

Investigation of Reversibility of Asphaltene Precipitation and Deposition for an Iranian Crude Oil

*Ashoori, Siavash *⁺; Jamialahmadi, Mohammad*

Faculty of Petroleum Engineering, Petroleum University of Technology, Ahwaz, I.R. IRAN

Müller Steinhagen, H.

Institute of Thermodynamics and Thermal Engineering, University of Stuttgart, Stuttgart, GERMANY

Ahmadi, Kaveh

School of Engineering, University of Kansas, Lawrence, USA

ABSTRACT: *In this work, the precipitation and re-dissolution of asphaltenes were studied for an Iranian relatively heavy crude oil. A series of experiments were designed and carried out to quantitatively examine the reversibility of asphaltenes precipitation upon the change in the solvent concentration along with the temperature. n-Heptane was used as the precipitant, and a temperature range of 30 to 70°C was applied to perform the temperature reversibility tests. Experiments were conducted in both porous and non-porous media. As a porous medium, a slim tube apparatus was used which is a one-dimensional model reservoir. Generally, the experiments showed that the precipitation is completely reversible for oil under study upon both composition and temperature changes.*

KEY WORDS: *Asphaltene, Precipitation, Deposition, Dissolution, Reversibility, Porous media, Temperature effect, Composition effect.*

INTRODUCTION

Asphaltene are high-molecular weight solids which are soluble in aromatic solvents (benzene and toluene) and insoluble in paraffinic solvents [1].

Asphaltene precipitation and deposition may take place during petroleum production, transportation, refining and processing as a result of change in pressure, temperature and composition of the crude oil. In addition to

these, asphaltene precipitates may deposit in the pore spaces of reservoir rock and form plugging, which is referred to as a type of formation damage.

In all cases above, it is of great importance to know under which conditions the asphaltene precipitate and to what extent precipitated asphaltene can be re-dissolved.

In other words, to what extent the process of asphaltene

* To whom correspondence should be addressed.

+ E-mail: Ashoori@put.ac.ir

1021-9986/06/3/41

7/8/2.70

precipitation is reversible with respect to change in thermodynamic conditions.

The subject of asphaltene precipitation has been studied for more than a half century, but there are still some controversies and disagreements between researchers and investigators. An important disagreement is in the nature of asphaltene in crude oil. There are two different models to describe the nature of asphaltene in the solution. The first approach is the solubility model which considers the asphaltene to be dissolved in a true liquid state. In the second approach, the colloidal model, asphaltenes are considered to be solid particles which are suspended colloiddally in the crude oil and are stabilized by large resin molecules. According to the solubility model, asphaltene precipitation is a thermodynamically reversible process, while in the colloidal model, precipitation of asphaltene is considered to be irreversible. The validity of each of these models depends on whether the precipitation process is reversible or not.

Pfiffer and *Saal* (1940) believe that asphaltene experimental observation of the colloidal behavior of asphaltene suspensions [2].

Hirschberg et al. (1984) observed reversibility of asphaltene precipitation with pressure at 94°C. They assumed that asphaltene precipitation is reversible but is likely very slow [3].

Andersen and *Stenby* (1996) studied the effect of temperature on asphaltene precipitation /dissolution. They used a mixed solvent (toluene and n-heptane) and performed solvent reversibility runs at 24, 50, and 80°C. Although the reversibility of precipitation with temperature was not explicitly investigated, the results demonstrated that asphaltenes partially re-dissolve with an increase in temperature [4].

Fotland (1996) and *Wang et al.* (1999) have speculated that asphaltene precipitation is less likely to be reversible for crude oils subjected to conditions well beyond those of the precipitation onset [5].

Rassamdana et al. (1996) performed experiments at room temperature to study the reversibility of asphaltene precipitation with respect to composition. They concluded that the asphaltene precipitation process is partially reversible [6].

Pacheco-Sanchez and *Mansoori* (1997) suggest that asphaltene flocculation is irreversible [7].

Hammami et al. (1999) used SDS (solids detection

system) for their works and concluded that asphaltene precipitation is generally reversible but is time dependent [8].

