



Review

Asphaltenes: Separations, structural analysis and applications

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ABSTRACT

Asphaltenes, complex aromatic compounds from various carbonaceous sources, could be obtained by solvent dissolution, filtration and adsorption. It was difficult to clarify the molecular structures and chemical properties of asphaltene due to its structural similarity, composition complexity and source dependences. Many techniques, like Mass spectrometry, Chromatography, Nuclear magnetic resonance spectroscopy, Infrared spectroscopy, Roman spectroscopy, Fluorescence spectroscopy, X-ray diffraction analysis and Small-angle scattering techniques and so on, have revealed some valuable descriptions of asphaltenes chemical compositions and fundamental structures. Moreover, advanced Mass spectrometry, Atomic force microscopy and Scanning tunneling microscopy could provide more clear and essential molecular compounds and structures in asphaltenes. In addition, several asphaltenes models have succeeded to illustrate aggregation properties asphaltene. In this work, the progress on asphaltene separation, characterization and application was summarized, and the similarities and differences between coal-derived asphaltenes and petroleum asphaltenes were compared. Furthermore, the reactivity of asphaltenes has been discussed in the aspect of hydroprocessing, pyrolysis and gasification. Asphaltene was excellent carbon precursor for functional carbon material due to its high aromaticity and carbon yield; several porous carbon nanosheets from asphaltenes that would be prospective electrode materials after being graphitized were shown. Pitch-based carbon fiber derived from coal-derived asphaltenes displayed a tensile strength of 1.0 GPa and elastic modulus of 350 MPa, respectively. These powerful advances will provide asphaltenes promising developments.

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Abbreviations: AFM, atomic force microscopy; APCI, atmospheric pressure chemical ionization; APPI, atmospheric pressure photoionization; ATR FTIR, attenuated total-reflection Fourier transform infrared; CW, continuous-wave; DBE, double bond equivalent; DEPT, distortionless enhancement by polarization transfer; DOSY, Diffusion ordered spectroscopy; DRIFT, diffuse reflectance Fourier transform infrared; ESI, electrospray ionization; ESR, electron spin resonance; EPR, electron paramagnetic resonance; FCS, fluorescence correlation spectroscopy; FD, Fluorescence depolarization; FDI, field desorption; FI, field ionization; FL, Fluorescence; FT-ICR, Fourier-transform ion cyclotron resonance; FTIR, Fourier transform infrared; GC, gas chromatograph; GC×GC, two-dimensional gas chromatograph; 1D-GC, one-dimensional GC; GPC, gel permeation chromatography; HDM, hydrodemetallization; HDN, hydrodenitrogenation; HDS, hydrodesulfurization; HRTEM, high resolution transmission electron microscopy; HPLC, high performance liquid chromatography; IR, infrared; LDI, laser desorption ionization; L2DI, laser desorption laser ionization; L-H, Langmuir-Hinshelwood; LIAD, laser-induced acoustic desorption; MALDI, Matrix-assisted laser desorption/ionization; MS, mass spectrometry; MSn, Multi-stage mass spectrometry; MW, Molecular weight; NCD, nitrogen chemiluminescence detector; NIR, near-infrared; NMP, N-Methyl pyrrolidone; NP HPLC, normal-phase HPLC; NPD, nitrogen phosphorus detector; NMR, nuclear magnetic resonance; PAHs, polycyclic aromatic hydrocarbons; PASH, polycyclic aromatic sulfur heterocycles; RP HPLC, reversed-phase HPLC; SALDI, surface-assisted laser desorption/ionization; SALS, small angle light scattering; SANS, small angle neutron scattering; SAXS, small angle X-ray scattering; SEC, size exclusion chromatography; SERS, surface enhanced raman spectroscopy; SFE, supercritical fluid extraction; SPE, single pulse excitation;



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spICP MS, single-particle inductively coupled plasma mass spectrometry; STM, scanning tunneling microscopy; TEM, transmission electron microscopy; THF, tetrahydrofuran; TLC, thin-layer chromatography; TOF, time-of-flight; TRFD, time resolved fluorescence depolarization; UV-vis, ultraviolet-visible; VO₂⁺, vanadyl porphyrin; VPO, vapor pressure osmometry; XANES, X-ray absorption near edge structure; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction; d_m , inter-aromatic layer distance; d_c , inter-chain layer distance; f_a , asphaltene molecular aromaticity; L_a , aromatic sheet diameter; L_c , cluster diameter, N_a , average number of aromatic rings per sheet; M , average number of aromatic sheets per stacked cluster.

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1. Introduction

Asphaltenes, a complex aromatic molecular mixture, is widely contained in crude oil, residues of petroleum and coal processing. It was firstly adopted asphaltene to indicate the distillation residue of bitumen in 1837 [1]. Fundamental knowledge of asphaltene is gradually enriched due to the development of separation and identification techniques. However, There are still challenges of how to determine the accurate molecular structure, constituent and structure-behavior relationships of asphaltene [2].

Asphaltene is initially obtained from crude oil by petroleum naphtha, n-pentane and n-heptane separation [3], it is generally defined by the solubility characteristics rather than chemical structures. Asphaltene means the fraction that is insoluble in n-alkanes with low carbon number (n-hexane, n-heptane or n-pentane) but soluble in light aromatic hydrocarbons (toluene and benzene) [4–6], besides, asphaltene also could be dissolved in other solvents with high surface tension, such as, pyridine, carbon disulfide, carbon tetrachloride [7]. The n-heptane/toluene is one of the most popular partners for asphaltene separation. Separated fractionation of asphaltene was primary determined by the order of used solvents and the polarity showed less effect on asphaltene composite. Anyhow, asphaltenes has no definite melting point and is the most aromatic, heaviest fraction in the crude oil; but it is not the most aromatic component of coal [8].

Typically, asphaltenes can be obtained from crude oil or petroleum pitch by solvent extraction [7,9–13]. Besides, it can be produced by thermal treatment of coal or shale oil, such as pyrolysis or catalytic hydrogenation [14,15]. Asphaltenes is not only a simple intermediate but also an important carrier for resource geochemistry [16], it was also called geological clock [7]. For example, changes of asphaltenes viscosity can monitor its stability which deteriorates on ageing, based on most partly oxidation in functionalized sites. The approximate age of oil also could be reckoned by properties of associated porphyrins.

Understanding physical and chemical nature of asphaltenes is the basis of its effective utilization. Separation technology, structural analysis and application of asphaltenes were widely investigated. However, these works were more concentrated on asphaltene from petroleum and less concerned about asphaltene from coal pyrolysis or direct liquefaction. It is necessary to summarize the asphaltene structures, chemical compositions, physiochemical properties, separations and characterization methods for better understanding the effect of original, technical processing (preparation and separation) on its physicochemical property and application.

This work reviews not only the profound properties of asphaltenes, but also the association between asphaltene and fossil fuels, the influence of asphaltenes on the thermal and catalytic conversion processes, and significant advances in asphaltenes molecular structures, separation, characterization and applications.

2. Asphaltene compositions

2.1. Asphaltene content measurements

Asphaltene content was measured according to traditional gravimetric techniques and ASTM D6560 [17], which was complained for long cycling time, tedious labor, poor reproducibility, environmental disturbance and incapability with asphaltene contents (<1%). The changes in optical absorption of oils/maltenes united with asphaltenes were used to quantify the asphaltenes [17], which spend little time (about 30 min) with higher accuracy ($\pm 2\%$ repeatability) [18,19].

2.2. Chemical compositions

Asphaltene is not uniform in chemical composition. Aromatic molecules commonly contain heteroatoms (N, O, S) and metals (V, Fe, Ni, etc.) in molecular structure [5,20,21]. Table S1 lists chemical composition of several representative petroleum and coal-derived asphaltenes from different origins. Asphaltenes has the similar properties that are regardless of source, MW, composition, and metal content. For example, the identical ratio of H to C atoms in asphaltenes varies from 1.0 to 1.3. While O, N and S contents fluctuate in bigger extent according to the literature are O, 0.3%–5.0%; N, 0.6%–3.0%; S, 0.3%–10%; V and Ni present in mg/g levels [11–13,22–25]. Another two common elements in trace amounts are Fe and Mo [26]. It is notable that the amount of heteroatoms (N, O and S) helps to identify a given asphaltene from coal or petroleum origin [7], N and O are essential for both origin, respectively. S is a basic part for petroleum origin.

2.3. Asphaltene structures

Asphaltenes does not have an "absolute" structure. How to ascertain the accurate and detailed asphaltene molecular structures, such as, alkyls and functional groups, the existence of naphthenic cycles and number of polycyclic aromatic hydrocarbons (PAHs) per molecule, has always been the focus issues, it will be detailed by many characterizations in Section 5. The structures could also be classified to microstructure and macrostructure. The microstructure is usually limited to short-range bonding with spacing from 0.05 nm to 0.2 nm, and the macrostructure refers to molecular interaction at farther distances between 2 nm and 200 nm, as the nanostructures illustrated in Section 3.2.

2.3.1. Structural parameters

Asphaltene could be elucidated by a series of the structural parameters due to its anisotropic nature. Generally, different asphaltenes, include coal-derived and petroleum asphaltenes, usually show some similar structural parameters derived from specific characterization means; moreover, one parameter could be obtained by different methods. For instance, the hydrogen substitution and aromaticity of the asphaltenes could be deduced by both IR and NMR. The producing process of asphaltene, such as temperature and pressure, also affect its properties, so, the structure and property of asphaltene can be adjusted by the process parameters [7].

Molecular reconstruction, namely integrating all authentic parameters in an average model molecule, is another way to figure asphaltene. The experimental data usually are verified by using known compounds or model systems for computation. Table 1

Table 1. Some structure parameters of asphaltenes.

Items	Values
Main distribution of molecular weights	200–2000
Number of PAHs in molecule	usually no more than 3 ring systems in small molecule
Hydrogen substitution	nearly 9 out of 10 hydrogen bonded to sp^3 carbon, mainly in methylene and some methyl
Heteroatom states	sulfur existing in thiophene, sulfide and a bit of sulfoxide; almost all nitrogen being aromatic, like pyrrolic and pyridinic
Number of condensed rings per PAH	ranging from 4 to 20, general acceptance with 4–10
Number of PAH stacks in nanoaggregate	4–5 condensed aromatic sheets
Aggregation number of nanoaggregates	4–10
Diameter of fused aromatic rings	1–2 nm
Critical nanoaggregate concentration of asphaltenes (CNAC)	10–150 $\mu\text{g}/\text{mL}$
Concentration of cluster formation	2–5 mg/mL
Nominal sizes of asphaltene aggregates in diluents	depending on temperature and concentration, for small clusters 2–6 nm, up to 400 μm

Table 2. Several prevailing structural models of asphaltenes.

Researchers	Predominant model	Ref.
Yen	island model, an condensed core with side chains, and aromatic layers with MW about roughly 1200 to 3600	[3,42]
Mullins and Montanari	island model, PAHs as the backbone, with a relatively concentrated MW about 500–1000 Da and island structure for the aromatic cores,	[2,6,43,44]
Strausz	archipelago structures, units of PAH and hydro-PAH with no more than twenty rings, units linked by aliphatic bridges, degree of aromatic condensation lower than that in Yen Model	[41]
Speight	multinucleate aromatic molecules with less than ten rings	[9]

summarizes kinds of asphaltene parameters, which will be detailed in the following sections.

2.3.2. Structural models

Numerous molecular structures of asphaltene have been illustrated in the literature. Carbon and hydrogen dominate complex structures, and aromatic carbons account for about 40%–50% in petroleum asphaltenes and 70%–90% in coal-derived asphaltenes [27,28]. Major nitrogen is aromatic in formation of pyrrole, pyridine and their derivatives. Content of pyrrolic nitrogen is usually more than that of pyridic nitrogen, and the saturated amine is negligible in asphaltenes [29]. As for sulfur in asphaltenes, thiophene (aromatic) is the most common form, followed by sulfide (saturated) structure; the oxidized sulfur is mostly sulfoxide. Moreover, sulfur content in coal-derived asphaltene is commonly less than that in petroleum asphaltene.

It is difficult to examine the metals in asphaltenes due to its less amount and existing as organic metal compounds, and the formation mechanism of organic metals has not reached a consensus [26]. Compared with other metals in asphaltenes, V and Ni are the richest and extensively researched. Usually, the metal ions are chelated with organic groups, and some are located at the defect centers of an imperfect aromatic sheet as porphyrins [30–32], and these possible structures were always hypothesis [32,33]. Meanwhile, amount of experiments confirmed metal compound to be nonporphyrin structure, existing as free molecule, or captured one in asphaltene nanostructure, or a component of asphaltene [34]. Recently, metallic nanoparticles and dissolved metals in asphaltene solutions have been distinguished more clearly by single-particle inductively coupled plasma mass spectrometry (spICP-MS) with *o*-xylene. For instance, Ni and V were not detected in nanoparticles, suggesting that they were very likely forming coordination complexes as porphyrins. Besides, most Mo was also dissolved, but Fe mainly presented as nanoparticles and the size was directly proportion to its total concentration [26].

Fortunately, two major classifications, namely “island” and “archipelago” models, summarized the broad range of asphaltene structures. Island configurations mainly contain a central single aromatic or heteroaromatic core with unpredictable alkyl chains; archipelago configurations usually include more than two fused aromatic and heteroaromatic rings, which interconnect by alkyl

bridges [10,35]. The predominant models and corresponding architectures of asphaltenes are shown in Fig. 1 and summarized in Table 2. The dominant position of island structure is verified by various methods. For example, Fourier-transform ion cyclotron resonance (FT-ICR) MS revealed only alkane fragments and no atomic carbon produced. Consistently, time resolved fluorescence depolarization (TRFD) evidenced one PAH per asphaltene molecule [2]. Laser desorption laser ionization (L_2 DIMS) MS [36] and surface-assisted laser desorption/ionization (SALDI) MS [35] also supported for the island geometry and could give unbiased information of all asphaltene components without aggregation. Meanwhile, the archipelago structure has been supported by NMR, FT-ICR MS/MS [37] and thermal cracking methods [10]. A continuum between island and archipelago structures was recently proved by a series results of FT-ICR MS and the ratios of island and archipelago structures were depended on the asphaltene sample [38]. It was surprised that cycloalkane linkages instead of linear alkane ones and bridged the whole in archipelago geometry [35]. Additionally, the island model compounds in asphaltenes were proved to be stable enough to endure electro/helium collision, or photo absorption by L_2 DIMS and Laser-induced acoustic desorption (LIAD) MS, but archipelago model compounds were fragmented under the same conditions, indicating that the low stability led to low abundance [2].

