

Review Article

Asphaltene Structure, Separation and Purification Steps: A Short Review

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ABSTRACT

Separation of asphaltenes into multiple sub-fractions is performed using different fractionation techniques which are investigated in this study. The method chosen depends on the parameter of interest such as solubility, molecular weight difference, polarity, etc. For this write-up, the methods reviewed include sequential elution fractionation, solvent extraction, sequential extraction, column chromatography, sequential precipitation, supercritical fluid extraction, etc.

The yield and the quality of the fraction are the two important subjects for choosing the separation procedure. For example, the yield is influenced using different hydrocarbon liquids as a significant factor. In addition, the method of choice will determine the presence of co-precipitated resins or not. The advantages of some of the methods were highlighted as well as the future prospects and application of asphaltene.

Introduction

Petroleum consists of a multifaceted mixture of organic fractions such as light gaseous molecules and much heavier sticky liquids. Usually, the main parameter for the separation of these fractions in refineries is the boiling point, giving rise to numerous commercial products. Petroleum composition is grouped in terms of their saturates, aromatics, resins, and asphaltenes (SARA) contents. Waxes generally account for up to 14%, branched and cyclical (naphthenic) compounds make up about 16%

and 30%, respectively, with aromatics (30%) and asphaltenes-resins 10% [1]. Asphaltene constitutes the most weight by molar mass and the most polar components in crude oil, with the quantity and properties of the asphaltene fraction depending more or less on the crude oil source. Asphaltene components are non-distillable during crude oil refining and remain as residue while removing the distillable fractions. This asphaltene content has great value and importance [2].

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They, however, pose major problems for the petroleum industry, chief among them being precipitation during production and transport, catalyst poisoning during refining and formation of water-in-oil emulsions [1], blockage of pipelines, and fouling of the internal surface of reservoirs. [2,3] The asphaltene component occurs as dark brown to black friable solids and does not melt and decompose easily at relatively higher temperatures of 300 to 400 °C (they have no definite melting point) [1,2]. When heated, they often foam and swell, leaving behind a carbonaceous residue. They contribute significantly to the crude oil's density and viscosity; a problem during transport and are also largely responsible for its very dark color.

Asphaltene constituents are gotten from petroleum by treating with a light nonpolar liquid (for e.g. hydrocarbons) with a surface tension lower than 25 dyne cm^{-1} at 25°C. Examples are low-boiling n-heptane, petroleum naphtha, iso-pentane, petroleum ether, n-pentane, etc. [4,5], giving rise to precipitates that dissolve in aromatic compounds e.g. toluene [6].

Asphaltene constituents are soluble in liquids with a surface tension greater than 25 dyne cm^{-1} , such as carbon disulfide, pyridine, benzene

and carbon tetrachloride but are insoluble in liquefied petroleum gases, such as C1, C2, and C3 gas; in fact, C3 (propane) is utilized commercially in processing petroleum residues for asphaltene constituents and resin constituents [2].

When using n-pentane and n-heptane as aggregating agents (floculant), the asphaltene isolates are called C5I and C7I respectively. A higher yield is achieved using n-pentane and this fraction constitutes molecules with a broader distribution of molar masses and polarities. One could say that asphaltenes C5I contains all molecules of asphaltenes C7I. [6,8].

Elemental Constituents and Composition

Asphaltene molecular weight covers a very broad range, from hundreds to millions, giving rise to the idea of self-aggregation [9]. Carbon and hydrogen are usually the most common, in excess of 90 % by weight. These values represent a hydrogen-to-carbon atomic ratio of 1.15 in n-heptane derived asphaltenes [3]. In contrasting manner, the content of undesired heteroatoms in asphaltenes usually varies greatly, with sulfur as the most common [3,9]. Sulfur contents vary from 0.05 to 7.0 wt%.

