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Advanced Analytical Techniques for Comprehensive Characterization of Vacuum Residue Oil (VRO): A State-of-the-Art Review

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ABSTRACT:

The characterization of vacuum residue oil (VRO) presents substantial challenges due to its complex and diverse composition, including a wide range of heavy hydrocarbons and high molecular weight compounds. Existing literature has extensively documented various advanced analytical techniques for assessing VRO, yet the complexity of this material continues to pose difficulties in fully understanding its properties and optimizing its industrial applications. This review builds on prior research by providing a comprehensive overview of the latest characterization methods, categorizing them into three primary areas: physical and chemical bulk property analysis, saturates, aromatics, resins, and asphaltenes (SARA) fractionation, and molecular modeling approaches. The report highlights global standards and variations in VRO properties, with particular focus on the intricate correlations between physical properties such as refractive index and density, and the molecular weight of specific fractions. By compiling and synthesizing these advancements, this review not only underscores the significant diversity within VROs but also clarifies the crucial role of advanced techniques, such as FTIR, NMR spectroscopy, and chromatographic methods, in enhancing our understanding and optimizing the processing of VROs in industrial applications. The insights provided here aim to bridge the gap between existing characterization methods and their practical application in optimizing conversion processes in commercial residual oil units.

1. Introduction

Vacuum residue oil (VRO) is a byproduct of the vacuum distillation process in petroleum refining. Its complex composition, characterized by a high boiling point and substantial viscosity, makes it an essential feedstock in various industrial applications [1,2]. VRO is indispensable in producing heavy fuel oil (HFO), asphalt, bitumen, and lubricants, and serves as a base material for creating solvents, detergents, and specialty chemicals [41]. Understanding and optimizing the use of VRO is crucial for the transportation, construction, manufacturing, and chemical sectors, highlighting the need for advanced characterization techniques to exploit its potential fully shown in (refer Fig 1.) VRO is composed of a myriad of hydrocarbons and non-hydrocarbons, including resins, asphaltenes, and a variety of aromatic compounds [4]. This complexity presents significant challenges in its analysis and utilization. The detailed characterization of VRO involves understanding its physical and chemical properties, the distribution of its molecular components, and the effects of various extraction and processing conditions on its composition [36].

Traditional methods of analyzing VRO, while useful, often fall short in providing comprehensive insights into its intricate structure. Consequently, sophisticated analytical methods have been created and improved to provide a more thorough and precise characterization. These methods include SARA (Saturates, Aromatics, Resins, and Asphaltenes) analysis molecular modeling, and a range of sophisticated spectroscopic and chromatographic techniques [123]. SARA analysis is a cornerstone for characterizing VRO [5,37]. It fractionates the oil into four main components: saturates, aromatics, resins, and asphaltenes [28,6]. This segregation allows for a clearer understanding of the oil's composition, facilitating targeted applications and processing methods. By determining the proportions of these fractions, researchers can predict the behavior of VRO in different industrial processes and improve the efficiency of its conversion into valuable products [38]. Molecular modeling procedures simulate the activity of VRO at the molecular level, providing an alternative

method to empirical investigation. These simulations can forecast VRO's behavior in a variety of scenarios, offering challenging insights to obtain through experimental methods alone. Molecular modeling is particularly useful in optimizing the refining process, enhancing the quality of the final products, and reducing the environmental impact of VRO utilization. To fully understand the molecular structure of VRO, spectroscopic techniques like GCMS, FTIR NMR are essential [2]. NMR spectroscopy provides detailed information on the hydrogen and carbon frameworks of VRO molecules, providing information about the different kinds of chemical bonds and atom arrangements [96]. On the other hand, functional groups in the oil can be found using FTIR spectroscopy, which helps to determine the chemical makeup of the oil. The accurate examination of the volatile components of VRO is made possible by GCMS, which combines the identification power of mass spectrometry with the separation capabilities of gas chromatography. Chromatographic methods are necessary for a thorough examination of VRO. TLC-FID is effective for confirming the purity of the oil and detecting impurities that might affect its performance [37]. GPC is employed for molecular weight analysis, providing insights into the size distribution of the oil’s molecular components. Because it has a major influence on the oil's overall characteristics, the characterisation of the heavy oil aromatic portion within VRO is particularly important [15,123]. PAHs are isolated and quantified using methods like HPLC, which are crucial in determining the reactivity and stability of VRO [85]. Molecular fragmentation analysis and API-Mass Spectra Examination further aid in identifying the specific aromatic compounds present, enabling more precise control over the refining process.

The composition of VRO is also influenced by enhanced oil recovery (EOR) techniques, which are used to extract more oil from reservoirs. The application of thermal, chemical, and gas injection methods alters the molecular structure and properties of the oil [91]. Understanding these changes is essential for optimizing the refining process and improving the quality of the end products. This review explores the impact of various EOR techniques on VRO composition, providing insights into the evolving nature of this complex feedstock.

This review aims to deliver an in-depth analysis of advanced techniques employed in VRO characterization, emphasizing their critical role in enhancing the understanding and optimization of VRO applications across diverse industrial sectors. This review aims to provide guidance for future research and development efforts in the field of VRO analysis by analyzing the advantages and disadvantages of each method. The integration of traditional and advanced analytical techniques promises to enhance the efficiency and sustainability of VRO processing, contributing to the development of higher-quality and more environmentally friendly products.

At the atomic level, NMR spectroscopy is a potent method for clarifying the structural specifics of VRO. NMR provides information on the hydrogen and carbon environments within the oil, enabling the identification of various functional groups and the types of chemical bonds present [97]. This technique is particularly useful in distinguishing between different types of hydrocarbons, such as alkanes, alkenes, and aromatics, and in detecting heteroatoms like sulfur, nitrogen, and oxygen. To determine the functional groups in VRO, FTIR spectroscopy is frequently utilized. By measuring the absorption of infrared light at different wavelengths, FTIR provides a fingerprint of the molecular vibrations within the oil. This information is critical for understanding the chemical composition of VRO and for identifying specific compounds that contribute to its overall properties. FTIR is especially useful for detecting polar compounds and heteroatomic species, which are often present in significant quantities in VRO. GCMS is a combination of mass spectrometry's identifying power and gas chromatography's separation capability. This method works very well for examining the volatile parts of VRO and precise yield details about the molecular weight and structure of each individual chemical. GCMS is invaluable for identifying trace components and impurities that can affect the performance and quality of VRO-derived products. The high sensitivity and specificity of GCMS make it a cornerstone technique for VRO analysis. A chromatographic method called TLC-FID is used to evaluate the purity of VRO and find contaminants. According to their affinity for the stationary and mobile phases, TLC divides the components of VRO, whereas FID provides quantitative detection of the separated components. This technique is

particularly useful for monitoring the refining process and ensuring the consistency and quality of VRO-derived products.

The molecular weight study of VRO is performed using GPC. GPC offers a distribution profile of the molecular weights within the oil by sorting molecules according to their size. This information is critical for understanding the rheological properties of VRO and for optimizing its processing and utilization. GPC is especially useful for characterizing high-molecular-weight fractions, such as asphaltenes, which significantly influence the viscosity and stability of VRO [35].

HPLC isolates and quantifies specific components within VRO, such as PAHs. HPLC offers high resolution and sensitivity, allowing for the precise identification and quantification of aromatic compounds. This technique is crucial for assessing the quality and reactivity of VRO, because PAHs have a big influence on how the oil behaves when it's processed and used.

The utilization of enhanced oil recovery techniques aims to optimize oil extraction from depleted oil reservoirs [92]. These techniques, including thermal, chemical, and gas injection methods, significantly impact the composition and properties of VRO. Understanding the changes induced by EOR is essential for optimizing the refining process and improving the quality of the end products. This review examines the effects of various EOR techniques on VRO composition, providing insights into the evolving nature of this complex feedstock.

Thermal EOR techniques, such as steam injection and in-situ combustion, increases the temperature of the reservoir to reduce the viscosity of the oil and enhances its flow. These methods can alter the molecular structure of VRO, leading to the formation of lighter fractions and the degradation of heavier components. Understanding these changes is crucial for optimizing the refining process and improving the quality of VRO-derived products.

Chemicals including polymers, alkalis, and surfactants are injected during chemical EOR procedures in order to increase the oil's displacement efficiency. The content and characteristics of VRO are changed by these chemicals' interactions with the oil and the reservoir rock. For instance, whereas polymers raise the viscosity of the injected water, surfactants can lower the interfacial tension between oil and water. To maximize the refining process and raise the caliber of the finished products, it is crucial to comprehend how these chemicals affect VRO. Gas injection EOR techniques, such as carbon dioxide (CO_2) injection, involve the injection of gases to increase the reservoir pressure and improve oil recovery. CO_2 injection, in particular, can significantly alter the composition of VRO by dissolving in the oil and reducing its viscosity. The interaction between CO_2 and VRO can lead to the formation of new compounds and the modification of existing ones. Understanding these changes is crucial for optimizing the refining process and improving the quality of VRO-derived products.

