INFLUENCE OF TETRALIN ON THE HYDROTREATING OF CRUDE OIL

I. A. Mohammed-Dabo, B. Sabiu and D. E. Ogboso*

Abstract

Hydrotreating of crude oil fractions has long been an important operation in petroleum refining; however, the hydrotreating of whole crude oil remains a relatively underexplored process. Although pure hydrogen is conventionally used as the hydrogen source, concerns regarding its safe handling have encouraged interest in alternative hydrogen-donor chemicals.

This study investigates the hydrotreating of crude oil using tetralin as a hydrogen-donor chemical. Experiments were conducted in a continuous-flow fixed-bed reactor under controlled operating conditions using a cobalt–molybdenum catalyst supported on alumina. The sulphur, nitrogen, and nickel contents of the crude oil were analysed before and after treatment. The sulphur content of the untreated crude oil decreased from 0.12 wt.% to 0.053 wt.% after treatment with tetralin. Similarly, nitrogen and nickel contents decreased from 0.09 wt.% and 0.985 ppm to 0.039 wt.% and 0.641 ppm, respectively. These results indicate that tetralin can serve as a viable hydrogen-donor medium for reducing key impurities during crude oil hydrotreating, offering a potentially safer alternative to direct handling of gaseous hydrogen.

Keywords: Crude oil; Hydrotreating; Tetralin; Hydrogen-donor chemicals; Cobalt–molybdenum catalyst; Impurity removal

Introduction

The petroleum refining industry plays a pivotal role in meeting global energy demands and providing essential products for various sectors. However, this industry is confronted with multifaceted challenges, including the need to produce cleaner, high-quality fuels, reduce environmental impacts, and enhance operational efficiency[1]. One of the cornerstone processes in petroleum refining is hydrotreating, which is employed to remove impurities, such as sulphur and nitrogen compounds, and to improve the quality of refined products, including gasoline, diesel, and jet fuel[2] .

Traditionally, hydrotreating has been the linchpin of petroleum refining, a cornerstone process that transforms raw crude oil into an array of valuable products, from cleaner fuels to essential petrochemicals[3]. Yet, even in its importance, the conventional methodology of hydrotreating has shown its limitations and marked areas ripe for innovation.

---

*Authors are of the Department of Chemical Engineering, Ahmadu Bello University, Zaria

[1] Korsten, H. and Hoffmann, U. Three-phase reactor model for hydrotreating in pilot trickle-bed reactors. AIChE Journal, 1996, 42 (5): 1350-1360.

[2] Ancheyta J.; Betancourt G.; Marroquin G.; Centeno G.; Castañeda L C.; Alonso F.; Muñoz J.A.; Gómez Ma. T.; Rayo P. Hydro-processing of Maya heavy crude oil in two reaction stages. Applied Catalysis A: General 233, 2002: 159–170.

[3] Gary, J. H.; Handwerk, G. E.; Kaiser, M. J. Petroleum Refining: Technology and Economics. 5th ed.; CRC Press: Boca Raton, FL, 2007.

This research endeavours to explore an unconventional path, one that pivots away from the conventional method of relying solely on gaseous hydrogen for hydrotreating. Instead, it thrusts forward with the daring proposition of utilizing hydrogen-donor chemicals to revolutionize the process. In doing so, it bridges the gap between tradition and innovation, offering a fresh perspective on an age-old refining practice.

Crude oil hydrotreating is a novel technology and a new challenge that has not received much attention. Hydrotreating procedures are applied to oil fractions rather than to the entire crude oil (that is, after the crude oil has been separated into its constituent fractions, such as light and heavy gas oils, gasoline, and kerosene)[4]. Subsequently, the HDT processes are implemented for every cut independently. This indicates that a substantial number of the contaminants, primarily S, N, V, Ni, and asphaltenes, will end up at the bottom of the atmospheric and vacuum distillation columns. Additionally, it is simple to process each section's HD independently. The crude oil hydrotreating process is considered highly challenging due to the diverse compounds and intricate structures present in crude oil, along with its multiphase nature and the asphaltenes it contains, which are rich in sulfur and metals that deactivate the catalyst's active sites[5] .

The study explores an innovative approach to hydrotreating the entire crude oil feedstock, moving beyond the conventional focus on individual petroleum fractions. This paradigm shift redefines refining processes by challenging established industry practices. By conducting hydrotreatment prior to distillation, the method enhances operational efficiency, optimizes resource utilization, and significantly improves environmental sustainability compared to traditional techniques

This research also focuses on the transformative concept of hydrogen donor chemicals. These compounds, with their exceptional ability to release hydrogen atoms under specific conditions, represent a paradigm shift in hydrotreating methodologies. They offer a powerful alternative to the traditional dependence on bulk hydrogen gas, presenting significant implications for the refining industry[6].

The use of hydrogen-donor chemicals challenges the established norms of hydrotreating by presenting an avenue toward improved energy efficiency, reduced environmental impact, and enhanced economic viability[7]. By rethinking the way we harness hydrogen for hydrotreating, this research positions itself at the forefront of innovation, offering a potential meaningful change for the refining sector.

This research embarks on a pioneering exploration into the untapped potential of hydrotreating the entire crude oil feedstock, coupled with the innovative application of hydrogen-donor chemicals. The study seeks to evaluate their effectiveness in impurity removal, product quality enhancement, and the promotion of sustainability within the refining process. Treating the

---

[4] Ancheyta J.; Betancourt G.; Marroquin G.; Centeno G.; Castañeda L C.; Alonso F.; Muñoz J.A.; Gómez Ma. T.; Rayo P. Hydro-processing of Maya heavy crude oil in two reaction stages. Applied Catalysis A: General 233, 2002: 159–170.

[5] Andari M. K., Behbehani H., Stanislaus A. Sulfur compound type distribution in Naphtha and gas oil fractions of Kuwaiti crude. Fuel Sci Technol Int, 1996, 14:939– 961.

[6] Areff, H.A. The effect of operating conditions on vacuum gas oil hydrotreating on sulfur and aromatics content. M.Sc. Thesis, University of Tikrit, Iraq. 2001.

Speight, J. G. (2019). The Chemistry and Technology of Petroleum (6th ed.). CRC Press.

[7] Speight, J. G. (2019). The Chemistry and Technology of Petroleum (6th ed.). CRC Press.

entire crude oil feedstock offers the promise of more efficient resource utilization, reduced waste, and streamlined operations.

Moreover, this approach holds significant economic promise. By optimizing the hydrotreating process on a whole-feedstock scale, the research aims to reduce operational costs, improve profitability, and enhance the economic sustainability of the industry. This innovative methodology challenges conventional practices and seeks to chart a course toward more sustainable and efficient energy solutions.

This study involved conducting HDS, HDN, and HDM reactions in a continuous-flow isothermal fixed-bed reactor (FBR), utilizing crude oil as the feedstock and cobalt-molybdenum supported on alumina (Co-Mo/γ-Al2O3) as the catalyst. The experiments were performed across varying reactor temperatures, hydrogen pressures, and liquid hourly space velocities (LHSVs), maintaining a constant hydrogen-to-oil ratio. Following hydrotreatment under optimal conditions, the crude oil was distilled into naphtha, kerosene, diesel, and reduced crude residue. The yield and properties of these fractions were then compared with those obtained through conventional methods.

Hydrotreatment of Crude Oil

Hydrotreating is a catalytic process used to stabilize petroleum products by hydrogenating unsaturated hydrocarbons and removing contaminants like sulfur, nitrogen, oxygen, and metals (such as nickel and vanadium) from feedstocks through reaction with hydrogen at elevated temperatures and pressures[8]. During this process, sulfur and nitrogen are converted into hydrogen sulfide (H_2S) and ammonia (NH_3), respectively[9]. Hydrotreating is crucial for complying with increasingly strict environmental and emissions standards, and it also prepares petroleum stocks for downstream processes like catalytic cracking and reforming, which require the removal of these contaminants to prevent catalyst poisoning[10]. The crucial factors that constitute and determine the nature of a hydrotreating process are highlighted in Figure 1. In brief, these factors include feed properties, catalyst, and process.

