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QUARTERLY TECHNICAL PROGRESS REPORT
FOR THE PERIOD
JANUARY 1 THROUGH MARCH 31, 1989

Development of Analytical Procedures for Coprocessing

by

J.W. Vogh
R.P. Anderson

Work Performed Under Contract DE-AC22-88PC88810

Prepared for the
U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

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SUMMARY

Coprocessing of coal with petroleum resid is a promising method for conversion of these low-grade materials to more easily refined liquids. As the supply of high quality petroleum diminishes and the use of lower grades of crudes increases, coprocessing could provide the means to convert the increasing amounts of resid to useful products and to initiate the utilization of coal for the production of distillate fuels.

This is the second quarterly technical report for a project designed to extend our understanding of coprocessing reactions. More specifically, this research is concerned with development of chemical analytical procedures needed to distinguish between materials and compound classes in the coprocessing products which are derived from the petroleum resid, the coal, or both. This project will provide new information on the structure of products derived from coprocessing and will aid in identification of the reaction mechanisms that affect conversion.

Carbon isotope ratios have been used to determine the relative contributions of coal and resid to various coprocessing fractions where the fractions were produced by distillation or solubility fractionation. In the current project, the carbon isotope technique will be utilized with chemical compound type fractionations which have been developed at NIPER. These comprehensive separation schemes have been extensively applied to petroleum but not to coprocessing products. These separation techniques will be used initially with coprocessing samples produced in-house with a 2-liter batch autoclave. Later in the project, these techniques will be applied to samples produced on process development units operated by other DOE contractors.

Materials selected for initial study were Maya >1000° F resid and Illinois #6 coal. Catalyst was introduced by aqueous impregnation of the coal with ammonium tetrathiomolybdate solution. Conditions for satisfactory conversion have been established and workup procedures have been developed. Runs with 20, 30, and 40 percent coal loadings were completed this quarter.

Initial carbon isotope results with the 20 percent coal run suggest a substantial isotope fractionation in the coprocessing reaction ($\delta^{13}C$ for hydrocarbon gases much more negative than for the coal, resid, or liquid products).

INTRODUCTION

Coprocessing of petroleum residuum and coal has attracted interest as a method for production of improved and more easily refined liquids. Although much has been accomplished in development of quality products and high yields, more information is needed on the specific contribution of coal and residue to the compound classes found in the products. Characterization methods developed at NIPER can provide detailed information on the composition of material such as petroleum and syncrudes. In addition to this, carbon isotope analysis can provide information on the contribution of coal and residue to the class fractions isolated from the coprocessing products.

The goal of this project is development of procedures by which the products of coal and residue individually in the coprocessing liquid may be determined. Some evidence of isotopic selectivity in coprocessing reactions has been demonstrated (1). Although this interferes somewhat with interpretation of isotope ratio results, samples prepared over a range of coal and residue compositions should help in determining the course of reaction. The products of coal liquefaction and petroleum residuum conversion show both similarities and compound classes unique to each. Products specific to coal or residue reactions will be present in amounts proportional to the composition of the reaction mix. This may change if the reactions of either is strongly affected by the presence of the other.

Coprocessing procedures have been shown to produce useful liquid products from various petroleum residues and coals. This project is intended to provide information on certain important aspects of coprocessing reaction chemistry. One uncertainty is the amount of useful product derived directly from the coal in the final product. While it is clear that coal does contribute to the liquid products, it is desirable to demonstrate that the amounts are adequate in relation to quantity of coal consumed. Also, the quality of the liquid product as related to refining operations is partly affected by the choice of residue and coal for the reaction. There will generally be more freedom of choice in selection of coal than of petroleum residue for the coprocessing reaction. Therefore, a clear understanding of the components derived from the coal could aid in a selection best suited for the ultimate processing of the liquid products.

