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Report

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DOE/PC/30302-2

SECOND QUARTERLY TECHNICAL PROGRESS REPORT

on

SYNTHETIC-FUEL AROMATICITY AND STAGED COMBUSTION

to

U. S. DEPARTMENT OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER

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

Period Covered: January 1, 1981-
March 31, 1981

April 30, 1981

by

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

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PATENT STATUS

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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). This program is directed to these two issues.

OBJECTIVES

The overall objective of this program is 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 is divided into five tasks. The title and objective of these tasks are as follows.

Task 1. Characterization of the Aromatics and the Fuel-N Components. The objective is to determine the volatility and to characterize the aromatic and fuel-N compounds present in a typical synfuel.

Task 2. Pyrolysis Studies. The objective is to determine the aromatic and fuel-N characteristics of narrow (50 C) distillation cuts of synfuel as a function of time, temperature and oxygen level.

Task 3. Oxidation of Pyrolysis Products. The objective is to determine the ease of oxidation of the pyrolysis products (the condensible fraction) of Task 2.

Task 4. Staged Combustion Studies. The objective is to define the burning characteristics of synfuel as a function of equivalence ratio, temperature and residence time in two-stage combustion.

Task 5. Modeling. The objective is to apply the results from Tasks 2, 3 and 4 into existing models for soot and NO_x formation in flames.

SUMMARY

In the second quarterly period the efforts were confined to Tasks 1 and 2. Five-gallon samples of naphtha, middle distillate, and heavy distillate were obtained. The middle and heavy distillate fractions were distilled into eleven 50 C-range cuts with boiling points ranging from <150 C to >450 C. Analyses were completed on all the samples to be used in the Task 2 pyrolysis study.

Initial pyrolysis experiments using the drop-tube furnace procedure are not as satisfactory as desired. A new approach is being devised which will vaporize the sample and allow for a gas phase pyrolysis.

PROGRESS

Task 1. Fuel Characterization

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. (It is not planned to use the SRC II naphtha sample in the current program.)

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

Sample	Boiling Point Range, °C, Corrected to 760 mm Hg	Sample Weight g/%
MD-1	<150	6.0/0.7
MD-2	150-200	124.6/15.0
MD-3	200-250	356.4/43.0
MD-4	250-300	298.2/36.0
MD-5	300-304	9.0/1.1
MD-6	>304 (residue)	34.6/4.2

The three largest fractions were analyzed for molecular weight, (by Vapor Pressure Osmometry VPO), elemental analysis, hydrogen distribution (by NMR), basic nitrogen (by titration with $HClO_4/CH_3COOH$) and simulated distillation (by gas chromatography). The procedures were discussed in detail in the First Quarterly Report.

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

Sample	Boiling Point Range, °C, Corrected to 760 mm Hg	Sample Weight g/%
HD-1	<300	82.1/8.2
HD-2	300-350	334.2/33.3
HD-3	350-400	293.9/29.3
HD-4	400-450	149.6/14.9
HD-5	>450	138.9/13.8

Fractions HD-2, HD-3, and HD-4 were also analysed as described above and will be used in the pyrolysis studies of Task 2. 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.

The results of these analyses are listed in Tables 1-3. 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 300-350 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 1. The boiling points of some typical aromatics 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 2) do not fall entirely within the boiling point ranges measured during distillation. The boiling point ranges measured by GC are indicated in Figure 1 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 1 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 1). The experimental variation in the NMR

TABLE 1. ANALYTICAL DATA FOR WESTINGHOUSE AND GULF MIDDLE DISTILLATE SRC SAMPLES

Sample	Westinghouse	MD-2	MD-3	MD-4	HD-2	HD-3	HD-4
Bp Range, °C		150-200	200-250	250-300	300-350	350-400	400-450
Molecular Weight[1] g/mole	138	147	176	184	177	196	262
Elemental Analyses (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	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
NMR Parameters							
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
Haromatic	0.24	0.17	0.21	0.22	0.32	0.37	0.37
H-Phenolic[2]	0.03	0.04	0.05	0.01	0.01	0.01	0.01

(1) Measured by Vapor Phase Osmometry.
(2) Based on the assumption O = OH.

Sample No. 2248; MD-2,-3,-4
Sample No. 2249: HD-2,-3,-4

TABLE 2. ANALYTICAL DATA FOR WESTINGHOUSE AND GULF MIDDLE DISTILLATE SRC SAMPLES

Boiling Point Distributions °C(1)

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	7.39	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 3. ANALYTICAL DATA FOR WESTINGHOUSE AND GULF MIDDLE DISTILLATE SRC SAMPLES

Sample	Westinghouse	MD-2	MD-3	MD-4	HD-2	HD-3	HD-4
Structural Parameters							
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
Molecular Formula							
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.

