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SYNTHETIC FUEL AROMATICITY AND STAGED COMBUSTION

Final Report for the Period September 23, 1980–September 23, 1982

By
James R. Longanbach
Lisa K. Chan
Arthur Levy

November 15, 1982

Work Performed Under Contract No. AC22-80PC30302

Battelle Columbus Laboratories
Columbus, Ohio

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FINAL REPORT

on

**SYNTHETIC FUEL AROMATICITY AND
STAGED COMBUSTION**

to

**U. S. DEPARTMENT OF ENERGY
Pittsburgh Energy Technology Center**

November 15, 1982

by

James R. Longanbach, Lisa K. Chan, and Arthur Levy

Period Covered: September 23, 1980-September 23, 1982

**Contract No. DE-AC22-80PC-30302
Battelle No. G-7662**

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PITTSBURGH ENERGY TECHNOLOGY CENTER

Contract No. DE-AC22-80PC-30302
Battelle No. G-7662

Period Covered: September 23, 1980 -
September 23, 1982

November 15, 1982

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James R. Longanbach, Lisa K. Chan, and Arthur Levy

INTRODUCTION

Synthetic liquid fuels, otherwise referred to as synfuels or coal-derived liquids, are probably best characterized from a combustion-environmental point of view as low in hydrogen, low in sulfur, high in nitrogen, and high in aromatics. As a consequence two of the more critical problems in synfuel combustion are NO_x formation and soot formation (and polycyclic organic matter).^(1,2) This program was directed to these two issues.

At first hand the solutions to burning synfuels high in aromatics and fuel-bound nitrogen are diametrically opposed, i.e., high temperature and excess air keep soot levels down and low temperatures and vitiated air keep nitrogen oxide levels down. Staged combustion however offers a logical solution to the above. This program separates and analyzes the synfuel combustion problem via its component parts and then puts them together again phenomenologically via the stage combustion process.

OBJECTIVES

The overall objective of this program was to elucidate the pyrolysis and oxidation behavior of synfuel and to integrate this behavior in staged combustion to determine the effects of staged combustion on the formation of soot and NO_x .

More specifically, this program was divided into five tasks. The titles and objectives of these tasks were as follows.

Task 1. Characterization of the aromatics and the fuel-N components. The objective was to characterize the aromatic and fuel-N compounds present in a typical synfuel.

Task 2. Pyrolysis Studies. The objective was to determine the behavior of aromatic and fuel-N components in narrow (50 C) distillation cuts of synfuel as a function of time and temperature.

Task 3. Oxidative-Pyrolysis Studies. The objective was to study the oxidation of the pyrolysis products from Task 2. However, the studies in Task 2 were simply extended to various levels of oxygen.

Task 4. Staged Combustion Studies. The objective was to define the burning characteristics of synfuel as a function of equivalence ratio, temperature and residence time in two-stage combustion. Only single-stage combustion studies were completed at various equivalence ratios. Residence time and temperature were not varied systematically.

Task 5. Modeling. The objective was to apply the results from Tasks 2, 3 and 4 into existing models for soot and NO_x formation in flames. No formal activity was carried out on this task but the data obtained were compared with results reported in the literature.

SUMMARY

Samples of middle and heavy SRC II distillates were obtained and distilled into 50 C boiling point range fractions. These were characterized by measurements of their molecular weight, elemental analysis and basic nitrogen content and calculation of average molecular structures by applying hydrogen distribution data obtained by H^1 -NMR to the Brown-Ladner correlations. The structures typically consisted of 1-3 aromatic rings fused to alicyclic rings with short, 1-3 carbon aliphatic side chains. The lower boiling fractions contained significant amounts (1 atom/molecule) of oxygen while the heavier fractions contained so few heteroatoms that they were essentially hydrocarbons. Basic nitrogen predominated in each of the SRC II distillate fractions.

Laboratory scale oxidative-pyrolysis experiments were carried out using the 50 C SRC II distillation cuts prepared in Task 1. Pyrolysis temperatures of 500-1100 C and oxygen concentrations from 0 to 100 percent of stoichiometry were used. The fuels were prevaporized and carried through a horizontal quartz reactor tube in flowing helium. The liquid products were collected in condensers cooled with liquid nitrogen and analyzed using procedures developed in Task 1.

The liquid product analyses showed that aromatization is a major reaction in the absence of oxygen. The oxygen containing materials (phenolics) seem to be more resistant to thermal pyrolysis than unsubstituted aromatics. Short aliphatic side chains are lost to produce unsubstituted aromatic liquids up to 900 C. These go on to solid products consisting almost entirely of carbon at 1100 C. In the presence of oxygen, oxygen is added to the aromatic ring at 900 C, decreasing the concentration of soot precursors.

Nitrogen converts from basic to nonbasic forms at about 500 C. The nonbasic nitrogen is more stable and survives up to 700 C after which it is slowly removed. Nitrogen content and basic/nonbasic nitrogen ratios were nearly unaffected by the presence of oxygen.

One area which requires significantly more research is the low temperature conversion between types of nitrogen compounds.

A recently constructed 50,000 Btu/hr staged combustor, equipped with a Sonicore nozzle to burn SRC and probes to take solid and liquid samples, HCN

and NH_3 , combustion gases, NO and unburned hydrocarbons, was used to study the chemistry of the nitrogen and aromatics in SRC II under actual staged combustion conditions. SRC II combustion was studied under fuel-rich, first-stage conditions at air/fuel ratios from 0.6 to 1.0 times stoichiometric. TFN (total fuel nitrogen) showed a minimum at $\phi = 0.8$ corroborating observations of others.

Analysis of the solid samples recovered from the combustion products showed that both oxygen and hydrogen concentrations increase with increasing air/fuel ratio, suggesting that oxygen is added to the fuel as OH resulting in the formation of phenols. The solids contained only about 1.7 hydrogens per 10 carbon atoms at $\phi = 0.8$. Nitrogen contents were low and no trend in nitrogen retention with increasing stoichiometry was observable.

The liquid samples contained very high molecular weight materials ($\text{MW} > 200$) with the majority containing more than 4 aromatic rings. Apparently only the most highly condensed aromatics survive to be captured by the sampling probe. Again, no trend in fuel nitrogen could be measured.

The chemistry of the fuel during combustion calls for further investigation in order to examine the mechanism by which HCN is evolved as a common intermediate for the formation of the nitrogen containing gaseous combustion products. In this way it may be possible to increase the formation of N_2 in competition with HCN formation and ultimately reduce NO_x emissions from the combustion of synthetic fuels.

RESULTS AND DISCUSSION

Task 1 - Characterization of SRC II Samples

Objectives

The objective of this task was to obtain suitable SRC II samples, distill them into narrow boiling point range cuts and characterize them with particular emphasis on the nitrogen content and aromatic structure.

SRC II Samples

Our initial activity was directed toward obtaining representative samples of SRC II for use in this program. We were also interested in defining suitable safety procedures for storing and handling SRC II in our laboratory.

Gulf and Westinghouse in Pittsburgh were visited to discuss safety procedures and SRC II samples. Gulf's safety procedures and the method and facilities used to transfer SRC II within their laboratory were explained. The names of people to contact at SRC International to obtain SRC II samples for use in the experimental program were also obtained. Battelle had a one-year old, 2-barrel sample of a blend of SRC II middle and heavy distillate from Westinghouse. Westinghouse provided analyses for this material and discussed their safety procedures for handling SRC II.

At a Workshop on Synthetic Fuel Combustion hosted by the Pittsburgh Energy Technology Center it was decided that standard SRC II samples would be provided through PETC. Since these would be available too late to fit into the Battelle program schedule, the Pittsburgh and Midway Coal Mining Company provided 5-gallon samples of SRC II naphtha, middle distillate, and heavy distillate. The Westinghouse sample and the three Pittsburgh and Midway samples were characterized, but only the Pittsburgh and Midway middle and heavy distillate SRC II samples were used in Tasks 2 and 3.

The standard SRC II sample provided by the Pittsburgh Energy Technology Center (PETC) was used in the Task 4 staged combustion studies.

Analytical Methods

Analytical methods developed for use in this program are discussed in detail below. No distillation cuts were made on the SRC II blend (Westinghouse) sample; it was used as received.

Elemental Analyses for C, H, N, S and O. A Perkin Elmer Elemental Analyzer was used initially for C, H, and N analyses. There are no problems with this method when low-ash liquid samples are used. However, it was found that this method did not give satisfactory results for total nitrogen and the samples were sent to an outside laboratory which used the Kjeldahl method. This is discussed in more detail later. Sulfur was measured by x-ray fluorescence and oxygen was calculated by difference. The sample size required was less than 10 ml, about 5 ml of which was used for the sulfur analysis and about 5 ml for the nitrogen analysis. Only a few milligrams were needed for the C and H analyses.

Basic Nitrogen. If typical nitrogen compounds are arranged in order of ionization constants in aqueous solution, those above a certain value are titratable with perchloric acid while those with lower ionization constants are not. The separation point is reported to be about $K_b = 1 \times 10^{-11}$.⁽³⁾ Most oxygen and sulfur compounds do not interfere. Examples of basic (titratable) nitrogen compounds include pyridines, quinolines, piperidines, and anilines (Figure 1). 2-Amino-benzothiazole is right on the separation point. Examples of nonbasic nitrogen compounds include pyrrole, indoles, carbazoles, urea, acetamide and cyanide (Figure 2).

Similar compounds are reported in SRC II.⁽⁴⁾ A list of basic and nonbasic nitrogen compounds found in SRC II is given in Table 1.

The titration of basic nitrogen with perchloric acid in acetic acid was tested successfully. The method⁽³⁾ consists of diluting an accurately weighed sample of SRC II (1.0 gram) with 100 ml of glacial acetic acid and

QUINOLINES

ISO-QUINOLINES

ACRIDINES

PHENANTHRIDINES

PHENAZINES

ANILINES

FIGURE 1. REPRESENTATIVE TYPES OF BASIC NITROGEN COMPOUNDS FOUND IN PETROLEUM

(From Axworthy, A.E., et al., "Chemistry of Fuel Nitrogen Oxides in Combustion", Rocketdyne Division, Rockwell International Report to EPA, February 1976, p. 23)

PYRROLES

INDOLES

CARBAZOLES

BENZCARBAZOLES

AMIDES

QUINOLONES

BENZONITRILES

FIGURE 2. REPRESENTATIVE TYPES OF NONBASIC NITROGEN COMPOUNDS
FOUND IN PETROLEUM

(From Axworthy, A.E., et al., "Chemistry of Fuel
Nitrogen Conversion to Nitrogen Oxides in Combustion",
Rocketdyne Division, Rockwell International report to
EPA, February 1976 (p. 24))

TABLE 1. BASIC AND NON-BASIC NITROGEN COMPOUNDS IN SRCII

<u>Basic</u>	<u>Non-basic</u>
Alkylpyridines	Phenolic pyridines
Quinolines	Alkyl indoles
Anilines	Phenolic amines
Aliphatic amines	Indoles
	Carbazoles
	Quinolenes
	Amides
	Benzocarbazoles
	Phenazines
	Nitriles

5 ml of toluene (to improve solubility) and titrating the mixture while stirring with 0.1N HClO₄ in glacial acetic acid. Water must be excluded from the system. After titration with a pH meter using a combination electrode, MV readings are plotted versus ml of acid added to find the breakpoint on the curve. A sample of pure pyridine was used to standardize the perchloric acid titrant. Analysis of the SRC II blend sample gave a value for basic nitrogen of 0.54 g/100 g sample. The total nitrogen content is 0.91 g/100 g. Thus, the ratio of basic/total nitrogen is 0.59. Ratios of 0.30 ± 0.05 are typical for crude oils.(5)

Simulated Distillation by Gas Chromatography. Simulated distillation by gas chromatography, similar to the method described in ASTM 2887, was used for this analysis. This technique requires much less sample, time and cost compared to even small scale conventional distillation techniques.

A comparison of a preliminary result of the Battelle GC simulation method with the results reported for the SRC II blend sample is shown in Table 2. The Battelle results are closer to the ASTM D86 results at all points up to the end point. The end point cannot be determined accurately using conventional distillation techniques because of the residue left in the equipment when the distillation pot is empty.

Aromatic Distribution by H¹ and C¹³ NMR. Brown and Ladner have developed a method for calculating several structural parameters of coal liquids based on the amounts of aromatic protons, aliphatic protons next to an aromatic ring and aliphatic protons not adjacent to an aromatic ring as measured by H¹ NMR.(6) Several assumptions were made in developing the equations which describe the molecular structures. They assumed that aromatic rings are not linked by C-C bonds or by C-O-C bonds. Recent studies suggest that these are reasonably good assumptions in depolymerized coal liquids such as SRC II.(7) We also assumed that all of the oxygen present in the SRC II is present as phenolic oxygen and appears under the aromatics in the NMR as found by Schwager, et al.(8) We corrected for this using the oxygen concentrations from the elemental analysis provided by Westinghouse. The fractions of total hydrogen measured were:

TABLE 2. COMPARISON OF DISTILLATION RESULTS
USING WESTINGHOUSE SRC II

Volume Distilled/ wt %	Method		
	Battelle	ASTM	
	GC Simulation, °C	D86, °C	2887, °C
IBP	114	104	136
5	172	194	166
10	183	207	181
30	211	223	207
50	235	237	229
70	252	255	250
90	293	303	282
95	331	338	312
EP	412	338	406

0.36 H_0 = aliphatic not adjacent to aromatic

0.37 H_α = aliphatic adjacent to aromatic

0.24 H_{aro} = aromatic

0.03 H_{OH} = phenolic.

sing these fractions, the elemental analyses and a molecular weight of 200 g/mole (discussed in the next section) the following molecular structure parameters were calculated for the Westinghouse SRC II blend.

f_a = fraction of total carbon which is aromatic = 0.556.

$\frac{H_{aro}}{C_{aro}}$ = ratio of substitutable edge atoms to total aromatic atoms = 0.998

α = fraction of edge atoms substituted = 0.474

C_A = total number of aromatic carbon atoms per molecule = 7.95

R_S = number of substituted aromatic ring carbons = 3.76

n = number of carbon atoms per saturated substituent = 1.97

R_n = number of aromatic rings per molecule = 1.01.

