Chapter-1

Crude Oil Stability and Compatibility Evaluation Using TLC-FID SARA: Correlating P-Value with Colloidal Insolubility Index

1.1 Introduction

1.1.1Crude Oil

Known as "black gold," crude oil is a naturally occurring liquid fossil fuel that is mostly made up of hydrocarbons, although it also contains other organic and inorganic substances. It is the basic raw material used to make petroleum products including lubricants, diesel, and gasoline [1]. The composition of crude oil differs greatly depending on where it comes from, therefore thorough classification is required for effective refining and use [2,3]. Crude oil is processed using a number of methods, such as distillation and cracking, to separate it into valuable fractions [4].

Based mostly on its API gravity a measurement of density in relation to water that has a big impact on its market value and refining behaviour crude oil is generally divided into light, medium, heavy, and extra-heavy categories [5]. While heavy and extra-heavy crudes (API gravity below 20°) contain larger, more complex compounds like asphaltenes and resins, light crude oils, which have higher API gravities (usually above 31.1° API), are rich in lighter hydrocarbons like gasoline and naphtha precursors [6].

Traditionally, heavier fractions obtained during vacuum distillation, such as vacuum residue and vacuum gas oil, have been considered low-value by-products due to their high viscosity, sulfur content, and refractory nature, which complicate refining and yield lower-value products [7].

However, recent advancements in material science and nanotechnology have enabled innovative approaches to upgrade these heavy fractions into high-value nanomaterials. For instance, heavy residues have been explored as precursors for carbon nanotubes, graphene derivatives, and other nanostructured carbons with applications in catalysis, energy storage, and advanced composites [8].

A thorough understanding of crude oil's complex chemical composition and physicochemical properties is essential for optimizing refining processes, improving conversion efficiency, and minimizing environmental waste. Characterization techniques such as Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), and gas chromatography-mass spectrometry (GC-MS) enable detailed profiling of hydrocarbons and impurities, guiding process adjustments to enhance economic viability and sustainability [9].

Crude oil compatibility plays a crucial role in the petroleum industry, particularly in the blending and processing of special crude mixtures. The ability to accurately predict and assess the compatibility of various crude blends is essential for ensuring efficient refining operations, preventing operational issues, and maintaining the quality of the final petroleum products [10,11]. Key parameters used to evaluate crude oil compatibility include the P-Value, Colloidal Instability Index (CII), and the Kuop component, which are recognized as critical indicators. These parameters provide valuable insights into the stability and behaviour of crude blends, enabling early identification of incompatibilities that could result in precipitation, sludge formation, or other processing challenges [10,12-14].

1.1.2 The crucial vital of Crude Oil Compatibility in present day Refining

The global petroleum industry serves as a fundamental pillar underpinning modern economies and the infrastructure of contemporary civilization. This vast sector encompasses a wide array of complex activities, including exploration, extraction, transportation, and refining of crude oil—each process deeply reliant on a comprehensive understanding of the intricate physicochemical properties inherent to different crude oils [15,16]. In this highly dynamic and multifaceted environment, the concept of crude oil compatibility emerges as a critical challenge, particularly in the context of blending diverse crude stocks sourced from different geographical regions and geological formations.

Refiners are increasingly compelled to engage in strategic crude blending driven by economic imperatives, which are shaped by volatile global market prices, geopolitical uncertainties, and the expanding availability of unconventional crude resources such as shale oils, heavy sour crudes, and bitumen-derived oils. This diversification of crude supply enhances flexibility and cost-effectiveness in feedstock procurement but simultaneously introduces complexities due to the heterogeneous nature of the crude blends [10,17].

The compatibility of these crude mixtures directly impacts refinery operations, as incompatible blends can precipitate physical and chemical instabilities. These may manifest as sludge formation, asphaltene precipitation, emulsion problems, or fouling, all of which can impair process equipment, reduce operational efficiency, and compromise the quality of refined products. Such disruptions can escalate operational costs and lead to substantial financial losses, highlighting the necessity for meticulous compatibility assessment and optimization strategies in crude oil blending [10,17].

Understanding and managing crude oil compatibility thus becomes paramount for refineries aiming to maximize profitability while ensuring smooth operations and meeting stringent product quality standards in an increasingly complex and competitive global market.

Crude oil is far from a uniform substance; rather, it is a highly complex, polydisperse mixture of hydrocarbons and non-hydrocarbon compounds, ranging from light gases like methane and ethane to heavy, high-molecular-weight species such as waxes, resins, and asphaltenes [18]. Among these, asphaltenes represent the most polar, aromatic, and structurally complex fraction of crude oil. They possess the highest molecular weight and are typically present in a metastable colloidal suspension, intricately dispersed within the oil matrix.

This suspension is stabilized primarily by resins and light aromatics, which act as peptizing agents. These molecules prevent the asphaltene particles from aggregating by adsorbing onto their surfaces, thereby maintaining dispersion and preventing precipitation [19,20]. However, this delicate thermodynamic equilibrium is highly sensitive and can be easily disrupted. Factors such as the blending of incompatible crude oils, changes in temperature or pressure, or the introduction of certain solvents or diluents (e.g., paraffinic diluents) can destabilize the system, leading to asphaltene flocculation and precipitation.

The consequences of asphaltene precipitation are both extensive and detrimental to refinery operations. Once destabilized, asphaltenes tend to form sticky, insoluble sludge that adheres to metal surfaces and internal components of processing units. This leads to: Fouling of heat exchangers and furnaces, which reduces heat transfer efficiency and results in increased energy consumption due to elevated furnace duty. Elevated operational costs, as cleaning, maintenance, and energy requirements rise. Increased greenhouse gas emissions, due to inefficient combustion and prolonged processing cycles. Potential equipment damage, particularly under severe fouling conditions, which can compromise the mechanical integrity of refinery units [5, 20–23].

Understanding the behaviour of asphaltenes and their interactions with other crude components is thus critical for predicting compatibility, preventing fouling, and maintaining stable, efficient refining operations.

1.1.3 P-value: A Foundational Metric for Asphaltene balance

In response to the critical need for assessing crude oil compatibility—especially during blending operations—the petroleum industry has historically relied on a range of empirical and semi-empirical parameters. Among the most fundamental and widely adopted of these is the P-Value, also known as the Peptizing Power Value [24,25]. This parameter stems from the understanding that asphaltenes exist as a colloidal dispersion within the crude oil matrix, and their stability is governed largely by the solvency characteristics of the surrounding medium [19,26-29].

The P-Value offers a relatively quick and straightforward metric that quantifies a crude oil’s inherent ability to maintain its asphaltenes in a stable, dissolved state. It effectively reflects the balance between precipitating tendencies and stabilizing components (such as aromatics and resins) within the crude. Oils with a high P-Value possess stronger solvency power and are better equipped to keep asphaltenes dispersed, thereby reducing the risk of precipitation during blending or processing.

Due to its simplicity and predictive reliability, the P-Value is often used as a preliminary screening tool in the selection and evaluation of crude oils for blending operations. It enables refiners to identify potential incompatibilities early in the decision-making process, minimizing operational risks such as sludge formation, fouling, and throughput reductions [28,29].

The P-Value is typically determined through a controlled titration method, wherein a known volume of crude oil is gradually diluted with a precipitating (paraffinic) solvent, such as n-heptane or n-pentane, until the onset of asphaltene flocculation is visually or instrumentally detected [30]. Simultaneously, a portion of the same crude oil is mixed with an aromatic solvent, such as toluene or xylene, to establish a baseline solubility reference for asphaltenes under ideal solvency conditions.

The P-Value is then calculated as the ratio of the volume of aromatic solvent (good solvent) to the volume of paraffinic solvent (poor solvent) required to maintain asphaltenes in a dispersed state under defined experimental conditions [31]. This dimensionless value serves as an indicator of the crude oil’s peptizing strength, reflecting the ability of the surrounding matrix to stabilize colloidal asphaltenes.

A higher P-Value indicates stronger peptizing capability, suggesting that the crude oil possesses a robust solvency environment—typically due to a higher content of aromatics and resins which effectively stabilizes asphaltenes and minimizes the risk of their precipitation. Conversely, a lower P-Value reflects weaker peptizing strength, indicating a higher tendency toward asphaltene aggregation and flocculation, which can pose significant operational challenges during storage, transportation, and refining [32].

The P-Value titration method is a two-phase solvent addition test used to evaluate the stability of asphaltenes in crude oil. Below is a simplified breakdown of the experimental procedure:

Sample Preparation:

A fixed volume of crude oil (e.g., 10 mL) is placed into a test tube or titration vessel.

Addition of Aromatic Solvent (Good Solvent):

An aromatic solvent (e.g., toluene or xylene) is incrementally added to fully dissolve asphaltenes.

This step establishes the baseline solubility of asphaltenes.

Titration with Paraffinic Solvent (Poor Solvent):

A paraffinic solvent (e.g., n-heptane or n-pentane) is added dropwise to the crude/aromatic solvent mixture.

The solution is continuously observed for asphaltene flocculation or haze formation, typically via visual inspection, light scattering, or turbidity measurement.

P-Value Calculation:

$$\text{P-Value} = \frac{V_{\text{good solvent}}}{V_{\text{poor solvent}}}$$

Where Vgood solvent is the volume of aromatic solvent used, and Vpoor solvent V poor solvent is the volume of paraffinic solvent added up to the flocculation point.

P-Value	Interpretation

High (>1.5–2.0)	Strong peptizing ability, low asphaltene precipitation risk
Moderate (~1.0–1.5)	Medium stability, some risk of incompatibility
Low (<1.0)	Poor peptizing power, high risk of asphaltene precipitation

The theoretical foundation of the P-Value is deeply rooted in the colloidal model of asphaltenes, which conceptualizes asphaltenes as complex, highly aromatic, polycondensed molecular structures with a strong tendency to self-associate into nano-sized aggregates or micelle-like clusters under certain conditions [14]. These aggregates form due to intermolecular interactions, such as π–π stacking and hydrogen bonding, and are inherently unstable without the presence of stabilizing agents.

Stability within the crude oil matrix is achieved through the adsorption of resins and polar aromatic compounds onto the surface of asphaltene aggregates [15]. This adsorbed layer serves as a protective shell, providing steric hindrance and/or electrostatic repulsion that prevents further aggregation and subsequent precipitation of asphaltenes. The continuous oil phase, predominantly composed of saturates and light aromatics, functions as the dispersion medium that hosts these colloidal structures.

The P-Value provides a quantitative measure of the solvency strength of this medium that is, its ability to maintain the dispersion of asphaltenes. A high P-Value indicates a crude oil composition that is rich in peptizing agents, particularly resins and aromatics, relative to its asphaltene content. Such crude oils possess sufficient solvency power to keep asphaltenes dispersed, reducing the likelihood of flocculation or deposition. In contrast, a low P-Value suggests a higher proportion of paraffinic (saturate) components, which are poor solvents for asphaltenes. This condition results in weaker peptizing forces and a greater risk of asphaltene precipitation, especially under changing operational conditions or during crude blending [19].

Standardized methodologies, such as ASTM D7112 (Standard Test Method for Asphaltene Precipitation from Crude Oil by Light Scattering) and the more recent ASTM D8253 (Standard Test Method for Asphaltene Precipitation from Crude Oil by Optical

Microscopy), provide established procedures for the experimental determination of the P-Value [5,20]. These protocols typically involve a dual-solvent titration technique, wherein a crude oil sample is diluted with a mixture of a good solvent (commonly toluene) and a poor solvent (such as n-heptane). The mixture is gradually adjusted until the onset of asphaltene flocculation is detected.

To identify this onset, advanced optical detection methods are employed. Techniques such as light scattering (in ASTM D7112) or optical microscopy (in ASTM D8253) are used to observe the emergence of asphaltene aggregates, marking the point at which the stabilizing capacity of the medium is exceeded. At this point, the relative concentrations of the good and poor solvents are recorded, and the P-Value is calculated accordingly. This value serves as an indicator of the overall solvency power of the crude oil matrix to keep asphaltenes in a dispersed, stable state.

