

Effect of Crude Oil Aging on Asphaltene Inhibitor Product Recommendation

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Aging refers to the deterioration of hydrocarbon fluids that manifests as changes in the physico-chemical characteristics of the fluid upon exposure to ambient conditions. In order to understand the effect of aging of crude oils on asphaltene inhibitor product recommendation, simulated aging studies were performed on a crude oil from Wyoming with known asphaltene issues. The results clearly show that aging of crude oil affects the stability of the oil with respect to asphaltenes and caution must be exercised when recommending asphaltene inhibitor if the evaluations were performed on fluids after long-term storage. A real case study where ambient storage in the lab adversely affects the stability of the crude oil and renders asphaltene inhibitor ineffective further confirms results from simulated aging.

Keywords Aging, asphaltene stability, fluid composition, inhibitor recommendation, optimization

1. INTRODUCTION

Asphaltene precipitation and deposition is considered a menace in the oil industry. In the oil fields asphaltenes are known to plug wells, pipelines, surface facilities and subsurface formations and can even bring production to a halt.^[1–5] Crude oil production in deepwater and ultra-deepwater (DW/UDW) is an extremely capital intensive process due to increasing tieback distances and water depth and the pressure and temperature regimes applicable in what is typically an immensely challenging environment. Operational problems associated with asphaltene deposition are projected to increase in severity in DW/UDW production systems and costs associated with intervention and remediation would be substantially higher.^[6–9] Asphaltenes can also derail downstream operations due to their propensity to adhere and foul hot surfaces in refineries and poison and deactivate hydrocracking catalysts used in refining and upgrading processes.^[3,4] In the upstream side of the business, determining the nature and content of asphaltenes in a crude oil is an important parameter to develop strategy and methodology to control and manage deposition and ensure reliable, efficient, and profitable exploitation of the reservoir. The refining strategies in the

downstream side are also dependent to a great extent on asphaltene content of the crude oil.

The problem of asphaltene deposition can be prevented by either modification of the production conditions or by chemical treatment where process alterations are not feasible. A proper understanding of the production conditions and fluid composition is, thus, essential for implementation of the mitigation technique.^[1,2,8–12] This can be achieved by suitable laboratory tests, utilizing deposition prediction models, design of the oil production and transportation systems accordingly and laboratory chemical screening tests on both live and dead crude oil to identify and select inhibitor and solvents for remediation. The development/selection of inhibitor package for resolution of asphaltene deposition relies on a suite of laboratory test methods. These techniques constitute detailed analysis of the crude oil and the deposit to quantify and characterize the nature and extent of the deposition, and screening for various dispersants, antifoulants and solvents. Although the efficacy of the inhibitors is dependent on their chemical architecture; fluid quality and uniformity of the fluid samples through each stage of laboratory analyses is a key factor in accurate assessment and qualification of the chemicals.^[1]

Most of the routine screening for chemical recommendation is performed on dead oil samples. It is, thus, vital for a successful flow assurance program that samples are of good quality and as representative of the reservoir fluids as possible. Further, the importance of sampling and sample preservation is extremely important and cannot be underestimated. Organic composition of petroleum is most complex, consisting of thousands of different chemical

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compounds of varying properties and reactivity that cannot be readily simulated by simpler mixtures of known components.^[13] Procuring crude oil samples during the early development of a reservoir especially the samples that are free of treatment chemicals can be difficult. They are usually available only in very limited amounts, and their composition may alter with time. In order to provide chemical solutions to the precipitation problem, it is important to preserve sample quality during all stages of laboratory testing and screening for inhibitors for qualitative evaluation and accurate optimization. Alteration of physical and chemical properties of hydrocarbon fluids is a common phenomenon that has been observed and extensively reported after prolonged storage for finished fuels and lubricants.^[14-24] Reactive products from oxidation, autoxidation, degradation and polymerization type reactions involving reactive hydrocarbons and organic compounds of sulfur, nitrogen and oxygen have been reported from hydrocarbon fluids leading to extensive sedimentation and change in the initial compositional matrix. These changes also manifest as changes in physical property such as viscosity, color, density, or pour point and tend to reduce the quality of the oil and lead to the product being off specification.^[14,24] Crude oil is largely hydrocarbon and if not properly preserved reactive crude oil components would be prone to chemical transformations upon protracted storage or exposure to the environment that can drastically alter its original chemical and physical properties and, thus, affect its response to the asphaltene inhibitors or other production chemicals that are applied. Such fluids stand the risk of erroneous analysis and interpretation, thus, inaccurate recommendation and optimization of production chemical. They may even fail to respond to chemicals, thus, projecting an overtly unmanageable situation and may even raise false alarms. The storage history of a crude oil is, thus, of immense importance from an oilfield chemical company's vantage in accurate assessment and credible chemical recommendation and optimization. A better understanding of the susceptibility of the fluids to aging and age-induced transformations is important to predict asphaltene deposition and select mitigation approach. The purpose of this study is to examine the effect of aging of a crude oil on its response to asphaltene inhibitors. In order to understand the aging phenomena and the effect of aging on the solubility of asphaltenes, simulated aging studies were performed on a crude oil from Wyoming with known asphaltene issues. We also report a real case study where an inhibitor that successfully inhibited asphaltene precipitation in a Gulf of Mexico crude oil in the laboratory failed to stabilize it at lower treat rates and needed higher dosage for stabilization after roughly 6 months of ambient storage. The results clearly show the age of the crude oil impacts the stability of the oil with respect to asphaltenes and caution must be exercised when