The molecular formula was calculated to be $C_{14.3}H_{17.4}N_{0.15}S_{0.01}O_{0.54}$.

These easy calculations provide sufficient characterization of the structures of the starting SRC II distillation fractions and pyrolysis and oxidation products to study the effects of aromaticity. These preliminary results suggested that almost all of the aromatics were single ring structures and that the substituents average two carbon atoms in length. In addition a sample was submitted for C^{13} NMR, which gives a measure of the ratio of aliphatic to aromatic carbon directly, and was used as a check on these calculations. The aromaticity by C^{13} NMR was $f_a = 0.60$. Other workers have also found that the Brown-Ladner equations agree very well with the C^{13} results so C^{13} NMR analyses were not used on the other samples.(9)

Molecular Weight Measurements. Most molecular weight measurements for coal liquids reported in the literature are obtained by Vapor Pressure Osmometry (VPO) in either benzene or THF. A sample of the SRC II blend sent out for VPO measurement of molecular weight gave a molecular weight of 138 g/mole. Since these measurements involve a long lag time it was preferable to find a method for determining molecular weight in-house. VPO yields a number average molecular weight. Number average molecular weights have been

obtained using two methods which could be done in-house: Gel Permeation Chromatography (GPC) and Gas Chromatography (GC).

GPC uses size exclusion of the adsorbed SRC II molecules dissolved in a solvent as they pass through a column containing a material with a known pore size distribution. Large molecules which cannot be adsorbed in the pores are eluted first. A polystyrene standard of known molecular weight distribution is run and used as an external standard to calibrate the molecular size distribution curve. Two problems occur. First, the results are based on molecular shape rather than weight and the polystyrene standard may have a different molecular size/weight ratio than the SRC II. Second, the SRC II must be totally soluble and must not be permanently adsorbed on the column. Both problems appeared to occur when the Westinghouse SRC II sample was analyzed using GPC. The number average molecular weight was found to be only 53 g/mole. This is clearly too low. Some of the SRC II was not eluted from the column and apparently the polystyrene polymer was not a good standard for SRC II as well.

GC was tried using the same column used for simulated distillation. This column elutes the compounds in order of their boiling point. The flame ionization detector (FID) used measures the mass of sample (carbon) passing through the flame. Standards of straight chain aliphatics of known boiling point and molecular weight were used to calibrate the results. The aliphatics mixture is not a good model for aromatics because aliphatics boil at lower temperatures for the same molecular weight compared to aromatics and phenols, as shown in Figure 3. The addition of aliphatic side chains to aromatics increases their boiling points, moving them into closer agreement with the n-aliphatic standards.

The number average molecular weight obtained by the GC method was 190 g/mole. This also seemed low but number average molecular weights are heavily influenced by the concentration of low molecular weight species present. One set of published values for PAMCO SRC molecular weights (by VPO) are propane soluble 307, pentane insolubles-benzene solubles 352, pentane soluble-propane insolubles 563, and carbon disulfide insolubles 600. These seem high considering the other properties of the Westinghouse SRC II such as viscosity (1.19 cs at 100 C) and pour point (-65 F).

FIGURE 3. BOILING POINT VERSUS MOLECULAR WEIGHT IN VARIOUS TYPES OF AROMATICS AND n-ALIPHATICS

Distillation of SRC II Samples

Three 5-gallon samples of SRC II product fractions, one each of naphtha, middle distillate, and heavy distillate, were received from the Pittsburg and Midway Coal Mining Company. (The SRC II naphtha sample was not used in the current program.)

The SRC II middle distillate was distilled at atmospheric pressure to 266 C and under reduced pressure (64 torr) from 264 to 304 C. Six fractions were obtained:

<u>Sample</u>	<u>Boiling Point Range, C, Corrected to 760 mm Hg</u>	<u>Sample Weight, g/%</u>
MD1	< 150	6.0/0.7
MD2	150-200	124.6/15.0
MD3	200-250	356.4/43.0
MD4	250-300	298.2/36.0
MD5	300-304	9.0/ 1.1
MD6	>304 (residue)	34.6/ 4.2

The three largest fractions were analyzed for molecular weight, elemental analysis, hydrogen distribution, basic nitrogen and simulated distillation.

The SRC II heavy distillate sample was distilled under reduced pressure (3 torr). Five fractions were obtained:

<u>Sample</u>	<u>Boiling Point Range, C, Corrected to 760 mm Hg</u>	<u>Sample Weight, g/%</u>
HD1	< 300	82.1/8.2
HD2	300-350	334.2/33.3
HD3	350-400	293.9/29.3
HD4	400-450	149.6/14.9
HD5	>450	138.9/13.8

Fractions HD-2, HD-3, and HD-4 were also analyzed as described above. Fraction HD-1 is assumed to be identical to fraction MD-4 since the middle and heavy distillates are presumably cuts from the same distillation at the Tacoma SRC II pilot plant.

Analysis of Distillation Cuts

The results of these analyses are listed in Tables 3-5. The results for a blend of middle and heavy SRC II distillate obtained previously from Westinghouse are also included.

The molecular weights obtained by VPO are number average molecular weights and are very sensitive to the low molecular weight compounds present. Thus, even though the HD-2 distillation fraction was obtained between 300 and 350 C, there are enough low molecular weight components to bring the number average molecular weight down to 177 g/mole. The molecular weights are plotted versus boiling point range in Figure 4. The boiling points of some typical aromatic compounds are included for comparison. Substitution of short aliphatic chains on a benzene ring raises the boiling point significantly. It is highly probable that virtually every compound in SRC II is a substituted aromatic.

The boiling point ranges as measured by GC (Table 4) do not fall entirely within the boiling point ranges measured during distillation. The boiling point ranges measured by GC are indicated in Figure 4 by dotted lines. When the boiling point ranges are extended the correlation of boiling point ranges with molecular weight agrees well with the known values for the substituted aromatics.

The elemental analyses listed in Table 3 show that carbon content increases and hydrogen content decreases with increasing molecular weight as expected. Nitrogen, sulfur and oxygen do not exhibit clear trends with increasing molecular weight. Basic nitrogen and the ratio of basic N/total N also do not follow clear trends with increasing molecular weight.

The fraction of aromatic hydrogen increases and the fractions of total aliphatic hydrogen and phenolic hydrogen decrease with increasing molecular weight (Table 3). The experimental variation in the NMR measurements is significant as shown by duplicate determinations.

The structural parameters calculated from the hydrogen distribution measurements are listed in Table 5. Aromaticity (f_a) increases from about 40 percent to 70 percent with increasing molecular weight. The ratio of substitutable aromatic positions to total aromatic carbon (H_{aro}/C_{aro}) decreases with increasing molecular weight as would be expected as the number of condensed

TABLE 3. ANALYTICAL DATA FOR WESTINGHOUSE AND GULF SRC II SAMPLES

Sample	Westinghouse	MD-2	MD-3	MD-4	HD-2	HD-3	HD-4
<u>Bp Range, °C</u>		150-200	200-250	250-300	300-350	350-400	400-450
<u>Molecular Weight</u> ⁽¹⁾ g/mole	138	147	176	184	177	196	262
<u>Elemental Analyses</u> (Wt. Percent)							
Ash	0.02	0.02	0.02	0.02	--	--	--
C	85.9	82.6	83.4	87.3	90.	90.	90.1
H	9.1	9.8	9.3	9.2	8.1	7.4	7.1
N ⁽²⁾	1.0	0.9	1.5	1.7	1.0	1.4	1.4
S	0.07	0.22	0.24	0.31	0.07	0.16	0.33
O	3.9	6.5	5.5	1.5	0.8	1.0	1.1
Basic N		0.49	0.75	0.80	0.42	0.56	0.76
Basic N/Total N		0.54	0.50	0.47	0.42	0.40	0.54
<u>NMR Parameters</u>							
H -α to Aromatic	0.37	0.31	0.42	0.43	0.40	0.36	0.37
Haliphatic	0.36	0.48	0.32	0.34	0.27	0.26	0.25
Aromatic	0.24	0.17	0.21	0.22	0.32	0.37	0.37
H-Phenolic ⁽³⁾	0.03	0.04	0.05	0.01	0.01	0.01	0.01

(1) Measured by Vapor Phase Osmometry.

(2) Measured by C-H-N analysis. Corrected results for MD-2, MD-3, MD-4 and HD-2 are listed in Table 9.

(3) Based on the assumption O=OH.

TABLE 4. ANALYTICAL DATA FOR WESTINGHOUSE
AND GULF SRC II SAMPLES

<u>Boiling Point Distributions</u>							
<u>°C(1)</u>							
Sample	Westinghouse	MD-2	MD-3	MD-4	HD-2	HD-3	HD-4
69	--	--	--	--	--	--	--
98	0.05	0.06	--	--	--	--	--
126	0.05	0.10	--	--	--	--	--
151	0.50	6.76	--	--	--	--	--
174	1.60	11.45	--	--	--	--	--
196	13.05	39.85	6.54	--	--	--	--
216	17.70	34.65	37.64	0.48	--	--	--
235	14.85	4.01	27.40	10.90	--	--	--
253	19.85	--	17.94	--	--	--	--
287	17.90	2.87	7.89	54.55	31.28	--	--
317	5.95	0.35	0.60	33.49	59.52	10.20	0.67
344	3.10	0.15	0.49	0.05	8.65	21.06	0.75
369	2.85	0.22	0.63	0.03	0.18	46.88	10.60
391	0.90	--	0.57	--	--	18.90	42.89
412	0.50	0.05	--	0.06	--	2.09	39.32
432	0.25	0.09	0.11	0.13	--	0.66	2.45
450	0.15	0.02	0.08	0.07	--	0.20	2.48
468	0.15	--	0.05	0.08	--	--	0.78
498	0.50	--	0.05	0.13	--	--	--
525	0.00	--	--	0.01	--	--	--
548	0.00	--	--	--	--	--	--

(1) Measured by GC simulation.

TABLE 5. ANALYTICAL DATA FOR WESTINGHOUSE
AND GULF SRC II SAMPLES

<u>Structural Parameters</u>							
Sample	Westinghouse	MD-2	MD-3	MD-4	HD-2	HD-3	HD-4
f_a (1)	0.54	0.44	0.51	0.51	0.64	0.69	0.71
H_{aro}/C_{aro} (2)	1.	1.	1.	1.	0.88	0.78	0.74
σ (3)	0.50	0.60	0.59	0.52	0.40	0.34	0.35
R_s (4,5)	2.6	2.7	3.6	3.6	3.0	2.7	3.6
n (6)	2.0	2.6	1.8	1.8	1.9	1.7	1.7
C_a (7)	5.3	4.4	6.2	6.9	8.5	10.2	13.9
R_a (8)	1.	1.	1.	1.1	1.5	2.1	2.8
<u>Molecular Formula</u>							
C	9.88	10.1	12.2	13.4	13.3	14.7	19.7
H	12.	14.4	16.4	16.9	14.3	14.5	18.6
N	0.10	0.09	0.19	0.22	0.13	0.20	0.26
S	0.00	0.01	0.01	0.02	0.00	0.01	0.03
O	0.34	0.61	0.61	0.17	0.09	0.13	0.18

(1) f_a = fraction of total carbon which is aromatic.(2) H_{aro}/C_{aro} = ratio of substitutable aromatics.(3) σ = fraction of the available aromatic edge atoms occupied by substituents.(4) R_s = number of substituted aromatic ring carbons.(5) R_s was calculated by assuming $H_{aro}/C_{aro} \leq 1$.(6) n = number of carbon atoms per saturated substituent.(7) C_a = total number of aromatic carbon atoms.(8) R_a = number of aromatic rings.

FIGURE 4. MOLECULAR WEIGHT - BOILING POINT DISTRIBUTION

rings per molecule increases. The higher molecular weight molecules have a lower fraction of substituted aromatic carbon atoms α , but about the same number of substituted aromatic carbon atoms per molecule (R_g). This shows that coal is not "chickenwire" but is made up of aromatic centers connected to each other by a limited number of aliphatic and heteroatom bridges which are broken and capped during liquefaction. The number of substituents per aliphatic side chain (n) does not change much with increasing molecular weight, remaining between one and two carbon atoms. This indicates that the connecting links are short, as would be expected for solid material such as coal. The number of aromatic carbon atoms (C_a) and the number of aromatic rings (R_a) per molecule increase with increasing molecular weight as expected.

The molecular formulas show that the molecules are largely hydrocarbons. Less than one in every 4-5 molecules contains nitrogen and less than one molecule in 20-30 contains sulfur. Oxygen decreases with increasing molecular weight and is assumed to be entirely phenolic. More than half of the lower molecular weight molecules contain a phenolic functional group.

Average molecular structures can be drawn for the various boiling point fractions. Some possibilities are shown in Figure 5. These structures contain 1-3 carbon aliphatic side chains. Alicyclic structures become more numerous as molecular weight increases. The number of aromatic rings per molecule is only 1-3 throughout the distillable range. These structures also correspond reasonably well with the structures of known boiling point shown in Figure 4.

Improvement in the Measurement of Total Nitrogen

The measurement of total nitrogen has been a problem in the past⁽¹⁰⁾ and a number of papers have been written describing improved methods of analysis.⁽¹¹⁻¹⁴⁾ We were not satisfied with the total nitrogen analytical data supplied by Battelle's analytical staff and as a result, a series of standards were made up consisting of a pyridine-type compound in No. 2 fuel oil and a pyrrole-type compound in No. 2 fuel oil. Each standard was analyzed several times using both the C-H-N analyzer and the micro-Kjeldahl method of nitrogen analysis to characterize each method in terms of nitrogen recovery

MD-2

MD-3

MD-4

HD-2

HD-3

HD-4

FIGURE 5. AVERAGE MOLECULAR STRUCTURES IN SRC II

(accuracy) and standard deviation (precision). The results are listed in Table 6.