While the P-Value offers a convenient, rapid, and practical metric for assessing crude oil stability, it is important to recognize its inherent limitations. As an empirical parameter, the P-Value provides only a simplified representation of the complex intermolecular interactions occurring within the crude oil system. It primarily reflects the bulk solvency behaviour of the crude but does not offer a detailed molecular-level breakdown of the individual constituents contributing to solvency.

For example, different crude oils may exhibit similar P-Values while possessing vastly different chemical compositions, particularly in terms of asphaltene structure and maltene fractions (saturates, aromatics, and resins). When such crudes are blended, unforeseen incompatibilities may arise due to specific interactions between the asphaltenes of one crude and the maltenes of another—interactions that the P-Value alone cannot predict.

Moreover, the P-Value is fundamentally a static measurement, determined under fixed laboratory conditions. It does not fully account for dynamic operational variables such as temperature fluctuations, pressure variations, or mechanical shear forces, all of which can significantly influence asphaltene stability and behaviour during actual refining or transport operations [16].

These limitations underscore the necessity of complementing P-Value analysis with more detailed compositional and molecular characterizations, including SARA analysis, NMR spectroscopy, and molecular modelling, to provide a comprehensive understanding of crude oil compatibility and to mitigate the risks associated with crude blending and processing.

1.1.4 SARA analysis: decoding the Molecular Blueprint of Crude Oil

To overcome the inherent limitations of empirical parameters such as the P-Value—and to develop a more fundamental understanding of crude oil behaviour, particularly in relation to asphaltene stability and compatibility—the SARA analysis (Saturates, Aromatics, Resins, and Asphaltenes) has emerged as a critical analytical technique in petroleum characterization [21]. Unlike single-value metrics, SARA analysis offers a quantitative compositional breakdown of crude oil by fractionating it into four chemically distinct groups based on molecular polarity and solubility.

This fractionation process is typically achieved through techniques such as liquid chromatography or IP-143 gravimetric methods, which separate the crude oil into:

Saturates – nonpolar alkanes and cycloalkanes with low solvency power,

Aromatics – mono- and polycyclic aromatic hydrocarbons with moderate polarity,

Resins – polar, high molecular weight compounds that act as peptizing agents,

Asphaltenes – the most polar, heaviest fraction, prone to aggregation and precipitation.

The relative proportions and chemical characteristics of these fractions are vital in determining the colloidal stability of asphaltenes within the crude oil matrix. For instance, a high resin-to-asphaltene ratio generally enhances asphaltene dispersion by providing sufficient steric stabilization, while a high saturate content may reduce solvency, promoting asphaltene flocculation [22].

SARA analysis thus provides a more nuanced and molecular-level perspective than empirical indices alone, enabling refiners and researchers to: Predict compatibility issues during crude blending, Understand the solvency environment of different crude oils, Design targeted mitigation strategies to minimize operational risks such as fouling and deposition.

When used in conjunction with tools like the P-Value and Colloidal Instability Index (CII), SARA data significantly improves the accuracy and reliability of crude oil compatibility assessments in both laboratory and operational settings.

1.1.5 Each SARA fraction plays a distinct role in the crude oil device

Saturates are the least polar fraction of crude oil and primarily consist of straight-chain alkanes (n-paraffins), branched alkanes (iso-paraffins), and cyclic alkanes (naphthenes) [23]. Due to their nonpolar nature and lack of aromaticity, saturates possess minimal solvency power for asphaltenes. In fact, they are considered poor solvents and are known to act as strong precipitants for asphaltenes. Crude oils with a high saturate content particularly rich in long-chain n-paraffins tend to exhibit reduced colloidal stability, increasing the risk of asphaltene flocculation and deposition. This destabilizing influence becomes especially significant during blending with more paraffinic crudes or under cooling conditions, where saturate solubility decreases.

Aromatics, on the other hand, are moderately polar hydrocarbons characterized by the presence of one or more aromatic rings. This group includes both monocyclic aromatics (e.g., benzene, toluene) and more complex polycyclic aromatic hydrocarbons (PAHs) [15]. Aromatics are excellent solvents for asphaltenes, as their π-electron systems interact favourably with the polyaromatic structures of asphaltene molecules. Consequently, aromatics contribute significantly to the peptizing strength of the crude oil, enhancing the colloidal stability of asphaltene aggregates and preventing their precipitation. The aromatic content of a crude is thus a key determinant in solvency balance, influencing both the P-Value and overall compatibility with other crude oils during blending operations.

Resins are a highly polar and chemically diverse fraction of crude oil, often comprising polycyclic aromatic compounds that include heteroatoms such as sulphur (S), nitrogen (N), and oxygen (O) in their molecular structures [15]. Compared to saturates and aromatics, resins exhibit greater polarity and molecular complexity, placing them functionally between the lighter oil components and the heavier, more polar asphaltenes.

Resins play a crucial role in stabilizing asphaltenes, acting as a transitional solvency layer that mediates the interaction between asphaltene aggregates and the bulk oil phase. They adsorb onto the surfaces of asphaltene micelles, forming a stabilizing shell that provides steric hindrance and, to a lesser extent, electrostatic repulsion, both of which help prevent further aggregation and precipitation. This adsorption is key to maintaining the colloidal dispersion of asphaltenes, especially under varying temperature and compositional conditions.

Resins are distinguished from asphaltenes in that they remain soluble in normal alkanes (such as n-pentane and n-heptane) even after the precipitation of asphaltenes. However, they are typically insoluble in the solvents used to isolate asphaltenes, such as excess n-heptane, once the asphaltene fraction is removed. This solubility behaviour allows for the analytical separation of resins during SARA analysis and underscores their intermediate role in the crude oil matrix bridging the compatibility gap between the oil phase and the asphaltene fraction.

Asphaltenes are operationally defined as the fraction of crude oil that is insoluble in an excess of light n-alkanes (typically n-heptane or n-pentane), but soluble in aromatic solvents such as toluene or xylene [14]. They represent the most polar, heaviest, and chemically complex component of crude oil, and are widely recognized as the central contributors to compatibility and stability issues in crude blending and refining operations.

Structurally, asphaltenes are thought to consist of polycondensed aromatic cores with peripheral alkyl chains, heteroatoms (e.g., N, S, O), and metal-containing functionalities (e.g., vanadium, nickel). These macromolecules have a strong propensity to self-associate via π–π stacking and hydrogen bonding, forming nano-aggregates under stable conditions.

However, when the colloidal balance is disrupted—by changes in composition, temperature, pressure, or blending with incompatible crudes these aggregates can grow into larger flocculates, ultimately resulting in asphaltene precipitation.

Asphaltenes are often referred to as the “heart” of the crude oil compatibility problem, as even minor shifts in the surrounding matrix can lead to destabilization. Their solubility and dispersion are highly dependent on the relative concentrations and properties of the other SARA fractions particularly resins and aromatics, which act as peptizing agents to maintain colloidal stability.

The relative proportions of saturates, aromatics, resins, and asphaltenes are therefore key indicators of a crude oil's overall compatibility and stability. A crude oil with high saturate content and low aromatic and resin content is likely to be “under-solvated,” meaning that its asphaltenes are on the verge of insolubility, increasing the risk of flocculation. In contrast, a crude rich in resins and aromatics relative to its asphaltene content is typically more stable, with a robust capacity to keep asphaltenes dispersed even under varying operational conditions.

SARA analysis the separation of crude oil into Saturates, Aromatics, Resins, and Asphaltenes is typically conducted using a range of chromatographic techniques, each offering varying degrees of resolution, speed, and accuracy. The traditional approach employs liquid adsorption chromatography, as standardized in methods such as ASTM D2007 and IP 143 [24]. In this technique, a crude oil sample is passed through adsorbent columns packed with silica gel or alumina, and the fractions are eluted sequentially using solvents of increasing polarity. This method relies on the principle that different SARA components exhibit varying affinities for the stationary phase based on their polarity, enabling their separation and quantification.

To improve analytical speed and resolution, more advanced chromatographic techniques have been adopted. One such method is High-Performance Liquid Chromatography (HPLC), which provides faster analysis times, higher resolution, and improved reproducibility. HPLC is especially valuable for handling complex crude mixtures and offers detailed insights into sub-fractionation within the SARA groups, particularly for resins and aromatics.

Another widely used technique is Thin-Layer Chromatography coupled with Flame Ionization Detection (TLC-FID), such as the Iatroscan method [25]. In this procedure, crude oil fractions are applied to a chromarod (a silica-coated rod), which is then developed in a solvent system. The separated fractions are quantitatively analysed using flame ionization detection, offering a rapid and semi-automated alternative to traditional column chromatography. TLC-FID is particularly advantageous for its speed and suitability for high-throughput sample analysis.

Despite their effectiveness, these SARA analysis methods are subject to inter-laboratory variability, stemming from differences in solvent systems, column materials, sample preparation, and operational definitions of the SARA fractions [22]. Such discrepancies can lead to inconsistent SARA values, which may complicate compatibility assessments and hinder data comparability across different institutions or studies.

These challenges underscore the ongoing need for methodological standardization, robust quality control protocols, and clear reporting practices to ensure data reliability and enhance the utility of SARA analysis in both research and industrial applications.

A higher Colloidal Instability Index (CII) indicates an increased risk of asphaltene precipitation, reflecting a chemical imbalance between precipitating components—primarily saturates and asphaltenes—and peptizing components, such as aromatics and resins [19]. The CII is calculated using the relative mass fractions of the SARA components, and it offers a more chemically grounded assessment of a crude oil's colloidal stability than empirical methods alone.

In parallel, the Resin-to-Asphaltene (R/A) ratio serves as another critical stability indicator. A higher R/A ratio typically correlates with enhanced asphaltene dispersion, as it implies a sufficient concentration of resins capable of adsorbing onto asphaltene aggregates and preventing their flocculation. Conversely, a low R/A ratio suggests that the stabilizing capacity of the crude may be insufficient, especially under stress conditions such as mixing, cooling, or pressure changes.

These SARA-derived indices, such as CII and R/A ratio, provide a more nuanced and chemically-informed prediction of crude oil compatibility, particularly when compared to empirical parameters like the P-Value [32]. They offer insights into the underlying intermolecular forces including π–π interactions, van der Waals forces, and steric effects that govern asphaltene stability in complex crude oil matrices. Such understanding becomes particularly vital in crude blending operations, where compatibility mismatches can result in severe operational issues such as precipitation, fouling, and pipeline blockages.

Beyond compatibility assessment, SARA analysis also informs key refining concerns such as: Coking tendency: Higher asphaltene or resin content increases coke formation during thermal processes.

Catalyst deactivation: Heavy metal-containing asphaltenes can poison catalysts used in hydro processing.

Product quality: Variations in aromaticity and saturate levels influence the yields and properties of refined fractions [33,34].

Thus, integrating SARA-based metrics with operational knowledge enables more informed feedstock selection, enhances refining efficiency, and mitigates risks associated with asphaltene instability.

1.1.6 The KUOP factor: Refining Predictive fashions

While SARA analysis and its associated indices—such as the Colloidal Instability Index (CII) and the Resin-to-Asphaltene (R/A) ratio—represent significant advancements in the assessment of crude oil compatibility, they are not without limitations in fully capturing the complex, non-linear behaviour exhibited by all crude oil blends [35,36]. The inherent variability in crude oil composition—stemming from geographical origin, maturity, and the presence of unconventional feedstocks—means that broad classifications and ratio-based indices may fall short in reliably predicting stability, especially when dealing with challenging or highly incompatible crude oils [17,37].

This complexity arises from the intricate intermolecular interactions among hydrocarbons and heteroatomic compounds, which are not always adequately described by simple bulk compositional metrics. For example, two crude oils may present similar SARA profiles but display markedly different behaviour when blended, due to subtle differences in molecular architecture, trace metal content, or functional group distribution.