For specific characterizations such as NMR and FTIR, numerous studies highlight their efficacy in analyzing vacuum residue oil [46,43]. NMR spectroscopy is a powerful tool used to determine the molecular structure, composition, and chemical bonding in residual oils, providing detailed insights into the aromatic and aliphatic content as well as other functional groups. FTIR spectroscopy, on the other hand, offers a comprehensive characterization of the chemical composition and functional groups in VRO, enabling the identification of various chemical moieties including hydrocarbons, aromatics, aliphatics, and heteroatoms. These techniques collectively enhance the understanding of VRO's structural and functional properties, making them indispensable in the study and application of vacuum residue oils.

The characterization of vacuum residue oil is essential for optimizing its utilization across various industries. Advanced analytical techniques, including spectroscopic and chromatographic methods, provide detailed insights into the complex composition of VRO [16,120] combined with molecular modeling and SARA analysis, these techniques provide a thorough comprehension of the chemical and physical characteristics of VRO [49]. The application of enhanced oil recovery techniques further emphasizes the need for such advanced characterization methods. EOR processes can alter the composition of VRO, making it crucial to understand these changes to optimize recovery and processing strategies. By integrating traditional and advanced analytical techniques, researchers can improve the efficiency and sustainability of VRO processing, contributing to the development of higher-quality and more environmentally friendly products.

2. Methods for Characterization of Residual Oils

2.1 Characterization Techniques

The characterization of vacuum residue oil is essential for optimizing its utilization across various industries. Advanced analytical techniques provide detailed insights into the complex composition of VRO [121]. These techniques can be segregated into physical characterization and chemical property characterization methods to provide a systematic understandings shown in Fig 2 and discussed in Table 1.

2.1.1 Physical Characterization Techniques

SARA analysis is a cornerstone for characterizing VRO. It fractionates the oil into four main components, allowing for a clearer understanding of the oil's composition. This segregation shown in (refer Fig 5a, b, c) is essential for predicting the behavior of VRO in different industrial processes and improving the efficiency of its conversion into valuable products [49].

Molecular modelling procedures simulate the activity of VRO at the molecular level. These simulations can forecast VRO's behavior in a variety of scenarios, offering insights that are challenging to obtain through experimental methods alone. This technique helps in understanding the interactions and stability of various components within the VRO, leading to better process optimization [16].

The graph shown in Fig 5a, depicts the hydrocarbon composition of the sample, detailing the weight percentages of Saturates, Aromatics, Resins, and C7-asphaltenes. Saturates, comprising slightly over 90%wt, are the predominant fraction, indicating a sample with a high concentration of non-polar, saturated hydrocarbons. This high level of saturates suggests a material with enhanced stability and lower reactivity, which is favorable for applications requiring resistance to chemical breakdown. Aromatics, constituting approximately 60%wt, represent hydrocarbons containing one or more aromatic rings, known for their greater chemical reactivity and potential impact on the thermal and oxidative stability of the sample. Resins account for around 70%wt, reflecting the presence of heavier, polar molecules that can significantly influence the viscosity and surface properties of the material. Lastly, C7-asphaltenes make up about 40%wt of the sample, indicating a considerable portion of the heaviest and most complex molecules, which are often associated with challenges such as precipitation, fouling, and increased viscosity in petroleum-derived products. The composition suggests a complex interplay of stable and reactive hydrocarbon species, with implications for processing, handling, and end-use applications.

Graph 5b, presents the boiling point distribution of hydrocarbon fractions in the sample, highlighting a range from light naphtha to vacuum gas oil. The light naphtha fraction, boiling between 30°C and 100°C and composed of C5 to C7 hydrocarbons, represents the lightest and most volatile components, but it constitutes a relatively small portion of the sample. Moving up the boiling range, the heavy naphtha fraction, between 100°C and 180°C (C7 to C10), shows a significant increase in content, indicating a substantial presence of hydrocarbons suitable for gasoline production or petrochemical feedstock. The kerosene fraction, boiling between 180°C and 240°C (C11 to C14), reflects a moderate level of hydrocarbons commonly used in jet fuel, showcasing the sample's potential for aviation fuel production.

The diesel fraction, which boils between 240°C and 360°C and consists of C15 to C22 hydrocarbons, is the most prominent in the sample, indicating a high potential for diesel production. This suggests that the sample is rich in middle distillates, making it particularly valuable for producing diesel fuel. Finally, the vacuum gas oil fraction, boiling between 360°C and 540°C (C23 to C46), represents the heavier components of the sample. This fraction is crucial for further processing in catalytic cracking units to yield lighter, more valuable products such as gasoline and diesel. Overall, the distribution emphasizes the sample's suitability for refining processes aimed at maximizing the yield of diesel and other middle distillates.

The chart shown in 5c) illustrates the elemental composition of the sample in terms of weight percentage (%wt). Carbon is the dominant element, constituting 87%wt of the total composition, which is typical for hydrocarbon-based materials. This high carbon content indicates that the sample is primarily made up of organic compounds, contributing to its energy-rich nature.

Hydrogen is the second most abundant element, making up 14%wt of the sample. The carbon-to-hydrogen ratio suggests a structure rich in hydrocarbons, which are crucial for energy production and chemical processing. Sulfur is present at 9%wt, indicating a significant level of heteroatoms that may require removal during refining to meet environmental regulations and to prevent corrosion in processing equipment. Nitrogen and oxygen are present in smaller amounts, at 3%wt and 1.5%wt, respectively. These elements can impact the stability and reactivity of the sample, with nitrogen contributing to the formation of NOx emissions and oxygen potentially leading to oxidative instability.

2.1.2 Chemical Property Characterization Techniques

NMR spectroscopy is a powerful tool used to determine the molecular structure, composition, and chemical bonding in residual oils. It provides detailed information on the hydrogen and carbon frameworks of VRO molecules, revealing the different kinds of chemical bonds and atom arrangements. This technique is crucial for understanding the aromaticity, aliphaticity, and the presence of functional groups in heavy oils [10].

FTIR spectroscopy serves as a powerful tool for comprehensive characterization of the chemical composition and functional groups in VRO. It identifies and quantifies various chemical moieties, including hydrocarbons, aromatics, aliphatics, and heteroatoms (see Fig 5a, b, c). FTIR provides essential data on the functional groups present, such as carbonyl, hydroxyl, and sulfide groups, by offering a fingerprint of the molecular vibrations within the oil.

GC-MS combines the identification power of mass spectrometry with the separation capabilities of gas chromatography to analyze the volatile components of VRO. This technique is invaluable for identifying and quantifying the various hydrocarbons and other compounds present in the oil. It enhances the resolution and identification of complex mixtures in heavy oils, making it possible to detect sulfur compounds and polycyclic aromatic hydrocarbons [116].

The application of enhanced oil recovery techniques further emphasizes the need for such advanced characterization methods. EOR processes can alter the composition of VRO, making it crucial to understand these changes to optimize recovery and processing strategies. By integrating traditional and advanced analytical techniques, researchers can improve the efficiency and sustainability of VRO processing, contributing to the development of higher-quality and more environmentally friendly products. This review highlights the significance of these methodologies in advancing VRO analysis and optimizing its utilization across various industrial applications.

2.2 SARA Analysis for Characterizing Residual Oils

SARA analysis is a fundamental technique employed to characterize the composition of crude and residual oils by separating them into four distinct fractions shown in Fig 3, Saturates, Aromatics, Resins, and Asphaltenes [52]. This method capitalizes on the differences in the polarizability and polarity of the oil components, enabling a detailed understanding of the oil's makeup, which is crucial for refining processes and predicting the behavior of oils in various applications [7]. The primary techniques for performing TLC, HPLC, and gravity-driven chromatographic separation are examples of SARA analytical techniques. Every approach has unique benefits and drawbacks that may influence the outcomes and how they are interpreted.

[53] complex mixture of hydrocarbon and non-hydrocarbon components that makes up residue oil has a boiling point range of about 760°C (for methane) and carbon numbers varying from 1 to over 100 atoms. [30,12] The final boiling temperatures of several types of residual oil have been observed to vary between 1000 and 2000°C using TBP distribution models. The number of acyclic alkane isomers that are feasible is about 36.7 million at a carbon atom number of 25 (boiling point = 402°C), and 5920 trillion at a carbon atom number of 100 (boiling point = 708°C). Although the precise count of constituents in a leftover oil mixture is uncertain, it is likely to surpass one million. For instance, just 5% of the components in the heaviest proportion of oil—vacuum residue—that boils at 540°C are known, and the other 95% are still unknown. The analysis of this intricate mixture poses considerable difficulties for experts in the petrochemical and refining sectors.

