



Effect of ultrasound irradiation on asphaltene aggregation and implications to rheological behavior of bitumen

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ABSTRACT

The present work investigates the contribution of asphaltene aggregation to bitumen viscosity subject to ultrasound irradiation. A West-African bitumen with a viscosity of 12043 cP at room temperature was sonicated at low (38 kHz) and mild frequency (200 kHz) under controlled gas environment including air, nitrogen (N₂) and carbon dioxide (CO₂). The rheology of the bitumen, asphaltene content analyses as well as spectral studies were conducted. Herein was found that sonicating the bitumen at 200 kHz under air-environment reduces the initial viscosity up to 2079 cP, which was twice larger than that obtained when a low frequency was used. In respect of the gas environment, it was shown that ultrasound irradiation under N₂ environment could lower the bitumen viscosity up to 3274 cP. A positive correlation between the asphaltene content and the viscosity reduction was established. The results from the spectral analyses including Fast Fourier Infrared and the observations from Scanned Electron Microscope were consistent with the rheological studies and led to the argument that the viscosity reduction results from either the scission of long chain molecules attached to the aromatic rings (when the applied frequency was altered under fixed gas environment) or the self-aggregation of asphaltene monomers (when gas environment was changed at fixed frequency).

1. Introduction

Bitumen has raised a considerable interest because of its potential to compensate the depletion of conventional resources in addition to the large reserves (~5,505 billion of barrels) reported to sit within the reach of existing fields [1]. Bitumen is an asphaltic, dense, and viscous hydrocarbon in its natural state. These attributes dictate its extraction, transportation, and to a certain extent its processing at the surface facilities [2,3]. Thermal methods are the most advanced and understood recovery techniques as far as bitumen recovery is concerned [4].

In a classical thermal approach, the heat is supplied to the oil-bearing matrix, causes the oil to vaporize and facilitates thereby the oil flow. Unfortunately, thermal recovery methods are not only energy-demanding but also, they are sensitive to the formation heterogeneity. More importantly, these methods are challenged by the poor sweeping efficiency of injected fluid [5]. Alternative approaches have been extensively investigated as part of efforts to propose cost-effective methods [6]. These include dilution of bitumen with light compounds [7], bitumen heating [8], formation of oil-in-water emulsions [9–11], drag reduction [12] or even viscosity reduction via annular flow through

pipelines [13] and more recently the electromagnetic waves [14,15].

In respect of the potential of electromagnetic waves, the literature reports that microwaves [16], gamma irradiation [17], as well as ultrasound treatment [18,19] have raised considerable interest; with the latter being the scope of this paper. Ultrasound waves are emitted at a frequency equal to (or greater than) 16 kHz. The fundamental mechanism of the ultrasound waves involves the stretching of the molecular spacing of fluid through which the propagation occurs [20]. The oscillations within the fluid are thus subsequent to a compression and rarefaction phenomena from which micro-bubbles are formed [21].

These microbubbles implode further violently during the compression stage releasing thereby a considerable amount of energy. The literature reports that the collapse of microbubbles creates the microvoids, high local pressures as high as 1000 atm, and high transitory temperatures that may reach up to 5000 K [22,23]. Both the chemical and physical effects of ultrasound waves have been well exploited in chemistry (sonochemistry) as the chemical effects have the ability to generate free chemical radicals [24], while the physical effects can enhance the reactivity of a catalyst by enlarging its surface area or even by increasing a reaction rate [25].

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Meribout (2018) reviewed that enhancing the oil production using ultrasonic treatment (1) was much cheaper than conventional recovery methods, (2) was less-energy demanding, and (3) allows a better control of the ultrasonic wave propagation. As per the same author, the primary challenge is the relatively limited range of ultrasonic radiation (up to 2 m) at the operational resonance frequency, which usually ranges from 20 to 40 kHz [26]. This is to say that this method still suffer from deeper understanding to make meaningful and consistent scientific elaborations despite the wealth of papers covering the topic [27–33].

To probe the mechanisms of oil viscosity reduction, one has to look at the molecular structure and/or the composition of the propagating medium, therefore [34,35]. Montes et al. (2018), and later Cui et al. (2020), showed that combining the ultrasound irradiation with addition of nanoparticle could disrupt the viscoelasticity of asphaltene, which leads to a decrease in viscosity [36,37]. Mansouri et al. (2021) combined ultrasonic waves with different frequencies and magnetic nanoparticles. They argued that the viscosity of heavy crude oil could be reduced from 87.2 to 65.7 cSt after sonicating the oil for 10 min at 20 °C, which was concomitant with a decrease in asphaltene concentration.

It appears from the literature that the viscosity reduction pertains to (1) asphaltene re-dissolution [18,38], (2) conversion of asphaltene molecules by dehydrogenation [27], or (3) conversion of asphaltenes to lighter aromatics [39,40]. At any rate, controlling the solubility of asphaltene under ultrasound irradiation, could provide significant insights on the reduction of bitumen viscosity. However, most of the reported works have emphasized either on the applied frequency or irradiation time (up to 2 h) or even the addition of foreign materials. The available literature seemingly disregards the influence of the environment under which the irradiation takes place.

This is particularly relevant if one recalls from a chemistry point of view that asphaltene monomers self-aggregate as a result of a decrease in their solubility within the dispersed medium, which itself depends strongly on the environment [41]. Thus, the present work investigates the contribution of asphaltene on viscosity reduction of bitumen. The further objective is to establish the extent to which both applied frequency as well as the gas environment impact the formation of asphaltenes and subsequently alter the viscosity.

To achieve this purpose, the viscosity of the bitumen was measured at different applied ultrasonic frequencies and gas-environments. The contribution of asphaltenes were then investigated and the mechanisms pertaining to viscosity reduction are equally discussed.

2. Material and methods

2.1. Material

The bitumen sample, used in the present work, was sampled from the surface equipment in an oilfield located in the Gulf of Guinea. The properties of the candidate bitumen are outlined in Table 1.

2.2. Methods

2.2.1. Sonication of the candidate bitumen

The ultrasound irradiation of bitumen was performed in two different apparatuses, whose schematics are depicted in Fig. 1.

A low (38 kHz) and a mild frequency (200 kHz) were considered.

Table 1
Physico-chemical properties of the investigated bitumen.

