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A Review of Asphaltenes: Composition, Structure, Properties, Behavior, and Applications

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Abstract

Asphaltenes are the highly aromatic and polar fractions of crude oil defined by their insolubility in n-alkanes and solubility in aromatics. They exhibit complex molecular compositions, broad molecular weight distributions, and a strong tendency to self-associate. Research using advanced analytical methods, like Fourier transform ion cyclotron resonance (FT-ICR MS), has shown that asphaltenes contain a lot of different atoms and structures, leading to the development of several molecular models, including the Yen–Mullins model and island/archipelago structures. Physiochemically, asphaltenes show high thermal stability and unique optical/electrical properties, and they play a key role in stabilizing water-in-oil emulsions. On the downside, asphaltene aggregation and deposition can cause serious flow assurance problems in petroleum production. This review comprehensively summarizes the composition, molecular structure, aggregation behavior, phase behavior, emulsification role, deposition mechanisms, and industrial handling of asphaltenes, including biodegradation. The aim is to provide an updated understanding of these complex substances and to discuss future outlooks for managing asphaltene-related challenges and harnessing their value.

Keywords: Asphaltenes; Composition; Aggregation behavior; Phase behavior; Applications.
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1. Introduction

Petroleum products play a crucial role in the economic development of any nation. As known petroleum reserves dwindle, previously underutilized energy resources are becoming increasingly attractive. Among these, bitumen represents a highly promising alternative, offering significant potential to meet the growing demand for petroleum-based feedstocks.[1] The organic part separated from the mineral parts of the oil sand is called natural bitumen, according to its global name. Bitumen or natural bitumen, like usual petroleum components, can be divided into multiple compounds and will contain a percentage of dissolved gases, liquids, and solids. Including liquids, they can be further divided into saturates, aromatics, and resins. Different types of solids may also exist in bitumen, such as asphaltene. It entails a time-consuming chromatographic separation of de-asphalted oil into saturates, aromatics, and resins known as Saturate, Aromatic, Resin and Asphaltene (SARA) analysis.[2]

Asphaltenes are high-molecular-weight aromatic compounds found in crude oil, typically composed of polycyclic aromatic cores, alkyl side chains, heteroatoms, and trace metals and their content is usually around 0-20% in hydrocarbons. Table 1 shows the content of asphaltene from different sources. Asphaltenes exhibit highly complex molecular structures and significant compositional diversity. Because of interactions like π–π stacking, hydrogen bonding, and van der Waals forces, asphaltene molecules often group together to form tiny clusters, leading to special behaviors that affect their stability and how they settle in a solution. These

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characteristics greatly affect how petroleum is produced, moved, and processed, as asphaltene clumping or settling can lead to blocked pipelines, buildup, and reduced effectiveness of catalysts (see Fig. S1). Moreover, asphaltene deposition poses serious flow assurance problems, making it one of the key operational challenges in the petroleum industry.[3] Recently, increasing attention has been paid to the potential applications of asphaltenes beyond traditional refining, leveraging their strong aromaticity, high carbon content, and tunable structures for the development of functional nanomaterials. Studies have demonstrated that asphaltenes can serve as precursors for carbon materials, conductive films, dye-sensitized solar cells, and other advanced materials, showing promising potential in fields such as energy and environmental applications.[4] A systematic review is necessary to clarify the connections between asphaltenes' multi-scale complexity, significance, structure, properties, behavior, and applications.

In this review, we use a framework that looks at structure, properties, behavior, and applications to clearly summarize the latest research on asphaltenes (Fig. 1). Topics discussed include what asphaltenes are made of and their molecular structure, their physical and chemical properties, how they behave in different phases, their role in oil-water mixtures, how they build up and ways to reduce that, challenges in industry and how to use them, how they break down in the environment. The objective is to deepen the scientific understanding of this complex multiphase system and to identify future research directions.

2. Methods

To build this review, we conducted a comprehensive literature search across databases including Scopus, Web of Science, ScienceDirect, Wiley Online Library, SpringerLink, and Google Scholar, covering the years 1990 to 2024. The search focused on studies addressing the structural evolution of asphaltenes, their aggregation and phase behavior, emulsification mechanisms, deposition prediction and control, industrial handling, and environmental remediation potential. Keywords like "asphaltenes," "asphaltene aggregation," "asphaltene deposition," "asphaltene phase behavior," "asphaltene in emulsions," "asphaltene biodegradation," and "coal-derived asphaltenes" were chosen to make sure the review stayed closely related to its main topics.

3. Composition and molecular structure of asphaltenes

3.1 Chemical composition and elemental distribution

The chemical composition of asphaltenes is highly complex, consisting primarily of carbon, hydrogen, oxygen, nitrogen, sulfur, and trace metals such as nickel and vanadium. Typically, asphaltenes contain over 80% carbon and around 8–10% hydrogen by weight, with the remainder comprising

Table 1: Comparison of asphaltene content from different sources

Hydrocarbon sources	Daqing	Shengli	Saudi medium	Iranian heavy	Oman	Athabasca bitumen	Munaily-Mola bitumen	Karazhanbas crude oil
Asphaltenes, %	0.00	2.20	9.30	10.80	2.00	15.59	6.2	5.9
References	[1]	[1]	[1]	[1]	[1]	[1]	[2]	[2]

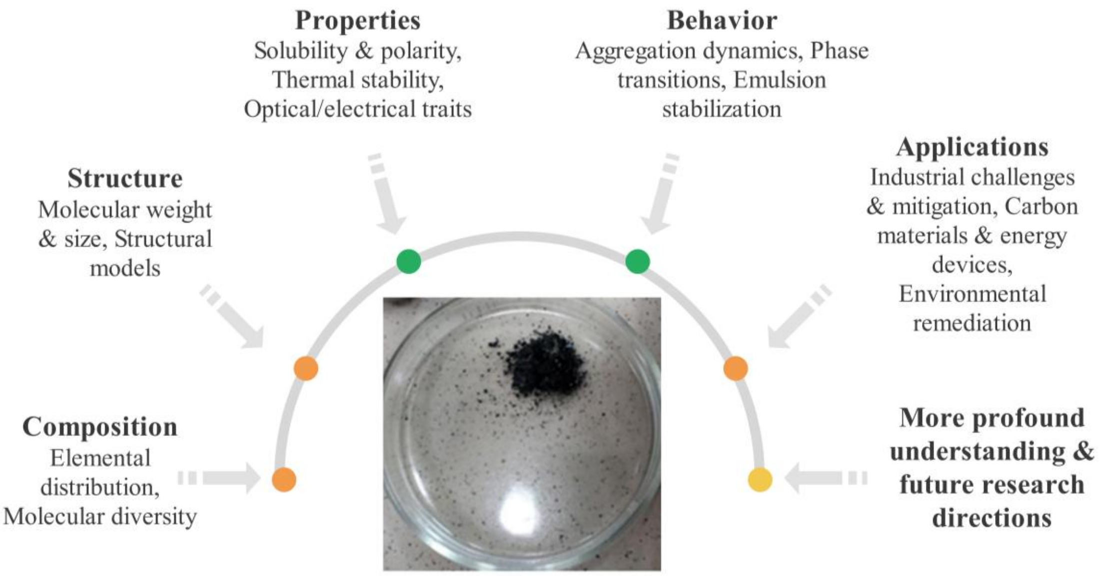


Fig. 1: Research diagram of review paper.

Table 2: Elemental composition of asphaltenes.

Element	Asphaltenes from Athabasca bitumen	Asphaltenes from Beke field oil sands bitumen	Cracking asphaltenes from Beke field oil sands bitumen
C	80.71	77.30	81.91
H	7.95	7.59	7.00
S	4.78	1.00	0.64
N	0.99	1.07	1.45
O	2.07	13.04	9.00
References	[1]	[10]	[10]

heteroatoms and trace metals.[5] Table 2 presents the results of elemental analysis. The forms of these heteroatoms significantly influence asphaltene properties. For example, oxygen in asphaltenes is often present as hydroxyl, carbonyl, or ether groups; nitrogen occurs mainly in pyrrolic and pyridinic structures; and sulfur appears as thiols, thioethers, and thiophenes.[6] These functional groups impart strong polarity to asphaltenes, affecting their solubility and reactivity. Moreover, metals like nickel and vanadium are frequently found in porphyrin complexes within asphaltene molecules, and the content and speciation of these metals can directly influence asphaltene catalytic behavior and deposition tendencies.[7] High-resolution mass spectrometry (*e.g.*, Electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) has revealed a wide distribution of heteroatom-containing species in asphaltenes, including N_1, O_1, and S-containing classes. These polar species increase the polarity and complexity of asphaltenes, significantly influencing their solubility and reactivity,[8] Fig. 2 shows the comparison of heteroatom compounds and their relative abundance in Munaily-Mola bitumen and Munaily-Mola asphaltenes in negative ion mode.[9]

3.2 Molecular weight distribution and structural features

Recently, industrial observations have shown that asphaltenes form colloidal aggregates in crude oil with a wide molecular weight range (1000–50,000 Da) and diameters of approximately 3–5 nm. In commercial separation processes, light hydrocarbons like propane and butane are used as solvents,[11] and how much asphaltenes are produced depends on the type of solvent, how well it dissolves,[12,13] and the ratio of bitumen to solvent. Asphaltene molecules stay separate in oil at very low amounts (less than 2.1 mg/L,[14] or less than 5.10 mg/L (according to some sources),[15] but when the concentration reaches a certain level (50–200 mg/L),[16-19] 6–10 molecules stick together to form stable groups called nanoaggregates that are 2–10 nm in size.[20] Increasing the concentration further creates more of these groups without changing their size; at 2–5 g/L, these nanoaggregates form larger clusters of 8–10 units,[20-21] which can range from 6 to 30 nm in size (sometimes even up to 100 nm).[11]

To study the structure and aggregation of the asphaltene surface, the produced samples were examined by scanning electron microscopy (SEM). The resulting surface images provide some information about the characteristics of asphaltogenic aggregation. As seen in Figs. 3A and 3B, derived asphaltenes have a medium-ordered structure, and the main component of the surface is represented by amorphous carbon.[11] There are more subtle aspects of carbon layers related to structure and aggregation that electron microscopy data cannot detect.

