TECHNICAL PROGRESS REPORT

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SOLVENT TAILORING
IN COAL LIQUEFACTION

Quarterly Report for the
Period May, 1982 - August 1982

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OBJECTIVE

The objective of this research program is to determine the effects of phase behavior of process components on coal liquefaction and of solvent composition on coal-dissolution behavior as well as their combined effects on second-stage upgrading. Through understanding the fundamentals of coal dissolution, this research will provide data for tailoring solvents to attain higher reaction rates, increased conversion, and higher product selectivity.

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SUMMARY

The initial objective of this work was to study the phase distribution of donor solvents and solvent mixtures during the liquefaction of coal, to investigate the effect of phase distribution on coal conversion, and to determine the advantages, if any, of operating at subcritical and/or supercritical conditions.

Computer simulations were used to predict the phase distribution, for various binary systems, as a function of temperature. The FLASH program was used to theoretically predict phase distribution for various model systems. Due to limitations in the computer program, success was achieved only in a few cases. Even in these cases, the existence of two-phase regions was observed only at temperatures and pressures far below normal liquefaction conditions.

An extensive review of the literature was carried out in order to survey methods of experimentally studying vapor-liquid equilibria.

Finally, some preliminary laboratory studies were carried out with the use of benzothiophene-dodecane as the model reaction system. It was felt that the study of the effect of reactor configuration on conversion would provide insight into whether phase distribution or mass transfer was the limiting consideration for coal conversion. However, no conclusive results were obtained from these studies.

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NOMENCLATURE

$$B = b_1 - b_1/T_r - b_3/T_r^2 - b_4/T_r^3$$

b_1, b_2
 b_3, b_4 = Constants in the BWR-Lee Kesler Equation

$$C = c_1 - c_2/T_r + c_3/T_r^3$$

c_1, c_2
 c_3, c_4 = Constants in the BWR-Lee-Kesler Equation

$$D = d_1 + d_2/T_r$$

d_1, d_2 = Constants in the BWR-Lee-Kesler Equation

$H-H_0$ = Isothermal enthalpy departure for the total mixture, J/g

$K(I)$ = Equilibrium constant of component 'i' in the mixture

k_{ij} = Binary parameter for the i-j pair in the mixing rule for the pseudo-critical temperature

P = Pressure, atm.

T = Temperature, K

V = Molar volume, cm³/g mole

$x(I)$ = Liquid phase molefraction of component 'i', x_i

$y(I)$ = Vapor phase molefraction of component 'i', y_i

$z(I)$ = Molefraction of component 'i' in the mixture

Z = Compressibility factor

β, γ = Constants in the BWR-Lee-Kesler Equation

W = Acentric factor

Subscripts

b = Boiling point

c = Critical property

i = Component 'i'

j = Component 'j'
m = Mixture property
r = Reduced property

Superscripts

L = Liquid phase
V = Vapor phase
(o) = Simple fluid
(r) = Reference fluid

I. COMPUTER SIMULATION STUDIES

INTRODUCTION

Since the beginning of the past decade, research in coal liquefaction has gained considerable interest. Coal, a naturally abundant resource, could possibly be a complementary energy source in the long run because any single energy source may not be able to meet future energy requirements.

The liquefaction of a non-uniform substance like coal is a highly involved process. During the early stages of coal liquefaction research, it was found that one of the serious drawbacks of the liquefaction process is the large amount of hydrogen required for the process because the ratio of hydrogen to carbon in coals is less than that in petroleum based fuels. Also, removal of oxygen, sulfur, and nitrogen is essential to obtaining clean liquid fuels and eliminating environmental pollution.

Past work in coal liquefaction has shown that the use of hydrogen-donating solvents can significantly reduce hydrogen consumption during coal liquefaction. Donor solvents used in liquefaction processes act both as hydrogen donors and as physical solvating agents. For example, tetralin, a partially unsaturated aromatic hydrocarbon, is a popular donor solvent. It has been reported that the aromaticity of coal could enhance the rate of dissolution of the liquefaction products in tetralin.

Majlessi (14) has reported that the phase behavior of hydrogen donor solvents could significantly affect the rate of dissolution of coal. Usually, liquefaction experiments are performed at temperatures and pressures above 400°C and 2000 psig, respectively. Under these operating conditions, many hydrogen donor solvents are near or above their critical properties. However, information on the phase behavior of donor solvents or donor solvent mixtures under liquefaction conditions is still in the early stages of its development.

Consequently, it was decided to study the phase behavior of donor solvents and solvent mixtures to determine the advantages, if any, of operating under supercritical and/or subcritical conditions. Such information would help to appropriately choose operating conditions for various solvents so as to maximize the yield of liquefied products.

THEORETICAL PREDICTION OF K-VALUES

Phase equilibria of light hydrocarbons and of mixtures of light hydrocarbons and hydrogen have received considerable attention from several investigators since the discovery of petroleum. Due to this interest, low-temperature vapor-liquid equilibrium data are abundant in the literature. However, reliable high temperature and high pressure vapor-liquid equilibrium data are seldom available.

Recently, a few authors have considered the phase behavior of gas-liquid systems, such as the hydrogen-tetralin system, methane-tetralin system, and so on, at elevated temperatures and pressures. Yet, phase equilibria of hydrogen donor solvents, most of which are heavy hydrocarbons and heavy hydrocarbon mixtures, at liquefaction conditions are almost non-existent.

Experiments have been performed at the Auburn Coal Conversion Laboratories (ACCL) to evaluate the effect of shifts in K-values, K being the vapor-liquid equilibrium constant, of tetralin and other solvent mixtures (14). During these experiments, a change in the phase behavior of tetralin was effected by the addition of various aliphatic and aromatic physical solvating agents. The results of these studies suggest that a difference in the K-values of tetralin could influence the yield of liquefied products. But no attempt has been made to determine the actual distribution of tetralin between the two phases when it is mixed with various solvents.

Several other examples were presented in the original proposal, for this project, to illustrate the significance of the phase behavior of solvents on reactivity during liquefaction and subsequent processing of the coal liquids. Thus, results of past works pointed to the need to study the distribution of solvents and hydrogen donors between the liquid and vapor phases at liquefaction conditions.

To achieve this objective, an attempt was made to theoretically predict the K-values of tetralin. For this purpose, the reprints of three computer programs were obtained from Prausnitz (20) for three types of vapor-liquid equilibrium calculations.

A few attractive features of the computational procedure described by Prausnitz (21) are:

- i) the procedure can be used even at high pressures, including pressures in the proximity of critical pressures;
- ii) it is not restricted to symmetric mixtures, but is also applicable to asymmetric mixtures;
- iii) the programs do not require mixture critical properties as input data, but need only pure component critical properties, acentric factors, and one binary parameter for each binary pair;
- iv) the procedure is applicable not only to binary systems but to ternary or higher systems as well (i.e., for a ternary system, no ternary parameters are necessary other than the binary parameter mentioned earlier).

However, care must be taken when calculations are performed in the critical region because uncertainties arise for the range $(T/T_{ct}) > 0.96$, where T_{ct} is the true critical temperature.

Three types of vapor-liquid equilibrium calculations can be made using these computer programs (20) (The sample input data cited at the end of the original program documentation was used during the test-run of these programs):

- i) bubble-point pressure
- ii) bubble-point temperature
- iii) FLASH calculations

When temperature T and liquid phase molefractions x_i (one for each component present) are given, the first step above can be used to calculate pressure, P , and vapor phase molefractions, y_i , while the second can be used to compute temperature, T , and vapor phase molefractions, y_i , when pressure, P , and liquid phase molefractions, x_i , are given. Although the first two programs have been stored for future use, they have not been used until now since both liquid and vapor molefractions are unknown for the problem at hand.

The present problem is related to the third program, FLASH calculations. This program requires the following input data: temperature, T , pressure, P , the binary interaction parameter, k_{ij} , for each i - j pair, and feed molefractions, z_i , of all components in the mixture. The program output contains liquid phase molefractions, vapor phase molefractions, the fraction of total vapor present, the isothermal enthalpy departure for the total mixture, and the K -values.

