

Advanced Acoustic Approach for Reservoir Solids Problems/Effects of Inhibitors on Solids Onset and EOS Modeling

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ABSTRACT

The production, transport, and refining of petroleum and gas are constantly affected by the deposition of unique phases such as wax, asphaltenes, diamondoids, hydrates and sulphur. The venue of the advanced acoustic resonance approach has been successfully tested to meet the challenges of solids problems in the new millennium. A mercury-free advanced acoustic resonance (AR) system, developed and tested at Hycal Energy Research Laboratories for reservoir applications, makes it possible to have fast, highly accurate, measurements during depressurization (9000 psia to 12000 psia) runs on dark live oil at reservoir temperature to identify the onset of asphaltene precipitation and bubblepoint during the same run. Black oil, a problem for visual and optical methods, is no barrier for this technology. Effects of inhibitors on solid-liquid equilibrium have been investigated at various concentrations and temperatures. The results are presented and discussed. EOS modeling of the AR results have been presented with comparisons. There is good agreement between measured and modeled data.

INTRODUCTION

Asphaltene precipitation from reservoir fluids causes severe operational problems in the wellhead equipment, separators, tanks and surface equipment¹. In offshore production, the clean-up costs have skyrocketed². Asphaltenes are dark brown to black solid compounds with no definite melting point. They decompose while heating and leave a carbonaceous residue. They are non-crystalline substances or mixtures of relatively high molecular weight fractions of bitumen with characteristics of strong aromatic polar substances. They are classified by the particular solvent (n-heptane, n-pentane) used to precipitate them³. Asphaltene precipitation can be measured experimentally. Light-scattering techniques⁴ and cross-polarization microscopy⁵ have been used to determine the onset of solids precipitation experimentally. Poor signal to noise ratio limits the dynamic range of operation in the case of N.I.R.

An advanced acoustic resonance system developed at Hycal has been successfully used in the determination of solids precipitation onset in live reservoir fluids. The

system exploits the time evolution of the acoustic response in fluids under variable and well-controlled conditions of pressure, volume and temperature^{6,7}. The system detects phase transitions on the basis of differences in orders of magnitude in sonic speeds of various fluid states (vapor/liquid/solid) when acoustic waves are propagated in a reservoir fluid going through phase changes.

EXPERIMENTAL DETAILS

Hycal's AR system, consisting of a cylindrical resonator (0.25 inches in diameter) is made of hastelloy with one transducer at the top to generate acoustic waves through the fluid in the resonator, and the other at the bottom to receive the signals that carry information about the fluids through the phase transitions. One can detect the onset of liquid-solid or liquid-vapor transitions in fluids by analyzing the acoustic responses.

The assembly is housed in a well-insulated circulating air-bath with precise temperature control from -40°C to 150°C. A digital pressure gauge is used to measure pressures up to 10,000 psia and a platinum resistance thermometer is used to measure temperatures precisely. A linear velocity displacement transducer arrangement is used to accurately measure the volume at any instant in time. The signal received at the receiver is processed through a low noise amplifier and then through a fast analog to a digital converter (ADC).

Acoustic data acquired by the ADC, at a sampling rate of 100 kHz, is synchronized by a trigger signal generated by a function generator. The acquisition computer interfaced to the control computer displays the acoustic spectrum through a graphic interface and shows the data. Pressure, temperature and volume data, gathered during acoustic data acquisition are also displayed. The frequency spectrum presents various excited modes of the fluid contained in the resonator. Hycal's custom software has been used to track one of the modes along with temperature, pressure and volume. The results show the liquid-solid or liquid-vapor transitions.

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

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

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 the length of the resonator and a is the radius of the resonator.

At the phase transition or onset due to the magnitude of difference between sonic speeds in different phases (liquids, solids and vapor), the acoustic response goes through a sharp, major change which is analyzed with the mode tracking utility.

