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FUELS RESEARCH

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FOREWORD

The Quarterly Technical Report, NIPER-621, is submitted in accordance with the provisions of Cooperative Agreement DE-FC22-83FE0149 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 April 1 - June 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: April 1 - June 30, 1992

Objectives

Generally, to identify compounds or classes of compounds with significant positive or negative effects on crude oil and/or product properties and characteristics and 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

Catalytic cracking experiments with the Wilmington 650°F+ resid and chromatographic fractions thereof were completed. A preliminary survey of the data indicated that material balances and run to run repeatability with the micro-confined bed unit (MCBU) were generally satisfactory. Descriptions of the unit and of the procedures employed were given in the two previous quarterly reports.

Figure 1 shows correlations of microcarbon residue (MCR, ASTM D 4530) versus coke yield for various blends of Wilmington fractions, the whole resid (Wil(W)), neutral fractions (N)
from both Wilmington and Maya resid, and a gas oil (2034GA). Points designated 1693A and 1693B represent blends of the Wilmington 650° F+ neutrals plus 650-1000° F acids and bases, respectively. Points designated 1694SA, 1694WA, 1694SB and 1694WB represent blends of the 650° F+ neutrals with 1000° F+ strong acids, weak acids, strong bases and weak bases, respectively. Points denoted 2034GA + 1693A and 1693B reflected data from blends of the whole 2034 gas oil plus Wilmington 650-1000° F acids and bases. The point designated Wil(W) + 1694SA denotes a blend of the whole resid and 1000° F+ strong acids; that designated BR(W) represents the whole Brass River 650° F+ resid.

The solid line correlation indicated in the figure encompasses feedstocks with minimal acid/base content (2034A, whole Brass River resid, Wilmington and Maya neutrals), whereas the dashed (broken) line correlates feeds with significant acid/base content (whole Wilmington resid, blends of neutrals or 2034GA with acid or base fractions). Two obvious features of the figure are: (1) the relationship between MCR and coke yield is essentially linear for each feedstock group, and (2) the y-intercepts for the two data sets are significantly different. The y-intercept indicates catalytic coke; i.e., coke formed through catalytic interactions from a zero carbon residue feed. As seen in the figure, this parameter is definitely affected by the acid/base content of the feed.

Figure 2 shows the nearly 1:1 correspondence (dashed line denotes true 1:1 correspondence) between MCR data and additive coke yield for each feedstock. The labeling scheme for points in the figure is the same as used in figure 1. Additive coke was calculated as the difference between total and catalytic coke (y-intercepts, figure 1). Through use of the respective values for catalytic coke from feedstocks with and without acids and bases, a single correlation was obtained which is applicable to all feeds. Additive coke yield should relate directly to MCR test results since both reflect non-catalytic high temperature free radical condensation of aromatics to form coke.

Since MCR yield for a blend of components is simply the weighted average of MCR for each component (\(J\)), it should be possible to similarly calculate MCBU additive coke yield for each component in blends depicted in figure 2. Thus, figure 3 illustrates the correlation between MCR yield (directly determined, see reference 1) and calculated additive coke yield for neat chromatographic fractions from Wilmington. The dashed line again denotes a true 1:1 correspondence. Given that the resulting calculated additive coke yield is subject to considerable error, the correlation obtained appears quite reasonable.

The major source of error in the above calculations arises from the relatively small proportion of acids or bases (10-20 wt %) diluted with either the Wilmington 650° F+ neutrals or 2034 gas oil. Thus, the correction for the contribution of either diluent to the observed coke yield for the blend is significant; the remaining additive coke attributable to the acid or base.
fraction carries a relatively high uncertainty since it is essentially a small difference between two relatively large quantities.

The poor agreement in the two points shown in figure 3 for the 1000°F+ strong acids (denoted 1694SA), obtained for blends containing 9 and 17 wt % of the fraction, potentially illustrates the magnitude of error in the calculations. However, some of the difference may result from invalidity of the initial assumption that the coke-make of the blend is simply the weighted sum of the blend components. In the case of the 650-1000°F base fraction (points designated 1693B), different diluents (Wilmington 650°F+ neutrals versus the 2034 gas oil) were used to obtain the points shown. It is not presently known whether the difference in the two results obtained reflects experimental error or effect of the diluent. The result for the whole Wilmington resid calculated from data for each fraction (Wil(W, calc)) agrees well with that determined directly on the resid (Wil(W)). This agreement suggests negligible interaction between components with respect to additive coke formation.

