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# Vapor-Liquid Equilibrium of Hydro-Treated Anthracene Oil (HAO61)

Michael J. Holmes

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VAPOR-LIQUID EQUILIBRIUM OF HYDRO-TREATED  
ANTHRACENE OIL (HA061)

by  
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Bachelor of Science, Mayville State College, 1984

A Thesis

Submitted to the Graduate Faculty

of the

University of North Dakota

in partial fulfillment of the requirements

for the degree of

Master of Science

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This thesis submitted by Michael J. Holmes 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.

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Department: Chemical Engineering

Degree: Master of Science

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## ABSTRACT

This thesis reports the equilibrium characteristics of the vapor and liquid phases of hydro-treated anthracene oil under conditions commonly used in coal liquefaction. These data should be useful in coal liquefaction studies and process designs.

The experiments were performed using the UND EERC's Hot Charge, Time Sample, Batch Autoclave System. Samples could be taken at desired temperatures and pressures with minimal disturbance to the system. The automated system allowed samples to be taken in a consistent manner.

Tests were conducted in temperature and pressure ranges of 300 to 440 °C and 2000 to 4000 psia, respectively. Sampling intervals were 20 °C for temperature and 500 psi for pressure.

Samples were analyzed to determine the fraction of the solvent present in the vapor state. The fraction of solvent in the vapor phase increased with increasing temperature. This is the expected effect of temperature, since increased temperature typically increases the vapor pressure of a solvent. The fraction of solvent in the vapor phase remained nearly constant as pressure was increased through the addition of nitrogen gas. The solvent behaved as could be expected, since changing the total pressure in this manner should have very little effect on the vapor pressure of a solvent.



The percentages of light, middle, and heavy oils present in the samples were also determined. The data show that the percentage of heavy oils in the liquid phase was nearly constant over the range of conditions tested. These data did not follow the expected trend for an increase in temperature and therefore vapor fraction. The liquid phase of the system would be expected to become richer in heavy oils as the vapor fraction increases, since the lighter, more volatile oils are the first to vaporize.

The results suggest, instead, that thermal cracking of the heavier organics may have occurred, since an increase in the percent heavy oils in the liquid phase did not coincide with increased vapor fraction. Additional analyses showed that for all of the autoclave runs, the mass percentage of heavy oils in the solvent decreased during testing. This provides further evidence that cracking of the solvent occurred.

## CHAPTER I. INTRODUCTION

The United States and its allies must continually work to develop alternative fuels because the countries we rely on for our oil supply are politically unstable. Coal is the most abundant fossil fuel available in the United States. Coal gasification, coal liquefaction, and coal water slurry production are three potential techniques for providing fuels to replace oil in the future. This research was conducted to support development of coal liquefaction techniques. The objective is to add information to the data base on the behavior of coal liquefaction solvents at typical process conditions.

This study investigated the behavior of Catalytically Hydrogenated Anthracene Oil - batch 61 (HAO61) under conditions of high temperature and high pressure. The HAO61 acts as a hydrogen donor solvent during the liquefaction process. In order for liquefaction solvents to be effective, they need to have hydrogen donor species present in the liquid phase. The vapor-liquid equilibrium of HAO61 under typical operating conditions was of primary interest in this study. In addition, the split between the light plus middle oils and heavy oils was determined over the range of conditions. The HAO61 was characterized under typical operating conditions to provide basic information for liquefaction processes.

The information gathered in this thesis can be combined with existing information and used to better understand coal liquefaction. This research is one part of a four part study to examine the behavior of common liquefaction solvents at typical operating conditions. Other solvents investigated included Anthracene Oil (AO4), a mixture of 25 percent by weight Solvent Refined Lignite (SRL) in AO4, and a phenolic solvent. The goal of these studies is to provide information that will help make more informed decisions on the type of catalysts, reactor design, and optimum conditions for the liquefaction process.

To get the desired information over a range of conditions, samples of both the liquid and vapor phases were taken while temperature and pressure were varied over time. Test conditions ranged from 2000 to 4000 psia and 300 to 440 °C with pressure and temperature increments of 500 psi and 20 °C, respectively. Samples taken at each test condition, were analyzed to determine the fraction of the solvent in the vapor phase, and the ratio of combined light and middle oils to heavy oils in each phase.

System parameters were controlled to minimize changes to the HAO61 solvent. Nitrogen gas ( $N_2$ ) and calcium carbonate ( $CaCO_3$ ) were the only two materials present in the system with the HAO61.  $N_2$  was used to control the pressure, and  $CaCO_3$  was used as a spike in the liquid phase to determine the fraction of vapor in the system.  $N_2$  and  $CaCO_3$  were chosen because they are both inert for the pur-



poses of this study and will not contribute to cracking of the heavier hydrocarbons. Although precautions were taken, the results indicate that some thermal cracking of the solvent occurred. It was important to minimize changes in the solvent composition during testing, and it is important to recognize any changes in the solvent that occur.

## CHAPTER II. BACKGROUND

This study is part of an investigation of the vapor-liquid equilibrium of coal liquefaction solvents. Catalytically hydrogenated anthracene oil (HAO61) is the solvent investigated in this thesis. This is one in a series of three such studies performed as part of the overall program. The other two of these studies involved similar characterizations of the solvent A04, and a mixture of 25 percent by weight SRL in A04 (1,2). The three studies were performed to build a data base and provide insight into the vapor-liquid characteristics of coal liquefaction mixtures.

### COAL LIQUEFACTION

Coal liquefaction is a generic term for processes that produce liquid fuels, often by the addition of hydrogen to coal. Coal and petroleum have hydrogen-to-carbon (H/C) ratios of  $\sim 0.7$  and  $>1.2$ , respectively (3). Liquid fuels can be formed by increasing the H/C ratio of coal.

Most coal liquefaction processes follow the basic principles of Bergius hydrogenation, which involves reacting pulverized coal or coal/oil slurries with hydrogen gas to form liquid hydrocarbons (3). This reaction requires conditions of high temperature and pressure and is, therefore, costly. It has since been found that liquefaction can be performed at lower temperatures and pressures by adding hydrogen donor solvents to the process. Processes

that rely more heavily upon hydrogen donor solvents are referred to as second generation liquefaction processes. Second generation processes offer economically more attractive conversions because of the lower temperature and pressure requirements.

#### VAPOR-LIQUID EQUILIBRIUM

The vapor-liquid equilibrium of second generation coal liquefaction solvents is important in understanding the reactions that occur. Design of reactors, selection of catalysts, and determination of operating conditions can be aided if this information is available.

Solvents in second generation coal liquefaction processes are very complex. Because most are derived from coal, which itself contains a broad spectrum of organic compounds, these solvents also contain numerous organic species. Furthermore, the composition of a liquefaction solvent is under continual change during the process.

Mathematically modeling a complex solvent's vapor-liquid equilibrium using conventional methods would be impractical. Modeling high pressure vapor-liquid equilibrium requires a knowledge of the solvent species and the relative amounts present (4). It is complicated and very expensive to analyze these solvents to determine their chemical compositions. In addition, the composition of the solvents continually changes during the liquefaction process.



## CHAPTER III. EXPERIMENTAL PROCEDURE

### Materials

The HAO61 solvent used in this study was produced in run sixty-one of the EERC's Continuous Process Unit (CPU). HAO61 is produced by catalytically hydrogenating anthracene oil from Crowley Chemical Company, batch four (AO4). Analyses of the chemical composition and microdistillation results at five torr are provided in Tables 1 and 2, respectively.

Tetrahydrofuran (THF), obtained from Fischer Scientific Company, was used to perform analyses and for cleanup. Calcium carbonate ( $\text{CaCO}_3$ ) was added to the solvent in order to determine the fraction of liquid in the reactor. Calcium carbonate is insoluble in THF and stable within the temperature ranges of the experiment. Nitrogen gas ( $\text{N}_2$ ) is inert at the conditions studied and was added to the reactor as a cover gas and to control pressure.

### Equipment

The apparatus used for this study was the EERC's one gallon batch autoclave system. A schematic of the system is provided in Figure 1.

The system contained a one gallon stainless steel charger equipped with pressure and temperature instrumentation. The charger was equipped with a piston which allows remote charging into a hot and pressurized autoclave. The

Table 1 Gas Chromatography Summary for HAO61

Component	Wt. %
Alkanes:	
C-10	0.004
C-11	0.017
C-12	0.036
C-13	0.058
C-14	0.047
C-15	0.065
C-16	0.073
C-17	0.180
C-18	0.141
C-19	0.116
C-20	0.061
C-21	0.032
C-22	0.022
C-23	0.016
C-24	0.013
C-25	0.009
C-26	0.010
C-27	0.007
C-28	0.008
C-29	0.008
C-30	0.007
C-31	0.007
C-32	0.005
C-33	0.004
pristane	0.051
phytane	0.058
5-methylindan	0.007
tetralin	0.837
naphthalene	1.553
2-Methyltetralin	0.239
1-Methyltetralin	0.127
1,1-dimethyltetralin	0.016
6-Methyltetralin	0.663
5-Methyltetralin	0.398
2-methylnaphthalene	2.087
1-methylnaphthalene	1.019
2,6-&R,7-dimethyltetralin	0.542
2-ethyltetralin	0.119
1,8-dimethyltetralin	0.036
6-ethyltetralin	0.246

Table 1 Gas chromatography Summary for HAO61 (continued).

Component	Wt. %
5-ethyltetralin	0.067
2A,3,4,5-tetrahydroacenaphthene	2.434
2-&1-ethylnaphthalene	0.915
2,6-&2,7-dimethylnaphthalene	0.575
1,6-dimethylnaphthalene	0.453
1,4-dimethylnaphthalene	0.635
1,2-dimethylnaphthalene	0.140
acenaphthene	5.758
1-phenylnaphthalene	0.075
1,3-dimethylnaphthalene	0.473
dibenzofuran	5.302
octahydrophenanthrene	0.587
phenanthrene	12.402
biphenyl	1.897
2,3-dimethylnaphthalene	0.113
fluorene	8.330
9,10-dihydrophenanthrene	2.214
anthracene	0.165
3-methylphenanthrene	0.456
2-methylphenanthrene	0.570
4,5-methylenephenanthrene	0.820
4,5-dihdropyrene	0.355
pyrene	1.625
4-methylbiphenyl	0.300
2-methylfluorene	0.590
1-methylfluorene	0.198
4-methylfluorene	0.204
4-methylphenanthrene	0.155
1-methylphenanthrene	0.196
4,5,9,10-tetrahydropyrene	1.121
/1,2,3,4-tetrahydrofluoranthene	
2-ethylphenanthrene	0.026
fluoranthene	3.236
3-methylbiphenyl	0.607
2-methylbiphenyl	0.182
9-methylfluorene	0.315
3,6-dimethylphenanthrene	0.006
2,7-dimethylphenanthrene	0.010
2-methylpyrene	0.062
4-methylpyrene	0.009
1-methylpyrene	0.016

Table 1 Gas Chromatography Summary for HAO61 (continued)

Component	Wt. %
2-phenylnaphthalene	0.378
stilbene	0.652
1-phenyltetralin	0.050
1,2-benzofluorene	0.305
2,3-benzofluorene	0.340
"-terphenyl	0.089
benz(c)anthracene	0.025
benz(a)anthracene	0.135
chrysene	0.288
benz(e)pyrene	0.105
benz(a)pyrene	0.081
phenyl ether	0.094
2-phenyltetralin	0.053
6-methylchrysene	0.009
perylene	0.032
1,2,3,4-dibenzanthracene	0.018
/dibenz(a,h)anthracene	
$\beta,\beta'$ -binaphthyl	0.010
TOTAL	65.201



Table 2 HAO61 Analyses.

	Sample	
	HAO61 <sup>a</sup>	
ASTM D-1160 Distillation @ 5 torr		
IBP, °C		42
Vol. % off at, °C		93
10		107
20		122
30		134
40		144
50		152
60		161
70		175
80		182
90		207
95		252
Max. Temp., °C		273
Vol. % off at Max. Temp.		97
Calculated from ASTM D-1160		
	HAO61 <sup>b</sup>	
IBP - 121 °C Fraction, Wt. %	21.0	19.2
121 - 260 °C Fraction, Wt. %	70.6	77.5
260 °C - Max. Temp. Fraction, Wt. %	0.0	1.3
Vacuum Bottoms, Wt %	5.5	2.0
Density, g/ml room temperature		1.05
Ultimate Analysis		
Carbon, Wt. %		90.3
Hydrogen, Wt. %		6.99
Nitrogen, Wt. %		0.37
Sulfur, Wt. %		0.15
Oxygen, Wt. %		2.20
H/C Ratio		0.93

<sup>a</sup>Results from anthracene oil catalytically hydrogenated in the EERC's Continuous Process Unit, Run 61.

<sup>b</sup>Same solvent retested for this study.

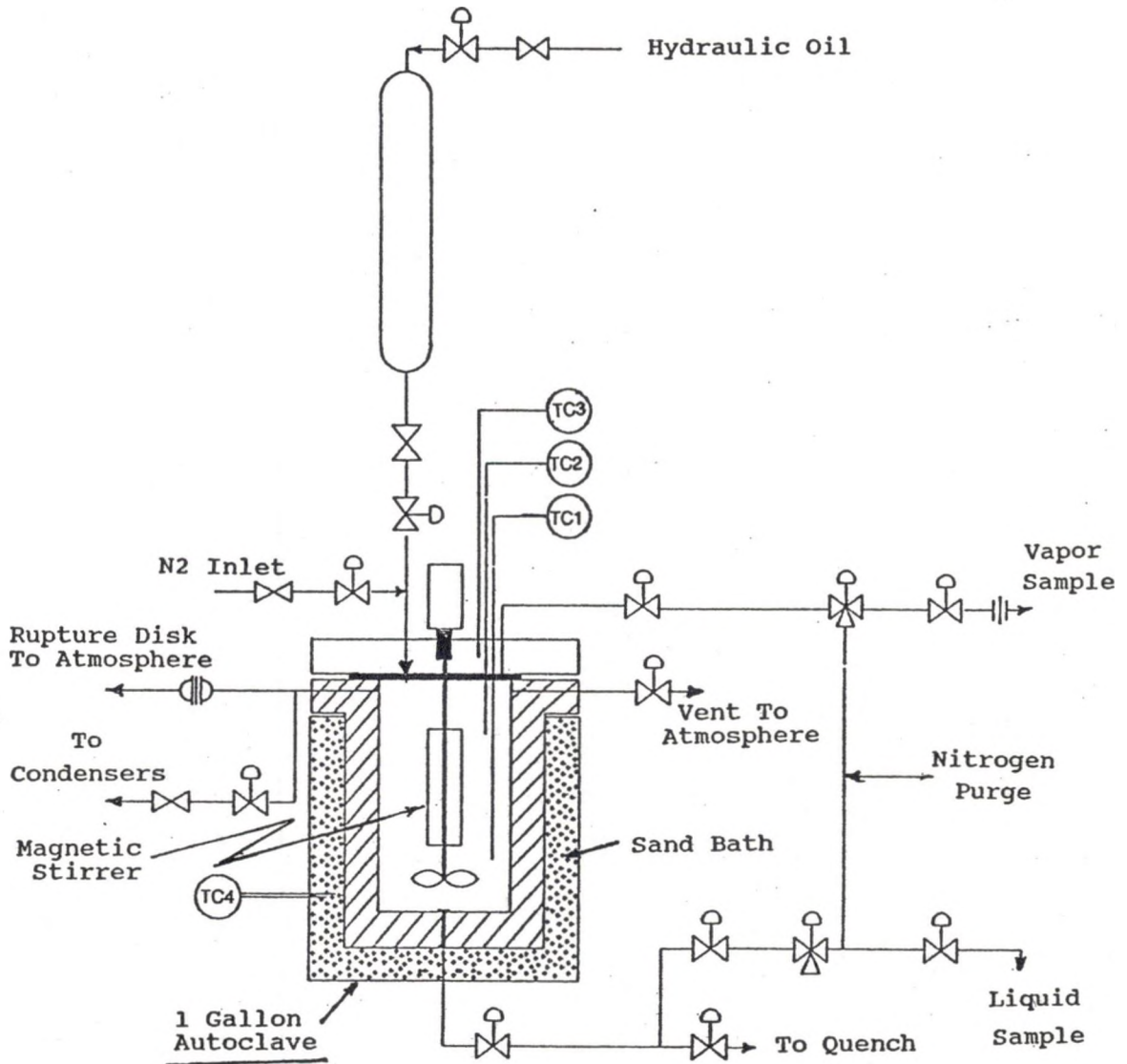


Figure 1. Schematic of EERC One Gallon Batch Autoclave System.



autoclave contained a magnetic stirrer to provide a well mixed system during the experiment. The apparatus was designed to allow simultaneous remote sampling of the liquid and vapor phases. The valve sequence for the sampling system was controlled using a Gould P-180 computer.

The system included a two gallon stainless steel quench vessel. The solvent was transferred to the quench vessel upon completion of a run to simplify its collection and to expedite cooling. Three condensers were placed in the gas venting line to collect any vapor released with the cover gas.

A vapor collection system was constructed out of stainless steel tubing connected to three-quarter inch pipe. The vapor samples were condensed in the pipe which was cooled using a mixture of iso-propyl alcohol and dry ice. Liquid samples were collected in 25 ml sample bottles.

#### Charge Preparation

The HA061 solvent was spiked with calcium carbonate before testing. About 1200 grams of total mixture was prepared containing approximately five percent calcium carbonate by weight. After mixing the contents of the solvent supply container, the desired amount of solvent was then removed and placed into a preweighed container. Then the calcium carbonate was added and the contents of the container were mixed well and weighed.

### Charging Procedure

The piston of the charger was set to provide the necessary volume for the mixture and leave room for only minimal air space. The HAO61 and calcium carbonate mixture was placed in the chamber of the charge vessel. The charger was then sealed and connected to the autoclave with one-quarter inch tubing.

Prior to charging the system, the autoclave was evacuated, preheated, and pressurized. A vacuum pump was used to remove most of the air from the reactor which was then sealed. The heater was set at 800 °C, and the reactor was pressurized to about 1000 psig. When the temperature reached 280 °C, the HAO61 charge was injected into the autoclave. The magnetic stirrer was turned on and set at 1500 rpm. The stirring rate was confirmed periodically using a tachometer.

