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Asphaltene Flocculation Inhibition with Ultrasonic Wave Radiation: A Detailed Experimental Study of the Governing Mechanisms

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Abstract
The concept of ultrasonic wave assisted asphaltene flocculation/deposition inhibition was earlier introduced by Najafi et al., (2011). Current study is based on a series of experimental analyses, rheological changes, flocculation behavior, and total asphaltene content of two types of crude oils.The role of ultrasonic wave radiation on these parameters are investigated in order to elaborate the changes in the kinetics of asphaltene flocculation which leads to inhibition of asphaltene flocs formation. Based on the results obtained from the experiments, one can conclude that ultrasonic wave radiation can be most effective if the wave is radiated up to an optimum time. Around this time the oil has its local minimum value of kinematic viscosity, the least value of asphaltene content, and least potential for formation of macro-structured flocsdue to reduction of aromatic to saturate ratio.
More detailed studiesrevealed that during radiation timetwo main mechanisms are active in asphaltenic crude oil: asphaltene particles disintegration and formation of asphaltene particles. Based on asphaltene content analysis, the optimum radiation time can be defined as the time at which the two mechanisms have an equal rate. The optimum radiation times are observed to be in the same time range in different tests. According to the results obtained, ultrasonic wave technology can be a potential method of flocculation inhibition and can have extensive industrial application.

Key words: Ultrasonic; Asphaltene; Flocculation inhibition

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Asphaltenes are heavy complex molecules which are soluble in aromatics and non-soluble in paraffins. They are the heaviest and the most polar fraction ofcrude oil. In petroleum chemistry it is predominantly accepted that asphaltenes are suspended in micelle form in petroleum and are stabilized by adsorbed resins in solutions (Gollapudi, 1994). The ratios of resin to asphaltene and aromatic to saturate are the key parameters that control the stability of asphaltene micelles in crude oil. When these ratios decrease, asphaltene micelles flocculate and form larger aggregates (Diallo et al., 2000). Injection of solvents into petroleum reservoirs in tertiary recovery methods can destabilize the micelle by stripping the resins from around the asphaltene molecules and would cause asphaltene depositions which will lead to drastic operation and economic complications in production, transport, and refining of crude oil.

In an earlier report (Najafi et al., 2011), the potential benefits of ultrasonic wave technology as a novel method of asphaltene flocculation/deposition inhibition was presented. This study is devoted to providing more information about the governing mechanisms in this method based on quantitative analyses.

In recent years, acousticwave technology's application to removing asphaltene deposits from near wellbore regions, cracking asphaltene molecules, etc. has been studied by many researchers. Champion et al. (2004) generated high power sound with a high voltage electrical discharge to investigate the applicability of acoustic waves for wellbore cleaning. They concluded that high power sound wave technology could be an effective method of removing wellbore plugging materials such as asphaltene. Gunel and Islam (2000) compared electromagnetic and ultrasonicwave's role on crude oil properties alteration. Their experiments showed that in the case of asphaltenic crude oil, ultrasonic waves can change the rheological properties of oil samples but these alterations are not long-lasting. The alterations made by electromagnetic waves are reported to last longer.

Dunn and Yen (2004) focused on the influence of ultrasonic waves on conversion of asphaltene molecules and concluded that sonication would lead to both dehydrogenation and cracking in bitumen. In 2009,Sawarkar et al. reported that a reduction in asphaltene content was observed due to conversion of refinery residues to lighter hydrocarbons in the boiling range of gasoil fractions. The reaction time in their experiments varied in a range of 15 to 120 minutes.