Heteroatom partitioning between gaseous, liquid, and solid (coke) products appears to be dependent on feedstock composition, but has not yet been investigated in detail. Table 1 compares nitrogen and sulfur contents of selected feedstocks and the corresponding liquid products. The ratio of nitrogen in feeds over products varies between 6 and 2, and that for sulfur ranges from 3 to 1.6. For all runs, the balance of the nitrogen carried over into coke (formation of ammonia was negligible), and the bulk of the non-liquid sulfur was in the form of H2S. Thus, the partitioning of each heteroatom may be inferred from the data in the table.

The greatest relative carryover of nitrogen into liquid products occurred during cracking of the blend of Wilmington 650°F+ neutrals plus 650-1000°F acids, while the liquid product from the sulfide-free neutrals retained the largest proportion of feed sulfur. These results are consistent with higher carryover of pyrrolic forms of nitrogen and thiophenic forms of sulfur, respectively, into liquid products. The decreased relative carryover of nitrogen during cracking of higher boiling acid/base fractions is consistent with the propensity of higher boiling nitrogen species to form coke. The comparable levels of sulfur in liquid products from 650°F+ neutrals versus sulfide-free 650°F+ neutrals suggest that much of the sulfur present in sulfide forms in the whole neutrals is converted to H2S.

Liquid chromatographic separation of nominal 650-1000°F distillates for future catalytic cracking work was also completed this quarter. Mass balances for all distillates, including those reported previously, are given in table 2. Inspection of those data reveals that the Wilmington distillate contains approximately twice the concentration of acids and bases as compared to the other distillates, and that the results for the other distillates are quite similar.

A procedure was devised for measuring ammonia content of offgas from MCBU runs. A portion of the gas was bubbled into dilute aqueous sulfuric acid and the resulting ammonium ions
A procedure was devised for measuring ammonia content of offgas from MCBU runs. A portion of the gas was bubbled into dilute aqueous sulfuric acid and the resulting ammonium ions were measured using ion chromatography. As noted earlier, results from all runs indicated negligible ammonia formation (typically 0.1 ppm). Aqueous extractions of liquid products, in an attempt to isolate ammonium sulfide, revealed negligible quantities of ammonia in that form as well. Therefore, it was concluded that feedstock nitrogen partitioned exclusively between liquid and solid (coke) products.

Reference

### TABLE 1. - Nitrogen and sulfur content of MCBU feedstocks and liquid products

<table>
<thead>
<tr>
<th>Feed</th>
<th>Nitrogen, wt %</th>
<th>Sulfur, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>Product</td>
</tr>
<tr>
<td>2034GA</td>
<td>0.16</td>
<td>0.026</td>
</tr>
<tr>
<td>650° F+ Brass River resid</td>
<td>0.16</td>
<td>0.029</td>
</tr>
<tr>
<td>650° F+ Maya neutrals</td>
<td>0.11</td>
<td>0.018</td>
</tr>
<tr>
<td>650° F+ Wilmington neutrals</td>
<td>0.44</td>
<td>0.12</td>
</tr>
<tr>
<td>650° F+ Wilmington neutrals minus sulfides</td>
<td>0.30</td>
<td>0.12</td>
</tr>
<tr>
<td>650° F+ Wilmington neutrals + 650-1000° F acids</td>
<td>0.70</td>
<td>0.34</td>
</tr>
<tr>
<td>650° F+ Wilmington neutrals + 650-1000° F bases</td>
<td>0.89</td>
<td>0.34</td>
</tr>
<tr>
<td>650° F+ Wilmington neutrals + 1000° F + strong acids</td>
<td>0.56</td>
<td>0.17</td>
</tr>
<tr>
<td>650° F+ Wilmington neutrals + 1000° F + strong bases</td>
<td>0.78</td>
<td>0.23</td>
</tr>
</tbody>
</table>

### TABLE 2. - Fraction yields from separation of 650-1000° F distillates

<table>
<thead>
<tr>
<th>Crude</th>
<th>Sample No.</th>
<th>Yield (wt %)(^1)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Acids</td>
</tr>
<tr>
<td>Brass River</td>
<td>3229</td>
<td>4.4 ± 0.1</td>
</tr>
<tr>
<td>Lagomedio</td>
<td>3293</td>
<td>3.5 ± 0.1</td>
</tr>
<tr>
<td>Wilmington</td>
<td>1693</td>
<td>10.7 ± 0.5</td>
</tr>
<tr>
<td>Maya</td>
<td>1740</td>
<td>4.2 ± 0.1</td>
</tr>
<tr>
<td>Mercy</td>
<td>3295</td>
<td>4.9 ± 0.1</td>
</tr>
</tbody>
</table>