Recognizing these nuances, researchers and industry practitioners have increasingly explored the development of more refined predictive tools. One such advancement is the Kuop factor (or Kuop index) a composite parameter that integrates a broader range of physicochemical properties, including density, aromaticity, viscosity, and boiling point distribution [17]. The Kuop factor aims to offer a more robust and comprehensive evaluation of crude oil compatibility, moving beyond purely compositional indicators to consider thermodynamic and molecular interaction potentials.

The continued pursuit of such integrated, multi-parameter models reflects a growing recognition that no single index can universally predict compatibility outcomes across the wide spectrum of crude oils encountered in modern refining operations. As blending strategies grow increasingly complex due to economic and logistical drivers, the need for hybrid models—combining empirical, compositional, and physicochemical data becomes ever more critical.

The Kuop factor, also known as the UOP K-value or Watson characterization factor (Kw), is a well-established parameter in petroleum engineering widely used to characterize the paraffinic or aromatic nature of crude oils and their fractions [5]. Originally developed for process design applications—such as predicting product yields and behaviour during refining—its utility has since been extended to address challenges related to crude oil compatibility.

The Kuop factor is empirically calculated using the following formula:

$K(UOP) = (3\sqrt{Tb}) / SG$

Where:

TB is the cubic average boiling point of the crude oil in degrees Rankine (∘R) [5].

SG60/60 is specific gravity at 60∘F/60∘F.

Interpretation of the Kuop factor is straightforward:

A higher Kuop value (typically above 12.5) indicates a more paraffinic crude, characterized by a higher content of straight-chain and branched alkanes. Conversely, a lower Kuop value (below 10) corresponds to a more aromatic or naphthenic crude [5].

In the context of crude oil compatibility, the Kuop factor offers critical insights. A highly paraffinic crude (high Kuop factor) tends to act as a strong precipitant for asphaltenes when blended with other crudes rich in asphaltenes but deficient in peptizing resins, thereby increasing the risk of destabilization and precipitation. On the other hand, more aromatic crudes (low Kuop factor) generally exhibit better solvency power for asphaltenes, promoting greater blend stability [11,38].

The expanded use of the Kuop factor in compatibility assessment stems from the understanding that the crude's "character", as reflected by this factor, directly influences its solvency capability [39]. While the P-value offers an empirical measure of asphaltene flocculation onset and SARA analysis provides detailed compositional breakdowns, the Kuop factor uniquely integrates bulk physical properties such as average boiling point and density—which correlate with the molecular size and chemical nature distribution within the crude.

This integration allows for a more holistic evaluation of the crude's inherent solvency and its interactive behaviour when blended with other crudes. For example, a crude possessing both a high asphaltene content and a high Kuop factor (indicating strong paraffinic character) would typically be flagged as particularly challenging to blend with other asphaltenic crudes, due to the poor solvency offered by its continuous phase.

1.1.7 Interdependence, challenges, and the point of interest of modern-day studies

In the intricate domain of crude oil refining, it is unequivocally evident that no single parameter can serve as a comprehensive solution to the complex challenge of crude oil compatibility. The P-value offers a rapid, empirical snapshot of a crude's inherent stability, serving effectively as an initial "pass/fail" screening tool [31]. In contrast, SARA analysis, through its detailed compositional breakdown and derived indices such as the Colloidal Instability Index (CII), provides a far more chemically informed perspective by elucidating the molecular-level interplay between dispersing and precipitating forces within the crudev[40,41]. The Kuop factor adds another dimension of refinement by integrating a broader spectrum of physicochemical properties, thereby enhancing the predictive accuracy of compatibility assessments [5]. Together, these parameters each contribute unique, complementary insights—no single metric alone can capture the full complexity of crude oil behaviour.

The synergistic application of these metrics is thus paramount. While the P-value offers a quick screening, a deeper examination of SARA fractions can clarify the underlying reasons for the observed stability or instability and quantify specific risks. For example, a low P-value often correlates with a high CII derived from SARA data, indicating an excess of saturates relative to peptizing resins and aromatics conditions conducive to asphaltene precipitation. Furthermore, a high Kuop factor, indicating a paraffinic crude, typically corresponds with elevated saturate content in SARA results, providing additional explanation for its propensity to destabilize asphaltenes. In this framework, the Kuop factor serves as a sophisticated integrator, often synthesizing SARA data with other physicochemical properties to yield a more holistic and predictive evaluation.

These integrative insights pave the way for the development of advanced, reliable models for crude oil blending optimization. Such models may form the foundation for next-generation machine learning algorithms capable of predicting compatibility in real-time, ultimately enhancing operational efficiency, minimizing fouling, and maintaining product quality across the global petroleum refining industry. The comprehensive understanding gained through this multifaceted analysis is essential for managing the complexities of modern crude oil blending, ensuring the long-term stability, profitability, and environmental sustainability of refinery operations.

1.2 Materials & Methods

In this study, the SARA (Saturates, Aromatics, Resins, and Asphaltenes) composition of crude oils was analyzed using the Thin Layer Chromatography with Flame Ionization Detection (TLC-FID) technique. This method provides a rapid and quantitative approach to determine the relative proportions of the major crude oil fractions, which are critical for assessing crude compatibility and stability.

1.2.1 Crude Oil Blends for SARA Analysis

A blend of three distinct crude oils, each mixed in equal weight percentages, was prepared for SARA characterization. The individual crude oils were selected based on their API gravity values to represent a broad spectrum of crude types:

Light Crude Oil (LCO): API gravity of 33.5°

Medium Crude Oil (MCO): API gravity of 24.0°

Heavy Crude Oil (HCO): API gravity of 17.5°

This blend was analysed to determine its overall SARA distribution and to understand how blending crudes of varying densities impacts the colloidal stability and solvency properties.

1.2.2 Extended Dataset for Correlation Study

To establish robust correlations among key crude oil compatibility parameters—namely the Colloidal Instability Index (CII), Kuop factor (Kw), and P-value—a comprehensive dataset comprising fifteen crude oils was utilized. These crudes span a wide range of API gravities and are designated as CO01 through CO15, with the following API values:

Crude Name	API Gravity (°API)
CO01	13.9
CO02	14.7
CO03	17.5
CO04	20.9
CO05	21.1
CO06	22.0
CO07	25.4
CO08	28.2
CO09	30.3
CO10	30.6
CO11	32.7
CO12	35.3
CO13	39.2
CO14	40.6
CO15	42.7

Table 1.1: Crude Oil Samples and Their API Gravity

This dataset enabled a detailed evaluation of how crude oil physical properties, molecular composition, and empirical stability parameters interact across a wide spectrum of crude types. Through statistical analysis of the TLC-FID derived SARA fractions and their corresponding CII, Kuop, and P-value measurements, predictive relationships were developed, enhancing the ability to forecast compatibility and optimize crude blending strategies.

1.2.3 Density & API

The ASTM D1298 standard establishes a rigorously structured hydrometer method for determining the density, relative density (specific gravity), or API gravity of crude oils and other petroleum liquids. This well-defined procedure is deeply rooted in meticulous temperature control and systematic corrections to ensure precision and repeatability.

Initially, both the sample and hydrometer are equilibrated to a specified temperature and transferred carefully into a calibrated hydrometer cylinder. Once thermal equilibrium is reached, the hydrometer reading is recorded from the scale, followed immediately by the measurement of the sample's temperature [10]. Any observed hydrometer reading undergoes essential corrections—accounting for the meniscus effect, the thermal expansion of glass, and any calibration temperature deviations—before being adjusted via Petroleum Measurement Tables to the reference temperature of 60 °F (15 °C)

To enhance accuracy under unstable thermal conditions, the hydrometer cylinder may be placed in a constant-temperature bath, and the measurement process repeated until temperature fluctuations remain within ±0.5 °C a threshold ensuring high fidelity in readings

The resultant API gravity (°API) value is calculated using the formula:

$$API = \frac{141.5}{SG} - 131.5$$

where SG represents specific gravity of petroleum liquid (measured at 60°F).

The significance of this method extends far beyond laboratory instrumentation it plays a critical role in volume-to-mass conversions, impacting both the valuation and custody transfer of petroleum products

Though API gravity serves as a key parameter in commercial and regulatory contexts, it is understood that it is only one component in assessing crude quality and must be correlated with other parameters for a truly comprehensive evaluation.

API gravity is commonly measured using the following techniques (Paliukaite et al., 2014):

Hydrometer Method:

This traditional technique uses a hydrometer, a weighted glass instrument that floats in the petroleum liquid. The depth to which the hydrometer sinks depends on the density of the fluid. By reading the scale on the hydrometer at the liquid surface, the specific gravity (density relative to water) is determined. This value is then converted into API gravity using the standard formula. This method is simple, cost-effective, and widely used in field conditions, though it may be less precise for very light or heavy oils.

Pycnometer Method:

The pycnometer is a laboratory device consisting of a precise volume container, usually made of glass. By measuring the weight of the pycnometer filled with the petroleum sample and comparing it with the weight when filled with distilled water, the exact density of the oil can be calculated. This method offers high accuracy and is typically used when precise measurements are required, such as in research or quality control laboratories.

Digital Density Meters (Oscillating U-Tube Method):

Modern digital density meters employ an oscillating U-shaped tube filled with the oil sample. The frequency of oscillation changes with the mass of the fluid inside the tube. Since the volume of the tube is constant, this frequency shift can be used to calculate the density with high precision. This technique is fast, requires minimal sample preparation, and is widely used in industrial laboratories for routine density and API gravity measurements.

Refractometry:

This indirect method measures the refractive index of the petroleum liquid, which is related to its composition and density. By passing light through the sample and measuring the angle of refraction, the refractive index is obtained. Using empirically derived correlations, the refractive index can be converted into an estimate of the density and, consequently, the

API gravity. While less direct than other methods, refractometry can be useful for rapid screening or when only small sample volumes are available.

API gravity values play a crucial role in classifying crude oil types, as they provide insight into the oil's density and quality (Asemani et al., 2020; Nazar et al., 2008). Lighter oils typically have higher API gravity values, indicating lower density and often higher value due to better refining characteristics. Conversely, heavier oils have lower API gravity values, signifying higher density and usually more complex processing requirements.

API Gravity (°API)	Type of Crude Oil	Characteristics
< 10	Extra heavy crude	Denser than water, does not float
10-22.3	Heavy Crude	High viscosity, difficult to refine
22.3-31.1	Medium Crude	Moderate viscosity widely used
>31.1	Light Crude	Low viscosity, high refining efficiency

Table 1.2: API of Crude Oil

1.2.4 P-Value

The Automated Stability Analyzer, manufactured by Zematra, utilizes the SMS 1600 method for determining the P-value of crude oil samples. In this method, a 10-gram sample of crude oil is placed into a titration beaker and titrated with n-heptane (also referred to as n-cetane). The process employs an optical detection device called an optrode to monitor the flocculation of asphaltenes.

Figure 1.1: P-Value Stability Analyser

During titration, n-heptane is gradually added to the crude oil sample. The volume of n-heptane added per gram of crude oil at the point just before asphaltene flocculation occurs is recorded as

. The P-value is then calculated using the equation:

$$\text{P-value}=1+X\ \text{min}$$

Where X min is the volume of n-heptane added per 1 gm of crude oil can be diluted until it just does not flocculate the asphaltene.

The sample is diluted incrementally with n-heptane at 10-minute intervals, and the optical probe continuously monitors for the presence of flocculated asphaltenes. When flocculation is detected, the titration stops, and the software calculates the P-value based on the recorded volume of n-heptane. This method provides a rapid and precise measurement of asphaltene stability in crude oils, which is crucial for predicting and managing deposition problems during production and processing.

1.2.5 SARA

1.2.5.1 TLC-FID coefficient for SARA analysis for crude oil & it's heavy fraction

In this study, three different crude oil blends with varying API gravities Light Crude Oil (LCO), Medium Crude Oil (MCO), and Heavy Crude Oil (HCO) were used. A weighed quantity of each crude oil sample (less than 100 mL) was distilled using an ASTM D86 apparatus to fractionate the crude oil into two fractions: The Initial Boiling Point (IBP) to 204°C cut, and the 204°C+ residue.