Physical Properties	API gravity (°)	7.700
	Specific gravity (-)	1.017
Chemical Properties	Total Acid number (mg KOH/g-oil)	6.587
	Total Base Number (mg HCl/g-oil)	0.435
	Mercaptan Content (wt.%)	5.742
	Asphaltene Content (wt.%)	85.04

When the sonication was performed either at 28 or 200 kHz, the ultrasound waves were generated by an ultrasonic generator (Kaijo TA-4021) and the submersible traducer ensured the sonication (Fig. 1a). On the other hand, an Ultrasonic Cleaner (C 100D, Kaijo, Japan) was used when the sonication of the bitumen was performed at 38 kHz (Fig. 1b).

The output power for 38 and 200 kHz were computed to be 19.3, and 25.2 W, respectively. These output powers were determined by calorimetric method, whose procedure is detailed elsewhere [42]. Five grams of oil were weighed, and loaded into a flat bottom flask, which was later immersed into a water bath (25 °C). The flat bottom flask was placed 3 cm above the submersible traducer; optimal distance at which the cavitation for the equipment used is maximal [24].

The bitumen was then allowed to reach the equilibrium temperature. The sonication environment was generated by flushing the gas of interest in the reactor cell through an 0.4- μm glass tube at rate of 0.2 ml. min^{-1} for a minimum of 15 min prior sonication. Three gases were considered including air, nitrogen (N_2 , 99.9% pure), and carbon dioxide (CO_2 , 99.9% pure). To investigate the influence of the gas environment, the applied frequency was fixed at 38 kHz. On the other hand, the effect of the applied frequency was evaluated under air environment.

In either case, ice floes were immersed into the water bath to mitigate the increase in temperature inherent to ultra-sound irradiation. The ultrasound irradiation was performed continuously for 1, 2, and 3 h. Fig. 2 shows sample photographs of sonicated bitumen using a 200 kHz frequency under air environment.

At the end of each respective sonication time, the rheological properties of the oil were measured as per the procedure described in the following section.

2.2.2. Rheological studies

At room temperature and before sonication, the sample appears solid (Fig. 3a).

The oil flow could only be initiated when the bitumen was heated at temperature equal or greater than 70 °C (Fig. 3b, c). For these reasons, viscosity measurements of the bitumen and those of sonicated bitumen were performed at 70 °C using a Brookfield programmable rheometer (Model DV-III) over the shear rate in the range from 4 to 30 sec^{-1} .

2.2.3. Asphaltene extraction

To extract the asphaltenes from the bitumen (or the sonicated bitumen), 1 g of oil was accurately weighed and transferred to a 100 ml Erlenmeyer flask. The oil was then diluted with toluene at a volume ratio of 1:10, oil:toluene. The mixture was stirred at 1500 rpm using a magnetic stirrer (D Lab, MS H280-pro) for 2 h and the resulting solution was then filtered through a 0.45 μm filter paper.

One volume of the filtrate was added to 20 volumes of pentane, followed by storage overnight at atmospheric conditions. The precipitates were separated from the supernatant fluid by vacuum filtration using a pre-weighed filter paper (0.45 μm). The filtered solids (asphaltenes) were then dried at ambient conditions; after this step, no further purification of the precipitated asphaltenes was performed.

The concentration in asphaltenes was computed as the quotient of the difference of the filter paper after and before the filtration to the initial mass of oil. Both toluene and pentane were purchased from Junsei (Japan) and were used as received.

2.2.4. Spectral analyses

The spectral analyses used in this study included Fourier Transform Infrared Spectra (FT/IR) and Scanning Electron Microscopy (SEM). The former was performed on fresh and sonicated bitumen, while the latter was used for asphaltenes extracted from oils.

Fourier Transform Infrared Spectra (FTIR) of the fresh bitumen and those of the sonicated bitumen were acquired using a Jasco spectrophotometer (Model 4100, Japan). All the absorption spectra were acquired from 400 to 4000 cm^{-1} with 48 scans and a resolution of 1 cm^{-1} . A baseline correction was performed prior to the analysis. It is worth

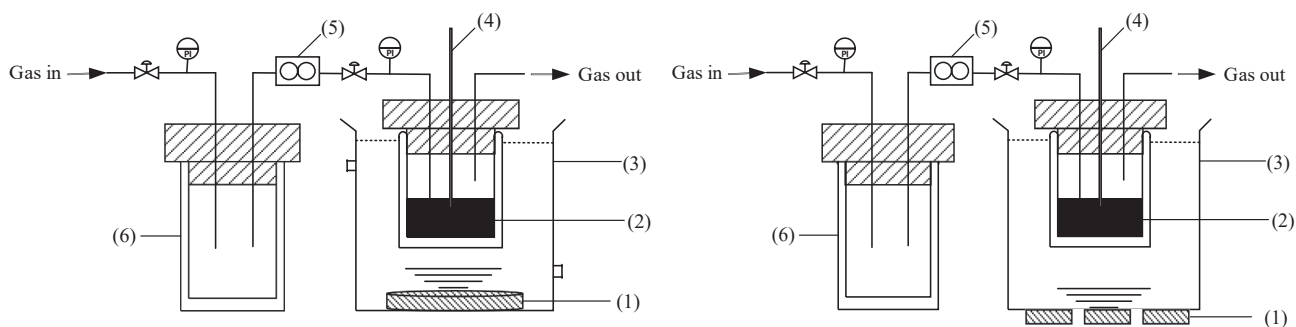


Fig. 1. Schematic representation of ultra-sonication equipment used for bitumen irradiation; (1) submersible transducer; (2) bitumen sample; (3) thermostatic water bath; (4) thermocouple; (5) gas flowmeter; (6) gas holding tank.

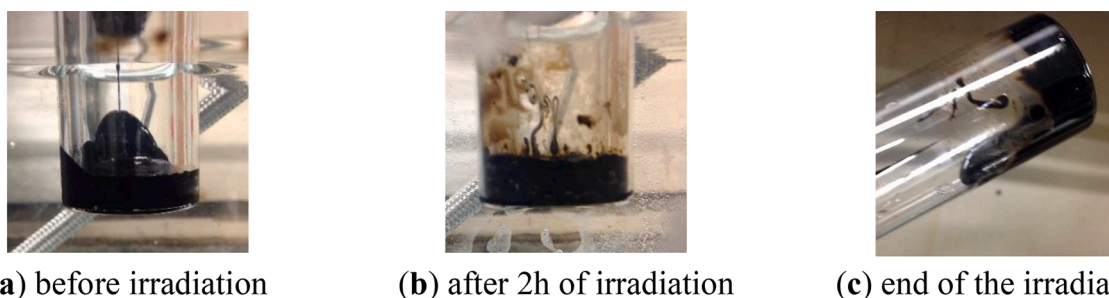


Fig. 2. Photographs of (a) fresh bitumen and sonicated bitumen after (b) 2 h and (c) 3hr; no efforts were performed to trap the light ends of the oil.

