The effect of cationic surfactants on bitumen's viscosity and asphaltene nanostructure under thermal partial upgrading

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Abstract
Bitumen extracted from oil sands is a highly viscous fluid; thus, its transportation via pipelines in its original form resembles a major challenge. Partial upgrading is a recently proposed approach that aims to reduce bitumen's viscosity to meet the pipeline specifications. To optimize the process and make it more cost-effective, a novel approach is proposed and researched in this study. Ionic surfactants were for the first time employed to promote thermal cracking reactions and dispersion of asphaltenes in bitumen at elevated upgrading temperatures. Three surfactants representing the cationic, nonionic, and anionic charges were studied at the thermal upgrading conditions (360–400°C) at their optimal addition ratios to mimic the bitumen partial upgrading conditions. The results demonstrated that the cationic surfactant (dodecyltrimethylammonium bromide, DTAB) surpassed the other two surfactants and that with the addition of only 0.25 wt% of it, it can effectively reduce the viscosity of bitumen by up to 60% more than the upgraded bitumen with no additives under the same upgrading temperature. The Saturates, Aromatics, Resins, and Asphaltene analysis revealed that the contents of saturates and aromatics within the upgraded bitumen were also enhanced when DTAB was added. Moreover, the detailed asphaltene nanostructural analysis using X-ray diffraction, high-resolution transmission electron microscope, and thermogravimetric analysis revealed that the addition of the cationic surfactant (DTAB) resulted in an increased asphaltene nanostructural disorder, smaller polycyclic aromatic hydrocarbons size, and increased fringe curvature, as compared with the upgraded bitumen's asphaltene with no surfactants. Hence, the results have suggested that DTAB, a cheap and readily available ionic surfactant, can serve as a potential upgrading additive for designing partial upgrading procedures to produce upgraded bitumen with much less viscosity at lower upgrading temperatures.
This upgrading technique will result in an upgraded bitumen that requires significantly reduced volumes of diluent for transportation.

**KEYWORDS**
asphaltene, oil sand bitumen, partial upgrading, surfactants, thermal cracking

# INTRODUCTION

With the continuous increase in energy demand, the conventional oil resources will stand insufficient on their own to fuel the world and fill the energy gap. Hence, new unconventional resources of energy have to be exploited worldwide. Canada, for instance, has a vast amount of oil reserves, ranking it as the fourth-largest oil producer and exporter in the world.\(^1\) Unconventional oil resources consist of heavy oil, extra-heavy oil, oil sand, tar sands, oil shale, and bitumen. Currently, more than half of the world’s oil reserves (~53.3%) are in the form of unconventional oil reserves.\(^2\) As a result, much attention has been directed towards the abundant yet inefficiently utilized petroleum resources such as oil sands and heavy “bitumen” oil. These unconventional resources present a much-under-utilized energy core, and with the expected increase in oil prices, their production and transportation present themselves as an increasingly economically viable solution. Oil sands are mainly defined as a mixture of sand, water, and bitumen, which are known to be physically separable. Bitumen is made up of a highly complex mixture of large hydrocarbon molecules infused with up to 5% sulfur compounds by weight and some minor heteroatoms impurities such as oxygen and nitrogen and metals (including vanadium and nickel).\(^3\),\(^4\)

Bitumen is a highly viscous fluid, and its transportation resembles a significant challenge, especially since it has a dynamic viscosity somewhere between \(2 \times 10^5\) and \(2 \times 10^6\) (mPa/s or cP), and a density of >1000 kg/m\(^3\) at atmospheric conditions.\(^5\) Such high viscosities make transporting bitumen via pipelines to the refineries in their original state very difficult. The Canadian pipeline specifications require the oil to have a dynamic viscosity of 300 cP (or equivalently, the kinematic viscosity of 350 cSt) or less and a density of ≤940 kg/m\(^3\) at the reference temperature of 7.5°C for winter.\(^6\) Table 1 below shows a comparison between the different types of oil as compared with the required Canadian pipeline specifications.

As a result of this limitation, there are currently two major strategies that are employed by producers to meet the pipeline specifications criteria to transport bitumen. These strategies are (A) diluting bitumen with expensive diluents (condensate or light naphtha) or (B) fully upgrading bitumen to synthetic crude oil using large upgrading and refining facilities.\(^8\) However, both methods have revealed some major drawbacks in the past few years. For instance, when considering Option A, the diluents used to transport bitumen to the United States usually result in an extra production cost of $14 per barrel of bitumen.\(^7\) Also, about 33% of the pipeline capacity is lost due to the additional volume of the diluents.\(^7\) Moreover, additional costs are needed for the final separation of the diluents from transported bitumen.

On the other hand, when considering Option B, despite having four full upgraders currently operating in Alberta, the government has no intentions for any additional full upgraders, because any investment in such plants is no longer cost-effective.\(^10\) The full upgrading plants are usually facilitated with catalysts and hydrogen gas, which allows them to highly improve the quality of the oil, reducing its viscosity, sulfur and nitrogen contents, and any other heavy metal content.\(^11\),\(^12\) However, the cost of operation is high and yet the four full upgraders can only treat 35% of Alberta’s bitumen before being sold to the market. Another drawback of the full upgraders is that they lead to significant greenhouse gas (GHG) emissions during the refining process. The oil sands operations currently emit 70 Mt of GHG per year, accounting for about 8% of Canada’s total GHG emissions.\(^13\) Therefore, a new alternative must be implemented on an industrial scale.

| Property          | Pipeline specs | Athabasca bitumen | Diluted bitumen | Fully upgraded synthetic crude oil |
|-------------------|----------------|-------------------|-----------------|----------------------------------|
| Viscosity (cSt)   | <350           | 1,000,000 (Average) | 200–300        | 10                               |
| Density (kg/m\(^3\)) | <940          | >1000             | 920             | 850                              |
| API (°)           | >19            | >8                | >20             | >30                              |

Note: *API is the API gravity which is a common used index of the density of a crude oil or a refined product.
to address the bitumen transportation demand and the older solutions’ drawbacks. The new approach of bitumen partial upgrading manifests as a good alternative when compared with the full upgrading techniques. Partial upgrading seems to be a more efficient and cost-effective strategy that aims to reduce the intensity and cost of upgrading, while producing bitumen that meets pipeline specifications. This technology not only will be more economically viable but also will generate substantial gains in employment, labor income, exports, and government revenue. Partial upgrading brings bitumen to something resembling a medium-heavy crude that can be easily transportable at a lower cost per barrel than full upgrading, while at the same time producing much lower GHG emissions.14

Although the idea of partial upgrading seems promising in principle, there is still a considerable need to demonstrate the viability of optimizing this technique. Against this background, the work reported herein is to develop a new approach to partially upgrade bitumen to pipeline transportable crudes at a low cost and reduced GHG emissions.

