ASPHALTENE ONSET, EFFECTS OF INHIBITORS AND EOS MODELING OF SOLIDS PRECIPITATION IN LIVE OIL USING ACOUSTIC RESONANCE TECHNOLOGY

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Abstract

Acoustic Resonance Technology is a newly emerging tool for obtaining high quality data on asphaltene onset in very dark live oil or dead oil at reservoir conditions. This mercury-free digital technology makes it possible to make fast highly accurate measurements during depressurization runs to identify the onset of asphaltene precipitation (solid-liquid equilibrium (SLE)) and the bubblepoint (vapor-liquid equilibrium (VLE)) during the same run.

Measurements were performed at temperatures from 71°C to 116°C and at pressures from 9000 psia to 1200 psia. Comparison of the VLE data obtained from optical methods showed excellent agreement. Effects of inhibitors on the solids precipitation onset have been investigated and discussed. EOS modeling results have been presented with comparisons. There is good agreement between measured data and theory.

Introduction

Wax and asphaltene precipitation from reservoir fluids has been a common problem for many years. These solids remain in solution under reservoir temperature and pressure conditions and begin precipitating when the production temperature or pressure drops below onset conditions. Wax formation occurs when the reservoir fluid cools below the cloud point temperature[1]. Asphaltene precipitation occurs due to the instability caused in the colloidal suspension due to changes in pressure, temperature or composition of the oil. Asphaltenes are classified by the particular solvent used to precipitate them[2 3]. Precipitation of waxes and asphaltenes poses severe operational problems during the life of producing wells in the subsurface, wellhead equipment in separators and tanks[4 5]. Cleanup costs can be very high in offshore oil production[6].

Asphaltene and wax precipitation can be determined experimentally. Several techniques such as fluorescence spectrometry[7], conductivity measurements[8], fibre optics[9], light scattering techniques[10] and cross polarized microscopy[11] are used to determine incipient solids precipitation experimentally. For black oil, most of the techniques become inadequate. In the case of NIR, the problems are due to alignment, poor signal to noise ratio and the dynamic range of operation is limited.

An advanced acoustic resonance technology (ART) has been successfully tested at Hycal Energy Research Laboratories Ltd. to identify solids precipitation onset conditions. The most powerful use of ART is to exploit the time evolution of the acoustic response in fluids under variable and well-controlled conditions of pressure, volume and temperature[12 13 14]. It offers a sensitive and objective method for probing phase transitions. The color of the fluid has no impact on the technique's ability to identify phase transition.

Experimental Details

The acoustic resonance assembly at Hycal consists of a cylindrical resonator of 0.25 inches in diameter made of Hastelloy to resist corrosion. The cylindrical cavity has two transducers: one at the top and the other at the bottom. The excitation of acoustic stimulation is applied through the top piezo-electric transducer by applying a voltage through an excitation source. The acoustic vibrations go through the fluids and the resultant vibrations are received by the receiver at the bottom of the resonator. The acoustic response carries information of the fluids through the phase transition. Hence, by analyzing the acoustic responses, one can detect the onset of liquid-solid or liquid-vapor transition in fluids.

Pressure, volume or temperature can be changed with alacrity in order to analyze potential phase transition with any one of these independent variables held constant. The assembly is housed in a well-insulated circulating air bath with precise temperature control from 150°C to -40°C. A digital pressure gauge is used to measure pressures up to 10000 psia and a platinum resistance thermometer is used to precisely measure temperatures. A linear velocity displacement transducer is used to accurately measure the volume at any instant of time. The acoustic response received by the receiver is processed through a low noise amplifier and then through a fast analog to digital convertor (ADC). Acoustic data, at a sampling rate of 100 khz, acquired by the ADC is synchronized by a trigger signal generated by a function generator. The acquisition computer interfaced to the control computer displays the acoustic spectrum (frequency domain) through a graphic interface and shows the data. Pressure, temperature and volume data gathered during acoustic data acquisition are also displayed. The finger print of the spectrum is the representation of various excited modes of the fluid contained in the resonator. Custom software has been used to track one of the modes along with temperature, pressure or volume and shows the liquid-solid or liquid-vapor transitions.