recommending asphaltene inhibitor if the evaluations were performed on fluids that have not been preserved properly.

2. EXPERIMENTAL

Simulated aging experiments were performed in a Wyoming crude oil with severe asphaltene deposition issues. The effect of aging on stability with respect to asphaltenes and the effect of inhibitors were evaluated with several techniques.

2.1. SARA Analysis

Crude oil samples before and after aging were submitted to Weatherford Laboratories (Shenandoah, TX, USA) for SARA analysis. Asphaltenes were precipitated from the fluids following a modified IP 143 procedure.

2.2. Total Acid Number

Total acid number (TAN) values of all the crude oil samples were determined following ASTM D664-04 Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration and reported as mg KOH/g of oil.

2.3. FTIR Spectroscopy

Information on the changes induced in the crude oil upon aging was followed with FTIR spectroscopy. All the spectra were recorded on a Thermo Scientific (Madison, WI, USA) Nicolet iS10 Spectrometer with DTGS detector and SpeculATR ZnSe Fresnel ATR cell. Interest was focused on the carboxylic region of the FTIR spectrum.

2.4. Simulated Aging

Accelerated aging tests are routinely performed laboratory tests to evaluate the storage stability of finished fuels and the effect of stabilizers in a reasonably short time. Long-term storage to evaluate the effect of aging is not always a feasible option because it does not give a reliable answer in a reasonably short period.^[14,15] Therefore, methods of increasing the rate of the chemical reactions involved in aging by artificial means are adopted. These tests simulate long-term storage of hydrocarbon fluids and are referred to as accelerated stability test methods as they include exposure of samples to elevated temperatures in the presence of air or oxygen under increased pressure. In order to determine the effect of aging on the properties of the crude oil and its response to inhibitors, accelerated stress test was conducted on the crude oil. 50 mL of crude oil was taken in a glass bomb liner and aged at 300°F (150°C) in a pressure bomb for 16 hours under 100-psia pressure of N₂, air and O₂, respectively.

2.5. Flocculation Point Analysis

Stability of the crude oil before and after simulated aging experiments was evaluated by fouling potential

analyzer (FPA) for asphaltene instability.^[27,28] When a crude oil is titrated with an excess of paraffinic hydrocarbons, it causes the asphaltene to precipitate out at a certain volume of the precipitant. This volume may vary for different crude oils and is an indicator of the instability associated with the asphaltene for that particular crude oil. The formation of larger asphaltene particles or agglomerates that absorb/scatter light causes the absorbance signal to turn upward which is sensed by a near-IR probe.^[29] A known amount (20 mL) of the crude oil is charged to a FPA glass container and iso-octane is added to the oil at a controlled, constant rate. The oil-solvent mixture is mixed continuously with a magnetic stirring device. The flow of precipitant is controlled by a peristaltic pump and maintained at 5 mL/min. The near-IR traces are obtained with the probe directly placed inside the mixture. The results are plotted on a graph with solvent (mL) consumed in the onset of flocculation of asphaltenes on the x axis and absorbance on the y axis.

2.6. Turbiscan and Separability Numbers

The samples were analyzed on Turbiscan for evaluating the effect of asphaltene inhibitors and aging on the crude oil, using a Turbiscan MA2000 from Formulation (Davie, FL, USA) that uses a pulsed near-infrared (IR) light source (850 nm). Turbiscan performs multiple light scattering to measure the average transmittance of a sample. It measures both the stability of the asphaltenes in a particular crude oil and the relative performance of asphaltene inhibitors in that crude oil. A computer automates this technique thereby diminishing the possibility of operator error. In a Turbiscan test, an efficient asphaltene inhibitor will lower the percent transmission compared to the blank and remain relatively unchanged during the full length of the test.