However, it is unavoidable resulting in mistakes and inaccurate asphaltene structure information by different characterization methods. Spectroscopic techniques could not distinguish two major configurations of asphaltenes [10]. Besides, the defect of some mainstream models lies in the high energies caused by unreasonable chemical bonding. Greenfield [39] successfully decreased repulsive forces and restored planar aromatic rings by changing the side-chain positions but keeping the overall structures. Furthermore, Clar sextet theory and density functional theory were applied to rearrange the distribution of π electrons of the fused aromatic molecule and the intramolecular energy was reduced by an order of kJ/mol [40].

2.3.3. Molecular weight (MW) distribution

MW-related parameters are the most important and fundamental information of asphaltenes. High aromaticity and high-boiling-point substance resulted in its high MW. The reported M_{WS} of

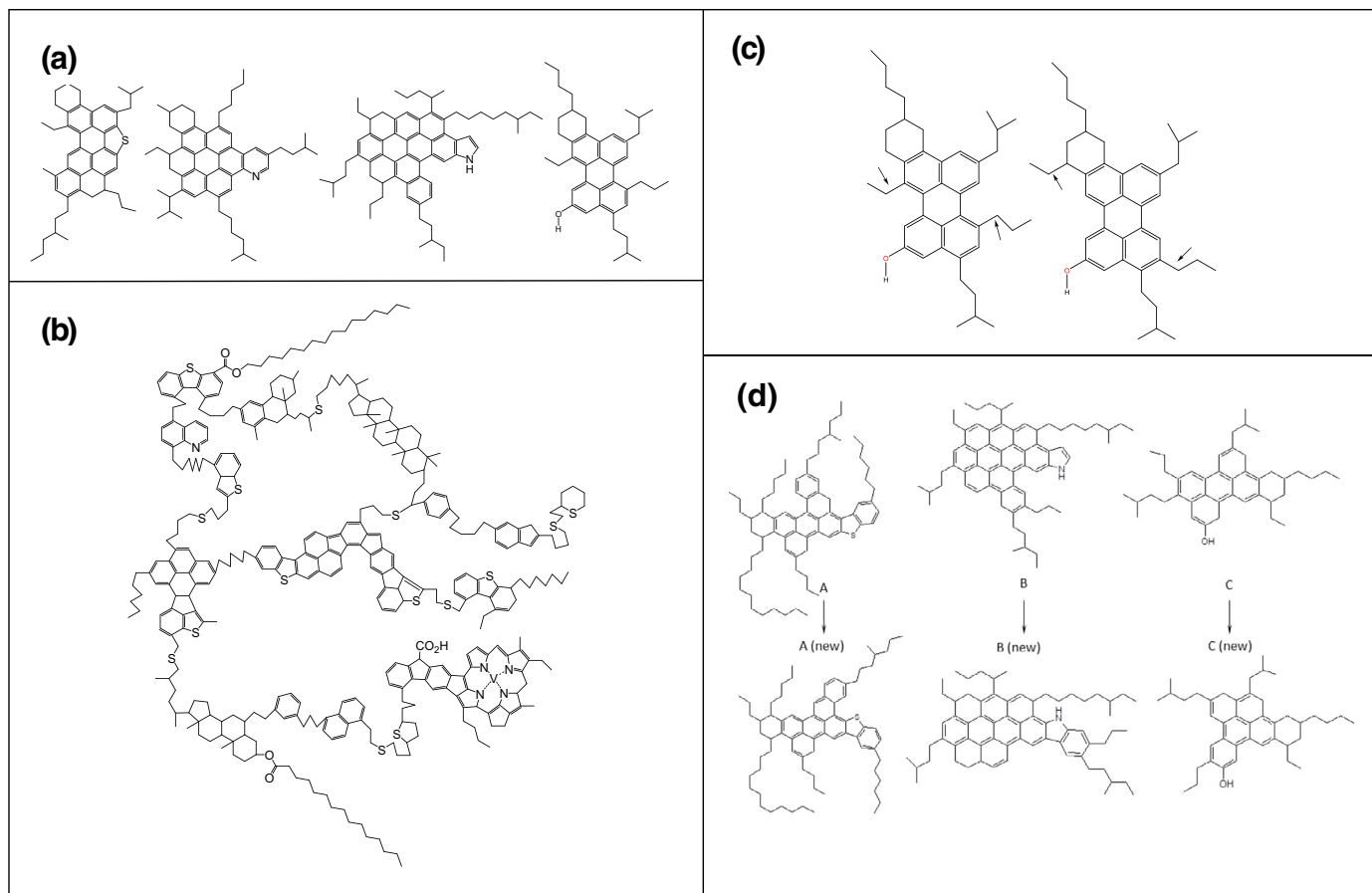


Fig. 1. Typical molecular architectures of asphaltenes. (a) Typical island molecular architectures of asphaltenes proposed by O. C. Mullins, (b) typical archipelago molecular architectures of asphaltenes proposed by O. P. Strausz, (c) modified structures of asphaltenes by Greenfield, (d) molecular structures optimized by M. J. Buehler et al. A refers to Asphaltene from previous Greenfield models; B and C denote Greenfield-modified models based on Yen–Mullins ones. A (new), B (new) and C (new) were optimized ones in order. All were reprinted with permission from Ref. [2,39–41], respectively.

asphaltenes change by several orders of magnitude because it is hard to evaluate the MW on behalf of monomeric asphaltene or polymeric asphaltenes.

Generally, MWs of asphaltenes vary from 5×10^2 to 2×10^3 with average value around 700 Da [20], but it may occasionally extend up to 10,000 [45–47]. While, MW is considered to be 4×10^3 – 10^4 for a cluster or particle weight and possibly 4×10^4 – 4×10^7 for a micelle [9,23]. MWs of asphaltenes are determined mostly by vapor pressure osmometry (VPO) [48], size exclusion chromatography (SEC) [44,49], TRFD [20,43] and various MS [47,50–52]. There is a consistent conclusion of molecular fragments, such as diameter of fused aromatic ring, number of fused rings in per PAH as listed in Table 2. The reliability of estimates is still argued because the MWs are affected by aggregation or macrostructures formed through intermolecular interactions, as well as technique limits such as fragmentations of covalent bonds, multiple ionizations, as well as production of cluster ions in MS analysis [23].

3. Asphaltene properties

3.1. Acid-base property

The acid-base surface characteristics of asphaltene were highly related with its precipitation and adsorption. It has been proven that all exchangeable protons in asphaltenes were contained in acidic component rather than basic component in coal-derived asphaltenes. Acidic and basic components were separated by

simply blowing HCl gas through the toluene solution. The acidic component remained in solution while the basic component precipitated as an insoluble HCl adduct. The acidic components could also be obtained with ion exchange separation [53] and potassium hydroxide treated silica column [54]. Meanwhile, acidic and basic groups have been identified by thin-layer chromatography (TLC), thin-layer electrophoresis (detecting the phenolic) [3], zetametry (the ratio of the electron donor and acceptor numbers representing the ratio of acid to base group numbers on surface) [55] and NMR [3]. The original acid and alkali of asphaltene is oxygen/sulfur and nitrogen functional groups, the typical acidic functional groups are phenols, carboxylic acids and naphthenic acids [56], and basic sites usually contain heteroatoms (N, O, S) in/near aromatic ring or on alkyl chain [57]. The amount and kinds of hydroxyl and carboxyl groups of Athabasca petroleum asphaltene were calculated by high resolution ^{13}C , ^{19}F , and ^{29}Si NMR spectra [58]. There were 4 to 8 hydroxyl groups (including COOH) per molecule on average (Fig. 2a). Some basic and non-basic N- and O-containing class of coal-derived asphaltene components was found by diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) and FT-ICR MS [59], some proposed chemical structures were shown in Fig. 2(b). Acidic-basic structures of model compounds were synthesized to simulate the interfacial properties of asphaltenes (Fig. 2c) [60]. The identical asphaltene may show different acid/alkali kinds and intensity due to various test conditions, and when the acid-base structures simultaneously exist in molecules [53], they inevitably interact and result in agglomeration or

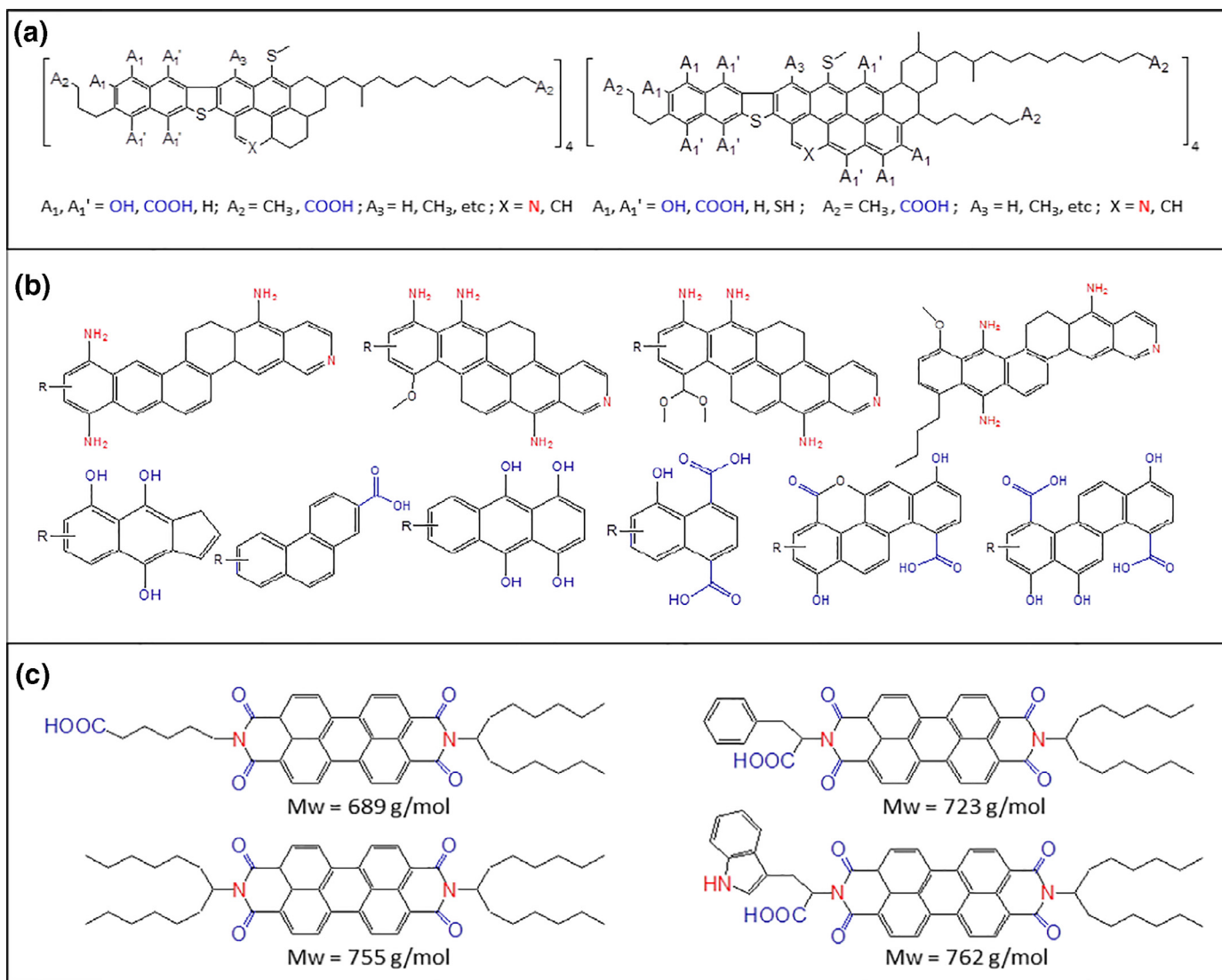


Fig. 2. Some proposed chemical acidic-basic structures of asphaltenes (Red, basic groups; blue, acidic groups; R, unsure groups). (a) Positions of carboxyl and hydroxyl groups in hypothetical average molecular structures of Athabasca petroleum asphaltene based on NMR (the top one MW \approx 2767–2800 Da; the bottom one MW \approx 3746–3824 Da. A, unhindered; and A', sterically hindered.); (b) the basic species (N_4 , N_4O and N_4O_2 class) and acidic species (O_2 – O_7 class) in coal-derived asphaltenes from China identified by FT-ICR MS; (c) acidic-basic structures of model compounds synthesized by E. L. Nordgard to mimic the interfacial properties of asphaltenes. Reprinted with permission from Ref. [58–60], respectively.

crosslinking of asphaltenes. For example, acid-base property had an influence on migration of asphaltenes from solution to colloid reversibly in non-polar solvents [57].

3.2. Association and aggregation

The aggregation of asphaltene was a stepwise process and it was firstly explained with crystallite structures by T.F. Yen [42]. A detailed stepwise description of asphaltene aggregation behaviors as following: nanoaggregates of asphaltene firstly appeared at common concentrations above 50–100 mg/L, it was then crosslinked into clusters with a size from 3 to 10 nm based on the results of X-ray and SANS analysis, the clusters grew up to flocs and precipitation finally happened. Besides these, several groups also have proposed asphaltene models of association and agglomeration, the most relevant issues are listed in Table 3 and shown in Fig. 3.

Summarily, association and agglomeration processing involved not only the asphaltene inherent structure (aromatic, functional groups, intermolecular forces etc.) but also surrounding conditions

(solvent polarity, pressure and temperature). Although great deals of meaningful achievements on association and agglomeration have been obtained, further study is still needed to illustrate the fine and widely-applicable agglomeration of asphaltenes.

4. Separation

Asphaltene widely exists in crude oils, coal liquefaction residues and coal pyrolysis products. The simplest separation method is solvent dissolution, filtration and solvent recovery. Supercritical extraction and adsorption is also commonly used to separate asphaltenes.

