DOE/BC/15107-5

Project Title: Enhancing the Effectiveness of Carbon Dioxide Flooding by Managing Asphaltene Precipitation

Quarterly Technical Report

April 1, 2001 – June 30, 2001

Principal Author: Milind D. Deo

Contract Number: DE-AC26-98BC15107

Department of Chemical and Fuels Engineering
University of Utah
Salt Lake City, UT 84112

Disclaimer:
This report was prepared an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Objectives

This project was an attempt at understanding the phenomenon of carbon dioxide induced asphaltene precipitation. The idea was that such an understanding would help in identifying solutions and in better managing the flooding process.

Summary of Work Done

A comprehensive coreflood was completed wherein 22 timed samples were collected for compositional analysis. The kinetic experiments and modeling with field asphaltene were continued.

Description of the Work and Results

Comprehensive Coreflood

A 1.5 –inch diameter Berea core, 6.88 inches long was used for the experiment. The core was mounted in a heat shrink Teflon sleeve, which was shrunk in place. The ends of the core along with the sleeve were clamped onto two specially designed end pieces of a triaxial core holder. Several measurements were made of the core pore volume. The average from all the measurements was 51 mL.

The coreflood was performed with live oil. The gas oil ratio was 155 scf/stb and the temperature was 160^0F. The core was first evacuated and charged with oil. The coreflood was performed without any water in the core. Two pore volumes of carbon dioxide was sent through the core at about 3000 psi. Twenty two (22) samples were collected as a function of time. Detailed compositional analyses were performed on each of the samples. The data was analyzed by simulated distillation (SIMDIS). Figure 1 shows the compositions of different samples as they eluted from the core. As is seen from the figure, until about CO_2 breakthrough, the compositions of the mixtures remain

unchanged. At and after CO_2 breakthrough, intermediate compounds go through a high and this high shifts to heavier and heavier compounds as more oil eluted from the sample. Compositions of the some of the key hydrocarbon constituents are shown in Figure 2, as a function of time. Lighter components (up to about C20) are produced at their original composition until CO_2 breakthrough. Thereafter, they go through an increase before declining in concentration. The intermediate compounds have the biggest increase after CO_2 breakthrough The heaviest of hydrocarbons are lower in concentration more or less throughout the run and their amounts are significantly higher in the oil left behind and obtained using a solvent flood (dichloromethane was the solvent used).

Kinetic Experiments

The solubility parameters of asphaltenes were determined by mixing different types of asphaltenes in different solvents and by determining the precipitation onset by Near Infrared Spectroscopy. Asphatenes separated by using pentane, heptane and also field asphaltenes from Rangely were mixed with a wide variety of solvents and reprecipitated using heptane. A simple model was used in calculating the solubility parameters.

The three different asphaltenes were initially mixed with three solvents, toluene, xylene and tetrahydrofuran (THF). Physical properties of the solvents are listed in Table 1. Fixed quantity of the solids (100mg) were mixed with 20-40 mL of the solvents. In each case, a single-phase mixture was generated. Heptane was added to the different mixtures at a rate of 1 mL/min and the mixture absorbance was monitored at 1600 nm using the Near Infrared Spectrometer. As discussed in the previous reports, the minimum in the absorbance at 1600 nm was determined to be the point of the onset of precipitation.

Onset trends for the three asphaltenes are shown in Figures 3-5. The initial solvent dilution (L of solvent/g of asphaltenes) is on the x-axis, while the precipitant (heptane) required (in L of heptane/g of asphaltenes) is on the y-axis. As the initial solvent dilution increases, the precipitant volume required to initiate precipitation also increases (more or less linearly) for all of the three solids examined. The onset volumes are the highest for THF and the lowest for xylene, and follow the order THF > TCE > toluene > xylene. This onset behavior appears well correlated with the solubility parameter of the solvents. Higher the solubility parameter of the solvent, harder it is to induce precipitation of a mixture of asphaltenes with that solvent. It is also clearly observed that it is much easier to induce precipitation from field asphaltenes compared to the pentane insoluble asphaltenes. The heptane insoluble asphaltenes fall between these two samples. It is hypothesized that the field asphaltenes are solvent washed and weathered and are thus of higher molecular weight and polarity.

