Viscosity of H_2-CO_2 Mixtures at (500, 800, and 1100) K

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The viscosity of H_2-CO_2 mixtures at 500 K, 800 K, and 1100 K, 3×10^5 Pa pressure, and (15, 30, 50, 70, and 85) mol % CO_2 has been measured experimentally. The experimental methods make use of the fact that in the laminar flow regime the flow rate is inversely proportional to the fluid viscosity for a given pressure gradient.

Introduction

The production of hydrogen and synthesis gas has become increasingly important as the world seeks to produce more and cleaner fuels. At the same time, capital constraints are requiring that equipment for hydrogen and synthesis gas production be designed to more exacting specifications. These requirements demand more accurate values for the transport properties of fluid mixtures containing hydrogen. Hydrogen is typically produced in a steam-methane reformer, while synthesis gas is produced by partial oxidation or autothermal reforming. In practice, each of these technologies is supported by a system of heat integration that recovers heat from the high-temperature product streams to increase the operating efficiency of the plant.

The process streams consist of mixtures of primarily hydrogen, steam, carbon dioxide, carbon monoxide, and methane. Invariably, industrial equipment is operated in the turbulent flow regime and viscosity plays a minor role in determining the pressure loss. However, heat transfer coefficients are a strong function of the Reynolds number (Re), which is inversely proportional to the fluid viscosity. So, accurate design of heat-transfer equipment, particularly when part of a complex integration scheme, requires accurate knowledge of fluid viscosity over a wide range of temperatures. Experimental data is required to aid in the development of accurate models for estimating the viscosity of mixtures containing hydrogen. The essential contribution of this work is the measurement of viscosity of H_2-CO_2 mixtures at much higher temperatures than reported before.

The theoretical analysis of gas-mixture transport properties is very complex. The knowledge of exact intermolecular potentials is needed to apply rigorous kinetic theory for the prediction of the mixture properties.[1] For viscosity, when pure-gas values are known, interpolation methods based on kinetic theory approximations may be used for predicting mixture values.[2] A commonly used method is that of Wilke;[3] however, the predictions have variable accuracy for mixtures of gases with greatly different molecular weights.[2] For $H_2 + O_2$ mixtures at 297 K, errors from the Wilke method are as high as 9%.[4] For $H_2 + N_2$ mixtures over the range 307 to 478 K,[5] errors are as high as 15% at 478 K, and the error increases with temperature. Since data are unavailable to test the interpolation method at the high temperatures of interest here, the accuracy of mixture viscosity prediction is uncertain for hydrogen-containing mixtures at reformer temperatures.

Experimental Section

The experimental setup is shown in Figure 1. The basis of the technique is measuring the rate of pressure decrease in a test volume during isothermal outflow of a gas. Experiments have been carried out in a test cell placed in special muffle furnace. The muffle furnace is a wire heater wrapped around a stainless pipe with a length of 50 cm and an internal diameter of 7 cm. The heater power can be varied up to 4 KW, which allows the test cell to be heated to 1100 K. Temperature was measured by five chromel−alumel thermocouples placed on the outer surface of the test cell. Well-known calibration table data for this thermocouple are used in data reduction. The uncertainty of temperature measurements is about 1 K. The temperature stability is attained by heating for up to 4 h at a particular power.

The test cell is made of stainless steel and has a length of 120 mm, diameter of 51 mm, and wall thickness of about 3.5 mm. Stainless plates (40) with a thickness of 0.3 mm and a 15-mm circular hole in the center are placed perpendicular to the axis as a heat exchanger to aid maintenance of isothermal conditions during gas outflow. Gases are supplied to the test cell by a gas supply and vacuum system. The purity of the gases used in experiments was better then 99.9% (supplier's data). Before the cell is filled with test gases, it is evacuated to a pressure of 1 Pa. Preparation of the gas mixture was accomplished in the test cell by consecutive filling of each gas. The composition of gas mixtures was fixed by controlling the partial pressure of the components, and the uncertainty in gas composition did not exceed 0.5%.