Separability numbers: The stability of the fluids was quantitatively measured by calculating the separability numbers from transmission, based on modified ASTM D7061-06.^[30] This method covers the quantitative measurement of how easily asphaltenes destabilize from a sample under analysis upon addition of heptane. This is measured as a separability number by the use of an optical scanning device or Turbiscan. The method, thus, allows us to quantify the performance of inhibitors also. The rate of the phase separation is determined by measuring the increase in transmittance in the sample from the bottom of a test tube to the top (or a portion thereof) over time. The standard deviation of the average transmittance from a number of scans gives a separability number.

2.7. Asphaltene Dispersancy Test

Asphaltene dispersancy test (ADT) evaluates the presence of asphaltenes and their tendency to precipitate in a crude oil. The test also enables determination of the

efficacy of various asphaltene inhibitors or dispersants. An aliquot of untreated and treated crude oil is added to ADT test tubes that contain 10 mL of heptane. The crude oil was treated with 250 ppm by weight (based on crude oil) of the asphaltene inhibitor. The percent sedimentation due to gravity after 10, 30, and 60 minutes is observed and recorded. Subsequently, all the samples are centrifuged for three minutes at 2500 rpm. The transmission of the blank oil sample and treated samples are measured with a colorimeter (PC 910 Colorimeter, Brinkman Instruments, Westbury, NY, USA) and recorded as %T_{blank} and %T_{treated}. The blank sample is shaken again on the vortexer such that all the asphaltenes are dispersed in the solution and transmission recorded as 100% Dispersion (100%D).

Percent inhibition (%I) is calculated from transmission measurements as per the equation-

$$\%I = 100 - \left[\frac{(\%T_{treated} - 100\%D)}{(\%T_{blank} - 100\%D)} \right] * 100$$

3. RESULTS AND DISCUSSIONS

3.1. Effect of Aging on Chemical Composition of Fluids: SARA, IR Spectroscopy, and TAN Analyses

Wyoming oil used in this study has known asphaltene problems in the field. All the crude oil samples before and after simulated aging were analyzed for saturates, aromatics, resins, and asphaltenes (SARA) to examine compositional changes. TAN and IR analyses were performed to check for changes in the polarity and acid characteristics of the crude oil after aging. All this analytical data shows increase in the polarity of the crude oil. TAN values and the polar NSO (resin) fraction increase upon increasing the severity of aging conditions. IR spectroscopy further corroborates this data.

Table 1 shows the SARA data for the Wyoming crude oil before and after aging under N₂, air and O₂ environment.

As seen from SARA values reported in Table 1, the polar NSO fraction of the crude oil significantly increases upon aging and the values are conspicuously higher upon

TABLE 1
SARA of Wyoming (WY) crude oil before and after aging under different conditions

Sample ID	Oil composition (weight %)			
	SAT	ARO	NSO	ASPH
Unaged WY oil	59.56	32.76	6.95	0.73
N ₂ aged WY oil	61.88	30.01	7.21	0.90
Air aged WY oil	59.46	29.51	10.36	0.67
O ₂ aged WY oil	60.95	27.19	11.33	0.53

aging in air and O₂ atmosphere. Although resin to asphaltene ratio has been used as an indication for asphaltene stability, the trend here seems to show otherwise. It shows that caution is needed in interpreting crude oil stability with respect to asphaltenes from resin to asphaltene ratios. The aromatic fraction decrease upon aging under air and O₂ and can be explained by the aromatics in the fluid reacting with oxygen and forming polar compounds that add to the NSO fraction.^[25,26] It is also expected that the aromatics lose the alkyl side chains due to high temperature and pressure conditions during aging. The difference in these polar fractions between unaged and N₂ aged fraction is not substantial probably because the sample is only subjected to thermal stress in a non-oxidizing environment, such that oxidative degradation is avoided. Aging under air and O₂ causes sedimentation which is significantly higher for O₂ than for air. About 5–6% of sedimentation was observed for aging in O₂ atmosphere, along with some residue that adheres to the walls of the glass bomb liner. This residue did not dissolve in either toluene or methylene chloride. About 1% sedimentation was observed for the air aged sample. The decrease in asphaltene fractions upon severe aging in the presence of air and O₂ can be attributed to this precipitation from the aged fluids so that the SARA analysis was actually performed on supernatant fluids minus the precipitated solids. It is widely acknowledged that O₂ absorption is one of key factors causing aging and deterioration in hydrocarbon fluids.^[25,26]

The TAN values for all the samples are reported in Table 2.