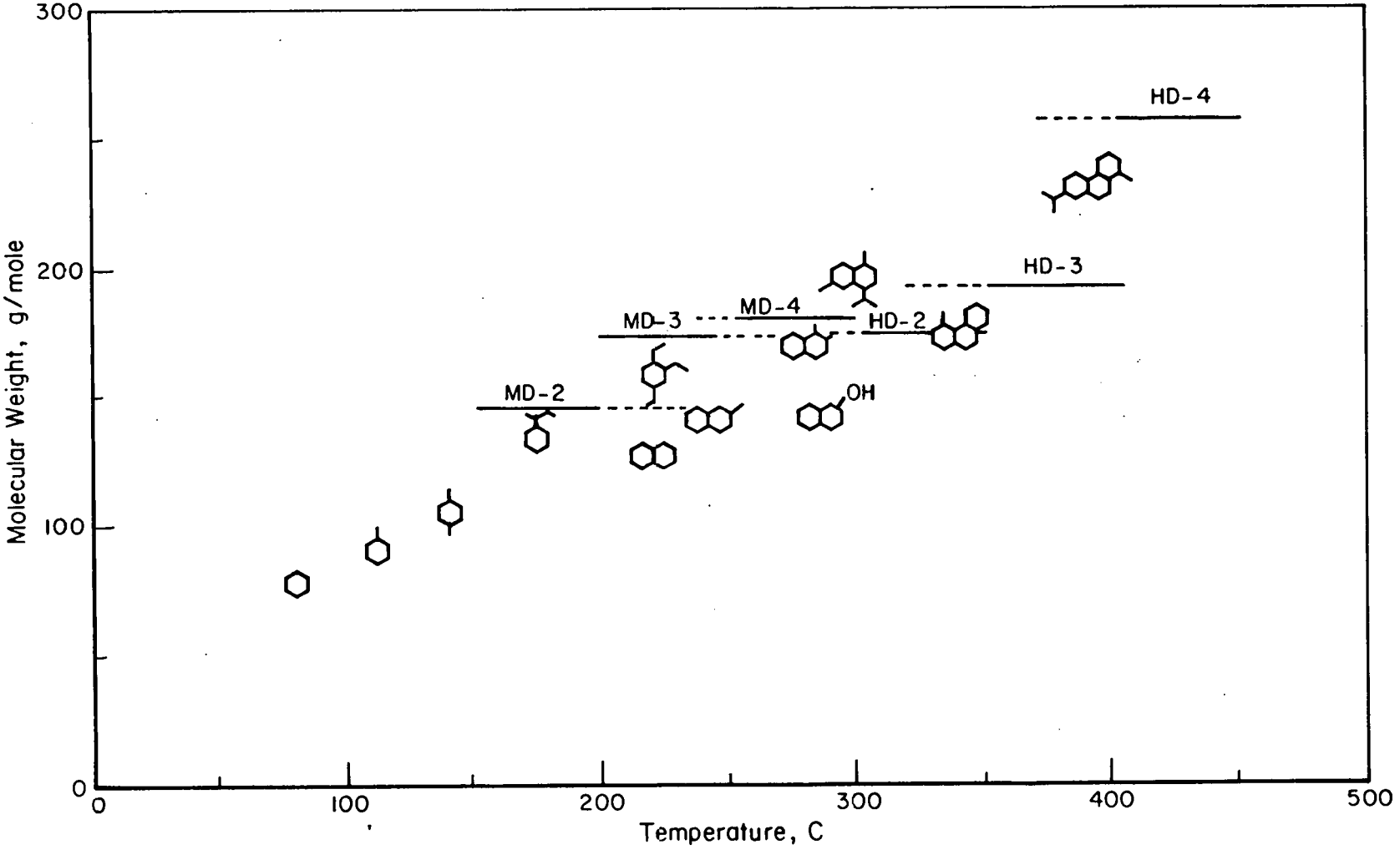


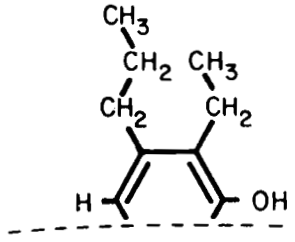
FIGURE 1. MOLECULAR WEIGHT - BOILING POINT DISTRIBUTION

measurements has been shown to be substantial by duplicate determinations. The actual variation and the effect of this variation on the structural parameters calculated using the Brown-Ladner equations will be calculated during the next quarter.