Peramanu et al. (2001) reported differences in the reversibility of solvent - and temperature-induced aggregation. Their investigation confirmed that solvent treatments can be an effective method for re-dissolving asphaltenes as long as there is sufficient turbulence to break-up the asphaltene particles; another result suggested that temperature treatments may not be the best method for re-dissolving asphaltenes [9].

To answer the question of reversibility of asphaltene precipitation/deposition processes, two sets of experiments were carried out in both non-porous and porous media. In the non-porous medium the behaviors of precipitated asphaltene in the crude oil under study following flocculant removal by vaporization and addition of fresh crude oil were investigated. The reversibility of asphaltene precipitation due to temperature change was also examined. In porous medium a flooding test was performed by injecting a mixture of n-heptane and crude oil and thereafter fresh oil was injected into the porous medium.

EXPERIMENTAL

Materials and apparatus

The crude oil under study was a relatively heavy tank oil with a gravity of 20°API sampled from one oil field in the southwest of Iran. The asphaltene content of the oil was found to be 8% by weight. The crude oil was stored under laboratory conditions for up to three months, to allow any volatile components to evaporate, in order to establish a stable condition and to obtain a crude with relatively fixed composition. The oil was then filtered by means of a standard filter paper (Wattman No. 42) to ensure that there is no sand or clay content, which are usually associated with the produced oils.

Extra pure n-heptane was obtained from Merck. In all experiments, n-heptane was used as the precipitant, and the gravimetric method was followed for measuring the amount of asphaltene precipitated.

Investigation of reversibility in non-porous media

Three series of tests (R-1, R-2, and R-3) were carried out to investigate the effects of composition and temperature on reversibility of asphaltene precipitation.

Tests R-1 and R-2 were conducted to investigate the effect of composition while Test R-3 were performed to investigate the effect of temperature. In Test R-1, several mixtures of oil and n-heptane were prepared with different dilution volume ratios, R_v . After 24 hours, the amount of precipitated asphaltene along with the density of each mixture was measured (precipitation process). Then a mixture was prepared with $R_v=15$ and kept in a dark place for 24 hours. The container cap was removed to allow n-heptane to vaporize. The amount of precipitated asphaltene and density were then measured at particular times (re-dissolution process).

Test R-2 involved the addition of enough fresh oil to different mixtures of oil and n-heptane. Four mixtures with dilution volume ratios of 2, 4, 7, and 10 were prepared and after 24 hours, samples of each mixture were collected. Then desired volumes of fresh oil were added to each mixture to obtain very dilute solutions, below the precipitation onset ($R_v=0.3$). The mixtures were left for a long time while their caps were closed. Again sampling and measurements of the sample's density and the amount of precipitated asphaltene were carried out in case of each mixture.

In test R-3, a mixture of n-heptane and oil with dilution ratio of 1 was prepared. Twenty samples were taken from this mixture and put in a temperature-controlled oven. First the temperature was set at 30°C. After 24 hours, 4 samples were collected and the amount of precipitated asphaltene of each sample was measured. Then an average value was calculated. The temperature was raised to 50°C while the other 16 samples remained in the oven for another 24 hours. Again 4 samples were collected and the amount of asphaltene precipitated was measured. This procedure was also repeated for 70°C. Experimental results showed that the amount of precipitated asphaltene decreases with temperature.

To examine the effect of temperature variation in reverse direction, the system temperature of 70°C was lowered to 50°C and the mixture was allowed to stay at this temperature for 24 hours and thereafter sample collections and precipitated asphaltene measurements were done. This procedure was also repeated for temperature of 30°C. Recent measurements showed that the amount of precipitated asphaltene increases as temperature decreases. The whole procedure was also repeated for mixtures with dilution volume ratios of 2/3, 7 and 12.

Investigation of reversibility in porous media

To study the reversibility of asphaltene precipitation and deposition in porous media, a Ruska slim tube was used. The slim tube is a narrow stainless steel tube coil of 7.9 mm O.D. and 6.2 mm I.D. The tube length is 18.3 m (60 ft), coiled to a diameter of roughly 20 cm. The tube is packed with 150 to 170-micron round-grained glass beads. The porous filling has an overall porosity of approximately 28% and an absolute permeability of 5 darcies. The total system pore volume, including lines and fittings, is 150 cm³. The slim tube is located in an oil bath equipped with an adjustable temperature controller with a resolution of 1°C. Upstream pressure is monitored with a precision pressure gauge, and a digital pressure gauge is connected downstream of the slim tube. Overall operating pressure is controlled by a downstream back pressure regulator after which the produced oil is flashed to atmospheric conditions. The schematic diagram of experimental setup is shown in Fig.1.

