Measurement of Viscosities of Liquids Saturated with Gases at High Pressures

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THE interest of the petroleum industry in increasing the yield of crude oil from producing formations has caused much thought to be given to the factors controlling its recovery. One of the most important of these appears to be the properties of the oil itself. Previous investigators found that dissolving natural gas in crude oil had a surprising effect on many of its physical properties. A general study of these changes was undertaken at the California Institute as Research Project 37 of the American Petroleum Institute. This paper describes the viscometer developed for the study of the effect of dissolved gas on the viscosity of crude oils.

INSTRUMENTAL REQUIREMENTS

In order to duplicate in some measure the range of conditions found in petroleum formations, saturation pressures up to 200 atmospheres (2940 pounds per square inch) and temperatures ranging from 20° to 95° C. (70° to 200° F.) must be attained. The work of other investigators (1), at
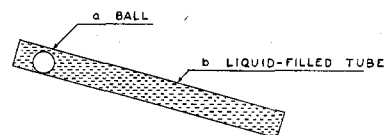

FIGURE 1. DIAGRAM OF BALL AND TUBE

lower pressures, indicated that the change in viscosity of the oil would be very large at saturation pressures of 200 atmospheres. An instrument is therefore required which will measure accurately a wide range of viscosities without requiring intermediate alterations or readjustments. There are several other requirements which must be met by an instrument suitable for this study. Some means must be provided for establishing equilibrium between the gas and oil within a reasonable time. The instrument should be of such a nature that its calibration is independent of pressure. There is also need for means of measuring the saturation pressure and of maintaining the temperature of the viscometer constant during a given set of measurements.

PRINCIPLE UTILIZED

The instrument which was found to satisfy most nearly the needs of this work was a modified form of the viscometer developed by Flowers (3) and Hersey (4). The sketch in
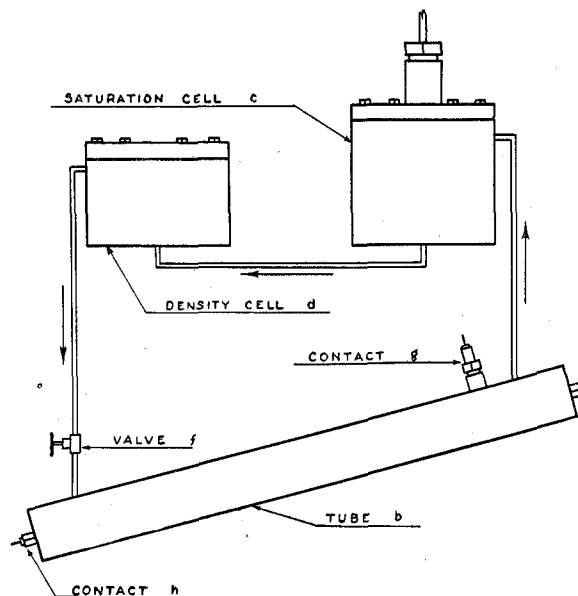

FIGURE 2. DIAGRAM OF VISCOSITY-MEASURING APPARATUS

Figure 1 illustrates the principle of the instrument. The ball a is at the upper end of the closed, liquid-filled tube b. As the ball moves down the tube (probably by both rolling and sliding), the displaced liquid must flow past it through the space between the ball and the tube. For any given ball with the tube held at a constant angle, the travel time of the ball multiplied by the difference between the density of the ball and that of the liquid is a linear function of the absolute viscosity of the liquid. This linear function breaks down, however, if the rate of movement of the ball is so great that the flow becomes turbulent.

