

CHARACTERIZATION OF RESIDUUM FRACTIONS
PREPARED BY FRACTIONAL DESTRUCTION

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ABSTRACT

Fractionation with supercritical fluids, termed fractional destruction, is being developed at the Pittsburgh Energy Technology Center (PETC) for use on liquefaction residua. In this process, the density of a supercritical fluid is used to promote reflux in a manner analogous to temperature in a conventional distillation. This paper presents elemental, spectroscopic, and chromatographic analyses of residuum fractions prepared by this method. Emphasis is on the use of liquid chromatography as a relatively rapid method for obtaining important characterization data, such as molecular weight and chemical functionality. Such data are necessary for monitoring the daily operation of the Fractional Destruction Unit at PETC.

INTRODUCTION

Characterization of fossil fuels by distillation is limited in application to the extent that nonvolatile components occur in the fluid. For complex fluids such as those derived from heavy crude oils, tar sands, shale oil, or coal, more than half of the fluid may be nonvolatile residuum (1). To overcome this limitation, PETC is currently developing a supercritical-fluid-based fractionation process. The process is termed either fractional destruction (2) or supercritical distillation (3). Using this procedure, a residuum may be fractionated according to the solubility of its constituent components in the supercritical fluid. The novel aspect of this approach is the incorporation of a system to promote a reflux of the less-soluble components onto a packed bed. The liquid reflux is caused by increasing the temperature of the fluid phase at constant pressure, thereby decreasing the density of the supercritical fluid and its carrying capacity for residuum. The use of reflux results in rectification of the residuum in a manner analogous to conventional distillation (2, 4). At PETC an experimental unit has been constructed to operate in this manner and has been used to fractionate coal-derived distillate and residuum (4, 5). This unit is called the Fractional Destruction Unit (FDU). The purpose of this report is to present chemical, chromatographic, and spectroscopic characterization data for a set of coal-derived residuum fractions prepared by this process.

Operation of the FDU required the development of appropriate analytical methods to monitor the fractionation of residuum. Procedures common to conventional distillation, such as GC-simulated distillation, are limited to distillates; and more sophisticated analytical techniques, such as field ionization mass spectrometry, are too time-consuming and expensive to use on a daily basis. To overcome these difficulties, liquid chromatographic procedures previously developed for distillable coal-derived materials were adapted for use with residuum. The object of this report is to present the chromatographic characterization data and the corresponding chemical and spectroscopic results for a set of coal-derived residuum fractions prepared by the fractional destruction process.

EXPERIMENTAL

Residuum Fractionation

The FDU basically consists of two major components: (a) the fractional destruction vessel (FDV) where the supercritical fluid and residuum come in contact; and (b) a separator that subsequently disengages the residuum from the solvent in the overhead stream from the FDV (5). The novel feature of the FDV is an integral column in which reflux is generated by means of a hot finger onto a packed bed. In the work reported here, 1000 g of residuum from the Wilsonville Advanced Coal Liquefaction Test Facility was fractionated using cyclohexane ($T_C = 553.4$ K, $P_C = 4.074$ MPa) as the supercritical fluid. This residuum was collected from the T102 vacuum distillation tower during Run 242. The run was made in a Short-Contact-Time Integrated Two-Stage Liquefaction mode using Illinois No. 6 coal from the Burning Star mine (6). During the time this sample was collected, the T102 vacuum tower was operated at 594 K and 3.4 KPa. The cyclohexane was obtained in drum quantities at greater than 99 percent purity and used as received.

Figure 1 summarizes the fractionation in terms of the residuum concentration in the overhead as a function of the extent of destruction. The residuum concentration value was calculated from the amount of residuum brought overhead and the amount of cyclohexane pumped through the FDV during that collection period. Most of the points in this figure represent 30-minute collection periods. The total time on stream was 19.06 hours, which spanned three working days. The gaps in the line in Figure 1 indicate the points at which the fractionation was terminated by shutting the FDU down at the end of each working day.

In the FDU, the residuum charge was contacted with cyclohexane at a T_r , or T/T_C , of 1.02 and a P_r , or P/P_C , of 1.3. An initial temperature difference of 60 K between the extraction section and the reflux section of the apparatus was established to promote reflux. As shown in Figure 1, this resulted in an initial overhead concentration of approximately 2.4 gram residuum per g-mole of cyclohexane. By contrast, the overhead concentration of residuum in the absence of reflux, i.e., isothermal operation, is approximately five times greater. Six fractions were collected as indicated in Figure 1. As the overhead concentration of residuum decreased, the temperature difference across the FDV was reduced to increase the density in the reflux section and thus permit more residuum in the overhead stream. During collection of the final fraction, the temperature in the reflux section was the same as that in the extraction zone.