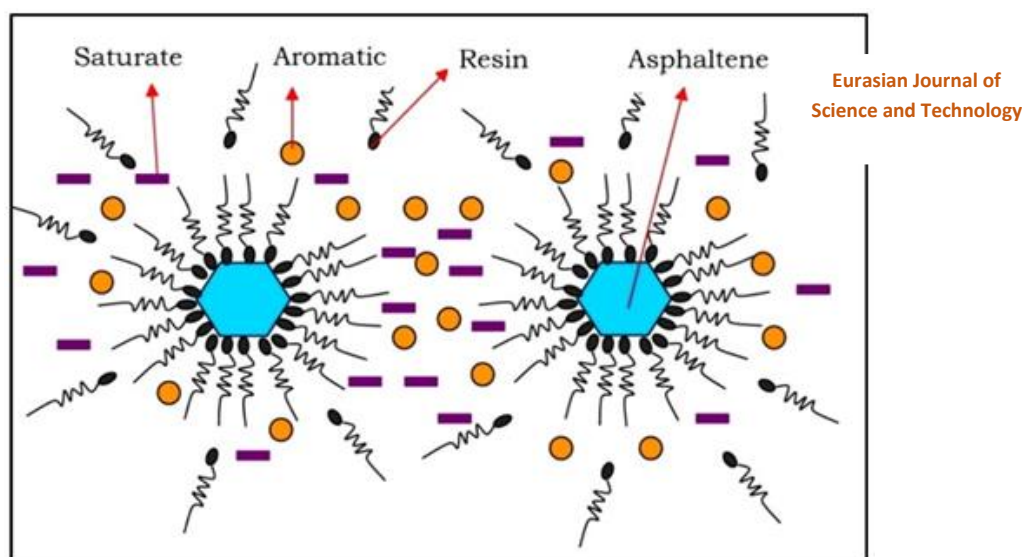


Figure 1 Interaction between the SARA fractions in petroleum [51]

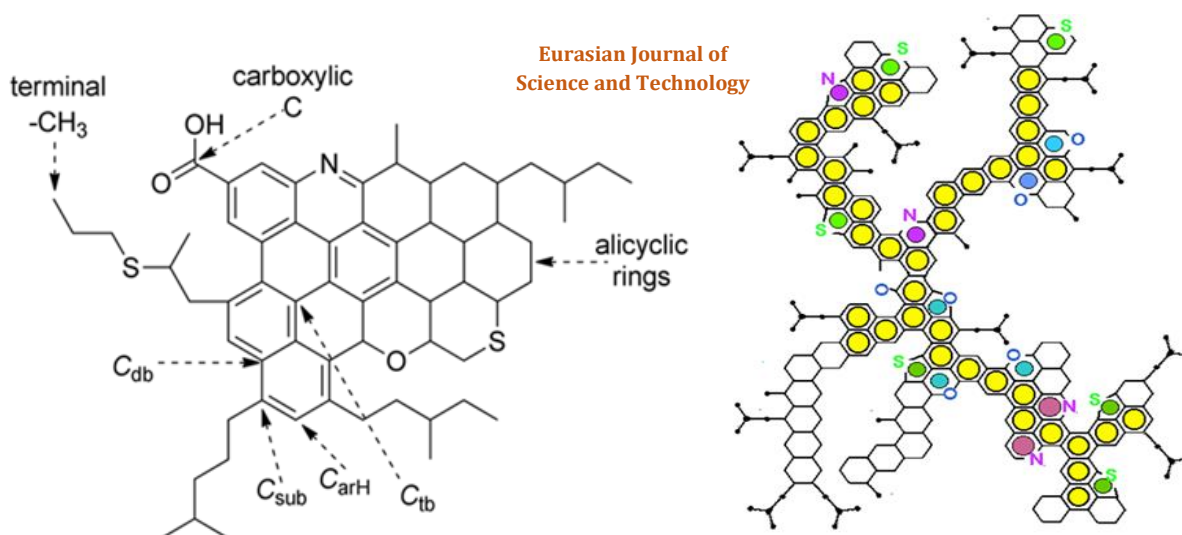


Figure 2 Hypothetical structures of asphaltene molecules [3]

In contrast, the nitrogen content has a somewhat lower variation (0.05–0.5 % by weight), and oxygen contents are usually lower than 1.0 % by weight. Adding to that, some metallic elements occur in asphaltenes and are distributed in the range of 0–4000 ppm, with vanadium and nickel being the most occurrence. Metal atoms in asphaltenes are usually present in the form of metalloporphyrins and as so-called “nonporphyrins”, which are yet to be proven [10].