[8] Wang, H., Song, H., Zhang, L., & Ma, X. (2016). Hydrotreating of crude oil at high pressure with a non-sulfided NiMo catalyst. Asia-Pacific Journal of Chemical Engineering, 11(5), 619-627

[9] Zhang, J., & Du, Z. (2016). Hydrotreating of Heavy Oils and Residua. Springer.

[10] Chen, H., Liu, S., & Liu, Y. (2017). The Role of Hydrogen Donor Chemicals in Hydrotreating and Their Potential for Upgrading Heavy Oils. Fuel, 205, 182-192

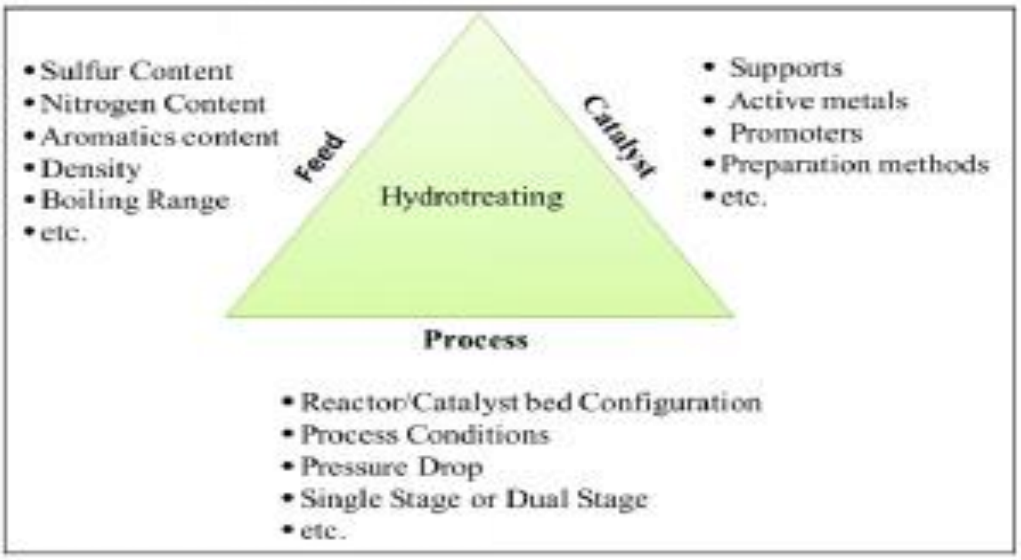


Figure 1: Key factors affecting hydrotreating activities

There are around thirty hydrotreating processes available for licensing[11], though most follow a similar process flow. A hydrocarbon feedstock mixed with hydrogen is heated to a specific inlet temperature before being fed into a fixed-bed reactor containing the catalyst. In the reactor, hydrogen reacts with the oil, primarily resulting in the formation of saturated hydrocarbons, hydrogen sulphide (H_2S), and ammonia (NH_3). The reactor effluent enters high- and low-pressure separators where the liquid and gaseous products are separated. The liquid product is sent to the fractionation unit for further separation. Unreacted H_2 is recovered from the gaseous product and recycled to the reactor[12] .

Hydrotreating Reactions

Impurities like nitrogen, sulphur, and metals, combined with carbon and hydrogen compounds, add complexity to the structure of crude oil. These impurities, along with hydrogen and carbon, vary in molecular structure, molecular weight, and both physical and chemical properties[13] . The primary reaction in hydrotreating is the removal of sulphur, known as hydrodesulfurization (HDS). However, other reactions can occur simultaneously depending on the operating conditions. These include hydrodearomatization (HDAM), hydrodemetallization (HDM), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO), and hydrogenation (olefin saturation). Hydrodeoxygenation is less significant as most crude oils contain little oxygen. Hydrodesulfurization is the most important hydrotreating process because sulphur content and

[11] Yang, H., Liu, J., & Zhang, C. (2021). Hydrogen Donor Chemicals for Clean Fuel Production: A Review. Frontiers in Energy Research, 9, 632468.

[12] Jarullah, A. T., Mujtaba, I., Wood, A.S., 2011, "Kinetic Parameter Estimation and Simulation of Trickle-Bed Reactor for Hydrodesulfurization of Crude Oil." Chemical Engineering Science 66 (5), 859-871

[13] Dry, M. E. (2002). The Fischer-Tropsch process: 1950-2000. Catalysis Today, 71(3-4)

API gravity have the greatest influence on the quality of heavy oil and residue[14] . The primary goal of HDS and HDN is to remove sulphur and nitrogen from the feedstock, converting them into hydrogen sulphide (H_2S) and ammonia (NH_3), respectively. Other reactions, such as HDM, HDN, and HDO, occur alongside HDS. Hydrodemetallization (HDM) is a thermo-catalytic process that forms metallic sulphides, such as nickel sulphide (NiS) and vanadium sulphide (V_3S_4), which deposit on the catalyst's active sites during the reaction. Hydrotreating reactions typically take place in a trickle bed reactor.

Hydrogen Donor Chemicals

Hydrogen donors are chemical substances that can donate hydrogen atoms to other molecules or chemical species. In many chemical reactions, the transfer of hydrogen atoms is an important step in the formation of new chemical bonds or the breaking of existing ones. Hydrogen donors play a vital role in such reactions by providing a source of hydrogen atoms that can participate in these processes.

Hydrogen donors can be classified into two main types: organic and inorganic. Organic hydrogen donors are typically organic compounds that contain one or more hydrogen atoms that can be readily transferred to other molecules or chemical species. Inorganic hydrogen donors, on the other hand, are typically metals or metal hydrides that can donate hydrogen atoms through various mechanisms[15].

Hydrogen donors are used in a variety of chemical reactions, including reduction reactions, hydrogenation reactions, hydrotreating, and radical reactions. They can also be used as fuels, as the combustion of hydrogen donors releases energy in the form of heat and light.

In general, the use of hydrogen donors in hydrotreating of petroleum products makes it possible not only to increase the yield of light fractions but also to suppress the processes of coke formation and the removal of heteroatoms such as sulphur, nitrogen, and oxygen.

The efficiency of their use depends on several factors, such as the nature of the oil, the catalyst, and the conditions for upgrading. In several works, hydrogen donors (tetralin and decalin) and gaseous hydrogen were compared during the cracking of heavy oil in the presence of nickel–molybdenum catalysts[16] .

Experimental Work

Sample Collection

The crude oil sample utilized in this study was collected from the Ahmadu Bello University Minirefinery, Zaria. The collection process adhered to industry-standard protocols, including proper storage and handling to preserve the sample's integrity. The key characteristics of the crude oil sample, such as its origin, composition, and properties, were documented for reference.

---

[14] Ancheyta, J., 2013, Modeling of Processes and Reactors for Upgrading of Heavy Petroleum. CRC Press: Taylor & Francis Group, Boca Raton, USA

[15] Gary, J. H., & Handwerk, G. E. (2001). *Petroleum Refining: Technology and Economics* (4th ed.). Marcel Dekker

[16] R. K., & Towler, G. (2009). *Chemical Engineering Design*. Elsevier.

Catalyst

The catalyst utilized for the hydrotreating (HDT) process in this study was a cobalt-molybdenum (Co–Mo) supported on gamma alumina (γ-Al_2O_3), a widely adopted formulation for hydrotreating applications. Fourier Transform Infrared (FTIR) spectroscopy was employed to verify the presence of the required functional groups, ensuring the catalyst's suitability for the process. Additionally, catalyst presulfiding was performed as an activation step to enhance the catalyst's performance under hydrotreating conditions.

Experimental Setup

A laboratory-scale hydrotreating (HDT) unit (shown in Figure 2) incorporating a fixed-bed reactor was set up to simulate processes commonly employed in petroleum refining, such as hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodemetallization (HDM), and hydrocracking (HDC) of crude oil feedstocks. The system comprises four main sections: the feed section, the reactor section, the product section, and the nitrogen gas module. The nitrogen gas module supplies high-pressure nitrogen to purge the system of oxygen and other impurities before the hydrotreating reactions commence. The feed system includes a liquid feed reservoir, and a metering pump integrated with a rotameter for precise monitoring of the feedstock flow rate. The liquid feed reservoir is a 500 mL round-bottom flask, and a low-pressure dosing pump introduces the feedstock and hydrogen donor chemical into the reactor.