One promising approach is to address bitumen’s heaviest and most polar molecular fraction, which is the asphaltene. Asphaltenes are defined as the fraction of oil that is insoluble in paraffin solvents (usually n-pentane or n-heptane) but soluble in aromatic solvents such as toluene or dichloromethane.15 The asphaltene component is generally associated with forming a colloidal suspension of aggregates and this is one of the leading causes for the elevated viscosity of bitumen. As a result, the degree of association and dispersion of the aggregates is an important factor in the microstructure and mechanical behavior of bitumen. Asphaltenes are considered a major problem due to their tendency to associate and precipitate during oil production, upgrading, and refining. They reduce the oil flow and can even cause blockages during production and have severe drawbacks during the processing of heavy ends such as the tendency to form coke deposits in heat exchangers and reactors and to deactivate or poison catalysts.10

Chemical surfactants are commonly used as dispersing agents for asphaltenes in crude oils to prevent their precipitation in pipelines during enhanced oil recovery. So, an interesting approach is proposed to investigate the effects of these surfactants at the operating conditions of bitumen partial upgrading. The strategy aims to modify the colloidal structure of bitumen to reduce the interactions between the asphaltene aggregates so that agglomeration is reduced. The addition of surfactants to oil for viscosity reduction purposes was recently reported in the literature17,18 but on a limited scope. In these studies, surfactants were tested for their abilities to deasphalt or to promote asphaltene dispersion under atmospheric or mild conditions. It was noted that the surfactant molecules can progressively get attached to the available sites on asphaltene molecules/aggregates, occupying most of the available sites and sterically hindering the interactions between the asphaltene aggregates. The surfactant molecules can also cover some layers on asphaltene aggregates that provide steric stability, preventing them from aggregating into larger structures. Ortega et al.17 found out that the addition of dodecylbenzenesulfonic acid as a chemical surfactant was sufficient enough to significantly enhance the viscosity of the bitumen at 60°C (mild condition). Also, it was noted that there was a more significant reduction in the viscosity curves when the samples were thermally treated at temperatures around 170°C. In another study, Kwon et al.18 found that the use of surfactants with a short alkyl chain was the best way to maximize the efficiency of asphaltene removal at atmospheric conditions. The viscosity of bitumen decreased by a factor of six times when it was compared with the cases in which surfactants were not used.

However, studies related to asphaltene cracking behavior in the presence of surfactants during high-temperature thermal upgrading (>350°C) have not been documented in the literature. There is no clear correlation between the charge or concentration of the surfactant and its efficiency in asphaltene cracking and dispersion at high temperatures. This might be justified due to the fear of thermally decomposing the surfactants at elevated temperatures greater than 250°C. However, most surfactants, such as the ones chosen in this study, might be able to initiate some desirable free radical reactions at lower temperatures before their degradation,19 which means that even if the thermal upgrading was carried out at the elevated temperatures of ~400°C, the effect of the surfactants in partial upgrading will remain a predominant factor. Any increase in temperature beyond 400°C would greatly reduce the influence of the surfactants, as most of them will be highly prone to decomposition. Therefore, the novel approach of studying the effect of the surfactant addition on the structure of asphaltene at the partial upgrading conditions between 360°C and 400°C is proposed. A series of anionic, cationic, and nonionic surfactants will be tested within bitumen and investigated through the thermal partial upgrading technique in a sealed autoclave reactor. In this study, surfactants will be preblended with bitumen at their optimum concentrations and tested at the elevated temperatures: 360°C, 380°C, 390°C, and 400°C to mimic the bitumen partial upgrading conditions and evaluate the effect of high thermal stress on the surfactant’s ability to alter the asphaltene fraction and improve its
rheological properties. It is important to note that temperatures >400°C were ignored in this study, because, in our preliminary experiments, it was noticed that upgrading bitumen at temperatures in the range of 400–500°C tends to generate a noticeable amount of coke. Hence, temperatures above 400°C were greatly decreasing the liquid yield of the upgraded bitumen and 360–400°C seems to be a more reasonable range that can significantly reduce the viscosity of bitumen, while at the same time maximize the liquid yield of bitumen.

2 | EXPERIMENTAL METHODOLOGY

2.1 | Materials

2.1.1 | Bitumen

Oil sand bitumen obtained from Alberta’s Athabasca reservoirs was used as the main feedstock for the experimental analysis presented in this study. Table 2 below represents the main physical properties of the bitumen used for this study. The viscosities of the samples were measured according to the ASTM D4402 standard using the ROTAVISC rotational viscometer (procured from IKA), a reproducibility of ±1%, and a measuring range of 100–4,000,000 cP. The density measurements were obtained using a specific gravity hydrometer purchased from Fisher Scientific following the ASTM E100 standard. The saturates, aromatics, resins, and asphaltene (SARA) analysis was performed according to the ASTMD2007‐98 standard procedure and the average measurements of the original bitumen fractions are also reported in Table 2.

2.1.2 | Surfactants

All the surfactants (in solid form) that were tested were purchased from Fisher Scientific with purities >97% and their chemical structures are summarized in Table 3. DTAB is a cationic surfactant that has the molecular formula of CH₃(CH₂)₁₁N(CH₃)₃Br. This surfactant has been previously proven to promote oil recovery in petroleum reservoirs. The improvement in the oil recovery was due to the ability of the surfactants to (a) reduce the oil/water interfacial tension; (b) generate foam in porous media; and (c) modify rock wettability so that it shifts toward water‐wet conditions. Furthermore, surfactants such as DTAB were proven by Kwon et al. to greatly improve the bitumen properties through an effective deasphalting mechanism at low temperatures.

Span 60 is a nonionic surfactant which is also known as “sorbitan monostearate,” it has the molecular formula of C₃₂H₆₄O₆, and it has no net charge. Span 60 has proven its ability to induce the cracking reactions in favor of converting asphaltene and resins to smaller hydrocarbon molecules hence, improving the gas oil to resin ratios.

SDS belongs to a group of surfactants called alkyl sulfates and it has the chemical formula of CH₃(CH₂)₁₁SO₄Na. SDS has a linear molecular structure that consists of 12 carbon atoms in the form of a hydrophobic chain attached to a negatively charged sulfate group. Thus, SDS can significantly interact with asphaltene molecules at the interface between asphaltene molecules. Moreover, it can potentially reduce the π−π interactions between asphaltene molecules, which are considered the main contributor to asphaltene stacking.

