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FOREWORD

The Quarterly Technical Report, NIPER-501, 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 to September 30, 1990.
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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 FY 1990: $300,000

Principal Investigator:
John Green

Project Monitor:
William D. Peters
Bartlesville Project Office

Reporting Period: June 1 - September 30, 1990

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 FY90 are: 1) to determine relative carbon-forming (coking) tendencies of compound classes in petroleum and to relate coke yield and heteroatom content to chemical structure, 2) to develop procedures for breaking associates formed between metal- and nonmetal-containing compounds which will ultimately lead to methods for isolation and identification of metal-containing compounds in petroleum, and 3) to further develop mass spectrometric methods for analysis of acidic compounds in petroleum.
Summary of Technical Progress

One status and two topical reports were completed and delivered to BPO this quarter. Their titles, report numbers and summary sections are reprinted below.

TOPICAL REPORT
NIPER-491

COKING TENDENCIES OF COMPOUND TYPES IN VACUUM RESIDS

ABSTRACT

Five vacuum resids from petroleums spanning a wide range of physical properties and refining characteristics were separated into compound types using liquid chromatographic methods. The microcarbon residue (MCR, ASTM D 4530) yields of the whole resids and their fractions were determined in addition to partition ratios for N and S between the MCR solid versus volatiles. MCR yield correlated well with the atomic H/C ratio for all resids and their fractions. Also, the sum of MCR yields for chromatographic fractions corresponded well with that of each whole resid. Thus, carbon deposition is simply a function of H/C and is largely independent of detailed chemical structure. Sulfur partitioning into MCR solids versus volatiles correlated well with solid yield but poorly with sulfur content of whole resids or their fractions. Also, the weighted sum of sulfur partition ratios for fractions agreed with those of the corresponding whole resids. Nitrogen partitioning was much more dependent on composition than sulfur. Partition ratios of fractions could not be correlated with those of whole resids, MCR solid yield, or nitrogen content of the fraction. In general, acidic forms of nitrogen (e.g., benzologs of pyrrole) deposited into the MCR solid to a greater degree than basic forms (e.g., benzologs of pyridine).
TOPICAL REPORT
NIPER-473

RETENTION INDICES, RELATIVE RESPONSE FACTORS, AND
MASS SPECTRA OF TRIFLUOROETHYL AND HEPTAFLUOROBUTYL ESTERS
OF CARBOXYLIC ACIDS DETERMINED BY CAPILLARY GC/MS

ABSTRACT

The GC/MS characteristics of carboxylic acid esters prepared from
fluorine-containing alcohols were compared to those of methyl esters. The GC
retention of 2,2,2-trifluoroethyl (TFE) esters was less than, and 2,2,3,3,4,4-
heptafluoro-1-butyl (HFB) esters approximately equivalent to that of methyl
esters. The peak shape of both TFE and HFB esters was slightly superior to
that of methyl esters. Mass spectra of TFE and HFB aliphatic esters show
significantly more intense molecular and key fragment ions than those of
methyl esters. Also, owing to their significantly higher molecular weights,
TFE or HFB ester molecular ions and most fragment ions of interest occur at
significantly higher m/z values than most potential interfering ions.

The GC retention indices, relative GC/MS total ion current response
factors, and 70 ev electron impact mass spectra of about 70 TFE and 70 HFB
carboxylic acid esters are reported. Results from analysis of a TFE/HFB
esterified petroleum carboxylic acid concentrate are discussed in detail.

STATUS REPORT
NIPER-477

DEVELOPMENT OF TECHNIQUES FOR DECOMPLEXATION, ISOLATION,
AND CHARACTERIZATION OF METALS COMPLEXES IN CERRO NEGRO 700° C+
ACID-BASE-NEUTRAL FRACTIONS

CONCLUSIONS

A preparative scale HPLC separation has been developed that gave vanadium
(V) (porphyrin and total metal) concentrates from a 700° C + resid Cerro Negro
neutrals fraction. This separation used a NIPER custom-designed (pyridyl)
packing which has an affinity for porphyrins. Two fractions contained 87.8%
of the porphyrinic V and 73.6% of the total V, indicating that the pyridyl
packing was successful in concentrating the V porphyrins. The concentration
of total V into these two fractions suggests that the "nonporphyrinic" V
complexes may be porphyrinic in nature but without absorbance in the visible
spectrum.
An attempt to further concentrate the V porphyrins using an amine column was unsuccessful. Recovery was poor and no great concentration of V porphyrins was achieved.