The reactor section is the core of the system, where the feedstock and hydrogen donor chemicals flow concurrently. The reactor tube, constructed from stainless steel with an inner diameter of 32 mm and a length of 45 cm, is divided into three sections. The first section (20 cm) is packed with 4 mm diameter glass beads, which preheat the mixture, ensure uniform flow distribution, and prevent end effects. The second section (10 cm) contains 10 g of catalyst, while the bottom section (15 cm) is packed with inert particles to serve as a disengagement zone. The reactor operates under isothermal conditions, maintained by an independently controlled electric furnace. The product recovery system comprises a condenser and a product collection unit. The reactor effluent is directed to the condenser, where vapor-phase products are condensed and separated into liquid and gaseous fractions for collection and subsequent analysis.

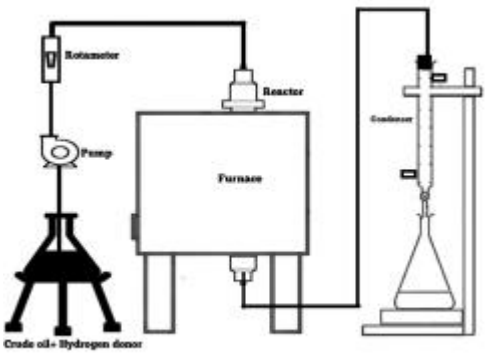


Fig 2: Schematic diagram for crude oil hydrotreating experimental setup.

Catalyst Loading

Before loading the reactor, the Co-Mo/γ-alumina was prepared and dried at 120°C for 2 hr on a heating mantle, and the dried solution was calcined in a furnace at 500°C for 4 hours to properly activate it and remove some soluble impurities. The bottom part of the reactor with a length of 15 cm was loaded with glass beads of 4 mm diameter. In the middle part of the reactor with a length of 10 cm, 20 g of catalyst was loaded, respectively. Finally, the top part of the reactor with a length of 20 cm was loaded with glass beads of 4 mm diameter. Figure 3 shows the catalyst loading schematic diagram.

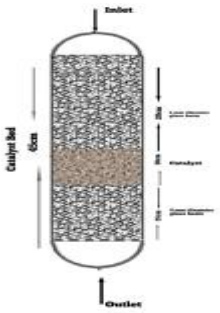


Figure 3: Catalyst loading schematic.

Experimental Procedures

The reaction was carried out in a continuous-flow fixed-bed reactor using crude oil as the feedstock and cobalt-molybdenum as the catalyst. Before any run was started, the fixed-bed reactor was purged using nitrogen gas for a duration of 5 minutes to remove oxygen and any other impurities.

500ml of the crude oil feedstock was measured using a measuring scale and then mixed with 100 mL of a hydrogen donor chemical. The mixture of crude oil and hydrogen donor chemical was thoroughly stirred with a magnetic stirrer for about 25 minutes to ensure that the hydrogen donor chemical was fully dissolved and a homogeneous mixture was achieved. The mixture of crude oil and hydrogen donor chemical was charged into the continuous-flow fixed-bed reactor containing 20 g of cobalt-molybdenum catalyst with the help of a low-pressure pump. The reaction occurred at a temperature range of 350–400 °C, a pressure of 20 bar, and an LHSV of 1.2 h^{-1}. The reactor temperature was maintained at 375 °C. Liquid products were collected and analyzed for sulphur, nitrogen, and metal contents. The entire hydrotreating process was systematically repeated using two different hydrogen donor chemical (Tetralin). These experiments followed the same rigorous conditions, and hydrotreated crude was collected.

Crude Distillation Unit

A borosilicate glass reaction vessel with a round bottom and a volumetric capacity of 500 mL was selected as the primary vessel for the distillation process. This vessel was selected due to its exceptional thermal stability and visibility, allowing for real-time monitoring of the reaction progress.

The reaction vessel was carefully placed onto a precision-controlled heating mantle. This heating mantle provided the controlled and uniform application of heat to the reaction mixture, ensuring optimal reaction conditions. A fine-wire thermocouple, positioned within the reaction vessel, was employed to continuously monitor and record temperature variations throughout

the course of the reaction. To recover and isolate the reaction products, a vertical Liebig-type fractionating condenser was securely attached to the reaction vessel. This condenser effectively condensed vaporized products, allowing for the separation and collection of liquid fractions. The reaction vessel was hermetically sealed to prevent any potential gas leakage, maintaining a closed system and ensuring the safety of the experiment.

The reactor vessel setup was meticulously purged using nitrogen gas for a duration of 5 minutes. This step was undertaken to eliminate any presence of atmospheric air or impurities within the vessel, ensuring an oxygen-free environment for subsequent hydrotreating.

350 mL of the hydrotreated feedstock was measured and charged into a 500 mL round-bottom flask on an electric heating mantle. The heating mantle, connected to an electric source, provides heat input adjustment. A thermocouple located at the top of the distillation column records the boiling point of the distilled fraction periodically. The hydrocarbons in the sample(s) were separated based on their boiling range. The range of temperatures needed was recorded, and fractions were continuously removed at intervals related to the temperature ranges. The recovered fractions were measured using a measuring cylinder to detect the volume of the recovered fractions. The recovered fractions were then separated into a reagent bottle. The procedure was repeated using the same conditions for different treated crude samples.

Results and Discussion

Physicochemical Properties of Raw Crude Oil

The Physicochemical Properties of the crude oil are shown in Table 1. From the table, the crude oil appeared to be in the category of a medium crude, having an API gravity of 31. It is also a sweet crude with a 0.12 wt% sulfur content. Both nitrogen and nickel contents are moderately low. From all these parameters, the crude oil is of high value; hence, it requires a less rigorous approach in its refining to valuable finished products.

Table 1. Physico-Chemical Properties of Crude Oil

S/N	PARAMETERS	UNIT	VALUES
1	Sulphur Content	(wt.%)	0.12
2	Nitrogen Content	(wt.%)	0.09
3	Metal Content (Nickel)	(ppm)	0.985
4	API Gravity	--	31
5	Density	g/cm^3	0.892
6	Specific gravity	--	0.872
7	Viscosity @40	^oC	1.2cp
8	Viscosity @100	^oC	0.5cp

Results of Catalyst Analysis

The FTIR spectrum of the Co-Mo/γ-alumina catalyst was analyzed, and the following characteristic absorption bands were identified, as depicted in Figure 4.

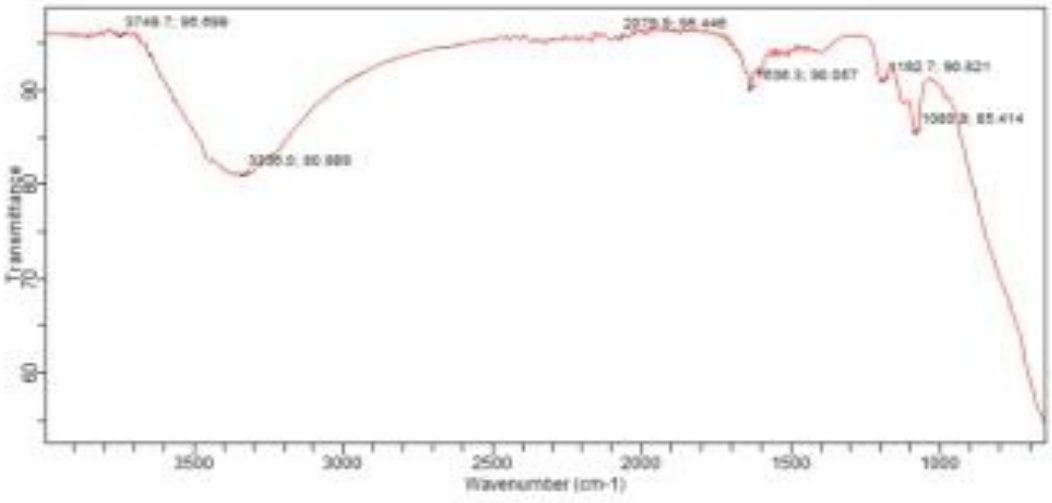


Figure 4: FTIR results for the catalyst.