4.1. Solvent extraction

Solvent extraction of asphaltenes is affected by solvent polarity, the ratio of solvents to asphaltenes, temperature and pressure to separate it from raw materials.

According to solubility parameter approach for solvent fractions, asphaltene is isolated from various carbonaceous sources [7].

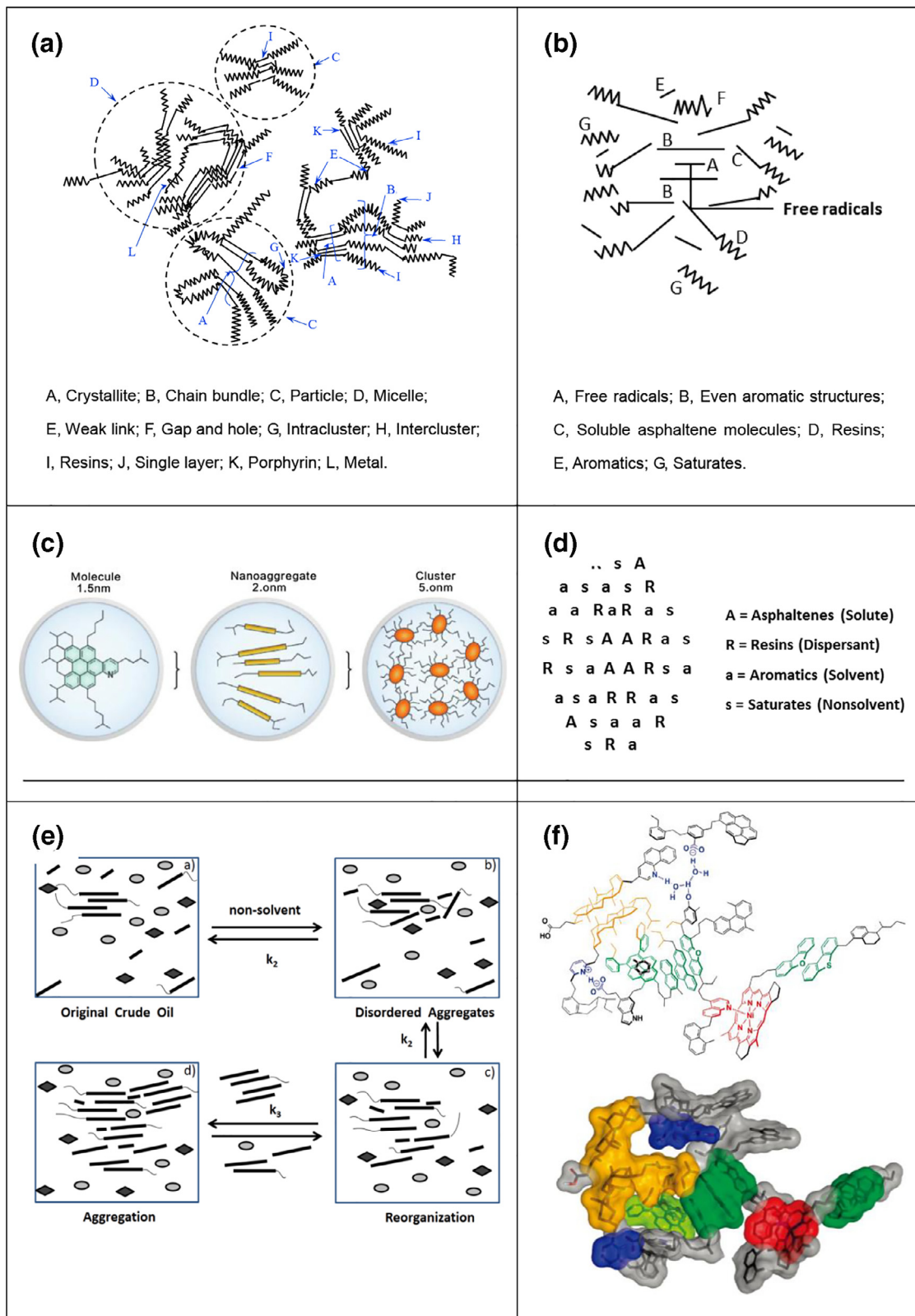


Fig. 3. The most relevant models of association and aggregation of asphaltenes. (a) Yen model; (b) micelle model proposed by Acevedo, etc. Schematic transversal cut of an asphaltene micelle; (c) Yen-Mullins model; (d) physical model of asphaltene in petroleum proposed by I.A. Wiehe; (e) aggregation model under poor solvent condition; (f) schematic representation of a supramolecular assembly composed of host and guest species in a representative asphaltene aggregate suggested by M. R. Gary. All reprinted with permission from Ref. [42,43,61,63–65], respectively.

Table 3. The most relevant models of association and aggregation of asphaltenes.

Asphaltene models	Main points	Diagrams	Ref.
Yen model	Layer view: micelle structure as the core, covered by resin molecule, meanwhile enclosed in aromatic and saturated molecules; Micelle size: 1.6–2.0 nm in high and 0.8–1.6 nm in wide.	Fig. 3(a)	[42]
Micelle model by Acevedo	Cage structures: free radicals wrapped inside by aromatic structures and avoiding intermolecular reactions, with other soluble molecules surrounded; Uncertainty of whether free radicals causing the signal as an unpaired electron captured by Electron Paramagnetic Resonance (EPR); the unpaired electron increasing intermolecular associations only if transannular electron delocalizing.	Fig. 3(b)	[61]
Yen-Mullins model	Stepwise aggregation: predominant molecule as “island structure”; molecules forming nanoaggregates with aggregation numbers about six, and with a single disordered stack of PAHs; nanoaggregates forming clusters with aggregation numbers about eight.	Fig. 3(c)	[6,62]
Compatibility model by Wiehe	Size of nanoaggregates: 2 nm; size of nanoaggregate clusters: 5 nm. A dynamic equilibrium: asphaltenes particle dispersed by resins in oil; asphaltene-resin association dissolved by small ring aromatics as solvents while saturates as nonsolvents; the balance easily broken by increasing saturates or reducing resins or aromatics, indicating changes in solubility causing aggregation.	Fig. 3(d)	[63]
Aggregation model under poor solvent condition by Rogel	Complex reorganization: composition of precipitated asphaltenes changing widely along with time by precipitating kinetics, and involving reorganization of the aggregates including expulsion and incorporation of molecules.	Fig. 3(e)	[64]
Supramolecular aggregate model by Gary	A supramolecular: molecules assembled by cooperative binding of hydrogen bonding, Brønsted acid-base interactions, metal coordination complexes, aromatic π - π stacking, and hydrophobic pockets. Porous networks and host-guest complexes existing simultaneously. Explained the advantage of aggregate phenomenon: aggregating over a large scale of concentrations and temperatures, adhering strongly to many surfaces, and being elastic under tension.	Fig. 3(f)	[65]

Preferentially, asphaltene is separated from residue of crude oil distillation, coal liquidation or pyrolysis. It could be precipitated by adding paraffins. Larger alkane yields less asphaltene. For instance, the yields of asphaltenes from Athabasca bitumen are 50%, 17%, 11%, and 9% by propane, n-pentane, n-heptane and n-decane extraction, respectively. Generally, the yield of asphaltenes obtained by n-paraffin precipitating is more than that of isoparaffin [66]. In order to fully separate asphaltenes, the volume ratio of solvent to asphaltene should be higher than 40:1. Meanwhile, shorter operation time (less than 8 h) was reasonable, it could avoid to introduce resins into asphaltenes because resin was a less polar and aromatic fraction of oil and similar solubility compared with asphaltenes [1]. Other components may precipitate simultaneously with asphaltenes, like inorganic salts, free radicals, metalloporphyrins, and solvents [67]. Trapped solvents could be eluted by an increasing carbon number of paraffins and sequentially polar solvents. For instance, the n-pentane-insoluble fraction could be extracted with n-hexane, followed by dealing with hexane-insoluble fraction with n-heptane, and so on. And about 85% of the inorganic components could be removed just by centrifugation [1].

4.2. Supercritical fluid extraction (SFE)

Asphaltenes could be dissolved by solubility change of supercritical CO₂, and different compositions could be separated by changing the pressure and temperature. Recently, some polar modifier can be added to CO₂ to improve the solubility of polar fractions in asphaltenes by SFE, like propane, heptane, and toluene. Furthermore, water, n-pentane and/or benzene and/or ethanol were also used as the solvents of SFE. The maximum content of asphaltene must be under the most effective condition, most likely in the vicinity of critical temperature of the solvent. The n-pentane/benzene (1/1, v/v) system was reported to get the relatively high yield of asphaltenes by SFE (24.3 wt%) at 383 °C [68]. Asphaltene extraction was prior to resins, and asphaltenes accounted more in residues than in original Athabasca bitumen after SFE with water under 360–380 °C and 15–30 MPa, maybe some fractions upgraded in the process [69].

4.3. Membranes filtration

As another way of separation, filtration (micro-, nano-, and ultrafiltration) could disorder physical states of asphaltenes. There are mainly two kinds of membranes, inorganic and organic

membranes, including zirconia membrane [70], Ultracel YM and nanopore membrane [71], asymmetric ceramic monolith membranes [72], and polyethersulfone and polyimide porous membranes [73,74], which are widely applied in separation process. Asphaltene was separated experimentally using mica membranes (pore radius 8–220 nm) and Wicke–Kallenback-type diffusion cell in early 1983 [1]. Then asphaltenes from types of Iranian crude oils [75] and Cold Lake oil [76] was successfully isolated by ceramic monolith membranes (pore radius 25–100 nm and 50–700 nm separately), with retention up to 80% for Cold Lake asphaltene. Flux of permeate and asphaltene rejection were main factors that was restricted by the membrane pore size initially during the fouling period, later a gel-layer formatting played a key role. As a result, asphaltene rejection increased with its content [75,77,78]. Ultrafiltration could also greatly reduce permeated density, viscosity and metal contents, which was correlated with permeated asphaltene content [1].

4.4. Asphaltenes adsorption

Adsorption is a simple and economic method to recovery asphaltene from crude oil or coal tar; it could avoid the introduction of impurity and high treatment temperature. The effect of asphaltene properties [79,80], sorbent features [81,82], water content [81,83,84], and temperature [85–87] on adsorption properties were summarized in Fig. 4. Adsorbent types and adsorption mechanism were listed in Table 4. Physically adsorbed asphaltenes were often desorbed by eluting sorbent with solvent which could not only dissolve asphaltene but also adsorb on active sites more strongly than asphaltenes. While chemical adsorptions of asphaltenes were mostly irreversible and similar to a chromatographic process [88,89].

Summarily, solvent extraction is expensive and tedious due to a heavy use of paraffinic or naphthenic solvents. What's worse it may regrettably loss much polar and valuable components. The solvents are recycled often by distillation under vacuum. Similarly, membranes filtration is also unfeasible, because adsorbed asphaltenes foul the membranes easily. Relatively, adsorption is more economic owing to its nonconsumptive desorption process and uncomplicated sorbent regeneration. Above all, a better understanding of sorbent-asphaltene interactions will promote commercial development of asphaltene adsorption more quickly.

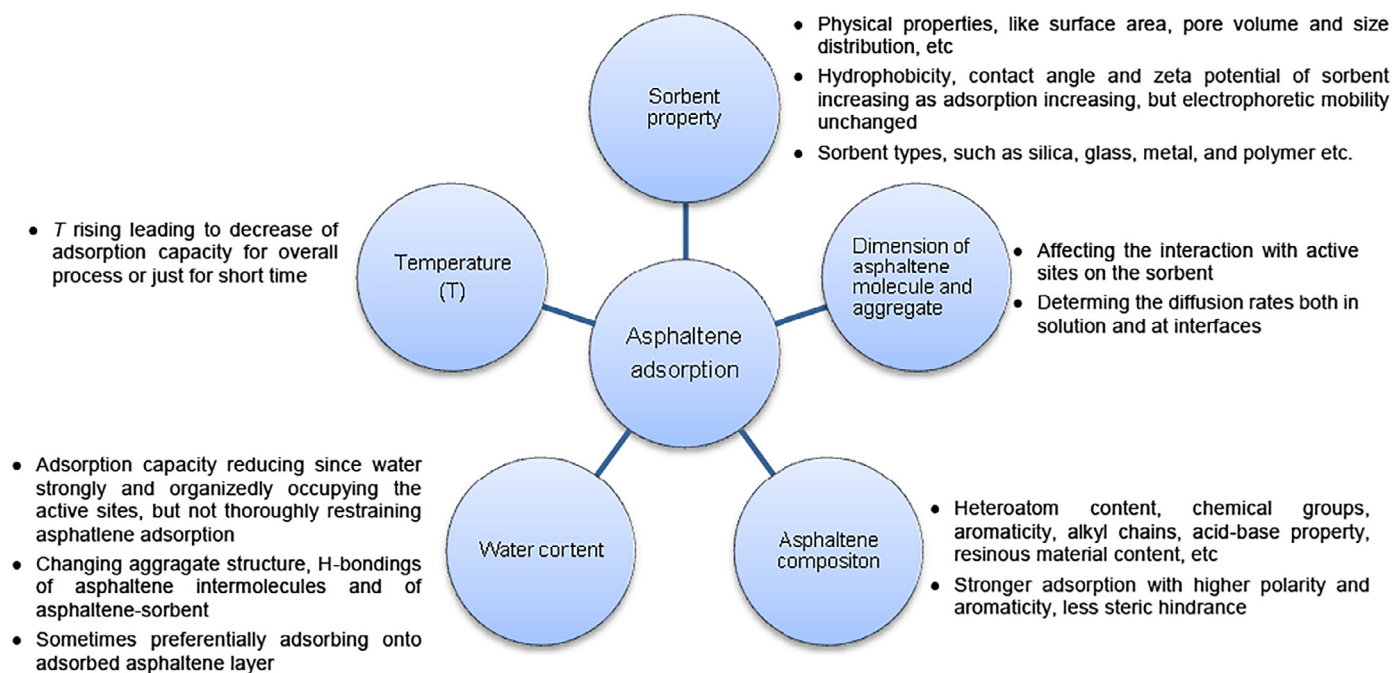


Fig. 4. The main factors of asphaltene adsorption.