Using the same pyridyl column, a similar separation was developed for the Cerro Negro 700°C + resid weak acid fraction. The results of this fractionation have not been completely evaluated because of incomplete analytical data. Vanadyl porphyrins were found in three of six fractions despite the fact that none were detected in the original weak acid fraction. This confirms that some of the V in the weak acid fraction was in porphyrinic form but was not detected by UV-VIS measurements.

The hydrogenation of a Cerro Negro 700°C+ strong acid fraction resulted in the appearance of VO (Vanadyl) porphyrins that were not previously detected in this fraction. The mechanism for this reaction is not known. The Wilmington and Mayan fractions and the Cerro Negro weak acid fraction showed no porphyrins after hydrogenation. The results from the other Cerro Negro fractions were inconclusive.
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

Topical Report NIPER-482, "The Thermodynamic Properties of 2-Aminobiphenyl (An Intermediate in the Carbazole/Hydrogen Reaction Network)" (1), was completed. This is the first in a series of reports on the thermodynamics of hydrodenitrogenation of three-ring compounds. The executive summary and conclusions are reproduced here.

"Catalytic hydrodenitrogenation (HDN) is a key step in upgrading processes for conversion of heavy petroleum, shale oil, tar sands, and the products of the liquefaction of coal to economically viable products. Organic
nitrogen and sulfur are commonly removed via reaction at 300 to 400 °C and 50 to 150 atm. of hydrogen. Under these severe conditions, hydrogen is consumed not only in breaking carbon-nitrogen and carbon-sulfur bonds, but also in saturating aromatic components in the feed. Hydrogen consumption in excess of 1500 scf/bbl (standard cubic feet per barrel) is common in hydrotreating shale oil, while the amount theoretically required for selective heteroatom removal is only about 600 scf/bbl. The problem is exacerbated as the number of rings in nitrogen and sulfur-containing molecules is increased. Hence, the saving in expensive hydrogen could be enormous, if a process for denitrogenation without saturation of the aromatic rings in the feedstock could be developed.

"This research program, funded by the Department of Energy (DOE) Office of Fossil Energy, Advanced Extraction and Process Technology (AEPT), provides accurate experimental thermochemical and thermophysical properties for "key" organic nitrogen-containing compounds present in the range of alternative feedstocks, and applies the experimental information to thermodynamic analyses of key HDN reaction networks (e.g., quinoline/hydrogen, indole/hydrogen, acridine/hydrogen, etc.) Thermodynamic analyses, based on accurate information, can be used to set the boundaries (e.g., temperature range, pressure range, etc.) for efficient processing of materials, and to provide insights for the design of cost-effective methods of nitrogen removal.

"Previous reports by this research group have discussed the two-ring systems; indole/H₂ and quinoline/H₂. This report is the first in a series that will lead to an analysis of a three-ring HDN system; the carbazole/hydrogen reaction network. 2-Aminobiphenyl is the initial intermediate in the HDN pathway for carbazole, which consumes the least hydrogen possible. In this report, thermodynamic-property measurements for this molecule are detailed, and the results are used in thermodynamic calculations to compare the feasibility of the initial hydrogenolysis step in the carbazole/H₂ network with that of its hydrocarbon and oxygen-containing analogues; i.e., fluorene/H₂ and dibenzofuran/H₂."
"Results of the thermodynamic calculations are compared with those of batch-reaction studies reported in the literature. The "crossover temperature" concept is shown to be a valuable tool in the interpretation of the reaction-study results, and the thermodynamic calculations and reaction studies are found to be in accord. For the hydrodenitrogenation of carbazole the reaction pathway using the minimum of hydrogen (carbazole + 2-aminobiphenyl + biphenyl) cannot probably be realized, but the pathway (carbazole + 2-aminobiphenyl + 2-phenylcyclohexylamine + cyclohexylbenzene) should be possible with proper catalyst selection.

