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Review

Asphaltene Modeling, Emulsion, and Aggregation: A Review

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Abstract: Asphaltene is a component of crude oil that, if mishandled, may create substantial transportation and industrial concerns. It is a solid by nature, with a diverse set of molecular compositions. Furthermore, the oil industry has identified emulsion generation and clogging precipitate as key concerns. The emulsified water droplets in the process are just what give the raw oil its increased viscosity; hence, power is squandered to transport the oil around. The information has been separated into sections based on simulation, solubilization, agglomeration, precipitation, and evidence of model chemicals in the literature. We have included research that investigates the bulk rheology and interfacial rheology of asphaltene to describe its interfacial activity more clearly.

Keywords: Asphaltene; emulsion generation; Pickering emulsion

1. Introduction

Petroleum fumes called asphaltenes are insoluble in n-alkanes but soluble in aromatic compounds [1-2]; the most plentiful substance in crude oil is asphaltene [3-8]. Molecules called asphaltenes can become problematic during the production, transportation, and refinement of crude oil. Asphaltene is a solid phase that, under reservoir conditions, is homogenized and fixed in crude oil. Contrary to the non-polar crude oil as a whole, it is one of the few polar solvent parts of crude oil[1]. Inside the papers, the molar weights of asphaltene, the polyaromatic portion of crude oil, has been estimated to vary from 700 to 40,000 [9], 1000-50,000 g/mol [10], 3200 400 g/mol [11], and 300-1400 g/mol [12], to mention a few. Mullins et al.[13] estimated that the most recent and likely figure was somewhere around 750 g/mol. Solubility factors are a different method of defining asphaltenes.

Asphaltene can facilitate formation of emulsion in oil and water through formation a layer at the interface. This skin is formed as a result of asphaltene crowding at the contact, which is aided by self-association at the liquid interface and results in layered formation[14]. These films become highly bendable after several hours of ageing, as measured by interfacial rheological characteristics. As a result of the excessive floc and sediments created by asphaltene in lakes, canals, or transportation conduits, associated with production challenges arise. It reduces the efficacy of the oil supply by emulsifying the oil in water; hence, it is critical to investigate these difficulties and propose remedies.

The potential of asphaltene to emulsion water systems is a problem for the petroleum sector. Due to its sluggish travel to the interface and ability to reside there indefinitely, asphaltene has been dubbed a “surface-active agent”. The asphaltene network's

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structure at the junction can be either liquid or solid, regardless of the solvent aromaticity, ageing period, or beginning bulk concentration. Yield stress of the film formed on the droplet may be present during the transitional stages as a possible energy barrier to drop coalescence. The elastic dilatational modulus of asphaltenes increases with effort and time. In fact, before the liquid film approaches the depth at which it ruptures, a yield stress of just 102 Pa is sufficient to stop the drainage[15]. The interface yield stress is buildup and cross linking at the interface.

In 2010, liquid crystalline domain like other known colloids have been observed in hydrocarbon rich resources. The domain were seen to be biplex[16]. The comprise a thin shell surrounding a hydrocarbon core dispersed in a hydrocarbon liquid. These shell display thermotropic properties with varying phase transition temperatures. For examples When heated for the first time, the crystalline forming temps for 340/423 K for *Maya C5 asphaltenes*, 338/435 K for *Athabasca C5 asphaltenes*, 341/433 K for *Safaniya C7 asphaltenes*, and 371/431 K for *Cold Lake C5 asphaltenes*. There were also reports of liquid crystal subdomains at oil-water interfaces, where they affect the strength of emulsification [17-18]. In steam-assisted gravity drainage facilities and laboratory tests, it has been shown that liquid crystal domains may be transferred from the Athabasca phase to a phase that is rich in water[19]. Model rag layers connected with a naphthenic froth treatment procedure[20] for mined Athabasca have similarly shown liquid-crystal-like behaviour [21].

Another problem that petroleum business faces; is asphaltene precipitation and aggregation that during process of extraction of oil or moving it into refineries causes various flow issues. To investigate aggregation and precipitation; state of the art characterization tools have been employed including using simulations, model compounds (synthetic and refined ones) and microfluidics among others [22-24]. The asphaltene in the oil products will continue to be stable under equilibrium circumstances. Nevertheless, the asphaltene will start to migrate from the oil solution whenever there is any disruption to the oil, such as production or solvent infusion. In the process of precipitation, the asphaltene solid emerges from solutions to form observable asphaltene particles suspended in the oil. If the asphaltene is floating in the oil, there is still no danger. As soon as the precipitation doesn't really rise more, the asphaltene will be transportable along with the oil.

Through the use of several molecular modelling techniques, many conclusions about the shape of asphaltene agglomerates have been satisfactorily addressed [25]. Asphaltene particles were seen as subunits in these modelling studies, and the aggregating of asphaltene was compared to the polymerization reaction [26]. Early computer studies assumed that asphaltene was a monodisperse system and suggested that the primary cause of asphaltene aggregates was stacking of Polycyclic Aromatic Hydrocarbons (PAH) sheets. It is plausible to assume that asphaltene molecules' alkane chains act as a repellent between the sheets of PAH[27]. Steric interference has a significant influence due to the alkyl chain. While medium-length alkyl chains function as a barrier to aggregation,

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the longer chain contributes additional binding force via - and - interactions, promoting the process. The capacity to handle several large molecules is critical for these simulations. However, it is still thought that these simulations are too early to explain asphaltene behaviour in general. When dealing with macromolecules like these, molecular modelling has three major limitations. (i) The asphaltene molecule is not described by a single chemical arrangement. (ii) The simulation box measurements and time periods are insufficient for the dynamics of the asphaltene aggregate. (iii) The rigour of these inquiries is called into question.

Despite these obstacles, the value of these simulations rests in their ability to provide insight into the immediate phenomena, leading to a better understanding of the fundamental stages of the nano-accumulation mechanism. The chemical configurations and polarity of asphaltene molecules influence how they behave in the toluene-water system[28]. Undefined hydrophilic and hydrophobic regions can be found in asphaltene. They therefore don't resemble traditional surfactants, and the emulsion only depends on the ability of asphaltene to aggregate. However, the parallel stacking of aromatic sheets, or sheets interplay, is not the sole interaction found in the aggregates. Other interactions, such as the heteroatoms found in the asphaltene core, have the capacity to alter the polarity of the molecule and oversee the development of hydrogen-bonded networks. In the case of asphaltene-water interaction, the crucial interaction is hydrogen bonding caused by functional groups[29]. The charged terminal model compounds show that this arrangement of hydrogen bonds dominates overstacking, but the neutral asphaltene model compounds do not. It appears that a charged moiety, or perhaps a zwitterion framework, is required for the induction of interfacial activity in molecules. This impression suggests that asphaltene aggregation behaves like diffusion. Despite their complexity, simulations are nevertheless vital in the creation of chemicals such as asphaltene, thus a section of this page is dedicated to them.

When researching the issues that asphaltene poses for the oil business, we look at numerous approaches that are regarded to be particularly sophisticated for analysing the behaviour of asphaltenes, such as microfluidic chips, rheology, and simulations. Microfluidics, for example, overcomes classic procedure difficulties such as long turnaround times, a lack of automation, and poor reproducibility. Because typical extraction procedures usually need vast volumes of solvents, big glass containers, and other apparatus, this approach has attracted a lot of attention in the literature. Microfluidics also provides a more efficient approach for testing and studying emulsion stability and transport.

In summary, this article evaluated the behaviour of asphaltene in terms of its role in emulsification, deposition, and inclusion in polymers; therefore, the current publication is a good reference for getting an illustrated overview on asphaltene-related subjects. Even though there are more studies in the literature, only a few have been highlighted here to emphasise the importance of asphaltene research. Asphaltene's propensity to affect reservoir wettability or to cause refinery catalyst deactivation due to adsorption at active sites are only two instances of uncontrolled regions of asphaltene that readers are encouraged to study in the references[30-32].As a result, effective mitigation strategies may be found, such as a surfactant-coating substance that is acceptable for surfaces exposed to asphaltene or operating circumstances.

2. Asphaltene

2.1 Aggregation and precipitation

Asphaltenes are a polycrystalline component found in crude oil that have a wide range of molecular properties and sizes. One of the issues in the oil business is the precipitation of asphaltene and asphalt during the production, transportation, and processing of crude oil. These precipitations' quantity and properties vary depending on the kind of solvent used, the oil-solvent ratio, duration, pressure, temperature, etc[33]. Along with modelling, the next sections examined some of the challenges produced by asphalt aggregation and the attempts done to solve them. We put asphaltene precipitation and aggregation in the spotlight here. Asphaltene deposition is a chronic problem in crude oil extraction. It might cause pore throat blockage, reducing oil recovery dramatically. Understanding the microscopic process is critical for successful crude oil extraction.

Several factors may have an influence on the stability of the asphaltene in the crude oil [34]. These variables may be divided into experimental parameters, which are supplied throughout reservoirs extraction, and reservoirs variables, which are variables that are native to the reservoir but change once production or fluid injection begins. The physics of the reservoir, which include pressure and temperature, as well as the characteristics of the oil, which include solutions gas, oil viscosity, and the categorization of the oil based on its API gravity, make up the reservoir conditions. In most cases, the reservoir's pressure and temperature remain constant and are therefore uncontrolled. The oil's characteristics will be affected by the manufacturing process, the liquids injected into the reservoir, and pressure fluctuations as the hydrocarbon is mobilised. A solvent is any material that may be dissolved in crude oil under different conditions depending on the solvent and reservoir parameters. Steamed, detergent, CO2, nitrogen, methane, and a variety of other solvents used to alter the properties of crude oil can all be poured into the reservoir. Once the solvent begins to interact with the asphaltene as a result of a change in the equilibrium conditions under which it was originally solubilized, the asphaltene may no longer be stable in the crude oil.

Numerous interfacial activities and occurrences in oil production and wastewater treatment depend on the interactions between asphaltene surfaces in aqueous systems[35]. To use a surface forces apparatus (SFA) and atomic force microscopy, the interaction processes among asphaltene surfaces in aqueous solutions were examined in this work (AFM) [35]. SFA showed long-range repulsion between two asphaltene at 1mM NaCl at pH 8.5 and the force range drop with increase in acidity. Calcium ion addition significantly reduced the attraction between asphatleen surfaces. The measured repulsion did not match the Derjaguin, Landau, Verwey, and Overbeek (DLVO) hypothesis as it was originally proposed. Due to the hydrophobicity of the surface, the attraction and interlocking of asphalten chains or agglomerates, or calcium ion-induced bridging, adhesion was seen when separating two surfaces under all solution conditions. The calcium ion, salinity, and acidity all had an impact on the adhesion strength. These results are remarkably like other nanofillers[36-42]. Results are depicted schematically in **Figure 1** displaying how AFM came into measuring the interaction between surface of asphaltene. Other notable studies employing AFM or similar device to measure adhesion with regards to asphaltene can be found in refs[43-45].

The electrokinetic effect, as its name implies, describes movements of a substance caused by a change in charges. Because asphaltene frequently contains a charged, the differential pressure between the deposit and the wellbore causes a dip during plant operation. This depletion and the asphaltene charges are primarily responsible for the electrokinetic action, which causes asphaltene instabilities in crude oil and, as a result, asphaltene precipitation. Solvent injection into crude oil is commonly used to increase the oil's mobility while decreasing its fluidity, especially in heavy crudes. The stability of asphaltene may be affected by the solvent's contact with the oil. Asphaltene stability may be gauged using an index called the solvent-to-bitumen ratio. Asphaltene will eventually start to precipitate at a certain solvent-to-bitumen ratio[28]. This point will vary greatly depending on the kind of solvent [46-47]. In ref, first direct quantification of asphaltene charge in air using electrostatic force microscopy (EFM) as also applied to other nanofiller thus this report is the first report on direct meausing native charge of asphaltene.

