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DIFFUSIVITIES OF SYNTHESIS GAS AND FISCHER-TROPSCH PRODUCTS IN SLURRY MEDIA

Final Report

By
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FINAL REPORT

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EXECUTIVE SUMMARY

Purpose

The Fischer-Tropsch synthesis is a process for which complex reactor design models have been developed. No matter how detailed these models are, they cannot be expected to generate successful reactor designs without accurate estimates of thermophysical properties such as density, viscosity, and the diffusion coefficient. Currently used estimates of these properties are extrapolated from limited ambient temperature data, and are probably highly inaccurate. Since a sound theory for diffusion in liquids does not exist, the primary purpose of this research was to measure diffusion coefficients in an actual sample of Fischer-Tropsch reactor liquid at typical reaction conditions. We also hoped to develop a predictive equation for diffusion coefficients which could confidently be used by design engineers.

Background

The Fisher-Tropsch Synthesis is a process by which a hydrocarbon mixture, consisting primarily of paraffins, olefins, and oxygenates, is produced from synthesis gas. Coal is usually gasified to supply the required hydrogen and carbon monoxide. These two gases are then reacted in either a gas/solid fixed bed or fluidized bed reactor, or in a liquid slurry containing a suspended catalyst. In addition to the primary products, carbon dioxide is formed as a side product by the water-gas shift reaction.

The task of estimating diffusion coefficients in a Fischer-Tropsch reactor is by no means elementary. The steady state liquid phase, often referred to as FT wax, is primarily a mixture of saturated hydrocarbons with an average carbon number of about 30, although it can range as high as 70. The melting point of the FT wax is typically in excess of 100°C, and reaction conditions of the normal process range from 473-573 K at 1 to 5 MPa. Prior to this study, diffusion coefficients in even the simplest pure low melting hydrocarbons had not been measured at these conditions. For this reason, we began our research by measuring diffusion coefficients in pure low molecular weight hydrocarbon solvents and progressed to measure diffusion in higher molecular weight solvents until we were ultimately able to measure diffusion coefficients in an actual sample of FT reactor wax.

The diffusion coefficients measured in this study are properly referred to as 'mutual diffusion coefficients at infinite dilution'. The mutual diffusion coefficient, D_{12}, is the most common type of diffusion coefficient and is the diffusion coefficient required for mass transfer calculations. Often the mutual diffusion coefficient is simply referred to as the diffusivity of solute A in solvent B. The mutual diffusion coefficient is actually a function of concentration. Since most gases are only sparingly soluble in liquids, mutual diffusion coefficients for gases in liquids are always reported as being at infinite dilution. Throughout this report, the terms diffusivity, diffusion coefficient, infinite dilution diffusion coefficient, and mutual diffusion coefficient are used interchangeably, except where noted.

Since liquid-liquid mixtures can exist over the entire concentration range, the effect of concentration on the liquid-liquid mutual diffusion coefficient can sometimes be important. However, for the case of diffusion in Fischer-Tropsch wax, the mutual diffusion coefficient at infinite dilution, D_{12}^{o}, is the proper diffusion coefficient for design calculations. In this case, D_{12}^{o}, represents the diffusion of infinitely dilute solute, 1, through the Fischer-Tropsch wax mixture, 2. This is precisely the situation occuring as a product or reactant diffuses to or from the surface of the FT catalyst.

Apparatus

To measure the diffusion coefficients reported in this study, we constructed a Taylor dispersion apparatus. In general, the apparatus works as follows. A narrow pulse of solute is quickly injected into a long uniform tube, in which a solvent is flowing in slow laminar flow. As the pulse is carried through the tube, it spreads due to the combined effects of laminar flow and molecular diffusion, although the peak center or maximum continues to flow at the mean velocity of the laminar profile. Eventually, the peak elutes from the end of the long tube, at which point the radially averaged concentration profile is measured as a function of time. From this recorded concentration vs. time data, the diffusion coefficient can be determined using mathematics derived by Taylor (1953). However, in any Taylor dispersion apparatus, concentration is not measured directly. Instead, a detector (a refractive index detector in this study) at the end of the diffusion tube outpu voltage which is proportional to solute concentration. Previous researchers using the same technique have used approximate mathematical models to extract the diffusion coefficient from the raw voltage vs. time data. We were able to develop a non-linear least squares model which directly fits the data to the full analytical solution originally given by Taylor (1953), thus improving the accuracy of the experiment. Our reported data is accurate to better than ±1.5%.

