

Coal Liquefaction Process Streams Characterization and Evaluation

Electron Microscopy Observations of Resids Obtained From Coal Liquefaction Experiments

Topical Report

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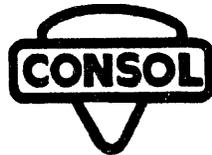
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PROJECT ASSESSMENT

Introduction

Under subcontract from CONSOL Inc. (U.S. DOE Contract No. DE-AC22-89PC89883), Vander Sande Associates studied the use of transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and energy dispersive X-ray (EDX) spectroscopy for analysis of dispersed catalysts in the insoluble portion of coal-derived materials. Dr. John B. Vander Sande, the principal investigator of this work, is vice president of Vander Sande Associates and professor of Materials Science and Engineering at Massachusetts Institute of Technology. The full report authored by Vander Sande Associates is presented here. The following assessment briefly highlights the major findings of the project, and evaluates the potential of the method for application to coal derived materials. These results will be incorporated by CONSOL into a general overview of the application of novel analytical techniques to coal derived materials at the conclusion of this contract.

Summary

This study demonstrated the feasibility of using scanning transmission electron microscopy (STEM) spectroscopy accompanied by energy dispersive X-ray (EDX) spectroscopy for the examination of the tetrahydrofuran (THF)-insoluble portion of distillation resid materials derived from direct coal liquefaction. The technique was able to determine the distribution, morphology, and elemental composition of dispersed catalyst components in the insoluble portion of the distillation resids. An attempt was made to use transmission electron microscopy (TEM) on these samples; however, detailed compositional information could not be obtained. Further development of STEM and EDX as aids to process development are justified based on these results.

Program Description

This report describes the work performed by Vander Sande Associates under a subcontract from CONSOL Inc., Research and Development. CONSOL's prime contract to the U.S. Department of Energy (Contract No. DE-AC22-89PC89883, "Coal Liquefaction Process Streams Characterization and Evaluation") established a program for the analysis of direct coal

liquefaction derived materials. The program involves a number of participating organizations whose analytical expertise is being applied to these materials. This Participants Program has two main objectives. The broad objective is to improve our understanding of fundamental coal liquefaction chemistry to facilitate process improvement and new process development. The specific approach to achieving this objective is to provide a bridge between direct coal liquefaction process development and analytical chemistry by demonstrating the application of various advanced analytical methods to coal liquefaction materials. The methodologies (or techniques) of interest are those which are novel in their application for the support of coal liquefaction and those which have not been fully demonstrated in this application. CONSOL is providing well-documented samples from different direct coal liquefaction production facilities to the program participants. The participants are required to interpret their analytical data in context to the processing conditions under which the samples were generated. The methodology employed is then evaluated for its usefulness in analyzing direct coal liquefaction derived materials.

Participant's Methodology

Vander Sande Associates used STEM and EDX to analyze the THF-insoluble portion of distillation resid (850°F) that were known to contain a molybdenum-based dispersed catalyst used in the liquefaction process. The insoluble portion of the resid is a solid at room temperature and contains organic material and mineral matter native to the coal as well as the added catalyst. The original samples were produced at the Wilsonville pilot plant. The major processing parameter which was considered in the choice of these samples was the concentration of the added catalyst. Samples were obtained from two processing runs which used the same feed coal. In one run, slurry-phase (dispersed) molybdenum catalyst was fed to the first reactor. In the other run, slurry catalyst was fed to the first reactor in the two-stage process and supported catalyst was used in the second reactor. Samples from Wilsonville were taken from three locations: between the reactors, after the second-stage reactor, and at the recycle oil vessel. These samples are expected to represent different extents of coal liquefaction and perhaps different catalyst morphology, composition, and activity. The samples were composites of

a number of samples taken during a single run day in a single operating run period. The STEM experimental procedure is described on pages 4-7 of the attached report. All experimental work reported here was performed at the Materials Science and Engineering Department of the Massachusetts Institute of Technology.

Participant's Major Findings

The following principal observations for the application of STEM and EDX to coal liquefaction materials were reported by Vander Sande Associates. An expanded discussion can be found in the attached report, pages 7-10. Preliminary examination of the samples using transmission scanning microscopy (TEM) provided insufficient compositional information; therefore, all work was accomplished with the STEM.

The STEM technique has a spatial resolution for imaging of about 0.5 nm and for compositional analysis of about 2.0 nm. Both "bright-field" and "dark-field" imaging modes were used, and compositional analysis of the features detected was accomplished via energy dispersive X-ray analysis. Molybdenum, introduced into the two processing runs as Molyvan L, a catalyst precursor, was detected in all of the samples of the processing run in which the Molyvan L was introduced at the 500 ppm MF coal level (Run 262), and only in the recycle sample from the run in which Molyvan L was introduced at the 100 ppm MF coal level (Run 263). The largest localized concentrations of Mo were detected in the recycle sample in Run 263. The Mo was rarely seen as a particle in the THF-insoluble portion of the resids; rather, it was typically seen in a diffuse state in which any existent particles are smaller than observable at the resolution of the instrument (<2nm). Sulfur was often found to be associated with the Mo. Iron was observed in all samples and it was always found in association with sulfur. The FeS were determined to be particulate (about 0.1-2.0 μm) in nature.

