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VAPOR-LIQUID EQUILIBRIUM OF AO4 SOLVENT

by

John J. Rolando

Bachelor of Science in Chemistry
St. John's University, 1983

A Thesis
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Vapor-Liquid Equilibrium of A04 Solvent

John Joseph Rolando, M.S.

The University of North Dakota, 1986

Faculty Advisor: Dr. Thomas C. Owens

The major purpose of this study was to determine the vapor-liquid equilibrium of A04 (anthracene oil #4) solvent at typical coal liquefaction operating conditions. The experimental apparatus used was the University of North Dakota's single-stage, hot charge, batch autoclave system which was specially designed to simultaneously sample both liquid and vapor phases. Six autoclave runs were made according to the following test matrix: (a) one run to determine the vapor pressure of A04 at temperatures ranging from 20 to 440 C, and (b) five time sample runs to determine the A04 vapor-liquid equilibrium distribution at temperatures ranging from 300 to 440 C and average autoclave pressures of 2100, 2560, 3050, 3635, and 4010 psia. Each autoclave run consisted of a 1200 gram charge of solvent, and nitrogen gas was used to build reactor pressures to the desired levels.

The vapor pressure of A04 increased with increasing temperature from a low value of 16 psia at 21.5 C to a high value of 354 psia at 443.7 C. This increase in vapor pressure occurred gradually at the lower temperatures (21.5 to 100 C) and with increasing slope as the temperature increased. The Clausius-Clapeyron relationship was used to

further analyze the pressure-temperature data. From this analysis, three distinct enthalpies of vaporization corresponding to the light, middle, and heavy oil components of A04 (assuming ideal gas behavior) were determined to be 979, 6316, and 30,920 Btu/lbmole, respectively. In addition, results indicate that the molar volume of A04 in the gas phase dramatically decreased from a high value of 239.8 cu.ft./lbmole at 16.5 psia to a value of 6.9 cu.ft./lbmole at 134 psia, and then leveled out at a final value of 0.5 cu.ft./lbmole at 328 psia. It was also found that as the temperature increased, the weight fraction of A04 in the vapor phase increased from 0.8 percent to a maximum of 68 percent. At the highest temperature studied (440 C), the weight fraction of A04 in the vapor phase varied from 45 percent at 4010 psia to 68 percent at 2560 psia. In addition, the fractions of light and middle oils present in the liquid phase decreased from 88 percent to 69 percent as the temperature increased.

This thesis submitted by John J. Rolando in partial fulfillment of the requirements for the degree of Master of Science from the University of North Dakota has been read by the Faculty Advisory Committee under whom the work has been done, and is hereby approved.

Thomas C. Owens

Dan T. Green

Donald E. Foster

This thesis meets the standards for appearance and conforms to the style and format requirements of the Graduate School of the University of North Dakota, and is hereby approved.

A. William Johnson 10/22/86

Title: Vapor-Liquid Equilibrium of A04 Solvent

Department: Chemical Engineering

Degree: Master of Science

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Signature John J Rolando

Date August 27, 1986

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Finally, I would like to dedicate this thesis to my mother and father. Only with their support, patience, and understanding, was I able to complete my college career. But it is their love for me and for each other that will give me faith, courage, and guidance throughout my life.

ABSTRACT

The major purpose of this study was to determine the vapor-liquid equilibrium of AO4 (anthracene oil #4) solvent at typical coal liquefaction operating conditions. The experimental apparatus used was the University of North Dakota's single-stage, hot charge, batch autoclave system which was specially designed to simultaneously sample both liquid and vapor phases. Six autoclave runs were made according to the following test matrix: (a) one run to determine the vapor pressure of AO4 at temperatures ranging from 20 to 440 C, and (b) five time sample runs to determine the AO4 vapor-liquid equilibrium distribution at temperatures ranging from 300 to 440 C and average autoclave pressures of 2100, 2560, 3050, 3635, and 4010 psia. Each autoclave run consisted of a 1200 gram charge of solvent, and nitrogen gas was used to build reactor pressures to the desired levels.

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CHAPTER 1 INTRODUCTION

Many liquid fuels can be produced by the process of coal liquefaction. Improvement and upgrading of this coal conversion technique is a continual process. One major aspect of coal liquefaction that is presently under scrutiny is the role of reaction solvents in the process. Reaction solvents play an important function in this coal conversion process, and understanding the physical and chemical characteristics of these solvents is vital to improving process efficiencies and product yields. The vapor-liquid equilibrium phase distribution of reaction solvents at the high temperatures and pressures of the coal liquefaction process are of particular interest.

As part of a comprehensive study that includes investigating the vapor-liquid equilibrium of four commonly used liquefaction solvents, this research examines the vapor-liquid equilibrium phase distribution of anthracene oil #4 (AO4) at temperatures ranging from 300 to 440 C and pressures ranging from 2000 to 4000 psia. The complete study involves these other reaction solvents: hydro-treated anthracene oil (HAO61), solvent refined lignite (SRL), and phenolic solvent.

The purpose of this study, then, was to determine the equilibrium phase distribution at the temperature and pressure conditions mentioned. In addition, weight distribution of light, middle, and heavy oils present in each of the liquid and vapor phases was determined. The experimental apparatus used was the University of North Dakota's single-stage, hot charge, batch autoclave system, which was capable of simultaneously sampling both liquid and vapor samples.

Chapter 2 discusses the background of coal liquefaction and the role that solvents play in the process. In addition, pressure and temperature equilibrium considerations are discussed, and previous work in this research area is briefly examined. Chapter 3 gives a detailed description of the experimental procedure and operating equipment utilized in this project. Chapter 4 presents and discusses the results of this study. Finally, Chapter 5 draws some conclusions about this project and makes some recommendations for further work in this research area.

CHAPTER 2 THEORETICAL BACKGROUND

This chapter examines the basic theory behind this research study. The first sections define coal liquefaction and the major role solvents play in this process. The solvent used in this study, AO4, is then described in detail. Finally, theoretical aspects of vapor pressure and temperature equilibrium are examined along with previous work done in this area.

I. COAL LIQUEFACTION AND THE ROLE OF SOLVENTS

This section is divided into two major areas: coal liquefaction and the role that solvents play in this process.

A. Coal Liquefaction

Coal liquefaction is a process by which coal is broken down and converted into liquid fuels by the direct or indirect addition of hydrogen. In other words, the large and complex structures in a coal molecule are broken down at high temperatures and pressures exposing many free radical carbon bonding sites. These bonding sites are then "capped off" with hydrogen that is present in the reaction system to form various liquid hydrocarbons. The key reaction, then, in coal liquefaction is the hydrogenative stabilization of radical fragments produced thermally from the coal (1).

The coal liquefaction processes currently under study are primarily "second generation" systems. Temperatures in these processes range from 350 to 450 C and pressures vary from 1400 to 4250 psia (2).

As mentioned earlier, stabilization of the free radical bonding sites by the addition of hydrogen is the key reaction in coal liquefaction. Therefore, the source of this hydrogen is a major concern in the process; these sources are: (1) molecular hydrogen in the gas phase, (2) the coal itself, and (3) a reaction solvent (1). This study stems from the fact that the reaction solvent is a source for hydrogen and, therefore, has a major role in coal liquefaction.

B. Role Of Solvents

Reaction solvents used in coal liquefaction processes have three central functions: (1) to initially break up the coal and aid in dispersing the coal into a slurry, (2) to act as a transfer agent for transporting coal into the reactor, and (3) to act as a hydrogen donor during the reaction. In addition, a good reaction solvent must be compatible with the products of this thermal dissolution of coal. The liquefaction solvent may function as a direct source of hydrogen (hydrogen donor), an indirect source of hydrogen (hydrogen shuttler), or as a hydrogen abstractor. In commercial processes, the solvent is derived from coal and must be suitable for recycle operation (3).

The selection and proper utilization of the reaction solvent affects both product yields and operability during the liquefaction process (4). Solvents generally comprise 75 percent of the mass of a typical liquefaction process, and therefore, greatly influence the reaction outcome. Because it has such an important function, a better understanding of some of the physical properties of the reaction solvent is necessary. Understanding the physical changes the solvent undergoes during the liquefaction process is vital to the improvement of yields and conversion.

One physical characteristic of reaction solvents that has drawn interest in recent years is the vapor-liquid equilibrium distribution of these solvents at liquefaction operating conditions. With an understanding of this distribution, proper selection of reaction catalysts could be made, reactor design could be improved, and ultimately, the efficiency of the coal liquefaction process could be increased. Vapor-liquid equilibrium distribution is the basis for a study to better understand the coal liquefaction process and the role of reaction solvents. This study concentrates on AO4 solvent, which is described in detail in the following section (5).

II. ANTHRACENE OIL #4 (AO4)

The solvent used in this study was anthracene oil, a coal-derived mixture from batch number four (AO4) obtained from Crowley Tar & Chemical Company, New York. It is a mixture of many solid hydrocarbon constituents at various concentrations that, when combined, form a liquid (6). Table 1 lists the constituents of A04 and their weight fractions based on gas chromatography analysis (7). As can be seen, A04 contains a multitude of components including straight chain alkanes and many ringed compounds. The major constituents are phenanthrene (16.59 percent), acenaphthene (9.54 percent), and fluoranthene (6.87 percent).

Table 2 gives a standard vacuum distillation analysis of A04 along with its elemental analysis. As the table shows, A04 contains only 3.1 percent light oils (boiling range of IBP to 120 C at 5 Torr) and 85.1 percent middle oils (boiling range of 120 to 260 C at 5 Torr) (8). The low boiling range light oils are compounds in the six- to eight-carbon structure range (example: benzene), while the higher boiling range middle oils fall into the ten- to twelve-carbon structure category (example: anthracene).

An understanding of the vapor-liquid equilibrium distribution of A04 at liquefaction operating conditions is important to improving conversions. The following section describes some of the basic pressure-temperature equilibrium theory that was used as a basis in this study.

III. PRESSURE-TEMPERATURE EQUILIBRIUM

The vapor-liquid equilibrium distribution of anthracene oil #4 (A04) was examined in this study. To understand this

TABLE 1 COMPONENTS OF A04

(Determined by GC Analysis of Silica Gel Fractions)

Component	Wt%	Component	Wt%
C-14	0.01	Acenaphthene	9.54
C-15	0.02	Biphenyl	0.81
C-16	0.05	Phenanthrene	16.59
C-17	0.11	1-methylphenanthrene	0.52
C-18	0.14	2-methylphenanthrene	0.84
C-19	0.14	3-methylphenanthrene	0.66
C-20	0.07	Dibenzofuran	4.95
C-21	0.04	4,5-methylenephenanthrene	1.60
C-22	0.02	Anthracene	2.02
C-23	0.02	Fluorene	6.67
C-24	0.01	2-methylfluorene	0.45
C-25	0.01	1,2 and 2,3 benzofluorenes	0.48
C-26	0.01	Pyrene	2.69
Pristane	0.09	Fluoranthene	6.87
Phytane	0.11	Benz(a)anthracene	0.26
Naphthalene	0.75	Chrysene	0.27
1-methylnaphthalene	0.86		
2-methylnaphthalene	1.44		
2-ethylnaphtalene	0.32		
2,6-dimethylnaphthalene	0.37		
2,3-dimethylnaphthalene	0.16		
1,3-dimethylnaphthalene	0.37		

TABLE 2
STANDARD VACUUM DISTILLATION ANALYSIS OF A04

ASTM-D1160 Distillation at 5 Torr	
IBP, C	94
Vol. % off at, C	
10	146
20	163
30	175
40	185
50	195
60	205
70	217
80	231
90	251
95	276
Max. Temp., C	288
Vol. % off at Max. Temp.	97
Distribution on weight basis:	
IBP - 120 C Fraction Wt.%	3.1
120 - 260 C Fraction Wt.%	85.1
260 - Max. Temp. Fraction Wt.%	7.6
Vacuum Bottoms, Wt.%	4.3
Density, g/ml at RT	1.1
Elemental Analysis:	
Carbon, Wt.%	90.66
Hydrogen, Wt.%	6.38
Nitrogen, Wt.%	0.78
Sulfur, Wt.%	0.59
Oxygen, Wt.%	1.59
H/C Ratio	0.79

Note: A04 is as received anthracene oil from Crowley Tar & Chemical Company, New York.

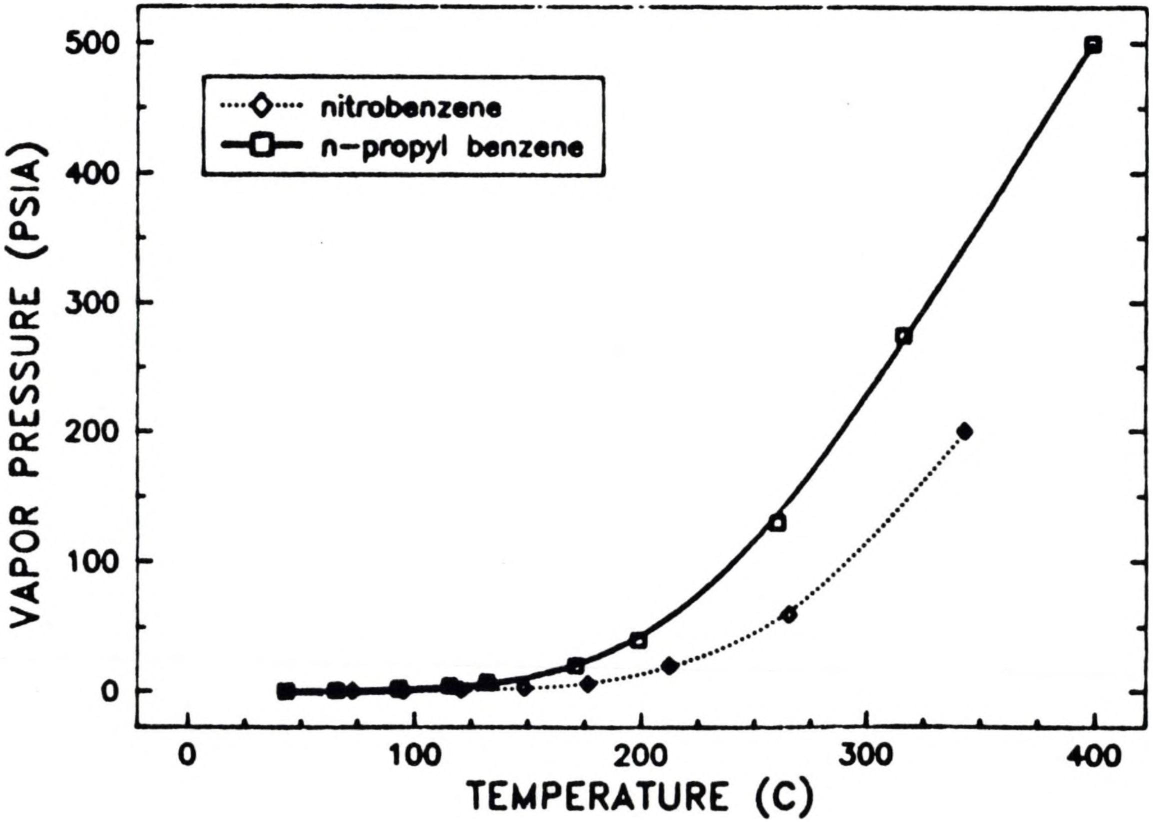
distribution, it is necessary to closely look at the theory behind this vapor-liquid equilibrium. First, the vapor pressure versus temperature relationship is discussed and how it applies to the A04 system under study. Secondly, the effects of pressure and temperature on a system in equilibrium are examined. Finally, some predictions of how A04 will respond to changes in pressure and temperature are made.

A. Vapor Pressure Versus Temperature

In general, the pressure exerted by the vapor in equilibrium with its liquid, at a given temperature, is called the vapor pressure of the liquid (9). The vapor pressure of a liquid increases with increasing temperature up to the critical point of the liquid. The increase in vapor pressure with temperature is easy to understand in terms of kinetic theory. As the temperature increases a greater proportion of the molecules acquires sufficient energy to escape from the liquid, and, consequently, higher pressure is necessary to establish equilibrium between the vapor and liquid. Above the critical temperature, the escaping tendency of the molecules is so high that no applied pressure is sufficient to keep any of them in the liquid phase, and the whole mass exists as a gas (10).

Figure 1 illustrates how vapor pressure vaires with temperature for two example compounds, nitrobenzene and n-propyl benzene. The vapor pressure increases gradually at

FIGURE 1 VAPOR PRESSURE AS A FUNCTION OF TEMPERATURE



the low temperatures, and the slope increases at the higher temperatures. This variation is expressed mathematically by the Clausius-Clapeyron equation:

$$dP/dT = \Delta H/T \times (V_G[\text{gas}] - V_L[\text{liquid}]) \qquad [1]$$

where P is the vapor pressure at temperature T, ΔH is the heat of vaporization of a given weight of liquid, V_L[liquid] is the liquid volume, and V_G [gas] is the volume of the same weight of vapor (11).

For vaporization processes at low pressures, approximations can be introduced into the above equation by assuming that the vapor phase is an ideal gas and that the molar volume of the liquid is negligible compared with the molar volume of the vapor. These assumptions are expressed as follows:

$$V_G - V_L = V_G = RT/P \qquad [2]$$

The Clapeyron equation becomes:

$$dP/dT = \Delta HP/RT^2 \qquad [3]$$

or

$$(dP/P)/(dT/T^2) = \Delta H/R \qquad [4]$$

or

$$\Delta H = -Rd(\ln P)/d(1/T) \qquad [5]$$

Equation 5 relates the latent heat of vaporization directly to the vapor pressure versus temperature curve. Specifically, this equation indicates that ΔH is given by the slope of a plot of ln (P) versus 1/T. This equation implies that ΔH is almost constant, independent of T. This is not true, and the assumptions on which the Clausius-

Clapeyron equation are based are only approximately valid at low pressures (11).

This vapor pressure versus temperature theory would have a similar effect on the A04 reaction solvent under study. Each component of the solvent exerts its own vapor pressure and the sum the individual vapor pressures gives the total vapor pressure of A04 at a particular temperature. As the reactor temperature is increased, the vapor pressure exerted by the A04 should increase in a manner similar to the illustration. However, the assumptions of the Clausius-Clapeyron equation may not be valid for A04. The results of this study will address these assumptions.

B. Pressure and Temperature Effects

Once the vapor pressure versus temperature relationship has been developed, it is interesting to see the effects that higher pressures and temperatures have on the vapor-liquid equilibrium of a liquid system. For example, if a sample system is allowed to come to equilibrium at a particular temperature, the liquid will exert a specific vapor pressure. At this temperature, a certain fraction of the sample will be in the liquid phase, and the remaining fraction will be in the vapor phase. In other words, the system would be in a state of vapor-liquid equilibrium.

If this system is slowly heated, the fraction present in the vapor phase will increase as more and more molecules vaporize. Heating the system will result in a vapor pressure curve similar to those illustrated earlier. A plot of the weight fraction of the sample in the vapor phase versus temperature would result in a similarly shaped curve. That is, as the temperature increases, the weight fraction of the sample in the vapor phase increases gradually at the lower temperatures and with increasing slope as the temperature increases.

Suppose the pressure was increased on a system at equilibrium. Le Chatlier's principle briefly states that when an outside force is applied to a system at equilibrium, the equilibrium must shift to adjust to this change. In this case, the pressure would prevent the liquid molecules from vaporizing and hold them in the liquid phase. The greater the pressure applied, the more sample that would be held or would remain in the liquid phase (9).

A04 should react to pressure and temperature effects in the same general way. The specific behavior of the vapor-liquid system, that is, the weight fraction of the liquid A04 sample that is in the vapor phase at various pressures and temperatures, is the primary consideration in this research project.

IV. PREVIOUS WORK

While much work has been done on the coal liquefaction process itself, only a limited number of studies have been conducted in the area of reaction solvent characterization and phase equilibrium. This section briefly outlines some of these studies and then discusses some of the important aspects.

A. Important Studies

There have been many studies in the area of vapor-liquid equilibrium as applied to petroleum products, but only a few studies have been conducted involving coal liquids and reaction solvents like AO4. Two of these studies are examined below.

1. Vapor Pressure of Coal-Liquid Fractions (12)

In this study, a method was developed to mathematically predict vapor pressure versus temperature relationships for coal and petroleum liquids based on minimum information about the system. The correlation used has worked well in the petroleum industry but has met with difficulty in the presence of hetero-compounds (like phenanthrene and anthracene) found in coal liquids.

The prediction of vapor pressure is based on the following equation:

$$\text{Pressure (Total)} = \sum (P_i)(x_i)(a_i) \qquad [6]$$

where x_i is the mole fraction of component i, p_i is its vapor pressure, and a_i is its activity coefficient in the liquid phase. It has been found that predicting the vapor pressure for all the individual components in coal liquids is very difficult and more work is needed in this area.

2. Equilibrium in a Simulated Coal System (13)

This project examined the vapor-liquid equilibrium of a simulated coal derived liquid system at temperatures ranging from 120 to 260 C and pressures ranging from 250 to 1500 psia. An estimation of equilibrium K values was the major result of this study, but one of the drawbacks was that the liquid system was fabricated with predominantly light aromatic compounds. This simulated mixture does not adequately represent the composition of coal liquids such as A04, which contains some heavier compounds.

B. Special Aspects

Only limited work has been done in the area of vapor-liquid equilibrium of coal liquids. Most of the studies provide predictive correlations, but it would be helpful to actually determine vapor-liquid equilibrium for coal liquids. The complex structures and chemistry of coal liquids, as represented by A04, make the prediction and determination of quantities such as equilibrium K-values or liquid activities very difficult. However, with the determination of the vapor-liquid phase distribution at liquefaction operating conditions, much information can be gained to improve coal conversion processes.

CHAPTER 3 EXPERIMENTAL PROCEDURE

This chapter describes the materials and equipment used as well as the experimental procedure employed in this study.

I. MATERIALS

Following is a list of materials that were utilized in this study.

A. Anthracene Oil #4

The solvent used in this study was an anthracene oil from batch number four (AO4) obtained from Crowley Tar and Chemical Company.

B. Nitrogen Gas

Nitrogen gas was obtained in 1700 psig cylinders from Dow Supply Company. This gas was used to pressure test the autoclave and quench vessels. In addition, because nitrogen is inert under the operating conditions studied, it was used to build autoclave pressures to the desired levels.

C. Calcium Carbonate

Calcium carbonate ($CaCO_3$) was used to indicate the vapor-liquid distribution. Calcium carbonate is a stable compound and is not soluble in tetrahydrofuran (THF). In addition, this compound does not vaporize at the temperature ranges studied and remains in the liquid phase. (See Appendix A for a discussion on the utilization of calcium carbonate.)

D. Tetrahydrofuran

Tetrahydrofuran (THF) was the solvent used to determine the phase distribution of A04 samples. In addition, it was used for clean up procedures as most components of A04 are readily soluble in THF.

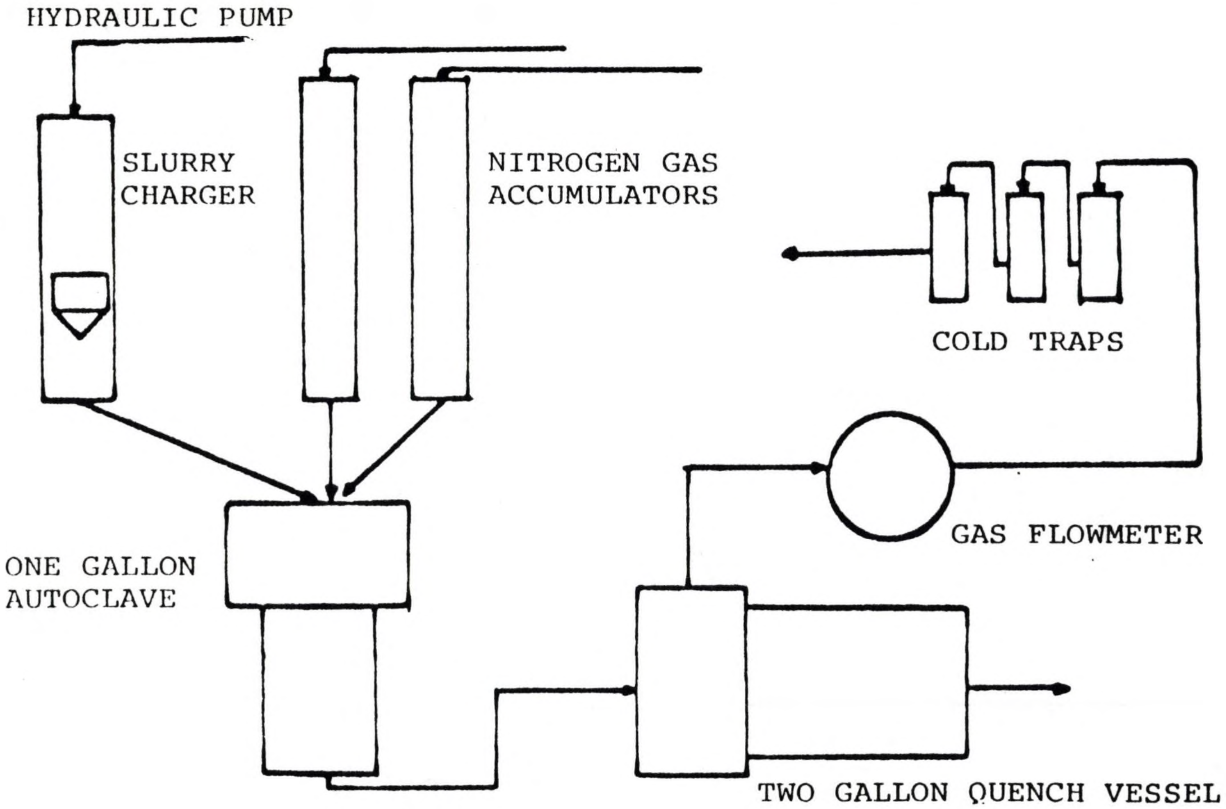
II. EQUIPMENT

The University of North Dakota's single-stage, hot charge, batch autoclave system was used in this study. Figure 2 is a schematic diagram of this autoclave system, and Figure 3 is a photograph of it.

The one-gallon A04 slurry charge vessel, constructed of stainless steel and equipped with a movable hydraulic piston, was rated at 10,000 psig. The nitrogen feed gas system consisted of two 2.5 gallon piston accumulators rated at 10,000 psig. The autoclave was constructed of stainless steel and had a void volume of approximately one gallon. (See Appendix B.) It was equipped with a magnetic stirrer, temperature and pressure detectors, and was capable of simultaneously sampling liquid and gas phases during operation. The autoclave let-down, or quench vessel, had a volume of about 2 gallons. (See Appendix B.)