Figure 1. Schematic of procedure in which colloidal behavior of asphaltene came under scrutiny. Adapted with permission from ref. [35]

Electrostatic Force Microscopy (EFM)[48-49] to determine the density of asphaltene native charge to approximately 43.7 nC/cm2 . Asphaltene charge in water with suspension was strongly influenced by pH and salt content; as a result, ionisation of the surface group resulted in their charging. Similar tests in a solvent (nonpolar media like toluene and heptane, for example) can add a solvent-dependent value, making it impossible to accurately quantify this native charge and comprehend the precise function of the solvent[50]. There are further studies that have quantified the charge of asphaltene, with their focus being quantification is the measurement of asphaltene charge in aqueous medium or water–oil interfaces, and the results indicate that asphaltene charge will substantially fluctuate as a function of buffer pH (from very extremely positive to very highly negative)[51]. Another study[52] looked at the electrokinetic characteristics of asphaltene particle. To measure the electric charge of the particles, a DC electric field was applied. Particles in n-heptane and its combination with toluene (heptol) had positive charges but no movement, indicating that toluene had a neutral charge. Although it is natural to expect larger asphaltene aggregates to have greater electric charges, the results showed that they are mainly governed by gravity rather than electrostatic force and that "aggregation" decreases the charge density of asphaltene particles. Another group conducted a similar experiment with crude oil and discovered that the asphaltene charge was negative[53]. Surprisingly, another group of researchers[54] discovered that the asphaltene molecule has a natural positive charge, but that at high current density circumstances, an induced negative charge may be seen. Deposition onto the cathode, anode, or both was seen depending on the concentration.

Figure 2a-b shows two asphaltene molecular structure “continental-type” and “archipelago-type” structure. The archipelago model, which is less popular, has several aromatic cores that are alkyl-bridged with different polar functions. The traditional island model represents asphaltenes as single core aromatic molecules with peripheral alkyl side chains. Authors findings show that island and archipelago themes coexist in petroleum asphaltenes, and that asphaltene filtration is necessary in order to identify and identify archipelago individuals by mass spectrometry, in contrast to readily available island motifs[55]. Since asphaltenes fall within the solubility class, the extraction technique has a significant impact on their molecular makeup[56]. The visual appearance of asphaltenes extracted using the two most used solvents, pentane, and heptane. On the figure, these asphaltenes have diverse textures and even colours. Additionally, the asphaltenes recovered using pentane (C5) contain compounds soluble in heptane, like resins. Similar to how two distinct asphaltene were evaluated in ref[57], morphology and rheology were both used to examine the apparatus. The appearance of the first sample is foamy whereas the second sample is grainy and resplendent. (**See Figure 2c-d**). Foamy appearance is an indication of material tendency to form structured porous[57]. The agglomerated structure associated with sample shown in **Figure 2c** as opposed to sample shown in **Figure 2d** that has spanned the whole TEM images. The viscosity graph also reflects the connection between structure and viscosity of these samples as structure sample shows more dramatic increase in viscosity as concentration of asphaltene increases **(See Figure 2e-f)**.

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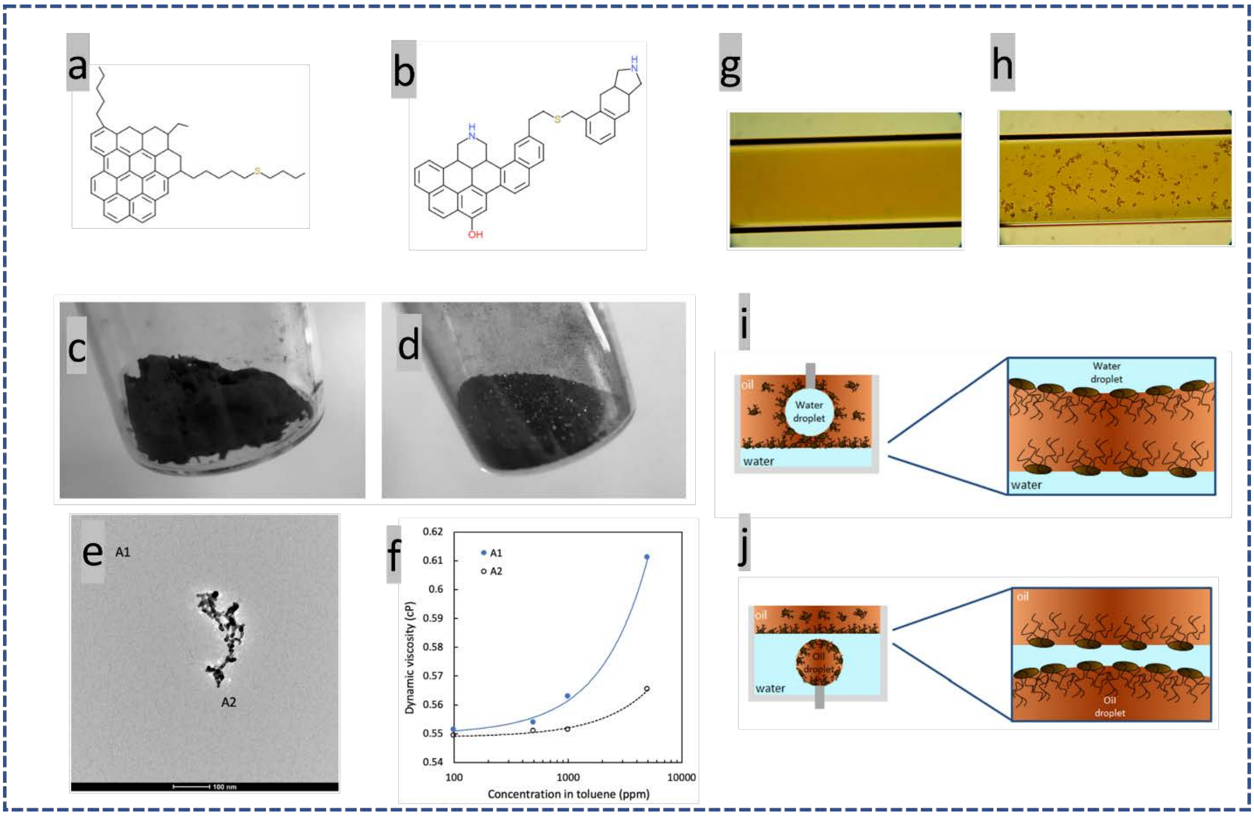

Figure 2. (a) Asphaltene molecular structure "continental-type" adapted with permission from ref. [58] **(b)** Asphaltene molecular structure "archipelago-type" adapted with permission from ref.[59] . **(c-d)** Simple photographs of asphaltene investigated in ref thus displaying appearance difference of the two samples. Adapted with permission from ref[57]. **(e)** A1 and A2 asphaltenes from Gibbs oil are shown in a TEM micrograph, and **(f)** their dynamic viscosity varies with toluene concentration With permission, modified from ref [57]. **(g-h)** Mixtures of oil A and n-C15 aged in microtubes at 50 °C with mixing ratio of 47:53 (stable) and 40:60 (unstable) (tubes are 200 μm across). Adapted with permission from ref [60]. **(i-j)** For each configuration, the interaction of asphaltene molecules with the oil/water contact. The employed ratio is 1:1.5 o/w, and volumes of water and oil solutions are drawn out of scale. Adapted with permission from ref[61].

To describe and simulate the behaviour of the asphaltene phase, methods have been devised. The Oliensis spot test is the oldest illustration of experimental onset characterisation[62]. In order to determine asphaltene instability in response to changes in the oil solubility parameter, the ASIST method[63] conducts microscopic observations. Data for a variety of n-alkanes can be utilised either directly or as inputs for characterisation of asphaltene in simulations to forecast onsets that would happen as a result of the presence of light ends, lift gases, etc[64]. An application of this method to a deep-water region in the Gulf of Mexico was proven by Montesi et al. [65]. To put asphaltene deposition under microscope, the oil and nonsolvent were combined, and the resulting liquid were then put into a glass capillary tube as shown **Figure 2(g-h)** [60]. Micrographs were acquired via the glass capillary as a function of time. Examples of both clearly stable and unstable mixtures are shown in **Figure 2(g-h)** [60]. Clearly as stated earlier solvent ratio here 47:53 vs 40:60 plays a key role in pushing particles out of their homogenized state.

It is thought that the configuration of asphaltene particles at the oil/water contact and the consequent interface-interface interactions, as illustrated in **Figure 2(i-j)**, are responsible for this departure from the behaviour of water droplets. The aliphatic component of asphaltene molecules penetrates the oil layer when water droplets are present, which causes a significant hydrophobic repulsion of the tails.[66] The literature reports the measurement of strong repulsive forces between asphaltene tails using a surface force instrument[67]. When it comes to droplets, the aromatic part of the asphaltenes is exposed to a water layer that is draining, creating a desirable interaction. The particle contact angle, which replaces the interface asymmetry in particle-laden interfaces[68], has a similar effect on coalescence time.

Aggregates are also susceptible to shear during shear[69]. If yield stress is not passed the aggregates stay unbroken; when shear fractures the structures at higher rates of shear; the differences found between different molecular structures of asphaltene vanishes as molecules are now separated. Similarly, to examine flow-precipitation joint action, asphaltene precipitation during multiphase flow with high resolution and in 3-D was examined, authors created an in situ micro-CT imaging capability. To cause the precipitation of asphaltene in a sample of sandstone rock, pure heptane and crude oil were concurrently injected [70]. The competitive adsorption of n-heptane onto quartz surfaces was investigated by the another group of authors[71]; report revealed that the quartz substrates' surface hydroxyl groups had a significant influence on the adsorption of asphaltene on the quartz surfaces, significantly increasing the flow of oil via SiO_2 nanopores[71].

At low Reynolds number asphaltene is troublesome for oil industry practices [72-74]. For instance, in ref [75], studies were conducted to correlate flow rate; precipitation as a function of solvent and concentration however they fail to forecast precipitation at industrial scale. For instance, in ref [75], the deposition development in the lab scale was monotonic and homogeneous, indicating that erosion and entrainment were absent. When this new data was scaled up to the field size, it revealed that waterflooding would result in a loss of more than half of the well production [76]. It is critical to precisely forecast the rate of deposition to help minimize and regulate this issue. The forecasting of asphaltene deposit in pipes has been the subject of a few research that have been reported in the literature. The creation of models to examine asphaltene deposition is described in the work of refs[77-79]. However, an examination of the body of research finds that there aren't any qualitative or quantitative comparisons of asphaltene deposition profiles predicted with deposition profiles at the lab and field scales. One way of remediation of these issues is to pay attention to kinetic of depiction; in fact, kinetic of deposition[73] can be modeled and investigated using variables that in large scale are hard to explore experimentally. At the flow lines, nanoscale behavior of asphaltene aggregates and cluster can come under scrutiny[80]. According to experts, these endeavour can pay the way for more accurate modeling approaches [80].

