

## FRACTIONAL DESTRUCTION OF COAL-DERIVED RESIDUUM

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### ABSTRACT

An apparatus has been developed to fractionate coal-derived residuum by exploiting the solvent power of fluids near their critical points. Termed Fractional Destruction, the method fractionates residuum according to the solubility of its constituent components in a supercritical fluid. The novel aspect of the approach is the incorporation of a system to promote reflux of less-soluble components onto a packed bed. Fractionation of residuum will facilitate the determination of previously unattainable information concerning the composition and process-related behavior of this complex material. This paper describes operation of the unit to fractionate a residuum sample produced at the Wilsonville Advanced Coal Liquefaction Test Facility.

### INTRODUCTION

Describing the behavior of undefined mixtures, whether from natural or synthetic sources, often begins with the separation of these complex systems into effective pseudocomponents by distillation (1). Each pseudocomponent is then characterized as if it were a pure compound, and its characterization data are used in appropriate correlations. The presence of nonvolatile residuum poses a serious limitation to such methodology. For coal-derived liquids, heavy crude oils, tar sands, and shale oil, more than 50 percent of the fluid may not be distillable (1). Since this nonvolatile residue cannot be separated using conventional techniques, new methods of separation and characterization must be developed to provide the necessary information for design and operation of plants utilizing the fossil fuels mentioned above (2).

Apart from the need to fractionate residuum-containing fossil fuels for the measurement and prediction of thermophysical properties, other important problems could be resolved better through the study of residuum pseudocomponents. Two examples in the area of coal liquefaction are the role of residuum (a) in hydrogen utilization and hydrogen transfer and (b) in the manifestation of harmful biological effects.

Work at the Pittsburgh Energy Technology Center has been directed at the development of novel technology for the separation of fossil fuel residuum into effective pseudocomponents. In this respect, application of supercritical fluids in a manner similar to that reported by Zosel (3) is being developed. This approach is similar to conventional distillation in that an apparatus is used not only to extract the residuum but also to cause part of the residuum in the fluid phase to return as reflux onto a packed bed. This liquid reflux is caused by increasing the temperature of the supercritical fluid phase at constant pressure, thereby decreasing the density of the supercritical fluid and its carrying capacity for the residuum. Operation of a system in this region of retrograde condensation has recently been reported in the literature (4). Other recent investigations support the hypothesis that supercritical solubility is a density-driven phenomenon in the absence of strong associating forces in the solvent (5). The method is called either Supercritical Distillation or, as Zosel suggested, Fractional Destruction. This report describes the use of this technology to

fractionate a coal-derived residuum from the Wilsonville Advanced Coal Liquefaction Test Facility.

## EXPERIMENTAL

The experimental unit, called the Fractional Destruction Unit (FDU), has been designed to contact a 3-4 kg charge of residuum with a continuous flow of supercritical fluid at conditions up to 673 K and 27.6 MPa. The heart of the FDU is the Fractional Destruction Vessel (FDV) shown in Figure 1. The FDV consists of a modified 3.8-L 316 stainless steel pressure vessel onto which is attached a 78-cm column fabricated of 316 stainless steel (6.03-cm o.d., 1.11-cm wall). The column contains a packed bed and a condenser section. In the experiments reported here, the 30-cm bed section was packed with 0.41-cm stainless steel Pro-Pak protruded metal distillation packing from Scientific Development Co., State College, Pa. This is the same packing used in a conventional Podbelniak distillation column. The condenser consists of a removable 38-cm finger made of 316 stainless steel (2.67-cm o.d., 0.78-cm wall) that is heated by an internal cartridge heater to promote reflux. A triple zone furnace is used to control the temperature in the extraction zone. Temperature control on the column is accomplished with independently controlled band heaters on the packed bed and condenser sections.