Owing to inefficiency in the separator, some of the residuum brought overhead is collected with the spent solvent. This material is recovered by distilling the solvent in a rotary evaporator. The overall efficiency of the separator during the fractionation reported here was 67 percent. In this study, the residuum recovered from the solvent was not combined with that recovered from the separator because independent analysis of this material will provide valuable information concerning operation of the separator. Current work is aimed at improving the separator efficiency through optimization of operational parameters and design.

Characterization

The elemental analyses were performed at PETC using ASTM techniques that were modified for use with coal-derived materials. The vapor pressure osmometry (VPO) molecular weights were single-point determinations in pyridine at 353 K and were performed at Huffman Laboratories, Inc., Wheatridge, Colo.

The gel permeation chromatography (GPC) was performed using PLgel 100A⁰ columns manufactured by Polymer Laboratories, Ltd., Shropshire, U.K., with THF as the eluent. An evaporative analyzer from Applied Chromatography Systems (USA), Inc.,

State College, Pa., was used in conjunction with a conventional refractive index detector to monitor the separation. The molecular weights reported here were calculated using the data obtained from the evaporative analyzer. In this detector, the eluent from a liquid chromatographic column is nebulized with a gas, the solvent is vaporized from the resulting droplets, and the remaining nonvolatile sample particles pass through a light-scattering photometer. This detector is more sensitive than the refractive index detector and is especially suited for GPC of high molecular weight coal derivatives (7). The calibration curve was constructed using polystyrene standards for molecular weights greater than 1000, and a series of pure aromatic compounds for the lower molecular weights. A correction for polystyrene molecular weights that was developed by Reerink and Lijzenga (8) with petroleum bitumens and asphaltenes was used in constructing the GPC calibration curve.

Chemical class fractionation was performed using a high performance liquid chromatography (HPLC) method similar to that proposed by Matsunaga (9). In this procedure, the residuum sample is dissolved in tetrahydrofuran, filtered to remove particulates, and separated on a μ -Bondapack NH_2 column from Waters Associates, Milford, Mass., using a hexane/THF gradient. Using this procedure, the sample is separated on the basis of the number of double bonds and functionality. One unresolved problem with this method is the extent to which the separation is affected by the solubility of the sample in hexane. This aspect is still under investigation.

Spectroscopic analyses included near-infrared, $^1\text{H-NMR}$, and field ionization mass spectrometry (FIMS). The near-infrared measurements were made on dilute methylene chloride solutions of the fractions. The $^1\text{H-NMR}$ spectra were acquired in d_5 -pyridine. The FIMS data were obtained from SRI International, Menlo Park, Calif.

DISCUSSION OF RESULTS

The elemental analysis and VPO data are summarized in Table 1 for the six fractions collected. Important trends to note in the elemental composition of the fractions as the destruction proceeds are the increase in heteroatom concentration and the decrease in the hydrogen-to-carbon ratio. The molecular weight data also exhibit a regular increase in going from the first to the last fractions. These observations indicate that the separation in the cyclohexane fractional destruction proceeds according to the relative volatility of the sample components. This may not be the case when associating solvents are used as supercritical fluids (10).

The number average molecular weights (\bar{M}_N) of the six overhead fractions calculated from FIMS and GPC are compared to the VPO determinations in Figure 2. The data are in good agreement except for the FIMS results for the higher molecular weight fractions. Except for the third fraction, sample volatilization exceeded 90 percent. The low results for the last two fractions are primarily due to termination of the spectra at 800 amu. Future FIMS data will be collected out to 2000 amu. The advantage of using GPC is that it is much faster and more easily automated than the other methods. This capability has been invaluable in making decisions concerning daily operation of the FDU.

The GPC profiles of the six fractions are compared in Figure 3. The weight average molecular weights are also shown. Similar data on fractions collected during a non-reflux, isothermal experiment show much broader distributions and little difference between the first and last fractions. Operation in the reflux mode, as shown in Figure 3, produces narrower fractions, with an obvious trend to larger molecules as the fractionation proceeds. The transition between Fractions 4 and 5 is noteworthy. Referring back to Figure 1, the overhead concentration also increases dramatically at this same time.

Figure 4 contains results for the chemical class fractionation performed using HPLC. Even though the development of this procedure is still in its early stages, the results yield important information concerning the molecular properties of the fractions obtained by supercritical fluid fractionation. The qualitative chemical class distinctions indicated in Figure 4 were estimated from the retention of neutral, acidic, and basic fractions obtained from an SRC II distillation cut (588 K to 755 K) by column chromatography. The neutral species are more concentrated in the first fractions (see Figure 4). The later fractions are depleted of neutral species and show increasingly higher concentrations of more polar compounds. These observations are tentative until the extent to which the separation is affected by the hexane solubility of the samples is determined.