EXPERIMENTAL

The plan of the project was described in detail in the first Quarterly Report. In brief, the reactions are based on Maya crude residuum, bp >1000° F, and Illinois No. 6 coal. All reactions are carried out at 445° C for one hour. The initial hydrogen pressure (cold) is 1800 psi and total pressure is maintained at no less than 3000 psi during the reaction period. Molybdenum catalyst is present in all reactions at a level of 0.1 weight percent Mo. It is added by impregnation of the coal with an aqueous solution of ammonium tetrathiomolybdate. The only variable in the reaction procedure is the content of coal in the reaction mixture. The values selected for preparation of coprocessing products are 2, 20, 30, and 40 percent coal loading. The first value represents an approximation of the reaction blank but contains some coal so as to produce the catalytic effect of coal ash as well as to provide a method of introducing the Mo catalyst. The other coal composition values encompass the usual range of coprocessing reactions.

The reactions are carried out in Hastalloy stirred batch autoclave having a capacity of 2 liters. A total of 667 grams of residue and coal are used in each reaction plus 1.8 grams of $(NH_4)_2MoS_4$ which is deposited on the coal. Methyl disulfide (0.5 mL) was added to the mixture in the autoclave to insure sulfiding of the catalyst. The amount of reactants was limited to this quantity on the basis of previous experiments that showed inadequate hydrogen partial pressure at greater autoclave loadings.

After the reaction is completed and cooled to room temperature, the gases are sampled to determine composition and to obtain material for isotope analysis of the hydrocarbons and carbon dioxide. Gas volume is determined by a volumetric meter. Cold traps at 0 and -80° C are attached to the autoclave and condensate is collected under vacuum. The liquid and solid products are transferred from the autoclave to a pressure filter equipped with a glass fiber membrane. Filtration is accomplished at 80° C under nitrogen at 20 psig. Solids obtained from the filtration are dispersed in tetrahydrofuran and refiltered. The tetrahydrofuran soluble material is recovered by evaporation of the solvent and the dry solids are obtained by air drying the insoluble material. The filtrate from the pressure filter represents the major part of the coprocessing products.

The light hydrocarbons and other gases are analyzed by gas chromatography. These analyses are carried out on a dual column system consisting of Poropak-T and molecular sieve columns. Hydrogen and the hydrocarbons are determined using argon as carrier and both thermal conductivity and flame ionization detectors. Carbon dioxide and hydrogen sulfide are determined in the same system using helium as carrier and the thermal conductivity detector alone. To collect samples of the hydrocarbons and CO_2 for carbon isotope analysis, the gas collected from the autoclave is passed through a series of scrubbers and traps for isolation of these components. Hydrogen sulfide is precipitated by a buffered copper acetate solution in the first scrubber in the train. Carbon dioxide is then collected in potassium hydroxide solution and precipitated as barium carbonate when collection is completed. Special care is taken to avoid contamination of the carbonate sample with atmospheric CO_2. Prior to CO_2 collection, a small quantity of barium hydroxide is added to the KOH solution and the mixture then centrifuged to remove carbonate impurity. This solution is then quickly transferred to a scrubber bottle under a stream of helium and kept under helium until the sample collection is started. After the collection is completed, an excess of barium chloride is added to precipitate the carbonate. The solution is then rinsed out of the bottle through the gas dispersion frit with several additions of freshly boiled water until the washings are neutral. The $BaCO_3$ is then filtered and dried.

The hydrocarbons are trapped and partially separated from hydrogen by condensation at liquid nitrogen temperature in two metal traps, the first empty and the second containing activated charcoal. The larger part of the hydrogen passes on through the collection system to waste. The hydrocarbons (primarily methane) are transferred to evacuated steel cylinders by warming the traps to room temperature. Sufficient hydrocarbons are collected to develop a pressure of 150 to 250 psi in the cylinders.

RESULTS AND DISCUSSION

Three coprocessing reactions were carried out during this reporting period. Runs at 20, 30, and 40 percent coal loading were conducted under the conditions described above and in the previous Quarterly Report. Table 1 contains yields determined for major fractions and some of the components of the products. These yields are expressed as percent of the total coal + resid charge. Conversion data, yields on a moisture and ash-free basis, and yields of distillate and soluble + 1000° F residue will be reported following completion of distillations during the next quarter.