The particular apparatus we constructed is capable of measuring diffusion coefficients in liquid solvents with melting points up to 400 K. In order to achieve this feat, the optics of the refractive index detector were separated from the electronics, producing a detector capable of operating with molten Fischer-Tropsch wax. Measurements can be obtaine temperatures to 573 K. This maximum limit is determined by the maximum temperature of an electrically heated enclosure which houses the coiled diffusion tube.

The apparatus was constructed with an in-line viscometer for solvent viscosity measurements at operating conditions. Since diffusion coefficients are a strong function of solvent molar volume (molecular weight divided by density), solvent density measurements were also required. During the course of the project a highly accurate method was developed which measures solvent density using the Taylor dispersion apparatus. The method relies on a simple mathematical relationship between the retention time of a Taylor dispersion peak and solvent density.

Two personal computers are dedicated to the Taylor apparatus. One computer controls the temperature of the enclosure containing the diffusion tube and monitors two pressure transducers which are located at each end of the viscometer. The second computer records the voltage output from the refractive index detector and the corresponding time. Measurements are recorded on floppy disk every five seconds during the course of each experiment.

Results

The experimental work was conducted in three phases. During the first phase of the project infinite dilution diffusion coefficients were measured for the normal alkane solutes octane, decane, dodecane, tetradecane, and hexadecane, and for the gases hydrogen, carbon monoxide, and carbon dioxide in the liquid n-alkane solvents heptane (C_7), dodecane (C_{12}), and hexadecane (C_{16}). Normal alkanes were chosen because they are a simple homologous series and are primary products of the FT synthesis. Hydrogen and carbon monoxide are reactants in the synthesis and carbon dioxide is a product of the water-gas shift. Measurements were made at temperatures between 298 and 573 K, and pressures from 0.1 to 3.45 MPa (14.7 to 500 psia). Prior to this study, the available data for alkane/alkane systems were primarily limited to the temperature range 290-343 K, and there were no data available for the diffusion of gases above 323 K. Results indicated that the diffusion coefficient was a very weak function of pressure, as expected. For this reason, all subsequent experiments were conducted at the same pressure (200 psi).

During the second phase of the experiments, we modified the Taylor dispersion apparatus so that we could collect data at similar conditions using solvents which are solids at room temperature. We proceeded to measure diffusion coefficients in the solvents n-eicosane (C_{20}) and n-octacosane (C_{28}) at several temperatures ranging from 373 to 534 K. Prior to this study, diffusion coefficients had never been measured in these solvents.

During the third and final phase of the experimental work, we measured mutual diffusion coefficients at infinite dilution for each of the selected alkane and gaseous solutes in an actual sample of FT wax which melted near 100°C. Measurements were made at 200 psia over the range 473-533 K, which are typical FT reactor conditions.

Solvent densities were measured at each experimental condition during all phases of the experimental work. Solvent viscosity was measured only during the first phase of the study. Most diffusion coefficient measurements were repeated three times to verify the reproducibility of the results. In this project we have measured diffusion coefficients in 40 different systems, resulting in 204 data points. Most data points represent an average of at least three replicate measurements, bringing the total number of measurements to well over 600. To the best of our knowledge, this is the largest and most comprehensive data base of diffusion coefficients in the literature.

Correlation and Discussion of Results

Since existing correlations for predicting diffusion coefficients were developed using data collected at near ambient conditions, these correlations failed miserably when used to predict our high temperature data. We investigated several theories to interpret the data and decided to use the Rough Hard Sphere (RHS) theory for diffusion prediction.

The RHS theory, which applies to dense gases and liquids, extends the kinetic theory for gases to liquids. The hard sphere kinetic theory for gases was developed by assuming that molecules are spherical and inelastic, colliding much like billiard balls, with only bimolecular collisions occuring. The hard sphere assumptions lead to an equation which predicts diffusion coefficients accurately in low pressure gases, but is not applicable to dense gases and liquid solvents.