The complex combination is divided into fractions according to their chemical similarities in order to make the chemical characterization and comprehension of leftover oil easier. Using a variety of solvents, eluents, and adsorbents, this separation into saturates, aromatics, resins, and asphaltenes (SARA) is based on the polarity of these fractions. [39,17]. Using n-heptane or n-pentane, the asphaltenes are precipitated from the oil mixture as the initial stage in the SARA fractionation process. [28,17] After the leftover oil combination has been de-asphalted, techniques like ASTM D2007, ASTM D4124, high-performance liquid chromatography (HPLC), or thin-layer chromatography with flame ionization detection (TLC-FID; IATROSCAN) can be used to check for saturates, aromatics, and resinous fractions [54].

Due to variances in the methodologies, the type of eluent, and the molecular weight of the solvents, which have a substantial impact on the relative proportions of each fraction, there have been documented considerable disparities between SARA results obtained by ASTM, HPLC, or TLC-FID procedures. [8] have predicted different qualities of residual oil, coke production, asphaltene stability, and other characteristics using the SARA composition results [19,29]. Many equations of state rely on the group hydrocarbon composition of residue oil as input data, and thermodynamic models that forecast sediment formation during residue oil extraction and refining are built upon this foundation [73]. Furthermore, the group hydrocarbon makeup of the feedstock used in different conversion processes to produce lighter, higher-value products offers important insights on how these processes work.

Consequently, there is a great deal of practical interest in researching techniques for determining the SARA composition of residual oil and its derivatives. Comparisons are difficult since different researchers analyze the SARA composition of residual oil and its byproducts using different analytical methodologies. The group hydrocarbon composition of extra light, light, medium, heavy, and extra heavy residue oil types, oil sands, and natural bitumen obtained using various techniques is covered in this review, which compiles a substantial body of data published in the literature [87]. It investigates the connections between SARA composition, residue oil's physicochemical characteristics, and several indicators that describe how residue oil behaves during extraction and refining. In this study, SARA composition in 308 residue oil samples that represented the following categories: extra light (specific gravity (SG) < 0.8017), light (0.8017 < SG < 0.855), medium (0.8600 < SG < 0.9220), heavy (0.9220 < SG < 1.000), and ultra-heavy (SG > 1.000). The specific gravity, aromatic structure content (which is the total of all fractions containing aromatic carbon, such as aromatics, resins, and asphaltenes), and group composition data (SARA) of the 308 residue oil samples are summarized in (refer Table 2) [20,65]. The percentage distribution of the five methodologies utilized for the SARA analysis of residue oil composition for a database including 308 residue oils from published sources.

According to the data cited, the HPLC method is the one that is most frequently used for SARA residue oil composition analysis. It has been used to analyze the group hydrocarbon composition of oil sands and natural bitumens, as well as extra light, light, medium, heavy, and extra heavy residue oil types [40,41]. The ASTM D2007 method, which applies to all types of residual oil, is the second most used approach. The liquid chromatography approach comes next and has also been employed to ascertain the SARA composition of each residual oil group. In terms of SARA technique application, TLC-FID (Iatroscan) comes in fourth place [54]. It has been used to analyze light, medium, and heavy residue oil types using SARA. The modified ASTM D4124 method, which has also been utilized for SARA analysis of light, medium, and heavy grades of residual oil, is the least applied in terms of applicability.

Gravity-Driven Chromatographic Separation:

This traditional method, often guided by ASTM D2007, utilizes large sample volumes and significant quantities of solvents. The process involves sequential adsorption on clay and silica columns to fractionate the oil into its SARA components. During this process, the oil sample is first treated to precipitate asphaltenes, which are then filtered and weighed [26]. The remaining maltenes are subjected to further separation on adsorption columns. However, a major limitation of this method is the potential loss of volatile materials during the separation, which can lead to inaccuracies in the final composition analysis. This method is labor-intensive and time-consuming, but it remains widely used due to its established protocol and ability to handle large sample sizes.

Thin Layer Chromatography (TLC):

Compared to gravity-driven techniques, TLC with flame ionization detection (TLC-FID) offers a quicker and less solvent-intensive solution [55]. This method uses quartz rods coated with silica for separation; the separated fractions are then detected and quantified using flame ionization. To characterize AR maltene and its MPLC fractions, MK-6S (Misthuibish, Japan) and silica chromarods (Misthuibish, Japan) were employed. To guarantee data repeatability, several silica rods were examined concurrently. Initially, methylene chloride was used to dilute each MPLC phase and AR maltene. A small volume of each diluted sample was then spotted onto the TLC silica rods for analysis. After a brief drying period for the dilution solvents, hexane was eluted to a specified distance and dried to remove residual solvent. Subsequently, toluene was eluted to a shorter distance and dried. Finally, methylene chloride with a small percentage of methanol was eluted to an even shorter distance and dried for a brief period.

High-Pressure Liquid Chromatography (HPLC):

HPLC stands out for its ability to provide faster and more reproducible results compared to traditional chromatographic methods shown in Fig 4. Utilizing NH_2^- bonded columns, HPLC effectively separates the oil components without the need for prior removal of asphaltenes. This method minimizes the loss of volatile materials, ensuring more accurate quantification of the fractions. HPLC's precision and efficiency make it particularly useful for detailed compositional analysis and research applications where high accuracy is required. Its reproducibility and reduced solvent usage further enhance its appeal for modern analytical laboratories.

The SARA study of three distinct crude oil types is shown in Fig 4 utilizing ASTM, HPLC, and TLC-FID analytical techniques. The proportion of volatiles, saturates, aromatics, resins, and asphaltenes varies significantly amongst the crude oil samples according to each method. [10,7] For A-95 crude oil, the ASTM method indicates a high saturate content of approximately 60 wt%, with low volatile content around 10 wt%, and minimal amounts of aromatics, resins, and asphaltenes. The HPLC method, however, shows a more balanced profile with moderate volatiles at about 25 wt% and saturates at roughly 35 wt%, while the amounts of aromatics and resins remain low. The TLC-FID method reveals a significantly higher volatile content of about 50 wt%, with moderate saturates around 20 wt% and similarly low levels of aromatics, resins, and asphaltenes. C-LH-99 crude oil follows a similar trend. The ASTM method reports high saturates (~55 wt%) and low volatiles (~15 wt%), with minimal aromatics and resins. HPLC results show increased volatiles (~30 wt%) and reduced saturates (~25 wt%). TLC-FID indicates high volatiles (~45 wt%) and moderate saturates (~25 wt%). C-R-00 crude oil demonstrates substantial variation among methods [54]. ASTM shows high saturates (~60 wt%), low volatiles (~15 wt%), and negligible aromatics and resins. HPLC and TLC-FID methods reveal moderate volatiles and saturates (~35 wt% and ~25 wt%, respectively) [55].

S-Ven-39 crude oil exhibits high saturates (~50 wt%) and low volatiles (~20 wt%) according to ASTM. HPLC and TLC-FID indicate increased volatiles (~35 wt%) and moderate saturates (~30 wt%). [55] SQ-95 crude oil shows high saturates (~55 wt%) and low volatiles (~20 wt%) with ASTM. HPLC and TLC-FID reveal higher volatiles (~40 wt%) and moderate saturates (~25 wt%). Tensleep-99 crude oil follows the trend of high saturates (~60 wt%) and low volatiles (~15 wt%) with ASTM. HPLC and TLC-FID show moderate volatiles (~30 wt%) and saturates (~25 wt%).

2.3 Advanced Analytical Techniques for Residual Oil Characterization

Advanced analytical techniques have catalyzed a paradigm shift in residual oil characterization, transcending the limitations of conventional methodologies. Amidst the vast array of traditional approaches, HRMS has emerged as a transformative force, similar to mass spectrometry and gas chromatography. HRMS's capacity for accurate mass measurement facilitates the discernment of intricate molecular structures within residual oil matrices, offering unparalleled resolution and sensitivity. In addition, two-dimensional gas chromatography (2D-GC) has become a powerful instrument for deciphering residual oil compositions. By its comprehensive separation capabilities, 2D-GC enables the dissection of highly intricate mixtures, surpassing the limitations of conventional GC techniques. Complementing these advancements, NMR stands out for its non-destructive probing of molecular architectures and functional groups present in residual oils [46,56]. Leveraging the inherent magnetic properties of nuclei, NMR affords unprecedented insights into the chemical bonding and composition of residual oil constituents [22,23]. Pyrolysis gas chromatography-mass spectrometry (Py-GC/MS), on the other hand, provides a unique thermal decomposition-based method, facilitating the identification and characterization of biomarkers and heteroatoms within residual oil samples [66]. These advanced techniques find versatile applications across diverse sectors, including petroleum refining, environmental monitoring, and biofuel production [79,88]. Their integration not only enhances process efficiency and product quality but also fosters strides towards environmental sustainability. As the trajectory of analytical innovation continues unabated, ongoing advancements in instrumentation and interdisciplinary collaborations hold the promise of further revolutionizing residual oil characterization, driving the frontiers of knowledge in this critical domain.