The FTIR analysis of the Co-Mo/γ-alumina catalyst reveals the presence of key functional groups that contribute to its structural and catalytic properties (enhanced adsorption, increased reactivity in nitrogen-involved reactions, improved reaction stability, versatility in reaction pathways, enhanced substrate interaction, and structural stability). The prominent O–H stretching vibrations observed at 3749.7 cm^{-1} and 3326.0 cm^{-1} indicate hydroxyl groups, which are integral to the catalyst's surface chemistry and adsorption characteristics. The presence of N–H stretching vibrations suggests nitrogen-containing groups, potentially enhancing its reactivity in nitrogen-involved reactions.

The observed C≡C and C≡N stretching vibrations at 2078.9 cm^{-1} highlight unsaturated carbon and nitrile functionalities, which are associated with high reactivity and catalytic stability. Additional C=C and C=O stretching vibrations at 1633.3 cm^{-1} confirm the presence of unsaturated carbon and amide groups, critical for diverse catalytic mechanisms. The C–H bending vibrations at 1383.2 cm^{-1} and C–N or C–O stretching vibrations at 1192.7 cm^{-1} further indicate methyl and organic functionalities, influencing the catalyst's hydrophobicity and substrate interactions. Moreover, Si–O stretching vibrations at 1080.8 cm^{-1} suggest silicon-containing compounds, contributing to the structural stability of the catalyst.

These findings underscore the catalyst's diverse functional groups and its potential applicability in reactions involving hydroxyl groups, nitrogen compounds, unsaturated carbons, and various organic molecules, broadening its utility in catalytic processes.

Even though as highlighted in Table 1, the sulphur, nitrogen and Nickel contents are not significantly high, direct hydrotreatment of the crude led to the reduction of these impurities. Table 2 indicates that, hydrotreatment of the crude separately using pure hydrogen and tetralin led to reduction of the sulfur contents of 63.3 and 55.8%, respectively. It can also be observed from the table that the utilization of pure hydrogen gave higher reductions in both nitrogen and metal (Ni) contents, which were 57% and 35%, respectively. However, from the safety and environmental perspectives of handling pure hydrogen, it may be safer to utilize tetralin as a source of hydrogen in the hydrotreating process.

Table 2. Impurities Reduction in Raw and Hydrotreated Crude Oils

S/N	Sample	Sulphur		Nitrogen		Metal (Ni)	
		Content, wt%	% Removal	Content, wt%	% Removal	Content, ppm	% Removal
1	Raw Crude Oil (Untreated)	0.12	-	0.09	-	0.985	-
2	Pure Hydrogen Treated Crude Oil	0.044	63.3	0.036	60	0.552	44
3	Tetralin Treated Crude Oil	0.053	55.8	0.039	56.7	0.641	35

Effects of Crude Oil Hydrotreatment on the Distillate Yield

In order to ascertain the economic viability of the direct crude oil hydrotreatment process, the hydrotreated crude was distilled, and the yields of the fractions were quantified. Table 3 indicates the yields of gasoline, kerosene, diesel, and the atmospheric fractions. From the table, it can be seen that there was an appreciable increase in the amounts of gasoline, kerosene, and diesel yields. The highest diesel yield (36.86%) was obtained when the crude oil was hydrotreated using tetralin. This increase in the light and middle distillates led to a corresponding decrease in the yield of atmospheric residue. This is favorable from the economic point of view, considering the fact that the residue has a low market value compared to the light and middle distillates.

Table 3. Yields of Distillation Fractions

S/N	Fractions	RCO		H2-HTCO		TL-HTCO	
		Vol (ml)	% Vol	Vol (ml)	% Vol	Vol (ml)	% Vol
	IBP	**92°C**		**91°C**		**93°C**	
1	1BP-150°C (Gasoline)	60	17.14	65	18.57	63	18
2	150-240°C (Kerosene)	90	25.71	95	27.14	92	26.29
3	240-350°C (Diesel)	125	35.71	127	36.29	129	36.86
4	>350°C (Residue)	60	17.14	50	14.29	53	15.14
5	Loss	15	4.29	13	3.71	13	3.71
Total		**350**	**99.99**	**350**	**100**	**350**	**9.97**

Effects of Crude Oil Hydrotreatment on the distillate quality

Each of the distillates obtained from the distillation of the hydrotreated crude oil samples was analyzed with a view to establishing the effects of the respective hydrotreatment on the quality parameters of the fractions

Physico-chemical properties of the various gasoline, kerosene, diesel, and atmospheric residue fractions are highlighted in Tables 4, 5, 6, and 7. From Table 4, it can be seen that the impurity contents were drastically reduced when the crude oil sample was hydrotreated using both pure hydrogen and tetralin. The octane numbers of the gasoline fractions increased appreciably by about 7.8–10.5 points. This implies that the gasoline fractions had better anti-detonation tendencies compared to the raw crude oil straight-run gasoline. From Table 5, it can be observed that the kerosene flame height increased by a unit, while the diesel index of the diesel fraction

(Table 6) for the pure hydrogen-hydrotreated crude oil was the highest (40) compared to those for the raw crude (34.92) and tetralin-treated crude oil (39.24). Table 7, which depicts the physico-chemical properties of the atmospheric residue, equally indicated that hydrotreatment of the crude oil improved its refining and safety status.

Table 4. Physico-Chemical Properties of Raw Crude Oil and Crude Oil Hydrotreated Gasoline Fractions

S/N	PARAMETER	CO	H-HT	TL-HT
1	Density g/cm^3	0.781	0.749	0.754
2	Specific Gravity	0.756	0.717	0.722
3	Sulfur (wt.%)	0.016	0.0064	0.007
4	Nitrogen (wt.%)	0.032	0.015	0.017
5	Metal (Nickel) (ppm)	0.323	0.163	0.169
6	RON Clear	77.8	88.3	85.6
	MON Clear	72.5	82.6	78.6
7	Flash Point (^{o}C)	65	62	63

Table 5. Physico-Chemical Properties of Raw Crude Oil and Crude Oil Hydrotreated Kerosene Fractions

S/N	PARAMETER	CO	H-HT	TL-HT
1	Density g/cm^3	0.820	0.780	0.789
2	Specific Gravity	0.784	0.746	0.751
3	Sulphur (wt.%)	0.045	0.015	0.021
4	Nitrogen (wt.%)	0.038	0.016	0.019
5	Metal (Nickel) (ppm)	0.384	0.189	0.196
6	Flash Point (^{o}C)	80	75	77
7	Flame Height (cm)	6	7	7

Table 6. Physico-Chemical Properties of Raw Crude Oil and Crude Oil Hydrotreated Diesel Fractions

S/N	PARAMETER	CO	H-HT	TL-HT
1	Density g/cm^3	0.877	0.838	0.853
2	Specific Gravity	0.839	0.802	0.818
3	Sulphur (wt.%)	0.083	0.042	0.055
4	Nitrogen (wt.%)	0.04	0.021	0.025
5	Metal (Nickel) (ppm)	0.387	0.198	0.221
6	Flash Point (^{o}C)	110	107	107
7	Diesel Index	34.92	40	39.24

Table 7. Physico-Chemical Properties of Raw Crude Oil and Crude Oil Hydrotreated Atmospheric Residue Fractions