Perhaps the most significant problem for petroleum chemistry has always been the composition and properties of asphaltenes. For many decades, various researchers have made efforts to characterize, analyze, and determine

the physicochemical characteristics of asphaltenes using different analytical techniques, but these efforts are barely a success, owing mainly to the complexity of asphaltenes.

Molecules of asphaltenes are very well closely packed and somewhat high in unwanted metals and heteroatoms, giving rise to stubborn self-aggregation. Different classes of asphaltene such as the solubility class and the chemical class differs, hence some variations among different asphaltenes are expected. Furthermore, there are bigger problems with different crude oil sources and preparation techniques giving asphaltenes of quite notable



Figure 3 A sample of liquid asphaltenes extracted in a lab from crude oil in n-C7 (left) and n-C5 (right) [3]

difference in composition. Asphaltene characterization still poses a major challenge. [3]

Asphaltene Fractionation

The study of asphaltenes via instrumental analysis is very vital to understanding their physicochemical properties. Combining these instrumental techniques with adequate pretreatments, such as fractionation, gives more information on molecular composition. Given that it represents the most problematic fraction of crude oil, many studies have made attempts, with various methods to separate asphaltene into groups of closely related fractions and then analyze their chemical and physical properties comparatively to better understand their structural makeup. Asphaltene is better explained by its solubility in solvents, or more specifically, by petroleum constituents that can dissolve in toluene or benzene but not in saturated hydrocarbons like n-heptane.

Since asphaltenes are "non-distillable" substances as well, their separation frequently relies on solubility. Additionally, different physical and chemical techniques are also used. However, matrices as complicated as asphaltenes might be separated using simple, efficient, and quick processes thanks to the advancement of analytical techniques and technology, and online fractionation techniques have even been developed. There are two significant benefits of fractionating asphaltenes:

(1) It makes research materials less difficult.

(2) Rather than just providing averages, it offers a property distribution.

This approach, which is based on the continuity model, has been effectively used to enhance the characterization of asphaltenes and exhibits regular changes in the functionality of various fractions. In general, lesser soluble fractions have a lower H/C ratio, more aromaticity, and more heteroatoms [3].

The physical and chemical characteristics that are relevant for the separation of the components of asphaltene include those listed

below. No single parameter alone is effective in this process [2,11].

(1) Polarity (existence of functional groups formed by present heteroatoms).

(2) Aromaticity (existence of polynuclear aromatic systems).

(3) Molecular weight (or size).

(4) The asphaltene micelle (with 3D structure) as it relates to the other crude oil constituents.

(5) The ability of the precipitating/extracting solvent utilized to dissolve the asphaltene for separation.

(6) The required time for the precipitating/extracting solvent to reach the micelle, and which relies on the hydrocarbon solvent's capacity to penetrate the micelle, showing that the process is diffusion-controlled.

(7) The yield and nature of the asphaltene product are determined by the ratio of crude oil to precipitating/extracting solvent.

(8) Temperature, which may shorten the induction period required for diffusion-controlled processes.

(9) Pressure, as used in numerous refinery processes to keep lower boiling hydrocarbon fractions in the liquid phase.

It has been identified that the variation in the solubility parameter of the hydrocarbon can be associated with the varied yields of the asphaltene fraction.^[11] The degree to which the asphaltene constituents can fluctuate with the hydrocarbon medium's solubility parameter is connected to the asphaltene constituents' polarity and aromaticity rather than the asphaltene constituents' molecular weight or dimensions. Other parameters that are subsets of those listed above can be defined. It is also worth noting that, to get rid of the entrained resin material, the asphaltene elements must often be precipitated from benzene or toluene. However, none of the characteristics used in petroleum separation can be connected to the separation of different chemical kinds [11,12].

Sequential Elution Fractionation (SEF)

For more than 70 years, crude oil and coal-related solvent fractionation has been

employed in separating non-distillable fractions. In general, solvent fractionation necessitates the use of Soxhlet and frequent washing, which might take many days. Boduszynski and colleagues [13] devised a speedier and more robust approach for solvent fractionation, which was first utilized in solvent-refined coal research. This method was later utilized to successfully make non-distillable petroleum fractions [14].