THE INSTRUMENT AND ITS OPERATION

Figure 2 is a sketch of the instrument developed upon the above principle. In order that equilibrium between the gas and oil may be reached, a closed circulating system is provided. The liquid flows from the saturation cell c to the density-measuring bomb d, thence to the bottom of the inclined tube b of the viscometer itself, returning from the top of the tube to the gas space of the saturation cell again. A small cam pump in the bottom of the saturation cell circulates
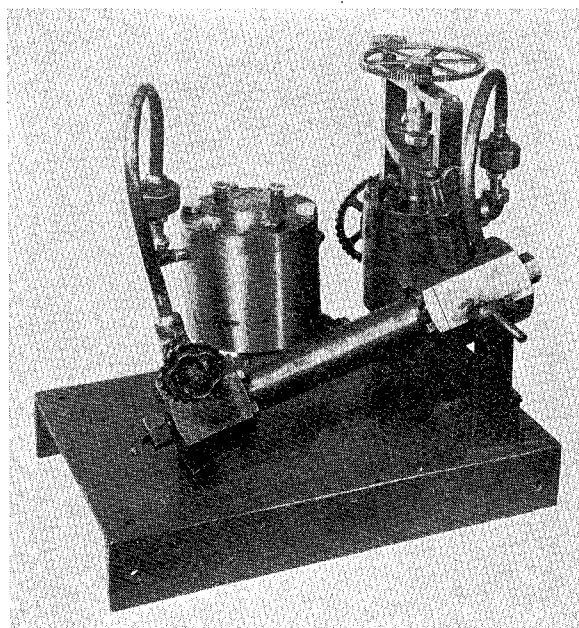

FIGURE 3. PHOTOGRAPH OF INSTRUMENT

261

the oil through the system as desired. A photograph of the actual instrument is shown in Figure 3.

The entire system, except the upper part of the saturation cell, is filled with the oil sample, the system being so arranged that any entrapped gas is swept out upon circulation. Liquid is pumped through the system after thermal equilibrium is
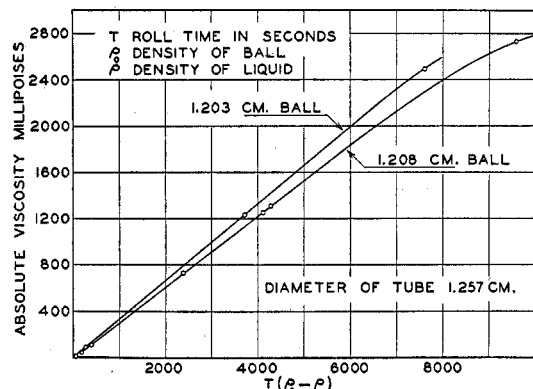

FIGURE 4. CALIBRATION CURVES FOR TWO BALLS

attained, the ball being forced to the upper end of the tube b above the outlet tube. When circulation is stopped, the ball is allowed to move part way down the tube. The upper contact g is then screwed down a small amount, and the circulation again started. The ball, moving up the tube, now wedges itself against the lowered contact, and is in position to start a measurement. This procedure of wedging the ball from below the contact gives a sharper and more reproducible release upon raising the contact than is the case with the ball above. The valve f at the lower end of the ball tube is now closed and the contact lifted, starting the ball down the tube. The break in contact is recorded on a chronograph. When the ball touches the lower contact h, another mark is made on the chronograph record. The valve f is again opened, circulation reëstablished, and the measurement repeated as often as desired. Next, gas is admitted to the top of the saturation cell and circulation maintained until the attainment of equilibrium is indicated by constancy of pressure reading. A new set of ball times is determined as before, more gas is then admitted, and the measurements are repeated at the resulting higher saturation pressure. This process is continued until the pressure approaches the upper limit of 200 atmospheres (2940 pounds per square inch). A series of determinations of this nature involving measurements at ten different pressures requires in the neighborhood of two hours after the initial thermal equilibrium has been reached.