The nitrogen compounds used were pyrrole, quinoline and 4-benzyl pyridine. Pyrrole was found to be unstable and was not analyzed using the C-H-N analyzer. A freshly prepared mixture was analyzed by the micro-Kjeldahl method however. Nitrogen recoveries were 89-94 percent using the Kjeldahl method. The incomplete recoveries were apparently due to the stability of the compounds, particularly quinoline, which did not break down completely under the conditions used. Nitrogen recoveries were 107-112 percent using the C-H-N analyzer. The reasons for the high nitrogen recoveries are unknown, but the presence of air in the sample cup can lead to significant errors on the high side. The nitrogen levels used were around 1 percent and these errors could be expected to increase with typical samples from the pyrolysis-oxidation studies which contain less than 1/2 percent nitrogen. It did not appear that these results were sufficiently accurate for use in this research program. The standard deviations were also too large.

It was therefore decided to send the samples outside Battelle for total nitrogen analyses. Several well known research groups, including those at Mobil and MIT, send their fuel samples to one outside laboratory for nitrogen analyses. A series of standard samples containing a stable pyrrole, 2,3-dimethylindole, and quinoline in No. 2 fuel oil were sent to this outside laboratory for analysis of total nitrogen using the Kjeldahl method. The results are listed in Table 7.

Nitrogen recoveries were low (71-73 percent) for quinoline and high (100-118 percent) for 2,3-dimethylindole. Standard deviations were also unsatisfactory for the quinoline.

Energy and Environmental Research Corporation (EER) personnel suggested that we try Truesdail Laboratories, Inc. for total nitrogen analyses. They have studied the analytical methods available for total nitrogen analyses in fuel oil and have concluded that the Kjeldahl method is the best method overall, although care must be taken to insure complete digestion of refractory organics such as quinoline.⁽¹⁵⁾ Their total nitrogen analyses appeared to be precise and accurate. The test samples consisted of No. 2 fuel oil spiked with quinoline (basic nitrogen) and 2,3-dimethylindole (nonbasic nitrogen). The results are shown in Table 8. With the exception of the sample containing

TABLE 6. RESULTS OF THE BATTELLE ANALYSES FOR
NITROGEN USING KJELDAHL AND C-H-N METHODS

Sample	Target Conc., %	Analytical Method	Nitrogen						
			Replicates				Statistics		
			1	2	3	4	Std. Dev.	Mean	% Recovery
Fuel Oil	--	Kjeldahl	.02	.02	.02	.02	--	--	--
Fuel Oil	--	CHN	.02	.07	--	--	--	--	--
Fuel Oil and Pyrrole ^(a)	1.04	Kjeldahl	0.99	0.98	0.95	--	.02	0.97	94.0
Fuel Oil and Quinoline	1.02	Kjeldahl	0.91	1.0	0.82	--	.09	0.91	89.
Fuel Oil and Quinoline	1.02	CHN	1.17	1.12	1.02	1.11	.06	1.1	107.
Fuel Oil and 4-Benzyl- pyridine	0.84	CHN	0.96	0.84	1.01	--	.09	0.94	112.

(a) Nitrogen was not determined on this sample by C-H-N because of the presence of two phases

TABLE 7. RESULTS OF OUTSIDE LABORATORY ANALYSES FOR TOTAL NITROGEN

Sample	Target Conc, N%	Replicates			Statistics		
		1	2	3	Std. Dev.	Mean	% Recovery
Fuel Oil	--	0.016	0.015		.00071	0.0155	----
Quinoline in Fuel Oil	1.04	0.70	0.83	0.70	.075	0.74	71.1
Quinoline in Fuel Oil	0.54	0.50	--				92.6
2,3-Dimethylindole in Fuel Oil	0.31	0.31					100.0
2,3-Dimethylindole in Fuel Oil	0.11	0.14	0.12	0.13	.01	0.13	118.2

TABLE 8. RESULTS OF ANALYSES FOR TOTAL NITROGEN
BY TRUESDAIL LABORATORIES, INC.

Sample	Target Conc., % N	Replicates			Statistics		
		1	2	3	Std. Dev.	Mean	Percent Recovery
Fuel Oil	-	0.019	0.023		0.0028	0.021	-
Quinoline in fuel oil	1.04	1.05	1.05	1.05	0.0000	1.05	101.0
Quinoline in fuel oil	0.54	0.56	-	-	-	-	103.7
2,3-Dimethylindole in fuel oil	0.31	0.31	0.32		0.0041	0.315	101.6
2,3-Dimethylindole in fuel oil	0.11	0.14	0.13		0.0071	0.135	122.7

a very low level of 2,3-dimethylindole, recoveries averaged 102 percent. The low level sample recovery was only 0.025 percent nitrogen above the actual value. The standard deviation on every sample was excellent.

The SRC II distillate fractions were submitted for total nitrogen analysis. The results, combined with the perchloric acid/acetic acid titration results for basic nitrogen are listed in Table 9. Total nitrogen content appears to peak in the 250-300 C boiling point range. Basic nitrogen is the principal component in all of the distillate samples but nonbasic nitrogen concentration increases with increasing boiling point.

The same samples were analyzed in-house using a gas chromatograph equipped with an effluent splitter leading to a FID detector, to measure total sample concentration, and a nitrogen specific thermionic detector to measure total nitrogen. The nitrogen specific detector conditions were optimized for nitrogen/carbon response. The results are shown in Figure 6. There is a significant difference in the detector response to basic and nonbasic nitrogen. Since it is likely that the basic N/nonbasic N ratio changes as pyrolysis or oxidative-pyrolysis progresses, our gas chromatograph was not used to determine total nitrogen.

Tests on the Method for Basic Nitrogen Determination

The precision of the perchloric acid titration procedure for basic nitrogen was checked by titrating one sample three times. The results were reproducible within 1 percent of the basic nitrogen percentage (± 0.006 percent absolute). Since the normality of the titrant is established by titrating pure pyridine samples under the standard titration conditions and since there is not an appreciable solvent blank, the accuracy of the method should also be good. The scatter in basic nitrogen content suggests that there are only a few basic N compounds present in each SRC II distillation cut and that their concentrations vary widely from cut to cut.

The titration method for basic nitrogen⁽¹⁰⁾ was also tested for selectivity on the same samples used for evaluation of total nitrogen analytical methods. Ideally, the titration method for basic nitrogen should recover 100 percent of the nitrogen in the samples containing quinoline but none of

TABLE 9. NITROGEN DISTRIBUTION IN
SRC II DISTILLATION FRACTION

Fraction	Boiling Point Range, °C	Total N	Basic N	Nonbasic N (by diff.)
MD-2	150-200	0.55	0.49	0.06
MD-3	200-250	0.81	0.75	0.06
MD-4	250-300	1.05	0.80	0.25
HD-2	300-350	0.64	0.42	0.22

FIGURE 6. ACTUAL PERCENT NITROGEN
VERSUS PERCENT NITROGEN BY NITROGEN
SPECIFIC DETECTOR / FID RESPONSE
USING GAS CHROMATOGRAPHY

the nitrogen in the samples containing 2,3-dimethylindole. The results are shown in Table 10.

The standard deviations for all of the samples are good. Nitrogen recoveries are 102.3-102.5 percent for the basic nitrogen samples. The slightly high recoveries are apparently due to an error in the standardization of the perchloric acid titrant. The recoveries for nonbasic nitrogen are 0-2.1 percent, which is also good. It appears that basic nitrogen titration method is acceptable.

Improvement in the Simulated Distillation Method

A mixture of aromatics was prepared to use as a standard for the simulated distillation by gas chromatography (GC) analysis. The standard does not extend to boiling points as high as can be obtained with the n-alkane standards. The aromatic standard mixture consists of the following:

<u>Component</u>	<u>Boiling Point, C</u>
Benzene	80
Toluene	111
p-Xylene	138
Indane	177
Naphthalene	218
Dibenzyl	285
Phenanthrene	340
Pyrene	(395)

The boiling point of 395 C for pyrene appears to be too high based on the curve of boiling point versus GC residence time. Other boiling points have been reported for pyrene.

An 18" x 1/4" O.D. column had been used for the GC simulated distillation analysis. Most of the SRC 1I distillation cut which passed through the pyrolysis zone boiled in the same range as the starting material. Although there were many peaks of higher and lower boiling points, it was difficult to tell what changes had taken place in the region where the starting material boiled. Typical results are shown in Figure 7.

TABLE 10. RESULTS OF BATTELLE ANALYSES FOR BASIC NITROGEN USING
TITRATION WITH PERCHLORIC ACID IN ACETIC ACID

Sample	Target Conc. N%	Replicates			Statistics		
		1	2	3	Std. Dev.	Mean	N% Recovery
Fuel Oil	--	0.002	0.008	--	0.0042	0.005	--
Quinoline in Fuel Oil	1.04	1.075	1.068	--	0.0049	1.072	102.5
Quinoline in Fuel Oil	0.54	0.555	0.555	0.562	0.0040	0.557	102.3
2,3-Dimethylindole in Fuel Oil	0.31	0.013	0.010	0.011	0.0015	0.011	2.1
2,3-Dimethylindole in Fuel Oil	0.11	0.000	0.007	--	0.0049	0.00	0.0

FIGURE 7. COMPARISON OF MD-3 (250-300 C) BOILING POINT DISTRIBUTION BEFORE AND AFTER PYROLYSIS AT 800 C (GC COLUMN 18" x 1/4") (NUMBERS ABOVE PEAKS ARE GC ELUTION TIMES IN MINUTES)

To improve the separation and to detect changes in composition occurring during pyrolysis, a 54" x 1/4" O.D. column was prepared using the same packing, 10 percent UCW-982 on 60/80 Chrom-PAW. Simulated distillations using this column clearly showed the changes in the composition of the SRC II distillation cut taking place during pyrolysis, as shown in Figure 8.

Development of a Gas Chromatographic Method for the Determination of Molecular Weight

Molecular weight analyses by Vapor Phase Osmometry (VPO) have also been found to give some spurious results, particularly for the higher molecular weight materials in which some solids are probably present. The molecular weight of each sample has also been obtained by summing the area percent obtained by simulated distillation by gas chromatography using a series of aromatic standard compounds of known molecular weight to calibrate the curves. These results seem to be more consistent than the VPO results. Molecular weights obtained by the two methods are compared in Figure 9. There are differences between the two methods. The area percentages obtained by GC have not been corrected by using response factors. As a result, most of the VPO molecular weights are higher than those obtained by GC. The best fit between the data is given by the dashed line in Figure 9 (omitting the data shown as squares). This correlation allows a GC molecular weight to be substituted for a VPO molecular weight and may be a preferable method of obtaining molecular weight for the SRC II type samples.

Comparison of Analytical Results With Literature Data

The analytical results for the SRC II distillation cuts agree well with detailed characterization of narrow boiling point cuts of SRC II reported by Gray, et al. (17). The most common structures they reported for the boiling point fractions used in this work are shown in Table 11. Tetralins, hydrophenanthrenes, and hydroxyrenes predominate depending on the boiling point range of the sample.

The Pittsburgh and Midway Coal Mining Company sent analytical data on SRC II distillation cuts for comparison. The analyses are in good agreement.

FIGURE 8. COMPARISON OF MD-3 (250-300 C) BOILING POINT DISTRIBUTION BEFORE AND AFTER PYROLYSIS AT 800 C (GC COLUMN 54" x 1/4")

FIGURE 9. COMPARISON OF LIQUID PRODUCT MOLECULAR WEIGHTS OBTAINED BY VAPOR PHASE OSMOMETRY AND SIMULATED DISTILLATION BY GAS CHROMATOGRAPHY

TABLE 11. STRUCTURAL TYPES VERSUS BOILING
POINT OF SRC II FRACTIONS

Fraction	MD-2	MD-3	MD-4	HD-2	HD-3	HD-4
Total Weight % of Sample						
Saturates	27.8	13.2	4.8			
Olefins	3.5	4.2	0.5			
Aromatics	68.8	81.2	93.5	69.6	72.3	65.2
Weight % of Aromatics						
Phenols	51.4	40.5	6.2			
Benzenes	24.8	3.9				
Tetralins	21.5	25.6	8.9			
Naphthalenes		21.1	17.8			
Diphenyls			7.9			
Octahydrophenanthrenes			12.9			
Tetrahydrophenanthrenes			23.4	32.7	8.2	
Phenanthrenes				10.8		
Decahdropyrene				5.4		
Octahdropyrene					5.2	8.3
Hexahdropyrene				17.5	10.6	9.4
Dihdropyrene				6.7	18.3	10.8
Pyrene					18.3	12.4
Octahydrochrysene					7.0	

Their data were obtained using Powhatan No. 5 coal; the SRC II samples supplied to Battelle were prepared using Powhatan No. 6 coal. The significance of slightly different coals on the SRC II elemental analyses is unknown, but presumed to be minor.

The number average molecular weight of the distillation cuts were obtained by VPO. For the P&M samples, which correspond most closely in boiling point range to the Battelle samples, the molecular weights correspond fairly well, as shown in Figure 10. The use of separate middle and heavy distillates to obtain the Battelle samples accounts for the largest variation between molecular weight which occurs in the fourth distillation cut.

The trends in carbon, hydrogen, and oxygen content in the SRC II cuts with increasing boiling point are the same for the Gulf and Battelle samples as shown in Figures 11-13. It should be noted that the contents of carbon and oxygen do not increase or decrease smoothly with increasing boiling point due to the large peak in oxygen content at 200 C.

The H/C atomic ratio decreases with increasing boiling point and the sulfur content is low but increases slowly with increasing boiling point as shown in Figure 14.

The total and basic nitrogen contents are shown in Figure 15. The total nitrogen content measured by Gulf increases gradually with increasing boiling point. The circled Battelle results in Figure 15 were obtained when the samples were sent out for analysis using the Kjeldahl method as discussed previously. The agreement between these results and the Gulf data is quite good.

Summary -- Task 1. Characterization of SRC II Samples

Five analytical tests were selected to analyze the SRC II before and after partial oxidation and pyrolysis, emphasizing characterization of the nitrogen species present and the aromatic structure. The analytical methods were tested and refined with the following results.