### Testing

Once the reactor was charged, test conditions were set. Heating continued until the reactor contents reached about 300 °C, where the first samples were taken. Tests were performed at temperature intervals of approximately 20 °C up to a final system temperature of about 420 °C. With the temperature steady, the reactor was brought to the test pressure with compressed nitrogen gas. Tests were performed at pressures ranging from 2000 to 4000 psig at 500 psi intervals.



Each vapor-liquid sampling sequence included purge samples, sample shots, and N<sub>2</sub> purging of the lines. With the temperature and pressure at the desired values a set of waste samples were taken. This was done to remove any residue from the previous conditions. Then the conditions were allowed to restabilize and the actual samples were taken. The run samples each included two liquid and two vapor shots to provide sufficient material for analysis. For all samples, including the waste shots, the magnetic stirrer was shut off for 15 seconds prior to sampling and data logging. Following sample collection, the sample lines were purged with nitrogen gas.

Waste material resulting from sampling and purging was collected to be included in the material balance. Waste vapor shots were collected in a gas sampling bomb and weighed to determine the mass. Similarly, waste liquid samples were collected in a glass vial and weighed. Material collected during purging and cleanup procedures was also weighed and accounted for in the material balance.

One solvent charge was used for each pressure condition. Remaining solvent was pneumatically transferred from the reactor into the quench vessel. This helped reduce cool down time so cleanup could begin. Any remaining gases were removed through the cold traps where the vapors were condensed and then measured.

Upon completion of testing and cool down, cleanup was performed and the material balance for that run was com-

pleted. All cleanup rags were weighed prior to use so that the net weight after cleanup could be accounted for in the material balance.

The quench vessel was drained into preweighed containers and remaining solvent was wiped out with clean-up rags. The reactor was then opened and its internals were wiped clean. All residue was removed from sample lines by covering the ends with waste rags and purging the lines with nitrogen gas. Finally, the area was cleaned with waste rags to account for spills and loose spray. All of the sample and clean-up masses were totaled and subtracted from the total mass charged, to complete the material balancing procedure.

The testing procedure for the partial pressure run differed in that no samples were taken, and nitrogen gas was not used to increase the system pressure. Since samples were not taken, it was not necessary to add calcium carbonate to the solvent for this run. Data were taken to provide the solvent vapor pressure as a function of temperature. These data were logged over the temperature range of 300 to 450 °C. Cleanup and the material balance for the partial pressure run were similar to those for the time sample runs except for the absence of sample masses.

#### Analytical Methods

Samples taken during testing were later analyzed to provide information at the sample conditions. The vapor-

liquid equilibrium was determined for each liquid sample using THF solubility tests. A description of the THF solubility test and calculation procedure is found in Appendix C. The split of the light, middle, and heavy oils was identified using the microdistillation analysis which is described in Appendix D. The results from these analyses were combined with system data to complete the data set at each condition.



## CHAPTER IV. RESULTS AND DISCUSSION

Data and findings of this research are presented in this section. Partial pressure run results are presented and discussed first, followed by results of the time sample runs.

### Partial Pressure Run results

The data for the partial pressure run are provided in Table 3. The pressures were determined by correcting for the gauge reading at atmospheric pressure and accounting for the residual air that remained in the evacuated autoclave. Details on the pressure corrections are provided in Appendix B. The pressures represent the vapor pressure of the HA061 solvent at the given temperatures. The temperature measurement locations (TC1 and TC2) are shown in Figure 1. Values from TC1 indicated the upper autoclave temperature, and the TC2 values indicated the lower autoclave temperature. The averages of TC1 and TC2 were used as the system temperature for data calculations and plots.

The partial pressure results were considered from various perspectives. First, Table 3 is a tabulation of the HA061 vapor pressure as a function of system temperature. These data were plotted and are shown in Figure 2. As can be seen, and as expected, vapor pressure increased with increasing temperature. There did not appear to be any points where the solvent made a sharp change in behavior.



Table 3 Data for Run N-312, Partial Pressure Run.

Run N-312

July 12, 1985

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Solvent	HA061
Mass Charged	1186.2 g
Mass Balance (% Recovered)	96.8%
Barometric Pressure	29.08 in. Hg
Initial Autoclave Pressure	-10 psig
Evacuated Autoclave Pressure	-22 psig
Ambient Temperature	22 C
Stirrer Speed	2000 rpm

---

<u>Reading Number</u>	<u>System Temperature (F)</u>	<u>System Pressure (psia)</u>
1	28.6	2.9
2	50.8	4.8
3	63.2	5.7
4	84.4	5.5
5	111.5	6.3
6	141.3	8.1
7	152.5	10.0
8	164.3	12.9
9	171.7	15.8
10	204.5	27.6
11	221.2	33.5
12	238.4	43.3
13	260.2	51.2
14	270.0	56.1
15	284.3	63.0
16	295.3	69.9
17	314.0	79.8
18	338.5	97.6
19	357.3	115.4
20	377.8	137.3
21	397.9	164.1
22	412.2	193.0
23	422.3	221.9
24	431.5	260.8
25	441.4	327.8
26	444.6	360.7
27	447.1	394.7

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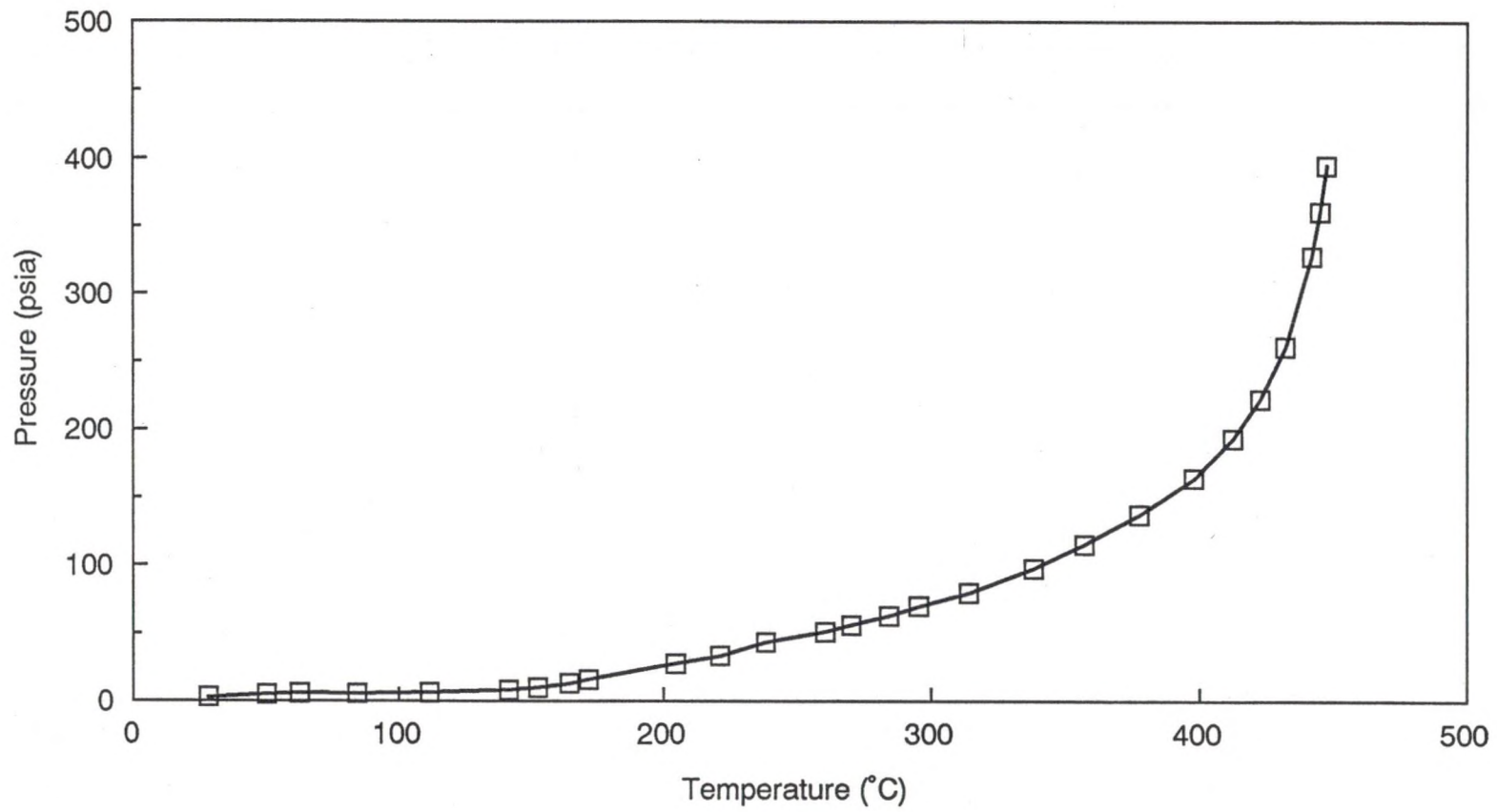


Figure 2. HAO61 Vapor Pressure Curve.

The smooth curve of pressure versus temperature is characteristic of a single component system. Since HA061 contains such a large number of components, some "stepping" in the behavior would not have been surprising.

Another way to examine the data is to fit it to the Clausius-Clapyron equation. The partial pressure data were fit to the Clausius-Clapyron equation. This was also done in similar research projects for A04 and a mixture of A04 and 25 percent by mass Solvent Refined Lignite (A04/SRL) by Rolando and Krause, respectively (1,2). Data from these investigations did not provide straight line fits over the entire range of investigation, but did provide fits over limited temperature ranges.

The Clausius-Clapyron equation was used as:

$$\ln P = - \Delta H/RT + C \quad [1]$$

Where,

- P = absolute pressure,
- T = absolute temperature,
- R = the ideal gas constant (1.987 calories/g-mole\*K),
- $\Delta H$  = heat of vaporization,
- C = constant specific to the solvent.

It is assumed that the vapor obeys the ideal gas law and that the volume of liquid in the system is negligible. The Clausius-Clapyron equation is normally used to evaluate single component systems.

The HAO61 partial pressure data fit of the Clausius-Clapyron equation is shown in Figure 3. The HAO61 results showed fits over limited temperature ranges similar to the results of Rolando (1) and Krause (2). The curve was fit over the temperature ranges from 111 to 412 °C and 421 to 446 °C. The resulting  $\Delta H$  values for these two ranges were 6,130 cal/g-mole and 22,800 cal/g-mole, respectively. The comparison of these results with those for AO4 and the AO4/SRL mixture is shown in Table 4.

Table 4 Comparison of Clausius-Clapyron Results From HAO61, AO4, and AO4/SRL Solvents.

	<u>Liquid Identification</u>		
	HAO61	AO4	AO4/SRL
$\Delta H$ - cal/g-mole T < 400 °C	6,130	6,316	7,200
$\Delta H$ - cal/g-mole T > 400 °C	22,800	30,920	28,000

The lower  $\Delta H$  values observed for the HAO61 solvent can be attributed to a higher ratio of hydrogen-to-carbon (H/C) in HAO61 than is present in either AO4 or the AO4/SRL mixture. Since it takes less energy to vaporize light oils, the  $\Delta H$  values of HAO61 are expected to be lower than for the other two solvents at the same temperature.

Krause (2) suggests that the fit below 400 °C represents the light oils, and the fit above 400 °C represents the middle oils. He supported this by showing that the en-



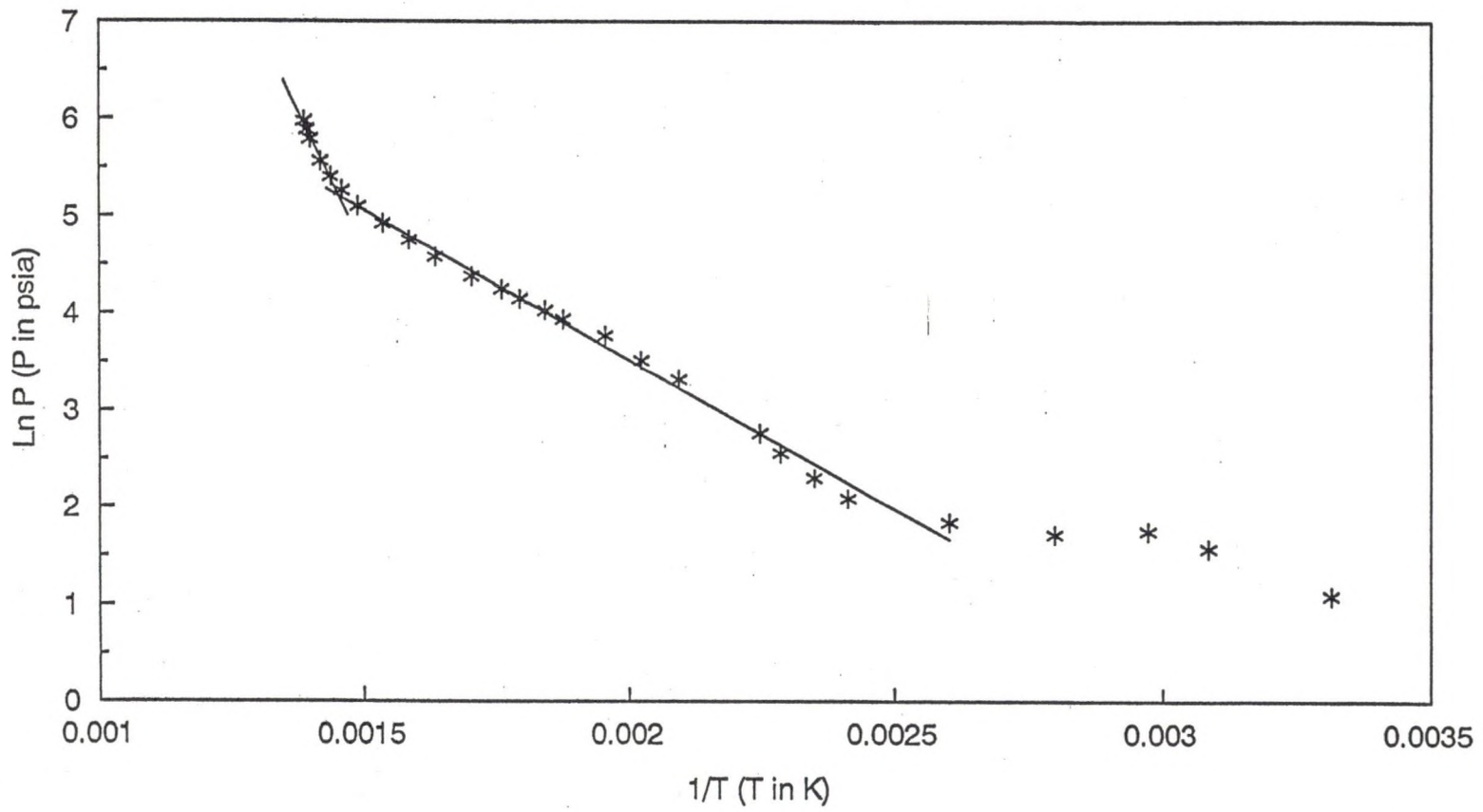


Figure 3. Clausius-Clapeyron Results for HAO61 Vapor Pressure Data

enthalpies of vaporization for some common light oils ( $\Delta H$  for benzene and toluene are 7352 and 7930 cal/g-mole, respectively) compared well to the 7200 cal/g-mole obtained for A04/SRL. The HAO61 provides good agreement with this, even though the light oil value was slightly lower. Again, the lower value for HAO61 was probably the result of higher concentrations of light oils as compared to the A04/SRL mixture. A better comparison to the 6130 cal/g-mole for HAO61 light oils is found with the heats of vaporization for iso-pentane and furane of 6386 and 6480 cal/g-mole, respectively (5).

### Results of Time Sample Runs

The following discussion contains results from time sample runs N-321, N-323, N-333, N-336, and N-347. The section is divided into discussions on test conditions, material balance calculations, vapor-liquid equilibrium, the light plus middle oil split with heavy oils, and an analysis of the data using the Clausius-Clapyron equations.

#### Test Conditions

The data for each time sample run includes system pressures and temperatures during each sample. Run conditions at which samples were taken are summarized in Tables 5 and 6. These tables contain the pressure and temperature conditions, respectively, for each of the five time-sample runs. The temperatures are the averages of TC1 and TC2. Pressures were determined by correcting gauge readings for barometric pressure and the deviation from zero at ambient conditions (See Appendix B). Each condition recorded represents the point at which a sample was taken.

#### Mass Balance Calculations

Mass balances were performed for each run to determine the quantity of solvent unaccounted for at the end of the run. The mass balance results are summarized in Table 7. Complete results from the mass balance calculations are provided in Appendix C.

Table 5 Corrected Sample Pressures.

	Run N-333	Run N-323	Run N-321	Run N-336	Run N-347
Sample Number	Pressure (psia)	Pressure (psia)	Pressure (psia)	Pressure (psia)	Pressure (psia)
1	2059	2760	3401	3534	3972
2	2066	2557	3323	3622	4057
3	2069	2560	3134	3623	3973
4	2054	2560	3033	3598	3997
5	2051	2604	2855	3580	3986
6	2068	2580	3221	3567	4041
7	2032	2563	3078	3531	4042
8	2127	2546	2964	3557	4046
9	2170	2560		3659	4036
average	2078	2588	3126	3586	4017
Sample (s)	43	67	183	43	34

Table 6 Test Matrix.

	Run N-333	Run N-323	Run N-321	Run N-336	Run N-347
Sample Number	Avg. Temp. (°C)	Avg. Temp. (°C)	Avg. Temp. (°C)	Avg. Temp. (°C)	Avg. Temp. (°C)
1	305.3	304.5	302.7	303.2	303.0
2	319.3	317.9	332.8	323.4	325.3
3	333.6	337.8	344.0	343.1	343.1
4	350.2	350.1	362.4	363.7	364.9
5	364.7	364.7	380.3	379.8	378.7
6	382.5	381.0	397.6	394.6	393.7
7	402.6	395.0	420.1	407.5	409.5
8	423.8	409.9	433.5	423.6	423.8
9	441.7	424.2		439.8	436.2
Average Pressure	2078	2588	3126	3586	4017



Table 7 Summary of mass balances.