The asphaltene solubilities can be calculated by a procedure described by Anderson (1999). The slope of the solubility line (Figures 4-6) is first determined and consequently, the volume fraction of the solvent phase. The critical solubility parameter is then found followed by an empirical determination of asphaltene solubility.

$$?_s ? \frac{1}{1 ? slope}$$

$$slope ? \frac{V_p}{V_s}$$

$$?_p ? 1 ? ?_s$$

V_p : volume of precipitant (heptane)
V_s : volume of solvent
$?_s$: volume fraction of solvent
$?_p$: volume fraction of precipitant

? ? $_i$? 1

? $_{cr}$? ? $_s$? $_s$? ? $_p$? $_p$

$?_a = ?_{cr} + 4\ Mpa^{1/2}$

The solubility parameters of the three asphaltenes determined thus are tabulated in Table 2. The field asphaltene solubility value is the highest followed by heptane asphaltenes and finally, the pentane asphaltenes. What the data shows is that the solubility of asphaltenes in solvents is based on differences between the solubility parameter of the solvent and that of the asphaltene in question. Smaller the difference, more compatible is the solvent and stronger the solubility.

References:

Anderson, S. I., 1999, Flocculation Onset Titration of Petroleum Asphaltenes, Energy and Fuels, Vol. 13, 315-322.

Table 1: Physical properties of the solvents

	MW	Solubility Parameter $(cal/mol)^{0.5}$	Molar volume (mL/mol)	BP (^oC)	MP (^oC)	Density (g/cm^3)
Heptane	100.20	7.50	147.48	98.4	-90.6	0.6837
Toluene	92.14	8.93	106.84	110.6	-95	0.8669
o-Xylene	106.17	9.06	121.12	144.4	-25.2	0.8802
m-Xylene	106.17	8.88	123.48	139.1	-47.9	0.8642
p-Xylene	106.17	8.82	124.00	138.3	13.3	0.8611
THF	72.1	9.48	81.7	66		0.882
Trichloro ethyelene	131.39	9.29		87	-73	1.4642

Table 2: Slope and solubility parameters of the asphaltenes studied

	Field-asphaltene		C7-asphaltene		C5-asphaltene	
	slope	solubility parameter	slope	solubility parameter	slope	solubility parameter
THF	1.30	10.33	1.85	10.16	3.30	9.92
TCE	1.10	10.32	1.95	10.07	3.30	9.88
Toluene	0.70	10.30	1.25	10.09	2.75	9.84
Xylene	0.60	10.35	1.20	10.10	2.80	9.83
average		10.32		10.11		9.87

Table 3. Hansen Parameters for solvents {unit : $Mpa^{0.5}$)

	$?_d$	$?_p$	$?_h$	$?_t$
Toluene	18.0	1.4	2.1	18.18
THF	16.8	5.7	8.0	19.4
Tri-chloro ethylene	18.0	3.1	5.3	19.0
Heptane	15.3	0	0	15.3