The pressure inside the test cell can be varied in the range of (10^5 to 10^6) Pa. The absolute pressure was measured by a pressure gauge with an uncertainty of 0.5%. The tubing used for measuring viscosity is placed inside the test cell and has a diameter of 0.9 mm and a length of 70 cm, resulting in a ratio of length to diameter of about 800. The capillary was in the shape of a coil with diameter of 1.5 cm. Both pressure gauges are placed outside the

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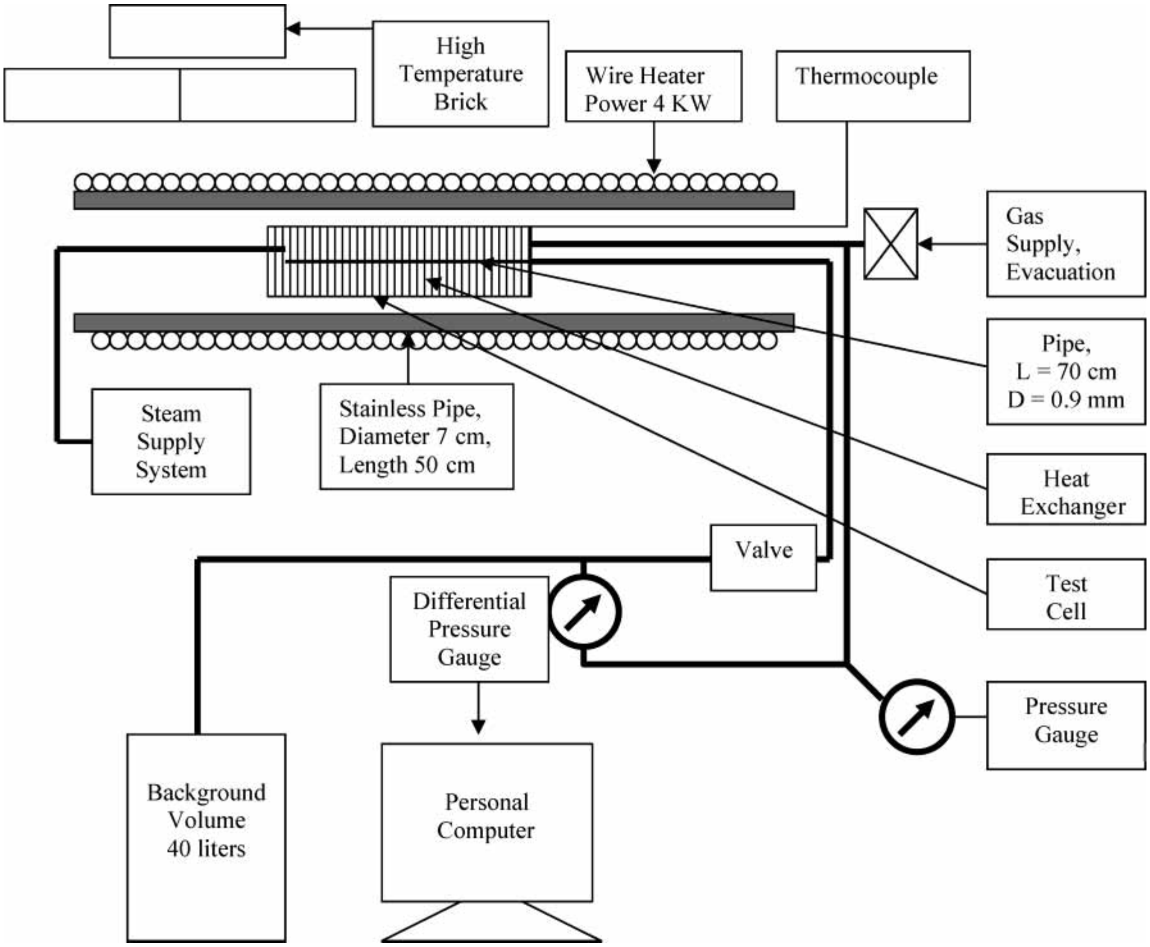

Figure 1. Experimental setup.

furnace. They are connected with the test cell by tubing with an internal diameter of 3 mm, which has negligible pressure drop compared to the tubing in the test cell. The cell is connected with a reservoir volume of 40 L through a valve. Initially the pressure inside the test cell was slightly (about 3×10^3 Pa) higher than that in the reservoir volume. After the valve was opened, the gas flowed from the test volume through the tube into the reservoir volume. Calculation of the flow Re confirmed that flows were laminar (Re < 2000) at all experimental conditions. The differential pressure gauge measures the time-dependent pressure drop through the tube. An analog-digital analyzer in a computer-automated measurement and control system was used to get the time-dependent pressure drop through the tube. The voltage resolution was 1 mV, which corresponds to approximately 1 Pa. The maximum repetition rate of data acquisition was 500 Hz (time resolution of 0.002 s). The repetition rate of pressure measurement was chosen depending on the gas composition and temperature. Normally, the total number of measured points was 2000 and the repetition rate is set so that the essential pressure change was distinguished in approximately the first 1000 points, which were used in data reduction.