\(^1\)Uncertainties given are average deviations from duplicate separations.
Figure 1. Correlation of MCR content versus Total MCBU Coke yield.
Figure 2. Correlation of MCR content versus Additive MCBU Coke yield.
Figure 3. Correlation of MCR content versus calculated additive Coke yield.
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

Density Measurements

Density measurements were completed for thianthrene between 450 K and near 570 K, and are in progress for phenoxathiin. The measurement range for phenoxathiin will be 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 vapor pressure of the standard, water. 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 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 can be correlated accurately with the corresponding-states equation of Riedel (1), as formulated by Hales and Townsend (2):

\[
\frac{n}{n_c} = 1.0 + 0.85\left(1.0 - \frac{T}{T_c}\right) + (1.692 + 0.986w)\left(1.0 - \frac{T}{T_c}\right)^{1/3}
\]

(1)

where \(n_c\), \(T_c\), and \(w\) are the critical density, critical temperature, and acentric factor, respectively. The acentric factor is defined as \(-\log(p/p_c)^{-1}\), where \(p\) is the vapor pressure at \(T_r = 0.7\) and \(p_c\) is the critical pressure. Accurate vapor pressures below 3 bar are measured routinely for all compounds in this research project. The Wagner equation is fit to these vapor pressures, and \(T_c\) can be adjusted to optimize agreement between the measured densities and those calculated with equation 1. Agreement is optimized when there is no trend with temperature for the percentage differences between the calculated and measured values. Once the percentage difference is adjusted to be nearly constant, the critical density \(n_c\) can be adjusted to minimize the remaining differences.

Figures 1 and 2 show deviations of fitted densities from those calculated with equation 1 for two hydropyrenes studied within another DOE project. The hydropyrenes decompose near 650 K, which is far below their critical temperatures, which are near 900 K. The deviations shown in figure 2 were obtained once the critical temperature for each compound was adjusted higher by only 15 K. Thus, measured densities over a wide temperature range provide a valuable tool in the estimation of critical properties even for compounds that decompose far below their critical temperatures. In the cases shown in figures 1 and 2, the upper-temperature limit of the densities is more than 300 K below the \(T_c\) values, yet the sensitivity to small shifts in the \(T_c\) values remains high.

**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, is 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.

**Adiabatic Heat-Capacity Calorimetry**

Heat-capacity and enthalpy measurements were finalized this quarter for two diheteroatom compounds: isoxazole (5 to 380 K) and phenazine (5 to 520 K). The heat-capacity versus temperature curves are shown in figures 3 and 4. Vapor pressures, densities, the enthalpy of combustion, and high-temperature heat-capacities by DSC were determined for isoxazole within
a separate industrially sponsored project. Preparations for these measurements for phenazine within this DOE project are in progress.

A preliminary comparison for isoxazole between the ideal-gas entropies derived from the calorimetric results and those derived from spectroscopic analysis and statistical thermodynamics shows a near constant difference between the values, which is outside the expected uncertainty in the measurements. It has been postulated by Dworkin (3) that nearly all molecules comprised of five-membered rings (thiophene, furan, cyclopentene, thiazole, etc.) retain disorder in their crystal structures to 0 K and, consequently, retain a zero-point entropy. A review of the calorimetry and spectral analysis for these materials is under way within a NIPER project for the Office of Energy Research.

References
FIGURE 1. - Deviations of measured densities for two hydropyrenes from those calculated with the corresponding-states correlation, equation 1.

FIGURE 2. - Deviations of measured densities for two hydropyrenes from those calculated with the corresponding-states correlation, equation 1. The estimated critical temperature is 15 K higher than that used to derive the deviations shown in figure 1.
FIGURE 3. - Heat-capacity versus temperature by adiabatic calorimetry for phenazine. The vertical lines indicate phase-transition temperatures.
FIGURE 4. - Heat-capacity versus temperature by adiabatic calorimetry for isoxazole. The vertical lines indicate phase-transition temperatures.
END

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12/4/92