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Spatially resolved micron-scale wrinkle structures at asphaltene films induced by mild thermal treatment and its impact on emulsion stability

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ABSTRACT

Mild thermal treatment is an important partial upgrading technique to enable bitumen pipeline transportation, but no attention has been paid to the impact of mild thermal treatment on the emulsification behavior of emerging partially upgraded bitumen. Asphaltene compounds are active emulsion stabilizers in bitumen oil. The emulsion stabilizing capacity of bitumen asphaltenes was investigated, before and after a mild thermal treatment at 400 °C. The structural morphology and mechanical property of the asphaltene interfacial films were analyzed by using a combination of cryo-SEM, Langmuir trough, and Brewster angle microscopy. The thermal treatment significantly enhanced the emulsion stabilizing capacity of bitumen asphaltenes; the interfacial films formed by the thermally treated asphaltene samples appeared to be rougher and thicker with more abundant micron-scale wrinkle structures. The interfacial corrugation may intensify the mechanical stability/flexibility of the asphaltene films and consequently strengthen the stability of emulsion droplet.

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1. Introduction

Driven by the emerge of novel technological developments and economic considerations, the unconventional petroleum, such as natural bitumen and heavy oils, become increasingly important and common in our energy structure (Montoya et al., 2016). Partial upgrading of bitumen attracted much attention in recent years, which aims to achieve the goal of pipeline transportation without diluent addition (Gray, 2019). Mild thermal treatment (at around 400 °C) is an effective method to reduce the viscosity and density of bitumen materials with no coke formation, and thus is used in the proposed partial upgrading technologies (Jia et al., 2016; Zachariah and Klerk, 2017; Gray, 2019; Sviridenko et al., 2020). In comparison to the conventional diluted bitumen, the emerging partially upgraded bitumen may be an attractive feed in refineries, providing new market opportunities. An in-depth investigation on the

properties and behaviors of partially upgraded bitumen is of crucial importance for expanding its usage.

The knowledge on the emulsification behavior of partially upgraded bitumen is important, considering that a contact with water is inevitable in the life cycle of bitumen production (Abdulredha et al., 2020; Glagoleva and Kapustin, 2020; Silva et al., 2020). For example, desalting and dewatering of crude oil is necessary before distillation. Usually 2–8 wt% of water is added to dissolve salts and subsequently separated with the aid of demulsifiers. The natural emulsifiers in bitumen, such as asphaltenes, have a significant impact on the efficiency of demulsification processes (Yarranton et al., 2000; Czarnecki et al., 2013; Rocha et al., 2018; Alade et al., 2019; Gorbacheva and Ilyin, 2021).

In addition, such knowledge is useful to optimize the methods of bitumen partial upgrading and thus to form an integral utilization strategy of partially upgraded bitumen materials. A combination of mild thermal treatment (visbreaking) and solvent deasphalting is commonly proposed in partial upgrading of bitumen (Gholami et al., 2021; Díaz-Boffelli et al., 2018), while how to utilize the asphalt residue remains unclear. Asphalt emulsions, consisting of

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asphalt, water, and emulsifier, have been widely employed in road pavement, showing the advantages of energy savings, low cost, and environmental protection compared with conventional hot mix asphalt (Ronald and Luis, 2016). Asphalt materials with strong emulsification property are required as feed for asphalt emulsions. Our preliminary study suggests that a mild thermal treatment can enhance bitumen emulsification. To our best knowledge, no studies have investigated the impact of thermal partial upgrading on the emulsification performance of bitumen materials.

Water-in-oil emulsions are commonly encountered during bitumen/heavy oil production (Gao et al., 2009; Wang et al., 2021). The stability of bitumen emulsions is largely ascribed to the structural strength of a rigid interfacial film, that prevents the coalescence of water droplets (Aske et al., 2002; You et al., 2019). Bitumen components, such as asphaltenes and resins, all play a vital role in the emulsion formation. Asphaltenes are the most polar and heaviest compounds in the bitumen oil, which are soluble in toluene but insoluble in short-chain alkanes (Gray, 2015; Liu et al., 2020). The rigid film at oil/water interfaces is believed to be predominantly composed by asphaltenes (Yarranton et al., 2000; Czarnecki et al., 2013; Rocha et al., 2018; Gorbacheva and Ilyin, 2021), while the resin compounds may also contribute acting as peptizers (Gafonova and Yarranton, 2001; Yudina et al., 2021). The present work focuses on the interfacial behavior of asphaltenes, and further research into the role of resins and resin-asphaltene interactions on interfacial stability is suggested.

The configuration and structure of asphaltenes at oil/water interfaces are still poorly understood (Chang et al., 2018; Singh et al., 2018; Chen and Liu, 2019; Rodríguez-Hakim et al., 2020), considering that micron-scale study of emulsion interfaces is a non-trivial work due to the strong mobility, thin film thickness, and thermolabile form of emulsion droplets. Yeung et al. (2000) introduced a micropipette technique to study the interfacial properties of emulsions, and they demonstrated the presence of a rigid asphaltene layer surrounding a water droplet, which crumpled with a reduction of the interfacial area. However, the water-in-oil “emulsion droplet” in their work was artificially formed and the rigid “skin” was visualized by withdrawing fluid back into the water-filled micropipette.