CONSOL Evaluation

The STEM and EDX technique were shown to be useful for the analysis of the THF-insoluble portion of the direct coal liquefaction resid samples. It was shown that localized distributions of the different elements and compounds in the sample could be determined. The morphology of the

detected elements and compounds was discernable. However, little difference was observed in the concentration or morphology of the Fe or Mo among the samples in which Fe and Mo were detected. It is, therefore, not possible, based on these six samples, to comment on the effect of processing conditions on the nature of the Mo catalyst.

The concentration of the highly dispersed Mo was below the detection limits of the STEM and EDX methods for two of the samples. In two of the three samples obtained from a processing run in which only 100 ppm (MF coal basis) of fresh Mo was introduced, the method was not able to detect the molybdenum that was present, even though the dispersed Mo catalyst was concentrated (~1300 ppm) in the THF-insoluble portion of the resid before examination.

There was an apparent discrepancy in the concentrations of Mo detected via the STEM and EDX techniques and conventional bulk methods. The STEM and EDX techniques indicate that the highest Mo concentration is in the recycle samples, but the bulk analysis indicates that those samples have low to medium Mo concentrations. This apparent discrepancy can be resolved if consideration is given to the fact that the STEM method, by experimental design, is reporting only on the Mo-enriched regions of the sample.

The STEM and EDX techniques appear to be powerful diagnostic tools for the analysis of these materials. The techniques are well-suited to the task of following the fate of dispersed catalysts through the liquefaction process.

Sample preparation was minimal; the dry powdered sample was distributed on a carbon film, which was supported by a Cu mesh grid, and placed directly into the microscope. The STEM instrument used to accomplish the work described in this report costs approximately \$650,000. The time required to run one sample is about one day. The operation of the equipment and the interpretation of the data are most commonly performed by highly trained professional personnel.

Further Development

Further development of the STEM technique for analysis of catalytic materials in coal liquefaction derived residu appears to be warranted. It is suggested that many additional samples containing iron and molybdenum based catalysts be examined to determine if processing trends affect the morphology of the materials. It is also suggested by Vander Sande Associates that electron energy loss spectroscopy (EELS) be tested with process derived samples to learn more about the local chemical environment of the Mo.

Participant's Statement of Work

Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM) are techniques which have been used for the investigation of ceramic materials, coal and coal ash. It has not, however, been demonstrated for its ability to answer questions pertaining to the chemistry of coal conversion. As such, it fits well within the scope of the participants program.

The application of TEM and STEM to a specified sample set (6 samples) will allow a demonstration of the value of this technique for the examination of the dispersed catalyst in coal liquefaction-derived residu. The samples are known to contain molybdenum, originally introduced as a catalyst precursor (Molyvan L), and dispersed iron. These samples have been selected (see attached list) so that the utility of TEM and STEM for addressing the issue of catalyst activity can be evaluated by obtaining information on the size, morphology, occurrence, and chemical nature of the molybdenum and the iron in the different samples. Examination of the samples will be done in two steps. First, the samples will be globally scanned by STEM to map the molybdenum and iron concentrations. Then the Mo- and Fe-rich areas will be examined in a point-by-point analysis at high magnification by TEM. The point-by-point examination will include microdiffraction analysis and either energy dispersive X-ray spectroscopy (EDX) or electron energy loss spectrometry (EELS). Examination of the samples by other techniques such as Auger electron spectroscopy and secondary ion mass spectroscopy (SIMS) also will be employed to provide additional information for each sample. The samples will be supplied to MIT with the following information, as

available: elemental analyses, ash content, ash elemental analysis, phenolic -OH concentration, calorific value, hydrogen classes by $^1\text{H-NMR}$, and the full history of the sample (plant, process conditions, age, and storage conditions). The samples are the tetrahydrofuran-insoluble portion of non-distillable residual materials. They contain THF-insoluble organic material and ash. Sample size will be at least 1g. The six insoluble resid samples will be solid materials that will be supplied as approximately minus 60 mesh powders. All experimental work will be performed at the Massachusetts Institute of Technology, Department of Materials Science and Engineering, Cambridge, Massachusetts.

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Resids Obtained from Coal Liquefaction Experiments

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ELECTRON MICROSCOPY OBSERVATIONS OF RESIDS
OBTAINED FROM COAL LIQUEFACTION EXPERIMENTS

Executive Summary

Scanning transmission electron microscopy (STEM) was accomplished on six tetrahydrofuran (THF) insoluble portions of solid 850°F+ materials (resids) from two Wilsonville direct coal liquefaction processing runs. Three samples are from a run employing a fresh molybdenum concentration of 500 ppm MF coal while the second set of three samples are from a run employing a fresh molybdenum concentration of 100 ppm MF coal. In each case Molyvan L was used as the slurry catalyst. In each of the two sample sets, one sample is from the "interstage" sampling point (between the first and second reactors), the second sample from the "recycle" sampling point (at the solvent surge tank) and the third sample from the "second stage product" sampling point (from a vessel after the second reactor).