Binary Mixtures

A number of binary mixtures were considered for the FLASH calculation purpose, in all of which tetralin was considered as the component 'i'. The second component, component 'j', was one of the following compounds:

1-Methylnaphthalene

Cyclohexane

Toluene

Xylene

Hexadecane

Dodecane

Undecane

n-Hexane

Critical Properties

Critical properties of these compounds were obtained from the literature except the critical volume of tetralin and that of hexadecane. The critical volume of tetralin was estimated using three group contribution methods. The methods used and the corresponding values of the critical volume are given in Table 1.

Details of these estimation procedures are available in reference 23. Of the three methods, Lydersen's method was reported to be the most reliable (23). Hence, the value obtained by this method was used in all subsequent calculations. Table 2 summarises the critical properties of the compounds of interest.

The Binary Interaction Parameter (k_{ij})

The binary interaction parameter k_{ij} for each i-j pair was obtained from Figure 1 which was obtained from reference 21. This figure presents k_{ij} parameters as a function of the dimensionless group $(T_{ci} V_{ci})/(T_{cj} V_{cj})$ for hydrocarbon-hydrocarbon systems including aromatics. For values of the ratio $(T_{ci} V_{ci})/(T_{cj} V_{cj}) \ll 1$, k_{ij} values are difficult to read from the figure and therefore, k_{ij} values were estimated only for $(T_{ci} V_{ci})/(T_{cj} V_{cj}) > 1$.

Table 1

Critical Volume of Tetralin Using
Different Calculation Methods

Method	Critical Volume of Tetralin (cm ³ /gmole)
Lydersen	438.0
Vetere	449.1
Riedel	444.6

Table 2
Critical Properties of Solvents¹

Solvent	Mol Wt (g/gmole)	T _c (K)	P _c (atm)	V _c (cm ³ /gmole)	Z _c	W
Tetralin	132.2	719	34.7	438*	--	0.303
1-Methyl naphthalene	142.2	772	35.2	445	0.250	0.334
Cyclohexane	84.2	553.4	40.2	308	0.273	0.213
Toluene	92.1	591.7	40.6	316	0.264	0.257
m-Xylene	106.2	617	35.0	376	0.260	0.331
Hexadecane	226.4	717	14.0	920*	--	0.742
Dodecane	170.3	658.3	18.0	713	0.240	0.562
Undecane	156.3	638.8	19.4	660	0.240	0.535
n-Hexane	86.2	507.4	29.3	370	0.260	0.296

* calculated

¹ Except otherwise stated, data were taken from reference 23.

FIGURE 1. CORRELATION OF BINARY PARAMETERS, K_{ij} FOR HYDROCARBON-HYDROCARBON - SYSTEMS, INCLUDING AROMATICS

SOURCE: REFERENCE 21.

However, for certain binary pairs for which $(T_{ci} V_{ci}) / (T_{cj} V_{cj}) < 1$, an approximate value of k_{ij} was obtained from the intersection of the curve shown in Figure 1 with the ordinate at a later time. The interaction parameters thus obtained, are given in Table 3. In all cases, tetralin was assumed as the component 'i'.

The binary pair tetralin-toluene was used to study the effect of the interaction parameter on phase equilibrium calculations. k_{ij} values were varied from 0.75 to 1.10, and all calculations were performed at a constant temperature of 683 K, which is close to the liquefaction temperature. For each k_{ij} value, the calculations were repeated for three different pressures, 130.25, 137.05, and 143.85 atm.

Only the vapor phase was observed to exist in all cases. In other words, no obvious changes were noted in the vapor-liquid equilibrium behavior. However, the calculated value of the reduced volume was negative when k_{ij} was 1.1. Also, the isothermal enthalpy departure for the total mixture was found to increase with an increase in k_{ij} .

Reduced Temperatures

The next attempt was to repeat the foregoing calculations for other binary pairs. Although the computational procedure used in the previous calculations is applicable to high system pressures, near the critical region, its applicability is questionable when $(T/T_{cm}) > 0.93$ (T_{cm} is the pseudo critical temperature of the mixture). Hence, before further calculations were performed, the pseudo critical temperatures of the binary systems of interest were estimated.

The required relationships for estimating the pseudo critical temperatures of various binary systems were taken from reference 21. Accordingly, T_{cm} values obtained for four binary systems are given in Table 4.

Table 3
Binary Interaction Parameters

Component 'j'	$(T_{ci} V_{ci}) / (T_{cj} V_{cj})$	k_{ij}
1-Methylnaphthalene	0.9167	-
Cyclohexane	1.8476	1.005
Toluene	1.6843	1.000
m-xylene	1.3575	0.997
Hexadecane	0.4774	-
Dodecane	0.6709	-
Undecane	0.7469	-
n-Hexane	1.6775	1.000

Table 4
Reduced Temperatures for Binary Systems

Binary System	T_{cm} (K)	$T_r = T/T_{cm}$
Tetralin-Toluene	620.09	1.10
Tetralin-Cyclohexane	590.6	1.15
Tetralin-m-xylene	640.67	1.06
Tetralin-n-Hexane	551.08	1.24

The temperature, T , was assumed to be 683 K as before. These four binary systems were chosen because estimated k_{ij} values were found to be reasonably accurate for these systems. It is evident from Table 4 that the results obtained from the FLASH program may not be accurate because T/T_{cm} always exceeds the safe limit of 0.93 at 683 K for all four binary systems considered. Hence, further computations on these binary systems were not performed.

Tetralin-1-Methylnaphthalene System

Since the dimensionless ratio $(T_{ci} V_{ci})/(T_{cj} V_{cj})$ for the tetralin-1-methylnaphthalene system is near unity, a fairly accurate estimation of the interaction parameter is possible compared to other systems shown in Table 3, whose dimensionless ratios are much less than unity. Subsequently, the pseudo critical temperature of this mixture was estimated to be 732.4 K. At 683 K, T/T_{cm} was calculated and determined to be approximately 0.93. Although T/T_{cm} is equal to the limiting value, the FLASH computational procedure was applied to this system, and the observations are described below.

The feed was assumed to consist of 1.5 gms of tetralin and 3.5 gms of 1-methylnaphthalene. The corresponding feed molefractions were 0.3155 and 0.6845. The temperature used in the calculations was 683 K, and the pressures used were 130.25, 137.05, and 143.85 atm. An approximate value of k_{ij} for this system was estimated to be 0.97. (The estimation procedure was described in previous paragraphs.) When k_{ij} values were varied from 0.75 to 1.25, the following behavior was observed.

1. When $k_{ij} = 0.75$, both components are completely in the vapor phase.
2. When $k_{ij} > 0.80$, only the liquid phase exists.

3. A transition from vapor phase to liquid phase occurs for a k_{ij} value between 0.775 and 0.776 (See columns 6 and 7 in Table 5).
4. As k_{ij} increases, the isothermal enthalpy departure for the mixture also increases (See column 3 in Table 5).
5. For a given $k_{ij} < 0.90$, the isothermal enthalpy departure for the mixture increases with increase in pressure. But, for k_{ij} between 0.90 and 0.95, the change in $\Delta H (H-H_0)$ with pressure is small. Contrary to the behavior for $k_{ij} < 0.90$, when $k_{ij} > 0.95$, ΔH appears to decrease with an increase in pressure.
6. A two-phase region was not observed to exist for any of the conditions studied.

Since the existence of a two-phase region was of considerable interest to this work, computations were performed to locate the two-phase region for the system tetralin-1-methylnaphthalene. The composition range studied is given in Table 6. For a given temperature and feed composition, six different pressures were used as shown below:

<u>P, psig</u>	<u>P, atm</u>
1000	69.02
1250	86.03
1500	103.04
1900	130.25
2000	137.05
2100	143.85