Table 2 shows the variations in acid numbers for the Wyoming crude oil before and after simulated aging at 300° F and in the presence of 100 psia of N₂, air and O₂, respectively. The TAN when the oil was thermally stressed under N₂ atmosphere does not change much in comparison to the unaged crude oil that can be due to the absence of O₂, an accelerant for the oxidation reactions that form acidic functional groups.^[25,26] A significant increase in total acidity is evident by higher TAN values for crude oil upon aging in an air and oxygen atmosphere. This is due to the formation of acidic species in the crude oil attributed to O₂ absorption. Almost exclusively carboxylic acid formation

during stressing of middle distillate fuels which accounts for acidity increase has been previously reported.^[25] The principal mechanism of aging for transformer oils under high temperature and moisture has been reported as oxidation, which results in the formation of acids and other polar species.^[26] As expected, aging under O₂ does increase total acidity in comparison to aging under air due to pure O₂ environment. TAN of 1.8 mg KOH/g for air stressed fluid is lower than that observed for O₂ stressed fluid, due to the increased severity for aging in purely O₂ environment. Severe stress under O₂ induces significant precipitation from the crude oil, as a result of formation of species that are no longer soluble in the bulk medium.

Zoom inset for the acid region in the FTIR spectra for the unaged and aged samples are shown in Figure 1 and reflect an increase in the carboxylic acidity of the oil samples with the severity of aging conditions. For aging under oxygen appearance of anhydride is also noticed.

FTIR spectra for the unaged and aged samples reflect an increase in the carboxylic acidity of the oil samples with the severity of aging conditions. The IR spectra corroborates the TAN numbers and the small shoulder for anhydrides in the IR spectrum of the O₂ aged crude oil shows that the aging in O₂ environment not only forms acidic species but also causes them to react further and condense to form anhydrides under severe stress and high temperature. The results from simulated aging, thus, provide evidence that long-term storage under atmospheric conditions can significantly lead to alterations at molecular level in a crude oil, thus, changing its compositional profile and physico-chemical properties.

A series of articles on the changes of the chemical group compositions and the structures of Chinese petroleum

TABLE 2
TAN values for the crude oil before and after aging under different conditions

Sample ID	Total acid number (mg KOH/g)
Unaged WY oil	0.1
N ₂ aged WY oil	0.1
Air aged WY oil	1.8
O ₂ aged WY oil	2.4

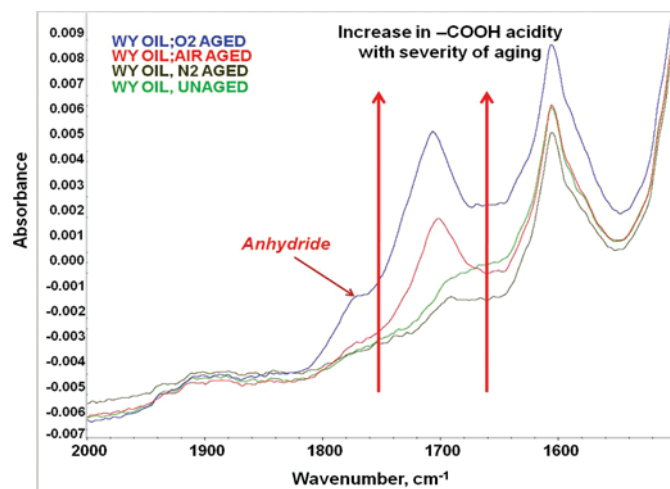


FIG. 1. Zoom inset of the carboxylic acid region (-COOH) in the FTIR spectra of the Wyoming crude oil before and after aging. (Color image available online.)

asphalts and their constituents during oxygen absorption were reported by Qi et al based on the oxygen absorption behaviors of the hydrocarbon material.^[31–33] They show that the resin and the asphaltene can easily absorb oxygen and they are more active constituents in petroleum asphalt, while the saturate hardly absorbs oxygen, which is the most stable constituent. Their research results demonstrated that asphalt constituent upon absorbing oxygen changes into the nearest heavy fraction with the exception of saturates. They reported resins conversion into asphaltene to be the highest and that oxygen molecules absorbed by samples are mainly converted into the molecules containing oxygen functionalities in the substrate. We notice similar increase in the NSO fraction (resins); however, asphaltene fraction for O₂ and air aged samples is decreasing. This can be attributed to the precipitation observed from the fluids which has not been taken into account in the SARA or other analyses that were performed in fluids minus the sediments.

3.2. Effect of Aging on Inhibitor Performance

3.2.1. Fouling Potential Analysis

Onset is defined as the minimum amount of precipitant necessary to induce the precipitation of asphaltenes. A number of methods have been developed to measure the onset of precipitation of asphaltenes in the laboratory based on conductivity, refractive index, and viscosity measurements.^[29] Optical detection via onset flocculation titration is often used to predict asphaltene destabilization. Direct measurements on asphaltene destabilization based on absorption in the UV and the near-IR region have been used in the laboratory to detect onset of precipitation as a function of the precipitant required to bring about the precipitation by titration of the oil with a paraffinic solvent (precipitant).