This stage of experiment (Test R-4) includes a set of flooding experiments to verify the reversibility of asphaltene precipitation in porous media.

Step 1: First, fresh oil was injected into the clean slim tube at a constant flow rate of 30 cm³/hr. The injection pressures were measured and recorded.

Step 2: The slim tube was cleaned, evacuated and the apparatus was set to perform injection of a mixture of 50% n-heptane concentration at 30 cm³/hr into the porous medium.

Step 3: The injection was followed by flooding four pore volumes (600 cm³) of fresh oil at 30 cm³/hr to completely displace the remaining mixture. By injection of such an amount of fresh oil, what remained from the previous mixture was asphaltene particles that already deposited in pore throats and on grain surfaces of the porous medium.

Step 4: After injection of four pore volumes of fresh oil, the pumps were turned off and the fresh oil was allowed to soak. The soaking period lasted 100 hours. During the soaking time the asphaltene particles re-dissolved in the fresh oil. After that, fresh oil was again injected at 20 cm³/hr.

REPEATABILITY OF THE EXPERIMENTS

Because of simplicity, experiments involving asphaltene precipitation in open media (e. g., beaker) are

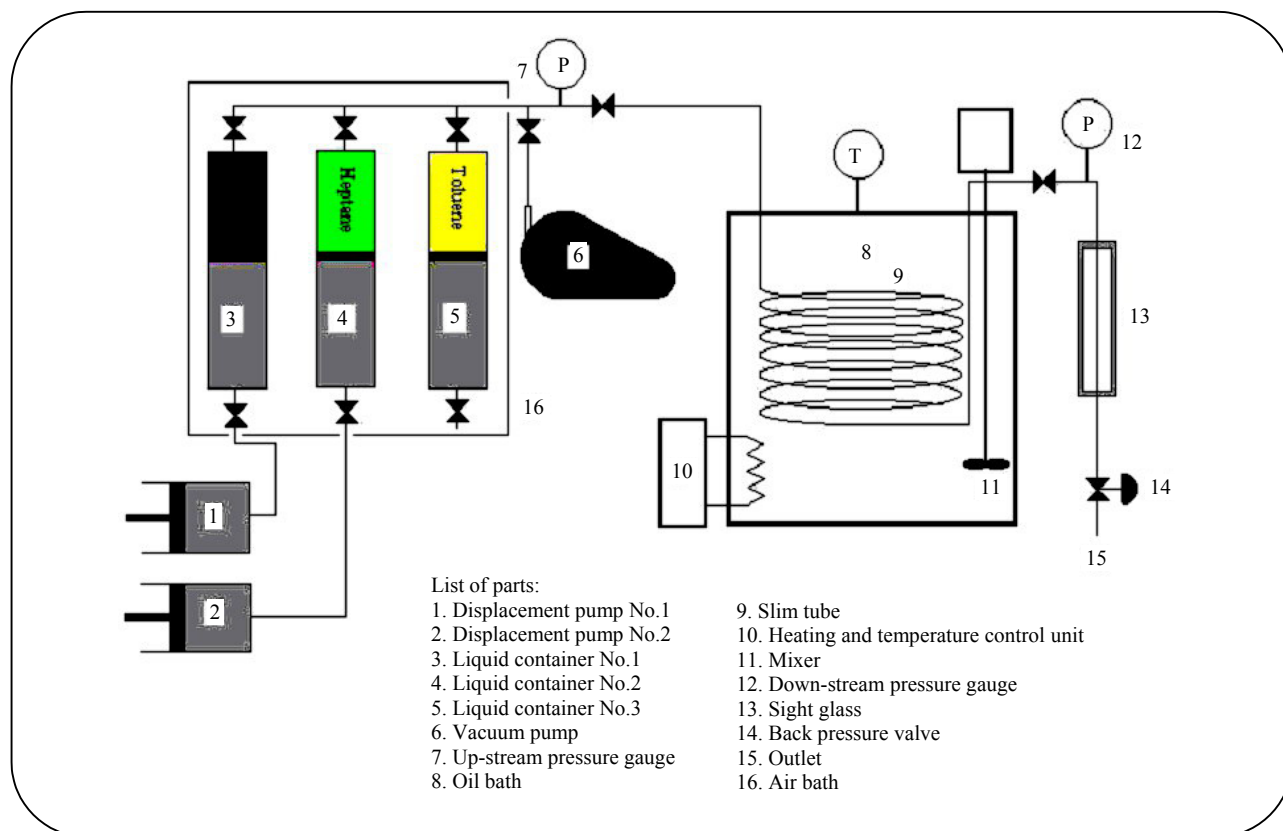


Fig. 1: Diagram of the experimental setup.

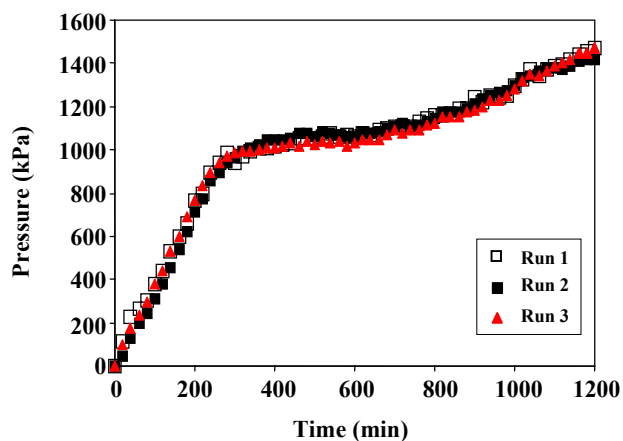


Fig. 2: Pressure change as a function of time for three runs with identical operational conditions.

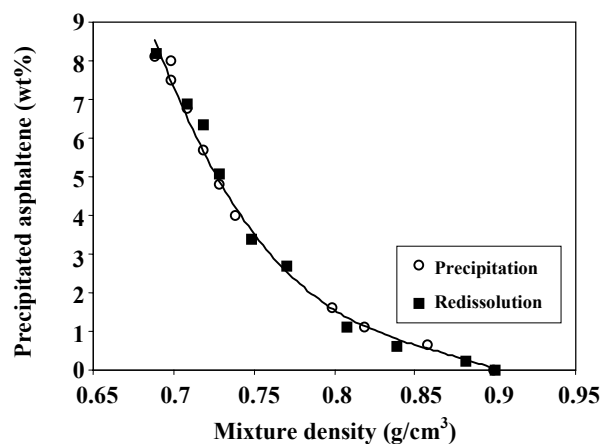


Fig. 3: Amounts of asphaltene precipitation/re-dissolution in test R-1.

repeatable, but in case of porous media, the situation is more complex. One of the runs was repeated to check the reproducibility of the experiments, which proved to be very good as demonstrated in Fig. 2. In this stage, mixtures of 50% n-C7 were injected into the slim tube in three runs with identical operational conditions.

RESULTS AND DISCUSSION

The amounts of asphaltene precipitated measured in Test R-1 are represented in Fig. 3. The circles show the amount of precipitated asphaltene in the first step of the test (i.e., precipitation), while the squares show the measured values during re-dissolution process.

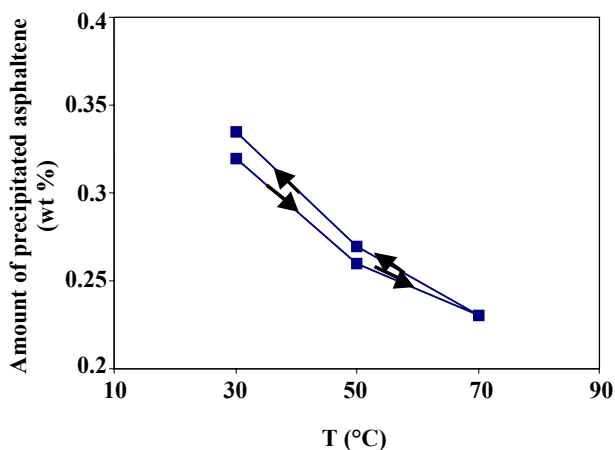


Fig. 4: Effect of temperature on reversibility of asphaltene precipitation for mixture of n-heptane and oil with $R_v = 2/3$.

