

Gamma Ray Viscometer-Densitometer for Oils at High Temperature and Pressure

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Introduction

The manufacture or reprocessing of liquid hydrocarbons derived from either coal or petroleum often involves high temperatures and pressures, notably in hydrogenation or reforming units. The accurate design of such units, particularly the liquid handling systems, thus depends heavily upon knowledge of the physical properties of the liquid inventories or oils at the rigorous conditions employed in the units. Viscosity and density data for liquids at very high temperatures and pressures are indeed sparse in the literature, for even the more familiar liquids. Such engineering data are almost certain to be completely unavailable for new products and processes so that the necessary data must be obtained directly on the new materials.

The instrument described here was developed, in particular, to measure the viscosity and density of coal oils at temperatures up to 450°C and pressure up to 5000 psig, conditions used for further hydrogenation. However, the instrument is of widespread interest since it can be used to gain data on any liquid under extreme conditions.

Gamma radiation is perhaps uniquely applicable to determine liquid properties under such drastic conditions. The necessary heavy equipment to maintain these conditions precludes the use of more conventional measuring techniques.

Experimental Equipment

A schematic diagram of the apparatus is given in Figure 1. The arrangement shown is that for viscosity measurements. The liquid is contained in a controlled temperature autoclave that can be maintained under high pressure. Basically, viscosity is determined by measuring the falling velocity of a plummet in the liquid. The special shape of the plummet facilitates measurement of the velocity. It consists of two wide disc ends connected by a thin stem. The gamma ray beam traverses the column of liquid. As the plummet falls through the gamma ray beam, the two heavy ends absorb much of the beam and the stem absorbs but little. Continuously recorded observation of the beam intensity yields two deflections and from their time separation and the size of the plummet, the velocity is easily calculated.

The clearance between plummet and inner wall of the vessel is small, of the order of 5 to 10 thousandths of an inch. This is to suit the low viscosities at high temperatures, i.e., to give a falling velocity slow enough to be accurately

measurable. For such close clearance, a very finely machined sleeve must be used as the inner wall to eliminate wall irregularities of the autoclave. Sleeve and plummet are of the same stainless steel (type 304) to avoid thermal expansion differences.

The gamma ray source is a 5 millicurie sealed source of cesium-137, encased in a 4-inch lead cylinder. A quarter-inch hole drilled through to the source serves as the collimated aperture for the gamma ray beam. Because of sensitivity, a scintillation counter is preferred for detecting the beam intensity and its output is measured by a count-rate-meter (Nuclear-Chicago Corp., Model DS-101 and Model 162OBS respectively). The count rate is continuously recorded on a 1 milliamp strip chart recorder (Esterline-Angus Model No. A. W.) to accurately obtain the time increment for the passage of the ends of the plummet.

The heater encased autoclave is mounted on a pivot. It can thus be inverted to allow the plummet to fall back and forth for repeated collection of velocity data.

Density is measured with the same unit, except that the autoclave is turned 90° into a horizontal position. The source, detector and gamma ray beam are thus lined-up axially with the liquid column. Liquid density is measured by gamma ray absorption. Doing so through the length of the column optimizes the sensitivity of the measured absorption to liquid density.

For the density measurements, the count-rate-meter and recorder are replaced by a gamma radiation analyzer and scaler (Nuclear-Chicago Corp. Model No. 1810 and Model No. 181 respectively). Radiation pulses or counts from the scintillation counter are discriminated by the analyzer which is set to select only those counts due to the primary 0.66 mev gamma rays from the cesium-137. This eliminates background scattered radiation from the counting. Otherwise, the count rate due to scatter so overwhelms small differences in primary ray absorption that small differences in liquid density cannot be discerned accurately. Discrimination thus enhances the accuracy of the method for measuring density by at least an order of magnitude. Discrimination is, of course, not possible with the less expensive Geiger Tube counters, making the scintillation counter necessary here.

Calibration

Empirical calibrations are used for both the viscosity and density measurements.

Some typical responses obtained on the counting recorder when calibrating the viscometer are shown in Figure 2. Note the well-marked deflections when the bottom and top of the plummet pass through the gamma ray beam. Measurement of time between deflections is quite accurate, to three significant figures. From these primary data, an empirical calibration of viscosity against observed falling time (velocity can be used if one chooses) is obtained as shown in Figure 3. An excellent straight line relationship is obtained on a logarithmic plot, confirming that terminal velocity of the plummet is being observed in the viscometer. This is predicted by fundamental viscosity relationships for terminal velocities of falling bodies. The five points plotted in this calibration were obtained by using trichloroethane, benzene, water and two NBS standard viscosity oils at 25°C. Similarly calibrating two more plummets with larger clearances yields a useful measurement range of 0.4 to 20,000 cp for this viscometer.

Both in the calibrations and measurements with the viscometer, the buoyancy effects on the plummet by liquids of different densities are corrected for by

$$\Delta T = \Delta T_0 \left(\frac{\rho_0 - \rho_x}{\rho_0 - 1.00} \right)$$

where

ΔT = corrected falling time

ΔT_0 = observed falling time

ρ_0 = density of steel (plummet)

ρ_x = density of liquid studied.

This equation refers all buoyancies to that of water at a density of 1.00, an arbitrarily chosen reference. Any other would serve as well. The equation derives from the first order approximation that the falling time is proportion to buoyancy. If the density of the liquid in the viscometer is not much different than 1, then the correction is negligible.