Cryo-scanning electron microscopy (cryo-SEM) is effective in studying samples containing moisture, and thus is used to characterize emulsions in the food, pharmaceutical, and biological systems (Isa et al., 2011; Wille et al., 2017). For instance, Wang et al. (2019) determined the microstructures of the hetero-aggregated food emulsions by using cryo-SEM. With the aid of cryo-SEM, Isa et al. (2011) measured the wetting properties of single-nanoparticles at oil/water interfaces. In contrast, cryo-SEM is less common in the petroleum industry (Mikula and Munoz, 2000; Jia et al., 2016).

The hypothesis of the present study is that a mild thermal treatment can enhance the emulsion stabilizing capacity of bitumen asphaltenes, by altering the structural conformation of asphaltene interfacial films. The emulsification behavior of bitumen asphaltenes, before and after a mild thermal treatment typically at 400 °C (Zachariah and Klerk, 2017; Gray, 2019; Kaminski and Husein, 2019), was investigated and compared. The micron-scale wrinkle structures on the asphaltene films were clearly visualized and spatially resolved by using cryo-SEM, enabled by freezing the naturally formed water-in-oil droplets. The effect of thermal treatment on the asphaltene interfacial films and consequently on the emulsion stability is discussed.

2. Materials and methods

2.1. Materials

The bitumen sample used in this study was a coker feed bitumen supplied by an oil sands operator in Alberta, Canada. Reagent-grade toluene and *n*-heptane were purchased from Fisher Scientific and used as received without further treatment. Milli-Q deionized water was used in all experiments.

2.2. Preparation of asphaltene samples

Bitumen can be generally separated into two fractions: the *n*-heptane soluble fraction, i.e., maltenes, and the *n*-heptane insoluble/toluene soluble fraction, i.e., asphaltenes (Gray, 2015; Hofko et al., 2016). The maltenes and asphaltenes were obtained from the bitumen sample using *n*-heptane extraction following ASTM D6560-12 (ASTM, 1958). Thermal treatment of the bitumen sample was carried out at 400 °C for 30 min under a nitrogen atmosphere using a Parr reactor (Chen et al., 2016), and subsequently, maltenes/asphaltenes from the treated bitumen (called “thermally treated maltenes/asphaltenes”) were separated using *n*-heptane following the same method of ASTM D6560-12 (ASTM, 1958).

2.3. Analytical methods

The CHNS elemental composition of the asphaltene samples was determined by a Thermo Scientific Flash 2000 elemental analyzer. A Nicolet 6700 FTIR spectrometer was used to obtain the transmission Fourier transform infrared (FTIR) spectra of the asphaltene samples within a wavenumber range of 4000–400 cm^{−1}, by using a KBr technique and a baseline correction method (Chen et al., 2017; Asemani and Rabbani, 2020).

2.4. Emulsification and visual observation

The toluene-water emulsification method of Chen et al. (2017a, b) was followed in the present work. In brief, 0.2 g of bitumen, maltenes, or asphaltenes was diluted by 20 mL toluene and then mixed with 20 mL water in a 50 mL glass bottle. The mixtures were gently hand-shaken for 2 min and left to stand to phase separate for 24 h. Li et al. (2015) compared the emulsion stability prepared by hand-shaking or using a homogenizer. They observed that the emulsions prepared by the above two methods showed similar characteristics. In the present work, hand-shaking method was used due to its simplicity and relatively low energy input (Chen et al., 2017). The outward appearance and internal structure of the as-prepared emulsions were imaged by a Huawei Nova 7 phone camera and a Zeiss Axiovert 200 M microscope, respectively. A dilution method presented by Binks and Lumsdon (2000) was used to infer the emulsion type. A drop of each emulsion was added to a volume of either pure toluene or pure water. Water continuous emulsions would disperse in water and remain as an intact drop in toluene, while toluene continuous emulsions would disperse in toluene and remain as an intact drop in water. A Hitachi S-3000N cold stage scanning electron microscope was used to visualize the micro-structure of the interfacial film at oil/water interfaces by a drop freezing technique. A drop of the formed emulsions (20 μL) was deposited on the cold stage at −20 °C. The film structures were observed and captured at different magnifications.

The interfacial properties of asphaltene films at the air/water

interface were analyzed using a KSV NIMA Langmuir trough (Biolin Scientific, Sweden). An EP3 Brewster angle microscope (BAM, Accurion GmbH, Germany) fitted with a CCD camera is interfaced to the Langmuir trough, enabling real-time observation of the morphology of the asphaltene interfacial films. A laser beam is reflected at the Brewster angle ($53 \pm 2^\circ$) and the resulting signal is captured by the CCD camera. The dark background of the captured BAM images represents the water surface with low reflectivity, and the bright regions correspond to the asphaltene domains. A great brightness indicates the formation of three-dimensional asphaltene structures with multiple layers (Álvarez et al., 2010; Hua and Angle, 2013).

The trough and the two barriers are fabricated from PTFE (polytetrafluoroethylene). The Langmuir trough has a maximum area of 260 cm^2 at the fully opened position of the barriers. The presence of the BAM setup limits the closest position that the two barriers can reach, which leads to a minimum trough area of 120 cm^2 . All the components are enclosed in a cabinet to mitigate dust contamination. An active vibration isolation system (Halcyonics, Germany) is installed to monitor and stabilize the entire apparatus.