	Partial Pressure	<u>Run Identification</u>				
		N-333	N-323	N-321	N-336	N-347
Average Pressure	N.A.	2078	2588	3126	3586	4017
Percent Accounted for	96.8	97.5	94.9	98.1	96.8	96.4

Unaccounted for solvent could include vapors not recovered in the cold traps, sampling losses, residue in lines, or material not recovered in the waste rags. The vapor samples were collected using three-quarter inch pipe cooled in a dry ice and iso-propyl alcohol mixture. While releasing the pressurized sample from this collection system, it was found that a small amount escaped as atomized liquid. Small losses during the sampling procedure can become significant when they are accumulated over all of the samples taken during the run.

#### Vapor-Liquid Equilibrium

Tables 8 through 12 provide the results of the vapor-liquid distributions at the various system conditions. The data are also presented graphically in Figures 4 through 8 as the results are discussed.

The run data show that the fraction of the solvent in the vapor phase increases as temperature increases over the range studied. This behavior is expected, since an in-

Table 8 Vapor-Liquid Distribution of HAO61 at Run N-333  
Test Conditions.

Mass Charged to Reactor = 1203.8 g  
Percent CaCO<sub>3</sub> in Charge = 5.1 %

Sample ID	<u>Test conditions</u>		CaCO <sub>3</sub> in liquid (%)	HAO61 vapor (wt. %)	HAO61 liquid (wt. %)
	Temp. (°C)	Pressure (psia)			
1	305.3	2059	7.17	31.0	69.0
2	319.3	2066	6.95	28.8	71.2
3	333.6	2069	7.71	36.3	63.7
4	350.2	2054	7.85	37.7	62.3
5	364.7	2051	9.59	50.2	49.8
6	382.5	2068	12.75	64.0	36.0
7	402.6	2032	11.35	59.5	40.5
8	423.8	2127	13.47	67.0	33.0
9	441.7	2170	12.63	65.0	35.0

Table 9 Vapor-Liquid Distribution of HAO61 at Run N-323  
Test Conditions.

Mass Charged to Reactor = 1222.6 g  
Percent CaCO<sub>3</sub> in Charge = 4.9 %

Sample ID	<u>Test conditions</u>		CaCO <sub>3</sub> in liquid (%)	HAO61 vapor (wt. %)	HAO61 liquid (wt. %)
	Temp. (°C)	Pressure (psia)			
1	304.5	2760	6.71	28.6	71.4
2	317.9	2557	7.41	35.9	64.1
3	337.8	2560	8.38	44.2	55.8
4	350.1	2560	9.77	53.1	46.9
5	364.7	2604	9.08	49.6	50.4
6	381.0	2580	11.60	61.9	38.1
7	395.0	2563	11.88	63.5	36.5
8	409.9	2546	14.44	71.3	28.7
9	424.2	2560	14.13	71.2	28.8

Table 10 Vapor-Liquid Distribution of HAO61 at Run N-321 Test Conditions.

Mass Charged to Reactor = 1205.5 g  
 Percent CaCO<sub>3</sub> in Charge = 5.1 %

Sample ID	<u>Test conditions</u>		CaCO <sub>3</sub> in liquid (%)	HAO61 vapor (wt. %)	HAO61 liquid (wt. %)
	Temp. (°C)	Pressure (psia)			
1	302.7	3401	6.87	27.2	72.8
2					
3	332.8	3323	8.25	40.3	59.7
4	344.0	3134	8.69	43.9	56.1
5	362.4	3033	9.57	49.8	50.2
6	380.3	2855	12.32	62.4	37.6
7	397.6	3221	14.16	68.3	31.7
8	420.1	3078	16.78	74.5	25.5
9	433.5	2964	18.46	77.8	22.2

Table 11 Vapor-Liquid Distribution of HAO61 at Run N-336 Test Conditions.

Mass Charged to Reactor = 1186.0 g  
 Percent CaCO<sub>3</sub> in Charge = 5.0 %

Sample ID	<u>Test conditions</u>		CaCO <sub>3</sub> in liquid (%)	HAO61 vapor (wt. %)	HAO61 liquid (wt. %)
	Temp. (°C)	Pressure (psia)			
1	303.2	3534	7.27	32.9	67.1
2	323.4	3622	7.57	35.9	64.1
3	343.1	3623	8.54	44.1	55.9
4	363.7	3598	11.09	58.4	41.6
5	379.8	3580	11.22	59.4	40.6
6	394.6	3567	12.02	62.9	37.1
7	407.5	3531	12.09	63.8	36.2
8	423.6	3557	14.84	71.9	28.1
9	439.8	3659	14.05	70.8	29.2



Table 12 Vapor-Liquid Distribution of HAO61 at Run N-347  
Test Conditions.

Mass Charged to Reactor = 1189.4 g  
Percent CaCO<sub>3</sub> in Charge = 5.1 %

Sample ID	<u>Test conditions</u>		CaCO <sub>3</sub> in liquid (%)	HAO61 vapor (wt. %)	HAO61 liquid (wt. %)
	Temp. (°C)	Pressure (psia)			
1	303.0	3972	6.79	26.3	73.7
2	325.3	4057	6.24	19.4	80.6
3	343.1	3973	8.65	43.2	56.8
4	364.9	3997	8.87	45.0	55.0
5	378.7	3986	9.78	50.9	49.1
6	393.7	4041	13.62	66.5	33.5
7	409.5	4042	13.68	67.2	32.8
8	423.8	4046	14.37	69.6	30.4
9	436.2	4036	14.97	71.6	28.4

Average Run Pressure = 2078 psia

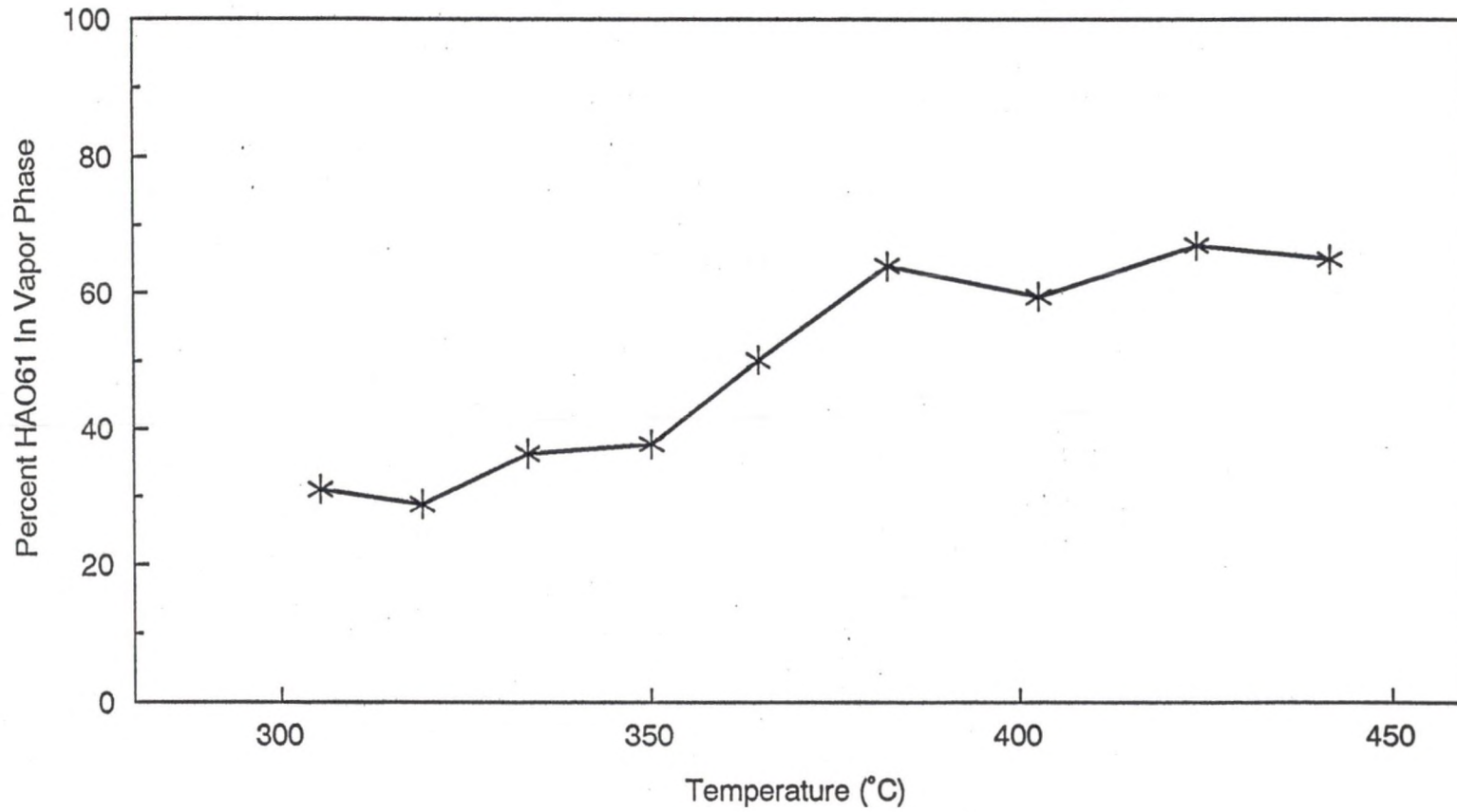


Figure 4. Percent of HAO61 in Vapor Phase as a Function of Temperature, Run N-333.

Average Run Pressure = 2588 psia

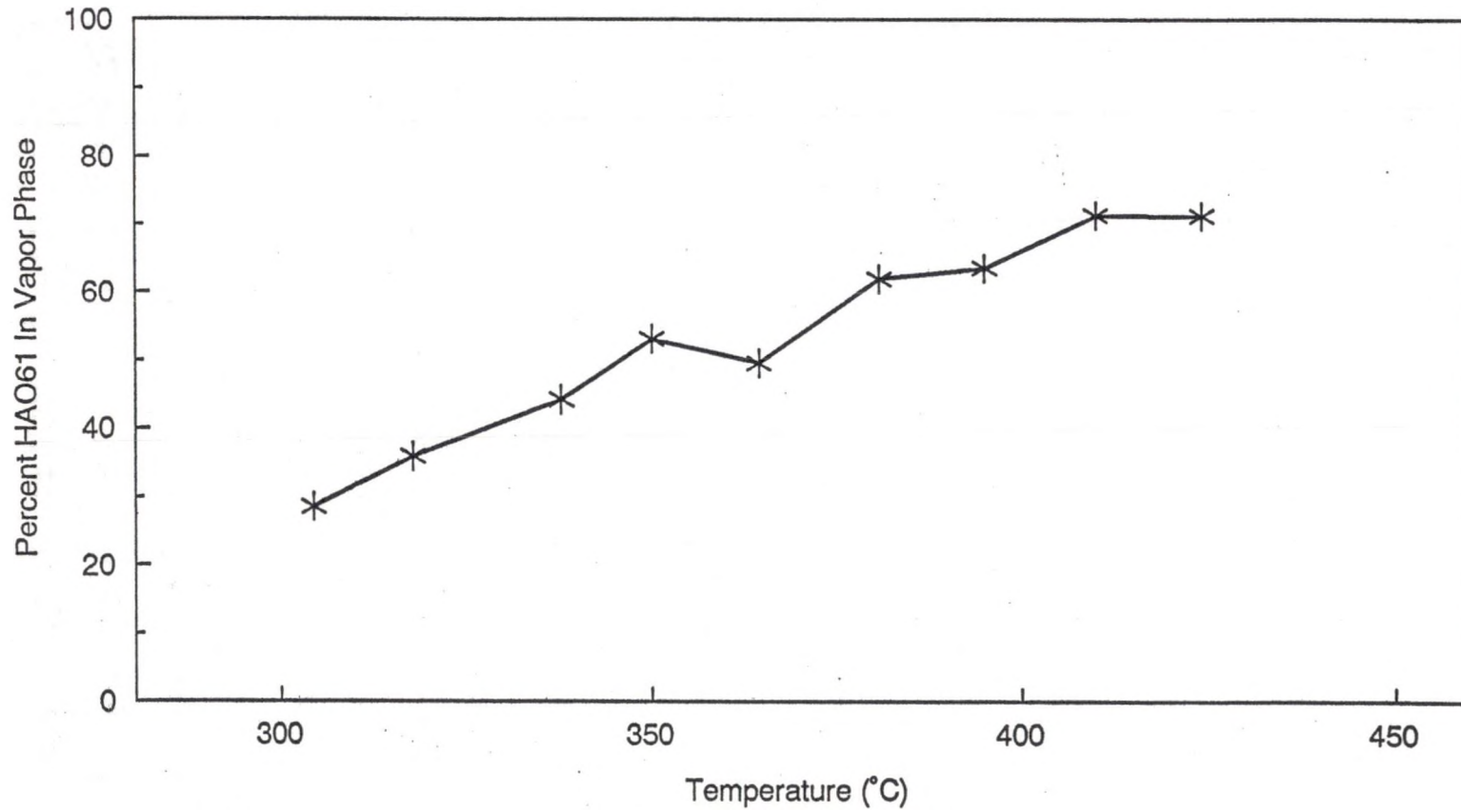


Figure 5. Percent of HAO61 in Vapor Phase as a Function of Temperature, Run N-323.



Average Run Pressure = 3126 psia

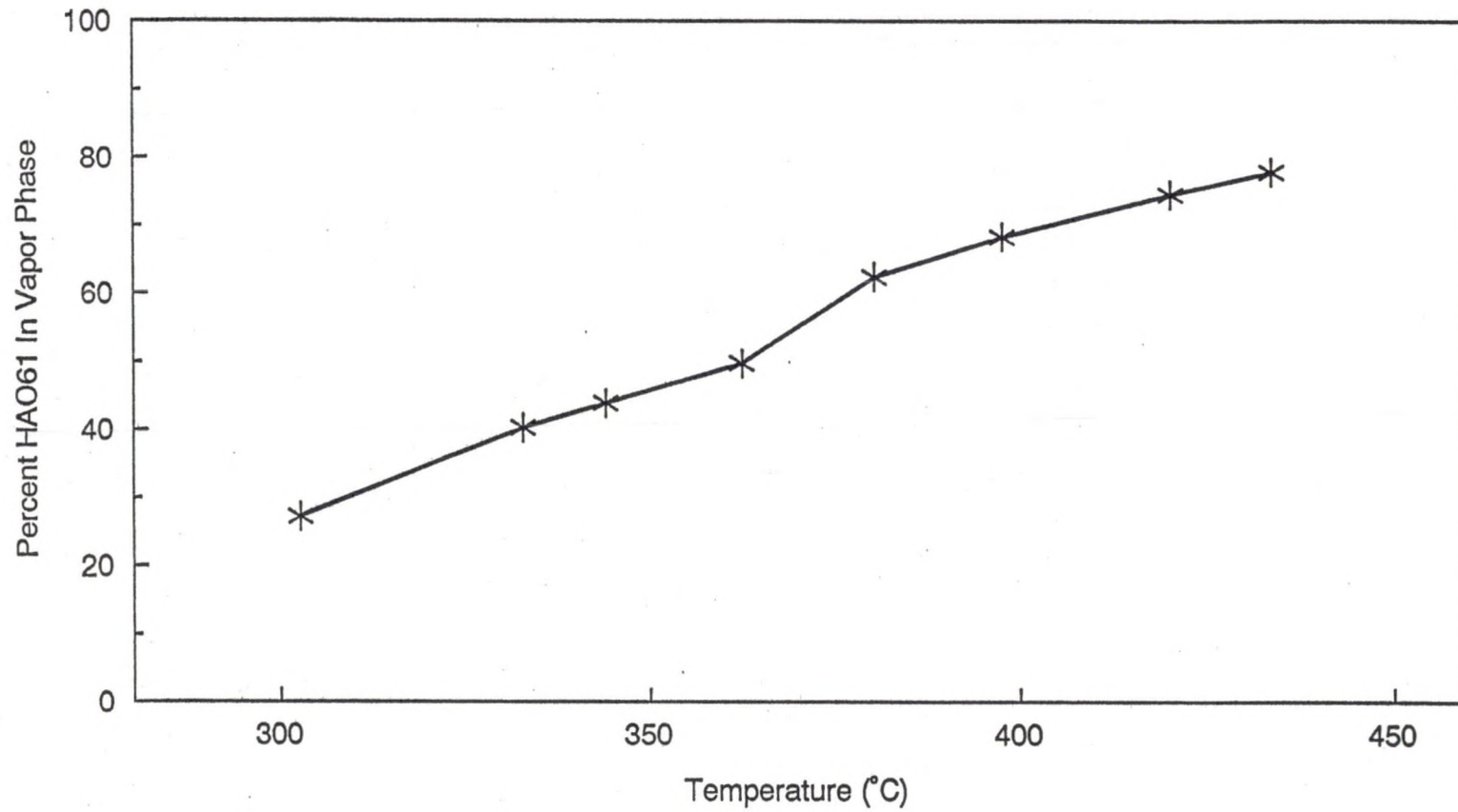


Figure 6. Percent of HAO61 in Vapor Phase as a Function of Temperature, Run N-321.