UV-Visible Spectroscopy (UV-VIS) is used for structural analysis, identifying asphaltenes, mono- and bicyclic hydrocarbons, and metal binding within the oil [67]. Infrared Spectroscopy (IR) focuses on molecular characterization, assessing the degree of aromaticity, identifying hydrocarbon compounds, and dividing the oil into SARA fractions. It also measures API gravity, viscosity, density, and sulfur speciation. Oil shale and additives, asphaltenes, hydrocarbon chemicals, and molecular vibrations can all be examined using GC-MS. Molecular vibrations, the structural state of carbon in bitumen and kerogens, distillation fractions, mono- and bicyclic hydrocarbons, and asphaltene dimensions are all examined using TLC-FID. Viscosity, asphaltenes, hydrocarbon compounds, soluble fractions, molecular structures, and atom counts can all be precisely determined using NMR. Together, these methods provide a thorough characterization of crude oils, aiding in their analysis and processing.

HRMS is an analytical technique that provides accurate mass measurement of ions, which is essential for identifying complex molecular structures and characterizing trace components in residual oils. This high level of precision allows for the detailed analysis of minute constituents within a sample. 2D-GC offers comprehensive separation of components, making it highly effective for resolving complex mixtures in residual oils. Its enhanced peak capacity facilitates a more detailed analysis compared to traditional gas chromatography, allowing for the identification of individual compounds within a complex matrix. NMR detects NMR signals from nuclei, enabling the determination of molecular structure, composition, and chemical bonding in residual oils [46]. The process of pyrolysis Py-GC/MS, or gas chromatography mass spectrometry, uses heat to break down samples in order to identify biomarkers, heteroatoms, and important constituents in leftover oils [50] as discussed in Table 3. By breaking down the sample into smaller fragments, Py-GC/MS can reveal detailed information about the chemical makeup and origins of the oil components, making it a powerful tool for oil analysis. Together, these techniques offer a comprehensive suite of methods for the detailed analysis and characterization of residual oils, providing insights into their composition, structure, and chemical properties.

2.4 Residual Oil Characterization through Molecular Modelling Processes

Residual oil characterization via molecular modeling processes represents a sophisticated approach leveraging computational techniques to elucidate the structural and chemical properties of residual oil components. Molecular modeling methods encompass a diverse array of computational tools, comprising molecular dynamics (MD), quantum mechanics (QM), and molecular mechanics (MM), each of which provides a different perspective on the behavior and interactions of molecules inside residual oil matrix. Techniques rooted in quantum mechanics, like density functional theory (DFT) and ab initio computations, provide precise electronic structure and energetics prediction shedding light on the molecular-level mechanisms underlying various chemical processes within residual oils [71]. Molecular mechanics approaches, on the other hand, employ simplified empirical force fields to simulate the conformations and interactions of complex molecular assemblies, facilitating the exploration of conformational landscapes and intermolecular forces governing residual oil behavior. Molecular dynamics simulations further augment these capabilities by providing a dynamic perspective on molecular motion and kinetics, enabling the study of phenomena such as diffusion, phase transitions, and reaction pathways in residual oil systems

[3]. The integration of molecular modeling techniques with experimental data, such as spectroscopic analyses and chromatographic profiles, allows for the refinement and validation of computational models, enhancing their predictive accuracy and reliability. Through the synergy of computational and experimental approaches, molecular modeling processes play a pivotal role in advancing our understanding of residual oil composition, reactivity, and behavior, with profound implications for applications spanning petroleum refining, environmental remediation, and renewable energy production [50,88].

3. Investigating the Impact of Enhanced Oil Recovery (EOR) Techniques on Residual Oil Composition

Enhanced Oil Recovery methods significantly influences both the molecular and macroscopic properties of residual hydrocarbons in oil reservoirs [9,93]. This investigation evaluates the effects of various EOR techniques, including thermal methods like steam flooding and in-situ combustion. These reduce oil viscosity and cause thermal cracking of long-chain hydrocarbons into lighter fractions, potentially affecting asphaltene stability [73,79]. Chemical EOR techniques, such as polymer flooding, surfactant flooding, and alkaline flooding, involve injecting chemicals that improve oil mobility and alter the wettability of the reservoir rock, leading to changes in molecular composition, emulsification, and interfacial tension. Gas injection methods, like CO_2 and nitrogen injection, cause oil swelling, reduce viscosity, and alter phase behavior, enhancing oil displacement. These EOR techniques induce specific changes in the residual oil's molecular structure, including variations in hydrocarbon chain lengths, aromaticity, and asphaltene precipitation, as well as alterations in physical properties like viscosity, density, and interfacial tension [51].

4. Characterization of Heavy Oil Aromatic Fraction

4.1. High-Performance Liquid Chromatography (HPLC)

Analyzing vacuum residue oil using HPLC involves a detailed process to separate and identify its complex mixture of high-boiling point hydrocarbons [107,81]. Initially, the vacuum residue oil sample is diluted in an appropriate solvent, typically toluene, to facilitate injection into the HPLC system. To remove particulates, the sample may undergo additional clean-up steps, such as filtration or centrifugation. In the HPLC system, the sample is injected into a column packed with a suitable stationary phase. The choice of stationary and mobile phases is critical, often utilizing reverse-phase HPLC due to the non-polar nature of many components in vacuum residue oil. As the sample components are transported through the column by the mobile phase, they are divided into groups according to how they interact with the stationary phase. Detection is typically achieved using a UV-Vis or refractive index detector, capable of identifying and quantifying the various fractions. The resulting chromatogram provides detailed information on the composition of the vacuum residue oil, including the presence and concentration of asphaltenes, resins, aromatics, and saturates, facilitating a comprehensive analysis of its chemical properties [101].

4.2. Identification and Quantification of Polynuclear Aromatic Hydrocarbons (PAHs)

The main theme of the survey on the latest in-depth techniques for the analysis of vacuum residue oil focuses on the identification and quantification of polynuclear aromatic hydrocarbons within this complex matrix. PAHs are significant due to their environmental impact and health risks, necessitating precise analytical methods. In order to fully characterize PAHs in vacuum residue oil, the survey assesses sophisticated techniques as FTIR, GC-MS, and HPLC. [57,58] These techniques provide high sensitivity and specificity, enabling the detection of trace levels of PAHs amidst a background of heavy hydrocarbons [59]. The study focuses on the developments in sample preparation techniques that improve the effectiveness and precision of PAH analysis, such as solid-phase extraction (SPE) and accelerated solvent extraction (ASE). Additionally, the survey examines the integration of hyphenated techniques, like HPLC-MS and GC-MS/MS, offering comprehensive insights into the molecular composition of vacuum residue oil [60]. This technical evaluation aims to inform the development of more effective analytical protocols, ensuring better environmental monitoring and risk assessment of PAHs in heavy oil fractions [47].

4.3. Molecular Fragmentation Analysis

molecular fragmentation analysis emerges as a pivotal tool for elucidating the complex molecular composition

of this heavy oil fraction [74]. By subjecting vacuum residue oil samples to mass spectrometry and analyzing the resulting fragmentation patterns, researchers can gain crucial insights into the structural characteristics and chemical constituents present in the oil. This method makes it possible to identify and measure a wide range of substances, such as species that contain heteroatoms, polynuclear aromatic hydrocarbons, and other complicated organic molecules. which are often challenging to characterize using conventional analytical methods. The ability to precisely determine the molecular composition of vacuum residue oil is paramount for understanding its properties, behavior, and environmental impact [60]. As such, molecular fragmentation analysis stands as an indispensable component of the analytical toolkit for investigating vacuum residue oil and developing strategies for its efficient utilization and environmental management [60].

4.4. API-Mass Spectra Examination

The examination of API-mass spectra holds significant relevance within the context of the survey on the latest in-depth techniques for the analysis of vacuum residue oil. Vacuum residual oil contains complex chemical components, and one effective analytical method for determining their molecular makeup is atmospheric pressure ionization mass spectrometry, or API mass spectrometry. By subjecting the oil samples to API-mass spectrometry, researchers can obtain detailed information about the mass-to-charge ratios of ions generated from the oil's molecular components. Numerous substances, such as heteroatom-containing species, polynuclear aromatic hydrocarbons, and other organic molecules found in the vacuum residue oil, can be identified and measured using this technique. The examination of API-mass spectra enables the elucidation of structural features, functional groups, and molecular fragments within the oil, providing crucial insights into its chemical composition and properties. Therefore, API-mass spectra examination serves as a vital technique in the comprehensive analysis of vacuum residue oil, contributing to our understanding of its complex molecular makeup and facilitating informed decision-making in various industrial and environmental applications.

5. Structural Analysis of Vacuum Residue

5.1. Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectroscopy is a powerful analytical tool used to gain detailed structural insights into the molecular composition of vacuum residue oil [32]. NMR characterize the chemical environment of nuclei within the oil's molecular structure, providing crucial information about aromaticity, aliphatic chains, and the presence of heteroatoms.

This detailed characterization discussed in Table 4. is essential for understanding the complex properties and behavior of vacuum residue oil, which in turn informs the development of more efficient processing methods.