The 204°C+ residue fraction was used for the determination of SARA (Saturate, Aromatic, Resin, Asphaltene) coefficients. Asphaltene analysis was performed on the residue fraction following the ASTM D6560 standard method to isolate the pure asphaltene fraction. The remaining maltene fraction was then subjected to chromatographic separation to isolate saturates, aromatics, and resins.

Chromatographic separation was conducted by eluting the maltene fraction through a column using successive solvents: n-heptane for saturates, toluene for aromatics, and a mixture of toluene and methanol for resins. After each elution, the solvents were evaporated to recover the individual component fractions. Multiple elution cycles were performed to improve the purity of the SARA fractions.

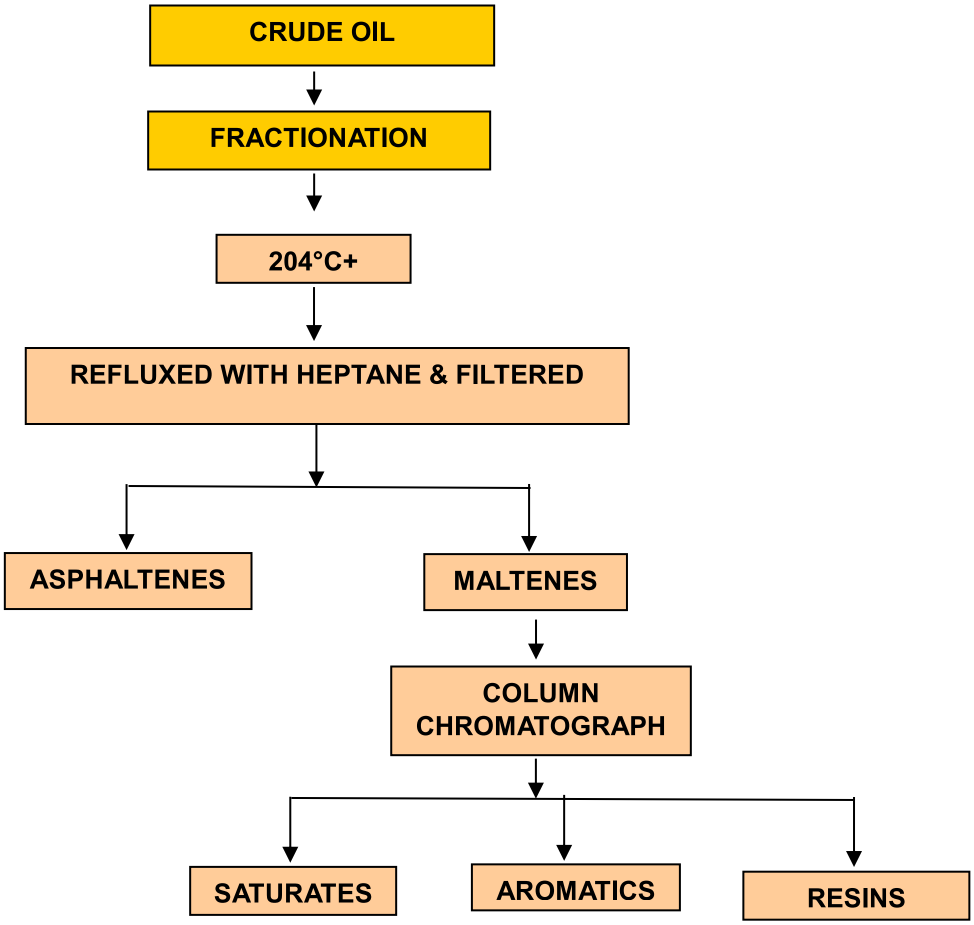

Figure 1:2: SARA Analysis Scheme

1.2.5.2 Thin Layer Chromatography Flame Ionization Detector (TLC-FID)

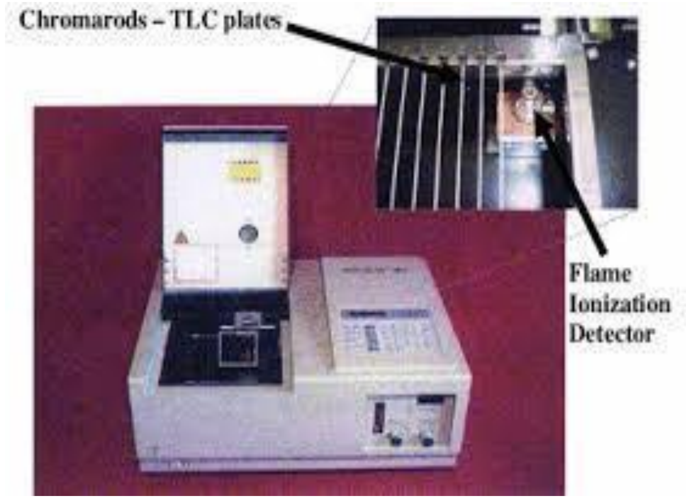

Figure 1:3: TLC-FID set up

The analysis of SARA components of crude oil is obtained by using TLC-FID on a latroscan MK-6S system. Residual fuel and crude oil sample 1% concentrated solution make in dichloromethane. The hydrogen gas flow rate was maintained at 160 mL/min, while the air flow rate was maintained at 2 L/min of air. Silica-coated quartz Chromarods were detected with a 1 μL solution. The data was guaranteed to be reliable and precise by spotting each SARA standard with a single concentration on all 10 Chromarods. Following this, the chromarods were placed in an oven at 80°C for a duration of 5 minutes. In order to elute the saturate components, the chromarods were maintained in n-heptane at a height of 100mm for 35 minutes. Immediately following n-heptane elution, the Chromarods were incubated in an oven at 80°C for 5 minutes. to elute aromatic components, the chromarods were maintained in toluene at a 50 mm height. For the purpose of solvent evaporation, the chromarods were once more deposited in an oven at 80°C for a duration of 10 minutes. To elute the resin components, the chromarods were maintained in a 25mm-high mixture of dichloromethane and methanol (95:5) following this stage. The asphaltene components do not elute and hence persist at the bottom of the Chromarods. The chromarods are deposited in an oven at 80°C for 10 minutes after the elution procedure has been completed. The chromarods were inserted into the Iatroscan for FID analysis after drying.

1.2.6 Colloidal Instability Index (CII)

Beyond the quantitative separation of crude oil into Saturates, Aromatics, Resins, and Asphaltenes (SARA) fractions, these compositional data form the basis for deriving advanced indices that assess crude oil stability and compatibility. One of the most widely applied parameters in this context is the Colloidal Instability Index (CII), which quantitatively evaluates the propensity of asphaltene precipitation by considering the relative proportions of the four SARA fractions[34].

The CII is defined as the ratio of the sum of destabilizing components—Saturates and Asphaltenes to the sum of stabilizing components Aromatics and Resins as shown in the equation:

CII = Saturates (wt%) + Asphaltenes (wt%) \ Aromatics (wt%) + Resins (wt%)

Saturates and asphaltenes tend to promote aggregation and precipitation due to their non-polar and high molecular weight characteristics, respectively. Conversely, aromatics and resins act as natural dispersants and stabilizers, preventing asphaltene flocculation by solvating or adsorbing onto asphaltene aggregates (Gray et al., 1999; Speight, 2014). Therefore, a higher CII value indicates a greater likelihood of colloidal instability and asphaltene precipitation, which can lead to operational challenges such as pipeline fouling and reservoir plugging (Larter et al., 2005). This index is widely used in both research and industry to predict crude oil behaviour during production and refining processes, providing a valuable tool for designing treatment strategies and optimizing processing conditions (Al-Sabagh et al., 2012).

1.2.7 Hight Temperature Simulated Distillation

The Agilent 780B Gas Chromatograph was utilized to perform the boiling point distribution analysis according to the ASTM D7169 method. This method employs an inlet and a capillary column operated under a programmed temperature gradient to separate the hydrocarbon fractions of the crude oil sample.

Figure 1.4: High Temperature Simulated Distillation Gas Chromatography

The procedure begins with the injection of the prepared sample solution into the chromatograph. The retention times of the individual sample components are converted to boiling point temperatures using established calibration data. Subsequently, response factors are applied to quantify the recovered amounts of each fraction. This enables the determination of the boiling point distribution of the sample up to the total recovered amount.

The ASTM D7169 method has been extended to cover a higher final boiling point range, from the Initial Boiling Point (IBP) up to 750°C, facilitating a more comprehensive characterization of heavy hydrocarbons. For sample preparation, approximately 0.2 g of crude oil is accurately weighed and diluted in 10 g of carbon disulphide (CS_2) to prepare the injection solution. A 1 µL aliquot of this solution is injected into the column. The initial column temperature is set at 100°C, with a controlled heating rate of 15°C per minute throughout the analysis. Helium is employed as the carrier gas to ensure efficient separation of components. This method provides detailed boiling point distribution profiles critical for understanding crude oil composition and refining behaviour.

1.2.8 Spot Method

The spot method relies on the visual observation of a crude oil (or crude blend) sample absorbed onto a filter paper. Asphaltenes, which are highly polar and insoluble components of crude oil, are kept dispersed by other components like resins. When incompatible crude oils are blended, or when conditions change, this delicate balance can be disrupted, causing asphaltenes to flocculate and precipitate. In-house method developed for analysing crude compatibility. In this method neat crude oil heated at 60℃ for 10 minutes and spotted on Whatman filter paper by dropper. Spotted filter paper dried in oven at 60℃ for 15 minutes.

1.2.9 High Performance Liquid Chromatography (HPLC)

For this study, an Agilent 1200 Series Isocratic HPLC system was employed. The sample preparation involved using a filtered and moisture-free sample. Approximately 0.9 g to 1.1 g of the sample was accurately weighed into a 10 mL volumetric flask, diluted to the mark with n-heptane, and thoroughly mixed by shaking. The solution was then allowed to stand for 10 minutes to ensure complete dissolution. If any insoluble material remained, the solution was filtered before analysis.

A 10 µL aliquot of the prepared sample was injected into the HPLC polar column. The analysis was carried out under isocratic conditions using n-heptane as the mobile phase at a flow rate of 1 mL/min. The column temperature was maintained at 35 °C, and detection was performed using a refractive index detector (RID).

Due to their inherent selectivity, aromatic hydrocarbons were effectively separated from non-aromatic hydrocarbons, producing distinct peaks that correspond to their unique ring structures. As the analytes eluted from the column, the RID detected changes in refractive index, and the electronic signals were continuously recorded by the data processor. Finally, the signal amplitudes obtained from the aromatic compounds in the sample were compared against those from the calibration standard, ensuring accurate quantification.

1.3 Results & Discussion

The quantification of asphaltenes in crude oil was performed in accordance with the ASTM D6560 standard method, as presented in Figure 1.2. Upon removal of the asphaltene fraction, the remaining maltenes were subjected to further separation using column chromatography. The chromatographic setup consisted of a glass column measuring 1150 mm in length, with an internal diameter of 15 mm and a bulb capacity of 500 mL, which was sufficient to accommodate a 10 g crude oil sample. The column was packed with a stationary phase comprising activated alumina oxide (100 mesh size) and FIA-grade silica gel, ensuring efficient retention and fractionation of the maltenes.

The separation of maltenes into saturates, aromatics, and resins (SAR fractions) was achieved through a sequential solvent extraction protocol. Initially, the saturate fraction was eluted with n-heptane, as its non-polar character effectively dissolves and mobilizes saturate hydrocarbons. This was followed by the elution of the aromatic fraction using toluene, a moderately polar solvent well-suited for aromatic compounds. Finally, the resin fraction was isolated by introducing a binary solvent mixture of toluene and methanol (1:1 v/v), which facilitated the recovery of the more polar constituents. Following solvent evaporation, the purified SAR fractions were obtained and subsequently analysed. Together with the asphaltenes, these fractions are collectively referred to as the SARA components, as schematically represented in Figure 1.5.

