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Influence of asphaltene inhibitors on asphaltene deposition in the porous media

Arnab Mandal[1], Vikas Mahto*[,1], Subodh Purohit[2] & M C Nihalani[2]

[1]Department of Petroleum Engineering, Indian Institute of Technology (Indian School of Mines), Dhanbad, Jharkhand 826 004, India
[2]Research & Development Department Oil India Limited, Duliajan, Assam 786 602, India

E-mail: vikas.ismpe@hotmail.com

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This article deals with organic asphaltene deposition in the reservoir rock, for crude oil having high asphaltene content and high apparent viscosity. The crude oil is characterized using thermal analysis through the thermogravimetric method. Crude oil is blended with heptane and flooded through the formation core at 55°C and 200-1200 psi pressure. With the rise in flow pressure, asphaltene precipitation became more significant with about four hundred times fall in the initial flow rate (flow rate at 200 psi) of crude oil at 1200 psi pressure. Phthalic acid and turpentine oil are used as asphaltene inhibitors for this crude oil. These asphaltene inhibitors are easy to procure, required less dosage for asphaltene dissolution and are relatively less toxic as compared to the other organic solvents used frequently as asphaltene inhibitor in oil industries. The asphaltene inhibitors are injected into the crude oil and flowed through the pores of the core. It is found that the crude oil treated with phthalic acid resulted in 88.23% increment its flow rate as compared to the turpentine oil, suggesting significant organic asphaltene dissolution in the formation rock.

Keywords: Asphaltene inhibitor, Core flow study, Crude oil characterization, SARA distribution

Accumulation of organic solids in the reservoir rock can be a trouble for oil industries. Organic solid deposit from the crude oil included high molecular weight compounds like asphaltene, paraffin, diamondoids etc. The path of crude oil through the pores of formation rock leads to localized pressure fluctuations and hence causes overall pressure depletion[1]. It results in an increase in the volume fraction of aliphatic compounds like pentane, heptane etc. that are insoluble in asphaltene. It initiates an increase in the accumulation of asphaltene molecules that precipitate as solid in the pores of the formation rock. Consequently, the flow rate of crude oil through the pores of the rock reduces and the production from the oilfield might stop owing to formation damage[2]. Bagheri *et.al* (2011) had carried out core flow studies at 4000 psi pressure and 150^{0}C for PVT analysis. They maintained a flow rate of the order of 10^{-8} m^3/s (0.6 mL/min). The flow rate of crude oil drops down signifying asphaltene deposition[3]. Ebrahimi *et al.* (2016) found that an increase in the injection pressure leads to an increase in the asphaltene precipitation[4].

Precipitation of solid asphaltene in the formation rock can be reduced by using chemical agents like asphaltene inhibitor. Aromatic solvents like toluene, xylene etc. dissolved asphaltene through the dissociation of asphaltene aggregates, replacing the π-π asphaltene molecular interaction with π-π orbital overlap between aromatic solvent and asphaltene[5]. Asphaltene dispersants have a tendency to reduce the size of flocculated asphaltene in crude oil, keeping them in suspension[6]. Madhi *et al.* (2017) screened asphaltene inhibitors like salicylic acid, cetyl trimethyl ammonium bromide, benzoic acid, naphthalene etc. for crude oil. They found that the asphaltene inhibitors interacted with asphaltene via hydrogen bonding and π-π interaction and acid-base interaction[7]. Luiz *et.al* (2006) worked on the reduction in the asphaltene precipitation from crude oil with the help of oil-soluble amphiphiles. They used a variety of inhibitors like dodecyl benzene sulphonic acid, sebacic acid, caprylic acid and vegetable oils like soy oil, sweet almond oil, coconut oil, Brazil nut oil etc. It was found that vegetable oils caused fair improvement in the viscosity of crude oil[8].

This paper highlights the effect of injecting different asphaltene inhibitors on developments in the flow behaviour of crude oil. Asphaltene precipitation is checked by flooding crude oil-heptane blend through a sandstone core. Asphaltene inhibitors are doped into the crude oil and asphaltene dissolution is checked using different experiments.