As a conclusion of the Experimental Section, we emphasize the advantages of this technique for measuring the viscosity of gases. In principle, the range of pressures and temperatures is defined by the condition that the gas be of constant compressibility. In the present work, the pressure range was (10^5 to 10^6) Pa, and the temperature range was (300 to 1100) K. The apparatus has no moving parts inside the cell, and it is made of stainless steel, which allows measurements at high temperatures and with corrosive gases. The measurement of transient outflowing eliminates the need to create a constant gas flow rate. Only the pressure drop is measured, which is automated and enables very rapid measurements. A disadvantage of this technique is that the measured value is relative and therefore requires calibration of the system at every temperature with a gas with well-known viscosity. The uncertainty of the measured viscosity values is determined by the uncertainties in measuring pressure (0.5%) and temperature (1 K), uncertainty in the calibration experiments, and uncertainty in calculated values of characteristic time. A comparison of measured values of the viscosity of simple gases with reference data shows this rather simple technique gives an uncertainty of about 3%, whereas other more complicated methods have demonstrated a higher accuracy.

Analysis of Data

In the laminar regime of flow, the gas consumption for the case where the change in density over the length of pipe is small is defined by the following equation[6−8]

$$Q = \frac{\pi \rho \Delta P R^4}{8 \mu L} \tag{1}$$

Here, Q is the mass flow rate, π the ratio of circumference to diameter, ρ the mass density, ΔP the pressure drop, R the radius of the pipe, μ the viscosity, and L the length of the pipe. Equation 1 shows that measuring the gas flow through a pipe of known radius and length allows the viscosity to be determined. The gas flow can also be related to the rate of pressure decrease within a known volume. Specifically, for isothermal flow of an ideal or constant compressibility gas, one has

$$\frac{dP}{dt} = \frac{d(znkT)}{dt} = \frac{zkT}{mV}\frac{d(mn)}{dt} = -\frac{zkT}{mV}Q \qquad (2)$$

Here, z is the compressibility factor, n the gas number density, k the Boltzmann's constant, T the temperature, t the time, m the molecular mass, and V the volume. Combining eqs 1 and 2, one obtains

$$\frac{dP}{dt} = -\frac{\pi R^4}{8lV}\frac{\rho}{m}\frac{zkT}{\mu}\Delta P = -\frac{\pi R^4 P}{8lV\mu}\Delta P \qquad (3)$$

The result of solving this equation is

$$\Delta P(t) = \Delta P_0 \exp(-t/\tau) \quad \text{where} \quad \tau = \frac{8lV}{\pi R^4 P}\mu = \alpha\mu \qquad (4)$$

τ can be determined from experimental data as the rate of change of the log of the pressure difference between the test cell and the reservoir (this is equivalent to determining the slope of the line when the pressure difference is plotted on a semilog scale). As shown in eq 4, τ is proportional to the gas viscosity. The proportionality constant, shown here as α, is constant for a specified pressure, temperature, and geometry. This is the theoretical basis for the viscosity measurements. α is determined by calibration measurements on gases with well-known viscosity.

Let us consider the factors that influence the uncertainty of the measured data. One factor is the uncertainty of pressure and temperature measurements, and another is the changing density along the pipe due to the gas compressibility. In addition, the measured pressure drop does not exactly define the actual pressure gradient in the pipe because kinetic-energy correction and end-correction factors[8] should be taken into account. The maximum pressure drop used in data reduction is 3000 Pa at the total pressure of 3×10^5 Pa. Therefore the density is constant within an uncertainty of 1%. Both the kinetic-energy correction and the end-correction factors are proportional to ρU^2, where U is the flow velocity. For a pressure drop of 3000 Pa, diameter $D = 0.0009$ m, length $L = 0.7$ m, and characteristic viscosity $\mu = 3 \times 10^{-5}$ Pa·s, one obtains flow velocity $U = PD^2/32\mu L = 4$ m/s. For the dynamic pressure correction factor for density $\rho = 2$ kg·m^{-3}, we get $\Delta P = \rho U^2/2 = 16$ Pa, which is less than 0.5% of the total pressure drop. This analysis shows that all uncertainties give a total uncertainty of a few percent, which corresponds to the value of 3% observed experimentally.