Models[77, 81-82] or simulations[83] have been attempted to predict aggregation and subsequent issues that asphaltene causes in oil extraction schemes; in one instance, researcher made a model[84-85] to correlate operational parameters and aggregation\precipitation of asphaltene. To provide an overview on system under which asphaltene bulk or interfacial behavior has been studied media can be summarized in broad terms into toluene\water[86], toluene\decane\water[23, 87], Crude oil\toluene\water [88], Crude oil[89], Crude oil and *p*-xylene[90], Decane\water[91], Crude oil[92-94], *p*-xylene and toluene[87], Ester oil\water[95] and xylene\water[96]; these system thus attempt to provide a situation similar to oil production.

Similarly, regarding the characterisation of the precipitated substance, the kinetics of asphaltene precipitation is investigated in one interesting report[97]. The mixing of various crude oil constituents results in aggregates with a varied composition that alter over time and is dependent on the solvent power of the heptane/oil mixture. The precipitate was discovered to include a large quantity of maltenes, whose relative composition changes with time. As time passed, the typical properties of the asphaltenes present in the precipitate changed. The distributions of these molecules altered when additional heptane molecules precipitated, lowering its average solubility parameter. A novel model that captures the intricate aggregation behaviour involved in precipitation was created based on the observations[97]. In one experiment, n-C5, n-C6, n-C7, n-C9, and n-C12 were each added to the oil individually, and the amount of precipitated solid was noted to increase with the solvent ratio (g solvent/g oil). The results indicated that n-C5 precipitated more solidly at all solvent ratios[98].

2.2 Emulsification

Beside precipitation and aggregation problem that asphaltene pose in petroleum industry, emulsification is another major issue. In fact, in oil and gas production, issues with flow assurance linked to asphaltene are already common. Water/brine-in-oil emulsion entrapment in porous media is characterised by hydrodynamic bridging and adhesion of emulsion droplets[99]. The research may result in improved processes for demulsifying and separating entrained water from generated crude oils[100]. Emulsions formed by salty water and crude oil are regularly encountered during in the manufacture and refining of petroleum liquids. To efficiently break and separate oil/water emulsions, it is critical to grasp the underlying processes that drive their formation and stability [57]. To quantify the emulsifying power of asphaltene, one study found that as the concentration of asphaltene increased to 4 kg/m3, the diameter of droplets in a helptol system in water drastically decreased once they reached an 8-micrometre diameter. Subsequent increases in asphaltene concentration had no impact on droplet sizes[101].

It is believed that these layers are what give asphaltene its "Pickering emulsion" type stability [102]. Pickering emulsions are O/W or W/O emulsions that contain solid particles to stabilise them[103]. It was given this name in honour of S.U. Pickering [104], who was the first to notice how small solid particles might stabilise such emulsions. Along with factors including nanoparticle volume fraction, salinity, and water phase pH, particle wettability is a crucial factor in determining the kind and durability of a Pickering emulsion[105] . O/W emulsions are more likely to be stabilised by water-wet particles than W/O emulsions are by oil-wet particles[106]. Elastic modulus increases significantly when the interfacial area expands or surfactants like asphaltene move across the interface. As a result, in an emulsion [107], coalescence is less likely to happen when two droplets contact. The Gibbs- Marangoni [108-109]is also efficient, and asphaltene migrates to less populous areas. Numerous attempts have been undertaken to assess the interfacial films' compressibility and elastic properties using Langmuir film balancing methods[110-111] using oscillatory drop measurements that may record asphaltene's progressive migration. Rheology, as a characterization tool, can investigate oil-water interplay; in one report[112], authors demonstrated that the asphaltene film form on the surface of water and oil can be liquid or solid depending on concentration, ageing, and the molecular structure of asphaltene; these findings were consistent with the results of ref[113].

Microfluidic chips can be used to accomplish this goal since they are tiny and allow for controlled flow under a microscope while studying the influence of the demulsifier during the flow of the emulsion, which is often necessary. Researchers can use micro-channels to investigate the effect of modifying Reynolds number, temperature, and other ingredients on emulsification behaviour. According to one report[24], demulsifier was added to bitumen prior to development or the water droplet developed and introduced demulsifier to the oil phase. The kind and concentration of demulsifier influenced coalescence; one addition increased coalescence more than the others. Demulsifiers guarantee that the surface is free of surfactants and pickering agent emulsifiers such as asphaltene. The author properly determined that demulsification owing to the action of bringing out chemicals from the interface is a diffusion restricted process based on data analysis.

In ref [112], droplet coalescence was discovered to be totally controlled by the system's viscoelasticity, since more solid-like behaviour encourages separation of droplets rather than merging. Yield stress at the interface is a non-Newtonian time-dependent characteristic that prevents droplets from perturbing the interface. Shear and dilatational rheology similarly demonstrated divergence behaviour, with shear rheology of interface showing a progressive transition in viscoelasticity towards solid-like behaviour, whilst dilatational rheology remained elastic dominating from the start. As explain earlier one way to neutralize this is to use demulsifiers[114-115] that can turn droplet interface from viscoelastic to viscose again. Demuslfication include variety of methods that has been enumerated in our previous publication[22].

Although spontaneous emulsion formation is helpful and desirable in many sectors, it causes various issues during oil extraction, such as corrosion of equipment and an unexpected increase in viscosity[116-118]. Emulsion development is almost inevitable during the extraction of crude oil. For instance, flow disturbances such submersible pumps and choke valves can easily emulsify a certain amount of created and crude water. In conclusion, as asphaltene interfacial behaviour has the potential to cause issues for the petroleum sector, it is crucial to research it is using rheology.

Asphaltenes, other nanoparticles, for instance, can all act as a “pickering” emulsion agent [119]. Although heating and the addition of flocculants can help with low viscosity and density conditions, they do not always produce efficient coalescence. Asphaltene mostly adsorbs as a monolayer of joined molecules at the contact, with thicknesses varying from 0.002-0.009 µm [120]. Over time, the asphaltene seems to restructure and form a solid film. These films have been seen to tumble down when interface is under stress [121-122]. The material that must be added to push asphaltene from the interface back to the solution may be determined by investigation like the one conducted before utilising AFM.

To address how to depopulate interface from asphaltene, a serrated edge biconical bob interfacial shear stress rheometer has recently been used to study asphaltenic coatings at model oil/water interfaces[117]. The elastic storage (G′) and viscous loss (G″) moduli were determined by the authors by tracking the film strength using frequency sweeps at 1-hour intervals. Due to an abundant supply of asphaltene, the interfacial shear elasticity (G′) in systems containing just asphaltene grew monotonically over hours to days. The molecular rearrangement of asphaltenes at the interface, which results in a cross-linked network, caused the elastic modulus to rise for an additional 8 hours after the asphaltene solution was replaced with new solvent. A resin solution was used in lieu of the asphaltene solution, and this caused an immediate decrease in elasticity followed by a gradual rise. This is most likely because asphaltenes were solvated and were being removed or replaced at the time.

The resilience of the water-in-crude emulsified is governed primarily by the solubilization of asphaltenes in oil, which is influenced by several factors including asphaltene concentration, resin to asphaltene ratio, aromaticity of the oil form of media, and the presence of compounds (such as -COOH). McLean and Kilpatrick [119, 123], researched this relationship. Those who later investigated the impact of asphaltene aggregation on emulsification using a model oil made of heptane and toluene (Heptol), coming to the conclusion that asphaltenes are most surface active[86] when they are present as fine dispersions (i.e., 1 micrometer) close to the point of precipitation [119, 123].

The literature on interfacial dilatational rheology of asphaltene is rich[23, 91, 96, 117, 124-127]. According to the literature [128], the dilatational modulus in such films is dependent on time and concentration of filler; this is an indication of delayed diffusion of asphaltene to the interface possibly due to interaction with neighboring asphaltenes during migration. When reaching to the interface second crowding can happen due to arrival of molecules to the interface this might further kinetically freeze the accumulation of asphaltene at the interface.

Rheology shows clearly that concentration of asphaltene in range of 0.2-0.5wt% is needed to create a strong interface [117, 126]. Rheology also shows concentration and time affect one another[113]; and rheological finger print of asphaltene at the interface is reminiscent of soft glassy materials[39-40, 129]. Interface stiffness gradually happened in one reference[112]; the storage modulus for toluene-heptane equal ratio mixture was lower for the sample that was devoid of heptane; clearly deposition of asphaltene and how out of balance it is in the phase affects its emulsification power. Authors also predict based on their observation that viscose character of interface is a stronger sign of asphaltene build up; however, network formation is more easily seen with elastic domination of viscoelasticity over time.

In a system where asphaltene migrates to the interface over time, the elastic modulus increases. For example, in one report, the elastic modulus significantly increased for 16 hours [120]. According to the study presented here, asphaltene displays complex time-dependent interactions at the interface in its role as a surface activating agent. Results further show that asphaltenes form monolayers on the interface, even at concentrations as high as 40 kg/m3, and that massive aggregates with molar masses more than 10,000 g/mol do not seem to be absorbed by the contact. The thickness of the monolayer ranged from 2 to 9 nm. While protein are polymers that are often coiled into spherical forms, asphaltenes, which are tiny molecules, have striking parallels to proteins in their behaviour at liquid interfaces[131]. In milk, proteins like casein clump to form micelles that are misnomerly referred to as such and have a radius of about 100 nm [132]. The well-defined size in asphaltene big conglomerates may result from a similar arrangement, with more polar asphaltene nanoaggregates in the middle and the less polar ones at the edges. Electrostatic repulsion is a different possibility: The overall charge rises and an ideal size is discovered when charged things gather [133]. The charges of asphaltene in oil, meanwhile, is relatively low (one charged molecule in 10^5 in toluene), and the average charge of the cluster is considerably lower than one. Thus, the charging pathway is implausible. The validity of the casein type of cluster for asphaltenes might be verified by molecular simulations (or not).

In one report, authors reported that films stabilized by asphaltene were thicker (40-90nm) than those stabilized with maltenes (~ 10nm)[15] as shown in **Figure 3**. Such a large range in the film's characteristics suggests several stabilising strategies for thin organic solvent films. Thin organic solvent films incorporating asphaltenes showed apparent ageing effects, such as a slow rise in film thickness, stiffness at the oil/water interface, and the production of sub-micrometer-sized aggregates. Films with bitumen and maltenes in toluene showed no signs of ageing. The unique capacity of asphaltenes to self-assemble and create 3D networks in the film is related to the enhanced stability and decreased drainage dynamics of thin liquid films containing asphaltene. Stable films often have lengths that are far longer than the smallest asphaltene molecules, nanoaggregates, or even clusters of nanoaggregates that have been described in the literature. The development of such a 3D structure changes the liquid film's rheological characteristics so that they are non-Newtonian increasing yield stress (gel like). Thin asphaltenes in toluene liquid films appear to drain more slowly because of the formation of such network structures. Before the film reaches the critical thickness at which film rupture occurs, the yield stress of a liquid film as tiny as 102 Pa is enough to stop the drainage.