This procedure is known as sequential elution fractionation (SEF), which entails precipitating and dissolving components in an inert column. This showed that non-distillable fractions takes similar patterns as distillation cuts and that solubility could be leveraged to accomplish similar distillation for non-distillable materials using this method.[15] In general, this technique requires asphaltene to be loaded onto the carrier before being eluted using various solvents liquids. The approach works by boosting the ability of the solvent used in dissolving the material. According to the cohesive-parameter technique, the fraction's

solubility parameter should grow from the first eluted fraction (SF-1) to the final (SF-6).

Solvent Extraction

Asphaltene solvent fractionation is guided by their equilibrium solubility in solution. Although sequential elution can produce a series of asphaltene fractions, effective separation of asphaltene can be achieved via a single solvent-extraction stage by carefully selecting the solvent and complementing it with a good physicochemical treatment [3].

Miller et al [16] used prolonged Soxhlet extraction in n-heptane to separate asphaltene into two fractions. The fraction so extracted was non-colloidal and unassociated in aromatic solvents, but the unextracted part was colloidal and had a high apparent molecular mass and larger aggregates in solution.

The degree of connection in solution was the most significant variation between these two fractions.

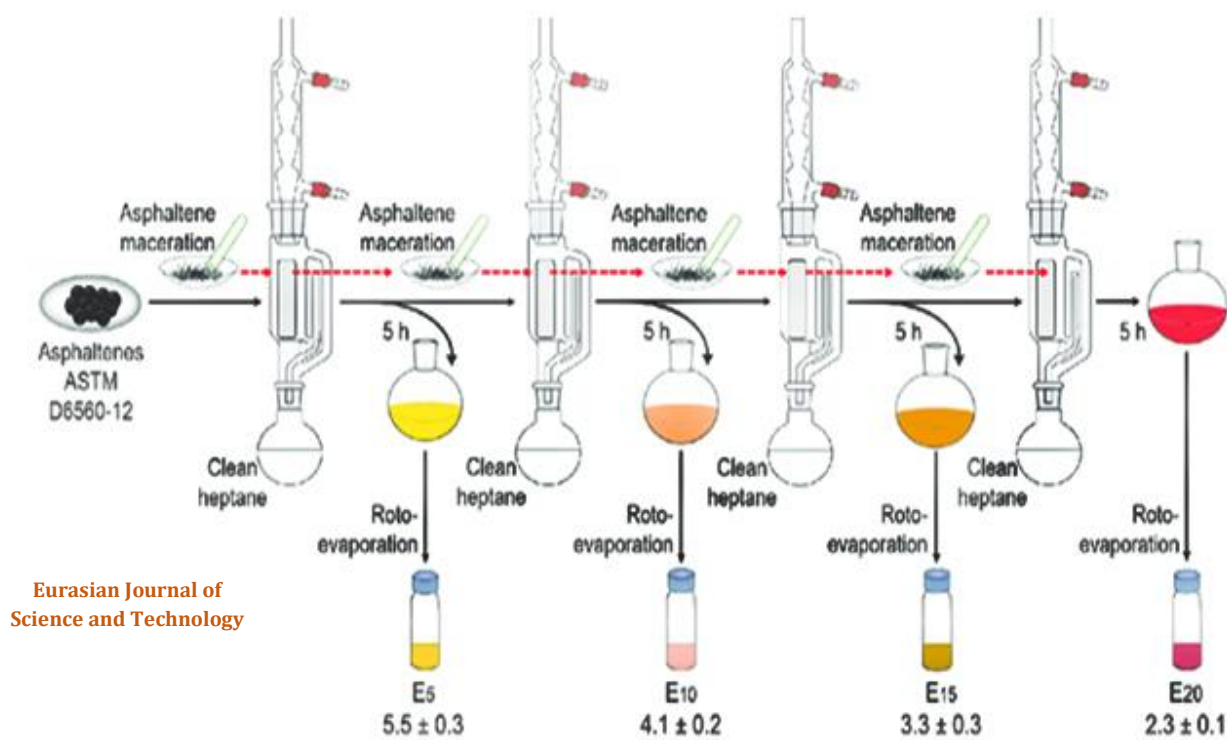


Figure 4 An illustration of occluded asphaltene compound [52]

Asphaltenes were separated by Gutiérrez et al [17] by forming a compound with p-nitrophenol (PNP). It was advised to make the similar combination using asphaltene so that precipitation would result. PNP has been known to produce complexes that can transfer charges with aromatic compounds [3].