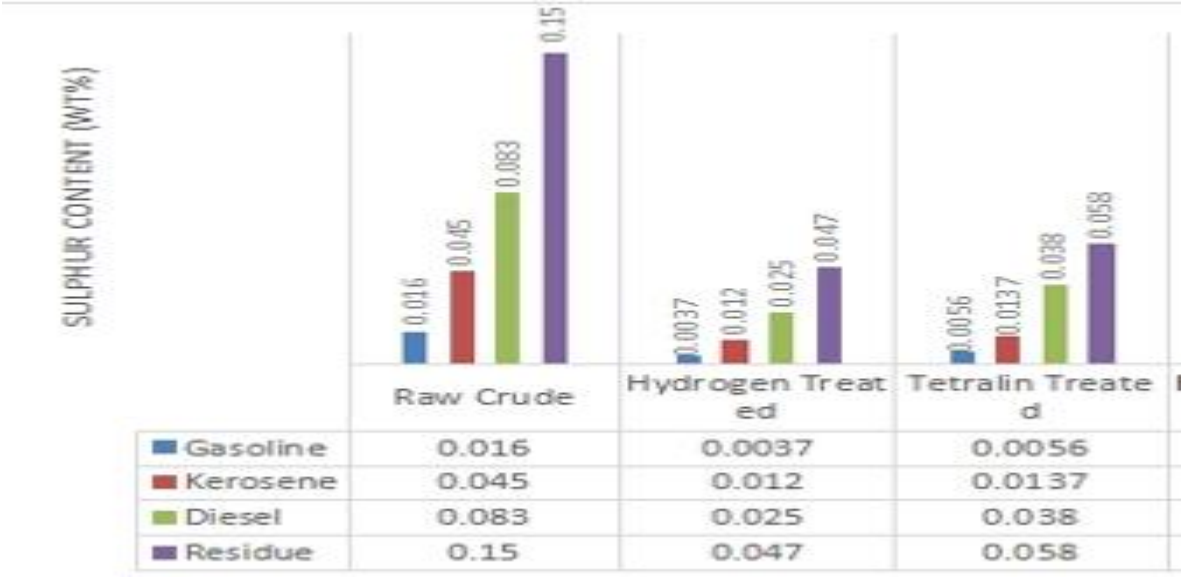
S/N	PARAMETER	CO	H-HT	TL-HT
1	Density g/cm^3	1.30	1.19	1.230
2	Specific Gravity	1.24	1.139	1.182
3	Sulphur (wt.%)	0.150	0.055	0.068
4	Nitrogen (wt.%)	0.06	0.034	0.040
5	Metal (Nickel) (ppm)	0.753	0.503	0.592
6	Flash Point (^{o}C)	205	200	205

Comparative Analysis of Impurity Concentrations in Crude Oil Fractions Under Different Treatment Processes

The comparative analysis of impurity concentrations in crude oil fractions under different treatment processes highlights the effectiveness of various methods in reducing sulfur, nitrogen, and metal content. Figures 5, 6, and 7, presented as bar charts, illustrate the differences in impurity levels across these processes, providing a clear visual representation of their impact on crude oil purification.

Comparison of Sulfur Content in Crude Oil Fractions Across Different Treatments

The bar chart below illustrates the sulfur content variation in crude oil fractions subjected to different treatments. It compares the sulfur levels across various fractions, providing insights into the effectiveness of each treatment method in reducing sulfur concentration.



	Raw Crude	Hydrogen Treated	Tetralin Treated
Gasoline	0.016	0.0037	0.0056
Kerosene	0.045	0.012	0.0137
Diesel	0.083	0.025	0.038
Residue	0.15	0.047	0.058

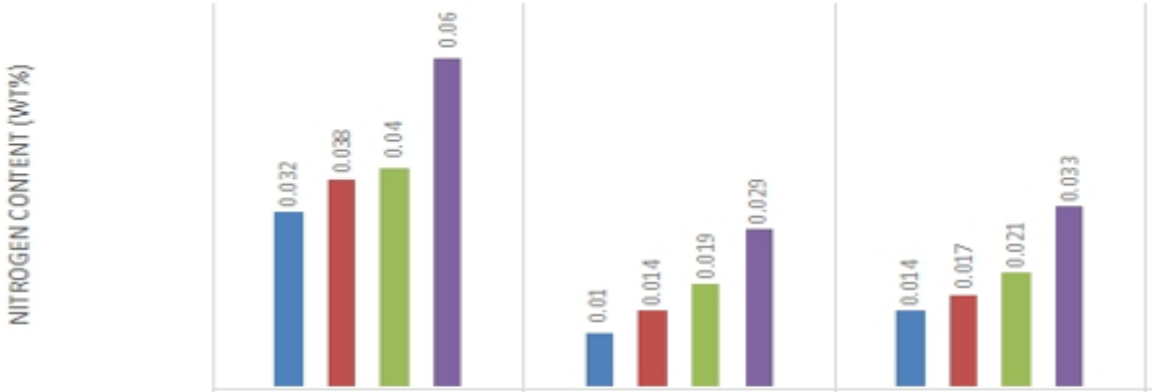
Figure 5: Comparison of sulfur content in crude oil fractions across different treatments

From Figure 5, hydrogen treatment demonstrates the most significant impact on reducing sulfur content across all crude oil fractions, showcasing its effectiveness as a desulfurization method. In the gasoline fraction, sulfur content decreases from 0.016 wt.% in raw crude to 0.0037 wt.% after hydrogen treatment. For kerosene, the sulfur content is reduced from 0.045 wt.% to 0.012 wt.% with hydrogen treatment. The diesel fraction also benefits from this treatment, with sulfur levels decreasing from 0.083 wt.% in raw crude to 0.025 wt.% post-treatment. The most substantial reduction was observed in the residue fraction, where sulfur content drops significantly from 0.15 wt.% in raw crude to 0.047 wt.% after hydrogen treatment. Compared with hydrogen treatment, Tetralin treatment is less effective but still demonstrates reductions in sulfur. For instance, in the residue fraction, Tetralin treatment reduced sulfur to 0.058 wt.%. This indicates that while all treatments contribute to sulfur reduction, hydrogen treatment is the superior choice for minimizing sulfur impurities across different crude oil fractions.

Comparison of Nitrogen Content in Crude Oil Fractions across Different Treatments

Figure 6 presents a comparative result of the nitrogen content in crude oil fractions after undergoing different treatment methods. It highlights the variation in nitrogen levels across the

fractions, offering a perspective on the efficiency of each treatment in reducing nitrogen concentration.



	Raw Crude	Hydrogen Treated	Tetralin Treated
Gasoline	0.032	0.01	0.014
Kerosene	0.038	0.014	0.017
Diesel	0.04	0.019	0.021
Residue	0.06	0.029	0.033

Figure 6: Comparison of nitrogen content in crude oil fractions across different treatments

From the figure, it can be observed that hydrogen treatment also proves highly effective in reducing nitrogen content in crude oil fractions, indicating its versatility in tackling multiple impurities. In the gasoline fraction, nitrogen content decreases from 0.032 wt.% in raw crude to 0.01 wt.%. after hydrogen treatment. Kerosene shows a similar trend, with nitrogen levels dropping from 0.038 wt.% to 0.014 wt.%. In the diesel fraction, the treatment reduces nitrogen from 0.04 wt.% to 0.019 wt.%. The residue fraction, which initially had the highest nitrogen content at 0.06 wt.% in raw crude, experiences a substantial decrease to 0.029 wt.% following hydrogen treatment. Although Tetralin treatment also lowers the nitrogen level, it is comparatively less effective. For example, Tetralin reduces nitrogen in the residue to 0.033 wt.%. These values underscore that hydrogen treatment is the most efficient method for reducing nitrogen across various crude oil fractions, especially in heavier fractions where impurities are more concentrated.

Comparison of metal (nickel) content in crude oil fractions across different treatments

Figure 7 presents a comparison of nickel contents in crude oil fractions subjected to various treatments. It demonstrates the variation in metal concentration across the fractions, providing insight into the effectiveness of each treatment in reducing nickel content.