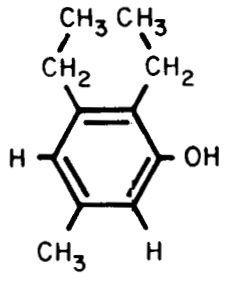
The structural parameters calculated from the hydrogen distribution measurements are listed in Table 3. Aromaticity (f_a) increases from about 40 percent to 70 percent with increasing molecular weight. The ratio of substitutable aromatic positions to total aromatic carbon (H_{aro}/C_{aro}) decreases with increasing molecular weight as would be expected as the number of condensed rings per molecule increases. The higher molecular weight molecules have a lower fraction of substituted aromatic carbon atoms (σ), but about the same number of substituted aromatic carbon atoms per molecule (R_s). 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 does 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.

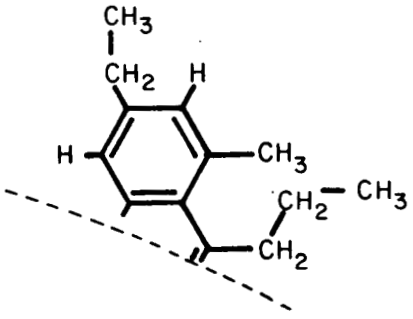
Average molecular structures can be drawn for the various boiling point fractions. Some possibilities are shown in Figure 2. These structures contain 1-3 carbon aliphatic side chains. Alicyclic structures become more numerous as molecular weight increases. The number of aromatic rings per molecule is only 1-3 throughout the distillable boiling point range. These structures also correspond reasonably well with the structures of known boiling point shown in Figure 1.



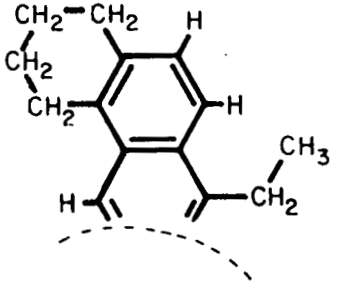
MD-2



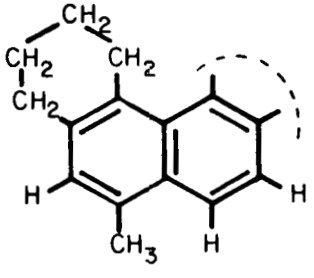
MD-3



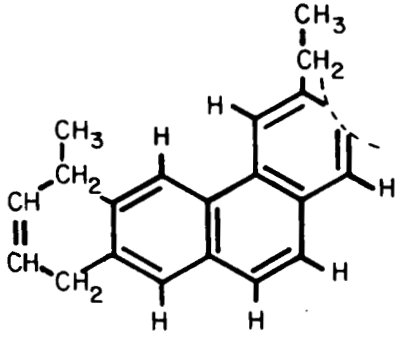
MD-4



HD-2



HD-3



HD-4

FIGURE 2. AVERAGE MOLECULAR STRUCTURES IN SRC II

Task 2. Pyrolysis Studies

The objective of this task is to determine the decomposition and conversion characteristics of the Task 1 distillate fractions as a function of temperature, time and oxygen level. Of particular interest are the distribution of aromatics and fuel-N constituents in the fractions before and after pyrolysis.

The effort this past quarter has been primarily exploratory, looking for the most practical way to examine the pyrolytic character of the SRC II cuts. As discussed last quarter a procedure was being devised to carry out this task in a drop-tube furnace. Basically the thought was to add droplets at a controlled rate, through a controlled heat up and at a fixed set of temperatures; then to collect the condensible portion of the stream to characterize it relative to the initial properties of the distillation cut. As a consequence of the problems encountered with this procedure and the results to date a different pyrolysis procedure is being devised. This new procedure, along with the results to date are presented below.

Results

Pyrolysis experiments were conducted at 400, 500 and 850 C with SRC II middle distillate and a 200-250 C cut, MD-3. The procedure was as described in the First Quarterly Technical Progress Report. Although it was desired to pass small drops, <200 μm, through the furnace, our 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 for the reason that extremely high flow resistance was encountered when fine needles were used and because the fuel is 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 constant flow syringe at rates between 0.1-0.9 g/min. 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. Boiling point distribution was essentially unchanged from that presented in Table 2. This was also the situation where 5.3 percent O_2 was added to the helium stream carrying the drops through the furnace.

The only marked change was in a small weight fraction of material in the 253-287 C region, which is only a tailing on the MD-3 sample, and not of significance in this experiment.

Modified Apparatus

Considering the nature of the experimental issues the pyrolysis apparatus is being modified to pre-vaporize the fuel prior to pyrolysis. The system being set up is similar to that of Blazowski[1] where 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 will be maintained by the syringe pump.

The collection system is also being modified. The vapor emitting from the furnace region will be passed through a cold trap system and to a GC unit. The GC unit will only be used to analyze the low molecular weight (gaseous) breakdown products.

