

ASPHALTENE-COMPATIBLE FLUID DESIGN FOR WORKOVER OPERATIONS

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ABSTRACT

Laboratory experiments were carried out to systematically evaluate the asphaltene-precipitation characteristics of heavy oil mixed with various multi-component light hydrocarbon mixtures (e.g., condensate, distillate, etc.). The objective of this work was to design an asphaltene-compatible fluid system for well workover operations. The onset of asphaltene precipitation was determined using the change in the light-scattering properties of the solutions due to the presence of solid asphaltene particles.

Results show that solid asphaltene particles precipitate out of solution when heavy oil is brought into contact with some condensate fluids. On the contrary, the distillate fluids do not cause asphaltene precipitation because they contain a lower proportion of lighter hydrocarbon components than the condensates. Based on the experimental results, an asphaltene precipitation compatibility factor was defined as a function of the ratio of cumulative mole percent of saturate (C_2 through C_{10}) contents to cumulative mole percent of aromatic contents. This factor can be used to design asphaltene-compatible fluids applicable for workover operations.

INTRODUCTION

Heavy oil produced from the Lindbergh area, Alberta, Canada, is highly viscous but sufficiently fluid at reservoir conditions to be produced under primary recovery using either progressive-cavity or reciprocating pumps. This oil is usually accompanied by formation sand. During the production life, these wells encounter various operational problems including rod parting, tubing leaks, pump wear, and well sanding. In the Lindbergh area, routine workover operations are carried out using lighter fluids, which include less viscous oil from another formation. This practice is not very cost-effective because these lighter fluids need to be transported a

significant distance by truck. In the past, the usual practice in this area was to use a blend of condensate fluid and produced Lindbergh oil.

The heavy oil produced in the Lindbergh area contains about 15 to 20% (w/w) asphaltenes in solution. Asphaltenes are defined as the *n*-pentane insoluble fraction of crude oil. Asphaltenes are polar molecules which aggregate together through aromatic π - π orbital association, hydrogen bonding, and acid-base interactions [1,2]. The presence of some heteroatomics (aromatics with nitrogen, sulphur, and oxygen atoms included in the structure) was reported [2]. Asphaltenes form flat aggregates whose size and molecular weight depend on temperature, composition, and solvent [3]. The growth of the aggregates is limited by the association of asphaltenes with resins in solution. The molecular weight of these aggregates can grow to several hundred thousand grams per mole.

Various asphaltene-solubility modelling studies have been reported [3,4,7-9,11] based on the principle of colloidal suspension. Some authors [10,12,14] have used these molecular models to predict the dynamics of asphaltene flocculation.

In general, asphaltene precipitates out of solution because of changes in pressure, temperature, and/or composition of the solution [3-17]. For instance, acidizing wells for cleanup or stimulation purposes has resulted in the precipitation of asphaltene [18]. Asphaltene preferentially deposits on pores containing kaolinite and this has been attributed to the positively charged asphaltene aggregates being attracted to the negatively charged clay [19].

Enhanced oil recovery techniques have also led to asphaltene problems. Waterfloods and CO_2 floods will upset the internal balance within the native oil. The presence of brine was shown to increase solids precipitation [9]. The use of CO_2 can support asphaltene solubility to a certain extent in dead oil [6]. However, in a live oil, CO_2 was found to have a destabilizing effect on asphaltenes [7,19,20].

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Two forms of asphaltene are reported [21] to precipitate in the field: hard, shiny, solid deposits, and dark sludges. The hard deposits are probably caused by the growth of asphaltene aggregates on a surface while the sludges are probably due to asphaltene forming large aggregates in solution, that settle out and drag other components with them. These deposits may cause problems anywhere in the oil circuit.

One of the mechanisms for asphaltene flocculation, besides changes in temperature and pressure, is compositional change. Changes in oil composition can occur when lighter hydrocarbon components (e.g., C_2 to C_{10}) are added to the asphaltene/oil system. Oils display different asphaltene precipitation characteristics when they are brought into contact with various single- or multi-component light hydrocarbons. During EOR, the changes in composition through solvent, gas, or water floods may lead to asphaltene deposition.