Experimental Section

Procurement of materials

Methanol, *n*-heptane, paraffin oil and toluene were bought from RankemAvantor Performance Materials (New Delhi, India). Chloroform and acetonitrile were bought from Merck Specialties Pvt. Ltd. (New Jersey, United States of America). Turpentine oil and phthalic acid were bought from Loba Chemie Pvt. Ltd. (Mumbai, India). All glassware wasbought from Merck Specialties Pvt. Ltd. (New Jersey, United Sates of America). Crude oil under investigation belonged to an Indian oilfield and core sample was procured from the same oilfield.

Experimental procedure

Determination of different properties of crude oil

Bingham Pycnometer was utilized to measure the API gravity of crude oil[9]. Crude oil is heated to 50°C and taken in a cork covered test tube covered provided with thermometer, surrounded by ice bath. The motion of crude oil was observed by inclining the test tube at each temperature drop of 3°C. The point at which the flow of crude oil comes to halt indicates its pour point[10]. Water and sediments are identified by mixing crude oil with toluene in 50:50 (v/v) with gradual heating in the round bottom flask. Toluene acts as a carrier fluid for crude oil in this experiment. The volume of water obtained after the distillation ceased, was calculated for water content[11]. Paraffin wax present in the oil sample was determined according to modification in standard procedure. Crude oil was mixed with n-pentane in the ratio 1:20 (w/v). Next acetone was added & system was frozen to –20°C for 24 hr. The sample was subjected to vacuum filtration in a Buchner funnel using Whatman filter paper 934 and washed with hot hexane[12]. The oil sample was added to n-heptane in the ratio 1:30 (w/v). The mixture was kept at 35 to 40°C and cooled to ambient temperature for 4 hours. The mixture was filtered under vacuum pressure and washed with hot toluene to determine the asphaltene content. For non-asphaltene components, the filtrate solution was passed through a silica gel bed partially wetted with heptane in a chromatography column. Extra volume of heptane was passed for the total elution of saturates and aromatics were eluted by passing toluene over the wetted gel bed. Resins were eluted using the following sequence: First 1:1 (v/v) mixture of methanol and toluene was passed, second 1:1 (v/v) mixture of methanol and chloroform was passed, third chloroform and at last acetonitrile was passed through this gel bed. Elutes were subjected to Soxhlet extraction for measuring the individual fractions collected from specific elution performed in the column[13].

Study of thermal profile of crude oil sample

Thermal analysis of theoil sample was carried out employingTGA method using NETZSCH STA 449 F3 Jupiter model (Germany) employing *Proteus* software. A few amount of crude oil was required for sampling. Purge gas used in the experiment was Nitrogen gas at an operating pressure of 8 kgf/cm^2 approximately. The temperature range was set from 25 to 600°C for the crude oil under study.

Identification of asphaltene solubilizers for crude oil sample

50:50 volumetric mixtures of phthalic acid and toluene was prepared, labelled as P and used as an asphaltene solubilizer for crude oil under investigation. Turpentine oil is used as another asphaltene solubilizer and labelled as Q. Phthalic acid is an aromatic carboxylic acid with the chemical formula of $C_6H_4(COOH)_2$. It is a white solid substance that is soluble in aromatic solvents like toluene.On the other hand, Turpentine oil is a viscous liquid, composed of terpenes, mainly α-pinene and β-pinene with lesser amounts of careen, camphene etc. Pinenes are bicyclic compounds with chemical formula $C_{10}H_{16}$. The general structure of the pinene is given in Fig. 1. Pinenes contain one carbon-carbon double bond unit.The other properties of phthalic acidand turpentine oil,employed as asphaltene solubilizers from crude oil under reservoir conditions are listed in Table 1.

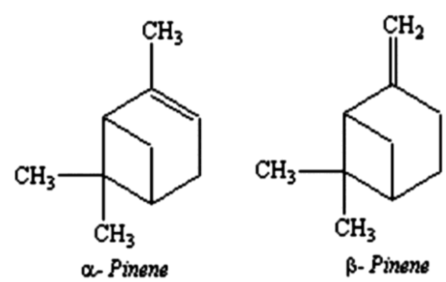

Fig. 1 — Chemical structure of pinenes present in Turpentine oil

Table 1 — Different characteristic properties of phthalic acid and turpentine oil

Parameter	Phthalic acid	Turpentine oil
Density (g/mL)	1.593	0.804
Melting point (°C)	207	-55
Boiling point(°C)	Not available	155-175
Flash point(°C)	Not available	36
Median Lethal Dose (mg/kg test sample)	7900	5760

Observing the parameters from Table 1, it is evident that turpentine oil at room temperature exists in the liquid state and under experimental conditions (55°C temperature), material loss due to vaporization does not occur. In addition, the median lethal dose for xylene is 4300 mg/kg test sample[14]. Based on median lethal dosage data, turpentine oil and phthalic acid, used as asphaltene inhibitor in the oilfield are relatively safer for application in environment/ ecosystemas compared to the conventional aromatic solvents used for asphaltene solubilisation like toluene or xylene alone.