The gas and liquid sampling loops, constructed of 1/4

FIGURE 2 UND'S AUTOCLAVE SYSTEM



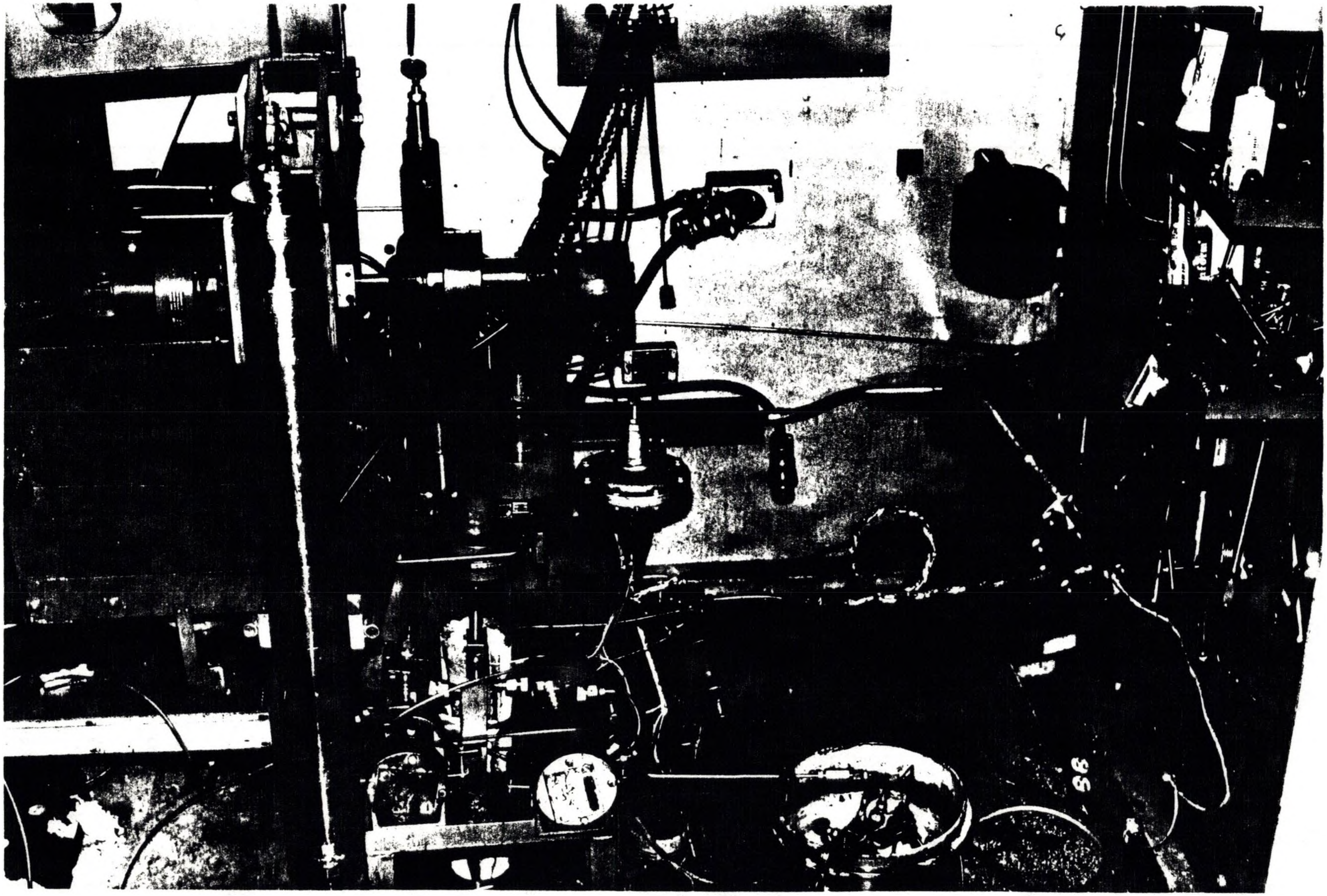


FIGURE 3 PHOTOGRAPH OF AUTOCLAVE APPARATUS

inch high pressure stainless steel tubing, were specially designed for this project. The gas samples were collected in a "make-shift" tubing bomb condenser as shown in Figure 4. All major valve operations were controlled using a Gould P-180 computer.

III. PROCEDURE

The following sections describe the experimental procedure employed in this study from the initial autoclave pressure test and sample preparation to final sample collection and analysis. Each experiment, or run, lasted approximately ten hours.

The test matrix included the following experiments:

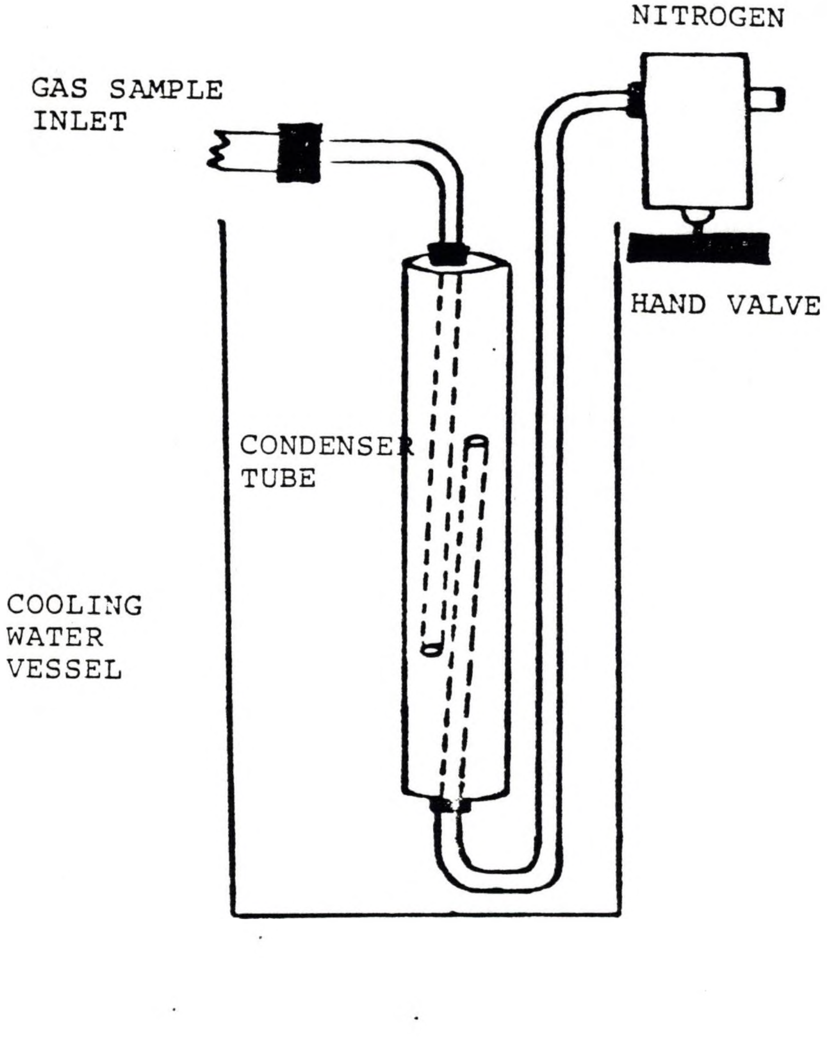
(1) One autoclave run: partial pressure of A04 determination. In this run, A04 was cold charged to the autoclave and heated from room temperature to 450 C. Partial pressure and temperature readings were taken periodically.

(2) Five autoclave runs: hot charge of A04. In these runs, the A04 charge was heated through the temperature range of 300 to 440 C at a constant reactor pressure. The five system pressures studied were 2000, 2500, 3000, 3500, and 4000 psia. Time samples were taken periodically during each run.

A. Pressure Test

The autoclave, quench vessel, and sample lines were

FIGURE 4 GAS BOMB CONDENSER



tested by charging the system with nitrogen gas to 4000 psig from the piston accumulators. This test was necessary to prevent, detect, and repair leaks before the system was used for each run. Nitrogen was selected as the pressure test gas because it was the gas used to build autoclave pressure once experiments were underway and A04 had been charged to the system.

B. Charge Preparation

The autoclave charge mixture, which consisted of A04 and calcium carbonate in a 95/5 ratio by weight, was prepared in the following manner. The A04 was preheated at low temperature (30 to 50 C) for one hour to ensure that all components of the solvent were in the liquid phase. After preheating, the A04 storage can was shaken vigorously to mix the solvent thoroughly. The A04 and calcium carbonate were then slowly combined under constant agitation. Each charge to the autoclave consisted of approximately 1140 grams of A04 and 60 grams of calcium carbonate.

C. Autoclave Charging Procedure

The autoclave charging procedure consisted of two main functions: (1) heat-up and evacuation of autoclave system and (2) injection of sample and nitrogen gas. While the charge mixture was being prepared, the autoclave system was set for charging. Gases present in the reactor were evacuated using a vacuum, and the autoclave was heated to about 250 C. Then nitrogen was forced into the autoclave from the accumulator gas feed system, building the autoclave pressure to the desired level. The A04 mixture was then charged to the heated autoclave from the hydraulic charger. This process is known as "hot charging" the autoclave, as opposed to "cold charging" in which the sample is placed in the autoclave and allowed to heat from an initial ambient state to the desired higher temperature level.

D. Sample Collection

After charging, the A04 mixture was slowly heated through the temperature range under study (300 to 440 C) while stirring at a constant rate of 1500 RPM. When a desired temperature and pressure level was reached the following sampling procedure was implemented:

1. The temperature and pressure were maintained constant for 15 to 20 minutes by adjusting the heater controller and monitoring the temperature and pressure gauges.
2. The stirrer was shut off for 20 seconds to allow droplets and entrained calcium carbonate to settle back into the liquid phase from the vapor phase.
3. The computer controlled automatic valve time sampling sequence was started. Liquid and vapor samples were simultaneously collected. Liquid samples, extracted from the bottom of the autoclave, were transported through a heated

sampling loop and collected in pre-weighed glass vials. Vapor samples, extracted from the top of the autoclave, were collected in the specially designed "gas bomb" condenser. Pressure was manually released from the condenser using a hand valve; this left the condensed sample in the gas bomb.

4. The liquid and vapor sample lines were flushed with nitrogen gas under high pressure (2000 psig) to clear the lines. This marked the end of the automatic valve sequence. (Time length about 20 seconds.) Steps 2 to 4 were then repeated resulting in two samples for each set of temperature and pressure conditions.
5. The stirrer was started and maintained at 1500 RPM. Autoclave heaters were increased to reach the next temperature level. The liquid sample vial and the gas condenser bomb were weighed, and the results were recorded.

This procedure was followed for each set of samples. However, to ensure that the sample lines were clear before sampling and contained no residual matter from the previous samples, one or two sample "waste shots" were collected at each set of temperature and pressure conditions before the actual samples were taken. The "waste shot" sequence was exactly the same as the steps mentioned above except special waste vials and a "gas waste bomb" were used.

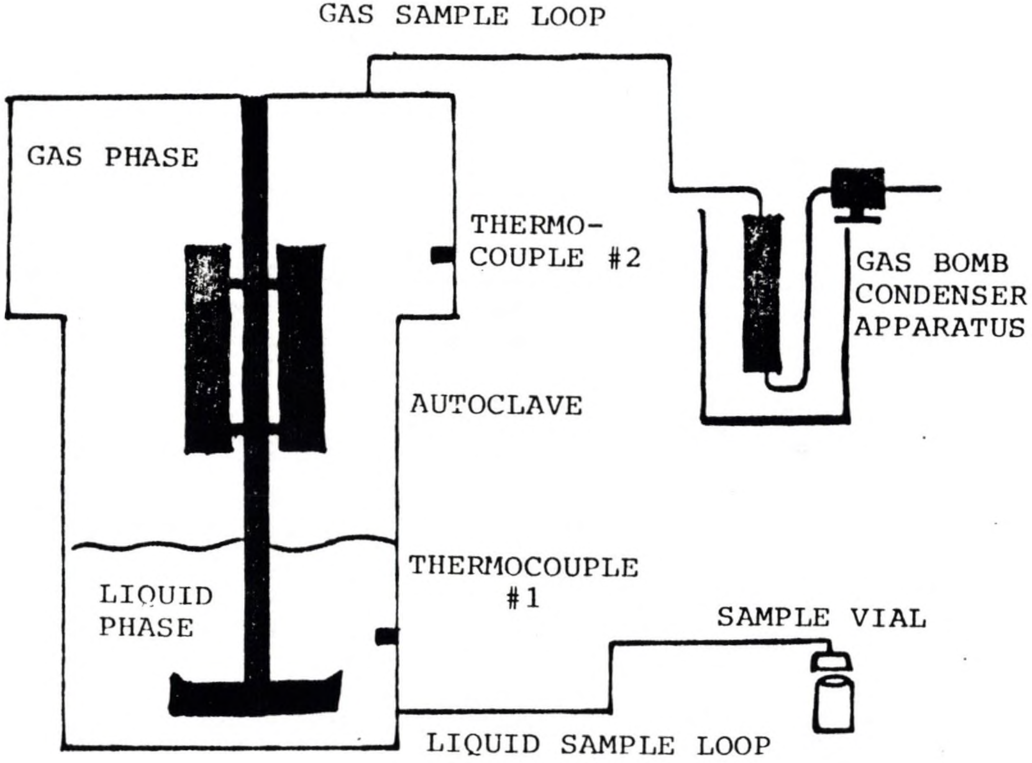
Figure 5 is a schematic diagram of the autoclave sampling system. The temperature in the autoclave was measured at two locations in the autoclave as shown in the same diagram. One of the thermocouples was located in the liquid phase near the bottom of the reactor, and the other thermocouple was positioned at the top of the autoclave in the vapor phase. It should be noted that, before sampling, these two thermocouple readings were allowed to "level out" to within a 4 to 7 degree difference using the automatic temperature controller. The liquid phase thermocouple had a higher temperature reading than the vapor phase thermocouple.

During each run, eight to ten liquid and vapor sample sets were collected at temperature intervals of 15 to 20 degrees. The pressure was maintained constant by adding nitrogen. While carrying out the sampling cycle, which consisted of two "waste shots" and two sample shots, the autoclave pressure would drop approximately 100 psig, and nitrogen was added to maintain the pressure at the desired level. Total run time was approximately six hours.

E. Quench and Material Recovery

After all samples had been collected, the remaining contents of the autoclave were released to the quench vessel and allowed to cool for ten hours. During this time A04 vapors condensed, leaving only nitrogen gas in the gas phase.

FIGURE 5 REACTOR SAMPLING SYSTEM



After completing a run, the clean-up procedure was conducted. All containers, disposable wipes, or cotton tip swabs used in the charging or clean-up operation were weighed before and after use. The difference in weight was added to the weight of the material lost from the system during the run.

The hydraulic charger vessel and valve assembly were cleaned with disposable wipes. After all surfaces were cleaned with these wipes, cotton tip swabs were used to remove any remaining material. All material that did not enter the autoclave was subtracted from the initial A04 slurry charge. The autoclave vessel was then cleaned in the same manner. Sample loops and connecting valve lines were flushed with THF to remove residual matter. The material collected in these operations was added to the liquid product weight.

The quench vessel was tilted to an upright position and the bottom valve opened to allow liquid to drain into a pre-weighed steel can. The sides were then scraped with a spatula and plunger and finally cleaned with disposable wipes. The net liquid weight from these cleaning procedures was added to the end product weight.

A series of three cold traps, followed by an in-line flow meter, was used in initial runs to recover the residual gas (nitrogen and A04 vapors left in the cooled product). However, no A04 condensed in these traps, and this step was eliminated from subsequent clean-up procedures. In all subsequent runs, nitrogen was still measured through an in-line flowmeter, and this reading was recorded. This clean-up procedure, while being time consuming, was essential to obtain material balances.

F. Analytical Procedure

Two testing methods were used for sample analysis. Liquid samples were analyzed using a THF solubility test and a standard vacuum micro-distillation. Only the micro-distillation test was used to analyze the condensed vapor samples.

sample analysis. Liquid samples were analyzed using a THF solubility test and a standard vacuum micro-distillation. Only the micro-distillation test was used to analyze the condensed vapor samples.

(1) **THF Solubility Test** - The THF solubility test was used to determine the percentage by weight of calcium carbonate in the liquid samples and, ultimately, to determine the vapor-liquid phase distribution. The procedure for the THF solubility test is detailed in Appendix C.

(2) **Micro-distillation** - The vacuum micro-distillation test was developed from the standard vacuum distillation (ASTM D-1160) and was used to determine weight fractions of distillate in both the liquid and gas samples. The micro-distillation test was developed to accommodate the large numbers of liquid and gas samples collected in each run.

This development and the procedures for standard vacuum distillation are also described in Appendix C. The results of this test gave the composition (light, middle, and heavy oils) of both the liquid and vapor phases.

High performance liquid chromatography (HPLC), which was examined as a possible analytical method, gives detailed analysis of the major constituents in each sample based on differences in molecular weight. Because of time and monetary restrictions, HPLC was not used. It is, however, briefly described in Appendix C.

G. Calculations

The calculations used in this study consisted of the material balance calculations and the calculations to determine the vapor-liquid distribution of the AO4 at each of the operating conditions.

1. Material Balance Calculations

Material balance calculations were done in three parts: (1) the determinination of mass charged into the autoclave, (2) the determination of mass leaving the autoclave, and (3) the material balance closure, which is the ratio of the mass leaving the autoclave system to the mass entering the system.

For liquid material balance calculations, the mass that was not recovered was assigned to the light oil category. These losses were assumed to be the result of the initial gas samplings in which the light oils, which comprise only 3.1 percent of the A04 charge, escaped from the system during the first sample extractions. That is, the samples may not have totally condensed in the gas bomb condenser assembly and, when the nitrogen pressure was released, a portion of the non-condensed sample escaped.

A04 vapor material balance calculations were not necessary because it was shown that the A04 samples would totally condense in the time period following each run. Therefore, only a liquid material balance calculation was necessary.

A nitrogen gas balance was also determined based on the amount of nitrogen charged into the system and the amount that was metered through the flowmeter after each run. However, this balance was flawed because, for each sample taken, an unmeasured quantity of nitrogen gas was released into the atmosphere. All nitrogen losses were assumed to be from this source. Material balance sample calculations are shown in Appendix D.

2. Vapor-Liquid Calculations

The vapor-liquid distribution calculations were based on the mass of initial charge, the mass of samples collected, and the results of the THF solubility test. The THF solubility test determined the percentage, by weight, of calcium carbonate present in each liquid sample. Using these data and the weights of the liquid and vapor samples, the vapor-liquid distribution could be determined for each temperature condition.

For calculation purposes, the liquid and gas waste shots were averaged over the total number taken. That is, the total mass of waste gas and liquid samples was divided by the number of waste shots taken in each run to obtain average gas and liquid waste shots. The computer program used in the vapor-liquid distribution calculations is shown in Appendix E along with sample calculations for this determination.

The results of the micro-distillation had to be adjusted to account for the presence of calcium carbonate in each sample. A simple calculation is shown in Appendix E as well.

Calculations dealing with the Clausius-Clapeyron equation and other minor calculations are shown in Appendix G.

CHAPTER 4 RESULTS AND DISCUSSION

This chapter outlines and discusses the major results of this study on the vapor-liquid behavior of A04 at the temperatures and pressures under consideration. In the first section of this chapter, the experimental data are presented, and the operating conditions are briefly examined. Results of the sample analysis techniques, THF solubility and micro-distillation, are given in the next section. Finally, statistical analysis on the operating conditions and sample analyses are discussed, and sources of error are pointed out and examined.

I. OPERATING DATA

The operating data for this study are given in this section. This experimental study of A04 vapor-liquid behavior consisted of six autoclave runs: one partial pressure run and five time sample runs. The operating conditions for these six runs are described below.

A. Partial Partial Run (N-311)

In the partial pressure run, A04 was charged to the autoclave at room temperature. The sample was gradually heated from the initial temperature to a maximum temperature of 445 C. As the sample was heated the pressure exerted by the A04 vaporizing in the autoclave increased. The temperature and pressure at specific points in the heat up were recorded. Table 5 in Appendix F gives the actual operating data for this autoclave run; it also contains the operating conditions at each reading. An explanation of the tabulated data for all runs is given in Appendix F.

B. Time Sample Runs (N-310,322,325,327, and 328)

Five autoclave runs were conducted in which liquid and vapor samples were simultaneously taken at selected temperatures while reactor pressure remained nearly constant. These five autoclave tests are listed below with the average system pressure for each run.

Run Number	Average Autoclave Pressure (psia)
N-310	2100
N-325	2560
N-322	3050
N-327	3635
N-328	4010

In each of these autoclave runs, the A04/calcium carbonate mixture was hot charged to the reactor and heated through the temperature range studied with periodic liquid and vapor phase sampling while maintaining a constant pressure. The operating data for each run are listed in the tables in Appendix F. Each set of conditions noted in each table indicates the temperatures and pressures at which the liquid and vapor samples were taken.

It should be noted that run N-310 (average autoclave pressure of 2100 psia) was the first of the time sample runs in this study. At the time, HPLC was to be used as the analytical technique to determine the liquid-vapor phase distribution. Therefore, no calcium carbonate was added to the A04 autoclave charge. It was later decided to replace this analytical method with the THF solubility and micro-distillation tests. All subsequent autoclave runs, N-322 through N-328, used calcium carbonate in the reactor charge mixture.

II. MAJOR RESULTS OF EXPERIMENTAL WORK

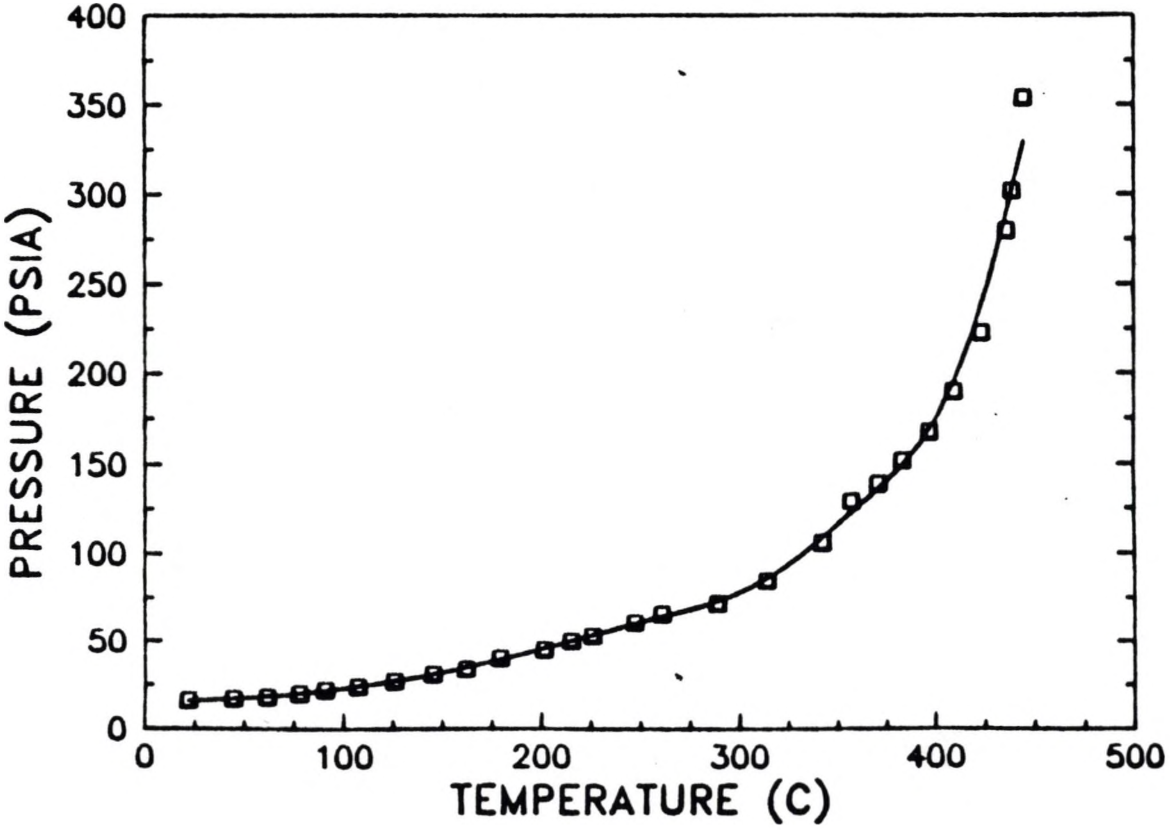
This section presents and examines the major results of this study. First, the results of the partial pressure run are covered followed by the discussion of the five time sample runs.

A. Partial Pressure Run

In the partial pressure run, the A04 sample was heated in the autoclave and the temperature and pressure were recorded at periodic intervals. Figure 6 is a plot of the partial pressure of A04 (in psia) versus the average autoclave temperature (in degrees C). It should be noted that the autoclave temperature is the average of the two thermocouple readings.

The curve illustrates that as the temperature increased, the pressure exerted by the A04 vaporizing gradually increased to about 300 C and then sharply increased up to a final pressure of 354 psia at about 445 C.

FIGURE 6 RUN N-311
PARTIAL PRESSURE OF A04



The shape of the curve is very similar to those curves illustrated in Chapter 2 and is typical for vapor pressure versus temperature data. It should be emphasized that theoretical arguments for vapor pressure versus temperature data are usually only applied to single component systems. A04 contains many components of varying concentrations, but it still yields a vapor pressure versus temperature curve that is similar to that of a single component system. The combined effect of each component of the "A04 mixture" results in this vapor pressure versus temperature relationship.

From the pressure and temperature data, the Clausius-Clapeyron equation can be used to further analyze these results and gain more information about the behavior of A04 at the study conditions. The Clausius-Clapeyron equation relates the enthalpy of vaporization to pressure and temperature data as follows:

$$dP/dT = (\Delta H)/[T(V_G - V_L)] \qquad [1]$$

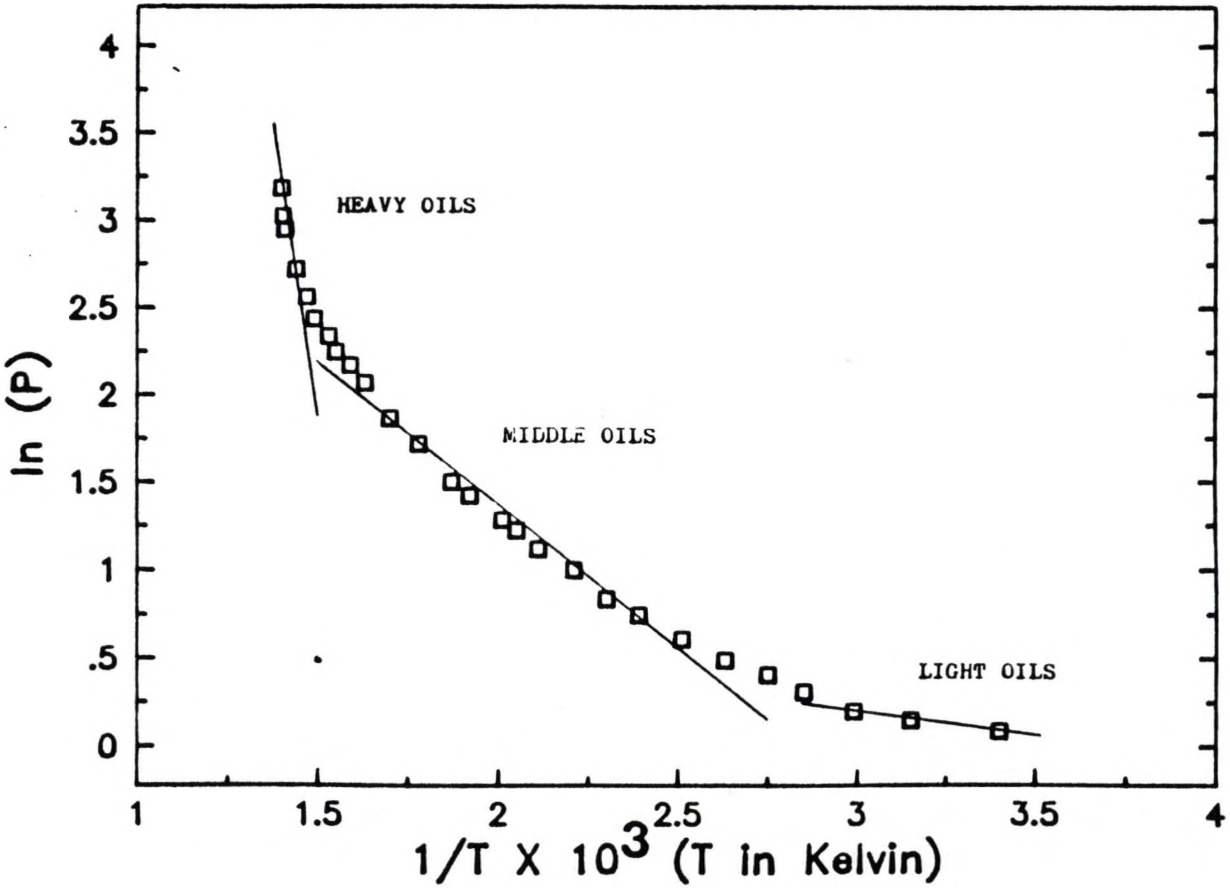
Assuming ideal gas behavior and $V_G >> V_L$, this equation becomes:

$$\Delta H = -Rd(\ln P)/d(1/T) \qquad [5]$$

ΔH can be determined from the slope of a plot of ln P versus 1/T. Figure 7 illustrates this relationship. Calculations for determining these slopes are given in Appendix G.