In the formation, asphaltene deposition can affect oil production in several ways. Pore throats can become blocked and cause a reduction in permeability. The formation can become more oil-wet and change the relative-permeability relationships. Asphaltenes can promote water-in-oil emulsions, leading to much higher viscosities. In the wellbore and surface facilities, asphaltene deposits will gradually reduce the area for flow, resulting in the need for higher pressure drops to maintain production. Deposition in downhole safety valves may interfere with their proper operation [17]. Buildup in the tubing may damage wireline tools or require different running procedures.

The oil industry has been focusing mostly on remedial measures to be implemented after the asphaltene precipitation has taken place. Remedial measures include mechanical scraping [22] and asphaltene solvent and dispersant injection [5,18,1,23,24]. An alternate option would be to focus on preventive measures. In heavy-oil wells, light hydrocarbon fluids are frequently used to carry out routine workover operations. In the Lindbergh area, condensate fluid alone or a mixture of oil and condensate was generally used as a workover fluid. These fluids were not only costly but also often caused asphaltene precipitation because of their higher light hydrocarbon (e.g., C_5 and C_6) content.

Norcen's cleaning plant at Elk Point produces distillate material from the atmospheric distillation of the Lindbergh heavy oil. These distillates generally contain lesser amounts of C_5 and C_6 than condensates. The distillate fluid was thought to be less instrumental in causing asphaltene precipitation than the condensate fluid. Preliminary asphaltene-precipitation tests were carried out using a filtration technique. In that study, the compatibility of the condensate/heavy oil and distillate/heavy oil mixtures was evaluated. The solid content was determined by measuring the weight of the filter paper (5- μ m filter paper) before and after the filtration experiments.

Results showed that the distillate/heavy-oil mixture at various ratios (i.e., 1:1, 1:2, 1:4) did not cause any solid precipitation. However, a seasonal variation of the distillate composition was observed and, therefore, a detailed solid precipitation study using a light-scattering technique [15] was carried out to establish a safe workover-fluid design criterion. The results are presented in this paper.

SAMPLE CHARACTERIZATION

The compositional analyses of both distillate and condensate systems are presented in Figure 1. As seen in the figure, compared to the condensate system, the distillate system does not contain as much C_4 , C_5 , or C_6 . The distillate system has more hydrocarbon components in the C_8 to C_{12} range than does the condensate. The aromatic components identified by GC are presented in Figure 2. As seen in the figure, the total aromatic content of the distillate system is greater than that of the condensate system. The physical properties and chemical composition of the Lindbergh oil are presented in Table 1.

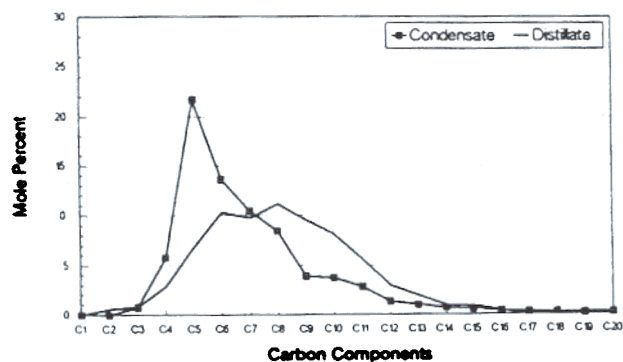


Figure 1. Comparison of condensate and distillate composition.