Samples were prepared for electron microscopy by distributing the dry powders on a thin carbon film which itself is supported on a Cu mesh grid. The observations presented in this report were obtained using a Vacuum Generators HB-5 STEM operating at 100 kV. This instrument has a spatial resolution for imaging of ~ 0.5 nm and a spatial resolution for compositional analysis of ~ 2.0 nm.

Imaging of samples was done in both bright-field and dark-field modes. Compositional analysis of features seen was accomplished by using a windowless energy dispersive X-ray

detector and associated analyzer. This analytical approach is based on the incident electron probe interacting with the thin, solid sample generating characteristic X-rays from the volume of the sample under electron irradiation. The X-rays produced are collected by the X-ray detector, sorted in terms of their (characteristic) energy, and presented in a plot of X-ray intensity versus energy. The X-ray intensity in a given peak can also be used to "drive" the CRT to produce an X-ray map of the sample as the electron beam scans the object.

Mo was detected in all of the samples from the 500 ppm MF coal Mo concentration samples but only from the "recycle" 100 ppm MF coal Mo concentration sample. The Mo concentration was locally the highest in the "recycle" 500 ppm MF coal sample. The Mo is rarely seen as a particle but rather appears as a diffuse, organic-like mass suggesting that Mo is in a "molecular" state rather than particulate state. In contrast to the form in which Mo was observed, Fe was always observed in conjunction with S and always in the form of a particle. The FeS has a particle size of 0.1-2.0 microns.

It is concluded that STEM is an extremely useful technique for analyzing the fine details of morphology and composition in coal liquefaction resid. As this analysis requires detailed information on local composition, transmission electron microscopy was determined to be a less useful technique compared to STEM.

ELECTRON MICROSCOPY OBSERVATIONS OF RESIDS
OBTAINED FROM COAL LIQUEFACTION EXPERIMENTS

Introduction

The goal of the research effort described in this report is to determine if transmission and scanning transmission electron microscopy are viable analytic techniques for investigating certain aspects of the direct coal liquefaction process. To this end, six samples were supplied to the author by CONSOL Inc. under a subcontract to DOE Contract DE-AC22-89PC89883. Sample Nos. 1-6 (see Tables 1-6) were tetrahydrofuran (THF) insoluble portions of solid 850°F+ materials (resids). All six samples are from the Wilsonville pilot plant. Each sample is the THF-insoluble portion of an individual sample taken during a single run period. Operating conditions were considered stable over the length of the period.

The first three samples (Nos. 1-3) are from Wilsonville Run 262. A description of the objectives of Run 262 and the experiences with this run are presented as Appendix A. Sample Nos. 1-3 were obtained during period B. The samples were taken from three different locations in the Wilsonville plant (refer to Figure 1). The samples taken at the three different sampling points during the same run are expected to represent different degrees of coal processing. The sampling point called "interstage" in Figure 1 (also refer to Tables 1-3) is between the first and second reactors. The sample designator for this sample is R1235. The sampling point called "Recycle" is at the

solvent surge tank, V131B. The third sample is obtained from vessel (V-1067) after the second reactor, but before the critical solvent deasher. It is designated "2nd stage product".

The second three samples (Nos. 4-6) are from Wilsonville Run 263 Period E. The objectives and experience with this run are presented as Appendix B. The sample designators, see Tables 4-6, have an identical definition to sample Nos. 1-3 and the reader is once again directed to Figure 1. The main difference between Runs 262 and 263 is that Run 262, Period B employed an added molybdenum concentration of 500 ppm MF coal whereas Run 263, Period E employed an added molybdenum concentration of 100 ppm MF coal. In both cases Molyvan L was used as the slurry catalyst. Data for Molyvan L is presented as Appendix C.

These six samples were observed by scanning transmission electron microscopy in an effort to determine differences (if any) between the three sampling points and the two different data sets (Nos. 1-3 versus Nos. 4-6).

Experimental Procedures

The samples were provided to the author as dry powders in sealed tubes. The background experimental procedures, provided with the samples, are presented as Appendix D.

Sample preparation for electron microscopy was straightforward. A thin (~ 50 Å) carbon film supported on a 3 mm diameter Cu mesh grid was immersed in a given vial and then

removed. The grid was lightly tapped to remove any loosely bound particles and then placed directly into the electron microscope. At least two different grids were observed for each sample. In addition it was observed that every grid square within a given grid had virtually an identical distribution of particles. The images presented below, although randomly chosen for analysis, are typical of all the observations made on that sample.

The majority of the work presented below was accomplished on a Vacuum Generators HB-5 scanning transmission electron microscope operating at 100 kV with a Link Systems windowless energy dispersive X-ray spectrometer and associated analyzer. On occasion, transmission electron microscopy of samples was performed on a JEOL 200 CX microscope operating at 200 kV. Early in the work it became clear that transmission electron microscopy alone would not provide sufficient information on composition to be useful and all work shifted to the STEM.

The STEM operates with a small probe (~ 1.5 nm) in a transmission mode. The X-rays generated when the electron beam interacts with the sample are detected by the energy dispersive X-ray detector. If the beam is scanning the sample and the instrument display (CRT) is being scanned synchronously and the CRT bright-up is being generated by a given X-ray intensity, then an X-ray map is produced. If the electron probe is stopped on a small area or feature, then a point analysis is produced. Numerous examples of each type of analysis are presented in the following.