2.2 | Sample processing method

The bitumen was preheated using hot water until it became flowable (oil temperature should be about 80°C); then, about 60 g of bitumen was added to the autoclave (Parr Bench Top Reactor of series 4590). After that, the surfactant was added to bitumen and stirred at 300 r.p.m. for 1 h at 60°C to form a homogenous blend. The bitumen sample was then thermally treated at the preset temperatures (360–400°C) for 2 h then was left to cool down to room temperature.

After each run, the upgraded bitumen was removed from the autoclave and its physical properties such as

| Properties | Measured values | Error bar (±) |
|------------|-----------------|---------------|
| Viscosity (cP) | 330,000 | 1% |
| TAN (mgKOH/g) | 4.32 | 0.1 |
| Density (kg/m³) | 1020 | 5 |
| API | 7.23° | |

Abbreviations: SARA, saturates, aromatics, resins, and asphaltene; TAN, total acid number.
viscosity, density, and asphaltene content were measured. Later, the asphaltene fraction (insoluble in \(n\)-pentane) was extracted from the treated bitumen and subjected to detailed characterization tests.

2.3 | Characterization

2.3.1 | Thermogravimetric analysis (TGA)

TGA was conducted on the liquid bitumen samples using the apparatus Pyris 1 TGA (Perkin-Elmer) under a nitrogen environment. Each run was conducted using ~10 mg of bitumen per run. During the TGA analysis, the samples were heated from 20°C to 600°C with a heating ramp of 30°C/min and \(N_2\) flow rate of 30 ml/min.

2.3.2 | X-ray diffraction (XRD)

The structural parameters of asphaltene particles were obtained by using the X-ray diffraction patterns within the range of 10°–60° with a step size of 0.02°/step using the Rigaku DMax diffractometer. Before the analysis, a portion of the asphaltene sample was ground for ~1 min and then mounted with the help of ethanol as a solvent. The XRD results obtained were used to calculate \(L_a\) (diameter of the aromatic sheet), \(L_c\) (height of the stack of aromatic sheets), and \(d\) (layer distance between the aromatic sheets).

2.3.3 | High-resolution transmission electron microscope (HRTEM)

The transmission electron microscope (Titan 80-300 LB), which is an HRTEM that operates at 80 and 300 keV accelerating voltage with an ultimate lattice resolution of 0.24 nm, was used to record the microstructural details of the upgraded asphaltene particles. After being ultrasonicated in ethanol for 10 min, the dried asphaltene samples were placed on a lacy carbon-coated copper grid, and the TEM images were obtained from different sites of the asphaltene samples.

3 | RESULTS AND DISCUSSION

3.1 | Oil sand bitumen physical properties

3.1.1 | The effect of temperature on bitumen partial upgrading with no additives

In the first step, bitumen was thermally upgraded at different temperatures within the range of 360–400°C with 10°C increment as described earlier in an autoclave reactor. This step will serve as a basis (control) to help compare the properties of the upgraded bitumen with and without the addition of surfactants. It was noticed that within the upgrading temperature range of interest, the liquid product yield of around 97%–98% can be easily achieved without any significant coke formation. The SARA analysis was then performed on all the samples, and a summary of the obtained results is included in Table 4. The SARA analysis for the thermally upgraded bitumen samples suggests that, as the upgrading temperature increases from 360°C to 400°C, the fractions of asphaltenes and resins continuously decrease reaching their minimum at 400°C. At the same time, the fraction of aromatics readily increases with temperature, which suggests that the asphaltene and resins were primarily thermally cracked into aromatics. Rapid reduction of resin content to aromatics was also observed within the 380–390°C range, indicating that the resin fraction was activated within this temperature range. Saturates were
slightly decreasing with temperature, which might be due to some polymerization reactions that might convert them to aromatics. The rheology and physical properties of the original and thermally upgraded bitumen were also measured and compared in Table 5. The trends of those physical properties suggest that the thermal treatment is one of the effective means to reduce bitumen’s viscosity. The viscosity of the original bitumen (measured at 25°C) decreased from an initial value of 330,000 cP steadily with temperature, reaching a minimum value of 1700 cP (for the upgraded bitumen at 400°C). Although similar trends were observed for the viscosity values measured at a lower temperature (7.5°C) that were mainly used to mimic the Canadian pipeline specification conditions, the lowest viscosity value observed at 400°C was 5500 cP (measured at 7.5°C). This viscosity value that was achieved by thermally upgrading bitumen at 400°C on its own still stands way above the required criteria of 300 cP.

### 3.1.2 The effect of surfactant addition to bitumen before thermal upgrading

To determine the effect of surfactant on bitumen before conducting the thermal cracking reactions, various bitumen samples were premixed with an equal amount of the three different surfactants, in the form of solid powder, with different concentrations and charges. Physical properties such as viscosity, density, total acid number (TAN), and SARA composition were measured for each sample accordingly. The results suggested that the viscosity and density measurements in addition to the SARA analysis were almost identical to the original bitumen samples. This means that the addition of small quantities of surfactants (up to 1 wt%) on their own is not enough to alter any physical property within the original unupgraded bitumen. Therefore, the properties of the original bitumen and the unupgraded bitumen with surfactants are identical and the two terms hereafter are interchangeable. A better indication of the preupgrading results is shown in Table 6.

### 3.1.3 The effect of surfactant charge on bitumen through thermal partial upgrading

To study the effect of the surfactant charge on the thermal upgrading of bitumen, the samples were premixed with an equal amount (0.5 wt%) of different surfactants with different charges. The samples were then thermally upgraded in the autoclave at 360°C (fixed temperature) for 2 h. Then, 360°C was chosen in this case, as it was the minimum thermal upgrading temperature in this study. A low temperature will assist in identifying the magnitude of surfactants’ effect on the bitumen’s viscosity for the best comparison. The viscosities of upgraded oil samples were measured and the obtained results are shown in Table 7.

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**TABLE 4** SARA analysis for the upgraded bitumen at various temperatures

| Fractions | Original bitumen | Bitumen upgraded at 360°C (%) | Bitumen upgraded at 380°C (%) | Bitumen upgraded at 390°C (%) | Bitumen upgraded at 400°C (%) | Error bar (±; %) |
|-----------|-----------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-----------------|
| Saturates | 18%             | 20%                           | 20%                           | 20%                           | 19%                           | 0.5%            |
| Aromatics | 29%             | 39%                           | 47%                           | 53%                           | 53%                           | 0.5%            |
| Resins    | 30%             | 23%                           | 19%                           | 14%                           | 10%                           | 1%              |
| Asphaltenes | 20%           | 15%                           | 14%                           | 14%                           | 13%                           | 0.5%            |

Abbreviation: SARA, saturates, aromatics, resins, and asphaltene.