The near-infrared spectra reveal only small differences in the amounts of free -OH and relative -NH functionality in the soluble fractions. The absolute weight percent of oxygen as free -OH only increased from 0.6 to 0.7 between the first and last fractions. The increase in pyrrolic N-H functionality paralleled the increase in nitrogen content of the fractions.

More interesting results were obtained from mean molecular parameters calculated using the $^1\text{H-NMR}$ data. A summary of some of the trends is shown in Figure 5. Going from left to right, the data points in this figure represent Fractions 1 to 6, respectively. Position on the abscissa indicates the mid-point of the fraction. The most notable change is in the calculated total number of rings (aromatic, heterocyclic, hydroaromatic, naphthenic) per average molecule, which shows the most marked change after Fraction 4. This is consistent with the molecular weight and GPC data. The trend in the number of aromatic rings per molecule parallels this observation. There is an increase of about one heterocyclic ring per average molecule between Fractions 1 and 6. The calculated number of ring (aromatic plus heterocyclic) clusters per average molecule is about 1.5 for the first four fractions but then increases to about 2 in the last two fractions.

CONCLUSION

The development of the fractional destruction concept was motivated by the need to extend distillation technology to coal-derived systems containing intractable residuum. In order to provide daily information on the operation of the FDU, GPC procedures were developed to rapidly characterize the residuum fractions. In the long term, alternate procedures such as GPC will be necessary to monitor the performance of demonstration and commercial plants that utilize or generate residuum-containing streams. The complexity of fossil fuels also demands similar procedures for monitoring the more polar, associating species. This provides impetus for the development of HPLC separations such as the one reported here.

In summary, the trends in the characterization data of a set of residuum fractions prepared by fractional destruction show that as the fractionation proceeds, the average composition of the fractions shifts to higher molecular weight, lower hydrogen-to-carbon ratio, and increased heteroatom content. The data also show an increase in both the average size and average number of aromatic ring clusters in the components, along with larger ring clusters, and more ring clusters per molecule. The transitions are generally smooth; however, an abrupt change occurs in some of these trends during the latter part of the fractionation.

DISCLAIMER

Reference in this report to any specific product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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TABLE 1. Analyses of the T102 Residuum and the Products of Fractional Destruction with Cyclohexane

	RUN 242 ^a		FRACTION NUMBER				RESIDUE	
	T102 RESIDUUM	1	2	3	4	5		6
C	79.1	88.1	87.7	87.3	87.8	87.6	87.3	73.0
H	5.9	8.0	7.7	7.5	7.4	7.4	6.7	4.7
O ^b	4.0	2.6	3.2	3.7	3.2	3.3	4.0	4.6
N	1.3	0.8	0.9	0.9	1.0	1.0	1.2	1.5
S	1.0	0.5	0.5	0.6	0.6	0.7	0.8	1.9
ASH	8.7	---	---	---	---	---	---	14.3
H/C	0.89	1.08	1.05	1.02	1.00	1.01	0.91	0.77
¹⁴ N (VPO, 353 K, PYRIDINE)		389	413	433	481	588	638	c

^aApproximately 8 percent unconverted coal content. ^bDetermined by difference. ^cNot completely soluble.

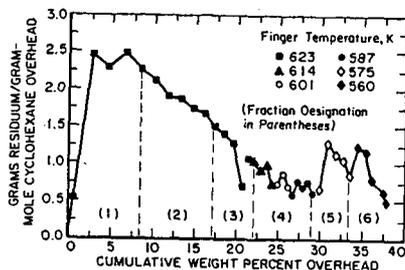


Figure 1. Summary of Fractional Destruction of Wilsonville T102 Residuum.

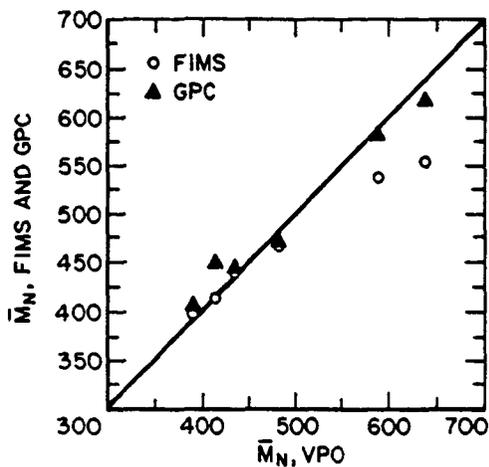


Figure 2. Comparison of Number Average Molecular Weight Determinations for Wilsonville Residuum Fractions Prepared by Fractional Destruction.