The effectiveness of the fractionation process was evaluated using Thin Layer Chromatography–Flame Ionization Detection (TLC-FID). The results, shown in Figure 1.5, revealed distinct retention times (RTs) for each fraction: saturates at 0.1 s, aromatics at 0.3 s, resins at 0.4 s, and asphaltenes at 0.5 s. The clear separation of retention times confirmed the reliability of the applied method. Furthermore, the saturate fraction exhibited a pronounced and sharp peak, often referred to as a "hump", which is characteristic of naphthenic hydrocarbons and indicative of its high purity. In contrast, the aromatic, resin, and asphaltene fractions demonstrated well-defined peaks without overlapping features, thereby confirming the successful and precise resolution of all four SARA components.

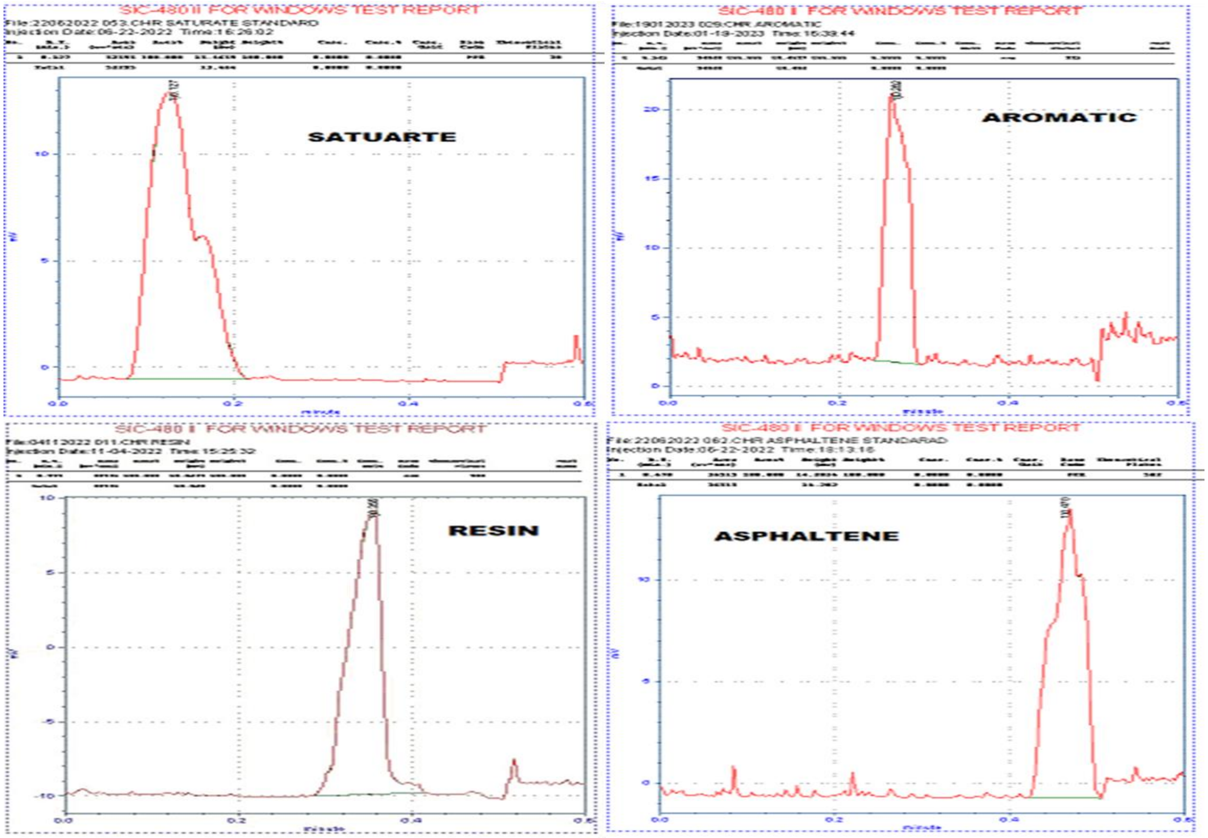

Figure 1:5: TLC-FID graph for SARA

Distillation (°C)	Saturates	Aromatics	Resin	Asphaltene
Initial Boiling Point (IBP)	328.5	265.0	295.0	493.0
5 wt.% Recovered at	515.5	368.0	515.0	540.0
10 wt.% Recovered at	540.0	437.5	539.5	560.5
20 wt.% Recovered at	561.5	528.0	568.0	618.5
30 wt.% Recovered at	576.0	562.0	594.5	***
40 wt.% Recovered at	589.0	588.5	624.0	***
50 wt.% Recovered at	602.0	615.5	657.5	***
60 wt.% Recovered at	615.5	644.5	705.0	***
70 wt.% Recovered at	631.0	678.0	***	***
80 wt.% Recovered at	651.0	717.5	***	***
90 wt.% Recovered at	681.5	***	***	***
95 wt.% Recovered at	704.0	***	***	***
Final Boiling Point (FBP)	737.0	***	***	***
Recovery @ 750°C	***	84.5	64.8	29.4

Table 1:2: HTSD of individual SARA fractions

According to the results obtained from ASTM D7169 high-temperature simulated distillation (HTSD), the separated SARA fractions exhibited distinct boiling point distributions, thereby validating the effectiveness of the applied fractionation methodology. As presented in Table 2, the saturate fraction was completely distilled within the HTSD range, which is consistent with its composition of relatively lighter hydrocarbons possessing lower boiling points. In contrast, the aromatic, resin, and asphaltene fractions displayed progressively lower recovery rates at the maximum HTSD temperature of 750 °C, with values of 84.5% for aromatics, 64.8% for resins, and only 29.4% for asphaltenes.

This systematic variation in distillation behaviour directly reflects the increasing molecular weight, polarity, and structural complexity of the fractions. The observed trend establishes a clear hierarchy, wherein saturates represent the lightest and most volatile constituents, followed sequentially by aromatics and resins, while asphaltenes comprise the heaviest, most condensed, and thermally stable fraction. Such a gradation confirms the characteristic order of molecular complexity and thermal stability among SARA components: Saturates < Aromatics < Resins < Asphaltenes. This finding is in strong agreement with the established physicochemical understanding of crude oil fractions, thereby reinforcing both the reliability of the separation technique and the accuracy of the HTSD analysis.

Sr. No.	**Known Blend %**			
	Saturate	**Aromatic**	**Resin**	**Asphaltene**
Set-I	48.1	33.0	13.3	5.6
Set-II	79.8	15.0	5.0	0.2
Set-III	30.0	45.0	20.0	4.9
Set-IV	15.0	55.0	20.0	10.0
Set-V	10.0	40.0	30.0	20.0

Table 1:3: Different proportion of SARA fraction for blend

Sr. No.	**Obtained Area**				
	Saturate	**Aromatic**	**Resin**	**Asphaltene**	**Total**
Set-I	18581	9861	13276	4309	46027
Set-II	30097	3780	5576	228	39680
Set-III	11231	25208	19647	5481	61567
Set-IV	5834	21632	19469	9436	56371
Set-V	4123	12696	19004	12803	48626

Table 1:4: SARA fractions obtained area on TLD-FID

Sr. No.	**Contributed %**				
	Saturate	**Aromatic**	**Resin**	**Asphaltene**	**Total**
Set-I	0.4035	0.2142	0.2886	0.0937	1.0000
Set-II	0.7580	0.0951	0.1413	0.0056	1.0000
Set-III	0.1824	0.4096	0.3190	0.0890	1.0000
Set-IV	0.1034	0.3843	0.3447	0.1676	1.0000
Set-V	0.0849	0.2604	0.3910	0.2637	1.0000

Table 1:5: SARA fractions contributed %

To establish reliable calibration parameters for TLC-FID analysis, the purified SARA fractions were blended in five distinct proportions, as outlined in Table 3. Each blend was carefully formulated by systematically varying the ratios of Saturates, Aromatics, Resins, and Asphaltenes, thereby enabling the development of a robust calibration model for quantitative determination.

The TLC-FID analysis of these calibration blends produced distinct peak areas for each SARA component, as reported in Table 4. For every blend, the peak area corresponding to each fraction was measured, and the cumulative area of the entire blend was determined. Subsequently, the area of each individual fraction was divided by the total blend area to calculate the relative response factor (RRF), also referred to as the calculated coefficient, for each SARA component.

The analysis revealed notable trends in detector response behaviour. The coefficients for saturates and resins remained highly consistent across all five calibration sets, underscoring the stability and reproducibility of detector sensitivity for these fractions. In contrast, the coefficients for asphaltenes exhibited only minor fluctuations, whereas the aromatic fraction demonstrated a comparatively higher degree of variability, with coefficient values ranging from 0.0018 to 0.0038. This variation suggests that the detector response is particularly sensitive to subtle compositional differences within the aromatic fraction, likely due to the structural diversity of its constituents.

To obtain reliable calibration factors, the coefficients derived from all blends were averaged for each SARA fraction. These average values were then normalized to the total coefficient sum, resulting in a final set of normalized TLC-FID response factors. The normalized values were determined to be 0.0034 for saturates, 0.0037 for aromatics, 0.0013 for resins, and 0.0016 for asphaltenes. These response factors constitute a critical calibration dataset, providing the basis for accurate quantification and comparative evaluation of SARA fractions in unknown crude oil samples.

1.3.1 Validation of Coefficient

Following the confirmation of calibration parameters through established verification procedures (Figure 1.6), the same calibration blend was subjected to TLC-FID analysis. The resulting chromatographic profiles, shown in Figure 1.5, demonstrated a high degree of analytical performance and method reliability. Notably, the technique exhibited exceptional repeatability, with deviations consistently maintained within ±1% across replicate measurements.

This level of reproducibility is highly significant, as it falls well within the generally accepted limits for analytical method validation recommended by organizations such as ASTM International and the International Union of Pure and Applied Chemistry (IUPAC), where repeatability below 2% is typically considered acceptable for chromatographic methods. The ≤1% repeatability observed in this study therefore confirms not only the robustness of the TLC-FID methodology but also the validity of the calibration approach established using SARA fraction blends.

Furthermore, the consistency of the profiles highlights the ability of TLC-FID to effectively resolve compositional variations among the different SARA fractions without compromising quantitative precision. This robustness is particularly valuable in crude oil characterization, where subtle differences in SARA composition can significantly influence refining behaviour, processing efficiency, and product yield. Thus, the observed repeatability reinforces the analytical reliability, industrial relevance, and scientific credibility of TLC-FID as a quantitative tool for SARA analysis.