The desired charge of residuum is placed in the extraction section of the FDV, and the entire unit is purged with nitrogen. The FDU is then brought up to the operating temperature before beginning solvent flow. The destruction fluid is then pumped as a liquid through a preheater to raise its temperature above the critical point before it is introduced into the FDV through the sparging device at the bottom. The pressure is controlled by a high-temperature Badger-Meter control valve located near the outlet of the FDV. After traveling up the column, the fluid stream, which now contains destructed residuum, exits at the top of the FDV and is partially depressurized through the heated control valve into a separator constructed of a 2.25 L (approximately 10.2-cm o.d., 42.5-cm long) 304 stainless steel cylinder. The separator is operated slightly above the critical temperature of the solvent ( $T_R \approx 1.02$ ) at a pressure of 0.8 MPa. Separation of the residuum from the supercritical fluid is accomplished by the reduction in pressure. The residuum is drained and collected from the bottom of the separator at periodic intervals, while the solvent is flashed to atmospheric pressure, condensed, and recovered as a liquid. The operation of the FDU will be reported in detail in a later publication.

Toluene ( $T_C = 591.7$  K,  $P_C = 4.115$  MPa) and cyclohexane ( $T_C = 553.4$  K,  $P_C = 4.074$  MPa) were used as the supercritical fluids in the work reported here. They were obtained in drum quantities at greater than 99 percent purity and used as received. Owing to inefficiency in the separator, some of the destructed residuum is collected with the solvent. This material is recovered in a rotary evaporator. The distilled solvent is then reused in the FDU. In the figures in this report that depict residuum overhead data, correction has been made for the residuum recovered in the spent solvent.

The residuum used in the work reported here was collected from the T102 vacuum distillation tower during Run 242 at the Wilsonville Advanced Coal Liquefaction Test Facility. This run was made using Illinois No. 6 coal from the Burning Star mine in what is termed a Short-Contact-Time Integrated Two-Stage Liquefaction (SCT-ITSL) mode (6). During the time this particular sample was collected, the T102 unit was operated at 594 K and 3.4 KPa. The residuum was crushed to minus 0.64 cm and mixed by riffing before use.

## DISCUSSION

Operation of the FDU with coal-derived residuum was preceded by tests on pure compounds and distillable coal liquids using n-pentane as the supercritical fluid (7). The results of tests with the coal-derived distillate showed that the FDU was basically performing as expected. Liquid reflux was generated by means of the hot finger when the device was operated at a temperature slightly above the critical temperature of the transport fluid. When reflux was established, fractionation based upon volatility was observed. Poorer separation was achieved in the absence of reflux.

The first work on the T102 bottoms involved operation in the non-reflux mode to obtain base-line data on the transport of this residuum in various hydrocarbon solvents. Using n-pentane, cyclohexane, and toluene at a  $T_R$  of 1.02 and at a  $P_R$  of 2, the residuum brought overhead was 23, 54, and 67 percent of that charged, respectively. Based on this information, further studies were performed using cyclohexane as the supercritical fluid, since a large portion of the residuum could be destructed at a temperature similar to or less than that in the T102 separator.

A two-step destruction procedure was developed to maximize the amount of T102 residuum brought overhead. In the first step, toluene is used in a manner similar to conventional supercritical extraction to produce a nearly ash-free material for subsequent fractionation. This first step is called the non-reflux mode because the column of the FDU is maintained at the same temperature as the extraction section. In the second step, called the reflux mode, the column and finger are heated to a higher temperature than the extraction section, which causes the density of the fluid to decrease as it travels up the column and thus promotes reflux of the less-soluble components. These two steps are described below.

In the non-reflux mode, the FDU was used to process five 800-gram charges of the T102 bottoms. Repetitive operation of the unit was performed to produce sufficient quantities of the final fractions for subsequent characterization and experimentation. Figure 2 summarizes the operation of the FDU during these five destructions. Shown is the amount of residuum brought overhead as a function of the time on stream at a  $P_R$  of 2. As previously mentioned, the residuum overhead data include residuum recovered from both the separator and the spent solvent. The FDU was maintained at a  $T_R$  of 1.02, with overall variance in temperature for the five tests being  $\pm 5$  K. Temperature variance during any one test was  $\pm 2$  K. The differences observed, especially in the final amounts destructed, appear to be due to this small temperature variance between runs. The higher yields were consistently obtained at temperatures nearer the critical point. This phenomenon appears to be particularly sensitive to the temperature of the extraction zone when the fluid is first introduced. The fact that the initial dissolution of the residuum in the fluid influences the overall yield suggests that components in the residuum may be acting as cosolvents.