Scanning electron microscopy does not give us complete information about the processes of aggregation of asphaltenes, and therefore, the paper studied by transmission electron microscopy (TEM).[11] Results of the TEM analyses of the

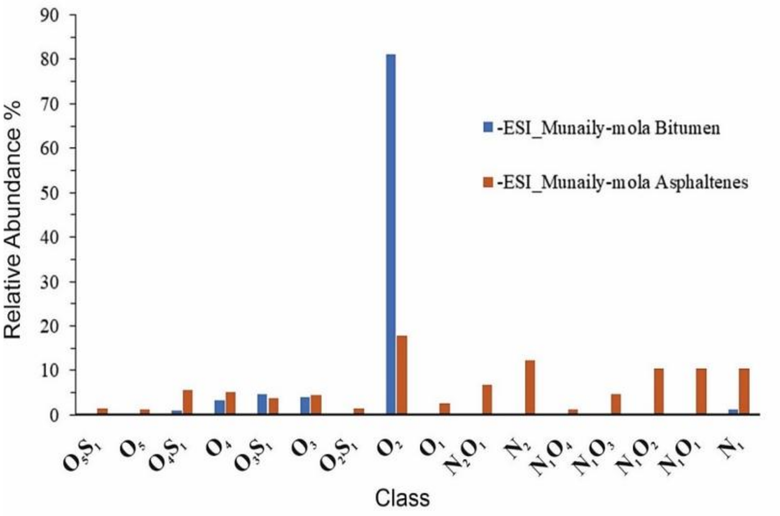


Fig. 2: Relative abundance of compound classes in Munaily-Mola bitumen and its asphaltenes.[9]

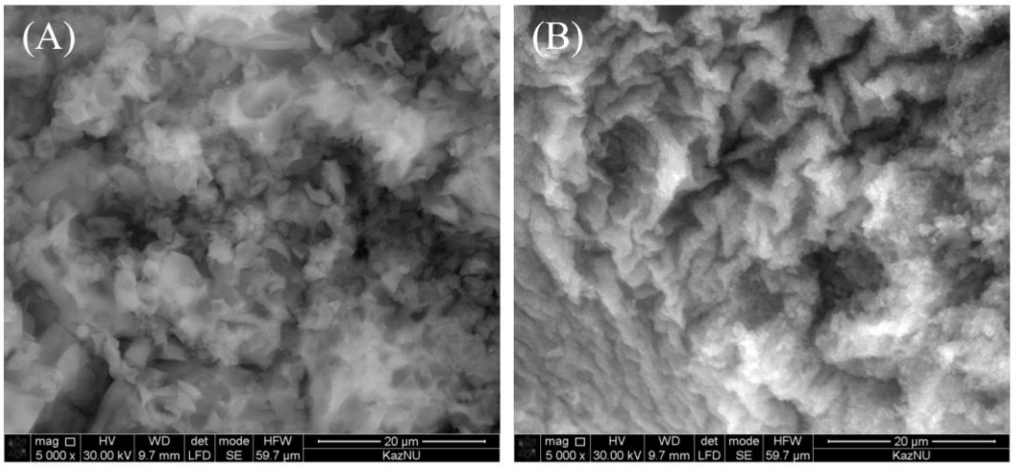


Fig. 3: SEM images of asphaltene surface precipitated from natural bitumen.[11]

asphaltene surface precipitated from natural bitumen are shown in Fig. 4. Asphaltene samples consist mainly of fragments of sufficiently dense films (Fig. 4A). For some annealing of the sample occurs thinning of the film and occasionally there are sample substances of formation having a crystal lattice. At the edge of the film may be dense, large and thin particles (Fig. 5B).

Studies using high-resolution TEM and energy-dispersive X-ray spectroscopy (EDX) reveal that well-separated asphaltene samples consist of carbon frameworks containing heteroatoms (S, V, Si) like fullerene-type structures. High-resolution (HR)-TEM images (Fig. 5) display graphene-like layers with ~0.39 nm spacing and 1.5 nm two-shell architectures.[11] As the electron beam keeps shining on them, "onion-like" fullerene layers and C@C structures appear and then break down,[11] showing that they are not very stable, probably because of the heteroatoms mixed in.[13]

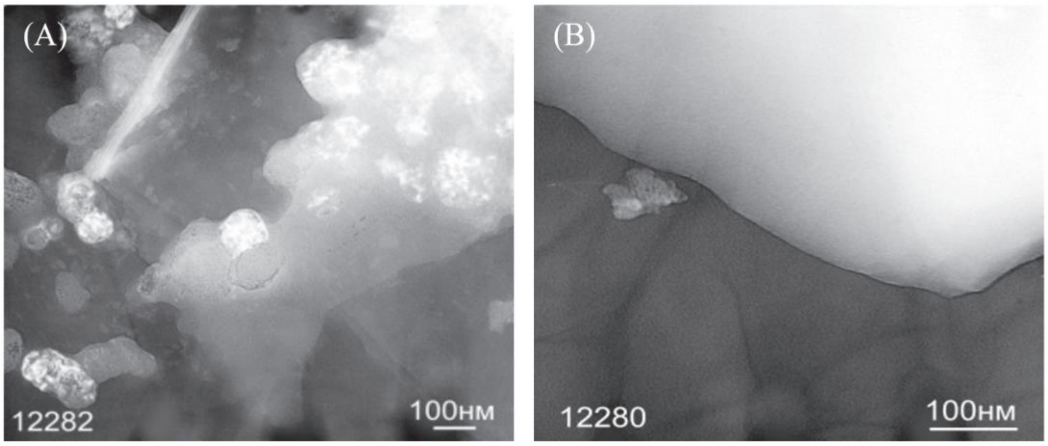


Fig. 4: TEM images of asphaltene.[11]

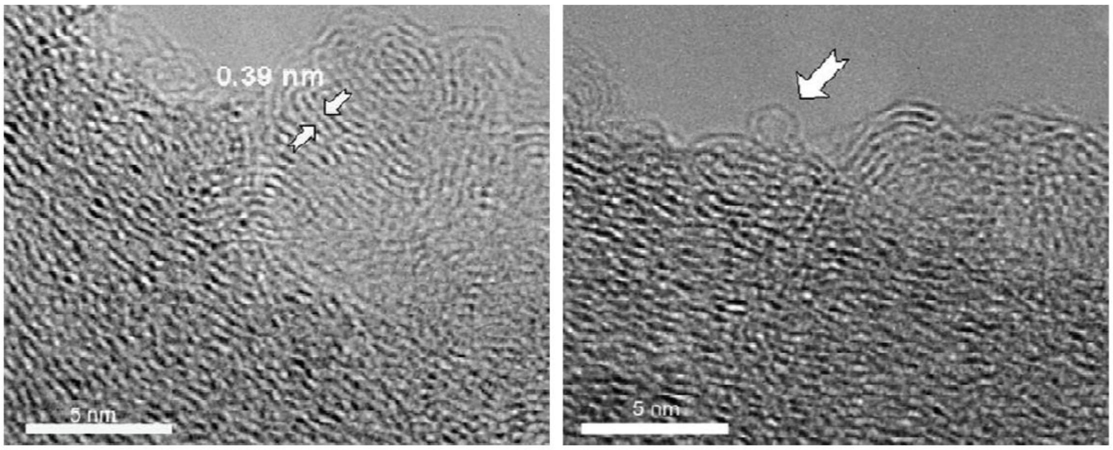


Fig. 5: High-resolution image of the structure of the asphaltene aggregates.[13]

3.3 Molecular structural models

Given the complexity of asphaltene molecules, various models have been proposed to describe their molecular architecture. Early on, the "island model" imagined each asphaltene molecule as one big polyaromatic center with side chains, while the different "archipelago model" suggested that an asphaltene molecule could be made up of several smaller aromatic parts connected by links (like methylene groups). These two models highlight different structural motifs in asphaltenes, as shown in Fig. 6.[21]

