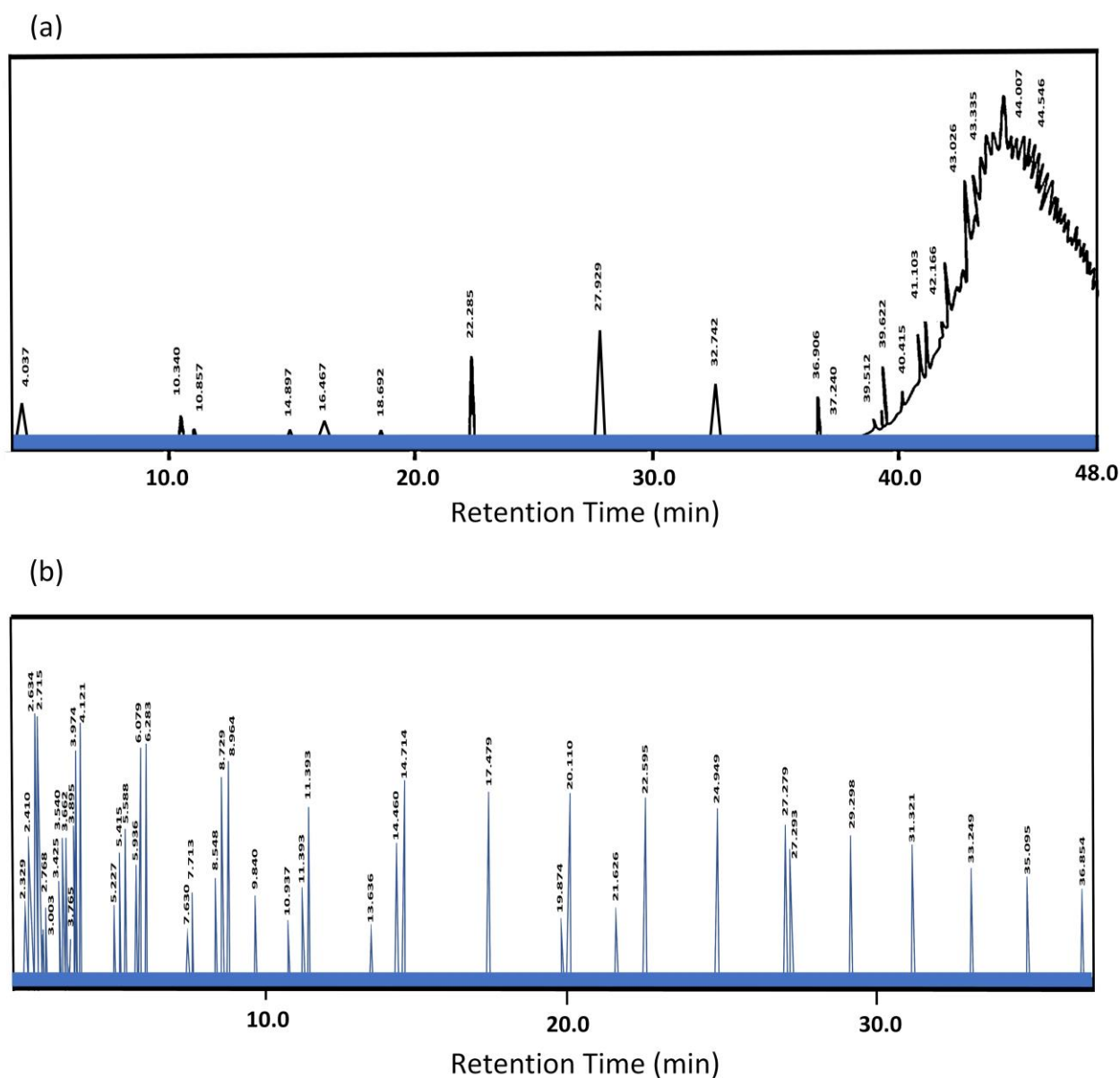


Figure 13. Comparative GC-MS chromatograms of waste lubricating oil (a), and pyrolysis oil obtained by using optimized FeNi/TiO₂ nanocatalyst (b).