Table 1 contains the elemental analysis of the T102 bottoms, the material brought overhead with toluene, the residue remaining after the toluene destruction, and the starting coal used at Wilsonville during Run 242. The toluene overhead represented 66.8 percent of the material charged to the FDU, and the residue accounted for 27.9 percent. Other material collected from the FDU includes 4.2 percent in the spent solvent and 2.7 percent recovered during cleaning of the FDU and separator with tetrahydrofuran. The total material balance is 101.6 percent. This number also includes any residual toluene or tetrahydrofuran in the various samples. The overhead collected from the five destructions was ground and combined before use in the reflux mode experiments.

As previously mentioned, cyclohexane was chosen for the fractionation solvent for the second step, since it could transport sufficient quantities of residuum at reasonable temperatures. In the reflux mode, the column of the FDU is operated at

a higher temperature than the extraction zone. As the carry-over of residuum decreases, the temperature of the column is reduced to cause the density in this region to increase and consequently more residuum is transported overhead. This is repeated until the column is at the same temperature as the extraction zone. In this work, four fractions were brought overhead by operating the column initially at 593 K and then decreasing the temperature to 578, 573, and 563 K as the residuum carry-over approached 1.0 gram per gram-mole of cyclohexane. This concentration value is calculated from the amount of residuum collected from the bottom of the separator after a 30-minute collection period and from the amount of cyclohexane pumped during that period. The column temperatures were selected both from density estimation and from actual experimentation. A more detailed discussion of the development of the operational parameters for the reflux mode will be presented in a future paper.

Figure 3 illustrates the difference between operation of the FDU in the non-reflux and the reflux modes with cyclohexane. This figure depicts the results in terms of the overhead concentration of residuum. The reflux mode data represent one of three replicate fractionations that were performed on the T102 toluene distraction overhead. Each point represents a 30-minute sample collection period. Owing to the limited quantity of toluene overhead produced, no non-reflux mode experiments were conducted using this material. From the earlier development work, however, several non-reflux mode experiments were performed on the T102 residuum sample from Run 242. The non-reflux mode data in Figure 3 were derived from one of these experiments and adjusted for comparability to the data from the reflux mode. The adjustment compensates for separator inefficiency and for residuum insoluble in supercritical toluene. All but the last three data points in the non-reflux mode data represent 15-minute sample periods. The only other difference between the two tests was the solvent delivery rate, which was 0.24 mole per minute for the non-reflux mode, and 0.43 mole per minute in the reflux mode.

As shown in Figure 3 the temperature of the column was initially 30 degrees higher than the pot, which produced the reduced carry-over rate by causing reflux to occur. An expanded view of the carry-over concentration is shown in Figure 4. This view shows more clearly how residuum carry-over is manipulated by changes in the column temperature. Figure 5 contains the same information for the three replicate cyclohexane fractionations performed on the toluene overhead. Conditions in all three experiments were similar; however, the small deviations due to inherent limitations of the process controllers produced some overlap between successive fractions. The amount of overlap is estimated at 2.6 percent between Fractions 1 and 2, 2.5 percent between Fractions 2 and 3, and 3.0 percent between Fractions 3 and 4. Also, 32 grams that should have been in the 573 K fraction were inadvertently collected in the 578 K fraction. The respective fractions and residues from the three fractional distractions were ground and combined before characterization.

Table 2 contains the analysis of the four overhead fractions and the residue. The overall material balance was 96.1 percent, with 57.2 percent of the charge being brought overhead (includes residuum recovered from spent solvent) and 31.7 percent remaining in the residue. An additional 7.2 percent was recovered upon cleaning the unit with tetrahydrofuran. The trends evident from the elemental analysis indicate that the components that have lower molecular weights, higher hydrogen-to-carbon ratios, and lower heteroatom contents are concentrated in the earlier fractions. Also note that the separator inefficiency is highest for the earlier fractions, indicating that the more volatile components are more readily carried through the separator with the solvent. The material carried through the separator with the solvent was not mixed with the respective fractions collected from the separator. Independent characterization of these samples will provide valuable insight into the operation of the separator.