Two different fractions (A1 and A2) with highly differing solubilities were separated using this process. A2 had a lower molecular weight (by VPO) than the low-soluble fraction A1, but a greater H/C mole. A model for an asphaltene colloidal solution in aromatic hydrocarbons was developed using research findings, where A1 the lower soluble fraction forms a colloidal phase and be distributed in the medium by A2 the higher soluble fraction. The analysis of A1 and A2 revealed that low aromatic hydrogen and high H-type hydrogens in A1 were consistent with a single, rigid, and flat core created by the fusion of polycyclic aromatic and naphthenic units, whereas high aromatic hydrogen and high H-type hydrogens in A2 were consistent with a more flexible structure where several smaller polycyclic aromatic and naphthenic units were joined by aliphatic chains [18]. With combinations of toluene and heptane, Spiecker et al.'s method [19] was able separate asphaltenes from four different samples of crude oil. Strong cooperative asphaltene contacts of a certain subfraction, showing polarity with hydrogen bonding, were revealed by the solubility profile data. They discovered that this subfraction contained the highest N, V, Ni, and Fe levels and the lowest H/C ratios. Additionally, they discovered that the aggregates generated by the lesser soluble subfractions were significantly bigger than those created by the higher soluble subfractions.

Sequential Extraction

Asphaltenes are continuously extracted from one another using liquids in the sequential extraction process. It doesn't need to load data first like the SEF approach; it just extracts. In this procedure, two-solvent mediums are employed for extracting, and a number of asphaltene fractions are produced based on a

charge of the mixture composition polarity. A strong solvent (such as toluene or THF) and a typical paraffin (such as n-heptane or n-hexane) are typically used [3, 20, 21].

Column Chromatographic Fractionation

For a very long period, petroleum asphaltenes have been studied using column chromatography, a crucial technique for studying petroleum and its constituents. To successfully achieve progressive asphaltene separation, this study was started on chromatographic separation in several chromatographic equipment, and by adsorbing on clay or silica [22] ion exchange [23], and gel permeation chromatography (GPC) [24].

The gradient separation was achieved using the adsorption method, which is given by the polarity difference of components. As the solvent's polarity and strength grew, so did that of the eluted fraction. [25]. Asphaltenes can be separated into basic, acidic, and neutral (acid- and base-free asphaltenes) molecules using ion-exchange chromatography. By contrasting the behavior of the three components, it is possible to learn a little bit about their chemical make-up. The properties of acid- and base-free asphaltenes and the original asphaltenes can also be directly compared [23]. By their apparent molecular size and with a potent eluent like THF, asphaltenes are fractionated by GPC [26]. The asphaltene association may be studied and the actual molecular weight can be determined using GPC fractionation and molecular weight measurements. [27]. Asphaltene failed to completely dissociate in less potent solvents like toluene and chloroform, which resulted in a high molecular weight. The weights of these fractions, which were measured in the most potent solvent, dioxane-chloroform, were around 1050, indicating that asphaltene molecules were made up of numerous linked unit sheets rather than a single, substantial peri-condensed aromatic ring system [3].

One way to ascertain asphaltene molecular weight distribution is GPC. In the early days of column chromatography, a column with an inner diameter of 2 cm and a length of roughly

100 cm was frequently utilized for separation. Small-volume chromatography columns and high-performance liquid chromatography (HPLC) have become commonplace thanks to the advancement of analytical techniques. HPLC has a number of benefits [26].

(1) First, it produces the greatest number of fractions in the shortest amount of time with the least solvent use.

(2) It also provides perfect sample recovery and repeatability.

(3) Thirdly, it provides flexibility because it can be quickly modified and improved.

(4) Fourth, it has simple work-up processes that prevent sample degradation and is simple to use.

