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Comparison of Experimental Techniques at Ambient and High Pressure Conditions for Evaluation of Chemistries against Asphaltene Aggregation and Deposition: New Application of HPHT-QCM

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Asphaltene deposition, Asphaltene inhibitors, Evaluation of Inhibitors

ABSTRACT

Asphaltene precipitation and deposition caused by temperature variation, pressure depletion and oil composition changes can result in formation damage, oil production reduction and increased operating costs. Use of chemical additives is probably the most effective option for preventing or reducing asphaltene problems. Selection of inhibitors for asphaltene deposition is commonly based upon simple tests conducted on stabilised crude oil samples at ambient conditions. The results obtained from the current testing techniques in the labs are sometimes in disagreement with the outcome at field conditions. Therefore, the current techniques which are employed to select the most appropriate asphaltene inhibitor based on their efficiency should be revisited to provide a better methodology for choosing the most suitable strategy for inhibitor/solvent injection.

This research study addresses this asphaltene challenge using a Quartz Crystal Microbalance (QCM) based technique, with emphasis on selection of chemical additives for remediation/prevention strategies to handle gas induced asphaltene deposition problems. The proposed technique can work at high pressure conditions, simulating the effect of pressure and dissolved gas on asphaltene phase behaviour and deposition tendencies with and without inhibitors. It can also assess the deposition rate onto the quartz crystal surface due to asphaltene deposition under real reservoir conditions. In this study, the ability of different asphaltene inhibitors to shift asphaltene onset points (AOPs) and reduce the amount of deposited asphaltenes in dead crude oils is investigated. A comparison between the results of the QCM technique at high pressure-high temperature and dead crude oil testing at ambient condition is presented. The results of this work indicate that the change in temperature, pressure and presence of gas could alter the ranking of chemistries for mitigating asphaltene challenges.

1. INTRODUCTION

Asphaltenes are referred to as functional molecules and the heaviest and most polar fraction of crude oil. These polydisperse molecules have a polyaromatic hydrocarbon core with aliphatic chains in their structure. They also contain different heteroatoms (e.g. N, O, and S) on the periphery which make acidic and basic moieties in asphaltenes and contribute to the asphaltene self-association and asphaltene-inhibitor interactions[1–5]. Additionally, asphaltenes contain trace amount of metals (e.g. Va, Ni, and Fe) on porphyrin like structures[6–8]. Asphaltenes are soluble in aromatics (e.g. toluene and xylene) and insoluble in aliphatics (e.g. n-heptane, n-pentane)[9]. Asphaltenes are recognised to be precipitated and aggregated typically as the fluid pressure is reduced due to reservoir pressure depletion towards the bubble point pressure and mixing with other crude streams and addition of gas or gas and liquids (e.g. for EOR purposes) which cause asphaltene deposition and restricted flow[10–12]. Restricted flow through porous media and subsea infrastructure caused by asphaltene deposition restricts the oil flow to the surface leading to deferred production[1,13] and causes formation damage and wellbore plugging which need costly treatments and deposition removal operations. Some of the significant parameters involved in the asphaltene deposition phenomenon are: asphaltene onset pressure (AOP), lower and upper asphaltene envelope, reservoir pressure and bubble point pressure[14–16]. Gas injection is one of the most common EOR approaches which increases ultimate oil recovery in many cases because of induced oil viscosity reduction or pushing the oil towards the wellbore[17]. One of the most effective agents in this type of EOR method is natural gas which leads to increase oil production although the natural gas injection into an oil reservoir could change the flow behaviour and the fluids equilibrium properties which cause asphaltene precipitation and deposition problems[18,19]. Despite several decades of R&D projects, gas induced asphaltene deposition is still a major flow assurance challenge[20,21]. There are different approaches for asphaltene remediation and inhibition including mechanical techniques (Pigging, mechanical/manual Striping, mechanical Vibration[22,23]), chemical treatments (dispersants, antifoulants, coagulants, polar co-solvents[24–28]) and thermal techniques (steam injection, hot chemical injection, microwave technique, in-situ combustion[22]). Between all these techniques, chemical injection is one of the most widely used strategies to tackle the asphaltene precipitation and deposition barrier[29,30]. Millions of dollars per year are astimated to be spent each year on installing and servicing asphaltene mitigation equipment and chemicals[31]. In this regard, development of a new reliable technique for evaluation of asphaltene inhibitors could help cut the costs and reduce the frequency of treatments. Using classical asphaltene analysis techniques, the chemical structures of asphaltenes and additives that affect inhibitors performance have been elucidated[32–37]. Despite these achievements, studying the effect of inhibitors on asphaltene precipitation and deposition mechanisms under real field conditions remains difficult due to the complex environment in which asphaltenes are destabilised and the lack of a reliable technique. The conventional tools and methodologies for evaluation of asphaltene inhibitors performance include filtration technique[36,38,39], UV-vis spectrophotometry[40], microscopy[41,42], spectroscopy techniques[43], light scattering[44,45] and solid detection system (SDS)[32]. Although these methods have provided detailed information about asphaltene formation and interactions with inhibitors, they might not be suitable for evaluation of chemicals with respect to asphaltene precipitation and deposition. All these techniques have particular strengths and weaknesses in terms of sample volumes, test time, accuracy; some work at ambient conditions using n-heptane titration. Therefore, in this study a new high pressure high temperature method has been developed in which chemicals are evaluated based on both precipitation and deposition inhibition in order to study their function at relevant conditions. In this study, a technique based on QCM is presented to rank three asphaltene inhibitors based on their efficiency in shifting asphaltene onset point and reducing deposition rate at high pressure. This technique is faster, more reliable and accurate compared to the available tests such as the Asphaltene Inhibitor Screening Test (AIST) and UV-vis-NIR spectrophotometry. Furthermore, we are able to evaluate the effect of inhibitors on the asphaltene deposition rate onto the crystal surface that is obtained by resonance frequency monitoring after precipitation onset point, using dead-oil samples at high pressure-high temperature QCM (HPHT-QCM). The experimental results reveals that the asphaltene inhibitors are able to shift the onset of asphaltene precipitation/aggregation and could reduce the rate of asphaltene deposition, and also the ranking of chemicals could be different from ambient to HPHT condition. In this research work, the influence of chemical additives dosage, ageing time and temperature on the asphaltene precipitation and aggregation phenomena are also investigated.

2. EXPERIMENTAL SECTION

2.1. Materials

Experiments were conducted at both ambient and high pressure-high temperature (HPHT) conditions on crude oil "P" from the North Sea. Table 1 shows the properties of crude oil "P". The commercial asphaltene inhibitors 6, 10 and 12 were utilised to treat the crude oil samples. These chemicals were selected based on their significant applications and contributions in mitigating asphaltene challenges in industry, which were received from operators. HPLC-grade anhydrous n-heptane (>99%), anhydrous toluene (>99.8%), HPLC grade acetone (≥99.9%) and ethanol (≥99.8%) were purchased from Sigma-Aldrich and used as received.