Average Run Pressure = 3586 psia

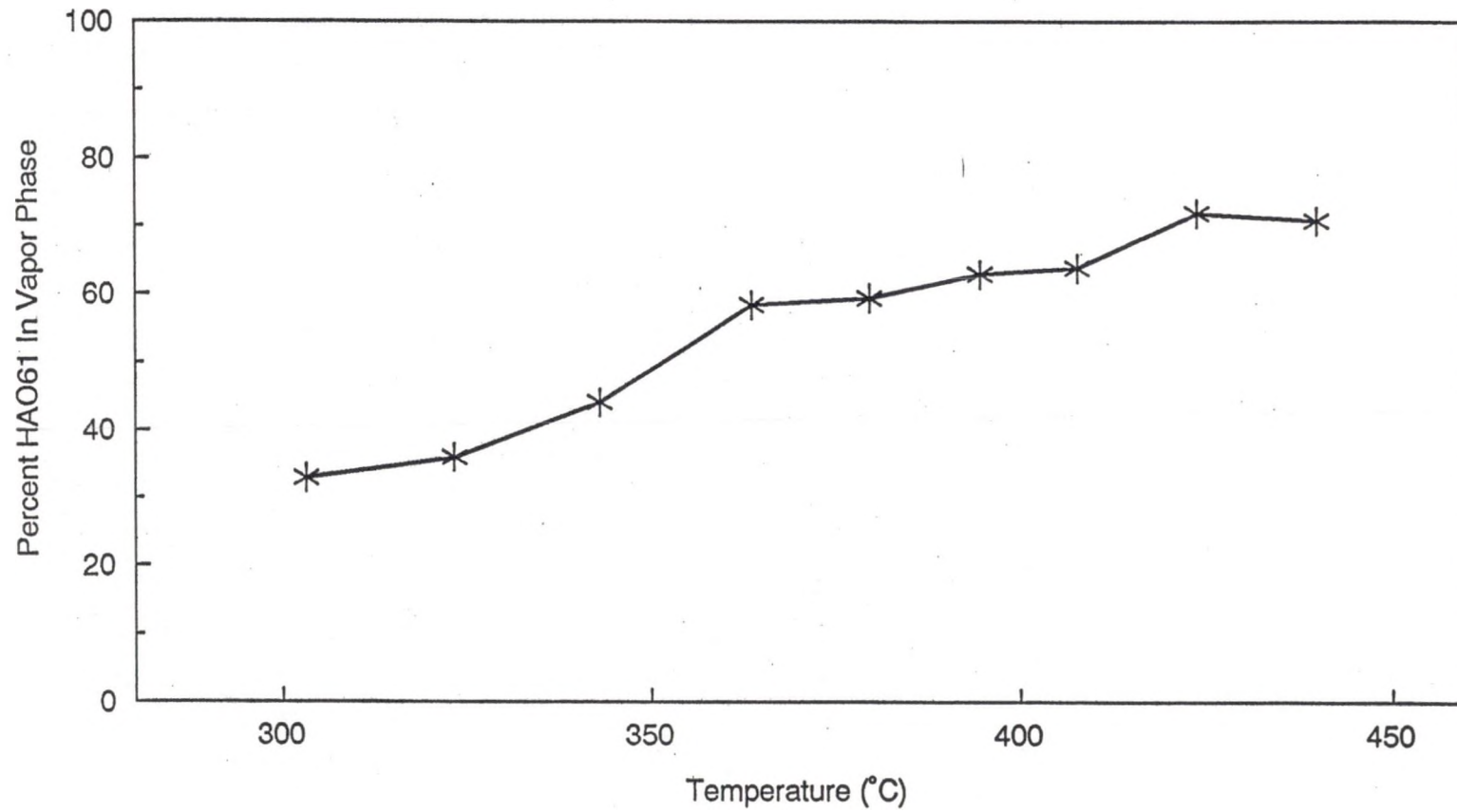


Figure 7. Percent of HAO61 in Vapor Phase as a Function of Temperature, Run N-336.

Average Run Pressure = 4017 psia

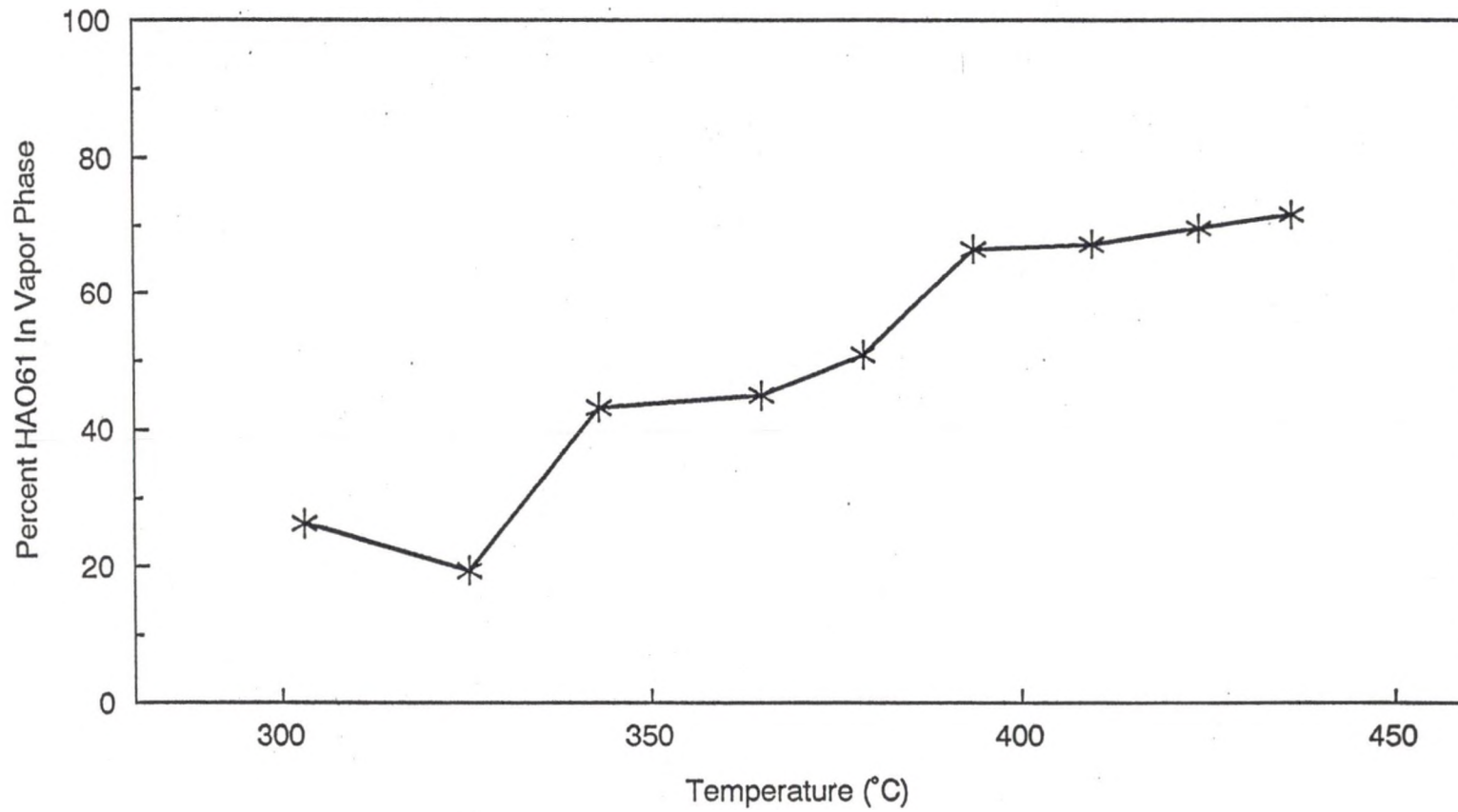


Figure 8. Percent of HAO61 in Vapor Phase as a Function of Temperature, Run N-347.



crease in temperature increases the vapor pressure of the solvent. The trend is shown graphically in Figures 4 through 8. As an example, Figure 6 and Table 10 (Run N-321) show that as temperature increased from 303 to 434 °C, the percent vapor increased from 27 to 78 percent at a constant nominal pressure of 3126 psia. Temperature affected the vapor-liquid equilibrium similarly for the other four time-sample runs shown.

The effect of pressure on the vapor-liquid equilibrium was not as pronounced. The results of this study showed that pressure affected the quantity of solvent in the vapor phase very little between pressures of 2000 and 4000 psia. To show this graphically, the percent solvent in the vapor phase is plotted as a function of temperature with all of the run pressures on the same graph (See Figure 9). The vertical distances between the curves represent the effect of pressure on the vapor-liquid equilibrium. As can be seen, there is no obvious effect of pressure for these data.

Since the increased system pressure was achieved by adding inert nitrogen gas, it could be expected that pressure would have almost no effect on the fraction of solvent in the vapor phase. At constant temperature, the vapor pressures of individual components in HAO61 should be affected very little by the addition of nitrogen. Therefore, the nearly constant percentage of solvent seen in the vapor phase as pressure was increased, was as it should be.

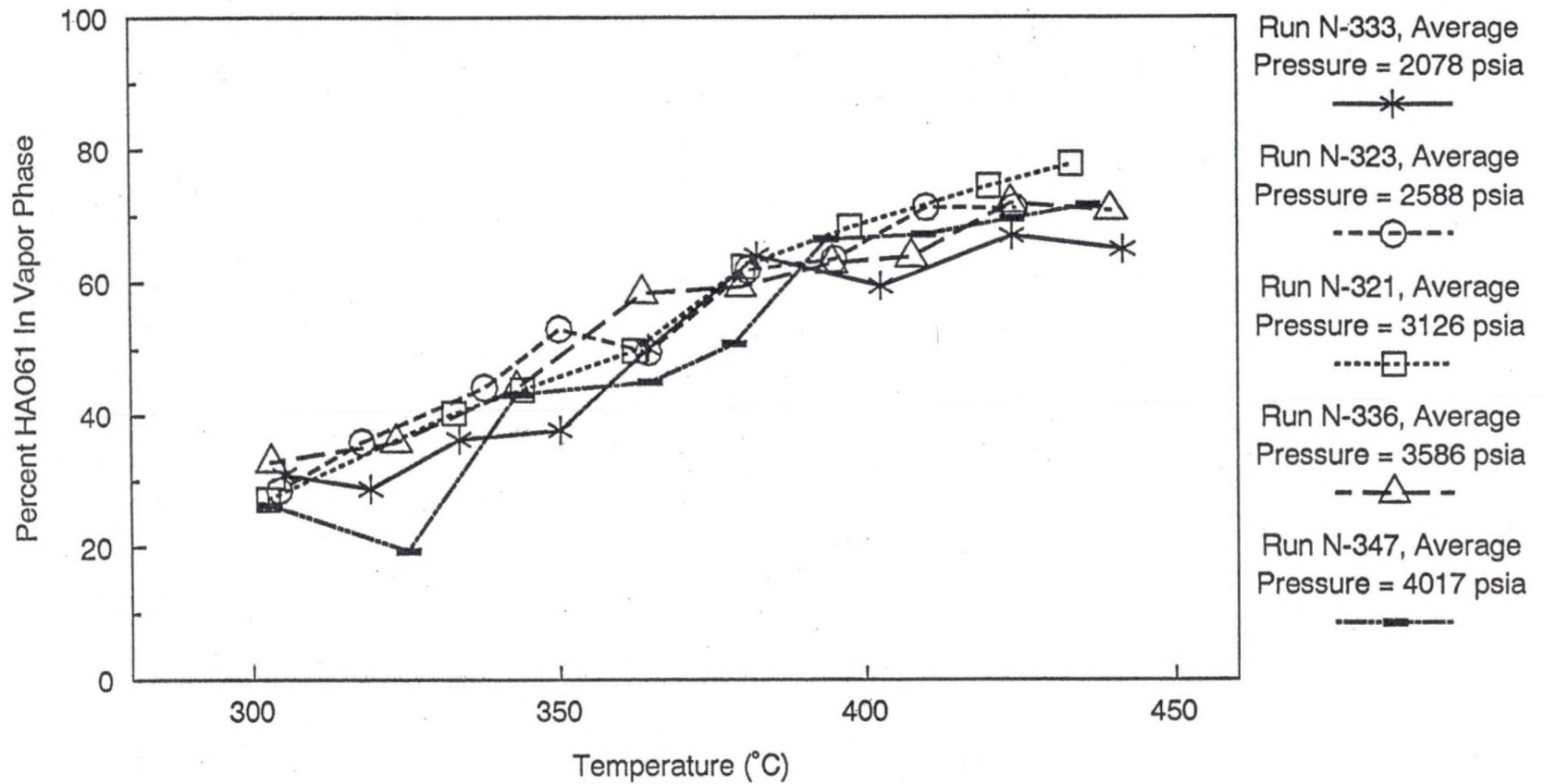


Figure 9. Percent of HAO61 in Vapor Phase as a Function of Temperature, All Runs.

An Analysis of Variance (ANOVA) was performed on the data to verify the effects of temperature and pressure on the vapor-liquid equilibrium. Results of the ANOVA verified the effect of temperature and also indicated that pressure had a barely significant effect on the vapor-liquid equilibrium at the 95 percent confidence level (See Appendix F).

Nominal conditions that were used for the ANOVA are summarized in Table 13 with percentages of solvent in the vapor phase. The rows in the table represent conditions of similar temperature and the columns represent similar pressures. Vapor yields averaged over all pressures increase with temperature similarly to runs conducted at a single pressure. Vapor yields averaged over all temperatures increase slightly with pressure initially and then decrease slightly.

Table 13 ANOVA Setup for Fraction HAO61 in Vapor Phase Results.

	Block (Avg Temp)	Treatment (Pressure)					Block Average
		1 2078	2 2588	3 3126	4 3586	5 4017	
1	304	31	29	27	33	26	29
2	324	29	36	40	36	19	32
3	346	38	53	44	44	43	44
4	364	50	50	50	58	45	51
5	380	64	62	62	59	51	60
6	395	60	64	68	63	67	64
7	423	67	71	75	72	70	71
Treatment Average		48	52	52	52	46	50 = Grand Average



The test results were combined to produce a three dimensional plot showing the effects of pressure and temperature on the system equilibrium. The general trends discussed in this section can be seen in Figure 10.

### Clausius-Clapyron Results

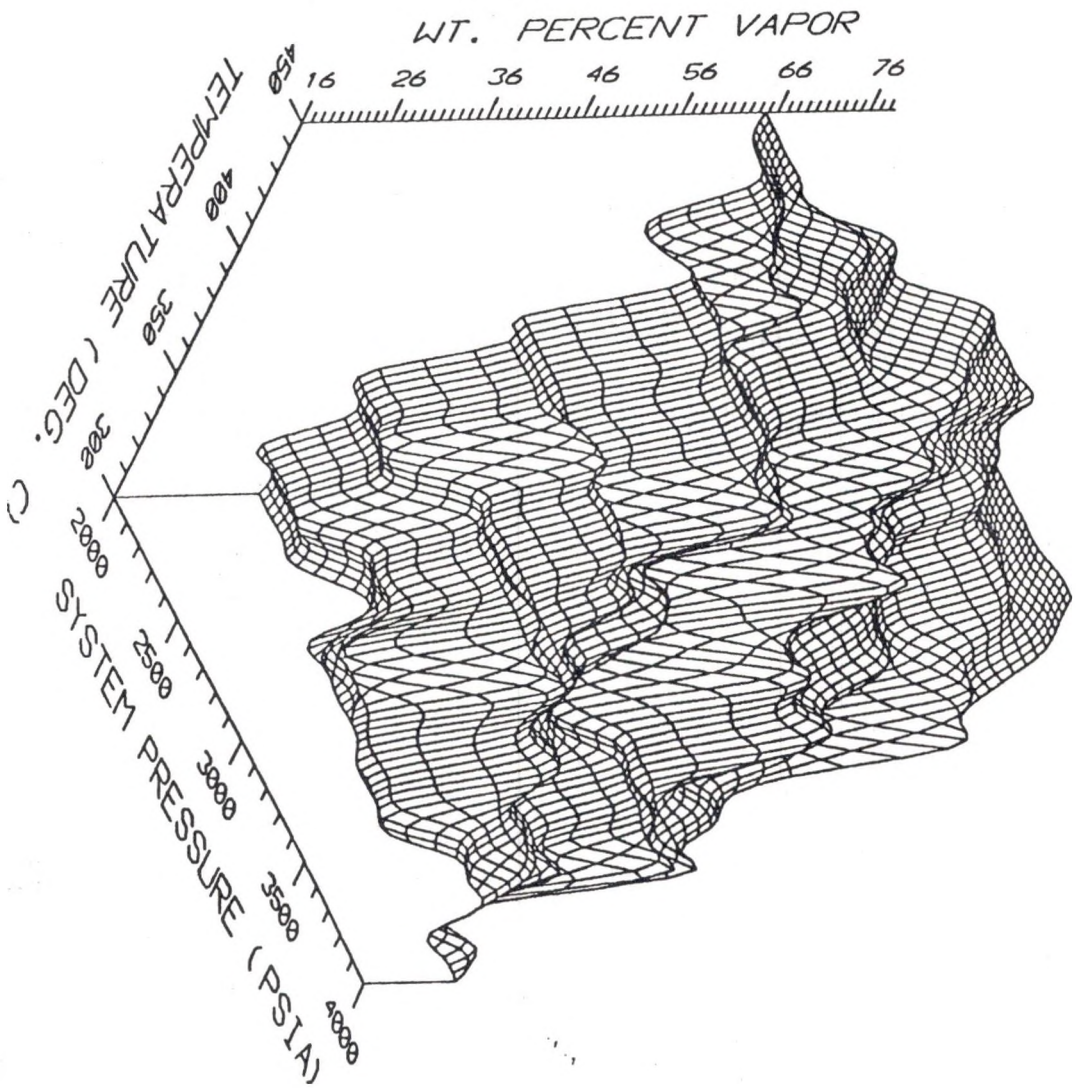
The HAO61 data were also reduced using the modified Clausius-Clapyron Equation (Equation 2).

$$\ln(Gp^*T) = -(\Delta H/zRT) + C \quad [2]$$

$G_p$  is defined as the mass percent of solvent in the vapor phase. Equation 2 was used, and is discussed in detail, in a study by Krause (2) involving the A04/SRL mixture. Equation 2 can be used as a simple model to describe mass of vapor at given conditions since fits to the equation yield nearly straight lines. Reduction of the HAO61 data using this equation also allows an additional comparison of the behavior of HAO61 to that of A04 and A04/SRL.

