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Asphaltene Deposition and Remediation in Crude Oil Production: Solubility Technique

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Abstract: Asphaltenes are heavy fractions of crude oil responsible for serious problems during crude oil production. These problems include blockage in the oil reservoir, well tubing, transport pipelines and equipments. The nature and behavior of asphaltene in crude oils is complex and changes in temperature, pressure and composition of crude oils during production can result in precipitation of asphaltene components. Potential solutions for these problems include physical removal of deposits, solvent washes and treatment with dispersant agents. The use of aromatic solvents provides the most effective but expensive solution for asphaltene deposits in the wellbore region. This research focuses on remediation methods that can be used for the treatment of asphaltene deposits in the near-and-around wellbore, tubing and oil production facilities. In this research, a test was conducted to determine the solubility of asphaltene in toluene, xylene and a mixture of toluene and xylene solvents in order to check for its solubility in these solvents. The results from the test showed that almost 100% asphaltene solubility was achieved within 150 min when pure toluene solvent was used but for the pure diesel solvent, the asphaltene solubility after 150 min was <15%. It also proved that aromatic solvents are good solvents for asphaltenes. The results from this test can be used to select the best and less expensive solvent or combination of solvents for removing asphaltene deposits from the near wellbore region.

Key words: Asphaltene, solubility, crude oil, deposition, pipelines, remediation

INTRODUCTION

Crude oil is a complex mixture consisting of ≥200 different organic compounds, mostly hydrocarbons (Havard, 2006). During the production of crude oil, the temperature and pressure of the produced fluid decreases along it is production pathway. This reduction disturbs the equilibrium of the oil composition particularly the heavier components like asphaltene and paraffin wax, leading to their separation, precipitation and deposition at in-and-around well bore and production tubing. Such a deposition can choke the flow passage from reservoir to well bore and reduce the production of oil appreciably (Ibrahim and Ali, 2005).

Other locations affected by the deposition along the production pathway include surface production facilities, flow lines, pipelines, pumps, storage tanks and even oil wells (Remy *et al*., 2007). Asphaltene deposition particularly in the near-and-around wellbore region and in production tubing can reduce the production of oil appreciably by restricting the flow passage from reservoir to wellbore, damaging pumps, plugging flow lines and pipelines and fouling production handling facilities. Asphaltenes are the heaviest constituents of crude oil and are believed to exist in crude oil in dissolved colloidal form under initial reservoir conditions. The presence of asphaltene in this form in crude oil accounts for it is dark-brown colouration. A steric-colloid is formed when asphaltene is stabilized in the solution by adsorption of resins on its surface. Asphaltene stability in crude oil depends to a large extent on the resin to asphaltene ratio in the oil.

The presence of paraffin hydrocarbon in a petroleum fluid can cause the flocculation of asphaltene particles out of solution but in the presence of excess amount of resins, steric-colloids can be formed. The major cause of blockage to the flow of petroleum fluids is due to the flocculation of asphaltene in highly-paraffinic crudes which is irreversible. The flocculated asphaltenes will precipitate out of the solution unless there is enough resin in the solution that can cover the surface of the asphaltene particles by adsorption and form steric-colloids (Mousavi-Dehghani *et al*., 2004).

Asphaltenes are responsible for numerous production problems during the production of crude oil. These problems include the formation of organic deposits in oil reservoirs, wellbore, tubing, transport pipelines and equipment leading to a significant increase in the

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production operational costs. Chemical remediation which involves the use of aromatic solvents and/or dispersants is an excellent method for the removal of asphaltene deposits near-and-around the wellbore region. Aromatic solvents like toluene and xylene are mostly used because of the high rate of solubility of asphaltene in these solvents.

For the removal of asphaltene deposits in the production tubing, mechanical methods such as pigging and wirelining have been proven effective. The injection of de-asphalted (heavy) crude oil as well as hot, visbroken heavy crude oil into the near-wellbore formation as a solvent has proven to be a less expensive and a more environmental-friendly method for the revival of wells closed due to wellbore and near-wellbore obstruction caused by asphaltene deposits (Marvin *et al*., 2008; Jamaluddin and Nazarko, 1995).