Many studies now agree on the molecular structure of asphaltene aggregates, and the updated Yen model (the Yen-Mullins model) has become one of the most accepted ways to represent asphaltene structure. The original Yen model was proposed by Professor Yen and colleagues in 1967 to describe chemical moieties in asphaltenes. It was revised in 2010 by Mullins *et al*. to incorporate both molecular-scale and colloidal characteristics, leading to the now widely accepted Yen–Mullins model.[22] The Yen–Mullins model describes asphaltenes in a hierarchical structure from monomers to nanoaggregates to clusters, depending on crude oil type (see Fig. 7). In light crude oils (high American Petroleum Institute (API) gravity), asphaltenes predominantly exist as small polyaromatic molecules ~1.5 nm in diameter at low concentrations, remaining largely unassociated. In medium or black oils (which have lower API), the amount of asphaltenes goes up, causing the molecules to stack together and form small groups about 2 nm wide. In heavy oils (very low API), a higher amount of asphaltenes causes them to group together into clusters made of several nanoaggregates, which can be about 5 nm wide. This model reflects the close relationship between asphaltene aggregation and crude oil density/API gravity and reveals the significantly negative impact of asphaltenes on crude oil properties (*e.g.*, decreasing API gravity). Overall, the Yen-Mullins model connects the behavior of tiny molecules and larger particles, giving a strong foundation for understanding how asphaltene structure and clumping affect crude oil properties.[23]

This model helps us understand how asphaltene size changes when concentration goes up and shows how asphaltenes can harm crude oil properties, like making it thicker and lowering its API gravity. It serves as a robust framework for interpreting the molecular and colloidal behavior of asphaltenes across a range of petroleum systems.[23]

Research has found that the molecular weight characteristics of asphaltenes are closely related to the content of heteroatoms and the degree of aromatic condensation; the incorporation of nitrogen, sulfur, and oxygen can increase

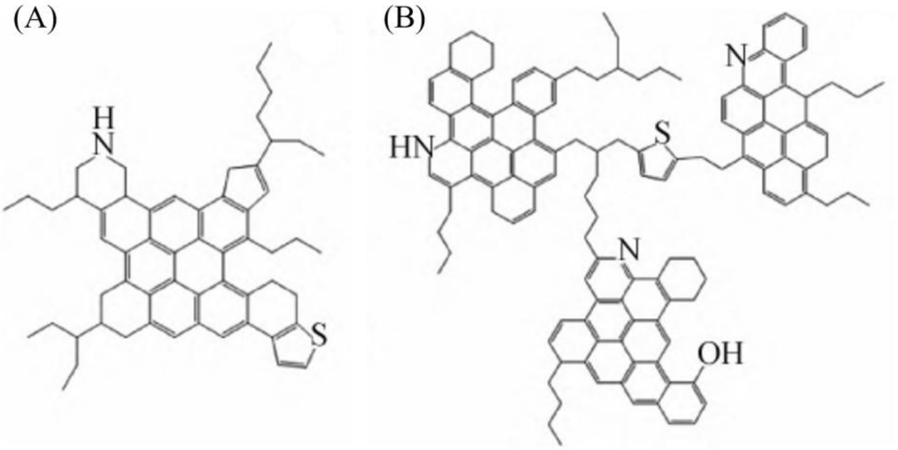


Fig. 6: Basic structural unit model of asphaltene molecule.[21] (A) Island molecule: (B) Archipelago molecule.

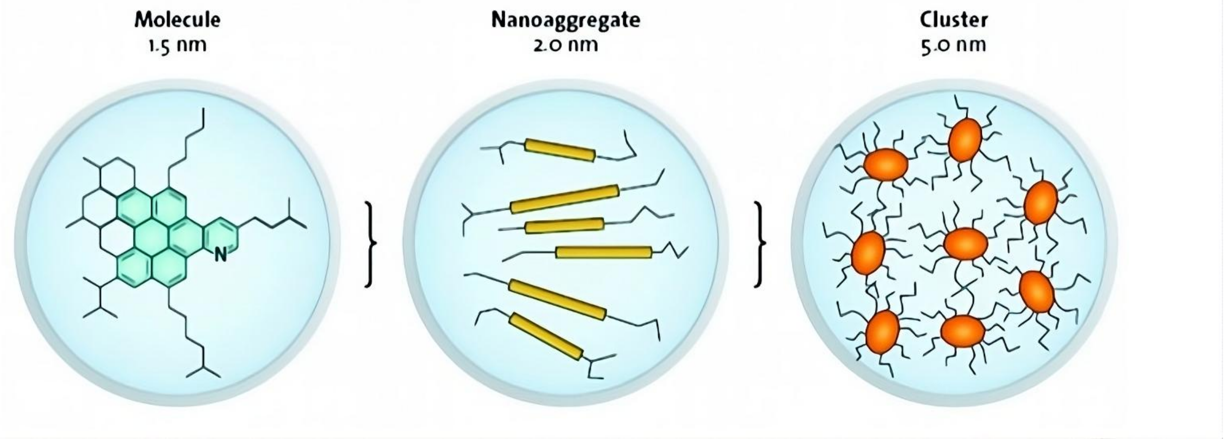
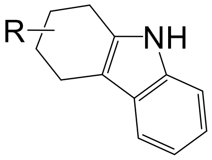
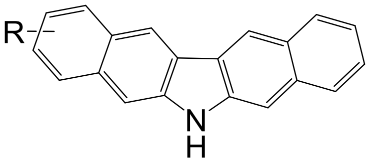
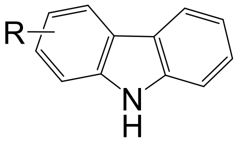
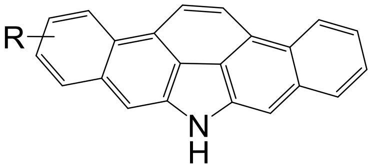
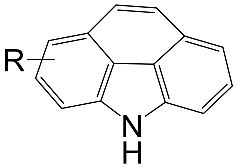
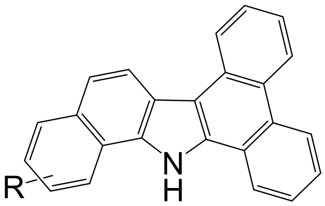
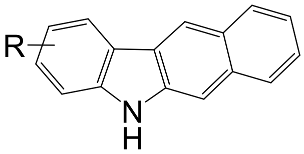
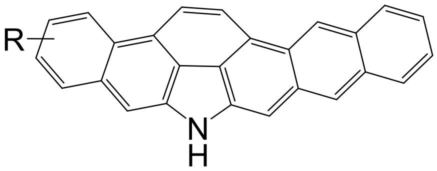
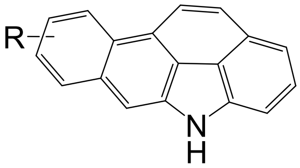
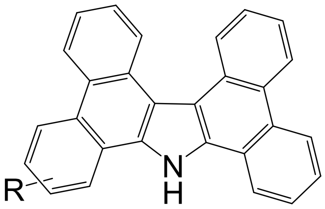


Fig. 7: Modified Yen model.[22]

Table 3: Possible molecular formula of the neutral nitrogen species of N_1 class.[9]

DBE	Structural formula	DBE	Structural formula
7		15	
9		17	
11		18	
12		20	
14		21	

molecular polarity and alter molecular weight distribution.

Based on the concept of double bond equivalents (DBE), the molecular formulas of N1 compounds observed in negative ion mode can be inferred, as illustrated in Table 3. When the DBE ranges from 9 to 18, these compounds are likely to be nitrogen-containing carbazoles. Those with a DBE value of 12 are more prevalent in bitumen and are likely structured as benzocarbazoles. Contrarily, asphaltenes more commonly contain compounds with a DBE of 18, which we presume to be nitrogen compounds of the tribenzocarbazole type. Furthermore, asphaltenes derived from different sources display unique structural traits; for instance, coal-derived asphaltenes typically contain a higher number of aromatic rings and nitrogen heterocycles, contributing to increased polarity and a distinct functional group profile compared to their petroleum-derived counterparts.[17]

4. Physical and chemical properties of asphaltenes

4.1 Solubility and polarity

One of the fundamental properties of asphaltenes is the extreme sensitivity of their solubility to the nature of the solvent. Operationally, asphaltenes are defined as insoluble in n-alkanes (*e.g.*, n-heptane or n-pentane) but soluble in aromatic solvents such as toluene or benzene.[5] Solvent aromaticity and polarity significantly affect their solubility: aromatic solvents can stabilize dispersed asphaltene molecules via π–π interactions, maintaining them in solution, whereas non-aromatic alkanes tend to induce aggregation and precipitation.[7, 24] In addition, naturally occurring surfactant-like components such as resins influence asphaltene solubility and phase equilibrium.[25] The impact of temperature is complicated: higher temperatures usually make substances dissolve better by breaking apart the forces between molecules, but too much heat can cause them to clump together and lower how well they dissolve. When temperatures rise, the weak forces in supramolecular aggregates turn into strong covalent bonds, which makes heavy oil more likely to form coke. A schematic illustration is shown in Fig. 8.[6,24] Pressure also alters the phase behavior of asphaltenes–depressurization (such as during oil production) often promotes their precipitation.[24] Importantly, the solubility of asphaltenes significantly decreases in saline environments; high salinity and specific ions (*e.g.*, Ca^{2+}) promote asphaltene precipitation,[26] which is particularly relevant in offshore reservoirs and high-salinity formations. Recent studies have also proposed quantitative parameters to describe asphaltene solubility, suggesting a solubility parameter range of 19–24 $MPa^{0.5}$.[3]