2.2. Asphaltene Inhibitor Screening Test (AIST)

Various dosage of inhibitor 6, 10 and 12 were injected to crude oil "P". In this regard, 100, 300 and 600 ppm of each inhibitor were provided and analysed. Concentrated solution of each inhibitor in crude oil (2000 ppm), were diluted with n-heptane and inserted in a beaker, then were mixed by magnetic stirrer at 1000 rpm for two hours to obtain a homogeneous solution. 10 mL of n-heptane plus 300 μL of the treated crude oil sample was placed in graduated centrifuge tubes to be centrifuged using a Heraeus Megafuge. The centrifuge tubes were left for a time interval (which is called ageing time hereafter) after which, the quantity of asphaltene aggregates at the bottom of each tube was measured in mL. A blank crude oil with no chemical additive was used as reference.

The applied aging times are 1 hr, 6 hr and 24 hr. The term "clear" is being utilised whenever no asphaltene aggregates were seen at the bottom of the tube and the term "trace" is used for the condition when the quantity of deposit is not high enough to be measured[11,46]. Comparing the quantity of sediment measured in mL for various injected inhibitors and dosages with reference to the untreated oil, which was the combination of crude oil and n-heptane without any chemical, is done to investigate the efficiency of inhibitors by utilising the AIST.

2.3. Detection of asphaltene appearance point using UV-vis-NIR Spectrophotometer

The mixtures of crude oil and precipitant, with and without inhibitor, were provided following the same approach which was described in Section 2.2. Mixtures with various proportions of treated or untreated crude oil and n-heptane varying from 0 to 85 vol% of n-heptane were provided. The test tubes were rigorously shaken manually to obtain a homogeneous solution which was then sealed to be preserved from atmosphere. To retain a uniform temperature the test tubes were held in a Stuart Scientific oven which was set at a particular temperature (25 °C and 60 °C were used in these tests). The test tubes were undisturbed for a particular ageing time. The ageing time is the duration between sample preparation and the determination of the NIR light transmittance number. In next step, the NIR transmittance was determined by Hitachi UV–Vis–NIR spectrophotometer Model U-3010. The transmittance numbers were recorded for 1100 and 1300 nm wavelengths. From this measurement it can be concluded that whenever the signal is not saturated, several wavelengths can be utilised to determine the onset point of precipitation. For wavelengths less than 1100 nm, evaluation cannot be done as the signal is saturated. The mass ratio of oil and precipitant exist in every mixtures were evaluated and by presuming an ideal mixing and knowing the density of the contents, their volumes were calculated. The light transmittance numbers of each sample were modified by subtracting the n-heptane transmittance and after that the influence of dilution was mathematically omitted[46,47]. By utilising the transmittance of the crude oil as reference, normalized amount of the corrected transmittance was calculated. These normalized values are often plotted as a function of the volume fraction of n-heptane or crude oil. Another method for illustrating similar results is to use light intensity instead of absorbance, which is more common for presenting results in direct spectroscopy. The normalized light intensity can also be plotted as a function of the volume fraction of crude oil and/or n-heptane. The obtained normalized light intensity was reduced as asphaltene aggregates barricade light rays through the cell, therefore this reduction trend indicates asphaltene aggregation happening, the first deflection from the linear line revealed the precipitation of asphaltenes which called asphaltene appearance point (AAP) hereafter. AAP represents the minimum amount of n-heptane added to crude oil to cause asphaltene precipitation that is discernible for the utilized technique.

The morphology and architecture of the asphaltene precipitates with and without chemical additives were investigated by Environmental Scanning Electron Microscopy (ESEM) in order to investigate the effect of inhibitors on asphaltene precipitates size and their morphology.

2.4. Quartz Crystal Microbalance (QCM)

This technique measures the resonance frequency for a quartz crystal surface inserted into crude oil with and without chemical additive to determine the asphaltene onset point (AOP) at a specific temperature, pressure and composition. Since the asphaltene precipitation is measured independently of deposition using the QCM technique, the effect of inhibitor on asphaltene precipitation and deposition phenomena was independently studied. The crude oil "P" was treated with inhibitors 6, 10 and 12 at various chemical dosages ranging from 119 to 1785 ppm. The blank oil without any inhibitor was considered as reference. Then the treated/blank crude oil samples were loaded into the QCM cell and stabilized at the temperature and pressure of interest. Then, the test fluid is pressurised by injecting natural gas at a constant rate of pressure increase. The composition of injected natural gas is presented in Table 2. The QCM technique can provide a robust, reliable method for evaluation of asphaltene inhibitors and deposition risks which has some advantages over other conventional techniques including; applying more realistic pressure and temperature conditions, small size of the sample, assessment of real time deposition rate, using live oil samples (in addition to dead/stabilised samples). It could be more automated and much cheaper compared to other utilised techniques in industry.

3. RESULTS AND DISCUSSION

Three commercial asphaltene inhibitors have been utilised to investigate their effect on asphaltene appearance point, aggregation and deposition phenomena using three different techniques: ‘‘AIST”, “UV-vis-NIR spectrophotometry” and ‘‘HPHT-QCM”, which have been described in Section 2. Natural gas injection was used to induce the asphaltene precipitation at HPHT conditions, which gives the driving force for asphaltene precipitation, instead of the n-heptane titration that is employed in the ambient tests. The results of all these experiments will be presented and discussed in following subsections.

3.1. Asphaltene Inhibitor Screening Test (AIST)

Crude oil “P” was treated with inhibitors 6, 10 and 12 at 100, 300 and 600 ppm as described in Section 2.2. The results are presented in Figure 1 and the volume of asphaltene sediments in the bottom of tubes obtained with/without inhibitors in various ageing times is presented in Table 3. With respect to the capability of inhibitors on dispersing the asphaltene aggregates in the mixtures the AIST ranks the inhibitors performance, which also decrease the particles velocity in Brownian motion and, as a result, the amount of deposited asphaltenes[11,46]. The more effective is the asphaltene inhibitor the less deposition will be seen. No asphaltene deposit was observed in sample with inhibitor 10 at 600 ppm after 24 h. Deposits appeared in the reference crude oil (oil without any additive) after 1 h and we had higher amount of asphaltene aggregates as time passed as reported in Table 3. However, for samples with all concentrations of asphaltene inhibitor 10 and 12, there is no asphaltene sediment after 1 hr. By conducting UV-vis-NI spectrophotometer tests it was shown that the amount of asphaltene precipitates decreases with higher concentration of inhibitors as shows in Section 3.2. Hence the ranking of asphaltene inhibitors based on dispersion of asphaltene aggregates obtained from AIST is as follows: AI. 10 > AI. 12 > AI. 6. In AIST technique, to get a transparent test solution in which asphaltene sediments on the bottom of centrifuge tubes can be detectable, AIST needs a high amount of n-heptane (>97 vol%). Therefore, due to inability of AIST in evaluation of inhibitors at the heptane concentration in which the highest amount of asphaltene precipitates and/or the largest asphaltene aggregates form, this method cannot be thoroughly reliable. In addition, this highly dilute solution is not a suitable representative of the real field conditions at which asphaltenes precipitate, aggregate and deposit. Hence we employ UV-vis-NI spectrophotometer technique to evaluate asphaltene inhibitors at ambient conditions which could give us more information about inhibitor efficiency.