Pyrolysis oil has properties similar to those of commercial diesel fuel, making it a viable alternative energy option. As shown in Table 5, the pyrolysis process increases the abundance of mid-chain hydrocarbons, which are the key constituents of diesel fuel. This change demonstrates that pyrolysis successfully decomposes long-chain hydrocarbons into lighter, more flammable compounds. Generally, shorter-chain hydrocarbons possess greater volatility, promoting more efficient combustion and enhanced energy output [36,37]. Additionally, the discovery of previously unidentified hydrocarbon fractions indicates that pyrolysis enhances fuel quality by producing a composition that is better aligned for combustion uses.

The reduction in long-chain hydrocarbon content in pyrolysis oil highlights its improved fluidity and superior combustion properties compared to conventional diesel fuel. The lower concentration of heavier components results in cleaner combustion, thereby decreasing soot formation and minimizing harmful exhaust emissions [39,40]. These features indicate that pyrolysis oil can serve as a practical replacement for diesel fuel in both industrial and transportation sectors while providing environmental advantages by re-

cycling waste lubricating oil in a more sustainable way. With additional enhancements, the pyrolysis method has considerable potential for generating an alternative fuel that is efficient and eco-friendly.

Table 5. Hydrocarbon composition of pyrolysis oil and diesel.

Compounds	Composition of Pyrolysis Oil	Literature
	After (%)	Diesel (%) [38]
C5	0.282	0.000
C6	2.911	0.201
C7	6.532	1.892
C8	8.826	1.464
C9	10.454	3.306
C10	9.967	2.880
C11	7.504	4.674
C12	4.911	7.961
C13	3.011	7.140
C14	4.570	7.130
C15	3.996	4.844
C17	4.588	4.725
C18	0.000	2.750
C19	6.464	1.613
C20	6.818	16.020
C21–40	19.164	33.400

According to Barra et al. [41], diesel fuel in Morocco typically falls within the C8–C24 hydrocarbon range, while Hidayanti [42]’s findings indicate that Indonesian diesel fuel consists of hydrocarbons ranging from C6 to C39. A comparison with documented diesel fuel compositions verifies that the hydrocarbon fractions, especially in the C7–C20 range, closely match those in traditional diesel fuel. This illustrates the promise of pyrolysis as a practical and sustainable method for transforming used lubricating oil into an alternative diesel-like fuel, providing both ecological advantages and economic viability.

4. Conclusions

This study successfully demonstrates the green synthesis of nanoflower FeNi/TiO₂ catalysts using grape seed extract (GSE) as a natural reducing and stabilizing agent. The key findings and their implications are summarized as follows. The GSE-mediated synthesis route produced a well-dispersed FeNi/TiO₂ nanocatalyst with a high surface area and a nanoflower morphology. This catalyst exhibited exceptional performance in the low-temperature (400 °C) catalytic pyrolysis of waste lubricating oil, significantly enhancing the breakdown of heavy hydrocarbons (C21–C40) into valuable lighter fractions (C6–C20). Under optimized conditions determined by Response Surface Methodology (RSM), the process achieved a high pyrolysis oil yield of up to 77.59%. The resulting oil possesses key properties, including calorific value (11,016 cal/g), density (829.4 kg/m³), and viscosity (2.27 cP), that align with commercial diesel standards (e.g., Indonesian Premium Diesel). GC-MS analysis confirmed the dominance of diesel-range hydrocarbons, underscoring the practical viability of oil. This work provides a sustainable and efficient pathway for managing hazardous waste lubricating oil by converting it into high-quality diesel-like fuel. The use of a bio-based reducing agent aligns with green chemistry principles, reduces reliance on toxic chemicals, and enhances the overall sustainability of the process. The findings highlight the potential of green-synthesized bimetallic nanocatalysts to advance waste-to-energy technologies, contributing to circular economy goals and reducing environmental pollution.

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