Additionally, NMR spectroscopy offers insights into molecular connectivity, stereochemistry, and conformational dynamics, revealing the intricate molecular architecture of vacuum residue oils. This ability to dissect the molecular structure has significant implications for industrial applications, such as improving refining processes, enhancing environmental management strategies, and optimizing quality control measures. Specifically, NMR analysis has shown that understanding the distribution and interaction of various chemical functionalities within vacuum residue oil can lead to more targeted and effective processing techniques, reducing environmental impact and improving product quality.

5.2. FTIR

FTIR spectroscopy is intricately linked to the survey on advanced techniques for analyzing vacuum residue oil [34]. In this survey, FTIR spectroscopy serves as a powerful tool for the comprehensive characterization of the chemical composition and functional groups present in vacuum residue oil [94]. By subjecting oil samples to FTIR analysis, researchers can obtain detailed information about the vibrational modes of molecular bonds present in the oil [76]. This technique allows for the identification and quantification of various chemical moieties, including hydrocarbons, aromatics, aliphatics, and heteroatoms. Moreover, FTIR spectroscopy provides valuable insights into the presence of functional groups such as carbonyl, hydroxyl, and sulfide groups, which are essential for understanding the reactivity and properties of vacuum residue oil. Examination of FTIR spectra

enables researchers to elucidate the molecular structure, composition, and properties of vacuum residue oil, thereby facilitating the development of efficient processing methods, environmental management strategies, and quality control measures in various industrial applications [43] (see Table 5.)

FTIR spectroscopy is a crucial analytical tool for characterizing the chemical composition and functional groups in vacuum residue oils [33]. Studies have shown that FTIR provides detailed information about the vibrational modes of molecular bonds, enabling the identification and quantification of various chemical moieties, including hydrocarbons, aromatics, aliphatics, and heteroatoms [94]. This capability is essential for understanding the reactivity of these oils, particularly in identifying functional groups such as carbonyl, hydroxyl, and sulfide, which play a significant role in oil processing and stability.

Moreover, FTIR has proven effective in detecting trace contaminants and offering enhanced sensitivity to minute compositional changes during oil processing, making it invaluable for quality control and environmental assessments. The correlation between FTIR data and physical properties like viscosity and density allows for a more comprehensive understanding of oil behavior, which is critical for optimizing processing methods and ensuring environmental compliance. However, challenges remain in fully leveraging FTIR for real-time monitoring and in developing standardized protocols for its application across different types of heavy oils [72].

5.3. GCMS

GC-MS serves as a cornerstone for the comprehensive characterization of the complex molecular composition of vacuum residue oil discussed in Table 6 [92]. GC-MS allows the isolation and identification of specific components within the oil sample based on their mass spectra and retention times by combining gas chromatography and mass spectrometry. This method makes it possible to identify and measure a wide range of substances, such as heteroatom-containing species, polynuclear aromatic hydrocarbons (PAHs), and other organic molecules present in vacuum residue oil. Additionally, GC-MS provides valuable insights into the molecular weight distribution, structural features, and chemical functionalities of the oil constituents. The examination of GC-MS spectra enables researchers to unravel the intricate molecular architecture of vacuum residue oil, facilitating the development of efficient processing methods, environmental management strategies, and quality control measures in various industrial applications.

GC-MS techniques have significantly enhanced the analysis of vacuum residue oils, enabling the development of methods for detailed hydrocarbon profiling. discuss new GC-MS techniques that provide comprehensive data on vacuum residues, leading to a deeper understanding of their composition [103]. The resolution and identification have improved capabilities of GC-MS for complex mixtures in heavy oils, essential for accurate characterization of these challenging materials [99]. The application of GC-MS in oil refinery product analysis, which enhances the detection of sulfur compounds and polycyclic aromatic hydrocarbons, thus aiding in quality control and refining processes [100]. The use of comprehensive two-dimensional GC-MS (GC×GC-MS) by facilitates the separation and identification of high-boiling compounds in vacuum residues, providing detailed compositional insights [98]. Focus on the optimization of GC-MS techniques, introducing new methodologies for sample preparation and chromatographic conditions, which improve the analysis of petrochemical products [112]. A detailed study provided on the biomarker composition of vacuum residues, offering insights into their origins and chemical characteristics, vital for geochemical and environmental studies [35]. Research by reveals the chemical complexity and molecular weight distribution in oil sands vacuum residue, contributing to a better understanding of these resources. A Review on recent advancements in GC-MS instrumentation and techniques, highlighting significant improvements in analyzing heavy oil fractions and reflecting the ongoing evolution in this field [59]. The application of GC-MS for sulfur compound analysis in vacuum residues, allowing for the identification and quantification of various sulfur-containing compounds, important for both environmental and industrial applications [31]. Finally, provided a comprehensive profiling of products obtained from heavy oil upgrading processes using GC-MS, offering valuable data for optimizing these processes and improving product quality [112].

6. Chromatographic Techniques

6.1. TLC-FID for Purity Confirmation

TLC-FID is highly relevant, particularly when discussing sophisticated methods of vacuum residue oil analysis. This method offers a rapid and effective means to confirm the purity of various compounds present in the oil sample. TLC separates individual components based on their affinity to the stationary phase, followed by visualization using a suitable detection method, in this case, Flame Ionization Detection. FID provides quantitative information about the separated compounds by measuring the ions generated upon combustion, thus enabling the determination of purity levels. In the analysis of vacuum residue oil, TLC-FID aids in confirming the absence of impurities or contaminants that may compromise the quality or performance of the oil. This technique is particularly valuable in quality control processes, ensuring that the oil meets specified purity standards for its intended application. Therefore, TLC-FID emerges as a crucial tool for purity confirmation within the realm of advanced analytical techniques for vacuum residue oil analysis, contributing to quality assurance and product integrity in various industrial sectors.

The evaluation of vacuum residue oil purity has seen significant advancements through improved TLC-FID methods, offering higher sensitivity and more accurate assessments of purity [104]. The development of advanced TLC-FID protocols has enabled precise purity measurements in heavy oil fractions, addressing the complexities inherent in these materials [121]. Enhanced resolution and quantification of various components in crude oil residues have been achieved using TLC-FID, as demonstrated in studies that optimize these methods for better analytical outcomes [102]. Novel approaches for purity confirmation in petrochemical products through optimized TLC-FID methods have provided more robust and reliable results, facilitating better quality control [97]. The continuous monitoring of purity levels during oil refinery processes has been improved by the application of TLC-FID, enabling real-time quality assessment and process optimization [113]. Detailed characterization of heavy oil fractions and their purity assessment using TLC-FID has provided critical insights into their composition, supporting more efficient utilization and processing of these resources discussed in Table 7 [104]. Recent advancements in TLC-FID techniques have enhanced the analysis and purity confirmation of petrochemicals, reflecting ongoing improvements in this field [105]. For the purpose of separating and verifying the purity of crude oil components, high-resolution TLC-FID techniques have been developed, which provide increased accuracy and dependability [55]. The utilization of TLC-FID for purity confirmation in oil sands-derived vacuum residues has highlighted its effectiveness in handling complex matrices found in these materials [60]. Finally, comprehensive studies on the use of TLC-FID for analyzing and confirming the purity of vacuum residue oil have consolidated its role as a crucial tool in petrochemical analysis, providing detailed and accurate data essential for industry applications [59].

6.2. Molecular Weight Analysis using GPC

Molecular Weight Analysis using GPC is a vital technique within the scope of advanced analyses for vacuum residue oil. GPC is adept at determining the distribution of molecular weights present in the oil sample. Using this technique, molecules are separated according to size as they move through a porous gel matrix. Smaller molecules take longer to elute than larger molecules, which elute earlier. Detection methods such as refractive index or ultraviolet absorption allow for the quantification of the separated fractions. In the analysis of vacuum residue oil, GPC provides essential insights into the distribution of molecular sizes, helping to characterize the complexity of the oil's composition. By determining the average molecular weight and polydispersity index, GPC facilitates the assessment of the oil's suitability for various industrial applications [44]. Moreover, it aids in understanding the relationship between molecular size and properties such as viscosity, thermal stability, and solubility. Thus, molecular weight analysis using GPC stands as a critical technique for gaining a comprehensive understanding of vacuum residue oil, guiding formulation, processing, and quality control efforts in the petroleum industry [108].

7. Discussions

The published reviews on characterization of residual oils highlights significant differences in the methods and results. For instance, the study emphasizes the importance of SARA analysis in understanding the properties of vacuum residual oils [15]. It notes that the

correlation between density and refractive index is strong, indicating a strong correlation between these properties. In contrast, other studies, focus on the use of advanced analytical techniques like petroleomics and molecular modeling to better understand the composition and properties of heavy petroleum mixtures [80]. Additionally, research explores the thermal cracking behavior and viscosity prediction of vacuum residues, highlighting the need for more comprehensive approaches to understanding residual oil properties [67] and [128]. These differences in focus and methodology underscore the complexity of residual oil characterization and the need for diverse approaches to fully understand these complex mixtures.

