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QUARTERLY TECHNICAL REPORT
for
July 1 - September 30, 1992
Volume I
Fuels Research

Work Performed for the
U.S. Department of Energy
Under Cooperative Agreement
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FOREWORD

The Quarterly Technical Report, NIPER-670 is submitted in accordance with the provisions of Cooperative Agreement DE-FC22-83FE60149 between the Department of Energy and the IIT Research Institute. The report is submitted in two volumes, Volume I representing the work accomplished under Fuels Research and Volume II the work for Energy Production Research during the period July 1 - September 30, 1992.

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FUELS RESEARCH

Dexter Sutterfield, Director

DEVELOPMENT OF ANALYTICAL METHODOLOGY FOR ANALYSIS OF HEAVY CRUDES

Cooperative Agreement DE-FC22-83FE60149, Project BFR2

National Institute for Petroleum and Energy Research
Bartlesville, Oklahoma

Contract Date: October 1, 1983
Anticipated Completion: Continuing
Funding for FY1992: $300,000

Principal Investigator: John Green

Project Monitor: William D. Peters
Bartlesville Project Office

Reporting Period: July 1 - September 30, 1992

Objectives

General objectives are: 1) to identify compounds or classes of compounds that significantly affect, either positively or negatively, crude oil and/or product properties and characteristics, and 2) to develop methods for their determination in conventional or low grade petroleum and syncrudes.

Specific objectives for FY92 are: 1) to determine catalytic cracking behavior of individual compound classes in petroleum, and 2) to further develop GC/MS methodology for speciation of nitrogen and sulfur compounds in petroleum.

Summary of Technical Progress

Gasoline range (82-430° F) components in liquid products from cat-cracking whole Wilmington >650° F resid, Wilmington >650° F neutrals, and blends of neutrals plus 650-1000° F acids and bases were determined by GC/MS. The results are shown in table 1. Peak identifications were largely based on published GC retention indices and mass spectra. However, the identifications of n-paraffins and most isoparaffins were confirmed via analysis of standards under identical conditions. Identification of selected olefinic, aromatic and naphthenic species, including cyclopentadiene, was similarly confirmed. A 100 m, 0.25 mm i.d., methyl silicone (0.5 µm film thickness) column was used; it was interfaced direct to a Kratos MS-80 mass spectrometer operated in the electron impact mode (70 ev).

The elemental compositions and microcarbon residue (MCR) data for feeds are listed in table 2. Acid, base and neutral fractions were generated from 650-1000° F and >1000° F boiling range fractions of Wilmington via nonaqueous ion exchange liquid chromatography. Table 3 shows the proportion of each fraction present in the whole resid.

The distribution of heteroatomic compounds in the feed exerts a greater impact on gasoline product composition than any other single feedstock parameter. For example, the higher concentration of alkylbenzenes and total aromatics from pure neutrals compared to neutral + acid or neutral + base feed reflects the greater activity of the catalyst when the inhibiting acidic or basic compounds are absent. Similarly, the lower concentration of n-paraffins left in the pure neutrals product reflects the higher conversion attained with that feed.

Olefins are formed as primary products from all cracking reactions; they undergo subsequent reactions to form isoparaffins, naphthenes and aromatics (1). As expected, the concentration of olefins is lowest in the gasoline from pure neutrals. The concentration of olefins increases with the other feeds in the following order: whole resid <acid + neutrals <base + neutrals. The relatively low olefin concentration in gasoline from the whole resid stems from a lower primary cracking reaction rate (overall gasoline yield from the whole resid was only 60-70% of that obtained from other feeds) and probable consumption in coke formation (coke yield from the whole resid was 1.5 - 1.8 times that of other feeds). The higher olefin content of base + neutrals compared to acid + neutrals product reflects the greater inhibition of bases on secondary cracking reactions.

The nearly equal concentration of isoparaffins from neutral and acid + neutral feeds indicates minimal acid inhibition of hydrogen transfer to form isoparaffins from the corresponding olefins. The substantially lower isoparaffin content of whole resid and base + neutral products indicates that basic compounds inhibit hydrogen transfer to a much greater extent than acids. Similarly, the ratios of saturated naphthenes to those with one or two double bonds decrease as follows: neutrals (3.6) >acids + neutrals (2.7) >bases + neutrals (1.5) >whole resid (0.9). The very low ratio obtained from the whole resid suggests that formation of high levels of coke on the catalyst further limits hydrogen transfer in addition to inhibition by bases.

The very low benzene, cyclohexane and cyclopentane content of the whole resid gasoline indicates that very little alpha cleavage of alkylbenzenes occurred in that case. This observation is further supported by the relatively high levels of ethyl-, n-propyl- and n-butylbenzenes observed. The rate of alpha cleavage of aromatics may be sensitive to the amount of coke formed on the catalyst (highest with whole resid) or the presence of higher boiling acid or base compounds (not present in other feeds).