The curve can be divided into three "linear" sections representing the light, middle, and heavy oil components of A04. The enthalpies of these three regions are as follows:

FIGURE 7 LN (P) VS. 1/T



Region	$\Delta \underline{H}$ (Btu/lb-mole)
Light Oils	979
Middle Oils	6,316
Heavy Oils	30,920

Comparing these values to actual light, middle, and heavy oils shows that the results are in reasonable agreement. Some examples of these oils contained in A04 are listed below with their enthalpies (14).

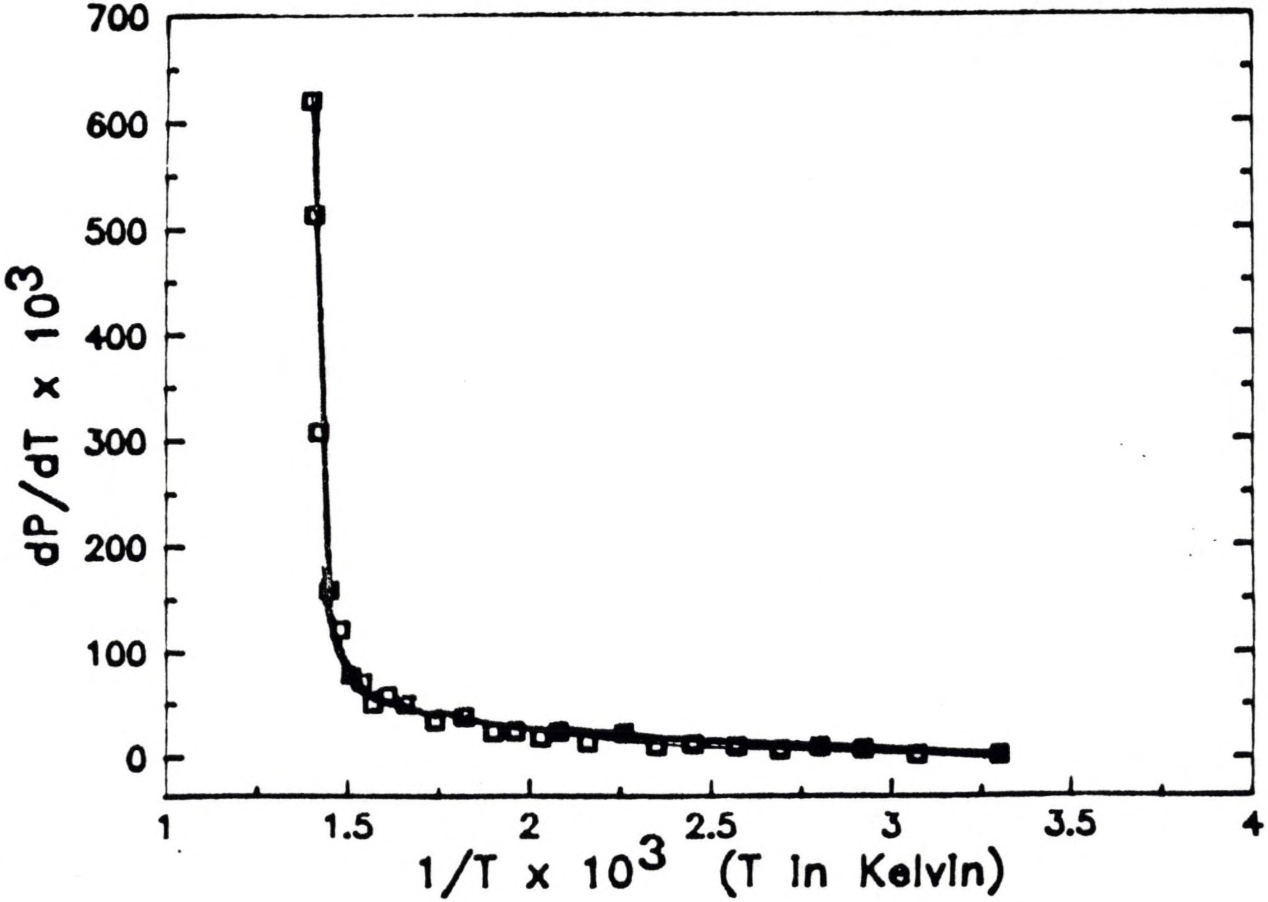
Compound	$\Delta \underline{H}$ (Btu/lb-mole)
Ethane	6,733
Naphthalene	22,168
Phenanthrene	25,539
C-25 Hydrocarbon	37,480

Another way to examine the pressure-temperature data is to use the Clapeyron equation without assuming the vapor is an ideal gas:

$$dP/dT = \Delta H/TV_G \qquad [7]$$

Figure 8 is a plot of dP/dT versus 1/T, which results from differentiating the pressure-temperature data and finding dP/dT at various temperatures. From this curve, $\Delta H/V_G$, the enthalpy of vaporization per molar volume of gas, may be determined. This differentiation and calculations for determining $\Delta H/V_G$ are shown in Appendix G. In Figure 8, the slope of the curve decreases dramatically at low values of 1/T (high temperatures) and tends to level off as the value of 1/T increases (low temperatures). Interpretation of this plot and calculations to determine $\Delta H/V_G$ indicate that the

FIGURE 8 dP/dT VS. 1/T



enthalpy of vaporization per molar volume of gas increases with temperature from a low value of 106.5 Btu/cu.ft. at 33.0 C to a high value of 49,794 Btu/cu.ft. at 441.0 C.

The effect of pressure on the molar volume of the gas is also examined. To determine this molar volume (in cu.ft./lb-mole), ΔH was assumed to be that of phenanthrene, the most abundant component in A04, and the molar volume was determined using equation 6. (See Appendix G for results and details of these calculations.) Figure 9 is a plot of molar volume of gas (cu.ft./lb-mole) versus pressure (psia). The curve shows that this molar volume dramatically decreases from a high value of 239.8 cu.ft./lb-mole at 16.5 psia to a value of 6.9 at 134 psia. This molar volume then levels out as the pressure increases to a final value of 0.5 cu.ft./lb-mole at 328 psia.

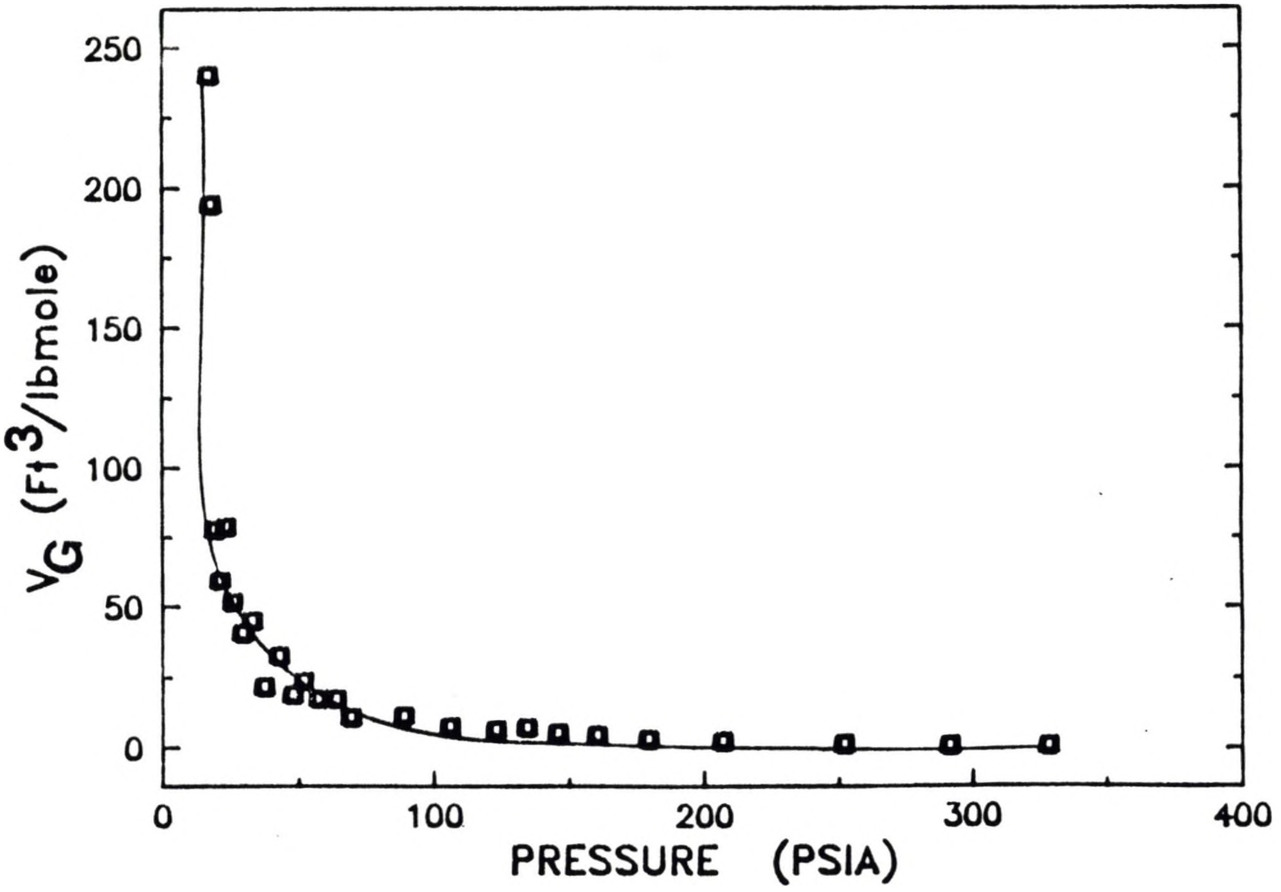
B. Five Time Sample Runs

The results for the five time sample runs were based on material balance calculations and the results from the analytical techniques (THF solubility and micro-distillation tests).

1. Material Balance Results

The material balance calculations gave the closure for each run based on the mass charged to the autoclave and the mass recovered. Tables 11, 12, 13, 14, and 15, in Appendix H, give the data necessary for material balance

FIGURE 9 MOLAR VOLUME VS. PRESSURE



calculations. These tables include the liquid and vapor sample weights, the mass of the waste liquid and vapor samples, and the mass of the clean-up materials.

A mass balance is then calculated for the run. (See Appendix D for sample calculations.) These material balance results, or closures, are also shown in the tables and are listed below.

Run Number	Closure (Percent)
N-310	96.3
N-325	96.6
N-322	96.4
* N-327	94.7
N-328	98.4

* Note: In this run, the quench can was accidently spilled onto the floor, thus lowering the material balance.

These values for the closure of the system are very high for this autoclave system. However, to be of value for a thermodynamic equilibrium study such as this, an explanation of the small loss is necessary.

The loss in each of the runs can generally be attributed to the light oils in the initial sample shots. The light oils vaporize at a low temperature at atmospheric pressure and probably did not reach condensation temperature in the gas bomb. These light oils, which comprise about 3 percent of the A04 charge, were lost when nitrogen pressure was released with the hand valve on the gas bomb condenser.

Additional losses may also be due to residual material that was left in the quench and autoclave vessels or material that was not flushed from the process and sampling lines after clean-up.

2. Analytical Techniques

The THF solubility test and the micro-distillation test were used to extensively analyze the liquid and vapor samples. (See Appendix C for detailed descriptions of these two techniques.) The THF solubility test was used to determine the calcium carbonate content in each liquid sample and, ultimately, the vapor-liquid distribution at the conditions studied. The micro-distillation was used to determine the oil distribution (light, middle, and heavy oils) of each sample.

a. THF Test Results:

The THF test indicated the calcium carbonate content present in each liquid sample. Results of this test, shown in tables in Appendix I, show that as the temperature increased, the percentage, by weight, of calcium carbonate present in each liquid sample increased. That is, as the temperature increased, more and more of the A04 vaporized, and the concentration of calcium carbonate present in the liquid phase increased. Calcium carbonate does not decompose and all of it remained in the liquid phase as indicated by the results. (Note: Run N-310, which did not use calcium carbonate in the A04 charge, was not analyzed using the THF solubility test.)

The results of this THF test were then used, in conjunction with the material balance data, to determine the vapor-liquid distributions of A04 at the temperature and pressure conditions studied. Tables 20, 21, 22, and 23 located in Appendix J give the results of this determination. Each table lists for each run the liquid sample number, the operating temperature and pressure conditions, and the percent by weight of vapor and liquid. (See Appendix E for sample calculations and the computer program used in these calculations.)

Because calcium carbonate was not used in run N-310, it was not possible to determine the vapor-liquid distribution from THF test results. Only the fractions of light, middle, and heavy oils from the micro-distillation test were determined for this run.

Figures 10, 11, 12, and 13 are graphs of the weight fraction of A04 present in the vapor phase versus temperature (in degrees Celsius) for each of the four time sample runs. In each autoclave run, the weight fraction of A04 in the vapor phase ranged from low values at 300 C and gradually increased to maximum values at about 440 C. The maximum weight fractions of A04 in the vapor phase ranged from about 47 percent in run N-328 (average pressure of 4010 psia) to about 68 percent in run N-325 (average pressure of 2560 psia).

FIGURE 10 RUN N–325
COMPOSITION VS. TEMPERATURE AT 2560 PSIA

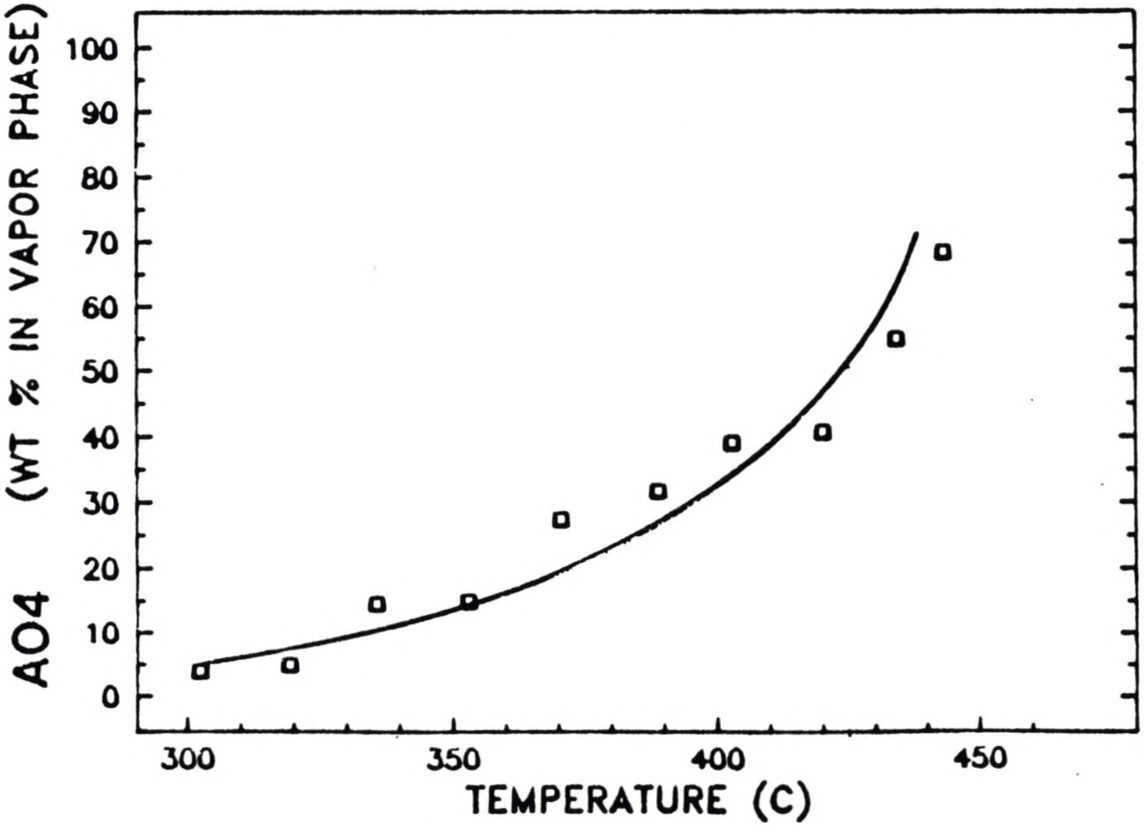


FIGURE 11 RUN N-322
COMPOSITION VS. TEMPERATURE AT 3050 PSIA

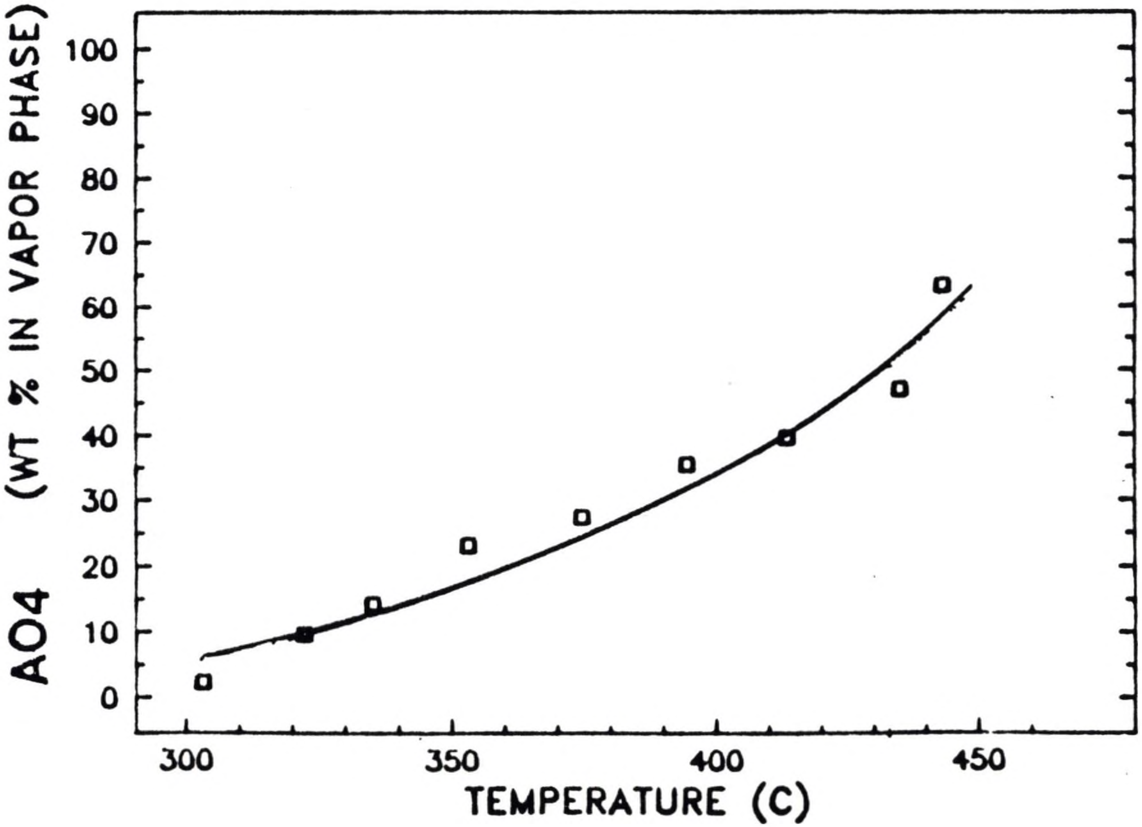


FIGURE 12 RUN N-327
COMPOSITION VS. TEMPERATURE AT 3635 PSIA

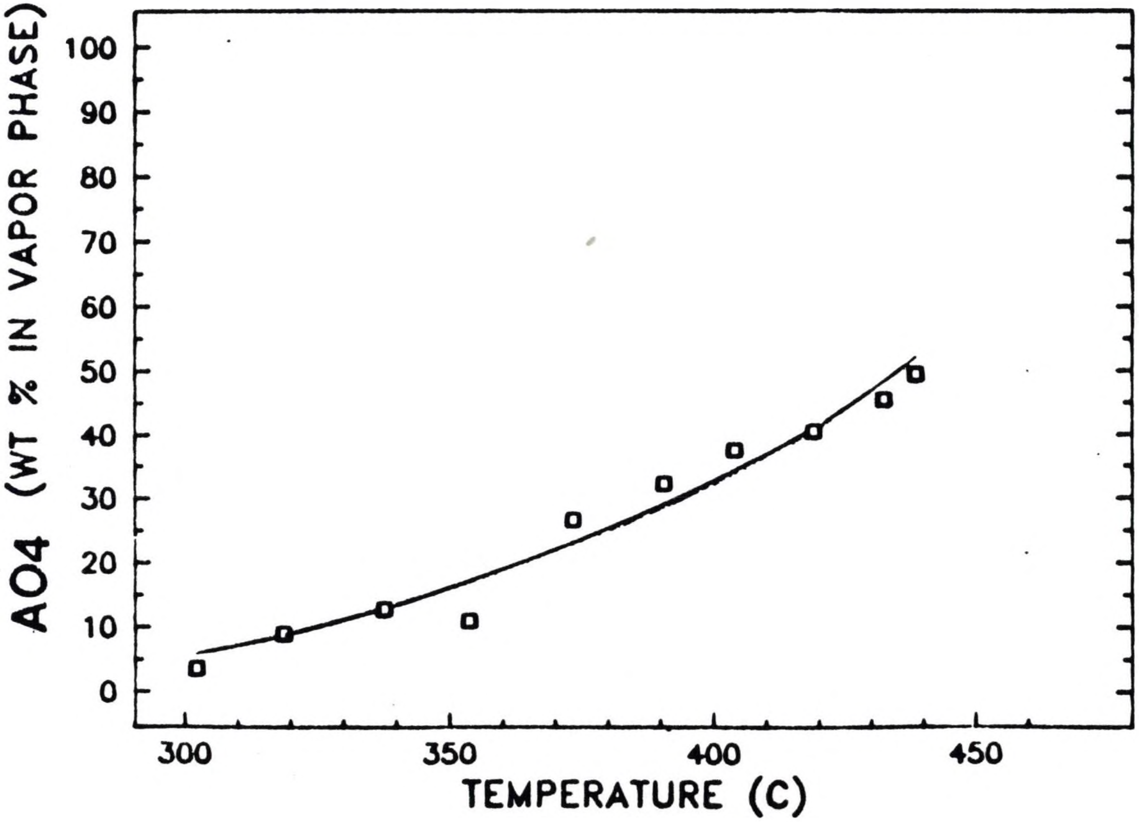
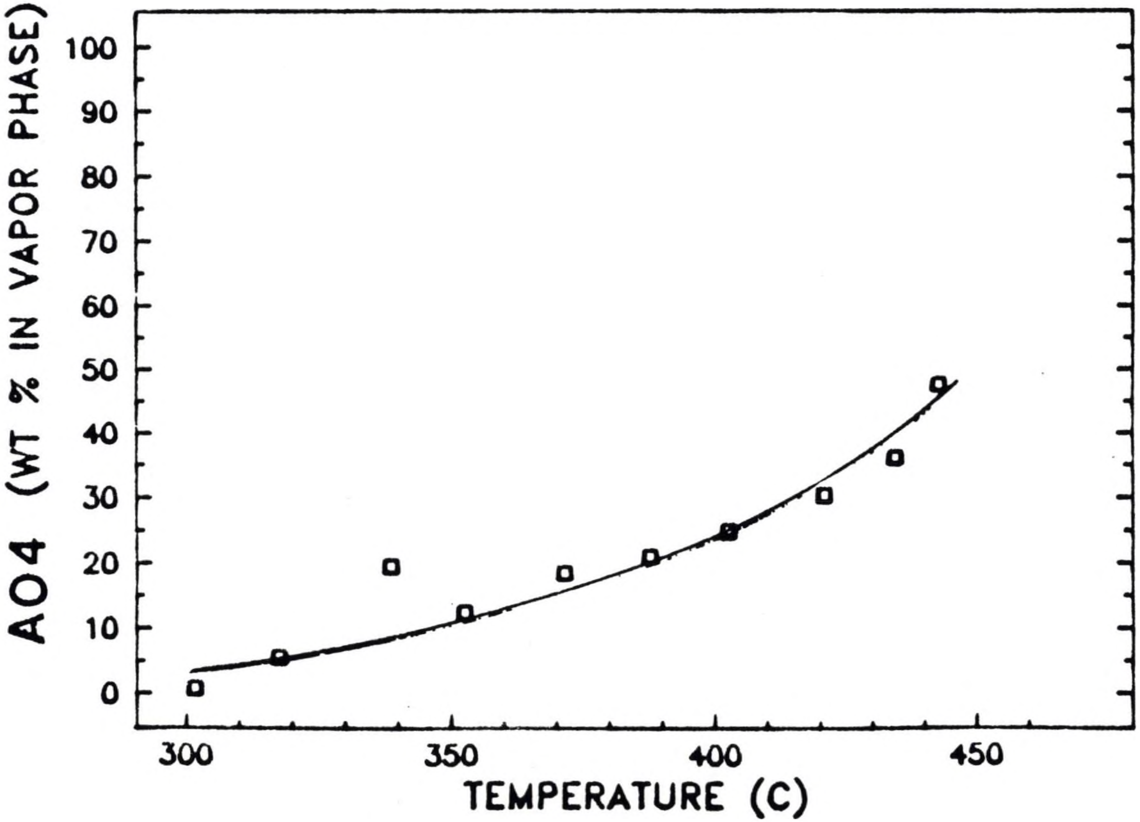


FIGURE 13 RUN N-328
COMPOSITION VS. TEMPERATURE AT 4010 PSIA



To further explain and compare these curves, two phenomena must be examined: the effect of temperature on the vapor-liquid distribution at constant pressure, and the effect of pressure on this distribution at constant temperature.