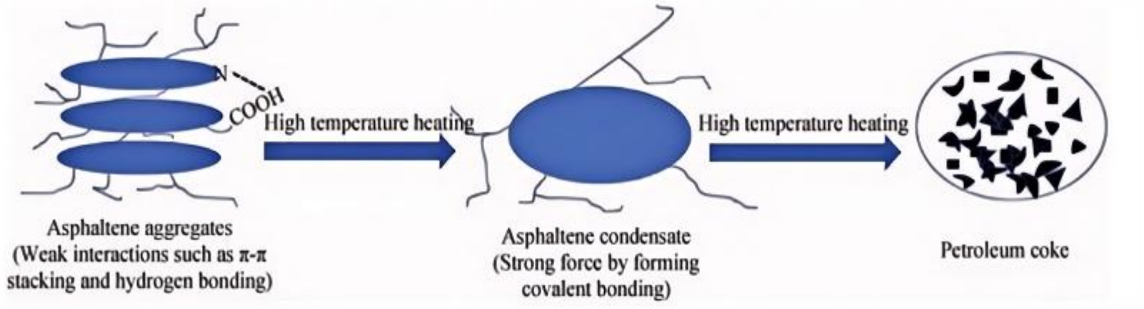


Fig. 8: Mechanism of petroleum asphaltene coking.[21]

4.2 Aggregation and dispersibility of asphaltenes

The self-assembly and aggregation of asphaltenes are driven by multiple non-covalent intermolecular forces—including acid–base interactions, hydrogen bonding, metal coordination, hydrophobic effects, and aromatic π–π stacking. Cooperatively, these weak forces form thermodynamically stable supramolecular aggregates (see Fig. 9).[21,22] Moreover, in the presence of water, hydrogen bonding becomes more pronounced, and van der Waals forces further enhance asphaltene adsorption onto solid surfaces.[3,20]

The proposed supramolecular assembly of asphaltenes illustrates various association mechanisms, each represented by a different color: blue for acid–base and hydrogen bonding interactions, red for metal coordination complexes, orange for hydrophobic pockets, and green for π–π stacking interactions.[27]

In crude oil or solvent systems, how stable asphaltene mixtures are relies on the interactions between natural dispersants like resins and asphaltene clumps. When resin levels are sufficient, they adsorb onto the aggregate surfaces, inhibiting excessive clustering and maintaining dispersion stability;[21] however, under resin deficiency or abrupt temperature–pressure changes, aggregates destabilize and precipitate, causing flow assurance issues.[6] It's important to fully understand how asphaltenes clump together and how they can be spread out to create better anti-aggregants/dispersants and enhance the flow of oil and gas during production and transport.[3]

4.3 Thermal stability and pyrolysis characteristics

Asphaltenes are very stable when heated because their tightly packed aromatic structures make them better at resisting heat than regular hydrocarbons.[6,21] Thermogravimetric analysis (TGA) reveals that significant weight loss only occurs above ~400 °C, primarily between 420–520 °C, indicating molecular stability at lower temperatures.[6] At higher temperatures (above 400–500 °C), asphaltene molecules break down and create new C–C covalent bonds, which results in more coke being produced. Having elements like sulfur and nitrogen leads to gas emissions such as H_2S and NH_3 and causes flaws in the resulting coke or carbon materials.[6,21]

In the petroleum industry, asphaltenes are the main precursors of coke. Their pyrolytic behavior significantly affects catalyst ouling, coking rates, and overall process

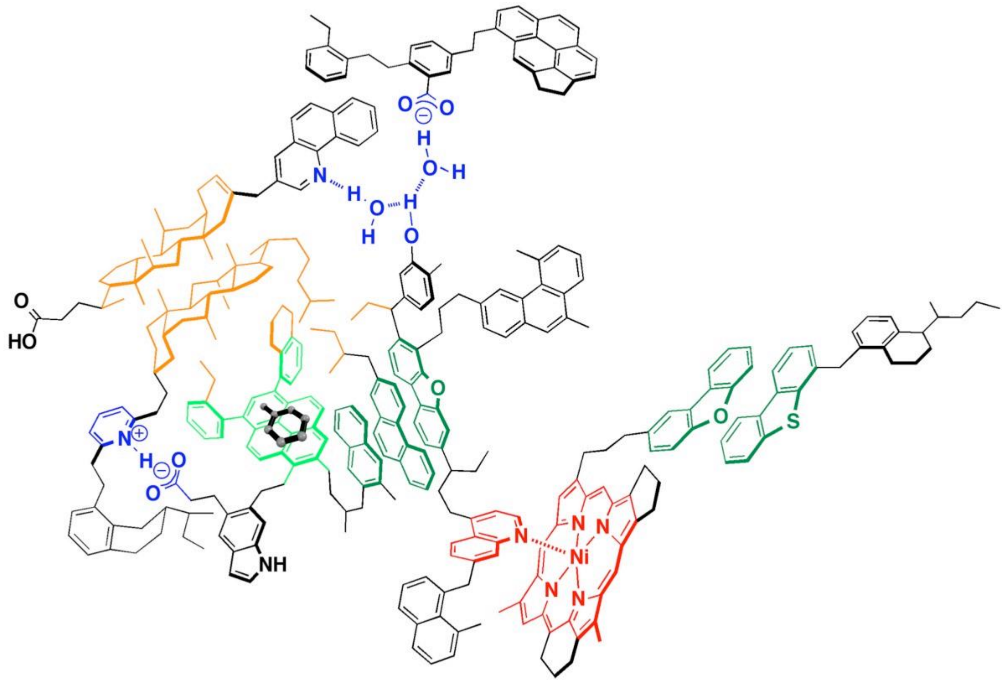


Fig. 9: Supramolecular assembly model of asphaltene.[22]

stability.[6] However, because asphaltenes have a lot of carbon and are aromatic, they can be good starting materials for useful carbon products like activated carbon, graphene-like nanostructures, and carbon fibers. Controlled thermal treatment enables the production of value-added materials for energy storage, electrodes, and adsorption applications.[28]

^{1}H Nuclear magnetic resonance (NMR) spectroscopy (Table 4) is used to characterize aromaticity and molecular evolution. The amount of aromatic carbon is an important sign—feed asphaltenes have 14.28 wt.% aromatic carbon, which is linked to a high coke yield.[10] Reactive side chains connected to aromatic or sulfur moieties decompose at high temperatures, releasing gas and reducing hydrogen content (Table 3).

During pyrolysis, the amount of aromatics in the liquid increases because aliphatic pieces are taken away while aromatic structures stay. Olefins generated from chain scission may undergo radical addition and rearrangement to form new aromatic species. Computational data confirm that molecules with more, smaller structural blocks are thermodynamically more stable than those with fewer, larger blocks. Layered molecular structures are also more stable than amorphous forms.[10] Fig. 10 shows the structure of the asphaltene product after being heated at 600 °C, and it has an amorphous carbon structure. It was formed 5.12 nm of nanoparticles at high-temperature heating.[11]

4.4 Optical and electrical properties

Asphaltenes exhibit unique optical and electrical properties due to their highly conjugated aromatic structures and the presence of heteroatoms.[3] In the ultraviolet-visible spectrophotometry (UV-Vis), they typically display broad and intense absorption bands, indicating the existence of large π-conjugated systems. Some asphaltene solutions can glow in the visible range when exposed to UV light, and how bright they glow, and the color of the glow depends on how the asphaltene molecules are grouped together and their chemical features. These optical features make fluorescence spectroscopy a useful method for studying how asphaltenes interact with each other and how they group together.[3]

Electrically, the delocalized π-electrons in the aromatic rings provide a basis for a certain degree of charge transport. Even though asphaltenes usually don't conduct electricity well, they can show some electrical conductivity when they clump together in certain ways, depending on how their molecules are arranged. For instance, modifying the aggregation morphology or introducing conductive additives can enhance their conductivity to some extent.[3] These electrical modulation mechanisms suggest that processed asphaltene materials could have potential applications in flexible electronics, sensors, or energy storage systems.[28] Thus, studying the optical and electrical properties of asphaltenes helps us learn more about their molecular structure and how they group together, and it also aids in finding ways to use them in creating useful materials.[3,21]

5. Phase behavior and thermodynamics of asphaltenes

The phase behavior of asphaltenes in crude oil systems is important when predicting their precipitation and aggregation. Researchers have extensively studied asphaltene phase behavior under various conditions through experimental and thermodynamic modeling approaches. When it comes to temperature, small increases usually help asphaltenes dissolve, but very high temperatures can cause asphaltene molecules to clump together and form large, insoluble particles.[24] In terms of pressure, decreases during reservoir production often cause asphaltenes to precipitate and deposit within wellbores and formations.[29]

Table 4: NMR results (wt. %) of macromolecular compounds.[10]

Sample	H			
	Aromatic	CH_3	CH_2	CH
Initial asphaltenes	14.28	24.97	45.94	14.81
Cracking asphaltenes	14.75	24.63	50.19	10.43