The overall indication is that gasoline range products are largely formed via secondary catalytic reactions from olefins. Polar compounds in the feed control the composition of the resulting gasoline through varying degrees of inhibition of these secondary reactions, as noted above. The hydrocarbon structure of the feed does have some impact on product composition, however. For example, the relatively high alkylbenzene content of the whole resid product must reflect some direct contribution from primary cracking reactions, since the observed degree of inhibition of secondary reactions effectively would prevent attainment of the observed concentration solely through secondary processes (the whole resid is the most aromatic feed, see table 2). Other isolated incidences of high concentrations of individual species or isomeric groups (e.g. C_2-indans from acid + neutrals) may reflect a particular aspect of feedstock structure. The relative importance of hydrocarbon structure versus polar compound distributions should become more quantifiable as data on feedstocks from the other crudes become available.

Finally, concentrations of unstable hydrocarbon species such as cyclopentadienes and other dienes were lower in gasolines from base-free feeds (neutrals, acid + neutrals). The presence of bases apparently inhibits further reaction of these intermediate species to more stable hydrocarbons. This aspect of composition may be important with respect to gum formation of the gasoline during storage and use since such highly reactive species are usually responsible for fuel quality problems.

Reference

1. Gary, J. H.; Handwerk, G. E. *Petroleum Refining*; M. Dekker: New York, **1975**; pp 95-97.

Table 1. - Composition of gasoline (C_5 - 430° F) from different feeds (Area%)

FEED	Whole >650° F Resid	>650° F Neutrals	Neutrals + 650-1000° F Acids	Neutrals + 650-1000° F Bases
AROMATICS				
Alkylbenzenes				
benzene	0.14	1.02	1.62	1.78
toluene	5.3	4.3	4.2	4.7
total C_2-benzenes	14.3	11.6	11.2	11.2
ethylbenzene	2.0	1.66	1.65	1.82
o-xylene	3.3	2.9	2.8	2.9
m + p-xylenes	9.0	7.0	6.7	6.5
total C_3-benzenes	17.0	14.8	13.7	12.8
isopropylbenzene	0.12	0.028	0.011	0.040
n-propylbenzene	0.99	0.78	0.84	0.87
1-ethyl-2-methylbenzene	1.14	1.02	0.93	0.86
1-ethyl-3-methylbenzene + 1-ethyl-4-methylbenzene	4.3	3.9	3.6	3.2
1,2,3-trimethylbenzene	2.0	1.7	1.6	1.7
1,2,4-trimethylbenzene	5.8	4.9	4.4	4.2
1,3,5-trimethylbenzene	2.6	2.5	2.3	1.9
total C_4-benzenes	9.7	10.8	9.5	7.0
n-butylbenzene	0.51	0.33	0.18	0.13
1-methyl-2-propylbenzene	0.32	0.56	0.51	0.28
1-methyl-3-propylbenzene	0.83	0.79	0.70	0.58
1-methyl-4-propylbenzene	0.18	0.23	0.23	0.47
1,2-diethylbenzene	0.012	0.007	0.014	0.022
1,3-diethylbenzene	0.47	0.67	0.62	0.49
1,4-diethylbenzene	nd[a]	0.06	0.06	0.03
1,2-dimethyl-3-ethylbenzene	0.22	0.48	0.38	0.16
1,2-dimethyl-4-ethylbenzene	1.31	1.52	1.39	1.11
1,3-dimethyl-2-ethylbenzene	0.006	0.09	0.05	0.016
1,3-dimethyl-4-ethylbenzene + 1,4-dimethyl-2-ethylbenzene	1.61	1.82	1.59	1.24
1,3-dimethyl-5-ethylbenzene	1.32	1.38	1.21	0.74
1,2,3,4-tetramethylbenzene	0.63	0.58	0.62	0.25
1,2,3,5-tetramethylbenzene	1.10	1.23	1.07	0.61
1,2,4,5-tetramethylbenzene	0.80	1.01	0.91	0.86
total C_5-benzenes (no. isomers)	3.2 (12)	5.0 (10)	3.4 (12)	2.7 (10)
total C_6-benzenes (no. isomers)	0.30 (1)	0.07 (1)	0.36 (1)	0.17 (3)
Total Alkylbenzenes	49.5	47.6	44.0	40.4

Table 1. - Composition of gasoline (C_5 - 430° F) from different feeds (Area%) (continued)

FEED	Whole >650° F Resid	>650° F Neutrals	Neutrals + 650-1000° F Acids	Neutrals + 650-1000° F Bases
Alkylindans				
indan	0.77	0.92	0.72	0.66
total C_1-indans	3.13	3.12	2.65	2.65
1-methylindan	0.51	0.53	0.47	0.47
4-methylindan	1.51	1.28	1.04	1.39
5-methylindan	1.11	1.31	1.14	0.79
total C_2-indans (no. isomers)	1.41 (4)	1.56 (2)	2.09 (4)	1.66 (4)
Total Alkylindans	5.3	5.6	5.5	5.0
Alkylindenes				
indene	0.14	nd	0.03	0.05
total C_1-indenes	0.02	nd	nd	nd
Total Alkylindenes	0.16	nd	0.03	0.05
Naphthalene	1.26	1.13	0.88	0.58
Alkylthiophenes				
thiophene	0.058	nd	nd	nd
methylthiophene	0.001	nd	nd	nd
Total Alkylthiophenes	0.06	nd	nd	nd
TOTAL AROMATICS	56.3	54.3	50.4	46.0
NORMAL PARAFFINS				
pentane	0.30	0.24	0.36	0.47
hexane	0.56	0.26	0.39	0.50
heptane	1.18	0.26	0.28	0.59
octane	0.94	0.85	0.78	0.96
nonane	0.55	0.32	0.25	0.39
decane	0.58	0.30	0.35	0.58
undecane	0.65	0.47	0.38	0.53
dodecane	0.37	0.056	0.12	0.22
TOTAL N-PARAFFINS	5.1	2.8	2.9	4.2