3.2. Evaluation of Asphaltene Inhibitors Using UV-vis-NIR Spectrophotometer

Figure 2 shows the results of asphaltene appearance point determination for the crude oil “P” with and without inhibitors 6, 10 and 12 at 100, 300 and 600 ppm at 25 ^{o}C and 24 hr ageing time. The crude oil without inhibitor was considered as reference. All plots in Figure 2 can be divided to two main trends: the first trend is approximately a horizontal line for low amount of n-heptane (precipitant) and high volume percentage of crude oil. In this part all systems show the same trend. Next, the second trend which has high amount of n-heptane and low volume of crude oil where the light intensity numbers deflects from the horizontal line. The intersection point between these two trend lines at which this deflection happens illustrates the volume fraction of n-heptane needed for determination of asphaltene appearance point (AAP). In the second trend line after determination of asphaltene appearance point, Figure 2 presents a progressive light intensity decline for the reference fluid. The light intensity reduction reveals an increment in the quantity and size of asphaltene aggregates. For test samples with inhibitors, the light intensity reduced more gently than the reference sample results in slower precipitation and aggregation process rates under the influence of inhibitors. Next, as the heptane concentration reached 60 vol.%, the treated mixture illustrated a second inflexion point at 60 vol.% where the light intensity raised again toward the horizontal base trend line that shows a stable solution with fewer and smaller asphaltene aggregates due to presence of inhibitors. As precipitant increased in the solutions it can influence the asphaltene precipitation mechanism in two ways: first it dilutes asphaltene concentration and in consequence decreases the light intensity, even at below 30 vol.% of n-heptane where there is no precipitation in the solution, second it decelerates the rate of precipitation and aggregation process. If inhibitors exist in the test solution the rate of precipitation and aggregation will slow down more which results in higher light intensity compared to the blank crude oil “P” after 24 hr ageing time.

The inhibitor efficiency on asphaltene precipitation and aggregation inhibition was determined by monitoring the asphaltene appearance point and normalised light intensity changes due to presence of different inhibitors at various dosages. Regarding to financial aspects low dosage inhibitors are more favourable. Figure 2 (a) shows that inhibitor 10 has a profound effect in shifting AAP from ~30.1 to ~38.4 vol% n-heptane at dosage of 100 ppm. While inhibitor 12 could not change the AAP significantly at this concentration (Figure 2 (b)). Figure 2 (c) illustrate that inhibitor 6 had limited effects at concentrations of 100 and 300 ppm, although at higher inhibitor dosage shifted the AAP from ~32.4 to ~41.6 vol% of n-heptane. As mentioned before in Section 3.1, no notable deposition was seen for inhibitor 10 at 300 and 600 ppm after 24 hr ageing time although from direct spectroscopy we observed the occurrence of asphaltene precipitation and aggregation for these systems. The reason of this observation is related to the slow rate of aggregation phenomenon for treated solution with inhibitor 10 at 300 and 600 ppm after 24 hr ageing time compared to the result obtained from the blank crude oil “P”. Unlike inhibitor 6, Figure 2 (a) and (b) present decline trend for asphaltene aggregation and thus higher light transmittance numbers due to dosage increment for inhibitor 10 and 12. They also decreased asphaltene aggregation to a drastically low level at 600 ppm. As can be seen from Figure 2, all asphaltene appearance points were shifted for the treated crude oil “P” with inhibitors 6, 10 and 12 at 600 ppm. The inhibitor 10 has better performance compared to inhibitors 6 and 12 at concentration of 100 ppm, thus it can be concluded that at concentration of 100 ppm inhibitor 10 might be the best option. Applying chemical additives at high concentrations in oilfields is not economically favourable and desirable solution. Determination of asphaltene appearance points for crude oil “P” which was blended with 100, 300 and 600 ppm of inhibitors after 24 hr ageing time is presented in Table 4. The control is crude oil S without adding any additives and is utilized as reference for discovering the effect of each inhibitor. A shift in asphaltene appearance point from its number in reference fluid (~30.5 vol% n-heptane) to higher values, stated the influence of utilised asphaltene inhibitor. We believe that there is one main mechanism which explains the change in asphaltene appearance point due to presence of inhibitors. This mechanism is that the inhibitors molecules have interaction with asphaltenes and decrease the asphaltene particle size (before aggregation phenomenon) and also delay the precipitation and aggregation steps, or change the hydrophobicity of asphaltene nanoaggregates by occupying their active sites. In order to investigate this further, the effect of inhibitor on asphaltene precipitates size and its morphology were investigated by ESEM micrographs. Figure 3 shows the effect of Inhibitor 6 on asphaltene particle size. The micrographs are all analysed using ImageJ and presented in Figure 3.

Figure 3 presents the size distribution of asphaltene precipitates with and without inhibitor. The employed inhibitor reduced the asphaltene particle size. For the samples with inhibitor (Figure 3.a), the sizes range from 100 to 800 nm averaging around 376 nm. The measurements without inhibitor have larger asphaltene particle sizes averaging around 584 nm, which is the size of the asphaltene aggregates that can be detected by commercial techniques used for determination of asphaltene precipitation onset. The ranking of asphaltene inhibitors based on AAP changes obtained from UV-vis-NI spectrophotometer technique is as follows: AI. 10 > AI. 12 > AI. 6 which is in consistent with AIST results in the same conditions. To investigate the influence of temperature on performance of inhibitors, several tests were performed with similar concentrations of inhibitors 6 and 12 at 25 °C and 60 °C and ageing time of 24 hr.

Since some oil properties like density, viscosity and asphaltene solubility depend on temperature. The solubility of asphaltenes in oil usually increases with increasing temperature[48]. In addition, asphaltene contents which precipitate out of the solution at high or low temperatures can be dissimilar with each other since asphaltene is a polydisperse molecule. The influence of temperature on asphaltene behaviour should be considered since each fraction of asphaltene has its own properties like diffusion rate and density. Asphaltene nanoaggregates might precipitate in higher temperatures as they get more unstable.

The results for influence of temperature on mixture of oil and n-heptane with and without inhibitors are presented in Figure 4. From Figure 4 it seems that the solution without inhibitor has more stable asphaltene nanoaggregates at 60 °C compared to the solution at 25 °C. It is obvious from the test results that the rate of aggregation and precipitation phenomena decreased as the temperature increased. Behaviour of the crude oil at higher temperatures shows that it performs as a more effective solvent for the asphaltene nanoaggregates and the solution requires more n-heptane to detect the asphaltene appearance point. The results for inhibitors 6 and 12 at concentration of 600 ppm at temperatures of 25 °C and 60 °C after 24 hr ageing time are illustrated in Figure 4 (a) and (b), respectively. As can be seen from Figure 4, it is clear that at 600 ppm, inhibitor 12 has the same performance at both 25 °C and 60 °C. So the increase in temperature has no effect on the inhibitor efficiency. Similar procedure was employed for inhibitor 6 at concentration of 600 ppm, 25 °C and 60 °C for ageing time of 24 hr. The efficiency of inhibitor 6 in shifting AAP is slightly lower than inhibitor 12 at same conditions. However inhibitor 6 at 60 °C is more effective on asphaltene aggregates dispersion and AAP changes compared to inhibitor 12 and its performance at 25 °C. The ranking of asphaltene inhibitors 6 and 12 based on AAP changes monitoring at higher temperature is: AI. 6 > AI. 12. Therefore, the efficiency and ranking of inhibitors might change at higher temperature. So we decided to evaluate the inhibitors not only at high temperature but also at high pressure in presence of gas, which is closer to real field conditions, in order to obtain the updated ranking of inhibitor based on operation condition.