Calibration

A simple data-reduction procedure is used to calculate the characteristic time of pressure reduction during gas outflow. The uncertainty of a single measurement is about 5%, but statistical data reduction of several repetitive measurements allows a decrease in the uncertainty of the average measured value. The calibration measurements include a test of isothermal conditions in the test cell and measurements of the viscosity of following gases, each with well-known values of viscosity: He,[9] Ar,[9] CO_2,[10] H_2,[11] and N_2.[12]

To check whether the outflowing conditions are isothermal, test measurements were carried out at different pressures. At elevated pressure, more heat must be supplied to keep the system isothermal as the pressure drops in the test cell. If the temperature were allowed to fall, the recorded pressure drop would not be solely a result of the gas flow. Experiments showed that for all temperatures at the pressure of 3×10^5 Pa, isothermal conditions are satisfied for all of the gases used. Only at 500 K and pressures greater than 5×10^5 Pa does the system fail to satisfy the isothermal condition. Maintenance of isothermal conditions is confirmed in Figure 2, where the measured values of viscosity are compared to reference values. Reference values (in the dilute-gas limit) and measured viscosity data for these gases for pressure of 3×10^5 Pa are presented in Table 1. The effect of the pressure difference is negligible at these conditions. As is seen from Table 1, the deviations of measured values from ref 1 are within 3%, which characterizes the accuracy of the technique described. Coefficient α was defined as the average value over all gases used for calibration; α was found to vary slightly with temperature, because the equipment sizes increased with temperature and geometry of the tube coil changed slightly with temperature.

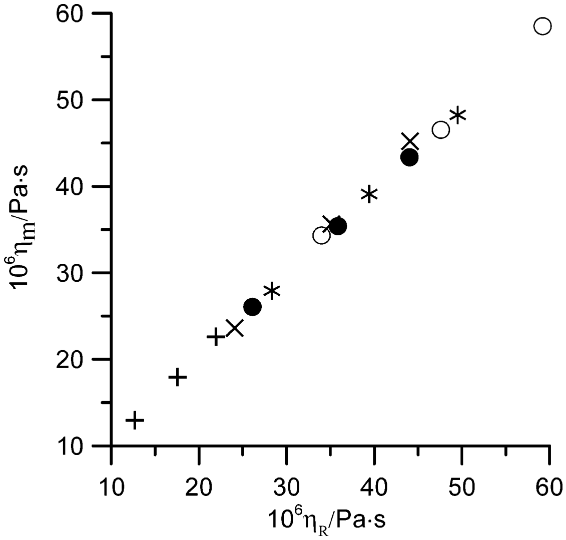

Figure 2. Calibration data (+, H_2; *, He; ○, Ar; ●, N_2; ×, CO_2).

Table 1. Results of Calibration Measurements (10^6 Pa·s)

	500 K		800 K		1100 K	
gas	reference	measured	reference	measured	reference	measured
He	28.32[9]	27.9	39.42[9]	39.1	49.52[9]	48.2
Ar	33.98[9]	34.3	47.60[9]	46.5	59.21[9]	58.1
CO_2	24.02[10]	23.6	35.09[10]	35.6	44.08[10]	45.2
H_2	12.69[11]	12.9	17.56[11]	17.9	21.95[11]	22.6
N_2	26.11[12]	26.1	35.85[12]	35.4	44.03[12]	43.4

Table 2. Viscosity (10^6 Pa·s) of H_2 (1)−CO_2 (2) Mixtures

$100x_1$	0	15	30	50	70	85	100
500 K	23.6	23.8	24.1	23.6	21.5	19.2	12.9
800 K	35.6	35.1	34.6	33.6	30.3	26.9	17.9
1100 K	45.2	43.8	43.1	42.2	40.3	34.6	22.6

Results and Discussion

The measurements on $CO_2 + H_2$ mixtures were carried out at a pressure of 3×10^5 Pa. Table 2 presents measured viscosity of CO_2−H_2 mixtures at different mole fractions for 500 K, 800 K, and 1100 K. Only the data obtained at 500 K can be compared with previous measurements.[13] This comparison is shown in Figure 3. Both data sets are very close to each other except in the region near 0.6 CO_2 mole fraction, where the present data are about 3% higher. Also, it is interesting to note the present data has a maximum viscosity in this region.