Table 1. - Composition of gasoline (C_5 - 430° F) from different feeds (Area%) (continued)

FEED	Whole >650° F Resid	>650° F Neutrals	Neutrals + 650-1000° F Acids	Neutrals + 650-1000° F Bases
ISOPARAFFINS				
isopentane	1.03	1.40	1.66	1.14
total C_6	3.0	3.5	4.2	3.3
2,2-dimethylbutane	nd	0.052	0.053	0.092
2,3-dimethylbutane	0.38	0.22	0.42	0.49
2-methylpentane	1.62	1.95	2.16	1.81
3-methylpentane	0.91	1.23	1.54	0.90
total C_7	3.4	3.8	3.8	3.0
2,3-dimethylpentane	0.002	0.013	0.002	0.013
2,4-dimethylpentane	0.040	0.008	0.006	0.008
2-methylhexane	2.02	2.23	2.24	1.77
3-methylhexane	1.33	1.58	1.59	1.23
total C_8	4.3	4.8	4.6	3.5
2,2,3-trimethylpentane	nd	nd	0.004	nd
2,3-dimethylhexane	0.13	0.026	0.021	0.095
2,4-dimethylhexane	0.65	0.80	0.86	0.64
2,5-dimethylhexane	0.32	0.40	0.37	0.35
3,4-dimethylhexane	nd	0.001	nd	nd
2-methylheptane	2.08	1.99	1.92	1.42
3-methylheptane	1.13	1.48	1.46	0.99
4-methylheptane	nd	0.019	nd	0.004
total C_9	2.1	3.2	3.0	1.9
2,3,4-trimethylhexane	nd	nd	0.011	0.013
2,4-dimethylheptane	0.26	0.32	0.34	0.094
2,5-dimethylheptane	0.63	0.89	0.83	0.63
2,6-dimethylheptane	0.36	0.64	0.61	0.45
2-methyloctane	0.19	0.41	0.33	0.13
3-methyloctane	0.70	0.91	0.86	0.64
total C_{10}	0.71	2.4	2.0	1.3
dimethyloctanes (no. isomers)	0.32 (3)	1.77 (5)	1.38 (5)	0.98 (5)
2-methylnonane	0.11	0.14	0.13	0.05
3-methylnonane	0.28	0.43	0.46	0.29
total C_{11} (no. isomers)	0.54 (5)	0.90 (5)	0.88 (6)	0.55 (6)
total C_{12} (no isomers)	0.20 (4)	0.30 (3)	0.32 (4)	0.014 (3)
TOTAL ISOPARAFFINS	15.3	20.3	20.5	14.7

Table 1. -Composition of gasoline (C_5 - 430° F) from different feeds (Area%) (continued)

FEED	Whole >650° F Resid	>650° F Neutrals	Neutrals + 650-1000° F Acids	Neutrals + 650-1000° F Bases
NAPHTHENES				
Saturated				
cyclopentane	0.06	0.87	0.79	1.14
total C_6	1.46	4.9	4.9	5.9
cyclohexane	0.093	3.1	3.0	4.2
methylcyclopentane	1.37	1.76	1.92	1.66
total C_7	2.75	3.3	3.5	2.76
c-1,2-dimethylcyclopentane	0.29	0.40	0.47	0.28
t-1,2-dimethylcyclopentane	0.67	0.58	0.62	0.66
c-1,3-dimethylcyclopentane	0.44	0.61	0.64	0.47
t-1,3-dimethylcyclopentane	0.67	0.79	0.83	0.69
methylcyclohexane	0.68	0.94	0.91	0.66
Total C_5-C_7 Saturated Naphthenes	4.2	9.1	9.2	9.8
One double bond				
cyclopentene	0.21	0.20	0.30	0.49
total C_1-cyclopentenes	2.0	1.03	1.26	2.0
1-methylcyclopentene	1.44	0.51	0.69	1.33
4-methylcyclopentene	0.52	0.52	0.57	0.70
total C_2-cyclopentenes (no. isomers)	2.3 (4)	1.3 (5)	1.8 (4)	4.0 (6)
Total C_0-C_2-Cyclopentenes	4.5	2.5	3.4	6.5
Two double bonds				
cyclopentadiene	0.018	nd	0.008	0.016
total C_6-cyclodienes (no. isomers)	0.20 (3)	0.04 (2)	0.04 (2)	0.075 (2)
total C_7 cyclodienes (no. isomers)	0.02 (1)	nd	nd	0.03 (1)
Total C_5-C_7 Cyclodienes	0.24	0.04	0.05	0.12
TOTAL C_5-C_7 NAPTHENICS^b	8.9	11.6	12.7	16.4
OLEFINS				
One double bond				
total C_5 olefins	1.65	1.56	2.60	3.3
2-methylbutene-1	0.27	0.23	0.37	0.52
3-methylbutene-1	0.038	0.036	0.057	0.089
2-methylbutene-2	0.74	0.69	1.17	1.34
pentene-1	0.092	0.11	0.18	0.26
c-pentene-2	0.18	0.17	0.26	0.38
t-pentene-2	0.33	0.32	0.56	0.72