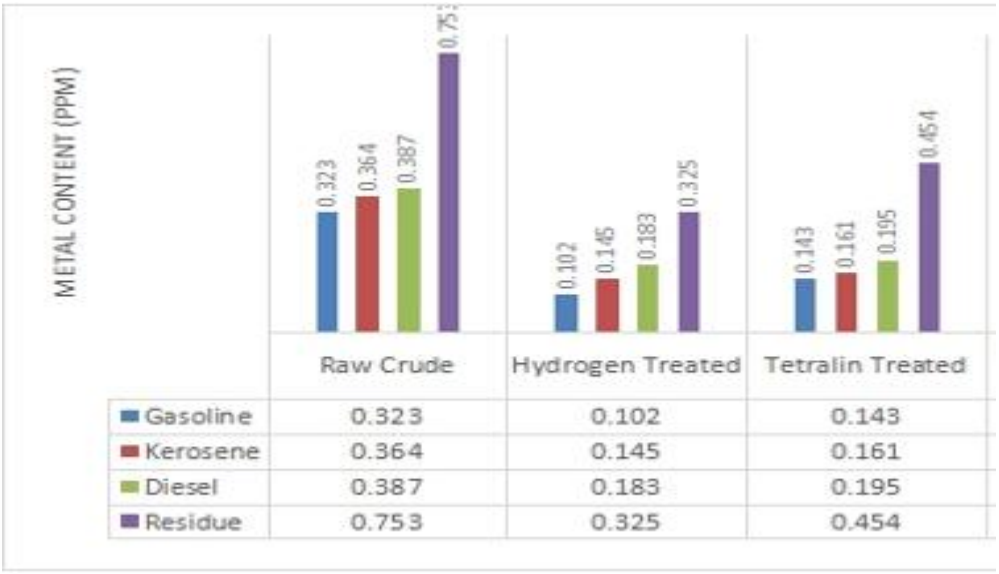


Figure 7: Comparison of metal (nickel) content in crude oil fractions across different treatments

From the figure, it can be noticed that hydrogen treatment is highly effective in reducing nickel (metal) content across all fractions, particularly in the heavier Residue fraction, where metal contamination is more pronounced. For the gasoline fraction, nickel content decreases from 0.323 ppm in raw crude to 0.102 ppm after hydrogen treatment. In the kerosene fraction, the content drops from 0.364 ppm to 0.145 ppm. Diesel undergoes a reduction in nickel from 0.385 ppm to 0.183 ppm with hydrogen treatment. The most dramatic reduction occurs in the residue fraction, where nickel content falls from 0.753 ppm in raw crude to 0.325 ppm post-treatment. Tetralin-based treatment shows less reduction in nickel content. In the residue fraction, Tetralin reduces nickel to 0.454 ppm. These values indicate that hydrogen treatment is the most effective in decreasing metal (nickel) content across various crude oil fractions, supporting its application in refining processes focused on metal impurity removal.

Comparison of physicochemical properties of crude oil fractions across different treatments

Table 8 provides a detailed comparison of the physicochemical properties of crude oil fractions under various treatment methods. The table highlights key parameters such as density, specific gravity, flash point, flame height, and diesel index, illustrating the impact of treatments like hydrogenation, tetralin, and formic acid on the quality and performance of the fractions. This analysis is essential for evaluating the efficiency and effectiveness of different refining processes.

The treatment methods applied to crude oil fractions significantly influence their physicochemical properties, including density, specific gravity, flash point, flame height, and diesel index. Generally, hydrogen treatment results in the lowest densities and specific gravities across the fractions, likely due to the reduction of heavier components. Flash points decrease slightly with treatment, particularly for lighter fractions like gasoline and kerosene, enhancing their volatility and making them more suitable for applications requiring quicker combustion.

Table 8: Comparison of Physicochemical Properties in Crude Oil Fractions across Different Treatments

S/N	DISTILLATION FRACTION	TREATMENT METHOD	DENSITY (g/cm^3)	SPECIFIC GRAVITY	FLASH POINT (^OC)	FLAME HEIGHT (cm)	DIESEL INDEX	RON Clear	MON Clear
1	GASOLINE	Raw Crude	0.781	0.756	68	--	--	77.8	72.5
		Hydrogen Treated	0.720	0.701	60	--	--	92.5	86.2
		Tetralin Treated	0.741	0.708	62	--	--	87.3	80.1
2	KEROSENE	Raw Crude	0.820	0.784	80	6.5	--		
		Hydrogen Treated	0.765	0.732	75	8	--		
		Tetralin Treated	0.775	0.741	74	7.6	--		
3	DIESEL	Raw Crude	0.877	0.839	110		34.92		
		Hydrogen Treated	0.805	0.784	100		44.97		
		Tetralin Treated	0.835	0.799	105		42.85		
4	RESIDUE	Raw Crude	1.40	1.25	205		--		
		Hydrogen Treated	1.06	1.01	195		--		
		Tetralin Treated	1.15	1.10	197		--		

For diesel, hydrogen treatment improves the diesel index, indicating better fuel quality. The residue fraction, with the highest density, specific gravity, and flash point, remains relatively unaffected in terms of volatility, maintaining its stability and suitability for heavy-duty applications.

In summary, the treatment methods allow for customization of fuel properties to meet specific industrial needs, with hydrogen treatment generally enhancing fuel quality, particularly in diesel, by reducing heavier hydrocarbon content.

Conventional Method of Hydrotreating

The conventional method of hydrotreating involves processing crude oil fractions, such as gasoline, kerosene, and diesel, in separate hydrotreating reactors to remove impurities like sulphur, nitrogen, and metals. This method ensures the production of cleaner fuels that meet environmental standards and enhance performance. Tables 9 and 10 provide detailed data on the operational parameters and outcomes of this method.

Table 9 presents the conventional hydrotreating process with hydrogen gas, outlining key operating conditions and analyzing impurity levels in hydrotreated crude oil fractions, including gasoline, kerosene, diesel, and residue.

Table 9: Conventional Hydrotreating Method Using Hydrogen Gas

Hydrotreating Temperature (°C)		350 – 400			
Hydrogen Partial Pressure		10bar			
Liquid Hourly Space Velocity		$1.2h^{-1}$			
S/N	**PARAMETER**	**FRACTIONS**			
		Gasoline	**Kerosene**	**Diesel**	**Residue**
1	Sulphur Content (wt. %)	0.0064	0.0150	0.042	0.055
2	Nitrogen Content (wt. %)	0.015	0.016	0.021	0.034
3	Metal content (Nickel)	0.163	0.189	0.198	0.503
4	Octane No. (RON Clear)	88.3			
	Octane No. (MON Clear)	82.6			
5	Density ($g/cm^{3)}$	0.749	0.780	0.838	1.19
6	Specific Gravity	0.717	0.746	0.802	1.139
7	Flash Point(oC)	62	75	107	200
8	Flame Height (cm)		7		
9	Diesel Index			40	

Table 10 provides an overview of the tetralin conventional hydrotreating process, emphasizing key operational parameters and assessing impurity levels in crude oil fractions—gasoline, kerosene, diesel, and residue—to evaluate its overall efficiency.

Table 10: Conventional Hydrotreating Method Using Tetralin

Hydrotreating Temperature (°C)			350 – 400		
Hydrogen Partial Pressure			10bar		
Liquid Hourly Space Velocity			$1.2h^{-1}$		
S/N	**PARAMETER**	**FRACTIONS**			
		Gasoline	**Kerosene**	**Diesel**	**Residue**
1	Sulphur Content (wt. %)	0.0070	0.0210	0.055	0.068
2	Nitrogen Content (wt. %)	0.017	0.019	0.025	0.040
3	Metal content (Nickel)	0.169	0.196	0.221	0.592
4	Octane No. (RON Clear)	85.6			
	Octane No. (MON Clear)	78.6			
5	Density ($g/cm^{3)}$	0.754	0.789	0.853	1.230
6	Specific Gravity	0.722	0.751	0.818	1.182
7	Flash Point(oC)	63	77	107	205
8	Flame Height (cm)		7		
9	Diesel Index			39.24	

Comparative Analysis of Impurity Concentrations of the Novel Method with Conventional

The comparative analysis of impurity concentrations between the novel method and the conventional method evaluates their efficiency in reducing sulfur, nitrogen, and metal content in crude oil fractions. This comparison highlights the advantages of the novel method in achieving lower impurity levels, demonstrating its potential as a more effective and sustainable alternative to conventional hydrotreating processes. The results are depicted in Figures 8 – 13.