Table 5

Effect of k_{ij} on the Tetralin-1-Methylnaphthalene System

T (K)	P (atm)	ΔH (H-Ho) (J/g)	I*	z(I)	x(I)	y(I)	k(I)
<u>k_{ij} = 0.775</u>							
683	130.25	201.18	1	0.3155	0.0	0.3155	0.0
			2	0.6845	0.0	0.6845	0.0
683	137.05	201.43	1	0.3155	0.0	0.3155	0.0
			2	0.6845	0.0	0.6845	0.0
683	143.85	201.62	1	0.3155	0.0	0.3155	0.0
			2	0.6845	0.0	0.6845	0.0
<u>k_{ij} = 0.776</u>							
683	130.25	201.39	1	0.3155	0.3155	0.0	0.0
			2	0.6845	0.6845	0.0	0.0
683	137.05	201.63	1	0.3155	0.3155	0.0	0.0
			2	0.6845	0.6845	0.0	0.0
683	143.85	201.83	1	0.3155	0.3155	0.0	0.0
			2	0.6845	0.6845	0.0	0.0

i = 1: tetralin; i = 2: 1-methylnaphthalene

Table 6

Composition Range of Tetralin-1-Methylnaphthalene System

Tetralin (grams)	1-Methylnaphthalene (grams)	Molefraction of Tetralin (z_1)	Molefraction of 1-methyl- naphthalene (z_2)
0.00	5.00	0.0000	1.0000
0.75	4.25	0.1595	0.8405
1.00	4.00	0.2119	0.7881
1.50	3.50	0.3155	0.6845
2.00	3.00	0.4176	0.5824
3.00	2.00	0.6174	0.3826
4.00	1.00	0.8114	0.1886
4.50	0.50	0.9064	0.0936
5.00	0.00	1.0000	0.0000

The temperatures employed were 500, 550, 600, 650, and 683°K. The interaction parameter was determined to be 0.97 from Figure 1. The observations based on these calculations can be summarized as follows:

1. When $k_{ij} = 0.97$, only liquid phase is observed to exist for the entire range of temperatures, pressures and compositions studied;
2. When k_{ij} is reduced to 0.75 and for a feed composition $z_2 = 0.6845$, only vapor phase exists at 683°K and for pressures greater than or equal to 2000 psig. At 1000 and 1500 psig, the program indicated cases of no convergence;
3. When the original subroutine VREDU was replaced by a modified subroutine VREDU to calculate the reduced volume, no more convergence problems were encountered. Even this new procedure was found to be incapable of detecting a distinct two-phase region. However, this modification showed a significant effect on the calculated isothermal enthalpy departure values for the mixture;
4. A shift from the liquid phase to the vapor phase was observed in the temperature range 763 to 675 K when k_{ij} was 0.75;
5. When the feed composition is $z_1 = 0.6174$ and $z_2 = 0.3826$, a similar transition from the liquid phase to the vapor phase occurs for the temperature range 650 to 652 K when k_{ij} is 0.75.

The effect of pressure on these transitions was not considered separately. Such transitions occurred irrespective of the pressures employed in these calculations.

Thus, after several trials, it was concluded that this computer program may not be directly applicable to the conclusive prediction of the phase behavior of mixtures of tetralin and other solvents. The uncertainty involved in using this program increases as the mixture reduced temperature T/T_{cm}

exceeds 0.93. But, it is clear from the foregoing discussion that the reduced temperatures for many solvent mixtures of interest in coal liquefaction are greater than unity under liquefaction temperature conditions. This fact, coupled with the high pressure required for liquefaction, complicates the problem of theoretical prediction of phase behavior of donor solvent mixtures.

The possibility of adapting the experimental tubing bomb reactions to determine the K-values of tetralin-solvent mixtures was also considered. The tubing bomb is a cylindrical microreactor commonly used to perform laboratory-scale coal liquefaction reactions. But, present experimental techniques do not incorporate pressure measurement, and it is difficult to obtain the actual distribution of tetralin in the liquid and vapor phases from an experimentally determined value of coal conversion. Hence, the idea of adapting tubing bomb techniques for use in the present study was abandoned at its rudimentary stage since it was found to be quite unpromising.

In order to devise adequate experimental procedures to measure equilibrium K-values for tetralin-solvent mixtures, a detailed literature search was conducted. The next two chapters are devoted to this aspect of the investigations.

II. LITERATURE REVIEW

STATIC METHODS FOR VAPOR-LIQUID EQUILIBRIUM MEASUREMENTS

It was pointed out earlier in this report that most of the high-pressure systems discussed in the literature are mixtures of light hydrocarbons which are gases under normal conditions. Since both physical solvating agents and hydrogen donors used in coal liquefaction are mostly heavy hydrocarbons, a prior knowledge of phase equilibria of heavy hydrocarbon mixtures is advantageous.

Phase equilibria of any system can be determined by either a static method or a flow method. A dynamic flow or continuous method is reported to be preferable for vapor-liquid equilibrium measurements at high temperatures and pressures. It is still worthwhile reviewing the literature on static methods, since static methods require less sophisticated equipment, are less expensive, and are simpler and easier to manage in laboratories than continuous methods.

A brief summary of the sources and some information regarding a few static techniques is presented in the following paragraphs. These techniques are suitable for moderate to high system pressures. However, a detailed discussion is not presented because these systems are gases under normal conditions, whose operating temperatures are very low as compared to liquefaction temperatures.

Benedict et al. (2) presented a detailed description of the equilibrium cell that they used to determine the vapor-liquid equilibria in the methane-ethylene-isobutane system. They measured equilibrium pressure using a

pressure gauge, equilibrium temperature, using a copper-constantan thermocouple, and compositions of gas and liquid phases in the cell. Although the apparatus was made of steel, the temperatures used were very low, 37.78 and 71.11 C, and the pressures employed were 34.02 and 68.05 atm.

Yudovich and others (33) studied the phase equilibria of carbon dioxide in the methane-carbon dioxide-n-decane system using a chromatographic technique to determine the equilibrium constants of carbon dioxide at infinite dilution in methane-decane solutions. The apparatus was reported to be designed for high-pressure systems. The pressure, in this case, ranged from 100 to 1750 psia, and the temperature range was 40 to 150 F.

Price and Kobayashi (22) employed a stainless steel cell to study the low temperature vapor-liquid equilibrium in the ternary methane-ethane-propane system. Their purpose was to investigate low-temperature phase equilibria at high pressures. Accordingly, they varied the operating temperature from 50 to -200 F and the operating pressure from 100 to 200 psi.

Besserer and Robinson (3) performed experiments in a 10 cm diameter type 316 stainless steel cylindrical equilibrium cell. They used a temperature of 37.7 C and pressures up to 80 atm. This high pressure apparatus was designed to measure the refractive index and the composition of each phase in equilibrium.

Manley and Swift (15) used a low temperature system, the propane-propene system. Their experimental equipment consisted of a volumetric metering system, a low-temperature system, and a weighing bomb. The investigators employed temperatures ranging from -20 to 100 F and pressures from 20 to 1600 psia.

Elliot and others (6) studied the methane-n-butane system at low temperatures and high pressures. In this study, the temperature ranged from 40 to -200 F and the maximum pressure used was approximately 2000 psia.

Sage and Lacey (25) reported a study of phase equilibria in hydrocarbon systems, in which pressures up to 200 atm. and temperatures from 20 to 100 C were employed. Katz and Hachmuth (11) studied the crude oil-natural gas system. Experiments were performed over a pressure range of 14.7 to 3000 psia and a temperature range of 40 to 200 F.

Bae and others (1) employed a 304 stainless steel constant volume cell to measure the vapor-liquid equilibria of the ethylene-1-butene system. The temperature ranged from -50 C to 50 C, and pressures up to 100 atm. were used.

Parisod and Plattner (19) described an apparatus to measure the vapour-liquid equilibria of the NaCl-H₂O system. The data were obtained for a temperature range of 300 to 400 C and pressures up to approximately 400 kg/cm².

Wichterle and Kobayashi (32) reported a study on the methane-propane system at temperatures ranging from -75 to -225 F and pressures from 25 to 950 psia.

Although the foregoing references contain valuable information, the discussion to follow is worth special mention because some of the techniques to be mentioned can be used in experiments incorporating extreme temperatures and pressures.

Legret and others (12) have described a static still having three main parts which include:

1. the equilibrium cell in its thermostat
2. the analyzer for the vapor phase
3. a special circuit used for the calibration of the transducer and for filling the still with gaseous components.

The still was reported to be operable up to a pressure of 50 bar (~ 49.4 atm.). The liquid phase composition was not directly analyzed but was evaluated from total quantities after a correction was made for the amount of substance in the vapor phase. The authors claimed that the apparatus could be used to study mixtures of components which are both liquids or both gases or one liquid and one gas at normal conditions. The binary system reported in this paper consisted of ethane and n-decane.