PROCEDURE

The stabilized live oil was charged to a pressure of 8500 psia into the resonator cell which was maintained at a temperature of 210°F (99°C). The resonator pressure was then decreased by changing the volume at a very slow rate of 50 psia per minute at constant temperature. The rate of depressurization decreased with time and reached approximately 5 psia per minute towards the end of the experiment. The acoustic data with volume, temperature and pressure were collected and subsequently analyzed to detect the onset of solids precipitation and bubble point. The system was then cleaned and prepared for another sample. The system temperature was changed to 220°F (105°C) and at this temperature, the cell was charged to a pressure of 8500 psia and the experiment was repeated as before. Measurements were completed at 230°F (110°C) and 240°F (116°C). Similar measurements were made for live oil with 20% deasphalted oil with 5000 ppm and 10,000 ppm Inhibitor X and the onset of asphaltene precipitation was determined using AR at three temperatures, 160°F (71°C), 210°F (99°C) and 240°F (116°C), respectively.

RESULTS AND DISCUSSION

The normalized acoustic response for the live oil versus pressure results are shown in Figure 1. The onset of asphaltene precipitation is clearly shown at P_S (pressure of 6855 psia). The acoustic response increased due to the increase in sonic speed when the nucleation of solid particles occurred in live oil (due to the liquid-solid transformation process). Further depressurization

leads to a liquid-vapor transition (bubblepoint) at P_b (pressure of 3221 psia).

Asphaltene onset pressures and bubblepoint pressures for similar runs for the live oil at four temperatures (210, 220, 230 and 240°F) are presented in Table 1. One can see the asphaltene precipitation onset has dropped from 6855 psia at 210°F to 6225 psia at 240°F. Recent AR data on live oil with 20% deasphalted oil confirmed the authors' view that these combinations strengthen the colloidal suspension and suppress the asphaltene precipitation pressures to some extent. Further attempts were made with an Inhibitor X at Hycal with various concentrations in live oil plus a 20% deasphalted oil mix to further suppress the solids precipitation onset pressure below the production pressure (5000 psia was desired).

AR results at 5000 ppm and 10,000 ppm of Inhibitor X in live oil plus 20% deasphalted oil are presented in Table 1. The results confirmed that, at 10,000 ppm levels, the solids precipitation onset dropped from 4062 psia at 160°F (71°C) to 3813 psia at 240°F (116°C), well below the production pressure of 5000 psia. The bubblepoint pressure increased from 1566 psia at 160°F (71°C) to 2586 psia at 240°F (116°C).

Preliminary results are promising. Figure 2 presents a comparison of the results presented in Table 1 and shows the effects of inhibitors on solids precipitation onset at various temperatures. Figure 3 presents the effects of inhibitors on the bubblepoint pressures at various temperatures.

EOS 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 210°F) was chosen as the reference point. The solid fugacity for this point was generated using the multiphase solid fugacity function of the Computer Modeling Group's (CMG) 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 EOS. The fugacity of the solid phase at other experimental conditions were then calculated from the following model.

where

$$\ln(f_S)_{PT} = \ln(f_S)_{PrTr} + \frac{V_S}{RT}(P - P_{TP}) - \frac{V_S}{RT}(P_R - P_{TP}) + \frac{C_{ps}}{R} \left[\ln\left(\frac{Tr}{T}\right) - T_{TP} \left(\frac{1}{T} - \frac{1}{Tr} \right) \right] - \frac{\Delta H_f}{R} \left[\frac{1}{T} - \frac{1}{Tr} \right]$$

- f_s = fugacity of solid (atm)
- V_s = molar volume of solid (lit/mol)
- P = pressure (atm)
- R = gas constant (cal/mol·K)
- C_{ps} = heat capacity of solid (cal/mol·K)
- T_r = reference temperature (K)
- T_{TP} = triple point temperature (K)
- P_{TP} = triple point pressure (atm)
- ΔH_f = 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 a comparison of AR experimental data with the results of modeled data and percent error. As shown, there was good agreement. Figure 4 presents a comparison of results.