As an example of X-ray mapping, Figure 2 from Sample

No. 3:262B, recycle is presented. An annular dark-field image is shown in the upper left hand corner of this image. Each of the other "images" is an X-ray map from the X-ray of the element shown in the legend. Notice the bright contrast in the Si and O maps, a result consistent with the presence of SiO₂ in this sample. Sample No. 3 will be discussed in more detail below. This series of maps is shown at this point for illustrative purposes only.

The result from a point analysis is an X-ray spectrum. An example is shown in Figure 3. It is noted that an energy dispersive X-ray spectrum (I vs. E) consists of peaks in intensity whose energy is characteristic of a certain element riding upon a background. This background is not associated with any given element but is associated with the X-ray photons generated when an incoming electron loses energy by any process. The generic process by which these background X-rays are produced is referred to as brehmstrahlung. An X-ray map is produced by choosing an energy window in a spectrum such as Figure 3 and having the CRT bright-up determined by the X-ray counts in that energy window. Note that a random background window would still show contrast in an X-ray map.

If background is subtracted from a spectrum then the ratio of X-ray peaks can be used to determine concentration by a relationship known as the Cliff-Lorimer equation

$$\frac{I_A}{I_B} = k_{AB}^{-1} \frac{C_A}{C_B} \quad (1)$$

where I_A and I_B are the X-ray intensities for elements A and B, C_A and C_B are the concentration of these elements, and k_{AB}^{-1} is the Cliff-Lorimer constant which can be determined experimentally or from first principles.

The way in which this equation is used can be demonstrated with reference to Figure 3 and Table 7. A "window" on the energy axis in Figure 3 is defined below a peak ("start keV" and "end keV" in Table 7). The number of X-ray counts in the window can then be determined (gross integral). A local background level for this peak can be established and the background counts subtracted to yield a net integral count. The k_{AB} factor is called the Eff. (efficiency) factor in Table 7. Equation (1) is then used to obtain "% age total", which is the weight percentage of the element whose X-ray peak had been undergoing this analysis. It is always assumed that the sum of all the elements will be unity. Thus, for N elements there are N-1 unique versions of Equation (1) plus the sum of N equal to unity yielding N equations with N unknowns.

Results and Discussion

This section will be constructed in the order of the six samples referred to above.

Sample No. 1: 262B, Recycle

A low magnification image of this sample is shown as

Figure 4. This is an annular dark-field image where the brightness of a feature in the image is an indication of the relative thickness of that feature, where greater thickness leads to brighter contrast. A higher magnification bright-field image is shown as Figure 5.

The series of X-ray maps for the region shown as Figure 5 are presented in Figure 6. The upper left hand corner is the annular dark-field image counterpart of Figure 5. The Fe, S, and Mo maps are also presented. If one superimposes the Fe and S maps it is generally seen that a strong Fe and S signal is produced from the same region. The nature of the contrast in these maps is consistent with particles of FeS. The Mo map, however, is much more diffuse and barely above background levels (brehmstrahlung). This suggests that Mo is not concentrated in the form of particles but is in the form of an organic-like solid. In this analysis a particle has a rather uniform, bright contrast and a well-defined edge. The Mo "contrast" is not uniform and has no well-defined perimeter. The Mo atoms are therefore distributed with a "particle size" that is smaller than the resolution of this instrument (~ 2.0 nm).

Point analysis from various regions in Figure 7, shown in Table 7, shows local enrichment of Mo.

Sample No. 2: 262B, Interstage

Figure 8 shows the annular dark-field image of a typical region of this sample. The associated X-ray map (for Fe, S,

and Mo) is shown as Figure 9. As in Sample No. 1, FeS particles are present and, for the most part, Mo is presented in a diffuse, non-particle way. The one exception is the bright Mo-rich particle seen in Figure 8 in the Mo map.

Sample No. 3: 262B, Second Stage Product

A low magnification annular dark-field image is shown in Figure 10. Two bright field images with associated X-ray maps are shown as Figure 11a and b. The contrast in the Mo map is from the larger amount of brehmstrahlung associated with the thicker sample region and is not to be interpreted as a local enrichment in Mo.

Point analysis from this sample (see Figure 12 and the data of Table 8) show some small amount of Mo enrichment. The "overall" scan from such areas shows the lowest Mo concentration to exist in this sample compared to Sample Nos. 1 and 2.

Sample No. 4: 263E, Recycle

An annular dark-field image and associated X-ray maps are shown as Figures 13a and b. Again, FeS is shown and it can be seen that the Mo map and the "background" map (marked Bk) show the same contrast level and, therefore, the Mo signal is not present above background.

Point analysis, however, as shown in Figure 14 and Table 9, show some local regions of Mo enrichment.

Sample No. 5: 263E, Interstage and
Sample No. 6: 263E, Second Stage Product

Figures 15 and 16 show annular dark-field images of these samples, respectively. In the case of both samples, Mo was not detected either in X-ray maps or in point counts.