A comprehensive overview of the challenges in petroleum characterization [17]. The authors discuss the various methods used to analyze petroleum crude oils, highlighting the importance of understanding the chemical nature of these complex substances. The article emphasizes that petroleum properties vary widely, making it difficult to measure them using a single standard method. It highlights the importance of understanding these variations to optimize oil refining processes and improve profitability. The authors discuss the use of the SARA (Saturates, Aromatics, Resins, and Asphaltenes) characterization method to analyze petroleum crude oils, and examine the application of the additive rule to predict asphaltene content from vacuum residue and TBP yield, which was found to be effective. The article also discusses the importance of accurate TBP (True Boiling Point) distillation data in refining processes, as it affects refining margins, and highlights the need for reliable TBP analysis to avoid underestimation or overestimation of refining margins, which can lead to incorrect crude oil selection. The authors examine the use of various analytical techniques, including chromatography, spectroscopy, and mass spectrometry, as well as chemometric approaches and modeling methods. The article emphasizes the significant impact of petroleum characterization on oil refining processes and the need for innovative techniques to improve profitability, as well as the importance of environmental regulations and the need for oil refining processes to be environmentally friendly.

8. Summary

The thorough examination of residual oils in this review makes it clear that there has been a substantial evolution in the characterization of VRO complex substances over time. The field started out with simple measurements of chemical and physical properties and has since advanced to more complex methodologies including molecular modeling, SARA analysis, and instrumental procedures. These developments have made it possible to comprehend residual oils' composition and characteristics better, which is essential for maximizing their use in a variety of industrial applications. Among these developments, SARA analysis stands out as a key technique that makes it easier to separate residual oils into four fractions: saturate, aromatic, resin, and asphaltene. The behavior and possible uses of these oils are significantly influenced by each fraction. The molecular weight ranges for the various SARA fractions are as follows: saturates ($350 \leq MW \leq 870$) < aromatics ($440 \leq MW \leq 1100$) < resins ($790 \leq MW \leq 1850$) < asphaltenes ($990 \leq MW \leq 2950$). These variations highlight the complexity and diversity of residual oils. These ranges demonstrate the wide variety of molecule structures that are present and their important influence on the characteristics of oil.

Crucially, the origin of the vacuum residual oil affects the composition of SARA fractions, which in turn affects attributes like density, hydrogen content, and Conradson carbon concentration. This diversity suggests that in addition to SARA analysis, careful consideration of the residual oils' provenance and the particular analytical techniques used are also necessary for a complete characterization of the oils. The observed differences in molecular weight among various oils highlight the necessity of customized analytical methods to completely understand their makeup and function. Beyond SARA analysis, sophisticated analytical methods have become essential for gaining molecular-level understanding of heavy oils, such as FT-ICR Mass Spectrometry. These methods are critical for creating comprehensive kinetic models that are necessary for industrial residue conversion process optimization. Despite these developments, the high viscosity, low volatility, and melting point of vacuum residual oils continue to pose difficulties for reliable analysis, frequently producing unexpected results in simple physical property evaluations. Although residual oil

characterization has advanced significantly, more study and technical advancement are needed to solve lingering issues and deepen our understanding. For chemical engineers working in commercial residual oil conversion units, further developments in analytical methodologies are essential to their ability to efficiently optimize conversion operations. In the end, thorough residual oil characterisation promotes the efficient and sustainable use of these priceless resources in the global energy landscape in addition to improving industrial applications.

9. Future Directions and Challenges

Future directions and challenges in the analysis of vacuum residue oil present exciting opportunities for advancement in the field.

- One promising direction involves the integration of advanced spectroscopic and chromatographic methods that improve data analysis and interpretation using artificial intelligence and machine learning algorithms. This interdisciplinary approach holds the potential for more accurate and efficient characterization of complex oil matrices, enabling deeper insights into their chemical composition and properties.
- Additionally, further research efforts could focus on developing novel analytical methods capable of addressing specific challenges associated with vacuum residue oil analysis, such as the characterization of high molecular weight compounds and the detection of trace-level impurities. Moreover, the exploration of greener and more sustainable analytical approaches, such as green chromatography and spectroscopy, could contribute to reducing the environmental footprint of oil analysis processes. However, several challenges remain, including the development of standardized protocols for vacuum residue oil analysis, the optimization of analytical techniques for real-time monitoring in industrial settings, and the interpretation of complex data obtained from advanced analytical instruments.

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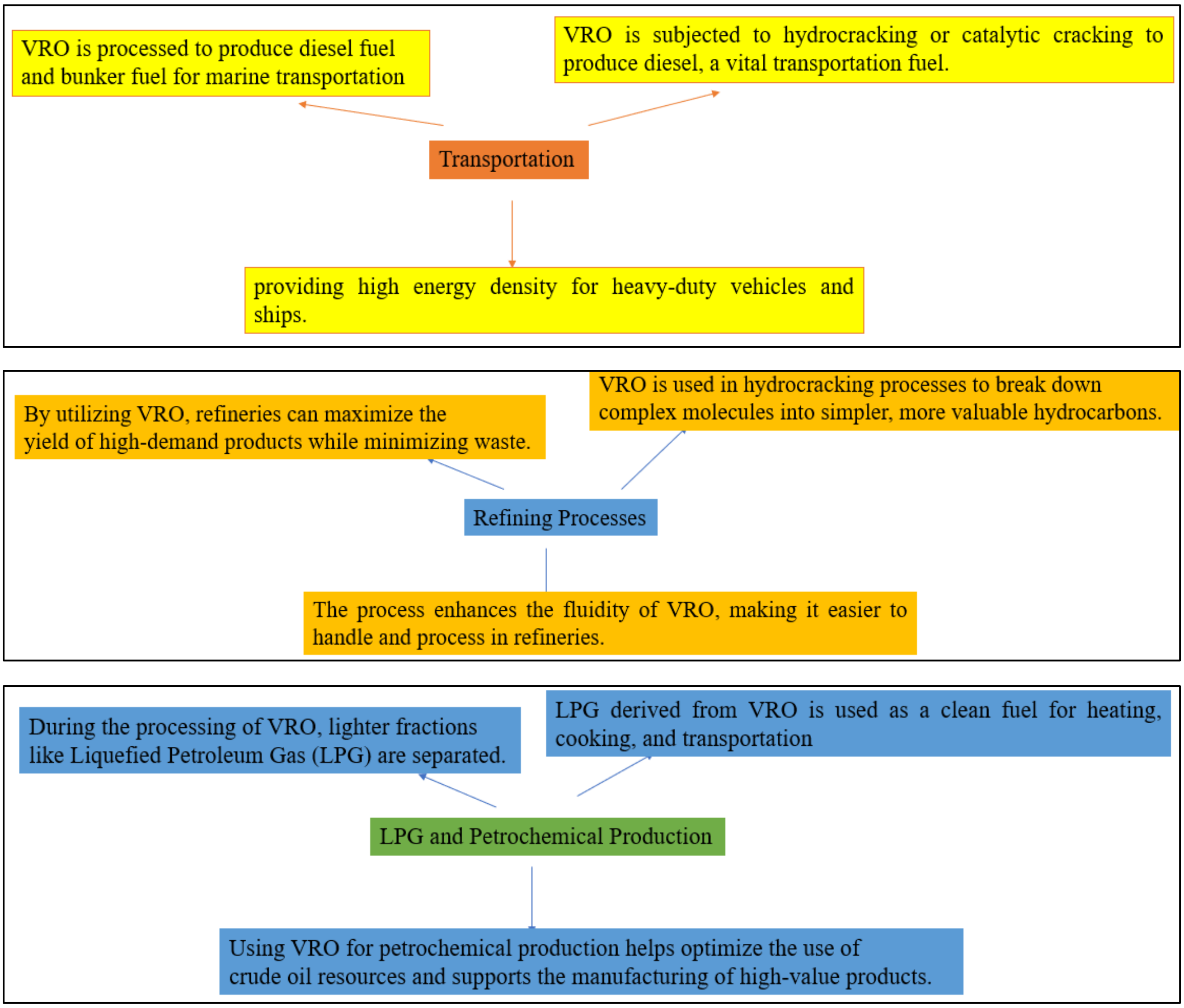
Figures and Tables



VRO is processed to produce diesel fuel and bunker fuel for marine transportation

VRO is subjected to hydrocracking or catalytic cracking to produce diesel, a vital transportation fuel.

Transportation

providing high energy density for heavy-duty vehicles and ships.

By utilizing VRO, refineries can maximize the yield of high-demand products while minimizing waste.

VRO is used in hydrocracking processes to break down complex molecules into simpler, more valuable hydrocarbons.

Refining Processes

The process enhances the fluidity of VRO, making it easier to handle and process in refineries.

During the processing of VRO, lighter fractions like Liquefied Petroleum Gas (LPG) are separated.

LPG derived from VRO is used as a clean fuel for heating, cooking, and transportation

LPG and Petrochemical Production

Using VRO for petrochemical production helps optimize the use of crude oil resources and supports the manufacturing of high-value products.