CONCLUSIONS

An advanced acoustic resonance technique has proven to be a useful tool to detect onset of asphaltene precipitation in live black oils. It is an ideal probe for evaluating the effects of various new inhibitors on the asphaltene onset pressures before testing in actual reservoirs. This will make it more cost-effective and one can make more efficient use of inhibitors. Modeling for future prediction of asphaltene precipitation can be achieved by incorporating high quality AR data.

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Table 1. Summary of Acoustic Resonance Results

No.	Sample	Pressure (psia)	Temperature °F (°C)				
			160 (71)	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 + 5000 ppm of Inhibitor X	Solids onset	7192	6050	-	-	5377
		Bubble point	1963	2385	-	-	2630
3	Live oil + 20% deasphalted oil + 10,000 ppm of Inhibitor X	Solids onset	4062	3932	-	-	3813
		Bubble point	1566	2344	-	-	2586

Table 2. EOS Model Results

Temperature °F (°C)	Sample: Live Oil		
	Experimental (AR) Solids Onset Pressure (psia)	Calculated Solids Onset Pressure (psia)	Percent Error
210 (99)	6855	6855	0
220 (105)	6588	6590	0.03
230 (110)	6419	6420	0.02
240 (116)	6225	6300	1.20

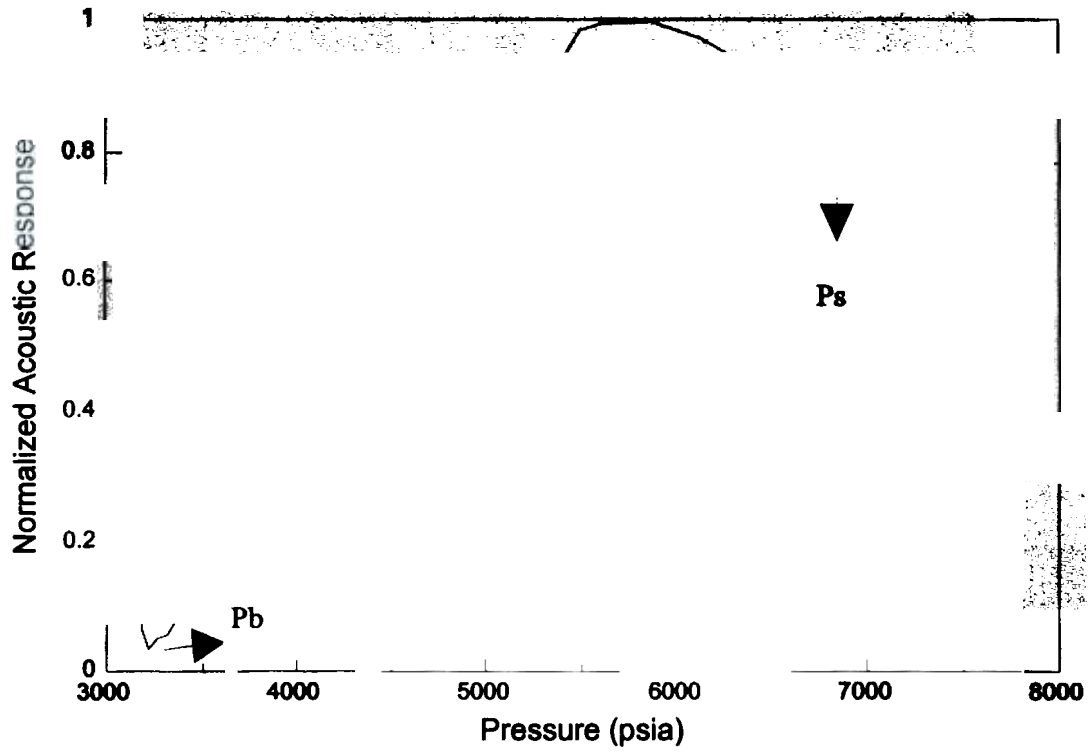


Figure 1. Acoustic Determination of Onset of Asphaltene Precipitation for a Live Oil at 210°F