(1) **Effect of Temperature-** As the graphs illustrate, the fraction of A04 present in the vapor phase increased as the temperature increased at constant pressure. It is interesting to note that the curves generally resemble the partial pressure curve.

(2) **Effect of Pressure-** The effect of pressure on the fraction of A04 present in the vapor phase is a very important result of these experiments. To illustrate this effect, data from runs made at different pressures, but at the same temperature, are compared. As the pressure increased, with the temperature held constant, the fraction of A04 present in the vapor phase decreased. That is, the increase in pressure tends to force or hold the A04 in the liquid phase and prevent it from vaporizing. This is best explained by Le Chatelier's principle which states, "If a stress (such as a change in concentration, pressure, or temperature) is applied to a system in equilibrium, the equilibrium shifts in a way that tends to undo the effect of the stress." (9) In other words, with the increase in pressure at constant temperature, the "stress" caused by this change in pressure is undone by holding the A04 in the liquid phase.

Figure 14 illustrates the effect of pressure in comparing runs N-328, N-322, and N-325 which were tested at average autoclave pressures of 4010, 3050, and 2560 psia, respectively. As the figure shows, increased pressure tends to hold the A04 in the liquid phase.

Figure 15 is a plot of the weight fraction of A04 in the vapor phase versus pressure at various constant temperature conditions. The graph again shows the effect of pressure at different temperatures. As the pressure increased at a constant temperature, the weight fraction of A04 in the vapor phase decreased.

Effects on Liquefaction

The A04 vapor-liquid phase distribution results are important to achieving a better understanding of coal liquefaction systems. Figure 16 is a three dimensionsl plot of these equilibrium results. It illustrates the temperature and pressure conditions studied versus the weight fraction of A04 present in the vapor phase.

A04 solvent is a major constituent of the reaction mixture in coal liquefaction; it comprises about 3/4 of a typical liquefaction charge. Therefore, by understanding the vapor-liquid equilibrium of A04 (at pressures and temperatures that are commonly found in liquefaction), it is possible to properly select reaction catalysts, improve reactor design, and increase process conversion.

FIGURE 14 EFFECT OF PRESSURE ON VAPOR-LIQUID DISTRIBUTION

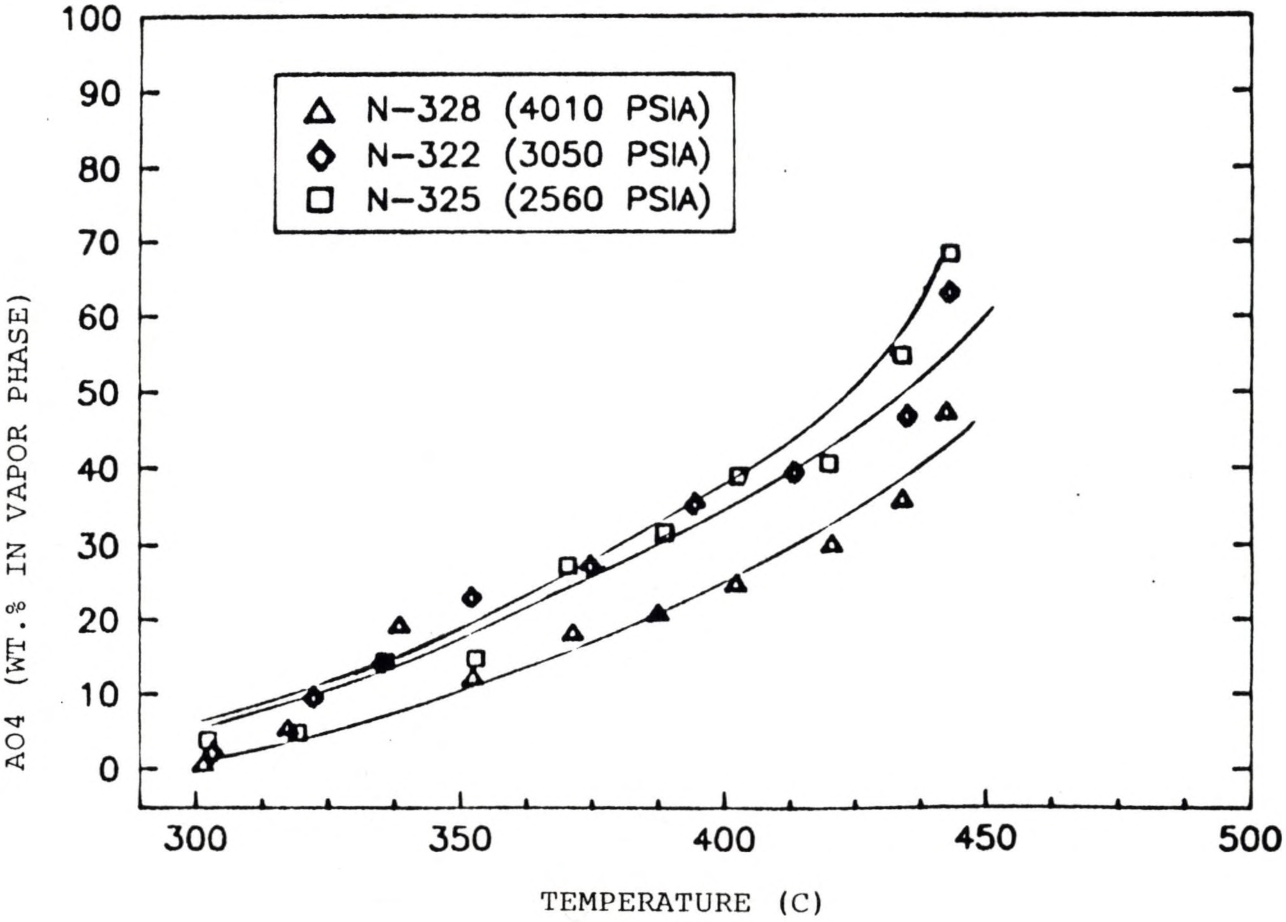


FIGURE 15 EFFECT OF TEMPERATURE ON VAPOR-LIQUID DISTRIBUTION

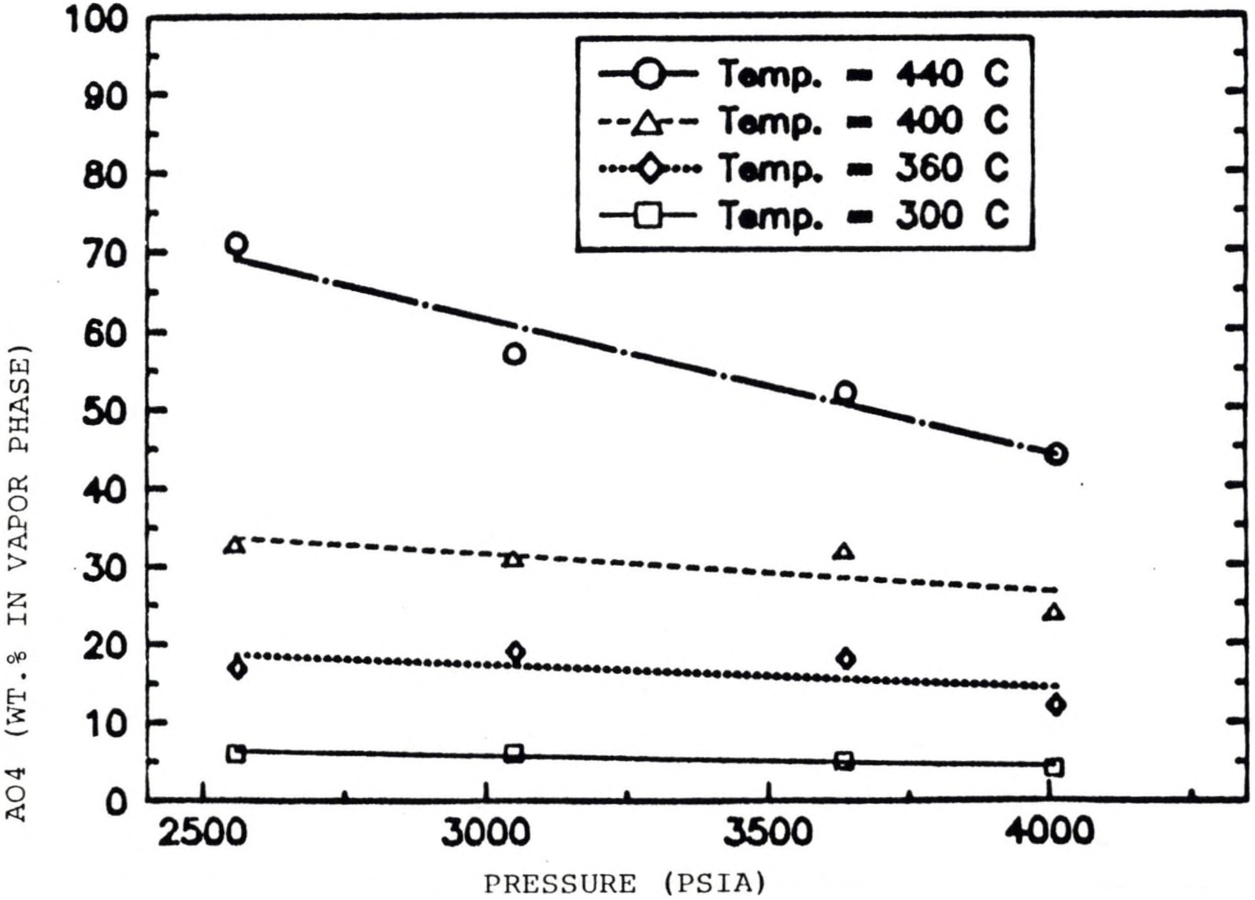
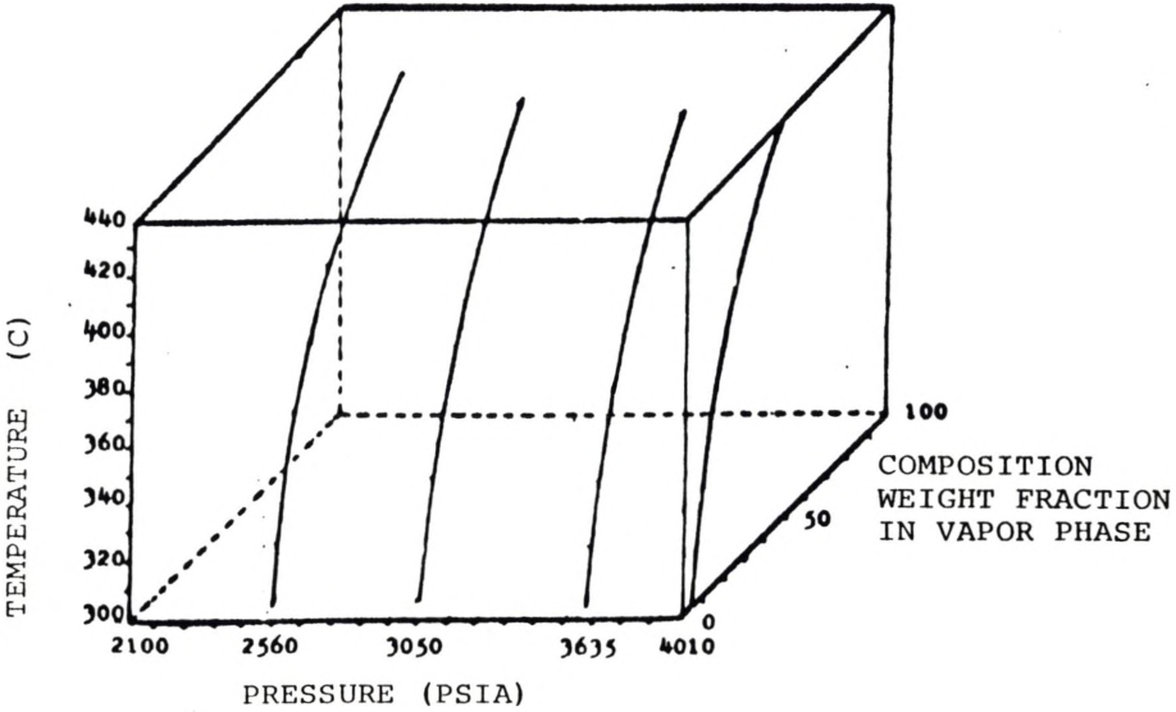


FIGURE 16 THREE-D EQUILIBRIUM PLOT



(a) Catalyst Selection- In coal liquefaction, a common yardstick used to measure a process is the conversion of coal to liquid products. The presence of an appropriate reaction catalyst can increase coal conversion. There are catalysts that improve conversion at low liquefaction temperatures (300 to 350 C), liquid phase catalysts, and catalysts that enhance conversion at higher temperatures (400 to 440 C), gas phase catalysts. Prior to this study it was not readily known why some catalysts (gas or liquid phase) performed better at some temperatures than at others. The results of this study provide some answers to that question.

Results of this study indicate that at low liquefaction temperatures (300 to 340 C), 80 to 95 percent, depending on the pressure, of the A04 is present in the liquid phase. This may explain why a liquid phase catalyst performs better than a gas phase catalyst at these low temperatures. That is, since most of the A04, which comprises most of a liquefaction charge, is in the liquid phase, a catalyst that is also in the liquid phase performs better. The opposite is true at the higher temperatures, where 50 to 70 percent of the A04 is present in the vapor phase. This may make it possible for a gas phase catalyst to perform more efficiently than a liquid phase catalyst at these elevated temperatures.

Therefore, with a better knowledge of the vapor-liquid equilibrium distribution of A04, it may be possible to make a better catalyst selection to improve the rate and conversion of coal liquefaction.

(b) <u>Reactor Design-</u> Knowledge of the vapor-liquid distribution of A04 at specific temperatures and pressures will assist in designing reactors for coal liquefaction. If the system is to be operated under conditions in which the reactants are in the gas phase, a special type of reactor, such as a tubular reactor or a fluidized bed, should be specified to enhance the gas phase reaction. Likewise, if the operating conditions are such that the reactor contents are in the liquid phase, a different type of reactor is needed.

(c) <u>Process Conversion-</u> The conversion of coal into liquid products can be greatly improved by knowing the vapor-liquid distribution of reaction solvents like A04 at particular operating conditions. A04 has a role in coal liquefaction of donating hydrogen to cap free radical bonding sites that result from the thermal cracking of coal. With an improved understanding of the phase distribution of A04, proper and effective use of this solvent may be possible.

b. Micro-distillation Results:

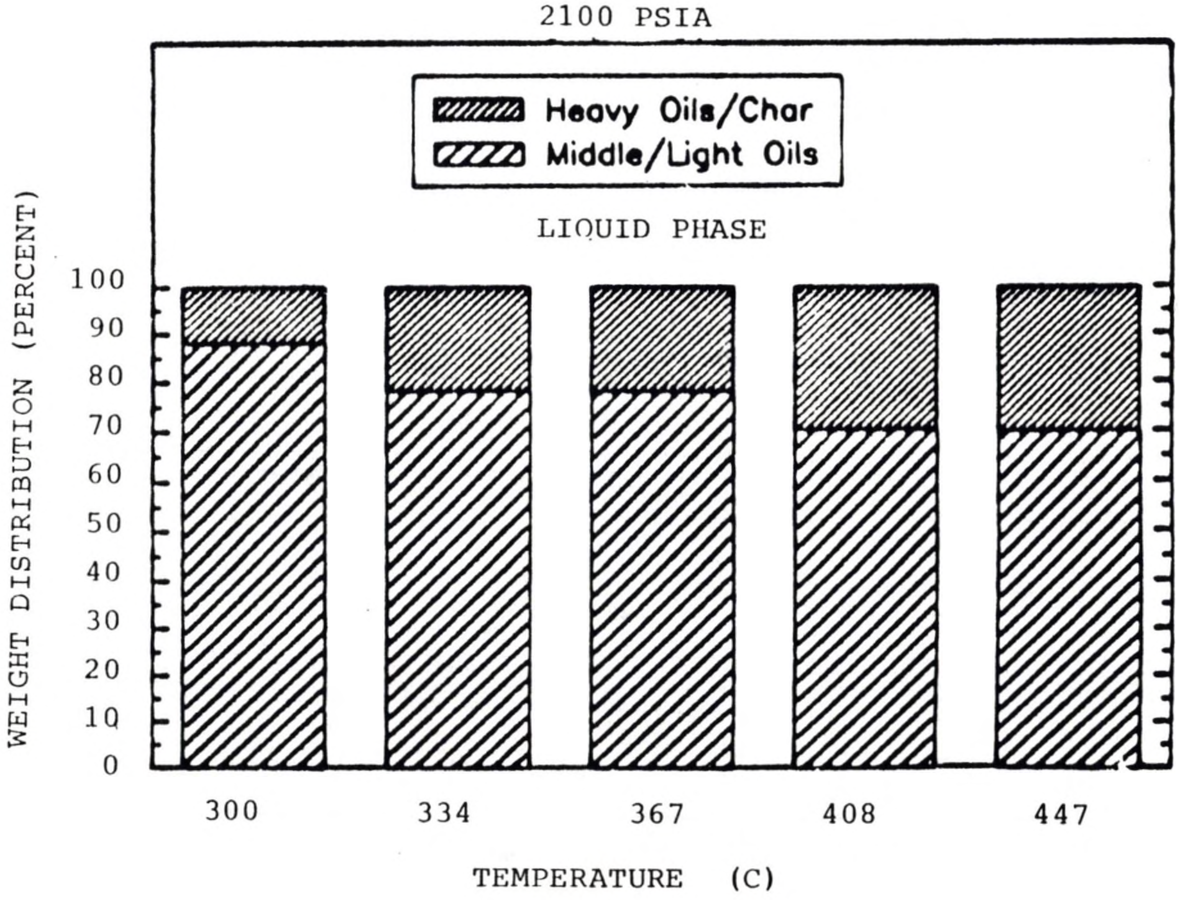
The micro-distillation test was used to determine the distillate cuts of the light, middle, and heavy oils present in each sample of the five time sample autoclave runs. Results of this test are shown in tables located in Appendix K. The results were adjusted to account for the calcium carbonate present in the liquid samples, except for run N-310, which did not utilize calcium carbonate. Calculations are shown in Appendix E.

Duplicate runs were made on most of the liquid samples. However, only a limited number of vapor samples were analyzed from each run. It was believed that the vapor samples should be 100 percent middle and light oils, and, as can be seen from the data, the average of the vapor samples analyzed was about 98 percent middle and light oils. For this reason, only a limited number of vapor samples were analyzed by micro-distillation.

The results of micro-distillation analyses are graphically illustrated in Figures 17, 18, 19, 20, and 21. In each run, the weight fraction of middle and light oils present in the liquid phase ranged from a high value of 88 percent, at the starting temperature of 300 C, and then steadily decreased as the temperature increased. The maximum weight fractions of middle and light oils obtained at the highest temperatures studied ranged from about 69 percent to 78 percent.

(1) **Effect of Temperature**-The illustrations indicate that as the temperature increased in each autoclave run, the percentage, by weight, of middle and light oils present in each liquid sample decreased, and the fraction of heavy oils