Vapor Pressure Osmometry (VPO) was first tried to obtain molecular weights but was found to be slow, expensive, and inaccurate in cases where some SRC II components were insoluble in the solvent used (THF). In addition,

FIGURE 10. MOLECULAR WEIGHT VERSUS AVERAGE BOILING POINT

FIGURE 11. PERCENT CARBON VERSUS AVERAGE BOILING POINT

FIGURE 12. PERCENT HYDROGEN VERSUS AVERAGE BOILING POINT

FIGURE 13. PERCENT OXYGEN VERSUS AVERAGE BOILING POINT

FIGURE 14. H/C ATOMIC RATIO AND PERCENT SULFUR VERSUS AVERAGE BOILING POINT

FIGURE 15. BASIC AND TOTAL NITROGEN VERSUS AVERAGE BOILING POINT

the number average molecular weights which result from VPO analysis were found to be heavily influenced by low molecular weight components in the mixtures. A method using the summation of molecular weights of components separated by gas chromatography (GC) was found to give more realistic and consistent values of molecular weight and was chosen as the preferred method. It could be done cheaply and quickly in-house with the same data used to obtain simulated distillation measurements. The GC curves were standardized using a mixture of aromatics of known molecular weight and boiling point.

Elemental analyses were done using microcombustion for C and H. Total nitrogen proved to be difficult to measure accurately on these samples and was obtained by sending the samples to an outside laboratory. The results obtained seemed to be precise and accurate, using a modified Kjeldahl technique, but the procedures required approximately 5 grams of sample.

Basic nitrogen was measured by titrating with perchloric acid in anhydrous acetic acid. The technique was found to be precise and accurate.

Aromatic structure was characterized by applying the Brown-Ladner correlations to hydrogen distribution data obtained by H^1 NMR. Using this data, the molecular weight and the elemental analyses, average structures could be drawn for each boiling point fraction of SRC II. These agreed well with more detailed structural studies done on SRC II fractions by other investigators.

Samples of middle and heavy SRC II distillate fractions obtained from Pittsburgh and Midway Coal Mining Company were distilled into 50 C boiling point range fractions and characterized using the tests developed in this Task for use in the oxidative-pyrolysis studies in Tasks 2 and 3.

TASKS 2 AND 3 - BENCH SCALE OXIDATIVE-PYROLYSIS STUDIES

Objective

The objective of this task was to determine the pyrolysis and oxidation behavior of the Task 1 SRC II distillate fractions as a function of temperature, time and oxygen level. The distribution of aromatics and fuel-N constituents in the fractions before and after pyrolysis was of particular interest.

Development of a Bench Scale Oxidative-Pyrolysis Apparatus

Steady-state or dynamic nonsteady-state procedures can be used to do bench-scale studies of the pyrolytic oxidative stability of SRC II distillate fractions. An advantage of the latter is the obvious similarity to what a droplet sees on entering the combustion zone. A disadvantage is the difficulty in carrying out informative experiments. If we compare these two approaches to the volatility problem in coal one notes that both procedures tend to lead to the same type of results. This is exemplified by the steady-state analysis of Solomon and Colket(18) and the rapid pyrolysis experiments of Suuberg, Peters, and Howard(19). Preliminary evidence obtained by Beér, et al.(20), shows a much higher fuel nitrogen loss per unit mass of the liquid fuel evaporated when 150 μm droplets of a residual petroleum fuel oil were rapidly pyrolyzed, whereas when the fuel oil was vaporized under normal distillation conditions, more nitrogen was retained in the residue. Also of consequence to this study are the facts that the dynamic system provides a better representation of the real combustor and independent variables in a flow reactor are more easily controlled.

Drop Tube Furnace. A drop tube apparatus was assembled as shown in the schematic in Figure 16. A two-inch-diameter quartz tube was positioned vertically and heated by a two-foot-long electric furnace. A smaller quartz tube was permanently attached to the top of the reactor, one end of which was sealed with a serum cap. The liquid flow rate was held constant by means of a syringe pump. Inlet gases were passed through the reactor via a connection on top. Product gases were cooled and separated from the condensables in the collector before passing into the analyzing instruments. The pyrolyzed droplets were collected in one of four sample bottles. The residence time of the fuel droplets was controlled solely by varying the drop size.

Preliminary experiments were carried out with the Westinghouse SRC II fuel oil sample blend. The purpose of these experiments was to determine the collection efficiency, the importance of drop size and the effect of gas flow. The collection efficiency was close to 100 percent when 2.65-mm diameter droplets were passed through the reactor at room temperature. The

FIGURE 16. A SCHEMATIC DIAGRAM OF THE FIRST EXPERIMENTAL SET-UP

experiments were also repeated at 800, 1000 and 1200 K under either a constant stream of nitrogen or a no-flow condition. Due to the large drop size used, only a maximum of 6 percent weight loss was recorded at 1200 K. Based on chromatographic analysis it appeared that the fuel was unchanged in these experiments. The residue collected at 1200 K and under a stagnant N₂ medium showed the same boiling point distribution, the same concentration of basic nitrogen and the same overall composition as the original oil. The percent weight loss was the same for the two cases of fuel oil dropping through a 5 liter/min N₂ stream or through a stagnant medium.

Gas flow, however, may have an effect on soot formation by limiting contact with the walls of reactor. When the reactor was purged with a constant stream of nitrogen during the pyrolysis experiments, carbon deposition on the reactor walls was not observed. However, under a no-flow condition, a layer of black residue, presumably soot, coated the heated section of the quartz tube. Parts of the residue were hard and parts were flaky. It burned off easily in the presence of oxygen.

Calculations assuming a uniform gas and droplet temperature and for the case of a droplet falling through a stagnant medium showed that the time required to heat a 2.65-mm diameter liquid fuel drop to within 63 percent of the gas temperature is approximately 40 sec. If the drop size is decreased by an order of magnitude, i.e., 265 μ m, the heating time reduces to only 0.4 sec.

Additional computations also indicated that the pyrolysis of the full droplet is controlled by heat transfer from the gas to the droplet. If all the heat convected to the drop were used solely to vaporize the oil, the time for complete evaporation of a 2.65-mm diameter droplet was calculated to be 5 and 9 sec for gas temperatures of 1200 and 800 K, respectively. Similar calculations gave a value of approximately 5 sec for the center of the drop to reach 63 percent of the outer surface temperature (assumed to be the same as the gas temperature). Both values are significantly smaller than the estimated 40 sec heat transfer time between the gas and the drop.

Additional pyrolysis experiments were conducted at 400, 500 and 850 C with SRC II middle distillate and a 200-250 C cut (MD-3). Although it was desired to pass small drops, < 200 μ m, through the furnace, efforts were unsuccessful. Due to surface tension, drop size produced by a fine needle

having diameters less than 200 μm was not significantly smaller than those produced from larger needles. For this reason and because extremely high flow resistance was encountered when fine needles were used and because the fuel was fairly volatile, preliminary experiments were carried out with a large needle which had an opening of 508 μm . Approximately 2-mm diameter drops were generated with this needle size. Fuel was fed via the syringe pump at rates between 0.1-0.9 g/min. The percent fuel vaporized increased with temperature, but the heating rates were insufficient to vaporize the drops, except at 850 C. At 400 C there was essentially no change in the properties of the MD-3 distillation cut. This was also the situation when 5.3 percent O_2 was added to the helium stream carrying the drops through the furnace.

Modification to Prevaporize the Fuel. A system was set up similar to that of Blazowski⁽²¹⁾ in which the fuel is vaporized in an aluminum block heater, mixed with a preheated gas stream, and then passed into the furnace region. The fuel feed rate in this system was also maintained by the syringe pump.

The collection system was also modified. The vapor emitting from the furnace region was passed through a cold trap system to a gas chromatograph for analysis of the low molecular weight (gaseous) decomposition products. A schematic of the modified experimental system is shown in Figure 17.

Preliminary Experimental Results. The 200-250 C (MD-3) SRC II distillation fraction was vaporized at 300 C and the helium/vapor mixture was passed through a 300 C pyrolysis zone. Under these conditions there was no change in the composition of the distillation cut. Analysis by simulated distillation using gas chromatography showed that the distribution of compounds in the distillation cut was identical before and after vaporization at 300 C. No other analyses were done on this product. Reaction conditions for this (Run 1) and all other preliminary experiments done with a vertical reactor are listed in Table 12.

The boiling point distribution from a pyrolysis experiment at 800 C clearly showed changes in product composition (Run 2). Three experiments (Runs 3, 4, and 5), at 800 C nominal temperature and three residence times,

FIGURE 17. A SCHEMATIC DIAGRAM OF THE MODIFIED EXPERIMENTAL SET-UP

TABLE 12. EXPERIMENTAL CONDITIONS FOR INITIAL PYROLYSIS EXPERIMENTS

Run Number	SRC II Distillation Cut	Temp., C ^(a)	Time, sec ^(b)	Helium Flow, l/min	Fuel Flow, ml/min	Fuel Vapor Concentration ^(c) , %
1 - 36485-15	MD-3	300	3.2	1.5	0.33	2.6
2 - 36485-16	MD-3	800	1.0	2.6	~0.40	1.8
3 - 36485-17	MD-3	800	1.0	2.6	0.33	1.5
4 - 36485-18	MD-3	800	0.7	3.7	0.48	1.6
5 - 36485-19	MD-3	800	0.3	8.5	0.99	1.4
6 - 36485-20	MD-2	900	0.9	2.6	0.33	1.9
7 - 36485-23	MD-4	900	0.9	2.6	0.33	1.5
8 - 36485-26	MD-4	900	0.9	2.6	--	--

(a) Nominal temperatures, measured on outside of reactor tube wall at center of zone 3.

(b) Nominal times, based on gas-flow thru hottest zone.

(c) Calculated, based on density and average molecular weight of distillation cut.

were carried out to obtain more specific information about the changes taking place in the pyrolyzed liquids. The products from Runs 3 and 5 were subjected to a complete set of analyses.

At 0.3-sec residence time and 800 C, no apparent change in boiling point distribution took place as shown by the GC simulated distillation (Figure 18). At 1.0-sec residence time, large amounts of benzene, toluene, and xylenes were produced as well as many materials of higher boiling point than the starting material. The results are listed in Table 13 and compared to MD-3 starting material.

Although the GC simulated distillations showed no changes in the product composition at 0.3 sec and extensive changes at 10 sec residence time, the molecular weights of the 0.3 sec (Run 5) and 1.0 sec (Run 3) residence time products were about the same.

As the extent of pyrolysis was increased, the liquid products contained increasing amounts of oxygen and nitrogen and decreasing amounts of carbon and hydrogen. The products were virtually sulfur free. Basic nitrogen remained approximately constant and the basic N/total N ratio decreased sharply. However, these total N results were obtained by C-H-N analysis.

The NMR parameters showed that most of the aliphatic hydrogen, α or farther from an aromatic ring, was removed and total aliphatic hydrogen decreased sharply. As a result the percentages of aromatic and phenolic hydrogen increased.

The structural parameters derived from NMR data showed that aromaticity (f_a), number of aromatic carbons (C_a), and number of aromatic rings (R_a) increased as expected while the number of carbons per saturated substituent (n) decreased.

The gaseous species in the pyrolyzed products were identified by means of gas chromatography and Dräger tubes. The experiments were carried out with the 150-200 C (MD-2, Run 6) and the 250-300 C (MD-4, Run 7) cuts at a nominal furnace temperature of 900 C and a residence time of 1 sec. Gas chromatographic analysis showed the presence of H_2 , C_2H_6 , C_2H_4 , N_2 , and CH_4 in the flue gas with methane as the predominant gaseous product. Both distillate cuts gave the same gaseous products. In Run 8 with MD-4 under similar conditions, HCN and a smaller amount of NH_3 were identified with the Dräger tubes.

FIGURE 18. COMPARISON OF BOILING POINT DISTRIBUTION IN MD-3 (250-300 C) BEFORE AND AFTER PYROLYSIS AT 800 C FOR 0.3 AND 1.0 SECONDS IN HELIUM

TABLE 13. ANALYTICAL DATA FOR MD-3 PYROLYSIS EXPERIMENTS (T=800 C)

Run No.	Starting Material	5	3
Residence time, sec	--	0.3	1.
Sample No. 36510-	MD-3	49-8,9	49-12
Molecular Weight, g/mole	176	148	147
<u>Elemental Analyses, wt. percent</u>			
Ash	0.02		
C	83.4	80.2	75.5
H	9.3	8.3	5.9
N	1.5	3.6	4.3
S	0.24	0.055	0.065
O (difference)	5.5	7.8	14.2
Basic N	0.75	0.75	0.83
Basic N/Total N	0.50	0.21	0.19
<u>Hydrogen Distribution, fraction</u>			
H α (a)	0.42	0.46	0.28
H aliphatic	0.32	0.33	0.02
H aromatic	0.22	0.15	0.55
H phenolic(b)	0.037	0.059	0.15
<u>Simulated Distillation (see Figure 9)</u>			
<u>Structural Parameters</u>			
f_a (c)	0.51	0.51	0.86
H_{aro}/C_{aro} (d)	0.77	0.93	0.75
σ (e)	0.57	0.76	0.42
R_s (f)	2.69	3.56	2.50
n (g)	1.76	1.72	1.07
C_a (h)	6.2	5.04	7.95
R_a (i)	1.70	1.18	1.99
<u>Molecular Formula</u>			
C	12.2	9.9	9.2
H	16.4	12.3	8.7
N	0.19	0.38	0.45
S	0.01	0.00	0.00
O	0.61	0.72	1.30

(a) Aliphatic α to aromatic ring.

(b) Based on the assumption O=OH.

(c) f_a = fraction of total carbon which is aromatic.(d) H_{aro}/C_{aro} = ratio of substitutable aromatics.(e) σ = fraction of the available aromatic edge atoms occupied by substituents.(f) R_s = number of substituted aromatic ring carbons.(g) n = number of carbon atoms per saturated substituent.(h) C_a = total number of aromatic carbon atoms.(i) R_a = number of aromatic rings.

Horizontal Furnace Modifications. With the preliminary identification of the pyrolysis products clarified and prior to carrying out more quantitative pyrolysis experiments, additional modifications were made to the experimental apparatus. Since the pyrolyses were more effectively conducted as vapor phase pyrolyses the reaction furnace was placed in a horizontal position. To specify the temperature and residence time more accurately, a set of thermocouples was introduced into the reactor volume. These two modifications allowed for a flatter temperature profile than with the vertical setup. Figure 19 is a schematic of the modified experimental apparatus. Figure 20 shows a schematic of the fuel vaporizer. The larger volume in the new vaporizer was designed to allow the fuel vapor to be fed, vaporized, and mixed with helium with no fractionation.