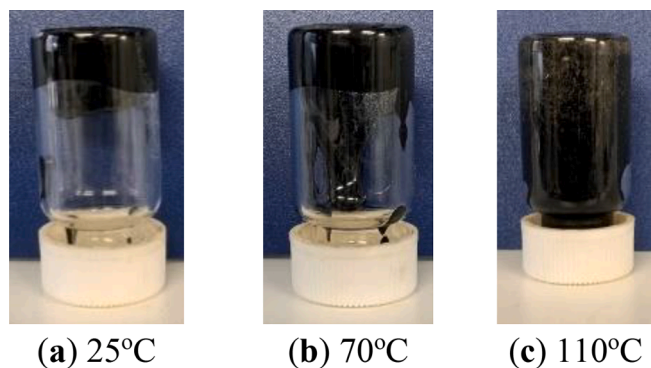


Fig. 3. Sample photographs of BT-1 exposed for 3 h at different temperatures.

mentioning that no sample preparation was needed and the FTIR spectra were obtained right after ultrasound treatment.

The surface morphology of the asphaltenes extracted from fresh and sonicated bitumen was investigated using a low vacuum high sensitivity scanning electron microscope (Model SU 3500). The extracted asphaltenes, with no further purification, were inserted in the vacuum chamber from where SEM photographs were taken by a low vacuum observation.

3. Results and discussion

3.1. Rheological properties of fresh and sonicated bitumen

Fig. 4 shows the apparent viscosity of bitumen before and after sonication under air environment.

It was seen that the apparent viscosity decreases over the range of investigated shear rates. Also, it was found that an extended sonication process (or period) led to a bitumen with a lower viscosity. These obvious observations were consistent with the literature, which reports that the ultrasound irradiation releases heat that dissipates into the oil

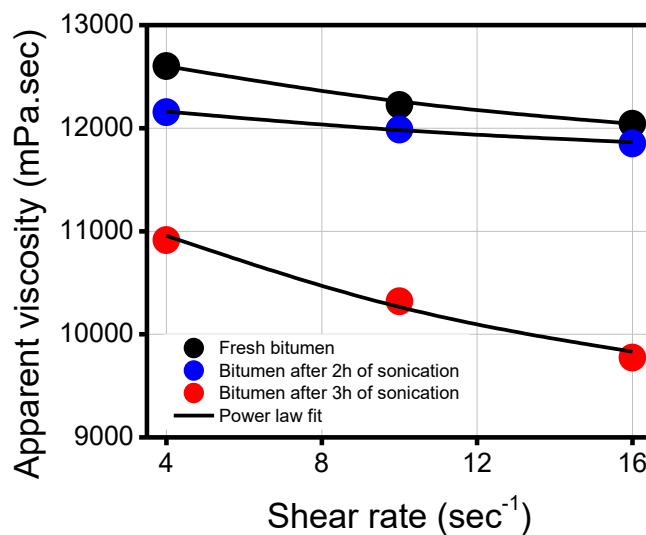


Fig. 4. Apparent viscosity of the bitumen before and after sonication under at 70 °C under air environment.

leading invariably to a less viscous bitumen [21,36,37].

To appreciate the influence of the sonication time on the viscoelastic behavior of the oil, one must apply the empirical models that describe the behavior of a time-dependent fluid. In this study, Power law model was selected because of the shear-thinning behavior of the bitumen in addition to its prominence in oil rheology [43]. The power law model is expressed as,

$$\mu = K\gamma^{n-1} \quad (1)$$

where μ is the apparent viscosity (mPa.sec), γ is the shear rate (sec⁻¹), K is the consistency index (mPa.sec²), n is the flow index (dimensionless) indicates the degree with which a material exhibits non-Newtonian flow behavior, the values of n close to 1 implied a Newtonian behavior and a

value of n close to 0 would indicate a departure from the Newtonian behavior.

The experimental data (Fig. 3) were then fitted and the statistical parameters including the root mean square error (RMSE) and the square root (R^2) were evaluated using equations (2) and (3) respectively,

$$RMSE = \sqrt{\frac{\sum_{i=1}^N (\mu_i^{\text{experiment}} - \mu_i^{\text{model}})^2}{N}} \quad (2)$$

$$R^2 = 1 - \frac{\sum_{i=1}^N (\mu_i^{\text{experiment}} - \mu_i^{\text{model}})^2}{\sum_{i=1}^N (\mu_{\text{average}} - \mu_i^{\text{model}})^2} \quad (3)$$

where N is the number of points (dimensionless). The results are shown in Table 2.

Under ambient conditions, Table 2 shows that a fresh bitumen behaves like a Newtonian fluid, which a n -value close to 1. These findings are consistent with the results presented by Ukwuoma and Ademodi (1999), who reported the influence of the temperature on a Nigerian oil sand Bitumen sampled from a deposit located in the same geological basin [44].

It was found that even after a prolonged sonication, the viscoelasticity of the bitumen was still fairly altered as evidenced by the values of n close to 1. This suggests at first sight that that the ultrasounds do not change the viscoelasticity of the oil. Furthermore, these preliminary observations suggested that viscosity of the bitumen even after ultrasound treatment was not low enough to be considered for an engineering application i.e., transportation. In fact, Martinez-Palou et al. (2011) reviewed that to transport bitumen, the viscosity of the oil should be lesser than 200 mPa.sec [45].

With an average bitumen viscosity equal to 10165 mPa.s after 3 h of continuous sonication at ambient conditions that is nearly 51-fold larger than the required value, it is evident that process parameters must be optimized to reach (or at least to get close to) the sought value.

In this regard, considerations were then given to both applied frequency and the gas environment. It is noteworthy to mention that the influence of either parameter will be addressed simultaneously, and the findings reported are those obtained after 3 h of continuous irradiation.

3.2. Effect of applied frequency and gas environment on bitumen viscosity reduction

The effect of applied gas and gas environment are shown in Fig. 5.