Shedid and Attallah (2004) focused on the influence of ultrasonic waves on rheological behavior of UAE crude oils in different solvent concentrations. Temperature and solvent concentration's role were investigated in series of experiments. Microscopic studies and differential thermal analyses were carried out to analyze the experimental results. Based on their work, ultrasonic wave radiation decreased the size of asphaltene flocs. This will reduce / prevent precipitation at 10 minutes of radiation or more. In their study, asphaltene content of oil samples were 1.76 weights percent.It seems that using crude oil with more asphaltene contents would lead to more apparent results. Based on a series of crude oil rheological properties and asphaltene flocculation confocal microscopy analysis, Najafi et al. (2011) reported the existence of an optimum radiation time at which asphaltenic crude oils reach the minimum kinematic viscosity. Experiments on asphaltene flocculation process in toluene-n¬-pentane mixtures showed that wave radiation can change both flocculation rate and flocs size distribution. Accordingly, they proposed the idea of asphaltene flocculation inhibition due to wave radiation.

1. THE PROCESS OF FLOCCULATION INHIBITION

The present investigation is a continuous effort to provide more information about the process of flocculation inhibition. Confocal microscopy and rheological analyses were performed on different crude oils to prove the repeatability of the observed phenomena. Asphaltene content analysis was done based on IP143 procedure, which will lead to more viable conclusions in this study.

If it is proved that ultrasonic waves can reduce the rate of flocculation and the tendency of asphaltene particles to floc, many of the production obstacles will be removed. The main focus in the next parts of this paper will be on the role of ultrasonic waves on flocculation of asphaltene particles due toreduction of aromatic to saturate ratios in solvent injection operations.

When a wave is radiated to a liquid it will cause cavitation and consequently some micro-streams form in the liquid environment. These two mechanisms can break down and resolve the asphaltene molecular structures in crude oil. This will lead to a change in crude oil composition which in turn results in changes in the rheological behavior of crude oil. To quantify the changes a series of viscometery tests are performed.

A Cannon-Fenske Routine Viscometer-100 was used to measure the viscosity variation of crude oil samples at different time intervals of ultrasonic radiation. As the asphaltene particles are colloidally suspended into the crude oil and there are no two separate solid and liquid phases, this type of viscometers seem to report accurate values. To be more confident about the results, the measurements were performed more than one time. The ultrasonic radiation was applied using a URG500 Wave Generator with 45-kHz frequency and 75-Watts output power. The value of output power is not the nominal output of the system and was calculated based on calorimeter experiments. To know more about the calorimetery method used, refer to Kikuchi and Uchida (2011).The proper power rating was achieved to mix the crude oil well. Two different crude oils were used in these experiments. The initial asphaltene content of the crude oils L and Hwas measured to be 10.2wt% and 12.3 wt% using IP-143 method. Toleune and n-heptane were used in this method. The API gravity of each of the crudes was reported to be 20 and 12 degrees, respectively. After the ultrasonic radiation to 200 ml of each crude oil for the specified time intervals, the oil samples were cooled to ambient temperature and the measurement was taken.

Based on previous studies, it can be inferred that ultrasonic wave can play three main roles in crude oil, (Suslick, 1989)

1. Dissolution of suspended soluble particles in crude oil, and
2. Increasing the temperature of crude oil,
3. Disintegration/formation of long chain molecules and asphaltene flocs.

The resultant of these three roles in this study leads to a total increase in crude oil viscosity in both samples. As is shown in Figures1 and 2 there is an optimum radiation time at which the value of viscosity has a local minimum. This time was recorded to be between 10 to 25 minutes for sample L and between 30 to 50 minutes for sample H.

In general three ranges could be determined by these figures, as is shown in Figures 1 and 2, at each range one or two of the mechanisms are dominant. Previously Argillier et al. (2002) mentioned the concept of critical concentration of asphaltenes, above which the overlap made between asphaltene particles would lead to an increase in viscosity. The rheological behaviors at each of these ranges can be justified based on the influence of ultrasonic waves on crude oil, as follows.

Range 1: In this range the main role is played by dissolution of unsolved suspended particles in crude oil which leads to an increase in viscosity.