Sequential Precipitation

Sequential precipitation is seen as the reverse of sequential extraction. Here, a mixture of a binary flocculent (typically paraffin, such as n-C5 and n-C7) and a "good" solvent, such as dichloromethane (DCM) and toluene, is used. A flocculating solvent is frequently added to a "good" solvent to disperse total asphaltene and cause partial precipitation. The dissolving capacity of the binary mixture reduces as the amount of flocculants increases. The more polar components of asphaltene precipitate out first, and as more flocculant is added, the less polar components also precipitate out. [28].

DCM and n-C5 mixture is another frequently used solvent combination. Using binary mixes of DCM and n-C5, Fogler et al. [29–31] separated asphaltenes into parts with various polarities. The more polar asphaltene fractions in their program precipitated first, and then fractions with lesser polarities precipitated by adding more flocculent. In order to separate asphaltene into different fractions, n-heptane was gradually added to naphtha as a "good" solvent. [32].

On-Column Method

The aforementioned lengthy and laborious experimental approaches were created to separate asphaltene by fractionation. The on-column approach, created by Schabron and colleagues. [33, 34], is a quicker and easier

fractionation process that uses asphaltene precipitation and redissolution to separate asphaltenes into solubility fractions. By using n-heptane as the carrier solvent, a crude oil sample or its asphaltenes is injected into a polytetrafluoroethylene (PTFE)-packed column in this method. Following the precipitation of asphaltenes on the column and the elution of maltenes, the solvent is first switched to cyclohexane, then toluene, and finally DCM. An evaporative light-scattering detector (ELSD) can measure fractions. The determination time for this approach is less than 30 minutes, and it has good reliability and reproducibility for quantifying asphaltene concentrations as low as 120 ppm. It can actually be mechanized and used online [35].

Ovalles *et al.* [36] refined this new solvent system, making the on-column approach more reliable and reproducible. In an effort to quantify and slow down changes in solubility parameters, they utilized combinations of heptane, DCM, and methanol. The analysis of processed materials using this improved approach was successful, and they discovered that asphaltene with a low-solubility-parameter was simple to react with [36].

For the purpose of determining the asphaltene content, they also utilized a filter rather than a PTFE column. The use of a filter, according to the findings, significantly improved the accuracy of asphaltene testing at low flow rates, enabling the coupling of asphaltene separation with other methods like GPC, MS, and ICP. [37].

Ultracentrifugation

To divide asphaltene dissolved in toluene into six fractions based on various masses, ultracentrifugation is used. Viscosity and X-ray scattering were employed in studying the structure of these fractions [38]. All of the asphaltene fractions had very slight changes in their mass densities. The separation of asphaltenes via ultracentrifugation, however, appears to be dependent on distinct masses rather than different densities as evidenced by the two-decade difference in mass between the smallest and largest aggregates of asphaltene. They discovered that asphaltenes produced

aggregates with a nanometer scale; however, they did not overlap [39].

Supercritical Fluid Extraction (SFE)

The technique known as supercritical fluid extraction (SFE) involves employing supercritical fluids as the extracting solvent to separate a component from the matrix. The most common supercritical fluid is carbon

dioxide (CO₂), which is occasionally altered by co-solvents. The critical temperature and critical pressure are not present during supercritical fluid extraction. Consequently, the supercritical fluid possesses both the properties of a gas and a liquid, with a high density and solubility, comparable to a liquid, and a strong penetrating force, similar to a gas.