The trough and barriers were thoroughly cleaned prior to each measurement (Yu et al., 2017). Forty (40) μL of 2 mg/mL asphaltene-in-toluene solution was deposited dropwise over the entire water surface ensuring the solution was evenly distributed. After a 30-min wait period for toluene evaporation, the asphaltene film at the air/water interface was compressed from 260 cm^2 to 120 cm^2 at a compression rate of $10 \text{ cm}^2/\text{min}$ to obtain the pressure-area isotherms. Images of the films were captured in real-time during the compression by using BAM and a CCD camera. All the measurements were carried out under room temperature (22°C).

Four compression-expansion cycles were performed to study the stability and reversibility of the films. First, each film was compressed to the minimum trough area (i.e. 120 cm^2). Immediately after reaching that position, the film was expanded by moving the barriers back to the initial position corresponding to the maximum trough area (i.e. 260 cm^2) at an expansion rate of $30 \text{ cm}^2/\text{min}$. This compression-expansion cycle was repeated for three additional times. The entire four-cycle compression-expansion test was repeated at least three times to ensure the reproducibility of the results. More details regarding this technique can be found elsewhere (Hua and Angle, 2013; Yu et al., 2018).

3. Results and discussion

3.1. Chemical composition of the asphaltene samples

The data of elemental analysis are presented in Table 1. A higher C/H ratio was observed after thermal treatment of the asphaltene sample, indicating that a chemical structure modification did occur; more specifically, a higher C/H ratio suggests an increase in aromaticity of the asphaltene sample (Ancheyta et al., 2003; Chiaberge et al., 2009). The heteroatoms (S and N) were slightly concentrated in the thermally treated asphaltenes, as presented in Table 1.

The FTIR spectra, along with band assignments (Chiaberge et al., 2009; Asemani and Rabbani, 2020), are presented in Fig. 1 and Table 2, respectively. The aromatic units are characterized by an

aromatic C–H stretching vibration band at 3050 cm^{-1} , aromatic double bond stretching bands at 1666 cm^{-1} and 1597 cm^{-1} , and aromatic C–H bending bands at 866 cm^{-1} , 812 cm^{-1} , and 754 cm^{-1} . In comparison to the untreated asphaltenes, a consistent increase of absorbance values at the above-mentioned bands indicates an increased aromaticity and polarity of the asphaltenes due to thermal treatment (McLean and Kilpatrick, 1997). In contrast, no significant changes were observed in the aliphatic chains as characterized by 2922 cm^{-1} , 2854 cm^{-1} , 1454 cm^{-1} , and so on. The increased asphaltene aromaticity deduced from FTIR data (Fig. 1 and Table 2) is consistent with the CHNS elemental analysis (Table 1).

3.2. Emulsification performance of asphaltene samples

The emulsification behavior of the bitumen, maltenes, and asphaltenes was examined using a toluene-water bottle test (Chen et al., 2017). For all the investigated samples, the formed emulsions became visually stable within 1 h after preparation. Fig. 2 shows the emulsification results, which were captured at 24 h after preparation. Emulsion layer was observed in the case of bitumen, but the quantity of emulsions was not high (Fig. 2a and b). In contrast, neither the untreated maltenes nor the thermally treated maltenes were able to form stable emulsions (Fig. 2c and d). As shown in Fig. 2e and f, a substantial amount of emulsions was formed by the asphaltene samples, consistent with the well-known hypothesis that the asphaltene component of bitumen was the main emulsion stabilizer (Aske et al., 2002; You et al., 2019). In comparison to the untreated asphaltene sample, the quantity of emulsions formed by the thermally treated asphaltene sample was much higher, indicating that thermal treatment can significantly enhance the emulsion stabilizing capacity of asphaltenes. The emulsion drops remained as intact droplets in water and dispersed in toluene, indicating that the produced emulsion was mainly a W/O type emulsion. This observation is consistent with the findings of Piroozian et al. (2021) and Velayati and Nouri (2021).

3.3. Micro-interfacial structures of asphaltene films

A magnified view of the asphaltene-stabilized emulsions (Fig. 3) allows a closer examination of the morphology of the emulsion droplets. The ageing time of the emulsions was 24 h after preparation. As illustrated in Fig. 3, the droplets stabilized by the untreated and thermally treated asphaltenes present very different characteristics, although the size distributions of the droplets are similar ($10\text{--}100 \mu\text{m}$). The emulsion droplets stabilized by the untreated asphaltenes had a spherical shape with visually smooth surface and no deformation (Fig. 3a and b). In contrast, the thermally treated asphaltenes produced emulsion droplets with a rigid and wrinkle morphology (Fig. 3c and d), corresponding to a higher emulsifying capability (Figs. 2 and 3).

Cryo-SEM was used to analyze the structural conformation of the asphaltene interfacial films at a higher resolution. As illustrated in Fig. 4, approximately $10\text{--}100 \mu\text{m}$ -sized emulsion droplets can be seen for both the untreated and thermally treated asphaltenes, consistent with the optical observations shown in Fig. 3. Indeed, the SEM images clearly illustrated the wrinkle structures (a variety features of troughs, fractures, folds, and cracks) on the asphaltene films and their spatial distributions (Fig. 4). The untreated and thermally treated asphaltenes showed significantly different wrinkle structures with varying morphological and structural conformations. In comparison to the untreated asphaltenes, the interfacial films formed by the thermally treated asphaltenes appeared to be enriched in micron-scale wrinkle structures and thus were much rougher and thicker. The thickness of the

Table 1
Elemental analysis of the untreated and thermally treated asphaltene samples.

