

Phase Equilibrium in Coal Liquefaction Processes

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Prepared by
Purdue University
West Lafayette, Indiana

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Final Report, October 1980

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ABSTRACT

Gas-liquid equilibria have been determined in simulation of coal liquefaction process conditions in mixtures of light gases + heavy hydrocarbons (polynuclear aromatics, N, S, and O containing aromatics, some paraffins, and naphthenes). The mixture systems experimentally investigated are:

- 32 binary mixture systems of a light gas (hydrogen, methane, or carbon dioxide) + a heavy hydrocarbon
- 2 ternary mixture systems of hydrogen + two heavy hydrocarbons
- 2 ternary mixture systems of hydrogen + methane + a heavy hydrocarbon
- 5 complex mixture systems of hydrogen + a coal oil fraction
- 4 complex mixture systems of methane + a coal oil fraction

Equilibrium data were determined at pressures up to 250 atm and temperatures up to 460°C which is substantially above the upper limit of previously reported investigations in the literature of about 220°C. A flow apparatus of special design made possible the attainment of the elevated temperatures at high pressures.


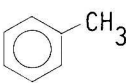
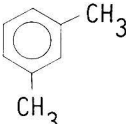
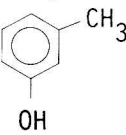
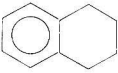
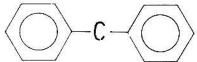
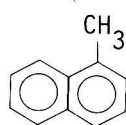
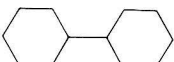
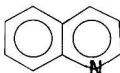
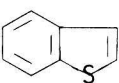
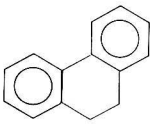
Vapor pressures were determined for eight hydrocarbons at superatmospheric pressures using the same flow apparatus.

A solubility parameter based correlation has been developed for the solubility of hydrogen. The hydrogen, methane, and carbon dioxide data have been analyzed and correlated with various degrees of success with the Soave equation of state, and Boublik-Alder-Chen-Kreglewski equation of state.

EPRI PERSPECTIVE

PROJECT DESCRIPTION

During the five years of research conducted on this project (RP367-2), extensive vapor-liquid equilibrium (VLE) data have been obtained on binary and ternary systems of light gases (H_2 , CH_4 , CO_2) in coal liquids and on pure liquid components which comprise coal liquids. Thirteen pure hydrocarbons have been used during this period to simulate coal liquids; these are:

- benzene 
- toluene 
- m-xylene 
- m-cresol 
- tetralin 
- diphenylmethane 
- 1-methylnaphthalene 
- bicyclohexyl 
- quinoline 
- thianaphtene 
- 9,10-dihydrophenanthrene 
- n-decane $CH_3(CH_2)_8CH_3$
- n-hexadecane $CH_3(CH_2)_{14}CH_3$

Specific data obtained include:

- Gas-liquid equilibria (including solubilities) of simple binary hydrogen mixtures, simple binary methane mixtures, and simple binary carbon dioxide mixtures
- Solubilities of hydrogen and methane in two Exxon Donor Solvent (EDS) coal liquids and three SRC-II (solvent-refined coal) coal liquids
- Gas-liquid equilibria of ternary mixtures of hydrogen in two pure hydrocarbon liquids
- Gas-liquid equilibria of ternary mixtures of two light gases ($H_2 + CH_4$) in a pure hydrocarbon liquid
- Vapor pressures of pure hydrocarbon liquids at superatmospheric pressures

The experimental conditions under which the data were taken simulate those found in liquefaction reactors and in the reactor effluent treatment section of a liquefaction plant. Pressures extend to 250 atmospheres (atm) and temperatures to 460°C.

The experimental data were used to test their applicability to coal liquefaction processes of existing correlations such as the Chao-Seader and the Grayson-Streed. These correlations have been used extensively in the petrochemical industry.