FIGURE 17 RUN N-310 OIL DISTRIBUTION VS. TEMPERATURE



2100 PSIA

FIGURE 18 RUN N-325 OIL DISTRIBUTION
VS. TEMPERATURE

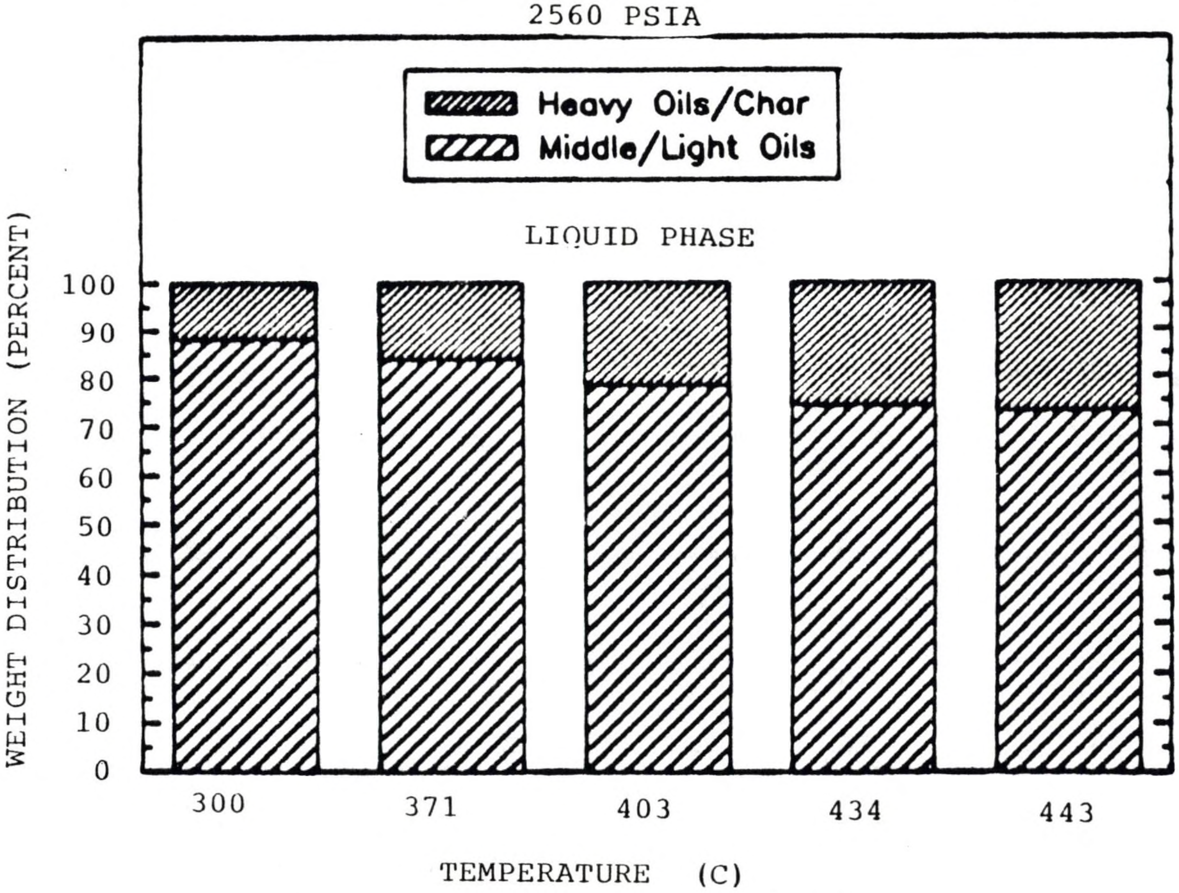


FIGURE 19 RUN N-322 OIL DISTRIBUTION VS. TEMPERATURE

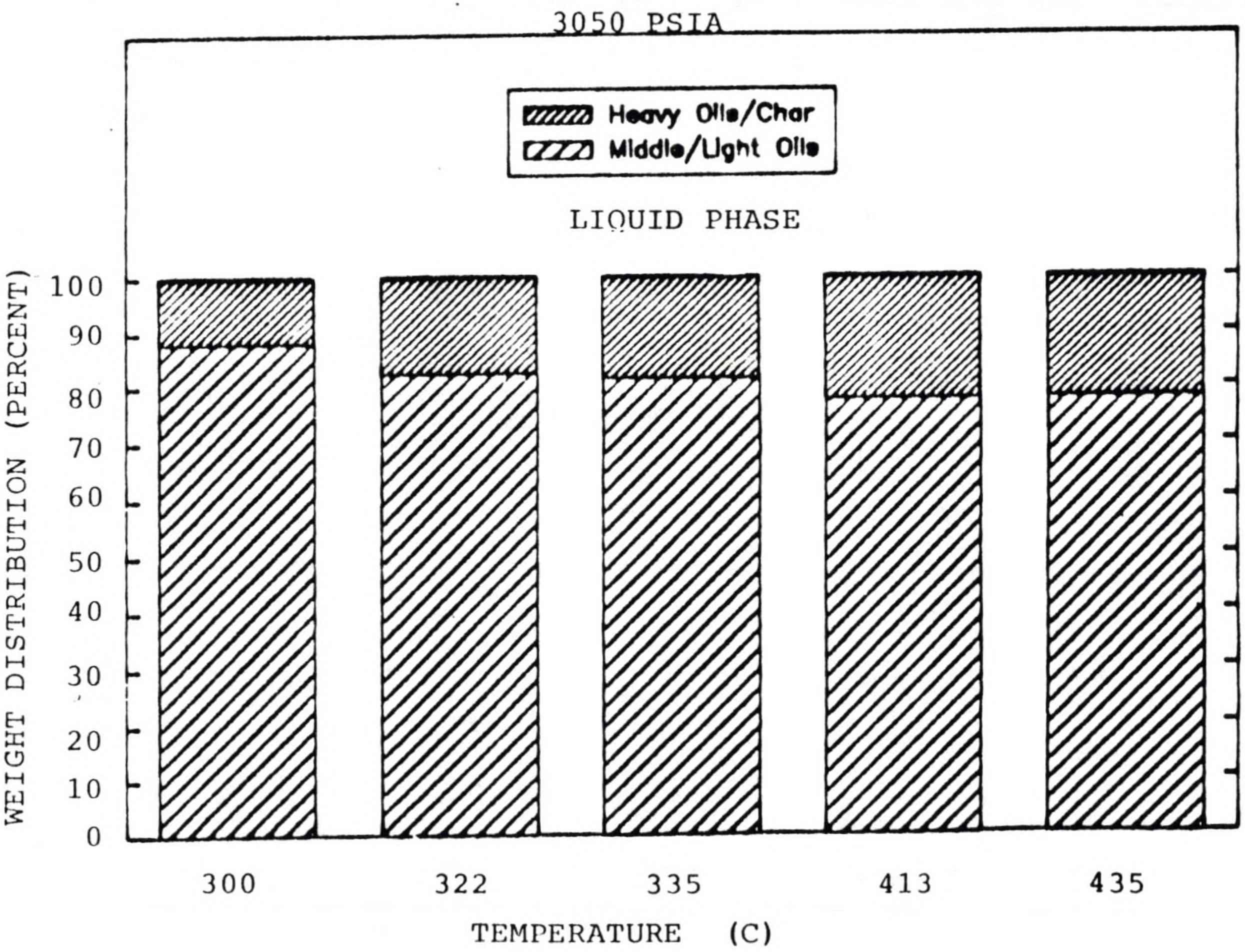


FIGURE 20 RUN N-327 OIL DISTRIBUTION
VS. TEMPERATURE

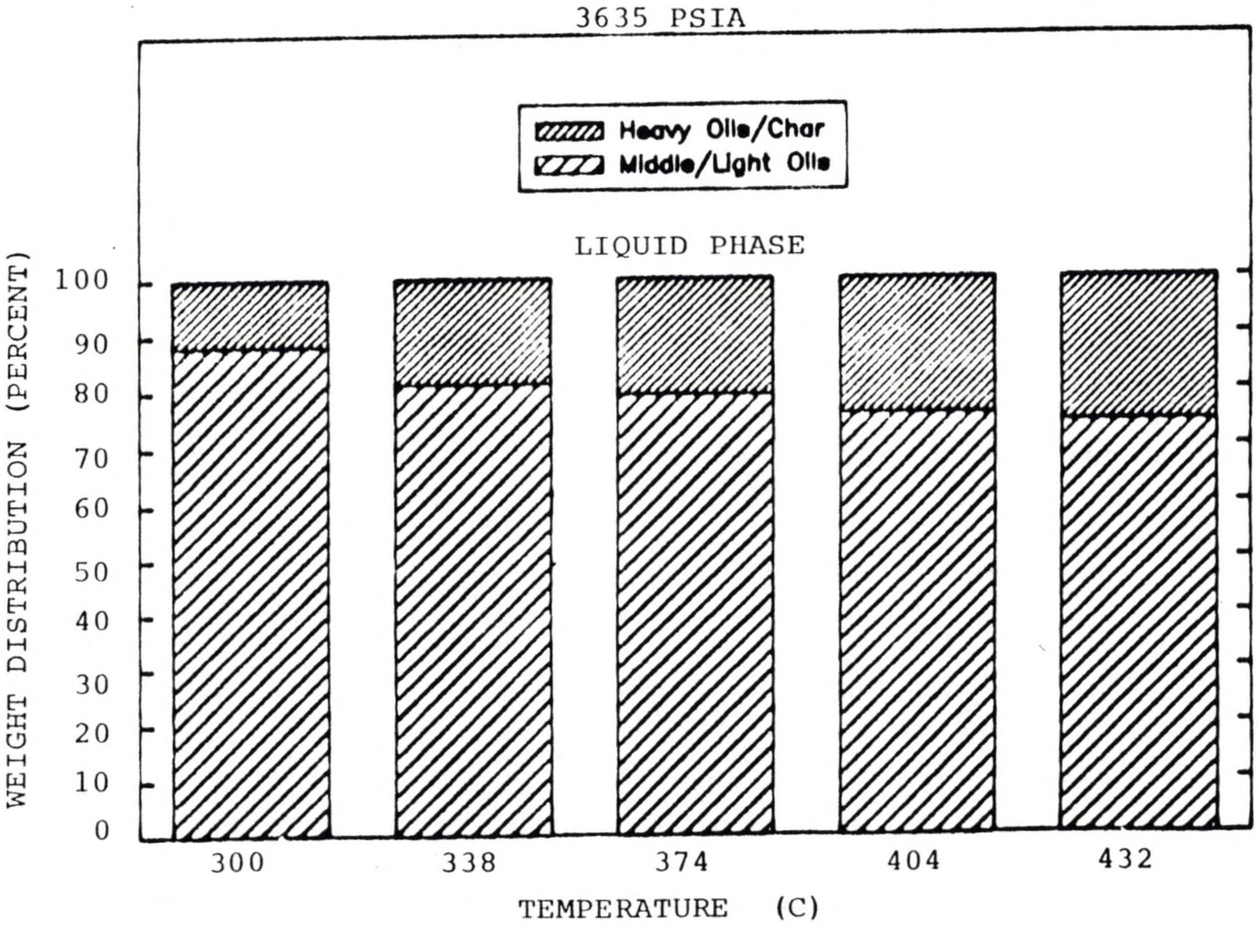
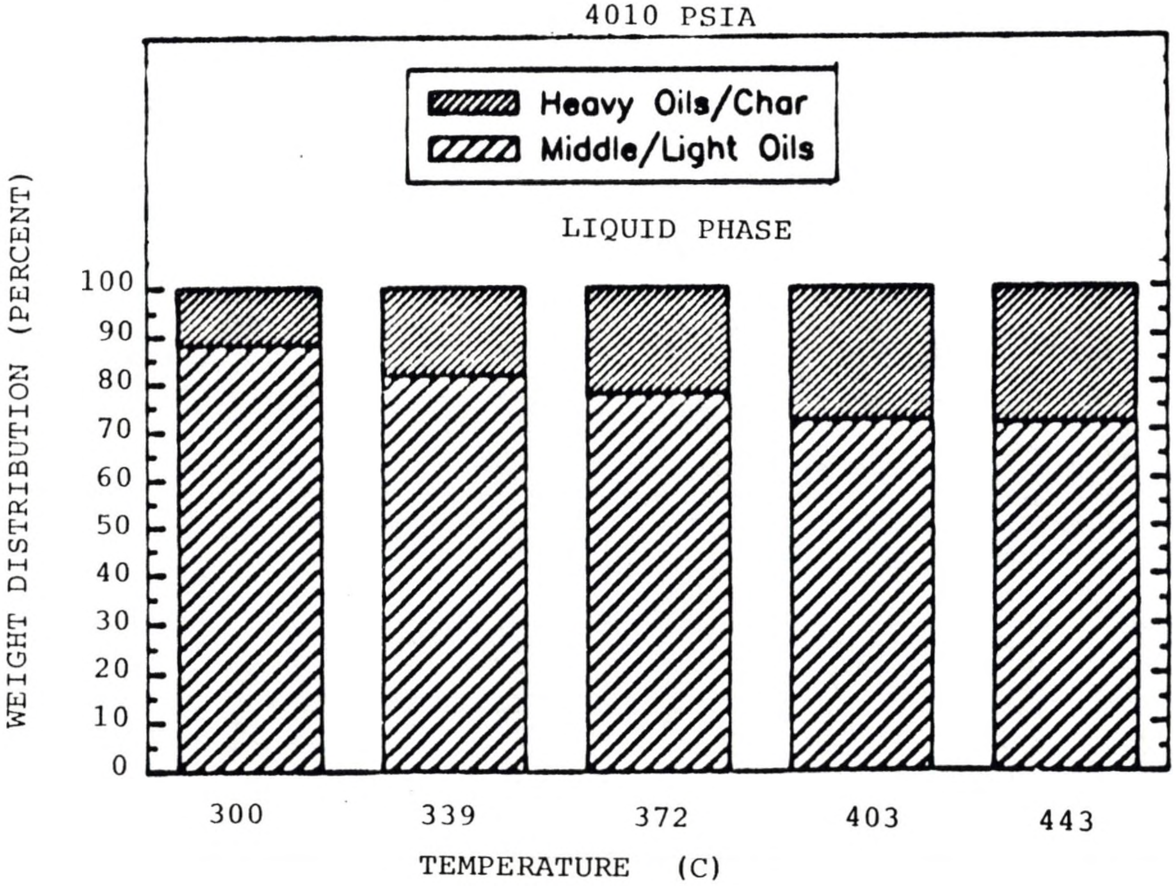


FIGURE 21 RUN N-328 OIL DISTRIBUTION
VS. TEMPERATURE



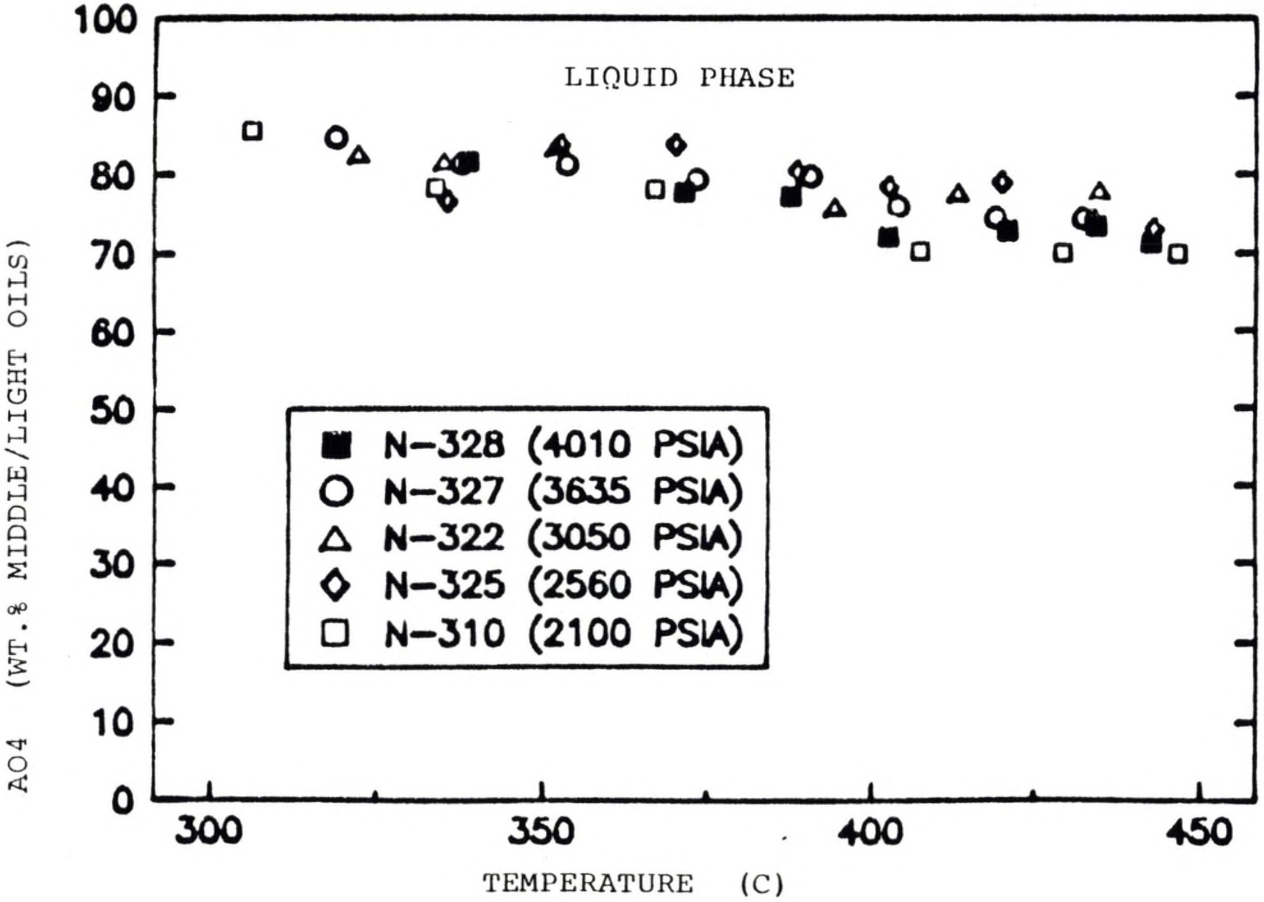
and solid residuum (or char) increased. This seems reasonable because as the temperature increased, the lower boiling range light and middle oils vaporized, leaving a liquid that is more and more concentrated with higher boiling range heavy oils and char.

(2) **Effect of Pressure-** It seems that as pressure increased at a constant temperature, the percentage, by weight, of middle and light oils present in the liquid phase should increase. Results from this study, however, do not agree as seen in Figure 22. It indicates there is no correlation for the effect of pressure on the fraction of middle and light oils present in the liquid phase. This discrepancy is shown statistically and will be discussed later.

Effects on Liquefaction

The previous results have some significance in the coal liquefaction process. The results imply that there is an effect of temperature on the middle and light oil distribution in both the liquid and vapor phases. With this knowledge of the oil distribution at different temperature conditions, it may be possible to predict the contribution of the A04 to the light, middle, and heavy oil products of a typical coal liquefaction run. In addition, it may be possible to better understand the chemistry of the liquefaction reaction and to determine the properties of the liquid and vapor phases by knowing the oil distribution at

FIGURE 22 EFFECT OF PRESSURE ON FRACTION OF MIDDLE/LIGHT OIL DISTRIBUTION



various operating conditions. That is, knowing the types of compounds present in one of the phases will help understand the chemistry and properties of that phase.

III. STATISTICAL ANALYSIS

This section describes the statistical analysis that was performed on the experimental operating conditions of this study and on the effects due to pressure and temperature on the results. In addition, this section discusses in detail the various sources of error associated with this experimental study.

A. Statistical Analysis of the Operating Conditions

The first section of this chapter listed the operating conditions for the five time sample autoclave runs, N-310 through N-328. In each run, liquid and vapor samples were collected at a "constant" pressure. A student t-test was performed on the "constant" pressure operating conditions to determine if the several operating pressures were statistically similar. The sample calculations and the results for this t-test can be found in Appendix L.

The t-tests were conducted at a significance level of 0.01. For the five runs it was found that some of the data in each run were taken at pressures that were statistically different from the average autoclave pressure. However, even by eliminating these data points from consideration, the graphs of weight fraction in the vapor phase versus temperature do not change. These pressure readings, while not being statistically similar to the average autoclave reading for each run, were numerically only about 150 psia units away from this average reading. A 150 psia deviation from the average is a small fraction when the total pressures ranged from 2000 to 4000 psia.

B. Analysis of Pressure and Temperature Effects

This section examines the results of the statistical analysis on the two analytical procedures: the THF solubility test and the micro-distillation test. The statistical analysis for these tests was based on the effects of pressure and temperature on the results of the tests.

1. THF Test:

The experiments in this study were set-up in a "semi-randomized" block design in order to determine the effects of temperature and pressure on the weight fraction of A04 in the vapor phase. That is, the average autoclave pressures were randomly varied through the range of 2100 to 4000 psia, but the temperature could only be increased through the range of 300 to 440 C. The limits of the equipment used in this study along with time and monetary constraints, only permitted "heat-up" processing and did not allow "cool-down" operation at the equilibrium conditions.

Based on this block design, results extracted from the weight fraction in the vapor phase versus temperature curves were placed in an Analysis of Variance (ANOVA) table, and the effects of pressure and temperature were determined. Appendix L contains this ANOVA table and calculations for the determination of pressure and temperature effects.

Results from the F-test conducted at a 0.01 significance level indicated there was a very large effect of temperature on the weight fraction of A04 present in the vapor phase. That is, as the temperature increased, the fraction, by weight, of A04 in the vapor phase also increased. Also, the F-tests indicated that there was a significant effect of pressure. In other words, when comparing runs, as the pressure increased at constant temperature, the weight fraction of A04 present in the vapor phase decreased.

2. Micro-distillation Test:

Statistical analysis of the results of the micro-distillation test indicated that there was a significant effect (at the 0.01 level) of temperature but no significant effect of pressure on the weight fraction of light and middle oils present in the liquid phase samples.

The statistical analysis for this test was similar to that used for the THF solubility test. Data at selected temperature and pressure conditions were extracted from the analytical results and were used to form an ANOVA table. F-tests were conducted at the 0.01 level to determine the effects of pressure and temperature on the weight fraction of light and middle oils present in the liquid phase samples. Appendix L contains this ANOVA table and calculations used in the determination of these effects.

Interpretation of the results shows that as the temperature increased at constant pressure, the percentage, by weight, of light and middle oils present in the liquid phase decreased. In other words, the lower boiling point range light and middle oils vaporized and left a higher concentration of heavy oils and char in the liquid phase. There does not seem to be an effect of increasing pressure on this oil distribution. It is believed, however, that as the pressure increases at a constant temperature, the weight fraction of middle and light oils present in the liquid phase should increase. That is, the higher pressures tend to hold, or force, these oils in the liquid phase. However, the results from this study do not confirm this prediction.

C. Sources of Error

The following list examines and discusses some of the major sources of error associated with this study.

1. Probably the most significant error is the simple fact that this was supposed to be a study of the vapor-liquid equilibrium of AO4. A problem develops when experimental data seems to indicate that the autoclave sampling system was not operating at true equilibrium

conditions. There was a 4 to 7 degree temperature difference between the top and the bottom of the autoclave. When sampling, this temperature difference was allowed to "level off" for only fifteen to twenty minutes. This is not an exact equilibrium condition. However, it a "functional" equilibrium and the data can be used as a basis for further work.

In addition, most thermodynamic vapor pressure versus temperature studies are carried out using a system containing only one or two components. From such a study, more precise data can be obtained to determine equilibrium constants and activities. Because A04 contains many constitutents in a range of concentrations, these data were impossible to obtain.

2. Another source of error is associated with the overall material balance determinations. For this type of study, it is vitally important to account for all of the mass present in the system. In these experiments, very high material balance closures were obtained (94 to 98 percent). It is possible, however, to account for the remaining material.

   (a) First, it was believed that the light oils, which have a relatively low boiling range, were lost in the gas bomb sampling system as mentioned earlier. This loss of light oils may have caused difficulties in obtaining meaningful results in the micro-distillation test.

(b) In addition, there was some residual matter that was trapped in sample and process lines when the run was complete. This material was not accounted for in the material balance closure.

(c) Finally, in one autoclave run, a spilled quench accounted for a lowered material balance.

Note: Since all results were in terms of "concentration," it is necessary to explain how the overall closure of the system is important. The micro-distillation test, which determines the fractionate cuts of light, middle, and heavy oils, relies on obtaining samples that are representative of the system. The loss in light oils, which comprise only 3 percent of A04, may have made it impossible to obtain these representative samples from the gas bomb system. Consequently, this may have caused difficulty in using the micro-distillation test.

3. All autoclave runs were run at the same nominal operating conditions. (See section on statistical analysis of operating conditions.) However, there were difficulties in maintaining constant pressure and temperature in the autoclave. To minimize effects due to the operating procedure, conditions such as sampling time, stirrer speed, and the length of a run were held constant. Even with these precautions, the limitations and capabilities of the equipment were of some concern.

4. There was also error associated with one of the analytical procedures used in this study. Results from the

micro-distillation test on the vapor samples indicated that about 98 percent of the sample was middle or light oil. This number should be 100 percent. This 2 percent difference, while not large, could be explained in two ways. First, this difference could be error in the micro-distillation test itself, or, probably, was associated with the autoclave vapor sampling system. This 2 percent deviation from 100 percent middle or light oils is accounted for in the heavy oil and char category. This seems to indicate that during the autoclave sampling procedure, each vapor sample contained 2 percent heavy oils and char. This is the result of the 20 second settling time before sampling not being long enough. That is, the heavy oils and char were not given sufficient time to completely settle into the liquid phase. In addition, the high reactor pressure may have forced some of the heavy oils and char to be entrained in the vapor when gas samples were taken.

In addition, the micro-distillation test was a very difficult test to duplicate results. The apparatus employed for this analytical procedure was difficult to maintain and operate consistently. This would help explain why the effects due to pressure on the fraction of light, middle, and heavy oils gave unexpected results. Also, the less than 100 percent material balance may have had an effect on the results obtained in this test as mentioned earlier. It should be noted that the THF solubility test was simple to conduct and to duplicate results.

5. There was also a small error associated with the decomposition of calcium carbonate at the operating conditions. This error was about 0.16 percent.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

This chapter lists the conclusions reached in this research project, and makes some recommendations for further study.

I. CONCLUSIONS

The following list contains the conclusions reached in this study. The conclusions are divided into two sections corresponding to the partial pressure run (N-311) and the five time sample runs (N-310 to 328).

A. Partial Pressure Run:

1. As the temperature increased, the vapor pressure of A04 increased from 16 psia to 354 psia in the temperature range of 20 to 440 C. The vapor pressure gradually increased at the lower temperatures and with increasing slope at the higher temperatures (300 to 440 C).
2. Assuming ideal gas behavior, the heat of vaporization for A04 is constant (independent of temperature) over three general ranges corresponding to light, middle, and heavy oil components of A04. These enthalpies are 979 Btu/lb-mole, 6316 Btu/lb-mole, and 30,920 Btu/lb-mole for the light, middle, and heavy oils, respectively.
3. In comparison, by assuming non-ideal gas behavior, the enthalpy of vaporization per molar volume of gas increases with temperature, gradually at the lower

temperatures and with increasing slope at the higher temperatures. The enthalpies per molar volume range from 106.5 Btu/cu.ft. at 33 C to a high value of 49,794 Btu/cu.ft. at 441 C.

4. Assuming that the heat of vaporization of A04 is represented by that of phenanthrene, the most abundant constituent in A04, the molar volume of gas decreases with pressure. This reduction is very dramatic at low pressures and tends to level out at the higher pressures. The molar volumes range from a high value of 239.8 cu.ft./lb-mole at 16.5 psia to a final value of 0.5 cu.ft./lb-mole at 328 psia.

B. Time Sample Runs

5. As the temperature of the system increased, the weight fraction of A04 present in the vapor phase increased to a maximum of 68 percent at the lower pressures studied.
6. In contrast, as the autoclave pressure increased at constant temperature, the weight fraction of A04 present in the vapor phase decreased. At 440 C, the fraction varied from 45 percent at 4010 psia to 68 percent at 2560 psia.
7. As the temperature of the system increased at constant pressure, the weight fraction of light and middle oils present in the liquid phase decreased from an initial concentration of 88 percent to a minimum of 69 percent.
8. The results of this study indicate that there was no

effect of pressure on the fractionate oil distribution.

II. RECOMMENDATIONS

The following is a list of recommendations for further studies in the area of reaction solvent vapor-liquid equilibrium.

1. Further work should be conducted to actually identify the components of A04 in the two phases. A possible analytical method for this is HPLC, a method abandoned in this project. By identifying the components in both the liquid and vapor phases, it may give a more detailed understanding of the chemistry of each phase and how each component contributes to coal liquefaction.
2. Because hydrogen is a reaction gas typically used in coal liquefaction, a series of similar vapor-liquid equilibrium autoclave runs should be conducted in which A04 and hydrogen gas are charged. This will indicate the behavior of hydrogen under the same temperature and pressure conditions, and how it affects the vapor-liquid equilibrium.
3. The comprehensive study involving the vapor-liquid equilibrium of A04, HA061, SRL, and phenolic solvent should be completed, compared, and analyzed. This comprehensive study will give a more complete understanding of reaction solvents.

APPENDICES

APPENDIX A

CALCIUM CARBONATE UTILIZATION

CALCIUM CARBONATE UTILIZATION

Calcium carbonate was used in this study as an indicator of the vapor-liquid distribution of the A04 solvent at various temperature and pressure conditions. A04 and calcium carbonate, in a 95:5 weight ratio, constituted a typical 1200 gram autocalve charge. As the temperature of this mixture increased through the range studied (300 to 440 C), the weight fraction of calcium carbonate present in the liquid phase increased as the light and middle oils vaporized.

Calcium carbonate was selected as the indicator because: (1) it does not decompose at the temperatures studied, and (2) it is not soluble in THF. With increasing temperature, calcium carbonate loses weight due to dissociation and volatization according to the following equation:

$$CaCO_3 \rightleftharpoons CaO\ (solid) + CO_2\ (gas) \qquad [8]$$

A laboratory test was conducted to determine if calcium carbonate decomposed at 500 C, well above the maximum temperature of this study. It should be noted that the CRC Handbook (14) predicts that dissociation should not occur until about 700 C. The test used to confirm this phenomena was called a "percentage ash" test. The procedure follows.

a) Weigh approximately 1.5 grams of calcium carbonate into a crucible and record the weight.

b) Heat the compound in an oven at 500 C for three hours. Remove from oven and place the sample in a desiccator. Cool to room temperature.

c) Weigh the calcium carbonate sample again and record the weight.

The percentage ash is calculated using the following equation:

$$\%\ ASH = \frac{\text{Initial Wt. Sample} - \text{Final Wt. Sample}}{\text{Initial Wt. Sample}} \times 100 \qquad [9]$$

Two calcium carbonate samples were analyzed using the above procedure. The results are shown on the next page. The results of the two tests indicate that only 0.16 percent of the calcium carbonate was lost to decomposition at 500 C. This is a very small loss and was not considered a major source of error. It also indicates that the calcium carbonate is very stable at 500 C.

The second factor involved in the selection of calcium carbonate as the vapor-liquid indicator was the fact that it is not soluble in THF. One of the analytical procedures used to calculate the vapor-liquid distribution was the THF solubility test (See Appendix C). For this analytical method to apply, it was vital that the calcium carbonate be insoluble in THF. The THF solubility test is based on the fact that A04 and all of its constituents are soluble in THF. The fraction of calcium carbonate, which is insoluble in THF, present in each liquid sample would be a direct indicator of the fraction of A04 that was present in both the liquid and vapor phases.

Percentage Ash Determination

The following are the results of the tests performed on calcium carbonate.

Title: Breakdown of Calcium Carbonate

Date: August 3, 1985

Test Parameters: Heat sample at 500 C for 3 hours

DATA:

Test #1:

Weight of crucible + sample = 14.6921 g

Weight of crucible = 13.3385 g

Weight of sample = 1.3536 g

After heating:

Weight of crucible + sample = 14.6712 g

% loss (or % ash) = .14%

Test #2:

Weight of crucible + sample = 15.5233 g

Weight of crucible = 13.7502 g

Weight of sample = 1.7731 g

After heating:

Weight of crucible + sample = 15.4964 g

% loss (or % ash) = .17%

Average % ash = .16%

APPENDIX B

VOID VOLUME DETERMINATION

VOID VOLUME DETERMINATION

This section describes the procedure used to determine the volume of the autoclave and quench vessel system. The volume of the system included sample loop lines as well as the cold traps. This volume determination was necessary for material balance calculations.

1. Procedure:

The procedure for finding the void volume of this system consisted of the following steps. As with all autoclave runs, the automatic control valve system was used to inject nitrogen gas into the system and all temperature and pressure readings were monitored on the digital displays.

1. The ambient temperature and barometric pressure were recorded along with the initial reading of the gas flowmeter and the pressure reading in the autoclave and quench system.
2. The vessels were charged with nitrogen gas from the piston accumulators to the desired pressure level and maintained at that level for roughly 30 minutes.
3. The nitrogen was then vented from the system through the flowmeter. When the flow of gas had stopped, the final flowmeter reading was recorded.

The difference between the initial and the final flowmeter readings was the actual volume (in cubic feet) of nitrogen present in the system.

2. Data:

Table 3 gives the data that was collected in the void volume test. Volumes of the autoclave and quench systems were determined.

3. Calculations:

The calculation to determine the volumes of the autoclave and quench vessels is based on the ideal gas law:

$$PV = nRT \qquad [10]$$

where P is the pressure in psia, V is the volume in cubic feet, n is the number of moles, R is the ideal gas constant with units of 10.73 psia-cubic feet/lb-mole R, and T is the temperature in degrees Rankine. Plots of volume (in cubic feet) versus pressure (in psia) for both autoclave and quench vessel data yielded straight lines with a correlation coefficient of 0.9995; this confirms that the ideal gas law is appropriate over the range of pressures used.

At a certain pressure, P_1, the following relationship exists:

$$P_1 = n_1 RT/V_1 \qquad [11]$$

and at another pressure, P_2:

$$P_2 = n_2 RT/V_2 \; . \qquad [12]$$

Since V_1 is equal to V_2 (the volume of the system is

TABLE 3 VOID VOLUME DATA

Date: June 10, 1985
Barometric Pressure: 29.15 inches mercury
Ambient Temperature: 24 C

Vessel	Pressure (psig)	Volume (cu.ft.)
Autoclave	403	4.009
	596	5.925
	217	2.096
Quench	403	7.823
	201	3.858
	600	11.128

constant) the equations yield:

$$P_1 - P_2 = (n_1 - n_2)RT/V \qquad [13]$$

where V is the volume of the system. By rearranging, the following equation results:

$$V \text{ (volume)} = (n_1 - n_2)RT/(P_1 - P_2). \qquad [14]$$

Using this last equation, the volume of each of the two vessels can determined using the data.