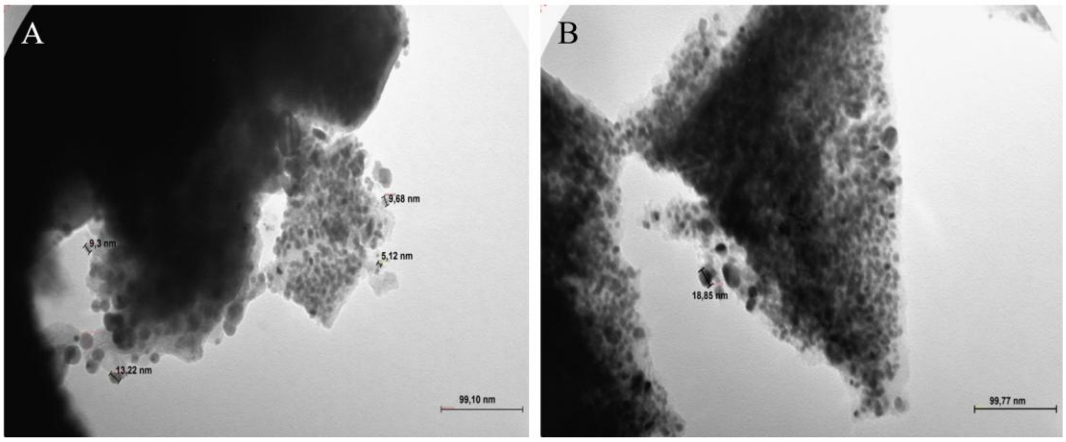


Fig. 10: SEM images of asphaltene products after heating at 600 °C.[11]

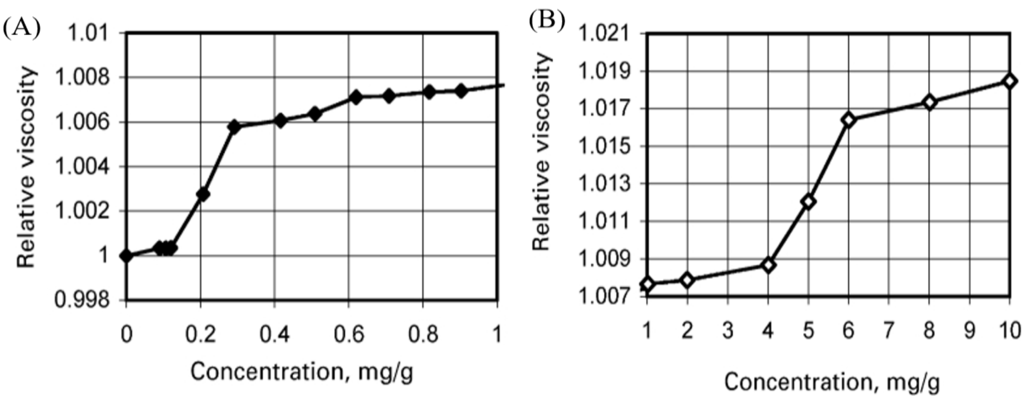


Fig. 11: (A) Variation of relative viscosity versus low asphaltene concentrations (0–1 mg/g), (B) Relative viscosity of asphaltene in the concentration range of 1–10 mg/g.[31]

Concerning solvent polarity, aromatic-rich systems have a stronger capacity to dissolve asphaltenes, whereas increasing the proportion of non-polar alkane components tends to trigger asphaltene precipitation.[24] Thermodynamic models that use equations of state, like Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT), have been successful in predicting how asphaltenes behave in different phases.[30] Studies show that elevated temperatures enhance the aggregation tendency among asphaltene molecules, thereby influencing their precipitation in produced fluids.[30] Additionally, certain enhanced oil recovery (EOR) operations can significantly alter asphaltene phase behavior; for example, in CO_2 flooding, the injected CO_2 reduces asphaltene stability in crude oil, causing large-scale precipitation, with the severity depending on injection pressure and oil composition.[29]

Furthermore, interactions between molecules, like hydrogen bonding, dipole–dipole interactions, and charge-transfer complexes, are important for how asphaltenes clump together and separate into different phases. Methods like ultrasonication or chemical additives can disrupt these interactions, altering asphaltene phase behavior and promoting disaggregation.[21]

5.1 Critical micelle concentration and coacervation point

The aggregation behavior of asphaltene in solution can be quantitatively characterized by two key parameters: the critical micellization concentration (CMC) and the micelle coacervation point (MCP).[31] As seen in Fig. 11A, at low concentrations (0–1 mg/g), the relative viscosity shows two clear changes that match the CMC and the micelle saturation point, showing a shift from single molecules to groups of molecules called micelles. Below the CMC, asphaltene molecules exist stably as monomers. Once the concentration exceeds the CMC, the molecules begin to self-assemble into micellar aggregates through π–π interactions between aromatic rings. With a further increase in concentration of MCP, these micellar aggregates coalesce into larger coacervate clusters, ultimately leading to macroscopic phase separation. As illustrated in Fig. 11B, two additional inflection points are observed in the higher concentration range (1–10 mg/g), corresponding to the MCP and the onset of phase separation.

Experimental evidence also shows that the solvent environment significantly influences aggregation behavior. In aromatic solvents like n-methylnaphthalene, asphaltene is more likely to form micellar structures, leading to a much lower CMC compared to non-aromatic systems.[31] Furthermore, temperature exerts a strong regulatory effect on micellization. As shown in Fig. 12, when the temperature goes up, the important concentration levels (CMC, MCP, *etc.*) come closer together, which reduces the stable colloidal area and speeds up the process of larger particles forming. These parameters provide an important basis for predicting and controlling asphaltene deposition behavior under various conditions.

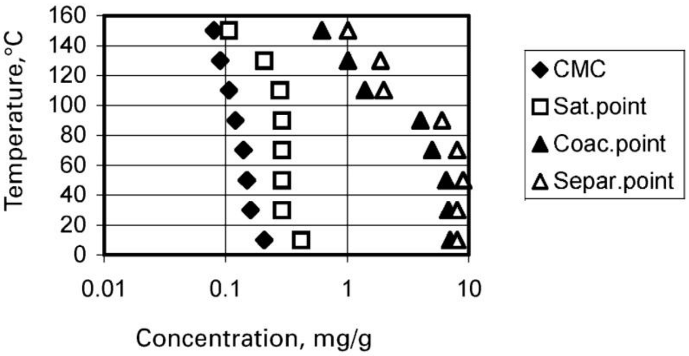


Fig. 12: Phase diagram of asphaltene in 1-methylnaphthalene showing CMC, MCP, and separation point at various temperatures, indicating a reduced stability zone as temperature increases.[31]

5.2 Thermodynamic modeling and deposition prediction

To predict the phase behavior and deposition risks of asphaltenes, various thermodynamic models and numerical simulation methods have been developed.[30,32] One commonly used method is the PC-SAFT equation, which comes from statistical thermodynamics, and it helps to understand and predict how asphaltenes behave in oil and gas systems. The model parameters can be calibrated with experimental data, enabling predictions of asphaltene precipitation under different temperatures, pressures, and compositions.[30] Moreover, by evaluating asphaltene stability under various temperature–pressure conditions, pressure management strategies in production facilities can be optimized to reduce deposition risks. The asphaltene deposition process usually involves clumping together, breaking apart colloids, sticking to surfaces, and finally settling down, as shown in Fig. 13. Overall, integrating experimental data with thermodynamic modeling significantly improves the quantitative prediction of asphaltene phase behavior and provides theoretical guidance for field operations.[32]

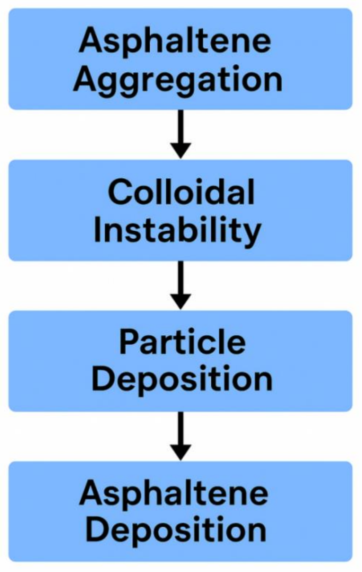


Fig. 13: Schematic diagram of the typical asphaltene deposition process.

6. Role of asphaltenes in oil–water emulsions

6.1 Interfacial adsorption and emulsion stability

Asphaltenes act as natural emulsifiers in oil–water systems and play a crucial role in the formation and stability of emulsions. Studies have shown that crude oil from which asphaltenes have been removed cannot form stable emulsions, underscoring the key role of asphaltenes in emulsion stabilization.[33] The presence of polar functional groups, like those containing oxygen and sulfur, in asphaltene molecules helps them stick to the oil-water boundary, creating strong films at that surface.[3,26] These interfacial films not only physically prevent direct contact between dispersed phase droplets but also effectively reduce interfacial tension, thereby improving emulsion stability.[30]

6.2 Temperature effects and interfacial behavior of functionalized asphaltenes

External physical conditions, such as temperature, have a significant impact on the interfacial behavior of asphaltenes. Research using the PC-SAFT model shows that asphaltenes are more likely to clump together and come out of solution at lower temperatures, which means that higher temperatures can help them mix better in crude oil systems. Table 5 clearly illustrates the effect of temperature on asphaltene precipitation. As the temperature goes up from 130 °F (about 54 °C) to 254 °F (about 124 °C), the amount of asphaltenes that settle out decreases a lot, showing that asphaltenes are more stable at higher temperatures.[30] In addition, chemically modified asphaltene particles have been shown to exhibit super-hydrophobicity and excellent interfacial activity, offering potential applications in controlling and separating crude oil emulsions.[34] These novel asphaltene-derived materials present promising new strategies for stabilizing or breaking emulsions.