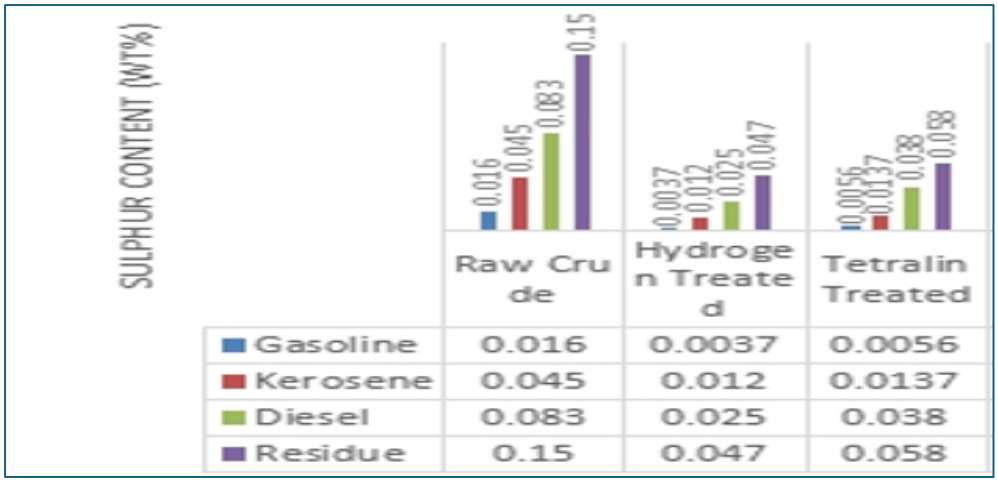


Figure 8: Sulfur content of fractions using the novel method

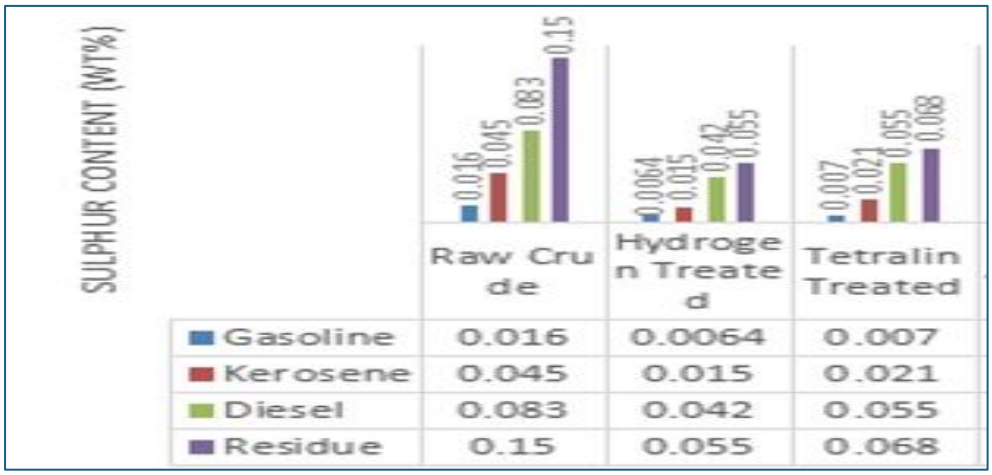


Figure 9: Sulfur content of fractions using the conventional method

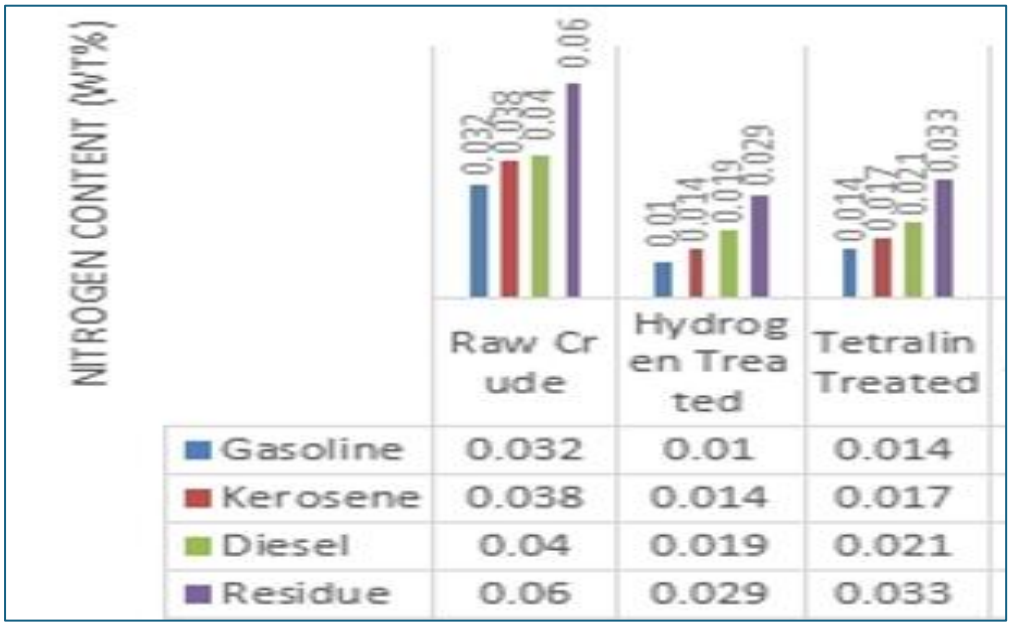
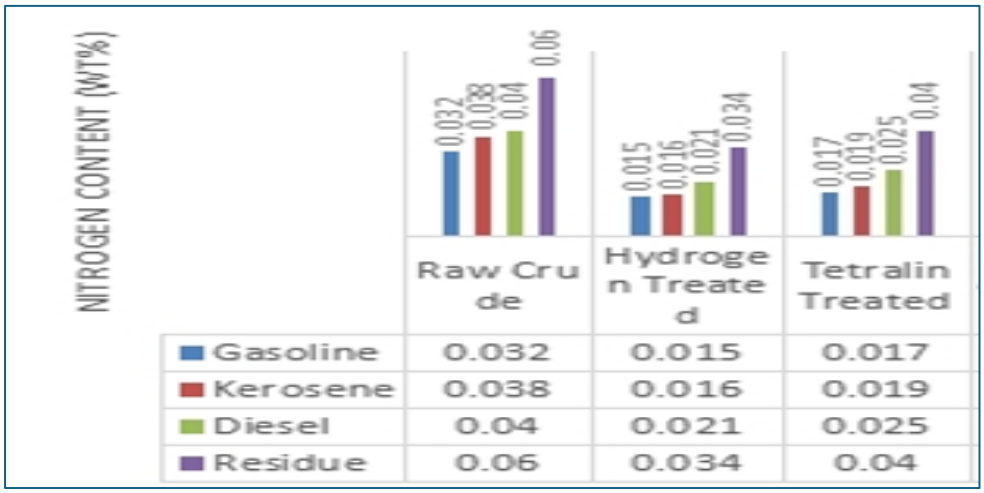
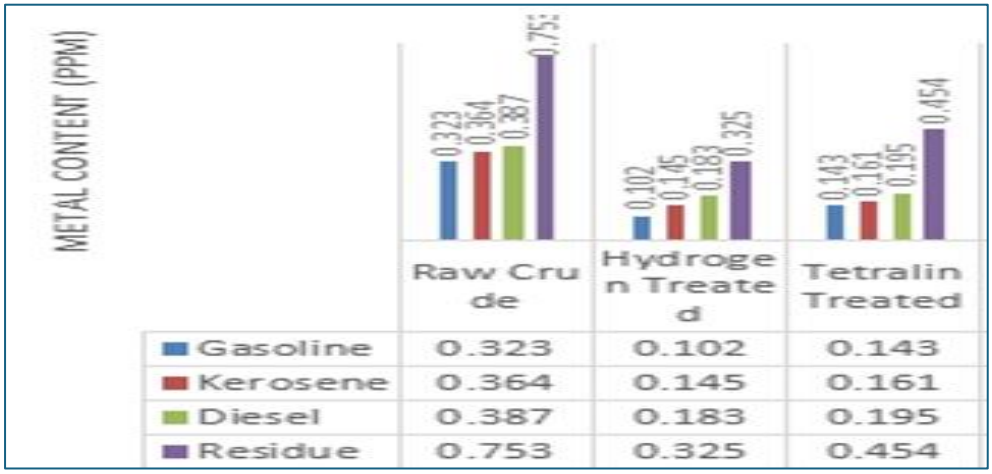