Table 4. Characters of different kinds of asphaltene sorbents.

Types of sorbent	Typical example	Adsorbing type	Reported maximum adsorption capacity	Ref.
Minerals	Clay minerals: hydrous aluminum phyllosilicates kaolinite, illite, montmorillonite	Exchangeable cations, negative charge	Dehydroxylated kaolinite: 7 mg/m ²	[90–93]
	Rock minerals: quartz, calcite, feldspar, dolomite, fluorite, hematite, sandstone and limestone	Slightly acidic, positive charge	Quartz: 4.4 mg/m ²	[90,94–96]
Silica, alumina, silica–alumina, crystalline zeolites	Modified silica or alumina, hydrophilic silica and alumina, silica hydroxyls	Hydroxyl silanol aluminol groups	Hydrophobic silica: 3.68 mg/m ²	[5,86,97,98]
Glass	Glass	Hydroxyl silanol	No details	[87,99,100]
Metals	Stainless steel, iron, aluminum	Physical absorption	4.9 mg/m ²	[87,100,101]
Metal oxides	Iron oxides, Al ₂ O ₃ , MoO ₃ , Co ₃ O ₄ , WO ₃ , Ta ₂ O ₅ , CoMo–Al ₂ O ₃ , Mo–Al ₂ O ₃ , Co–Al ₂ O ₃ , NiMo–Al ₂ O ₃ , NiO–Al ₂ O ₃	Catalytic oxidation	NiO–Al ₂ O ₃ : 7–9 mg/m ²	[97,102,103]
Carbon based materials	Activated carbon	Physical absorption, catalytic oxidation	Carbon CG6	[104]
Polymers	Naphthenic acids, poly (methyl methacrylate) hydrophobic poly (n-hexyl methacrylate)	Physical absorption	No details	[105,106]

5. Analysis and characterization technique

Now, asphaltene structures, M_w s and aggregations have been investigated at molecular scale, asphaltenes structure could be understood more deeply with almost continual developing techniques. This work illustrates and emphasizes the breakthroughs and advancements of systematic analytical methods for petroleum and coal-derived asphaltenes characterization. The discussion of analytical methods is primarily focused on VPO, MS, chromatography, NMR, spectroscopy and X-ray techniques based on references cited therein.

5.1. Vapour phase osmometry (VPO)

VPO is the most typical and wide way for MW test [9,11–13], and its result is easily effected by temperature and solvent nature (like o-dichlorobenzene) [107]. Table S1 lists MWs of several typical petroleum and coal-derived asphaltenes using VPO. It is replaced by Gel permeation chromatography (GPC) and SEC since the association phenomenon founded in VPO. Rogel reduced the number of asphaltene molecules per aggregate by adding inhibitors in

the asphaltenes model, while this did not always reduce the actual (or the apparent) size of the aggregates measured by VPO [48].

5.2. Mass spectrometry (MS)

MS has identified tens of thousands of unconventional compounds in asphaltenes, moreover, it elucidates the carbon number of alkyl chains, aromatic core sizes, functional heteroatom groups, M_w distributions, and interactions between asphaltenes and rock surfaces as “wettability state” and so on [28,52,108–112].

5.2.1. Ionization technology

Integral to advances in MS mainly owe to developments of ionization technology. Different ionizations are aim to transform gaseous, liquid and solid samples into gaseous ions efficiently, but they also have matrix effect on analytes [38]. Table 5 lists common characterizations of different ionizations applied in asphaltenes analysis. It was impossible to ionize all asphaltene molecules with single ionization [113], and none of any ionization could completely assess all compositions by electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), atmospheric

Table 5. Characterizations of different ionizations applied in asphaltene analysis.

Ionizations		Characterizations	Disadvantages	Typical applications	Ref.
Solution-phase ionization	ESI	Suitable for polar molecules, extending to nonpolar components with new reagents	Poor solubility; precipitation; missing high-MW species	Resolving and identifying $C_cH_nN_nO_oS_s$ of N, S, O-containing compounds	[59,109,114]
	APPI	Lower polarity ones which are inaccessible to ESI, like substituted hydrocarbon cycloalkanes, PAH, thiophenes and furans		Classing V-porphyrin structures; exploring occluded compounds and their interactions with asphaltene networks; yield only stable molecular ions (M^{+})	[28,46,115]
	APCI	Similar to APPI, producing radical cations $[M]^{+}$ and protonated molecules $[M+H]^{+}$		Identifying the preferred fragmentation pathways for the island and archipelago models	[112,113]
Laser-based ionization	LDI/L ₂ DI	Yield only stable molecular ions (M^{+}), providing relative unbiased measurements of all species	Aggregation; interference with parameters, like laser wavelength, pulse width, laser fluency/intensity and the chemical characteristics of the analyte	Bolstering island geometry; finding stable asphaltene nanoaggregates contained approximately seven molecules	[35,116]
	MALDI	Transferring all compounds from solid or solution state directly into the gas phase as ions, especially for macromolecular compounds		Macromolecular compounds, identifying $C_cH_nN_nO_oS_s$, aggregates, fullerene clusters formation	[23,117,118]
	SALDI	Variation of MALDI, samples bounded to a surface		MW distributions; nanoaggregates formation	[35,119]
	LIAD	Ionize neutral asphaltene molecules by electron bombardment (does not use direct irradiation of the sample)		MW distributions; structural information for asphaltene components	[120]
Others	FI/ FDI	Fit for polar, non-evaporable and thermally instable compounds	Harsh conditions	MW distributions; Compositional characterization	[121]

Notes: FI/ FDI, Field /field desorption ionization.

pressure photoionization (APPI), laser desorption ionization (LDI) and Matrix-assisted laser desorption/ionization (MALDI) [110]. All above five ionizations together only gave partial information about asphaltene (Fig. 5). However, all of these five ionizations required concentrations of asphaltene about 250–1000 $\mu\text{g/mL}$, since asphaltene nanoaggregates happened at concentration about 50 $\mu\text{g/mL}$, indicating the formation of stable nanoaggregates ($m/z > 2000$) (monomers, $m/z < 2000$) [108]. Obviously, aggregation happened in solution-phase ionization methods (ESI, APCI and APPI), and asphaltene solution would be concentrated after it was dripped over MALDI, LD or LD₂ targets with solvent evaporating. Therefore, all mass spectral techniques could observe only a subset of asphaltene compositions and structures, which are not tightly bound in stable aggregates.

5.2.2. Time-of-flight mass spectrometry (TOF-MS) and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS)

TOF-MS fits well for identifying asphaltene aggregates due to its detecting ability of singly charged ions up to 20 kDa [52,108], and FT-ICR MS owns unparalleled mass resolution and accuracy to measure asphaltene molecule. Both of them can provide precise chemical compositions, like identification of $C_cH_nN_nO_oS_s$ compounds, heteroatomic content, isotopic distribution, double bond equivalent (DBE) and classify components by heteroatom and aromaticity [28,47,50,51,109–111]. MWs of asphaltene were directly given from 300 to 20,000 with low-MW components only accounting for a little by hybrid magnetic sector-TOF tandem MS. Although high-MW molecules would be reduced by in-source collisional activation, most asphaltene were high-MW species [108]. Specific molecular analysis required ultrahigh resolution ($m/\Delta m_{50\%} > 800,000$ at $m/z = 400$, in which $\Delta m_{50\%}$ was the full mass spectral peak width at half maximum peak height), which realized only by FT-ICR MS [59,108]. FT-ICR MS is also one of the few extremely sensitive technology by which samples could be assayed even at background levels [122]. The aromaticity degree of asphaltene could be obtained by the slopes of DBE versus carbon number from different magnitude of the viscosities of oils

by APPI(\pm)-FT-ICR MS [28]. 4000–8000 peaks were sorted into 18 heteroatomic classes and subtle differences of asphaltene compositions could reflect the properties of oils and asphaltene, indicating the chance for ESI-FT-ICR MS on geochemistry research [108,114].

5.2.3. Others

Multistage mass spectrometry (MS_n), also called tandem mass spectrometry, is a unique way to define individual ionized asphaltene molecule without prior separation, as long as only a molecule is ionized and convoluted with no fragmentation or aggregation. Coupling APCI/CS₂ with MS₂ provided a good way to detect molecular structure of asphaltene, like alkyl chain length and size of aromatic cores. For example, MS_n produced plenty of stable molecular ions of PAHs with long alkyl chains of asphaltene in comparison with model compounds [10].

MS_n was applied to compare structure differences between coal and petroleum asphaltene by comparing the fragmentation pathways of molecular ions with linear quadrupole ion trap and FT-ICR spectrometry. The fragmentation patterns were produced by isolating molecular ions of varying m/z values and subjecting them to collisionally activated dissociation. The results revealed longer alkyl chains and smaller aromatic cores in petroleum asphaltene in contrast to their coal-derived counterparts with the same MW. The differences of chain lengths and core sizes between the two types of asphaltene were quite subtle at low MW and it creased with MW. In consideration of the most abundant molecules in petroleum and coal-derived asphaltene, they were similar in 8 rings-sized aromatic core, but a great difference of alkyl side chains (a total length of ~ 22 for petroleum asphaltene, a total length of ~ 4 for coal-derived asphaltene) [123].

Inductively coupled plasma MS (ICP MS) has become a popular detector in liquid chromatography study of asphaltene, especially for its endurance with absolutely tetrahydrofuran (THF) and xylene [124]. For example, SEC-ICP MS demonstrated metal (Ni, V) distributions with different proportions in asphaltene fractions. Additionally, precise isotope ratio of metals (like Pb, Re and Os) in asphaltene was measured by ICP MS; multi-collector ICP MS and

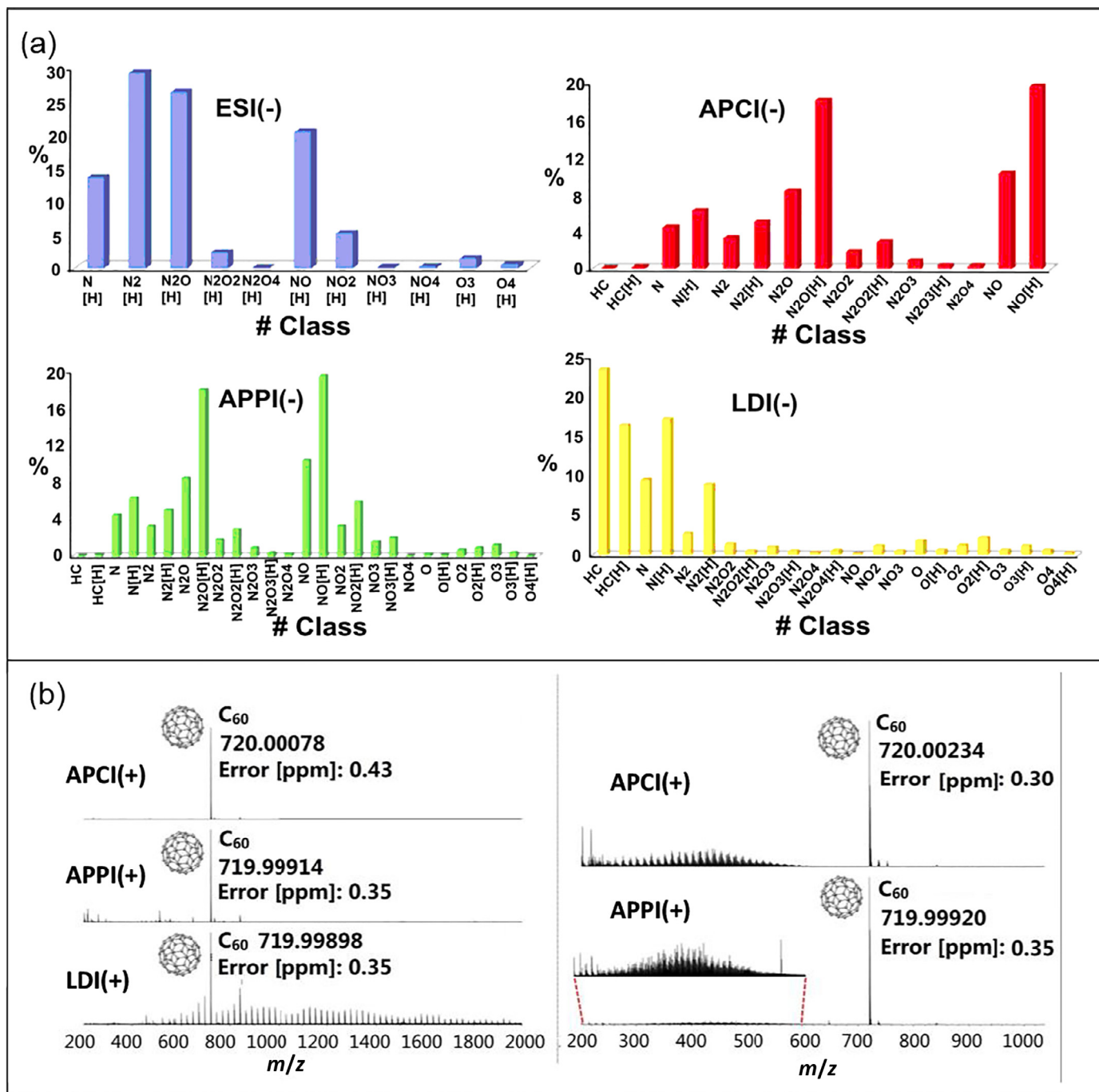


Fig. 5. FT-ICR MS analyses of asphaltenes using four different ionization methods. (a) A wider scale of class distribution generated from APCI(-) and APPI(-) compared with ESI(-) and LDI(-) FT-ICR MS data; (b) APCI(+), APPI(+), and LDI(+), FT-ICR MS for the fullerene solution (left), and APCI(+), APPI(+), FT-ICR MS for the asphaltene sample doped with fullerene C₆₀ (right). A 24 Da interval homologous compounds corresponding to fullerene clusters (ranging from C₄₄ (m/z 528.0011) to C₂₃₄ (m/z 2808.0022), C₆₀ (m/z 719.99914) as the most abundant allotropic) by LDI, but none by APCI(+), APPI(+). Both reprinted with permission from Ref. [110].

negative thermal ionization MS has been applied for geochronology of asphaltenes, kerogen, and petroleum source rocks [25,125].