The acoustic response in a fluid in a cylindrical resonator, can be represented by the resonance frequency and is related to sonic speed by the following equation:

$$f = \frac{C}{2}\left[\left(\frac{n_z}{\ell}\right)^2 + \left(\frac{\alpha_{mn}}{a}\right)^2\right]^{1/2}$$

Where C is the sonic speed in the fluid, n_z is an integer which defines the modes ($n_z = 1$, first radial and $n_z = 2$, second radial, etc.), α_{mn} is an Eigen value ($\alpha_{mn} = 0$ for radial mode), l is length of resonator and a is the radius of the resonator.

At the phase transition, due to the magnitude of difference between sonic speed in solids, liquid and vapor, the acoustic response goes through a major change which is analyzed with the mode tracking utility.

Procedure

The stabilized live oil was charged to a pressure of 9000 psia into the resonator cell which was maintained at a temperature of 105°C. The system was then depressurized at a rate of 50 psi per minute. The rate of depressurization decreased with time and reached approximately 5 psia/minute towards the end of the experiment. The acoustic data with volume, temperature and pressure were collected and subsequently analyzed to detect the solids precipitation onset and bubblepoint. The system was cleaned and prepared for another sample.

Results and Discussion

Figure 1 shows the normalized acoustic response for the live oil versus pressure. At a pressure P_S (6588 psia) incipient precipitation occurred. The acoustic response increased due to the increase in sonic speed when the nucleation of solid particles occurs in crude oil (due to the liquid-solid transformation process). Further depressurization leads to liquid-vapor transition at P_b (pressure 3284 psia).

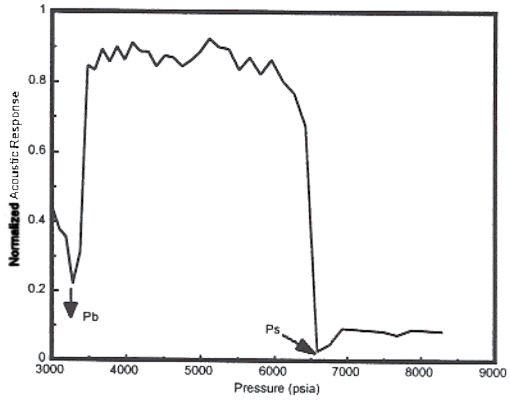

Figure 1. Acoustic Determination of Onset of Asphaltene Precipitation for Bottomhole Sample (Live Oil) at Temperature 105 C

Table 1 presents the solids onset and bubblepoint results for similar runs for live oil at four temperatures (99°C, 105°C, 110°C and 116°C). One can see the asphaltene precipitation onset has dropped from 6855 psia 99°C to 6225 psia at 116°C. The bubblepoint increased from 3221 psia at 99°C to 3290 psia at 116°C.

Table 1. Summary of Acoustic Resonance Results

Set No.	Items	Pressure (psia)	Temperature °F (°C)					
			160 (71)	190 (88)	210 (99)	220 (105)	230 (110)	240 (116)
1	Live Oil	Solids Onset	-	-	6855	6588	6419	6225
		Bubble Point	-	-	3221	3284	3276	3290
2	Live Oil + 20% Deasphalted Oil	Solids Onset	7276	6886	6463	-	-	5798
		Bubble Point	1999	2368	2469	-	-	2660
3	Live Oil + 40% Deasphalted Oil	Solids Onset	6526	6026	5687	-	-	5237
		Bubble Point	1812	2132	2324	-	-	2498
4	Live Oil + 20% Deasphalted Oil + 5000 ppm of Inhibitor X	Solids Onset	7192	-	6050	-	-	5377
		Bubble Point	1963	-	2385	-	-	2630
5	Live Oil + 20% Deasphalted Oil + 10000 ppm of Inhibitor X	Solids Onset	4062	-	3932	-	-	3813
		Bubble Point	1566	-	2344	-	-	2586

There have been several opinions about the effects of deasphalted oil on asphaltene precipitation onset pressures but no data has been found. Recent AR data on live oil with 20% deasphalted oil and 40% deasphalted oil confirmed the authors' view that these combinations strengthen the colloidal suspension and suppress the asphaltene precipitation onset pressures to some extent as shown in Table 1. The solids onset pressure in live oil + 20% deasphalted oil dropped from 7276 psia at 71°C to 5798 psia at 116°C and the bubblepoint increased from 1999 psia at 71°C to 2660 psia at 116°C respectively. The AR results for live oil + 40% deasphalted oil indicated further reduction in solids onset from 6526 psia at 71°C to 5237 psia at 116°C and a bubblepoint increase from 1812 psia at 71°C to 2498 psia at 116°C. Further attempts were made with an Inhibitor X at Hycal with various concentrations in live oil + 20% deasphalted oil to further suppress the solids precipitation onset pressure (5000 psia was desired). AR results at 5000 and 10000 ppm of Inhibitor X in live oil + 20% deasphalted oil are presented in Table 1. The results confirmed that at 10000 ppm levels, the solids precipitation onset dropped from 4062 psia at 71°C to 3813 psia at 116°C (well below the production pressure of 5000 psia), and increased the bubblepoint from 1566 psia at 71°C to 2586 psia at 116°C. Preliminary results are promising. Figure 2 presents the comparison of the results presented in Table 1.