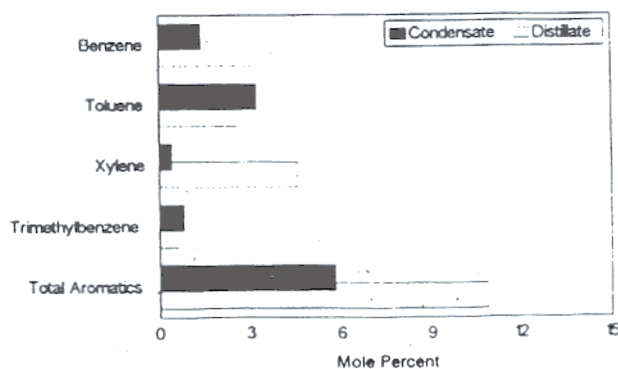


Figure 2. Comparison of aromatics content of condensate and distillate.

Table 1. Characteristics of Lindbergh oil

Parameters	Lindbergh oil
Density (g/mL)	0.965
Viscosity (mPa·s @ 20°C)	10,000
Molecular weight	503
SARA analysis (% w/w)	
Saturates	26
Aromatics	25
Resins I	19
Resins II	16
Asphaltene	14

EXPERIMENTAL WORK

It is difficult to determine *a priori* whether a given distillate will precipitate asphaltenes when added to a given oil, since this is probably a complex function of a number of factors including distillate and oil composition. The tendency for asphaltene precipitation to occur for a given distillate-oil pair may be determined experimentally using a light-scattering technique [15]. The experimental setup used to measure the change in light-scattering properties of the solutions, due to the presence of asphaltenes, consisted of a Guided Wave Spectrophotometer (Model 260). The apparatus was equipped with a fibre optics probe of 1 to 10 mm adjustable path length. In these experiments, a near-infra red (NIR) light source was used with measurements carried out at 1600 nm. A 150-mL Metrohm titration cell was used to contain the solution of oil in the distillate to be tested, which in turn was titrated with *n*-pentane using a 150-mL autoburette.

In a typical experimental run, a 25-g sample at a predetermined ratio of Lindbergh oil and distillate was added to the titration cell in which the fibre optics probe was placed. The contents of the cell were mixed using a magnetic stirrer. Pentane was slowly titrated and the light absorbance was recorded with time. An example of titration of a solution containing distillate and oil at a ratio of 0.30 is shown in Figure 3. As seen in the figure, as pentane was added the absorbance decreased because of dilution effects. After the addition of 34 mL of pentane, asphaltene particles began to appear and at this point the effective absorbance increased (or, more correctly, transmittance decreased) because of the scattering of the light by the asphaltene particles as evidenced by the sharp rise in the absorbance curve in Figure 3. The composition of the distillate was varied by adding known amounts, 11 and 25 percent of distillate by weight each, of *n*-pentane and *n*-hexane to the samples of distillate. The onset condition (mL of *n*-pentane) of asphaltene precipitation for all distillate/oil mixtures is tabulated in Table 2.

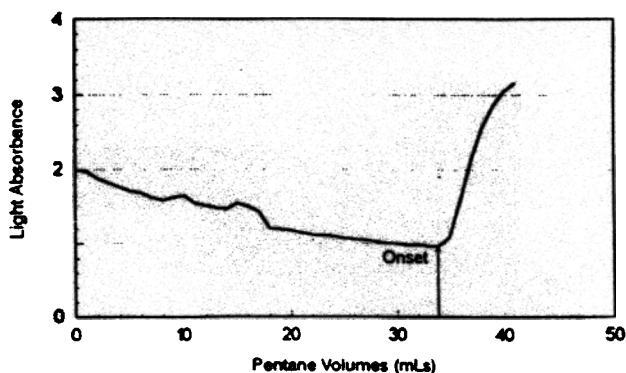


Figure 3. Titration with pentane (distillate to oil ratio: 0.30).