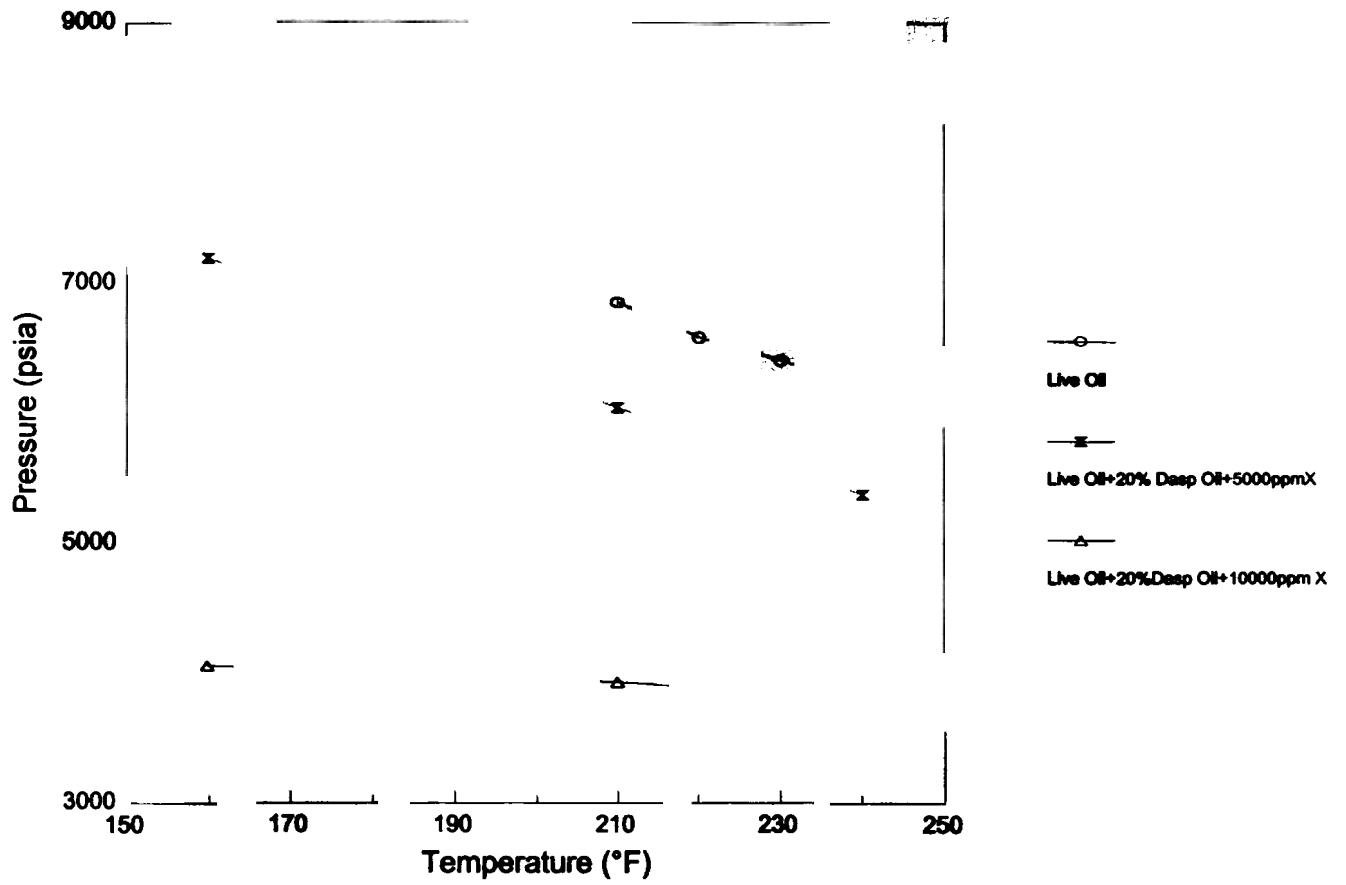


Figure 2. Acoustic Determination of Effects of Inhibitors on Solids Precipitation Onset at Different Temperatures