Asphaltenes	C, w/w%	H, w/w%	S, w/w%	N, w/w%	C/H
Untreated	82.03	8.13	5.79	1.18	0.84
Thermally Treated	84.39	7.64	5.82	1.27	0.92

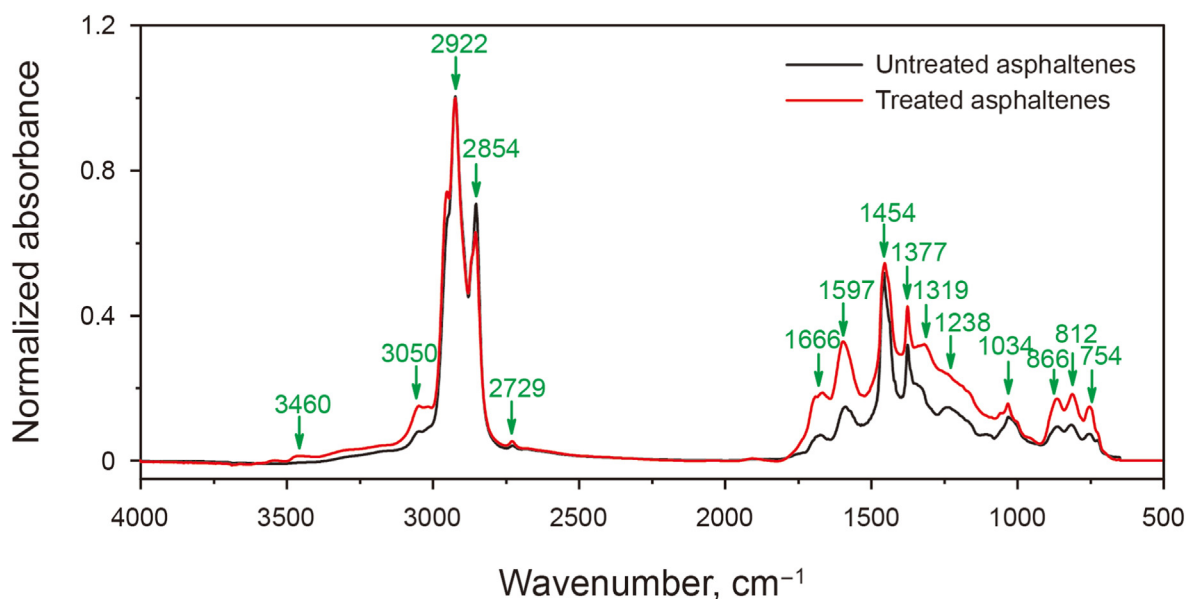


Fig. 1. FTIR spectra of the untreated and thermally treated asphaltene samples.

Table 2

FTIR band assignments based on references (Chiaberge et al., 2009; Asemani and Rabbani, 2020).

Wavenumber, cm^{-1}	Functional group
3460	O–H and N–H stretching
3050	Aromatic C–H stretching vibration
2922 and 2854	Asymmetrical stretching of C–H bond in CH_2
2729	Stretching of C–H bond in aldehyde hydrogen
1666	Breathing stretching in aromatic double bond-stretching of $\text{C}=\text{O}$
1597	Stretching of $\text{C}=\text{C}$ bond in aromatic rings
1454	Symmetrical bending of C–H in CH_2 , asymmetrical bending of C–H in CH_3 , asymmetrical stretching of $\text{C}=\text{C}$ bond in aromatic rings
1377	Symmetrical bending of C–H bond in CH_3
1319	Bending of C–H bond in CH_3 and stretching of C–O bond in carboxylic acid
1238	C–O stretching
1034	Stretching of S=O bond in sulfoxides
866, 812, and 754	Out of plane bending of C–H bond in aromatic ring structure

untreated and treated asphaltene film were determined to be $0.096 \pm 0.012 \mu\text{m}$ and $0.524 \pm 0.021 \mu\text{m}$, respectively, based on Fig. 4c and f. Yuan et al. (2020) found that the MXene/Polyurethane composite with wrinkle structures exhibits stable and stretchable mechanical properties. The observed higher stability of the treated asphaltene-stabilized emulsions (Fig. 2e and f) is most likely due to the formation of more apparent wrinkle structures (Fig. 4), which enhanced the mechanical stability/flexibility of the resulted interfacial films and consequently, created a strong spatial barrier inhibiting the coalescence of emulsified droplets.

3.4. Film formation behavior of asphaltenes at air/water interfaces

Due to the difficulty of separating and identifying the asphaltene films at the oil/water interfaces, many researchers studied the film formation behavior of asphaltenes at air/water to deduce the asphaltene behavior at oil/water interfaces, considering the fact that asphaltene behaved similarly at an oil/water interface to an air/water interface (Lawrence et al., 2004; Langevin and Argillier, 2016; Fajardo-Rojas et al., 2020). The asphaltene films at air/water interfaces were analyzed by using a combination of Brewster angle microscopy (BAM) and Langmuir trough (Pensini et al., 2014). The asphaltene-in-toluene solution was spread drop by drop ($40 \mu\text{L}$ per drop) over the air/water interface to form an evenly-distributed

thin layer on the water surface. An asphaltene film was formed following the evaporation of toluene. With the compression of Langmuir trough barrier, the BAM can provide a real-time observation of the resulting film structures at the surface of the trough. The typical snapshots are presented in Fig. 5, together with the corresponding surface pressures.

