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'Basic Properties of Coals and Other Solids'
Duke Univ.

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Eighth Quarterly Report

During the past quarter we have been occupied with a variety of activities.

I. Manuscripts published - Two articles describing research done with support from this grant were published in the Journal of the American Chemical Society. Reprints are attached.

a) Thermochemical Comparison of Solid and Homogeneous Acids and Bases...Pyridine and Polyvinylpyridine as Prototype Bases by Edward M. Arnett, Tanweer Ahsan and Kalyani Amarnath, and

b) Heats of Interaction of Strong Brönsted Acids With Silica by Edward M. Arnett and Tanweer Ahsan.

II. Completion of research on the Basic Properties of Pittsburgh #8 Bituminous Coal - Table 1 is largely a recapitulation of Table 1 from our second yearly report of 8/30/91 except that the column under Pittsburgh #8 has now been filled completely by the addition of the lower nine heats of immersion which are enclosed within the ruled box. Figures 1, 2 and 3 provide comparisons of Pittsburgh #8 with polyvinylpridine (PVP) Illinois #6 and Wyodak subbituminous coals respectively.

Previous comparisons in the Second Yearly Report showed generally much better correlations between the response of the different coals with aliphatic acids than to the aromatic acids. Figure 1 of this report correlating ΔH imm for Pittsburgh #8 with ΔH imm for polyvinylpyridine, the prototype solid base, in a series of acids is reminiscent of a similar plot for Argonne Wyodak coal. Both plots give R correlation coefficients of 0.97 for aliphatic acids. Again, Figure 2 shows a much better correlation (R = 0.96) between ΔH imm for Pittsburgh #8 and Illinois #6 in aliphatic acids than aromatic ones (R = 0.79). Figure 3 shows exactly the same correlation coefficients for comparing Pittsburgh #8 and Wyodak subbituminous.

Considering the large, but varied aromatic components in coals as a function of rank, some discrimination on this basis is not surprising, but it is interesting to see it repeated so exactly from one comparison to another.

Table 2 presents our first results for heats of immersion of North Dakota Beulap-Zap lignite coal, just received from the Argonne coal bank, in strong acids. These values are reminiscent of the values for Exxon Rawhide, a Wyoming coal with the same acids (Table 1) except that the Rawhide coal is slightly more exothermic. Dr. Ahsan has had considerable difficulty getting reproducible values for interactions of the North Dakota coal with acids. Work with this coal will be continued during the coming quarter.

An important part of our present study on the basic properties of coals has been extended from the comparison of solid coal slurries to thermometric titrations of a series of coal liquids. These comparisons using several Wilsonville coal liquids and a coal liquid, YP35, from Exxon were compared in Figures 3-6 in the second yearly report which portrayed in general, a roughly parallel response of the coal liquid to that of the coal slurry, at least through the first increments of addition for the various acids. In all cases the heats of interaction of the acids with the coal liquids was greater than with the coal slurries.

Recently Dr. Ahsan has been comparing several of these coal liquids with their related coals in their response to titration with n-butylamine as a standard organic base. The results so far are summarized in Table 3 which demonstrates the interesting fact that the coal slurries are more acidic towards this strong base than are the coal liquids in contrast to the results mentioned above for their titration with strong acids solutions. It is interesting to note that Dr. Ahsan's heat of titration (ΔHtitr) for n-butylamine into slurries of Wyodak (12.57 $\pm$ 1.07 kcal/mol) and Illinois #6 (12.46 $\pm$ 0.95) are within experimental values of the published values 12.70 $\pm$ 1.80 kcal/mol and 12.90 $\pm$ 0.40 obtained four years ago in this laboratory by Gumkowski and Liu (Energy & Fuels, (1988), 2, 295).

Coal liquids are obtained by high temperature vacuum distillation under a variety of conditions (see Figure 4) and may be expected to contain the acidic and the basic residues from components of coal many of which are probably hydrogen-bonded to each other both in the coal and in the liquid. If they are titrated with an organic base or acid that is stronger than the corresponding base or acid in the hydrogen-bonded complex there will be some displacement of the weaker component by the stronger one. The comparisons shown above indicate that the coal liquids studied so far carry a higher content of basic components than of acidic ones.

III. Future Work - An important concern about our acid-base research on coal slurries is that some of the most basic components which are reacting with strong acids are inorganic ones such as alkali, oxides and carbonates. Of course these have nothing to do with the organic compounds that are of significance in the distilled coal liquids.