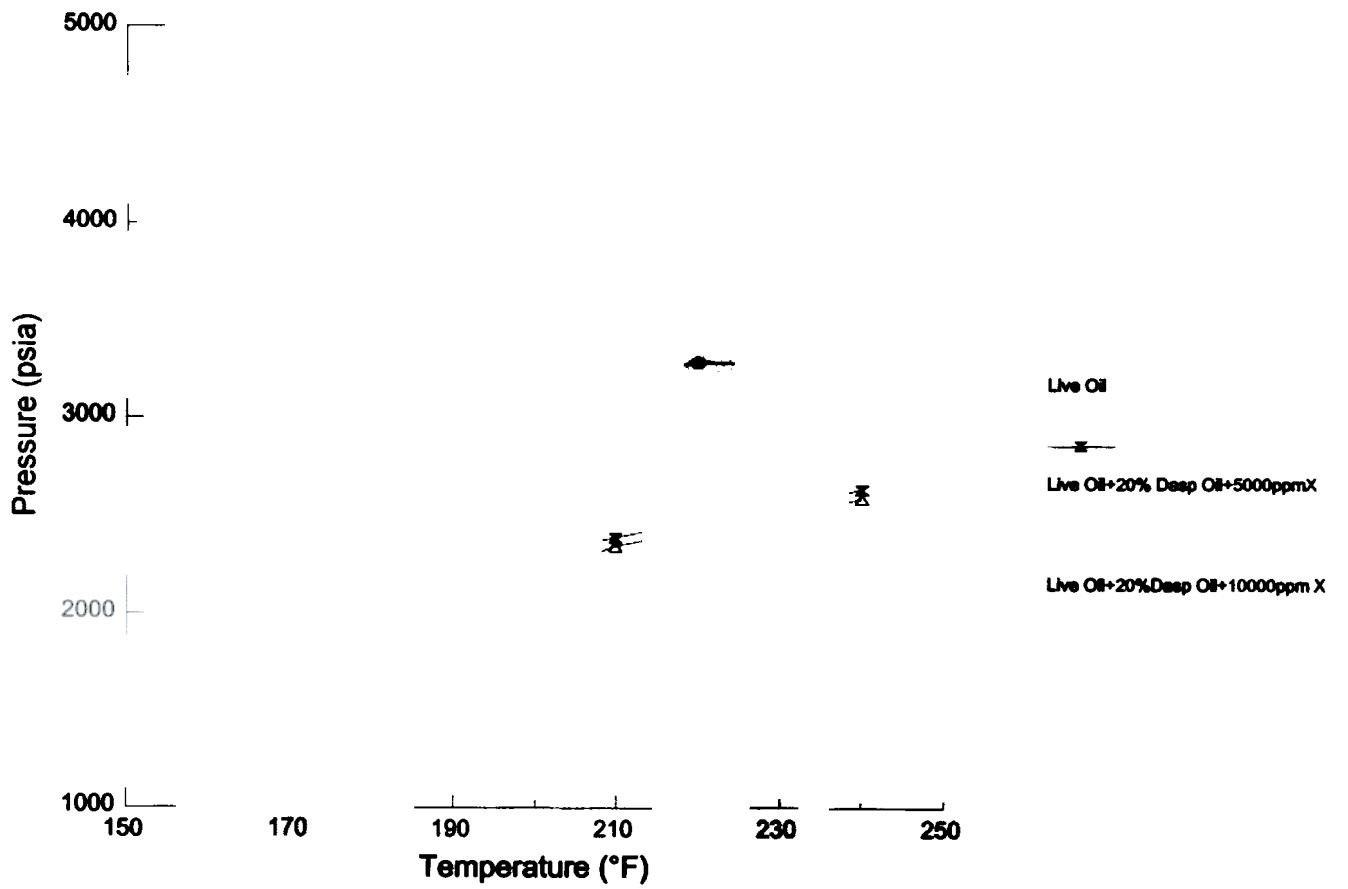


Figure 3. Acoustic Determination of Effects of Inhibitors on Bubble Point Pressures at Different Temperatures