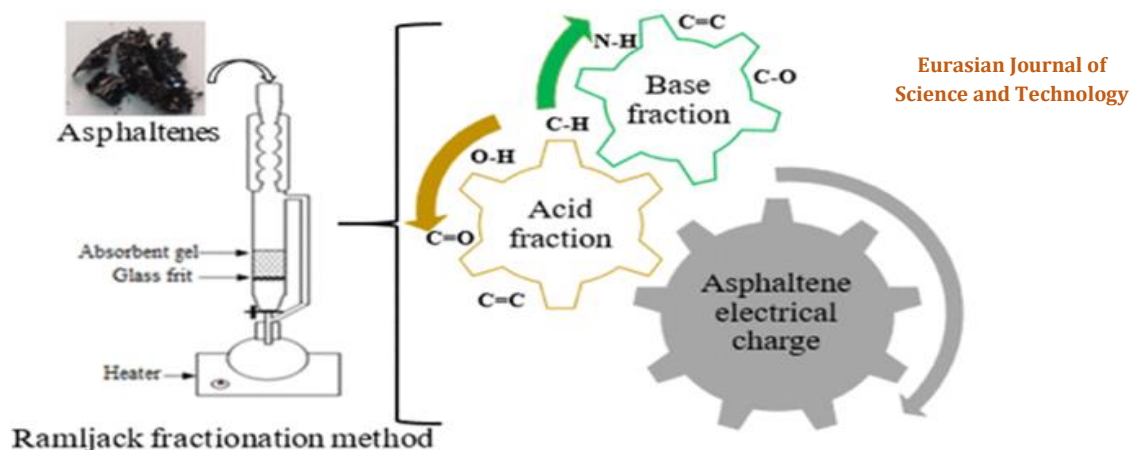


Figure 5 Column separated asphaltene fractions with their component functional groups [53]

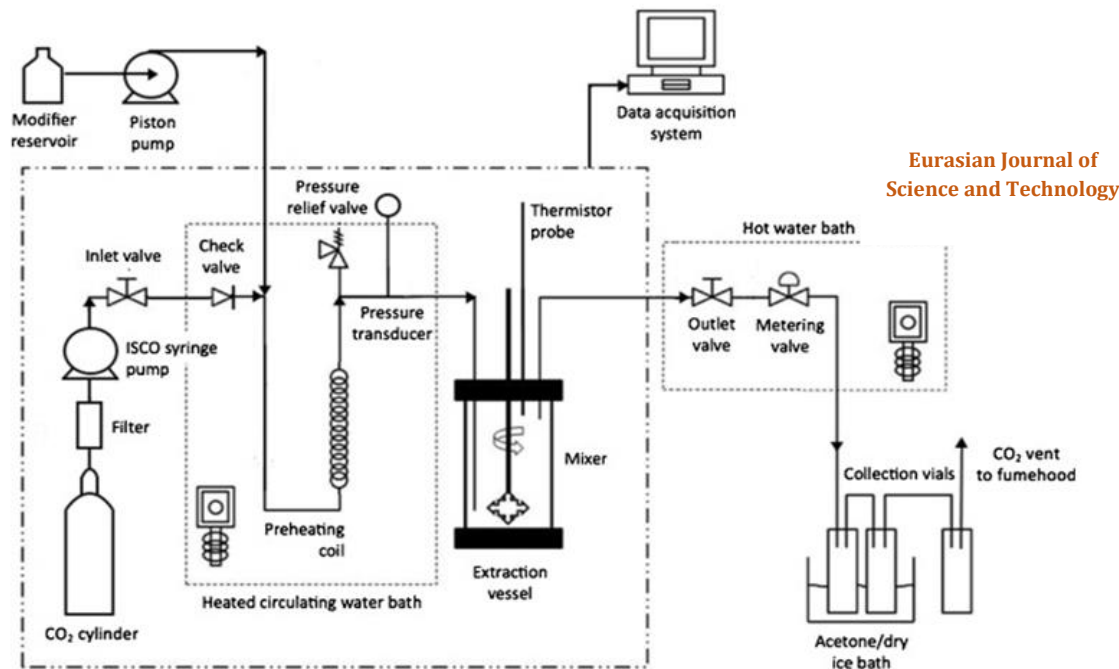


Figure 6 Schematics of Supercritical fluid extraction system for bitumen using chemically modified CO₂ [54]

Under varied experimental circumstances, SFE on asphaltene was carried out utilizing CO₂ as a solvent. The extracts contained alkanes, aromatics, and polar chemicals, making up to 12% of the entire asphaltenes. [40]. For a deeper and cleaner separation of heavy hydrocarbons using lower alkanes (such as C₃, C₄ & C₅) as supercritical solvents, the supercritical fluid extraction fractionation (SFEF) process was devised [41]. Heavy oil, residue, and oil sand separation were the main focus of SFEF. Following that, a number of narrow SFEF subfractions' characteristics were examined, including solubility parameters, impeded diffusion, information on alkyl side chains, molecular composition, and average structure [42].