Table 1. -Composition of gasoline (C_5 - 430° F) from different feeds (Area%) (continued)

FEED	Whole >650° F Resid	>650° F Neutrals	Neutrals + 650-1000° F Acids	Neutrals + 650-1000° F Bases
total C_6 olefins	2.6	1.8	2.6	3.8
2-methylpentene-1	0.30	0.18	0.13	0.60
3-methylpentene-1	0.029	0.017	0.022	0.022
4-methylpentene-1	0.07	nd	nd	nd
c-3-methylpentene-2	0.50	0.41	0.70	0.84
t-3-methylpentene-2	0.46	0.37	0.46	0.68
c-4-methylpentene-2	nd	nd	0.006	nd
t-4-methylpentene-2	nd	nd	0.006	nd
hexene-1	0.30	0.17	0.09	0.15
c-hexene-2	0.35	0.11	0.39	0.50
t-hexene-2	0.38	0.29	0.55	0.62
c + t-hexene-3	0.19	0.26	0.26	0.41
total C_7 olefins (no. isomers)	1.1 (10)	1.2 (10)	1.6 (5)	1.8 (9)
Total C_5-C_7 Olefins	5.4	4.5	6.8	8.9
<u>Two double bonds</u>				
total C_5 dienes (no. isomers)	0.009(1)	0.003(1)	nd	nd
total C_6 dienes (no. isomers)	0.006(1)	nd	nd	nd
total C_7 dienes (nd isomers)	0.022(1)	0.01 (2)	0.006(2)	0.007 (1)
Total C_5-C_7 Dienes	0.04	0.02	0.006	0.007
TOTAL C_5-C_7 OLEFINICS[b]	5.4	4.5	6.8	8.9
TOTAL ALL CATEGORIES[c]	**91.0**	**93.5**	**93.3**	**90.2**

[a] None detected.

[b] At C_8 and above, naphthenes generally cannot be differentiated from olefins.

[c] Species not accounted for are predominantly $\geq C_8$ naphthenes and olefins.

Table 2. - Feedstock Parameters

FEED	Elemental Composition (wt%)					MCR (wt%)	H/C (atomic ratio)
	C	H	N	S	O[a]		
Whole >650° F resid	85.03	10.57	1.05	2.42	0.93	13.4	1.481
>650° F neutrals	85.33	11.21	0.44	2.59	0.43	5.81	1.565
>650° F neutrals (85.3 wt%) + 650-1000° F acids (14.7 wt%)	84.81	10.94	0.69	2.39	1.17	5.66	1.537
>650° F neutrals (86.9 wt%) + 650-1000° F bases (13.1 wt%)	85.13	11.04	0.89	2.41	0.53	5.29	1.545

[a] Oxygen by difference.

Table 3. - Compound-type Distribution in Wilmington as a Function of Boiling Range (wt%)[a]

Sample No.	1693	1694	1693/94
Boiling Range, ° F	650-1000	>1000	>650[b]
Acids			
strong	-	11.2	7.4[d]
weak	-	15.5	10.2[d]
total	10.7 ± 0.5[c]	26.7	21.2[e]
Bases			
strong	-	11.7 ± 0.3	7.7[d]
weak	-	9.4 ± 0.1	6.2[d]
total	4.4 ± 0.1	21.1 ± 0.4	15.4[e]
Neutrals			
polar-neutral	2.1 ± 0.1	10.7 ± 0.7	7.7
sulfide	7.3 ± 0.2	10.7 ± 1.0	9.5
nonsulfide	77.3 ± 0.2	33.2 ± 1.3	48.3
total	86.7 ± 0.5	54.6 ± 2.0	65.5
Total	101.8	102.4	102.1

[a] From LC mass balances.

[b] Calculated from data for 650-1000° (34.3 wt% of >650° F) and >1000° F (65.7 wt% of >650° F) boiling ranges.

[c] Uncertainites given are average deviations from duplicate separations.

[d] Includes >1000° F portion only.

[e] Total >650° F acids or bases.

THERMOCHEMISTRY AND THERMOPHYSICAL PROPERTIES OF ORGANIC NITROGEN- AND DIHETEROATOM-CONTAINING COMPOUNDS

Cooperative Agreement DE-FC22-83FE60149, Project BFR3

National Institute for Petroleum and Energy Research
Bartlesville, Oklahoma

Contract Date: October 1, 1983
Funding for FY92: $350,000

Principal Investigator: W. V. Steele

Project Monitor: William D. Peters
Bartlesville Project Office

Reporting Period: July 1 - September 30, 1992

Objectives

To provide, interpret, and correlate with molecular structure and polarity of molecules, precise and accurate values of thermodynamic properties of organic nitrogen and diheteroatom-containing compounds that occur in or are readily derivable from heavy petroleum and oil shale. The results will enable the prediction of chemical equilibria for conceptual as well as current processes.