**TABLE 5** Viscosity and density measurements for the upgraded bitumen at various temperatures

| Sample                | Density (kg/m³) | Measured @ 40°C | Viscosity (cP) measured @ 25°C | Measured @ 7.5°C |
|-----------------------|-----------------|-----------------|-------------------------------|-----------------|
| Original bitumen      | 1020            | 200,000         | 330,000                       | NA              |
| Upgraded @ 360°C      | 1000            | 12,000          | 45,000                        | 150,000         |
| Upgraded @ 380°C      | 990             | 3000            | 7000                          | 22,500          |
| Upgraded @ 390°C      | 985             | 1250            | 4000                          | 9000            |
| Upgraded @ 400°C      | 980             | 132             | 1700                          | 5500            |

Abbreviation: NA, not available.
As shown in Table 7, the bitumen sample that was premixed with the cationic surfactant (DTAB) and thermally upgraded at 360°C recorded the minimum viscosity of 7000 cP (measured at 40°C). That is, the cationic surfactant was able to promote about a 42% reduction in viscosity as compared with the viscosity of the bitumen cracked at the same temperature with no additive (12,000 cP). The anionic surfactant was able to reduce the viscosity to about 8000 cP (33% reduction), while the nonionic surfactant has the least influence on the viscosity of the bitumen, which was reduced only by about 16.7%. This concludes that the addition of surfactants to bitumen before upgrading indeed promotes viscosity reduction. The results of the thermally cracked bitumen viscosity versus surfactant concentration are shown in Figure 1.

Figure 1 shows that the optimum surfactant concentration recorded was about 0.25 wt%. At this concentration, the viscosity of the cracked oil was reduced to a minimum of 17,000 cP from initially 45,000 cP (measured at 25°C). That is, the viscosity was reduced by about 62% as compared with the original sample at the same upgrading conditions. It is important to note that as the surfactant concentration increases beyond 0.25 wt%, the viscosity of the thermally cracked oil tends to increase as well. This can be explained by the fact that higher surfactants concentrations can promote the development of large-sized aggregates or flocculates due to the increased surfactant-asphaltene interactions. Consequently, greater shear forces will be required to overcome these interactions and, hence, larger viscosity values are recorded.

### 3.1.4 | The effect of surfactant concentration on bitumen’s properties via thermal partial upgrading

Bitumen samples were premixed with different concentrations of DTAB (cationic surfactant) from 0 to 1.0 wt% and thermally cracked at 360°C (fixed temperature). The viscosities of the cracked oil samples were then measured to determine the optimum surfactant concentration for viscosity reduction. The results of the thermally cracked bitumen viscosity versus surfactant concentration are shown in Figure 1.

Table 7 shows that the optimum surfactant concentration recorded was about 0.25 wt%. At this concentration, the viscosity of the cracked oil was reduced to a minimum of 17,000 cP from initially 45,000 cP (measured at 25°C). That is, the viscosity was reduced by about 62% as compared with the original sample at the same upgrading conditions. It is important to note that as the surfactant concentration increases beyond 0.25 wt%, the viscosity of the thermally cracked oil tends to increase as well. This can be explained by the fact that higher surfactants concentrations can promote the development of large-sized aggregates or flocculates due to the increased surfactant-asphaltene interactions. Consequently, greater shear forces will be required to overcome these interactions and, hence, larger viscosity values are recorded.

### 3.1.5 | The effect of the temperature of partial upgrading on surfactant activity

To study the effect of surfactants on bitumen under various thermal stresses and how the temperature affects the performance of the surfactants, a fixed
A concentration of 0.25 wt% of DTAB (optimum concentration) was selected and premixed with bitumen samples and thermally upgraded under 360, 380, 390, and 400°C. The viscosities of the upgraded samples were then measured and tabulated in Table 8. Similarly, even with the addition of surfactant, as the upgrading temperature increases, the viscosity of the oil products also decreases proportionally. The addition of DTAB enhanced the viscosity reduction by 62.5% at 360°C (from 12,000 to 4500 cP); however, the effect of the surfactant reduced as the upgrading temperature increased to the 380–390°C range. At this range, the surfactant was still able to reduce the viscosity of bitumen by around 53%. As the temperature reached 400°C, the thermal cracking dominated the reactions. The effect of the surfactant at this high temperature was further reduced and resulted in a viscosity reduction of only 22.7% from 132 to 102 cP (measured at 40°C) and 27% reduction from 5500 to 4000 cP (measured at 7.5°C).

The SARA analysis was performed on the upgraded oil samples with surfactants to study the effect of the surfactant (DTAB) on the compositional changes within the upgraded bitumen. The SARA results were summarized in Table 9 below. The results suggest that the addition of DTAB greatly affected the resins fraction which was mainly cracked into lighter fractions (aromatics and saturates). There is still a tiny fraction of aggregates formed due to the increased DTAB-asphaltenes interactions which led to a slight increase in the asphaltene content as compared to the samples upgraded without surfactant. The sum of the heavy fractions of resins and asphaltenes decreased with elevated temperatures, from 33% at 360°C down to 22% at 400°C. Thus, it can be concluded that the overall contribution to the thermal cracking reactions induced by DTAB was more than the contribution of the polymerization reaction resulting in a net reduction in the shear forces within the hydrocarbon molecules and, hence, reducing the viscosities. Compared with the summation of resins and asphaltenes shown in Table 4, the addition of the surfactant is deemed effective in the reduction of resins and asphaltenes at relatively low temperatures. As the temperature increases, there is a slight reduction in the saturate fraction accompanied by a slight increase in the aromatics. Furthermore, the increased temperature resulted in further cracking reactions within the heavier fractions (resins and

| Bitumen partially upgraded at | Measured @ 40°C | Viscosity (cP) measured @ 25°C | Measured @ 7.5°C |
|-------------------------------|----------------|--------------------------------|-----------------|
| 360°C                         | 12,000         | 45,000                         | 150,000         |
| 360°C + DTAB                  | 4500           | 17,000                         | 55,000          |
| 380°C                         | 3000           | 7000                           | 22,500          |
| 380°C + DTAB                  | 1400           | 3200                           | 10,500          |
| 390°C                         | 1250           | 4000                           | 9000            |
| 390°C + DTAB                  | 570            | 1850                           | 5150            |
| 400°C                         | 132            | 1700                           | 5500            |
| 400°C + DTAB                  | 102            | 1300                           | 4000            |

Abbreviation: DTAB, dodecyltrimethylammonium bromide.
asphaltenes), which were readily decreasing with temperatures reaching their minimum values at 400°C.