$*?_t ? \sqrt{?_d^2 ? ?_p^2 ? ?_h^2}$

* factor 2.046 to transfer from $(cal/mol)^{0.5}$ to $MPa^{0.5}$

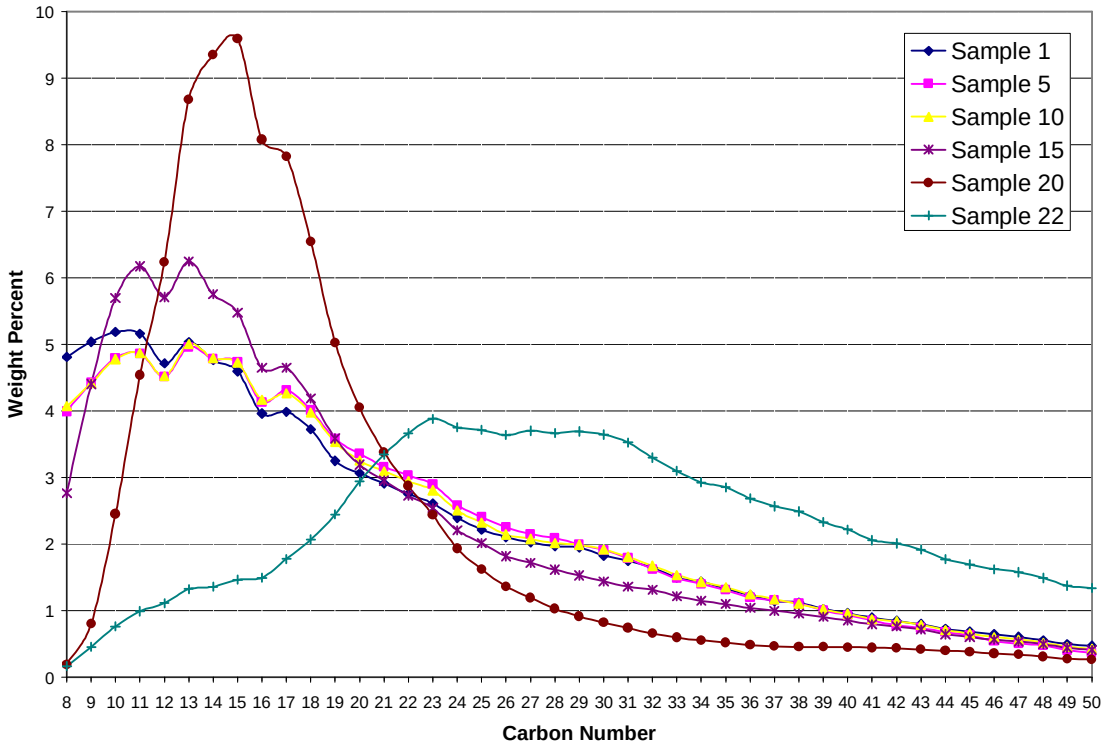

Figure 1: Coreflood results from a live oil experiment. Compositions of the oil samples were obtained using simulated distillation. The sample numbers indicate when they were collected. Higher numbers indicate later times. The carbon dioxide breakthrough occurred at around a sample number of 15.