During the past six months two postdoctoral students from Dr. John Larson's laboratory at Lehigh University have joined our group, both of them have worked on coal chemistry. They recommended that we try treating some of our coals by citric acid or HF wash in order to remove the inorganic components so that we may study the acid-base properties of the purely organic material. I believe this would be an important addition to the work which we have been doing and hope to have some trial results for the next quarterly report.

IV. Presentation - An invited lecture on the work supported by this grant was given on August 26, 1991 in a symposium on "Novel Analytical Techniques for Fossil Fuels" at the National A.C.S. meeting in New York. This is being prepared for publication in a special issue of Fuel. article from C+E News

V. Fowkes Festschrift - I wish to draw attention to a special festschrift volume entitled "Acid-Base Interactions: Relevance to Adhesion Science and Technology" edited by K. L. Mittal and H. R. Anderson, Jr., V. S. P., Utrecht which was put together in honor of the 75th birthday of Professor Frederick M. Fowkes of Lehigh University. Professor Fowkes was a leader in the calorimetric study of solids of many kinds, including coals. Unfortunately he passed away before this volume actually appeared for sale, but it is an appropriate memorial to his scientific work.

Table-1. Heats of immersion (ΔH_{imm}) of coals and Polyvinylpyridine in (0.65M) acid solutions in acetonitrile.

Acids	pka [a]	PVP	Exxon Rawhide	Wyodak	IL#6	Pittsburgh#8
		$-\Delta H_{imm}$ (cal/g)				
Ethanesulfonic	-1.68	148.33 ±17.0	37.35 ± 0.84	44.62 ± 1.56	22.86 ± 0.48	21.28 ± 2.13
Methanesulfonic	-1.92	147.55 ± 1.47	37.99 ± 1.46	44.79 ± 2.00	21.56 ± 0.24	21.98 ± 1.19
Triflic	-5.90	130.54 ± 9.54	59.16 ± 2.85	60.16 ± 1.61	45.08 ± 2.36	29.39 ± 1.47
Trifluoroacetic	0.54	85.75 ± 0.72	32.19 ± 0.86	35.69 ± 1.15	18.53 ± 0.48	12.62 ± 0.60
Trichloroacetic	0.69	80.82 ± 1.40	28.17 ± 0.03	23.89 ± 0.88	14.71 ± 0.72	08.07 ± 0.70
Difluoroacetic	1.30	74.99 ± 1.89	29.73 ± 0.56	31.55 ± 0.66	16.44 ± 0.45	10.03 ± 0.66
Dichloroacetic	1.36	70.56 ± 0.82	29.06 ± 0.22	26.52 ± 0.49	16.38 ± 0.38	09.90 ± 1.50
4-Toluenesulfonic	-6.55	66.89 ± 1.99	24.81 ± 1.02	24.81 ± 0.95	20.39 ± 0.41	08.92 ± 1.25
Benzenesulfonic	-2.70	62.08 ± 0.53	30.55 ± 0.94	29.30 ± 0.22	23.79 ± 1.87	18.58 ± 0.24
Chloroacetic		60.00 ± 0.82	27.25 ± 0.07	26.72 ± 0.94	16.75 ± 0.59	07.60 ± 0.66
4-Chlorobenzensulfonic		53.26 ±1.37	24.89 ± 0.94	24.09 ± 1.21	19.14 ± 0.98	10.82 ± 0.66
4-Nitrobenzenesulfonic	-4.00		23.24 ± 0.27	26.23 ± 1.00	20.81 ± 0.79	07.13 ± 0.71
Boron trichloride [b]			12.09 ± 0.58	11.34 ± 1.36	33.78 ± 2.23	16.94 ± 0.27

[a] Acidic dissociation constants of sulfonic acids in water at 25 °C from Grumrine et al; *J.Org.Chem.* 1986,51,25,5013. and J.P.Guthrie; *Can J Chem* 1978,56,2342. which describes the unusual difficulties of comparing the strengths of very strong acids. [b] Hexane as solvent.

Table 2.

Heats of immersion (ΔH_{imm}) of N. Dakota coal sample in strong acid solutions in acetonitrile at 25 ^oC

acids	ΔHimm (cal/g)
Methanesulfonic	35.41 ± 1.64
Ethanesulfonic	32.59 ± 0.49
Trifluoroacetic	27.52 ± 1.24
Difluoroacetic	28.43 ± 1.50
Dichloroacetic	24.42 ± 0.23
Trichloroacetic	17.14 ± 1.38

Table 3.