3.1.6 | The effect of surfactant addition on bitumen transportation properties

As previously mentioned, to decrease the viscosity of bitumen to a value acceptable by the Canadian pipeline specification (i.e., 300 cP), about 33 wt% of diluent must be premixed with bitumen before its transportation. Given this requirement and with the help of the diluent concentration correlation provided by Gray,7 the amount of diluent required by bitumen at various upgrading conditions was interpolated from the diluent concentration graph in Gray7 and tabulated in Table10 below.

According to the calculated diluent concentrations presented in Table 10, there is a continuous decrease in the diluent requirement with the increase in upgrading conditions. The addition of a small amount of DTAB has a noticeable effect in reducing the diluent requirement for the upgraded bitumen. At 390°C, for instance, with the addition of 0.25 wt% DTAB, the upgraded bitumen sample had a viscosity of 1850 cP measured at 25°C. This viscosity now requires only 12 wt% of diluent to reach the required pipeline specification of 300 cP instead of the earlier 33 wt% that was needed. Thus, 21% of the diluent required for blending with original bitumen can be reduced, resulting in 21% of the pipeline capacity freed (originally occupied by the extra diluent), which can be used to transport more bitumen every time the partially upgraded bitumen is pumped.

To confirm that the addition of 0.25 wt% of the DTAB surfactant will not worsen the corrosivity of resulted bitumen, the TAN of the upgraded oil products did not increase with the addition of 0.25 wt% of the tested surfactants. As a result, little to no extra corrosion is expected in this case.

3.2 | TGA

3.2.1 | The effect of temperature on bitumen partial upgrading with no surfactant addition

The oil vaporization tendency is a crucial parameter in identifying the changes within the oil fractions through determining the rate of weight loss as a function of temperature. Therefore, to identify those changes within the hydrocarbon fractions of both the original and upgraded bitumen samples, TGAs were performed. The variations in oil weight loss versus temperature for the original and upgraded bitumen samples, alongside their derivatives (differential thermogravimetry [DTG]) were measured and plotted in Figure 2. It can be observed from the plots in Figure 2 that the original oil sand bitumen (represented by the black line) is quite heavy that weight loss is not observed until temperature reach ~200°C. After the thermal treatment, bitumen is partially cracked into lighter products. Higher the treatment temperature more lighter products are obtained. This is evidenced by the TGA results that the starting point for weight loss moves to a lower temperature as the thermal
treatment temperature is increased. At the same time, the thermal stress initiated some heavier fractions (resins and asphaltenes) to get cracked into lighter products. Looking at the DTG curves, it is observed that the maximum derivative (decomposition temperature) occurs at the temperature range between 480°C and 490°C. At this temperature range, most of the oil fraction is decomposed into lighter fractions. Moreover, with the increase in upgrading temperature, the value of the maximum derivative peak tends to decrease and the curve tends to flatten more over a wider temperature range. This phenomenon occurs, as the original bitumen were cracked into lighter hydrocarbons during thermal partial upgrading.

3.2.2 | The effect of surfactant charge on bitumen’s TGA

The variations in oil weight loss versus temperature for upgraded bitumen with the three differently charged surfactants at a fixed temperature of 360°C alongside their derivatives (DTG) were measured and plotted in Figure 3.

From the TGA graph, one can see that all the differently charged surfactants had almost the same effect on the thermal degradation of bitumen. The presence of surfactant (regardless of its charge) within the upgraded oil samples slightly lowered the maximum decomposition temperature. This can further be witnessed by looking at the DTG peaks of the upgraded samples in which the derivative peaks are slightly shifted to a lowered temperature. Moreover, the surfactants caused a significant reduction in the (residue) coke fraction to about 10 wt% as compared with the “no surfactant” sample, which yielded about 18 wt% at 600°C. These results further ascertain the hypothesis of the attachment of surfactant molecules to the asphaltenic fraction, which promoted the initiation of free radical reactions and ultimately resulted in the enhanced rheological properties of the upgraded bitumen.

3.2.3 | The effect of surfactant concentration on bitumen’s TGA

The variations in oil weight loss versus temperature for upgraded bitumen with different concentrations of the surfactant (DTAB) at 360°C alongside their derivatives (DTG) were also measured and plotted in Figure 4. From the thermograms, one can see that regardless of the surfactant concentration used, the temperature shift that occurred to all the upgraded bitumen samples with different surfactant concentrations was very similar to each other. The presence of the surfactant even in very low concentration is still enough to result in a shift in the

| TABLE 11 Measurements of the TAN of the upgraded bitumen products |
|---------------------------------|----------------|-----------|
| Bitumen upgraded at            | TAN (mgKOH/g) | Error bar (±) |
| Unupgraded bitumen             | 4.32           | 0.2       |
| 360°C                           | 3.46           | 0.2       |
| 360°C + 0.25 wt% DTAB          | 3.41           | 0.2       |
| 360°C + 0.25 wt% Span 60        | 3.98           | 0.2       |
| 360°C + 0.25 wt% SDS           | 3.02           | 0.2       |

Abbreviations: DTAB, dodecyltrimethylammonium bromide; SDS, sodium dodecyl sulfate; TAN, total acid number.
maximum decomposition temperature from 500°C to about 480°C. This shift is more visible as the concentration of the surfactant increases. Moreover, the surfactants caused a significant reduction in the coke formation as they reduced the coke yield from 18 wt% to 9 wt%.