The viscosity of the bitumen decreases with the applied frequency with the largest viscosity reduction observed for 200 kHz (Fig. 5a). For example, at the fixed shear rate of 20 sec^{-1} , the viscosity of the fresh bitumen was 9654 cP. Irradiating the same bitumen continuously for 3 h at the frequency of 38 kHz and 200 kHz gave a bitumen with an apparent viscosity of 2798 cP and 1744 cP respectively (Fig. 5a). Similar results were reported by Mohapatra and Kirpalani (2016), who argued that sonicating a Canadian Bitumen at a frequency as high as 378 kHz could lower the viscosity of the oil up to 15% from its original value [28].

The influence of the gas environment was also noticeable (Fig. 5b). On the average, the viscosity was threefold lower than that of the fresh bitumen when the irradiation was performed under either gas environment. However, it was found that the bitumen with the lowest

Table 2
Parameters for rheological models used for sonicated and fresh bitumen.

Parameters	Fresh bitumen	Sonicated bitumen	
		2 h	3 h
$K \cdot 10^{-2} (\text{Pa} \cdot \text{sec}^2)$	13.19	124.7	122.1
$n (-)$	0.967	0.982	0.922
RMSE (-)	3.040	15.65	80.64
$R^2 (-)$	0.999	0.984	0.970

viscosity was obtained when the irradiation was performed under N_2 environment. Comparing the viscosity reduction obtained after altering either the applied frequency (Fig. 5a) or the gas environment (Fig. 5b), it appears that the former parameter is the conspicuous parameter. For instance, the bitumen sonicated with an applied frequency of 200 kHz gives a viscosity, on average, twice lower than those obtained when the gas environment was altered.

Table 3 summarizes the rheological parameters under different applied frequencies and gas-environment.

Table 3 suggests that simulating the flow by altering either the frequency or the gas environment, the bitumen would flow easily. Also, as the applied frequency increases, it could be seen that the bitumen departs from the Newtonian behavior. This trend, however, was less noticeable when the gas environment was altered. For all the cases, bitumen behaved like a Newtonian fluid.

Considering the sonication process as the conversion of electrical power into vibrational energy i.e., heat and cavitation [46], these results suggested that the extent to which the viscosity is altered dependent somewhat on either heat supplied or induced cavitation, which are sensitive to operating conditions. Therefore, it was then sought to probe the extent to which former form of energy (heat) contributes to the viscosity alteration.

3.3. Probing the mechanisms of viscosity reduction

Both the temperature of bitumen and that of the water bath in which the sonication was carried were recorded to investigate the influence of the heat supplied to the oil by either the applied frequency or the gas environment. The difference between the two temperatures was then plotted against the apparent viscosity. The results are shown in Fig. 6.

It could be seen that the apparent viscosity decreases exponentially with the increase in temperature. The curvature of the decay appeared less pronounced when the influence of the applied frequency was investigated (Fig. 6a), which contrasted with the influence of the gas environment (Fig. 6b). Therein, the decay approaches seemingly an equilibrium. Eyring (1936) argued that viscosity decay implies the existence of an energy, termed as activation energy of flow (E_a) [47].

Per the literature, E_a is a measure of the height of a potential energy barrier associated with the force needed to produce elemental quantum steps [48]. In this study, the flow activation energy should be then regarded as the minimum energy required by the molecules to be set in motion against the frictional forces subsequent either to a change in gas environment or applied frequency. From the viscosity theory of Eyring viscosity, the Arrhenius equation was then employed to compute E_a ,

$$\mu_s = \mu_o \exp\left(-\frac{E_a}{R} \left(\frac{1}{T_s} - \frac{1}{T_o}\right)\right) \quad (4)$$

where μ_s and μ_o are the apparent viscosity of sonicated and fresh bitumen at 16 sec^{-1} , respectively (in mPa.sec), E_a is the activation energy of flow (in kJ/mol), R is the gas constant ($R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), T_s is the temperature of the bitumen after sonication (in K), and T_o is the initial temperature of the bitumen (in K).

E_a is determined from the plot $\ln(\mu_s/\mu_o)$ versus $(1/T_s - 1/T_o)$. The results are shown in Fig. 7.

The minimum energy requires to initiate the flow increased with the applied frequency (Fig. 7a). It could be seen that applying a frequency equal to 38 kHz yielded the lowest activation energy (35.6 kJ/mol), which was four-fold lower than that of a mild frequency (200 kHz). As opposed to the applied frequency, changing the gas environment did not have a striking influence on the activation energy (Fig. 7b). Nonetheless, the lowest energy of activation was obtained for when the irradiation was conducted under CO_2 -rich environment ($\sim 29 \text{ kJ/mol}$). Looking at the results from Fig. 5 and Fig. 7, the viscosity reduction seems to be inversely proportional to the activation energy of flow. The probable reasons could be drawn out from the chemical effects of ultrasound

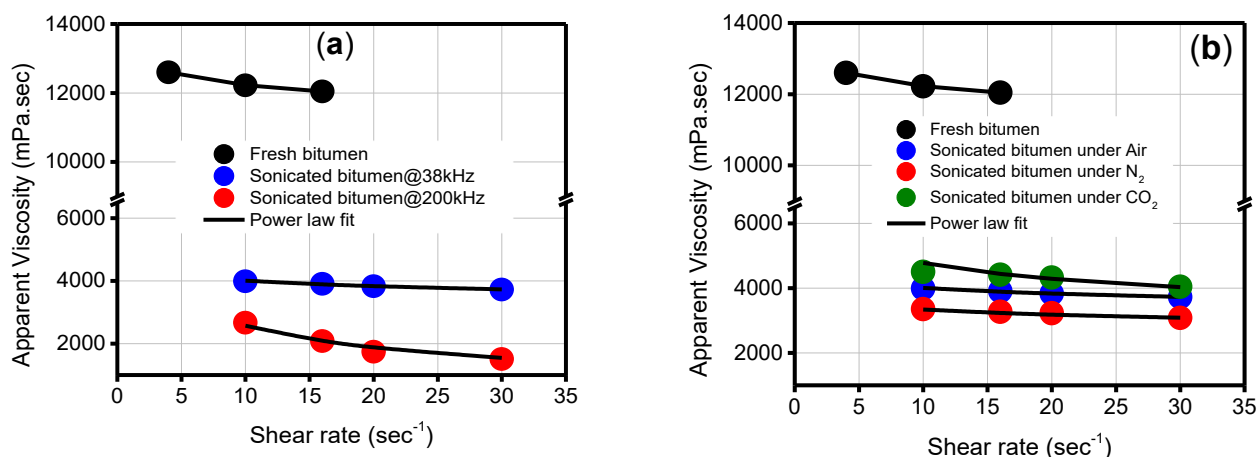


Fig. 5. (a) Influence of applied ultra-sound frequency conducted under air environment and (b) influence of gas environment on viscosity alteration after 3 h.

