Cloud Point Determination Using a Thickness Shear Mode Resonator

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Introduction

Crude oils and crude oil products contain substantial amounts of petroleum waxes, consisting of a distribution of high molecular weight hydrocarbons. These waxes or paraffins have limited solubility in oil and tend to precipitate out at a temperature determined by the concentration and constituents of the wax. Precipitation and deposition of wax results in narrowing of pipelines, making crude oil recovery difficult.

A parameter of practical importance is the wax precipitation temperature, traditionally known as the *cloud point*, at which visible crystallization occurs. Deposition problems arise in oil field operations at or below this temperature. Several techniques can be used to determine the cloud point [1]: (1) visual observation, (2) viscosity measurement, (3) differential thermal analysis, and (4) pulsed nuclear magnetic resonance.

In this paper we describe a new technique for measuring cloud point based on measuring properties of the fluid and accumulated deposit using a quartz resonator. The thickness shear mode (TSM) resonator consists of a thin, highly polished disk of AT-cut quartz with circular electrodes on both sides (Figure 1). Applying an RF signal to the electrodes causes the piezoelectric quartz crystal to be excited into a shear mode of vibration in which crystal faces undergo in-plane displacement.

The TSM resonator is instrumented as a sensor by incorporating it as the frequency-control element of an oscillator circuit. Wessendorf [2] has described an oscillator circuit capable of exciting the crystal in liquid media. This oscillator tracks the resonant frequency of the crystal and has level-control circuitry to measure the amplitude of the oscillation voltage; it provides a feedback voltage to maintain this at constant level. The level control compensates for changes in resonator damping caused by (1) changes in the viscosity of the contacting fluid and/or (2) deposits that form on the crystal. Since both of these changes occur with oil at the cloud point, the feedback voltage is a good indicator of the cloud point.

When a TSM resonator operates in contact with a fluid, the shear motion of the surface radiates a critically damped shear wave into the contacting fluid (Fig. 2). This mechanical coupling causes both a change in stored and dissipated energy in the crystal, leading to a change in resonant frequency and crystal damping (oscillator feedback voltage). Kanawaza and Gordon showed that resonant frequency decreases proportionally with $(\rho\eta)^{1/2}$, where ρ and η are liquid density and viscosity, respectively [3]. The change in crystal damping or feedback voltage due to liquid contact is also proportional to $(\rho\eta)^{1/2}$ [4].

A rigid film deposited onto the resonator surface moves synchronously with the oscillating surface. This causes a change in the stored (kinetic) energy of the resonator. This results in a decrease in resonant frequency proportional to the areal mass density (density times thickness) contributed by the layer [5]. Since moving the rigid layer does not result in dissipation of energy, however, there is no change in crystal damping or oscillator feedback voltage.

A compliant film deposited on the resonator surface behaves differently than a rigid one. While the lower film surface moves synchronously with the resonator surface, the upper film region may lag behind [6]. This induces a shear strain in the film. Since compliant films are typically viscoelastic, i.e., having both elastic and viscous character, strain in the film leads to both energy storage and dissipation. As the thickness of the compliant film increases, it initially leads to a decrease in resonant frequency; at larger thicknesses, however, the film causes an increase in frequency [6]. Thus, frequency alone is not a good indicator of deposit thickness. Initially, the feedback voltage increases with film thickness; at larger thicknesses, voltage tends to saturate. At the cloud point, the precipitation of wax results in both a change in the viscosity of the fluid, as well as formation of a viscoelastic deposit on the resonator surface. Since both effects lead to an increase in crystal damping, this parameter is a good indicator of the cloud point.

System Description

Figure 3 is a block diagram describing the cloud point detector system. The system consists of a test cell and peripheral equipment for temperature control and data acquisition. The temperature controller allows sample temperature to be easily varied to determine the cloud point of the test fluid. The data acquisition system is made up of a voltmeter (HP 3478A), frequency counter (HP 5384A), and scanning thermometer (Keithley 740). A personal computer acquires data from these instruments.

The test cell, shown in Fig. 4, has two parts: the cell body and the cell head. The cell body holds a glass sample cup with a volume of 25 cm^3. The body, made of stainless steel, has thermoelectric coolers on each of the four vertical surfaces. Heat sinks are attached to the coolers so that waste heat can be efficiently transferred to the room air, facilitated by a fan. The thermoelectric units heat and cool samples over the range of 5°C to 85°C. A stir bar is inserted in the sample cup to maintain sample uniformity; this is driven magnetically from below. The cell body also contains an o-ring seal on the surface that maintains pressure and prevents the loss of the more volatile sample constituents. Overpressurization is prevented by a 100 psi pressure-relief valve.

The cell head includes the sensor, oscillator, a thermocouple, and electrical connectors to output the oscillator frequency and feedback voltage. The electrical connector that holds the sensor was designed to allow rapid sensor changeout.