Experimental Results

The focus of this study was the chemistry of the partially pyrolyzed and oxidized liquid fuel which survives as pyrolysis and oxidative pyrolysis proceed. The experiments were designed so that these products were not completely destroyed and could be recovered for analysis.

Each of the four SRC II distillation cuts was pyrolyzed at 500, 700, and 900 C for approximately 5 sec residence time in helium. The fuel vapor concentration averaged 1.45 volume percent in helium in these experiments.

Recoveries of liquid products averaged 95 percent at 500 C, 74 percent at 700 C, and 54 percent of fuel weight fed at 900 C. Visually, there appeared to be very little reaction at 500 C. No solids were deposited on the pyrolysis tube and virtually no gases were detected. Chemically, the most notable change at 500 C was a decrease in sulfur content from an average of 0.21 weight percent in the distillation cuts to 0.06 weight percent in the liquid products. Other chemical changes were small.

The initial oxidation experiments were conducted with MD-4 at two substoichiometric levels of oxygen in the helium flow gas. These corresponded

FIGURE 19. SCHEMATIC OF THE MODIFIED EXPERIMENT APPARATUS

FIGURE 20. SCHEMATIC OF THE FUEL VAPORIZER

to about 8 and 24 percent of the oxygen required to convert the fuel to CO₂ and H₂O. (a) Temperatures of 500, 700, and 900 C, at about 5 sec residence times, were used to compare with the corresponding pyrolysis experiment results to study the effects of oxygen.

A series of experiments were carried out to extend the reaction temperature to 1100 C and the oxygen level to almost 100 percent stoichiometric oxygen.

Problems were encountered with these conditions which necessitated some changes and limitations in the usual analytical procedures. The products obtained at 1100 C were nonvolatile solids. The only analyses which could be run on these samples were elemental analyses including total nitrogen and C¹³ NMR for aromaticity. Basic nitrogen determinations using the perchloric acid/ acetic acid titration technique were tried and the results are reported but recoveries are unknown. The solids were not soluble in the titration system.

The samples obtained at approximately 100 percent stoichiometric oxygen contained large quantities of water. These were dried before analysis by evacuating at room temperature in a dessicator charged with Drierite until a constant weight was obtained. The liquid samples were then analyzed routinely although limited sample sizes decreased the precision of some analyses.

The average residence time for these experiments was 6.6 ± 1.7 sec. Average substoichiometric oxygen concentrations were 6.6, 20.4, and 73.0 percent at the three levels of oxygen used. However, the range at each level was quite large. Fuel vapor concentrations averaged 1.43 ± 0.33 volume percent.

Since the products at 1100 C were entirely solids and gases, this was an upper temperature limit for these experiments. At the lower limit of 500 C, relatively little chemical reaction was found to occur at the residence times used. At approximately 100 percent of stoichiometric oxygen required for formation of CO₂ and H₂O small amounts of organic products survived but sample sizes were limited.

(a) MD-4 - molecular formula assumed = C₁₃H₁₆

$$\text{Stoichiometric } \left(\frac{\text{Fuel, moles}}{\text{O}_2, \text{ moles}} \right) = .006$$

$$\text{Stoichiometric oxygen} = 17 \text{ moles O}_2$$

Summary of Tasks 2 and 3 Reaction Conditions

Table 14 is a summary of reaction conditions for the Tasks 2 and 3 experiments and Table 15 is a summary of product recoveries and mass balances. These include the weight of fuel fed, the weight of condensed liquid products, the weight of solids deposited on the reactor tube (based on collected weights of CO₂ resulting from the carbon burnoff), the weight of gas condensed and revolatilized (based on the assumption that all of the gas is methane and the PVT relationship for the vapor collection system), and the weight of uncondensed gases (based on the volume of gas fed to the system and periodic analyses of the noncondensed gases by gas chromatography). The gas chromatographic analyses are also shown.

For some experiments, Dräger tubes were used to obtain approximate concentrations of HCN, NH₃, and NO in the condensed gases.

Mass balances (for the seven completely analyzed experiments) averaged 96.4 percent.

Oxygen conversions were also calculated for the pyrolysis-oxidation experiments based on the level of oxygen remaining in the uncondensed gas stream.

Average total gas, liquid, and solid recoveries are shown in Table 16 on a normalized basis. The data show definite trends. Gas production increased with increasing temperature at all oxygen concentrations. Solids formation also increased with increasing temperature. It was assumed that there were no solids left on the tube at 100 percent stoichiometric oxygen. Liquid production declined with increasing temperature at all oxygen concentrations.

Solids formation decreased with increasing oxygen concentration at 700, 900, and 1100 C. At 500 C no solids were formed. Liquid product formation decreased and gaseous product formation increased with increasing oxygen concentration at all temperatures. The overall trends are as expected.

Summary of Liquid Product Properties

Table 17 summarizes the molecular weights, elemental analyses, and nitrogen-type analyses for the condensed products. The molecular weights obtained by GC are considered to be more accurate.

TABLE 14. OXIDATIVE-PYROLYSIS REACTION CONDITIONS

Run No.	Fuel	Vaporizer/Reactor Temp., C	Total Gas Flow, l/min	Fuel Flow, ml/min	O ₂ Conc., % (GC)	Fuel ⁽¹⁾ Vapor Conc., %	Residence Time, sec	Stoic. O ₂ , ⁽²⁾ %	Fuel Equiv. Ratio, ⁽³⁾ ϕ
21	MD-2	265/502	3.9	0.32	0	1.23	7.2	---	---
18	MD-2	247/699	3.1	0.34	0	1.48	7.2	---	---
22	MD-2	252/896	2.6	0.33	0	1.87	7.1	---	---
25	MD-3	303/505	3.9	0.47	0	1.62	7.2	---	---
24	MD-3	243/698	3.1	0.39	0	1.69	7.2	---	---
23	MD-3	288/896	2.6	0.33	0	1.70	7.1	---	---
60-28	MD-4	344/493	3.9	0.33	0	1.04	7.3	---	---
58-24	MD-4	/(700)	3.4	0.32	0	1.15	6.6	---	---
19	MD-4	343/898	2.6	0.33	0	1.55	7.1	---	---
32	MD-4	332/1104	2.2	0.35	0	1.99	7.1	---	---
17	HD-2	389/500	3.9	0.37	0	1.08	7.2	---	---
16	HD-2	404/699	3.1	0.35	0	1.28	7.2	---	---
14	HD-2	399/905	2.6	0.33	0	1.44	7.1	---	---
26	MD-4	293/513	4.26	(0.33)	1.6	0.98	6.5	9.5	11
27	MD-4	293/704	3.32	0.31	1.4	1.18	6.7	6.9	14
28	MD-4	347/897	2.82	0.34	1.5	1.51	6.6	5.7	18
34	MD-4	371/1066	1.92	0.31	1.5	2.02	8.4	4.3	23
31	MD-4	357/513	3.92	0.41	5.0	1.32	7.1	22.0	4.5
30	MD-4	338/710	3.31	0.30	4.6	1.14	6.7	23.5	4.2
29	MD-4	343/899	3.25	0.32	4.9	1.24	5.7	22.9	4.4
35	MD-4	349/1096	2.19	0.34	4.4	1.94	7.2	13.1	7.6
39	MD-4	(300)/515	3.80	0.32	15.5	1.06	7.3	84.8	1.2
38	MD-4	329/704	3.80	0.25	15.6	0.83	5.9	109.	.91
40	MD-4	352/899	2.80	0.35	15.2	1.57	6.6	56.0	1.8
36	MD-4	343/1096	2.20	0.33	14.1	1.88	7.2	43.3	2.3

(1) MD-4, molecular formula assumed = C₁₃H₁₆, MW = 172, density = 0.98 g/ml.

(2) Stoichiometric Oxygen for MD-4 = 17 moles O₂/mole.

(3) Fuel equivalence ratio,
$$= \frac{\text{Fuel/Air, actual}}{\text{Fuel/Air, stoichiometric}} = \frac{100}{\text{stoichiometric oxygen}}$$

TABLE 15. PYROLYSIS AND OXIDATIVE PYROLYSIS PRODUCT RECOVERIES AND BALANCES

Run No.	Fuel/ Temp., C	Wt. Fed, g	Wt. Gas Trapped, g Methane	Wt. Carbon Deposition, g	Wt. Liquids Trapped, g	Measured Mass Balance, Out/In %	Noncondensed Gases, g	% O ₂ Conversion	Noncondensable Gas Concentrations, vol. %			Condensed Nitrogen Gases, ppm		
									CO ₂	CH ₄	CO	HCN	NH ₃	NO
21	MD-2/500	21.41	0.89	0.0	20.24	98.6	NM	--	NM	NM	NM	NM	NM	NM
18	/700	25.85	1.13	0.0	19.41	79.5	NM	--	NM	NM	NM	NM	NM	NM
22	/900	21.34	0.96	2.35	11.38	68.8	NM	--	NM	NM	NM	NM	NM	NM
25	MD-3/500	20.59	1.11	0.0	19.29	99.1	1.30	--	NM	NM	NM	NM	NM	NM
24	/700	19.7	0.64	1.28	11.51	68.1	NM	--	NM	NM	NM	NM	NM	NM
23	/900	32.56	1.16	4.77	18.42	74.5	NM	--	NM	NM	NM	NM	NM	NM
60-28	MD-4/500	10.47	0.01	NM	8.49	81.2	NM	--	NM	NM	NM	NM	NM	NM
58-24	/700	12.72	NM	NM	9.68	76.1	NM	--	NM	NM	NM	NM	NM	NM
19	/900	29.93	0.87	5.4	16.17	75.0	NM	--	NM	NM	NM	NM	NM	NM
32	/1100	21.89	0.85	5.81	8.72	70.3	NM	--	NM	NM	NM	>150	4000	0
17	MD-2/500	13.66	0.02	0.0	9.11	66.8	NM	--	NM	NM	NM	NM	NM	NM
16	/700	25.95	0.86	NM	20.68	83.0	NM	--	NM	NM	NM	NM	NM	NM
14	/900	22.26	1.13	NM	10.54	52.4	NM	--	NM	NM	NM	NM	NM	NM
26	MD-4/500	30.45	0.2	0.0	29.44	100.6	1.04	25	NM	NM	NM	NM	NM	NM
27	/700	23.22	1.28	0.76	19.1	108.3	3.94	100	1.34	0.63	0.98	>150	~150	ND
28	/900	29.24	1.26	4.05	17.19	97.4	5.96	100	1.24	1.21	1.96	150	7000	ND
34	/1100	14.05	0.2	NM	4.59	56.4	3.15	97	2.59	0.60	3.74	NM	NM	NM
31	MD-4/500	22.73	0.6	0.0	15.15	69.8	0.14	Low	0	0	0.31	NM	NM	NM
30	/700	~14.1	NM	NM	10.16	NM	NM	NM	ND	Tr	2.4	Pr	Pr	Tr
29	/900	18.84	1.28	1.88	9.97	94.2	4.62	100	0.72	1.16	2.8	>150	~7000	NM
35	/1100	18.7	0.47	3.87	6.70	85.5	4.95	97	2.06	0.65	5.45	NM	NM	NM
39	MD-4/500	24.81	1.43	0.0	20.92	90.0	0	33	ND	ND	ND	NM	NM	NM
38	/700	28.29	0.19	NM	36.83	181.6	14.33	100	ND	0.67	5.93	NM	NM	NM
40	/900	28.44	0.0	NM	13.65	96.2	13.7	99.5	0.75	0.67	9.82	NM	NM	NM
36	/1100	16.97	1.1	NM	4.98	87.3	8.73	99	1.31	0.44	12.73	NM	NM	NM

NM - Not measured

ND - None detected

Tr - Trace

Pr - Present

S - Solids trapped

TABLE 16. NORMALIZED AVERAGE RECOVERIES OF SOLIDS, LIQUIDS AND GASES FROM
PYROLYSIS AND OXIDATIVE-PYROLYSIS OF SRC II DISTILLATE FRACTIONS

Av. Percent of Stoich. Oxygen Temp, °C	0%			7%			20%			73%		
	Gas	Liquid	Solid	Gas	Liquid	Solid	Gas	Liquid	Solid	Gas	Liquid	Solid
500	3.2	96.8	0.0	4.0	96.0	0.0	4.6	95.4	0.0	6.3	93.7	0.0
700	4.4	87.7	7.9	20.8	76.2	3.0	(24.6) ⁽¹⁾	72.1	(3.4) ⁽¹⁾	28.3	71.7	(0.0) ⁽²⁾
900	4.8	74.7	20.5	25.4	60.4	14.5	33.2	56.2	10.6	50.1	49.9	(0.0) ⁽²⁾
1100	5.5	0.0	94.5 ⁽³⁾	23.8	0.0	(76.2) ^(3,4)	33.9	0.0	66.1 ⁽³⁾	66.3	0.0	(33.7) ^(2,3)

(1) Based on averages of data at conditions of higher and lower oxygen concentrations.

(2) Based on assumption that no solids remained in tube at high oxygen levels.

(3) Solids caught in condenser traps combined with solids left on reactor wall.

(4) By difference.