Comments

Auger spectroscopy was not attempted on these samples because the STEM results demonstrated that the spatial resolution for compositional analysis in Auger spectroscopy (~ 500 nm) would not be sufficient to "observe" the Mo-rich regions seen here. Electron energy loss spectroscopy (EELS) was not routinely used in this work because its utility as a semi-quantitative analysis technique is very sample thickness dependent, a potential problem for particle analysis as was required here where large changes in thickness were observed. It was felt that scoping work of the type done here was best accomplished using energy dispersive X-ray spectroscopy. However, future research employing EELS to learn more about the local chemical environment of the Mo would be extremely useful.

Conclusions:

- (1) Scanning transmission electron microscopy (STEM) has been used for the analysis of various elements and compounds in distillation resids. This analysis has been accomplished with a spatial resolution for

compositional analysis of order 2.0 nm. Transmission electron microscopy alone does not provide sufficient capability for compositional analysis of these samples.

- (2) Mo from the Molyvan L slurry catalyst has been thoroughly analyzed by STEM in the six samples provided. The largest localized concentrations of Mo were found from the "Recycle" sampling point (V-131B).
- (3) The Mo present is, in nearly every case, observed as a diffuse thin layer with the Mo atoms being either in a molecular state or in "particles" with a "particle" size below the resolution of the STEM (2.0 nm).
- (4) Mo was observed in each of Samples No.1-3 with a fresh Mo concentration of 500 ppm MF coal. Again, the largest localized concentrations were observed in Sample No. 1. Mo was only observed in Sample No. 4 in the second suite of samples with a fresh Mo concentration of 100 ppm MF coal.
- (5) Conventional compositional analysis (Tables 1-6) suggest that the Mo concentration is least at the "Recycle" sampling point and largest at the "Second Stage Product" (V-1067) sampling point, in apparent conflict with the results of this work. In fact, the data of Tables 1-6 and the data in this

report are undoubtedly both correct inasmuch as the STEM determines the morphology of the Mo-concentrated regions, whereas the gross compositional analysis of Tables 1-6 speak to total concentration independent of distribution. In addition, the Mo concentration variations from point to point in the reactor, as shown in Tables 1-3 and 4-6, are quite small and might be considered, for each run, to be constant.

- (6) S was often observed in conjunction with Mo.
- (7) Fe and S were observed together, as FeS, in the form of particles between 0.1-2.0 microns in size in all samples.

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TABLE 1: ANALYSIS OF THF-INSOLUBLE DISTILLATION RESID

| | | |
|--|--------------------------------|-------|
| Ref. No. 1 | | |
| | Ultimate | |
| Run Number:262 B | Ash, wt% dry | 47.79 |
| Sample Designator:V-131B | C, wt % dry | 45.56 |
| Sampling Point:Recycle | H, wt % dry | 2.77 |
| Feed Coal:Wyodak and Anderson Seam | N, wt % dry | 0.82 |
| Black Thunder Mine | S, wt % dry | 4.52 |
| Insoluble Organic Material | | |
| (as % of Parent Resid): 10.1 | | |
| Major Ash Elementals (wt% of ash) | | |
| | Na ₂ O | 0.40 |
| | K ₂ O | 0.24 |
| | CaO | 16.28 |
| | MgO | 3.50 |
| | Fe ₂ O ₃ | 22.49 |
| | TiO ₂ | 0.87 |
| | P ₂ O ₅ | 1.74 |
| | SiO ₂ | 21.50 |
| | Al ₂ O ₃ | 11.49 |
| | SO ₃ | 19.86 |
| | Unaccounted | 1.63 |
| Trace Ash Elementals (ppm of dry sample) | | |
| | Mo | 2411 |

TABLE 2: ANALYSIS OF THF-INSOLUBLE DISTILLATION RESID

| | | |
|------------------------------------|--------------|-------|
| Ref. No. 2 | Ultimate | |
| Run Number:262 B | Ash, wt% dry | 49.05 |
| Sample Designator:R-1235 | C, wt % dry | 44.54 |
| Sampling Point:Interstage | H, wt % dry | 2.67 |
| Feed Coal:Wyodak and Anderson Seam | N, wt % dry | 0.76 |
| Black Thunder Mine | S, wt % dry | 4.61 |

Insoluble Organic Material
(as % of Parent Resid): 11.9

| | |
|-----------------------------------|-------|
| Major Ash Elementals (wt% of ash) | |
| Na ₂ O | 0.41 |
| K ₂ O | 0.25 |
| CaO | 16.20 |
| MgO | 3.48 |
| Fe ₂ O ₃ | 22.17 |
| TiO ₂ | 0.86 |
| P ₂ O ₅ | 1.92 |
| SiO ₂ | 22.16 |
| Al ₂ O ₃ | 11.43 |
| SO ₃ | 19.33 |
| Unaccounted | 1.79 |