3.3. Evaluation of Asphaltene Inhibitors Using HPHT-QCM

A QCM has been utilised in this study to evaluate the effectiveness of asphaltene inhibitors on asphaltene precipitation and deposition rate at high pressure-high temperature (HPHT) condition (up to 6000 psia and 60 ^{o}C) in presence of gas. The QCM resonance frequency (RF) was measured for one day during continuous natural gas injection to investigate the effect of inhibitors on asphaltene onset point, gas oil ratio (GOR) and deposition rate at various inhibitors concentrations. The RF is inversely proportional to the mass of quartz crystal surface. If the mass of the QCM surface alters because of the asphaltenes adhered onto the solid surface then a reduction in RF will be observed. The Sauerbrey equation[49] explains how the alteration in RF can be related to the change in mass which is as follows:

$$\Delta f = -f_u^{3/2}\left[\frac{\rho_L \eta_L}{\Pi \rho_q \mu_q}\right]^{1/2} \qquad (1)$$

Where Δf is frequency change (Hz), f_u is frequency of oscillation of unloaded crystal (in air), ρ_L is density of the liquid in contact with the electrode, η_L is viscosity of the liquid in contact with the electrode, ρ_q is density of quartz, and μ_q is shear modulus of quartz for AT-cut crystal. In an ideal condition, the asphaltene deposits with amount of 1 nanogram will give 1 Hz reduction in RF. The initial asphaltene test with no inhibitor was performed on crude oil "P" at 60 ^{o}C and various pressures because of continuous natural gas injection. The effects of asphaltene inhibitors on asphaltene onset point (AOP) and gas oil ratio which is required to detect the asphaltene precipitation onsets are presented in Figure 5. The RF increases due to the reduction in density and viscosity of the test fluid as pressure increases with injection of gas. The RF declines when asphaltene precipitate out of the solution on the QCM surface. The pressure at which the RF begins to decline represents the asphaltene onset point that is 1195 psi at GOR of 193.04 cf/bbl for blank crude oil "P" without any inhibitor. The AOP/GOR is 1753 psia/290.08 cf/bbl for AI.12, 1790 psi/296.50 cf/bbl for AI. 6 and 1268 psia/205.67cf/bbl for AI.10 with concentrations of 660 and 714 ppm, respectively. Figure 6 presents the AOP and GOR obtained by HPHT-QCM versus various concentrations of inhibitors.

As can be seen inhibitor 6 has better performance compared to the other two inhibitors on AOP shifting and the GOR at which AOP occurs. Inhibitor 10 has a negative effect on asphaltene precipitation at low concentration and has some limited effects at higher concentrations. The results regarding the effect of employed asphaltene inhibitors on deposition rate after the AOP are shown in Figure 7, which is RF reduction versus time for crude oil “P” with and without inhibitors at different concentrations. The obtained results show that all utilised inhibitors have a positive impact on reducing the asphaltene deposition rate onto the QCM surface after exceeding the AOP. As can be seen, there is a dramatic difference in the plotted curves between the blank oil “P” without any inhibitor and the same oil with 119 and 180 ppm of inhibitor 6, 10 and 12, respectively. The AI. 6 has better efficiency in reducing the deposition rate from -690.3 Hz/hr to -203.6 Hz/hr compared to inhibitors 10 and 12 at the same concentration which decreases the deposition rate from -256.7 Hz/hr to -201.2 Hz/hr and from -199.7 Hz/hr to -155.7 Hz/hr, respectively. A sudden change in RF is observed during the first 4 hrs of the test without inhibitor compared to the test with inhibitors. A significant reduction in the rate of asphaltene deposition could be seen in the tests with inhibitor after beginning of deposition phenomenon. The inhibitors might cover the asphaltene’s aromatic cores through π-π interactions between inhibitors aromatic rings and asphaltene’s aromatic cores which intercept the stacking of asphaltenes molecules into nanoaggregates which causes its better efficiency in AOP shifting and deposition rate reduction. The inhibitors usually can also form H-bonding with active sites of asphaltene nanoaggregates (e.g. carboxylic, sulfoxide groups), the asphaltene aggregates are not able to move toward each other due to the created steric repulsion between the aliphatic tails of inhibitors that curb the asphaltenes growth into larger aggregates. The ranking of asphaltene inhibitors based on AOP/GOR changes and deposition rate reduction using HPHT-QCM technique is as follows: AI. 6 > AI. 12 > AI. 10. Therefore, the ranking of inhibitor obtained at ambient condition (AIST and UV-vis-NIR spectrophotometry) is totally different compared to ranking of inhibitors achieved at HPHT condition in presence of gas. Table 5 presents the ranking of utilised asphaltene inhibitors obtained from different techniques.

Based on our recent study which is in preparation to be submitted to Journal in near future, we found that chemical structure of gas induced asphaltenes is different from structure of n-alkane induced asphaltenes. This could result in having different ranking of inhibitors based on operation conditions. For avoiding EOR induced asphaltene problems, evaluation of chemicals using techniques at ambient condition may not be representative of real performance and efficiency of chemistries which would be found in the field.

4. CONCLUSIONS

In order to identify appropriate asphaltene inhibitors to avoid or mitigate deferred oil production caused by asphaltene deposition, it is crucial to evaluate the inhibitors by using accurate and reliable techniques which could represent the real or close to real field condition. Based on the obtained results in this research study the commercial asphaltene inhibitors interact with the asphaltene nanoaggregates in the oleic phase to change the asphaltene appearance point which is detected by employed techniques and also decrease the rate of asphaltene aggregation phenomenon accordingly. The HPHT-QCM experiments results presented in this study provide experimental data that do not agree with asphaltene inhibitor evaluation techniques at ambient conditions. The ranking of inhibitors based on their performance could be significantly affected by pressure and presence of gas at which the tests are performed. On the other hand, the experiments conducted at 25 ^oC and 60 ^oC and ambient pressure reveal that the ranking of inhibitors used in this study is different for each temperature condition. This could be as the result of the effect of temperature on the ability of the chemistries to interact with asphaltenes and make them stable in the solution. Therefore, a reliable technique is needed to truly evaluate inhibitor chemistries and their effects on deposition rate based on inhibitor-asphaltene molecules interactions which could be actually differed from n-C_7 to CO_2 injection at high temperature. The

HPHT-QCM technique can investigate the effect of inhibitors on the apparent asphaltene deposition rate which is an important indicator of performance. All studied inhibitors could reduce the deposition rate. Additionally, the QCM is ideal for measuring ashaltenes at realistic P/T conditions as they have a high adhesion tendency and it is this property which causes the most problems downhole i.e pipeline restrictions and costly remediation procedures.