Table 3

Parameters of rheological model for fresh and sonicated bitumen at different frequencies and gas environment.

Parameters	Fresh bitumen	Applied frequency		Gas-environment		
		38 kHz	200 kHz	Air	N ₂	CO ₂
$K \cdot 10^{-2}$ (Pa. sec ²)	13.19	46.56	75.06	46.56	39.3	68.27
n (-)	0.967	0.935	0.535	0.935	0.929	0.845
RMSE (-)	3.040	12.6	76.89	12.6	37.58	25.52
R ² (-)	0.999	0.991	0.967	0.991	0.999	0.999

waves.

Suslick (1989, 1999) reported that the ultrasound breaks the long chain molecules and dissolves the suspended soluble particles, presumably asphaltenes [21,22]. This would mean that the decrease in energy of activation (Fig. 6) should be regarded rather as an increase in solubility of heavy components initially in suspension. With the knowledge that bitumen is highly asphaltic, it is reasonable to think that the viscosity reduction pertains perhaps to the solubilization of asphaltenes suspended in the oil as either monomers or nanoaggregates [34].

This statement could be verified qualitatively by monitoring the intensity of aromatic carbon peak (sp² C = C) and that of bonds from aliphatic carbon (sp³ C-H) on FTIR spectra [49,50]. Thus, FTIR spectra of the fresh bitumen and those of sonicated bitumen under different gas-

environment and applied frequency were acquired (Fig. 8).

The spectrum of the native bitumen and those of the sonicated bitumen features characteristic stretching peaks at (i) ~ 3100 cm⁻¹ due to an aromatic sp² C-H, (ii) ~ 2900 cm⁻¹ assigned to an aliphatic sp³ C-H, (iii) ~ 1600 cm⁻¹ due to a sp² C = C. Also, bending peaks characteristic of an aliphatic (or alkyl) sp³ C-H and aromatic sp² C-H were observed respectively at ~ 1450 cm⁻¹ and ~ 750 cm⁻¹ respectively. It could be seen that the vibration stretches of C = O bonds from a functional group appearing around ~ 1700 cm⁻¹ was noticeable for all the samples.

Rogel (2015, 2017) proposed that computing the ratio of the integrated intensity of the peak of sp² C = C vibrating at ~ 1600 cm⁻¹ to that of sp³ C-H appearing at ~ 2900 cm⁻¹ could enable the quantification of the molar ratio of aromatic rings to aliphatic side chains [51,52]. Alh-reez and Wen (2019) proposed that the ratio 3100 cm⁻¹/2900 cm⁻¹ is an indicator of the number of carbon atoms per alkyl chain [53]. However, it should be noted the determination of these ratios would assume that the extinction coefficients of the functional groups do not change among the fraction [51,54].

Therefore, the peaks appearing within the FTIR band 1400–1700 cm⁻¹ and 2700–3100 cm⁻¹ were baseline-corrected, deconvoluted, and fitted using Gaussian functions (Fig. S1, Fig. S2 supplementary file). The ratios 1600 cm⁻¹/2900 cm⁻¹ and 3100 cm⁻¹/2900 cm⁻¹ were then computed from the integrated peaks (Table 4).

As per Table 4, it seems that the molar ratio of aromatic rings to aliphatic side chains (i.e., 1600 cm⁻¹/2900 cm⁻¹) is fairly altered by either the change in applied frequency or gas environment evidenced by a value ~ 0.050. A different trend was observed for the number of

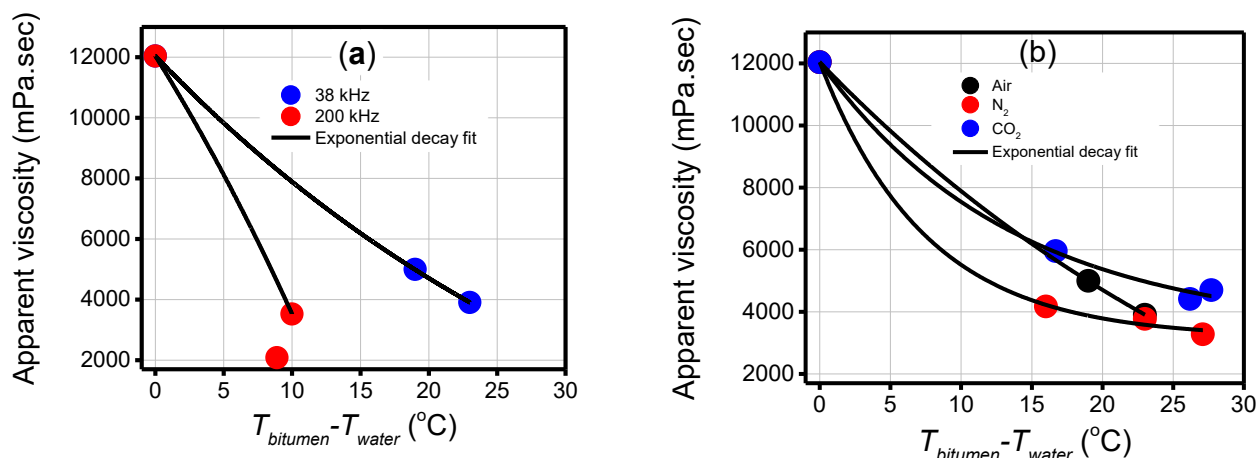


Fig. 6. Viscosity alteration as function of temperature of (a) applied ultra-sound frequency and (b) gas environment.