Figuiere and coauthors (8) studied hydrogen-hydrocarbon systems at high pressures and temperatures. Their method was said to be especially suitable for mixtures of at least one permanent gas and one high boiling liquid between 150 and 400 C and between 5000 and 40,000 kPa (~49 to 395 atm.). The advantage of this method is that only microquantities of samples are required for analysis. However, there is one limitation in this case, i.e., the sampling and analytical method require the liquid sample to be in the vapor phase. This condition fixes the lowest possible operating temperature. Upper limits for pressure (40,000 kPa) and temperature (400 C) were determined using the pressure transducer. The authors reported that pressures greater than 2000 kPa (~20 atm.) have been found to provide better accuracy.

Scheeline and others (27) described a high-pressure apparatus which was made of glass and was said to withstand pressures of up to 1500 psia at room temperature. The reaction of gases with mercury in the trap and the weakening of glass at high temperatures, were the main drawbacks encountered. Also, if a larger sample was necessary for analysis, the lengths of the still and the trap had to be increased.

Rigas and others (24) described a static experimental set-up in which 2 to 4 hours were required to ensure equilibrium depending on the magnitude of the pressure change imposed on the system and the proximity to the critical

pressure. Pressures up to 2000 psia (approximately) were applied in this work. Although the authors used this apparatus for low temperature measurements, they suggested that higher operating temperatures (>150 C) could be employed with the use of heat resistant gaskets.

Ellis and coworkers (7) presented the description of another relatively low-temperature (<100 C) static equilibrium cell of stainless steel. A characteristic feature of this cell was the provision of a magnetic stirring mechanism to agitate the contents of the cell. When vapor and liquid samples were collected, mercury was allowed to flow into the cell to keep the equilibrium pressure constant. The pressures in this study ranged from 1000 to 3000 psia.

Griswold and others (9) presented a schematic of a high-pressure vapor-liquid equilibrium apparatus in which the sample bombs were 60 cc in capacity. The temperature range specified was 100 to 250 C and the pressure range was from a very low value to nearly 1200 psia. No details about the apparatus were available.

Legret and others (13) presented a detailed description of a new static cell made of stainless steel, which has a capacity of 100 cc. Pressure equilibrium was said to be reached within 10 minutes of stirring. It was further reported that neither a displacement fluid nor a circulation pump was needed during sampling. Pressures up to 100 MPa and temperatures between 233 and 433 K were specified. The reproducibility of measurements was claimed to be excellent for the system studied.

In general, in a static method, the equilibrium cell is first evacuated and then half-filled with the system to be studied. The cell is then immersed in a constant temperature bath to bring the temperature up to the equilibrium value. Uniform conditions are maintained within the cell usually with the use

of a magnetic stirring mechanism. Stirring must be stopped during sampling to avoid entrainment. In any case, a static method requires at least 1 hour to attain equilibrium.

It is quite apparent from the foregoing discussion that a batch or static operation is especially suitable for low temperature experiments. The main drawback of a batch technique is the large residence time required to attain equilibrium. Such large residence times are especially damaging for systems which undergo excessive thermal decomposition at high temperatures.

FLOW METHODS FOR VAPOR-LIQUID EQUILIBRIA

A few static methods for measuring vapor-liquid equilibria have been the main consideration so far, and now a discussion on dynamic or flow methods for measuring phase-equilibria at elevated temperatures and pressures follows.

Flow methods for phase equilibrium measurement are different from circulation ones, in which a steady stream of constant composition is fed to the equilibrium chamber. A few distinct advantages of flow techniques are cited below.

1. Flow techniques are suitable for the study of partially miscible systems.
2. A number of vapor samples of varying sizes can be collected to check the approach to equilibrium.
3. The presence of equilibrium can be insured by the collecting of samples at various times.
4. The approach to equilibrium is quick. In other words, residence time is smaller, and thus, thermal decomposition at elevated temperatures can be inhibited.
5. Equilibrium conditions are not disturbed by the process of sampling.

Literature dealing with flow techniques is very limited. A brief discussion of some flow techniques is given below.

Wan and Dodge (30) described a flow apparatus which was used to study the solubility of carbon dioxide in benzene up to a maximum temperature of 60 C and a maximum pressure of 95 atm. The equilibrium cell was made of steel, the contents of which were agitated by means of a magnetic stirrer operated by a solenoid. The cell was heated by an electric immersion heater. The authors experienced troubles with vapor and liquid sampling in this apparatus. Specifically, initial entrainment of liquid in the vapor phase was reported to be substantial. Also, this apparatus was not suitable for studying immiscible liquids.

Miller and Dodge (17) modified the apparatus described by Wan and Dodge (30) for use at high temperatures. For this purpose, the constant temperature oil baths were lagged with magnesia, and all pressure tubing outside the baths was heated with the use of resistance wires. The maximum temperature and pressure, in this case, were 125 C and 300 atm, respectively. The authors reported that consistent results for the liquid phase were obtained only up to 125 C. Furthermore, at higher temperatures, cooling in the sampling valve during expansion was said to cause discrepancies in the results.

Mertes and Colburn (16) and Stutzman and Brown (29) presented two continuous methods of measuring phase equilibria. In both cases, the temperatures of operation were too low. However, a special advantage of the method of Mertes and Colburn is that it can handle vapors which form immiscible condensates. The advantage of the method of Stutzman and Brown is that the liquid level can be viewed through a sight glass.

Brandt and Stroud (4) gave the description of another low-temperature flow measurement technique. The apparatus, which was made of brass and was of

rectangular cross-section, was equipped with a windowed cell, a stirring device, and a temperature control system. Equilibrium was reported to have been attained in 10-15 minutes with this system.

White and Brown (31) gave the detailed description of a flow apparatus developed by them. In the equilibrium separator of this apparatus, the vapor sample was subjected to rotary motion to allow the entrained liquid to flow downward. A molten salt bath was used to provide constant-temperature conditions, and a capacitance measuring device served as the basis for a liquid level indicator. Finally, the operating temperatures and pressures ranged from 300 to 820 F and 50 to 700 psi, respectively.

Simnick and others (28) developed a flow type of apparatus. All parts of this apparatus which were exposed to high temperatures and high pressures were made of stainless steel. The authors have studied the vapor-liquid equilibrium of the hydrogen/tetralin system at elevated temperatures and pressures. Hydrogen was supplied to the system directly from a high pressure cylinder. Only above 120 atm, was a compressor found necessary. The gas and the liquid streams were heated before they were admitted into the equilibrium cell. The equilibrium chamber was reported to have an internal volume of 90 ml and was capable of withstanding temperatures up to 430 C. Insulated heating wires were provided to obtain a uniform temperature which was measured with the use of a calibrated chromel-alumel thermocouple. A constant liquid level was maintained to avoid entrainment. This level indicator was similar to that described by White and Brown (31). During sampling, the liquid weights and the gas volumes were determined. In this study of the hydrogen/tetralin system, the temperatures and pressures which were used are given below:

Temperature: 189.6, 268.7, 348.6, and 381.9 C

Pressure: 20, 30, 50, 100, 150, 200, and 250 atm

Nasir and Kobayashi (18) employed a vertical cell with a magnetic pump as the equilibrium cell. Known quantities of fluids were displaced during sampling by the advancement of a piston. The authors did not, however, present a description of their apparatus in this paper. The maximum temperature and pressure used were approximately 620 K and 100 atm. respectively.

Chao and others (5) developed a flow apparatus, which seemed to be a modification of the one described by Simnick and others (28), to study gas-liquid equilibrium. All parts of this apparatus exposed to high temperature and high pressure were made of type 316 stainless steel. Further details regarding the equilibrium cell were presented in the author's report. The gases were fed directly from high pressure cylinders through pressure regulators. A compressor was found necessary only above 150 atm. The liquid streams were metered with the use of a metering pump at rates of 500-3000 ml/hour. Preventive measures to avoid flow fluctuations in the liquid line were also provided. In this case, too, a capacitance measurement technique was adopted to control the liquid level in the equilibrium cell. The residence times were reported to vary from 12 to 33 seconds, which were based on a liquid flow rate of 0.6 ml/sec.

Henson (10) used an external circulation type apparatus in which equilibrium was said to be achieved in 30 minutes. This apparatus was used to study the solubilities of hydrogen and carbon dioxide in coal-derived liquids. The maximum temperature and pressure used were 400 C and 3000 psia, which are comparable to coal liquefaction conditions. The equilibrium cell used was an autoclave equipped with a turbine agitator, gas inlet, solvent charging, liquid sampling, and gas sampling. An external circulation system was provided to eliminate the effect of the large pressure drop between the equilibrium cell and the sample bomb.