The weight ratio of distillate to heavy oil is plotted as a function of the weight ratio of pentane to heavy oil in Figure 4. The relation is presented as a compatibility plot. With the addition of data from two other experiments (Runs 2 and 3), a straight line is drawn (Figure 4). It is observed from this plot that pentane is always required to initiate asphaltene precipitation, and that the higher the distillate to heavy-oil ratio the more pentane is required. That is, the distillate and the crude are compatible in all proportions. The slope of the line can be viewed as a compatibility factor (CF). A positive slope such as that in Figure 4 indicates an asphaltene-compatible system. The larger the CF, the better the asphaltene-solubility properties. A negative CF would show an incompatible system and cause asphaltene precipitation at some defined ratio of distillate to heavy oil given by the intersection of the line with the x-axis. A series of compatibility plots like that shown in Figure 4 are constructed and are presented in Figures 5 through 8.

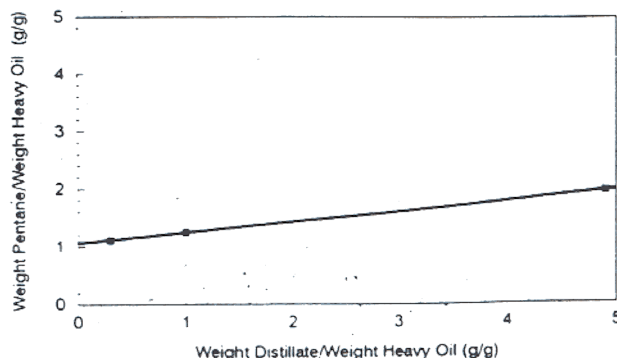


Figure 4. Compatibility plot — distillate and heavy oil.

Table 2. Summary of the experimental runs¹

Run #	Additional hexane or pentane (% w/w of distillate)	Asphaltene onset (pentane vol, mL)	Ratio of distillate to heavy oil (g/g)	Ratio of pentane ² to heavy oil (g/g)
1		34	0.30	1.11
2	0.0	25	1.00	1.25
3		13	4.90	1.95
4		34	0.30	1.11
5	11% hexane	23	1.00	1.15
6		10	4.98	1.50
7		34	0.30	1.11
8	25% hexane	22	1.00	1.09
9		7	5.00	1.05
10		36	0.30	1.17
11	11% pentane	24	1.00	1.20
12		10	5.00	1.49
13		34	0.31	1.11
14	25% pentane	22	1.00	1.10
15		6	5.00	0.90

¹ Total weight (distillate, added pentane/hexane, heavy oil) is roughly about 25 g.

² Pentane density is considered to be 0.6262 g/mL @ 20°C

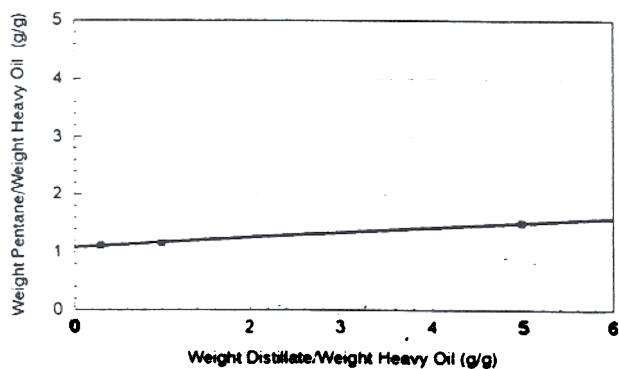


Figure 5. Compatibility plot — distillate + 11% hexane and heavy oil.

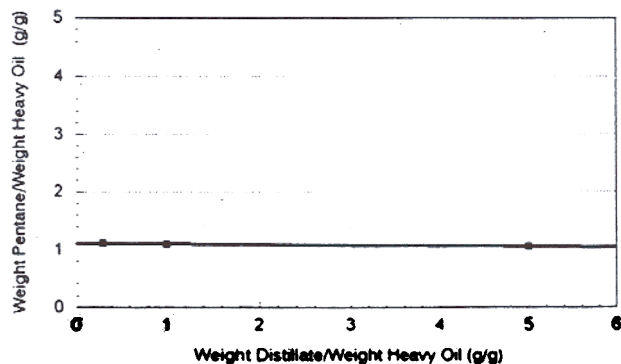


Figure 6. Compatibility plot — distillate + 25% hexane and heavy oil.