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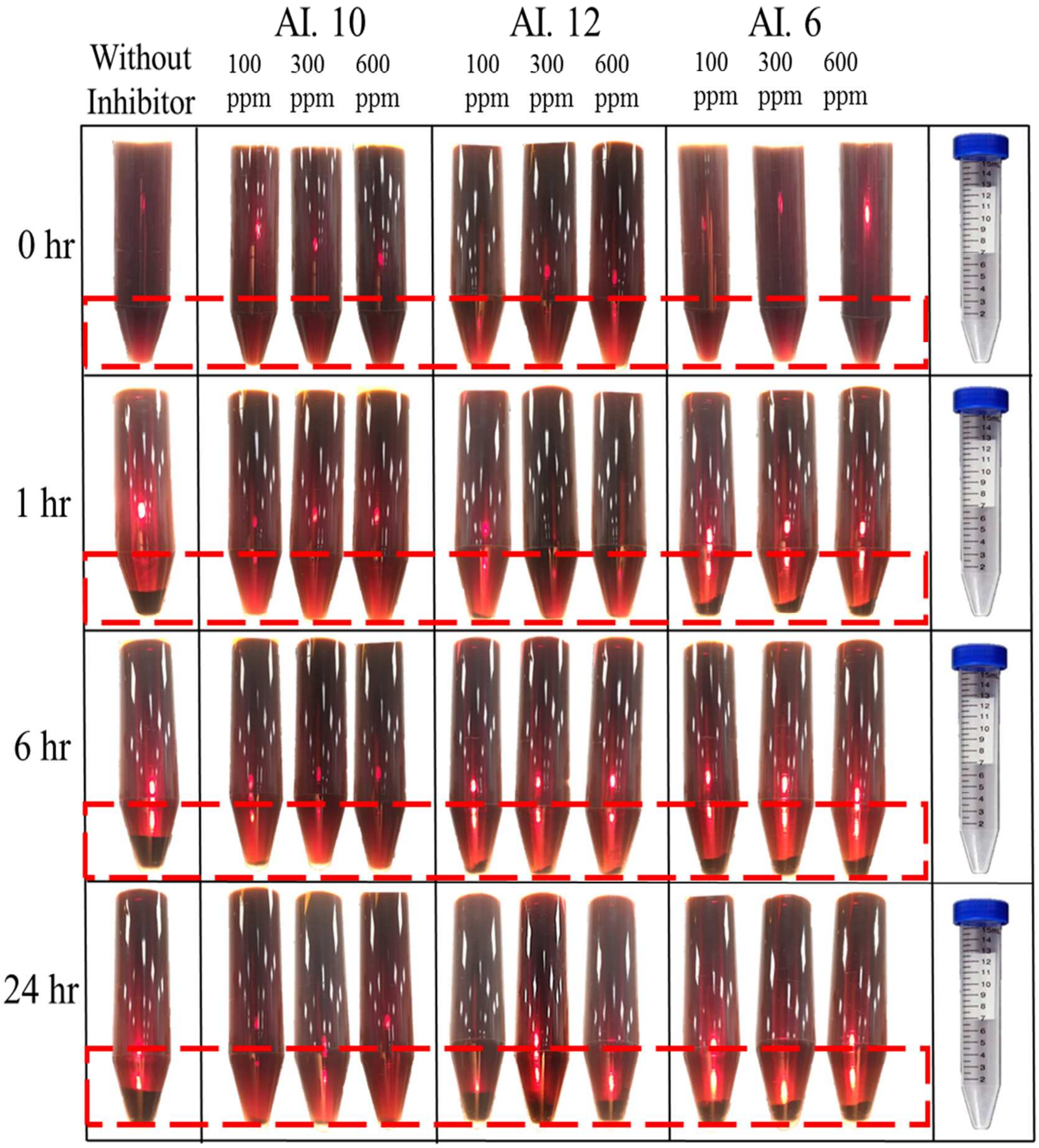

Figure 1. AIST results for crude oil "P" treated with inhibitors 6, 10 and 12 at 100, 300 and 600 ppm for different ageing times of 0 hr, 1 hr, 6 hr and 24 hr.

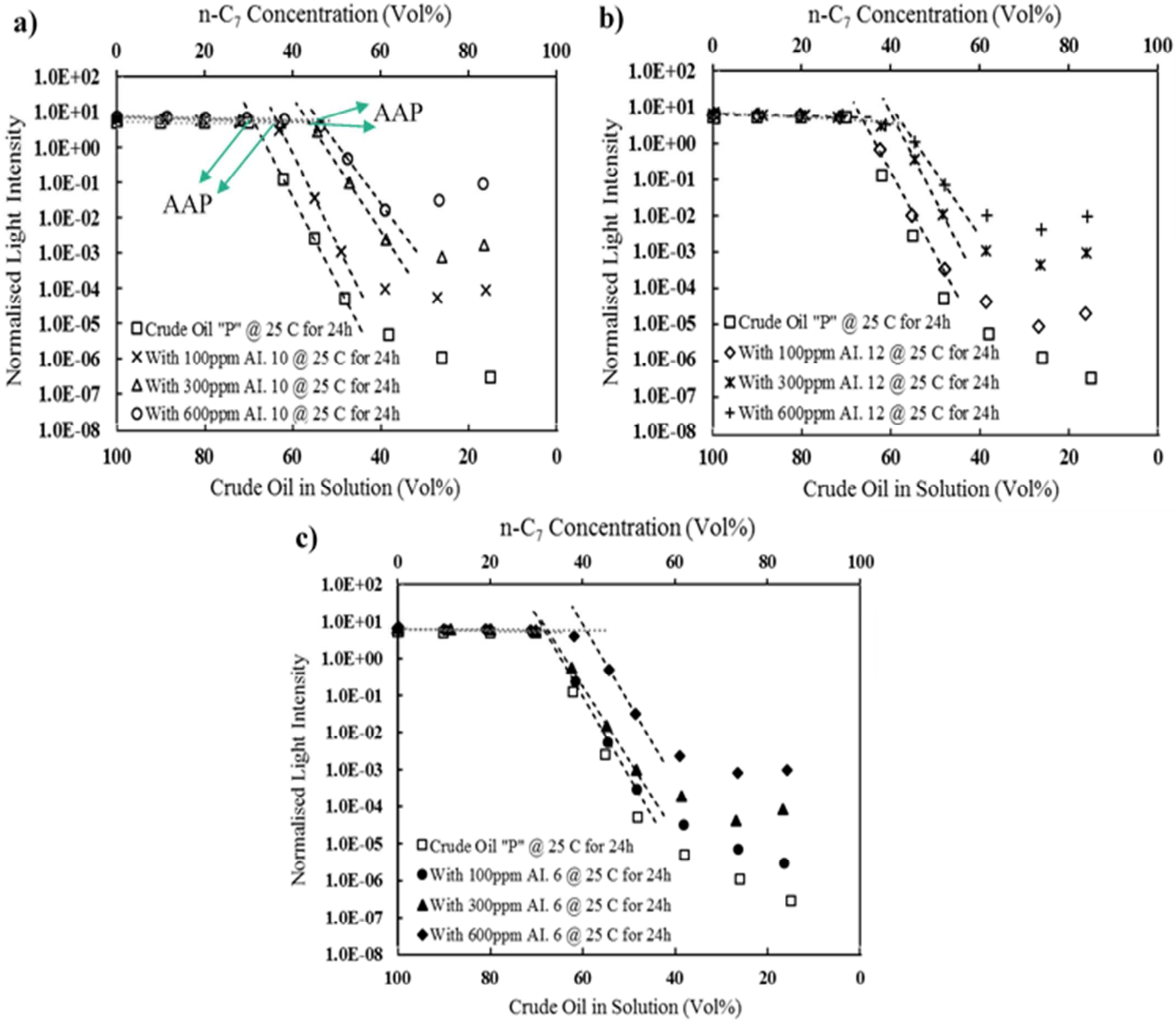

Figure 2. Results of the UV-vis-NIR spectrophotometer technique for the crude oil "P" with, (a) inhibitor 10, (b) inhibitor 12, and (c) inhibitor 6 at 100, 300 and 600 ppm, after mixing with n-heptane and ageing time of 24 hr at 25 ^{o}C.