Experimental Section

A clean and dry TSM resonator was installed in the cell head and reference measurements were made of the resonant frequency and oscillator feedback voltage. A crude oil simulant, consisting of Shell wax 300 and kerosene, was then placed in the test cell at room temperature. The lid, with sensor attached, was bolted onto the cell, sealing the test volume. At the start of a test, the cell temperature was elevated to 80°C. After the temperature stabilized, the controller was set for a certain cooling rate and final temperature; data acquisition was initiated.

The cloud point of the sample was also determined by visual observation. This was done by placing a mirror beneath the sample cup and observing a change in clarity as the sample was cooled. The sample was initially heated to 80°C and then cooled to 40 °C with the lid on to contain volatile components. The lid was removed at 40°C so that the cloud point could be observed.

Figure 5 shows the change in oscillator feedback voltage and resonant frequency vs. temperature for two different cooling rates for a wax/kerosene sample. A dashed line indicates the visually-determined cloud point at an intermediate cooling rate of 1°C/min. The oscillator damping voltage, in particular, shows an abrupt increase at the visually-observed cloud point due to the onset of wax precipitation. This is due to increased resonator damping from a combination of increased fluid viscosity and wax depositing on the resonator. The resonant frequency also shows an abrupt change at the cloud point. It is clear that the best indication of cloud point (i.e., agreement with visual observation) obtained from the resonator measurement is the point at which the damping voltage first changes slope during cooling.

The cloud point determined from resonator measurements is slightly higher for the lower cooling rate. This is to be expected since the lower rate provides more time for the nucleation of wax crystals to occur. Below the cloud point, the responses are quite dependent upon the cooling rate. This may be due to a dependence of the crystal properties on the cooling rate. Graham [7] has noted that slower cooling rates lead to crystals that are larger, more irregularly-shaped, and more aggregated.

Figure 6 shows the change in oscillator feedback voltage and resonant frequency vs.

temperature for two wax concentrations. The samples are both cooled at a rate of 1°C/min. The "original" sample shows a cloud point of 34.4°C, while the sample with added wax shows a cloud point of 36.6°C. As expected, the higher concentration of wax precipitates out at a higher temperature. The oscillator voltage clearly indicates the onset of wax precipitation in each case. The oscillation frequency shows a more complicated behavior, resulting from the fact that oscillation frequency initially decreases with accumulated layer thickness, then increases.

Conclusion

The resonator exhibits large responses in both oscillator feedback voltage and resonant frequency at the cloud point. The temperature at which the feedback voltage first changes slope during the cooling process is an indication of cloud point that is consistent with visual determination. This technique is less subjective and operator dependent than visual means and works equally well with opaque samples. Moreover, since the resonator operates at extremely low shear rates, it perturbs the sample less than a rotating-cup viscometer.

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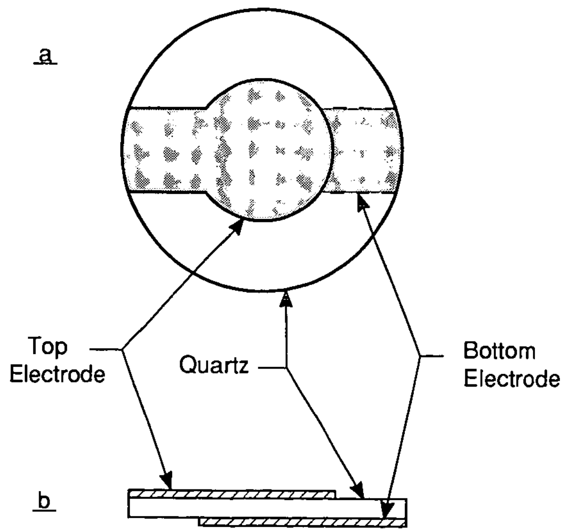

Fig. 1. *Top (a) and side (b) views of a quartz thickness shear mode (TSM) resonator.*

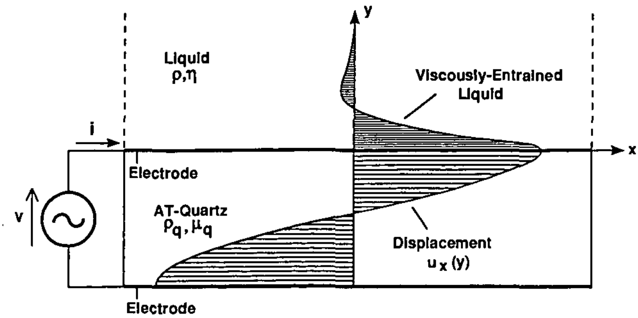

Fig. 2. *Cross-sectional view of a smooth TSM resonator with the upper surface contacted by a liquid. Shear motion of the smooth surface causes a thin layer of the contacting liquid to be vicously entrained.*