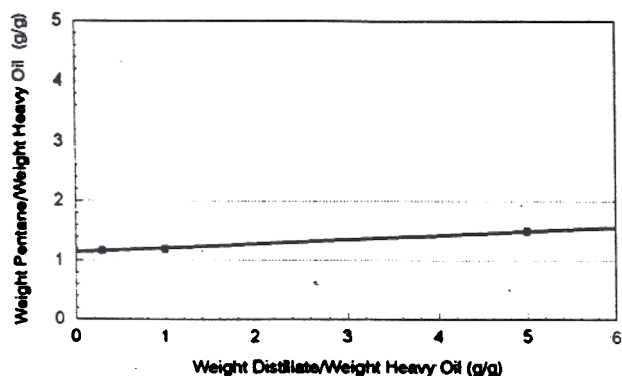


Figure 7. Compatibility plot — distillate + 11% pentane and heavy oil.

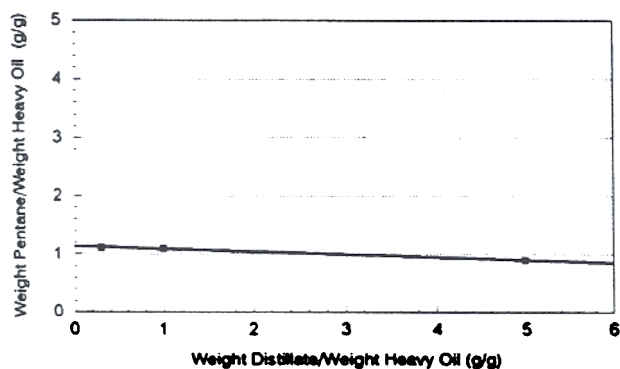


Figure 8. Compatibility plot — distillate + 25% pentane and heavy oil.

RESULTS AND DISCUSSION

Fifteen experimental runs were carried out. The experimental conditions are summarized in Table 2. The pentane concentrations at the asphaltene-onset conditions are extracted from the titration curves similar to that of Figure 3 and are tabulated in Table 2 for all runs. The compatibility plots are presented in Figures 5 through 8. As seen in Figure 5, the addition of 11% (w/w) hexane to the distillate still yields a positive CF. The compatibility factor becomes slightly negative when 25% (w/w) of hexane is added to the distillate system (Figure 6).

The addition of 25% (w/w) pentane (Figure 8) results in a negative slope or negative compatibility factor of -0.047 . This compatibility factor corresponds to an x-intercept of 25, which means that about 25 g of distillate per g of Lindbergh oil would be required to precipitate asphaltenes when the distillate system contains 25% (w/w) extra pentane. The calculated component data of the distillate system with the addition of the various amounts of pentane and hexane are summarized in Table 3. The compatibility factors are summarized in Table 4 along with the total saturate (*i.e.*, C_2 to C_{10}) and aromatic contents of the system.

In practical terms, no asphaltene precipitation occurs when the distillate material is mixed with the Lindbergh oil at a weight ratio of 0.30, as suggested by the operators. However, the addition of 25% (w/w) extra pentane to the distillate would cause asphaltene precipitation at a high distillate to oil ratio as indicated above (25 g distillate per g oil). This is the

Table 3. Calculated component data of the distillate

Component	Mole percent				
	Original	Hexane added		Pentane added	
		A	B	A	B
C_2	0.6	0.5	0.5	0.5	0.5
C_3	0.8	0.6	0.6	0.6	0.6
C_4 (i+n)	2.9	2.6	2.1	2.5	2.1
C_5 (i+n)	6.8	6.0	5.1	20.0	32.8
C_6	10.3	21.0	31.5	8.6	7.5
C_7	9.7	7.8	7.6	8.6	7.5
C_8	11.1	8.2	8.1	9.2	7.9
C_9	9.6	7.5	7.3	8.2	7.2
C_{10}	8.1	6.3	6.2	6.9	6.0
Total aromatics (toluene, benzene, xylene, TMB)	10.9	9.7	8.4	9.5	8.3