In Fig. 5, the dark background represents the water surface with low reflectivity. The first images on the left-hand side were taken following a 30-min interface stabilization before compression. The asphaltene clusters moved freely at the air/water interface and were nearly invisible inside the visual field of BAM, corresponding to a surface pressure of 0 mN/m. With the compression of Langmuir trough barrier, the plate-like asphaltene domains were observed at a surface pressure of 0.5 mN/m. The platy and rigid domains dispersed randomly in a black water background and moved randomly at the water/air interface. A further compression and consequently, a reduced available area for the asphaltene domains, led to a decreased movement and a higher surface pressure due to the collision between the asphaltene domains.

The asphaltene domains appeared a uniform brightness at low surface pressure ($< 15 \text{ mN/m}$), suggesting that they probably had the same film thickness (Fan et al., 2010; Hua and Angle, 2013). As shown in Fig. 5, regions with a brighter field of view appeared at higher surface pressure, consistent with the observations of Hua

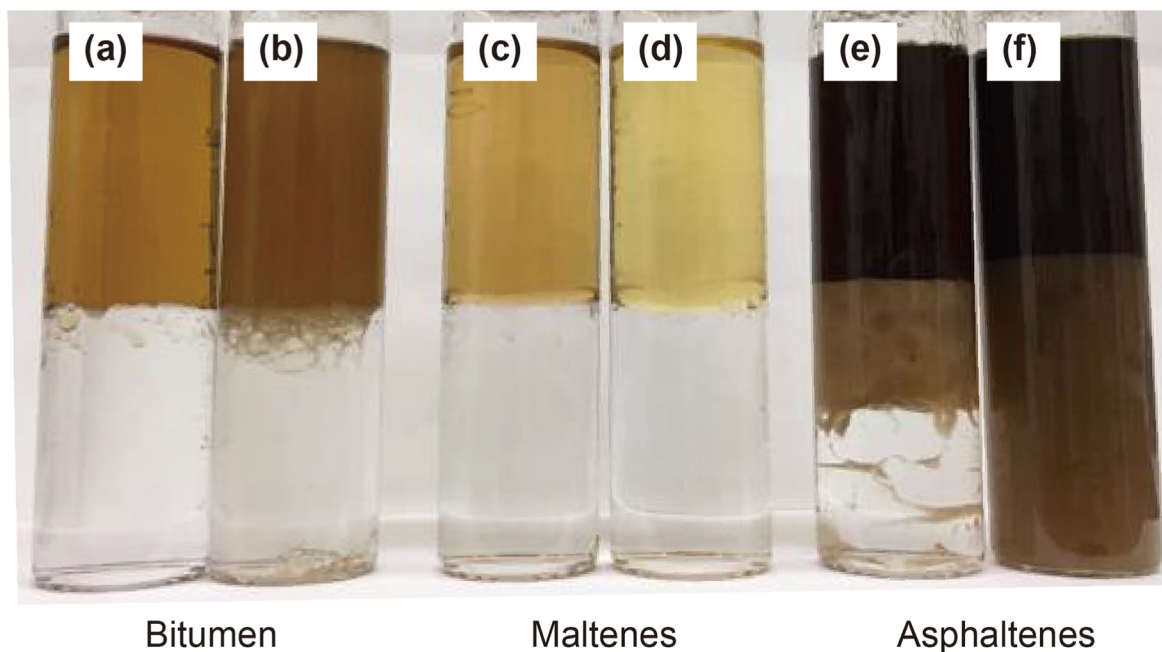


Fig. 2. Toluene-water emulsions stabilized by bitumen (a, b), maltenes (c, d), and asphaltenes (e, f) before (a, c, e) and after (b, d, f) thermal treatment. Images were taken 24 h after preparation.

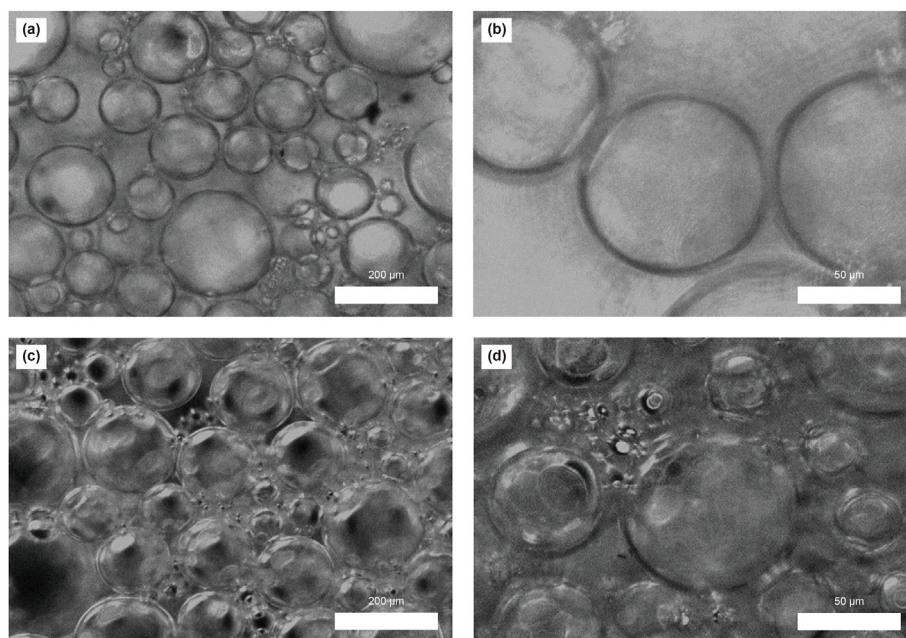


Fig. 3. Optical images of emulsion droplets stabilized by asphaltenes: untreated asphaltenes (a, b) and thermally treated asphaltenes (c, d).