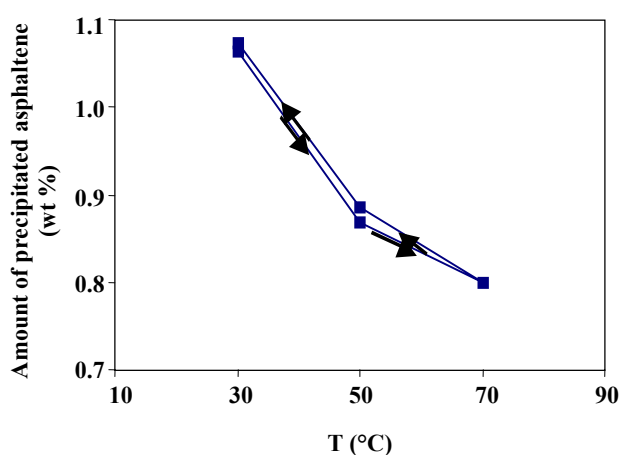


Fig. 6: Effect of temperature on reversibility of asphaltene precipitation for mixture of n-heptane and oil with $R_v = 7$.

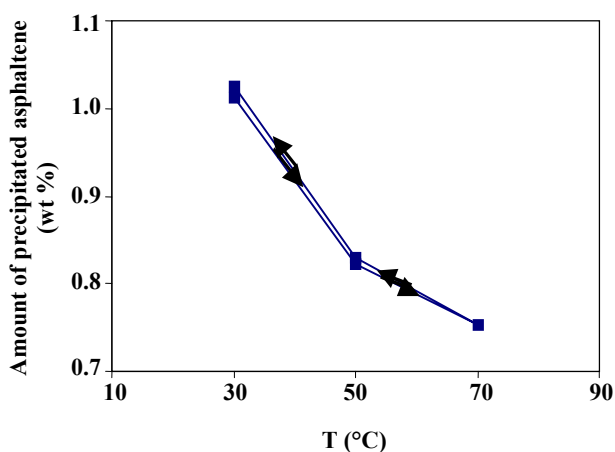


Fig. 5: Effect of temperature on reversibility of asphaltene precipitation for mixture of n-heptane and oil with $R_v = 1$.

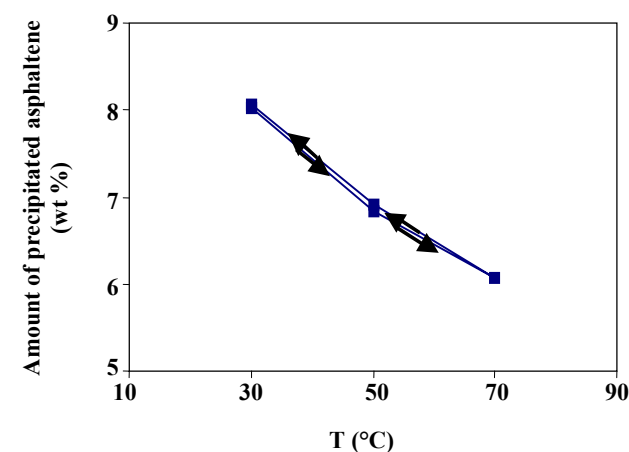


Fig. 7: Effect of temperature on reversibility of asphaltene precipitation for mixture of n-heptane and oil with $R_v = 12$.

There is a good agreement between the amounts of asphaltene precipitated measured in two precipitation and re-dissolution processes, which reveals that the asphaltene precipitation is reversible upon the addition and removal of the precipitant.

In Test R-2 measurements show that there was no precipitated asphaltene in different mixtures after addition of enough fresh oil. This reveals that the process of asphaltene precipitation is completely reversible for the oil under study.

Results of Test R-3 are presented in Figs. 4 to 7. The arrows indicate the direction of the temperature variation. As these figures show, every pair measured values of precipitated asphaltene at each particular temperature is approximately equal regardless of whether the temperature

is increasing or decreasing. This test showed that asphaltene precipitation is reversible with respect to temperature, and from the excellent agreement between each sets of data, it is concluded that the process has no hysteresis.