<u>Sample Calculation:</u>

A sample calculation for determining the volume using the above equations follows:

$$n_1 = \frac{(14.28 \text{ psia})(4.009 \text{ cu.ft.})}{(10.73 \text{ psia cu.ft./mole R})(535.2 \text{ R})} = .00997 \text{ moles}$$

likewise,

$$n_2 = .01473 \text{ moles}$$

Now using the last equation, the volume of the autoclave can be calculated as follows.

$$V = \frac{(.00997 - .01473)(10.73)(535.2)}{(403 - 596)}$$

$$= .1417 \text{ cubic feet or } 1.060 \text{ gallons}$$

The calculations for the quench vessel are carried out in the same manner. Table 4 summarizes the results for these calculations.

TABLE 4 VESSEL VOLUME

Vessel	Trial Number	Volume (gallons)
Autoclave	1	1.060
	2	1.098
	3	1.079
Quench	1	2.043
	2	1.997
	3	1.949

Average Autoclave Volume................. 1.079
Average Quench Volume.................... 1.996

Total Volume (Autoclave + Quench)........ 3.075

APPENDIX C

ANALYTICAL PROCEDURES

THF SOLUBILITY TEST

The solubility of the liquid samples in THF was used to determine the vapor-liquid distribution. The liquid time samples contained light, middle, and heavy oils as well as calcium carbonate. A description of this analytical test and a sample calculation for determining the weight fraction of THF insolubles follows.

The constituents in these liquid samples, except for the calcium carbonate, are readily soluble in THF. By dissolving a representative portion of a liquid sample in THF, filtering the undissolved calcium carbonate, and weighing the calcium carbonate residue, the vapor-liquid distribution of each time sample set could be calculated. For this test, the soluble constituents were those that passed through a 0.5 micron filter.

1. Equipment:

The following equipment was used in this experimental method.

- Millipore Fluoropore Type FH Filters (0.5 micron pores)
- AP Mitrex Prefilters
- Watchglass
- Desiccator
- Vacuum Filtration Apparatus
- Tweezers
- THF

2. Procedure:

1. Use Millipore fluoropore type FH filters with 0.5 micron pore size and type AP Mitrex prefilters.

2. Dry the prefilters in an oven for one hour at 105 C on a watchglass prior to use.

3. Remove the prefilters and watchglass from the oven using a tweezers and place in a desiccator to cool to room temperature. Add a 0.5 micron filter, weigh, and record the weight.

4. Place filters in the filter clamp holder. The 0.5 micron filter rests on the support screen, and the prefilter lies on the top of the filter. The assembly should be tightly snug. Turn on vacuum. Figure 23 is a schematic diagram of this filtration assembly.

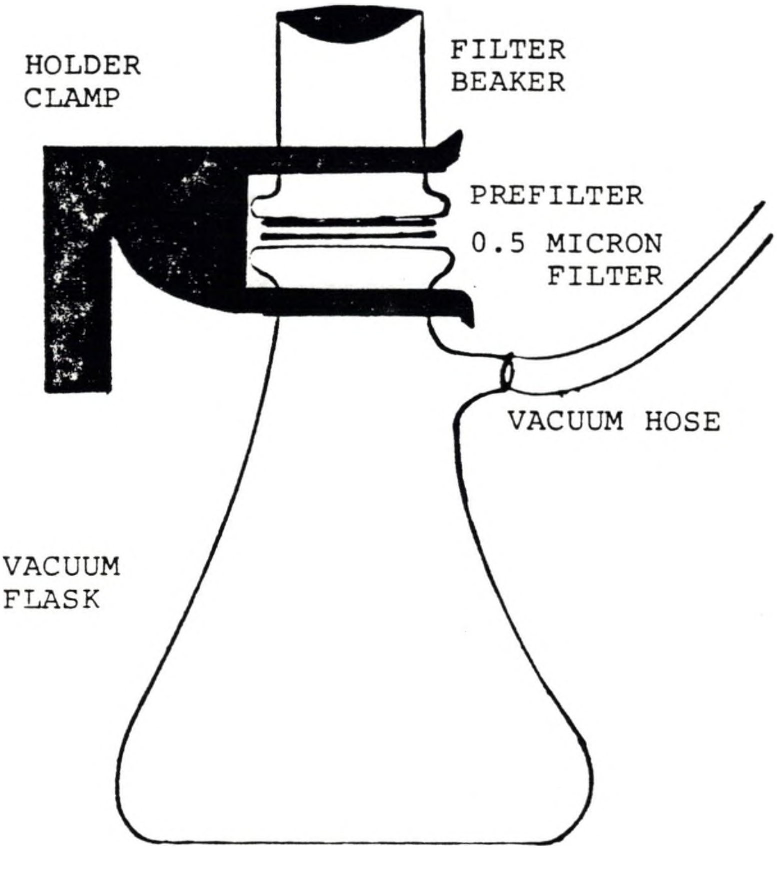
5. Weigh approximately 0.2 grams of the liquid sample material into a 50 ml beaker. If the sample is in solid form, pre-heat at low temperature until it is in liquid form. Record the weight.

6. Dissolve the sample in THF and pour into filter assembly. A quantitative transfer of the solution from the beaker to the filter is necessary. Therefore, rinse the beaker with additional THF and add this solution to the filter apparatus.

7. As the vacuum filtration continues, rinse the sides of the filter holder with THF and wash the solid deposits on the filter with THF until the filtrate is clear.

8. When all THF has been forced through the filters, remove

FIGURE 23 THF FILTRATION ASSEMBLY



the filters from the holder and transfer them and the insoluble residue quantitatively to the watchglass. Dry in the oven at 105 C for 20 minutes, cool in the desiccator, weigh, and record the weight.

3. Calculations:

The data collected from the above procedure is used to calculate the weight percent of THF insolubles present in the samples. This determination is based on the weight of the sample, weight of the residue, and weight of the filters. The calculation is carried out as follows:

$$\%\text{THF INSOLUBLES} = \frac{\text{Wt.Residue + Filter - Wt.Filter}}{\text{Wt. Sample}} \times 100 \qquad [15]$$

This weight percent of THF insolubles was assumed to be the same as the weight percent of calcium carbonate present in the samples. Calcium carbonate is insoluble in THF while the other constituents of A04 are readily soluble.

Special Notes:

(a) Tests should be duplicated for each liquid time sample.

(b) If filter holder leaks, the test must be repeated.

(c) For calculation purposes, the 0.5 micron filters, which are made of a "teflon-like" material containing some water weight, lose approximately .0015 grams from their initial weight during the final drying procedure. This correction factor should be taken into account when the calcium carbonate content of each sample is determined.

VACUUM DISTILLATION

The vacuum distillation test was used to determine the fractions of light, middle, and heavy oils present in both the liquid and vapor samples. This test is based on the fact that these various oils have a difference in their boiling temperature ranges under vacuum.

1. Test Development:

The vacuum distillation test used to analyze samples in this study was not the standard vacuum distillation (ASTM D-1160) carried out at a vacuum pressure of 5 Torr. Instead, a micro-distillation test was utilized (operating at 1.6 Torr) to accommodate the large numbers of samples. Because the vacuum pressures were different, however, the boiling ranges of the light, middle, and heavy oils were different at the two pressures. For the ASTM D-1160 standard vacuum distillation, the boiling ranges for these distillate cuts are as follows:

1) Initial Boiling Point (IBP) to 121 C ------ Lights
2) 121 to 260 C ------------------------------ Middles
3) 260 C to Maximum Temperature ------------- Heavies

Note: These are under 5 Torr vacuum.

The micro-distillation test utilized in this study was under different vacuum pressure (1.6 Torr) and, therefore, the light, middle, and heavy oils had lower boiling temperature ranges. It was necessary to determine the boiling temperature ranges for this test using a sample of A04, analyzing it with the standard test (D-1160), and using these data to determine the cut-off temperatures for the different distillate cuts with the micro-distillation test.

The following sections give detailed descriptions of both the standard vacuum distillation test and the micro-distillation tests utilized in this study. In addition, results from distillations used in the development of the micro-distillation test from the standard test are given and discussed.

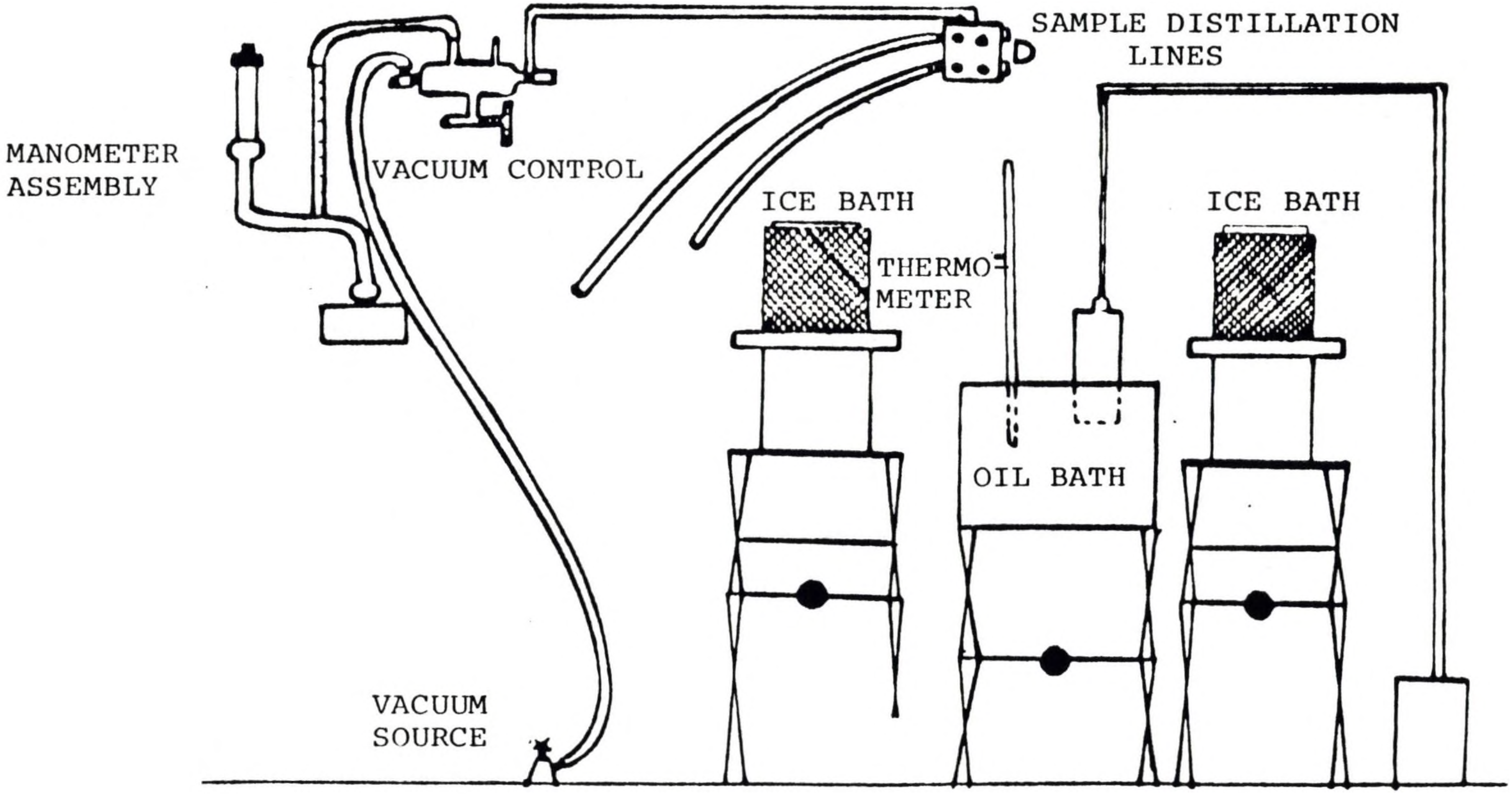
2. Micro-distillation:

The micro-distillation test used to analyze the samples in this study was developed from the standard vacuum test. In this section, the micro-distillation is described in great detail, from the operating equipment and materials utilized to the actual procedure and methods for calculating the fractions of the distillate cuts. Figure 24 is a schematic diagram of the micro-distillation apparatus. The advantages of this analytical technique, as mentioned earlier, are the ability to handle large numbers of samples, the relatively short distillation times, and the small sample size as compared with that required in the standard test.

a. Equipment:

The following is a list of equipment utilized in the

FIGURE 24 MICRO-DISTILLATION ASSEMBLY



micro-distillation test.

Oil Bath System

- Aluminum vessel (aluminum with welded seams)
- Automotive soft plug heater
- Variac heater controller
- Magnetic stirrer and stir bar
- Mercury thermometer
- Ring stand and thermometer clamp
- Variable jack (5 inches, 100 pounds capacity)

Vacuum System

- Vacuum pump
- Manometer, trap, and catch basin
- Support frame and clamps
- Vacuum lines
- Vacuum nipples and hoses

Cold Trap System

- 2 large Dewar flasks
- 2 variable jacks (5 inches, 100 pounds capacity)

Ventilation System

- Ventilation hood

Other Equipment

- Fabricated condenser tubes
- Brass sleeve connectors
- Rubber O-rings
- Stainless steel plungers
- Mallet, container, and spoon for crushing dry ice

b. <u>Materials:</u>

The following is a list of materials that were needed for this analytical testing method.

- -Dow DC-710 heat transfer fluid
- -Isopropanol
- -Dry ice
- -Latex gloves
- -Acetone
- -Microwipes
- -Micro pipettes
- -Mercury for manometer
- -THF
- -Sample tubes

c. <u>Operating Procedure for Micro-distillation:</u>

The following sections describe the operating procedure for the micro-distillation test from the preparation of samples and the distillation apparatus to the actual distillation procedure and methods to calculate the results.

Preparation of the Oil Bath

Prior to beginning the micro-distillation, the oil bath must be prepared according to the following procedure. (1) To heat the oil, flip the toggle switch on the variac heater controller to the 140 volts position and set the dial at 70. (2) The oil bath stirrer should be started and set at the #4 setting until the oil begins to heat. The oil will foam if it is agitated too vigorously. To prevent this, the operator should periodically lower the stirrer setting. A final setting of #2 will provide good circulation of the oil. (3) When the oil reaches 200 C, flip the toggle switch on the variac to 120 volts and turn the dial back to 60. It should take approximately one to two hours for the oil to reach 200 C.

Sample Preparation

While the oil bath is heating, the samples are prepared for distillation. The following procedure is implemented to prepare these samples. (1) Place a small amount of glass wool into the bottom of each sample tube. The role of the glass wool is to prevent entrainment of the sample during the distillation and to provide greater surface area for the separation. (2) Clean the prepared sample tubes using a disposable wipe, preweigh the tubes, and record the weight. (3) Stir the sample with a thin stainless steel rod, scraping the sides of the sample vial to mix the sample well and ensure that a representative sample is analyzed. (4) Using a micro-pipette weigh approximately 0.1 to 0.2 grams of sample into the sampling tube and record the weight. The sample is now ready to be analyzed by the micro-distillation technique.

Cold Trap Preparation

While the oil bath is heating, the cold traps are prepared as well according to the following steps. (1) Fill each of two Dewar flasks with isopropanol to within approximately three inches of the mouth. (2) Add crushed dry ice to the isopropanol in the flask. Because isopropanol bubbles violently with the addition of the dry ice, it should be added very carefully and slowly.

Final Preparation

After the oil bath has reached a temperature of 200 C, the micro-distillation is ready for final preparation before the test actually begins. (1) Put two oiled O-rings into the brass fitting on each condenser tube. Twist the sample tube into the fitting, making certain that the sample tube is firmly in place. The O-rings form an air-tight seal, allowing the vacuum distillation to occur. (2) Record the number of the brass fitting corresponding to each sample number. (3) Attach the other end of the condenser to the latex tubing and place the condenser in the cold trap submersing the condenser. (4) Clamp off any rubber tubing not in use. (5) Adjust the vacuum to 1.6 Torr using the regulator valve assembly.

Distillation

The following steps are followed in actually carrying out the micro-distillation. (1) Check and maintain the temperature of the oil bath at 200 C. (2) Position the sample tubes over the oil bath and lower them into the oil. Raise the oil bath until the oil covers the top of the brass adapters. (3) Check all sample tubes. If bubbles appear, it indicates that the air-tight seal has been broken. To solve this problem, remove this sample tube and clamp off the latex tube to maintain the vacuum level in the system. (4) Open the vacuum pressure to the sampling system and adjust the pressure to 1.6 Torr. (5) Distill for one hour from the moment the vacuum is applied to the samples.

Post Distillation

After one hour, the distillation is complete and the apparatus is disassembled. (1) Lower the oil bath and raise the cold traps. (2) Shut off vacuum to the sampling system. (3) Allow 10 minutes for the condensers to cool down and check the samples for leaks. If leaks had occurred, these samples will have to be removed from consideration. (4) Remove the samples from the condenser tubes and clean them of residual oil from the bath with disposable tissues. (5) Reweigh the sample tubes and record the weight. Shut off vacuum and oil bath heater when distillation tests are completed.

d. Sample Calculations:

The following is an example of the calculations to determine the distillate cuts based on the data collected from the micro-distillation.

(Tube wt. + Sample wt.) - Tube wt. = Sample wt.(grams) [16]

(Tube + Residue wt.) - Tube wt. = Residue wt.(grams) [17]

PERCENT DISTILLATE = (Residue wt/Sample wt) x 100 [18]

Special Notes:

(a) Tests should be duplicated for each liquid sample, or until consistent results are obtained.

(b) In some instances, it was not necessary to put glass wool in the sample tubes prior to micro-distillation, particularly when analyzing the vapor samples. In some instances, portions of the vapor samples were being trapped in the sample tube because the glass wool packing was too tight.

(c) Only a limited number of gas samples were analyzed by this method. Representative samples from two runs were analyzed and gave the same results and it was, therefore, assumed that all gas samples would give similar results.

3. Standard Vacuum Distillation (ASTM D-1160)

The Standard Vacuum Distillation test is briefly outlined and described below. In this technique, samples are distilled at 5 Torr under conditions that provide approximately one theoretical plate fractionation. Data are obtained from which a distillation curve relating weight distilled and boiling point at the controlled pressure can be prepared. Weight percent (sample weight basis) of fractions boiling over the range from initial boiling point to 121 C, 121 C to 260 C, and above 260 C are determined.

a. Equipment:

The following is a list of equipment that is used in this distillation technique.

- ASTM D-1160 distillation equipment kit
- Potentiometer
- Kovar tip thermocouple
- Dewar flask
- Cartesian Diver Manometer
- Thermometer
- Variac
- Magnetic stirrer

b. Operating Procedure:

The operating procedure for this standard vacuum distillation test is given in the following steps.

1) Assemble distillation apparatus empty. Turn vacuum pump on and off to check for leaks. Turn vacuum pump on again and set vacuum pressure at 5 Torr.
2) Record the ambient temperature and atmospheric pressure before and after the distillation.
3) Add approximately 100 ml of sample and a magnetic stir bar to the distillation flask.

4) Mount the distillation flask containing the sample on the distillation apparatus, lightly greasing the glass joints. Install 250 ml heating mantle on lower half of the flask and an unconnected upper half heating mantle jacket on the upper half of the flask.
5) Insert Kovar tip thermocouple in distillation column head, turn on vacuum pump, and adjust pressure to 5 Torr.
6) Set variac at 65, start timer, and record the initial boiling point (IBP) temperature when the first drop of distillate is visible at the top of the drip chain in the receiver.
7) Adjust the heating rate to maintain a distillate collection rate of 4 to 5 ml per minute.
8) Record the weight of distillate received corresponding to IBP to 121 C, and 121 C to 260 C. These figures will be used later to compute the weight percent of each fraction in the sample.
9) Continue distillation until 260 C is reached or an abrupt drop in temperature occurs.
10) Weigh all sample collection vials and the original sample flask and record the weights.
11) Turn off vacuum pump and clean all equipment with acetone.

c. Calculations:

From the data collected in the above procedure, the weight percent of each fraction can be determined according to the following calculation.

Calculate the weight percent of IBP to 121 C, 121 C to 260 C, and above 260 C residue fraction as follows.

a. Weight % light oils: (IBP to 121 C)

WT% = (wt. light oils/wt. of sample) x 100 [19]

b. Weight % middle oils: (121 C to 260 C)

WT% = (wt. middle oils/wt. of sample) x100 [20]

c. Weight % heavy oils/char: (260 C and above)

WT% = 100 - sum of above WT%'s [21]

4. Results of Micro-distillation Development

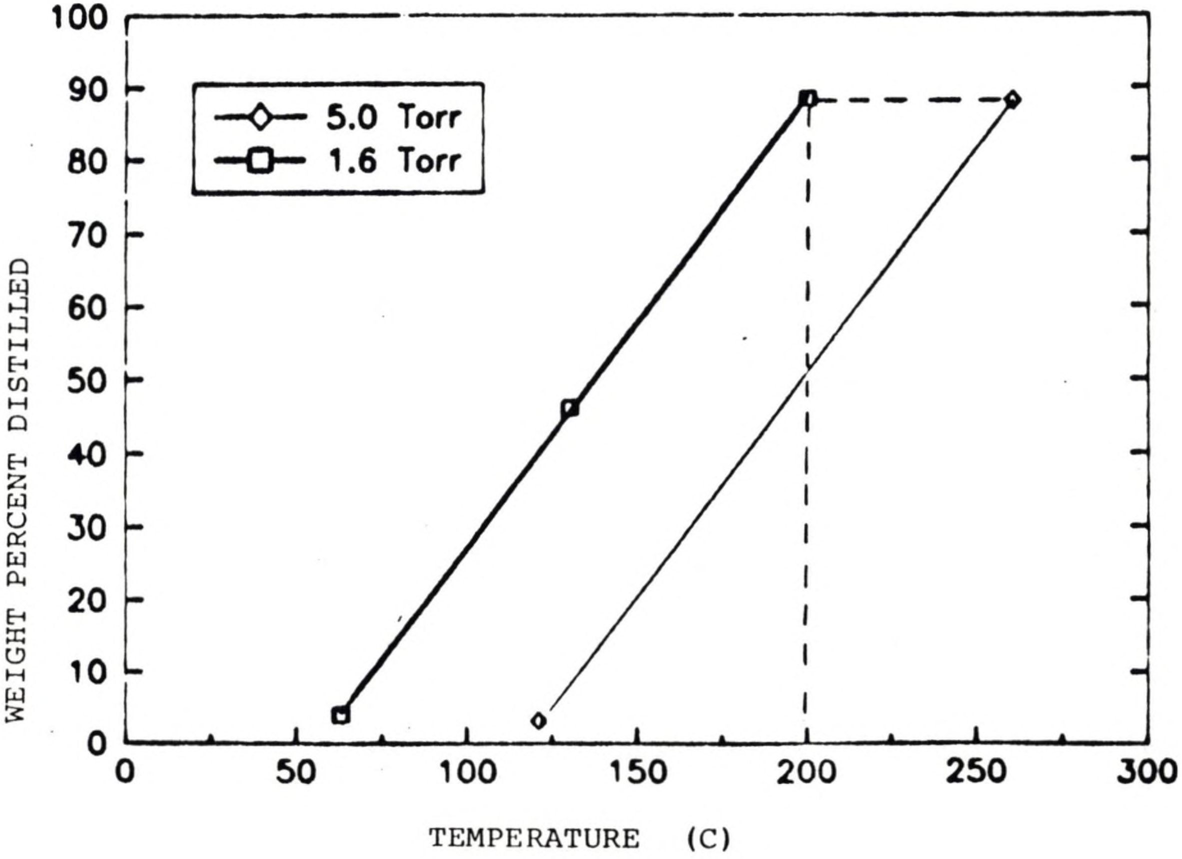
The standard vacuum test was conducted on a sample of A04 and the results were consistent with the literature values for A04 (8). That is, at a vacuum of 5 Torr, the fractions of distillate were:

1)	Light oils	3.0 %
2)	Middle oils	85.0 %
3)	Heavy oils/Char	12.0 %
	TOTAL	100.0 %

For the purposes of this study, this standard test was impractical because only one sample could be analyzed at a time. It was necessary to adapt the micro-distillation, which could accommodate large numbers of samples. Therefore, it was necessary to find the temperature ranges at 1.6 Torr that correspond with those at 5 Torr. The micro-distillation had to be operated at a lower temperature because the oil bath used in the test could only be heated to about 220 C.

To determine the new temperature levels at which to run the micro-distillation test, a series of samples were distilled on the distillation apparatus at 1.6 Torr at various temperatures, and the weight fractions were determined at each temperature level. A curve was constructed depicting weight fraction distilled versus temperature. From these data, the temperature ranges corresponding to middle and light oils were determined to be approximately 200 C. That is, only middle and light oils would vaporize at this temperature and pressure. Above 200 degrees Celsius, heavy oils would begin to vaporize. Figure 25 shows this distillation plot comparing the two pressures, 5 Torr and 1.6 Torr.

FIGURE 25 DISTILLATION CURVES AT 1.6 AND 5.0 TORR VACUUM PRESSURE



HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

HPLC, or molecular weight distribution analysis, was initially used to identify the major constituents present in both the liquid and vapor samples. This test is based on the principle that separation will occur because of differences in the molecular weight of each constituent present in a sample. That is, as samples were analyzed in the liquid chromatograph, retention times for the components present in each sample would vary with molecular weight. The following sections briefly describe the procedure for HPLC analysis and give some of the results obtained from this testing method. As mentioned earlier, this technique was not used because of time and monetary constraints. Over two hundred samples needed to be tested and each HPLC analysis requires one hour per sample. In addition, the cost of starting and operating this equipment was very high.

1. Equipment:

The following is a list of equipment used in HPLC. It is divided into two categories: sample preparation equipment and sample analysis equipment.

a. Sample Preparation Equipment:

-Vacuum filtration assembly

- -Filters and prefilters (0.5 micron)
- -Desiccator
- -30 ml beaker
- -Pipettes
- -THF
- -Sample Concentrator
- -Spatula

b. **Sample Analysis Equipment:**

- -Waters Associates Liquid Chromatograph (Model ALC/GPC-201)
- -Injector (Model U6K)
- -Solvent Pumps (Model M6000)
- -3 Ultra Stryagel Columns: 1000, 500, and 100 Angstrom pore size
- -ISCO Model UA-5 U-V Detector and Pen Recorder (Wavelength set at 254 nm)

2. Procedure:

The procedure used for HPLC analysis is divided into two main areas: sample preparation and sample analysis.

a. **Sample Preparation:**

Each vapor and liquid sample was prepared according to the following procedure (15).

1. Dry a coarse filter, watchglass, and vial for each

sample in oven at approximately 105 C for 20 minutes. Then cool in desiccator for 20 minutes.