Figure 10. Nitrogen content of fractions using the novel method



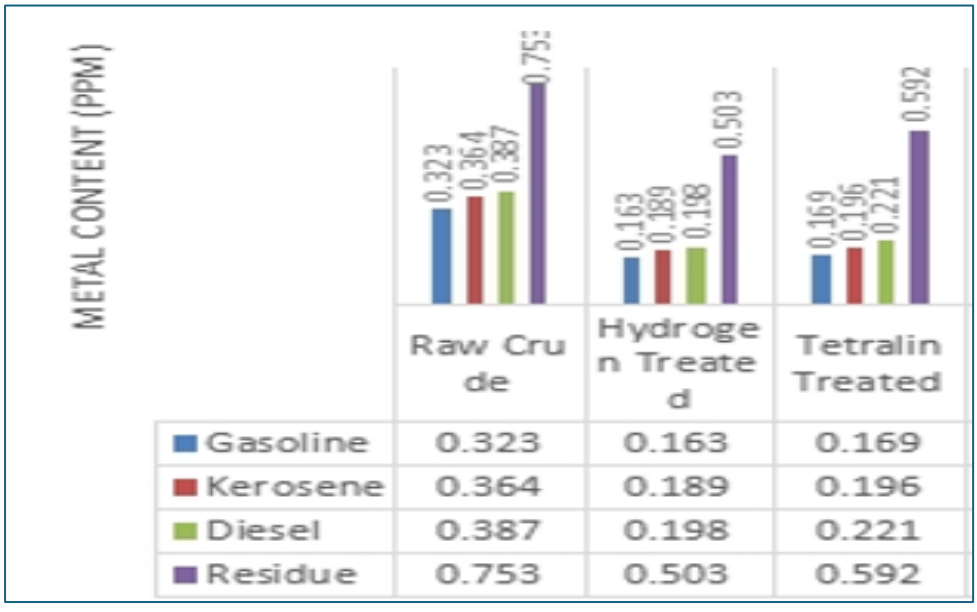
	Raw Crude	Hydrogen Treated	Tetralin Treated
Gasoline	0.032	0.015	0.017
Kerosene	0.038	0.016	0.019
Diesel	0.04	0.021	0.025
Residue	0.06	0.034	0.04

Figure 11. Nitrogen content of fractions using the conventional method



	Raw Crude	Hydrogen Treated	Tetralin Treated
Gasoline	0.323	0.102	0.143
Kerosene	0.364	0.145	0.161
Diesel	0.387	0.183	0.195
Residue	0.753	0.325	0.454

Figure 12. Metal (Ni) content of fractions using the novel method



	Raw Crude	Hydrogen Treated	Tetralin Treated
Gasoline	0.323	0.163	0.169
Kerosene	0.364	0.189	0.196
Diesel	0.387	0.198	0.221
Residue	0.753	0.503	0.592

Figure 13. Metal (Ni) content of fractions using the conventional method

The analysis of the bar charts above highlights the effectiveness of different treatment methods in reducing sulphur, nitrogen, and metal content across various fractions (gasoline, kerosene, diesel, and residue) of crude oil. Comparing the novel and conventional methods, it's evident that the novel method generally achieves a more substantial reduction in both sulphur, nitrogen, and metal content for each fraction, with hydrogen treatment being the most effective across both methods. The results for each fraction show consistent patterns in the impurity levels, but the degree of reduction varies by treatment type and method.

Sulfur Content

For sulphur content, the novel method demonstrates significant improvements, particularly with hydrogen treatment. For gasoline, the sulphur level drops from an initial value of 0.016 wt.% in raw crude to 0.0037 wt.% after hydrogen treatment under the novel method. This contrasts with a reduction to only 0.0064 wt.% in the conventional method. Similarly, kerosene sees its sulphur content reduced from 0.045 wt.% in raw crude to 0.012 wt.% with hydrogen treatment in the novel method, compared to 0.015 wt.% with the conventional method. Diesel, initially at 0.083 wt.%, shows a marked reduction to 0.025 wt.% with hydrogen treatment in the novel method, while the conventional method achieves a reduction to 0.042 wt.%. Lastly, the residue fraction has the highest initial sulphur content at 0.15 wt.%, and the novel method reduces this to 0.047 wt.% with hydrogen treatment, whereas the conventional method only achieves a reduction to 0.055 wt.%.

The results indicate that hydrogen treatment under the novel method is the most effective in reducing sulphur levels across all fractions. The tetralin treatment also reduces sulfur, but its effectiveness is comparatively lower. For instance, in gasoline, the sulphur content drops to 0.0056 wt.% with tetralin in the novel method. This value, while improved, does not match the level of reduction achieved by hydrogen treatment. Across all fractions, the conventional method generally yields higher sulphur levels than the novel method, suggesting that the novel method may provide a superior approach for sulphur reduction.

Nitrogen Content

A similar trend is observed in nitrogen content reduction, where the novel method, especially with hydrogen treatment, yields better results than the conventional method. In gasoline, nitrogen content decreases from 0.032 wt.% in raw crude to 0.010 wt.% with hydrogen treatment using the novel method, whereas the conventional method reduces it to 0.015 wt.%. %. In kerosene, nitrogen content falls from 0.038 wt.% to 0.014 wt.%. with hydrogen treatment in the novel method, as opposed to 0.016 wt.% in the conventional method. The diesel's nitrogen level, initially at 0.040 wt.%, drops to 0.019 wt.% with the novel method and hydrogen treatment, while the conventional method reduces it to 0.021 wt.%. %. For the residue fraction, which starts with a nitrogen content of 0.060 wt.%, the novel method lowers it to 0.029 wt.% through hydrogen treatment, whereas the conventional method only achieves a reduction to 0.034 wt.%.

Once again, hydrogen treatment within the novel method demonstrates superior efficacy in reducing nitrogen content across all fractions. Tetralin and formic acid treatments, while also

effective, result in higher nitrogen content compared to hydrogen treatment. For instance, in gasoline, nitrogen levels after tetralin and formic acid treatments are 0.014% and 0.018%, respectively, with the novel method. Despite these improvements, they still fall short of the reduction achieved by hydrogen treatment.

Metal Content

In terms of metal (nickel) content, the novel method achieves a 68% reduction using hydrogen gas compared to the conventional method, which achieves only a 50% reduction. Tetralin-treated achieves a 55% metal reduction compared to the conventional method, which is 47%. Meanwhile, the conventional method achieves a 43% reduction, resulting in an 11% higher efficiency in metal removal using the novel method.

The novel method is more efficient in reducing nickel content across all fractions, notably in the heavier fractions, thereby improving the feedstock quality for downstream processing.

Conclusion

From the findings of this research work, the following conclusions are drawn:

1. Physicochemical properties of the raw crude oil were altered, resulting in an increase in its refining value.
2. Hydrotreatment of the crude oil prior to its distillation led to an increase in the yield of light and middle distillates, with a corresponding decrease in atmospheric residues. Gasoline, kerosene, and diesel fractions were 18–18.6 wt%, 26.3–27 wt%, and 36.3–37 wt%, respectively. Pure hydrogen-based crude oil hydrotreatment yielded more distillates compared to the tetralin-based process.
3. Contents of impurities such as sulphur, nitrogen, and nickel in the distillates were significantly decreased after direct crude oil hydrotreatment.
4. Utilization of pure hydrogen appeared to be more effective in impurity removal. However, tetralin can be considered an alternative hydrogen supplier because it is safer to handle and is more environmentally friendly.