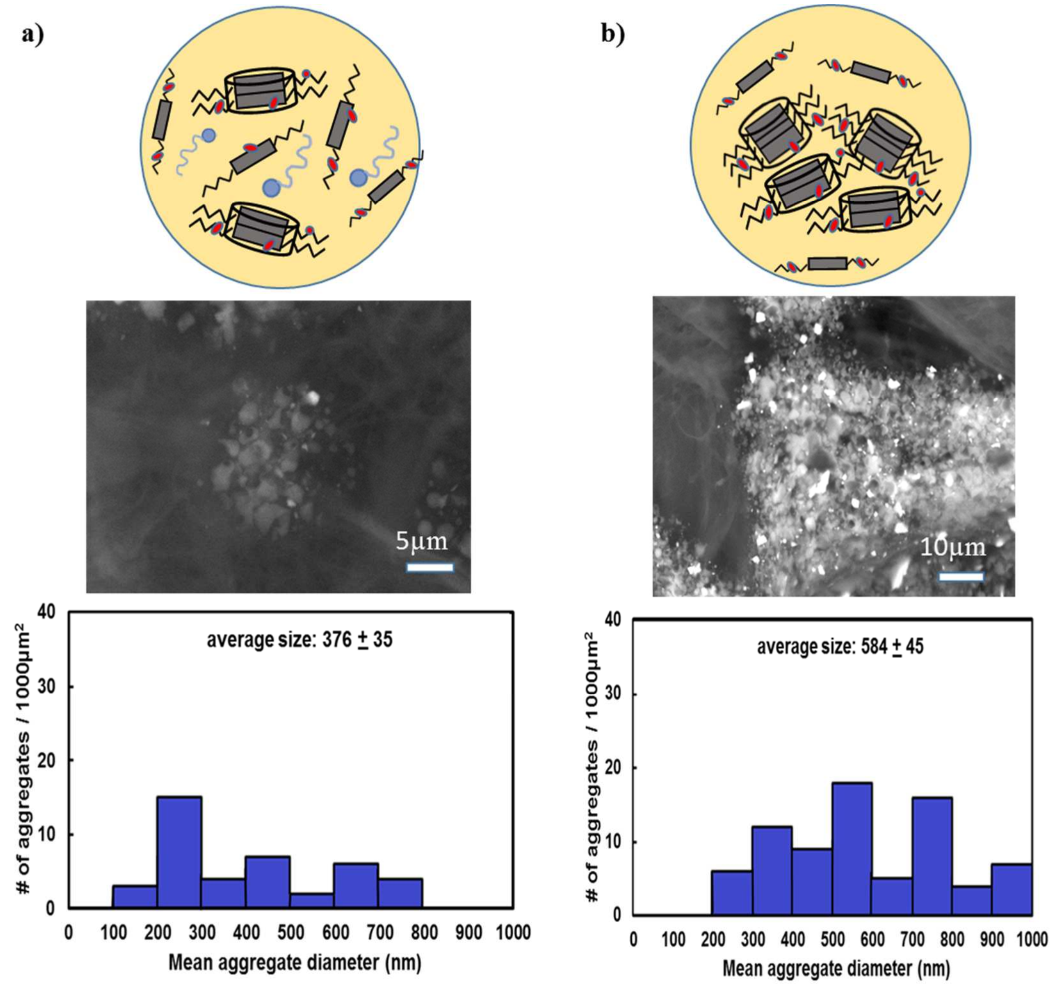

Figure 3. Effect of asphaltene inhibitor on asphaltene particle size obtained by ESEM micrographs: a) with AI. 6, b) without inhibitor. All pictures are analysed using ImageJ. This figure also presents schematic diagram of possible inhibitors interaction with asphaltenes which curbs the asphaltene-asphaltene nanoaggregate interactions to form larger particles. (▬): asphaltene monomer, (▨): asphaltene aggregates, (●): heteroatoms, (∿): inhibitor

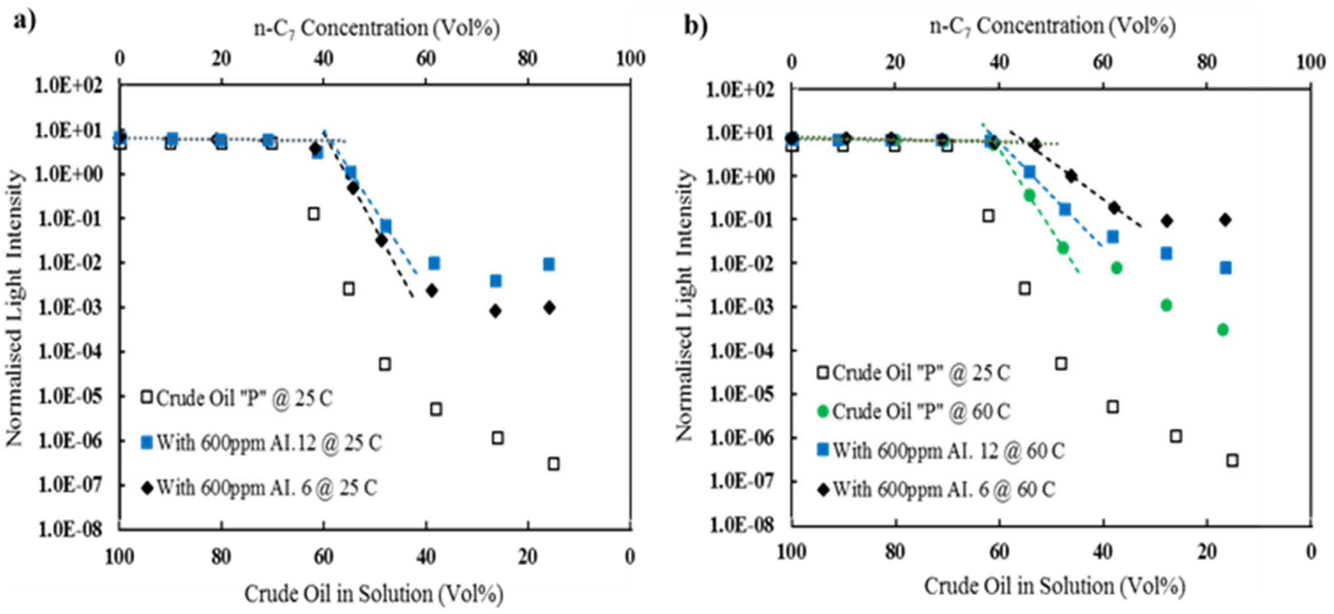

Figure 4. Effect of temperature on performance asphaltene inhibitors for crude oil “P”, a) crude oil “P” with and without inhibitors 6 and 12 at 600 ppm at 25 ^{o}C, b) Crude oil “P” with and without inhibitors 6 and 12 at 600 ppm at 60 ^{o}C, after blending with n-heptane for 24 hr ageing time.