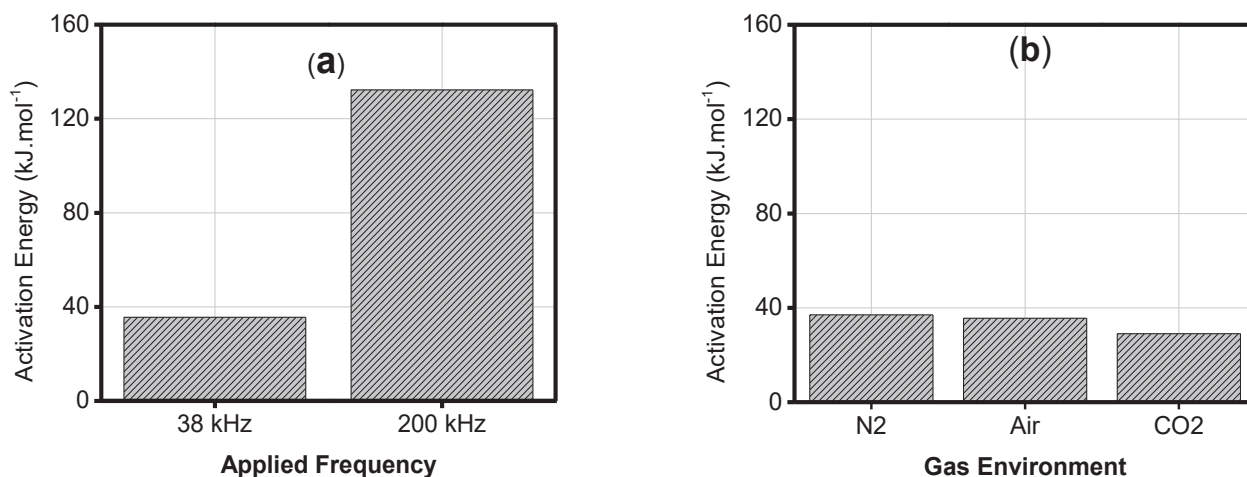


Fig. 7. Influence of (a) applied frequency and (b) gas sonication environment on activation energy estimated from Arrhenius equation (Eq. (4)).

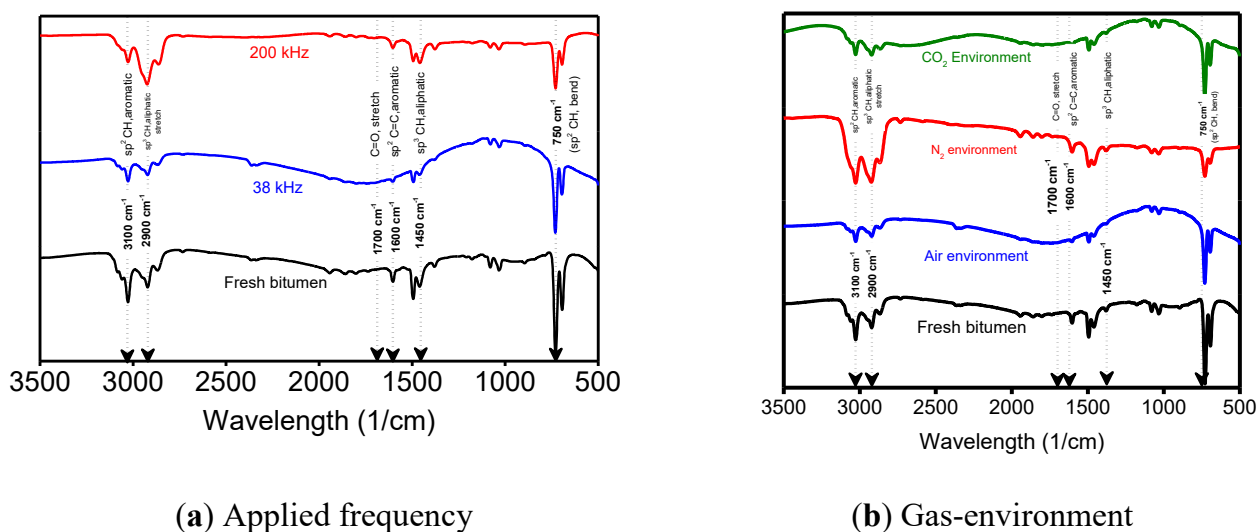


Fig. 8. Infrared spectra of fresh and sonicated bitumen under different (a) applied frequency and (b) different gas-environment; the spectra were acquired after 1 h of sonication.

Table 4

Molar ratio of aromatic rings to aliphatic side chains ($1600\text{ cm}^{-1}/2900\text{ cm}^{-1}$) and the number of carbon atoms per alkyl chain ($3100\text{ cm}^{-1}/2900\text{ cm}^{-1}$) for fresh and sonicated bitumen.

IR band	Ratio	Fresh bitumen	Applied frequency		Gas-environment		
			38 kHz	200 kHz	Air	N ₂	CO ₂
1600 cm ⁻¹ / 2900 cm ⁻¹	sp ² C = C/sp ³ CH	0.050	0.047	0.062	0.047	0.049	0.055
3100 cm ⁻¹ / 2900 cm ⁻¹	sp ² C-H/ sp ³ C-H	0.218	0.231	0.034	0.231	0.398	0.287

carbon atoms per aromatic ring. In the fresh bitumen, the number of carbon atoms per alkyl chain was computed to be 0.22.

The sonication at a mild frequency decreases the number of carbons per alkyl side chain to 0.03, suggesting either the presence of a large concentration in carbon atoms in the alkyl chain or a decrease in the size

of the aromatic rings. Considering that the molar ratio of aromatic ring to aliphatic side chain was fairly altered, it is reasonable to think that a value of 0.03 implies a scission of long chain molecules attached to the aromatic rings, which is supported by the findings of Luo and Gu (2007).

They argued that the energy supplied by the ultrasound degrades the hydrogen bonds between the resins and the asphaltene particles at the outmost layers [38]. In respect of the gas environment, one could observe that the gas-environment has a reverse effect on number of carbon atoms per alkyl chain. In fact, it was found an average increase of 40% from the initial value. This suggests that the gas environment prompts the formation of aggregates.

Table 4 confirms further a direct correlation between the asphaltene content and the viscosity reduction.

3.4. Contribution of asphaltene content and sonochemical enhancement

3.4.1. Monitoring the asphaltene concentration

Table 5 summarizes the asphaltene concentration monitored during the sonication at different applied frequencies and gas-environment.

For all the investigated samples, the concentration in asphaltene increases with the sonication time, which is somewhat consistent with

Table 5
Monitoring of asphaltene concentration under different applied frequencies and gas-environment^a.

Sonication time (min)	Fresh bitumen	Applied frequency (38 kHz)			Air-environment	
		Air	CO ₂	N ₂	38 kHz	200 kHz
0	3.21	3.21	3.21	3.21	3.21	3.21
60	0.73	11.3	13.6	13.9	11.3	8.39
120	2.22	24.2	12.8	6.99	24.2	25.6
180	2.37	7.94	15.1	16.3	7.94	1.15

^a All concentrations are expressed in weight per cent (wt.%)

the results presented in Table 4. In respect of the gas environment, the asphaltene concentration at the end of the experiments (3 h of irradiation) was computed to be six-fold larger compared to the fresh bitumen; the largest concentration was obtained when the sonication was performed under N₂-environment.