Summary of Technical Progress

Reports and Publications

Submission of a topical report concerning measurements of the thermodynamic properties of the two 3-ring diheteroatom-containing compounds, phenoxathiin and thianthrene, was delayed to allow completion of the density measurements. Heat-capacity measurements by both adiabatic and differential-scanning calorimetry (DSC), enthalpies of combustion, and vapor pressures by ebulliometry and inclined-piston manometry were completed previously within this project. Final data analysis is progress, and the report will be submitted to the BPO in the coming quarter. (See Density Measurements below.)

Compilation of a status report summarizing research completed within this project in FY92 is in progress.

Density Measurements

Density measurements were completed last quarter for thianthrene between 450 K and near 570 K, and were completed this quarter for phenoxathiin between 348 K and 548 K. The measurement range for phenoxathiin is greater because of the lower melting point (329 K) of that compound. The upper-temperature limit of this new densitometer is presently near 300 °C (573 K) as imposed by the temperature-controlled bath containing the apparatus. The densitometer was designed and built based on a design provided by Dr. J. M. Simonson of Oak Ridge National Laboratory within the DOE project, "Process-Engineering Property Measurements on Heavy Oil Components." Results obtained in that project for several hydropyrenes (1) highlighted the importance of the density measurements, particularly when critical properties cannot be measured due to sample decomposition, as was true for phenoxathiin and thianthrene.

Liquid-phase densities for thianthrene and phenoxathiin were correlated with the corresponding-states equation of Riedel (2), as formulated by Hales and Townsend (3):

$$(r/r_C) = 1.0 + 0.85\{1.0 - (T/T_C)\} + (1.692 + 0.986w)\{1.0 - (T/T_C)\}^{1/3}, \qquad (1)$$

where r_C, T_C, and w are the critical density, critical temperature, and acentric factor, respectively. The acentric factor is defined as $\{-\lg(p/p_C)-1\}$, where p is the vapor pressure at $T_r = 0.7$ and p_C is the critical pressure. Vapor pressures below 3 bar were measured in this research project. The Wagner equation was fit to these vapor pressures, and T_C was adjusted to optimize agreement between the measured densities and those calculated with equation 1. Agreement was optimized when there was no trend with temperature for the percentage differences between the calculated and measured values. Once the percentage difference was adjusted to be nearly constant, the critical density r_C was adjusted to minimize the remaining differences.

Figures 1 and 2 show deviations of fitted densities for thianthrene and phenoxathiin from those calculated with equation 1 evaluated for several different T_C values. Even though the upper-temperature limit of the densities is more than 300 K below the T_C values, the sensitivity to small shifts in the T_C values remains high. The estimated uncertainty for the critical temperatures is approximately 10 K. These materials decompose near 650 K, which is far below their critical temperatures. The estimated T_C values are 920 K for thianthrene and 863 K for phenoxathiin.

Adiabatic Heat-Capacity Calorimetry

Heat-capacity and enthalpy measurements were begun this quarter for the dinitrogen compound 1,10-phenanthroline. Results obtained to date are shown in figure 3. Liquid-phase heat capacities to 450 K as well as final checks of the experimental results will be completed early in the coming quarter. Vapor pressures, densities, enthalpies of combustion, and high-temperature heat-capacities by differential-scanning calorimetry (DSC) are planned.