Extensive correlation of the VLE data obtained in this project has been done to generate various forms that are best suited for different purposes and needs.

PROJECT OBJECTIVE

VLE data for light gases in coal liquids are needed for the reliable and accurate design of coal liquefaction plants. For various operating conditions of temperature and pressure, it is necessary to know when and where multiphases are expected to coexist in the liquefaction plant. The quantity and distribution of the phases will be highly dependent on the chemical constituents present at any given operating condition. Having this information is vital, not only for accurate sizing of equipment, vessels, and piping, but also for determining the dynamic response of the plant. This VLE information is also needed for further processing or refining of the coal liquids.

The collection and correlation of coal-related VLE data was undertaken to meet a major industry need. Prior to this project, the design of coal conversion processes was based on petroleum data and correlations which were rarely representative.

Thus, the objective of this project was to successfully collect and correlate data which were representative of coal liquefaction processes.

PROJECT RESULTS

A solubility apparatus of the flow type was designed and built under this project, and it has since been used extensively in the collection of coal-related solubility and vapor pressure data. The apparatus is a considerable improvement over previously available equipment in the high temperatures (460°C) and pressures (300 atm) it can achieve, and the short residence time it offers (which in turn means considerably less component degradation). The apparatus gives consistently reliable results. The equilibrium apparatus is also able to accommodate systems with mixed gases.

Extensive data have been collected for the experimental determination of VLE in diverse mixtures of light gases and heavy hydrocarbons (including coal liquids). These data have substantially extended the state-of-the-art knowledge of phase equilibria of high-pressure mixture at significantly higher temperatures. These data form a basic design tool for coal liquefaction plants.

Accurate new correlations of the data have been developed in three ways to generate results in various forms.

The Boublik-Alder-Chen-Kreglewski (BACK) equation of state has been used to correlate phase equilibria data of hydrogen mixtures, methane mixtures, and carbon dioxide mixtures. All data found in the literature and the data from this project were included. This equation is exceedingly accurate in representing pure fluid properties.

The Soave equation of state has also been used for the correlation of gas solubility data. The Soave equation offers the great advantage of convenience and economy while achieving reasonable accuracy. Using the Soave equation, the correlation of hydrogen mixtures, methane mixtures, and carbon dioxide mixtures has been completed. For this correlation, a slightly larger data base was used than for the BACK equation.

Correlation of gas solubility data has been accomplished also with solubility parameters. This correlation is quite accurate for all systems, and, of all the correlations, gives the best accuracy for hydrogen. The disadvantage is that the correlation applies only to the liquid phase and only to the dissolved gases in the liquid.

To provide the needed liquid density data for the correlation of solubilities, a new density apparatus was designed and constructed.

This project is continuing with extensive work on the determination of:

- Equilibrium flash vaporization of coal liquids
- Equilibrium flash vaporization of coal liquids in the presence of high-pressure hydrogen gas
- Solubilities of gases in coal liquids

and the correlation of:

- Vaporization properties of coal liquids
- Hydrogen solubility in coal liquids

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Section 1

INTRODUCTION

Accurate prediction of gas-liquid equilibrium is required for the engineering design of coal liquefaction plants. It is necessary to know in order to build a plant the phase states of the various fluid streams in the plant - if they are gases, liquids, or both, and in the latter case to know the proportions of the phases, and the distribution of components among the phases. All these predictions must be made for diverse conditions of temperatures and pressures, some of which may be extremely severe. And the components can be highly unusual.

The objective of the present research is to develop this predictive capability, for it is upon this capability that the design of plant equipment must ultimately depend for the sizing of the vessels, piping, compressors, separators, and gas-liquid absorbers and fractionators.