The stability of many crude oil emulsions is primarily attributed to asphaltenes. Besides the effects of functional groups mentioned earlier, the tiny structure and variety in size of asphaltenes also affect how well they can stabilize emulsions. Studies have found that some asphaltene molecules can adopt fullerene-like arrangements at interfaces, forming densely packed structures that further reinforce the interfacial film's strength and stability.[13] Moreover, modifying asphaltenes – for example, creating modified asphaltene nanoparticles (MA-NPs) – can impart superhydrophobic properties; such nanoparticles can stabilize emulsions in a manner similar to solid particles (Pickering emulsions).[34]

Zeta potential is considered an important indicator of asphaltenes' ability to stabilize emulsions: a high zeta potential indicates stronger electrostatic repulsion between asphaltene colloids, helping prevent coalescence and leading to more stable emulsions, whereas asphaltenes with low zeta potential tend to aggregate, resulting in emulsion destabilization.[35] Experimental evidence shows that asphaltenes in crude oil form aggregates on the order of 20–30 Å (approximately 2–3 nm), and these nanoaggregates can reorganize at the oil–water interface to form stable adsorption layers.[7] Some supramolecular aggregates of asphaltenes form interfacial films with high elasticity and viscosity, making them difficult to rupture. Therefore, asphaltenes help keep emulsions stable in several ways, like acting as surfactants and stabilizing particles, and they are essential for creating naturally stable emulsions.

6.4 Influence of metallic impurities on emulsion stability

Asphaltenes in crude oil usually contain a lot of metal impurities, especially Ni, V, and Fe, which are mainly found in the asphaltene part and greatly affect how they behave at the oil-water boundary in emulsions.[22] Studies have shown that metals such as Ni and V can form stable coordination complexes with asphaltenes, enhancing their adsorption at the

Table 5: Variation of asphaltene content in the precipitated phase of crude oil at different temperatures, based on PC-SAFT modeling results.[30]

Temperature (°F)	Mole % of asphaltene in precipitated phase	Weight % of asphaltene in precipitated phase
130	15.2	72.45
165	11.8	66.91
254	7.9	57.24

oil–water interface and contributing to the formation of more robust interfacial films.[22,27] However, if there is too much metal, it can cause large clumps of asphaltenes to form, which then lead to merging and settling at the interfaces, making the emulsions unstable.[22]

Furthermore, metal oxide nanoparticles like Fe_3O_4 can accumulate at the oil–water interface as "seeds," promoting asphaltene deposition and affecting the structural integrity of Pickering emulsions. Consequently, in treating highly stable emulsions, the role of metallic impurities must be considered. Removing or passivating these metal particles (for example, via magnetic separation or functional additives) has been shown to significantly improve demulsification efficiency.[27]

6.5 Demulsification strategies targeting asphaltene interfacial films

In petroleum production and processing, demulsification is a critical step for achieving efficient oil–water separation. Asphaltenes create strong layers at the oil-water boundary that make it hard to separate them, so it's important to specifically break down these layers during demulsification.[5] Common strategies include: (1) heating the crude or injecting hot oil to weaken the asphaltene film and promote water droplet coalescence;[24] (2) applying physical methods such as ultrasonication or centrifugation to disrupt the asphaltene-stabilized interface and improve coalescence of the dispersed phase; and (3) utilizing supercritical fluid extraction (*e.g.*, supercritical CO_2) to effectively remove asphaltenes and metallic surface-active species, thereby improving overall dehydration efficiency.[36] These strategies represent interface-chemistry-oriented approaches that specifically target asphaltene stabilization mechanisms for efficient demulsification.

7. Asphaltene deposition mechanisms and mitigation

7.1 Mechanisms and impacts of deposition

Asphaltene deposition occurs when asphaltenes come out of crude oil and stick to the insides of pipelines, the tiny openings in reservoirs, or production equipment. This deposition phenomenon typically occurs during crude oil production and transportation, resulting from asphaltene instability caused by variations in pressure, temperature, and composition. The key influencing factors include: pressure drop (for example, a reduction in bottomhole or pipeline pressure reduces oil solvency, causing asphaltenes beyond their solubility limit to precipitate); temperature reduction (cooling of crude oil lowers asphaltene solubility, and co-precipitation with wax is particularly common in subsea pipelines);[37] and changes in oil composition (such as gas injection or blending with diluents that alter the solvent power of the oil).[38]

Recent laboratory experiments have shown that cyclic, miscible N_2 injection in ultra-low-permeability shale cores (198 nD) can recover about 33 % of residual oil but also trigger progressive asphaltene precipitation within the pore network. This precipitation reduces pore size and alters wettability (contact angle increases from ~83° to 92–108°), leading to steadily declining oil recovery in later cycles.[39] Once formed, asphaltene deposits cause multiple adverse effects: in wellbores and pipelines, deposits narrow flow paths or even block them, significantly reducing oil mobility;[32] in reservoirs, deposits clog pore throats, leading to decreased permeability and production loss;[40] asphaltenes also stabilize water-in-oil emulsions, increasing the difficulty of crude oil dehydration;[27] in surface facilities like heat exchangers, storage tanks, and separators, asphaltene deposits hinder normal operations and necessitate frequent cleaning.[32,36] Additionally, when using CO_2 huff-and-puff or other methods to get more oil, adding CO_2 can make asphaltenes in crude oil unstable, causing them to settle in the reservoir and making it harder to recover oil.[29] Therefore, understanding the mechanisms of asphaltene deposition is crucial for developing effective prevention and remediation strategies.

Various standardized and experimental methods are currently available for asphaltene precipitation and isolation. These methods vary in the type of solvent used, the ratio of solvent to oil, the time taken for processing, and the way filtration is done, all of which affect the size and amount of asphaltene particles produced. Table 6 presents several representative standardized methods and their key experimental parameters.

7.2 Microscopic factors in deposition

In addition to macroscopic factors, the inherent properties of asphaltenes themselves determine their deposition tendencies. The structure of asphaltenes has a lot of aromatic rings, which makes them stick together and settle out of solution more easily; the more aromatic rings and the heavier the molecules are, the harder it is to keep them dissolved, and even small changes can cause them to settle out. Moreover, heteroatoms and metals in asphaltenes also play roles: for instance, sulfur- and oxygen-containing functional groups enhance the polarity of asphaltenes, strengthening interactions in polar solvents but promoting association and precipitation in non-polar media; metals like nickel and vanadium, if present as insoluble

Table 6: Comparison of different asphaltene precipitation methods.

Method	Solvent	Solvent/Oil Ratio	Operating Conditions	Filter Media	Reference
ASTM D-3279-07	n-heptane	100:1	Reflux for 30 min, settle at ambient for 1 h, filter at 38–49 °C	Fiberglass, 1.5 μm	[22]
ASTM D-4124-01	n-heptane	100:1	Heat in the steam bath for 30 min, settle at ambient overnight	Slow/medium paper, ~10 μm	[22]
ASTM D-4124-09	iso-octane	100:1	Reflux for 2 h, settle at ambient for 2 h	Medium glass frit, 10 μm	[22]
WRI	n-heptane	40:1	Heat to 80 °C for 5 min, stir at ambient for 16 h, settle for 30 min	Medium glass frit, 10 μm	[22]
ASTM D-6560-00	n-heptane	30:1	Reflux for 60 min, settle at ambient for 90–150 min	Whatman 42 paper, 2.5 μm	[22]
ASTM D-2007-03	n-pentane	10:1	Settle at ambient for 30 min	Rapid paper, 20 μm	[22]
IFP 9313	n-heptane	20:1–200:1	Heat to 80 °C for 5 min, filter at ambient	Cellulose ester filter, 0.45 μm	[22]
Our experimental methods	Benzene + Petroleum ether	~40:1 (Petroleum ether/bitumen)	Soxhlet extraction with benzene; dissolve in toluene; add 40× petroleum ether; settle in dark; repeated redissolution and settling until stable residue	Medium glass frit, 7 μm	[41]

complexes, can serve as nuclei for deposition particles.[22] The presence of water also changes how asphaltenes deposit: in systems with water, the amount of salt and the acidity can change the surface charge of asphaltene particles, which affects how stable they are. For instance, high salt levels (especially from sulfate or magnesium ions) can make the electrical layer around the particles smaller, leading to asphaltene clumping and settling.[26] Thus, from molecular structure to the surrounding environment, multiple factors jointly govern when and where an asphaltene deposit occurs.

7.3 Deposition monitoring and laboratory evaluation

To prevent and control asphaltene deposition, it is necessary to monitor and evaluate the conditions under which it occurs. In the laboratory, typical methods include hot filtration tests (filtering oil with asphaltenes at different temperatures and pressures to see how likely they are to deposit), visual high-pressure cell tests (watching asphaltenes form directly), and light scattering techniques (checking how the clarity of the solution changes under varying conditions).[32] In field operations, downhole deposition probes, pipeline pressure drops, and flow rate changes can serve as indicators to warn of asphaltene deposition. Additionally, advanced techniques such as nuclear magnetic resonance (NMR) imaging and pore-scale microscopic imaging have been employed to observe asphaltene distribution within reservoir cores.[40] These monitoring and experimental tools are crucial for spotting asphaltene buildup early and creating specific plans to reduce it.