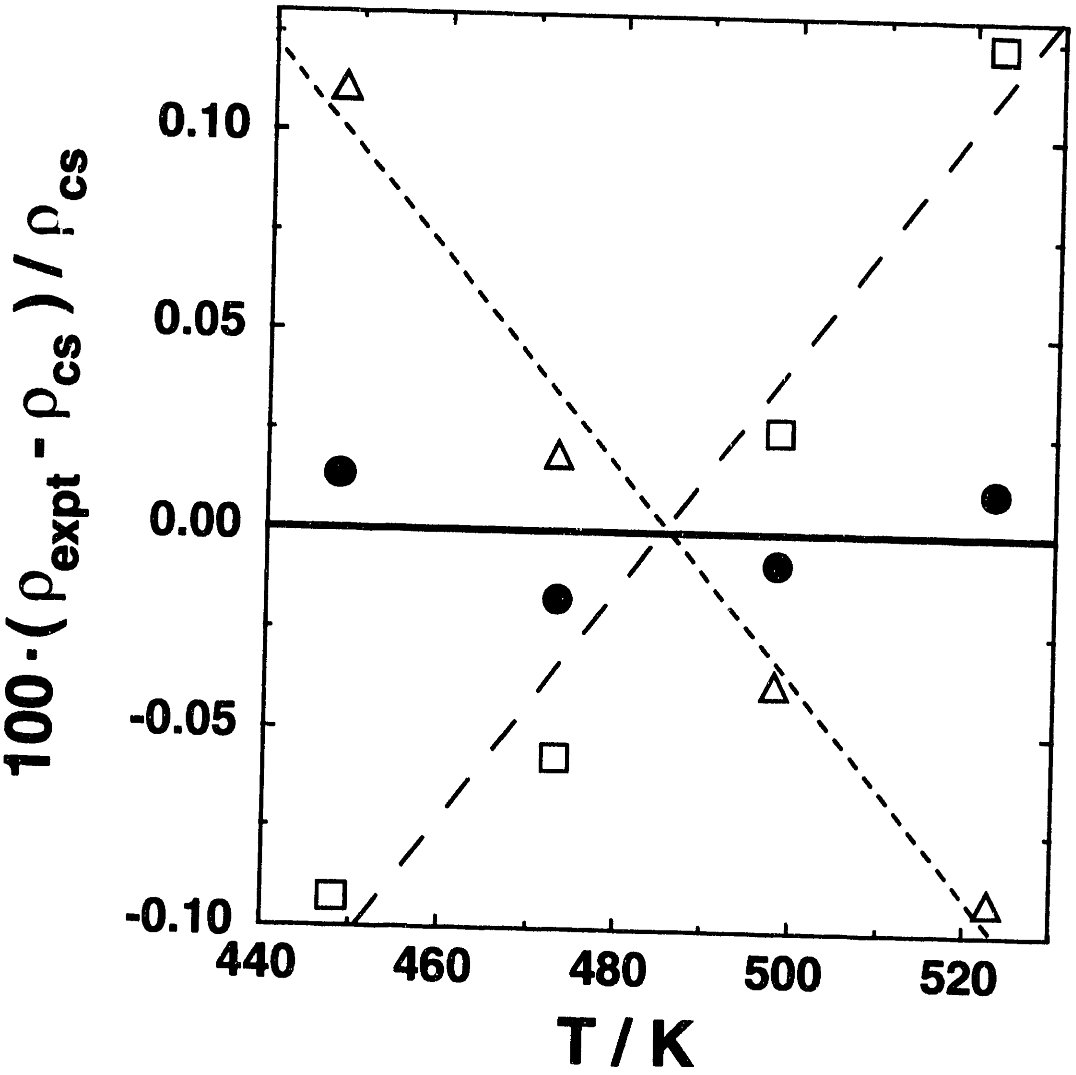

FIGURE 1. Deviation of measured densities r_{expt} for thianthrene from values calculated with corresponding states r_{cs} {equation (1)} for several values of the critical temperature T_C. ●, T_C = 920 K; △, T_C = 940 K; □, T_C = 900 K. The short dashes represent a straight-line fit to the results for T_C = 940 K; long dashes, T_C = 900 K; and uninterrupted line, T_C = 920 K. The estimated uncertainties in the measured densities are 0.1 percent.