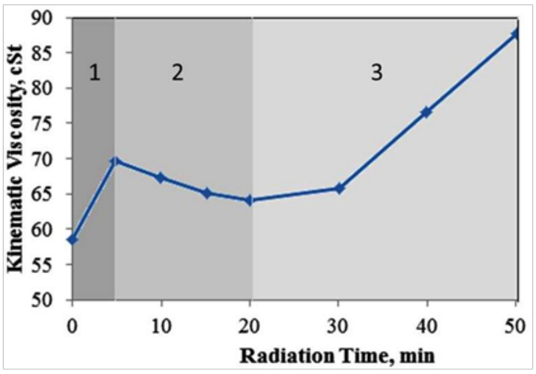

Figure1
Viscosity Changes Versus Radiation Time for Crude Sample L

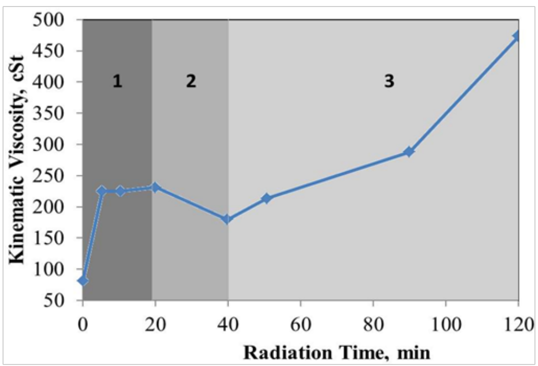

Figure 2
Viscosity Changes Versus Radiation Time for Crude Sample H

Range2: The main reasons for viscosity reduction in this range are temperature increase and asphaltene molecules disintegration. Ultrasonic wave cracks the long chain and heavy molecules and forms free radicals which leads to a reduction in viscosity.

Range 3: In all periods of sonication two mechanisms are active in crude oil system. These mechanisms are molecules disintegration into free radicals and hydrocarbons with shorter chain length, and integration of free radicals. Respectively these mechanisms cause formation of free radicals and formation of heavy molecules. This means that sonication can change the composition of crude oil. Based on the viscosity curves on Figures1 and 2,it is deduced that after the local minimum point, namedthe optimum radiation time, the dominant factor is reintegration of free radicals to each other. The next part of this paper is devoted to verify these justifications.

Comparing Figures 1 and 2 shows that an increase in API will result in an increase in optimum radiation time. For Sample H the optimum time is at about 40 minutes while it appears to be in the range of 10 to 20 minutes for Sample L.

If sonication can change the composition of a crude oil, kinetics of asphaltenic particles flocculation for crude oil samples radiated at different periods of time are anticipated to be diverse. To prove this, confocal microscopy experiment were performed. The procedure was the same as that in Najafi et al. (2011).

To study flocculation kinetics of asphaltene particles, 15 ml of n-pentane was added to 10 ml of 5% crude oil in toluene mixture; this ratio of crude oil/n-pentane ensures the flock formation. At selected times of flocculation 3 drops of the sample were taken to be observed in the confocal microscope. The light source consisted of a Tungsten lamp. The samples were observed with a magnification of 500. The microscope was connected to a PC and images of the flocculated asphaltenes were stored in raw format of 640×480 pixels. To obtain a statistically reliable particles size distribution curve, more than 10 images were taken per sample. More than 10000 images were stored to analyze the size as a function of time. Each value representing the size of flocks is an average of more than 150 particles in each sample. Photoshop software was used to determine the size of asphaltene flocks in different samples.

As it is shown in Figure 3the radiation of ultrasonic waves changed the irreversible mechanism of flocculation to a reversible phenomenon in both samples. This means that the asphaltene particles in the sonicated crude oil and n-pentane mixture have a greater tendency to separate and disintegrate flocs, rather than forming new flocs. The phenomenon was not observed in the same crude oil which is not sonicated. This shows that although irreversible models of flocculation like DLVO models can predict the flocculation behavior of asphaltene particles in non-sonicated crude oils, these models cannot be applied to the sonicated samples of the same crude. Figure 4 shows that for crude Samples L and H the least value of average flocsradius and rate of flocs growth are for Sample L3 and Sample H3.These samples were radiated for 10 minutes and 40 minutes respectively. These figures are showing the period of flocculation time at which the flocs formation rate is more than the disintegration rate.