In phase equilibrium measurements, the contamination of one phase with the other is a serious hazard, and the maintenance of a constant liquid seal is hence crucial. But proper liquid-level control in the equilibrium cell of a flow apparatus is extremely tedious and calls for expensive control accessories. Thus, the main hindrance to the use of a flow method is its demand for sophisticated control accessories which render the operation of a dynamic method more expensive and more difficult to control in a laboratory. The final decision as to the selection of a particular method of measurement, however, depends on the ease of operation and the accuracy or reliability of information obtainable from that method.

Continuous operation is preferable in the present case because of the high temperature involved. Thermal dissociation of tetralin occurs between 300-450 C, and hence, it is essential to reduce the residence time of the sample in the high temperature zone, to minimize thermal degradation. Continuous operation is attractive not only because of the short time of exposure of the sample to the high temperature zone but also because of its ease in collecting relatively large samples for analysis. Thus, results of the literature review indicated that a continuous system for the study of phase equilibria would be ideal.

III. FURTHER COMPUTER SIMULATION STUDIES

MODEL COMPOUND STUDIES

In the literature cited in the previous two chapters, the authors considered phase-equilibrium measurements from a thermodynamic point of view. However, in the field of coal liquefaction, the prime consideration is to know the advantages, if any, of operating under supercritical or subcritical conditions. Since model compounds are extensively used in liquefaction experiments, it was felt that the previously mentioned 'Flash' program might help yield information on model compound systems. Such information might help avoid expensive and tedious phase equilibrium measurements.

Coal, which is extremely complex in nature, yields a number of products upon liquefaction. The analysis and identification of these products are prerequisites to providing insight into the liquefaction mechanism. Such analyses are not easy to accomplish. Hence, a model compound, which constitutes one of the principal organic compounds in coal liquids, must be chosen to simulate the behavior of coal at given operating conditions. At the same time, this model compound should yield products whose analyses are not as cumbersome as that of actual coal liquefaction products.

The model compound used in this study was benzothiophene, a heteroaromatic compound and one of the principal organosulphur compounds in coal liquids. The next few paragraphs describe the results of the computer calculations done on the systems benzothiophene-hexadecane and benzothiophene-n-hexane where hexadecane and n-hexane serve as physical solvating agents.

Since the critical properties of pure benzothiophene are not available in the literature, these values were estimated using Lydersen's method (23). The Lee-Kesler vapor pressure relationship was used to estimate the acentric factor of benzothiophene (23). The critical properties of benzothiophene are shown in Table 7.

Again, Lydersen's method (23) was used to estimate the critical volume of hexadecane which has already been reported. The interaction parameters estimated for the two systems are given in Table 8. Once again the k_{ij} values in Table 8 were obtained from Figure 1, where the value for the system benzothiophene-hexadecane was approximated.

Benzothiophene-Hexadecane System

FLASH calculations were performed for a wide range of feed compositions of this system. The molefraction of benzothiophene was varied by changing the number of grams of benzothiophene while the total weight was kept constant. The compositions that were considered are presented in Table 9.

The temperatures employed were 500, 550, 600, and 625 K so that the reduced temperature for the mixture, T/T_{cm} , was less than 0.93. The pressures used were 69.02, 86.03 and 103.4 atm. At these conditions, both components were found to be always in the liquid phase for the entire molefraction range considered.

Calculations were repeated for a given feed composition and for constant temperature, but for different pressures. The feed molefraction selected was $z_1 = 0.1579$ (10% benzothiophene by weight) and $z_2 = 0.8421$ (90% hexadecane by weight). The results of these calculations were as follows:

1. At 500 K, both components are completely in the liquid phase up to 25 atm.

Table 7
Critical Properties of Benzothiophene*

	T_b (K)	T_c (K)	P_c (atm)	V_c (cm ³ /g mole)	W	Mol Wt (g/g mole)
Benzothiophene:	494	755.6	40.85	379	0.293	134.2

*Obtained from reference 23.

Table 8

Interaction Parameters for Benzothiophene-Hexadecane and
Benzothiophene-N-Hexane Systems.

i - j pair	$(T_{ci} V_{ci}) / (T_{cj} V_{cj})$	k_{ij}
Benzothiophene-hexadecane	0.4341	0.95
Benzothiophene-n-hexane	1.5254	1.0

Table 9

The Range of Composition of Benzothiophene-Hexadecane System

Grams of BT*	Grams of HD*	Molefraction	Molefraction
0.01	0.99	0.0168	0.9832
0.02	0.98	0.0333	0.9667
0.03	0.97	0.0496	0.9504
0.04	0.96	0.0657	0.9343
0.05	0.95	0.0816	0.9184
0.06	0.94	0.0972	0.9028
0.07	0.93	0.1127	0.8873
0.08	0.92	0.1280	0.8720
0.09	0.91	0.1430	0.8570
0.10	0.90	0.1579	0.8421
0.20	0.80	0.2967	0.7033
0.30	0.70	0.4197	0.5803
0.40	0.60	0.5294	0.4706
0.50	0.50	0.6279	0.3721
0.60	0.40	0.7168	0.2832
0.70	0.30	0.7975	0.2025
0.80	0.20	0.8710	0.1290

*BT: Benzothiophene; HD: Hexadecane.

2. At 550 K, while both components are in the vapor phase at 1 atm., they exist only in the liquid phase at 2 atm.
3. At 625 K, pure vapor phase is changed to pure liquid phase as the pressure is changed from 4 to 5 atm.

Once again, these calculations failed to show a two-phase region in any of the cases considered. The coexistence of the two phases was found to be very sensitive to even small changes in temperature and pressure.

For the same temperatures as before, pressures of 1, 10, and 15 atm were employed. The amount of benzothiophene was increased from 0.01 grams to 0.08 grams at increments of 0.01 grams. Table 10 summarizes the phase distribution for the benzothiophene-hexadecane system. Two phases were found to coexist at the reaction conditions shown in Table 11.

At temperatures higher than 550 K, a transition from the vapor phase to the liquid phase occurred at a pressure between 1 and 10 atm. The precise value of this pressure was not determined.

Benzothiophene-n-Hexane System

In the same way as for the previous system, the two phase regions for benzothiophene-n-hexane were located. The interaction parameter for this system was taken as 1.0. The temperatures chosen so as to satisfy the condition $T/T_{cm} < 0.93$ were 425, 450, and 460 K, and pressures used were 1, 10, and 15 atm. The molefractions employed are given in Table 12. It can be seen from Table 13 (analogous to Table 12) that at 450 K and 10 atm., two phases exist over a wide molefraction range for this system.

For both systems, the vapor phase and the liquid phase molefractions (x_i 's and y_i 's) at a given temperature and pressure were found to be independent of the feed molefraction used. In other words, they were constant for a given temperature and pressure.

Table 10

Phase Distribution for Benzothiophene-Hexadecane System

T (K)	P (atm)	I*	z(I)	x(I)	y(I)	k(I)
550	1	1	0.0657	0.0196	0.1337	6.8252
		2	0.9343	0.9804	0.8663	0.8836
550	1	1	0.0816	0.0196	0.1337	6.8253
		2	0.9184	0.9804	0.8663	0.8836
550	1	1	0.0972	0.0196	0.1337	6.8251
		2	0.9028	0.9804	0.8663	0.8836
550	1	1	0.1127	0.0196	0.1337	6.8252
		2	0.8873	0.9804	0.8663	0.8836
550	1	1	0.1280	0.0196	0.1337	6.8251
		2	0.8720	0.9804	0.8663	0.8836

I = 1: benzothiophene
 2: hexadecane

Table 11
Temperature, Pressure, and Feed Molefractions for
Two Phases in BT-HD System

T (K)	P (atm)	Benzothiophene (g)	Hexadecane (g)	z_1	z_2
550	1	0.04	0.96	0.0657	0.9343
550	1	0.05	0.95	0.0816	0.9184
550	1	0.06	0.94	0.0972	0.9028
550	1	0.07	0.93	0.1127	0.8873
550	1	0.08	0.92	0.1280	0.8720