Conventional asphaltene treatment techniques involves the continuous treating of asphaltene in the well tubing and flow lines and batch treatment for cleaning dehydrating equipments and tank bottoms. Asphaltenes comprise the heaviest polar fraction of crude oil. The classification of asphaltenes is based on it is solubility characteristics in various solvents. Asphaltenes belong to a class of soluble compounds found in petroleum fluids and are functionally defined as a precipitate obtained from petroleum by adding an excess of n-heptane (Rajagopal and Silva, 2004).

Due to the tendency of self-aggregation, the molecular weight of asphaltene molecules has been difficult to measure but molecular weights in the range of 500-2000 g mole^{-1} are believed to be reasonable. Asphaltene monomer molecular size is in the range 12-24Å (Narve, 2002). On heating >300-400°C, asphaltenes are not melted but decompose, forming carbon and volatile products. The colour of dissolved asphaltenes is deep red at very low concentration in benzene as 0.003% makes the solution distinctly yellowish. The black colour of crude oil and residues is due to the combined effect of neutral resins and asphaltenes which are not properly stabilized. Asphaltene can assume various forms when mixed with other molecules depending on the relative sizes and polarities of the particles present.

They are soluble in aromatic solvents and insoluble in aliphatic solvents. Asphaltene deposition occurs due to pressure reduction, temperature drop and change in fluid composition during crude oil production. As pressure decreases during reservoir production, the composition of the light components increases leading to a decrease in asphaltene solubility in the crude oil. This decrease in solubility continues until it reaches a maximum at the bubble point pressure. Below this point, asphaltenes become soluble again due to the evaporation of the light components. The reduction in temperature below the cloud point causes the precipitation/ crystallization of asphaltene out of the solution. This eventually leads to reduction in flow rate and deposition of asphaltene in production facilities.

For light crude oils as evaporation takes place due to pressure decrease, the percent by volume of the crude is reduced in favour of the asphaltene constituents leading to deposition but heavy crude oils, despite their high asphaltene content, generally possess higher amounts of resin (Narve, 2002).

When the amount of adsorbed resins on the asphaltenes is in too low quantity, the asphaltenes become only partly-covered by the resins. This will lead to the instability of the asphaltenes and hence, deposition. Also, the presence of light paraffin components in crude oil lowers the solubility power of the asphaltene molecules leading to their precipitation and deposition (Garshol, 2005).

MATERIALS AND METHODS

Asphaltene solubility test: This test on asphaltene solubility was conducted using toluene, diesel and a mixture of toluene and diesel solvents to determine the rate at which asphaltene dissolves in these solvents in order to select the most suitable solvent for removing asphaltene deposits in the near-wellbore region and well tubing.

Experimental procedure: The precipitated asphaltenes were ground and a fixed amount (5 g) was added to a solvent in a conical flask and left to stand for 30 min. The solution was not stirred. After 30 min, the solution was filtered through a filter paper apparatus weighing 0.87 g. The asphaltene residue was collected on the filter paper and was dried at 25°C after which the filter paper-asphaltene residue was weighed using a weighing balance and the weight of the asphaltene residue determined. The amount of asphaltene soluble in the solvent was gotten by subtracting the amount of insoluble asphaltene from the 5 g of asphaltene initially added to the solvent. The insoluble asphaltene (residue) after drying was added to the solution. The same procedure was repeated for at t = 30, 50, 70, 90, 120 and 150 min, respectively. The experimental procedure was conducted using 100% toluene, 100% diesel, 75:25, 50:50 and 25:75 toluene-diesel solvent mixtures.

RESULTS AND DISCUSSION

For each of the solvents and solvent mixtures used in the experiment, it was observed that more of the asphaltene got dissolved in the solvent as more time was allowed, leading to a higher solubility with time. From Table 1, it can be seen that asphaltene solubility increases with time and this will help to know the effect of contact time on the use of a particular solvent in cleaning organic deposits in the wellbore region.

Figure 1 shows a plot of percentage solubility against time (min) for the 100% toluene, 100% diesel and mixture of toluene and diesel in various proportions. From Fig. 1, the 100% toluene solubility curve displays an excellent increase in solubility as the solvent soaking time is increased. This shows that toluene (an aromatic solvent) is an excellent solvent for cleaning asphaltene deposits in the near-and-around wellbore region. This method can be used for asphaltene remediation but it is an expensive method due to the extra amount spent by the affected companies in purchasing this solvent.