As opposed to the gas influence, the concentration in asphaltenes decreases when a mild frequency was applied. These observations agree well with the results from FTIR and the literature [55–57]. It could be further highlighted that aggregation (or dissolution of asphaltene) and thus the viscosity reduction depends on operating conditions as it could be seen in Fig. 9 and Fig. 10.

Therefrom, large flocs and macro-aggregates could be observed when a low frequency was applied to the bitumen (Fig. 9a), which differ from the porous appearance when the gas was changed (Fig. 10). The different shapes of the extracted asphaltenes could be attributed either to the scission of long chain molecules [57] or the self-aggregation of asphaltene monomers, which leads to the formation of macro aggregates [58]. Either reason seems to corroborate with FTIR spectra.

3.4.2. Viscosity reduction, asphaltene yield, and sonochemical enhancement

Herein was evaluated the relationship between ultrasound irradiation, the oil viscosity reduction and the asphaltene aggregation. To do so, two dimensionless parameters were introduced namely viscosity reduction and asphaltene yield. Both terms were selected by analogy to sonochemical enhancement, which expresses the quotient of the product yield with sonication to that without sonication [59]. The mathematical expressions are shown in equations (4) and (5) respectively,

$$\text{Viscosity reduction (-)} = 1 - \frac{(\mu_{@16\text{sec}^{-1}})_{\text{after sonication}}}{(\mu_{@16\text{sec}^{-1}})_{\text{before sonication}}} \quad (5)$$

where $\mu_{@16\text{sec}^{-1}}$ is the apparent viscosity of the bitumen (cP) expresses the apparent

$$\text{Asphaltene Yield (-)} = \frac{\text{Concentration after sonication}}{\text{Initial asphaltene concentration}} \quad (6)$$

Per Eqs. (4) and (5), a viscosity reduction (or an asphaltene yield) equal or close to 0 would express a poor influence of the sonication, while a value close to 1 would imply otherwise. The results of the viscosity reduction and those of the asphaltene yield when the applied frequency (or the gas environment) were plotted against the sonication time (Fig. 11).

Fig. 11a shows the results of the fresh and unsonicated bitumen. Fig. 10b-c show those obtained when the applied frequency was changed under air-environment, and Fig. 11 d-f are the results obtained when the gas environment was changed at the applied frequency of 38 kHz. Irrespective of the investigated process parameter, the decrease in viscosity during sonication treatment was found proportional to aggregation in asphaltenes.

At ambient conditions, the yield in asphaltene was the lowest in addition to the fair alteration in viscosity (Fig. 10a). This suggests a poor scission of long chains of aliphatic groups attached to the asphaltenes or a poor solubilization (Table 4). However, in the event in which the sonication is conducted under a controlled gas-environment i.e., Fig. 11 d-f, it could be seen that for the bitumen to flow, more asphaltenes must be segregated from the bulk oil.

Fig. 11 suggests that the bitumen that flows consists of lighter molecules that have been separated from the asphaltic materials. Within the limit of the present work, it appears that either mild frequency (200 kHz) or an N₂-environment are suitable for bitumen viscosity reduction and it could be extrapolated to crude oil upgrading [60].

Storm et al. (1995), and later Rahimi et al. (2017) reported that the viscosity improvement also pertains to a separation of resins from asphaltene particles [18,61]. This means that beyond asphaltene content, concerns should be also given to the resins, which will be addressed in a future work.

4. Conclusions

The present work investigated the contribution of the asphaltene aggregation to the viscosity reduction of bitumen sampled from an oil-field located in Gulf of Guinea. The effects of applied frequency (38 kHz, 200 kHz) and the gas environment (air, nitrogen, and carbon dioxide) were investigated.

It was shown that the viscosity of bitumen decreased proportionally

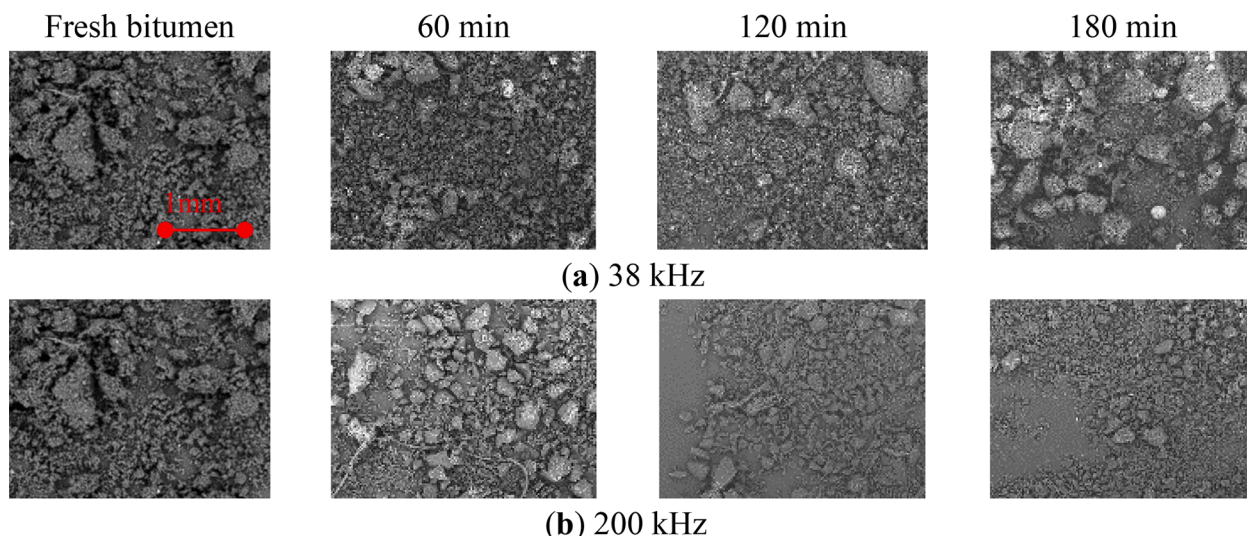


Fig. 9. SEM photographs of asphaltene precipitation at different ultrasound frequencies.