The molecular weight data in Table 2 were determined by vapor pressure osmometry (VPO) and gel permeation chromatography (GPC). The molecular weight increases

regularly from Fraction 1 to the residue. In comparison, the VPO molecular weights for six fractions collected in the non-reflux mode cyclohexane destraction shown in Figure 3 range from 441 to 471, with no consistent trend. The polydispersity values ( $M_w/M_n$ ) shown for the four fractions in Table 2 are less than those for the non-reflux mode fractions, which ranged from 1.47 for the first fraction to 1.88 for the sixth fraction. This number is a measure of the breadth of the molecular weight distribution and shows that operation in the reflux mode produces fractions with narrower molecular weight distributions than those prepared without reflux.

In Figure 6 the GPC traces for the four fractions and for the residue from each of the three cyclohexane fractional destractions are overlaid. The trend to higher molecular weight distributions as the fractionation proceeded is evident, as well as the reproducibility of the fractionation process. Additional characterization of similar samples produced in the FDU is the subject of another paper (9).

### CONCLUSIONS

The main conclusion to be drawn from the experimental data presented here is that fractionation of residuum through the use of a supercritical fluid system incorporating internal reflux produced by retrograde condensation results in sharper fractions than those obtained by ordinary supercritical extraction. The capability of the FDU to process coal-derived residuum in the internal reflux mode has been demonstrated. The density-driven separation does appear to fractionate the residuum on the basis of volatility, with lower molecular weight species preceding larger ones.

Other methods of fractionation with supercritical fluids are conceivable. One such possibility could involve manipulation of the pressure during the destraction or upon subsequent separation of the fluid and residuum. The relative merits of such possibilities remain to be explored. Successful development of such technology will result in the ability to fractionate and characterize material currently intractable by conventional methods.

### 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. Analysis of Feed Coal to Run 242, T102 Bottoms After Grinding and Mixing, and Materials Produced by Supercritical Extraction of T102 Bottoms With Toluene in the Non-Reflex Mode.

	ILLINOIS <sup>a</sup> NO. 6 COAL	RUN 242 <sup>b</sup> T102 BOTTOMS	TOLUENE OVERHEAD	TOLUENE RESIDUE
C	68.4	79.1	87.4	60.3
H	4.4	5.9	6.7	3.5
O	11.9 <sup>c</sup>	4.0 <sup>c</sup>	4.0 <sup>d</sup>	7.1 <sup>d</sup>
N	1.4	1.3	1.3	1.4
S	3.2	1.0	0.7	0.9
Cl	0.1	---	---	---
ASH	10.6	8.7	<0.1	29.4
H/C	0.77	0.89	0.91	0.69
M <sub>N</sub> (VPO, 353 K, PYRIDINE)	---	---	574	e

<sup>a</sup>Analysis from Wilsonville report, see reference 6. <sup>b</sup>Approximately 8 percent unconverted coal content. <sup>c</sup>Determination by difference. <sup>d</sup>Direct determination. <sup>e</sup>Insufficient solubility in pyridine.

TABLE 2. Characterization of Materials Produced From the Cyclohexane Fractional Destruction of the Toluene Overhead Sample in Table 1.

	FRACTION DESIGNATION <sup>a</sup>				RESIDUE
	593 K	578 K	573 K	563 K	
C	87.8	87.3	87.4	87.0	87.0
H	7.6	7.5	7.2	6.5	5.9
O <sup>b</sup>	3.5	3.7	3.3	3.7	4.9
N	0.9	0.9	1.2	1.4	1.8
S	0.5	0.6	0.6	0.7	0.9
ASH	---	---	---	---	<0.1
H/C	1.03	1.02	0.98	0.89	0.81
RESIDUAL CYCLOHEXANE, % <sup>c</sup>	0.5	0.5	0.8	0.6	0.5
RECOVERY, % <sup>d</sup>	23.9	13.0	13.8	6.4	31.7
SEPARATOR INEFFICIENCY, % <sup>e</sup>	27.5	17.8	8.4	11.1	---
MELTING RANGE, K	333-338	363-373	393-403	448-463	~573
M <sub>N</sub> , VPO <sup>f</sup>	393	479	578	645	1226
M <sub>N</sub> , GPC <sup>g</sup>	407	449	527	564	715
M <sub>w</sub> , GPC	504	601	851	1010	1996
M <sub>w</sub> /M <sub>N</sub>	1.24	1.34	1.62	1.79	2.79