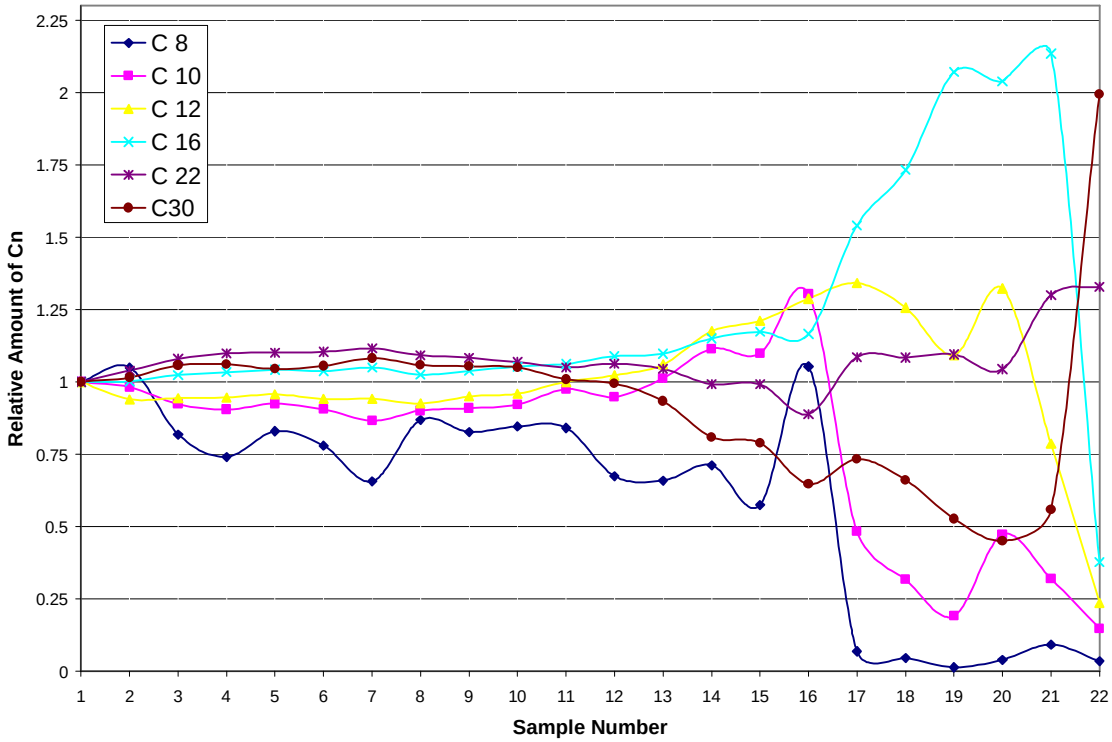

Figure 2: Plots of different carbon numbers in the samples as they eluted from the core with respect to their original concentration in the oil.

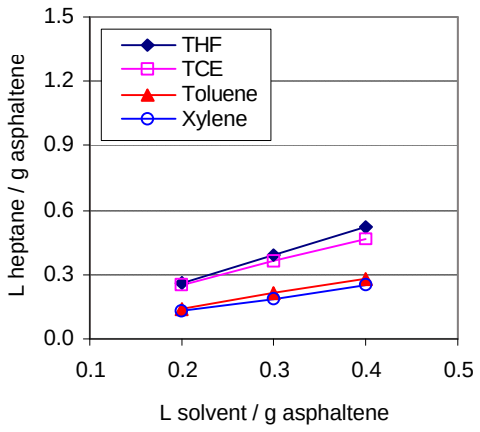

Figure 3: Onset of precipitation as a function of initial solvent dilution for asphaltenes from the Rangely Field.

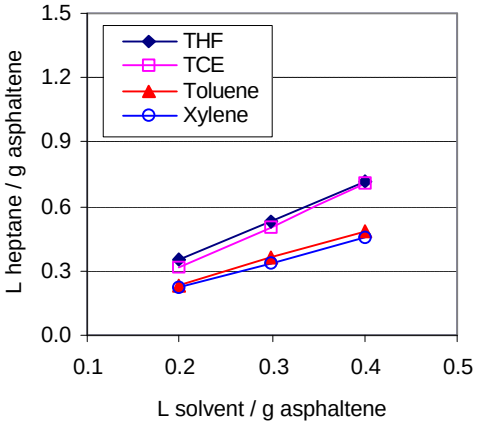

Figure 4: Onset of precipitation as a function of initial solvent dilution for asphaltenes separated by heptane (heptane insolubles from the Rangely crude oil)

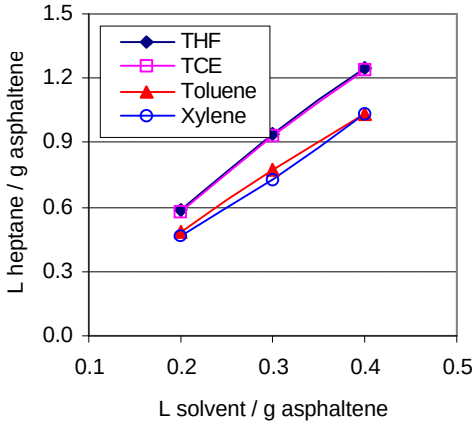

Figure 5: Onset of precipitation as a function of initial solvent dilution for asphaltenes separated by pentane (pentane insolubles from the Rangely crude oil)