and Angle (2013). The heterogeneity of asphaltene films is mainly ascribed to the varying thickness of asphaltene domains due to their overlaps under external compression. At the endpoint of Langmuir barrier (corresponding to the highest compression in this study), the asphaltene films became very compact without any visible gaps.

In Fig. 5, the untreated and thermally treated asphaltene domains appeared to have similar shapes but very different morphology. The asphaltene plates formed by the untreated asphaltenes are smooth and uniform, consistent with the

observations about asphaltene films at the water/oil interface shown in Fig. 4a–c. In contrast, a number of bright spots (i.e., high BAM reflectivity regions) are seen on the floating plates formed by the thermally treated asphaltenes. Lobato et al. (2017) observed similar phenomenon and attributed it to the aggregation of asphaltenes; they concluded that the formation of bright spots in BAM images were due to the occurrence of strong asphaltene self-aggregation. As shown in Fig. 5b, the abundance of bright spots is most likely due to the strong self-aggregation of the thermally treated asphaltene molecules (Cadena-Nava et al., 2007; Lobato

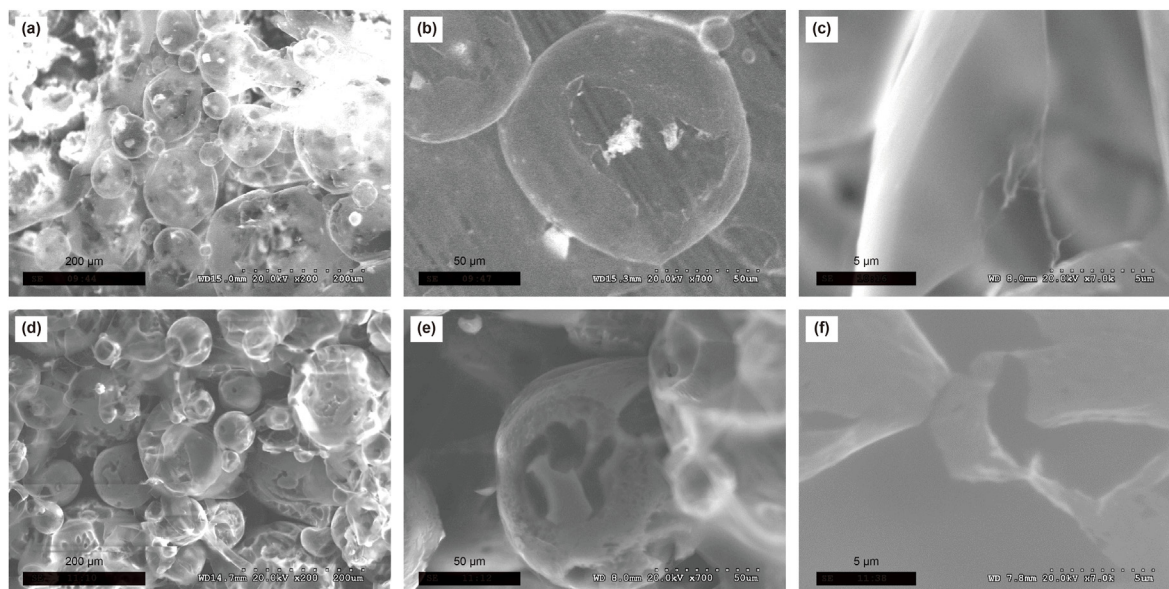


Fig. 4. Cryo-SEM images of emulsion droplets stabilized by asphaltenes: untreated asphaltenes (a–c) and thermally treated asphaltenes (d–f).