TABLE 1. - Yields of Coprocessing Products, Weight Percent

	20% Coal	30% Coal	40% Coal
CH_4	2.2	2.0	2.9
C_2-C_7	1.9	2.6	4.0
CO_2	0.1	0.3	0.6
H_2S	1.2	1.7	2.3
Condensate	3.3	7.3	3.0
Filtrate	63.6	66.1	62.3
THF Soluble	12.3	8.1	12.7
Dry Solids	4.8	6.1	8.5
Total	89.4	94.2	96.3

Yields of the gaseous products were determined from the composition determined by gas chromatography and the volumes of gas received in each run. Table 2 shows gas compositions for each of the runs. Both Tables 1 and 2 show a strong trend of carbon dioxide and hydrogen sulfide levels with coal loading. Also, Table 1 shows levels of C_2-C_7 hydrocarbons approximately proportional to coal loading.

The liquid and solid products were filtered under nitrogen pressure at 80-90° C. As shown in Table 1, the liquid filtrate was the major product from each reaction. The wet solids remaining in the filter contained some semi-solid pitch that was extracted with tetrahydrofuran. This was identified as THF soluble in Table 1. The remaining solids are granular, and are presumed to be a mixture of coal mineral matter, coal-derived insoluble organic matter, coke products of the reaction (either from coal or petroleum) and catalyst.

TABLE 2. - Gas Product Composition, Percent

	20% Coal	30% Coal	40% Coal
Hydrogen	61.27	54.22	30.28
Methane	21.54	21.05	30.41
Ethane	5.38	6.81	10.42
Propane	2.03	3.22	5.03
Butanes	0.55	0.99	1.60
Pentanes	0.15	0.28	0.47
Hexanes	0.04	0.09	0.14
Heptanes	0.01	0.02	0.03
CO_2	0.44	0.95	2.23
H_2S	5.37	8.35	11.25

Table 3 shows results of carbon isotope analysis for the products of the 20 percent coal reaction and for the coal and residue reactants. On the basis of the isotope ratios and the carbon elemental values of the coal and residue, the mean value for the reactant mix should be about $\delta^{13}C = -27.07$. It can be seen that all liquid and solid products are more positive than this with the major product, the filtrate, showing the greatest difference. The hydrocarbon gases are much more negative, indicating substantial isotopic fractionation. This gas sample was collected by partial condensation under cryogenic conditions and was composed of about 75 percent methane and the remainder C_2 to C_4 hydrocarbons. These light hydrocarbons represent about 4 percent of the total products.

TABLE 3. - Carbon Isotope Ratio Results, 20% Coal Reaction

Fraction	$\delta^{13}C$, PDB, o/oo
Hydrocarbon Gases	-37.60
CO_2	-18.87
Liquid Filtrate	-26.17
THF Soluble	-26.85
Dry Residue	-26.38
Maya Crude >100° F	-27.56
Coal, IL No. 6	-24.56

The δ value for carbon dioxide is significantly more positive than the reactant mix. Efforts were made to eliminate carbonate impurity in the potassium hydroxide absorbant and to avoid contact with atmospheric CO_2. The nominal $\delta^{13}C$ value for atmospheric CO_2 is about -7, indicating that the observed value could have been caused by air contamination. However, it may also indicate origin of the CO_2 by such means as thermal decomposition of mineral carbonates in the coal ash.

The carbon isotope ratio results suggest a substantial isotope fractionation in the coprocessing reactions. This may cause problems in interpretation of a single reaction product composition but it is expected that trends determined over the reaction conditions being prepared will define the contributions of coal and residue.

REFERENCES

1. Burke, F. P., R. A. Winschel, and M. S. Lancet. Stable Carbon Isotope Analysis of Coprocessing Materials Quarterly Technical Progress Report, July-September 1988, Consolidation Coal Co., DOE/PC88800-6.