### 3.2.4 The effect of temperature and surfactant on bitumen’s activation energy

Further analysis of the thermal stability of the upgraded oil was performed by calculating the activation energy of oil-cracking conversion using the kinetic model discussed in reference [27]. In this model, the oil fraction conversion ($\alpha$) is defined as $\alpha = \frac{(M_0 - M_T)}{(M_0 - M_L)}$, with $M_0$ being the initial mass of the oil sample, $M_T$ is the mass of partially converted oil at temperature $T$, and $M_L$ is the leftover mass. The reaction model or conversion function is denoted by $g(\alpha)$ and it can be related to the oil fractional conversion ($\alpha$) by the following equation:

$$\ln(g(\alpha)) = \ln\left(\frac{A}{B}\right) - \left(\frac{E_a}{RT}\right)$$

where

$$g(\alpha) = 1 - \frac{2\alpha}{3} - (1 - \alpha)^{2/3}.$$
While obeying the Arrhenius equation, $k = A e^{(E_a/RT)}$, $A$ is the pre-exponential factor, $B$ is the constant heating rate $dT/dt$, $E_a$ is the activation energy of oil conversion, and $T$ is the temperature in °K. Then, $-\ln (g(\alpha))$ is plotted against $1000/T$ for all the oil samples (original, upgraded, and upgraded with surfactant) and the activation energies ($E_a$) were calculated from the slope of the best tangent lines to the curves. The plots of the conversion functions versus temperature are presented in Figure 5 and the calculated activation energies are shown in Table 12. The $E_a$ plot for the original bitumen is different from those obtained for the thermally treated bitumen. Three sections of linearity appear to be for the original bitumen, whereas, on the other hand, two linear sections were observed for all the partially upgraded bitumen. This suggests that thermal cracking has modified the molecular structure of bitumen. The two sections in the upgraded bitumen samples represented the two activities (high temperature and low temperature) separated at a critical point, where a change in the slope occurs. This observation confirms that the thermal cracking process is preceded by a vaporization stage, but as the temperature increases more chemical cracking reactions are induced. The thermal reaction stages in the TGA results are represented by the activation energies $E_{a1}$ and $E_{a2}$, corresponding to the vaporization and thermal cracking stages, and can be calculated from the slopes $-E_a/R$ of the straight lines. The kinetic parameters of the vaporization and thermal cracking sections were obtained by linear regression. The activation energies, $E_{a1}$ and $E_{a2}$, which are calculated for all the upgraded bitumen samples at various conditions showed the coefficient of determination $R \geq 0.98$.

Significant differences in the activation energies of the bitumen samples were observed, starting with the lowest activation energy for the original bitumen which required 16 kJ/mol ($E_{a1}$) to initiate its vaporization phase and 38 kJ/mol ($E_{a2}$) to initiate the cracking phase beyond the critical temperature of 352°C. It is to be noted that there is an intermediate phase for the original bitumen (between the normally identified two phases) denoted with $E_{a3}$, the value of the activation energy of this intermediate phase was about 25 kJ/mol. However, after the partial upgrading of bitumen, this intermediate phase almost vanished. From the activation energy plots of the upgraded samples, one can see that there was a gradual increase in activation energies proportionally with the increase in upgrading temperatures reaching a maximum of 104 kJ/mol for $E_{a1}$ and 56 kJ/mol for $E_{a2}$ at 400°C. On the other hand, the bitumen sample upgraded at only 360°C with 0.25 wt% DTAB had the activation energies of 99 and 56 kJ/mol for $E_{a1}$ and $E_{a2}$, respectively. That means that the addition of surfactant indeed promoted further cracking reactions and generated a more stable partially upgraded oil that almost has the same properties and activation energies as the oil samples processed at much higher upgrading temperatures such as 390°C and 400°C.

Surfactants tend to disassemble normally is not good. Among the three surfactants DTAB, Span 60, and SDS, Span 60 is more stable than the other two surfactants, 90% of which was decomposed by the temperature reaching 300°C (as shown in Figures S1–S3 shown in the supplementary materials. About 50% of Span 60 can survive until temperature beyond 400°C. The viscosities of bitumen samples with addition of DTAB and SDS are much lower than the one with addition of Span 60, as shown in Table 7. This observation may suggest that surfactants may indeed act as a reaction activator/initiator in the thermal upgrading process of bitumen. Addition of surfactants to bitumen, the alkyl chains of surfactant, are expected to strongly interact with asphaltene-resin colloid. At elevated temperatures, surfactant molecules are expected to thermally fracture to generate radicals, which can initiate the thermal cracking reaction, and promote the reactivities of resins and asphaltenes that are absorbed on surfactant molecules. Compared with the SARA results of thermally treated bitumen shown in Tables 4 and 9, one can note that, with the presence of DTAB, more resins were converted to aromatics at lower temperatures (e.g., 360°C and 380°C). The structure changes of asphaltenes, confirmed by the XRD and HRTEM results shown in the Section 3.3, support the proposed mechanism. The effect of surfactant to the reactivity of asphaltenes aggregates is well agreed with the reports in the literature. Ortega et al. demonstrated that ionic surfactants such as dodecylbenzene sulfonic acid were able to affect the reaction mechanism of asphaltenes through the protonation of heteroatomic components in the asphaltenes.

### 3.3 XRD of asphaltene

#### 3.3.1 The effect of temperature on bitumen’s asphaltene structure after partial upgrading

To further understand the effect of temperature and surfactant addition on the heavier fractions of bitumen, the asphaltene fractions were extracted from the thermally upgraded bitumen and dried in the oven overnight until the asphaltene particles were solidified and became retrievable. The XRD analysis was then
performed on the asphaltene particles and the results are shown in Figure 6. The results of the analysis mainly showed two peaks at the 2θ scale at around 22° and 44° for the asphaltene treated at 360°C; however, only one peak was observed at 44° for the unupgraded sample. Although the peaks for the 380°C and 400°C samples were located at around 25° and 45°, respectively. The peak in the range of 22–25° is assigned to the (002) plane and it contains information about the interlayer spacing and the layer distance between the aromatic sheets.29 The peak in the range of 44–45° is assigned to the (100) plane and is an indicator of the average sizes of the aromatic sheets in the asphaltene sample. The quantitative analysis of these two peaks provides information about the nanostructure of the asphaltene fraction of bitumen under various thermal stresses. These
parameters manifest in the \( d_{002} \) value as per Bragg's law (see equation Equation 3), the nanocrystallite height \( (L_c) \), which indicates the height of the stack of aromatic sheets, using the Scherer formula (see Equation 4), and the nanocrystallite width \( (L_a) \), which provides the average diameter of the aromatic sheet using Equation 5. Moreover, the number of aromatic sheets per stack or stacking number \( (M) \) and the number of aromatic rings per aromatic sheet \( (N_{OAr}) \) are also calculated using Equations 6 and 7, respectively, as shown below:

\[
d_{002} = \frac{\lambda}{2 \sin \theta_{002}},
\]

\[
L_c = \frac{0.9\lambda}{B_{002} \cos \theta_{002}},
\]

\[
L_a = \frac{1.84\lambda}{B_{100} \cos \theta_{100}},
\]

\[
M = \frac{L_c}{d_{002}} + 1,
\]

\[
N_{OAr} = \frac{L_a}{2.667}.
\]