Study of asphaltene deposition in the formation rock

Asphaltene deposition of crude oil in the formation core was carried out with the help of an experimental core flow set up. It consistedof a crude oil tank equipped with electric coils for heating, a storage tank containing Hassler core holder containing core sample, surrounded by a rubber sleeve which served as a protecting sheath against pressure fluctuations. It also contained a pressure gauge at the inlet and outlet section of the total flooding path with back pressure regulator and a hydraulic pressure control system to monitor the overburden pressure. It was essential so that the fluid flow would be confined to the pores only. Double acting syringe pump was used to transport the crude oil from oil tank to the core sample serving as a porous medium present at a definite temperature and pressure. Paraffin oil acted as a driving fluid in this pump. The pump had a maximum flow rate of two hundred millilitres per minute and maximum injection pressure of 3750 psi. Core sample under investigation is a sandstone rock whose properties are listed in Table 2.

About two hundred millilitres of crude oil-heptane mixture and the crude oil-heptane mixture blended with additives utilized as asphaltene solubilizers was flooded through the core at pressures ranging from 200-1200 psi and at a temperature of 55^0C based on the average temperature and pressure existing in this oil reservoir. For further assessment of asphaltene precipitation, the syringe pump was operated at constant flow rate and the drop in the pressure was monitored with respect to time. A labelled processflow diagram for core flow studies is shown in Fig. 2.

Results and Discussion

Crude oil has a BS & W of 1.9 % (v/v) as shown in Table 3. The purpose of measuring BS & W of the crude oil sample is to roughly assess the requirement

Table 2 — Physical properties of core sample

S No.	Parameter	Magnitude
1.	Length	5.53 cm
2.	Diameter	3.76 cm
3.	Porosity	12.45 %

Table 3 — Physiochemical properties of crude oil

S No.	Test	Observed value	Method
1.	API gravity	25.03^0	ASTM D 1480-15(2016)[9]
2.	Pour point	30^0C	ASTM D 97 (2017)[10]
3.	BS & W	1.8 % (v/v)	Sharma et al (2018)[11]
4.	Wax content	12 % (w/w)	Sharma et al (2019)[12]
5.	Asphaltenes	3 % (w/w)	Deka et al (2018)[13]
6.	Saturates	45 % (w/w)	
7.	Resins	8.5 % (w/w)	
8.	Aromatics	16.5 % (w/w)	

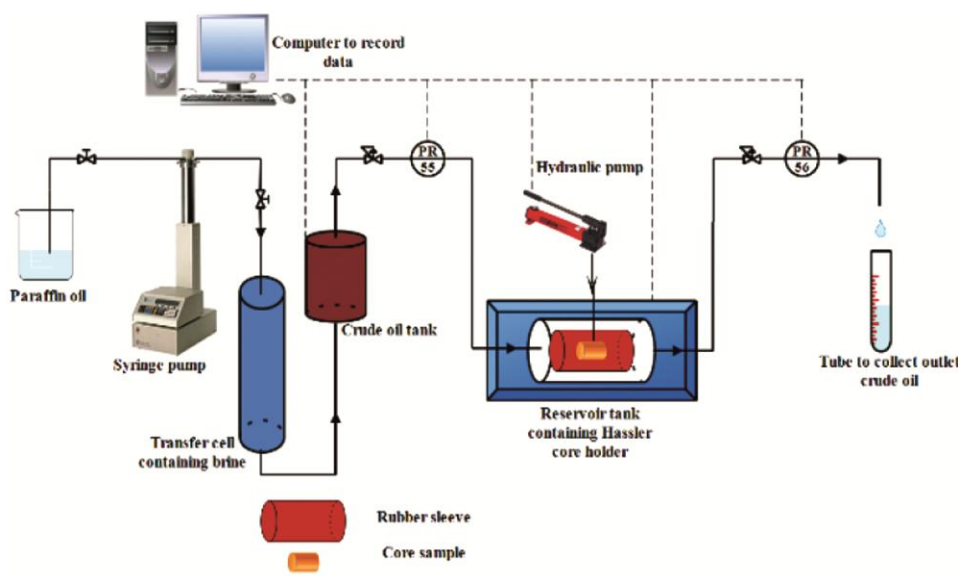

Fig. 2 — Experimental set up to study asphaltene deposition through the formation core