The measurements in test R-4 include injection pressure of the fluid flowing through the slim tube while the pump provides a steady, constant flow rate. In the first step the injection pressure of the fresh oil was measured and plotted as indicated in Fig. 8. As this figure shows, the pressure starts increasing until the first pore volume of the fluid is injected. Then pressure reaches a maximum value of 7.579 MPa and remains constant which shows that no deposition occurs in the porous medium.

Fig. 9 represents the variation of injection pressure with respect to time for mixture of oil and n-heptane

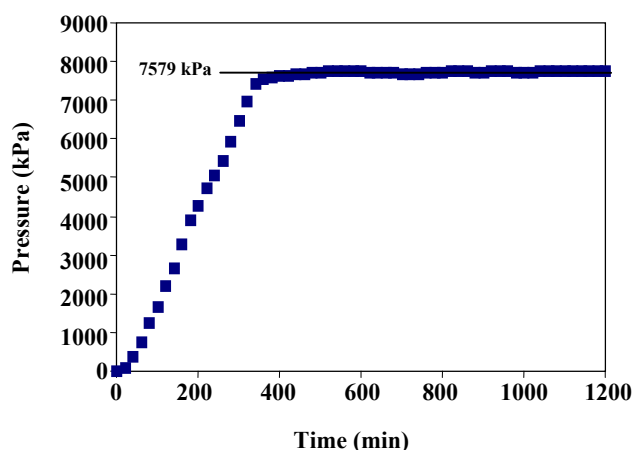


Fig. 8: Pressure variation during injection of fresh oil at rate of $30 \text{ cm}^3/\text{hr}$ (Step 1 of Test R-4).

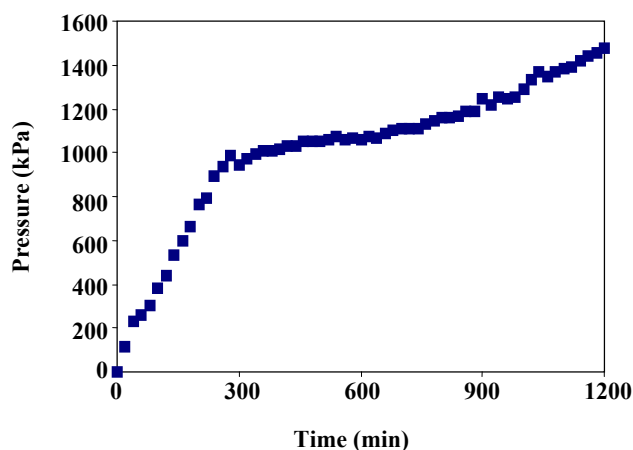


Fig. 9: Pressure variation during injection of a mixture of 50% *n*-heptane (Step 2 of Test R-4).

(Step 2). Gradual increment of pressure after injection of the first pore volume of fluid is an indication of deposition of asphaltene particles in the system. *n*-heptane causes asphaltene molecules to aggregate and deposit in porous medium and thereby some pore throats are partially or completely plugged. So more pressure drop occurs across the porous medium to maintain the same flow rate.

Fig. 10 is the plot of injection pressure versus time for the fresh oil injected in Step 3. This figure shows a non-uniform, zigzag pattern of pressure variation curve. The fluctuation was mainly due to presence of asphaltene particles and also turbulency thereafter occurred.

Step 4 was followed after a soaking time of 100 hours. As depicted in Fig. 11, pressure decreased slowly but in a

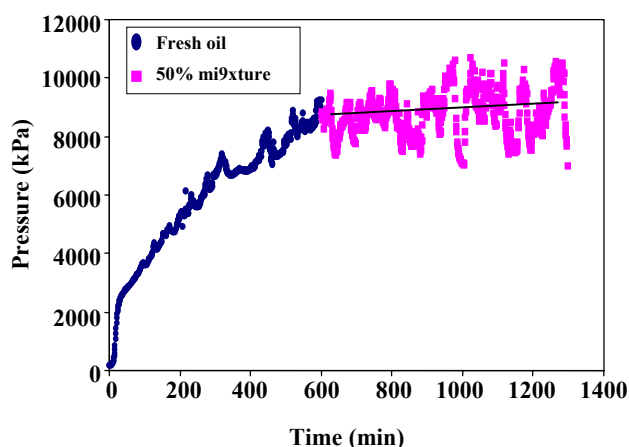


Fig. 10: Effect of particles remaining from injecting a mixture of 50% *n*-heptane on flowing pressure of fresh oil (Step 3 of Test R-4).