When a crude oil is titrated with an excess of paraffinic hydrocarbons, it causes the asphaltene to precipitate out at a certain volume of the precipitant. Absorbance is monitored as a function of the precipitant added and is an indicator of the instability associated with the asphaltene for that particular crude oil. The Wyoming crude oil sample before and after aging under N₂ was subjected to fouling potential analysis. Absorbance data were collected every second when iso-octane was added to the oil. The initial decrease in absorbance is due to dilution of the oil. The precipitant used in this experiment was *iso*-octane. Figure 2 shows the absorbance spectra for the Wyoming crude oil before and after aging (under N₂, 300° F, 16 hours) crude oil.

The downward trend in absorbance at the beginning of the titration represents the dilution effect. As the titration progresses, it induces asphaltene destabilization in the crude oil sample. The formation of larger asphaltene particles or agglomerates that absorb/scatter light causes a

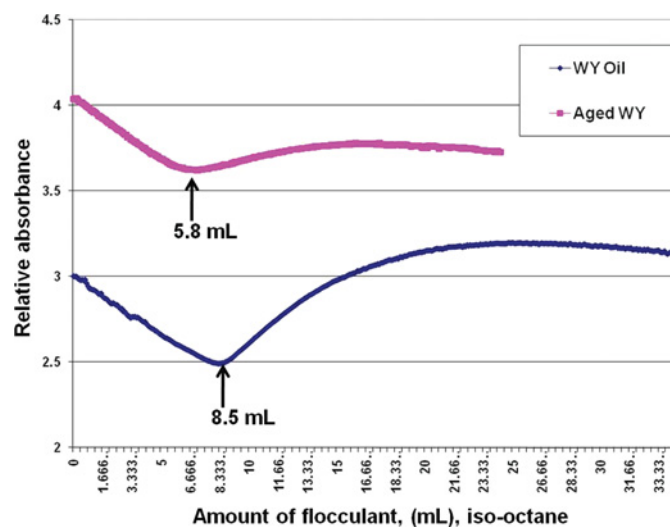


FIG. 2. Absorbance curves for representative crude oil before and after thermal stress in N₂ atmosphere. (Color image available online.)

sharp increase in the absorbance signal. The minimum in the absorbance curve, thus, corresponds to the flocculation point for the crude oil under study. Continued growth and agglomeration of asphaltene particles leads to precipitation. This precipitation is seen as a slight decrease in absorbance as the titration continues as observed from the mild maximum in the absorbance curve. Figure 2 shows the precipitation onset points for the crude oil, and it is observed that after thermal stressing, even in an inert N₂ environment, only 5.8 mL of solvent causes onset of asphaltene flocculation as opposed to 8.5 mL of the precipitant for the unstressed oil. The change in relative absorbance between the unaged and N₂ aged sample is insignificant. This contradicts observation by Wattana et al. where they report point of onset flocculation for aged crude oil at higher precipitant volume fraction.^[34] They cite loss of volatile light hydrocarbons upon aging as the reason for higher precipitant consumption to induce precipitation. However, in our study simulated aging is conducted in a sealed pressurized system and guarded against the loss of the volatile fractions. We infer that the aromatics, polar and the asphaltenic fractions of the crude oil are highly reactive and susceptible to aging that actually alters the crude oil compositional matrix. Similar observation was made from a Gulf of Mexico crude oil that will be discussed later in the text.

3.2.2. Turbiscan Measurements

3.2.2.1. Turbiscan Behavior of Unaged and Aged Crude Oil Samples. Turbiscan data from Figure 3 shows the stability trends for Wyoming crude oil before aging and after aging at 300° F, and 100 psia of N₂, air, and O₂ respectively. As the oil is destabilized, the transmission

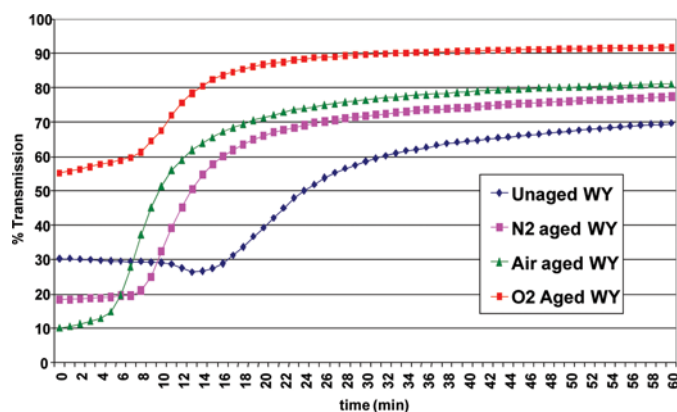


FIG. 3. Turbiscan graph of representative crude oil before aging and after aging under N_2 , air and O_2 . (Color image available online.)