In dense gases and liquids, molecules collide more frequently than in a low pressure gas, and also exchange rotational energy as they collide. The Rough Hard Sphere theory accounts for these differences and therefore is more applicable to dense gases and liquids than the Hard Sphere theory. However, until this study, the theory had rarely been tested with experimental data covering a wide temperature range.

We found that the general form of the RHS theory equation fits our diffusion data very well. In general, the RHS theory predicts that the ratio of the diffusion coefficient to the square root of temperature is proportional to the molar volume of the solvent. Starting with this general form, we were able to develop a simple semi-empirical correlation which predicts diffusion coefficients in the gaseous solutes hydrogen, CO, and CO_2 and alkane solutes ranging from n-octane (C_8) to n-hexadecane (C_{16}) in alkane solvents ranging fr n-heptane (C_7) to n-octacosane (C_{28}). The correlation predicts the data accurately over the entire temperature range of the measurements.

The Fischer-Tropsch wax sample used in this study was obtained from a Union Carbide pilot plant reactor and had a mean carbon number of 28. As might be expected, the diffusion coefficients for all solutes measured in the FT wax agreed closely with diffusion coefficients measured in pure n-octacosane, which has a carbon number of 28. For this reason, we recommend using our correlations to predict diffusion in Fischer-Tropsch wax, by assuming that the wax can be modelled as a pure alkane with carbon number equal to the mean carbon number of the FT wax. In the report we discuss the validity of this assumption and demonstrate that the method provides reasonable estimates of diffusi coefficients even when the mean carbon number of the wax is not known exactly.

Conclusions and Recommendations

Diffusion coefficients were successfully measured for hydrogen, carbon monoxide, carbon dioxide, and several n-alkanes in n-alkanes ranging from n-heptane to n-octacosane, and in FT reactor wax. The results of the measurements in pure alkane solvents were used to develop a single correlation based on the Rough Hard Sphere theory which accurately predicts the data over the entire temperature range of the experiments. The correlation was then used to verify the hypothesis that FT wax may be modelled as a pure alkane with carbon number equal to the mean carbon number of the wax. The correlation is recommended for estimating diffusion coefficients for use in engineering design calculations.

In future studies, we recommend that the measurements be extended to branched alkanes, α-olefins, alcohols, and other oxygenates. In addition, we believe that the role of water in FT synthesis is not clear and that diffusion measurements of water in FT wax may yield valuable information regarding its effect on the process.

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ABSTRACT

A Taylor dispersion apparatus was constructed which is capable of measuring diffusion coefficients in liquid solvents with melting points up to 400 K. Infinite dilution mutual diffusion coefficients of hydrogen, carbon monoxide, carbon dioxide, and several n-alkane solutes were measured in the solvents n-eicosane, n-octacosane, and Fischer-Tropsch reactor wax at 200 psia at temperatures to 533 K. Diffusion coefficients were also measured for the same set of solutes in the solvents n-heptane, n-dodecane, and n-hexadecane at both 200 and 500 psia at temperatures to 567 K. Using a novel technique developed during the course of this project, solvent density was measured at all experimental conditions for each solvent. Solvent viscosity was also measured for n-heptane, n-dodecane, and n-hexadecane.

All diffusion coefficient data were analyzed using a computer model based on the analytical solution to the Taylor dispersion problem. The model was developed as a part of this study and is superior to the approximate mathematical models used in previous Taylor dispersion research. An improved technique for collecting gaseous solute data using the Taylor dispersion apparatus was also developed.

Finally, the results of this study were used to develop a single correlation based on the Rough Hard Sphere theory which predicts diffusion coefficients in alkane solvents ranging from n-heptane ($CH_3(CH_2)_5CH_3$) through n-octacosane ($CH_3(CH_2)_{26}CH_3$). The correlation was then used to test the hypothesis that diffusion coefficients in Fischer-Tropsch wax can be estimated by assuming that the wax behaves as a pure alkane with chain length equal to the mean chain length of the mixture.