Figure 1. Positive perspectives for utilization of VRO

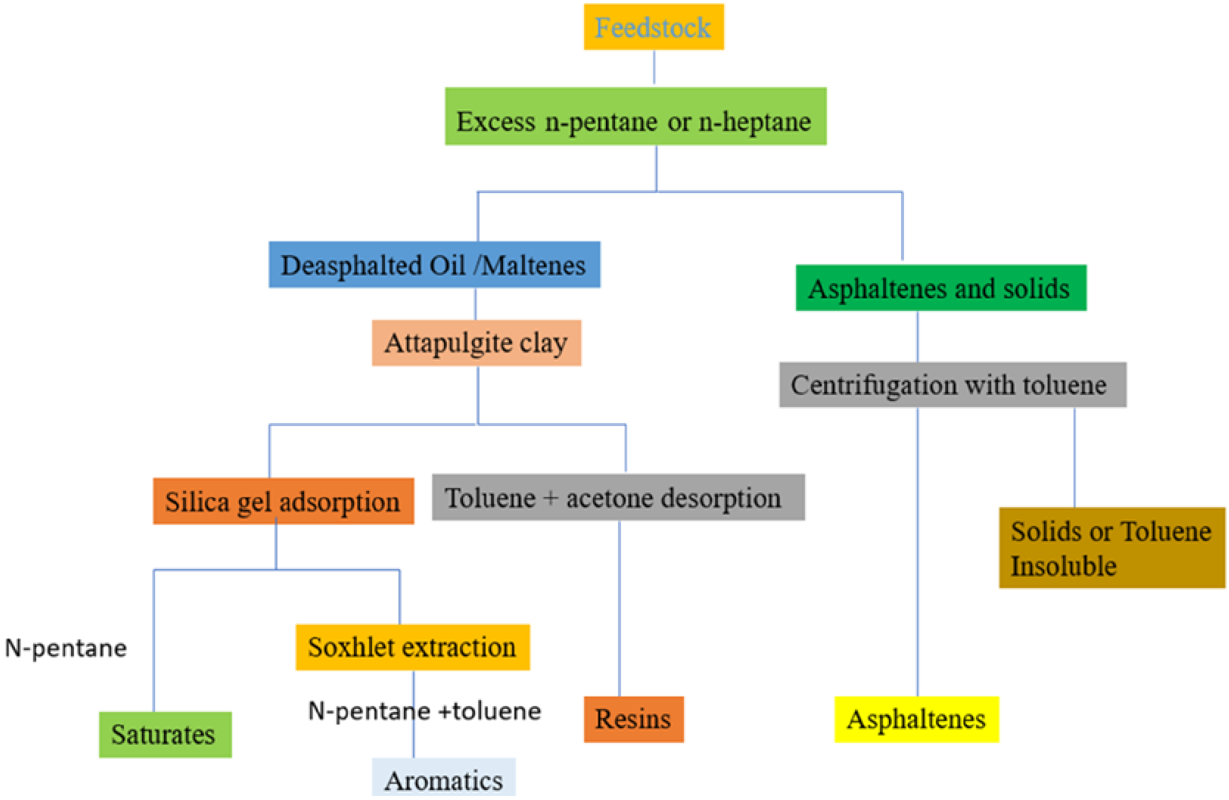
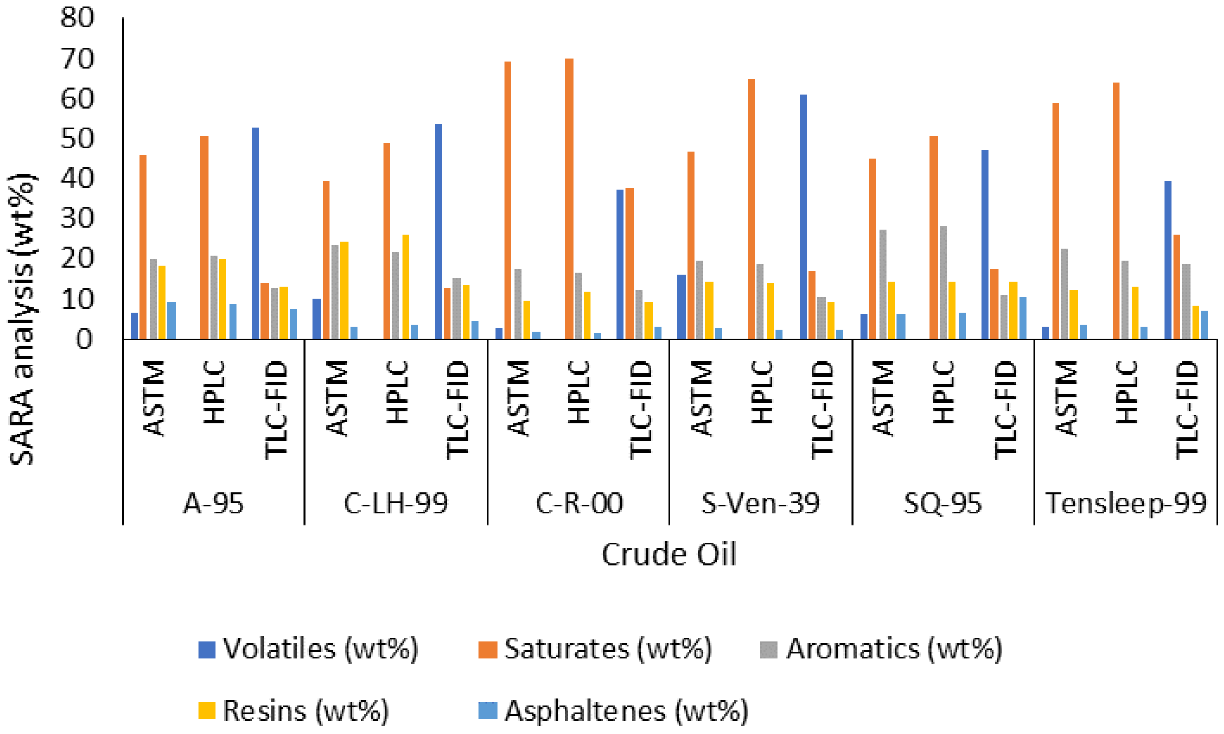
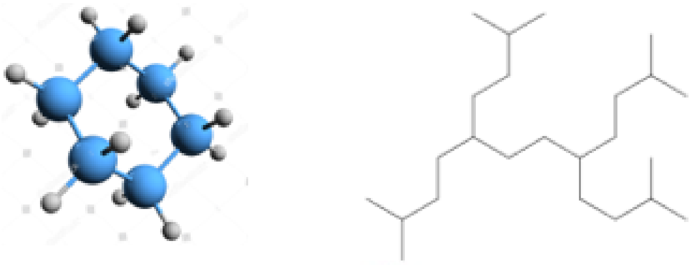


Figure 2. Schematic Procedure for SARA fractionation.