Samples L1 to L4 were radiated for 0, 5, 10, and 20 minutes, respectively. The histograms of asphaltene flocs size at different flocculation times are depicted in Figure 5. An observed shift of the diagram to the left hand side could be due to radiation of ultrasonic wave. This means that at a specified time of flocculation the crude oil which was treated with ultrasonic wave has less potential for generating macrostructure flocs.

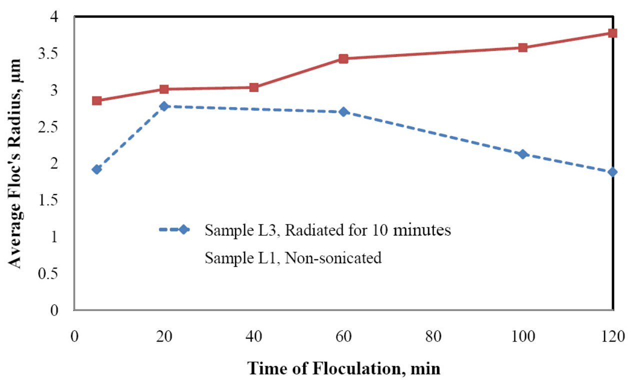

Figure 3
A Sphaltene Flocs Average Radius in Crude Sample L in Different Flocculation Times

It is known that flocs with lower sizes have a lower tendency to precipitate. As is shown in Figure 5, the trend of shifting to the left hand side, i.e. smaller flocs, is observed for the first three samples of crude oils. The third samples are the ones which are radiated for the optimum time. It was shown that the fourth sample had more tendencies for formation of bigger flocs than third sample. Based on these histograms, it can be concluded that before optimum time, radiation decreases the potential of asphaltenes for being precipitated while after this time the trend changes. It seems that radiation can make the asphaltene molecules smaller, by breaking down the chemical bonds until optimum radiation time. The result of this would be formation of free radicals which can rejoin by collision together. As the radiation time increases, these radicals' formation rate will decrease and reintegration rate will increase. After optimum time, it seems that reintegration of free radicals led to formation of heavier components and the asphaltene molecules with more branches.

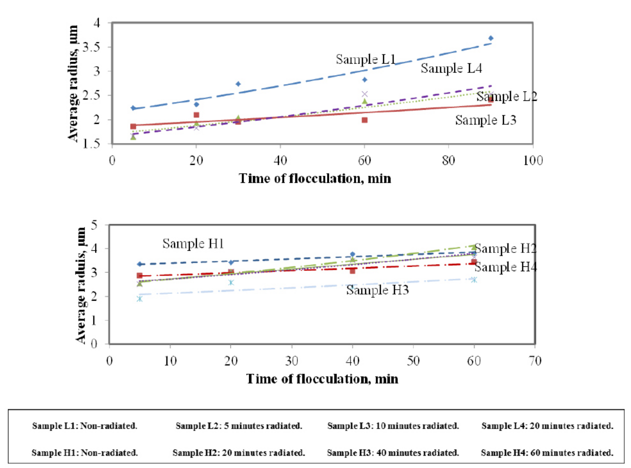

Figure4
Trend of Asphaltene Particles Radius Increase Versus Time of Flocculation in Presence of Alkane for L and H Crude Oils

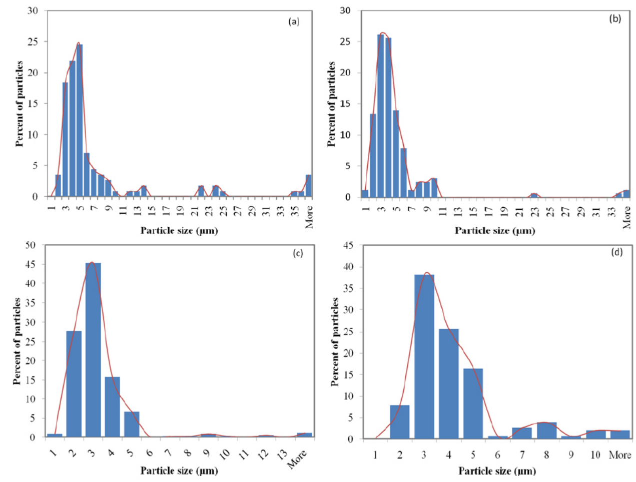

Figure 5
Particles Size Distribution Curve for Four Samples L Crude Oil Flocculated with 60% n-Pentane after 120 Minutes of Flocculation. (a) Sample L1, (b) Sample L2, (c) Sample L3, (d) Sample L4