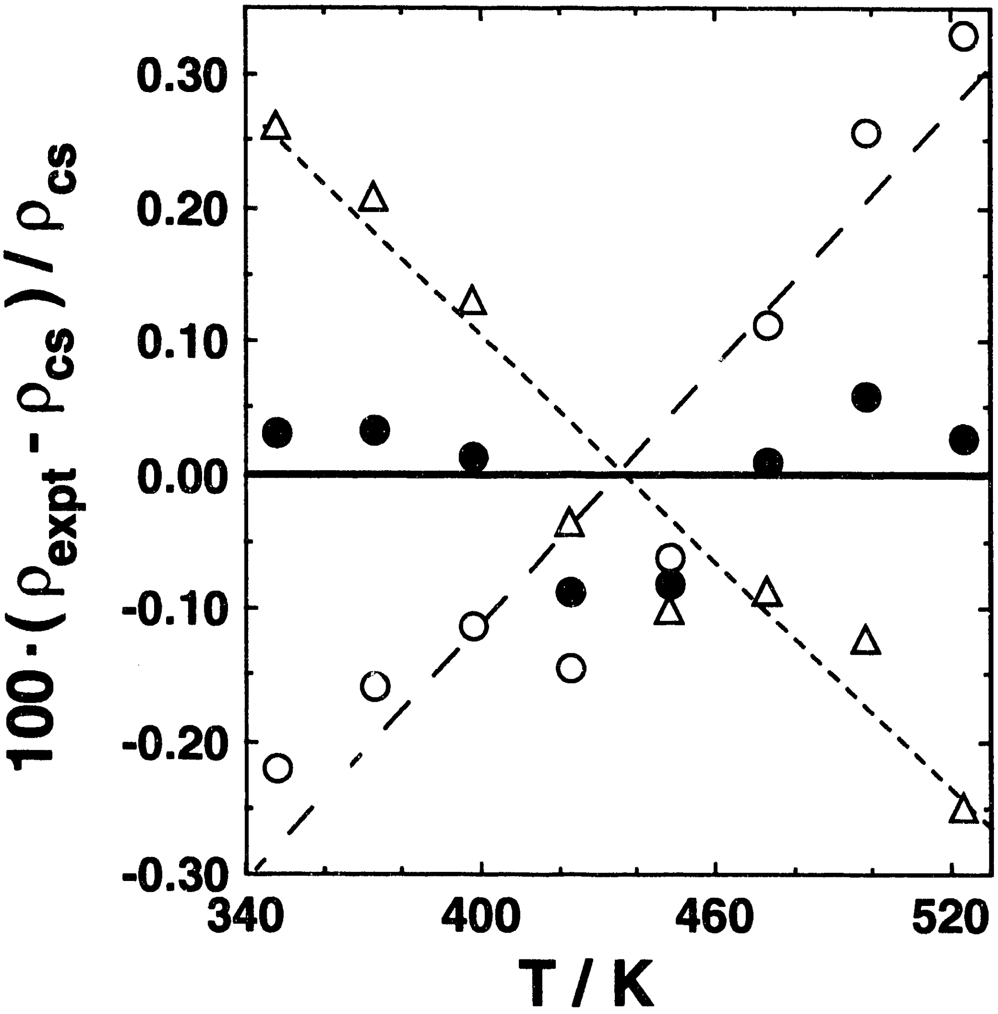

FIGURE 2. Deviation of measured densities r_{expt} for phenoxathiin from values calculated with corresponding states r_{cs} {equation (1)} for several values of the critical temperature T_c. ●, T_c = 863 K; △, T_c = 883 K; ○, T_c = 843 K. The short dashes represent a straight-line fit to the results for T_c = 883 K; long dashes, T_c = 843 K; and uninterrupted line, T_c = 863 K. The estimated uncertainties in the measured densities are 0.1 percent.

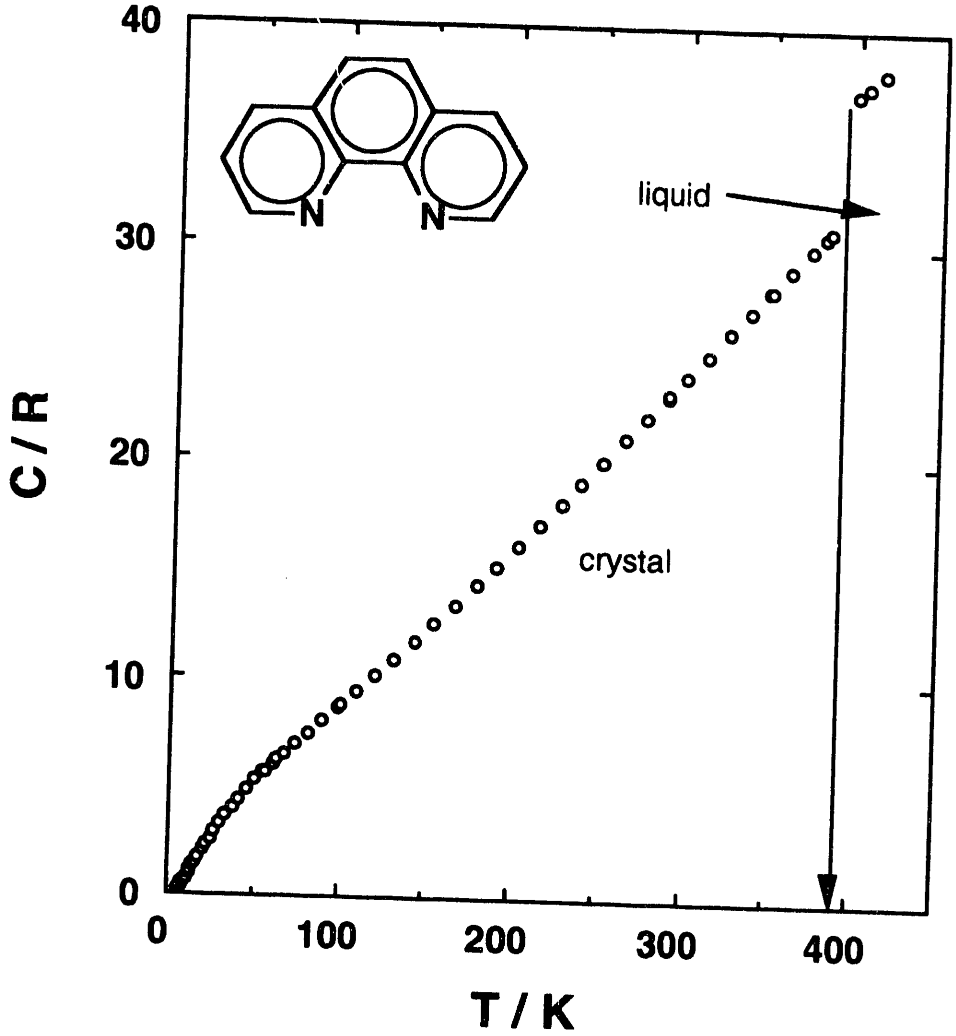

FIGURE 3. Heat-capacity versus temperature by adiabatic calorimetry for 1,10-phenanthroline. The vertical lines indicate phase-transition temperatures.