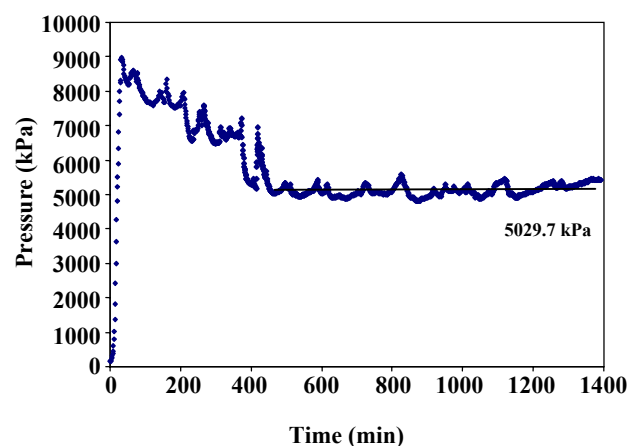


Fig. 11: Effect of re-dissolution of asphaltene particles on flowing pressure of fresh oil (Step 4 of Test R-4).

non-uniform manner and then reached an approximately constant value of 5029.7 kPa.

Comparison of flow properties of the fresh oil in the Step 4 of this experiment (i.e., $q = 20 \text{ cm}^3/\text{hr}$ and $P = 5029.7 \text{ kPa}$) with those of the first step (i.e., $q = 30 \text{ cm}^3/\text{hr}$ and $P = 7579 \text{ kPa}$) shows a ratio of 2/3 between both pressures and flow rates. This shows that the difference in pressures is due to the difference in the flow rates. For this reason, one can conclude that in the last step of Test R-4, there is no deposited asphaltene in porous medium to restrict the flow path, and all particles already deposited have been re-dissolved in the fresh oil during the soaking time.

This is a good indication that the process of asphaltene precipitation/deposition is reversible in porous media.

CONCLUSIONS

The precipitation of asphaltene was found to be completely reversible for the oil under study. The reversibility was verified for both composition and temperature changes. In addition to this, hysteresis was not observed in any experiment.

For the porous medium, reversibility of asphaltene precipitation and deposition was examined. After injection of several pore volumes of fresh oil and allowing the oil to soak, all deposited asphaltenes re-dissolved completely in the crude oil. The porous medium had its initial permeability after re-dissolution of deposited asphaltenes, so injection of fresh oil back to the damaged reservoir is recommended for remedial of permeability impairment.

Received : 9th March 2004 ; Accepted : 17th April 2006

REFERENCES

- [1] Speight, J. G., "The Chemistry and Technology of Petroleum", Marcel Dekker Inc., New York, p. 39, (1980).
- [2] Pfeiffer, J.P. and Saal, R.N.J., *J. Phy. Chem.*, **49**, p. 139, (1940).
- [3] Hirshberg, A., Dejong, L.N.J., Schipper, B.A., and Meijer, J.G., *SPE J.*, p. 283, June (1984).
- [4] Andersen, S. I. and Stenby, E.H., *Fuel Sci. & Tech. Intl.*, **14**(1&2), p. 261 (1996).
- [5] Fotland, P., *Fuel Sci. & Tech. Intl.*, **14**(1&2), p. 313 (1996).
- [6] Rassamdana, H., Dabir, B., Nematy, M., Farhani, M. and Sahimi, M., *AIChE, Journal*, **42** (1), p. 10 (1996).
- [7] Pacheco-Sanches, J. H. and Mansoori, G. A., *SPE paper* No. 38966, Proceeding the Fifth Latin American and Caribbean Petroleum Engineering and Exhibition Held in Rio de Janeiro, 30 August-3 September (1997).
- [8] Hammami, A., AIChE 1999 Spring National Meeting, Houston, Texas, March 14-18, (1999).
- [9] Peramanu, S., Singh, C., Agrawala, M. and Yarranton, H. W., *Energy & Fuels*, **15**, p. 910 (2001).