Figure 11 provides a plot of the  $\ln(Gp^*T)$  as a function of  $1/T$  for the five nominal pressures. The slopes from plots of this type can be expected to provide  $-(\Delta H/zR)$  values and the intercepts provide values for the constant (C). As can be seen in Figure 11, there is little difference between the slopes at the five different pressures. This indicates that the heat of vaporization for HAO61 remained nearly constant as pressure was increased. This

Figure 10. HA061 Vapor-Liquid Equilibrium



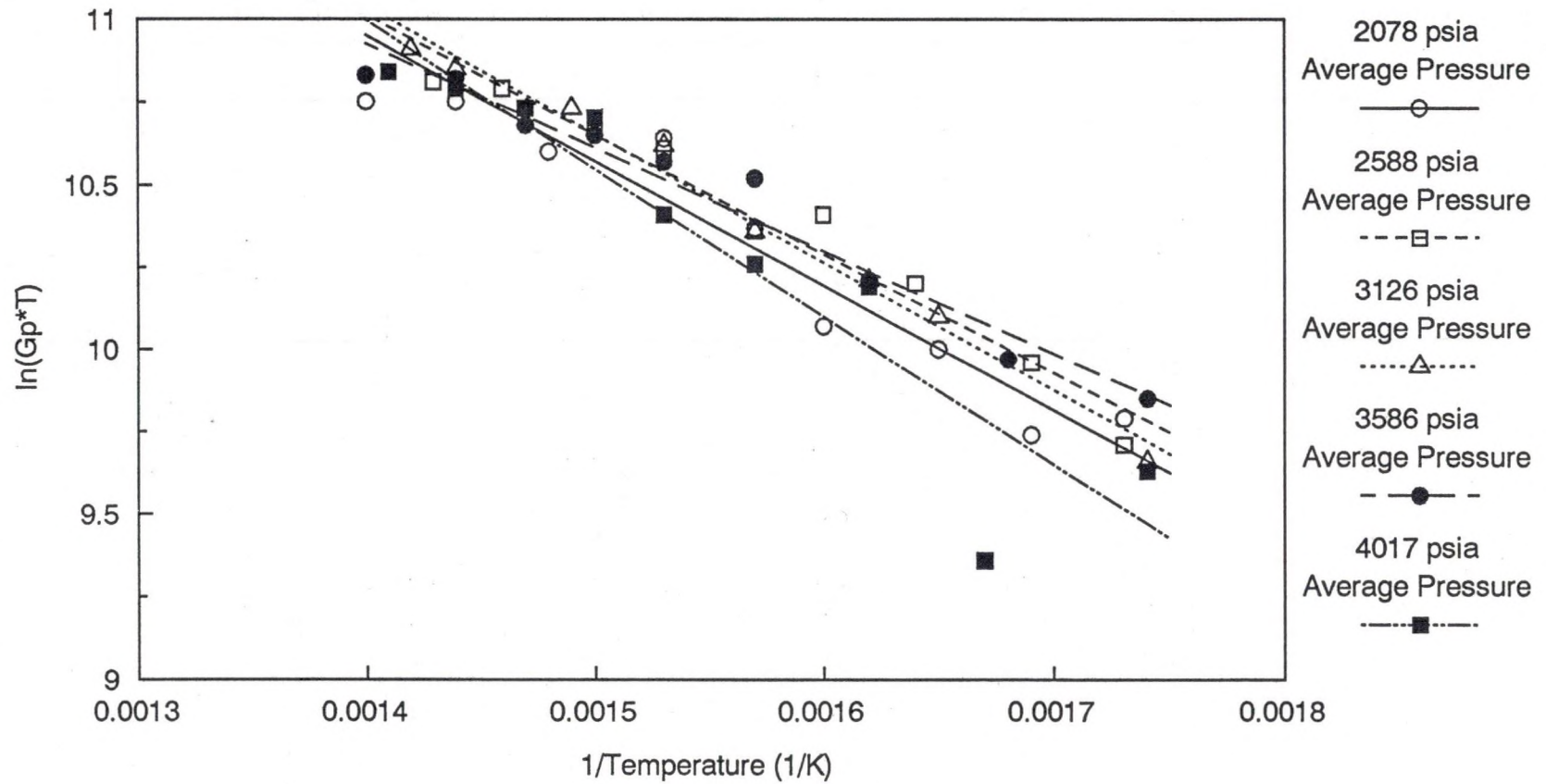


Figure 11. Modified Clausius-Clapyron Results.



could be expected, since percentages of solvent in the vapor phase were similar for all five pressure runs, and therefore, the components vaporized at a given temperature were also similar.

The values of  $\Delta H/zR$  determined using the modified Clausius-Clapyron equation are tabulated in Table 14 for each of the nominal run pressures. Results from A04 and the A04/SRL mixture are included in the table to allow further comparison of HA061 with the other solvents.

Table 14 Comparison of Modified Clausius-Clapyron Results From HA061, A04, and A04/SRL Solvents.

Nominal Pressure	HA061 Intercept	$\Delta H/zR$		
		HA061	A04	A04/SRL
2000	16.25	3,462	N/A	4,449
2500	16.08	3,616	8765	5,474
3000	16.49	3,889	8549	6,798
3500	15.31	3,134	7926	8,201
4000	17.28	4,491	10314	9,135

Table 14 shows that values of  $\Delta H/zR$  are higher for both the A04 and the A04/SRL solvents as compared with that of HA061 over the entire range of pressures. This can be explained by the larger relative quantity of hydrogen in the HA061. The larger H/C ratio of HA061 indicates the presence of relatively more light oils than in either A04 or the A04/SRL mixture and, therefore, less energy is required for vaporization.



### Microdistillation Results

Liquid and vapor samples from the time-sample runs were subjected to microdistillation analyses. A description of the technique and the results are provided in Appendix D. Microdistillation analyses provide a quantitative measure of the percent of a sample that can be considered either light, middle, or heavy oil. For this discussion, the combined quantity of light and middle oils is used.

Analyses of the samples showed that the percentages of the various oils remained nearly constant in both the vapor and liquid phases as the autoclave pressure or temperature were changed. As an example, Figure 12 shows the microdistillation results for samples generated in Runs N-323 and N-336 at average pressures of 2588 and 3586 psia, respectively. In general, the percent light plus middle oils ranged between 90 and 97 percent for the vapor phase and from about 84 to 90 percent for the liquid phase. Variations from measurement error are nearly large enough to make any small effects between the two pressures insignificant. An ANOVA performed on the results indicated that at the 95 percent confidence level, temperature effects were insignificant and pressure effects were just significant.

The nearly constant level of combined light and middle oils in the liquid phase contradicts the expected results for HA061. The liquid phase of the system would be expected to become richer in heavy oils as the autoclave tem-

perature is increased. Increased temperature could be expected to increase the quantity of solvent in the vapor phase for a non-reacting system. The lighter, more volatile oils are the first to vaporize, leaving the liquid phase richer in the heavy oils.

One explanation for the observed results is that the HAO61 was cracking in the autoclave, to form lighter hydrocarbons. Note that the solid line in Figure 12 represents the 85.2 percent light plus middle oils found in HAO61 using microdistillation. Average values for both the liquid and vapor phase samples were consistently above this value. This could only be the case if the percentage of light and middle oils had increased. In addition, microdistillation analysis of quench samples showed the percent heavy oils varying from 7.8 to 9.5 percent compared to 14.8 percent found in the HAO61. Since it appears that the solvent composition changed during testing, with an overall increase in light and middle oils, cracking is a plausible explanation for these observations.

The evidence that cracking was occurring in the solvent during testing should be considered when evaluating and making use of these data. Some of the effects observed could have resulted in part from these changes in composition. It is recommended that future testing include a run to determine the effect of cracking on the vapor-liquid equilibrium results. The run could be made over the same temperature range used in this study and at a nominal pres-

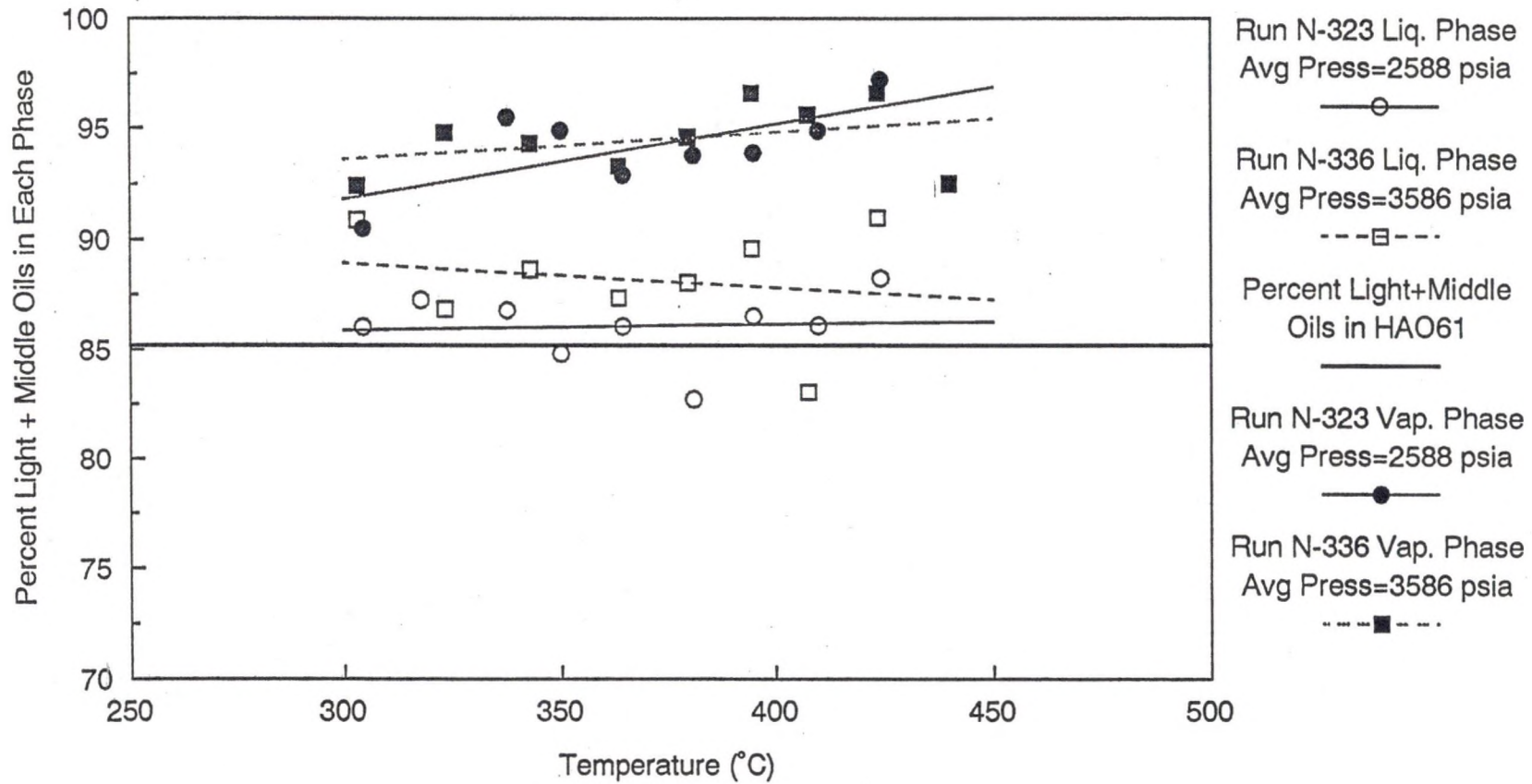


Figure 12. Microdistillation Results, Runs N-323 and N-336.



sure of 2000 psia, after the solvent is first allowed to react at 4000 psia and 450 °C. This would allow changes in composition to occur prior to taking the first data point. Any differences between data from such a run and the 2000 psia run data from this study, could then be attributed to cracking.



## CHAPTER V. CONCLUSIONS AND RECOMMENDATIONS

### Conclusions

1. As expected, the vapor pressure of HAO61 increased with temperature. As temperature was raised from 29 °C to 447 °C, the vapor pressure increased from 5 psia to 400 psia.
2. The fraction of solvent in the vapor phase increased with temperature. The quantity of solvent in the vapor phase averaged over all pressures, increased from 29 to 71 percent as temperature increased from 300 to 420 °C.
3. Examination of the partial pressure data using the Clausius-Clapyron equation provided linear fits over two temperature regions. At temperatures from 111 to 412 °C and temperatures from 421 to 446 °C, the values of  $\Delta H$  were determined to be 6,130 and 21,800 cal/g-mole, respectively.
4. The fraction of HAO61 in the vapor phase remained nearly constant as pressure was increased from 2000 to 4000 psia.
5. Analysis of the time-sample data using the modified Clausius-Clapyron equation showed that varying pressure had little effect on the heat of vaporization.

6. The percentages of the combined light and middle oils and heavy oils in the liquid phase remained nearly the same regardless of the run conditions.

7. The vapor and liquid samples taken during testing had more light and middle oils than did the HAO61 solvent. The quench samples also contained more of the lighter oils than did the original solvent. This provides evidence that cracking occurred during testing.

#### Recommendations

1. React the HAO61 with itself at various conditions and analyze the resulting liquids using microdistillation. The results would indicate the degree to which thermal cracking occurred. In addition, gas chromatography could be run on some of the samples to identify changes in chemical makeup.

2. Some autoclave runs should be made on HAO61, A04, or the A04/SRL mixture using hydrogen gas ( $H_2$ ) in place of  $N_2$  to identify the effects. The  $H_2$  would be present in the actual liquefaction process.

3. Combine vapor-liquid equilibrium data from the similar studies to provide comparisons between the various solvents. The combined data may allow development of a simple model for predicting vapor-liquid equilibrium of

liquefaction solvents. The (H/C) ratios or percentages of light, middle, and heavy oils in the solvents are potential parameters for such a model.

4. Repeat the 2000 psia data for each of the liquefaction solvents studied, after first bringing the reactor to 4000 psia and 450 °C for a period of time. Increases of the solvent fractions in the vapor phase over those for the original 2000 psia data would indicate that cracking of the solvent occurred at the elevated conditions.

## APPENDICES



## APPENDIX A

### Notation

A04	Anthracene oil from Crowley Tar and Chemical Company.
A04/SRL	Mixture of 25 percent SRL in A04.
C	Constant.
CPU	Continuous Process Unit at the EERC.
EERC	Energy and Environmental Research Center.
Gp	Solvent fraction in the vapor phase.
HA061	Hydro-treated anthracene oil from batch 61 of the EERC's CPU.
n.a.	Not applicable.
P	Pressure (absolute basis unless otherwise stated).
R	Ideal gas constant - 1.987 calories/g-mole*K
s	Standard deviation.
SRL	Solvent Refined Lignite.
T	Temperature (absolute basis unless otherwise stated).
TC1	Thermocouple #1 - in the upper portion of the autoclave.
TC2	Thermocouple #2 - in the lower portion of the autoclave.
THF	Tetrahydrofuran.
Z	Compressibility of a gas.
$\Delta H$	Heat of Vaporization.

## APPENDIX B

### Run Data

Raw data for the partial pressure run and the five time-sample runs are provided in this appendix. Table 15 contains the data for the partial pressure run, and the time-sample data are contained in Tables 16 through 20. Values provided in these tables are the numbers that were read during testing.

The data presented in the body of this thesis were obtained by correcting the raw data in this appendix. Temperatures were determined by taking the average of TC1 and TC2 as described in Chapter II. Pressure readings were corrected by correcting for atmospheric pressure and the offset of the gauge reading. The absolute pressure of the system for any data point was calculated as:

$$P = P_g + P_a - P_{g,e} \quad [3]$$

where,

$P_g$  = The gauge pressure read for the data point,  
 $P_a$  = The ambient pressure in psi,  
 $P_{g,e}$  = The gauge pressure of the autoclave nearly evacuated at the beginning of the run.

The partial pressures for run N-312 were calculated similarly except, it was necessary to account for the effect of air that remained in the autoclave after the evacuation procedure. As the temperature increased during a run, the pressure effect of this residual air also increased. The pressure due to the residual air was then

Table 15 Experimental Run Data for Run N-312, Partial Pressure Run.

Run N-312

July 12, 1985

Solvent	HAO61			
Mass Charged	1186.2 g			
Mass Balance (% Recovered)	96.8%			
Barometric Pressure	29.08 in. Hg			
Initial Autoclave Pressure	-10 psig			
Evacuated Autoclave Pressure	-12 psig			
Ambient Temperature	22 C			
Stirrer Speed	2000 rpm			
Reading #	Heater Setting	TC #1	TC #2	Pressure
1	999	29.5	27.7	-19
2	999	59.9	41.7	-17
3	999	76.3	50.0	-16
4	999	103.0	65.8	-16
5	999	133.4	89.5	-15
6	500	167.6	115.0	-13
7	500	178.8	126.2	-11
8	500	189.0	139.5	-8
9	601	195.0	148.4	-5
10	701	225.0	184.0	7
11	701	240.0	202.3	13
12	701	250.9	225.8	23
13	801	269.8	250.6	31
14	801	278.4	261.6	36
15	801	291.3	277.3	43
16	801	300.0	290.6	50
17	901	315.8	312.1	60
18	901	340.5	336.5	78
19	901	360.2	354.3	96
20	999	380.1	375.5	118
21	999	400.0	395.7	145
22	999	414.0	410.3	174
23	999	423.7	420.8	203
24	999	433.0	430.0	242
25	999	442.7	440.1	309
26	999	445.8	443.3	342
27	999	448.3	445.8	376



Table 16 Experimental Run Data for Run N-333.

Run N-333

September 4, 1985

Solvent	HAO61			
Mass Charged	1203.8 g			
Mass Balance (% Recovered)	98.1 %			
Barometric Pressure	29.18 in. Hg			
Initial Autoclave Pressure	-12 psig			
Ambient Temperature	22 C			
Stirrer Speed	1500 RPM			
Reading #	Heater Setting	TC #1	TC #2	Pressure
1	800	309.5	301.1	2033
2	780	322.8	315.7	2040
3	810	337.2	329.9	2043
4	820	353.4	347.0	2028
5	850	367.8	361.5	2025
6	880	385.5	379.5	2042
7	920	405.6	399.5	2006
8	985	426.7	420.8	2101
9	999	444.1	439.2	2144

Table 17 Experimental Run Data for Run N-323.

Run N-323

August, 1985

Solvent	HAO61			
Mass Charged	1222.6			
Mass Balance (% Recovered)	95%			
Barometric Pressure	29.36 in Hg			
Initial Autoclave Pressure	-26 psig			
Ambient Temperature	22 C			
Stirrer Speed	1500 RPM			
Reading #	Heater Setting	TC #1	TC #2	Pressure
1	730	307.3	301.7	2720
2	770	320.9	314.8	2517
3	830	341.1	334.4	2520
4	850	353.4	346.8	2520
5	880	368.3	361.1	2564
6	900	384.8	377.1	2540
7	930	398.4	391.5	2523
8	970	413.3	406.4	2506
9	970	427.2	421.2	2520



Table 18 Experimental Run Data for Run N-321.