In these equations, \( \lambda \) = wavelength of X-rays (0.154 nm for Cu K\( \alpha \)), the Bragg angles are \( \theta_{002} \) and \( \theta_{001} \), and the full width at half maximum (FWHM) values are \( B_{002} \) and \( B_{100} \) for the two peaks. The Bragg angles and the FWHM were then obtained by the Gaussian fitting of the respective peaks using Matlab software as was done by Abdrabou et al. in reference [30]. The obtained values are listed in Table 13. To verify the repeatability of the results, each XRD result was repeated at least three times and then the arithmetic mean of the calculated values was reported in addition to their SDs. The SD \( (\sigma) \) was calculated by subtracting each result from the mean, then squaring the difference and adding the results. Then the sum of squares was divided by the number of trials minus one and taking the square root of the result.
As evident from Table 13, the interlayer distance between the aromatic sheets is slightly decreasing with temperature due to the thermal stress exerted on the asphaltene particles, although the difference is still minor. Substantially, the reduced \( L_c \) values confirm that the nanocrystallites present in the thermally cracked asphaltene samples contains thinner and finer hydrocarbon stacks with a reduced number of graphene layers per stack compared with the original asphaltene sample. This decrease in aromatic sheet thickness was attributed to the loss of aliphatic carbon in the side chains and, consequently, resulting in a decrease in the number of aromatic sheets per stack, aka stacking number (\( M \)). Similar results were also obtained in reference [31].

On the other hand, the increasing values of \( L_a \) at elevated thermal stresses imply that the increase in thermal upgrading severity drives the asphaltene molecules towards the core nature structure. The asphaltene fraction is known to have an asphaltenic core, which is sometimes referred to as the coke fraction in some studies.\(^{31,2,3}\) The asphaltenic core in extreme thermal upgrading conditions tends to undergo secondary reactions such as dealkylation of side aliphatic chains, cyclization of alkyl chains, and combination of aromatic ring radicals via polymerization.\(^{32}\) These reactions are the possible reason for the noticeable increase in the diameter of the aromatic sheet (\( L_a \)) and hence the increase in the number of aromatic rings in a single aromatic sheet (\( \text{NO}_{\text{ar}} \)).

### 3.3.2 The effect of surfactant on the upgraded asphaltene nanostructure

The XRD analysis was performed on the asphaltene samples recovered from the thermally cracked bitumen at a fixed temperature (360°C) with and without the addition of DTAB surfactant, and the results are shown in Figure 7. The results showed some similarities to the previous analysis with two peaks at the \( 2\theta \) scale at around 22° and 44°. However, it is noticed that there might be a third peak at 25° for the surfactant blended

| TABLE 13 Asphaltene parameters calculated from XRD plots |
|---------------------------------------------------------|
| Properties | Definition | \( \sigma \) |
|------------|------------|---------------|
| \( d_{002} \) (nm) | Layer distance between the aromatic sheets | 3.6 ±0.01 nm |
| \( L_a \) (nm) | Diameter of the aromatic sheet | 35 ±0.5 nm |
| \( L_c \) (nm) | Thickness of the stack of aromatic sheets | 9 ±0.5 nm |
| \( \text{NO}_{\text{ar}} \) | Number of aromatic rings in the aromatic sheet | 13.12 |
| \( M \) | Mean stacking number | 3.50 |

Abbreviation: XRD, X-ray diffraction.

**FIGURE 7** X-ray diffraction (XRD) pattern of asphaltene samples from cracked bitumen at 360°C with and without dodecyltrimethylammonium bromide (DTAB).
sample that did not appear earlier. This additional peak is identified as the γ-band and it is usually attributed to the loosely held long-chain aliphatic structure (i.e., highly amorphous carbon structure attached to the aromatic rings). Equations E3–E7 were again used in collaboration with the Matlab code to obtain the Bragg angles and the FWHM via Gaussian fitting of the XRD plots and the calculated parameters are shown in Table 14 below:

The addition of 0.25 wt% of DTAB to bitumen followed by thermal treatment resulted in an asphaltene that has a slightly greater layer distance between the aromatic sheets ($D_m$).

The addition of the surfactant caused the $L_c$ value to decrease to about 50% of its original value mimicking the effect of increasing the upgrading temperature, which exerted additional stress on the asphaltene particles, the reduced $L_c$ values confirm that the nanocrystallites present in the surfactant-containing asphaltene samples contains thinner and finer hydrocarbon stacks with a reduced number of graphene layers per stack as compared with the asphaltene sample with no surfactant. Similarly, the increase in the value of $L_a$ to double the value with the addition of surfactant implies that the surfactant induced a similar effect on the asphaltene nanostructure as the increase in thermal upgrading severity due to temperature increase initially did. To verify the conclusions drawn from the XRD analysis, TEM images were obtained and carefully analyzed.

### 3.4 HRTEM of asphaltene

Figure 8 represents the HRTEM images of the original (unupgraded) bitumen’s asphaltene obtained at different magnifications (20, 10, and 5 nm scale). These images will be considered as the basis and will be used to draw comparisons with the thermally and chemically treated asphaltene particles under various conditions. Figure 9 represents HRTEM images of the asphaltene nanoparticles extracted of the partially upgraded bitumen at 360, 380, and 400°C at different magnifications (20, 10, and 5 nm scale) without the use of surfactant. It is clear from the micrographs that as the upgrading temperature increases, the severity of the cracking reactions within the asphaltene fragments also increases; hence, more tortuous and smaller fragments are observed. To further analyze the effect of the surfactant “DTAB” on the nanostructure of the asphaltene at low partial upgrading conditions, HRTEM images of the bitumen’s asphaltene upgraded at 360°C with 0.25 wt% DTAB were obtained and shown in Figure 10. The images in Figure 10 suggest that the addition of DTAB to the upgrading process of bitumen could indeed enhance the degree of cracking, leading to a reduction in the size of the asphaltene particles. Qualitatively from the images, it can be

| Properties | Upgraded at 360°C | Upgraded at 360°C with 0.25 wt% surfactant (DTAB) | SD (σ) |
|------------|------------------|---------------------------------|--------|
| $D_m$ (nm) | 3.82             | 4.15 ±0.01 nm                   |        |
| $L_a$ (nm) | 12.00            | 22                              | ±0.5 nm|
| $L_c$ (nm) | 11.55            | 5.7                              | ±0.5 nm|
| NOar       | 4.50             | 8.25                            |        |
| $M$        | 4.02             | 2.37                            |        |

Abbreviation: DTAB, dodecyltrimethylammonium bromide; XRD, X-ray diffraction.
FIGURE 9  High-resolution transmission electron microscopy (HRTEM) images of the asphaltene of the partially upgraded bitumen at 360, 380, and 400°C at different magnifications (20, 10, and 5 nm scale) without surfactant.