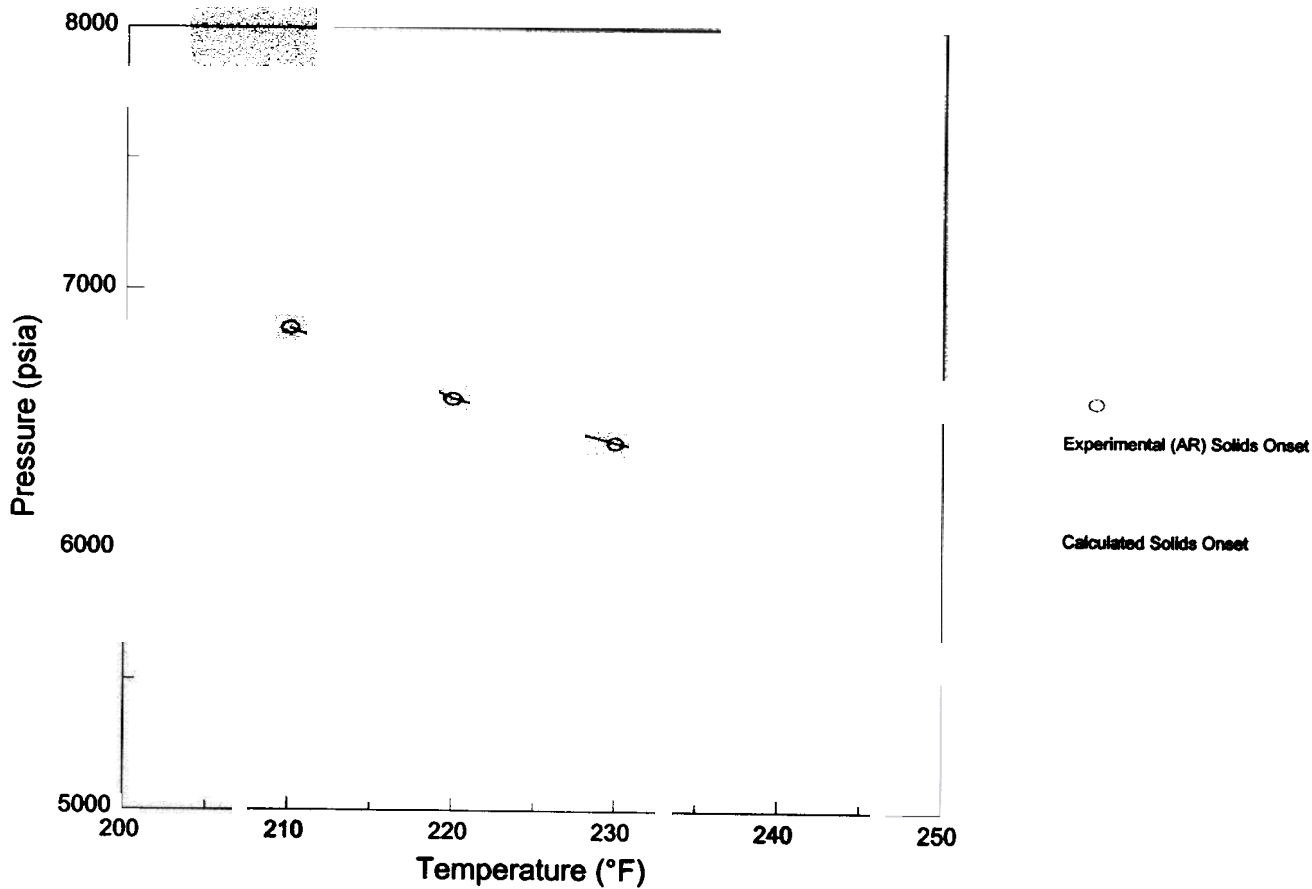


Figure 4. Comparison of Experimental (AR) Solids Precipitation Onset Data with EOS Modeled Data