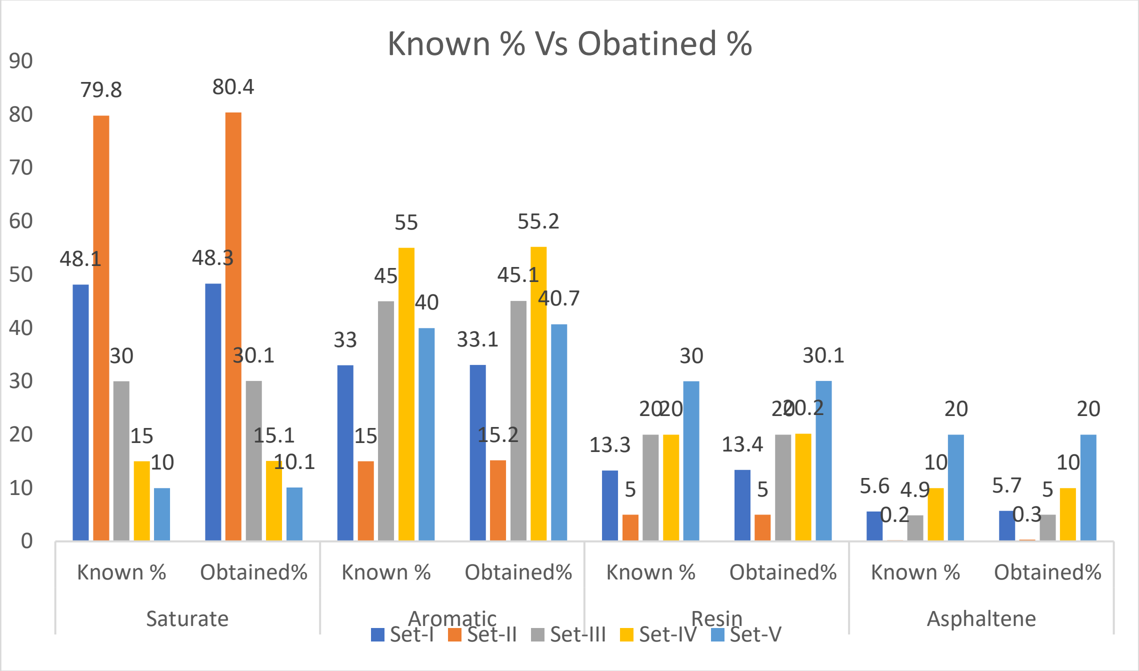

Figure 1:6: SARA verification known vs obtained %

To validate the accuracy of the TLC-FID response factors, the prepared SARA calibration blends were analysed using established reference methods (Figure 6). The TLC-FID results obtained from these blends were directly compared against known standard values in order to evaluate consistency and reliability. The comparative analysis, presented in Figure 6, demonstrated a high level of agreement between the TLC-FID–derived values and the reference data. The observed variation was consistently within ±1%, confirming the excellent repeatability, robustness, and analytical precision of the TLC-FID technique. These findings underscore the reliability of the calibration coefficients derived from the blended sets and affirm the suitability of TLC-FID for the accurate quantification of SARA fractions in crude oil.

To further strengthen the validation of the derived response factors, the saturate and aromatic fractions were cross-examined using High-Performance Liquid Chromatography (HPLC) in accordance with IP 391. This comparison served as an additional benchmark, enabling the precision of TLC-FID–derived coefficients to be assessed against a well-established and widely recognized analytical methodology. As shown in Table 6, the deviations between TLC-FID and HPLC results were found to be less than 3% for both saturates and aromatics. Notably, this deviation remained consistent across repeated measurements, indicating no significant systematic discrepancies between the two techniques.

The close agreement observed between TLC-FID and HPLC outcomes provides strong evidence of the methodological reliability and precision of TLC-FID, particularly for the quantification of saturates and aromatics. By aligning with the performance of a validated reference method, TLC-FID is confirmed as a dependable analytical tool for SARA characterization. Moreover, the integration of TLC-FID with cross validation procedures enhances the credibility of the overall analytical framework, ensuring that the results obtained are both scientifically robust and industrially relevant for crude oil analysis.

Verification of factor (TLC-FID VS HPLC (IP391)				
Sample	TLC-FID		HPLC (IP391)	
	Saturate	Aromatic	Saturate	Aromatic
Known Blend	25.6	74.4	27.9	72.1
	25.3	74.7	28.1	71.9
	25.0	75.0	28.0	72.0
	25.4	74.6	27.9	72.1

Table 1:6: Saturate and aromatic coefficient verification by HPLC

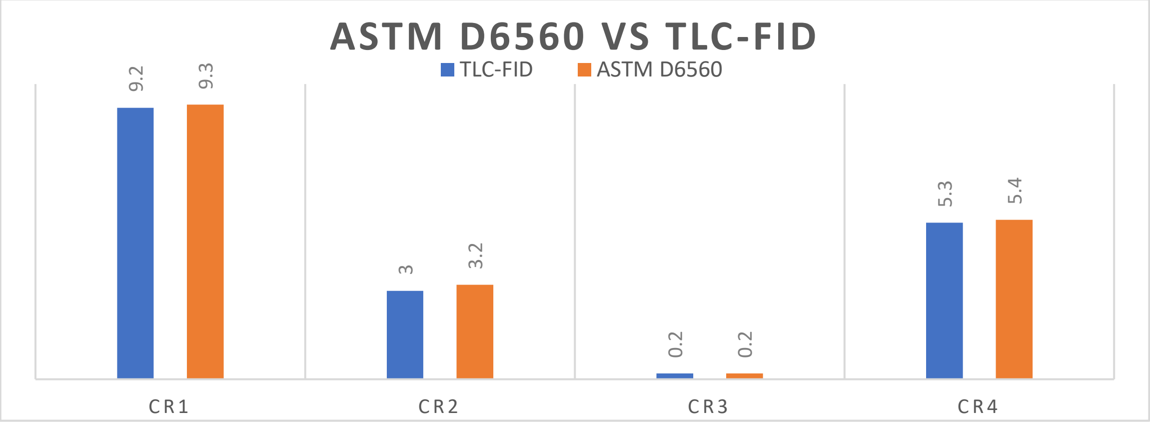

Figure 1:7: Asphaltene verified by ASTM D6560 Vs TLC-FID

The asphaltene response coefficient obtained through TLC-FID was further validated against the standard gravimetric procedure specified in ASTM D6560. To ensure the robustness and applicability of the method across diverse feedstocks, four crude oil samples with varying asphaltene contents were selected for verification.

As presented in Figure 7, the asphaltene concentrations determined using TLC-FID exhibited excellent agreement with those obtained from the ASTM D6560 method. The deviations between the two techniques were consistently within ±0.2%, indicating minimal variation and confirming the high accuracy and reproducibility of the TLC-FID–derived response coefficient.

These results provide strong evidence that, when appropriately calibrated, TLC-FID can serve as a reliable and precise alternative to gravimetric methods for asphaltene quantification. Moreover, the consistency of results across crude oils of differing compositions underscores the robustness and versatility of TLC-FID, reinforcing its suitability for the comprehensive analysis of SARA fractions in both research and industrial applications.

1.3.4 Co-relation between CII, P-Value & KUOP factor.

Sr. No.	**Crude Name**	**Saturates (Wt. %)**	**Aromatics (Wt. %)**	**Resin (Wt. %)**	**Asphaltene (Wt. %)**	**Asphaltene/Aromatic-Resin**	**KUOP**	**CII**	**P-Value**	**API**
1	CO1	25.8	38.8	25.7	9.5	0.15	11.57	0.55	1.95	13.9
2	CO2	33.8	42.2	17.3	6.7	0.11	11.25	0.68	2.15	14.7
3	CO3	38.3	32.4	17.9	11.5	0.23	11.55	0.99	1.65	17.5

4	CO4	35.7	36.3	21.0	7.1	0.12	11.66	0.75	2.25	20.9
5	CO5	35.5	37.2	20.1	7.2	0.13	11.64	0.75	1.25	21.1
6	CO6	40.5	33.5	20.7	5.2	0.10	11.72	0.84	2.25	22.0
7	CO7	32.4	47.2	14.2	6.2	0.10	11.61	0.63	1.45	25.4
8	CO8	46.8	42.4	8.7	2.1	0.04	11.73	0.96	1.45	28.2
9	CO9	53.7	33.1	11.0	2.2	0.05	11.92	1.27	1.35	30.3
10	CO10	75.7	15.5	8.5	0.3	0.01	12.42	3.16	1.25	30.6
11	CO11	48.6	41.3	8.0	2.1	0.04	11.87	1.03	1.45	32.7
12	CO12	74.4	19.7	5.6	0.3	0.01	12.25	2.95	1.05	35.3
13	CO13	66.3	25.9	7.5	0.3	0.01	12.02	2.00	1.05	39.2
14	CO14	62.5	30.2	7.0	0.3	0.01	11.98	1.69	1.05	40.6
15	CO15	72.8	20.8	6.1	0.3	0.01	11.95	2.71	1.05	42.7

Table 1:7: SARA, KUOP, CII, P-Value & API of fifteen different crude oils

As shown in Table 1.7, crude oils with a relatively higher API gravity are characterized by elevated values of the Crude Instability Index (CII), KUOP factor, and saturate content. In contrast, the proportions of aromatics, resins, and asphaltenes (ARA fractions), as well as their associated ratios, are significantly lower in these lighter crudes. Conversely, crudes with lower API gravity exhibit higher concentrations of aromatics, resins, and asphaltenes, together with an increased P-value, reflecting their heavier and more structurally complex molecular composition.

This inverse relationship highlights the intrinsic differences in chemical character between light and heavy crude oils. Higher-API crudes, being richer in saturates, generally exhibit better stability and higher hydrogen-to-carbon ratios, which translates into greater refining efficiency and higher yields of valuable distillates (Speight, 2014) [5]. In contrast, lower-API crudes, enriched in aromatics, resins, and particularly asphaltenes, are associated with poorer stability, higher tendency toward fouling, and reduced processability (Yen & Chilingarian, 1994). The elevated ARA content in these heavy crudes has been widely reported to contribute to challenges such as coke formation, sludge precipitation, and instability during blending (Leontaritis & Mansoori, 1987).

Furthermore, the observed correlation between API gravity and compositional ratios underscores the practical significance of SARA characterization in predicting crude oil behavior during refining. A higher proportion of saturates and elevated KUOP factor in light crudes indicates their suitability for producing lighter fractions such as gasoline and kerosene, whereas the abundance of aromatics and resins in heavier crudes necessitates more severe upgrading processes (e.g., hydrocracking, coking) to achieve comparable yields. Thus, the present findings not only validate the established inverse relationship between API gravity and ARA content but also emphasize the critical role of compositional analysis in guiding refinery selection, blending strategies, and process optimization.

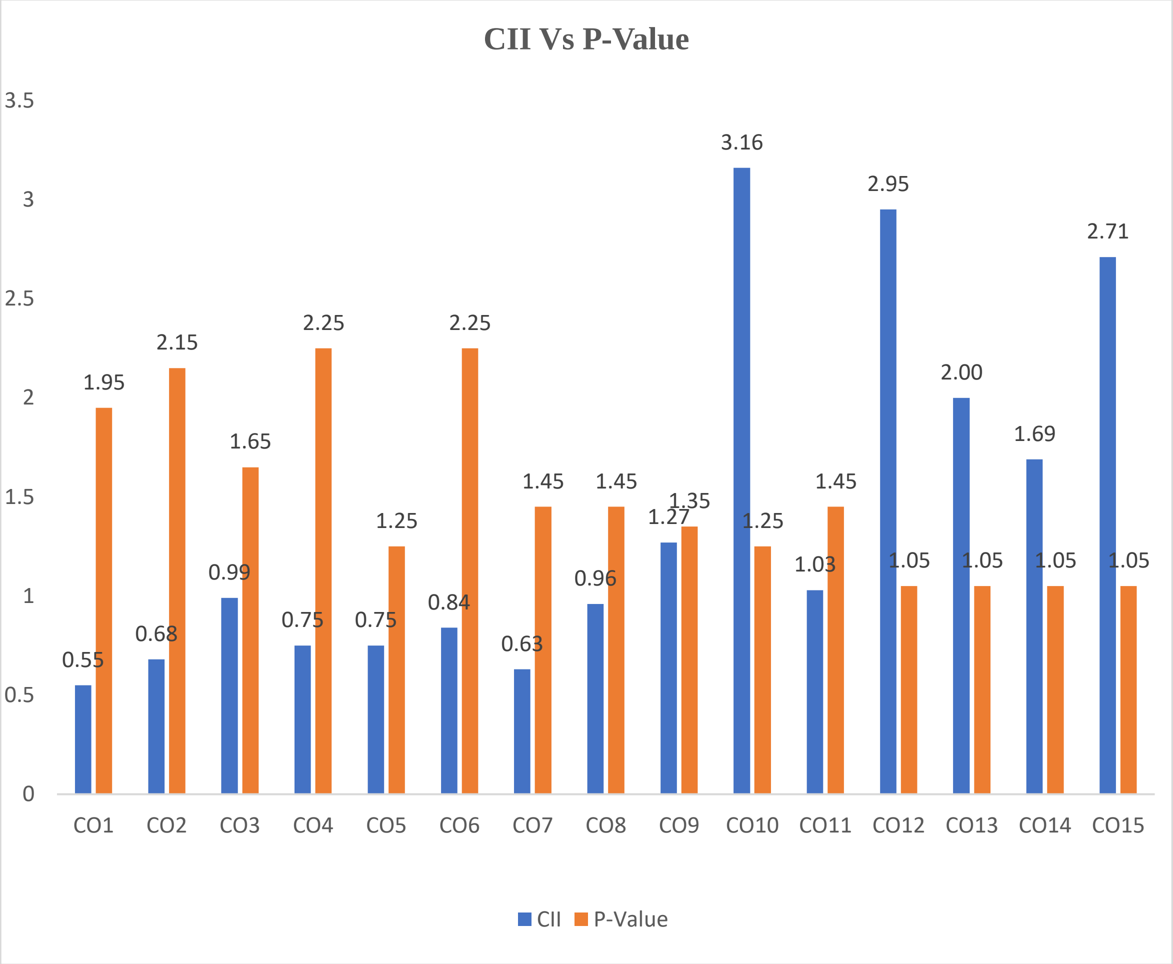

Figure 1.8: CII Vs P-Value

As illustrated in Figure 1:8, a clear inverse relationship is observed between the Crude Instability Index (CII) and the P-value. Specifically, a reduction in CII corresponds to an increase in P-value, whereas an elevated CII is consistently associated with lower P-values. This reciprocal trend is consistently demonstrated across the dataset, confirming the strong interdependence of these two stability parameters.