FIGURE 10  High-resolution transmission electron microscopy (HRTEM) images of the asphaltene of the partially upgraded bitumen with 0.25 wt% dodecyltrimethylammonium bromide (DTAB) at 360°C at different magnifications (20, 10, and 5 nm scale).
witnessed that the effect of DTAB at 360°C in terms of asphaltene nanostructural disorder is very similar to that resulting from the upgraded bitumen at 400°C; however, this assumption must be proven further qualitatively. Therefore, this possibility of the nano-structural disorder within the asphaltene particles can be confirmed by analyzing the small stacking lines commonly referred to as the fused aromatic ring structures. This process can be performed by estimating the graphene layers (fringes) length distribution and degree of tortuosity within the upgraded bitumen’s asphaltene micrographs. A quantitative analysis of the fringe length and tortuosity was performed using the Matlab code based on the algorithms reported by Yehliu et al., where the HRTEM images were subjected to negative transformation and grayscale. The negative transformation is defined as $I_{\text{negative}} = L - I_{\text{original}}$, where $I_{\text{original}}$ is the image pixel values before transformation and $L'$ is the discrete intensity levels. On selected multiple regions of interest, operations such as Gaussian filter, histogram

FIGURE 11 Matlab images, fringe length, and tortuosity index of asphaltene particles, for (A) bitumen upgraded with no surfactant and (B) bitumen upgraded with 0.25 wt% dodecytrimethylammonium bromide (DTAB)
equalization, and Tophat transformation were performed to eliminate errors due to nonhomogeneous illumination across the image, as well as to improve the fringe contrast. The branches from fringes were removed by a process called skeletonization using built-in functions in Matlab that uses a parallel thinning algorithm. Relative to these branch points, fringe length was determined in all directions. The smallest branch was identified, and the branch connections were broken by setting the first pixel to this branch as zero. The detailed procedure, equations, and algorithms used are listed in detail in reference [34].

For each sample, an HRTEM image consisting of 50–100 particles is chosen for homogeneity of the primary particle structure, of which 5 high-resolution microstructural images of each primary particle are randomly chosen and subjected to Matlab image processing as discussed above. The mean values of the fringe length and fringe tortuosity are then calculated using the Matlab code. The analysis was repeated five times for each image and the arithmetic mean values were reported in addition to their error bars. Samples of the processed fringe images for the asphaltene particles are shown in Figure 11.

From Table 15, one can conclude that asphaltene particles obtained from the original bitumen had a mean fringe length of 0.81 nm which decreases to 0.72 nm in the case of upgraded bitumen using DTAB. Moreover, the analysis of the tortuosity index also suggests that the short fringes in the surfactant treated asphaltene had a higher curvature (2.06) as compared to original bitumen asphaltene (1.76). The tortuosity index measures the curvature of fringes within the planar aromatic framework of graphene layers. Such curvatures in aromatic layers prevent the development of long-range graphitic stacks, resulting in the reduction in the overall particle size of the asphaltene particle. Therefore, it is more evident that the shorter fringe length and largely curved fringes make the asphaltene particles retrieved from the bitumen upgraded with DTAB surfactant highly disordered and amorphous. This suggests that the effect of increasing the upgrading temperatures on the asphaltene nanostructure can similarly be mimicked by adding a small quantity of DTAB to the bitumen and upgrading it at a much lower temperature.

### 4 | CONCLUSION

A systematic investigation of the effect of adding ionic surfactants to bitumen before its thermal partial upgrading was performed. Bitumen was partially upgraded within the temperature range of 360–400°C with surfactants of different charges and concentrations. The physical properties such as viscosity, density, and SARA composition of the upgraded bitumen at all upgrading conditions were then measured. The results revealed that the addition of 0.25 wt% of the cationic surfactant “DTAB” was the optimum condition for maximizing the reduction in bitumen’s viscosity. DTAB was able to reduce the viscosity of the upgraded bitumen by 62%, 53%, and 27% at the upgrading conditions of 360, 380, and 400°C, respectively, as compared with the bitumen upgraded without any additives. To further understand the hydrocarbon fractions compositional changes within the bitumen samples, TGA was performed on the partially upgraded bitumen samples both with and without surfactant. The results revealed that the addition of surfactants led to a significant reduction in the Heavy Gas Oil (R3) fraction and induced an earlier mass reduction plateau as compared with the original samples. This indicates that the surfactants were able to promote more cracking reactions at high temperatures and cause the heavier hydrocarbon fractions (R3 and R4) to break down into smaller and lighter fractions within the upgraded bitumen. Furthermore, the upgraded bitumen with surfactants showed significantly higher initial activation energies as compared with samples with no surfactant. This $E_a$ calculation acts as an indicator for the

| Asphaltene sample                  | Mean fringe Length (nm) | Mean fringe tortuosity |
|------------------------------------|-------------------------|------------------------|
| Original (unupgraded) bitumen      | 0.81 ± 0.01 nm          | 1.76                   |
| Upgraded at 360°C                  | 0.78 ± 0.01 nm          | 1.78                   |
| Upgraded at 380°C                  | 0.78 ± 0.01 nm          | 1.94                   |
| Upgraded at 400°C                  | 0.78 ± 0.01 nm          | 1.97                   |
| Upgraded at 360°C with 0.25 wt % DTAB | 0.72 ± 0.01 nm          | 2.06                   |

Abbreviation: DTAB, dodecyltrimethylammonium bromide; HRTEM, high-resolution transmission electron microscope.
enhanced stability that the surfactants induced within the upgraded bitumen samples. Solid asphaltene samples were then recovered from the upgraded bitumen and subjected to XRD and HRTEM analysis to understand the effect of surfactants on bitumen’s heaviest fractions. The detailed morphological characterization of the asphaltene samples using HRTEM and XRD techniques revealed an increase in the hydrocarbon structural disorder (greater fringe tortuosity and shorter fringe length), within the asphaltene nanostructure with the addition of DTAB. This change in the asphaltene nanostructure may be an indication of the additional cracking reactions that the surfactants induced during the thermal upgrading process.

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Additional supporting information can be found online in the Supporting Information section at the end of this article.

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