In order to quantify the changes in asphaltene content of crude oil in a direct way a series of IP143 tests were done. In these tests the total asphaltene content of crude oils were measured. The radiation time to each sample was selected based on the results of previous experiments. Crude Sample Lwas radiated for 5, 10, 15, 20 and 25 minutes and Sample H was radiated for 10, 20 , 40, 50 and 60 minutes. For measuring asphaltene content of crude oil IP143 procedure with n-heptane and toluene as solvents, was applied.

Based on our previous experiment it was shown that ultrasonic wave radiation for a specified time can reduce asphaltene content of crude oil. As is shown in Figures 6 and 7, this reduction is measured to be about 11% for sample L and 27% for sample H. It proves that before optimum radiation time ultrasonic could break down the asphaltene particles. Focusing on Figure 7 one can see that the slope of the curve reduces and tends to zero. At the optimum point, the slope is zero and it means that the rate of asphaltene particles disintegration is equal to the rate of asphaltene formation. After this point, asphaltene formation process is dominant.

The results obtained by IP143 tests are in accordance with the results of the confocal microscopy and viscosity tests.

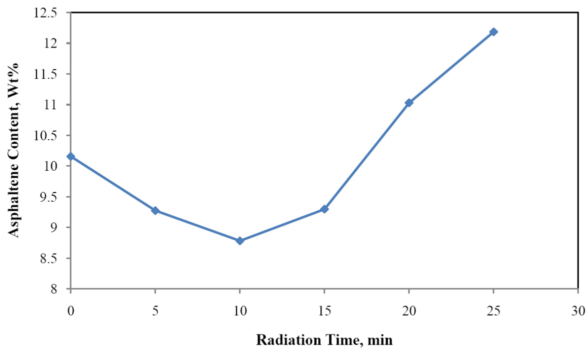

Figure 6
Asphaltene Content of Sample L Crude Oil Radiated for Different Times

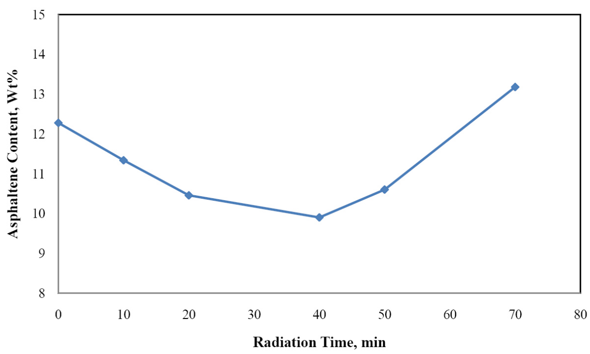

Figure 7
Asphaltene Content of Sample H Crude Oil Radiated for Different Times

CONCLUSIONS

In this study, viscometery tests, confocal microscopy and IP143 asphaltene content analysis are performed to justify the role of sonication on asphaltene flocculation in two samples of asphaltenic crude oils and the following conclusions are made:

1. Two mechanisms are always active while ultrasonic radiation, which are asphaltene particles disintegration and rejoining of free radical to form new asphaltene particles. Optimum radiation time is the time at which the rate of formation is equal to the rate of disintegration. Before optimum radiation time disintegration and after that formation is dominant.

2. It seems that heavier crude oils will have greater optimum radiation time. This time was measured to be 10 minutes for sample L and 40 minutes for sample H. Optimum radiation time measured was in accordance together in different tests.

3. It seems that performing a successful ultrasonic radiation operation requires a good knowledge of the fluid characteristics of the well and the optimum condition varies from well to well.

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