The significance of this relationship lies in the fact that both indices serve as complementary indicators of crude oil stability and compatibility. A higher CII reflects a greater propensity of the crude to undergo instability, often due to elevated concentrations of polar and heavy fractions such as resins and asphaltenes. In contrast, the P-value, being derived from solubility balance considerations, increases with improved crude stability and decreases when the crude exhibits a tendency toward precipitation or phase separation. Thus, the observed inverse trend not only validates the internal consistency of the calculated indices but also reinforces their diagnostic value for evaluating fouling potential, blending behaviour, and overall refining suitability of different crudes.

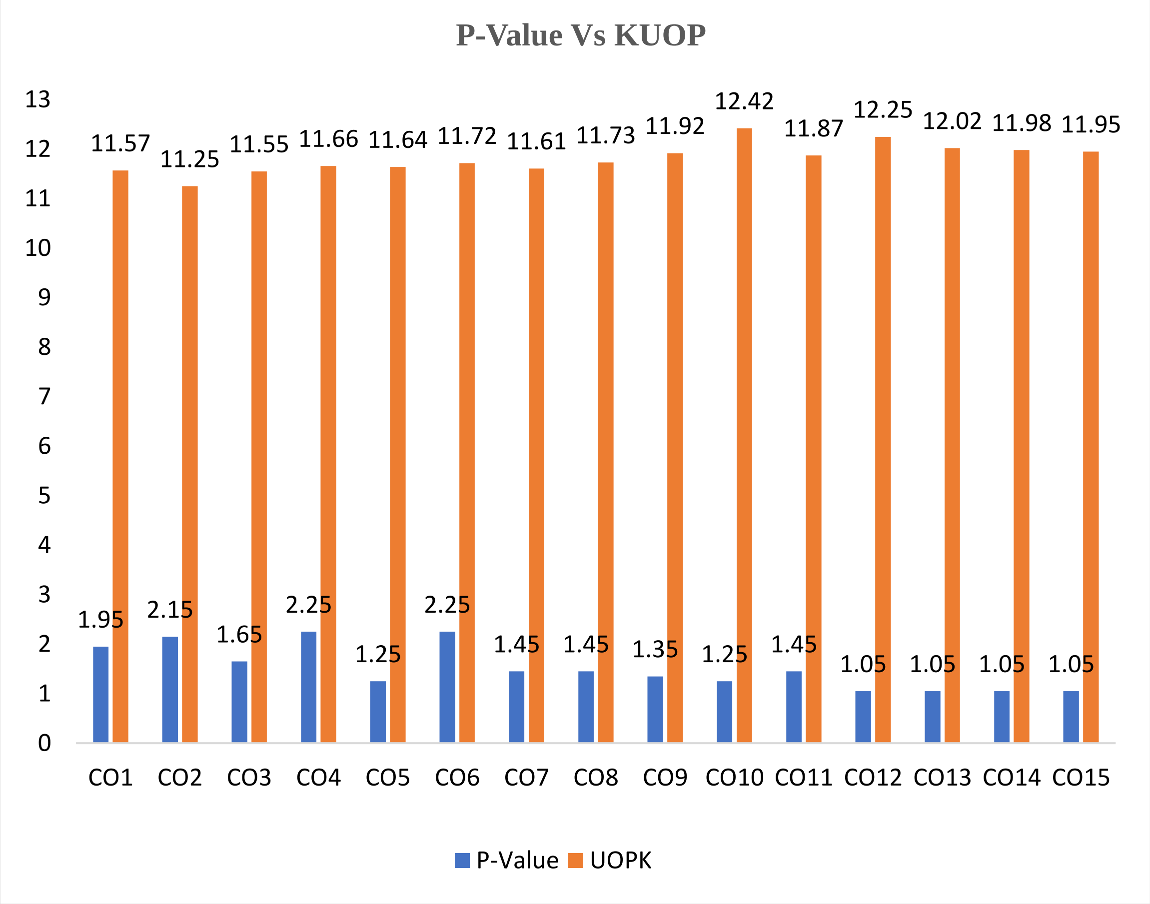

Figure 1.9: P-Value Vs KUOP

As shown in Figure 1:9, an inverse correlation is evident between the P-value and the KUOP factor, a parameter widely employed in crude oil characterization. Specifically, an increase in the P-value is accompanied by a reduction in the KUOP factor, whereas a lower P-value corresponds to a higher KUOP factor. This reciprocal trend mirrors the relationship previously identified between CII and P-value, thereby reinforcing the consistency of these stability and characterization indices.

The significance of this correlation lies in its reflection of the underlying molecular composition and stability characteristics of crude oils. The KUOP factor, which is strongly influenced by the relative abundance of saturates versus aromatics, tends to be higher for crudes with lighter, more paraffinic character and lower for those enriched in aromatics and resins. In contrast, the P-value increases with crude stability, particularly when the balance between solubilizing (aromatics/resins) and destabilizing (asphaltenes) fractions favours stable dispersion. Thus, the inverse relationship observed between the P-value and KUOP factor highlights the complementary diagnostic utility of these indices in assessing crude oil type, compatibility, and processing behaviour.

As illustrated in Figure 1.9, a distinct trend in phase separation behaviour was observed across the tested crude oil samples. Samples CO1 through CO7 exhibited stable behaviour, with no visible evidence of phase separation on paper, indicating a well-dispersed state of asphaltenes within the maltene matrix. A marginal onset of phase separation was first detected in CO8, marking a critical transition point in crude oil stability. Beyond this threshold, samples CO8 through CO15 consistently demonstrated progressive and pronounced phase separation, reflecting increasing instability within the crude matrix.

This observed transition is consistent with the solubility balance concept, whereby the ability of aromatics and resins to effectively stabilize asphaltenes diminishes as their relative proportions decrease or as asphaltene content increases. The emergence of phase separation in CO8 and its persistence through CO15 highlights the compositional shift from stable, saturate-rich crudes toward heavier crudes enriched in aromatic, resin, and asphaltene fractions. Such a trend is of particular significance, as phase separation is directly linked to operational challenges in refining, including sludge formation, fouling, and reduced process efficiency.

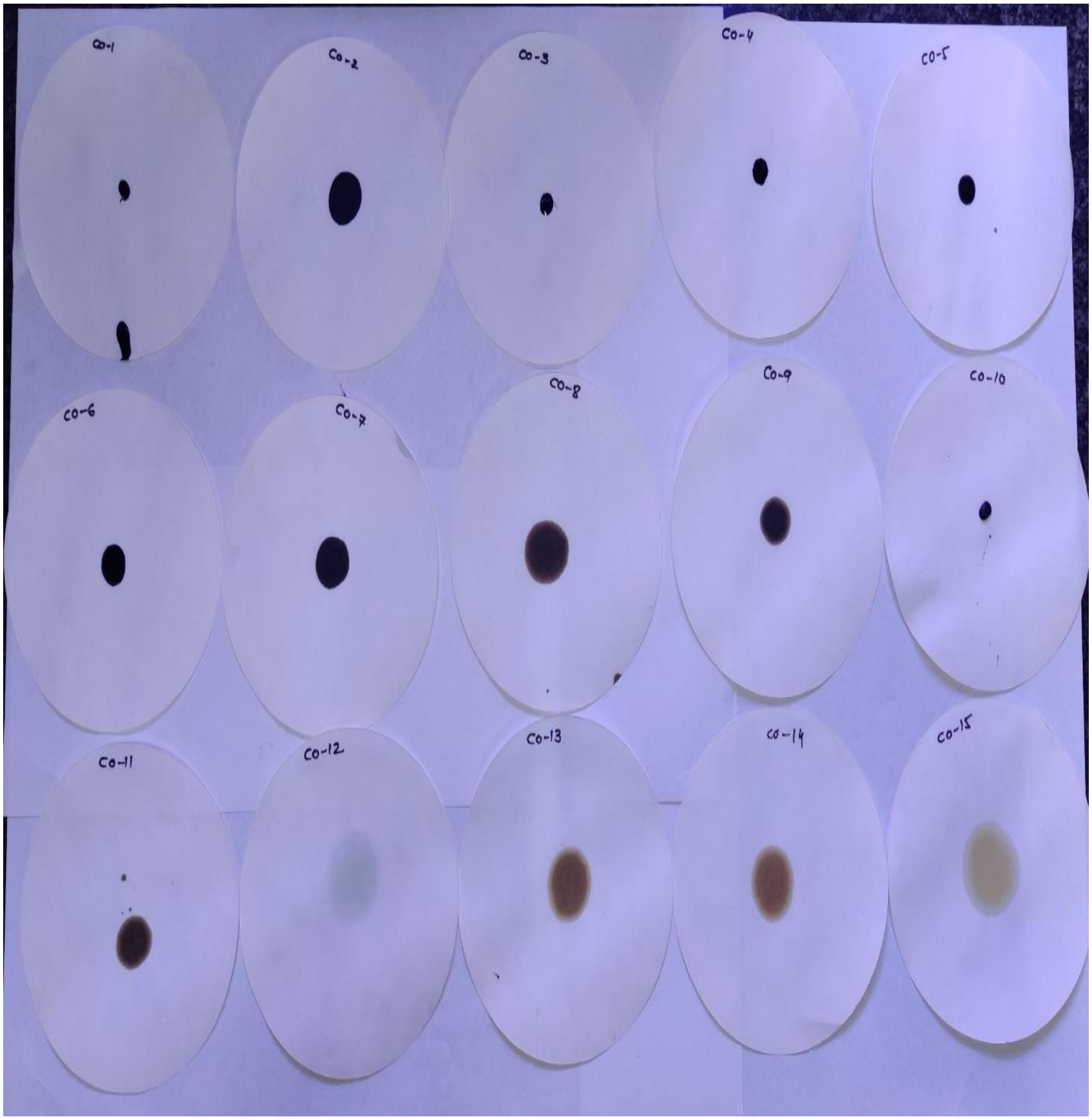

Figure 1.10: Spot test of crude oil

1.4 Conclusion

1.4.1 Methodological Contributions

This study has successfully established the TLC-FID technique as a robust, accurate, and efficient analytical method for the quantification of SARA fractions in crude oils. A set of carefully derived and validated response coefficients enabled precise quantification, overcoming one of the primary limitations associated with conventional TLC-FID approaches. The methodological framework was rigorously tested against standard reference methods (ASTM D6560, IP 391, and HTSD), ensuring reproducibility and reliability across a diverse set of crude samples. This methodological advancement offers an important step forward in refining crude oil analysis, combining simplicity, rapidity, and analytical precision.