Modeling

A single solid component asphaltene model states that solid precipitation occurs when the fugacity of the solid component in the liquid phase is greater than the fugacity of the fluid of the component as a solid. For this model, the first data point (6855 psia and 99°C) was chosen as the reference point. The solid fugacity for this point was generated using the multiphase solid fugacity function of CMG's WINPROP. The solid fugacity at this point was then set equal to the fugacity of the asphaltene component in the liquid phase predicted by the equation of state. The fugacity of the solid phase, at other experimental conditions, were then calculated from the following model.

$$\ell n(f_S)_{PT} = \ell n(f_S)_{\mathrm{Pr}\,Tr} + \frac{V_S}{RT}(P - P_{TP}) \quad \frac{V_S}{RT}(P_R \quad P_{TP})$$

$$+\frac{C_{ps}}{R}\ \ell n\left(\frac{Tr}{T}\right) - T_{TP}\left(\frac{1}{T} - \frac{1}{T_r}\right) - \Delta\frac{H_f}{R}\left[\frac{1}{T} \quad Tr\right.$$

where	f_S	is fugacity of solid (atm)
	V_S	is molar volume of solid (lit/mol)
	P	is pressure (atm)
	R	is gas constant (cal/mol·K)
	C_{ps}	is heat capacity of solid (cal/mol·K)
	T_r	is reference temperature (K) and pressure (atm)
	T_{TP}	is triple point temperature (K)
	P_{TP}	is triple point pressure (atm)
	ΔH_f	is the heat of fusion (cal/mol)

The solid heat capacity and the heat of fusion were also tuned to match the other experimental data parameters. Table 2 presents the results of modeled data along with AR experimental data and deviations. As shown there was good agreement. Figure 2 presents the comparison of results.

Table 2. Comparison of Experimental Solid Onset Pressures with EOS Modeled Results

Temperature °F (°C)	20% Deasphalted Oil			40% Deasphalted Oil			Live Oil		
	Experimental	Modeled	% Error	Experimental	Modeled	% Error	Experimental	Modeled	% Error
160 (71)	7276	7276	0	6526	6526	0	-	-	-
190 (88)	6886	6850	0.52	6026	6050	0.40	-	-	-
210 (99)	6463	6500	0.57	5687	5700	0.23	6855	6855	0
220 (105)	-	-	-	-	-	-	6588	6590	0.03
230 (110)	-	-	-	-	-	-	6419	6420	0.02
240 (116)	5798	5800	0.03	5237	5250	0.25	6225	6300	1.2

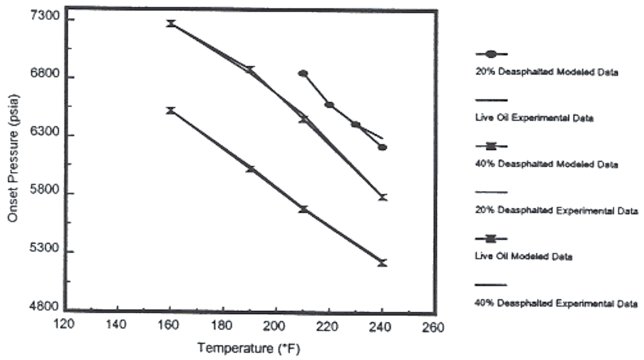

Figure 2. Comparison of Experimental Solids Onset Pressures with EOS Model Results

Conclusions

The state-of-the-art advanced acoustic resonance technique is a useful tool to determine the asphaltene onset conditions for a live or dead oil. It has been an ideal probe to study the effects of inhibitors on asphaltene precipitation. Solid-liquid equilibrium and vapor-liquid equilibrium conditions can be defined in a live reservoir fluid using the data obtained from this advanced AR system. Modeling for future prediction of asphaltene precipitations can be achieved by incorporating high quality AR data.

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