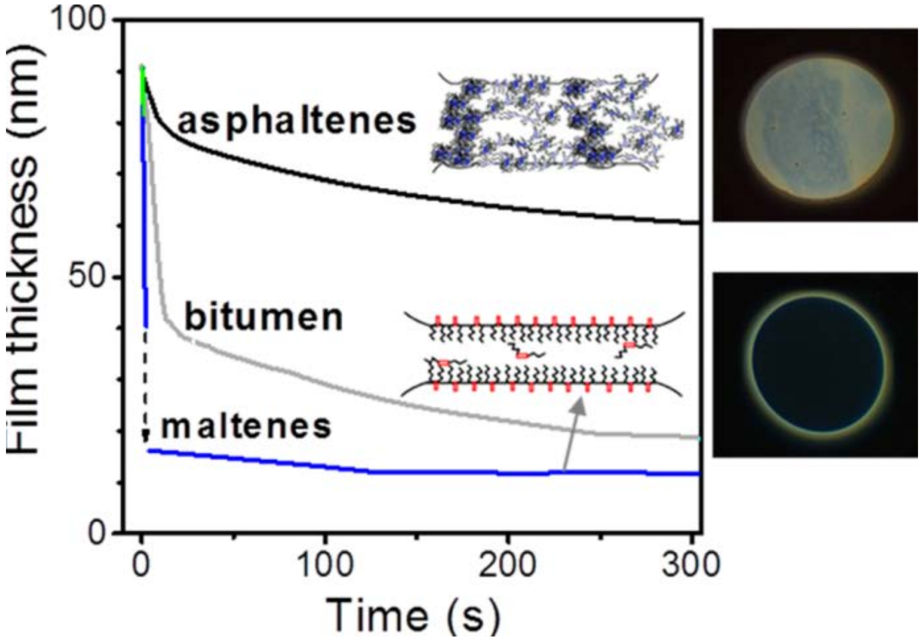

Figure 3. The films stabilized by asphaltenes are much thicker (40−90 nm) than those stabilized by maltenes (~10 nm). Adapted with permission from ref[15].

Prior research on the effects of solvent type, time, and continuous elemental composition on interfacial stiffness as well as certain simulations of interfacial rheology have been conducted[134-135]. For instance, a recent study by Freer and Radke[121] examined the adsorption of asphaltene and toluene at the water-toluene interface. Their findings imply that the Lucassen-van den Tempel [128]or Maxwell viscoelastic modulus[136] may be used to accurately describe a toluene-water contact with asphaltene concentrations less than 0.005 wt percent. The importance of asphaltene's permanent sorption effect (Rigid film) [137] is shown by the need for a mechanical component in their model. Asphaltene sorption at oil-water interfaces is permanent at bulk concentrations below and over the threshold nanoaggregate concentration at even brief times when the interfacial layers have not yet formed. You may find other rheological modelling attempts on the topic of asphaltene in references [23, 90, 128, 136].

2.4 Asphaltene with polymers

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Polymers are equally impressive class that can greatly benefit from inclusion of asphaltene. Similar to other reinforcement agent asphaltene can be employed as a filler [38, 138-139] inside polymers. There are footprints of application of asphaltene in major plastics such as polystyrene (PS), polypropylene (PP), and low-density polyethylene (LDPE) [140-141]. In these matrices mechanical and viscoelastic properties greatly improve with addition of asphaltene[38, 142]. Asphaltene improves mechanical properties of Bitumen as well [143].

Polymers can also attach to asphaltene aggregates and form complexes in the bulk oil phase, according to small-angle x-ray scattering[124]. As a result, the inclusion of polymer was beneficial in preventing the formation of additional emulsification sites. As state earlier deposition of asphaltene should be avoided one way of doing that is to add polymer to stop precipitation. At clean-up doses of 1,000 to 10,000 ppm polymer's capacity to occupy the active stacking sites of asphaltenes was found to be what made it the most efficient[144]. A series of organometallic polymers that have been demonstrated to be efficient as bactericidal corrosion inhibitors and asphaltene dispersants were examined by Hernández-Altamirano et al. [145]. The best chemical for preventing asphaltene aggregation was a butyl substituted bis-di-organotin (IV) compound, at 0.1 g/L of dispersant concentration in liquid heptane, asphaltene aggregation was reduced by about 30%. The n-butyl chains were assumed, as in previous investigations, to govern strengthening the steric repulsion between the asphaltene aggregates [145-146].

Asphaltene deposition has been successfully avoided by polymer with both aromatic parts and extremely polar functional units like amide or carbonyl [147-148]. Employing crude oil in heptol solution, Ghaffer et al. evaluated a series of propoxylated dodecyl phenol formaldehyde polymers with three distinct molecular weights [147-148]. Whereas the light absorbance was being measured, the oil mixtures in toluene were gently adjusted using heptane to cause precipitate. The findings demonstrated that as polymer molecular weight grew, asphaltene precipitation started sooner. Propoxy (C_3H_7O) side and end chains allowed for more contact with asphaltenes, leading to overall higher absorbance and enhanced efficiency compared with the non poly (dodecyl phenol formaldehyde) component. Similar research examined several dendronized polyamidoamine (PAMAM) polymers utilising the very same light absorbance test, DLS, and rheological tests as potential asphaltene solvents [147]. The findings indicated that the third-generation dendrimer of the PAMAM polymer was where the polymer performed at its best, most likely as a result of the dendrimer's significant level of branched, which causes inhibition among aggregates. Overall, the PAMAM polymers outperformed the propoxylated polymers in terms of their ability to disperse. As a method of reducing the viscosity of heavy oil, Castro et al. employed a terpolymer of styrene, n-butylacrylate, and vinyl acetate. Results showed that greater styrene content in the terpolymer improved flowability as a result of the positive aromatic contacts with the asphaltenes [148].

This section examined the relationship between asphaltene and polymers. Asphaltene, when used as a filler, can strengthen polymers and, because of its conductivity, can make polymer composites conductive as well. In addition, it has been demonstrated through experiments, some of which are discussed here, that asphaltene deposition can be prevented if specific polymers are added to crude oil prior to solvent or gas injection.

2.3 Compounds that mimic

The model compound approach involves choosing and researching model compounds that have been synthesised and have a structure comparable to asphaltene, as well as possessing characteristics that are typical of genuine asphaltene molecules. There are two approaches to take (i) The traditional method involves breaking down the full substance of asphaltene into several sub-fractions and examining each sub-fraction separately to determine which sub-fraction is mostly to blame for undesirable qualities [149-150]. (ii) using model molecules with established chemical structures and physicochemical characteristics to mimic native asphaltene is the model compound approach[66].

The first method allows the results of the studies to be extrapolated to the tested asphaltenes with reasonable estimations while still capturing the intricacy of the unknown structures of asphaltenes to some extent[66, 127, 151]. The main criticism of this approach however is that asphaltene's molecular structure is greatly influenced by the method of extraction and the kind of liquid used. So, because architecture and design of molecules are not clear and transparent using this approach, it has been difficult for instance to examine the aggregation of asphaltene and to propose models of their process in various solvents. Due to this, researchers take the second method, employing model compounds, and, in addition to labs, have investigated the characteristics and chemical connections between asphaltenes using computational and simulation techniques[25, 152].

In ref[153-154], using microfluidic chips impact of emulsification of asphaltene was examined using model molecules of VO-79 and coronene; VO-79 was shown to be a greater emulsion stabiliser than the latter. Even while the zeta potential VO-79, coronene, and ordinary asphaltene from crude oil were all the same, the rate of emulsion droplet coalescence varied greatly. This study shed light on the challenge of simulating asphaltene transport dynamics with imitating molecules.

By controlling volatiles, aromatization, and carbonation of asphaltene aggregated compounds, refineries and blending terminals may tune viscous flow and rheology[155]. Another notable candidate for studying asphaltene its sorption and rheological fingerprint is an acidic polyaromatic compound (C5PeC11)[127, 156-157]. Other similar compounds able to be used instead of asphaltene can be found in our previous publications [22]. Some of the compounds used in the industry to mimic asphaltene behavior are shown in **Figure 4** [156]. These molecular compounds have been shown to precipitate after addition of n-alkanes and therefore meet the solubility conditions of asphaltenes[156].

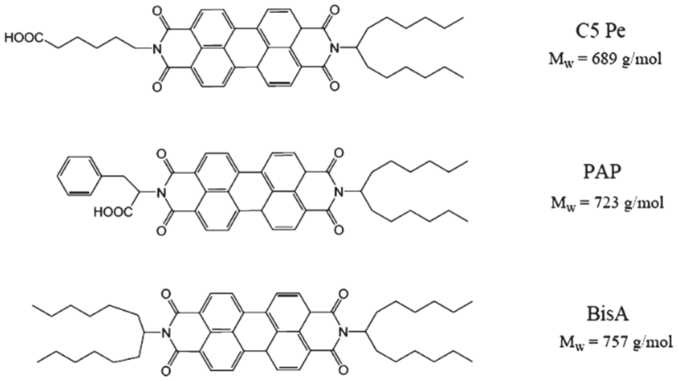

Figure 4. Three molecules were created as model compounds for studying asphaltene, and their structures, acronyms, and molecular weights are listed below. The correct terminology is N-(1-hexylheptyl)-N0 -(5-carboxylicpentyl) perylene-3,4,9,10-tetracarboxylic bisimide, using C5 Pe as an example. Adapted with permission from ref[156].

C5Pe, a linear molecule model with high emulsion stability over long period of 5 hours (shape and size of the molecule is shown in **Figure 4**).

The average molecular size of C5Pe was determined by Adsorption confirmed the NMR measurement and suggested a configuration tilted with the aromatic core at interfaces with relation to the interface's perpendicular plane. the current-NMR is used in this work to provide an unique method for determining the droplet sizes of such densely packed model emulsions. benefits over the conventional microscopy technique. The examination of the data is made more difficult by the development of free water. The studies given from an industrial perspective demonstrate the presence of acidic or comparable hydrogen-bonding groups. An asphaltene structure is significantly enhancing its ability to stabilising crude oil and water emulsions, and one such subfraction described by authors as a "surface-active

2.4 Simulation approach

Computer simulation is among the most effective techniques for understanding complex systems in industrial engineering and the industrial sector. Simulated data may also be used to assess process operations, which are very complex systems that are constantly affected by uncertainty. The use of simulation in process activities has a variety of advantages, including the ability to predict clogs, determine production and enhance it, manage resources more effectively, optimise stochastic responses to unforeseen conditions, and react to random and vibrant features in the system's operation. There are 10^5–10^6 distinct kinds of organic molecules in crude oil, each with a unique molecular weight and composition[158]. The molecular class of asphaltenes contains the most intricate, polar, and substantial of these molecules. These compounds include heteroatom distribution, saturated alkyl chains, and polyaromatic units.

Because of asphaltene's extraordinarily complicated structural makeup, which was previously discussed, no universal model formula has been created to predict asphaltene behaviour in crude oil. Since the formulas in this section were created using a particular series of experiments, they cannot be used with certainty for all types of crude oils and asphaltene geometries. These equations that used fitting or scaling variables to try to generalise the generated model are the ones that come closest to the general model. The Hildebrand and Flory-Huggins models are two of the most well-known equations that have been employed as a benchmark by several researchers throughout the years [159]. The soluble factor, which serves as a gauge of suitability, was defined by the Hildebrand model and is its most famous feature. Asphaltene is often stable if the high solubility of a solution exceeds the asphaltene offset pressure. The asphaltene will start to dissolve as soon as the high solubility drops below the offset pressure. Obtaining the chemical reactivity is mostly done using the Flory-Huggins model[159]. This model's fundamental flaw is that it wouldn't include an interactions coefficient; as a result, its accuracy is only as accurate as the equation of state that was used to get the solubility parameter[159].