A schematic of the modified experimental system is given in Figure 3.

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(1) Blazowski, W. S., "Dependence of Soot Production on Fuel Structure in Backmixed Combustion", Combustion Science and Technology, 21, 87 (1980).

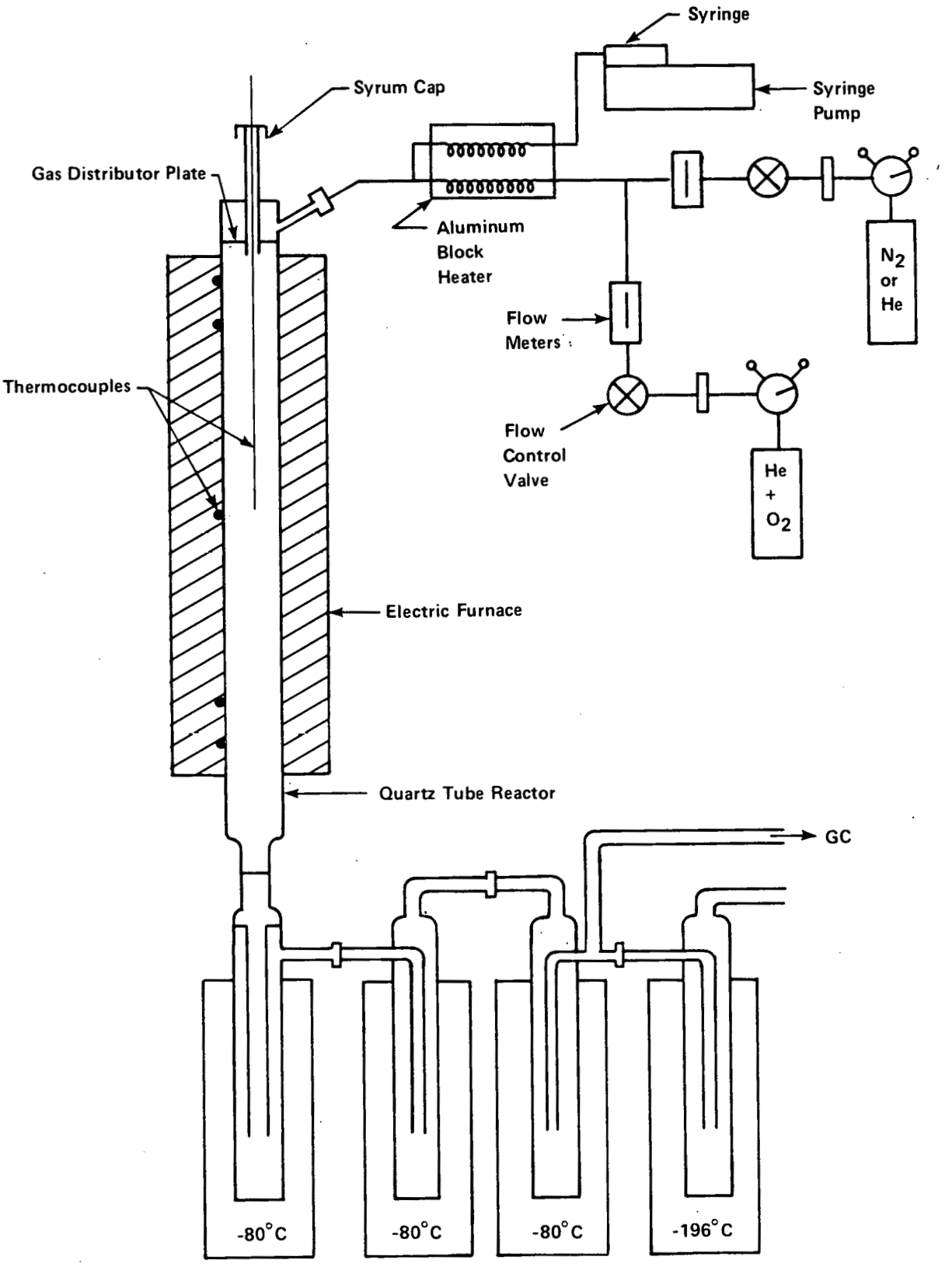

FIGURE 3. A SCHEMATIC DIAGRAM OF THE MODIFIED EXPERIMENTAL SET UP

PLANS FOR NEXT QUARTER

Task 1 is complete. No work is planned on the SRC II naphtha sample. It may be necessary to prepare additional samples of middle distillate and heavy distillate boiling range fractions but this will be minimized

Task 2 will concentrate on the pyrolysis of the middle distillate cuts (MD-2, -3, -4).

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