Vapor-Pressure Measurements

Vapor-pressure measurements were completed this quarter for the 4-ring nitrogen-containing compound benzo[c]carbazole. Vapor pressures were determined with both the inclined-piston apparatus (455 to 520 K; 0.03 to 0.49 kPa) and the ebulliometric apparatus (560 to 637 K; 2.0 to 16.7 kPa). Vapor pressures were determined also for thianthrene with both the inclined-piston apparatus (395 to 495 K; 0.02 to 2.8 kPa) and the ebulliometric apparatus (485 to 639 K; 2.0 to 101.3 kPa).

Experimental information on the methyl and dimethyl pyridines provides the basis for the accurate estimation of properties for nearly all substituted aromatic nitrogen compounds. In the coming fiscal year a major review of all of the thermodynamic properties of the dimethylpyridines is planned. Heat-capacity, density, vapor-pressure, and critical-property results obtained at NIPER will be included.

In this quarter, vapor pressures of 2,3-dimethylpyridine were measured by comparative ebulliometry. A comparison with values obtained at the National Physical Laboratory in England (4) is shown in figure 4. The deviations are small and may result from a combination slightly different experimental procedures and sample purities. The new measurements extend to both higher and lower temperatures than the earlier study.

Critical Properties and High-Temperature Heat Capacities by DSC

Critical temperatures and high-temperature (to near T_C) heat capacities are being determined for the six dimethylpyridines with a DSC. These results will be used to derive reliable critical pressures and critical densities that form the basis for the correlation of many key engineering properties through corresponding-states correlations.

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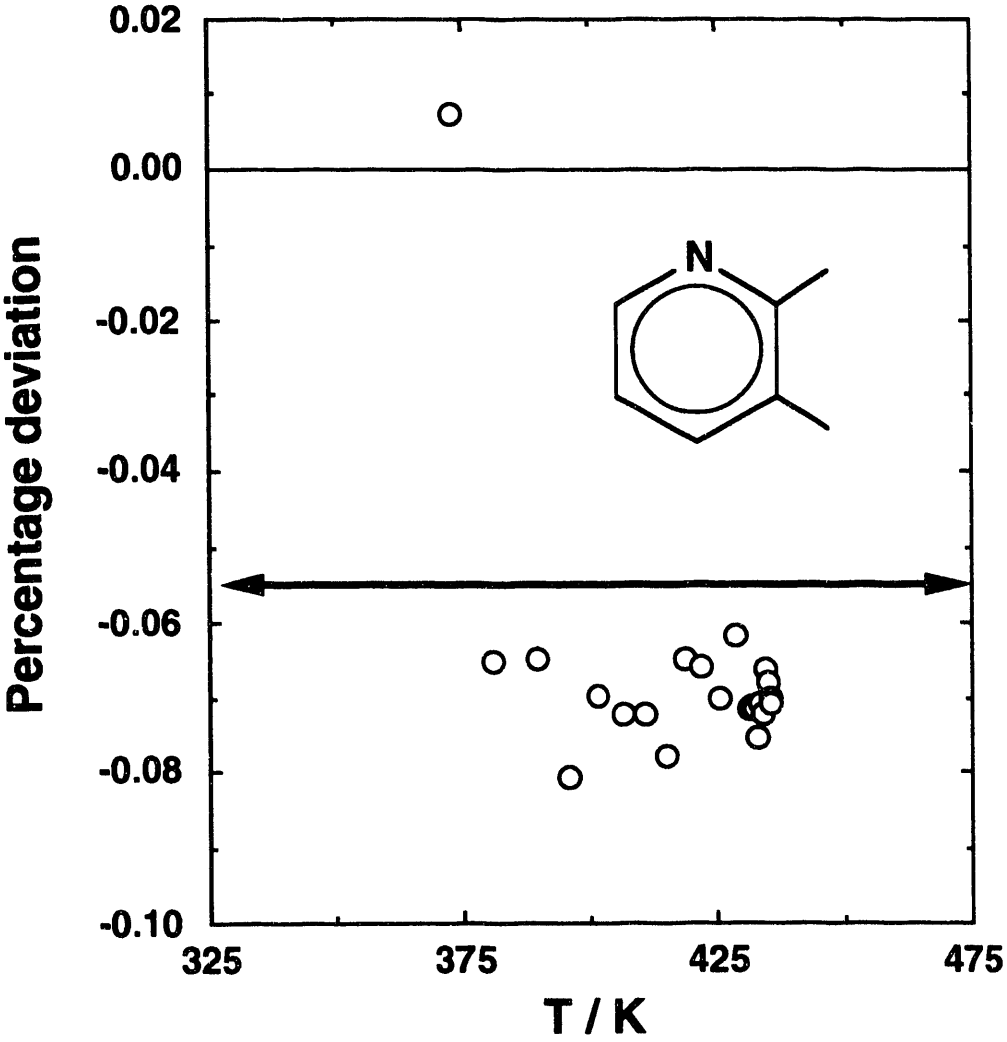

FIGURE 4. Percentage deviation of vapor pressures of 2,3-dimethylpyridine measured at the National Physical Laboratory in England (4) from values determined in this research at NIPER. The double-headed arrow indicates the temperature of the NIPER measurements.

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