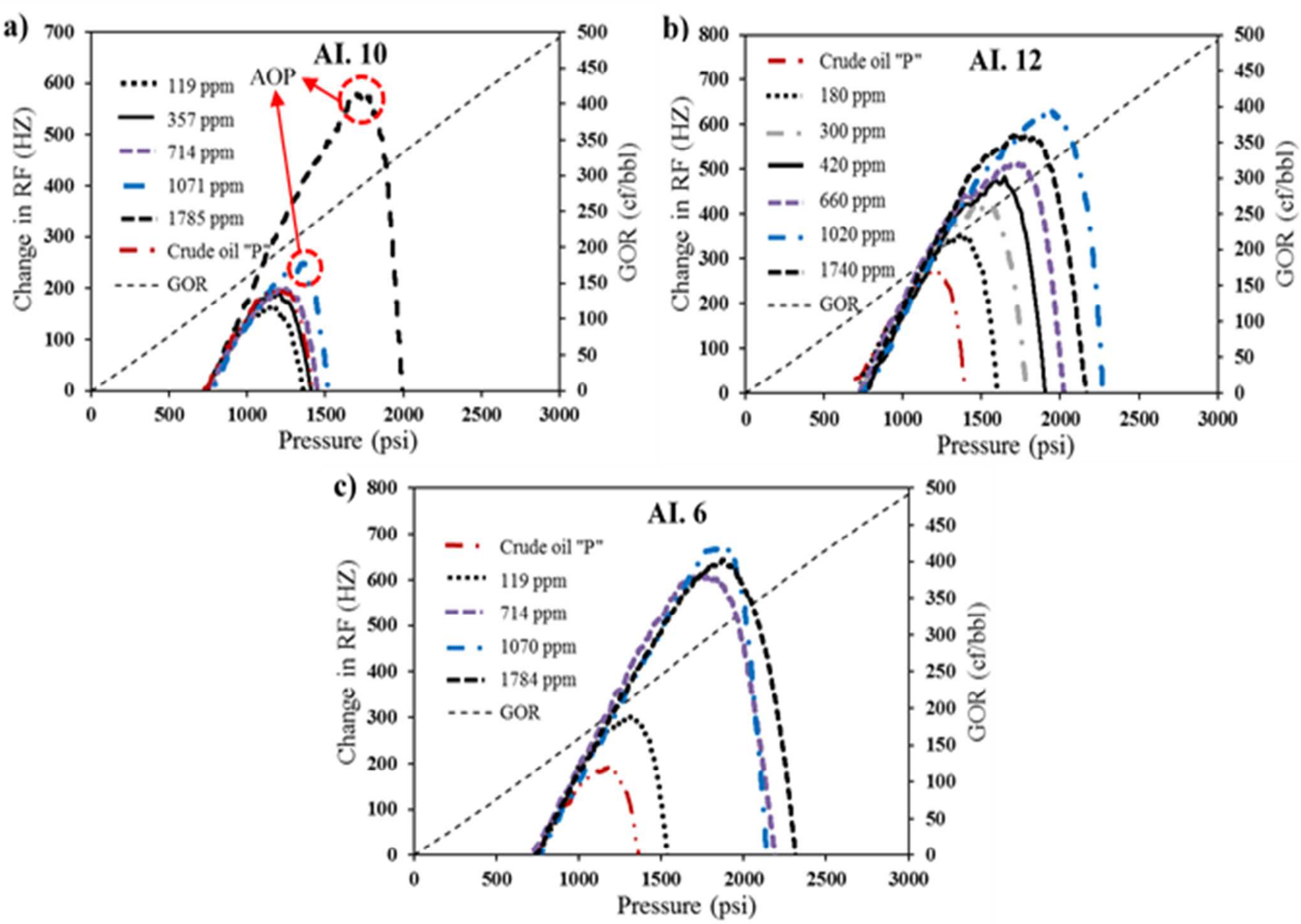

Figure 5. Results of the HPHT-QCM technique for the crude oil “P” with, (a) inhibitor 10, (b) inhibitor 12, and (c) inhibitor 6 at various concentrations, after injecting natural gas at 60 ^{o}C.