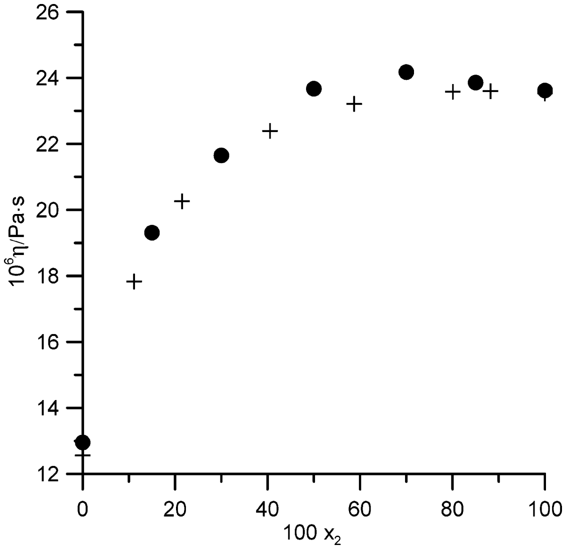

Figure 3. Comparison of present data for H_2 (1)−CO_2 (2) (●) with results of ref 13 (+).

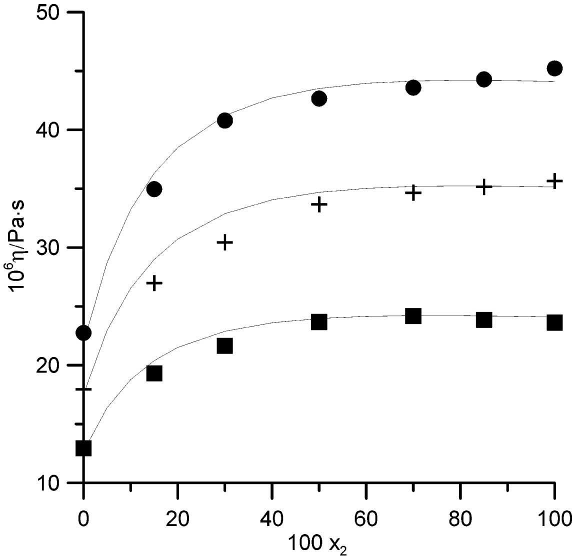

Figure 4. Comparison of present data (●, 1100 K; +, 800 K; ■, 500 K) with Wilke's method (solid line)[3].

For systems where the pure-component viscosities are known, the well-known method by Wilke[3], which is commonly used for industrial design, can be used to calculate mixture values. For a binary mixture, Wilke's method is

$$\mu_m = \frac{y_1\eta_1}{y_1 + y_2\phi_{12}} + \frac{y_2\eta_2}{y_2 + y_1\phi_{21}} \tag{5}$$

where μ_m is the mixture viscosity, y_1 and y_2 are the mole fractions, and ϕ_{ij} is defined by

$$\phi_{ij} = \frac{[1 + (\eta_i/\eta_j)^{1/2}(M_j/M_i)^{1/4}]^2}{(4/\sqrt{2})[1 + (M_i/M_j)]^{1/2}} \tag{6}$$

A comparison between mixture predictions by the Wilke method and our data is in Figure 4. The reference values of the pure-gas viscosities from Table 1 were used in eqs 5 and 6, and therefore the mixture predictions are completely independent of our data. The predicted mixture values are higher than the data, by a maximum of 8%.

Conclusion

The viscosity of H_2−CO_2 mixtures at different mole fractions at 500 K, 800 K, and 1100 K was measured. Calibration measurements and comparison with known data show that the error in measured data obtained does not exceed 3%. Prediction of the mixture viscosities by the Wilke method is within 8% of the data.

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