through the sample increases. This increase is most likely due to particle flocculation in the oil and consequently flocculation and sedimentation of asphaltenes. The rate by which the transmission changes gives a measure of how quickly the oil is destabilized, that is, the faster the transmission increases the less stable is the oil. For treated samples, if the dispersant is effective, it will keep the asphaltenes well solubilized in the solution and prevent from precipitation, which will keep the average transmittance unchanged. On the other hand, if the asphaltene dispersant is ineffective, the asphaltene particles will flocculate and deposit, resulting in a rapid increase in the average transmission.

The optical properties of crude oil change upon simulated aging as clearly evident from the shift in behavior from Turbiscan measurements reported in Figure 3. There is a rapid increase in transmission relative to the unaged crude oil, indicating increased instability of the asphaltenes. The instability for air-aged sample is significantly higher than that for N_2 , as would be expected due to severity of the reaction conditions in terms of exposure to O_2 . O_2 aging

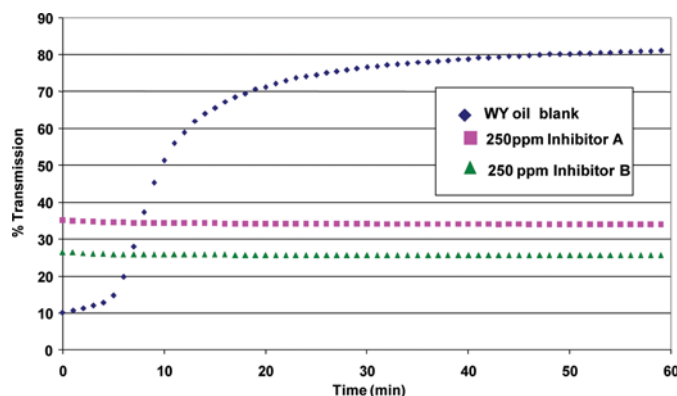


FIG. 4. Effect of inhibitors on unaged crude oil. (Color image available online.)

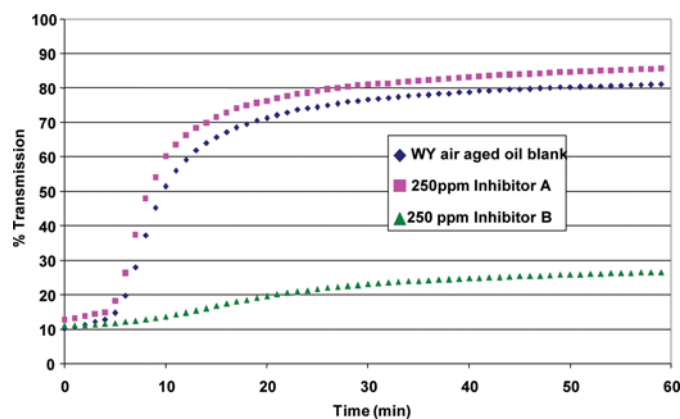


FIG. 5. Effect of inhibitors on air-aged crude oil. (Color image available online.)

conditions are as already observed most severe for the crude oil which can cause reactive crude oil components to undergo chemical transformations and induce fouling and sedimentation probably due to formation of a fraction that is no longer solvated by the crude oil. As with other analyses the Turbiscan data was recorded from the supernatant liquid, thus, accounting for most increase in transmittance. From this data it is clear that the oil's compositional matrix drastically alters upon aging.

3.2.2.2. Response to Inhibitors. The effect of aging on the response to asphaltene inhibitor chemistry was evaluated with Turbiscan on unaged and aged oil samples. Some of our best performing asphaltene inhibitor chemistries were screened on the crude oil before and after aging.

Figure 4 reports the Turbiscan curves for unaged crude oil before and after treatment with 250 ppm of Inhibitor A and Inhibitor B. Both the chemistries effectively stabilize asphaltene in the crude oil before it was subjected to simulated aging conditions.

In Figure 5, Turbiscan data for the crude oil exposed to simulated aging in the presence of air shows that Inhibitor A fails to inhibit asphaltene destabilization but Inhibitor B at 250 ppm is marginally effective in controlling asphaltene precipitation.

Figure 6 shows the effect of aging on the response to Inhibitor A, a highly successful asphaltene inhibitor chemistry. The chemistry at 250 ppm treatment rate ceases to be effective on crude oil samples aged under air and oxygen, which is due to aging induced fouling. This shifts the initial compositional matrix of the crude oil and subsequently its response to the inhibitor. The results indicate that the crude oil changes its characteristics when exposed to simulated aging conditions. It is, thus, difficult to make recommendations based on aged oil samples since oil's chemistry is expected to change over time and the oil may be compositionally different from when it was initially drawn from the reservoir.