For example in Eastern Venezuelan where severe asphaltene deposition problem is experienced, each solvent treatment event using aromatic solvents costs the oil producing company US $50,000 (Cenegy, 2001). The 75% toluene and 25% diesel mixture also show that asphaltene solubility is increased as the time is increased, thus this solvent combination can be used in cleaning asphaltene deposits in the wellbore region. Here, the diesel which is readily available and cheap is acting as a dispersant while the quantity of toluene required is reduced. This method is not a very expensive one compared with using 100% aromatic solvent due to the lesser amount spent on purchasing the solvent.

Table 1: Asphaltene solubility data using various solvent proportions

	Solubility				
Time (min)	100% toluene	75% toluene, 25% diesel	50% toluene, 50% diesel	25% toluene, 75% diesel	100% toluene
30	70.0	48.0	27.8	24.6	6.2
50	84.6	57.0	43.4	28.8	8.0
70	89.4	66.0	48.6	32.8	9.0
90	95.0	80.6	58.0	34.4	10.6
120	97.6	85.2	65.4	36.2	12.4
150	98.8	90.4	75.6	38.4	13.2

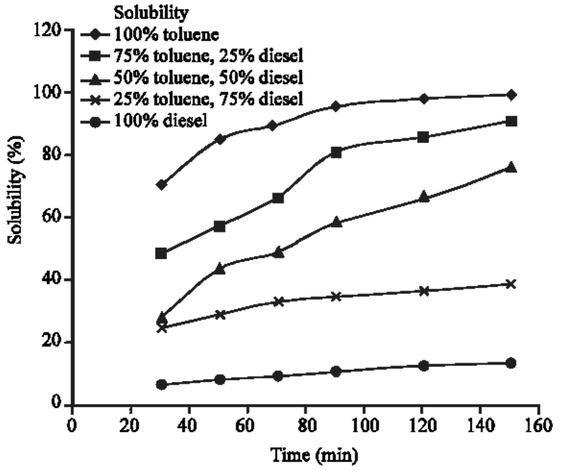

Fig. 1: Plot of solubility (%) against time (min) for various solvents

The 50% toluene and 50% diesel mixture show a good increase in asphaltene solubility with time from the results. This mixture can be used for cleaning the wellbore region if enough soaking time is allowed. This will require a shutdown of production for some time for a more effective cleaning to take place. It is a less expensive but time consuming treatment method and not economical for production.

From the 25% toluene and 75% diesel solvents data, it can be observed that as the time was increased, the difference in solubility is not appreciable. This can be explained from the low percentage of toluene (an aromatic solvent) with respect to the percentage of diesel used. This method is very time consuming and will lead to a very long time of shutdown of production and hence, losses. It is not an advisable solvent for asphaltene deposition treatment in the wellbore. From the results obtained, 100% diesel presents a very poor result for the solubility of asphaltene with time. Even with the time increase, the increase in solubility is insignificant. This shows that pure diesel is not a recommended solvent for asphaltene deposition treatment.

Thus, the 100% toluene solvent is the most favourable solvent for cleaning the near-and-around wellbore region which is the most damaging location for asphaltene deposition. Although, it is the most expensive method, a lesser shutdown time is required and enhanced oil recovery is achieved.

CONCLUSION

Asphaltene solubility tests were conducted on toluene, diesel and a mixture of toluene and diesel solvents in order to select appropriate solvents for cleaning plugged asphaltenes in the Wellbore region and production tubing. The test results showed that diesel is not a very good solvent and <15% of the asphaltenes dissolved after soaking for 2 h, 30 min (150 min). On the other hand, about 99% solubility was attained with pure toluene in under 150 min and if more soaking time was allowed, 100% solubility would be achieved.

These results have helped to prove that aromatic solvents are the best solvents for asphaltene treatment. For each of the toluene-diesel mixtures, it can be seen from the results that asphaltene solubility rate can be increased using these solvents if more solvent soaking time is allowed. In other words for these solvent mixtures, complete solubility can be achieved if the contact time between the asphaltene deposits and the mixture is increased in the Wellbore region.

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