In one report, side alkly chains are placed face to face in the simulation study, demonstrating that side chains prevent rod clusters from aggregating[160]. The results were consistent with our prior findings that asphaltene's characteristics affect how it deposits, aggregates, and precipitates. Tetralin was also employed to create smaller aggregates because of how its aromatic ring interacted with asphaltene's aromatic cores to prevent aggregation. Simulation provides insight on how to lower aggregate size and how leverage oil-water mixture to stabilize or destabilise asphaltene. Additionally, modelling provided insights untenable or costly with experiment as those longer chains decreased aggregation as predicted. It is well known that the degree to which the aromatic core of asphaltene is hydrogenated determines how well it aggregates. To deepen the knowledge of aggregation of asphaltene authros in ref [161], reported that asphaltenes' radial distributions and dimer contact energies calculations shows that the aggregation propensity is governed by the size, shape, and steric hindrance of the cyclic ring sheet. Contrary to the theory of "like attracts like," each form of asphaltene preferred to aggregate with its own kind above the other sorts. This simulation-based analysis revealed a lot about how asphaltenes function; it will be fascinating to watch if these findings are confirmed in further research by the development of compounds that may replace asphaltene.

Regarding reduction in aggregate size, surfactants can also reduce asphaltene aggregate sizes; different synergistic interactions between surfactants and asphaltene molecules can reduce interfacial tension[162]. The breakdown of the asphaltene molecular aggregation structure occurs for the surfactants sodium dodecylbenzene sulfonate (SDBS) and octylphenol polyoxyethylene ether (OP-10) as the interfacial concentration increases. Dodecyltrimethylammonium bromide (DTAB), however, demonstrated the opposite result. Asphaltene aggregation rose in response to an increase in surfactant interfacial concentration[22, 40, 129]. The action of surfactant and asphaltene is not favourable to further reducing the interfacial tension as the concentration of surfactant at the interface rises[162]. In tight light oil reservoirs, CO2 injection frequently occurs in conjunction with asphaltene precipitation. This study looked at how various reservoir types affected porosity, permeability, and wettability. Surfactant can be introduced into a reservoir to lower the asphaltene-induced wetability reversal index. Type I reservoirs have the greatest and lowest wettability reversal indices, respectively. To lessen the wettability reversal index brought on by asphaltene precipitation, the surfactant can be introduced into the reservoir[163]. Therefore, here reduction in aggregation size and its effect on well bore came under scrutiny.

Simulation can also give insight about structure-property relationship inside the solution\matrix that asphaltene. In ref [69], a dissipative particle dynamics (DPD) simulation was used to assess the impact of various concentrations and solvents on asphaltene characteristics. The structural analysis supported the parallel stacking between asphaltene layers as being predominant. The time-dependent development of aggregates showed the aggregate count decreased over time; so, aggregation was found to be time dependent behavior. Investigations into viscosity revealed that while the solvent-solvent interaction is initially crucial, its power gradually diminishes when entropy takes control due to a higher mass fraction. Molecular dynamics was also used to evaluate the viscoelasticity of a suspension of asphaltene. When molecule displacement is evaluated in terms of aggregate dynamics, it exhibits a sudden spike in motion that is quickly followed by a dramatic drop in motion due to paused phases. Thus aggregation occurs during the sol-gel transition. Similar to real experiments, because molecules become less mobile when a bigger mass fraction is grown, slower aggregation takes place due to sluggish movement of cluster of asphaltenes[164]. The diffusion coefficient for toluene containing 5% asphaltene was determined to be 300 micrometres per second, which is within the acceptable experimental range. In another DPD based simulation, authors (Ahmadi et al., 2018a) studied the effects of Brownian dynamics on suspensions of asphaltene in heptane and hetptol (mixture of heptane and toluene). Although percolated structures were discovered at larger volume fractions, fractal nanoaggregates were discovered at lower volume fractions. The self-diffusion of asphaltene particles diminishes with increasing volume percentage, which is consistent with other nanoparticle rotation and translational motions being controlled by volume fraction. In conclusion, the Brownian dynamics and DPD simulations presented here have the ability to provide information that experiments were unable to.

Solvent influences the size of the asphaltene aggregates according to molecular dynamic insights as aggregates were discovered to be more stable and denser in hexane compared to o-Dichlorobenzene. It is reasonably argued that based on temperature and the existence of polar groups, molecules and solvents interact with each other significantly [165]. Moreover, inhibitors can affect asphaltene aggregate size; similarly, a study based on simulation showed that the core of the aggregates' active sites interacts with inhibitors. In general, aggregates can assume any sizes [155] in presence of inhibitor.

3. Conclusions

This study reviews the stability of asphaltene in crude oil as well as the elements that have the most effects on it. The many models that have been used to attempt to characterise the asphaltene structure were discussed, along with the most modern and extensively used model, the Yen-Mullins model. The stages of asphaltene that may occur in crude oil, such as asphaltene precipitation, flocculation, dissociation, and deposition, were also highlighted and thoroughly described. asphaltene instability's primary influencing elements, such as operational and reservoir factors, were also discussed. Along with the many studies carried out to investigate asphaltene permeability decrease and pore plugging, the principal chemical techniques utilised to examine asphaltene structural features were also described. Finally, several field studies that faced asphaltene issues were highlighted, along with the approaches they used to address the issue and the results of each approach.

Asphaltene can also be used as filler to enhance the temperature-dependent attributes of matrix materials, as an adsorbate in separation processes because of its exceptional sensitivity and thermal properties, or as a carbon-rich material to synthesize advanced carbon-based materials or to adjust the surface of various nanomaterials [166]. In this regard, it can be viewed similarly to graphene quantum dot applications [167]. Finally, asphaltene seems to display a number of different behaviours that seem to be adequately covered by the available characterisation techniques. Systems using asphaltene seem to have a promising future. The oil business just must perform more research into the literature to get rid of concerns regarding precipitation, deposition, and emulsification in order to resolve the asphaltene problem.

References

1. Zhang, Y.; Siskin, M.; Gray, M. R.; Walters, C. C.; Rodgers, R. P., Mechanisms of asphaltene aggregation: puzzles and a new hypothesis. *Energy & Fuels* **2020,** *34* (8), 9094-9107.
2. Gray, M. R.; Yarranton, H. W.; Chacón-Patiño, M. L.; Rodgers, R. P.; Bouyssiere, B.; Giusti, P., Distributed Properties of Asphaltene Nanoaggregates in Crude Oils: A Review. *Energy & Fuels* **2021**.

3. Mozaffari, S.; Tchoukov, P.; Atias, J.; Czarnecki, J.; Nazemifard, N., Effect of asphaltene aggregation on rheological properties of diluted athabasca bitumen. *Energy & Fuels* **2015,** *29* (9), 5595-5599.

4. Mozaffari, S.; Tchoukov, P.; Mozaffari, A.; Atias, J.; Czarnecki, J.; Nazemifard, N., Capillary driven flow in nanochannels–Application to heavy oil rheology studies. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2017,** *513*, 178-187.

5. Kor, P.; Kharrat, R., Prediction of the asphaltene deposition profile along a wellbore during natural production from a reservoir. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* **2016,** *38* (19), 2837-2844.

6. Kor, P.; Kharrat, R., Modeling of asphaltene particle deposition from turbulent oil flow in tubing: Model validation and a parametric study. *Petroleum* **2016,** *2* (4), 393-398.

7. Ghahfarokhi, A. K.; Kor, P.; Kharrat, R.; Soulgani, B. S., Characterization of asphaltene deposition process in flow loop apparatus; An experimental investigation and modeling approach. *Journal of Petroleum Science and Engineering* **2017,** *151*, 330-340.

8. Nwadinigwe, C.; Anigbogu, I.; Ujam, O., Studies on precipitation performance of n-heptane and n-pentane/n-heptane on C 7 and C 5/C 7 asphaltenes and maltenes from 350° C atmospheric residuum of three Nigerian light crudes. *Journal of Petroleum Exploration and Production Technology* **2015,** *5* (4), 403-407.

9. Ratovskaya, A., Determination of the molecular weight of asphaltenes by the thermoelectric technique. *Chemistry and Technology of Fuels and Oils* **1968,** *4* (10), 773-776.

10. Ali, L. H.; Al-Ghannam, K. A., Investigations into asphaltenes in heavy crude oils. I. Effect of temperature on precipitation by alkane solvents. *Fuel* **1981,** *60* (11), 1043-1046.

11. Acevedo, S.; Gutierrez, L. B.; Negrin, G.; Pereira, J. C.; Mendez, B.; Delolme, F.; Dessalces, G.; Broseta, D., Molecular weight of petroleum asphaltenes: A comparison between mass spectrometry and vapor pressure osmometry. *Energy & fuels* **2005,** *19* (4), 1548-1560.

12. Akbarzadeh, K.; Hammami, A.; Kharrat, A.; Zhang, D.; Allenson, S.; Creek, J.; Kabir, S.; Jamaluddin, A.; Marshall, A. G.; Rodgers, R. P., Asphaltenes—problematic but rich in potential. *Oilfield review* **2007,** *19* (2), 22-43.

13. Mullins, O. C.; Sabbah, H.; Eyssautier, J.; Pomerantz, A. E.; Barré, L.; Andrews, A. B.; Ruiz-Morales, Y.; Mostowfi, F.; McFarlane, R.; Goual, L., Advances in asphaltene science and the Yen–Mullins model. *Energy & Fuels* **2012,** *26* (7), 3986-4003.

14. Verruto, V. J.; Le, R. K.; Kilpatrick, P. K., Adsorption and molecular rearrangement of amphoteric species at oil–water interfaces. *The Journal of Physical Chemistry B* **2009,** *113* (42), 13788-13799.

15. Tchoukov, P.; Yang, F.; Xu, Z.; Dabros, T.; Czarnecki, J.; Sjoblom, J., Role of asphaltenes in stabilizing thin liquid emulsion films. *Langmuir* **2014,** *30* (11), 3024-3033.

16. Bagheri, S. R.; Masik, B.; Arboleda, P.; Wen, Q.; Michaelian, K.; Shaw, J. M., Physical properties of liquid crystals in Athabasca bitumen fractions. *Energy & fuels* **2012,** *26* (8), 4978-4987.

17. Horváth-Szabó, G.; Masliyah, J. H.; Czarnecki, J., Friberg correlations in oil recovery. *Journal of dispersion science and technology* **2006,** *27* (5), 625-633.

18. Horváth-Szabó, G.; Czarnecki, J.; Masliyah, J. H., Sandwich structures at oil–water interfaces under alkaline conditions. *Journal of colloid and interface science* **2002,** *253* (2), 427-434.

19. Qin, C.; Becerra, M.; Shaw, J. M., Fate of Organic Liquid-Crystal Domains during Steam-Assisted Gravity Drainage/Cyclic Steam Stimulation Production of Heavy Oils and Bitumen. *Energy & Fuels* **2017,** *31* (5), 4966-4972.

20. Czarnecki, J.; Moran, K.; Yang, X., On the “rag layer” and diluted bitumen froth dewatering. *The Canadian Journal of Chemical Engineering* **2007,** *85* (5), 748-755.

21. Rao, F.; Liu, Q., Froth treatment in Athabasca oil sands bitumen recovery process: A review. *Energy & fuels* **2013,** *27* (12), 7199-7207.

22. Moud, A. A., Asphaltene induced changes in rheological properties: A review. *Fuel* **2022,** *316*, 123372.

23. Chang, C.-C.; Nowbahar, A.; Mansard, V.; Williams, I.; Mecca, J.; Schmitt, A. K.; Kalantar, T. H.; Kuo, T.-C.; Squires, T. M., Interfacial rheology and heterogeneity of aging asphaltene layers at the water–oil interface. *Langmuir* **2018,** *34* (19), 5409-5415.

24. Nowbahar, A.; Whitaker, K. A.; Schmitt, A. K.; Kuo, T.-C., Mechanistic study of water droplet coalescence and flocculation in diluted bitumen emulsions with additives using microfluidics. *Energy & Fuels* **2017,** *31* (10), 10555-10565.