Table 12

Feed Molefractions for Benzothiophene-n-Hexane System

Benzothiophene (g)	n-Hexane (g)	Benzothiophene z_1	n-Hexane z_2
0.01	0.99	0.0064	0.9936
0.02	0.98	0.0129	0.9871
0.03	0.97	0.0195	0.9805
0.04	0.96	0.0261	0.9739
0.05	0.95	0.0327	0.9673
0.06	0.94	0.0394	0.9606
0.07	0.93	0.0461	0.9539
0.08	0.92	0.0529	0.9471
0.09	0.91	0.0597	0.9403
0.10	0.90	0.0666	0.9334
0.20	0.80	0.1383	0.8617
0.40	0.60	0.2998	0.7002
0.60	0.40	0.4906	0.5094
0.80	0.20	0.7198	0.2802

Table 13
Temperature, Pressure, and Feed Molefractions for
Two Phases in BT-n-H System

T (K)	P (atm)	Gram BT (1)	Gram n-H (2)	z1	z2
450	10	0.03	0.97	0.0195	0.9805
450	10	0.04	0.96	0.0261	0.9739
450,460	10	0.05	0.95	0.0327	0.9673
450,460	10	0.06	0.94	0.0394	0.9606
450,460	10	0.07	0.93	0.0461	0.9539
450,460	10	0.08	0.92	0.0529	0.9471
450,460	10	0.09	0.91	0.0597	0.9403
450,460	10	0.10	0.90	0.0666	0.9334
450,460	10	0.20	0.80	0.1383	0.8617
425	1	0.40	0.60	0.2998	0.7002
460	10	0.40	0.60	0.2998	0.7002
425,450,460	1	0.60	0.40	0.4906	0.5094
425,450,460	1	0.80	0.20	0.7198	0.2802

1: Benzothiophene

2: n-hexane

Estimation of the Total Volume

It was stated earlier that the existing experimental techniques used in our laboratory do not incorporate the measurement of the actual pressure at liquefaction temperatures. Yet, the theoretical value of the total volume of a system can be compared with the experimental one because the experimental volume for a given tubing bomb size is constant. Hence the possibility of using a computer program to predict the total volume of a system was considered next.

The program calculates the compressibility factor of a simple fluid $Z^{(0)}$ and that of a reference fluid $Z^{(r)}$ using the modified Benedict-Webb-Rubin equation of state as follows (21):

$$Z = \frac{P_r V_r}{T_r} = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^5} + \frac{C^4}{T_r^3 V_r^2} \left(\beta + \frac{\gamma}{V_r^2} \right) \exp \left(\frac{-\gamma}{V_r^2} \right)$$

In the equation $Z = \frac{P_r V_r}{T_r}$, V_r is defined as (21)

$$V_r = \frac{P_c V}{RT_c}$$

Now, since $P_r = \frac{P}{P_c}$ and $T_r = \frac{T}{T_c}$, Z becomes

$$Z = \frac{PV}{RT}$$

Therefore, the compressibility factor calculated is the actual compressibility factor of a system instead of the reduced one as it may appear to be at first.

Now the compressibility factor for a mixture is obtained from the following equation (21):

$$Z_m = Z(o) + \frac{W_m}{W(r)} (Z(r) - Z(o))$$

where W_m is the acentric factor for the mixture. ($W_m = \sum_{j=1}^n z_j W_j$; z_j is the molefraction of compound 'j', and W_j is the acentric factor of pure 'j'.) $W(r)$ (=0.3978) is a constant given in the program documentation (21).

One of the subroutines (FUGI) estimates Z_m , for the liquid phase ($Z_m^{(L)}$) and for the vapor phase ($Z_m^{(V)}$). Now, the equation of state $Z = PV/RT$ can be rearranged to calculate the volume per mole as

$$V = \frac{ZRT}{P}$$

Hence the liquid and the vapor volumes are obtained from the following relationships.

$$\text{Liquid volume (VOLL)} = Z_m^{(L)} \frac{RT}{P} \text{ (The total number of moles in the liquid phase)}$$

and

$$\text{Vapor volume (VOLV)} = Z_m^{(V)} \frac{RT}{P} \text{ (The total number of moles in the vapor phase)}$$

Here, FUGI calculates

$$Z_m^{(L)} = Z(oL) + \frac{W_m^{(L)}}{W(r)} (Z(rL) - Z(oL))$$

and

$$Z_m^{(V)} = Z(oV) + \frac{W_m^{(V)}}{W(r)} (Z(rV) - Z(oV))$$

For a closed system and in the absence of chemical reactions, it is reasonable to assume that the total number of moles are conserved. Since the total number of moles in the feed are known, the total number of moles in the vapor phase can be obtained using the fraction of the total vapor determined by the program. The difference between the total number of moles in the feed and that in the vapor phase constitutes the total moles in the liquid phase. Consequently, the liquid and the vapor volumes can be evaluated and therefore, the total volume of the system is given by the sum of the vapor and the liquid volumes. Accordingly, a subroutine TOTVOL was incorporated in FLASH to estimate the total volume of a system.

The next attempt was to compare the total volume obtained theoretically with the tubing bomb volume. Several trials of various compositions and pressures were required to adjust the calculated total volume to the value of the tubing bomb volume. Since it would be easier to supply the amount in grams of the components in the feed as the program input, a subroutine FRAMOL was added to calculate the molefractions of the components in the feed from their respective amounts in grams.

1. Benzothiophene-n-Hexane System. Several trials gave the compositions, temperatures, and pressures presented in Table 14 so that the total volume of this system was very near to the tubing bomb volume which is 17.5 cm^3 .

2. Benzothiophene-Hexadecane System. Table 15 shows the results of similar calculations on the benzothiophene-hexadecane system.

It is clear from Table 15 (See column 5) that the estimated volume is significantly different from the actual tubing bomb volume which is 17.5 cm^3 . Attempts to reduce this difference failed because this system was very sensitive to even small changes in the operating conditions. For example, when the amount of benzothiophene was changed from 0.09 to 0.088 and when the

Table 14

Total Volume for Benzothiophene-n-Hexane System

BT grams	n-H grams	T (K)	P (atm)	V (cm ³ / gmole)	I	Feed Mole Fraction z(I)	Liquid Mole x(I)	Vapor Mole y(I)
0.0809	0.919	425	7.0	17.524	1	0.0535	0.0798	0.0058
					2	0.9465	0.9202	0.9942
0.1695	0.8305	450	9.5	17.507	1	0.1159	0.2098	0.0200
					2	0.8841	0.7902	0.9800
0.1965	0.8035	460	10.5	17.506	1	0.1357	0.2670	0.0282
					2	0.8643	0.7330	0.9718
0.6185	0.3815	425	3.7	17.510	1	0.5100	0.6379	0.0370
					2	0.4900	0.3621	0.9630
0.8273	0.1727	425	2.0	17.507	1	0.7547	0.8488	0.0754
					2	0.2453	0.1512	0.9246

1: Benzothiophene; 2: n-Hexane

Table 15
Total Volume for Benzothiophene-Hexadecane System

BT grams	HD grams	T (K)	P (atm)	V (cm ³ / gmole)	I	Feed Mole Fraction z(I)	Liquid Mole x(I)	Vapor Mole y(I)
0.4	0.96	600	2.6	44.318	1	0.0657	0.0216	0.0955
					2	0.9343	0.9784	0.9045
0.09	0.91	600	3.0	32.823	1	0.1430	0.0621	0.2287
					2	0.8570	0.9379	0.7713
0.15	0.85	625	5.0	25.465	1	0.2295	0.1134	0.3009
					2	0.7705	0.8866	0.6991

1: Benzothiophene; 2: n-Hexane

temperature and the pressure were still the same, it was found that the two-phase region ceased to exist. Again, for 0.09 grams of benzothiophene and at 600 K, when the pressure was changed from 3.0 to 3.1 atm, only the liquid phase was present.

To summarize, the benzothiophene-hexadecane system seemed to be extremely sensitive to changes in the operating conditions, and hence further calculations were not performed on this system.

3. Effects of Changes in the Operating Conditions on the Benzothiophene-n-Hexane System. The effects of changes in the interaction parameter, the temperature, and the feed compositions on the benzothiophene-n-hexane system were considered, and the observations are summarized below.

- For a given temperature and feed composition, when the interaction parameter is changed by $\pm 5\%$, the total volume is affected by $< \mp 30\%$ at high pressures ($\sim > 5$ atm.). At low pressures (< 5 atm.), a change in the interaction parameter has a pronounced effect on the calculated total volume. In general, the interaction parameter has considerable influence on the system at lower pressures compared to higher pressures.
- When the temperature is varied by ± 5 K, there are significant variations in the total volume (in some cases the volume decreases by 60%), and for certain feed molefractions, the coexistence of a two-phase region is no longer observed.
- There is only little change in the estimated total volume as long as the feed composition (by weight) is accurate to the second significant digit.