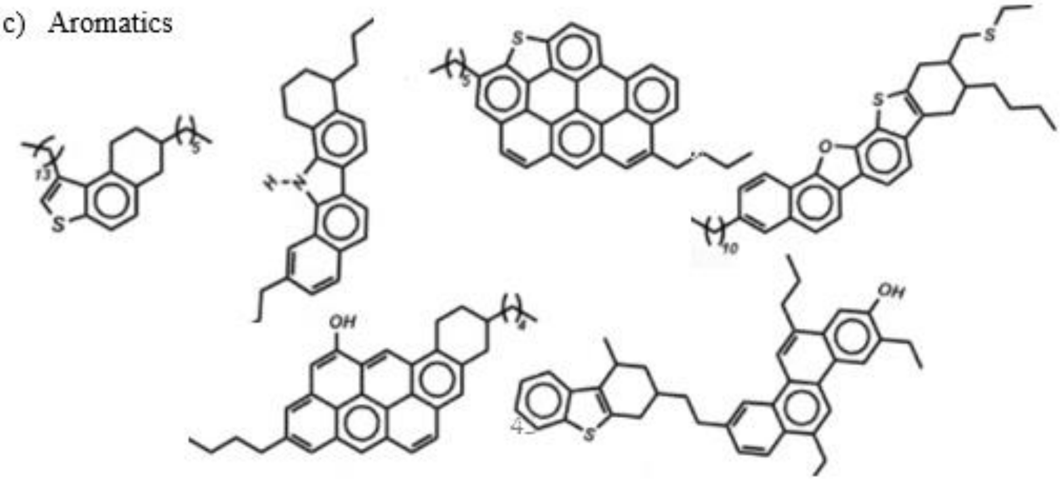


a) Volatiles

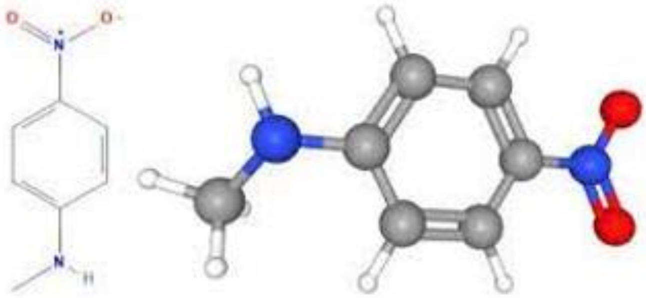
b) Saturates



c) Aromatics



e) Resins



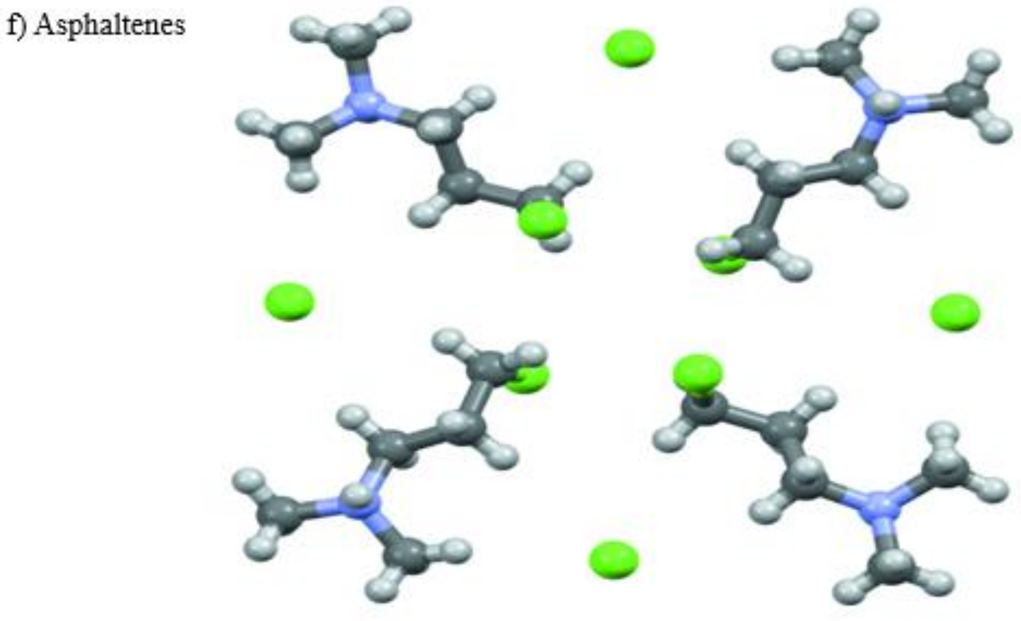


Figure 3. a. SARA analysis of various crude oils b. Fractions presents in the respective analysis.

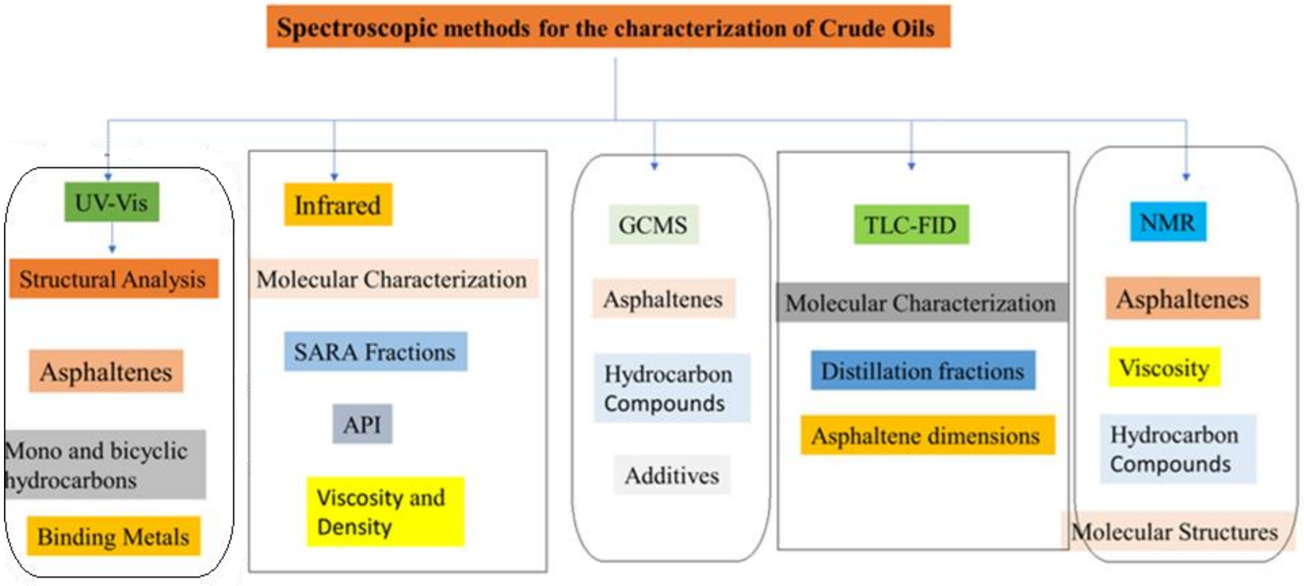
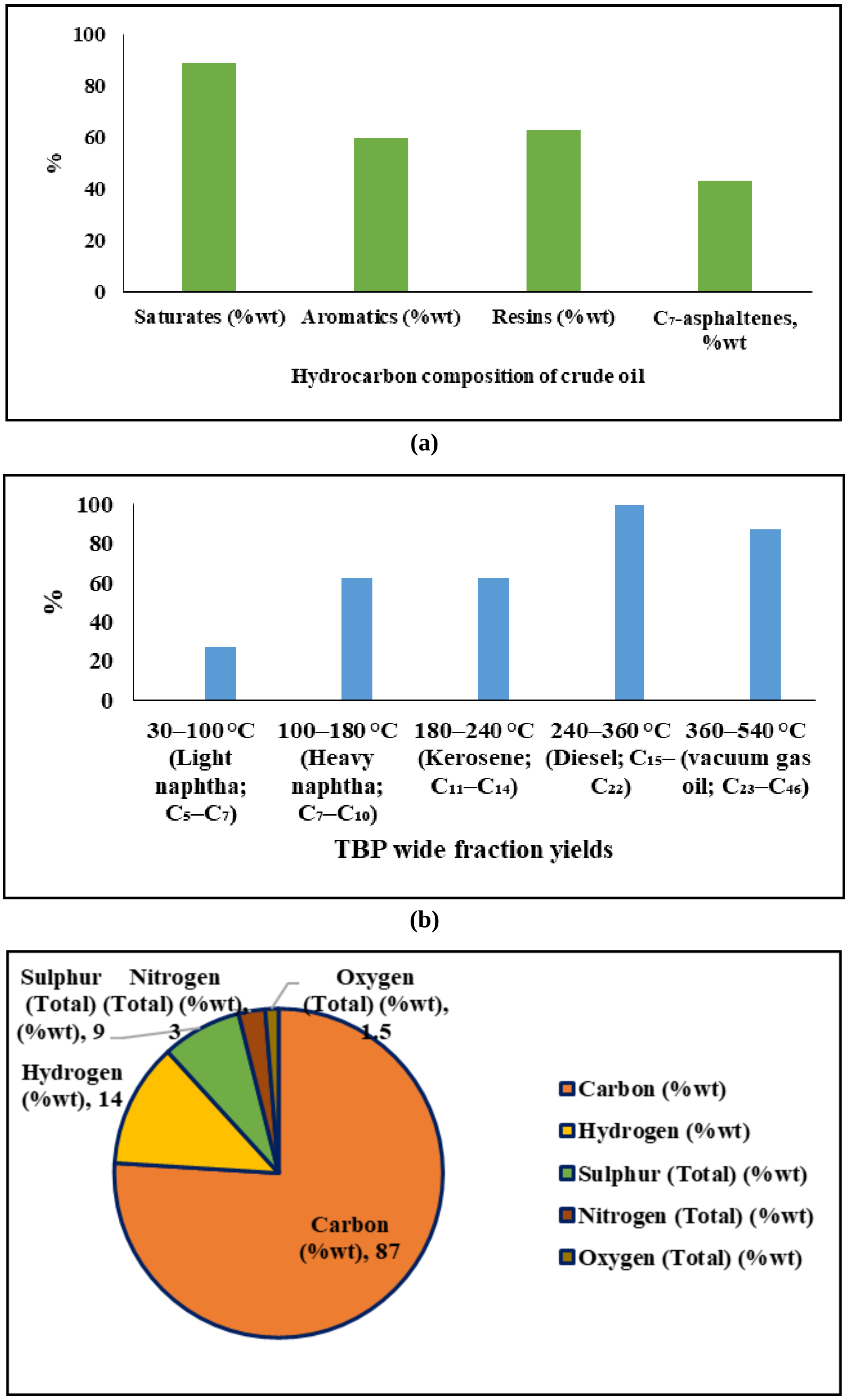


Figure 4. Spectroscopic methods for crude oil properties.



(a)

(b)

(c)

Figure 5. a) Hydrocarbon values of VRO; b) Maximum values of fractions in VRO; c) Group hydrocarbon composition of crude oil