Heats of titrations ($\Delta H_{titr.}$) of coal liquids and coal slurries with n-butylamine in acetonitrile at 25 ^oC

Coal liquids/slurries	$\Delta H_{titr.}$ (kcal/mol)
Coal liquids:	
Exxon CMEV YP35	3.62 ± 0.17
IL#6 R261 V161 lower fraction	0.22
Black Thunder R260 V161 lower fraction	1.00 ± 0.20
Black Thunder R260 V182 higher fraction	1.40 ± 0.06
Pittsburgh#8 R260 V161 lower fraction	no measureable heat
Coal slurries:	
Exxon Rawhide	12.57 ± 1.07
IL#6	12.46 ± 0.95
Black Thunder	12.86 ± 0.86
Pittsburgh#8	14.20 → 2.32

Fig 1. Comparison of ΔHimm of Argonne Pitts#8 and PVP in strong acids

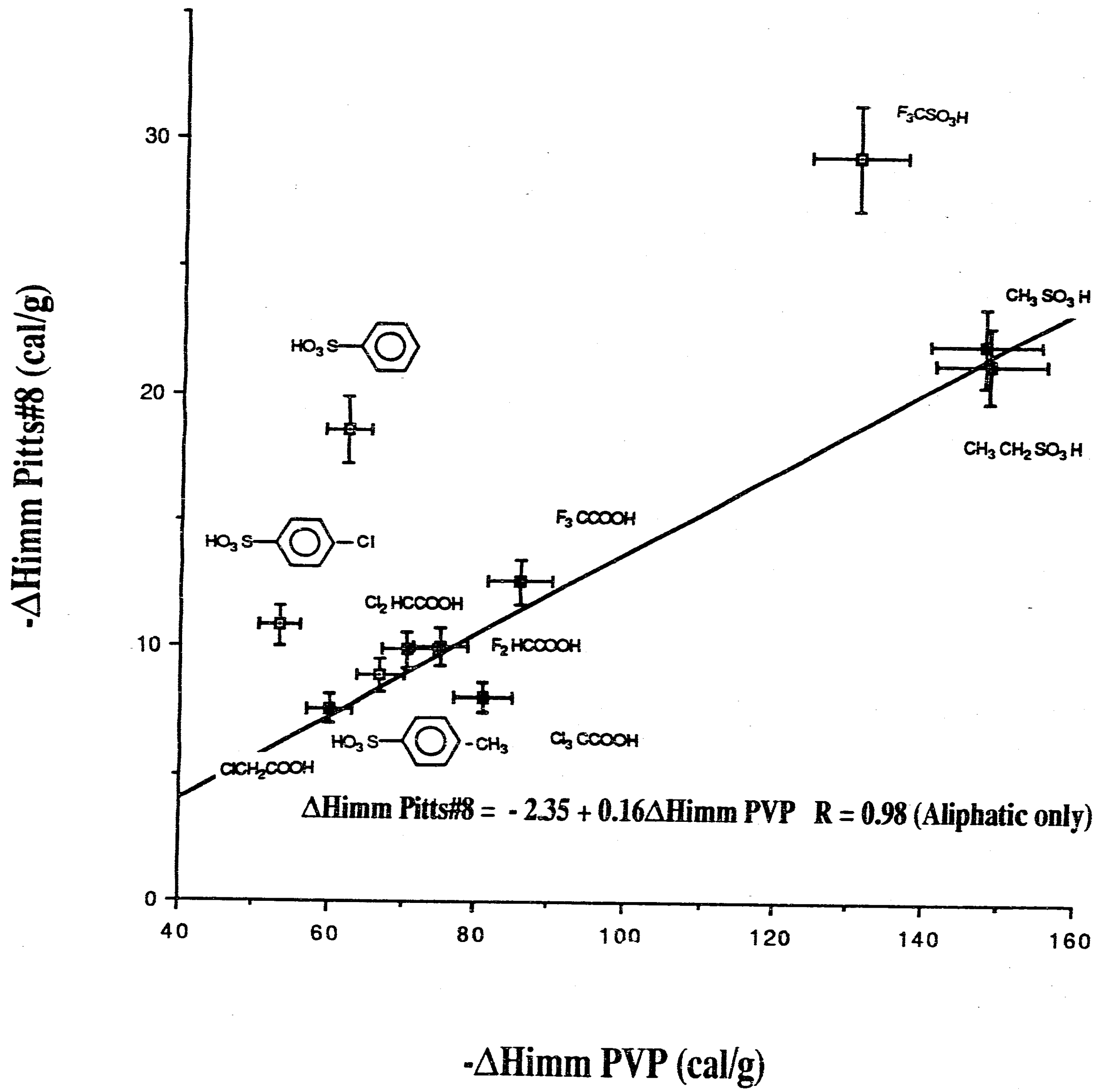


Fig 2. Comparison of ΔHimm of Argonne Pitts#8 and IL#6 coals in strong acids

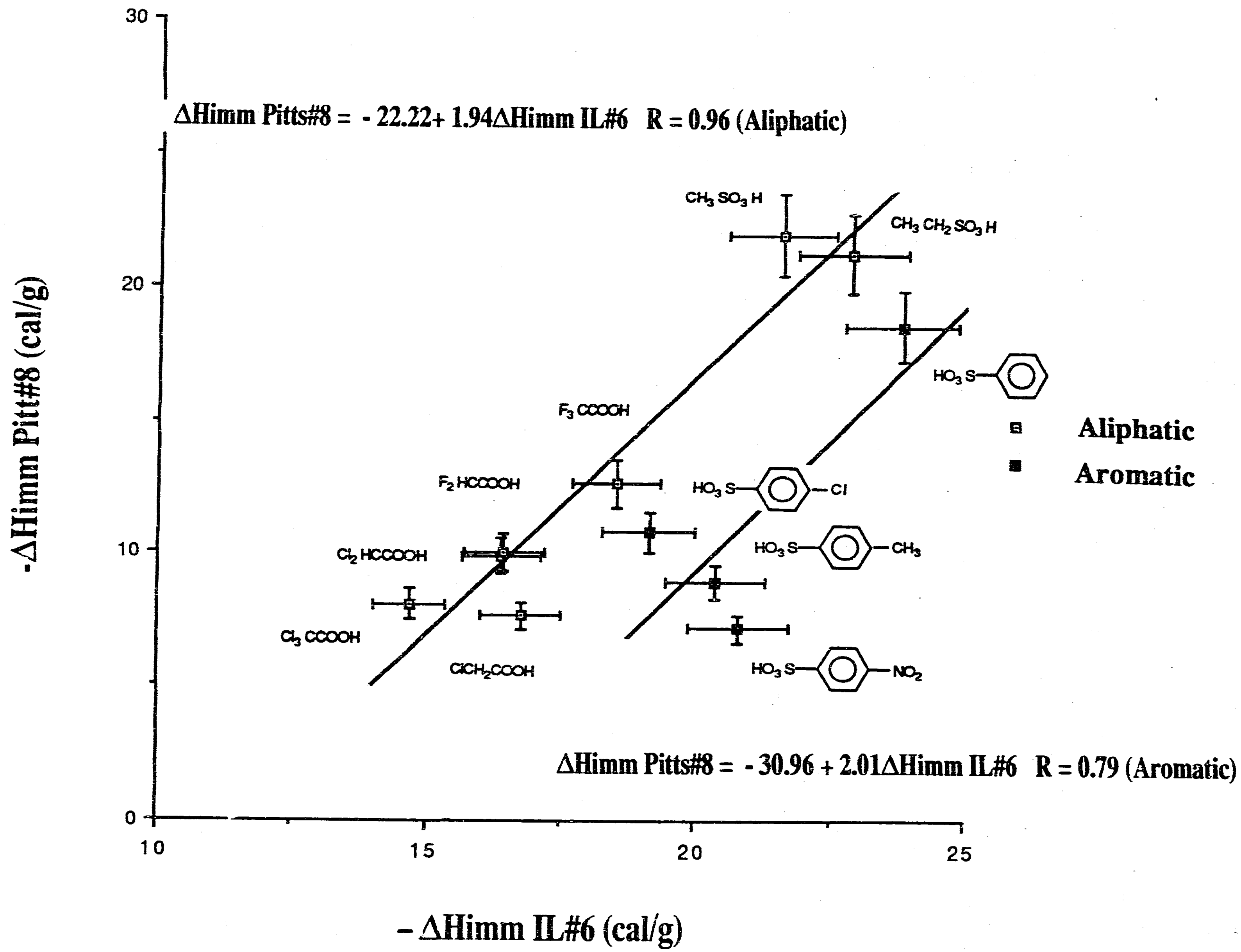


Fig 3. Comparison of ΔHimm of Argonne Pitts#8 and Wyodak coals in strong acids

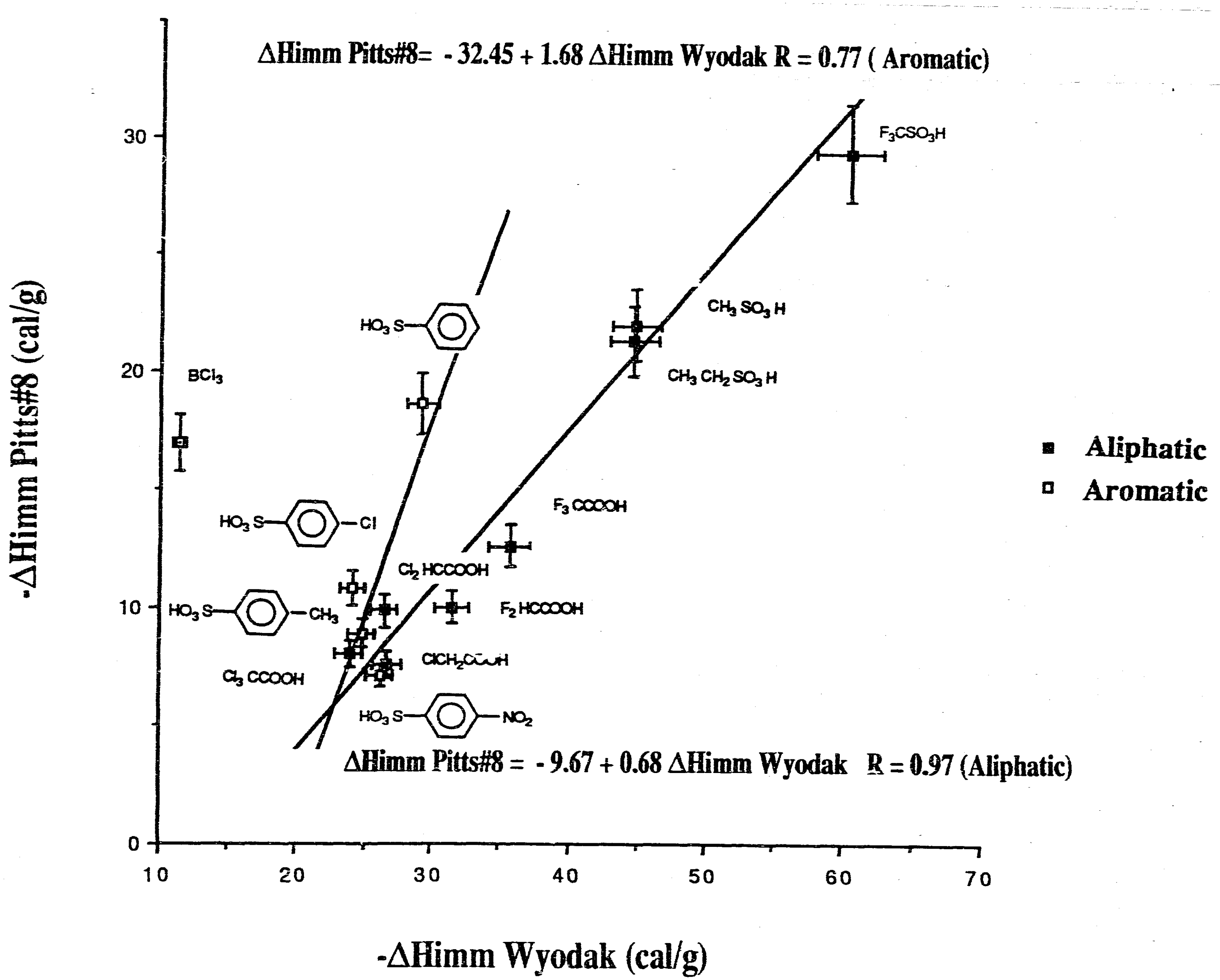
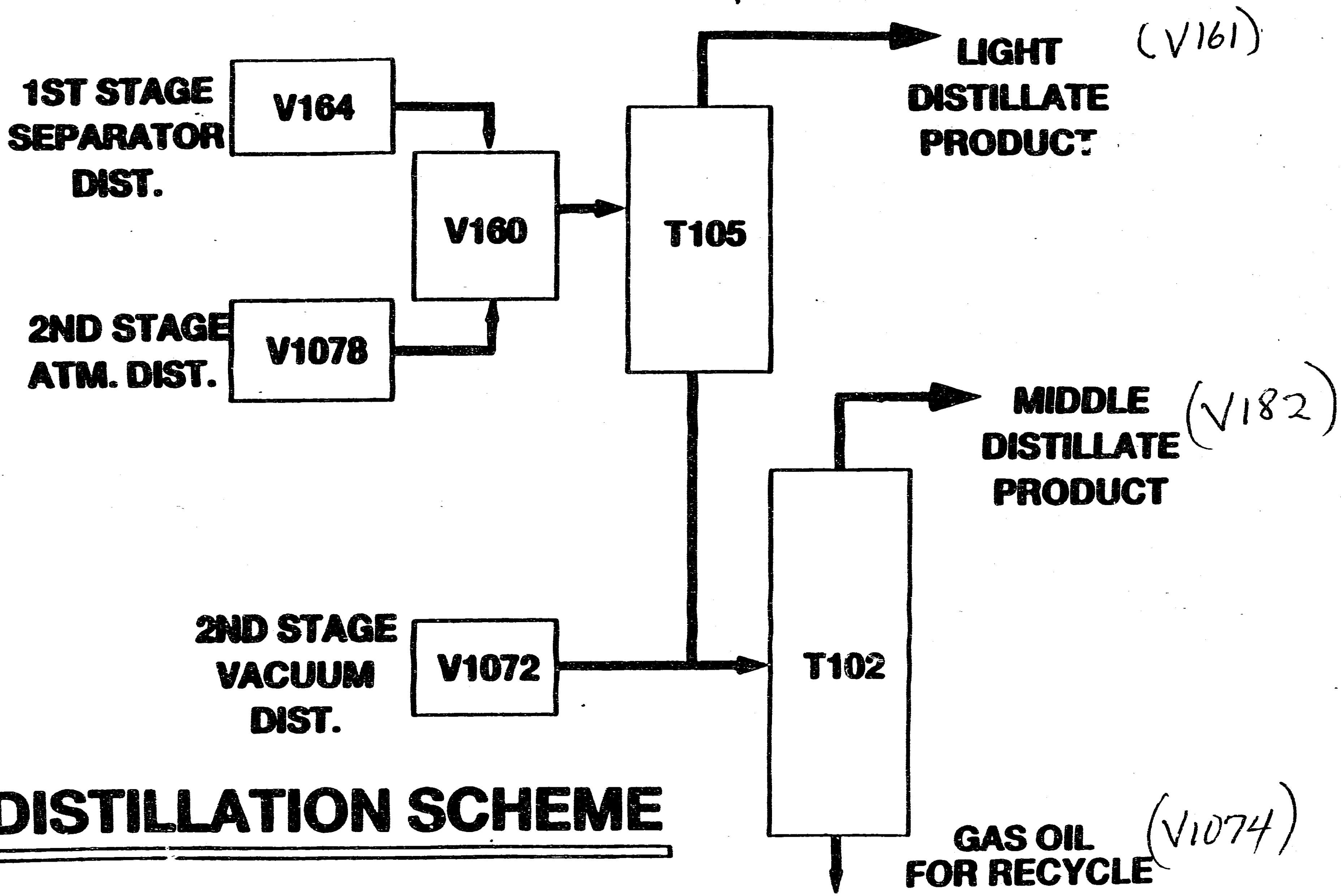


Figure 4



DISTILLATION SCHEME

DISTILLATION SCHEME: SAMPLE DESCRIPTION

V164 - First stage reactor product. Can be high in phenols and heteroatoms. Boiling range 100-800°F.

V1078 - Second stage reactor product. More hydrogenated than first stage product. Lower in heteroatoms. Boiling range 100-800°F.

V160 - A combination of V164 and V1078.

T105 - An atmospheric distillation column.

V1072 - A heavy second stage product boiling from 650-1000°F. High (>0.50 wt %) in nitrogen and low in sulfur.

V161 - Naphtha product from atmospheric column. Boils from 75-500°F. A major product from the process. I have sent samples of naphtha before.

V182 - Middle distillate from the vacuum column boiling from 400-800°F. A major product from the process. I have sent samples of it before.

V1074 - Bottoms product from vacuum column. Boils from 650-1000°F. Used primarily as a recycle solvent for coal slurry preparation.

T102 - Vacuum column.

Product - The product from each experimental run, which may last for twelve months, is a combination of the V161 and V182 samples. I have sent product samples before.

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