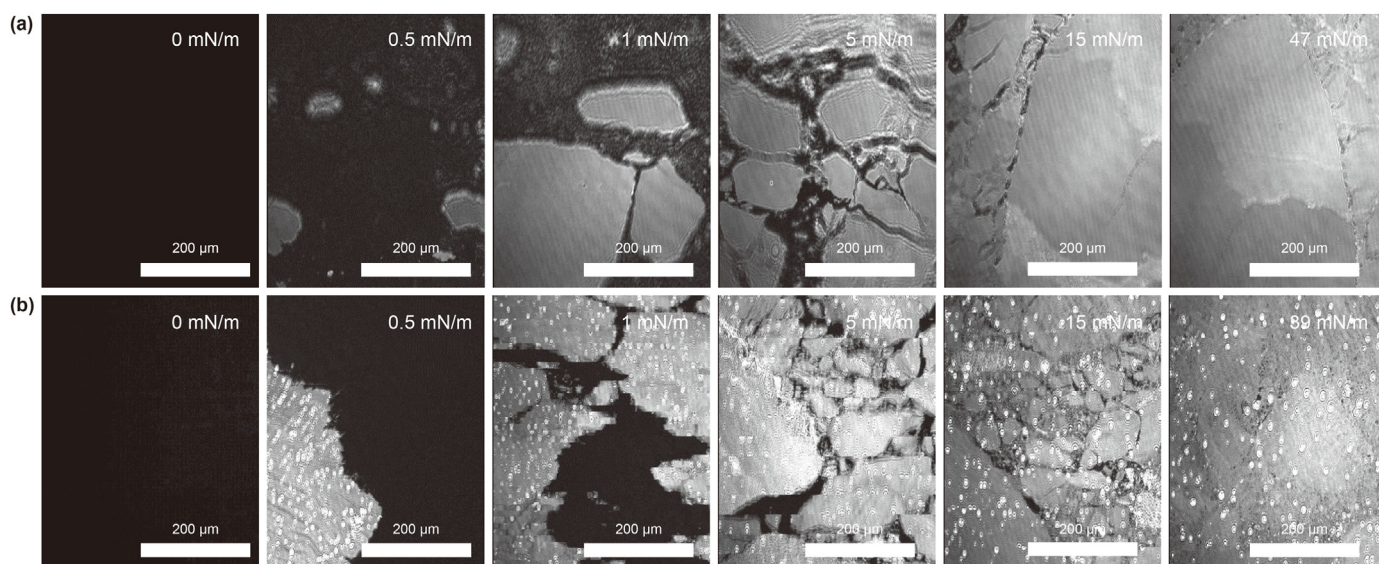


Fig. 5. BAM images of asphaltene films at different surface pressures during compression of the Langmuir trough: (a) untreated asphaltenes and (b) thermally treated asphaltenes.

et al., 2017). The presence of the colloid-like regions may provide active positions for the formation of wrinkle structures and thus favor the formation of a stable interfacial film (Zhang et al., 2017; Tian et al., 2018).

At the endpoint of compression, the maximum attainable surface pressure of the thermally treated asphaltenes was 39 mN/m, lower than the 47 mN/m of the untreated asphaltenes (Fig. 5). This observation suggests that a higher degree of three-dimensional overlap structures formed in the case of thermally treated asphaltenes, leading to a lower value of maximum attainable surface pressure (Fan et al., 2010; Hua and Angle, 2013).

The rigidity of the as-formed asphaltene films was further investigated by successive compression-expansion cycles. Fig. 6 shows the pressure-area isotherms of asphaltene films, corresponding to four compression-expansion cycles. Hysteresis was observed, likely due to the irreversible changes on the asphaltene

film caused by compression (only the compression curves are presented in Fig. 6). For the untreated asphaltenes (Fig. 6a), the surface pressure began to increase when the surface area was compressed to 225 cm²; while the surface pressure of the thermally treated asphaltenes remained at 0 mN/m until the surface area reached 180 cm². This observation indicates that the thermally treated asphaltenes formed more adaptable association structures, consistent with their substantial wrinkle structures on the interfacial films (Fig. 4d–f) (Wang et al., 2018; Yan et al., 2019). In comparison to the untreated asphaltenes, a repeated compression tests up to four times of the thermally treated asphaltene films exhibited a reduced hysteresis (i.e., a reduced variation from the initial state), suggesting that the wrinkle films of thermally treated asphaltenes had a higher rigidity and stability (Álvarez et al., 2010). No significant difference was observed after the third compression for both the untreated and thermally treated asphaltenes,

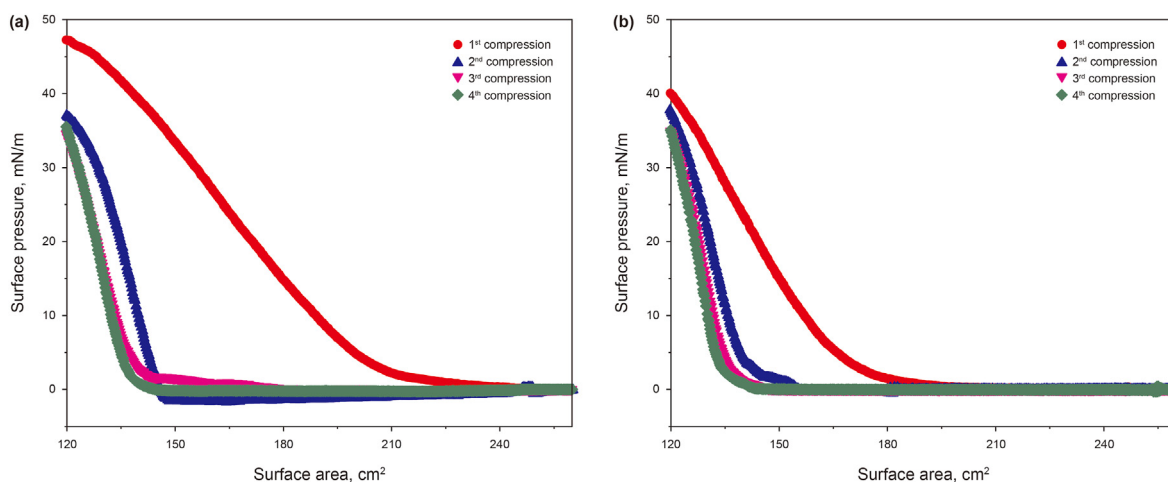


Fig. 6. Pressure-area isotherms of asphaltenes at air/water interfaces: (a) untreated asphaltenes and (b) thermally treated asphaltenes.

consistent with the rigid nature of asphaltenes as reported by many researchers (Zhang et al., 2007; Singh et al., 2018; Ismail et al., 2020).