<sup>a</sup>The temperature refers to the reflux and packed bed zone. The residue is the material remaining in the extraction zone. <sup>b</sup>Direct determination. <sup>c</sup>Determination by Headspace Chromatography, see reference 8. <sup>d</sup>Total recovery of material based upon weight of toluene overhead charged to the unit. Except for the residue this includes both residuum recovered from the fraction receiver and from the spent solvent. <sup>e</sup>Percent of total material overhead recovered in the spent solvent. <sup>f</sup>Determination in pyridine at 353 K. <sup>g</sup>Determination on PLgel 100A column with THF eluent.

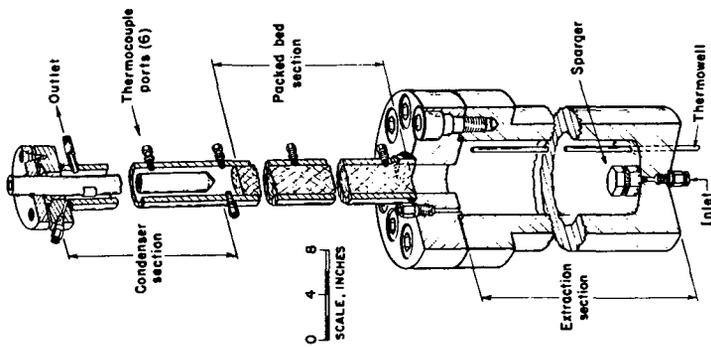


Figure 1. Sectional view of fractional distraction unit.

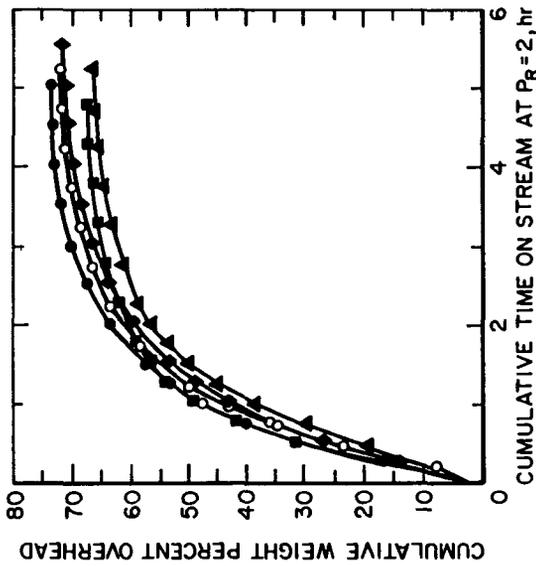


Figure 2. Comparison of five replicate distractions (non-reflux mode) of Wilsonville Run 242 T102 residuum using toluene.

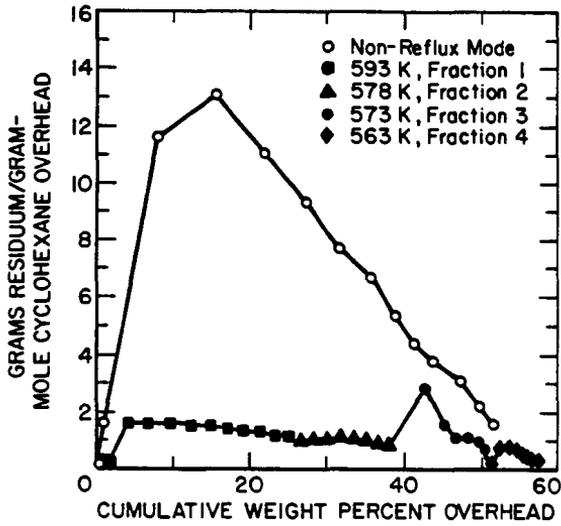


Figure 3. Comparison of non-reflux and reflux modes of operation using cyclohexane. Temperatures indicated are those of the column in the reflux mode. Pot temperature was 563 K in both modes.