The density of the liquid is measured in the density bomb at each of the saturation pressures by means of a small torsion-mounted balance. Since the two ends of the beam are constructed of materials of different density, the volume displaced is different and the force required to bring the beam into balance is a function of the density of the liquid in which it is immersed. This force is supplied by two solenoid coils, one mounted on the beam, and the other held in a fixed position. When current is passed through the coils a repelling force is exerted between them. By measuring the current flowing through the coils when the beam is in balance, a measure of the density of the liquid in which the beam is immersed is obtained. The instrument is calibrated by immersing it in a series of liquids of known density.

The saturation pressures are measured by means of a fluid pressure scale connected to the gas space of the system through a mercury trap. The trap is necessary to prevent contamination of the gas by the oil used in the fluid pressure scale. The temperature of the viscometer is held at any predetermined value by means of an oil bath controlled by a mercury regulator. The temperature of the bath can be varied between 20° and 95° C. (70° and 200° F.); the maximum variation from the desired temperature during a run is about 0.03° C. (0.05° F.).

CALIBRATION

The viscometer is calibrated by measuring the roll time at atmospheric pressure for liquids of known viscosity. The liquids used in this work were standardized by the Bureau of Standards. The viscosities of these liquids were known at several temperatures, so that the effect of temperature on the calibration of the instrument could be determined.

Figure 4 shows calibration curves for two balls of slightly different sizes. The curves are straight lines over the greater part of the range but flatten off at roll times over twelve to fifteen minutes. This may be due to the break-down of the film between ball and tube. The effect of turbulence can be seen at the short roll times on the upper curve. The instrument gives satisfactory results in this range if enough calibration liquids are used to give the location of the curve with the desired certainty. The marked divergence of the two curves for a small change in ball size points to the need of high accuracy in the machining of both the ball and the tube. It is also evident that change in the surface condition of either the ball or the tube will change the calibration of the instrument to a marked extent. The balls used in this work were spherical to within 0.0001 inch, this degree of accuracy being necessary to obtain duplication of roll times of 0.25 per cent.
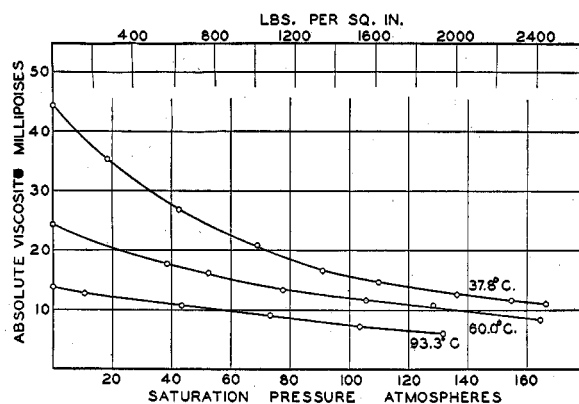

FIGURE 5. VISCOSITY CURVES AT DIFFERENT TEMPERATURES

The effect of pressure on the calibration of the instrument was investigated by comparing the small measured increase in viscosity of water under pressure with that expected from the work of Bridgman (2). This comparison indicated that at 170 atmospheres (2500 pounds per square inch) any change in calibration due to pressure could be neglected.

The range of measurable viscosities covered with one ball is quite large, from about 2500 millipoises down to 10 millipoises. However, the long roll times encountered at the higher viscosities make a smaller ball desirable when working in this range.

From the measured roll time and the density of the liquid, it is a simple matter to read the absolute viscosity from the calibration curve. The kinematic viscosity can then be computed from the absolute viscosity and the density.

An illustrative set of results is shown in Figure 5. These

viscosity curves are for a sample of Santa Fe Springs oil and dry natural gas at three temperatures. The decreased effect of the dissolved gas at the higher temperatures is probably due to the lower solubility of the gas under these conditions.

CONCLUSIONS

The use of this instrument has indicated that:

1. The viscometer described may be satisfactorily applied to the study of the effect of dissolved gas upon the viscosity of crude oil at relatively high pressures.

2. The instrument is satisfactory for use at temperatures up to 100° C. (212° F.).

3. A wide range of viscosities can be measured with one ball, and to extend such range greatly, only a simple change of ball sizes is needed.