of demulsification prior to characterization. Presence of water content reduces the effectiveness of additive in the particular crude oil.Based on API gravity value it can be classified as medium heavy crude oil by nature. The asphaltene content of crude oil under investigation is 3% (w/w). Observing the SARA distribution, the resin asphaltene ratio comes out to be 2.83, which signifies a high probability for asphaltene deposition in the crude oil. Presence of a high proportion of saturates indicates the potential for wax precipitation in addition to asphaltene deposition. Therefore, experimental conditions for core flow studies with the crude oil sample is adjusted in such a way that results confine to precipitation of organic solid asphaltene in the pore channels of the core.

Figure 3 represents TGA plot for the crude oil. The entire thermal analysis of crude oil consists of two oxidation regions- LTO (Low Temperature Oxidation) and HTO (High Temperature Oxidation). LTO involves oxygenation of liquid phase hydrocarbons. The products of LTO are oxygenated hydrocarbons which are denser, viscous and less volatile than crude oil. A significant amount of oxygen is consumed in the LTO phase[15]. LTO reactions are heterogeneous with a fewer amount of carbon dioxide produced. HTO reactions produce a large amount of carbon dioxide. HTO contributes to maximum exothermic heat of reaction. LTO is observed with lesser weight loss because asphaltene molecules are so heavy and resistant that oxygen does not affect these fractions until a high temperature is attained[16]. The temperature range 105°C to 350°C represents the distillation range. It can be attributed to the distillation of maltene fraction (the fraction left after filtration of asphaltene) of crude oil. The mass of crude oil sample remaining at 160°C is 70% due to distillation. Lower weight components like decane and hexadecane undergo vaporization in this regime. Heavy weight components like C20 and C36 undergo vaporization in the region 160°C to 250°C[17]. At 250°C, the mass of oil sample remaining is almost 40 %. Before the onset of HTO (350°C), 6.78 % of the oil sample weight is left out in the crucible.

Figure 4 presents the influence of pump pressure on the flow ability of crude oil pumped through the sandstone core at hundred and two hundred millilitres of flooding collected at the outlet section. It is found that at 200 psi injection pressure, post hundred millilitres of crude oil flooded results in its flow rate about 1.4 mL/min, while post 200 mL of crude oil collected, the flow rate becomes 0.28 times its value under 100 mL flooding, indicating initiation of asphaltene deposition. Injection of crude oil at 600 psi pressure yields the flow rate to be 0.075 times its value at 200 psi pressure and at 1200 psi, the flow rate becomes 0.0025 times its value at 200 psi injection. Increase in the pumping pressure enhances the entrapment of asphaltene in the pores of the core[4].

Observing variation in the flow properties of crude oil-heptane blend with respect to elevation in the concentration of asphaltene inhibitors in Fig. 5 reveal that crude oil-heptane mixture flows at higher magnitude reaches an optimum value at 1.5 vol. % blending and afterwards remains more or less constant. The increment in the flow rate of crude oil indicates asphaltene solubilisation in the pore channels of the core, additionally shown by a decrease in the slope of the curve of pressure drop versus time in Fig. 6.

The dissolution of solid asphaltene from the pore spaces of formation core can be explained on the basis of fact that π-π orbital overlap between asphaltene