25. Kuznicki, T.; Masliyah, J. H.; Bhattacharjee, S., Aggregation and partitioning of model asphaltenes at toluene–water interfaces: Molecular dynamics simulations. *Energy & Fuels* **2009,** *23* (10), 5027-5035.

26. Mousavi, M.; Abdollahi, T.; Pahlavan, F.; Fini, E. H., The influence of asphaltene-resin molecular interactions on the colloidal stability of crude oil. *Fuel* **2016,** *183*, 262-271.

27. Breure, B.; Subramanian, D.; Leys, J.; Peters, C. J.; Anisimov, M. A., Modeling asphaltene aggregation with a single compound. *Energy & fuels* **2013,** *27* (1), 172-176.

28. Czarnecki, J.; Moran, K., On the stabilization mechanism of water-in-oil emulsions in petroleum systems. *Energy & fuels* **2005,** *19* (5), 2074-2079.

29. Daaou, M.; Bendedouch, D., Water pH and surfactant addition effects on the stability of an Algerian crude oil emulsion. *Journal of Saudi Chemical Society* **2012,** *16* (3), 333-337.

30. Al-Maamari, R. S.; Buckley, J. S., Asphaltene precipitation and alteration of wetting: the potential for wettability changes during oil production. *SPE Reservoir Evaluation & Engineering* **2003,** *6* (04), 210-214.

31. Trimm, D. L.; Akashah, S.; Bishara, A.; Absi-Halabi, M., *Catalysts in petroleum refining 1989*. Elsevier: 1990.

32. Trimm, D. L., The formation and removal of coke from nickel catalyst. *Catalysis Reviews Science and Engineering* **1977,** *16* (1), 155-189.

33. Nikookar, M.; Omidkhah, M. R.; Pazuki, G. R.; Mohammadi, A. H., An Insight into Molecular Weight Distributions of Asphaltene and Asphalt Using Gel Permeation Chromatography. *Journal of Molecular Liquids* **2022**, 119736.

34. Rogel, E., Asphaltene stability in crude oils. Soc Pet Eng. 1999.

35. Zhang, L.; Xie, L.; Shi, C.; Huang, J.; Liu, Q.; Zeng, H., Mechanistic understanding of asphaltene surface interactions in aqueous media. *Energy & Fuels* **2017,** *31* (4), 3348-3357.

36. Abbasi Moud, A.; Sanati-Nezhad, A.; Hejazi, S. H., Confocal analysis of cellulose nanocrystal (CNC) based hydrogels and suspensions. *Cellulose* **2021,** *28* (16), 10259-10276.

37. Moud, A. A.; Nezhad, A. S.; Hejazi, S. H., Confocal Analysis of CNC based Hydrogels and Suspensions. **2021**.

38. Abbasi Moud, A.; Javadi, A.; Nazockdast, H.; Fathi, A.; Altstaedt, V., Effect of dispersion and selective localization of carbon nanotubes on rheology and electrical conductivity of polyamide 6 (PA 6), Polypropylene (PP), and PA 6/PP nanocomposites. *Journal of Polymer Science Part B: Polymer Physics* **2015,** *53* (5), 368-378.

39. Moud, A. A., Fluorescence Recovery after Photobleaching in Colloidal Science: Introduction and Application. *ACS Biomaterials Science & Engineering* **2022,** *8* (3), 1028-1048.

40. Abbasi Moud, A.; Hatzikiriakos, S. G., Kaolinite colloidal suspensions under the influence of sodium dodecyl sulfate. *Physics of Fluids* **2022,** *34* (1), 013107.

41. Moud, A. A.; Kamkar, M.; Sanati-Nezhad, A.; Hejazi, S. H., Suspensions and hydrogels of cellulose nanocrystals (CNCs): characterization using microscopy and rheology. *Cellulose* **2022**, 1-33.

42. Abbasi Moud, A.; Possion, J.; Hudson, Z. M.; Hatzikiriakos, S. G., Yield stress and wall slip of kaolinite networks. *physics of Fluids* **2021,** *33*, 000000.
43. Balabin, R. M.; Syunyaev, R. Z.; Schmid, T.; Stadler, J.; Lomakina, E. I.; Zenobi, R., Asphaltene adsorption onto an iron surface: combined near-infrared (NIR), Raman, and AFM study of the kinetics, thermodynamics, and layer structure. *Energy & Fuels* **2011,** *25* (1), 189-196.
44. Shi, C.; Zhang, L.; Xie, L.; Lu, X.; Liu, Q.; Mantilla, C. A.; van den Berg, F. G.; Zeng, H., Interaction mechanism of oil-in-water emulsions with asphaltenes determined using droplet probe AFM. *Langmuir* **2016,** *32* (10), 2302-2310.
45. Castillo, J.; Vargas, V.; Piscitelli, V.; Ordoñez, L.; Rojas, H., Study of asphaltene adsorption onto raw surfaces and iron nanoparticles by AFM force spectroscopy. *Journal of Petroleum Science and Engineering* **2017,** *151*, 248-253.
46. Yeung, A.; Dabros, T.; Czarnecki, J.; Masliyah, J., On the interfacial properties of micrometre–sized water droplets in crude oil. *Proceedings of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences* **1999,** *455* (1990), 3709-3723.
47. Xu, Y.; Dabros, T.; Hamza, H.; Shefantook, W., Destabilization of water in bitumen emulsion by washing with water. *Petroleum science and technology* **1999,** *17* (9-10), 1051-1070.
48. Leng, Y.; Williams, C., Electrostatic characterization of biological and polymeric surfaces by electrostatic force microscopy. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **1994,** *93*, 335-341.
49. Martin-Olmos, C.; Stieg, A. Z.; Gimzewski, J. K., Electrostatic force microscopy as a broadly applicable method for characterizing pyroelectric materials. *Nanotechnology* **2012,** *23* (23), 235701.
50. Gaikwad, R.; Hande, A.; Das, S.; Mitra, S. K.; Thundat, T., Determination of charge on asphaltene nanoaggregates in air using electrostatic force microscopy. *Langmuir* **2015,** *31* (2), 679-684.
51. Szymula, M.; Janusz, W.; Jabloriski, J., Electrochemical properties of asphaltene particles in aqueous solutions. *Journal of dispersion science and technology* **2000,** *21* (6), 785-802.
52. Azari, V.; Abolghasemi, E.; Hosseini, A.; Ayatollahi, S.; Dehghani, F., Electrokinetic properties of asphaltene colloidal particles: determining the electric charge using micro electrophoresis technique. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2018,** *541*, 68-77.
53. Belhaj, H.; Khalifeh, H. A.; Al-Huraibi, N., Asphaltene stability in crude oil during production process. *J. Pet. Environ. Biotechnol* **2013,** *4* (142), 1-5.
54. Xia, S.; Veony, E.; Kostarelos, K., A novel electro-deposition based asphaltene removal strategy. *Fuel* **2019,** *244*, 508-516.
55. Chacón-Patiño, M. L.; Rowland, S. M.; Rodgers, R. P., Advances in asphaltene petroleomics. part 1: asphaltenes are composed of abundant island and archipelago structural motifs. *Energy & fuels* **2017,** *31* (12), 13509-13518.
56. Fossen, M.; Kallevik, H.; Knudsen, K. D.; Sjoblom, J., Asphaltenes precipitated by a two-step precipitation procedure. 2. Physical and chemical characteristics. *Energy & Fuels* **2011,** *25* (8), 3552-3567.
57. Goual, L.; Zhang, B.; Rahham, Y., Nanoscale characterization of thin films at oil/water interfaces and implications to emulsion stability. *Energy & Fuels* **2020,** *35* (1), 444-455.
58. Headen, T. F.; Boek, E. S.; Skipper, N. T., Evidence for asphaltene nanoaggregation in toluene and heptane from molecular dynamics simulations. *Energy & Fuels* **2009,** *23* (3), 1220-1229.
59. Yaseen, S.; Mansoori, G. A., Molecular dynamics studies of interaction between asphaltenes and solvents. *Journal of Petroleum Science and Engineering* **2017,** *156*, 118-124.
60. Buckley, J. S., Asphaltene deposition. *Energy & Fuels* **2012,** *26* (7), 4086-4090.
61. Bochner de Araujo, S.; Merola, M.; Vlassopoulos, D.; Fuller, G. G., Droplet coalescence and spontaneous emulsification in the presence of asphaltene adsorption. *Langmuir* **2017,** *33* (40), 10501-10510.

62. Oliensis, G. In *A qualitative test for determining the degree of heterogeneity of asphalts*, Proc. ASTM, 1933; pp 715-721.

63. Buckley, J. S.; Wang, J.; Creek, J. L., Solubility of the least-soluble asphaltenes. In *Asphaltenes, heavy oils, and petroleomics*, Springer: 2007; pp 401-437.

64. Ting, P. D.; Gonzalez, D. L.; Hirasaki, G. J.; Chapman, W. G., Application of the PC-SAFT equation of state to asphaltene phase behavior. In *Asphaltenes, heavy oils, and petroleomics*, Springer: 2007; pp 301-327.

65. Montesi, A.; Pinnick, R. A.; Subramanian, S.; Wang, J.; Creek, J. L. In *Asphaltene management in GOM DW subsea development*, Offshore Technology Conference, OnePetro: 2011.

66. Andrews, A. B.; McClelland, A.; Korkeila, O.; Demidov, A.; Krummel, A.; Mullins, O. C.; Chen, Z., Molecular orientation of asphaltenes and PAH model compounds in Langmuir− Blodgett films using sum frequency generation spectroscopy. *Langmuir* **2011,** *27* (10), 6049-6058.

67. Natarajan, A.; Kuznicki, N.; Harbottle, D.; Masliyah, J.; Zeng, H.; Xu, Z., Understanding mechanisms of asphaltene adsorption from organic solvent on mica. *Langmuir* **2014,** *30* (31), 9370-9377.

68. Stancik, E. J.; Kouhkan, M.; Fuller, G. G., Coalescence of particle-laden fluid interfaces. *Langmuir* **2004,** *20* (1), 90-94.

69. de Oliveira, F. C.; Khani, S.; Maia, J. o. M.; Tavares, F. W., Concentration and solvent effects on structural, dynamical, and rheological properties of asphaltene suspensions. *Energy & Fuels* **2019,** *34* (1), 1071-1081.

70. Zhang, Y.; Lin, Q.; Raeini, A. Q.; Onaka, Y.; Iwama, H.; Takabayashi, K.; Blunt, M. J.; Bijeljic, B., Pore-scale imaging of asphaltene deposition with permeability reduction and wettability alteration. *Fuel* **2022,** *316*, 123202.

71. Hong, X.; Yu, H.; Xu, H.; Wang, X.; Jin, X.; Wu, H.; Wang, F., Competitive adsorption of asphaltene and n-heptane on quartz surfaces and its effect on crude oil transport through nanopores. *Journal of Molecular Liquids* **2022,** *359*, 119312.

72. Salimi, F.; Salimi, J.; Abdollahifar, M., Investigation of asphaltene deposition under dynamic flow conditions. *Petroleum Science* **2016,** *13* (2), 340-346.

73. Duran, J.; Schoeggl, F.; Yarranton, H., Kinetics of asphaltene precipitation/aggregation from diluted crude oil. *Fuel* **2019,** *255*, 115859.

74. Broseta, D.; Robin, M.; Savvidis, T.; Féjean, C.; Durandeau, M.; Zhou, H. In *Detection of asphaltene deposition by capillary flow measurements*, SPE/DOE Improved Oil Recovery Symposium, OnePetro: 2000.