3.5. Possible mechanism

The impact of thermal treatment on the emulsion stabilizing capacity of bitumen asphaltenes was investigated in the present work. Thermal treatment at 400 °C under nitrogen atmosphere altered the asphaltene aromaticity (Table 1 and Fig. 1) and resulted in asphaltene samples with a higher aromaticity, which is consistent with prior studies using NMR and TGA techniques (Chiaberge et al., 2009; AlHumaidan et al., 2016, 2017). The interfacial behavior between the two investigated asphaltenes samples exhibited significant difference, as shown both at an oil/water interface (Figs. 3

and 4) and at an air/water interface (Figs. 5 and 6). As schematically depicted in Fig. 7b, an abundance of wrinkle structures was formed at oil/water interfaces in the case of thermally treated asphaltenes. The formation of the observed rigid and wrinkle interfacial film is likely due to the increased aromaticity of the thermally treated asphaltene samples (Li et al., 2002; Xie et al., 2010; Gu et al., 2020). In comparison to the untreated asphaltenes, the thick and rigid interfacial films formed by the thermally treated asphaltenes enhanced the stability of emulsion droplets, thereby producing a larger volume of emulsions (Figs. 2 and 7).

The results of the present study suggest that the contact of partially upgraded bitumen with water during transportation and downstream refining processes may result in emulsions with high stability. The strong emulsification property may be undesirable for the desalting and dewatering pretreatment of crude oil before distillation.

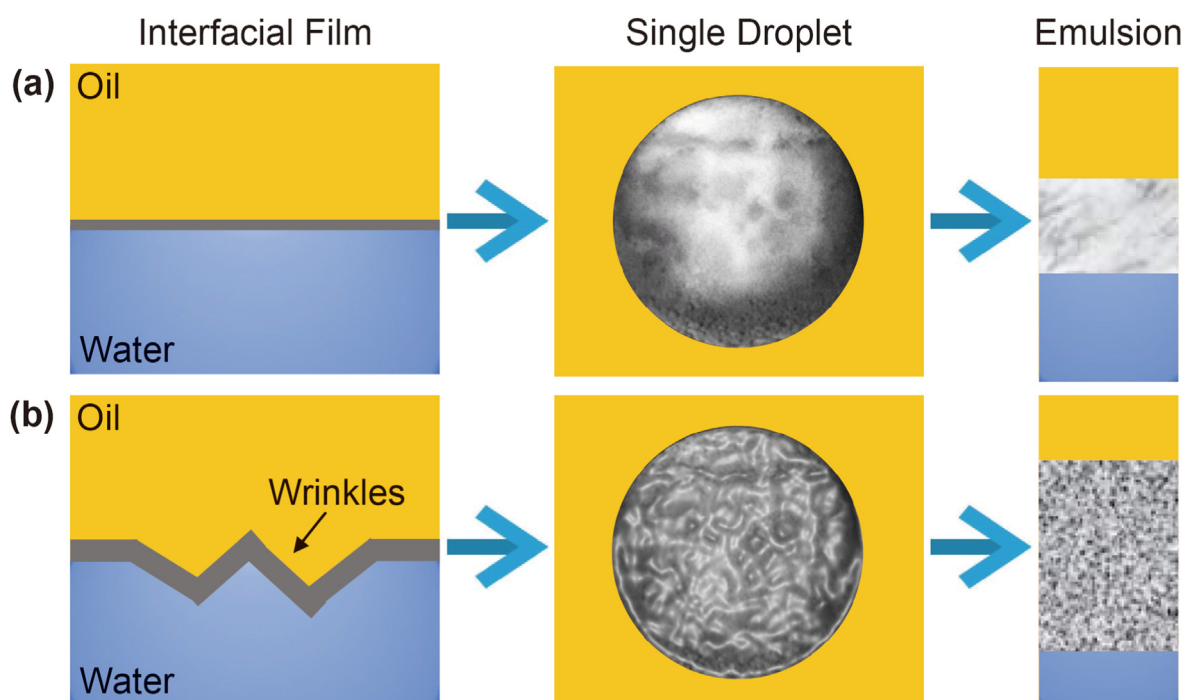


Fig. 7. Schematic depiction of emulsions stabilized by untreated asphaltenes (a) and thermally treated asphaltenes (b), showing asphaltene films at oil/water interfaces, single emulsion droplets, and an appearance of the resulted emulsion layer.

4. Conclusions

The formation of rigid asphaltene films at oil/water interfaces is largely responsible for the stability of bitumen emulsions. We investigated the influence of a mild thermal treatment on the emulsion stabilizing capacity of bitumen asphaltenes, specifically the structural morphology and mechanical property of the asphaltene interfacial films. The asphaltene emulsion-stabilizing capacity was significantly enhanced after thermal treatment at 400 °C. As visualized under cryo-SEM, the asphaltene films exhibited a micron-scale wrinkle feature. The thermally treated asphaltene samples gave larger volume of emulsions, likely due to the formation of thicker and more rigid interfacial films.

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