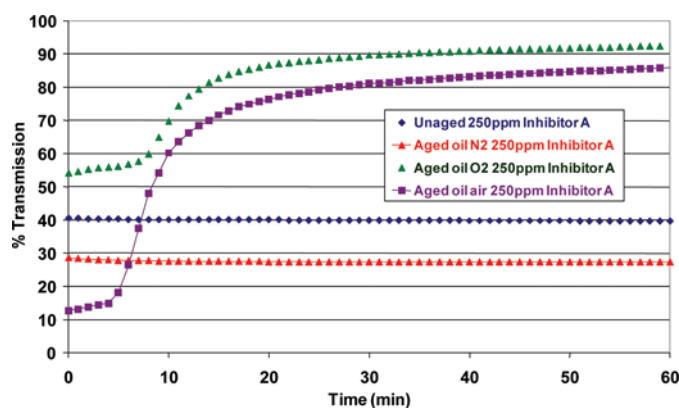


FIG. 6. Performance of Inhibitor A upon aging. (Color image available online.)

3.2.2.3. Separability Numbers. Separability numbers quantify the stability reserve or the ability of the crude oil to keep asphaltenes in suspension. A low value of the separability number indicates that there is good stability reserve within the oil and asphaltenes are not likely to flocculate and high separability number suggests that the stability reserve of the oil is very low and asphaltenes will easily flocculate, or have already started to flocculate.

Table 3 reports the separability numbers for the crude oil before and after simulated aging and the effect of the inhibitors.

Table 3 shows that the separability numbers for the crude oil increases from 19.4 to 20.7 under nitrogen stressing. In the presence of air the conditions are relatively more severe and the separability number is increased further to 22.5. The drop in the stability number after aging under O_2 stress can be attributed to the heavy sedimentation caused by the severity of aging under the presence of oxygen. Oxygen promotes severe oxidation, and instability at high temperature.^[25,26] Hence, the Turbiscan measurements in case of O_2 aged crude oil are performed on the supernatant liquid. However, O_2 stressing is too severe and would not be representative of aging under ambient storage.

As can be seen from the table, the separability number is decreasing for the unstressed and N_2 stressed oil samples

TABLE 3

Separability numbers for Wyoming crude oil, unstressed and stressed under different conditions and the effect of treatment with 250 ppm of inhibitors

	Unaged WY oil	N_2 aged WY oil	Air aged WY oil	*O_2 aged WY oil
Blank	19.4	20.7	22.5	12.1
Inhibitor A	0.3	0.3	22.0	13.0
Inhibitor B	0.2	0.2	5.1	1.1

TABLE 4

SARA of unaged and aged Gulf of Mexico (GoM) crude oil. Older sample was exposed to ambient conditions for roughly 6 months

Sample ID	Oil composition (weight %)			
	SAT	ARO	NSO	ASPH
Unaged GoM oil	38.23	49.93	9.00	2.85
Aged GoM oil	40.16	46.38	10.87	2.59

upon addition of stabilizing chemistry. It seems that thermal stressing under N_2 atmosphere does not foul the crude oil to the extent where the inhibitors are ineffective. This emphasizes the exposure to oxygen as critical to fouling of the crude oil samples. The severity of stress and fouling increases with air exposure. Inhibitor A is unable to control asphaltene precipitation. Inhibitor B, however, is effective for both air and O_2 stressed crude oil.

3.2.2.4. Real Case Study. A crude oil sample for a Gulf of Mexico oil that was successfully stabilized for asphaltene deposition in the lab with lower dosage of an asphaltene inhibitor failed to respond to the treatment chemical only upon 6–7 months of storage in a cabinet in the lab under air-conditioning. The crude oil was analyzed for its SARA composition that is reported in Table 4.

Increase in NSO fraction of the Gulf of Mexico crude oil upon 6 months of ambient storage is reported in SARA analysis (Table 4). This concurs with our observations from the simulated aging where similar trend was observed. The absorbance curves obtained from fouling potential analysis (Figure 7) of the two samples clearly show that less volume fraction of heptane is needed to induce destabilization in