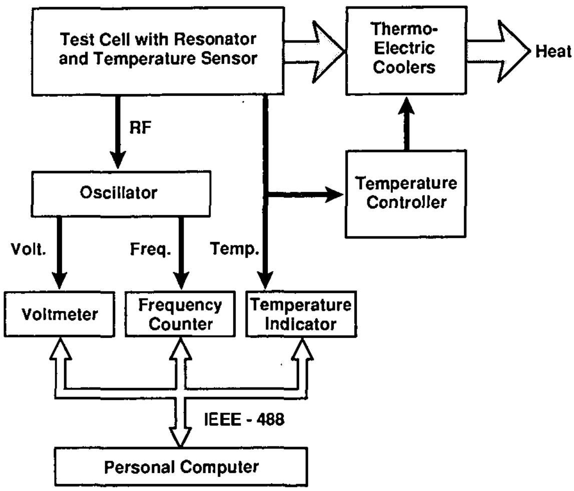

Fig. 3. *Block diagram of the cloud point detector system used for TSM resonator and visual cloud point determinations.*

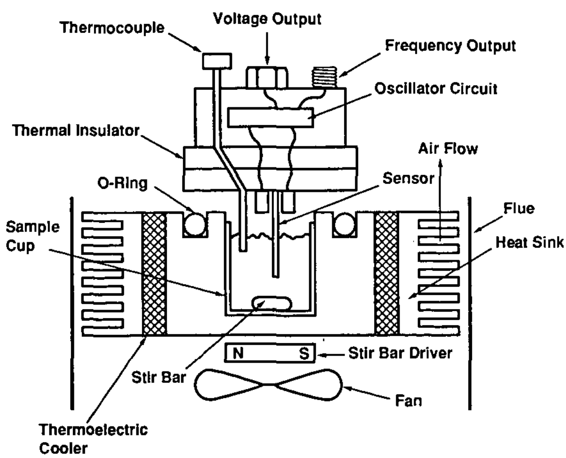

Fig. 4. *Cloud point detector test cell with TSM resonator (sensor), oscillator circuit, thermocouple, sample cup, stir bar with driver, thermoelectric coolers, heat sinks and fan.*

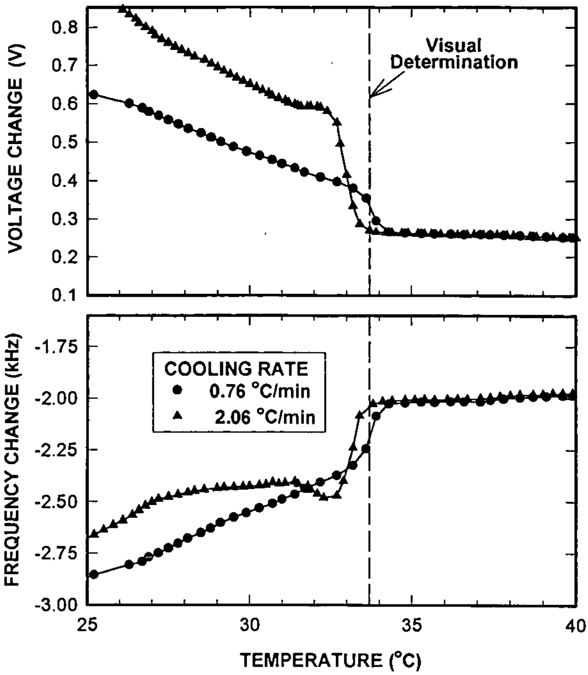

Fig. 5. *Voltage change and frequency change measurements of TSM resonator vs.temperature for a Shell wax 300/kerosene mixture cooled at two rates. Dashed line indicates the visually determined cloud point.*

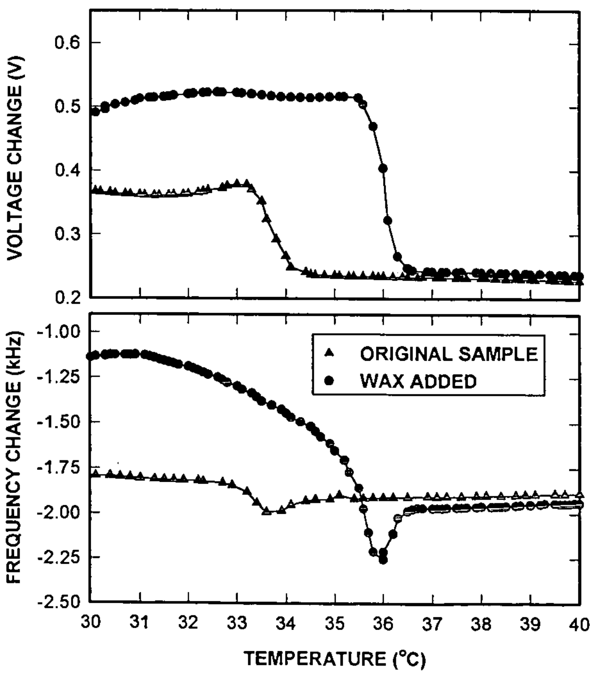

Fig. 6. *Voltage change and frequency change measurements of TSM resonantor for two different Shell wax 300/kerosene concentrations cooled at the same rate.*