To develop this predictive capability we have carried out a program of research as follows:

- We have performed experimental determination of gas-liquid equilibrium in diverse mixtures of light gases + heavy hydrocarbons (including coal liquids) in simulation of coal liquefaction process conditions at pressures up to 250 atm and temperatures up to 460°C. The experimental apparatus and procedures are described in Section 2, and the results in Section 3.
- We have developed correlations for the solubilities of hydrogen based on the use of solubility parameters, and have additionally analyzed and correlated the hydrogen, methane, and carbon dioxide data with the Soave equation of state, and the Boublik-Alder-Chen-Kreglewski equation of state. The correlations are described in Sections 4 and 5.

Section 2

EXPERIMENTAL APPARATUS AND PROCEDURE

2.1 INTRODUCTION

A flow apparatus has been built for the determination of gas-liquid equilibrium at temperatures from the ambient to 460°C and pressures from ambient to 300 atm. The apparatus has been checked out to give consistently reliable results and phase equilibrium data have been obtained for:

- 12 binary mixture systems of hydrogen + a heavy hydrocarbon
- 11 binary mixture systems of methane + a heavy hydrocarbon
- 9 binary mixture systems of carbon dioxide + a heavy hydrocarbon
- 2 ternary mixture systems of hydrogen + two heavy hydrocarbons
- 2 ternary mixture systems of hydrogen + methane + a heavy hydrocarbon
- 5 complex mixture systems of hydrogen + a coal oil fraction
- 4 complex mixture systems of methane + a coal oil fraction

For each binary system data have been taken, to the extent permitted by the nature of the system, at the fixed grid points of four temperatures and seven pressures as follows:

- temperatures at 190, 270, 350, and 430°C
- pressures at 20, 30, 50, 100, 150, and 250 atm.

The use of the same T-p grid facilitates interpolation and extrapolation with respect to solvent properties in the development of correlations.

For ternary systems of hydrogen + methane + a heavy hydrocarbon, the proportion of hydrogen to methane in the feed gas is systematically varied to reveal the effect of gas composition on K-values.

For ternary systems of hydrogen + two heavy hydrocarbons, the proportion of the hydrocarbons in the liquid feed is approximately equi-molal to reveal the liquid mixing effects.

For complex mixtures of a light gas + a coal oil, bubble point conditions and the solubility of the gas in the liquid are determined while vaporization of the oil is suppressed to insure the identity of the equilibrium liquids with that of the feed oil.

2.2 APPARATUS

A flow-type design was adopted for the equilibrium apparatus in order to reduce residence time of the sample in the high temperature zone and thereby to minimize thermal decomposition. Figure 1 shows the scheme of the apparatus. All parts exposed to high temperature and high pressure are made of stainless steel type 316.

Starting with the feeds to the apparatus as shown in Figure 2 the gases (hydrogen, methane, and/or carbon dioxide) are supplied from high pressure cylinders through pressure regulators. A Matheson gas blender (Dyna-Blender model SP-1601) provides a mixed binary gas stream at a set composition from two individual cylinders. Composition of the mixed gas has been found to stay constant within ± 0.5 mole %. The blender is bypassed when a single gas is used.

Downstream from the blender two vessels of about 1 liter each are placed in series in front of the compressor in order to promote mixing and to reduce pressure fluctuations at the blender due to operation of the diaphragm compressor.

A Hofer diaphragm compressor rated at $0.1 \text{ M}^3/\text{hr}$ compresses the gas from 25-150 atm to a pressure of up to 500 atm. The compressor is bypassed when pure carbon dioxide gas is used.

Downstream from the compressor is a 500 ml pressure vessel equipped with a pressure regulator at the exit. The presence of this vessel greatly reduces fluctuations of pressure caused by the compressor.

The liquid feed flows from the feed tank to a Hills-McCanna U-type metering pump (maximum capacity 5,450 ml/hr, maximum pressure 350 atm) at rates of 500-3000 ml/hr. The Hills-McCanna pump is of the reciprocating type causing uneven flow. To reduce flow fluctuations, a cylindrical vessel of 75 ml is installed in a vertical position