TABLE 17. MOLECULAR WEIGHTS AND ELEMENTAL ANALYSES OF PYROLYSIS AND PYROLYSIS-OXIDATION PRODUCTS

Run No.	Molecular Weight, g/mole		Elemental Analyses, %						
	VPO	GC	C	H	S	N (Diff.)	Total N	Basic N	Nonbasic N (Diff.)
21	117	139	82.7	9.6	0.05	7.08	0.59	0.36	0.23
18	138	137	84.7	8.0	0.04	11.8	0.67	0.37	0.30
22	(423)	167	84.2	5.6	0.12	10.1	0.37	0.15	0.22
25	130	129	80.5	8.8	0.07	10.6	0.77	0.48	0.29
24	143	147	84.0	7.1	0.07	8.8	1.01	0.54	0.47
23	(347)	136	87.5	5.4	0.21	6.9	0.92	0.24	0.68
60-28	211	176	86.2	9.1	0.09	2.3	1.04	0.54	0.50
58-24	200	167	88.9	6.9	0.09	1.6	1.25	0.62	0.63
19	94	153	81.0	5.0	0.21	12.5	0.95	0.23	0.72
32	NM(a)	NM(a)	97.8	0.9	NM(b)	1.0	0.31	0.03(c)	0.28(c)
17	213	197	89.2	8.4	0.04	1.3	0.63	0.29	0.34
16	203	172	87.7	6.5	0.08	3.8	0.73	0.33	0.40
14	285	223	77.0	3.8	0.41	25.8	0.65	0.08	0.57
26	172	179	87.6	8.9	0.10	2.3	1.05	0.52	0.53
27	170	165	85.0	7.1	0.13	6.4	1.20	0.47	0.73
28	(87)	178	79.4	4.6	0.46	14.6	0.95	0.28	0.67
34	NM(a)	NM(a)	98.9	0.7	NM(b)	0.1	0.28	0.01(c)	0.27(c)
31	199	176	87.0	8.6	0.15	3.0	1.00	0.44	0.56
30	240	166	87.2	6.9	0.17	4.4	0.97	0.37	0.60
29	(349)	182	84.8	6.5	0.32	7.4	0.83	0.29	0.54
35	NM(a)	NM(a)	95.	1.0	NM(b)	3.7	0.28	0.02(c)	0.26(c)
39	NM(b)	141	77.8	6.5	NM(b)	14.6	1.12	0.49	0.63
38	NM(b)	129	83.	5.0	NM(b)	9.3	2.72	0.92	1.80
40	NM(b)	241	57.2	3.9	NM(b)	38.3	0.56	0.11	0.45
36	NM(b)	NM(a)	96.	1.3	NM(b)	2.5	0.29	0.10(c)	0.19(c)

(a) Not measurable due to solid sample.

(b) Not measured.

(c) Value in doubt - solid sample.

Basic nitrogen analyses for the 1100 C experiments were based on the perchloric acid/acetic acid titration method on the solid samples obtained in the condensers, but the accuracy of these results is questionable because the samples were not soluble in the titration solvent.

In Table 18 the hydrogen distributions measured by H^1 NMR are listed. The structural parameters obtained by the Brown-Ladner correlations and molecular formulas derived from the elemental analyses and GC molecular weights are listed in Table 17. Only aromaticity, obtained by C^{13} NMR, could be obtained for the solid samples obtained in the condensate traps at 1100 C.

The amounts of representative unsubstituted aromatics in the liquid products, as measured by gas chromatography, are listed in Table 19. These results are not corrected for response factors and are percentages of total liquid product peak areas. These analyses also could not be done on the solids obtained at 1100 C.

Aromaticity. Aromaticity, the ratio of aromatic carbons to total carbon, increases from an average of 0.53 in the starting material and 0.56 at 500 C to 0.83 at 700 C and 0.95 at 900 C, as shown in Figure 21. The number of aromatic rings increases proportionately. There is almost uniform behavior between the different boiling point fractions. Aromatization of the ring systems is an important reaction during pyrolysis.

Figure 22 shows the relationship between aromaticity of the unburned products at each temperature and the stoichiometric amount of oxygen available during oxidative pyrolysis. Aromaticity does not appear to increase with increasing concentration of oxygen at any temperature.

The number of aromatic ring substituents and the average substituent length decreases with increasing pyrolysis temperature as shown in Figures 23 and 24, respectively. These numbers include aliphatic rings attached to aromatic rings at two points, such as in tetralin-type molecules. The number of substituents decreases from approximately three per ring in the starting material and at 500 C to approximately one per ring at 900 C. The aliphatic substituents are very short, ranging from an average of less than two carbon atoms at low temperature to less than one carbon atom per substituent at 900 C. (Phenolic substituents are counted as O-carbon substituents.)

TABLE 18. HYDROGEN DISTRIBUTION, STRUCTURAL PARAMETERS AND MOLECULAR FORMULAS FOR PYROLYSIS AND OXIDATIVE PYROLYSIS PRODUCTS OF SRC II DISTILLATION FRACTIONS

Run No.	21	18	22	25	24	23	60-28	58-24	19	17	16	14	32 ^(b)	26	27	28	34 ^(b)	31	30	29	35 ^(b)	39	38	40	36 ^(b)
Hydrogen Distribution, %																									
Aliphatic H	39	3	5	32	2	11	32	8	23	32	13	19	NM	34	4	16	NM	27	1	3	NM	25	5	51	NM
α to Aromatic H	31	32	0	38	32	0	44	28	0	33	21	0	NM	40	26	4	NM	39	19	0	NM	47	31	1	NM
Aromatic H	24	65	95	26	61	89	23	64	77	35	66	81	NM	25	69	80	NM	31	80	97	NM	28	66	46	NM
Phenolic H	5	0	0	4	5	0	1	0	0	0	0	0	NM	2	0	0	NM	3	0	0	NM	0	0	4	NM
Structural Parameters																									
Aromaticity, f _a	0.51	0.80	0.98	0.54	0.83	0.96	0.52	0.83	0.91	0.63	0.85	0.94	0.97	0.55	0.81	0.93	1.0	0.61	0.91	0.99	NM	0.64	0.87	0.79	1.0
Aro. Edge/Total aro., H _{aro} /C _{aro}	1.	1.	0.77	1.	0.94	0.69	1.	0.87	0.63	0.92	0.80	0.56	NM	1.	0.97	0.69	NM	1.	0.94	0.90	NM	0.81	0.67	0.46	NM
Substituted edge/total edge, σ	0.51	0.32	0.12	0.59	0.31	0.09	0.52	0.31	0.20	0.34	0.19	0.54	NM	0.48	0.23	0.27	NM	0.43	0.15	0.80	NM	0.73	0.34		NM
Substituted ring carbons, R _s	2.5	2.3	1.1	2.8	2.5	0.6	3.4	2.8	1.2	2.9	1.6	3.7	NM	3.3	2.2	2.0	NM	3.8	1.6	0.9	NM	3.5	1.8		NM
Carbon atoms/substituent, n	1.9	0.8	0.2	1.4	0.7	0.7	1.8	0.8	0.8	1.9	1.2	0.2	NM	1.9	1.2	5.	NM	1.7	1.1		NM	1.5	1.2		NM
Total aromatic carbons, C _a	4.9	7.2	11.5	4.7	8.5	9.5	6.5	10.3	9.3	9.2	10.7	12.2	NM	6.9	9.8	12.0	NM	8.8	11.0	12.7	NM	5.9	7.8	9.1	NM
No aromatic rings, R _a	1.	1.	2.3	1.	1.3	2.5	1.	1.7	2.7	1.4	2.1	3.7	NM	1.	1.2	2.7	NM	1.	1.3	1.6	NM	1.6	2.3	3.5	NM
Molecular Formula ^(a)																									
C	9.6	9.7	11.7	8.7	10.3	9.9	12.6	12.4	10.3	14.6	12.6	14.3	NM	13.1	11.7	11.8	NM	12.8	12.1	12.9	NM	9.1	8.9	11.5	NM
H	13.6	11.0	9.4	11.4	10.4	7.3	16.0	11.5	7.7	16.5	11.2	8.5	NM	15.9	11.7	8.2	NM	15.1	11.5	11.8	NM	9.2	6.5	9.4	NM
N	0.06	0.07	0.04	0.07	0.11	0.09	0.13	0.15	0.10	0.04	0.09	0.10	NM	0.13	0.14	0.12	NM	0.13	0.12	0.11	NM	0.11	0.25	0.10	NM
S	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.03	NM	0.01	0.01	0.00	NM	0.01	0.01	0.02	NM	NM	NM	NM	NM
O	0.6	1.0	1.1	0.9	0.8	0.6	0.3	0.2	1.2	0.2	0.6	3.6	NM	0.3	0.7	1.7	NM	0.3	0.3	0.2	NM	1.3	0.7	5.8	NM

(a) Based on GC molecular weights.

(b) Solid.

TABLE 19. UNSUBSTITUTED AROMATICS IN PRODUCTS OF PYROLYSIS
AND OXIDATIVE-PYROLYSIS OF SRC II DISTILLATION
FRACTIONS (PERCENTAGES)

Run No.	Benzene	Naphthalene	Phenanthrene	Pyrene
21	0.0	3.4	1.2	0.0
18	6.1	6.6	0.4	0.1
22	26.9	19.8	6.8	1.5
25	0.0	3.7	0.0	0.0
24	4.1	16.7	1.0	0.2
23	52.9	18.2	2.6	0.8
60-28	0.0	0.3	1.6	0.0
58-24	1.0	7.8	3.5	0.3
19	25.2	31.8	10.3	2.6
32	NM(a)	NM	NM	NM
17	0.0	0.0	31.5	0.5
16	0.5	1.3	20.8	1.3
14	4.3	18.4	43.7	5.6
26	0.0	1.1	2.7	0.1
27	2.9	9.1	3.8	0.4
28	11.5	30.9	8.9	4.0
34	NM(a)	NM	NM	NM
31	0.0	1.4	2.1	0.0
30	4.5	12.3	4.5	0.5
29	5.4	27.8	7.1	2.5
35	NM(a)	NM	NM	NM
39	15.0	0.0	0.0	0.0
38	10.0	0.0	3.8	0.0
40	0.0	0.0	0.0	0.0
36	NM(a)	NM	NM	NM

(a) Solid sample.

FIGURE 21. AROMATICITY OF LIQUID PRODUCTS
VERSUS PYROLYSIS TEMPERATURE

FIGURE 22. AROMATICITY VERSUS FRACTION OF STOICHIOMETRIC OXYGEN

FIGURE 23. NUMBER OF AROMATIC RING SUBSTITUENTS (R_s) VERSUS PYROLYSIS TEMPERATURE

FIGURE 24. SUBSTITUENT LENGTH (n) VERSUS PYROLYSIS TEMPERATURE

Molecular Weight. Aromatization, involving C-H bond breakage, rather than removal of aliphatic substituents, which involves aromatic carbon-aliphatic carbon bond breakage is suggested to explain the observations because the weight per molecule remains approximately constant with increasing temperature, as shown in Figure 25. The molecular weight measurements were determined by summation of the peak areas in the simulated distillation by gas chromatography analysis. Molecular weight could not be extended to 1100 C because the products formed at 1100 C were solids. However, the solids may be assumed to represent a significant increase in molecular weight above the 150-170 g/mole range obtained from 500-900 C.

The relationship between molecular weight and fraction of stoichiometric oxygen is shown in Figure 26. At 500 and 700 C molecular weight declines, but at 900 C the molecular weight increases with increasing fraction of stoichiometric oxygen. At 900 C oxygen appears to cause a relative increase in ring condensation. No data could be obtained at 1100 C.

Elemental Composition. The weight percent of carbon is roughly constant from 500 to 900 C but jumps significantly at 1100 C, as shown in Figure 27. The 1100 C sample was collected in the condensers and was probably obtained in approximately the same residence time as the samples obtained at lower temperatures. Hydrogen drops to less than one weight percent and oxygen (by difference) also drops to about one weight percent at 1100 C. Compounds containing oxygen and hydrogen are destroyed between 900 and 1100 C at the residence times used in these experiments (about 7 sec). A highly carbonaceous material, presumably with a graphitic structure, is obtained at 1100 C. There appears to be little difference in the carbonaceous products obtained at 1100 C from the different SRC II distillation fractions.

Up to 900 C there is a significant increase in the concentration of other elements. Direct oxygen determinations were not made, but this material is assumed to be primarily oxygen since the liquid products are nearly ash and sulfur free and the nitrogen content did not change significantly. The oxygen increase must result from preferential retention in the liquid products of the oxygen in the SRC II distillation cuts. There is no other source of oxygen in the system. This is not surprising since the nonliquid products consist of

FIGURE 25. MOLECULAR WEIGHT AND ELEMENTAL COMPOSITION VERSUS PYROLYSIS TEMPERATURE

FIGURE 26. MOLECULAR WEIGHT VERSUS FRACTION OF STOICHIOMETRIC OXYGEN

FIGURE 27. CARBON, HYDROGEN AND OXYGEN CONTENT VERSUS PYROLYSIS TEMPERATURE

soot (carbon) and light gases (primarily methane). Most or all of the oxygen in the SRC II distillation cuts is phenolic. The phenolic substituent apparently inhibits soot formation, possibly by quenching free radicals formed thermally during pyrolysis.

The hydrogen distribution is shown in more detail versus temperature in Figure 28. The average number of hydrogen atoms per molecule decreases and aliphatic hydrogen decreases to no more than one per molecule at 900 C. There is an increase in the number of aromatic hydrogens per molecule.

The changes in elemental composition of the partially pyrolyzed and oxidized fuel with increasing fraction of stoichiometric oxygen are shown in Figures 29-31. Carbon and hydrogen decline slightly while oxygen content increases. This is apparently due to oxygen incorporation in the molecules by oxidation. A mechanism such as the one described by Santoro and Glassman, in which dihydroxy benzenes are intermediates, is in agreement with this observation.(22)

Nitrogen Concentration. As shown in Figure 32, nitrogen is unchanged from room temperature to 500 C, is preferentially retained in the unpyrolyzed liquids between 500 and 700 C and is destroyed at an increasing rate from 700 to 1100 C. There is a conversion of basic to nonbasic nitrogen below 500 C and basic nitrogen appears to be less stable than nonbasic nitrogen at all temperatures. This is a surprising result when the simplistic view is taken that basic nitrogen is primarily pyridine and quinoline-type compounds, which are relatively stable, and nonbasic nitrogen is pyrrole and similar compounds which are generally thought to be less stable. These assumptions are apparently not correct and this is an area where more research is needed.

Figure 33 indicates that nitrogen distribution remains approximately constant as the level of stoichiometric oxygen is increased.

Unsubstituted Aromatics. The data indicate that the liquid product evolves during pyrolysis until it consists primarily of unsubstituted aromatics such as benzene, naphthalene, phenanthrene, and pyrene and phenolics. Of course, aromatization is not the only mechanism occurring since liquid products with both higher and lower molecular weights than the starting

FIGURE 28. HYDROGEN DISTRIBUTION VERSUS PYROLYSIS TEMPERATURE..