2. Weigh filters (coarse and 0.5 micron) on a numbered watchglass and vial (use gloves or tweezers).
3. Weigh 20 mg of sample into a dried 30 ml beakeer.
4. Assemble filter apparatus placing 0.5 micron filter on filter holder screen before the coarse filter (prefilter) which is placed over it.
5. Add several ml of THF to sample and decant into filter which is attached to vacuum line (turn on vacuum first). Add more THF and decant as before. This may have to be done as many as 5 to 6 times. Rinse beaker with small portions of THF three times (do not exceed capacity of vial; prefer 2/3 full or less) and filter.
6. Turn off vaccum, disassemble the filter apparatus placing filters on watchglass.
7. Place filters in 105 C oven for 15 minutes.
8. Cool in desiccator for 20 minutes and weigh.
9. Put the THF soluble portion in the concentrator and evaporate to approximately 1 ml.
10. Weigh vial with soluble portion adding THF to 0.25% by weight.

b. **Sample Analysis:**

The following is a very basic procedure that was used in operating the HPLC apparatus.

1. The liquid chromatograph and U-V detector were

turned on and allowed to warm up for approximately 2 hours. Start the vacuum pump.

2. During the two hour warm up, the Stryagel separation columns were purged with THF to remove any entrained material. The solvent pumps were utilized for this process.
3. Following the heat up, the pen recorder was turned on and the base line was set at zero. The attenuation was adjusted based on the size and concentration of the sample. The chart speed was set at one inch per minute.
4. Twenty five micro-liter samples were injected into the column and separation based on molecular weight difference occurred. Results were recorded on the U-V graphing system.
5. Each sample had a retention time of approximately 35 to 40 minutes.
6. After sampling, the machines were turned off.

3. Results and Discussion of HPLC:

The results for this analytical technique were very qualitative but not readily quantitative. However, with the addition of a high molecular weight polymer to each sample to act as a standard "spike" for peak height comparison, some quantitative data could be obtained. The quantification of this data was difficult, and the results are no more reliable than those of the micro-distillation test. Therefore, these results are not included with this report. The qualitative results could be used in conjunction with the micro-distillation test to give a more detailed view of the major constituents in each of the vapor-liquid sample pairs analyzed.

The graphs shown at the end of this discussion depict the spectra of A04 and some of the vapor-liquid samples from run N-310. On each spectrum, the peaks correspond to the different molecular weight components present in each sample. The retention time for each peak is a direct indicator of the molecular weight of that particular constituent. That is, the higher molecular weight substances had the shortest retention times in the chromatographic columns, and those peaks were the first to appear in the spectrum. Likewise, the lower molecular weight substances had the longest retention times and appeared later in the spectrum. Peaks could be identified by analyzing known compounds (pure components of A04 preferably) and comparing the known peak retention times with retention times of the test samples.

The relative concentration of each species could be determined by comparing relative peak heights. This was made possible by spiking each sample with a known concentration of a standard high molecular weight polymer. In this manner, relative peak heights could be quantified by comparison with the standard polymer peak. As stated earlier, this technique for determining concentrations was complex and results are not mentioned.

The location of these peaks in the spectrum also indicates whether that constituent falls into the light, middle, or heavy oil range. In general, the high molecular weight components fall into the heavy oil category while the lower molecular weight components fall in the middle and light oil range. However, this rule is only a generalization and not always true. There are compounds with high molecular weight that would be classified as middle or even light oils based on their boiling points.

As mentioned earlier, more work was needed to further develop this analytical technique, but a shortage of resources (time and money) prevented this from happening and eliminated this testing method from consideration. Figures 26 to 28 show the spectra of A04 and a corresponding pair of liquid and vapor samples. Each figure contains two spectra of the same sample at different recorder attenuations. Some of the peaks are identified on each figure as well. The peak heights for the heavy oils are larger for the liquid sample indicating that the concentration of heavy oils in the vapor phase is lower than in the liquid phase, a result proven by the micro-distillation tests. As can be seen from the figures, the spectra of A04 and the two samples are very complex with many components located in a narrow molecular weight range. Identification of particular peaks is difficult.

FIGURE 26 AO4 HPLC SPECTRA

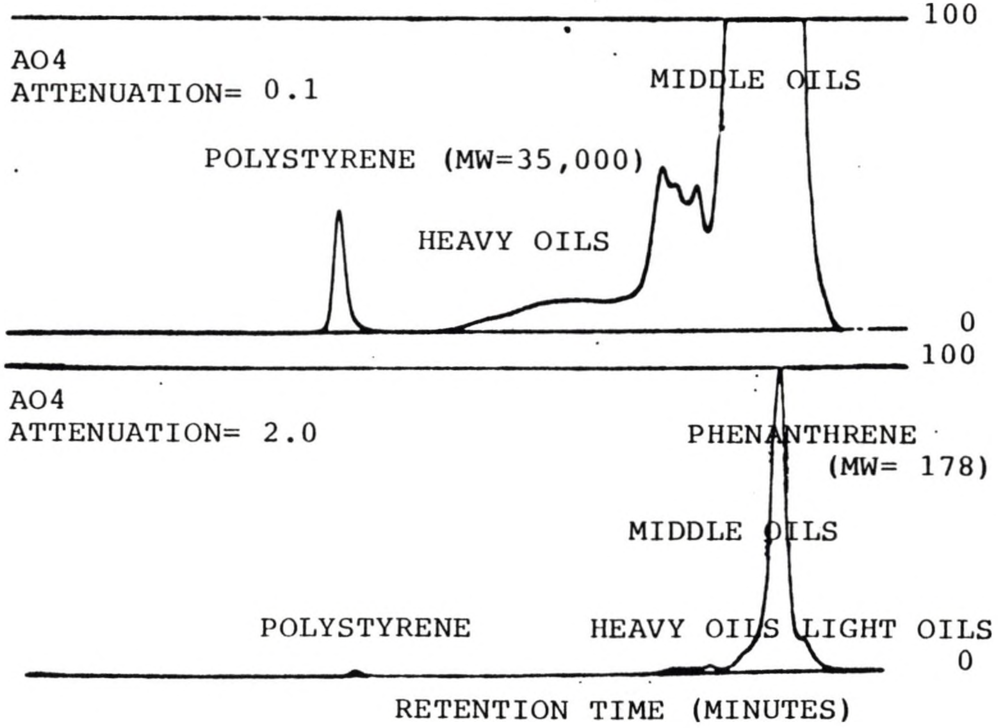


FIGURE 27 LIQUID SAMPLE SPECTRA

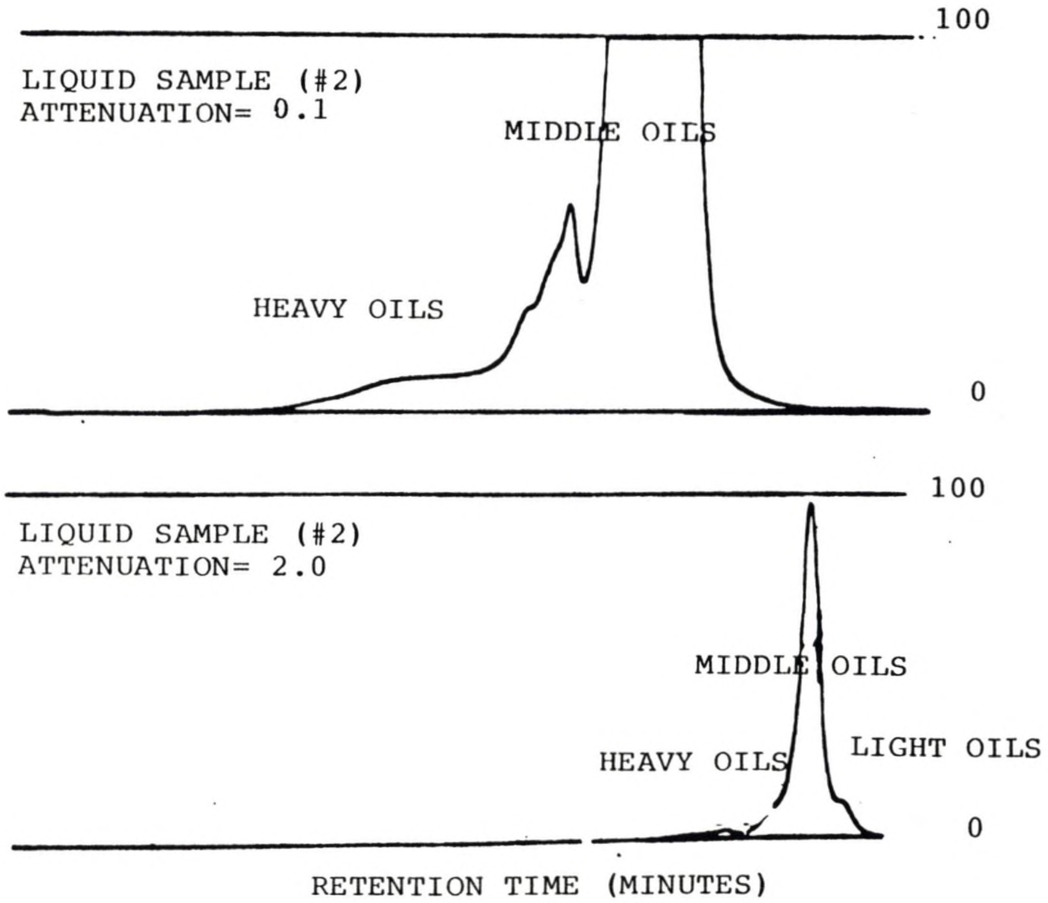
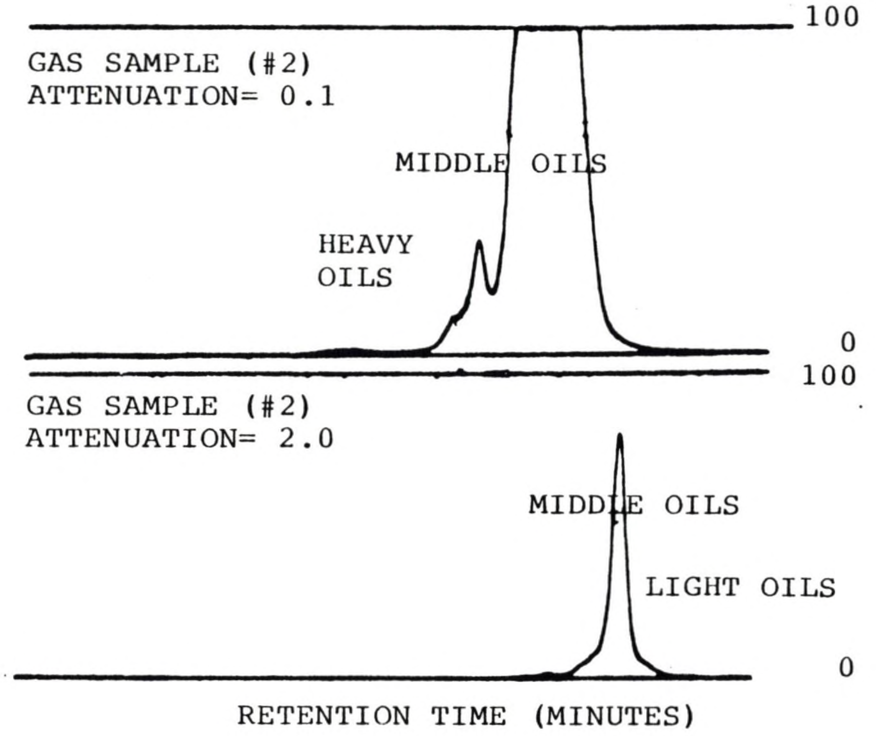


FIGURE 28 GAS SAMPLE SPECTRA



APPENDIX D

MATERIAL BALANCE CALCULATIONS

MATERIAL BALANCE CALCULATIONS

Following are the calculations used to determine the mass balance closure for each experimental run. First, a sample calculation for the liquid material balance is shown followed by a nitrogen gas material balance.

I. A04 LIQUID MATERIAL BALANCE (RUN N-328)

This balance was done to determine the closure of the system based on the mass charged to the autoclave and the mass recovered.

A. Mass Charged to Autoclave:

A04 + Calcium Carbonate	= 1214.1 grams

B. Mass Out Of Autoclave:

Total Time Samples	= 65.8 grams
Total Waste Liquid Samples	= 74.5 grams
Total Wastd Gas Samples	= 14.9 grams
Quench Vessel Clean-up	= 1001.6 grams
Autoclave Clean-up	= 26.0 grams
Total Mass Recovered	= 1182.8 grams

System Closure = (Mass Out / Mass In) x 100

= (1182.8 g / 1214.1 g) x 100

= 98.4 %

System Loss = 100 - 98.4

= 1.6 %

II. NITROGEN GAS MATERIAL BALANCE

Only the nitrogen gas balance for run N-328 is shown. Because losses were so great, this balance was believed to be unnecessary and meaningless.

A. Nitrogen Into System:

Initial Charge Into Accumulator	= 2428 psig
Reading After Processing	= 1382 psig
Net (Amount Used In Run)	= 1046 psig

B. Nitrogen Out Of System:

Initial Flowmeter Reading	= 995.395 cu ft
Final Nitrogen Meter Reading	=1005.998 cu ft
Net (Out)	= 10.603 cu ft

Calculation:

Moles Out = (P x V)/(R x T)

= (14.7 psia x 10.603 cu ft)/(10.73x 533.4 R)

= .0272 Moles Out

Moles In = (1396.7psia x .4111 cu ft)/(10.73x 533.4 R)

= 0.1003 Moles In

* Note: .4111 cubic feet is the volume of the autoclave and quench system.

Recovery (%) = (Moles Out/Moles In) x 100

= (.0272/.1003) x 100

= 27.2 %

* Note: The large loss is attributed to sampling technique. (See Chapter 3 for explanation.)

APPENDIX E

VAPOR-LIQUID DISTRIBUTION CALCULATIONS

VAPOR-LIQUID DISTRIBUTION CALCULATIONS

The vapor-liquid distribution of A04 was determined from the operating data and the results of the THF solubility test. The computer program shown on the following pages was used to aid in these calculations. A line by line sample calculation following the program is shown below. Run N-328 is used as the example for this calculation.

1. Mass charged into autoclave = 1214.1 grams
2. Weight percent calcium carbonate = 5.0 %
3. Number of gas/liquid samples = 10
4. Average liquid waste shot mass: (LW)

   LW = Total liquid waste / 20 waste shots

   = 74.44 grams / 20

   = 3.722 grams

5. Average gas waste shot mass: (GW)

   GW = Total gas waste / 20

   = .7415 grams

6. Calculate mass of calcium carbonate present in charge:

   1214.1 grams x 0.05 = 60.703 grams

7. Calculate (in line 280 of program) amount of solution present in autoclave after liquid and gas waste shots:

   (1214.1 - 3.722 - 0.7415) grams = 1209.59 grams

COMPUTER PROGRAM

```
10 REM THIS PROGRAM CALCULATES THE VAPOR-LIQUID DISTRIBUTION
20 REM OF AO4, BY WEIGHT PERCENT, AT SPECIFIC TEMPERATURES
30 REM AND PRESSURES.  IT TAKES INTO ACCOUNT THE INITIAL
40 REM AUTOCLAVE CHARGE, THF SOLUBILITY TEST RESULTS, MASS
50 REM OF VAPOR AND LIQUID SAMPLES, AND THE MASS OF WASTE
60 REM SAMPLE SHOTS.
70 DIM O(15,5)
80 PRINT "ENTER RUN NUMBER"
90 INPUT S$
100 PRINT "ENTER SOLVENT USED"
110 INPUT R$
120 PRINT "ENTER MASS CHARGED INTO AUTOCLAVE IN GRAMS"
130 INPUT A
140 PRINT "ENTER PERCENT CALCIUM CARBONATE IN CHARGE"
150 INPUT C
160 PRINT "ENTER NUMBER OF GAS/LIQUID SAMPLES TAKEN"
170 INPUT N
180 PRINT "ENTER AVERAGE LIQUID WASTE SHOT MASS IN GRAMS"
190 INPUT I
200 PRINT "ENTER AVERAGE GAS WASTE SHOT MASS IN GRAMS"
210 INPUT S
220 REM M1 IS THE MASS, IN GRAMS, OF CALCIUM CARBONATE
230 REM PRESENT IN THE INITIAL CHARGE.
240 M1=A*C/100
250 Z=0
```

COMPUTER PROGRAM (continued)

```
260 REM A IS THE MASS OF SOLUTION IN THE AUTOCLAVE LESS
270 REM THE LIQUID AND GAS WASTE SHOTS.
280 A=A-I-S
290 Z=Z+1
300 PRINT "ENTER MASS, IN GRAMS, OF LIQUID SAMPLE # ";Z
310 INPUT L
320 PRINT "ENTER MASS, IN GRAMS, OF GAS SAMPLE # ";Z
330 INPUT G
340 PRINT  "ENTER PERCENT CALCIUM CARBONATE IN LIQUID SAMPLE
    # ";Z
350 INPUT D
360 PRINT "ENTER PRESSURE (PSIA) AND TEMPERATURE (C)"
370 INPUT B,T
380 GOSUB 600
390 M=M1-(D*I)/100
400 F=(M//D)*100
410 H=A-F
420 REM P  IS THE MASS PERCENT OF AO4 PRESENT IN THE  LIQUID
    PHASE.
430 P=((F-M)/(A-M))*100
440 REM Q IS THE MASS PERCENT OF AO4 PRESENT IN THE VAPOR
    PHASE.
450 Q=100-P
460 X=Z+1
470 O(X,1)=Z
```

COMPUTER PROGRAM (continued)

```
480 O(X,2)=P
490 O(X,3)=Q
500 O(X,4)=B
510 O(X,5)=T
520 A=A-L-G
530 M1=M-(L*D)/100
540 IF Z<N GOTO 280
550 PRINT"RUN NUMBER:";S$
560 PRINT"SOLVENT:";R$
570 PRINT "SAMPLE     %LIQ    %VAP    P(PSIA)    T(C)"
580 FOR V=1 TO N
585 PRINT" "O(V+1,1);"      "O(V+1,2);"     "O(V+1,3);"
586 PRINT"          "O(V+1,4);"             "O(V+1,5)
590 NEXT V
595 STOP
600 PRINT Z
610 PRINT"1 LIQUID SAMPLE = ",L
620 PRINT"2 GAS SAMPLE = ",G
630 PRINT"3 %CALCIUM CARBONATE = ",D
640 PRINT"4 PRESSURE = ",B
650 PRINT"5 TEMPERATURE = ",T
660 PRINT
670 PRINT "ANY ERRORS? Y/N"
680 INPUT I$
690 IF I$<>"Y" THEN RETURN
```

COMPUTER PROGRAM (continued)

```
700 PRINT "ENTER # TO CORRECT"
710 INPUT I
720 PRINT"ENTER CORRECTED INFORMATION"
730 IF I=1 THEN INPUT L
740 IF I=2 THEN INPUT G
750 IF I=3 THEN INPUT D
760 IF I=4 THEN INPUT B
770 IF I=5 THEN INPUT T
780 GOTO 600
790 END
```

8. Mass of liquid sample #1 = 5.66 grams
Mass of gas sample #1 = 2.70 grams
Weight percent calcium carbonate
in liquid sample = 5.04 %
Pressure = 3891 psia
Temperature = 301.7 C

9. Calculate (line 390) remaining calcium carbonate in liquid sample after loss in liquid waste samples:
calcium carbonate = 60.703 grams - (3.722 x .0504) grams
= 60.515 grams calcium carbonate remaining in autoclave

10. Calculate (line 400) total mass in liquid phase in system:
Total mass = (60.515 grams / .0504 grams)
= 1200.703 grams

11. Calculate (line 420) weight percent of A04 in liquid phase:
Wt % = ((1200.703 - 60.515)/(1209.59 - 60.515) x 100)
= 99.23 % in the liquid phase

12. Calculate the weight percent of A04 present in the vapor phase:
Wt % = 100 - 99.23 grams = 0.77 % vapor

13. The program then subtracts out the mass of the liquid and gas samples to give the resulting mass in the autoclave:

    New autoclave mass = 1209.59 - 5.66 - 2.70 grams

    = 1201.23 grams

14. The amount of calcium carbonate left in system after sampling is:

    60.515 - (5.66 x .0504) = 60.23 grams

The program then loops back to line 280 and continues to calculate through the ten samples. The results for these calculations are shown in Appendix J.

MICRO-DISTILLATION ADJUSTMENTS

In determining the fraction of middle and light oils present in the A04 liquid phase, it was necessary to subtract out the presence of calcium carbonate in these samples. A sample calculation of this follows. Liquid sample #3 of run N-325 was selected for this sample calculation.

Mass of sample #3 = 5.1431 grams

Weight % calcium carbonate = 5.81 %

Mass of calcium carbonate
in sample = (.0581 x 5.1431) = .2988 grams

Original micro-distillation results:

Wt% middle/light oils = 72.0%

Mass of middle/light oils
in sample = (.72 x 5.1431) = 3.703 grams

Mass of heavy oils
and char = 5.1431 - .2988 - 3.703 = 1.141 grams

Corrected Total Mass(minus calcium carbonate) = 4.844 grams

Corrected Micro-distillation result:

Wt% middle/light oils = (3.703/4.844) x 100 = 76.4 %

Note: The corrected results are those given in this report and are shown in Appendix K.

APPENDIX F

OPERATING DATA

OPERATING DATA

The data listed in the tables in this appendix can be explained as follows: (1) Column one contains the test set number. (2) The two thermocouple readings (TC#1-bottom of the autoclave and TC#2-top of the autoclave) are reported in degrees Celsius in columns two and three. (3) These two readings are averaged in column four; this the system pressure. (4) The autoclave pressure is given in the fifth column of the table and recorded in psig. (5) Finally, the autoclave heater temperature (in degrees F) is shown in the last column of the table. The table also includes the ambient temperature, atmospheric pressure, the magnetic stirrer speed, and the mass charged to the autoclave.

TABLE 5 RUN N-311 OPERATING DATA

Date: July 11, 1985
Solvent: A04
Atmospheric Pressure: 29.19 inches mercury
Room Temperature: 18 C
Stirrer Speed: 1500 RPM
Autoclave Charge: 1205.2 grams
Subject: Partial Pressure Run

Sample	TC#1(C)	TC#2(C)	Avg (C)	P(psig)	Heater (F)
1	23.3	19.7	21.5	-24	999
2	52.5	36.3	44.4	-23	500
3	72.8	50.6	61.3	-22	300
4	91.5	63.5	77.5	-20	500
5	106.7	74.2	90.5	-18	500
6	125.3	88.9	107.1	-16	500
7	144.5	106.5	125.5	-13	500
8	165.5	124.3	145.0	- 9	601
9	182.6	140.8	161.7	- 6	601
10	198.5	159.2	178.9	0	701
11	220.4	181.9	201.2	5	701
12	233.1	196.4	214.8	10	701
13	243.1	207.9	225.5	13	701
14	261.7	231.8	246.8	21	801
15	275.0	246.0	260.5	26	801
16	300.6	276.5	288.6	42	801
17	325.5	301.7	313.6	55	851
18	350.0	333.6	341.8	76	901
19	362.9	350.0	356.5	89	999
20	375.1	365.1	370.1	99	999
21	387.7	376.8	382.3	112	999
22	399.6	392.5	396.1	128	999
23	411.7	405.1	408.4	150	999
24	425.0	420.0	422.5	183	999
25	437.1	433.0	435.1	240	999
26	440.0	436.0	438.0	262	999
27	445.5	441.9	443.7	314	999

TABLE 6 RUN N-310 OPERATING DATA

Date: July 9, 1986
Solvent: A04
Atmospheric Pressure: 29.09 inches mercury
Room Temperature: 21 C
Stirrer Speed: 1500 RPM
Average Autoclave Pressure: 2100 psia
Autoclave Charge: 1170.0 grams

Sample	TC#1(C)	TC#2(C)	Avg (C)	P(psig)	Heater (F)
1	308.5	304.2	306.4	2100	730
2	311.1	306.3	309.1	2056	730
3	312.4	308.2	310.3	2100	730
4	313.6	308.8	311.2	2089	730
5	323.6	319.7	321.7	2102	750
6	336.2	331.7	326.4	2098	790
7	349.7	345.7	347.7	2105	820
8	369.4	365.4	367.4	2100	860
9	385.5	381.5	383.5	2110	890
10	409.7	405.2	407.5	2105	930
11	431.2	427.4	429.3	2102	965
12	448.6	444.7	446.7	2125	980

TABLE 7 RUN N-325 OPERATING DATA

Date: August 20, 1985
Solvent: A04
Atmospheric Pressure: 29.12 inches mercury
Room Temperature: 24 C
Stirrer Speed: 1500 RPM
Average Autoclave Pressure: 2560 psia
Autoclave Charge: 1201.9 grams

Sample	TC#1(C)	TC#2(C)	Avg (C)	P(psig)	Heater (F)
1	305.8	298.9	302.4	2616	750
2	322.9	315.6	319.3	2460	780
3	339.7	331.7	335.7	2510	820
4	356.7	349.2	353.0	2509	840
5	374.5	366.5	370.5	2522	870
6	392.5	385.0	388.8	2551	900
7	406.3	399.2	402.8	2585	930
8	423.5	416.4	420.0	2488	960
9	437.7	430.3	434.0	2572	999
10	446.6	439.6	443.1	2558	999

TABLE 8 RUN N-322 OPERATING DATA

Date: August 16, 1985
Solvent: A04
Atmospheric Pressure: 29.11 inches mercury
Room Temperature: 19 C
Stirrer Speed: 1500 RPM
Average Autoclave Pressure: 3050 psia
Autoclave Charge: 1238.8 grams

Sample	TC#1(C)	TC#2(C)	Avg (C)	P(psig)	Heater (F)
1	306.9	299.4	303.2	3048	800
2	326.3	318.3	322.3	2868	830
3	339.0	331.3	335.2	3061	830
4	355.9	348.4	352.2	2896	850
5	378.3	371.1	374.7	3167	890
6	398.6	390.3	394.5	3017	920
7	417.4	409.2	413.3	2910	960
8	438.5	431.0	434.8	3123	999
9	445.0	441.0	443.0	3000	999

TABLE 9 RUN N-327 OPERATING DATA

Date: August 24, 1985
Solvent: A04
Atmospheric Pressure: 29.32 inches mercury
Room Temperature: 23 C
Stirrer Speed: 1500 RPM
Average Autoclave Pressure: 3635 psia
Autoclave Charge: 1181.1 grams

Sample	TC#1(C)	TC#2(C)	Avg (C)	P(psig)	Heater (F)
1	305.7	298.8	302.3	3369	750
2	321.8	315.8	318.8	3666	800
3	340.2	335.1	337.7	3734	800
4	357.5	350.1	353.8	3604	860
5	376.3	370.6	373.5	3682	890
6	393.4	387.7	390.6	3600	920
7	406.9	401.0	404.0	3617	940
8	422.0	415.8	418.9	3634	999
9	435.3	429.2	432.3	3579	999
10	441.2	435.5	438.4	3658	999

TABLE 10 RUN N-328 OPERATING DATA

Date: August 26, 1985
Solvent: A04
Atmospheric Pressure: 29.26 inches mercury
Room Temperature: 23 C
Stirrer Speed: 1500 RPM
Average Autoclave Pressure: 4010 psia
Autoclave Charge: 1214.1 grams

Sample	TC#1(C)	TC#2(C)	Avg (C)	P(psig)	Heater (F)
1	305.4	298.0	301.7	3874	730
2	320.2	315.0	317.6	4008	790
3	341.7	335.6	338.7	3876	830
4	355.3	349.9	352.6	3960	860
5	374.3	368.9	371.6	4122	880
6	390.5	384.9	387.7	4086	920
7	405.4	399.6	402.5	4088	950
8	423.5	417.9	420.7	3988	980
9	436.9	431.5	434.2	3974	999
10	445.2	439.8	442.5	3942	999

APPENDIX G

CLAUSIUS-CLAPEYRON CALCULATIONS

CLAUSIUS-CLAPEYRON CALCULATIONS

The data from run N-311 were analyzed using the Clausius-Clapeyron relationship. The following sections show the calculations and the results of this analysis.