Ultra-filtration Fractionation

Asphaltene size polydispersity was reduced and its properties were revealed via membrane filtration [43,44]. The findings show that membrane filtration may more effectively separate asphaltene particles of various sizes than solvent flocculation. Asphaltene diffusion through porous membranes is accelerated by the concentration gradient, which implements their size segregation. Compared to large aggregates, small asphaltene aggregates feature shorter alkyl chains, a higher aliphatic content, and lower aromaticity.

Adsorption onto Porous Medium

In recent times, a brand-new technique of fractionation was created using CaCO₃ as the porous media on which asphaltenes were adsorbed. The bulk asphaltene that remained in the bulk solution, the adsorbed asphaltene obtained by desorbing asphaltenes adsorbed on CaCO₃ using THF, and the irreversibly adsorbed asphaltene that was obtained after CaCO₃ dissolution were the three asphaltene fractions that were obtained [45–47]. According to research, the irreversibly adsorbed fraction, which had the highest concentration of carboxylic acid, carbonyl, or derivative groups, had a significantly higher tendency to self-

associate and form larger aggregates than the other fractions, which shared the same properties as the fraction that first sequentially precipitated [46]. Other media that can adsorb asphaltene include iron oxide and lime nanoparticles [55], dolomite [56], and magnetite [57].

Microwave Treatment

The efficiency of the microwave electromagnetic field in asphaltene fractionation is demonstrated by how well it may stimulate molecular mobility [48]. Microwave irradiation and a polar solvent were used to quickly separate an asphaltene solution into soluble and insoluble components. In the soluble fraction, vanadyl porphyrins were liberated and enriched, exhibiting greater UV-vis characteristic absorption. This could develop into a substitute technique for removing petroporphyrins from asphaltenes and crude oils. Fractionation is an essential step in pre-processing of asphaltenes. However, integrating this process with effective analytical methods can improve understanding of the physicochemical characteristics of asphaltenes. [3].

Applications of Asphaltenes

Numerous industries, including the polymer industry, nanomaterial synthesis and surface modification, electronics, emulsions and interfaces, organic photovoltaics, organic-based dye-sensitized solar cells, graphene-based structures, etc. have effectively exploited asphaltene. Amphiphilic asphaltene ionic liquid polymers have successfully been used to demulsify heavy petroleum crude oil emulsions [58]. It also serves as a precursor for the synthesis of graphene-like carbon nano-sheets [59]. Asphalt or bitumen by-products from refining processes are used to pave roads, make shingles for roofs, and waterproof construction foundations [7].

The resolution of asphaltene structures and dynamics has sparked the development of a new field of Reservoir Fluid Geodynamics (RFG), new thermodynamic applications in reservoirs,

and new knowledge of tar mats [49]. Petroleum asphaltene has also been effective in the adsorption of phenols and their derivatives from aqueous solutions [60].

Conclusion

For a better knowledge of asphaltene composition and properties, fractionation and separation are crucial since they simplify the compound and provide property distributions rather than just averages. Effective analytical methods are essential for determining the physicochemical characteristics of asphaltenes, which are classified as a solubility class representing the most polar part of crude oil and having very high metal and heteroatom concentrations. The abundance of polar functional groups is caused by the presence of these unwanted components. Along with contacts between aromatic cores, these polar functional group interactions also act as driving forces in the formation of aggregations. Asphaltene aggregation and deposition result in catalyst deactivation, pipeline obstruction, and fouling/scaling of the internal surface of reservoirs, which pose serious issues for the oil industry. One of the most crucial concerns for petrochemistry has always been gaining a thorough grasp of the chemical makeup and aggregation process of asphaltene. There are numerous distinct supply materials and preparation techniques for asphaltenes, which further complicates the situation. As a result, certified fractionation processes and analytical methods are crucial.

Future Prospects

As technology develops and study advances, new knowledge will be revealed. Future research should focus on creating a separation method that can produce representative samples of the components of asphaltene. Because results on asphaltene are frequently incomparable because they were obtained with various samples, the first development of "standard" asphaltene samples, Asphaltene 2017 [50], was a useful starting point. Future copies of this first rudimentary asphaltene reference material are recommended. The

success of more sophisticated fractionation and analytical methods should be aided by this, and research indicates that high-resolution mass spectrometry and spectroscopy may hold the breakthrough in resolving these asphaltene issues.

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