Run N-321

August, 1985

Solvent	HAO61
Mass Charged	1205.5 g
Mass Balance (% Recovered)	89 %
Barometric Pressure	29.09
Initial Autoclave Pressure	-12 psig
Ambient Temperature	22 C
Stirrer Speed	1500 RPM

Reading #	Heater Setting	TC #1	TC #2	Pressure
1	750	305.6	299.7	3375
2	780	335.4	330.2	3297
3	820	346.7	341.3	3108
4	850	365.1	359.6	3007
5	880	383.0	377.5	2829
6	910	400.3	394.8	3195
7	970	422.9	417.2	3052
8	990	436.2	430.8	2938

Table 19 Experimental Run Data for Run N-336.

Run N-336

September 7, 1985

Solvent	HAO61
Mass Charged	1186.0
Mass Balance (% Recovered)	96.8 %
Barometric Pressure	29.20 in. Hg
Initial Autoclave Pressure	-19 psig
Ambient Temperature	21 C
Stirrer Speed	1500 RPM

Reading #	Heater Setting	TC #1	TC #2	Pressure
1	800	306.9	299.5	3501
2	820	326.3	320.4	3589
3	840	346.1	340.0	3590
4	870	366.2	361.1	3565
5	900	382.3	377.2	3547
6	920	396.9	392.2	3534
7	940	409.7	405.3	3498
8	980	426.0	421.1	3524
9	999	438.2	441.4	3626

Table 20 Experimental Run Data for Run N-347.

Run N-347

October 31, 1985

Solvent	HAO61			
Mass Charged				
Mass Balance (% Recovered)				
Barometric Pressure	29.29 in. Hg			
Initial Autoclave Pressure	-2 psig			
Ambient Temperature	20 C			
Stirrer Speed	1500 RPM			
Reading #	Heater Setting	TC #1	TC #2	Pressure
1	800	305.8	300.2	3956
2	820	327.8	322.7	4041
3	840	345.5	340.7	3957
4	880	367.2	362.5	3981
5	900	380.9	376.4	3970
6	920	395.9	391.4	4025
7	950	411.6	407.3	4026
8	999	426.1	421.4	4030
9	999	437.9	434.5	4020

taken as the pressure at ambient conditions times the ratio of the run temperature to ambient temperature. Partial pressure of the solvent during the vapor pressure run was then calculated as:

$$PP = P - (P_{\text{air}} * T / T_i) \quad [4]$$

where,

$P_{\text{air}}$  = The absolute pressure of the evacuated system,  
 $T$  = Absolute system temperature for the data point,  
 $T_i$  = The absolute system temperature before heating.

This correction was used to arrive at the values that were presented in Table 3 and used in analyses for the vapor pressure run.

Calculation of data point number 5, from the vapor pressure run is performed below. First, the system pressure is found from equation 3 as:

$$P = -15 \text{ psi} + 14.3 \text{ psi} - -10 \text{ psi} = 9.3 \text{ psia}$$

Next, the partial pressure of the solvent is determined from equation 4 as:

$$PP = 9.3 \text{ psi} - (2.3 \text{ psi} * 384.7 \text{ K} / 295.2 \text{ K}) = 6.3 \text{ psi}$$

Calculations for the time-sample runs use equation 3 only since the system pressure is the variable of interest.

## APPENDIX C

### Mass Balances

Mass balance calculations were made to account for as much of the solvent charge as possible. Results for the partial pressure run are shown in Table 21. Results for the time sample runs are given in Tables 22 through 26. The percentage of mass accounted for was calculated as:

$$\% \text{ mass recovered} = \frac{\text{total mass recovered}}{\text{total mass charged}} * 100 \quad [4]$$

The total mass charged was equal to the net mass of solvent and  $\text{CaCO}_3$  prepared minus the net mass collected on the preparation equipment and charge clean up rags. The net mass prepared was determined by weighing the prepared mixture and preparation equipment and subtracting the mass of the preparation equipment. After the charger was filled the dirty preparation equipment and charge clean up rags were weighed. The mass charge lost was determined as total mass of dirty preparation equipment minus mass of preparation equipment clean plus the mass gained by the charge clean up rags.

The total mass recovered included all mass accounted for at the completion of the run. This value was determined from:



Table 21 Material Balance Results From Run N-312, Partial Pressure Run.

Run N-312	Mass Charged		1186.2 g
July 12, 1985	Mass Balance (% Recovered)		96.8 %
Solvent - HAO61	Percent CaCO <sub>3</sub> in Charge		N/A %
<hr/>			
Solvent Charged:			
Total Weight of Solvent + Beaker + Spatula			1679.2 g
-Weight of Beaker + Spatula + Adhered Solvent			-477.5 g
Charge rags	Gross	286.1 g	
	-Tare	270.6 g	
	=Net		15.5 g
			<u>-15.5 g</u>
Total Solvent Charged			1186.2 g
CaCO <sub>3</sub> in Prepared Charge	=Net	N/A	
Liquid Product:			
Autoclave rags	Gross	681.0 g	
	-Tare	680.3 g	
	=Net		0.7 g
Quench Can(s)	Gross	1421.2 g	
	-Tare	287.9 g	
	=Net		1133.3 g
Quench Rags	Gross	546.8 g	
	-Tare	543.9 g	
	=Net		2.9 g
Samples, Waste Shots, & Clean Up			
Net Liquid Samples		6.0 g	
Net Gas Samples		5.3 g	
Combined Sample Mass			11.3 g
Total Liquids Recovered			1148.2 g

Table 22 Material Balance Results From Run N-333.

Run N-333	Mass Charged	1203.8 g
September 4, 1985	Mass Balance (% Recovered)	98.1 %
Solvent - HA061	Percent CaCO <sub>3</sub> in Charge	5.1 %

## Solvent Charged:

Total Weight of Solvent + Beaker + Spatula		1693.6 g
-Weight of Beaker + Spatula + Adhered Solvent		-474.8 g
Charge rags	Gross	97.7 g
	-Tare	82.7 g
	=Net	15.0 g
		<u>-15.0 g</u>
Total Solvent Charged		1203.8 g
CaCO <sub>3</sub> in Prepared Charge	=Net	61.7 g

## Liquid Product:

Autoclave rags	Gross	128.3 g	
	-Tare	106.0 g	
	=Net		22.3 g
Quench Can(s)	Gross	1170.9 g	
	-Tare	144.7 g	
	=Net		1026.2 g
Quench Rags	Gross	69.4 g	
	-Tare	60.4 g	
	=Net	9.1	9.1 g
Samples, Waste Shots, & Clean Up from below:			
Net Liquid Samples		94.1 g	
Net Gas Samples		28.8 g	
Combined Sample Mass			122.9 g

Total Liquids Recovered 1180.5 g

## Sample Weights (g)

Samp. #	Gross	Gas Samples		Liquid Samples		
		Tare	Net	Gross	Tare	Net
1	1010.9	1009.2	1.8	18.9	16.9	2.0
2	1010.4	1009.2	1.3	18.1	16.7	1.4
3	1010.6	1009.2	1.5	18.5	16.7	1.8
4	1010.8	1009.2	1.7	20.0	16.7	3.3
5	1010.6	1009.2	1.4	18.6	16.7	1.9
6	1011.8	1009.1	2.7	20.2	16.7	3.5
7	1012.0	1009.2	2.8	19.7	16.4	3.3
8	1013.2	1009.2	4.1	20.2	16.5	3.7
9	1013.6	1009.2	4.4	19.0	16.6	2.4
Waste	150.6	147.6	3.0	145.7	126.8	18.9
Shots	1038.6	1034.4	4.3	142.4	129.2	13.2
Rags				130.7	92.0	38.6
Totals			28.8			94.1

Table 23 Material Balance Results From Run N-323.

Run N-323	Mass Charged	1222.6 g
August, 1985	Mass Balance (% Recovered)	94.9 %
Solvent - HAO61	Percent CaCO <sub>3</sub> in Charge	4.9 %

## Solvent Charged:

Total Weight of Solvent + Beaker + Spatula		1698.5 g
-Weight of Beaker + Spatula + Adhered Solvent		-470.5 g
Charge rags	Gross	63.4 g
	-Tare	58.0 g
	=Net	5.4 g
		-5.4 g
Total Solvent Charged		1222.6 g
CaCO <sub>3</sub> in Prepared Charge	=Net	60.0 g

## Liquid Product:

Autoclave rags	Gross	100.7 g
	-Tare	92.6 g
	=Net	8.1 g
Quench Can(s)	Gross	1123.9 g
	-Tare	142.9 g
	=Net	981.0 g
Quench Rags	Gross	70.8 g
	-Tare	59.8 g
	=Net	11.0 g
Samples, Waste Shots, & Clean Up from below:		
Net Liquid Samples		123.3 g
Net Gas Samples		37.3 g
Combined Sample Mass		160.7 g

Total Liquids Recovered 1160.7 g

## Sample Weights (g)

Samp. #	Gross	Gas Samples		Liquid Samples		
		Tare	Net	Gross	Tare	Net
1	1010.9	1009.1	1.8	18.48	16.60	1.88
2	1010.3	1009.2	1.2	20.90	16.65	4.26
3	1011.0	1009.2	1.8	21.01	16.57	4.44
4	1011.4	1009.2	2.2	18.13	16.67	1.45
5	1012.2	1009.2	3.0	20.47	16.81	3.66
6	1012.4	1009.3	3.1	20.93	16.59	4.33
7	1013.3	1009.3	4.1	20.71	16.62	4.09
8	1012.6	1009.2	3.4	19.68	16.71	2.97
9	1014.2	1009.2	4.9	21.02	16.81	4.21
Waste	2076.5	2068.9	7.6	157.40	125.76	31.64
Shots	2073.4	2069.1	4.3	153.71	127.98	25.73
Rags				149.45	114.78	34.67
Totals			37.3			123.33



Table 24 Material Balance Results From Run N-321.

Run N-321	Mass Charged	1205.5 g				
August 21, 1985	Mass Balance (% Recovered)	97.5 %				
Solvent - HAO61	Percent CaCO <sub>3</sub> in Charge	5.1 %				
<hr/>						
Solvent Charged:						
Total Weight of Solvent + Beaker + Spatula		1693.1 g				
-Weight of Beaker + Spatula + Adhered Solvent		-470.4 g				
Charge rags	Gross	73.9 g				
	-Tare	56.7 g				
	=Net	17.2 g				
		<hr/>				
		-17.2 g				
Total Solvent Charged		1205.5 g				
CaCO <sub>3</sub> in Prepared Charge	=Net	62.3 g				
<hr/>						
Liquid Product:						
Autoclave rags	Gross	*(Combined with liquid				
	-Tare	sample rags).				
	=Net					
Quench Can(s)	Gross	1346.4 g				
	-Tare	286.7 g				
	=Net	1059.7 g				
Quench Rags	Gross	152.4 g				
	-Tare	149.2 g				
	=Net	3.2 g				
Samples, Waste Shots, & Clean Up from below:						
Net Liquid Samples		86.5 g				
Net Gas Samples		26.5 g				
Combined Sample Mass		113.0 g				
Total Liquids Recovered		1175.9 g				
<hr/>						
Sample Weights (g)						
Samp. #	Gross	Gas Samples		Liquid Samples		
		Tare	Net	Gross	Tare	Net
1	1012.8	1009.3	3.5	19.1	16.6	2.6
2	1009.6	1009.2	0.4	18.4	16.6	1.8
3	1010.1	1009.2	1.0	18.1	16.5	1.5
4	1011.2	1009.2	2.1	18.2	16.6	1.6
5	1011.7	1009.2	2.4	18.0	16.6	1.4
6	1012.4	1009.2	3.2	19.1	16.7	2.4
7	1011.8	1009.2	2.6	18.2	16.7	1.5
8	1013.8	1009.2	4.5	18.3	16.7	1.6
9						
Waste	1036.8	1034.2	2.6	147.9	129.5	18.4
Shots	1038.6	1034.5	4.2	136.6	129.8	6.8
Rags				196.5	149.6	46.9
<hr/>						
Totals			26.5			86.5



Table 25 Material Balance Results From Run N-336.

Run N-336	Mass Charged	1186.0 g
September 7, 1985	Mass Balance (% Recovered)	96.8 %
Solvent - HAO61	Percent CaCO <sub>3</sub> in Charge	5.0 %

## Solvent Charged:

Total Weight of Solvent + Beaker + Spatula		1680.9 g
-Weight of Beaker + Spatula + Adhered Solvent		-469.8 g
Charge rags	Gross	124.2 g
	-Tare	99.1 g
	=Net	25.1 g
		<u>-25.1 g</u>
Total Solvent Charged		1186.0 g
CaCO <sub>3</sub> in Prepared Charge	=Net	60.5 g

## Liquid Product:

Autoclave rags	Gross	120.6 g
	-Tare	97.2 g
	=Net	23.5 g
Quench Can(s)	Gross	1096.1 g
	-Tare	143.9 g
	=Net	952.2 g
Quench Rags	Gross	182.3 g
	-Tare	152.7 g
	=Net	29.7 g
Samples, Waste Shots, & Clean Up from below:		
Net Liquid Samples		97.2 g
Net Gas Samples		45.5 g
Combined Sample Mass		142.7 g

Total Liquids Recovered 1148.1 g

## Sample Weights (g)

Samp. #	Gross	Gas Samples		Liquid Samples		
		Tare	Net	Gross	Tare	Net
1	1011.7	1009.2	2.6	19.9	16.5	3.5
2	1011.8	1009.2	2.6	20.4	16.7	3.7
3	1012.6	1009.2	3.4	20.1	16.5	3.6
4	1012.9	1009.2	3.7	19.9	16.5	3.3
5	1012.8	1009.2	3.6	20.0	16.7	3.4
6	1014.1	1009.2	4.9	19.3	16.7	2.7
7	1014.3	1009.2	5.0	20.1	16.8	3.3
8	1013.1	1009.2	3.9	19.0	16.4	2.5
9	1014.6	1009.2	5.3	20.0	16.8	3.2
Waste	151.7	143.2	8.4	145.3	129.7	15.6
Shots	1036.4	1034.4	1.9	145.6	130.1	15.5
Rags				211.9	174.9	37.0
Totals			45.5			97.2

Table 26 Material Balance Results From Run N-347.

Run N-347	Mass Charged	1189.4 g				
October 31, 1985	Mass Balance (% Recovered)	96.4 %				
Solvent - HAO61	Percent CaCO <sub>3</sub> in Charge	5.1 %				
<hr/>						
Solvent Charged:						
Total Weight of Solvent + Beaker + Spatula		1672.9 g				
-Weight of Beaker + Spatula + Adhered Solvent		-469.9 g				
Charge rags	Gross 117.6 g					
	-Tare 104.0 g					
	=Net 13.6 g	-13.6 g				
Total Solvent Charged		1189.4 g				
CaCO <sub>3</sub> in Prepared Charge	=Net 61.3 g					
Liquid Product:						
Autoclave rags	Gross 81.7 g					
	-Tare 79.4 g					
	=Net 2.3 g					
Quench Can(s)	Gross 1114.1 g					
	-Tare 142.2 g					
	=Net 971.9 g					
Quench Rags	Gross 68.6 g					
	-Tare 64.3 g					
	=Net 4.3 g					
Samples, Waste Shots, & Clean Up from below:						
Net Liquid Samples	120.8 g					
Net Gas Samples	47.5 g					
Combined Sample Mass	168.3 g					
Total Liquids Recovered		1146.8 g				
Sample Weights (g)						
Samp. #	Gas Samples			Liquid Samples		
	Gross	Tare	Net	Gross	Tare	Net
1	1036.0	1034.2	1.7	21.5	16.6	4.9
2	1037.4	1034.4	3.0	22.6	16.5	6.1
3	1037.0	1034.4	2.6	22.6	16.5	6.1
4	1037.5	1034.3	3.2	23.0	16.3	6.7
5	1037.2	1034.4	2.8	23.1	16.6	6.5
6	1038.5	1034.3	4.2	22.8	16.5	6.3
7	1038.5	1034.4	4.2	23.0	16.7	6.3
8	1038.6	1034.3	4.3	23.1	16.8	6.2
9	1038.2	1034.4	3.8	21.5	16.5	5.0
Waste	149.0	136.7	12.3	140.1	127.9	12.2
Shots	1014.6	1009.2	5.4	142.8	128.7	14.1
Rags				167.1	126.7	40.4
<hr/>				<hr/>		
Totals			47.5	120.8		

- o the mass collected in the quench can(s),
- o the mass collected on the quench clean up rags,
- o the mass collected from the sampling procedure,
- o the mass collected on the autoclave clean up rags,
- o and the mass collected in the cold traps.

Solvent that was not recovered in the mass balances could include vapors not recovered in the cold traps or sampling setup, residue in lines, or cleanup losses not recovered in the waste rags. The vapor samples were collected using three-quarter inch pipe cooled in a dry ice and iso-propyl alcohol mixture. While releasing the pressure from this collection system, it was found that a small amount of the sample escaped as atomized liquid. Small losses during the sampling procedure can become significant when these losses are accumulated throughout the run sequence.



## APPENDIX D

### Microdistillation Determinations of the Vapor and Liquid Phase Compositions

Microdistillation analyses were used to identify the mass fraction of light, middle, and heavy oils in each of the vapor and liquid samples. The analyses were performed using the EERC microdistillation setup. The technique provides a quantitative measure of percent sample mass which leaves as vapor at particular temperatures and pressures.

#### Measurement Conditions

Typically vacuum distillation measurements are made at 5 torr pressure, and temperature settings of 121 and 260 °C (ASTM D-1160). The oil bath used for these analyses could not be taken above 200 °C, and a lower system pressure had to be used to offset the lower temperature range. The pressure used for microdistillations on the HA061 samples was 1.6 torr. The EERC microdistillation procedure called for temperatures of 90 and 200 °C at this pressure (1,2,6).

#### EERC Microdistillation Procedure

The EERC microdistillation setup was used because as many as twelve samples could be analyzed at a time and only 0.2 grams of sample were needed for this technique. A schematic of the setup is provided in Figure 13.