Percentage Distribution of Benzothiophene

Once the component molefractions in the two phases are known, the actual distribution (% by weight) of benzothiophene between the two phases was to be determined. This factor was evaluated for the benzothiophene-n-hexane system which showed a relatively broad range of operating conditions. The percentage distribution thus obtained is given in Table 16.

It is clear from Table 16 that at the conditions considered, the percentage of benzothiophene present in the vapor phase was not appreciable; the maximum was 11% (see column 9 in Table 16). However, at the same conditions, all the benzothiophene fed would be in the liquid phase for the benzothiophene-hexadecane system. Thus, in one case, benzothiophene is present predominantly in the liquid phase while in the other at least 11% of benzothiophene is in the vapor phase. The advantages and/or disadvantages of reacting benzothiophene in one phase as opposed to the other are yet to be investigated.

Table 16

Percentage Distribution of Benzothiophene Between the Two Phases
for the Benzothiophene-n-Hexane System

BT grams	n-H grams	T (K)	P (atm)	V (cm ³ / gmole)	I	x(I)	y(I)	% BT in vapor (by wt.)	% BT in liquid (by wt.)
0.0809	0.9191	425	7.0	17.524	1	0.0798	0.0058	3.8	96.2
					2	0.9202	0.9942		
0.1695	0.8305	450	9.5	17.507	1	0.2098	0.0200	8.5	91.5
					2	0.7902	0.9800		
0.1965	0.8035	460	10.5	17.506	1	0.2670	0.0282	11.42	88.58
					2	0.7330	0.9718		
0.6185	0.3815	425	3.7	17.510	1	0.6379	0.0370	1.5	98.5
					2	0.3621	0.9630		

I = 1: Benzothiophene; I = 2: n-Hexane

IV. EXPERIMENTAL STUDIES

EXPERIMENTAL WORK ON THE BENZOTHIOPHENE-DODECANE SYSTEM

Introduction

Our initial objective was to study the phase behavior of donor solvents and solvent mixtures; to determine the advantages, if any, of operating under supercritical and/or subcritical conditions because previous work conducted in this area suggested that the distribution of reactants between the liquid and vapor phases at liquefaction conditions was an important factor.

For example, the hydrodesulfurization of benzothiophene dissolved in various solvents was conducted in the presence of a sulfur scavenger, Fe_2O_3 . The results are shown in Figure 2. According to this figure, the desulfurization proceeds at a slow rate in hexadecane, which has a high critical point (441°C). This behavior was thought to be due to liquid-gas mass transfer resistances. Since hexadecane is a liquid at the reaction temperature, the gaseous hydrogen has to overcome the liquid film resistance before it can react with benzothiophene dissolved in hexadecane. On the other hand, other solvents are in their supercritical state at liquefaction conditions, and hence mass transfer resistance through the liquid film is not present.

Figure 3 shows an increase in the benzothiophene conversion with an increase in the agitation rate. The effect of the agitation rate on the benzothiophene conversion shown in Figure 3 further led us to believe that mass transfer was important.

Recently, Shah (26) repeated the benzothiophene hydrodesulfurization experiments. He employed dodecane and hexadecane as solvents to evaluate the difference in benzothiophene conversion with changes in the reaction temperature. Figures 4 and 5 show the effect of temperature on hydrodesulfurization of benzothiophene using dodecane and hexadecane respectively as diluent

Figure 2. Effect of Reaction Temperature on Benzothioephene Conversion In Solvents With Different Critical Points (26)

Reaction Conditions: 410°C, 5 min, 1000 rpm, 0.5g Fe_2O_3 , 4.5g Solvent with 10% Benzothioephene, Two Steel Ball Agitators, 2000 psi H_2 Initial Pressure

Figure 3. Effect of Agitation Rate on Benzothiophene Conversion (26)

Reaction Conditions: 410 C, 30 min, 0.5g Fe_2O_3 , 4.5g Dodecane With 10% Benzothiophene, 2000 psi H_2 Initial Pressure

Figure 4 : Effect of Temperature on HDS of Benzothiophene using Dodecane as Diluent Solvent. (26)

Figure 5: Effect of Temperature on HDS of Benzothiophene using Hexadecane as Diluent Solvent. (26)

solvents. Shah (26) did not observe an abrupt increase in conversion as was shown in Figures 2 and 3, but obtained the same benzothiophene conversion with either solvent. Further studies indicate that mass transfer resistance is insignificant, and that hydrodesulfurization of benzothiophene is kinetically controlled under liquefaction conditions. Hence, at present, the phase behavior of solvents seems to be unimportant.

The question that arises is why, then, the benzothiophene conversion is found to increase with increased agitation rate as shown in Figure 2. A suggestion yet to be verified is that the difference in the benzothiophene conversion is probably due to poor catalyst dispersion, which in turn provides less exposed area for reaction. Consequently, the objective of this part of the work was to determine the effect of catalyst dispersion on the benzothiophene conversion during the hydrodesulfurization of benzothiophene in the presence of iron oxide as sulfur scavenger.

Materials Used

Specifications for the chemicals used are given below:

- 1) dodecane: 99% pure from Aldrich Chemical Company Inc.
- 2) benzothiophene: 97% pure from Aldrich Chemical Company Inc.
- 3) iron oxide (Fe_2O_3): red-anhydrous from Fisher Scientific Company
- 4) 1-methylnaphthalene: 96% pure from Aldrich Chemical Company Inc.

Iron oxide was used as a sulfur scavenger here, but it was sometimes referred to as the catalyst also. Iron oxide was dried overnight in a vacuum oven at 100 C and 25 inches of mercury and used immediately. 1-methylnaphthalene was used as an internal standard during the chromatographic analysis of the reaction products. Finally, dodecane and benzothiophene were the diluent solvent and the main reactant respectively.

Specifications of the Horizontal Tubing Bomb

outside diameter : 0.75 inch
thickness : 0.065 inch
length : 3.7 inches
material : stainless steel 316
internal volume : ~ 21.6 cc

Specifications of the Vertical Tubing Bomb

outside diameter : 0.5 inch
thickness : 0.035 inch
length : 9 inches
material : stainless steel 316
internal volume : ~ 21.7 cc

Feed Specifications and Temperature

4.5 grams of 10% benzothiophene in dodecane
0.5 gram of iron oxide
H₂ at 1250 psig at room temperature

The temperature used in all runs was 405 C. The 10% benzothiophene in dodecane solution was sonicated for 30-40 minutes to ensure complete dissolution of benzothiophene in dodecane.

Experimental Procedure

The tubing bomb was provided with a fine metering valve which was connected to the reactor body through 0.25 inch tubing Swagelok fittings and reducing unions were used to assemble the whole unit. Figure 6 shows the schematic representation of a vertical tubing bomb in the sand bath.

Figure 6: Schematic Representation of a Vertical Tubing Bomb in the Sand Bath

4.5 grams of 10% benzothiophene in dodecane (feed) and 0.5 gram of iron oxide were accurately weighed and transferred into the bomb. The bomb was sealed after the addition of two steel balls. These steel balls might not have any mixing effect because the experiments were performed without any agitation. However, steel balls were added to keep a consistent procedure. Later, H_2 was admitted into the bomb through the metering valve, and the bomb was checked for any possible leaks using soap water. The temperature was monitored using a multipoint Omega digital indicator.

The temperature of the fluidized sand bath was initially kept about $5^\circ C$ above the reaction temperature. Then, the tubing bomb was quickly immersed in the sand bath, and the temperature was reset to the desired reaction temperature and held constant throughout the reaction. During that period, the temperature fluctuation was within $\pm 1^\circ C$. At the end of the reaction, the tubing bomb was quenched in cold water, and the gases were carefully vented to a fume-hood. The liquid products were collected in small glass vials via vacuum filtration, and later analyzed using gas chromatography (GC). Finally, the tubing bomb was thoroughly washed with tetrahydrofuran (THF), and the washings were vacuum filtered to collect the spent iron oxide residue.