Overall, the wide MW distribution (originally several hundreds to tens of thousands) of asphaltenes had been compressed mainly from 200 to 2000. And more molecular details could be got from MS besides MW.

5.3. Chromatography

Chromatograph coupled with MS is quite adequate to separate and detect multi-components of coal and petroleum derivatives. It

also faces the problems surrounding monomeric MW of asphaltene, molecular aggregation, and characterization of isomers and so on.

5.3.1. Gas chromatograph (GC)

GC is a primary method for identifying low-MW and thermally stable hydrocarbons in asphaltenes. One-dimensional GC (1D-GC) is largely employed for analyzing heteroatomic (like N and S) compounds in asphaltene with selective detectors, such as nitrogen chemiluminescence detector (NCD), nitrogen phosphorus detector (NPD), sulphur chemiluminescence detector, pulsed flame

photometric detector and atomic emission detector [126–129]. The limits of detection were usually about 0.4 pg N/s and 0.5 pg S/s for nitrogen and sulfur, respectively [126,129,130]. However, the co-elution of asphaltene components limits 1D-GC applications.

To overcome the co-elution and improve sensitivity, a heart-cutting and comprehensive two-dimensional system (GC×GC) is complemented with non-polar×polar columns, the separation property was improved and a clear classification based on the visual inspection of the contour plots was provided [131]. Lots of literatures emphasized qualitative and quantitative analysis of N-containing compounds in asphaltenes by GC×GC-NCD/NPD, but with unsatisfactory “roof-tile effect” [132]. Besides, molecular identification by GC and GC×GC required authentic standard substances. GC×GC coupled with MS became a powerful complement for some fully separated but unexpected compounds. For instance, GC×GC/TOF MS could successfully detect 112 N-polyaromatic compounds in a coal tar without prior isolation [127], especially detecting trace level nitriles, distinguishing anilines and quinolines from phenols and PAHs separately, and avoiding interference from co-elution. GC×GC/TOF MS could also identify chemical structures of O- and S- compounds in asphaltenes [132,133], mainly containing diols, phenolic compounds, benzofurans, naphthols, and indanols. Additionally, GC×GC assisted by stable isotope determination (δ D and δ 13 C) were applied to affirm homogeneity of equilibrated liquid-phase components of similar chemical property and equilibrated asphaltene isotopes in Saudi Arabian oilfield [128].

5.3.2. High performance liquid chromatography (HPLC)

Asphaltenes is often separated by adsorption chromatography. GPC and SEC have shown great feasibility in reflecting MW distribution of asphaltene aggregates or monomers because of concentration-dependent self-association [44,64,108]. It achieves a separation due to hydrodynamic volume, MW, only when a calibration standard is available. Polystyrene is a common but inappropriate standard for asphaltenes due to big the differences in stereostructures, thus, the actual calibration is got via iterative operation whether with broad calibration or universal calibration. THF and N-methyl pyrrolidone (NMP) were used as the eluent. Adsorptive interactions between solute molecules and packing particles were not complete within columns in THF, while NMP could well dissolve most coal derivatives and wipe off any depositions caused by THF, so, molecular aggregations in dilute solution is avoided [134]. But, NMP is incapable with aliphatic compounds, for example, up to 50% of petroleum asphaltene was insoluble in NMP and with no UV-FL absorption [135]. Mixtures of NMP, dichloromethane and chloroform have also been tried on petroleum asphaltenes [9].

Additionally, TLC, column chromatography on silica and solvent extraction were taken before GPC or SEC to reduce complexity. It was reported that fractionation by GPC or SEC was the only to access high species with suitable detectors. It was clear that SEC required concentrations exceeding the critical micelle concentration detected by diode array detector [136]. UV-fluorescence was not sensitive for high-mass fractions and could not detect asphaltene with MW higher than 3000 Da. As mentioned above, only MS could accurately achieve MW of low- and high-MW fractions for size-separated fractions [137].

Besides GPC and SEC, reversed-phase HPLC (RP HPLC) and normal-phase HPLC (NP HPLC) also have been applied in analyzing asphaltenes. RP HPLC accompanied by EI MS was commonly used to investigate polar compounds. Lighter PAH and polycyclic aromatic sulfur heterocycles (PASH) were analyzed by NP HPLC, like by a column packed with β -cyclodextrin or a polar aminocyanobonded silica [138]. NP HPLC-ICP MS found that Ni and V mostly appeared in non-porphyrin congeners with different polarities. SEC connected with NP HPLC served as an improved

prior purification of metal analysis by MS [124]. Besides, argentation chromatography was used to compare asphaltene PAH with or without heteroatoms (N, O, S) and monitor the change of molecular components and achieve isomers separation with APPI/APCI MS [138]. Instead of a conventional column, HPLC with filtration realized on-column separation of asphaltenes, which could retain the precipitated asphaltenes that were to be quantified [139].

5.4. Nuclear magnetic resonance (NMR) spectroscopy

High resolution NMR spectrum can offer aromaticity degree, carbon distribution and hydrogen distribution of asphaltene [28,110,140,141]. Table S2 summarizes the belongings of specific regions in 13 CNMR and 1 HNMR spectra [142–144]. Petroleum asphaltene contained approximately 50% aromatic carbon according to 13 CNMR result [7,145,146]; while some coal-derived asphaltenes showed 85% aromatic carbon [147]. Another typical feature among the average structural parameters of petroleum asphaltene was its smaller aromaticity factor, but more H γ content compared with coal-derived asphaltenes, which also revealed alkyl side chains in petroleum asphaltene were long but very short in coal-derived aromatic layer, mainly in the form of methyl, methylene, methine and ethyl groups [148]. The degree of substitution of two kinds of asphaltenes was all depended on their origins and processing.

The protonated, outer and inner quaternary aromatic carbons in asphaltenes could be quantified by the combination of distortionless enhancement by polarization transfer (DEPT) and single pulse excitation (SPE) [144]. The ratio of alkyl carbon to aromatic carbon in aromatic region and their chemical shifts could be directly got from DEPT-45 and 13 C SPE spectra. Diffusion ordered spectroscopy (DOSY) could give chemical shift and molecular diffusion in a two-dimensional spectrum [143]. Different diffusion coefficients reflected the types of aggregates as macroaggregate, microaggregate and nanoaggregate. Except for these primary structure information, chemical composition, aromatic core number and carbon center distribution were also necessary for a structural construction and often connected with MS analysis [28].

5.5. Electron paramagnetic resonance (EPR) and electron spin resonance (ESR) spectroscopy

There has been an inspiring research in paramagnetic centers of petroleum derivatives for last five years by EPR and ESR, especially for vanadyl porphyrin (VO $_2^+$). The high sensitivity of EPR and ESR could detect low concentrations of vanadium species in asphaltenes, provide in situ information of sizes of vanadium molecules and their aggregates, distinguish different types of environments of vanadium species, and monitor environmental dynamics [31,149–151]. The mechanisms of hydrodemetallization were also investigated using EPR [149,152]. In particular, the evolution of V-containing asphaltene molecules during the different steps of hydrotreatment was tested both qualitatively and quantitatively by hyperfine sublevel correlation and continuous-wave (CW) EPR, respectively. It was proved that VO $_2^+$ influenced the formation of asphaltene aggregates since VO $_2^+$ was only a few nanometers away from free radical of asphaltene polyaromatic condensed nuclei by analyzing twelve different kinds of asphaltenes using high-frequency (W-band, $\nu_{MW} \approx 94$ GHz) pulsed EPR spectroscopy [153]. Asphaltene sizes could be quantitatively estimated in situ by correlating paramagnetic particle size with the responding rotational time using ESR [154]. Besides, ESR could offer the transformation between anisotropic and isotropic vanadium and 14 to 20 kcal/mol was needed to associate a metallo-complex with asphaltenes, which was calculated by adding vanadyl indicators to asphaltenes [7].

5.6. Fluorescence (FL) spectroscopy

FL spectroscopy is powerful measure for monitoring asphaltene aggregations [110,140,145,155], and approximate size of asphaltene aromatic nucleus could be deduced using synchronous FL spectroscopy. Different types of asphaltenes had similar absorption and emission spectrum, and their chromospheres changed little with concentration varying. Aggregation began with red shift and quenching of the largest FL peak even in every diluted solution (50 mg/L) [140].

Fluorescence depolarization (FD) and time-resolved fluorescence depolarization (TRFD) are performed to measure asphaltene molecular size and minute difference in molecular size [20,108,111,156]. Coal-derived asphaltenes exhibited similar trends with the petroleum asphaltenes on FD spectra. Compared with petroleum asphaltenes, coal-derived asphaltenes showed the shorter wavelength of emission peak (about 100 nm less than that of petroleum), smaller decay time of the anisotropy (about 0.2 ns less than that of petroleum at the same emission peak) and lack of longer wavelength absorption by FD, which confirmed the smaller fused ring systems of coal-derived asphaltenes [8]. Another example, predominant island structures of asphaltenes with an average MW around 700 Da could be proposed using TRFD [43]. However, TRFD is only suitable for molecules bigger than octaethyl porphyrin. Taylor dispersion and VPO were alternatively ways for small molecules, like coal-derived asphaltenes, but they required high asphaltene concentrations (0.1 g/L) accompanied with inevitable aggregation. While this problem was well settled with the translational diffusion coefficient by fluorescence correlation spectroscopy (FCS) at diluted solutions (0.03–3.0 mg/L), and proved that molecular size of coal-derived asphaltene was obviously smaller than that of petroleum asphaltene [156].

5.7. Ultraviolet-visible (UV-vis) spectrometry

UV-vis absorption spectrum is another valid way to determine asphaltene chromophore content aggregation degree [157], interaction between asphaltenes and other compounds [158], but usually in dilute solution with fluorescence spectrum [20,23,159]. Bigger aromatic nucleuses and molecular size would lead to lower UV-FL intensity [160]. The gradual formation of aggregate was proved to be different from micellisation formation. In detail, asphaltene molecular aggregation in solution was determined by its concentration, monomolecule existed when its concentration less than 1 mg/L, dimers prevailed at concentration from 5 to 15 mg/L, and finally stable “nanocrystallites” (dimer pairs) dominated at concentration roughly 90 mg/L [136]. Recently, near-UV-vis spectroscopy was used to illustrate how vanadyl porphyrins existed in different concentrations of asphaltene solution. As concentration of asphaltenes increasing, porphyrins were gradually attached to asphaltene molecules with one to three rings, wrapped in porous supramolecular aggregates and micelles, and free porphyrins existed at concentration from 4 to 12 mg/L [34]. Besides, the combination of UV-vis and EPR proved that the non-porphyrinic structure of V-containing asphaltene molecules also existed [152].

5.8. Infrared spectroscopy (IR) and near-infrared (NIR) spectroscopy

IR and NIR mainly indicated the functional groups, chemical bonds and hydrogen bonding in asphaltenes. IR practically scans from 4000 to 400 cm^{-1} , while NIR generally ranges from 10,000 to 4000 cm^{-1} [161,162]. The wavelengths of functional groups usually very little, like carboxyl, formyl, olefin, C-H stretching vibration, etc. Sometimes, absorption bands due to overtones or carbon-hydrogen stretching vibrations made NIR more suitable than IR.

It was photon absorption via excitation of aromatic C-H stretching vibrations that urged light weaken (13,700 to 10,000 cm^{-1}) when asphaltene concentrations < 30–40 mg/L, while Rayleigh scattering worked when asphaltene concentration increased more than 120 mg/L [162]. There was a well-established way to detect asphaltene precipitation based on the change of absorbance at wavelength of 6250 cm^{-1} in NIR spectra. Recently, precipitation of a petroleum asphaltene was found to be almost unaffected by pressure, temperature, and flocculant addition, except compound interaction, and it was conducted online also using NIR spectrometer at desalter condition [161].

Quantitative analysis is usually based on the proportionality between signal integrated areas and the content of compound of particular group in IR spectra. E. Rogel compared the asphaltene fractions by normalizing against the aliphatic stretch signal on condition of unchanged extinction coefficient to obtain concentrations of the function groups [141,163]. Vibrational spectra of asphaltene were determined by the characteristic band at 1600 cm^{-1} with electronic structure means [164]. Phenol and piperidine were used to estimate the strength of hydrogen bonding between -OH, -NH groups and asphaltenes by IR spectroscopy shown in Fig. S1 [165].

Fourier transform infrared (FTIR) spectroscopy is well used to analyze chemical composition of asphaltene, although the relative IR transparency is hard for these black heavy substances. More than 90% of hydrogen was found substituted on aliphatic groups. Especially, -OH absorption bands were divided into six types on FTIR spectra as shown in Table S3. Up to several micrometers deep of asphaltene deposit layer could be observed in situ by chemical imaging mode of attenuated total-reflection Fourier transform infrared (ATR FTIR) spectroscopy. Furthermore, asphaltene precipitation was affected by oxidation of molecular layer, which could also be accessed by comparing reflectance versus transmittance mode on FTIR spectra [166].

The FTIR spectrum of coal-derived asphaltene differed from those of petroleum asphaltenes [167]. Specifically, strong absorption peaks in the region of 3600–3300 cm^{-1} were arised from ether oxygen, OH functional groups, and self-associated N-H/O-H hydrogen bonds. And C-O bond in ethers, alcohols, and phenols also caused intense signals in the regions of 1300–1100 cm^{-1} [168]. While, long aliphatic chains of petroleum asphaltene usually had intense signals in the regions of 3000–2800 cm^{-1} (saturated C-H stretching), 1500–1300 cm^{-1} (saturated C-H bending), and 725–720 cm^{-1} (CH_2 of $-(\text{CH}_2)_n-$, $n \geq 4$ rocking vibration) [169,170]. Additionally, obvious bands at about 2500 cm^{-1} and 1032 cm^{-1} , corresponding to S-H vibrations and S=O groups of petroleum asphaltene, but they were insignificant in spectrum of coal-derived asphaltene [167].