As a densitometer, the apparatus was empirically calibrated by alternately filling it with materials of known density, namely, air, benzene, water, trichloroethane and carbon tetrachloride and observing the gamma ray transmission. The transmission, T, is arbitrarily defined as $T = C/C_0$ where C is the counts per minute observed for the discriminated gamma beam after passing through the filled autoclave and C_0 is the count rate obtained from a small reference radiation source attached to the scintillation counter in fixed geometry that can always be duplicated. T is thus put on a common basis which eliminates effects of instrumental sensitivity drifts during an extended study. As expected, an almost straight line relationship is obtained for the logarithm of transmission versus density as shown in Figure 4. Perfect linearity is not expected because of absorption in the autoclave walls and heater. The plummet may remain during densitometer calibration and use.

Results

Some exemplary data are given in Figure 5, on the temperature dependence of viscosity of high molecular weight oils obtained by partial hydrogenation of coal. The plots approximate the rough empirical law for liquid viscosity dependence on temperature, i.e., $\log \eta = \frac{A}{T} + B$, where A and B are constants. Strict linearity isn't expected for mixtures of compounds as here studied. These results serve here only to illustrate the type of data that can be obtained with this viscometer; data that are difficult to obtain otherwise. Oils A and B differ in boiling range. In practice, the data were used to determine throughput rates in reactors containing solid catalysts at up to 450°C.

A correlation study of the effects of temperature and pressure on the viscosities of liquids and vapors was made by Smith and Brown⁽¹⁾. Though the correlation is based on low molecular weight hydrocarbons up to hexane, a rough comparison may be made with the present data. The correlation is a plot of $\eta/\gamma M$ vs. reduced pressure ($P/P_{critical}$) with a reduced temperature

($T/T_{critical}$) isotherms. If assumptions are made for a critical pressure of 80 atm, critical temperature of 600°C and an average molecular weight (M) of 144, the correlation predicts a viscosity of 0.3 cp at 340°C and 5500 psig for oil B. The measured value for these conditions is 0.2 cp, a fair comparison in view of the extensive extrapolation of the correlation and rough assumptions made for the critical parameters and molecular weight.

The accuracy of density measurements at high temperatures was tested with the pure compound tetralin. The points shown on the graph in Figure 6 were measured experimentally by gamma ray absorption in this densitometer. The curve drawn on the graph was calculated from established equations⁽²⁾ for this particular compound. The agreement is excellent, lending confidence in density measurements on new materials. Densities of various coal oils have been measured from ambient temperature up to 450°C and pressures up to 5500 psig. All show a slow linear decrease of density with temperature of about 1.25×10^{-3} gm/cc per °C in this thermal range.

In conclusion, it has been demonstrated that satisfactory density and viscosity data can be obtained with this gamma ray apparatus, at quite drastic physical conditions.

Bibliography

- (1) Smith, A. S., and Brown, G. G., *Ind. Eng. Chem.*, 35, 705-711 (1943).
- (2) Reid, R. C., and Sherwood, T. K., *Properties of Gases and Liquids*, McGraw-Hill, 1958.

Figure 1

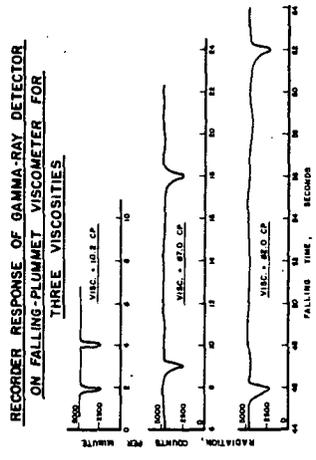


Figure 2

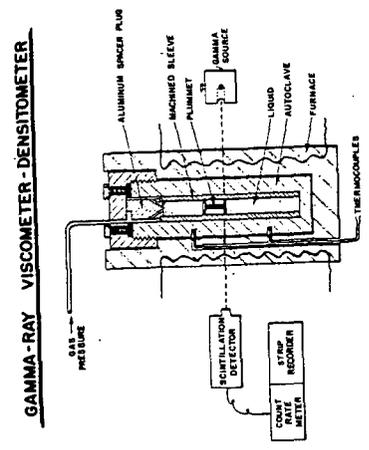


Figure 3

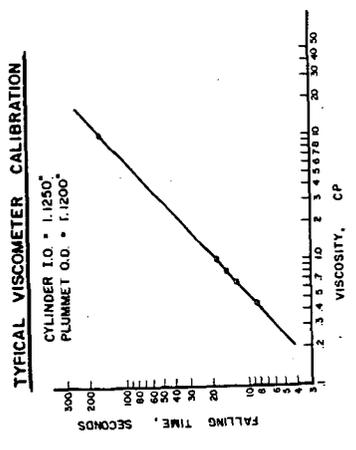


Figure 4

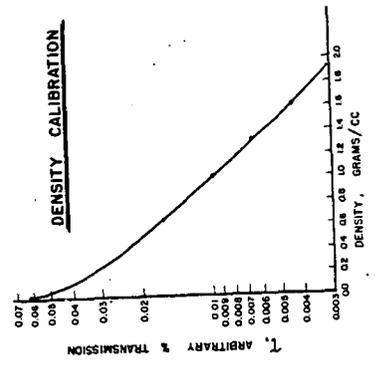


Figure 5

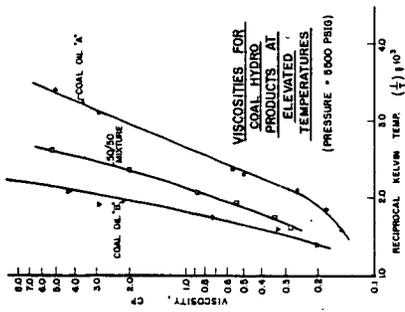


Figure 6