The liquid samples were analyzed on a Varian 3700 gas chromatograph with helium as the carrier gas and with an ionization detector. Separation was achieved in a stainless steel column 8 feet long and 0.125 inch outside diameter, and packed with 3% SP-2250 on 100/120 supelcoport.

For 10 and 20 minute runs, dodecane was taken as the internal standard. An implied assumption for using dodecane as the internal standard was that the dodecane remained unchanged during the reaction. Since cracking of dodecane during the reaction is a possibility, 1-methylnaphthalene was used as the

internal standard for all later calculations. For this purpose, 1% 1-methylnaphthalene in dodecane was prepared and stored separately.

Before the analysis was performed, 1 gram of standard was mixed with 0.2 gram of sample solution each time so that the concentration of the unknown component and that of the internal standard were close enough to give consistent results. In order to calculate the benzothiophene conversion, the response curve was assumed to be linear, i.e.,

$$y = mx$$

where

y = weight ratio of benzothiophene and
dodecane or 1-methylnaphthalene,
whichever was the internal standard.

x = GC peak area ratio of benzothiophene
to dodecane or 1-methylnaphthalene,
whichever was the internal standard.

m = slope of y versus x plot
(response factor of benzothiophene)

Again, dihydrobenzothiophene was assumed to have the same chromatographic response factor as benzothiophene.

The percentage sulfur present in the spent iron oxide was determined by total sulfur analysis on SC-32 Leco, system 780-600. Approximately 0.2 gram of the sample to be analyzed was weighed and combusted with the use of oxygen in an induction furnace. The furnace temperature was maintained at 2500 F for these analyses. The resulting combustion product, SO_2 , was carried by the oxygen through a dust filter and a moisture trap. The moisture and dust free SO_2 was irradiated with infrared energy in a measuring cell. An infrared

detector selectively measured the SO₂ present, and the detector output was amplified, integrated, linearized, and displayed as percent sulfur on an electronic digital voltmeter. Before an unknown sample was analyzed the instrument was calibrated using a standard in which the percent sulfur present was known.

Results and Discussion

It has already been stated in the introduction that the present objective is to determine the effect of iron oxide dispersion and available area on benzothiophene conversion during the hydrodesulfurization of benzothiophene in the presence of iron oxide. In order to achieve this objective, a few experiments were carried out in tubing bombs or microreactors, vertical and horizontal, without shaking and under identical conditions of temperature, pressure, feed, and iron oxide loadings. The following reaction scheme was proposed:

The idea behind these experiments is that in the vertical bomb, the available area for reaction is restricted to the cross sectional area of the bomb while in the horizontal bomb, the iron oxide is spread out, in the ideal case, so that the surface available for reaction is increased. As expected, we got more conversion of benzothiophene in the horizontal bomb for given reaction conditions than the conversion in the vertical bomb. Table 17 presents the conversions for various reaction times.

It is premature now to draw definite conclusions from the few data points presented in Table 17. However, it can be seen that there is a significant

increase in conversion in the horizontal tubing bomb. For example, for a reaction time of 20 minutes, there was no appreciable conversion that could be detected in the vertical bomb, but in the horizontal bomb, it was possible to obtain 58% conversion of benzothiophene. Moreover, it was found that in one hour, the reaction was nearly complete in the horizontal bomb while in the vertical one, the conversion was far from complete even after four hours.

Since one mole of benzothiophene contains one mole of sulfur, the percentage of sulfur removed from benzothiophene could be calculated once the percentage conversion of benzothiophene was known. Thus, the calculated values of the percentage sulfur removed are shown in columns 3 and 6 of Table 17. Observed percentage sulfur present in the spent iron oxide was obtained via Leco analysis, and is shown in columns 4 and 7 in Table 17. The values agree within experimental error. Slight discrepancies were noticed at higher reaction times, which may be due to the formation of H_2S . Since gases were not analyzed after the reaction, the sulfur present in H_2S went undetected. This undetected sulfur might be responsible for the lower value of the observed percentage sulfur.

Work in Progress

Although the conversion obtained in the horizontal bomb is much greater than that in the vertical bomb, it is not possible to conclude now that the difference in conversion is primarily due to the difference in the available area alone. In fact, it was pointed out that the diffusion path for the reactants is longer in the vertical bomb than in the horizontal one. So it was necessary to determine whether or not the diffusion resistance is large enough to control the reaction.

Table 17

Percentage Conversion of Benzothiophene and Percentage of Sulfur
Removed for Reactions in Vertical and Horizontal
Tubing Bomb Reactors

Run time (minutes)	% BT Conversion	<u>Vertical Tubing Bomb</u>		% BT Conversion	<u>Horizontal Tubing Bomb</u>	
		<u>% Sulfur</u> Calculated	<u>% Sulfur</u> Observed		<u>% Sulfur</u> Calculated	<u>% Sulfur</u> Observed
10	0.0	-	-	36.85	7.22	7.25
20	0.0	-	-	57.94	11.11	9.66
30	14.54±1.49*	2.41±0.43*	1.40±0.21*	86.46±1.02*	17.38±0.32*	15.16±1.26*
60	25.43	4.74	3.34	96.82	19.46	16.40
240 (4 hrs)	82.86	16.17	10.82	-	-	-

*Standard deviation

glass tube of 0.25 inch inside diameter. In both cases, a reduction in the conversion was observed which shows that the effect of the available surface is not insignificant (See Table 18). However, more work is needed to ascertain the extent of its significance.

Table 18

Percentage Benzothiophene Conversion When
Iron Oxide Is Confined to a Reduced Area

% Benzothiophene Conversion					
Vertical bomb			Horizontal bomb		
iron oxide in the bomb	iron oxide in a tube		iron oxide in the bomb	iron oxide in a boat	
	(1)	(2)		(1)	(2)
14.54	3.95	2.16	86.46	66.34	64.95

*Reaction time: 30 minutes; other reaction conditions were the same
as before.

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APPENDIX

PROCEDURE FOR THE CALCULATION OF THE PERCENTAGE SULFUR REMOVED FROM BENZOTHIOPHENE

One mole of benzothiophene contains one mole of sulfur. Therefore,

$$\begin{aligned}\text{moles of sulfur present before reaction} &= \text{moles of benzothiophene charged} \\ &= 0.0034 \text{ mole}\end{aligned}$$

$$\text{moles of sulfur present after reaction} = 0.0018 \text{ mole}$$

This value is obtained using response factors from GC data, and contains the number of moles of sulfur present in the unreacted benzothiophene and in the dihydrobenzothiophene formed during the reaction.

$$\begin{aligned}\therefore \text{moles of sulfur removed by iron oxide} &= 0.0034 - 0.0018 \\ &= 0.0016 \text{ moles} \\ \text{gram of sulfur removed} &= 0.0016 \times 32 \\ &= 0.0512 \text{ gram}\end{aligned}$$

Since iron oxide is a very good sulfur scavenger, iron oxide is assumed to react with the sulfur removed to form only iron sulfide (FeS). Now, an elemental iron balance gives the iron oxide left unreacted.

One mole of FeS contains one mole of Fe and one mole of S.

$$\begin{aligned}\therefore \text{moles of Fe in FeS} &= \text{moles of S in FeS} \\ &= \text{moles of S removed} \\ &= 0.0016 \text{ mole} \\ \text{Fe}_2\text{O}_3 \text{ charged} &= 0.50113 \text{ gram} \\ \text{moles of Fe in Fe}_2\text{O}_3 &= 2/160 \times 0.50113 \\ &= 0.0063 \text{ mole}\end{aligned}$$

$$\begin{aligned} \text{moles of Fe remaining in Fe}_2\text{O}_3 &= 0.0063 - 0.0016 \\ &= 0.0047 \end{aligned}$$

$$\text{grams of Fe}_2\text{O}_3 \text{ remaining} = 0.0047/2 \times 160$$

(An implied assumption is that the reduction of Fe_2O_3 to FeO is not present)

$$\begin{aligned} \text{grams of FeS} &= 0.0016 \times 88 \\ &= 0.1408 \text{ gram} \end{aligned}$$

Spent catalyst is assumed to be FeS and Fe_2O_3

$$\begin{aligned} \therefore \text{amount of spent catalyst} &= 0.0376 + 0.1408 \\ &= 0.5168 \text{ gm} \end{aligned}$$

$$\therefore \% \text{ sulfur calculated} = 0.0512/0.5168 \times 100 = \underline{9.91\%}$$