75. Lawal, K. A.; Crawshaw, J. P.; Boek, E. S.; Vesovic, V., Experimental investigation of asphaltene deposition in capillary flow. *Energy & fuels* **2012,** *26* (4), 2145-2153.

76. Mehana, M.; Abraham, J.; Fahes, M., The impact of asphaltene deposition on fluid flow in sandstone. *Journal of Petroleum Science and Engineering* **2019,** *174*, 676-681.

77. Ramirez-Jaramillo, E.; Lira-Galeana, C.; Manero, O., Modeling asphaltene deposition in production pipelines. *Energy & fuels* **2006,** *20* (3), 1184-1196.

78. Jamialahmadi, M.; Soltani, B.; Müller-Steinhagen, H.; Rashtchian, D., Measurement and prediction of the rate of deposition of flocculated asphaltene particles from oil. *International Journal of Heat and Mass Transfer* **2009,** *52* (19-20), 4624-4634.

79. Vargas, F. M.; Creek, J. L.; Chapman, W. G., On the development of an asphaltene deposition simulator. *Energy & Fuels* **2010,** *24* (4), 2294-2299.

80. Elkhatib, O.; Chaisoontornyotin, W.; Gesho, M.; Goual, L., Nanoscale investigation of asphaltene deposition under capillary flow conditions. *Energy & Fuels* **2019,** *34* (5), 5148-5158.

81. Eskin, D.; Ratulowski, J.; Akbarzadeh, K.; Pan, S., Modelling asphaltene deposition in turbulent pipeline flows. *The Canadian Journal of Chemical Engineering* **2011,** *89* (3), 421-441.
82. Paes, D.; Ribeiro, P.; Shirdel, M.; Sepehrnoori, K., Study of asphaltene deposition in wellbores during turbulent flow. *Journal of Petroleum Science and Engineering* **2015,** *129*, 77-87.
83. Boek, E. S.; Ladva, H. K.; Crawshaw, J. P.; Padding, J. T., Deposition of colloidal asphaltene in capillary flow: experiments and mesoscopic simulation. *Energy & fuels* **2008,** *22* (2), 805-813.
84. Alhosani, A.; Daraboina, N., Modeling of asphaltene deposition during oil/gas flow in wellbore. *Fuel* **2020,** *280*, 118617.
85. Shirdel, M.; Paes, D.; Ribeiro, P.; Sepehrnoori, K., Evaluation and comparison of different models for asphaltene particle deposition in flow streams. *Journal of Petroleum Science and Engineering* **2012,** *84*, 57-71.
86. Sztukowski, D. M.; Yarranton, H. W., Rheology of asphaltene− toluene/water interfaces. *Langmuir* **2005,** *21* (25), 11651-11658.
87. Moncayo-Riascos, I.; Taborda, E.; Hoyos, B. A.; Franco, C. A.; Cortés, F. B., Theoretical-experimental evaluation of rheological behavior of asphaltene solutions in toluene and p-xylene: Effect of the additional methyl group. *Journal of Molecular Liquids* **2020,** *303*, 112664.
88. Rane, J. P.; Pauchard, V.; Couzis, A.; Banerjee, S., Interfacial rheology of asphaltenes at oil–water interfaces and interpretation of the equation of state. *Langmuir* **2013,** *29* (15), 4750-4759.
89. Oldham, D.; Qu, X.; Wang, H.; Fini, E. H., Investigating change of polydispersity and rheology of crude oil and bitumen due to asphaltene oxidation. *Energy & Fuels* **2020,** *34* (8), 10299-10305.
90. Moncayo-Riascos, I.; Taborda, E.; Hoyos, B. A.; Franco, C. A.; Cortés, F. B., Effect of resin/asphaltene ratio on the rheological behavior of asphaltene solutions in a de-asphalted oil and p-xylene: A theoretical–experimental approach. *Journal of Molecular Liquids* **2020,** *315*, 113754.
91. Lin, Y.-J.; Barman, S.; He, P.; Zhang, Z.; Christopher, G. F.; Biswal, S. L., Combined interfacial shear rheology and microstructure visualization of asphaltenes at air-water and oil-water interfaces. *Journal of Rheology* **2018,** *62* (1), 1-10.
92. Nguele, R.; Okawa, H., Effect of ultrasound irradiation on asphaltene aggregation and implications to rheological behavior of bitumen. *Ultrasonics Sonochemistry* **2021,** *80*, 105811.
93. Ariza, E.; Chaves-Guerrero, A.; Molina V, D., Effect of average molecular parameters of asphaltenes on the rheological properties of crude oils from Colorado oil field. *Energy & Fuels* **2018,** *32* (6), 6557-6564.
94. Li, T.; Xu, J.; Zou, R.; Jiang, H.; Wang, J.; Li, L.; Cohen Stuart, M. A.; Prud'homme, R. K.; Guo, X., Effect of spacer length between phenyl pendant and backbone in comb copolymers on flow ability of waxy oil with asphaltenes. *Industrial & Engineering Chemistry Research* **2017,** *56* (44), 12447-12455.
95. Gorbacheva, S. N.; Ilyin, S. O., Structure, rheology and possible application of water-in-oil emulsions stabilized by asphaltenes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2021,** *618*, 126442.
96. Oliveira, P. F.; Santos, I. C.; Vieira, H. V.; Fraga, A. K.; Mansur, C. R., Interfacial rheology of asphaltene emulsions in the presence of nanoemulsions based on a polyoxide surfactant and asphaltene dispersant. *Fuel* **2017,** *193*, 220-229.
97. Rogel, E.; Moir, M., Effect of precipitation time and solvent power on asphaltene characteristics. *Fuel* **2017,** *208*, 271-280.
98. Behbahani, T. J.; Ghotbi, C.; Taghikhani, V.; Shahrabadi, A., Experimental investigation and thermodynamic modeling of asphaltene precipitation. *Scientia Iranica* **2011,** *18* (6), 1384-1390.

99. Li, J.; Liu, W.; Cong, S.; Li, Y.; Zheng, K.; Luo, X.; Luo, W.; Su, X., The flow of water-in-oil emulsion in heterogeneous parallel model. *Journal of Petroleum Science and Engineering* **2022,** *208*, 109209.

100. Lin, Y.-J.; Zhang, Z.; Biswal, S. L., Entrapment of Asphaltene-Stabilized Emulsions in Microfluidic Porous Media. *Energy & Fuels* **2022**.

101. Gafonova, O. V.; Yarranton, H. W., The stabilization of water-in-hydrocarbon emulsions by asphaltenes and resins. *Journal of Colloid and Interface Science* **2001,** *241* (2), 469-478.

102. Low, L. E.; Siva, S. P.; Ho, Y. K.; Chan, E. S.; Tey, B. T., Recent advances of characterization techniques for the formation, physical properties and stability of Pickering emulsion. *Advances in colloid and interface science* **2020,** *277*, 102117.

103. Chevalier, Y.; Bolzinger, M.-A., Emulsions stabilized with solid nanoparticles: Pickering emulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2013,** *439*, 23-34.

104. Pickering, S. U., Cxcvi.—emulsions. *Journal of the Chemical Society, Transactions* **1907,** *91*, 2001-2021.

105. Binks, B. P.; Lumsdon, S. O., Stability of oil-in-water emulsions stabilised by silica particles. *Physical Chemistry Chemical Physics* **1999,** *1* (12), 3007-3016.

106. Aveyard, R.; Binks, B. P.; Clint, J. H., Emulsions stabilised solely by colloidal particles. *Advances in Colloid and Interface Science* **2003,** *100*, 503-546.

107. Wang, Z.; Babadagli, T.; Maeda, N., Generation of pickering emulsions by activating natural asphaltenes as nano materials: An experimental analysis for cost-effective heavy-oil recovery. *Journal of Molecular Liquids* **2021,** *339*, 116759.

108. Firouzi, M.; Nguyen, A. V., The Gibbs-Marangoni stress and nonDLVO forces are equally important for modeling bubble coalescence in salt solutions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2017,** *515*, 62-68.

109. Hayat, T.; Khan, S. A.; Alsaedi, A.; Fardoun, H. M., Marangoni Forced Convective Flow of Second Grade Fluid with Irreversibility Analysis and Chemical Reaction. *International Journal of Thermophysics* **2021,** *42* (1), 1-21.

110. Schüer, J. J.; Wölk, C.; Bakowsky, U.; Pinnapireddy, S. R., Comparison of Tanaka lipid mixture with natural surfactant Alveofact to study nanoparticle interactions on Langmuir film balance. *Colloids and Surfaces B: Biointerfaces* **2020,** *188*, 110750.

111. Sosnowski, T. R.; Kubski, P.; Wojciechowski, K., New experimental model of pulmonary surfactant for biophysical studies. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2017,** *519*, 27-33.

112. Harbottle, D.; Chen, Q.; Moorthy, K.; Wang, L.; Xu, S.; Liu, Q.; Sjoblom, J.; Xu, Z., Problematic stabilizing films in petroleum emulsions: Shear rheological response of viscoelastic asphaltene films and the effect on drop coalescence. *Langmuir* **2014,** *30* (23), 6730-6738.

113. Samaniuk, J. R.; Hermans, E.; Verwijlen, T.; Pauchard, V.; Vermant, J., Soft-glassy rheology of asphaltenes at liquid interfaces. *Journal of Dispersion Science and Technology* **2015,** *36* (10), 1444-1451.

114. Pensini, E.; Harbottle, D.; Yang, F.; Tchoukov, P.; Li, Z.; Kailey, I.; Behles, J.; Masliyah, J.; Xu, Z., Demulsification mechanism of asphaltene-stabilized water-in-oil emulsions by a polymeric ethylene oxide–propylene oxide demulsifier. *Energy & Fuels* **2014,** *28* (11), 6760-6771.

115. Niu, Z.; Yue, T.; He, X.; Manica, R., Changing the interface between an asphaltene model compound and water by addition of an EO–PO demulsifier through adsorption competition or adsorption replacement. *Energy & Fuels* **2019,** *33* (6), 5035-5042.

116. Kar, T.; Hascakir, B., The role of resins, asphaltenes, and water in water–oil emulsion breaking with microwave heating. *Energy & Fuels* **2015,** *29* (6), 3684-3690.