I. ENTHALPY DETERMINATION

This section shows the calculations used to determine the enthalpy of vaporization of A04 using the Clausius-Clapeyron equation. The temperature and pressure data from run N-311 was first converted to units of degrees Kelvin and atmospheres of pressure. A plot of ln P versus 1/T was constructed from the data and is shown in Figure 7 of Chapter 4. The graph is broken down into three sections corresponding the light, middle, and heavy oil components of A04. The slope of each region and correlation coefficient are as follows:

Region	Slope	Correlation
Light Oils	-273.8	-.9978
Middle Oils	-1765.5	-.9908
Heavy Oils	-8643.0	-.9657

The enthalpy of vaporization for each region is calculated from the Clausius-Clapeyron relationship. These calculations are shown below:

$$\Delta H = -R(\text{slope}) \qquad [22]$$

For the light oils,

$$\Delta H = (-1.987 \text{ cal/gmole K})(-273.8 \text{ K})\times(454 \text{ gmole/lbmole})\times$$
$$(3.966 \times 10 \quad \text{Btu/cal})$$
$$= 979.6 \text{ Btu/lbmole.}$$

Likewise, for middle oils,

$$\Delta H = 6316.2 \text{ Btu/lbmole}$$

and heavy oils,

$$\Delta H = 30{,}920.5 \text{ Btu/lbmole.}$$

It should be noted that this determination is based on the assumption of ideal gas behavior of A04.

II. DIFFERENTIATION OF P-T DATA

The pressure and temperature data collected in run N-311 was differentiated and evaluated at specific temperatures in this section. From this differentiation, the data can be further analyzed using the Clausius-Clapeyron equation.

To find dP/dT at a specific temperature, the following equations are used.

$$dP/dT = (P_2 - P_1)/(T_2 - T_1) \qquad [23]$$

and

$$T = (T_2 + T_1)/2 \qquad [24]$$

For example, using samples at consecutive data points,

$$dP/dT = (3.06 - 2.72)/(474.2 - 451.9)$$
$$= .0152 \text{ atm/K}$$

and

$$T = (474.2 + 451.9)/2$$
$$= 463.1 \text{ K}$$

Substituting into the Claypeyron equation, the enthalpy per unit volume can be determined as follows:

$$\Delta H/V_G = .0152(T) = 7.04 \text{ cal/cm}^3$$

Converting to Btu/cu.ft yields:

$$\Delta H/V_G = 790.7 \text{ Btu/cu.ft.}$$

Using the same example, assume that ΔH is equal to that of phenanthrene, the most abundant constituent of A04. The molar volume of the gas at 463.1 K can be determined as follows:

$$V_G = (25{,}539 \text{ Btu/lbmole})/(961.4 \text{ Btu/cu.ft.})$$

$$V_G = 32.3 \text{ cu.ft./lbmole}$$

The molar volume of the gas was then plotted versus pressure as shown in Figure 9 of Chapter 4.

APPENDIX H

MATERIAL BALANCE DATA

TABLE 11 RUN N-310
MATERIAL BALANCE DATA

Average Autoclave Pressure: 2100 psia
Initial Charge: 1170.0 grams

Sample No.	Mass (grams)
LIQUID TIME SAMPLES	
1	2.0
2	5.9
3	5.7
4	3.5
5	5.2
6	5.0
7	4.8
8	4.5
9	4.5
10	4.2
11	4.0
12	4.0
GAS TIME SAMPLES	
1	0.1
2	0.8
3	0.7
4	0.9
5	1.5
6	2.2
7	2.2
8	2.0
9	5.1
10	2.5
11	2.2
12	3.2

Total Time Samples........................	76.7
Waste Liquid Samples......................	56.0
Waste Gas Samples.........................	12.9
Quench Clean-up...........................	983.4
Autoclave Clean-up........................	2.9
TOTAL MATERIAL BALANCE....................	96.3 %

TABLE 12 RUN N-325
MATERIAL BALANCE DATA

Average Autoclave Pressure: 2560 psia
Initial Charge: 1201.9 grams

Sample No.	Mass (grams)
LIQUID TIME SAMPLES	
1	4.9
2	5.3
3	4.8
4	5.1
5	4.8
6	4.2
7	4.9
8	4.9
9	5.2
10	5.7
GAS TIME SAMPLES	
1	1.6
2	1.0
3	0.9
4	1.4
5	2.4
6	2.8
7	3.5
8	4.0
9	4.3
10	4.0

Total Time Samples........................	75.7
Waste Liquid Samples......................	89.3
Waste Gas Samples.........................	8.7
Quench Clean-up...........................	971.9
Autoclave Clean-up........................	15.2
TOTAL MATERIAL BALANCE....................	96.6 %

TABLE 13 RUN N-322
MATERIAL BALANCE DATA

Average Autoclave Pressure: 3050 psia
Initial Charge: 1238.8 grams

Sample No.	Mass (grams)
LIQUID TIME SAMPLES	
1	2.3
2	2.0
3	2.3
4	2.3
5	2.3
6	2.5
7	2.6
8	1.4
9	1.4
GAS TIME SAMPLES	
1	1.7
2	0.7
3	1.6
4	1.6
5	2.3
6	2.2
7	1.8
8	2.6
9	1.7

Total Time Samples.........................	35.1
Waste Liquid Samples.......................	91.8
Waste Gas Samples..........................	6.7
Quench Clean-up............................	1046.3
Autoclave Clean-up.........................	14.8
TOTAL MATERIAL BALANCE.....................	96.4 %

TABLE 14 RUN N-327
MATERIAL BALANCE DATA

Average Autoclave Pressure: 3635 psia
Initial Charge: 1181.1 grams

Sample No.	Mass (grams)
LIQUID TIME SAMPLES	
1	5.5
2	4.5
3	2.1
4	4.4
5	4.6
6	2.4
7	2.6
8	5.3
9	4.8
10	5.1
GAS TIME SAMPLES	
1	1.9
2	1.8
3	2.1
4	3.0
5	3.1
6	3.0
7	4.0
8	4.4
9	5.1
10	4.5

Total Time Samples..........................	74.3
Waste Liquid Samples........................	76.8
Waste Gas Samples...........................	12.5
Quench Clean-up.............................	936.4
Autoclave Clean-up..........................	18.8
TOTAL MATERIAL BALANCE......................	94.7 %

TABLE 15 RUN N-328
MATERIAL BALANCE DATA

Average Autoclave Pressure: 4010 psia
Initial Charge: 1214.1 grams

Sample No.	Mass (grams)
LIQUID TIME SAMPLES	
1	5.7
2	7.0
3	2.4
4	1.4
5	2.0
6	2.1
7	2.0
8	2.4
9	2.4
10	2.6
GAS TIME SAMPLES	
1	2.7
2	2.6
3	1.8
4	4.8
5	4.4
6	4.4
7	3.0
8	3.5
9	3.8
10	4.8

Total Time Samples	65.8
Waste Liquid Samples	74.5
Waste Gas Samples	14.9
Quench Clean-up	1001.6
Autoclave Clean-up	26.0
TOTAL MATERIAL BALANCE	98.4 %

APPENDIX I

THF TEST RESULTS

TABLE 16 RUN N-325
THF SOLUBILITY TEST RESULTS

Liquid Sample No.	Temperature (C)	Pressure (psia)	Weight % Ca. Carbonate
1	302.4	2639	5.19
2	319.3	2485	5.25
3	335.7	2533	5.81
4	353.0	2532	5.83
5	370.5	2545	6.76
6	388.8	2574	7.15
7	402.8	2608	7.93
8	420.0	2511	8.12
9	434.0	2595	10.38
10	443.1	2581	14.03

Note: Analysis of gas samples 5 and 10 yielded 0.0 percent calcium carbonate.

TABLE 17 RUN N-322
THF SOLUBILITY TEST RESULTS

Liquid Sample No.	Temperature (C)	Pressure (psia)	Weight % Ca. Carbonate
1	303.2	3087	5.10
2	322.3	2906	5.50
3	335.2	3099	5.78
4	352.2	2934	6.40
5	374.7	3205	6.74
6	394.5	3055	7.52
7	413.3	2948	7.99
8	434.8	3161	8.99
9	443.0	3000	12.40

TABLE 18 RUN N-327
THF SOLUBILITY TEST RESULTS

Liquid Sample No.	Temperature (C)	Pressure (psia)	Weight % Ca. Carbonate
1	302.3	3390	5.18
2	318.8	3687	5.48
3	337.7	3755	5.71
4	353.8	3625	5.61
5	373.5	3703	6.73
6	390.6	3621	7.25
7	404.0	3638	7.82
8	418.9	3655	8.18
9	432.3	3600	8.84
10	438.4	3679	9.44

TABLE 19 RUN N-328
THF SOLUBILITY TEST RESULTS

Liquid Sample No.	Temperature (C)	Pressure (psia)	Weight % Ca. Carbonate
1	301.7	3891	5.04
2	317.6	4025	5.30
3	338.7	3893	6.17
4	352.6	3977	5.70
5	371.6	4139	6.12
6	387.7	4103	6.33
7	402.5	4105	6.66
8	420.7	4005	7.15
9	434.2	3991	7.76
10	442.5	3959	9.30

APPENDIX J

VAPOR-LIQUID DISTRIBUTION RESULTS

TABLE 20 RUN N-325
VAPOR-LIQUID DISTRIBUTION RESULTS

Sample No.	Wt Pct Liquid	Wt Pct Vapor	Pressure (psia)	Temperature (C)
1	96.2	3.8	2639	302.4
2	95.2	4.8	2483	319.3
3	85.5	14.5	2533	335.7
4	85.2	14.8	2532	353.0
5	72.7	27.3	2545	370.5
6	68.4	31.6	2574	388.8
7	61.0	39.0	2608	402.8
8	59.3	40.7	2511	420.0
9	45.1	54.9	2595	434.0
10	31.6	68.4	2581	443.1

TABLE 21 RUN N-322
VAPOR-LIQUID DISTRIBUTION RESULTS

Sample No.	Wt Pct Liquid	Wt Pct Vapor	Pressure (psia)	Temperature (C)
1	98.7	2.2	3087	303.2
2	90.4	9.6	2906	322.2
3	85.7	14.3	3099	335.2
4	76.9	23.1	2934	352.2
5	72.7	27.3	3205	374.7
6	64.6	35.4	3055	394.5
7	60.4	39.6	2948	413.3
8	53.0	47.0	3161	434.8
9	36.7	63.3	3000	443.0

TABLE 22 RUN N-327
VAPOR-LIQUID DISTRIBUTION RESULTS

Sample No.	Wt Pct Liquid	Wt Pct Vapor	Pressure (psia)	Temperature (C)
1	96.4	3.6	3390	302.3
2	91.0	9.0	3687	318.8
3	87.3	12.7	3755	337.7
4	89.1	10.9	3625	353.8
5	73.5	26.5	3703	373.5
6	67.8	32.2	3621	390.6
7	62.5	37.5	3638	404.0
8	59.5	40.5	3655	418.9
9	54.5	45.5	3600	432.3
10	50.6	49.4	3679	438.4

TABLE 23 RUN N-328
VAPOR-LIQUID DISTRIBUTION RESULTS

Sample No.	Wt Pct Liquid	Wt Pct Vapor	Pressure (psia)	Temperature (C)
1	99.2	0.8	3891	301.7
2	94.4	5.6	4025	317.6
3	80.5	19.5	3893	338.7
4	87.6	12.4	3977	352.6
5	81.6	18.4	4139	371.6
6	79.0	21.0	4103	387.7
7	75.0	25.0	4105	402.5
8	69.6	30.4	4005	420.7
9	63.8	36.2	3991	434.2
10	52.4	47.6	3959	442.5

APPENDIX K

MICRO-DISTILLATION TEST RESULTS

TABLE 24 RUN N-310
MICRO-DISTILLATION TEST RESULTS

Sample No.	Wt Pct Middle/ Light Oils	Wt Pct Heavy Oils & Char	Press. (psia)	Temp. (C)
Charge	88.0	12.0	--	--
1	85.5	14.5	2122	306.4
2	78.2	21.8	2100	334.0
3	78.0	22.0	2122	367.4
4	70.2	29.8	2127	407.5
5	70.0	30.0	2124	429.3
6	69.9	30.1	2147	446.7

TABLE 25 RUN N-325
MICRO-DISTILLATION TEST RESULTS

Sample No.	Wt Pct Middle/ Light Oils	Wt Pct Heavy Oils & Char	Press. (psia)	Temp. (C)
Charge	88.0	12.0	--	--
1	76.4	23.6	2533	335.7
2	83.5	16.5	2532	353.0
3	83.6	16.4	2545	370.5
4	80.1	19.9	2574	388.8
5	78.2	21.8	2608	402.8
6	78.8	21.2	2511	420.0
7	74.1	25.9	2595	434.0
8	72.9	27.1	2581	443.1

TABLE 26 RUN N-322
MICRO-DISTILLATION TEST RESULTS

Sample No.	Wt Pct Middle/ Light Oils	Wt Pct Heavy Oils & Char	Press. (psia)	Temp. (C)
Charge	88.0	12.0	--	--
1	82.4	17.6	2906	322.3
2	81.4	18.6	3099	335.2
3	83.3	16.7	2934	352.2
4	75.7	24.3	3055	394.5
5	77.5	22.5	2948	413.3
6	77.8	22.2	3161	434.8

TABLE 27 RUN N-327
MICRO-DISTILLATION TEST RESULTS

Sample No.	Wt Pct Middle/ Light Oils	Wt Pct Heavy Oils & Char	Press. (psia)	Temp. (C)
Charge	88.0	12.0	--	--
1	84.6	15.4	3687	318.8
2	81.3	18.7	3755	337.7
3	81.2	18.8	3625	353.8
4	79.3	20.7	3703	373.5
5	79.7	20.3	3621	390.6
6	75.9	24.1	3638	404.0
7	74.5	25.5	3655	418.9
8	74.4	25.6	3600	432.3

Note: Analysis of gas samples 1, 4, 5, 7, and 9 yielded 96.7, 98.8, 99.0, 99.2, and 98.8 weight percent middle and light oils.

TABLE 28 RUN N-328
MICRO-DISTILLATION TEST RESULTS

Sample No.	Wt Pct Middle/ Light Oils	Wt Pct Heavy Oils & Char	Press. (psia)	Temp. (C)
Charge	88.0	12.0	--	--
1	81.6	18.4	3893	338.7
2	77.7	22.3	4139	371.6
3	77.2	22.8	4103	387.7
4	72.1	27.9	4105	402.5
5	72.9	27.1	4005	420.7
6	73.5	26.5	3991	434.2
7	71.4	28.6	3959	442.5

APPENDIX L

STATISTICAL ANALYSIS

STATISTICAL ANALYSIS

The following details the statistical analyses performed in this study. The first section deals with the operating conditions and the second the experimental results.

I. STATISTICAL ANALYSIS ON THE OPERATING CONDITIONS

Statistical analysis was performed on each of the five time sample runs to determine if the time samples were collected at a statistically similar operating pressure. A student t-test was conducted to see if each sampling point was similar to the average pressure for each run. The results for this test and a sample calculation follow. All tests were performed at a 0.01 significance level.

A. Results:

The results for the student t-tests on the operating conditions are shown in Tables 29, 30, 31, 32, and 33. Each table gives the sample number and the operating pressure at which samples were taken. The tables also include: deviation from the average, the deviation squared, and the resulting t-value. If the absolute value of the actual t-value was greater than the t-critical value, the data point was considered to be statistically different at the 0.01 level. In each table, a * denotes that the point is not statistically similar at the 0.01 level.

TABLE 29 RUN N-310
STATISTICAL ANALYSIS OF OPERATING CONDITIONS

Sample No.	Press. (psia)	$x - \overline{x}$	$(x - \overline{x})^2$	t-value
1	2122	22	484	2.11
2	2078	22	484	2.11
3	2122	22	484	2.11
4	2111	11	121	1.06
5	2124	24	576	2.30
6	2020	80	6400	* 7.68
7	2127	27	729	2.59
8	2122	22	484	2.11
9	2132	32	1024	3.07
10	2127	27	729	2.59
11	2124	24	576	2.30
12	2147	47	2209	* 4.51

Average................ 2100 psia
Variance............... 1300
Standard Deviation..... 36.1

* Denotes t-test rejects

TABLE 30 RUN N-325
STATISTICAL ANALYSIS OF OPERATING CONDITIONS

Sample No.	Press. (psia)	$x - \bar{x}$	$(x - \bar{x})^2$	t-value
1	2639	79	6241	* 5.24
2	2483	77	5929	* 5.11
3	2533	27	725	1.79
4	2532	28	784	1.86
5	2545	15	225	0.99
6	2574	14	196	0.93
7	2608	48	2304	3.18
8	2511	49	2401	3.25
9	2595	35	1225	2.32
10	2581	21	441	1.39

Average............	2560 psia
Variance...........	2275
Standard Deviation.	47.7

* Denotes t-test rejects

TABLE 31 RUN N-322
STATISTICAL ANALYSIS OF OPERATING CONDITIONS

Sample No.	Press. (psia)	$x - \bar{x}$	$(x - \bar{x})^2$	t-value
1	3087	37	1369	1.06
2	2906	144	20,736	* 4.14
3	3099	49	2401	1.41
4	2934	116	13,456	3.33
5	3205	155	24,025	* 4.45
6	3055	5	25	0.14
7	2948	102	10,404	2.93
8	3161	111	12,321	3.19
9	3000	50	2500	1.44

Average............... 3050
Variance..............10,905
Standard Deviation.... 104.4

* Denotes t-test rejects

TABLE 32 RUN N-327
STATISTICAL ANALYSIS OF OPERATING CONDITIONS

Sample No.	Press. (psia)	$x - \bar{x}$	$(x - \bar{x})^2$	t-value
1	3390	245	60,025	* 7.95
2	3687	52	2704	1.69
3	3755	120	14,400	* 3.89
4	3624	10	100	0.32
5	3703	68	4624	2.21
6	3621	14	196	0.45
7	3638	3	9	0.10
8	3655	20	400	0.65
9	3600	35	1225	1.14
10	3679	44	1936	1.43

Average................ 3635 psia
Variance............... 9513
Standard Deviation..... 97.5

* Denotes t-test rejects

TABLE 33 RUN N-328
STATISTICAL ANALYSIS OF OPERATING CONDITIONS

Sample No.	Press. (psia)	$x - \bar{x}$	$(x - \bar{x})^2$	t-value
1	3891	119	14,161	* 4.38
2	4025	15	225	0.55
3	3893	117	13,689	* 4.31
4	3977	33	1089	1.21
5	4139	129	16,641	* 4.75
6	4103	93	8649	3.42
7	4105	95	9025	3.50
8	4005	5	25	0.18
9	3991	19	361	0.70
10	3959	51	2601	1.88

Average.............. 4010 psia
Variance............. 7385
Standard Deviation... 85.9

* Denotes t-test rejects

B. Sample Calculation:

Following is a sample calculation showing details of the t-test on the experimental data.

(1) Calculation of the Variance:

The variance of each set of run data is calculated by summing the squares of the deviations from the average and dividing by the number of degrees of freedom minus one. For run N-310:

Variance = S^2 = 14,300/(12 -1) = 1300

(2) Standard Deviation:

The standard is calculated by taking the square root of the variance as follows:

Standard Deviation = S = 36.1

(3) t-test:

The t-test calculation is shown as follows for sample number one of run N-310:

Ho (null hypothesis): $x = \bar{x}$

Ha (alternate): $x \neq x$

t(actual) = $(x - \bar{x})/(s/\sqrt{n})$ = 22/10.42 = 2.11

t(critical) = $t_{\alpha/2, 11}$ = 3.106 (from t-tables)

Since t(critical) > t(actual), accept Ho.

That is, at a 0.01 confidence level, sample number one (pressure = 2122 psia) is statistically similar to the average pressure of 2100 psia.

II. STATISTICAL ANALYSIS OF THE RESULTS

The following randomized block designs were used to determine the effects of pressure and temperature on the results of the THF and micro-distillation tests. Both were performed at the 0.01 significance level. Tables and sample calculations are shown on the next pages.

A. THF Solubility Test:

The data for this study are shown in Table 34. Note that it is arranged in a randomized block design with the following parameters: (1) Treatments- average autoclave pressure, (2) Blocks- temperature, and (3) Yield- weight fraction of A04 in the vapor phase. The columns and rows are totaled, and these totals are added to give the grand total. The statistical analysis is based on the sums of squares for the blocks, treatments, and residuals which are arranged in an ANOVA table. From this table, an F-test is performed at the 0.01 level to determine the various effects. The calculations for this test are divided into two parts: (1) calculations for forming the ANOVA table and (2) calculations for the F-test.

(1) Forming the ANOVA Table:

From Table 35, the various sums of squares can be

TABLE 34 RANDOMIZED BLOCK DESIGN (THF DATA)

		Pressure (psia)				
		2560	3050	3635	4010	Total
Temp. (C)	300	6	6	5	4	21
	320	8	8	8	6	30
	340	12	13	12	9	46
	360	17	19	18	12	66
	380	24	25	24	18	91
	400	33	31	32	24	120
	420	48	43	40	33	164
	440	71	57	52	44	224
Total		219	202	191	150	762

Treatments: Average Autoclave Pressure
Blocks: Temperature
Yield: Weight Fraction of A04 in the Vapor Phase

TABLE 35 ANOVA TABLE
(THF DATA)

Source	Sum of Squares (SOS)	Degrees of Freedom (DOF)	Mean Square
Blocks	$S_B = 8746.5$	7	$S_B^2 = 1249.5$
Treatments	$S_T = 323.3$	3	$S_T^2 = 107.8$
Residuals	$S_R = 305.2$	21	$S_R^2 = 14.5$
Totals		31	

$S_B^2/S_R^2 = 86.2$ $S_T^2/S_R^2 = 7.43$

calculated to be used in the ANOVA table. The calculations follow:

Correction Factor:

This is calculated by squaring the grand total and dividing by the number of data points as follows:

Correction Factor = $S_A = (762)^2/32 = 18,145$

In the following sums of squares, the correction factor is subtracted from each to give the correct value.

Total Sum of Squares:

This is calculated by squaring each data point in the table and then summing these figures:

Total Sum of Squares = $S = 6^2 + 6^2 + \ldots + 44^2 = 27,520$

Treatments Sum of Squares:

This is calculated by squaring each of the column totals and dividing by the number of rows as follows:

Treatments Sum of Squares = $S_T = (219^2 + 202^2 + \ldots + 150^2)/8$
$= 323.3$

Blocks Sum of Squares:

This is calculated by squaring each of the row totals and dividing by the number of columns as follows:

Blocks Sum of Squares = $S_B = (21^2 + 30^2 + \ldots + 224^2)/4$

$= 8,746.5$

Residual Sum of Squares:

This is calculated from the difference of the total sum of squares and the others mentioned above as follows:

Residual Sum of Squares = $S_R = S - S_B - S_T - S_A$

$= 27,520 - 8746.5 - 323.3 - 18,145$

$= 305.2$

These values are then used to form the following ANOVA table.

(2) F-test:

The following F-test was performed at the 0.01 level.

Ho: Blocks have zero effect

Ha: Blocks have an effect

F(critical) = $F_{.01, 7, 21} = 3.64$

From the ANOVA table:

F(actual) = $S_B^2/S_R^2 = 86.2$

Since F(actual) > F(critical) Reject Ho.

Therefore, there is an effect due to an increase in temperature on the weight fraction of A04 in the vapor phase at the 0.01 level.

Ho: Treatments have zero effect

Ha: Treatments have an effect

F(critical) = $F_{.01, 3, 21}$ = 4.87

From the ANOVA table:

F(actual) = S_T^2/S_R^2 = 7.43

Since F(actual) > F(critical) Reject Ho.

Therefore, there is an effect of an increase in pressure on the weight fraction of A04 in the vapor phase at the 0.01 level.

B. Micro-Distillation Test:

Table 36 contains the randomized data for the micro-distillation test. The parameters are as follows: (1) Treatments- pressure, (2) Blocks- temperature, and (3) Yield- weight fraction middle/light oils in the liquid phase.

(1) **Forming the ANOVA Table:**

The following are the results used in the formation of the ANOVA table. The table is shown on the page following these results.

TABLE 36 RANDOMIZED BLOCK DESIGN (MICRO-DISTILLATION DATA)

		Pressure (psia)					
		2100	2560	3050	3635	4010	Total
Temp. (C)	300	88.0	88.0	88.0	88.0	88.0	440.0
	335	78.2	76.4	81.4	81.3	81.6	398.9
	370	78.0	83.6	79.5	79.3	77.7	398.1
	405	70.2	78.3	76.6	75.9	72.1	373.0
	440	69.9	72.9	77.8	74.4	71.4	366.4
Total		384.3	399.1	403.3	398.9	390.8	1976.4

Treatments: Average Autoclave Pressure
Blocks: Temperature
Yield: Weight Fraction of Middle and Light Oils in the Liquid Phase

Total Sum of Squares =	$S = 157{,}042$
Correction Factor =	$S_A = 156{,}246$
Treatment Sum of Squares =	$S_T = 47$
Block Sum of Squares =	$S_B = 671$
Residual Sum of Squares =	$S_R = 78$

(2) F-test:

Ho: Blocks have zero effect

Ha: Blocks have an effect

F(critical) = $F_{.01,4,16}$ = 4.77

From ANOVA table:

F(actual) = S_B^2/S_R^2 = 34.3

Since F(actual) > F(critical) Reject Ho.

Therefore, there is an effect due to an increase in temperature on the weight fraction of middle and light oils that are present in the liquid phase of A04 at the 0.01 level.

Ho: Treatments have zero effect

Ha: Treatments have an effect

F(critical) = $F_{.01,4,16}$ = 4.77

TABLE 37 ANOVA TABLE (MICRO-DISTILLATION DATA)

Source	Sum of Squares (SOS)	Degrees of Freedom (DOF)	Mean Square
Blocks	$S_B = 671$	4	$S_B^2 = 168.0$
Treatments	$S_T = 47$	4	$S_T^2 = 11.8$
Residuals	$S_R = 78$	16	$S_R^2 = 4.9$
Totals		24	

$S_B^2/S_R^2 = 34.3$ $S_T^2/S_R^2 = 2.41$

From ANOVA table:

F(actual) = S_T^2/S_R^2 = 2.41

Since F(critical) > F(actual) Accept Ho.

Therefore, there is no effect due to an increase in pressure on the weight fraction of middle and light oils in the liquid phase of A04 at the 0.01 level.

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