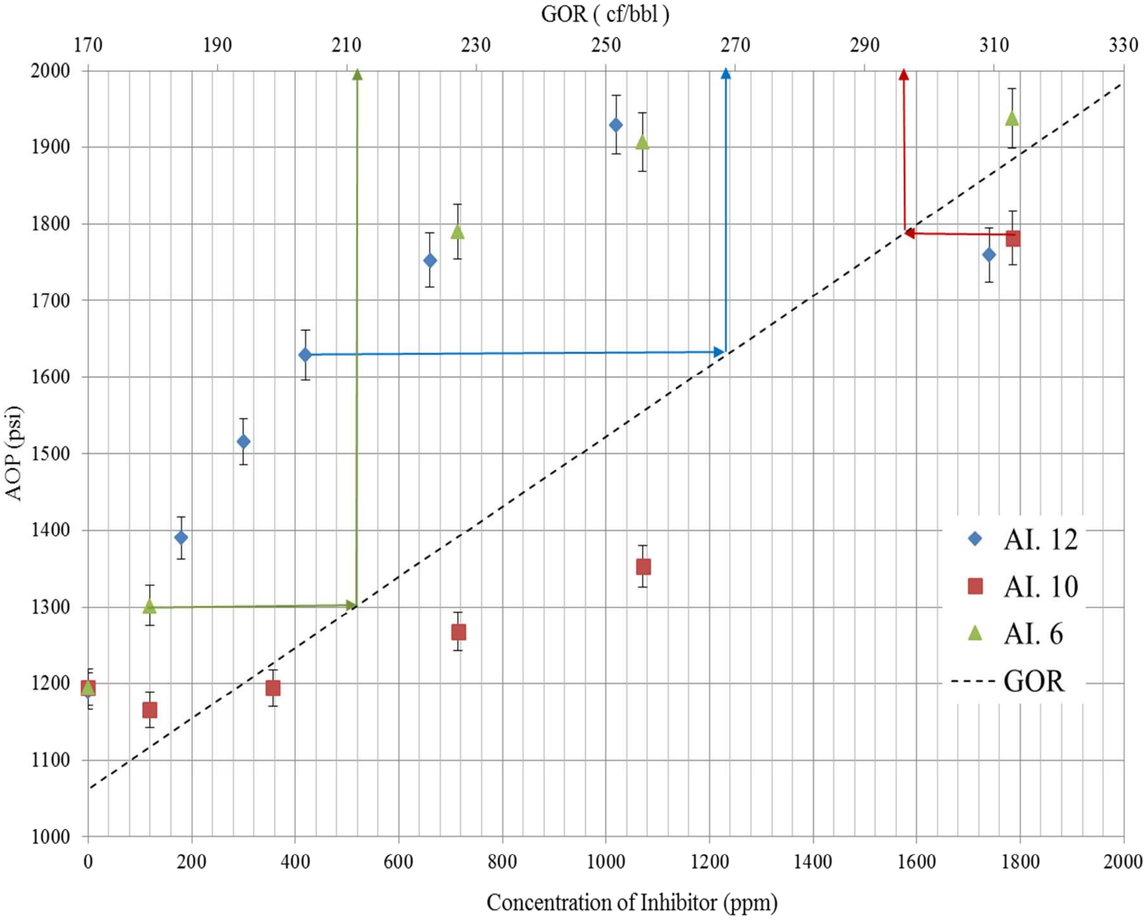

Figure 6. AOP/GOR versus concentration of three inhibitors 6, 10 and 12

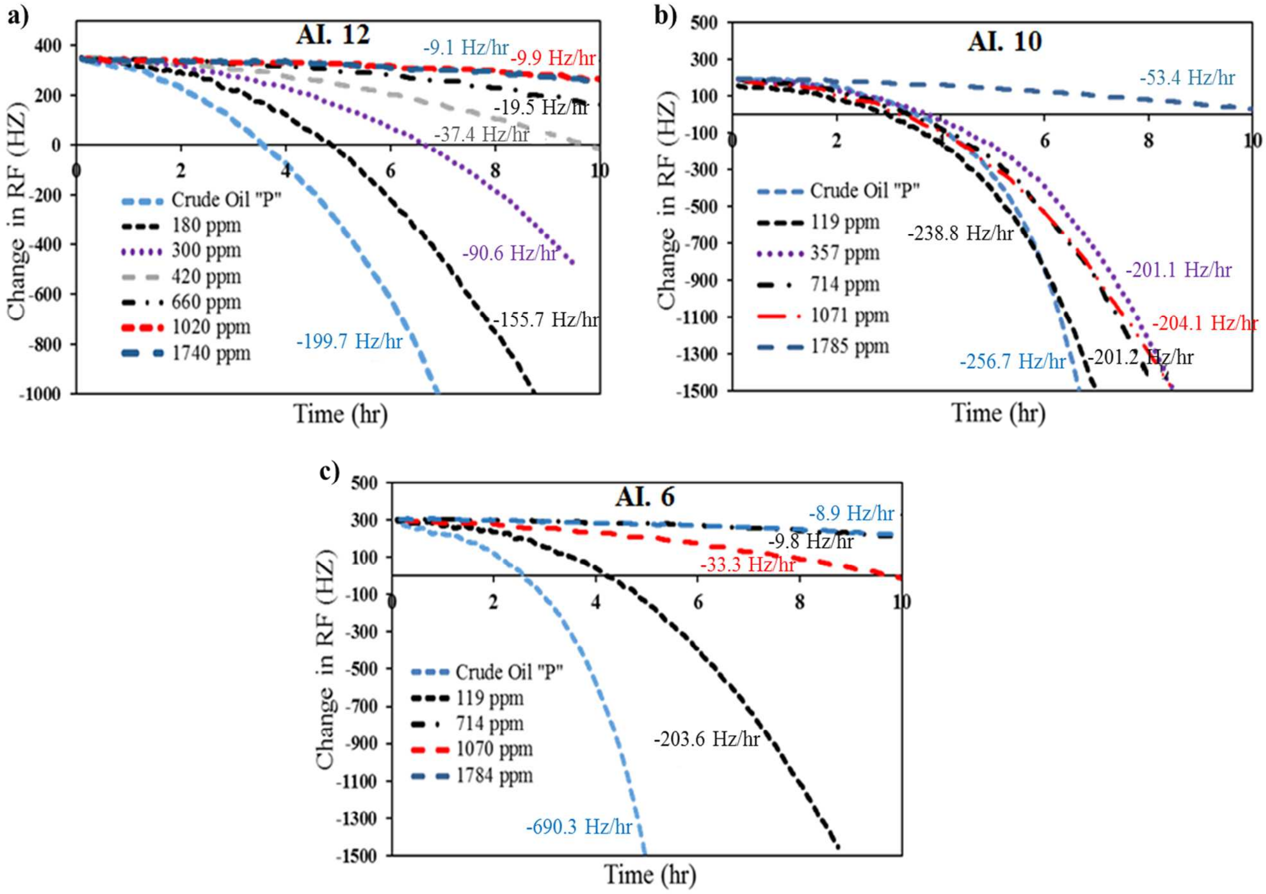

Figure 7. Results of the effect of asphaltene inhibitors on deposition rate at various concentrations, a) AI. 12, b) AI. 10 and c) AI. 6.

Table 1. Properties of Crude Oil “P” Used in This Study

Petroleum Fluid	f (g.g^{-1})	ρ_o (g.mL^{-1})	MW$_o$ (g.mol^{-1})	μ_o (cP)
B	0.0397	0.836	181	13.44

Table 2. Natural gas composition

Component	Mole%
N_2	1.84
C_1	89.94
CO_2	0.91
C_2	5.32
C_3	1.45
iC_4	0.20
nC_4	0.21
iC_5	0.07
$(nC_5) + C_6^+$	0.06

Table 3. AIST results for crude oil “P” treated with inhibitors 6, 10 and 12 at 100, 300 and 600 ppm for various ageing times

Sample	AI Conc. (ppm)	0 hr (mL)	1 hr (mL)	6 hr (mL)	24 hr (mL)
Crude oil “P”	0	Clear	0.3	0.4	0.5
With AI. 6	100	Clear	0.1	0.2	0.3
	300	Clear	Trace	0.1	0.2
	600	Clear	Trace	0.1	0.1
With AI. 10	100	Clear	Clear	Clear	Trace
	300	Clear	Clear	Clear	Clear
	600	Clear	Clear	Clear	Clear
With AI. 12	100	Clear	Clear	Trace	0.3

	300	Clear	Clear	Trace	0.2
	600	Clear	Clear	Trace	0.2

Table 4. Detection of asphaltene appearance point of crude oil "P" with 100, 300 and 600 ppm dosage of different asphaltene inhibitors, after mixing with n-heptane and aging for 24 hr at 25 ^{o}C.

Test Solution	Detection of asphaltene appearance point (n-heptane Vol %)		
	100 ppm	300 ppm	600 ppm
Blank Crude Oil "P"	30.5 ± 1.2	30.5 ± 1.2	30.5 ± 1.2
With inhibitor 6	31.8 ± 2.4	32.4 ± 1.7	41.6 ± 1.5
With inhibitor 10	36.4 ± 1.9	43.3 ± 2.0	45.7 ± 2.1
With inhibitor 12	33.2 ± 1.8	41.1 ± 1.4	42.5 ± 2.2

Table 5. Ranking of asphaltene inhibitors obtained from different techniques

Ranking	AIST	Detection of AAP @ 1 atm and 25 ^{o}C (UV-vis-NIR Spectrophotometer)	HPHT-QCM
1	AI. 10	AI. 10	AI. 6
2	AI. 12	AI. 12	AI. 12
3	AI. 6	AI. 6	AI. 10