FIGURE 29. CARBON COMPOSITION VERSUS FRACTION OF STOICHIOMETRIC OXYGEN

FIGURE 30. HYDROGEN COMPOSITION VERSUS FRACTION OF STOICHIOMETRIC OXYGEN

FIGURE 31. HYDROGEN COMPOSITION VERSUS FRACTION OF STOICHIOMETRIC OXYGEN

FIGURE 32. NITROGEN DISTRIBUTION VERSUS PYROLYSIS TEMPERATURE

FIGURE 33. NITROGEN DISTRIBUTION VERSUS FRACTION OF STOICHIOMETRIC OXYGEN

liquids, as well as gases and carbon, are formed. However, substantial amounts of the unsubstituted aromatics are formed. At 900 C, more than 50 percent of each liquid product is unsubstituted aromatics. The amounts of one, two, and three ring molecules (i.e., benzene, naphthalene, and phenanthrene) vary with the molecular weight of the starting material. For example, the liquid product of MD-3 at 900 C is more than 50 percent benzene while naphthalene is more than 30 percent of the liquid product from MD-4 at 900 C.

Figure 34 shows the concentrations of unsubstituted aromatics in the recovered liquid as a function of pyrolysis temperature. The concentration of each unsubstituted aromatic ring compound increased from 700 to 900 C. At 1100 C no liquid products were obtained. Apparently these unsubstituted aromatics are graphitic, are more stable than substituted aromatics, and are carbon precursors and, therefore, probably soot precursors in the combustion of coal-derived synthetic liquid fuels.

Figure 35 shows the amounts of unsubstituted aromatics in the liquid products versus fraction of stoichiometric oxygen present. At the highest levels of stoichiometric oxygen, the amounts of unsubstituted aromatics decreased, apparently due to the formation of molecules with oxygen substituted on the aromatic rings.

Tasks 2 and 3 Conclusions

Conclusions from Tasks 2 and 3 can be summarized as follows:

- The reactions of the distillation fractions of varying molecular weight under the pyrolysis and oxidative-pyrolysis conditions studied are similar.
- The principal reaction due to temperature alone is aromatization of the hydroaromatics which decreases the number and length of aliphatic side chains on aromatic rings.
- Unsubstituted aromatics are a principal intermediate in the pyrolysis of coal-derived synthetic liquid fuels.
- Nonbasic nitrogen is more stable than basic nitrogen. Total nitrogen content of the partially pyrolyzed and oxidized fuel increases up to 700 C and then decreases from 700 to 1100 C.

FIGURE 34. PERCENT OF UNSUBSTITUTED AROMATICS VERSUS PYROLYSIS TEMPERATURE

FIGURE 35. CONCENTRATION OF UNSUBSTITUTED AROMATICS IN THE LIQUID PRODUCT VERSUS FRACTION OF STOICHIOMETRIC OXYGEN

- Carbon and hydrogen contents decline as oxidation increases oxygen content. Aromaticity remains nearly constant. The destruction of unsubstituted aromatics is increased by oxidation, presumably by the formation of oxygen substituted aromatics.
- The nitrogen content and basic/nonbasic distribution are nearly unchanged in the presence of increasing amounts of oxygen.
- The most likely survivors of fuel-rich, first-stage pyrolysis are unsubstituted and oxygen substituted aromatics and nonbasic nitrogen compounds. These are the precursors to soot and NO_x formation during oxygen-rich, second-stage combustion.

Application of Results to Staged Combustion

The conditions used in the Tasks 2 and 3 studies were designed to allow the collection of significant amounts of partially pyrolyzed and oxidized fuel for chemical analyses. Nevertheless, they can be related to the fuel-rich stage of staged combustion and the results can be used in the selection of conditions and experiments needed to study NO_x and soot formation under actual staged combustion in Task 4.

The heatup rate used in these studies is some 10-100 times slower than typical combustion heatup rates. The maximum temperature was within 100 C of the maximum temperature expected in fuel-rich combustion (1200 C) and the maximum levels of oxygen used were similar to those expected in fuel-rich combustion ($\phi = 1.0 - 1.4$). Residence times were much longer than those expected in first-stage combustion (1 sec). The types of reactions which have been observed with increasing temperature and oxygen concentration are summarized in Figure 36.

Based on the results from Tasks 2 and 3, the following are suggested to achieve less soot and NO_x formation during staged combustion.

- Preheat in the presence of oxygen to suppress the conversion of unstable basic N to stable nonbasic N, which is more likely to survive to oxidizing conditions where NO_x can be formed.
- Operate at low temperatures where aromatization to unsubstituted aromatics, which are presumed to be soot precursors, is slower.
- Operate at higher oxygen concentrations where the destruction of unsubstituted aromatics by oxidation predominates.

FIGURE 36. CHEMISTRY OF UNBURNED COAL DERIVED LIQUID

- Add oxygen at low temperatures to react with aliphatic hydrogen before it is lost in subsequent pyrolysis. This loss of hydrogen negates the value of a high H/C ratio in the starting fuel. Early addition of oxygen could make the partially pyrolyzed and oxidized fuel more reactive and less likely to soot.

Task 4 - Staged Combustion Studies

Objective

The objective of this task was to examine the burning characteristics of SRC II as a function of residence time, temperature, and equivalence ratio in a two-stage combustion process, and to establish optimum combustion conditions for minimizing the production of soot and NO_x .

Staged Combustion Apparatus

Battelle's small laboratory scale furnace was used for this study. The combustor is a modification of the Babcock and Wilcox Laboratory Ashing Furnace⁽²³⁾ and is designed to fire both solid and liquid fuels. A schematic of the staged combustor is shown in Figure 37.

The combustor consists of an inner combustion chamber separated by a silicon carbide lining from a surrounding annular burner. The annular burner helps to maintain a constant temperature for the inner furnace. Combustion products from a natural gas flame fired into the bottom of the annular combustor pass through the gap and exit at the top of the furnace. The annular furnace is designed for a maximum firing rate of 300,000 Btu/hr. It is lined with Cerachrome insulation to minimize heat loss.

The inner combustion chamber has a diameter of 4 in. and a length of 52 in. Coal and fuel oil can be fired at maximum rates of 4 lb/hr or 0.5 gal/hr (~50,000 Btu/hr). Residence time for the first stage of the combustor can be from 0.5 to 1.5 sec and from 1 to over 2 sec, depending on load, for the overall combustor. The combustor is equipped with a sighting port. Air for the second stage is introduced by means of an inconel tube bent in the

FIGURE 37. SCHEMATIC OF THE TWO-STAGE COMBUSTOR

shape of an L and inserted into and along the wall of the furnace (not shown in Figure 37). Holes drilled on both sides of the elbow enable air to enter the furnace in a plane perpendicular to the direction of flow.

Combustion air entering the furnace can be preheated if necessary. Exhaust from the annular burner is used as the heating medium for the swirl air before being released to the stack.

The exhaust system from the main burner consists of a bare metal pipe section, a water-cooled section and an afterburner. The bare metal pipe is installed at a 60° angle to the main burner in order to minimize ash deposition along the tube wall and to allow insertion of the staged air and sampling probe(s). The afterburner is used to oxidize any unburned SRC II in the combustion products.

Nozzle Assembly. The nozzle assembly is shown in detail in Figure 38. A Sonicore nozzle, Model 052H-A is used. Air flows through the center to the top of the nozzle and atomizes the fuel which passes through the outer annulus of the nozzle. The jet coming out from the nozzle undergoes further atomization when it impinges on the resonator cup. Surrounding the Sonicore nozzle and its holder is an outer annulus. Combustion air enters this annulus and passes through a flow straightener before exiting through eight 45° swirl vanes. Preliminary testing of the nozzle system with kerosene showed that a 2 in. diameter, 3 in. long, blue flame could be achieved.

Liquid Fuel Feed System. The piping diagram for the liquid fuel feed system is given in Figure 39. Due to safety concerns, the fuel feed system was isolated from the remaining apparatus by confining it inside a well ventilated enclosure. Details of this enclosure are described below.

The fuel feed system allows SRC II to be pumped from the 55-gal drum in which it was shipped to a 5-gal can on the balance, pumped to the combustor, and rinsed from the lines with No. 2 fuel, without any manual handling. A variable speed pump was used to smooth the fuel flow by minimizing the pressure and recycle rate in the fuel feed system. The burner can also be brought to temperature by burning No. 2 fuel oil. The feed line, up to within 6 in. of the burner nozzle, can then be filled with SRC II before burning so that

FIGURE 38. NOZZLE ASSEMBLY

FIGURE 39. FUEL FEED SYSTEM

fuel changeover can be accomplished quickly. All of the experiments were completed without exposure of operating personnel to fumes or liquid spills.

A rotameter was calibrated for each fuel and used to measure the fuel feed rate. An electronic balance, capable of measuring ± 5 grams, was used to measure cumulative fuel feed and to obtain average fuel feed rates.

Three orifice plates regulated the flows of atomizing air, first-stage combustion air and second-stage combustion air. One of the orifice plates was calibrated using a wet test meter. The calibration agreed satisfactorily with the air flow calculated on the basis of the pressure drop across the orifice plate.

Ventilated Enclosure. The two-stage combustor is located in a laboratory which is open to various other working areas. For this reason, a ventilated enclosure was built to store fuel and any contaminated waste, and also to isolate the pumping system from the rest of the combustion apparatus. Contaminated solid waste such as paper towels, gloves and clothing, and liquid waste solvent were disposed of in separate 5-gal sealable metal drums before storing in this enclosure. Any maintenance on the pump assembly was confined within this area. A negative pressure was maintained in this enclosure at all times, and controlling and metering equipment were mounted on one of the walls outside the enclosure.

Probe Design, Sampling and Analysis

Three types of samples were taken using three separate probes. They were (1) solid and liquid samples, (2) HCN and NH_3 , and (3) combustion gases (CO , CO_2 , and O_2) and product gases (NO and unburned gaseous hydrocarbons). The probe design, sampling train and analytical method for each are discussed in detail below.

Solid and Liquid Product Probe and Sampling System. A water-quench probe was used to collect particulate and liquid samples (Figure 40). A stream of water flowed down the interior of a water-cooled probe. The quench water flow rate was controlled by varying the back pressure on the cooling water. The solid samples were collected on a 47 mm diameter Millipore filter.

FIGURE 40. WATER QUENCHED PROBE FOR PARTICULATE SAMPLING

A 5 μm pore size was used so that water would pass through readily. The filtered quench water was then collected in a large glass vessel and saved for extraction of organic liquids. The rest of the sampling system consisted of ice/water traps, a Drierite filter, a vacuum pump to control the gas flow rate, a carbon filter and a gas meter to measure the amount of gas which passed through the system (Figure 41).

The particulate samples were extracted with methylene chloride to remove soluble organics, dried and analyzed for carbon, hydrogen and nitrogen using a microcombustion analyzer. The typical weight of solid collected was 10-20 mg in 30-60 minutes. The quench water was extracted with methylene chloride and the extract was analyzed by gas chromatography to obtain boiling point distribution, nitrogen distribution, and molecular weight. Only a few milligrams of liquid samples were collected.

It has been suggested that the quench water used in the particulate sampling probe can be used to analyze for HCN and NH_3 using specific ion electrode techniques. Comparison of the results of analyses for both HCN and NH_3 from the quench water and the HCN/ NH_3 probe sampling system described later indicated that this does not appear to be a good method. The pH of the quench water was 5.4 (both before and after passing through the system). Under these conditions the quench water was shown to contain much less cyanide per volume of gas passed through the probe and as much or more ammonia than was obtained by the HCN- NH_3 probe and sampling system. Thus, a separate probe and sampling system were used for hydrogen cyanide and ammonia.

Hydrogen Cyanide and Ammonia Probe and Sampling System. The hydrogen cyanide-ammonia (HCN- NH_3) probe was air cooled to keep the gas temperature above the condensation temperature of water ($>100^\circ\text{C}$) to avoid the loss of either cyanide or ammonia by absorption in liquid water before the impingers (Figure 42). The gas passed through a heated glass thimble filter and then was divided into three streams (Figure 43). One stream was vented through a vacuum pump, ice/water condenser and carbon filter. The purpose of this stream was to keep the gas flow through the probe high enough to avoid water condensation. The remaining gas flowed to the cyanide and ammonia impingers in parallel and then Drierite traps, vacuum pumps, which controlled the flow

FIGURE 41. PARTICULATE AND LIQUID PRODUCT PROBE AND SAMPLING SYSTEM

FIGURE 42. COOLED SHEATH PROBE FOR GAS SAMPLING

FIGURE 43. HYDROGEN CYANIDE AND AMMONIA PROBE AND SAMPLING SYSTEM

rates, carbon filters and gas meters, which measured the flow rates (Figure 43).

The three cyanide impingers connected in series were each filled with 150 ml of 0.1N NaOH and 2 g/liter of CdCO_3 (to remove S^{2-} which interferes with the measurement of cyanide ion concentration by the specific ion electrode method). Collection efficiency was not satisfactory. The concentration of cyanide collected in the second and third impingers was not very much lower than the concentration collected in the first impinger. Measured cyanide concentrations in the gas varied from 0 to 1000 ppm, depending on the combustion stoichiometry, and gas flows averaged 2.3 scfh through the impingers. However, the collection efficiency appeared to be independent of both gas flow rate and cyanide concentration, probably due to the fact that HCN is a relatively weak acid and the acid-base reaction by which cyanide is collected is incomplete.

The two ammonia impingers connected in series were each filled with 150 ml of 0.05M H_2SO_4 . The same gas flow rates were used. The ammonia collection efficiency was much higher. Of the total NH_3 collected in the two impingers in series, 96.3 percent was collected in the first impinger. Ammonia concentrations measured in the combustion gas were much lower, ranging from 0-100 ppm.

The specific ion electrode measurements of CN and NH_3 appeared to be satisfactory. Titration of carefully prepared standards showed accuracies within ± 5 percent for both NH_3 and CN, although these were obtained immediately after reconditioning the electrodes, standardizing, etc.

Instrument Gas Probe and Analysis System. A third, water-cooled probe was used for sampling gases for instrumental analyses. The gases passed through a heated glass thimble and ice-water impingers before the flow was regulated for entry to the various analyzers (Figure 44). After analysis the gases were passed through separate carbon filters and vented. Separate instruments, listed in Table 20, were used to analyze for CO , CO_2 , O_2 , NO , and volatile hydrocarbons. This equipment has been used routinely in previous studies and has been debugged. The results are recorded on a digital data logger along with system temperatures.