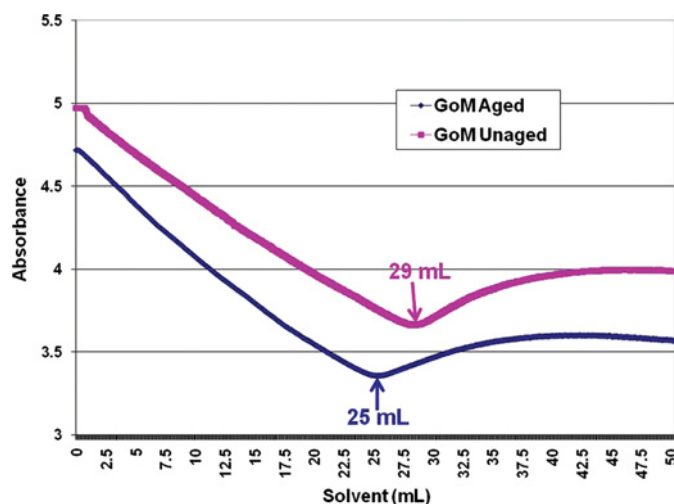


FIG. 7. Onset flocculation absorbance curves for a Gulf of Mexico crude oil before and after ambient storage. (Color image available online.)

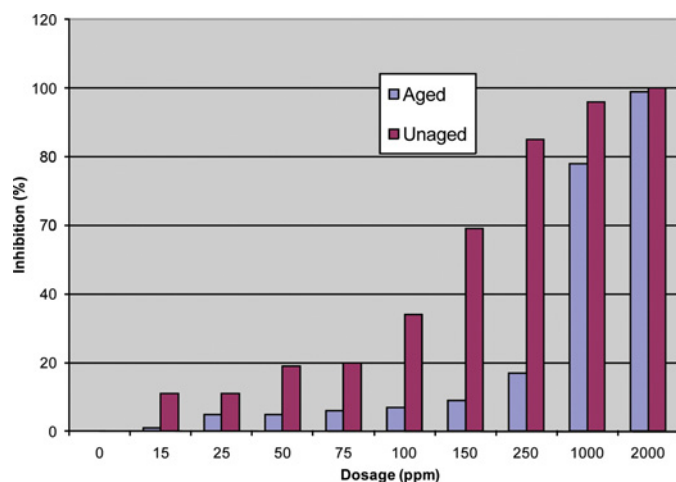


FIG. 8. Shift in the response to the inhibitor in the Asphaltene dispersion test for the Gulf of Mexico crude oil before and after ambient storage. (Color image available online.)

the older samples (25 mL as against 29 mL for the new crude oil), a difference of 4 mL which is significant.

The acidity of the sample that had been in the storage longer was higher than the acidity of fresh crude oil sample as observed with TAN values with ASTM D664. The stored sample has a TAN of 1.2 mg KOH/g against a TAN of 0.8 mg KOH/g for the fresh crude oil sample.

The percent inhibition for the new and old samples upon treatment with Inhibitor C is reported in Figure 8 as observed with asphaltene dispersion test (ADT). The ADT is a widely used laboratory test to determine the relative performance of different asphaltene control chemicals and is also based on the fact that asphaltene destabilization in a crude oil can be induced by addition of low molecular weight alkanes. The dose response chart highlights the differing response to the inhibitor for the fresh vs. stored samples. The asphaltene inhibitor is able to effectively stabilize fresh crude oil at all treat rates compared to the stored sample which shows poor response at all dosages up to 250 ppm based on the weight of the sample (crude oil). However, treatment with higher dosage (1000 and 2000 ppm) of the chemical significantly improves the stabilization of asphaltenes for the stored sample as evident from the 78% and 96% inhibition for 1000 ppm and 2000 ppm of the inhibitor, respectively. It is evident that analyses performed on aged samples would affect field treatment guidance and correct treatment level that optimizes cost and performance. Chemical optimization is vital to ensure best practice implementation in the field along with reduced costs.

Here, we demonstrate the significance of crude oil storage history on product evaluation and accurate recommendation and optimization. We infer that prolonged storage changes the compositional profile of the hydrocarbon fluids

and hampers qualitative evaluation of inhibitor chemistries and accurate product recommendation.

4. CONCLUSIONS

In order to evaluate the effect of protracted storage on crude oils and the response to inhibitors, Wyoming oil with known asphaltene issues was subjected to simulated aging in the lab. The results emphasize that storage and aging definitely changed crude oils' compositional profile. The response of the aged samples to the stabilizing chemistry also shifts, thus, hampering accurate inhibitor evaluation and recommendation if the samples were not preserved properly. The results are further supported by a Gulf of Mexico crude oil that shows different response to inhibiting chemistry after only 6 months of ambient storage. The asphaltenes for the aged crude oil could only be stabilized at higher treatment rates, thus, asserting the importance of fluid quality on chemical optimization and cost minimization. This change in behavior is due to compositional changes affected by prolonged storage at atmospheric conditions. To ensure a successful flow assurance program, particular care is needed to maintain sample integrity at all stages of testing and samples should be stored such that exposure to the atmosphere is minimum.

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