1.4.2 Key Findings and Validation

The accuracy and robustness of the derived coefficients were validated through comparative studies with both synthetic blends and real crude oils. The findings, as illustrated in Table 8 and Figure 7, clearly distinguish between stable and unstable crudes. Samples CO1 to CO7 demonstrated excellent stability, with no signs of phase separation, while samples CO8 to CO15 consistently exhibited incompatibility, as confirmed by both spot testing and SARA fraction analysis. Quantitative thresholds were established, indicating that a CII value below 1.0 and a P-value above 1.45 are strong predictors of crude oil compatibility. Moreover, the relationship between API gravity, asphaltene-to-resin ratio, and stability indices was clearly defined: higher-API (lighter) crudes, despite being saturate-rich, generally exhibited lower stability, whereas the asphaltene-to-resin ratio emerged as a critical determinant of compatibility. Collectively, these findings underscore the strong diagnostic power of SARA characterization when combined with stability indices.

1.4.3 Industrial Significance and Implications

From an industrial perspective, the validated TLC-FID approach provides a rapid and reliable tool for predicting crude oil compatibility, enabling refineries to make informed decisions in blending operations, feedstock selection, and fouling risk mitigation. The ability to detect incompatibility at an early stage offers significant operational and economic benefits, reducing the likelihood of unplanned shutdowns, maintenance costs, and product quality issues.

Furthermore, the establishment of quantitative thresholds for compatibility (CII < 1.0; P-value > 1.45) provides the industry with clear, actionable criteria for assessing the stability of crude blends. This study thus not only enhances analytical methodology but also contributes directly to improving operational efficiency, process optimization, and refinery economics.

1.5 References

1. Shishkova, I.; Stratiev, D.; Kolev, I. V.; et al. "Challenges in Petroleum Characterization—A Review." *Energies* **2022**, 15(20), 7765. https://doi.org/10.3390/en15207765.
2. Ivleva, N. P.; et al. "Molecular Characterization of Hydrocarbons in Petroleum by Advanced Mass Spectrometry: A Review." *Energies* **2023**, 16(11), 4296. https://doi.org/10.3390/en16114296
3. Känzig, D. R.; et al. "Not All Oil Types Are Alike in Trade Substitution." *Nature Communications* **2024**, 15, 6760. https://doi.org/10.1038/s41467-024-51786-9
4. Kinsara, R. A., & Demirbaş, A. (2016). *Upgrading of crude oil via distillation processes*. **Petroleum Science and Technology, 34**(14), 1300–1306.
5. Speight, J. G. (2014). The Chemistry and Technology of Petroleum (5th ed.). CRC Press. https://doi.org/10.1016/B978-0-12-396456-2.00001-2
6. Patel, P. et al. (2021). "Characterization and upgrading of heavy and extra-heavy crude oils: A review." Fuel, 285, 119524. https://doi.org/10.1016/j.fuel.2020.119524
7. Al-Hassan, S., et al. (2020). "Challenges and opportunities in the utilization of vacuum residue in refining industry." Energy, 196, 118369. https://doi.org/10.1016/j.energy.2020.118369
8. Maiti, S., et al. (2022). "Nanomaterials from petroleum residues: synthesis and applications." Carbon, 190, 1–22. https://doi.org/10.1016/j.carbon.2022.01.013

10 Zhao, Y., et al. (2021). "Advanced analytical techniques for crude oil characterization and refining optimization." Fuel, 290, 119634. https://doi.org/10.1016/j.fuel.2021.119634

11 Stratiev, D., Shishkova, I., Georgiev, G., Dinkov, R., Nedelchev, A., Nikolova, R., ... & Toteva, V. (2025). The Incompatibility Pitfall in Refining Opportunity Crude Oils. Processes, 13(2), 593. https://doi.org/10.3390/pr13020593

12 Shishkova, I. K., Stratiev, D. S., Tavlieva, M. P., Dinkov, R. K., Yordanov, D., Sotirov, S., Sotirova, E., Atanassova, V., Ribagin, S., Atanassov, K., Stratiev, D. D., Todorova-Yankova, L., & Nenov, S. (2021). Evaluation of the Different Compatibility Indices to Model and Predict Oil Colloidal Stability and Its Relation to Crude Oil Desalting. Resources, 10(8), 75. https://doi.org/10.3390/resources10080075

13 Heithaus, J. J. (1962). Measurement and prediction of asphaltene flocculation in n-alkane-diluted crude oils. Journal of the Institute of Petroleum, 48(460), 45-53

14 Lee, E., Hench, K., Miao, T., & Rudenko, J. (2024). Determination of Compatibility Parameters of Crude Oils by Near-Infrared Spectroscopy. Energy & Fuels, 38(17), 16049-16055. https://doi.org/10.1021/acs.energyfuels.4c02387

15 Watson, K. M., & Nelson, E. F. (1935). Characterization of petroleum fractions. Industrial & Engineering Chemistry, 27(12), 1460-1464. https://doi.org/10.1021/ie50312a018

16 Gary, J. H., Handwerk, G. E., & Kaiser, M. J. (2007). Petroleum Refining: Technology and Economics (5th ed.). https://doi.org/10.4324/9780203907924

17 Manning, F. S., & Thompson, R. E. (1991). Oilfield Processing of Petroleum: Volume One: Natural Gas. PennWell Books.

18 Krzysztof Bambinek, Andrzej Przyjazny, Grzegorz Boczkaj, Compatibility of Crude Oil Blends─Processing Issues Related to Asphaltene Precipitation, Methods of Instability Prediction─A Review. Industrial & Engineering Chemistry ResearchVol 62/Issue 1. December 19, 2022. https://doi.org/10.1021/acs.iecr.2c02532

19 Asomaning, S. (2003). Test Methods for Determining Asphaltene Stability in Crude Oils. Petroleum Science and Technology, 21(3–4), 581–590. https://doi.org/10.1081/LFT-120018540

20 Mullins, O. C. (2010). The Asphaltenes. Annual Review of Analytical Chemistry, 3, 233–254. https://doi.org/10.1146/annurev.anchem.111808.073758

21 Leontaritis, K. J., & Mansoori, G. A. (1988). Asphaltene Flocculation during Oil Production and Processing: A Thermodynamic Collodial Model. SPE Production Engineering, 3(4), 409–416. https://doi.org/10.2118/16258-PA

22 Mansoori, G. A. (1997). Asphaltene Formation and Deposition. Journal of Petroleum Science and Engineering, 17(1–2), 101–111. https://doi.org/10.1016/S0920-4105(96)00052-2

23 Hirschberg, A., De Jong, L. N. J., Schipper, B. A., & Meijer, J. G. (1984). Influence of Temperature and Pressure on Asphaltene Flocculation. Society of Petroleum Engineers Journal, 24(3), 283–293. https://doi.org/10.2118/11202-PA

24 Akbarzadeh, K., Hammami, A., Kharrat, A., Zhang, D., Allenson, S., Creek, J. L., & Mullins, O. C. (2007). Asphaltenes—Problematic but Rich in Potential. Oilfield Review, 19(2), 22–43.

25 Kawanaka, S., Leontaritis, K. J., & Mansoori, G. A. (1991). Flocculation of Asphaltenes from Petroleum Fluids. Journal of Petroleum Science and Engineering, 5(1), 33–41. https://doi.org/10.1016/0920-4105(91)90030-Y

26 Kashou, S. F., et al. (1996). Crude Oil Blending and the Use of Stability Indexes to Predict Asphaltene Precipitation. Presented at the International Symposium on Oilfield Chemistry. SPE-35378-MS. https://doi.org/10.2118/35378-MS

27 Fan, T., & Buckley, J. S. (2002). Acid Number Measurements Revisited. SPE 71456-MS. https://doi.org/10.2118/71456-MS

28 Buenrostro-Gonzalez, E., Lira-Galeana, C., Wu, J., & Yarranton, H. W. (2004). Asphaltene Precipitation and Solvent Properties of Crude Oils. Energy & Fuels, 18(3), 934–939. https://doi.org/10.1021/ef034072j

29 Yan Peng,Xiangyu Zhang, Lihua Cheng, Hong Zhang, Jieyun Tang, Hong Chen, Qinzhen Fan and Xinping Ouyang. Effect of Asphaltenes on the Stability of Water in Crude Oil Emulsions, Materials 2025, 18(3), 630; https://doi.org/10.3390/ma18030630

30 Saboor, A., Yousaf, N., Haneef, J. et al. Performance of asphaltene stability predicting models in field environment and development of new stability predicting

model (ANJIS). J Petrol Explor Prod Technol 12, 1423–1436 (2022). https://doi.org/10.1007/s13202-021-01407-8

31 Hernández, E. A., Lira-Galeana, C., & Ancheyta, J. (2023). Analysis of Asphaltene Precipitation Models from Solubility and Thermodynamic-Colloidal Theories. Processes, 11(3), 765. https://doi.org/10.3390/pr11030765

32 Speight, J. G., & Long, R. B. (1996). THE CONCEPT OF ASPHALTENES REVISITED. Fuel Science and Technology International, 14(1–2), 1–12. https://doi.org/10.1080/08843759608947559

33 L.G.M. Moura, M.F.P. Santos, E.L. Zilio, M.P. Rolemberg, A.C.S. Ramos, Evaluation of indices and of models applied to the prediction of the stability of crude oils, Journal of Petroleum Science and Engineering, Volume 74, Issues 1–2, 2010, Pages 77-87, ISSN 0920-4105, https://doi.org/10.1016/j.petrol.2010.08.011

34 Chandra Mohan Sinnathambi and Norhusna Mohamad Nor, 2012. Relationship Between SARA Fractions and Crude Oil Fouling. Journal of Applied Sciences, 12: 2479-2483.

35 Phuong T.H. Pham, Cham Q. Pham, Thi-Tam Dam, Quang-Anh Nguyen,Tung M. Nguyen, A comprehensive review of catalyst deactivation and regeneration in heavy oil hydroprocessing, Fuel Processing Technology, Volume 267, March 2025, 108170. https://doi.org/10.1016/j.fuproc.2024.108170

36 Xiong R, Guo J, Kiyingi W, Feng H, Sun T, Yang X, Li Q. Method for Judging the Stability of Asphaltenes in Crude Oil. ACS Omega. 2020 Aug 19;5(34):21420-21427. doi: 10.1021/acsomega.0c01779

37 Stratiev, D., Shishkova, I., Georgiev, G., Dinkov, R., Nedelchev, A., Nikolova, R., Veli, A., Bureva, V., Atanassov, K., Berg, F. v. d., Yordanov, D., & Toteva, V. (2025). The Incompatibility Pitfall in Refining Opportunity Crude Oils. Processes, 13(2), 593. https://doi.org/10.3390/pr13020593

38 Ruiying Xiong, Jixiang Guo,Wyclif Kiyingi, Hengshui Feng, Tongcheng Sun, Xiaohui Yang, Qing Li, Method for Judging the Stability of Asphaltenes in Crude Oil, ACS Omega Vol 5/Issue 34, August 19, 2020. https://doi.org/10.1021/acsomega.0c01779

39 Antonio Carlos da Silva Ramos, Marlus Pinheiro Rolemberg, Lyzette Gonçalves Moraes de Moura, Evaldo López Zilio, Maria de Fátima Pereira dos Santos, Gaspar González, Determination of solubility parameters of oils and prediction of oil compatibility, Journal of Petroleum Science and Engineering, Volume 102, 2013, Pages 36-40, ISSN 0920-4105. https://doi.org/10.1016/j.petrol.2013.01.008

40 Irwin A. Wiehe, Asphaltene Solubility and Fluid Compatibility, Energy & Fuels Vol 26/Issue 7, June 11, 2012. https://doi.org/10.1021/ef300276x

41 Pasadakis N., Roumeliotis, P., & Voutsas, E. (2001). A new method for the determination of SARA fractions in crude oils. Fuel, 80(10), 1435-1440.