FIGURE 44. INSTRUMENT GAS PROBE AND ANALYSIS SYSTEM

TABLE 20. CONTINUOUSLY MONITORED GASES

Species	Method
O ₂	Paramagnetic
CO ₂	NDIR
CO	NDIR
NO	Chemiluminescence
THC	Flame Ionization

Process Monitoring. In addition, the following process parameters were continuously monitored:

- Combustion chamber exit temperature
- Annular exhaust temperature
- Steel skin temperature
- Burner heat temperature
- Fuel weight change.

During the combustion experiments, manometers and pressure gauges were used to monitor the following parameters:

- Atomizing air flow
- Combustion air flow
- Annular burner gas flow
- Annular burner air flow
- Staged air flow.

Staged Combustion Operating Conditions

Fuel Characterization. The elemental analyses obtained for the SRC II supplied by PETC and No. 2 fuel oil were used to calculate the air/fuel ratios required for complete combustion. The results are listed in Table 21. SRC II has a slightly lower heat content and requires slightly less air for complete combustion than No. 2 fuel oil.

These air/fuel ratios were used to set the combustion conditions for the stoichiometries desired in the combustion experiments.

TABLE 21. ELEMENTAL ANALYSES OF
SRCII AND #2 FUEL OIL

Fuel	SRCII ⁽¹⁾	#2 Fuel Oil
Elemental Analyses, wt %		
C	85.8	85.3
H	9.4	11.8
N	0.61	0.29
S	0.28	2.52
O (Diff.)	3.91	
lb air/lb fuel required for complete combustion ($\phi = 1$) ⁽²⁾	13.0	13.8
BTU/lb fuel ⁽³⁾	18,145	19,712

(1) SRCII supplied by PETC.

(2) Calculated using:

$$\text{lb air/lb fuel} = (2.67 \text{ C} + 8 \text{ H} + 1.14 \text{ N} + \text{S} - \text{O}) \times 0.0431$$

where C = wt % carbon,
 H = wt % hydrogen,
 N = wt % nitrogen,
 S = wt % sulfur,
 O = wt % oxygen in fuel.

(3) Calculated using: BTU/lb (HHV) = 146.5 C + 621 (H -

$$\frac{(\text{N} + \text{O} - 1)}{8}) + 40.0 \text{ S.}$$

Agreement Between Calculated and Measured Stoichiometry. Stoichiometry in the system was determined by noting the fuel and air feed rates in effect when no CO and O₂ were present. The system stoichiometry was calculated and compared to the measured stoichiometry. Much effort was spent trying to obtain agreement between the measured and calculated stoichiometries. As shown in Table 22, the measured stoichiometries were 5 to 10 percent higher than the calculated values. Literature values for both SRC II and No. 2 fuel oil show higher stoichiometries than the calculated values based on the analyses and it is possible that part of the discrepancy is a result of inaccurate analyses.

TABLE 22. AGREEMENT BETWEEN CALCULATED AND MEASURED
STOICHIOMETRIES IN THE STAGED COMBUSTOR
(Lb Air/Lb Fuel)

	Calculated	Measured	<u>Measured Calculated</u>
No. 2 Fuel Oil	13.8	14.5	1.05
SRC II	13.0	14.2	1.09

For the combustion experiments, the atomizing air-to fuel weight ratio was 2 to 1, the fuel feed rate was 2 lb/hr and the sampling probes were lowered to approximately 6 in. from the bottom of the combustion zone.

It was noted that placing the sampling probes at the bottom of the combustion zone resulted in an increase in the static combustion zone temperature (the temperature when the annular burner is on, but no fuel is being fed to the combustion zone) from about 800 F to 1800 F. This is apparently due to decreased heat loss through the cooling water and air flows in the probes.

Discussion of Staged Combustion Results

A total of 34 runs were made on the staged combustor. Of the 18 runs made with SRC II supplied by PETC, 8 were good enough to analyze. A summary of the operating conditions and gaseous product concentrations is listed in Table 23 for these runs.

The experimental plan was to study the first, fuel-rich stage of staged combustion by varying the air/fuel ratios so that $\phi = 0.6, 0.7, 0.8, 0.9$ and 1.0 . Duplicate runs were attempted at each equivalence ratio. As a result of failure to collect some data at some points, only the runs shown were usable. Stoichiometry was controlled by changing the fuel feed rate rather than the air feed rates in most cases. Run times varied from 1-3 hours. Total fuel nitrogen (TFN) is the sum of the concentrations of HCN, NH_3 and NO.

Total Fuel Nitrogen. The results for TFN and the nitrogen-containing gases are plotted in Figure 45. TFN appears to go through a minimum near a stoichiometry of $\phi = 0.8$ as a result of a decline in HCN and NH_3 concentrations and an increase in NO concentration with increasing air to fuel ratio. England, et al., have reported exactly the same result for the first stage combustion of a SRC II heavy distillate oil.⁽²⁴⁾ At the minimum they reported NO levels of 200 ppm, HCN concentrations of 100-200 ppm and NH_3 concentrations of 80-120 ppm compared to levels of 180-250 ppm, 20-50 ppm, and 15-30 ppm, respectively, in this work.

Lanier has also reported nitrogen conversions of 25 percent at $\phi = 0.8$ with TFN consisting of 18 percent NO, 4 percent HCN, and 3 percent NH_3 .⁽²⁵⁾ The nitrogen conversion obtained in this study at $\phi = 0.8$ was 22.8 percent with the TFN consisting of 18% NO, 3% HCN, and 2% NH_3 . These results suggest that the experimental conditions in the Battelle staged combustor are similar to those used by other investigators.

Elemental Analyses of Solid Samples. The water quench probe was used to collect partially reacted fuel and product samples. The solids were collected on the filter described earlier and the liquids were retained in the bulk of the quench water. The quench water and the solids were extracted

TABLE 23.

SUMMARY OF OPERATING CONDITIONS AND GASEOUS
PRODUCT CONCENTRATIONS FOR THE SRCII COMBUSTION EXPERIMENTS

Run No.	Stoichiometry (air/fuel)	Fuel Feed Rate lb/hr	Air Feed Rate (lbs/hr)		Average Temperature, °F		Run Time, min	Gas Concentrations (volume percent or ppm [cc/cc])							
			Atomizing	Combustion	Combustor	Annular Burner		CO (%)	CO ₂ (%)	O ₂ (%)	HC (%)	NO (ppm)	HCN (ppm)	NH ₃ (ppm)	TFN (ppm)
28	0.60	3.33	1.77	24.8	2195	1421	70	10.9	7.8	0.0	4152	64	399	158	621
27	0.62	3.21	1.77	24.8	2117	1454	61	6.0	8.1	0.1	3471	72	316	156	544
25	0.70	2.84	1.77	24.8	2182	1431	60	9.7	9.3	0.0	2806	100	194	65	359
26	0.72	2.73	1.77	24.8	2091	1423	60	9.5	9.7	0.0	1220	118	145	93	356
24	0.82	1.98	1.77	19.8	2045	1447	60	7.3	12.1	0.0	151	249	7	15	272
16 ⁽¹⁾	0.87	4.1	2.18	44.2		1375	50	7.6	11.8	0.0	0	300	20	0	320
20	0.99	3.60	1.79	44.6	2133	1391	185	3.7	14.8	0.1	20	595	0	3	598
21	0.99	1.94	1.00	25.4	2164	1477	193	1.3	16.0	0.3	11	877	1	0	878

(1) Sample probes were positioned midway in the combustor.

FIGURE 45. CONCENTRATION OF NITROGEN CONTAINING GASES VERSUS STOICHIOMETRY

several times each with methylene chloride. These extracts were dried, combined and air evaporated to remove methylene chloride, resulting in 5-10 mg samples of liquids. These were typically thick, brown, tarry substances, probably heavier than the starting SRC II. The solid samples were typically 50-100 mg of black powder.

The solids were sent for C, H, and N analyses by microcombustion. The nitrogen analyses are probably not very accurate based on our previous experience described earlier. Oxygen was calculated by difference assuming both sulfur and inorganics were negligible. The results are listed in Table 24.

The oxygen content increases as the air/fuel ratio increases. This was also observed in the Task 2-3 bench-scale oxidative-pyrolysis studies. Hydrogen also increases as air/fuel ratio increases. This suggests that oxygen is added as -OH groups, again as suggested by Santoro and Glassman.⁽²¹⁾

Unfortunately the nitrogen analyses appear to have such large uncertainty that no trend can be developed for fuel nitrogen.

¹³C NMR measurements were not made on the samples due to insufficient sample size. However, based on the extremely low hydrogen to carbon ratios, which were also seen in the Task 2 and Task 3 results, the solids are expected to be highly aromatic.

Gas Chromatographic Analyses of Liquid Samples. The liquid samples were subjected to gas chromatographic analysis, using a Varian 3700 gas chromatograph equipped with a 50 m x 0.25-mm fused silica capillary column coated with polydimethylsiloxane OV-1, SE-30. Conditions were as follows:

Injector temperature: 300 C

Detector temperature: 310 C

Column temperature: 35 C for 3 min raised to 305 C at 10 C/min and held for 15 min

Helium carrier gas flow rate: 6 cc/min.

The effluent from the column was split into an FID detector to measure the amount of carbon (mass) versus time and a thermionic specific detector to measure the amount of nitrogen versus time. Two Hewlett Packard 3390A Integrators were used to record and integrate the signals from the two detectors.

TABLE 24. RESULTS OF ELEMENTAL ANALYSES ON SOLIDS RECOVERED FROM COMBUSTION

Number	Stoichiometry	Carbon	Weight Percent of		Oxygen (diff)	H/C	O/C
			Hydrogen	Nitrogen			
28	0.60	91.7	0.89	0.21	7.2	0.12	0.059
27	0.62	91.1	0.95	0.26	7.7	0.13	0.063
23	0.70	90.1	0.69	0.10	8.1	0.092	0.067
26	0.72	89.1	0.82	0.12	10.0	0.11	0.084
24	0.82	86.7	1.23	0.23	11.8	0.17	0.11
16	0.87	81.8	1.16	0.11	16.9	0.17	0.15
20	0.99	70.7	1.51	0.36	27.4	0.26	0.29
21	0.99	62.5	1.17	0.07	36.3	0.22	0.44

Each of the liquid samples was slurried in ether. They were not completely soluble but it is likely that a representative sample could be injected onto the column. (Tetrahydrofuran might have been a better choice as a solvent.)

The response was calibrated with an aromatic standard, an aliphatic standard, and a standard consisting of a mixture of cyanonaphthalene, quinine, and indole to measure an average nitrogen/carbon response. It was hoped that it would be possible to get some information on the nitrogen content, the boiling point range, and the average molecular weights of the very small (10-20 mg) liquid samples.

The nitrogen contents showed so much scatter that it was not even possible to obtain a good average value using the GC data. All of the significant nitrogen peaks on the TSD detector appeared to be in molecules with higher molecular weights than pyrene. These peaks are believed to be from the liquid samples but the possibility that they were an anomaly in the gas chromatographic setup cannot be entirely ruled out. This technique needs more development since it has the potential to significantly improve the understanding of the chemistry which the nitrogen in the fuel molecule undergoes before it is converted to one of the gaseous nitrogen products during combustion.

The molecular weights of the liquid samples were divided into materials boiling below benzene (less than 1 aromatic ring), between benzene and naphthalene (1 aromatic ring), between naphthalene and anthracene/phenanthrene (2 aromatic rings), between anthracene/phenanthrene and pyrene (3 aromatic rings), and above pyrene (4 or more aromatic rings). The results are summarized in Table 25.

There were no compounds present with boiling points below naphthalene. This may have been due to the way the samples were collected and prepared. There were increasing amounts of material of higher boiling point with the majority of the material being much heavier than pyrene.

Most of the liquid samples were obtained from extraction of the solid samples rather than from extraction of the water, as estimated by the color of the extracts. The fact that the samples are extremely heavy is not surprising. No trend in molecular weight/boiling point could be established as a function of stoichiometry because of the scatter in the data.

TABLE 25. AVERAGE BOILING POINTS/MOLECULAR WEIGHTS OF LIQUID COMBUSTION SAMPLES

No. of Aromatic Rings	Percent of Sample
<1	0
1 - 2	0
2 - 3	8
3 - 4	11
>4	81

NMR data could not be obtained on the samples because of insufficient funds.

Task 4 Conclusions

This work has shown, as has the work of others, that a minimum in total fuel nitrogen emissions ($\text{HCN} + \text{NH}_3 + \text{NO}$) occurs at an air/fuel ratio of 0.8 of the amount of air required to completely burn SRC II to CO_2 and H_2O . The total TFN emissions resulting from complete combustion of the SRC II under both stages of staged combustion have not been measured.

Analyses of solid and liquid samples obtained from the combustion zone have indicated that, for the most part, very heavy materials survive to second-stage combustion. There is a continuum of liquids and solids. The solids contain an average of only 0.18 weight percent nitrogen. As air/fuel ratio increases and combustion approaches completion the oxygen/carbon ratio and the hydrogen/carbon ratio both increase, indicating that oxygen is added as OH, as others have suggested.

No information was obtained on the nitrogen types which survive in the solids and liquids but, based on the results of Tasks 2 and 3, they are probably predominantly nonbasic, possibly cyano compounds.

The aromatic structure was not observed directly but most of the molecules contained four or more aromatic rings, substituted with an average of one oxygen for every 10 carbons (2 aromatic rings) at $\phi = 0.8$ and almost 4 oxygens per 10 carbons at $\phi = 1.0$.

ACKNOWLEDGMENTS

The assistance of the following people contributed to the successful completion of this program and is gratefully acknowledged. Don Hupp, Terry Sullivan, Bruce Rising and Paul Webb performed much of the experimental studies carried out during this program.

Discussions of SRC II safety and handling procedures with Dr. Jon Haebig of Gulf and Dr. Egon DeZubay and P. Richard Mulik of Westinghouse were helpful in implementing similar systems at Battelle.

Dr. David Schmalzer of the Pittsburg & Midway Coal Mining Company provided the samples of SRC II naphtha, middle distillate and heavy distillate used in this program. Dr. Douglas M. Jewell of the Pittsburg & Midway Coal Mining Company provided analytical data on narrow boiling range SRC II distillation cuts for comparison.

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