5.9. Raman spectroscopy

As complementary to IR, Raman is caused by molecular vibration of polarizability changes and mainly for measuring average size of aromatic fused rings and their boundaries in asphaltenes, while IR absorption is due to molecular vibration of dipole moment changes [164]. Asphaltenes and microcrystalline graphite-like substances are alike in Raman spectrum since both of them have aromatic fused rings [112]. The common bands and applications are listed in Table 6 [112,145,155].

Surface Enhanced Raman Spectroscopy (SERS) could be applied to detect asphaltenes at low concentrations, besides FT-ICR MS. Minimum value of asphaltene concentration significantly was reduced to smaller than 50 ppm by a common Raman spectrometer equipped with 514 nm light source and gold covered substrate, which was the best among the similar researches [122].

Table 6. Characteristic bands and applications of “twin-techniques” (Raman spectroscopy and XRD analysis).

Characteristic bands		Wave-numbers	Molecular vibration ascriptions	Particular parameters	Conclusions
Raman	G band	1580 cm ⁻¹	Stretching vibration of sp ² C–C bonds of ordered aromatic fused rings	Tuinstra and Koenig equation L_{α} (Å) = 4.4 I_G/I_{D1}(1), I_G , I_{D1} : integrated intensities of G, D1 bands, but G band limited at 1575–1610 cm ⁻¹ ; D2 not involved due to its extrinsic property of Raman scattering	Average parameters: L_{α} : 1.1–2.1 nm with approximately 7 to 8 aromatic fused rings; Bigger L_{α} larger aromatic cores, but lower stability, because of increased molecular self-association
	D1 band	1350 cm ⁻¹	Vibration of sp ² C in aromatic fused rings changed by in-plane defects or heteroatoms, intensity increasing linearly with peripheral atom numbers		
	D2 band	1600 cm ⁻¹	Vibration caused by intravalley process, like edge of graphene-like molecule next to aromatic fused rings		
XRD	Graphene band (002 band)	$2\theta = 26^\circ$; Bragg's angle where peak centers	Spacing between aromatic layers, sometimes as a shoulder peak (not a distinct peak) due to alkyl ordering	(L_{α}) , inter-aromatic layer distance (d_m), inter-chain layer distance (d_{γ}), cluster diameter (L_c), average number of aromatic rings per sheet (N_{α}), average number of aromatic sheets per stacked cluster (M), asphaltene molecular aromaticity (f_{α}),	Average parameters L_{α} : 1.0–2.0 nm d_m : 0.34–0.37 nm; d_{γ} : 0.44–0.62 nm L_c : 1.4–3.6 nm N_{α} : 4 to 16 aromatic rings M : 5 to 8 f_{α} : not actual aromaticity because C_A only refers to number of stack cluster aromatic carbons affecting 002 band, not all aromatic carbons
	γ -Band	$2\theta = 20^\circ$	Distance between aliphatic layers (alkyl chains or saturated rings)		
	(10) Band (11) Band	$2\theta = 40^\circ$	Weaker than 10 band		

Table 7. C 1s, N 1s, O 1s, S 2p_{3/2} signals and their chemical forms for asphaltenes in XPS.

C 1s		N 1s		O 1s		S 2p _{3/2}	
Chemical group	Binding energy (eV)	Chemical group	Binding energy (eV)	Chemical group	Binding energy (eV)	Chemical group	Binding energy (eV)
Aliphatic	284.8	Pyridinic	398.6	Ketones, O=S=O, S=O,	531.8	Aliphatic	163.3
Ether, amine	285.8, 285.9	Amine	399.4	Ether	532.3	Thiophenic	163.9, 164
Alcohol	286.5, 287	Pyrrolic/ pyridone	400, 400.2, 400.5	Alcohol, S–OH, S–O–R, C–OH	533.1, 533.3	Sulfoxide	165.4, 165
Ketones, amide	287.5, 288.3	Quaternary	401.4 ± 0.1	Carbonyl, O=C–OR, O=C–OH	534.8, 535	Sulfone	165.9
Carboxylic acids/ester	289.1, 290	Pyridine N-oxide	402.3	Occluded O ₂	536.9	Sulfite/Sulfate	166.5
πe^- , $\pi-\pi^*$	290.6, 291.5, 293	Other oxidized nitrogen	>402.7			Sulfonic acid	168, 169.3

5.10. X-ray diffraction analysis (XRD)

XRD gives an insight into the crystallite properties of asphaltene particles and is often called “twin-technique” of Raman spectroscopy. It has been used to measure the interlamellar spacing in petroleum asphaltenes since 1961 [3]. A whole set of literatures focus on a hypothetical cross-sectional sketch of asphaltene in Fig. S2. The aromatic sheets were theorized to be stacked in levels with alkyl chains or cycloalkanes sticking out from the edges. Quantitative analysis was calculated by the peak intensity and position and the particular parameters are list in Table 6 [4,145,171]. Compared average value of aromatic sheet diameter (L_{α}) obtained by Raman spectroscopy with that by XRD analysis, the value falls into similar scale, so L_{α} can be summed up from 1.0 nm to 2.1 nm.

XRD coupled with GPC, UV, Raman spectroscopy, elemental (C, H, N and S) analysis and metal (Ni and V) analysis were used to investigate how asphaltene molecules changed under different thermal process [30,172–174]. The harshly thermal cracking increased the aromaticity, but decreased asphaltene M_w and L_c with alkyl

chains broken and aromatic sheets reduced. And d_m , d_{γ} or L_{α} changed not so much with cracking severity increasing [171]. Additionally, stack diameter was found to be insensitive to subfractionation of asphaltenes.

5.11. X-ray photoelectron spectroscopy (XPS)

XPS is committed to analysis the chemical states of carbon, oxygen, sulfur and nitrogen in asphaltenes [175]. Table 7 lists the binding energy for C 1s, N 1s, O 1s, S 2p_{3/2} and their different chemical forms, respectively [29,175].

XPS studies showed the types of C–C and C–H were the most carbon-containing compounds both in coal-derived asphaltene and petroleum asphaltene [167]. But, it was difficult to distinguish carbon in aromatic from carbon in non-aromatic structures by XPS. With regard to oxygen, oxygen in coal-derived asphaltene was mainly in the form of C–O (C–OH and C–O–C), few in the C=O and COO–compounds. While asphaltenes from residue oils was more likely in the form of C=O and COO–groups [29]. Pyrrolic-nitrogen and pyridinic-nitrogen were the two main kinds also both in coal-

derived asphaltene and petroleum asphaltene. Coal-derived asphaltene contained little amino-nitrogen because such type of nitrogen was easily lost during pyrolysis for coal [167]. Quaternary-nitrogen in coal-derived asphaltene was more than that in petroleum asphaltene. This was because quaternary-nitrogen was thought as protonation of pyridinic-nitrogen connected with carboxyl oxygen or hydroxyl group by a H-bridge, and coal-derived asphaltene had more acidic phenolic groups to form H-bridges more easily [176].

5.12. Small angle neutron scattering (SANS), small angle X-ray scattering (SAXS) and small angle light scattering (SALS)

SANS, SAXS and SALS are conducted with neutrons, X-ray and light, respectively, all of them belong to small-angle scattering techniques. The mechanism by which the incident radiation acts on asphaltene makes them essentially different [11], as shown in Table S4. But with any of the three techniques, scattering pattern produced by radiation could give an unambiguous determination of sizes and shapes of asphaltene components, like semi-crystalline structure of asphaltene aggregates, described as a prolate ellipsoid or a sphere or an oblate cylinder building a dense, or fractal physical network [11,70,154]. SAXS analysis revealed that the size was nearly 2 nm for asphaltene nanoaggregates and about 5 nm for nanoaggregate clusters [81]. Additionally, SANS coupled with several other measurements suggested asphaltene aggregates could form at sub-ppm concentrations [108]. Solvent enlarged the size of colloidal aggregates by three times from initially a few nanometers by a serial of SAXS or SANS studies [177].

Furthermore, K-edge X-ray absorption near edge structure (XANES) spectroscopy was used for sulfur speciation, present in alkyl sulfoxide, sulfide, thiophene groups and fused ring system [146,178]. Also nitrogen in different valences presented typical resonance positions on XANES spectra, and pyrrolic nitrogen generally dominated the aromatic nitrogen in asphaltene [179].

5.13. Atomic force microscopy (AFM)

AFM technique is another way to analyze micro- and nanometer-scaled asphaltene aggregates [177], heterogeneity, and surface force [180,181]. AFM showed that if asphaltenes were well dissolved, two surfaces absorbing asphaltene repelled each other due to steric repulsion of de Gennes model. It turned to attraction when asphaltene was badly dissolved because of van der Waals forces. Changes of asphaltene colloidal particle size were directly observed caused by addition of inhibitors or flocculants with different AFM modes (topography and phase modes). AFM has been more frequently coupled with scanning tunneling microscopy than ever before, providing direct images of asphaltene molecules in Section 5.14. For example, recently, individual asphaltene molecule has been visualized with high-resolution noncontact AFM on CO-functionalized tips by B. Schuler etc., except for creation of fingerprinting of molecular groups by AFM, like alkyl groups and aliphatic rings [182].

5.14. Scanning tunneling microscopy (STM)

STM has developed rapidly for asphaltene molecular orbital study. The dimension of asphaltene aromatic structure was found to be 1 nm amount to 6–7 aromatic cores by STM more than twenty years ago and validated by high resolution transmission electron microscopy (HRTEM) later [145]. It is worth mentioned that more than 100 single asphaltene molecules from both one type of petroleum asphaltenes and two kinds of coal-derived asphaltenes were observed on ultrathin insulating film by low-temperature AFM coupled combined with STM [183]. The findings were consistent with Yen-Mullins model and absolute support for

smaller size of coal-derived asphaltene compared with petroleum asphaltene. B. Schuler further confirmed asphaltene structure of central aromatic core with peripheral alkyls irrespective of sources and processing by AFM/STM [184]. Although not all structures could be assigned, repetitive and differentiating structural motifs were clear enough, like representative groups, their relative occurrence and obvious locations. Moreover, AFM/STM and FT-ICR MS agreed with each other well about size distributions and the degree of unsaturation. Distinguishing features between the four pairs of samples and within each pair of samples are illustrated in Fig. 6, which were fully or partially identified by AFM/STM on a single-molecule basis with atomic-resolution.

5.15. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM)

TEM could provide the intuitive morphology of asphaltene molecules, and show locally ordered/disordered structure of asphaltenes. Besides, HRTEM could effectively observe direct stacking and the destruction of asphaltene nanoaggregates and fused aromatic ring systems [146,177,185]. For example, 2 to 3 fused ring systems were found in stacks, of which the size was nearly 1 nm in height and slightly bigger than 1 nm in width, and asphaltene dissolvability essentially decided the stacking invariants [146]. TEM showed that aggregate dimensions of asphaltene became more elongated with the addition of dispersant, which was in the range of 0.9–3.7 nm. The spacing of the π - π stacking distance of asphaltene molecules has been measured to be approximately 0.37 nm with 7 rings on average [146]. By addition of a bio-based modifier, the spacing was reduced to 0.35 nm by HRTEM, which was shorter than the typical distances of PAH molecules [186]. Furthermore, HRTEM showed the fused aromatic ring systems in linear dimension were about 1 nm of petroleum asphaltenes, and about 0.7 nm of coal-derived asphaltenes [8].

Integral to gradually advanced understanding of asphaltenes was constantly depended on the enhancements of analysis technology, especially about MS, NMR, X-ray techniques and AFM/STM and so on. Particularly, MS could track the structural differences of asphaltenes with MW changing by evolution of ionizing techniques. NMR yielded information about the average molecular parameters of asphaltenes, such as aromatic rings, carbons, and length of alkyl side chains. XRD reflected the variations of asphaltenes lamellar structures on interchain spacing, interlamellar spacing, number of layers and layer diameter. SAXS and AFM/STM could give unambiguous imaging of ships and molecular structures of asphaltenes, respectively. But there were still some challenges. For example, any technique (VPO, SEC even some kinds of MS) to determine M_w in solutions needed to considerate aggregation; all mass spectroscopy except LDI exhibited only part of asphaltenes molecular masses. And laser desorption techniques faced enormous baseline subtraction issue. For grossly different source materials, coal vs. petroleum or crude oil, more subtle differences in asphaltenes would be revealed due to the above analysis. In a word, the advantage and disadvantage of various analysis techniques for asphaltenes are compared in Table 8.

6. Coal-derived asphaltenes and petroleum asphaltenes

The coal-derived asphaltenes were commonly extracted from residues of direct coal liquefaction. Almost all oxygen is lost and pendant alkanes are also susceptible to cracking in the hydrogenation process. The petroleum asphaltenes were usually without chemical processing [187].

The most popular opinion between coal-derived asphaltenes and petroleum asphaltenes is that the former has lower MW and exhibits a much higher diffusion coefficient than that of the later.