| | |
|--|------|
| Trace Ash Elementals (ppm of dry sample) | |
| Mo | 2852 |

TABLE 3: ANALYSIS OF THF-INSOLUBLE DISTILLATION RESID

| | | |
|--|--------------------------------|-------|
| Ref. No. 3 | | |
| Run Number:262 B | Ultimate | |
| Sample Designator:V-1067 | Ash, wt% dry | 52.01 |
| Sampling Point:2nd Stage Product | C, wt % dry | 42.50 |
| Feed Coal:Wyodak and Anderson Seam | H, wt % dry | 2.55 |
| Black Thunder Mine | N, wt % dry | 0.77 |
| | S, wt % dry | 4.94 |
| Insoluble Organic Material | | |
| (as % of Parent Resid): 11.2 | | |
| Major Ash Elementals (wt% of ash) | | |
| | Na ₂ O | 0.39 |
| | K ₂ O | 0.26 |
| | CaO | 16.30 |
| | MgO | 3.53 |
| | Fe ₂ O ₃ | 22.20 |
| | TiO ₂ | 0.86 |
| | P ₂ O ₅ | 1.96 |
| | SiO ₂ | 21.70 |
| | Al ₂ O ₃ | 11.55 |
| | SO ₃ | 19.84 |
| | Unaccounted | 1.41 |
| Trace Ash Elementals (ppm of dry sample) | | |
| | Mo | 3133 |

TABLE 4: ANALYSIS OF THF-INSOLUBLE DISTILLATION RESID

| | | |
|------------------------------------|--------------|-------|
| Ref. No. 4 | Ultimate | |
| Run Number:263 E | Ash, wt% dry | 65.37 |
| Sample Designator:V-131B | C, wt % dry | 34.36 |
| Sampling Point:Recycle | H, wt % dry | 1.84 |
| Feed Coal:Wyodak and Anderson Seam | N, wt % dry | 0.51 |
| Black Thunder Mine | S, wt % dry | 6.31 |

Insoluble Organic Material
(as % of Parent Resid): 9.2

| | |
|--|---------|
| Major Ash Elementals (wt% of ash) | |
| Na ₂ O | 0.22 |
| K ₂ O | 0.35 |
| CaO | 16.35 |
| MgO | 3.26 |
| Fe ₂ O ₃ | 22.76 |
| TiO ₂ | 0.84 |
| P ₂ O ₅ | 1.30 |
| SiO ₂ | 21.67 |
| Al ₂ O ₃ | 13.10 |
| SO ₃ | 19.76 |
| Unaccounted | 0.39 |
| Trace Ash Elementals (ppm of dry sample) | |
| Mo | 1312.50 |

TABLE 5: ANALYSIS OF THF-INSOLUBLE DISTILLATION RESID

Ref. No. 5

| | Ultimate | |
|------------------------------------|--------------|-------|
| Run Number:263 E | Ash, wt% dry | 62.37 |
| Sample Designator:R-1235 | C, wt % dry | 35.93 |
| Sampling Point:Interstage | H, wt % dry | 1.97 |
| Feed Coal:Wyodak and Anderson Seam | N, wt % dry | 0.52 |
| Black Thunder Mine | S, wt % dry | 5.99 |

Insoluble Organic Material
(as % of Parent Resid): 10.2

Major Ash Elementals (wt% of ash)

| | |
|--------------------------------|-------|
| Na ₂ O | 0.22 |
| K ₂ O | 0.35 |
| CaO | 16.76 |
| MgO | 3.29 |
| Fe ₂ O ₃ | 22.75 |
| TiO ₂ | 0.85 |
| P ₂ O ₅ | 1.31 |
| SiO ₂ | 21.35 |
| Al ₂ O ₃ | 13.07 |
| SO ₃ | 19.70 |
| Unaccounted | 0.35 |

Trace Ash Elementals (ppm of dry sample)

| | |
|----|---------|
| Mo | 1265.50 |
|----|---------|

TABLE 6: ANALYSIS OF THF-INSOLUBLE DISTILLATION RESID

Ref. No. 6

| | Ultimate | |
|-------------------------------------|--------------|-------|
| Run Number:263 E | Ash, wt% dry | 65.79 |
| Sample Designator:V-1067 | C, wt % dry | 33.73 |
| Sampling Point:Second Stage Product | H, wt % dry | 1.80 |
| Feed Coal:Wyodak and Anderson Seam | N, wt % dry | 0.52 |
| Black Thunder Mine | S, wt % dry | 6.20 |

Insoluble Organic Material
(as % of Parent Resid): 10.4

Major Ash Elementals (wt% of ash)

| | |
|--------------------------------|-------|
| Na ₂ O | 0.22 |
| K ₂ O | 0.35 |
| CaO | 16.31 |
| MgO | 3.26 |
| Fe ₂ O ₃ | 22.49 |
| TiO ₂ | 0.85 |
| P ₂ O ₅ | 1.29 |
| SiO ₂ | 22.38 |
| Al ₂ O ₃ | 13.18 |
| SO ₃ | 20.30 |
| Unaccounted | -0.63 |

Trace Ash Elementals (ppm of dry sample)

| | |
|----|---------|
| Mo | 1315.50 |
|----|---------|

Table 7: X-ray point analyses of points 5, 6, and 7 from Figure 7. Note Mo enrichment.