4. Both the ball and the tube must be made with a high degree of accuracy.

5. The density of the liquid must also be measured in order to arrive at either the kinematic or the absolute viscosity.

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Use of a Selenium–Mercuric Oxide Combination in Determination of Nitrogen in Feed Materials

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IN 1931 Lauro (2) reported that the time required for digestion of the sample in the Kjeldahl method for the determination of nitrogen can be materially reduced by the substitution of selenium oxychloride for the more commonly used catalysts, copper and mercury, or their compounds. Since then a number of papers have appeared (3–6) in which the authors have given the results of comparative studies of the efficiency of various catalysts, or combinations of catalysts, in the reduction of the time required for complete digestion. The data thus far reported have, for the most part, been obtained in analyses of cereal grains or their products and are somewhat at variance. This laboratory has had occasion in the past to investigate the efficiency of metallic selenium in the Kjeldahl determination of nitrogen in materials commonly used in animal feeds, and the data presented herein may prove of interest to laboratories engaged in similar work.

A series of analyses was made in which the relative catalytic efficiencies of mercuric oxide, metallic selenium, and a mercuric oxide–selenium combination were compared. The Kjeldahl-Gunning-Arnold method (1) was followed, the digestion times being varied from 30 to 90 minutes. In the case of the mercuric oxide and selenium comparisons 1-gram samples of the materials were analyzed with the usual amounts of sulfuric acid and sodium sulfate, together with the addition of 0.7 gram of mercuric oxide or 0.15 gram of powdered selenium. The mercuric oxide–selenium catalytic combination was added in the form of a flux modified slightly from that described by Messman (3): 100 parts of sodium sulfate ($Na_2SO_4 \cdot 7H_2O$), 7 parts of mercuric oxide, and 1.5 parts of selenium. Ten grams of this flux were added to a 1-gram sample. All digestions were started on cold 600-watt burners.

Table I presents the data obtained.

It will be observed that, with the exception of the wheat bran and wheat shorts, the percentage of nitrogen obtained after 30 minutes' digestion in the presence of the mercuric oxide–selenium flux is in better agreement with that value obtained after 90 minutes' digestion with mercuric oxide alone, than are the nitrogen percentages obtained when mercuric oxide or selenium, alone, was used with an equal digestion time. These data are therefore in agreement with those of Osborn and Krasnitz (4). No significant differences exist between the relative efficiencies of mercuric oxide and selenium when each is used alone. This fact is also in accord with findings of previous investigators (4, 6).

TABLE I. RESULTS OF COMPARATIVE ANALYSES

MATERIAL	CATALYST	NITROGEN DETERMINED			
Time of digestion		30 min.	45 min.	60 min.	90 min.
		%	%	%	%
Cottonseed meal	HgO	6.80	6.91	6.95	6.94
	Se	6.86	6.90	6.94	6.93
	HgO-Se	6.90	6.96	6.94	6.94
Corn oil meal	HgO	3.71	3.71	3.77	3.78
	Se	3.70	3.75	3.74	3.77
	HgO-Se	3.75	3.76	3.78	3.76
Linseed meal	HgO	5.79	5.83	5.84	5.86
	Se	5.81	5.82	5.84	5.84
	HgO-Se	5.82	5.84	5.87	5.87
Wheat bran	HgO	2.57	2.59	2.60	2.62
	Se	2.58	2.59	2.59	2.60
	HgO-Se	2.58	2.62	2.62	2.62
Meat and bone scraps	HgO	8.62	8.73	8.74	8.80
	Se	8.65	8.72	8.71	8.81
	HgO-Se	8.72	8.74	8.78	8.76
Wheat shorts	HgO	2.87	2.89	2.91	2.90
	Se	2.87	2.88	2.89	2.90
	HgO-Se	2.87	2.90	2.90	2.90

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