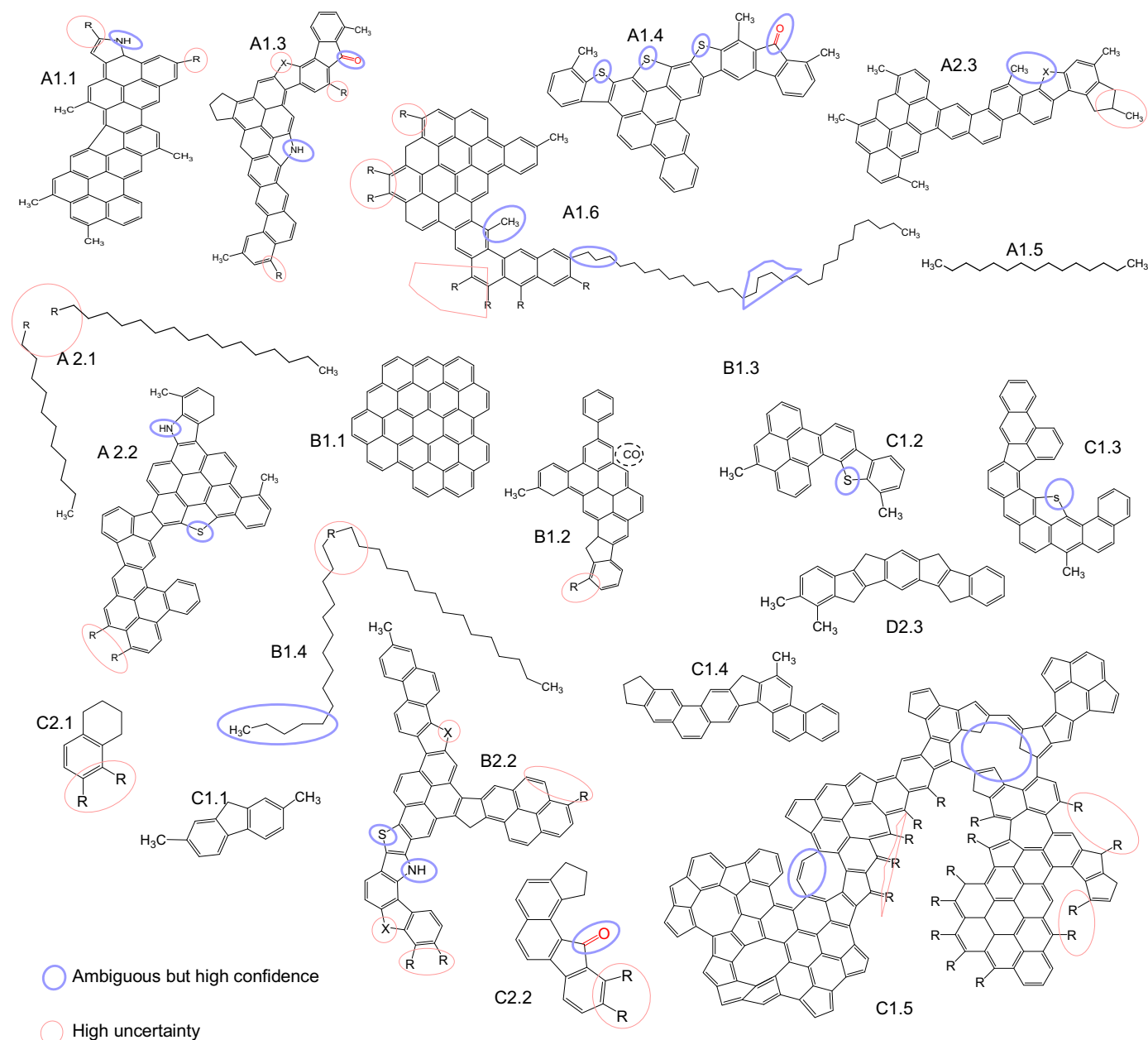


Fig. 6. Structure proposals based on AEM/STM measurements. The labels denote the sample name and molecule number. Samples: crude oil asphaltene (A1), asphaltene from deposit from A1 oilfield (A2), vacuum resid asphaltene from a heavy oil (B1), asphaltene from hydroconverted product from B1 oil (B2), asphaltene from steam cracker tar (C1), vacuum residue after asphaltene removal (C2) and two immature shale asphaltenes (D1 and D2). X and R mean uncertain heteroatoms and branched chains, respectively. Reprinted with permission from Ref. [184].

Specifically, asphaltene molecules from crude oils were two times size, and seven times carbon in long chains (>9 carbons) of that from coal by TRFD [147,188], FCS [27,156], LDIMS [47], L₂MS [189], and ¹³CNMR [187]. There were structural differences between them even with the same isolation method. Further, asphaltene isolated from original coal and native petroleum was even different from their refining products, respectively, but their dependence of aromaticity to H/C atomic ratio and aggregation behaviors were quite similar [7]. Asphaltene solubility was correlated with a balance between attractive and repulsive molecular forces. The short alkyl side chains in coal-derived asphaltene yields small intermolecular repulsion by ¹³C NMR [147]. Consequently, the smaller static repulsion must be balanced by smaller intermolecular attraction to maintain constant solubility intermolecular attractive

force in coal-derived asphaltene indicating the smaller fused ring systems relative to petroleum asphaltene. The two types of asphaltene have the same adsorption constants, and coal-derived asphaltene has the bigger adsorption saturation concentration on porous alumina than that of petroleum asphaltene. Fig. 7 shows the full or partial chemical structures of coal-derived asphaltene and petroleum asphaltene by AFM and STM on a single-molecule basis with atomic-resolution. Some typical differences between them are compared in Table 9 [3,8,15,47,144,156,184]. The comparison between coal-derived asphaltene and petroleum asphaltene offers the prospect of synthetic materials because of the difference between molecular architectures, which will be detailed in Section 7.2.

Table 8. The comparisons of analysis techniques in asphaltenes.

Methods	Applications	Advantages	Disadvantages
VPO	Determination of molecular weights	Fast, reliable, colligative, wide temperature range	Asphaltenes association effects
MS	Identification of individual components, MW distribution, metal detection	High-resolution, high sensitivity, convenient	Limited by ionization ways, asphaltenes aggregations; unable to distinguish fused-from separate-ring systems
GPC/SEC/HPLC	Qualitative and qualitative detection of functional groups; determination of mws	Yielding M_w distributions as well as average M_w	Requiring appropriate mobile phase and calibration standard; irreversibly adsorption on different substrates; time consuming, rather large estimation, concentration excess CMC
NMR	Estimation of aromaticity, condensation, average chain length	Information about individual atomic	Overlapping, uncertainty in deconvoluting, the observed peaks sensitive only to species with a detectable ^1H NMR signal
EPR/ESR	Founding the free radical content and the heteroatom sits, especially information of V-containing asphaltene molecules and their aggregates	High sensitivity, qualitative and quantitative, nondestructive	Limited by compounds only with electron paramagnetic
IR/NIR/ATR FTIR	Indicating the functional groups, hydrogen bonding, monitoring precipitation	Qualitative and quantitative, universal, nondestructive	Low sensitivity, low transparency
UV	Confirmation of aromatic structures	Qualitative and quantitative, universal, nondestructive	Low sensitivity
FL	Confirmation of aromatic fused structures CNAC; determination of molecule sizes and their subtle differences by TRFD	Qualitative and quantitative, relative high sensitivity, fast	Self-absorption, sensitive only to compounds with fluorophore; unsuitable for molecules smaller than octaethyl porphyrin by TRFD, like coal-derived asphaltenes
Raman spectroscopy	Average aromatic sheet diameter	Applied to different sample matrices	G band limited to 1575–1610 cm^{-1} by Tuinstra and Koenig equation, concentrations for detecting beyond CMC
AFM	Direct imaging of morphology and molecular force of surface	Stable, universal	Only the surface detecting, not suitable for soften samples, probably destructive
TEM/HRTEM	Direct molecular imaging of morphology and structures	Fast	Local property
STM	Size and structure of individual molecule	Inimitable	Samples with electricity, careful sample handling
XPS	Identifying the functional groups of the surface of the solid	Suitable for all elements except h and he, high sensitivity	Only the surface detection, lacking in-depth study
XRD	Detecting mesophase, crystallite structures, clusters parameters	Universal, convenient	Stack diameter is found to be insensitive to subfractionation of asphaltenes
SANS/SAXS/SALS/XANES	Examination of size and shape of aggregates, degree of intermolecular association, sulfur and nitrogen speciation	High accuracy	High requirements, high cost

Table 9. Typical differences between Coal-derived asphaltenes and Petroleum asphaltenes.

Items	Coal-derived asphaltene	Petroleum asphaltene
Asphaltene contents	8–15 wt% of coal tar	Less than 2 wt% of crude oil
Carbon aromaticity	70%–90%	40%–50%
Carbon aliphaticity	10%–30%	50%–60%
Heteroatom content	Low sulfur	High sulfur
Molecular diameter	10.5–14 Å	10–20 Å
MW distribution	300–700 Da	200–2000 Da
Average MW	400	750
Substituent	Shorter and less with aromatic system sparingly substituted (35% to 45%)	Longer, with aromatic system extensively substituted (70% to 80%); average of 4 or 5 carbons long; naphthenic rings fused to aromatic rings
Polarity	Strong polarity	Weak polarity
Association	Less	More highly associated
3D structures	Planarity and small content of flexible side chains	Less planar, more complex

7. Reactivity

7.1. Hydroprocessing, pyrolysis and gasification

Asphaltene complex reactivity is determined by its multiple properties, such as broad sources, different isolation ways, and wide MW distributions, etc. Hydroprocessing, pyrolysis and gasification are always the focus. The factors, like temperature and ratio of asphaltene internal aromatic carbon to peripheral one [1], greatly influence the yields and selectivity of hydroprocessing products [13]. The reduction of asphaltene molecular weight,

molecular size and H/C atomic ratio was caused by the rupture of C–C bonds in the molecules and alkyl chains during the hydroprocess [190]. A series of reactions of cycloalkane aromatization, hydrocracking, and heteroatom elimination happened simultaneously under hydroprocessing [174,191]. Changing temperature was thought to be the most cost-effective way to control the process. High temperature led to more hydrocracking reaction than hydrogenation. The dealkylation and polycondensation of fused aromatic rings produced bigger molecules, decreased the interaromatic layer distance and some agglomerated to coke. XRD and NMR founded that, with the temperature increase, L_α , d_m , total

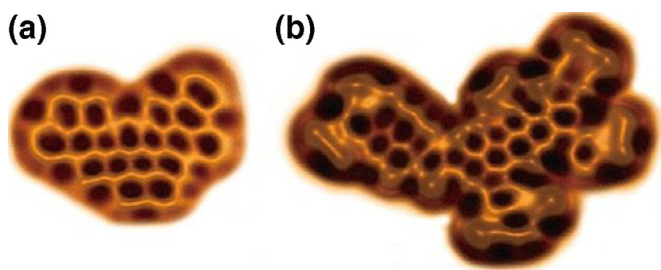


Fig. 7. AFM/STM images of coal-derived asphaltene (a) and petroleum asphaltene (b). Reprinted with permission from Ref. [183].

carbon number and average alkyl chain length decreased, while f_{α} and aromatic carbon number increased [190]. The heteroatom removal usually contains hydrodesulfurization (HDS) [29,191,192], hydrodenitrogenation (HDN) [12,191,193], and hydrodemetallization (HDM) [24,192], which is not as easy as desirable since the nucleus system remained with and/or without heteroatoms. Single-lump model was more adequate than Langmuir-Hinshelwood (L-H) models for specific asphaltenes [193].

In the hydroprocessing, the yield and selectivity is bound upon with hydrogen-donor solvents and catalyst. Savage et al have compared the yield of maltenes and coke in hydrogen and inert atmosphere, in the presence of and in absence of hydrogen-donor solvents and catalyst, it found that hydrogen only is negligible in hydrogenation, the presence of hydrogen-donor solvents led to higher selectivity to maltenes, and further addition of catalyst could maintain this high selectivity at high conversions [194]. In the case, hydrogen-donor solvents act as the medium of H_2 diffuses to the surface of catalyst for hydrogen supply and transfer, and prevents the condensation of free radical fragments.

The catalyst is necessary and considerably reducing the energy requirement for hydroprocessing [195]. The pore structure of a catalyst was designed to resist asphaltenes on its active surface to slow down the catalyst deactivation caused by metals and asphaltene deposits, etc. [196]. In principle, the asphaltene molecules need flow from the bulk phase to the internal surface of the catalyst, and then reaction in active site in hydroprocessing. In the process, the intrapore diffusion is the closest related to the performance of the catalyst. Compared to the petroleum asphaltenes, the effective diffusion coefficient of coal derived asphaltenes is ten times higher mainly due to smaller aggregate size [197]. Traditionally, hydrogenation of heavy petroleum fraction was carried out with industrial catalysts consisted of Mo, Ni/Co and loaded on γ -alumina, zeolites, or silica. And they could remarkably affect the molecular structures in HDS, HDN and hydrogenation of molecules [13]. The acidic property of silica-alumina catalyst deeply hydrogenated asphaltene aromatic rings and released more wrapped metals compared with alumina catalyst [198]. Table 10 lists literatures on hydroprocessing of asphaltenes.

The thermal cracking commercially produces high-value liquids and pitch, because of practical application in processing vacuum asphaltene residues, as well as in refinery industry such as delayed coking, visbreaking and flexicoking, etc. The research of asphaltene pyrolysis reaction involves in temperature and reaction time in the inert atmosphere [174,200–202], and a series of kinetic models are developed [196,203]. The pyrolysis may undergo a multi-step process, so do asphaltenic core and maltene [171,201]. Asphaltene conversion, gas yield, coke formation, S, N-specie reactivity, metal releasing, as well as asphaltene structure and its aromaticity mainly change with temperature and reaction time [24,171,174,202].

Additionally, asphaltene pyrolysis has been apportioned to elucidate its structure, analysis fragmentation products and investigated yields on pyrolysis temperature. When the temperature was

higher than 400 °C, C–C bonds were broken easily and saturated hydrocarbons cracked profitably; this results in the formation of polyaromatic rings. In addition, C–C bonds in short aliphatic side-chain of coal-derived asphaltene was relatively more stable and harder to cleave, and less condensed aromatic macromolecule free radicals produced compared with long groups in petroleum asphaltene. So asphaltene from coal had lower coking reactivity to some degree [190]. The products yielded on temporal variations, which made it possible to discriminate primary and secondary reaction products and offered a view for pyrolysis pathway and the inference of structural features. The research of major pyrolysate of asphaltenes founded that some portion of sulfur and oxygen atoms might exist at the periphery of the fused aromatic nucleus based on the nearly constant yields of H_2S and CO_2 , as well as independent of temperature [204]. Besides, long alkanes (up to C_{26}) of asphaltene were perceived as chemical-bonded structures and the chain length was proportional to its weight, which was consistent with Schucker and Keweshan asphaltene models. Three-lump models were prevalent to evaluate rate constants of parallel experiments for oil+gas and coke formation [107,196]. Every resulting composition will degrade again to lighter products, gas and char, presumably [196]. The conversion paths of asphaltenes were summarized in Fig. S3.