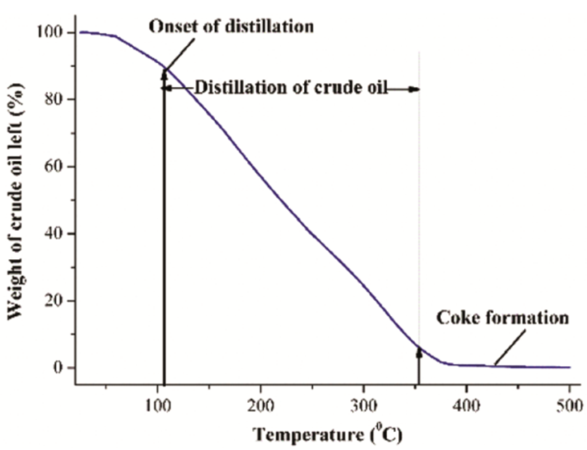

Fig. 3 — TGA plot of crude oil

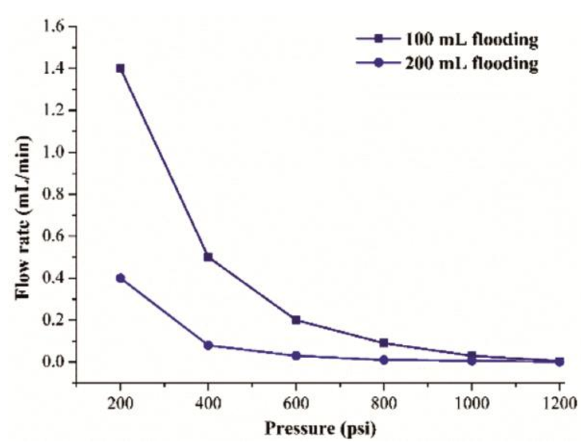

Fig. 4 — Effect of injection pressure on the flow rate of crude oil

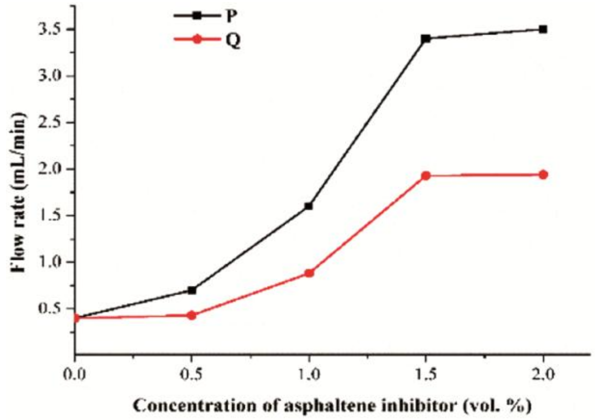

Fig. 5 — Effect of concentration of asphaltene inhibitors on the flow rate of crude oil

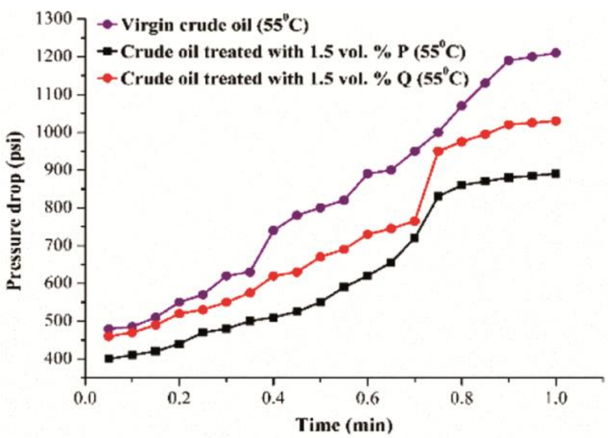

Fig. 6 — Pressure drop across the sandstone core for crude oil beneficiated with asphaltene inhibitors

molecules gets replaced by the π-π orbital overlap between the double bond of asphaltene molecule and double bond present in the asphaltene inhibitor[5]. The crude oil treated with asphaltene inhibitor P has 1.76 times flow rate of oil sample treated with asphaltene inhibitor Q at 1.5 volume percent concentration in the oil sample. It means asphaltene inhibitor P has relatively more efficiency in porous asphaltene solubilisation as compared to asphaltene inhibitor Q.

Conclusion

The experimental set up to study the core flow studies through the formation core, yielded in precipitation of asphaltene only, with flow rate at 1200 psi being reduced by 99.75 % of the flow rate at 200 psi injection post 200 mL flooding, which is the initial pressure used for flow study of crude oil in this porous medium. Elevation in the flow speed of crude oil through the pore spaces of formation rock increases 8.5 times its initial value in case of additive P as compared to Q. In addition, the pressure drop across the core sample is lower in the case of oil sample treated with 1.5 volume percent asphaltene inhibitor P as compared to 1.5 volume percent asphaltene inhibitor Q. Therefore, the asphaltene inhibitors used in this research work can be used to mitigate asphaltene precipitation in the petroleum reservoir rock.

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