TMB: Trimethylbenzene

A: 11% (w/w) hexane or pentane added to distillate

B: 25% (w/w) hexane or pentane added to distillate

Table 4. Compatibility factors as a function of distillate composition

Compatibility factor	Total saturates C ₂ to C ₁₀ (mole %)	Total aromatics (mole %)	Ratio of saturates to aromatics
0.181	59.9	10.9	5.50
0.085	60.5	9.7	6.24
0.069	65.1	9.5	6.85
-0.012	69.0	8.4	8.21
-0.047	72.1	8.3	8.68

Compatibility factor: slope of the compatibility plots

worst-case scenario observed in this work. The extra 25% by weight of pentane in the distillate added to what was there originally corresponds to a total molar concentration of 32% pentane in the distillate (Table 3). Therefore, this doped (25% pentane) distillate is still theoretically asphaltene compatible when mixed with the Lindbergh oil at a distillate to oil ratio of 0.30 (Run #13, Table 2). In the field, however, the mixing of this distillate with oil at a ratio of 0.30 may cause much higher localized ratios. Therefore, a criterion for asphaltene onset based on a negative slope or CF is still considered very conservative.

Previous results [15] have shown that the saturates in the range up to C₁₀ have the greatest negative effect on the CF. Aromatics, on the other hand, can counteract the effect of the saturates. Therefore, to take the additions of pentane and hexane into account, "new" values for the saturates up to C₁₀ and for the aromatics were calculated for these "new" or doped distillates. The results of the calculations are shown in Table 3. The compatibility factors with the varying ratios of saturates to aromatics are shown in Table 4. The ratios of the C₂ to C₁₀ saturate content to aromatic content in the distillate were plotted against CF using the data from Table 4 in Figure 9. It can be seen from the results in Figure 9 that there is a general decrease in CF with increasing ratio.

Using the negative slope criterion as suggested above, a saturates to aromatics ratio of between 7 to 8 should provide a useful flag for possible asphaltene problems. The component analysis (C₃₀⁺ analysis) can be carried out routinely and an operator can easily calculate the ratio of total C₂ to C₁₀ saturates to aromatics. If the ratio is greater than 8, there will be a tendency for asphaltene precipitation. In that case, it is suggested that a small portion of aromatics (e.g., toluene or xylene) be added to the distillate system before making the blend. Based on this analysis, the ratio of C₂ to C₁₀ saturates to aromatics was calculated from the known composition of the condensate (seen in Figures 1 and 2); and the ratio was 11.77. This condensate when mixed with Lindbergh oil, as stated earlier, precipitated asphaltenes.

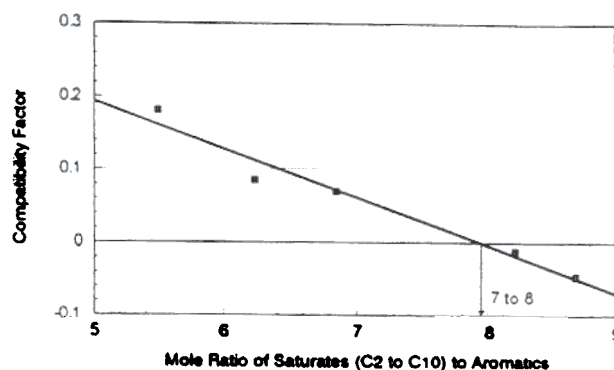


Figure 9. Asphaltene compatibility factor chart.

CONCLUSIONS

The Lindbergh oil shows asphaltene-precipitation characteristics when mixed with condensates containing relatively high proportions of C₅ and C₆. However, the distillate systems were less likely to result in asphaltene precipitation. The distillate material should be safe for field application as a workover fluid as long as the total molar ratio of C₂ through C₁₀ saturate content to aromatic content of the distillate system is below 8.

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