Gasification could translate carbonaceous fuel to syngas with a useful heating value, hydrogen and liquid products by air/oxygen and steam in an oxygen-deficient atmosphere at high temperatures; it has been a good choice to effectively use the byproduct asphaltene. It begins with pyrolysis, and pyrolysis starts with volatile combustion leading to cracking reactions. Besides, metals concentrates in the products of carbon oxidation, devolatilization and depletion of the droplet itself [30,205]. Table 11 lists literatures on pyrolysis and gasification of asphaltenes. The main factors, reactions, and products of hydroprocessing, pyrolysis and gasification are summarized in Table S5.

7.2. Synthesis of carbon materials

Due to its enriched polycyclic aromatic hydrocarbons, asphaltenes is considered to be a promising molecular precursor for functional carbon materials. Coal-derived asphaltenes have a higher aromaticity, narrower MW distribution than petroleum asphaltenes, as shown in Table 9. Therefore, the prepared carbon materials by coal-derived asphaltene as precursor are easier graphitized, which makes it promising to prepare porous carbons with excellent electrical conductivity for using as electrode materials. The carbon materials derived from asphaltene, for example, active carbon [207–209], carbon foam [210,211], carbon nanosheets [212], carbon fibers [213,214], and versatile composite or doped carbon materials [208,215,216], which successfully applied in water purification, gas adsorption, electrodes, etc. The intensive interfacial interaction between functionalized asphaltenes and epoxy resins produced a novel reinforcing filler with significantly increased storage modulus [155]. Furthermore, coal-derived asphaltene can be oxidized and dispersed in KOH solution to synthesize functional carbon materials, different morphologies of porous carbon nanosheets were obtained after carbonization at 800 °C. SEM images of typical several porous carbon nanosheets are shown in Fig. 8.

In addition, we selected coal-derived asphaltene as precursor to prepare spinning asphalt by thermal polymerization, the soft point could reach up to 280 °C, and it realized continuous spinning, the tensile strength and elastic modulus of resultant carbon fiber were 1.0 GPa and 350 MPa, respectively.

Table 10. Literatures on hydroprocessing of asphaltenes.

Asphaltene resources	Conditions <i>T</i> , atmosphere, <i>t</i>	Catalyst	Kinetics and conversions	Results	Ref.
Athabasca Cold Lake, Maya, Safaniya, Athabasca, and Venezuelan	430, 450, 480 °C in tetralin, H ₂ (initial 4.1 MPa)	FeSO ₄ on sub-bituminous coal	Distillates (<538 °C material) Asphaltene yields: 50%–60% Coke yields: <10 %	Saturates, 1-3-ring aromatics, >4-ring aromatics, and nitrogen- and sulfide-containing molecules	[13]
Maya heavy crude oil	380–440 °C; H ₂ (7 MPa)	NiMo/Al ₂ O ₃	No details	Nitrogen and metals content, asphaltene aromaticity, and H/C molar ratio increasing, sulfur contents decreasing	[193]
Athabasca crude oil	380 °C, H ₂ (5.51 MPa); 6 h	NiW/Al ₂ O ₃	No details	Sulfur, not nitrogen, removed by catalyst and sulfur concentrated at the surface	[29]
Direct liquefaction of a Spanish subbituminous coal	425–475 °C; H ₂ (containing 10 vol% of H ₂ S, 15 MPa); 5–40 min	Harshaw HT-500 E (15 wt% MoO ₃ and 3.5 wt% NiO)	First-order kinetics conversion ≤ 47 wt%; oil formation ≤ 46.2 wt%, gas ≤ 4.1 wt%, coke content remained 14.8 wt%	H/C atomic ratio increased, S/C atomic ratio decreased, little change of N/C ratio; a sharp decrease in viscosity	[195]
Athabasca bitumen	430 °C; H ₂ (initial 4.2 MPa); 2–60 min	NiMo/γ-Al ₂ O ₃	Second-order kinetics; Conversion ≤ 56%, ≤ 83% (catalyst); Rate constants 2.435×10 ⁻² and 9.360×10 ⁻² wt/(frac·min)(with catalyst)	Catalyst suppressing the formation of coke, reducing sulfur content in liquid products, and promoting the production of sulfuric gases	[107]
Bitumen	350–430 °C; H ₂ (initial 4.2–4.7 MPa, 10 MPa during reaction)	NiMo/γ-Al ₂ O ₃	First-order, 134.8 kJ/mol deviation of first-order kinetic at higher temperatures	Dominant products varying from gases to liquids to gases, reaction from C–C bonds cleavage to C–C bonds cleavage	[199]

Table 11. Literatures on pyrolysis and gasification of asphaltenes.

Asphaltene resources	Conditions <i>T</i> , atmosphere, <i>t</i>	Asphaltene conversions and yields	Conclusions	Ref.
California crude oil	350, 400, 450, 565 °C; argon; 5 to 150 min	Conversion < 10%; total gas yield 1.0%, maltene yield 10%	Producing H ₂ S, CO ₂ , CH ₄ , cycloalkane, n-paraffin series up to C ₂₆ , polynuclear aromatics, coke	[204]
California crude oil	350, 400, 450 °C; 60 min; with catalyst Co-Mo/Al ₂ O ₃	Conversion ~71%, total gas yield 1%–3%, ultimate maltene yield ~60%	C ₇ soluble 50%–60%, no toluene insoluble (<i>t</i> = 400 °C, <i>t</i> ≤ 2 h), <i>k</i> = 0.021 min ⁻¹	[204]
Maya oil	350, 400, 450 °C; N ₂ , constant flow at 1 atm	No details	Significant alteration of aliphatic molecule; Ni and V occurring as porphyrins, organic nitrogen concentrated in the nonvolatile coke, ~1% of the nitrogen lost	[24]
Direct liquefaction of subbituminous Spanish coal	425, 435, 450, 475 °C; N ₂ ; 5, 10, 20, 30, 40 min	Conversion 55.9%, oil yield: 70%, coke yield: 30%	Second-order kinetics, α-cleavage of the alkyl side chains being preferred over β-scission, H _β firstly decreasing and then increasing at 475 °C by H NMR	[196]
Vacuum residues of Kuwaiti oil Ratawi–Burgan, Lower-Fars, Eocene	400, 415, 430 °C; N ₂ , 1 NL/min; 30, 50, 60 min	No details	Decreasing in molecular size of asphaltene and H/S ratio, concentrating the metals in polyaromatic entities, no significantly affecting N content	[202]
Vacuum residues of Kuwaiti oil, Ratawi–Burgan, lower-Fars, Eocene	400, 415, 430 °C; N ₂ , 1 NL/min; 30, 50, 60 min	No details	No substantially effects on the layer distances between aromatic sheets, aliphatic chains and naphthenic sheets, the diameter of the aromatic sheet, except cluster diameter decreasing	[171]
Heavy oil from southeastern part of Turkey	350, 400, 450 °C; argon; 10 to 120 min	Conversion up to 93%, gas yield: 4%–16% (isolated asphaltene pyrolysis), 10%–38.6% (oil pyrolysis)	A decrease in H/C ratios, an increase in N/C ratios and S/C ratios with temperature increasing; H/C ratios and s content of reacted asphaltene from heavy oil pyrolysis higher than those of asphaltene from isolated asphaltene pyrolysis	[174]
Three kinds of Chinese coal tar	420 °C, 440 °C for 20 min; in N ₂ of 0.1 MPa or in supercritical water (SCW) of 26 ± 1 MPa	Conversions at 420 °C: 46.5% (SCW), 38.4% (N ₂); at 440 °C 69.7%–76.9% (SCW), 48.9% (N ₂); Maltene selectivity at 420 °C: 62.4% (SCW), 35.6% (N ₂); at 440 °C 56.5%–78.9% (SCW), 31.9% (N ₂);	Asphaltene conversion and maltene selectivity in SCW higher than that in N ₂ ; the presence of maltene suppressing the formation of char; aromatic nucleus of asphaltene molecule mainly composed of 2–4 rings aromatic hydrocarbons	[14]
Athabasca basin	1000, 1200, 1400 °C; N ₂	Char yield: 17.42%–18.29%, gas yield: 75.86%–72.98%, soot yield: 6.72%–8.73%	Soot containing more trace metals than char, reversibly at 1400 °C; V and Ni liberated into gas phase; V content increasing in both char and soot	[30]
Heavy oil and extra heavy oil, Colombian	127–827 °C; steam	Greater than 93%	The bimetallic active phase increasing the decomposition of the heavy compounds by an increase in aliphatic chains decomposition and the dissociation of heteroatoms bonds. Also, coke forming after steam gasification process reduced.	[206]

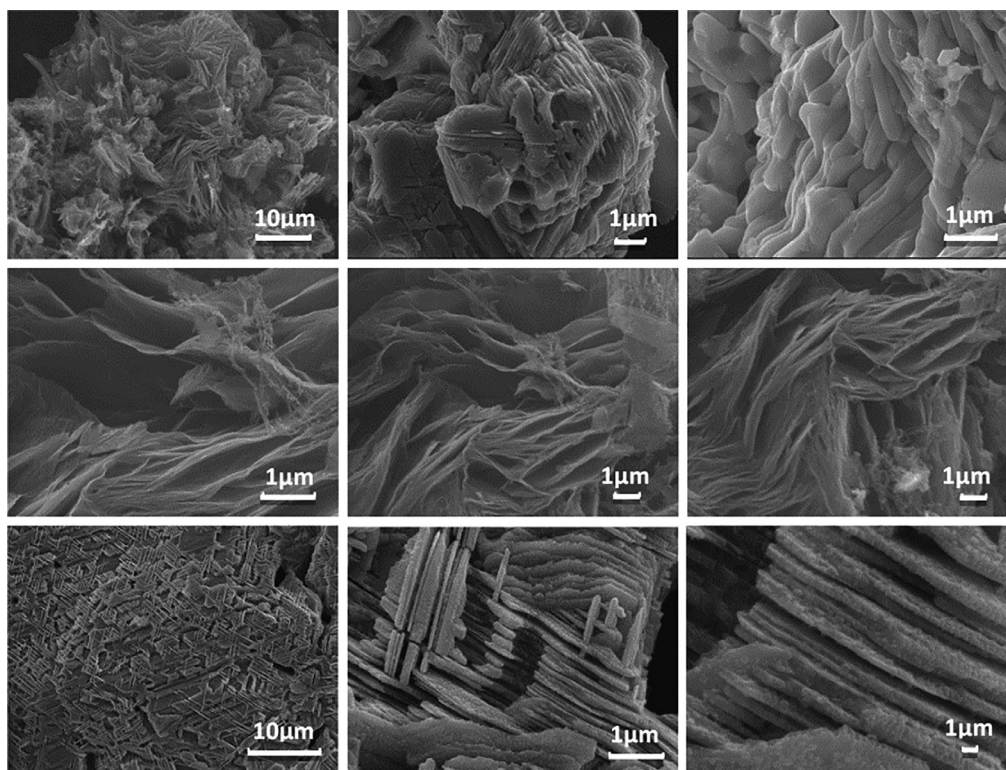


Fig. 8. The morphologies of porous carbon nanosheets by SEM.

8. Perspective and outlook

Asphaltene widely exists petroleum refining, coal tar, coal direct liquefaction products, it is mainly composed of C and H elements, different sources of asphaltenes all consists of polycyclic fused aromatic hydrocarbons and alkylations and has high average MW and aromaticity. Thus, it is easy to polymerize or crosslink due to its high carbon contents. Asphaltenes with controllable structure and concentrated MW distribution could be a perfect precursor to prepare new functional carbon materials. The structure of asphaltenes determines its chemical properties and application features, understanding its formation mechanism and realizing structure control is the basis of efficient use of asphaltenes. Over the years, various experiments and numerical simulations have been tried to study structures and properties of different sources asphaltene, but it is only to a certain extent, to known, researchers still can't accurately describe the composition and structure due to the complexity of asphaltene components, structural uncertainty. So, it can't provide more effective guidance for controlling the composition and structure of asphaltene.

Asphaltene is mainly derived from petroleum and coal liquefaction residues, the separation process affects its structure and chemical composition. Among the different solvents that can dissolve different structures of asphaltenes, the solvent with stronger dissolving ability can obtain a higher yield of asphaltenes, but it also caused the resultant asphaltene with various molecular species and wider MW distribution; Multiple solvents can selectively separate and regulate the composition and structure of asphaltenes.

In addition, some condensed ring compounds contained in asphaltenes can be separated, crystallized and purified by solvent extraction, which can be used as drug intermediates or model compounds to achieve high added value.

As a complex mixture, there are a lot of works about analysis and characterization of asphaltenes, but the obtained messages

are the apparent statistics data, it is difficult to give precise composition and relative content of different components of asphaltenes only using one analytic method/technology; it is only possible to obtain the comprehensive information of asphaltenes by combination of various analytical techniques and characteristics methods, then, achieving the qualitative and semi-quantitative analysis results.

Acid and alkalinity is stemmed from the functional groups of heteroatoms in asphaltenes. On the one hand, it can cause the association and agglomeration of asphaltenes. On the other hand, it provides polar sites for the reactions of asphaltenes. The acid-base reaction or coordination is expected to separate these acidic or alkaline asphaltenes.

Asphaltene can be used to synthesize macromolecule by thermal polycondensation. Only with high aromaticity, narrow MW distribution and proper amount of alkyl side chains and naphthenic structures, it is a promising plat-precursor for functional carbon materials, such as, spinning asphalt, impregnating pitch, high temperature binder.

Unlike polymer, coal and biomass as precursors of carbon materials, asphaltenes has the advantages of abundant raw materials, easy doping and compositing. The polymerization of asphaltenes in nonpolar solvents is related to its molecular properties, concentration, solvent parameters and polymerization temperature. Heteroatoms in asphaltenes endows that it is easily doped and modified, moreover, the presence of heteroatoms, such as N, S and O in resultant carbon materials are also easy to introduce chemical groups on its surface. But it is difficult to order structures during asphaltenes is polymerized and carbonized due to its complex mixture and wider MW distribution.

In summary, asphaltenes is abundant and accessible polycyclic aromatic hydrocarbons enriched sp^2 -hybridized carbon species, it is widely applied in chemical engineering and materials. Fine separation and fractional utilization of asphaltenes is the mainstream direction. We believe that more novel physicochemical properties

and applications of asphaltene will be discovered with the development of more universal and powerful analysis and separation ways.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jechem.2018.10.004.

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