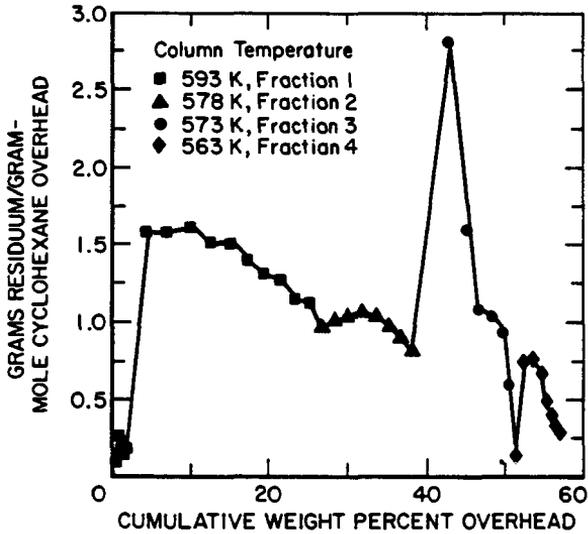


Figure 4. Fractional distraction of toluene overhead using cyclohexane.

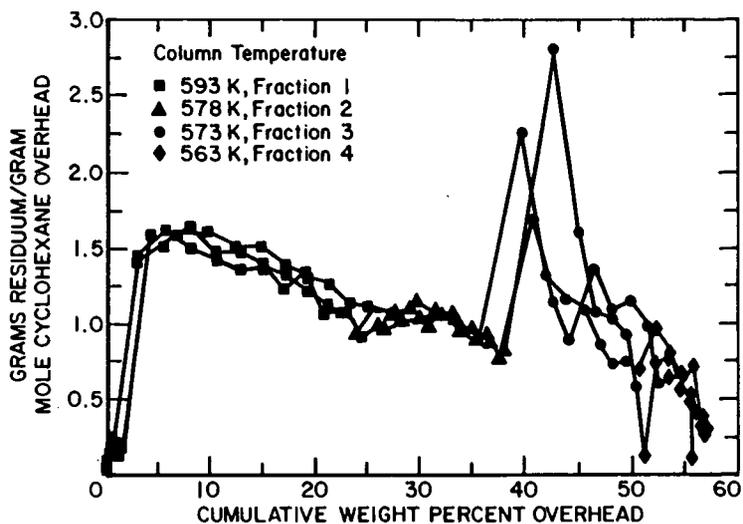


Figure 5. Comparison of three replicate fractional distractions (reflux mode) of toluene overhead using cyclohexane.

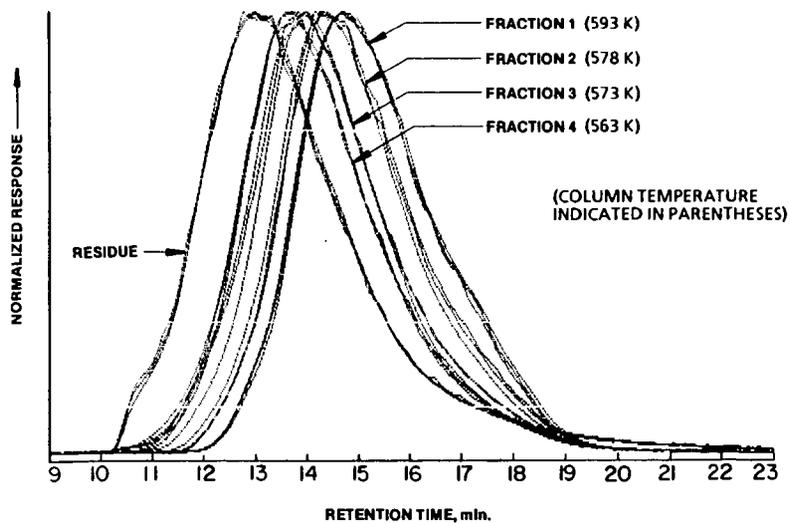


Figure 6. Comparison of the GPC results for the three replicate fractional distractions of toluene overhead using cyclohexane.