117. Spiecker, P. M.; Kilpatrick, P. K., Interfacial rheology of petroleum asphaltenes at the oil− water interface. *Langmuir* **2004,** *20* (10), 4022-4032.
118. Sahu, R.; Song, B. J.; Im, J. S.; Jeon, Y.-P.; Lee, C. W., A review of recent advances in catalytic hydrocracking of heavy residues. *Journal of Industrial and Engineering Chemistry* **2015,** *27*, 12-24.
119. McLean, J. D.; Kilpatrick, P. K., Effects of asphaltene aggregation in model heptane–toluene mixtures on stability of water-in-oil emulsions. *Journal of Colloid and interface Science* **1997,** *196* (1), 23-34.
120. Sztukowski, D. M.; Jafari, M.; Alboudwarej, H.; Yarranton, H. W., Asphaltene self-association and water-in-hydrocarbon emulsions. *Journal of colloid and interface science* **2003,** *265* (1), 179-186.
121. Freer, E.; Radke, C., Relaxation of asphaltenes at the toluene/water interface: diffusion exchange and surface rearrangement. *The Journal of Adhesion* **2004,** *80* (6), 481-496.
122. Freer, E.; Svitova, T.; Radke, C., The role of interfacial rheology in reservoir mixed wettability. *Journal of Petroleum Science and Engineering* **2003,** *39* (1-2), 137-158.
123. McLean, J. D.; Kilpatrick, P. K., Effects of asphaltene solvency on stability of water-in-crude-oil emulsions. *Journal of colloid and interface science* **1997,** *189* (2), 242-253.
124. Rodríguez-Hakim, M.; Anand, S.; Tajuelo, J.; Yao, Z.; Kannan, A.; Fuller, G. G., Asphaltene-induced spontaneous emulsification: Effects of interfacial co-adsorption and viscoelasticity. *Journal of Rheology* **2020,** *64* (4), 799-816.
125. Alicke, A.; Simon, S.; Sjöblom, J.; Vermant, J., Assessing the Interfacial Activity of Insoluble Asphaltene Layers: Interfacial Rheology versus Interfacial Tension. *Langmuir* **2020,** *36* (49), 14942-14959.
126. Fan, Y.; Simon, S.; Sjöblom, J., Interfacial shear rheology of asphaltenes at oil–water interface and its relation to emulsion stability: Influence of concentration, solvent aromaticity and nonionic surfactant. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2010,** *366* (1-3), 120-128.
127. Pradilla, D.; Simon, S.; Sjoblom, J.; Samaniuk, J.; Skrzypiec, M.; Vermant, J., Sorption and interfacial rheology study of model asphaltene compounds. *Langmuir* **2016,** *32* (12), 2900-2911.
128. Liu, F.; Darjani, S.; Akhmetkhanova, N.; Maldarelli, C.; Banerjee, S.; Pauchard, V., Mixture effect on the dilatation rheology of asphaltenes-laden interfaces. *Langmuir* **2017,** *33* (8), 1927-1942.
129. Gahrooee, T. R.; Moud, A. A.; Danesh, M.; Hatzikiriakos, S. G., Rheological characterization of CNC-CTAB network below and above critical micelle concentration (CMC). *Carbohydrate Polymers* **2021,** *257*, 117552.
130. Yarranton, H. W.; Sztukowski, D. M.; Urrutia, P., Effect of interfacial rheology on model emulsion coalescence: I. Interfacial rheology. *Journal of colloid and interface science* **2007,** *310* (1), 246-252.
131. Freer, E. M.; Yim, K. S.; Fuller, G. G.; Radke, C. J., Interfacial rheology of globular and flexible proteins at the hexadecane/water interface: comparison of shear and dilatation deformation. *The Journal of Physical Chemistry B* **2004,** *108* (12), 3835-3844.
132. Walstra, P., On the stability of casein micelles. *Journal of dairy science* **1990,** *73* (8), 1965-1979.
133. Groenewold, J.; Kegel, W. K., Anomalously large equilibrium clusters of colloids. *The Journal of Physical Chemistry B* **2001,** *105* (47), 11702-11709.
134. de Araujo, S. B.; Reyssat, M.; Monteux, C.; Fuller, G., Ablation of water drops suspended in asphaltene/heptol solutions due to spontaneous emulsification. *Science advances* **2019,** *5* (10), eaax8227.
135. Ballard, D.; Qiao, P.; Cattoz, B.; Dowding, P.; Prevost, S.; Alshamsi, M.; Charpentier, T.; Roberts, K.; Xu, Z.; Harbottle, D., Aggregation Behavior of E-SARA Asphaltene Fractions Studied by Small-Angle Neutron Scattering. *Energy & Fuels* **2020,** *34* (6), 6894-6903.
136. Kelbaliyev, G.; Tagiyev, D.; Rasulov, S.; Mustafayeva, G.; Kerimli, V., Rheology of structural oil disperse systems. *Theoretical Foundations of Chemical Engineering* **2017,** *51* (5), 729-735.

137. Cagna, A.; Esposito, G.; Quinquis, A.-S.; Langevin, D., On the reversibility of asphaltene adsorption at oil-water interfaces. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2018,** *548*, 46-53.

138. Moud, A. A., Recent advances in utility of artificial intelligence towards multiscale colloidal based materials design. *Colloid and Interface Science Communications* **2022,** *47*, 100595.

139. Sharif, F.; Arjmand, M.; Moud, A. A.; Sundararaj, U.; Roberts, E. P., Segregated hybrid poly (methyl methacrylate)/graphene/magnetite nanocomposites for electromagnetic interference shielding. *ACS applied materials & interfaces* **2017,** *9* (16), 14171-14179.

140. Siddiqui, M. N.; Redhwi, H. H.; Younas, M.; Hussain, S.; Achilias, D. S., Use of asphaltene filler to improve low-density polyethylene properties. *Petroleum Science and Technology* **2018,** *36* (11), 756-764.

141. Siddiqui, M. N. In *Asphaltene used for enhancing polymer properties*, ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY, AMER CHEMICAL SOC 1155 16TH ST, NW, WASHINGTON, DC 20036 USA: 2015.

142. Wu, H.; Thakur, V. K.; Kessler, M. R., Novel low-cost hybrid composites from asphaltene/SBS tri-block copolymer with improved thermal and mechanical properties. *Journal of materials science* **2016,** *51* (5), 2394-2403.

143. Hofko, B.; Eberhardsteiner, L.; Füssl, J.; Grothe, H.; Handle, F.; Hospodka, M.; Grossegger, D.; Nahar, S.; Schmets, A.; Scarpas, A., Impact of maltene and asphaltene fraction on mechanical behavior and microstructure of bitumen. *Materials and Structures* **2016,** *49* (3), 829-841.

144. Schantz, S.; Stephenson, W. In *Asphaltene deposition: development and application of polymeric asphaltene dispersants*, SPE Annual Technical Conference and Exhibition, OnePetro: 1991.

145. Hernández-Altamirano, R.; Mena-Cervantes, V. Y.; Chávez-Miyauchi, T. E.; Nieto-Álvarez, D. A.; Domínguez-Aguilar, M. A.; Zamudio-Rivera, L. S.; Barba, V.; Fernández-Perrino, F. J.; Pérez-Miranda, S.; Beltrán, H. I., New bis-di-organotin compounds derived from aminoacid-imine-hexadentate ligands. Multifunctional evaluation as corrosion inhibitors, antibacterials and asphaltene dispersants/inhibitors. *Polyhedron* **2013,** *52*, 301-307.

146. Li, J.-j.; Wang, X.; Tang, X.-d.; Wang, F.; Qing, D.-y., Effect of transition metal polymers with varying side alkyl chain on viscosity reduction of crude oil and aggregation behavior of asphaltene. *Energy & Fuels* **2015,** *29* (12), 7771-7780.

147. Kabel, K. I.; Abdelghaffar, A. M.; Farag, R. K.; Maysour, N.; Zahran, M. A., Synthesis and evaluation of PAMAM dendrimer and PDPF-b-POP block copolymer as asphaltene inhibitor/dispersant. *Research on Chemical Intermediates* **2015,** *41* (1), 457-474.

148. Castro, L. V.; Flores, E. A.; Vazquez, F., Terpolymers as flow improvers for Mexican crude oils. *Energy & fuels* **2011,** *25* (2), 539-544.

149. Zheng, C.; Zhu, M.; Zhang, D., Characterisation of asphaltenes extracted from an Indonesian oil sand using NMR, DEPT and MALDI-TOF. *Energy Procedia* **2015,** *75*, 847-852.

150. Wattana, P.; Fogler, H. S.; Yen, A.; Carmen Garcìa, M. D.; Carbognani, L., Characterization of polarity-based asphaltene subfractions. *Energy & fuels* **2005,** *19* (1), 101-110.

151. Mierau, J. M.-B.; Zhang, N.; Tan, X.; Scherer, A.; Stryker, J. M.; Tykwinski, R. R.; Gray, M. R., Catalytic hydrodenitrogenation of asphaltene model compounds. *Energy & Fuels* **2015,** *29* (10), 6724-6733.

152. Goual, L.; Sedghi, M.; Wang, X.; Zhu, Z., Asphaltene aggregation and impact of alkylphenols. *Langmuir* **2014,** *30* (19), 5394-5403.

153. Zhang, Z.; Perrard, A.; Trabelsi, S.; Biswal, S. L., Evaluation of Asphaltene Remediation Using Microemulsion Formulations in a Porous Media Microfluidic Device. *Energy & Fuels* **2021,** *35* (14), 11162-11170.

154. Zhang, Z.; Song, J.; Lin, Y.-J.; Wang, X.; Biswal, S. L., Comparing the Coalescence Rate of Water-in-Oil Emulsions Stabilized with Asphaltenes and Asphaltene-like Molecules. *Langmuir* **2020,** *36* (27), 7894-7900.

155. Rogel, E.; Ovalles, C.; Vien, J.; Moir, M., Asphaltene characterization of paraffinic crude oils. *Fuel* **2016,** *178*, 71-76.

156. Nordgård, E. L.; Sørland, G.; Sjöblom, J., Behavior of asphaltene model compounds at W/O interfaces. *Langmuir* **2010,** *26* (4), 2352-2360.

157. Wang, J.; van der Tuuk Opedal, N.; Lu, Q.; Xu, Z.; Zeng, H.; Sjoblom, J., Probing molecular interactions of an asphaltene model compound in organic solvents using a surface forces apparatus (SFA). *Energy & fuels* **2012,** *26* (5), 2591-2599.

158. Speight, J. G., *The chemistry and technology of petroleum*. CRC press: 2006.

159. Flory, P. J., Thermodynamics of high polymer solutions. *The Journal of chemical physics* **1941,** *9* (8), 660-660.

160. Lee, H.; Lee, Y.-K., Effects of the asphaltene structure and the tetralin/heptane solvent ratio on the size and shape of asphaltene aggregates. *Physical Chemistry Chemical Physics* **2017,** *19* (21), 13931-13940.

161. Park, J. W.; Lee, K. B., Molecular dynamics simulations of asphaltene aggregation in heavy oil system for the application to solvent deasphalting. *Fuel* **2022,** *323*, 124171.

162. Peng, B.; Xiao, S.; Wang, Y.; Qu, Z.; Yuan, L.; Liu, W.; Hou, Q.; Tang, X.; Pei, Y., On the synergistic effect of asphaltene and surfactant to reduce n-dodecane–water interfacial tension: insights from molecular dynamics simulations. *Molecular Simulation* **2022**, 1-10.

163. Huang, X.; Zhang, Y.; He, M.; Li, X.; Yang, W.; Lu, J., Asphaltene precipitation and reservoir damage characteristics of CO2 flooding in different microscopic structure types in tight light oil reservoirs. *Fuel* **2022,** *312*, 122943.

164. Solomon, M. J.; Spicer, P. T., Microstructural regimes of colloidal rod suspensions, gels, and glasses. *Soft Matter* **2010,** *6* (7), 1391-1400.

165. Oguamah, I. A. U.; Isehunwa, S.; Ndubisi, O.; Stephen, U.; Jude, O., Molecular Dynamics Study of Solvent Effect on the Structure and Characteristics of Asphaltene aggregates. **2022**.

166. Soulgani, B. S.; Reisi, F.; Norouzi, F., Investigation into mechanisms and kinetics of asphaltene aggregation in toluene/n-hexane mixtures. *Petroleum Science* **2020,** *17* (2), 457-466.

167. Peng, J.; Gao, W.; Gupta, B. K.; Liu, Z.; Romero-Aburto, R.; Ge, L.; Song, L.; Alemany, L. B.; Zhan, X.; Gao, G., Graphene quantum dots derived from carbon fibers. *Nano letters* **2012,** *12* (2), 844-849.