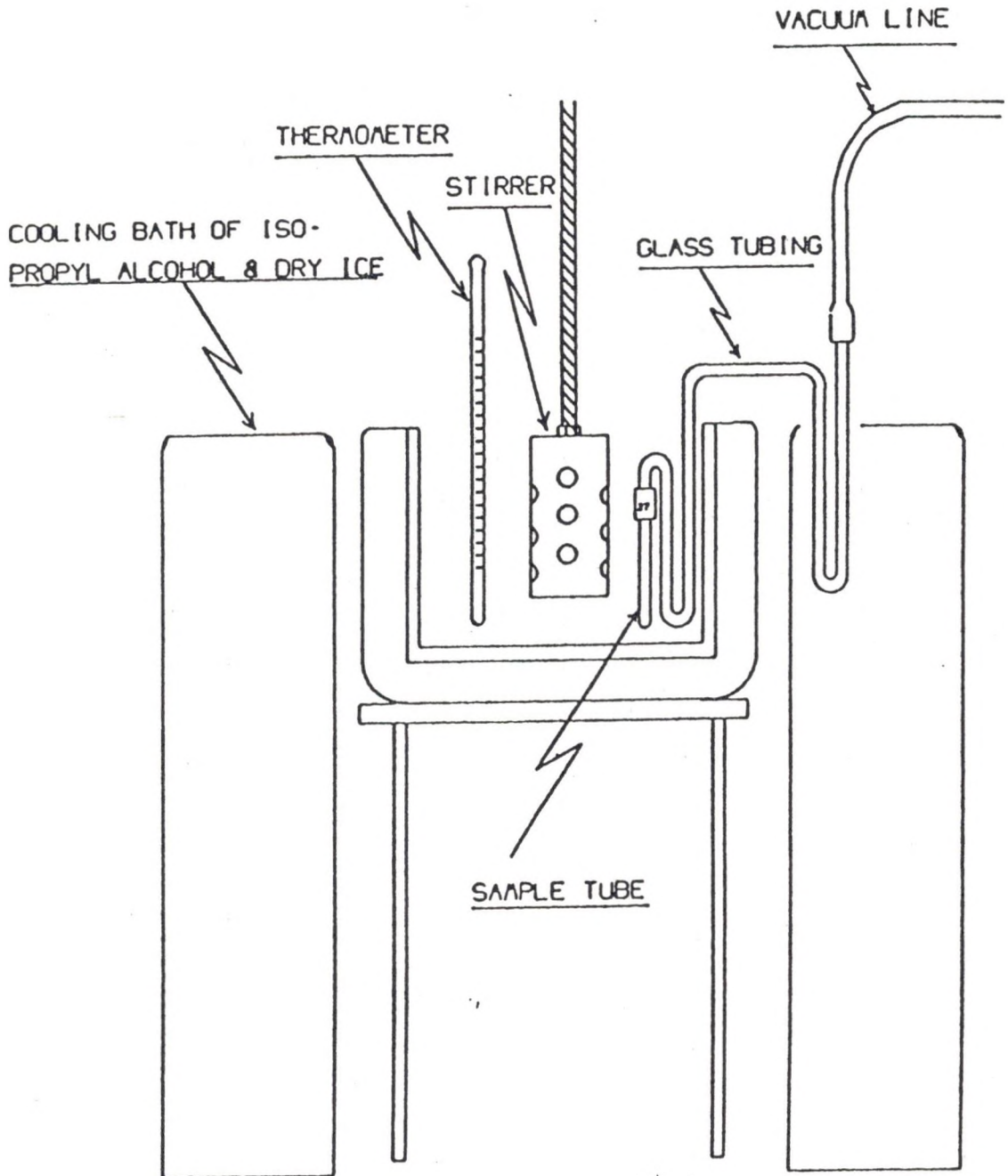


Figure 13. Schematic of EERC 5-torr Microdistillation Apparatus.

Before preparation of the distillation sample, a few strands of glass wool were placed in each sample tube to minimize sample loss from bumping. Each of the sample tubes was then weighed. Approximately 0.2 grams of sample were placed into each sample tube. The tubes were then reweighed and the sample masses were determined by difference (mass of tube with sample - mass of tube and glass wool). The sample tubes were then joined to the glass tubing using a metal collar. A seal was maintained by using vacuum grease between an o-ring in the collar and the tube.

When all of the samples were in place, the vacuum pump was started and the system pressure was reduced to 1.6 torr. The oil bath, which was preheated to 90 °C, was raised until the sample tubes were completely submerged. The height was set to cover as much of the glass tubing as possible to minimize condensation in the line prior to the cooling bath. The samples remained in the oil bath at 90 °C for 30 minutes. At the end of this time the tubes were reweighed and the bath temperature was increased to 200 °C. Once the bath reached temperature, the pressure was again reduced to 1.6 torr and the samples were submerged for another 30 minutes. The samples were again weighed. More complete documentation of the EERC microdistillation process was provided in previous work by Rolando (1).

### Calculation of Results

The following discussion explains the calculations used to reduce the microdistillation data. These calculations were performed on both liquid and vapor phase samples to determine the fractions of light, middle, and heavy oils present.

The mass fractions of the vapor phase samples were determined by straight differences in the masses before and after being submerged at each temperature. The liquid phase samples however, contained  $\text{CaCO}_3$  which had to be subtracted from the sample mass. The calculation of oil mass fractions in the vapor phase were performed as:

$$\text{Mass \% light oil} = 100 * (\text{mass1}-\text{mass2})/(\text{mass1}-\text{mass0}) \quad [6]$$

$$\text{Mass \% middle oil} = 100 * (\text{mass3}-\text{mass2})/(\text{mass1}-\text{mass0}) \quad [7]$$

$$\text{Mass \% heavy oil} = 100 * (\text{mass3}-\text{mass0})/(\text{mass1}-\text{mass0}) \quad [8]$$

Where:

mass 0 = mass of the tube and glass wool,

mass 1 = mass of the tube and sample,

mass 2 = mass after 30 minutes at 90 °C,

mass 3 = mass after 30 minutes at 200 °C.

Calculations for the liquid phase samples were similar except the mass of  $\text{CaCO}_3$  was subtracted from the sample mass term. Tables 27 through 32 contain the microdistillation results of the liquid phase samples from the time-sample

runs and Tables 33 through 37 contain the result for the vapor phase samples.



Table 27 Microdistillation Test Results for Run N-333, Liquid Samples.

Sample ID	Percent Light-Mid Oils			Percent Heavy Oils		
	point	avg	var	point	avg	var
N-333, 1L	88.6	90.4	6.42	11.4	9.6	6.42
N-333, 1L	92.2			7.8		
N-333, 2L	86.7	89.7	17.90	13.3	10.3	17.90
N-333, 2L	92.7			7.3		
N-333, 3L	86.0	88.7	14.53	14.0	11.3	14.53
N-333, 3L	91.4			8.6		
N-333, 4L	90.2	87.2	17.04	9.8	12.8	17.04
N-333, 4L	84.3			15.7		
N-333, 5L	81.6	84.4	15.26	18.4	15.6	15.26
N-333, 5L	87.1			12.9		
N-333, 6L	94.2	93.8	0.34	5.8	6.2	0.34
N-333, 6L	93.4			6.6		
N-333, 7L	92.6	91.6	1.88	7.4	8.4	1.88
N-333, 7L	90.7			9.3		
N-333, 8L	86.3	86.2	0.02	13.7	13.8	0.02
N-333, 8L	86.1			13.9		
N-333, 9L	84.5	84.1	0.20	15.5	15.9	0.20
N-333, 9L	83.8			16.2		

Table 28 Microdistillation Test Results for Run N-323, Liquid Samples.

Sample ID	Percent Light-Mid Oils			Percent Heavy Oils		
	point	avg	var	point	avg	var
N-323, 1L	83.6	86.0	11.22	16.4	14.0	11.22
N-323, 1L	88.4			11.6		
N-323, 2L	89.0	87.2	6.06	11.0	12.8	6.06
N-323, 2L	85.5			14.5		
N-323, 3L	85.5	86.8	3.36	14.5	13.2	3.36
N-323, 3L	88.1			11.9		
N-323, 4L	83.5	84.8	3.57	16.5	15.2	3.57
N-323, 4L	86.2			13.8		
N-323, 5L	92.0	86.0	71.28	8.0	14.0	71.28
N-323, 5L	80.1			19.9		
N-323, 6L	81.8	82.7	1.66	18.2	17.3	1.66
N-323, 6L	83.6			16.4		
N-323, 7L	84.6	86.5	7.02	15.4	13.5	7.02
N-323, 7L	88.4			11.6		
N-323, 8L	88.2	86.1	8.94	11.8	13.9	8.94
N-323, 8L	84.0			16.0		
N-323, 9L	85.4	88.2	16.31	14.6	11.8	16.31
N-323, 9L	91.1			8.9		

Table 29 Microdistillation Test Results for Run N-321, Liquid Samples.

Sample ID	Percent Light-Mid Oils			Percent Heavy Oils		
	point	avg	var	point	avg	var
N-321, 1L	82.4	82.6	0.03	17.6	17.4	0.03
N-321, 1L	82.7			17.3		
N-321, 2L	85.7	85.9	0.09	14.3	14.1	0.09
N-321, 2L	86.1			13.9		
N-321, 3L	81.3	78.7	13.09	18.7	21.3	13.09
N-321, 3L	76.1			23.9		
N-321, 4L	86.3	86.1	0.06	13.7	13.9	0.06
N-321, 4L	86.0			14.0		
N-321, 5L	87.2	88.3	2.32	12.8	11.7	2.32
N-321, 5L	89.3			10.7		
N-321, 6L	77.0	85.5	144.48	23.0	14.5	144.48
N-321, 6L	94.0			6.0		
N-321, 7L	88.1	87.7	0.35	11.9	12.3	0.35
N-321, 7L	87.3			12.7		
N-321, 8L	87.6	86.0	4.82	12.4	14.0	4.82
N-321, 8L	84.5			15.5		

Table 30 Microdistillation Test Results for Run N-336, Liquid Samples.

Sample ID	Percent Light-Mid Oils			Percent Heavy Oils		
	point	avg	var	point	avg	var
N-336, 1L	92.6	90.9	5.71	7.4	9.1	5.71
N-336, 1L	89.2			10.8		
N-336, 2L	85.8	86.8	2.23	14.2	13.2	2.23
N-336, 2L	87.9			12.1		
N-336, 3L	88.2	88.6	0.32	11.8	11.4	0.32
N-336, 3L	89.0			11.0		
N-336, 4L	86.1	87.3	3.16	13.9	12.7	3.16
N-336, 4L	88.6			11.4		
N-336, 5L	86.8	88.0	2.75	13.2	12.0	2.75
N-336, 5L	89.2			10.8		
N-336, 6L	91.5	89.6	7.33	8.5	10.4	7.33
N-336, 6L	87.6			12.4		
N-336, 7L	83.0	83.0	0.00	17.0	17.0	0.00
N-336, 7L	83.0			17.0		
N-336, 8L	91.5	91.0	0.61	8.5	9.0	0.61
N-336, 8L	90.4			9.6		

Table 31 Microdistillation Test Results for Run N-347, Liquid Samples.

Sample ID	Percent Light-Mid Oils			Percent Heavy Oils		
	point	avg	var	point	avg	var
N-347, 1L	83.5	83.9	0.37	16.5	16.1	0.37
N-347, 1L	84.4			15.6		
N-347, 2L	86.0	86.7	0.90	14.0	13.3	0.90
N-347, 2L	87.3			12.7		
N-347, 3L	80.7	84.3	25.08	19.3	15.7	25.08
N-347, 3L	87.8			12.2		
N-347, 4L	90.4	88.8	5.34	9.6	11.2	5.34
N-347, 4L	87.2			12.8		
N-347, 5L	87.3	87.3	n/a	12.7	12.7	n/a
N-347, 6L	91.3	91.4	0.01	8.7	8.6	0.01
N-347, 6L	91.4			8.6		
N-347, 7L	91.8	89.0	15.86	8.2	11.0	15.86
N-347, 7L	86.2			13.8		
N-347, 8L	89.7	90.1	0.32	10.3	9.9	0.32
N-347, 8L	90.5			9.5		
N-347, 9L	87.7	89.3	4.93	12.3	10.7	4.93
N-347, 9L	90.8			9.2		

Table 32 Microdistillation Test Results for Miscellaneous Liquid Samples.

Sample ID	Percent Light-Mid Oils			Percent Heavy Oils		
	point	avg	var	point	avg	var
N-321, Q*	91.5	91.5	0.01	8.5	8.5	0.01
N-321, Q	91.4			8.6		
N-323, Q	90.5	90.5	N.A.	9.5	9.5	N.A.
N-323, Q						
N-333, Q		N.A.	N.A.	N.A.	N.A.	N.A.
N-333, Q				N.A.		
N-336, Q	92.7	91.1	5.03	7.3	8.9	5.03
N-336, Q	89.5			10.5		
N-347, Q	90.5	92.2	5.58	9.5	7.8	5.58
N-347, Q	93.8			6.2		
HAO61	87.7	85.2	6.08	12.3	14.8	6.08
HAO61	82.8			17.2		

\*The Q indicates that the liquid was a quench sample from the particular run.



Table 33 Microdistillation Test Results for Run N-333 Vapor Samples.

Sample ID	Percent Light-Mid Oils			Percent Heavy Oils		
	point	avg	var	point	avg	var
N-333, 1G	87.8	87.8	n.a.	12.2	12.2	n.a.
N-333, 1G						
N-333, 2G	N-333, 2G					
N-333, 3G	88.3	88.3	n.a.	11.7	11.7	n.a.
N-333, 3G						
N-333, 4G	94.8	94.8	n.a.	5.2	5.2	n.a.
N-333, 4G						
N-333, 5G	94.6	94.6	n.a.	5.4	5.4	n.a.
N-333, 5G						
N-333, 6G	93.8	95.0	1.29	6.2	5.0	1.29
N-333, 6G	96.1			3.9		
N-333, 7G	94.4	93.8	0.35	5.6	6.2	0.35
N-333, 7G	93.2			6.8		
N-333, 8G	96.4	95.1	1.76	3.6	4.9	1.76
N-333, 8G	93.8			6.2		
N-333, 9G	95.4	95.5	0.01	4.6	4.5	0.01
N-333, 9G	95.6			4.4		

Table 34 Microdistillation Test Results for Run N-323 Vapor Samples.

Sample ID	Percent Light-Mid Oils			Percent Heavy Oils		
	point	avg	var	point	avg	var
N-323, 1G	90.5	90.5	n.a.	9.5	9.5	n.a.
N-323, 1G						
N-323, 2G	N-323, 2G					
N-323, 3G	95.5	95.5	n.a.	4.5	4.5	n.a.
N-323, 3G						
N-323, 4G	94.2	94.9	0.41	5.8	5.1	0.41
N-323, 4G	95.5			4.5		
N-323, 5G	96.8	92.9	15.00	3.2	7.1	15.00
N-323, 5G	89.0			11.0		
N-323, 6G	94.6	93.8	0.65	5.4	6.2	0.65
N-323, 6G	93.0			7.0		
N-323, 7G	93.1	93.9	0.70	6.9	6.1	0.70
N-323, 7G	94.7			5.3		
N-323, 8G	94.3	94.9	0.35	5.7	5.1	0.35
N-323, 8G	95.5			4.5		
N-323, 9G	96.9	97.2	0.09	3.1	2.8	0.09
N-323, 9G	97.5			2.5		



Table 35 Microdistillation Test Results for Run N-321 Vapor Samples.

Sample ID	Percent Light-Mid Oils			Percent Heavy Oils		
	point	avg	var	point	avg	var
N-321, 1G	90.6	90.8	0.04	9.4	9.2	0.04
N-321, 1G	91.0			9.0		
N-321, 2G						
N-321, 2G						
N-321, 3G						
N-321, 3G						
N-321, 4G	82.4	82.4	n.a.	17.6	17.6	n.a.
N-321, 4G						
N-321, 5G	91.6	93.4	3.16	8.4	6.6	3.16
N-321, 5G	95.2			4.8		
N-321, 6G	91.0	91.3	0.08	9.0	8.7	0.08
N-321, 6G	91.6			8.4		
N-321, 7G	86.6	89.9	10.48	13.4	10.1	10.48
N-321, 7G	93.1			6.9		
N-321, 8G	89.9	90.8	0.78	10.1	9.2	0.78
N-321, 8G	91.7			8.3		
N-321, 9G						
N-321, 9G						

Table 36 Microdistillation Test Results for Run N-336 Vapor Samples.

Sample ID	Percent Light-Mid Oils			Percent Heavy Oils		
	point	avg	var	point	avg	var
N-336, 1G	91.3	92.4	1.16	8.7	7.6	1.16
N-336, 1G	93.5			6.5		
N-336, 2G	96.6	94.8	3.04	3.4	5.2	3.04
N-336, 2G	93.1			6.9		
N-336, 3G	94.3	94.3	n.a.	5.7	5.7	n.a.
N-336, 3G						
N-336, 4G	94.7	93.3	1.95	5.3	6.7	1.95
N-336, 4G	91.9			8.1		
N-336, 5G	94.2	94.6	0.18	5.8	5.4	0.18
N-336, 5G	95.0			5.0		
N-336, 6G	95.6	96.6	1.02	4.4	3.4	1.02
N-336, 6G	97.6			2.4		
N-336, 7G	96.4	95.6	0.69	3.6	4.4	0.69
N-336, 7G	94.7			5.3		
N-336, 8G	95.7	96.6	0.70	4.3	3.4	0.70
N-336, 8G	97.4			2.6		
N-336, 9G	91.6	92.5	0.79	8.4	7.5	0.79
N-336, 9G	93.4			6.6		

Table 37 Microdistillation Test Results for Run N-347 Vapor Samples.