7.4 Asphaltene Inhibition or Removal Techniques

Asphaltene deposition in oil and gas production and transportation systems can lead to blockages in pipelines, surface and downhole equipment, and wellbores, compromising flow assurance and operational safety. Current mitigation methods are classified into four main categories:

Chemical inhibition & solvent washing. Injection of aromatic solvents (like toluene and xylene) or special surfactants helps dissolve asphaltenes or prevents them from clumping together; this allows existing deposits to be dissolved and cleaned out using solvent sweeps while the system is running or when it's turned off.[32]

Mechanical & high-pressure cleaning. Mechanical tools such as pipeline pigs, wax scrapers, and high-pressure water jets physically remove stubborn deposits from pipelines, heat exchangers, and separators with minimal process interruption.[32]

Advanced physical removal:

– Laser cleaning: High-energy laser pulses vaporize or decompose organic deposits in a non-contact, inline process.[24]

– Microwave heating: This method uses heat to specifically warm up areas with a lot of carbon, speeding up the breakdown of materials and helping to remove deposits.[24]

– Ultrasonic vibration: High-frequency elastic waves disrupt the microstructure of deposits and enhance desorption.[32]

Catalytic degradation and reservoir management:

Application of nanocatalysts to deposit surfaces catalyzes asphaltene breakdown into soluble or low-viscosity products under mild conditions;[42] low-salinity or tailored-ion waterflooding in the reservoir destabilizes asphaltene colloids, reducing near-wellbore and pipeline deposition.[26] Table 7 illustrates these techniques.

8. Industrial challenges and application technologies of asphaltene

Table 7: Classification of asphaltene inhibition or removal techniques.

Category	Techniques	Reference
Chemical inhibition & solvent washing	Aromatic solvent injection; surfactant addition; solvent sweeps	[32]
Mechanical & high-pressure cleaning	Pipeline pigs; wax scrapers; high-pressure water jets	[32]
Advanced physical removal	Laser cleaning; microwave heating; ultrasonic vibration	[24, 32]
Catalytic degradation & reservoir management	Nanocatalyst application; low-salinity water flooding	[26, 42]

8.1 Challenges in oilfield production

During oilfield development, significant concerns have arisen due to a series of challenges caused by asphaltenes. The most prominent issues are asphaltene deposition and emulsion stability. Deposition in wellbores and reservoirs can reduce oil production and necessitate frequent remedial interventions.[24] Stable water-in-oil emulsions increase the difficulty of crude oil dehydration and transportation.[27] Field experience shows that asphaltene behavior varies greatly among reservoirs, and crude oils with high asphaltene content often require customized process designs.[22] For example, in surface gathering systems, hot oil circulation is used to heat pipelines to prevent low-temperature deposition;[32] for highly emulsified crude, chemical demulsifiers are added to disrupt the asphaltene interfacial films.[42] Research also shows that some surfactants that interact with asphaltenes can change the surface structures and influence how well oil and water separate.[43] Additionally, CO_2 huff-and-puff and other enhanced oil recovery methods may induce asphaltene deposition, further impacting reservoir flow and recovery efficiency.[29] The destabilization of asphaltenes may occur at any stage within the oil production and processing infrastructure, extending from the near-wellbore region to downstream operations such as petroleum refining (Fig. 14).

8.2 Role of asphaltenes in refining processes

In petroleum refining, asphaltenes present both challenges and opportunities. On one hand, asphaltenes are very likely to create coke, which is a solid carbon substance, when heavy oil is heated: during high-temperature cracking and delayed coking, the large molecules in asphaltenes can combine to form this non-volatile coke, causing equipment to get dirty and harming catalysts. Different types of asphaltenes contribute differently to coke yield: even minor differences in aromatic structure can significantly affect coking tendency, explaining the varied behavior of asphaltenes from different sources in cracking processes. Refineries often take steps before processing to lower the amount of asphaltenes in the oil they use, like using solvent deasphalting to separate asphaltenes from vacuum residue, which can then be used for asphalt or fuel oil, making the later processes of catalytic cracking and hydrotreating work better.[6] On the other hand, asphaltenes can also be used as precursors for high-value products, such as producing carbon nanomaterials via pyrolysis,[44] or extracting contained metals for catalyst manufacturing.[22] The resulting coke-based and carbon-containing nanomaterials also can be used in the bitumen modification process. Therefore, managing asphaltenes in refining involves both mitigating their negative impacts and exploring their potential value.

8.3 Asphaltene recovery and pretreatment techniques

To enable efficient utilization of recovered asphaltene-rich feedstocks, specialized downstream recovery and pretreatment processes are required.[45] Supercritical fluid extraction (SCFE) uses CO_2 at high temperature and pressure to carefully pull out asphaltenes along with metals, sulfur, and certain compounds, allowing for a clean separation without leftover organic solvents.[22] Plasma pyrolysis or thermal cracking rapidly heats asphaltene molecules in plasma reactors or cracking furnaces, breaking them apart into valuable gases (H_2, CH_4) and producing highly graphitized carbon nanomaterials such as carbon nanotubes and carbon onions.[44] In addition, microwave or electromagnetic-assisted cracking utilizes volumetric heating effects of electromagnetic waves to

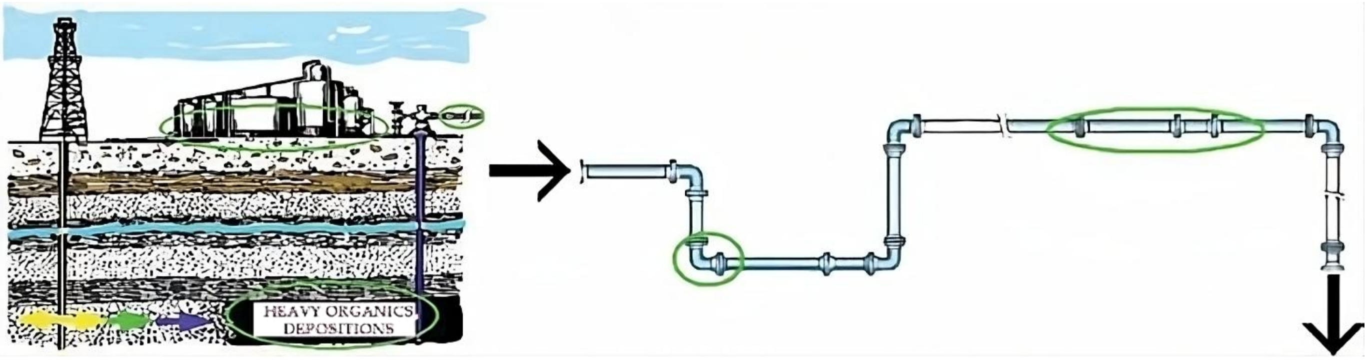


Fig. 14: Schematic illustration of potential sites (highlighted in green) where heavy organic deposits are most likely to form within petroleum fluid production and transportation systems.[32]

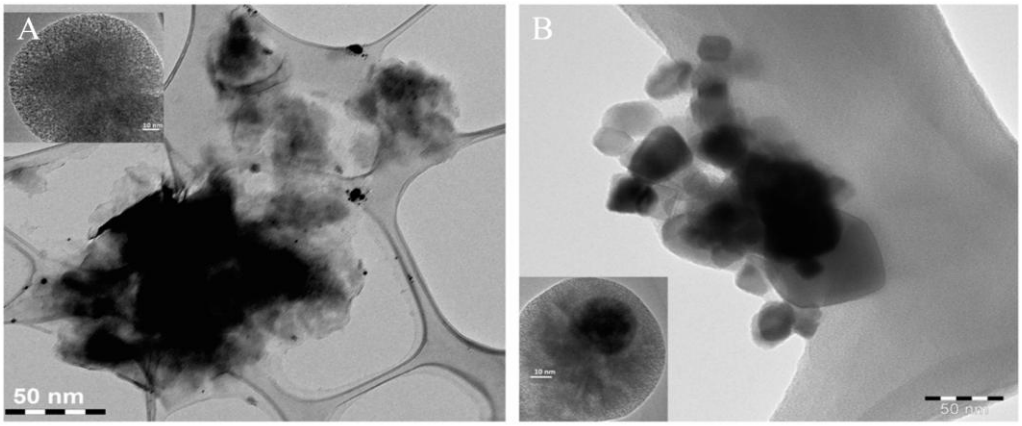


Fig. 15: TEM images of (A) HSNP-1 and (B) HSNP-2. The HSNP-2 particles show a uniform spherical core–shell structure.[34]

significantly reduce reaction time and improve cracking efficiency.[32] Solvent and resin cyclic recovery combines using a solvent to extract materials with resin that captures them, repeating this process several times to improve the purity and cost-effectiveness of recovering asphaltene.[22]

8.4 High-value functional material development

Recovered and purified asphaltenes can serve as precursors for various functional carbon-based materials:

Carbon nanosheets and graphene: By carefully heating asphaltenes, their layered structure can change into high-quality carbon nanosheets or graphene, which can be used in supercapacitor electrodes and conductive materials.[10]

Fluorescent carbon dots and carbon nanoparticles: Chemical oxidation or hydrothermal synthesis can produce size-tunable fluorescent carbon dots and carbon nanoparticles, which show potential for applications in anti-counterfeiting, data encryption, and bioimaging.[10]

Fullerenes and their derivatives: By using the structure of asphaltenes, fullerenes like C_{60} and C_{70} can be made through heat or chemical processes, allowing them to be used in solar panels and advanced electronic materials.[13]

Dye-sensitized solar cells (DSSC) offer low-cost alternatives to conventional solar cells and are commercially promising because of the promise of low-cost materials and roll-to-roll manufacturing.[4] Compared to conventional solar cells, DSSCs have the promise of easy fabrication at a low cost in an environmentally friendly way and have high-energy conversion efficiency, as shown in Fig. S2.