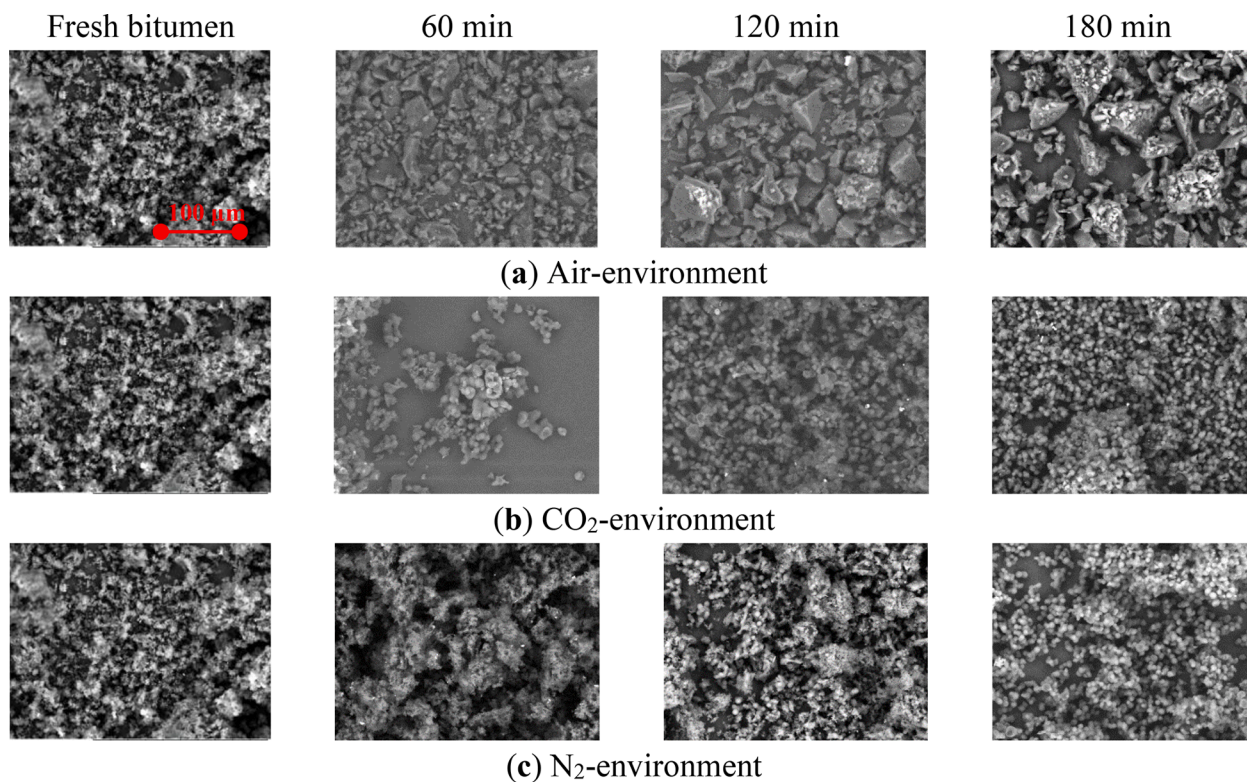


Fig. 10. SEM images of the surface morphology of asphaltenes under different gas environment.

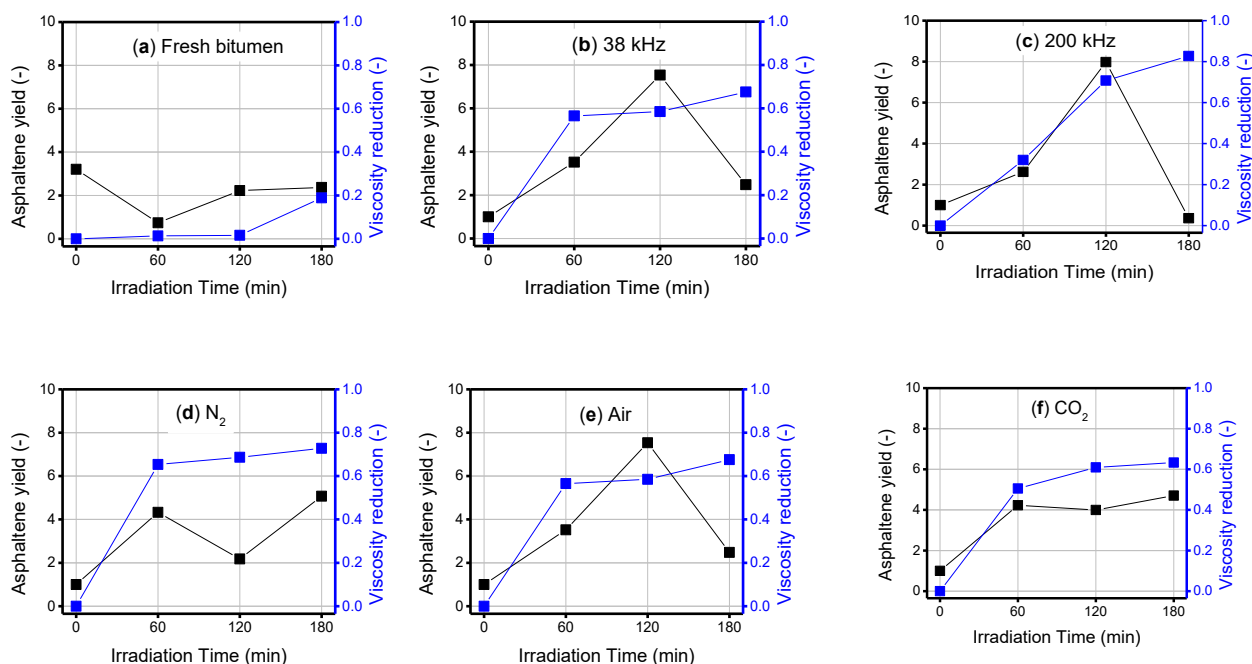


Fig. 11. Effect of applied frequency (b, c) and gas environment (d, e, f) on viscosity enhancement and asphaltene yield.

with the sonication time and the asphaltene aggregation. With an apparent viscosity of 12043 cP at ambient conditions, the bitumen viscosity could be as low as 2853, and 3274 cP upon sonication with an applied frequency of 200 kHz under air-environment and 38 kHz under nitrogen environment, respectively.

At any rate, the yield in asphaltene (and thus the viscosity reduction) was larger for a mild frequency and the sonication gas environment respectively due to the scission of long chain molecules attached

to the aromatic rings and the self-aggregation of asphaltene monomers. This study argued that ultrasound irradiation at ambient conditions or a low frequency are less efficient.

CRedit authorship contribution statement

Ronald Nguete: Conceptualization, Writing – original draft. **Hirokazu Okawa:** Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Author Contribution

All authors have given approval to the final version of the manuscript.

Appendix A. Supplementary data

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