"The report concludes that if minimization of hydrogen consumption is the goal of hydroprocessing of liquids containing compounds with carbazole and/or dibenzofuran moieties present, then catalysts other than those used in present refineries will be required. However, as was noted in the previous topical report on the hydrodenitrogenation of quinoline (NIPER-468), the presence of sulfur compounds in the processing liquid will restrict the operation of such a catalyst. Upgrading of such liquids will require new processing technology such as "Staged Upgrading." "Staged Upgrading" as used in this context is where different compound types are removed under conditions which favor their individual removal. For example, remove sulfur compound types first followed by nitrogen compound types under a completely different set of conditions of catalyst, hydrogen pressure, and temperature. This concept will be the subject of a future topical report from this group."

The highlights listed in the report were:

- Thermochemical and thermophysical properties for 2-aminobiphenyl are reported. The properties measured included an energy of combustion, and vapor pressures and heat capacities over an extended range of temperatures. Gibbs energies of formation for equilibria calculations were derived.
• Values for the critical properties of 2-aminobiphenyl were determined. The results, which illustrate the inherent thermal stability of the amine, are the first such experimental measurements reported for a 2-substituted biphenyl.

• Ideal-gas thermodynamic properties for 2-aminobiphenyl were determined based on the accurate calorimetric measurements. No previous calorimetric measurements on this important hydrodenitrogenation intermediate have been reported in the literature.

• Thermodynamic equilibria calculations were made on the carbazole/2-aminobiphenyl/hydrogen system and the results compared with those for the fluorene/2-methylbiphenyl/hydrogen and the dibenzofuran/2-hydroxy-biphenyl/hydrogen systems. The results give the following reactivity order for of ring-opening (hydrogenolysis) reaction:

  carbazole < fluorene < dibenzofuran.

• The thermodynamic equilibria results are confirmed by batch-reaction studies reported in the literature. For the hydrodenitrogenation of carbazole the reaction pathway using the minimum of hydrogen (carbazole + 2-aminobiphenyl + biphenyl) cannot probably be realized but the pathway (carbazole + 2-aminobiphenyl + 2-phenylcyclohexylamine + cyclohexylbenzene) should be possible with proper catalyst selection. The literature results confirm the minimum hydrogen pathway for fluorene. For dibenzofuran, the literature results confirm the possibility of the minimum hydrogen usage pathway using an oxide based catalyst. On an oxide catalyst the selectivity for two-ring products (biphenyl and cyclohexylbenzene) was >75 percent.

• If minimization of hydrogen consumption is the goal of hydroprocessing of liquids containing compounds with carbazole and/or dibenzofuran moieties present, then catalysts other than those used in present refineries will be required. However, as was noted in our previous Topical Report on the hydrodenitrogenation of quinoline, the presence of sulfur compounds in the processing liquid will restrict
Adiabatic Heat-Capacity Calorimetry

Following completion of heat-capacity and enthalpy measurements reported earlier this fiscal year on thianthrene, the calorimeter suspension system was modified, and a Kevlar cord was installed in place of the stainless steel chain used previously. This modification eliminated problems with slow equilibration of the calorimeter. The system was recalibrated in preparation for measurements on a four-ring nitrogen-containing heterocyclic compound.

Vapor-Pressure Measurements

Vapor-pressure measurements were determined ebulliometrically for benzoxazole (347-502 K; 2.0-270 kPa) in the third quarter of FY90. In the fourth quarter, the inclined-piston gauge was used to measure vapor pressures of the liquid to the triple-point temperature, as well as vapor pressures of the solid and supercooled liquid. Through application of the Clapeyron equation, these measurements (in combination with earlier heat-capacity results) will provide a rigorous test of the NIPER procedures for the measurement and calculation of sublimation pressures. This type of measurement will become increasingly important to this program as molecules of continuously higher molecular weight are studied.

References

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