Sample ID	Percent Light-Mid Oils			Percent Heavy Oils		
	point	avg	var	point	avg	var
N-347, 1G	92.8	90.0	7.93	7.2	10.0	7.93
N-347, 1G	87.2			12.8		
N-347, 2G	95.5	94.8	0.48	4.5	5.2	0.48
N-347, 2G	94.1			5.9		
N-347, 3G	95.7	95.8	0.01	4.3	4.2	0.01
N-347, 3G	95.9			4.1		
N-347, 4G	94.0	95.1	1.23	6.0	4.9	1.23
N-347, 4G	96.2			3.8		
N-347, 5G	91.5	94.5	8.62	8.5	5.5	8.62
N-347, 5G	97.4			2.6		
N-347, 6G	95.2	95.1	0.01	4.8	4.9	0.01
N-347, 6G	95.1			4.9		
N-347, 7G	93.5	91.8	2.74	6.5	8.2	2.74
N-347, 7G	90.2			9.8		
N-347, 8G	89.7	90.0	0.09	10.3	10.0	0.09
N-347, 8G	90.3			9.7		
N-347, 9G	95.9	95.9	n.a.	4.1	4.1	n.a.
N-347, 9G						

## APPENDIX E

### THF Solubility Tests

The vapor-liquid equilibrium profiles were determined using THF solubility tests. A known mass of  $\text{CaCO}_3$  was added to the HAO61 before each autoclave run.  $\text{CaCO}_3$  was found to be inert for the purposes of this study and is insoluble in THF. Since HAO61 was found to be THF soluble, THF insolubles represented only the  $\text{CaCO}_3$  in the sample. Knowing the percent  $\text{CaCO}_3$  in both the charge and the sample allowed calculation of the split of solvent into the vapor and liquid phases for the sample condition.

#### Procedure

THF solubility tests were performed on the samples by quantitatively filtering a small quantity of the sample through preweighed filters. A schematic of the apparatus used for the THF solubility tests is provided in Figure 14.

The sample and select labware were first weighed and prepared for the analysis. A nominal 0.2 grams of sample was weighed into a 50 ml beaker. The sample was to be filtered using a paper prefilter and a 0.5 micron Millipore type FH filter. The paper prefilter and a watchglass were dried in a laboratory furnace and cooled in a desiccator to ambient. The watchglass and the two filters were then weighed. The filters were placed into a filter housing seated above a vacuum flask as shown in Figure 14.

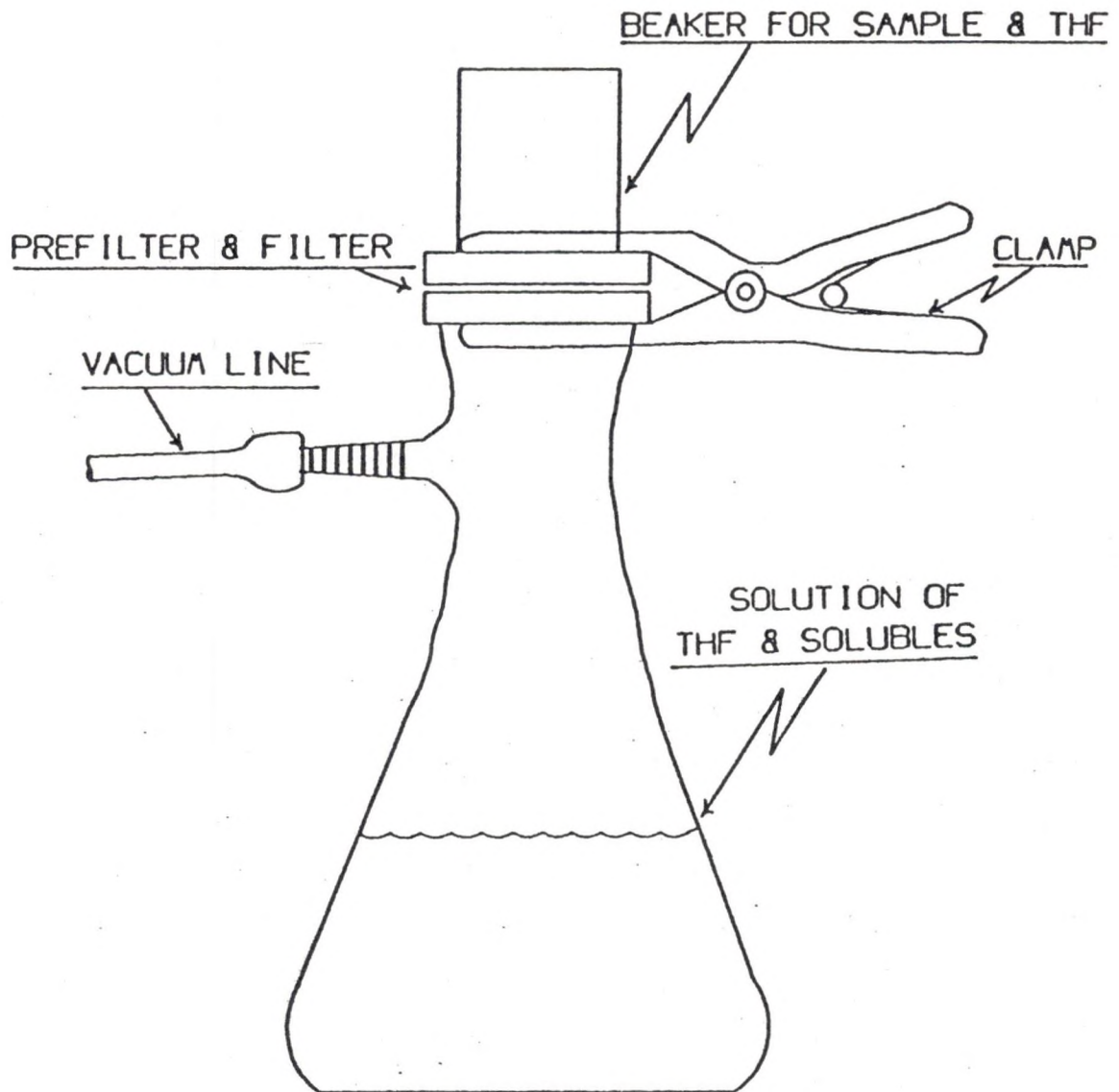


Figure 14. Schematic of Setup for THF Solubility Tests.



The mass of insolubles in the sample was determined by dissolving the sample in THF and filtering it. A water venturi was started to provide a slight vacuum below the filters and the sample was dissolved and rinsed from the beaker onto the filters using THF. Additional THF was then used to dissolve any remaining solvent on the filters and rinse it through the filters. The vacuum was applied until the solvent and solubles were pulled through the filters.

The apparatus was disassembled and the two filters containing the insolubles were placed back on the watch-glass and into the oven. The 0.5 micron filters could not be dried before use but it was found that these filters lose about 1.5 milligrams during the drying procedure. The dried filters were cooled in a desiccator and reweighed to identify the increase in mass. This increase in mass was assumed to be  $\text{CaCO}_3$  since THF solubility tests performed on the solvent showed no insolubles. The percentage of THF insolubles ( $\text{CaCO}_3$ ) was determined by difference as:

$$\% \text{CaCO}_3 = 100 * \frac{\text{mass of filters \& CaCO}_3 - \text{mass of filters}}{\text{mass of sample}} \quad [9]$$

where 0.0015 grams is subtracted from the filter mass to account for moisture lost from the .5 micron filter in the final drying.

THF solubility tests were performed on each of the liquid samples taken during testing. Tests also were per-

formed on the charge and quench liquids from various runs to identify any overall change. Results of these analyses are provided in Table 38.

Table 38 THF Solubility Test Results.

Sample ID	N-333			N-323		
	CaCO <sub>3</sub> %	AVG	Samp. Var	CaCO <sub>3</sub> %	AVG	Samp. Var
1L	7.231	7.170	0.007	6.922	6.714	0.087
1L	7.109			6.506		
1L						
2L	7.057	6.955	0.021	7.380	7.406	0.001
2L	6.852			7.432		
2L						
3L	7.725	7.707	0.001	8.693	8.379	0.197
3L	7.688			8.065		
3L						
4L	7.763	7.849	0.015	10.466	9.768	0.976
4L	7.935			9.069		
4L						
5L	9.618	9.593	0.001	9.195	9.080	0.027
5L	9.569			8.965		
5L						
6L	9.519	12.747	13.520	11.800	11.597	0.082
6L	16.750			11.394		
6L	11.973					
7L	11.194	11.354	0.052	12.253	11.878	0.282
7L	11.515			11.502		
7L						
8L	13.209	13.468	0.134	14.619	14.439	0.065
8L	13.727			14.258		
8L						
9L	13.649	12.629	1.979	13.828	14.125	0.177
9L	13.214			14.423		
9L	11.024					

Table 38 THF Solubility Test Results (continued).

Sample ID	N-321			N-336		
	CaCO <sub>3</sub> %	AVG	Samp. Var	CaCO <sub>3</sub> %	AVG	Samp. Var
1L	7.404	6.870	0.991	7.334	7.271	0.008
1L	7.485			7.207		
1L	5.722					
2L	8.678	8.247	0.372	7.634	7.570	0.008
2L	7.816			7.506		
2L						
3L	9.116	8.694	0.357	8.520	8.540	0.001
3L	8.271			8.560		
3L						
4L	10.111	9.571	0.583	11.135	11.093	0.004
4L	9.031			11.052		
4L						
5L	12.863	12.323	0.584	11.387	11.220	0.056
5L	11.782			11.053		
5L						
6L	13.976	14.165	0.071	12.156	12.021	0.037
6L	14.354			11.885		
6L						
7L	16.946	16.782	0.054	12.141	12.094	0.004
7L	16.618			12.047		
7L						
8L	18.505	18.464	0.003	14.869	14.837	0.002
8L	18.424			14.805		
8L						
9L				14.018	14.048	0.002
9L				14.078		
9L						



Table 38 THF Solubility Test Results (continued).

N-347				Miscellaneous Runs			
Sample ID	CaCO <sub>3</sub> %	AVG	Samp. Var	Sample* ID	CaCO <sub>3</sub> %	AVG	Samp. Var
1L	6.590	6.789	0.079	C - 323	4.740	4.826	0.015
1L	6.988			C - 323	4.912		
1L				C - 321	4.184	4.352	0.057
2L	6.932	6.242	1.089	C - 321	4.520		
2L	5.042			C - 336	4.652	4.519	0.036
2L	6.752			C - 336	4.385		
3L	8.707	8.647	0.007	C - 347	4.467	4.324	0.041
3L	8.587			C - 347	4.181		
3L							
4L	9.484	8.867	0.779	dry run	0.000	0.000	0.000
4L	9.260			dry run	0.000		
4L	7.856						
5L	12.284	9.781	12.723	Q - 323	4.167	4.188	0.001
5L	11.361			Q - 323	4.208		
5L	5.697			Q - 321	5.056	4.612	0.394
				Q - 321	4.168		
6L	13.560	13.621	0.007	Q - 336	4.287	4.283	0.000
6L	13.682			Q - 336	4.280		
6L							
7L	13.708	13.676	0.002	Q - 347	4.988	4.417	0.652
7L	13.645			Q - 347	3.846		
7L							
8L	14.314	14.369	0.006	HAO-61	0.152	0.051	0.020
8L	14.424			HAO-61	-0.050		
8L							
9L	14.973	14.971	0.000				
9L	14.968						
9L							

\*Q represents quench sample, C represents charge, and dry runs are with no liquid.

## APPENDIX F

### Analysis of Variance

Analysis of Variance (ANOVA) was used as a tool in analyzing the time sample data. The ANOVA was used to determine the significance of the temperature and pressure effects on the system. ANOVA tables were formed for both the fraction of solvent in the vapor phase and the percent of combined light and middle oils in the liquid phase (See Tables 37 and 38, respectively).

When using a block design for an experiment it is beneficial to change the treatments and blocks in a randomized order. A randomized design helps eliminate the effects of variation in the variables on each other (7). It should be noted that the design used for the experimental runs in this thesis was not completely randomized. While pressures were run in a randomized fashion temperatures were not. Instead, run temperatures were chosen in ascending order. This was done because of large amount of time it takes for the autoclave to cool down. Many more data points could be taken in a day with the procedure that was used.

The ANOVA for the fraction of solvent in the vapor phase showed that there was a significant effect from both temperature and pressure. This is shown in Table 37, where blocks represent temperature and treatments represent pressure. The ANOVA was performed using F-tables at the 95

Table 37 Analysis of Variance for the Fraction of HAO61 in the Vapor Phase.

	<u>Y<sub>ti</sub></u>					<u>Grand Average</u> <u>Y<sub>avg</sub></u>					<u>Block Deviations</u> <u>(Y<sub>i,avg</sub> - Y<sub>avg</sub>)</u>					<u>Treatment Deviations</u> <u>(Y<sub>t,avg</sub> - Y<sub>avg</sub>)</u>					<u>Residuals</u> <u>Y<sub>ti</sub> - Y<sub>tavg</sub> - Y<sub>iavg</sub> + Y<sub>avg</sub></u>				
	31	29	27	33	26	50	50	50	50	50	-21	-21	-21	-21	-21	-2	2	2	2	-4	4	-2	-4	2	1
	29	36	40	36	19	50	50	50	50	50	-18	-18	-18	-18	-18	-2	2	2	2	-4	-1	2	6	2	-8
Analysis of	38	53	44	44	43	50	50	50	50	50	-6	-6	-6	-6	-6	-2	2	2	2	-4	-5	7	-3	-2	3
Observations	50	50	50	58	45	= 50	50	50	50	50	+ 0	0	0	0	0	+ -2	2	2	2	-4	+ 1	-3	-3	6	-1
	64	62	62	59	51	50	50	50	50	50	10	10	10	10	10	-2	2	2	2	-4	6	0	0	-2	-5
	60	64	68	63	67	50	50	50	50	50	14	14	14	14	14	-2	2	2	2	-4	-3	-2	2	-3	7
	67	71	75	72	70	50	50	50	50	50	21	21	21	21	21	-2	2	2	2	-4	-2	-1	1	-1	3

ANOVA Table for Fraction of HAO61 in the Vapor Phase.

source of variation	sum of squares	degrees of freedom	mean square	ratio of mean squares
between blocks (temperature)	SB = 7574	(n-1) = 6	sB <sup>2</sup> = 1262	sB <sup>2</sup> /sR <sup>2</sup> 65.7
between treatments (pressure)	ST = 240	(k-1) = 4	sA <sup>2</sup> = 60.0	sA <sup>2</sup> /sR <sup>2</sup> 3.1
residuals	SR = 460	(n-1)(k-1) = 24	sR <sup>2</sup> = 19.2	
total (corrected)	S = 8274	N - 1 = 34		

Test for block and treatment differences using the F - tables:

Test the null hypothesis at 95 percent probability. To discredit the null hypothesis for the block deviations, it must be proven that  $F(.05,6,24) < 65.7$ .  
From F-tables  $F(.05,6,24) = 2.51$  and is less than 65.7, so the null hypothesis is discredited by the experiment.

Test the null hypothesis at 95 percent probability. To discredit the null hypothesis for the treatment deviations it must be proven that  $F(.05,4,24) < 3.1$ .  
From F-tables  $F(.05,4,24) = 2.78$  and is less than 3.1, so the null hypothesis is discredited by the experiment.



Table 38 Analysis of Variance for the Percent Light and Middle Oil in the Liquid Phase.

	<u>Y<sub>ti</sub></u>					<u>Grand Average</u> <u>Y<sub>avg</sub></u>					<u>Block Deviations</u> <u>(Y<sub>i,avg</sub> - Y<sub>avg</sub>)</u>					<u>Treatment Deviations</u> <u>(Y<sub>t,avg</sub> - Y<sub>avg</sub>)</u>					<u>Residuals</u> <u>Y<sub>ti</sub> - Y<sub>tavg</sub> - Y<sub>iavg</sub> + Y<sub>avg</sub></u>				
Analysis of Observations	90	86	83	91	84	87	87	87	87	87	-1	-1	-1	-1	-1	2	-1	-2	2	0	2	1	-2	2	-3
	90	87	86	87	87	87	87	87	87	87	-0	-0	-0	-0	-0	2	-1	-2	2	0	1	1	1	-2	-1
	87	85	79	89	84	87	87	87	87	87	-3	-3	-3	-3	-3	2	-1	-2	2	0	1	1	-4	2	-1
	84	86	86	87	89	= 87	87	87	87	87	+ -1	-1	-1	-1	-1	+ 2	-1	-2	2	0	+ -4	1	2	-1	2
	94	83	88	88	87	87	87	87	87	87	1	1	1	1	1	2	-1	-2	2	0	4	-4	3	-2	-1
	92	87	85	90	91	87	87	87	87	87	2	2	2	2	2	2	-1	-2	2	0	1	-1	-1	-1	2
	86	88	88	91	90	87	87	87	87	87	1	1	1	1	1	2	-1	-2	2	0	-4	1	1	1	1

ANOVA Table for Percent Light + Middle Oils in the Liquid Phase.

source of variation	sum of squares	degrees of freedom	mean square	ratio of mean squares
between blocks (temperature)	SB = 62	(n-1) = 6	sB <sup>2</sup> = 10.3	sB <sup>2</sup> /sR <sup>2</sup> 1.63
between treatments (pressure)	ST = 90	(k-1) = 4	sA <sup>2</sup> = 22.5	sA <sup>2</sup> /sR <sup>2</sup> 3.57
residuals	SR = 151	(n-1)(k-1) = 24	sR <sup>2</sup> = 6.3	
total (corrected)	S = 303	N - 1 = 34		

Test for block and treatment differences using the F - tables:

Test the null hypothesis at 95 percent probability. To discredit the null hypothesis for the block deviations, it must be proven that  $F(.05,6,24) < 1.63$

From F - tables  $F(.05,6,24) = 2.51$  and is greater than 1.63, therefore the null hypothesis is not discredited.

Test the null hypothesis at 95 percent probability. To discredit the null hypothesis for the treatment deviations it must be proven that  $F(.05,4,24) < 3.57$

From F-tables  $F(.05,4,24) = 2.78$  and is less than 3.57, so the null hypothesis is discredited by the experiment.



percent probability level. For temperature, the effect is found to be highly significant since the ratio of mean squares (65.7) is much greater than the F-value of 2.51. The pressure effect not as notable with a ratio of mean squares of 3.1 and an F-value of 2.78.

The ANOVA tables for percent light plus middle oils in the liquid phase showed that there was no temperature effect and only a slight effect due to pressure. The original belief was that the liquid phase would become more lean in the lighter oils as either temperature increased or pressure decreased. However, as discussed in Chapter III, it is suspected that thermal cracking of the solvent occurred. Since cracking changes the makeup of a solvent there is no longer an opportunity to "track" a set quantity of each cut of oils.

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