| MEM1: WINDOW LABEL | START keV | END keV | WIDTH CHANS | GROSS INTEGRAL | NET INTEGRAL | EFF. FACTOR | %AGE TOTAL |
|--------------------------|--------------|------------|----------------|-------------------|-----------------|----------------|---------------|
| O | .38 | .64 | 14 | 303 | 23 | .88 | .61 |
| Mg | 1.10 | 1.36 | 14 | 513 | 275 | .66 | 5.46 |
| Al | 1.38 | 1.60 | 12 | 599 | 323 | .57 | 5.53 |
| SiSr | 1.66 | 1.92 | 14 | 997 | 395 | .62 | 7.37 |
| P | 1.94 | 2.14 | 11 | 487 | 135 | .64 | 2.60 |
| S | 2.18 | 2.48 | 16 | 2168 | 1464 | .60 | 26.45 |
| Cl | 2.50 | 2.76 | 14 | 277 | -45 | .65 | -.88 |
| Ca | 3.56 | 3.82 | 14 | 1239 | 924 | .74 | 20.62 |
| BaTi | 4.32 | 4.62 | 16 | 139 | 27 | 1.00 | .82 |
| Fe | 6.20 | 6.56 | 19 | 235 | 131 | 1.00 | 3.95 |
| Sr | 13.78 | 14.44 | 34 | 36 | -15 | 2.83 | -1.28 |
| Mo | 17.12 | 17.66 | 28 | 328 | 230 | 4.14 | 28.76 |

POINT
5

| MEM1: WINDOW LABEL | START keV | END keV | WIDTH CHANS | GROSS INTEGRAL | NET INTEGRAL | EFF. FACTOR | %AGE TOTAL |
|--------------------------|--------------|------------|----------------|-------------------|-----------------|----------------|---------------|
| O | .38 | .64 | 14 | 268 | -12 | .88 | -.41 |
| Mg | 1.10 | 1.36 | 14 | 408 | 226 | .66 | 5.81 |
| Al | 1.38 | 1.60 | 12 | 495 | 231 | .57 | 5.12 |
| SiSr | 1.66 | 1.92 | 14 | 663 | 250 | .62 | 6.04 |
| P | 1.94 | 2.14 | 11 | 326 | 73 | .64 | 1.82 |
| S | 2.18 | 2.48 | 16 | 1786 | 1178 | .60 | 27.58 |
| Cl | 2.50 | 2.76 | 14 | 218 | -69 | .65 | -1.75 |
| Ca | 3.56 | 3.82 | 14 | 868 | 637 | .74 | 18.42 |
| BaTi | 4.32 | 4.62 | 16 | 113 | 17 | 1.00 | .67 |
| Fe | 6.20 | 6.56 | 19 | 193 | 127 | 1.00 | 4.95 |
| Sr | 13.78 | 14.44 | 34 | 31 | -3 | 2.83 | -.33 |
| Mo | 17.12 | 17.66 | 28 | 268 | 198 | 4.14 | 32.08 |

POINT
6

| MEM1: WINDOW LABEL | START keV | END keV | WIDTH CHANS | GROSS INTEGRAL | NET INTEGRAL | EFF. FACTOR | %AGE TOTAL |
|--------------------------|--------------|------------|----------------|-------------------|-----------------|----------------|---------------|
| O | .38 | .64 | 14 | 301 | 63 | .88 | 1.14 |
| Mg | 1.10 | 1.36 | 14 | 476 | 189 | .66 | 2.56 |
| Al | 1.38 | 1.60 | 12 | 503 | 221 | .57 | 2.58 |
| SiSr | 1.66 | 1.92 | 14 | 678 | 265 | .62 | 3.38 |
| P | 1.94 | 2.14 | 11 | 526 | 130 | .64 | 1.71 |
| S | 2.18 | 2.48 | 16 | 3468 | 2388 | .60 | 29.45 |
| Cl | 2.50 | 2.76 | 14 | 361 | -87 | .65 | -1.16 |
| Ca | 3.56 | 3.82 | 14 | 979 | 727 | .74 | 11.08 |
| BaTi | 4.32 | 4.62 | 16 | 163 | 19 | 1.00 | .39 |
| Fe | 6.20 | 6.56 | 19 | 248 | 153 | 1.00 | 3.16 |
| Sr | 13.78 | 14.44 | 34 | 40 | -11 | 2.83 | -.64 |
| Mo | 17.12 | 17.66 | 28 | 655 | 543 | 4.14 | 46.36 |

POINT
7

Table 8: X-ray point analyses of points 10, 11 and 13 from Figure 12. Note very modest Mo enrichment at points 10 and 13 and lack of Mo at point 11 (negative value).