Road construction, textiles, oil–water separation, batteries, anti-fouling coatings, and many other fields use superhydrophobic coatings.[46,47] In the development of superhydrophobic coatings, asphaltene-derived silane precursors (ASAS) were co-condensed with tetraethoxysilane (TEOS) and an amino-oleyltriethoxysilane (AOS) via sol–gel chemistry. The resulting core–shell nanoparticles (HSNP-2) exhibit uniform spherical morphology under TEM (Fig. 15). The strong connection between the water-repelling alkyl chains of ASAS and the silica network creates a bumpy surface. By tuning ASAS content up to 40 wt%, the HSNP-2 films become superhydrophobic, with a maximum water contact angle of about 170°.[34] Moreover, solid residue particles participate in surface structuring and forming the mentioned roughness.[48]

These HSNP-2 nanoparticles were applied as coatings to sand grains and polyurethane (PU) sponges, creating rough superhydrophobic surfaces. Water droplets form nearly spherical beads on these surfaces with contact angles approaching 170°. As shown in Fig. 16, a water droplet on a treated sand surface remains non-wetting, illustrating the high hydrophobicity. The coated sand and sponge therefore strongly repel water while exhibiting high affinity for oil. This combination of superhydrophobicity and oleophilicity enables rapid and selective oil uptake.[34]

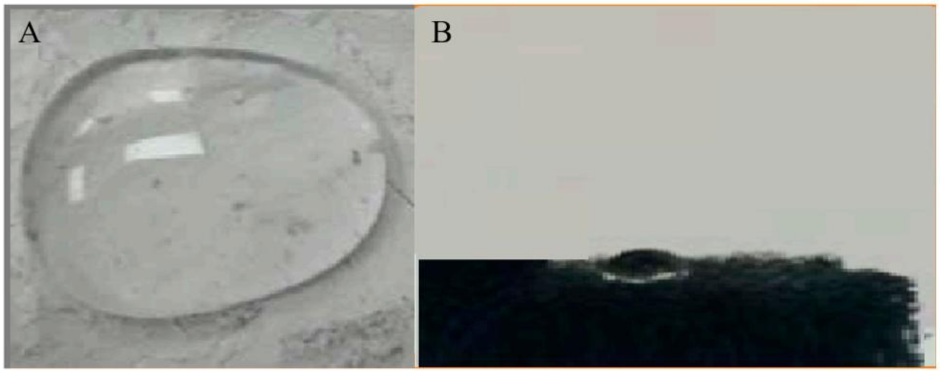


Fig. 16: Water droplet on (A) HSNP-2 modified sand and (B) HSNP-2 modified polyurethane sponge surfaces (water contact angle ~170°).[34]

Overall, this work demonstrates a low-cost, sustainable approach to upcycling asphaltene byproducts into value-added functional materials. The raw materials (petroleum asphaltenes and simple silanes) are inexpensive, and the sol–gel coating process is facile and scalable.

8.5 Outlook for innovative technologies

As the understanding of asphaltene composition and behavior deepens, multidisciplinary approaches are being employed to tackle industrial issues. Smart sensor and infrared laser detection technologies have been used to monitor asphaltene deposition in real time and are combined with production data to build trend models and forecasts.[36] At the same time, the growth of eco-friendly technologies has led to the creation of biodegradable demulsifiers and renewable ionic liquid-based solvents to lessen the environmental effects of using chemicals.[42,43] In materials science, asphaltenes can be converted into carbon nanomaterials or used as precursors for catalysts in energy storage or catalytic processes, showing enormous potential.[42,44]

9. Biodegradation of asphaltenes

9.1 Overview of microbial degradation

Biodegradation of asphaltenes refers to the process by which microorganisms (bacteria, fungi, *etc.*) metabolize these complex macromolecular organic substances into smaller, simpler products. This process occurs slowly in nature and is considered part of the natural biodegradation of crude oil. Microbial degradation of asphaltenes usually happens in several steps: microorganisms first release enzymes to break down asphaltenes, and then they process the smaller products inside their cells. Both anaerobic and aerobic microbes have been found capable of degrading asphaltenes, with aerobic degradation generally more effective. Asphaltene biodegradation is viewed as an environmentally friendly and economically feasible treatment strategy, but it proceeds slowly, often requiring months or even years to achieve significant transformation.[32] Therefore, in practical applications, conditions are optimized to accelerate the process, such as selecting highly effective microbial strains, controlling temperature and pH, and supplying necessary nutrients.[43]

9.2 Degradation pathways and mechanisms

Microorganisms are capable of degrading macromolecular organic substances such as asphaltenes, primarily targeting the more labile side chains and aromatic structures.[32] Studies have indicated that certain bacteria and fungi can metabolize asphaltenes as carbon and energy sources.[43] Under aerobic conditions, asphaltenes can progressively break down into carbon dioxide, water, and biomass assimilated by microbial cells. This process relies on enzymes like oxidases secreted by microbes. Also, the different elements in asphaltenes (like nitrogen and sulfur) can affect how they break down; for instance, parts that contain sulfur might turn into sulfates or hydrogen sulfide during the breakdown process.[32]

9.3 Microorganisms and degradation performance

Researchers have isolated various microorganisms capable of degrading asphaltenes. Some dominant strains include Pseudomonas aeruginosa and Enterobacter cloacae, which can utilize asphaltenes as the sole carbon and energy source. Studies have shown that Pseudomonas aeruginosa can achieve an asphaltene biodegradation rate of up to ~49% under optimal conditions. Additionally, researchers have explored mixed microbial consortia for synergistic degradation, where different microbes degrade different parts of the asphaltene molecules, thereby improving overall efficiency. Furthermore, choosing and adapting microbial strains that can handle high levels of asphaltenes is a common way to make them stronger and better at breaking down asphaltenes.[43]

9.4 Environmental factors influencing degradation

The biodegradation rate of asphaltenes is affected by various environmental conditions, including oxygen availability, nutrients, temperature, and pH. Most highly efficient degrading strains are aerobic, so a sufficient oxygen supply can significantly improve degradation efficiency. Studies have shown that asphaltene degradation is highest at 40 °C and pH 6.86, indicating that these parameters are key factors affecting the degradation rate. Additionally, adding surfactants can significantly improve the bioavailability of asphaltenes. For instance, when there is 50 ppm of SDBS (a surfactant), the way microbial cells interact with water changes, which helps them get closer to asphaltenes and speeds up their breakdown.[43]

9.5 Degradation products and potential applications

The final products of asphaltene biodegradation under aerobic conditions are mainly CO_2, water, and microbial biomass.[32] Furthermore, the process may yield intermediate products like organic acids, alcohols, and ketones. These intermediates are usually further metabolized by the microorganisms, but they may accumulate under certain conditions.[43] Biodegradation of asphaltenes shows potential as an eco-friendly treatment method, but due to the complex structure of asphaltenes and the slow degradation rate, current challenges remain in terms of efficiency and cost.[32,43] If future improvements can greatly speed up degradation rates and lower costs, bioremediation might become a valuable, eco-friendly option for dealing with refinery asphaltene residues.[43]

10. Conclusion

Asphaltenes, as a complex multi-component system, have significant impacts on both the petroleum and coal chemical industries. This review has systematically summarized their chemical composition, molecular structure, and physicochemical properties, along with phase behavior under various conditions.

We discussed the roles of asphaltenes in stabilizing water-in-oil emulsions, promoting deposition and catalyst deactivation, and the associated challenges in oil transport and refining. The complicated nature of asphaltenes can cause problems like blocking pipelines, stabilizing emulsions, and harming catalysts, but their complex structures and adjustable chemical groups also offer chances to create new materials and make better use of these resources. Future research should focus on leveraging advanced characterization tools (like synchrotron X-ray techniques, ultrahigh-resolution mass spectrometry and other) to better understand the structures and behaviors of asphaltene molecules, which will help improve theoretical models. It is also important to develop efficient, smart, and eco-friendly asphaltene control strategies (such as novel dispersants, electromagnetic field manipulation, or laser treatments) to effectively address aggregation and deposition. Additionally, using asphaltene resources in real-world applications can result in significant advancements in areas like nanocarbon materials, superhydrophobic coatings, energy storage, and catalyst supports.

In summary, through continuous technological innovation and interdisciplinary research, our scientific understanding and engineering control of asphaltenes will steadily improve, which will not only support sustainable development of the oil industry but also provide valuable materials and inspiration for new technologies and processes.

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Applicable.

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