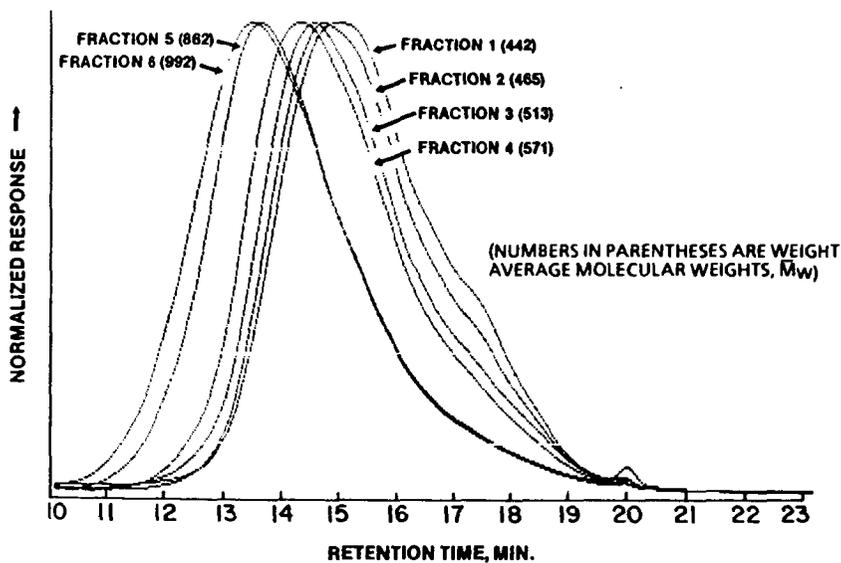


Figure 3. GPC of Wilsonville Residuum Fractions Prepared by Fractional Destruction.

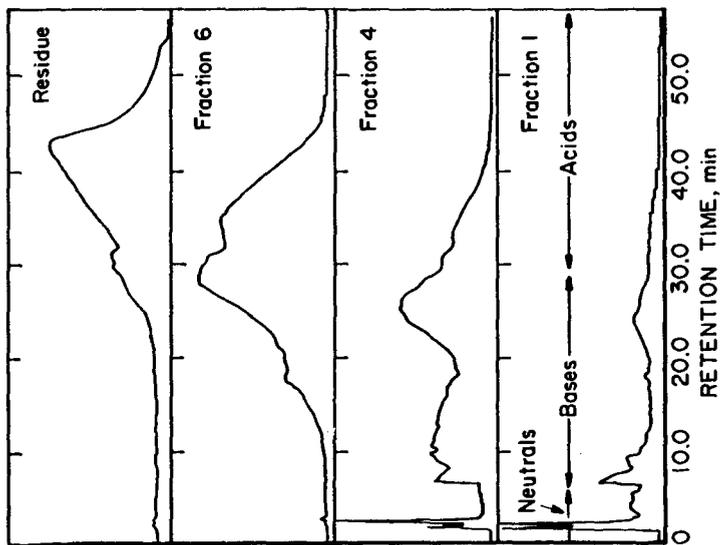


Figure 4. HPLC Separation of Wilsonville Residuum Fractions Prepared by Fractional Destruction.

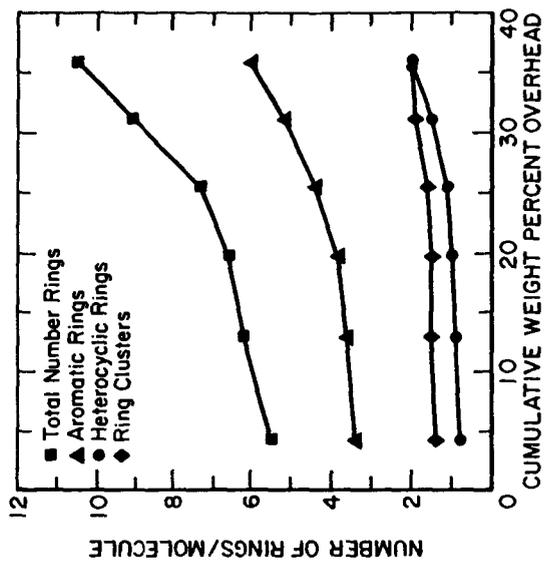


Figure 5. Summary of Average Molecular Ring Parameters for Wilsonville Residuum Fractions Prepared by Fractional Destruction.