| MEM1: WINDOW LABEL | START keV | END keV | WIDTH CHANS | GROSS INTEGRAL | NET INTEGRAL | EFF. FACTOR | %AGE TOTAL |
|--------------------------|--------------|------------|----------------|-------------------|-----------------|----------------|---------------|
| O | .38 | .64 | 14 | 3158 | 1940 | .88 | 32.63 |
| Mg | 1.10 | 1.36 | 14 | 1376 | 718 | .66 | 9.02 |
| Al | 1.38 | 1.60 | 12 | 1742 | 1214 | .57 | 13.16 |
| SiSr | 1.66 | 1.92 | 14 | 518 | 168 | .62 | 1.98 |
| P | 1.94 | 2.14 | 11 | 377 | 69 | .64 | .84 |
| S | 2.18 | 2.48 | 16 | 882 | 474 | .60 | 5.42 |
| Cl | 2.50 | 2.76 | 14 | 434 | 133 | .65 | 1.65 |
| Ca | 3.56 | 3.82 | 14 | 2620 | 2081 | .74 | 29.40 |
| BaTi | 4.32 | 4.62 | 16 | 285 | 125 | 1.00 | 2.39 |
| Fe | 6.20 | 6.56 | 19 | 192 | 97 | 1.00 | 1.86 |
| Sr | 13.78 | 14.44 | 34 | 78 | 10 | 2.83 | .54 |
| Mo | 17.12 | 17.66 | 28 | 28 | 14 | 4.14 | 1.11 |

POINT
10

| MEM1: WINDOW LABEL | START keV | END keV | WIDTH CHANS | GROSS INTEGRAL | NET INTEGRAL | EFF. FACTOR | %AGE TOTAL |
|--------------------------|--------------|------------|----------------|-------------------|-----------------|----------------|---------------|
| O | .38 | .64 | 14 | 33361 | 28552 | .88 | 44.78 |
| Mg | 1.10 | 1.36 | 14 | 2748 | -724 | .66 | -.85 |
| Al | 1.38 | 1.60 | 12 | 31988 | 24302 | .57 | 24.56 |
| SiSr | 1.66 | 1.92 | 14 | 41678 | 27664 | .62 | 30.47 |
| P | 1.94 | 2.14 | 11 | 1267 | -42 | .64 | -.05 |
| S | 2.18 | 2.48 | 16 | 1610 | 242 | .60 | .26 |
| Cl | 2.50 | 2.76 | 14 | 972 | 83 | .65 | .10 |
| Ca | 3.56 | 3.82 | 14 | 1073 | 289 | .74 | .38 |
| BaTi | 4.32 | 4.62 | 16 | 631 | 39 | 1.00 | .07 |
| Fe | 6.20 | 6.56 | 19 | 799 | 220 | 1.00 | .39 |
| Sr | 13.78 | 14.44 | 34 | 328 | -12 | 2.83 | -.06 |
| Mo | 17.12 | 17.66 | 28 | 190 | -6 | 4.14 | -.04 |

POINT
11

| MEM1: WINDOW LABEL | START keV | END keV | WIDTH CHANS | GROSS INTEGRAL | NET INTEGRAL | EFF. FACTOR | %AGE TOTAL |
|--------------------------|--------------|------------|----------------|-------------------|-----------------|----------------|---------------|
| O | .38 | .64 | 14 | 13901 | 7874 | .88 | 16.41 |
| Mg | 1.10 | 1.36 | 14 | 2333 | 884 | .66 | 1.38 |
| Al | 1.38 | 1.60 | 12 | 2384 | 1016 | .57 | 1.36 |
| SiSr | 1.66 | 1.92 | 14 | 1985 | 291 | .62 | .43 |
| P | 1.94 | 2.14 | 11 | 1585 | 83 | .64 | .13 |
| S | 2.18 | 2.48 | 16 | 19915 | 15491 | .60 | 21.95 |
| Cl | 2.50 | 2.76 | 14 | 1352 | -552 | .65 | -.85 |
| Ca | 3.56 | 3.82 | 14 | 9798 | 7761 | .74 | 13.58 |
| BaTi | 4.32 | 4.62 | 16 | 589 | -35 | 1.00 | -.08 |
| Fe | 6.20 | 6.56 | 19 | 20758 | 18754 | 1.00 | 44.46 |
| Sr | 13.78 | 14.44 | 34 | 261 | 40 | 2.83 | .27 |
| Mo | 17.12 | 17.66 | 28 | 254 | 100 | 4.14 | .98 |

POINT
13

Table 9: X-ray point analyses of points 6 and 8
from Sample No. 4, Figure 14.

| MEM1: WINDOW LABEL | START keV | END keV | WIDTH CHANS | GROSS INTEGRAL | NET INTEGRAL | EFF. FACTOR | %AGE TOTAL |
|--------------------------|--------------|------------|----------------|-------------------|-----------------|----------------|---------------|
| O | .38 | .64 | 14 | 22378 | 10002 | .88 | 31.10 |
| Mg | 1.10 | 1.36 | 14 | 7933 | 3950 | .66 | 9.17 |
| Al | 1.38 | 1.60 | 12 | 16799 | 10895 | .57 | 21.83 |
| SiSr | 1.66 | 1.92 | 14 | 13026 | 7524 | .62 | 16.43 |
| P | 1.94 | 2.14 | 11 | 1861 | 233 | .64 | .52 |
| S | 2.18 | 2.48 | 16 | 4258 | 2130 | .60 | 4.50 |
| Cl | 2.50 | 2.76 | 14 | 1303 | -132 | .65 | -.30 |
| Ca | 3.56 | 3.82 | 14 | 4541 | 2882 | .74 | 7.53 |
| BaTi | 4.32 | 4.62 | 16 | 1643 | 645 | 1.00 | 2.28 |
| Fe | 6.20 | 6.56 | 19 | 1941 | 1153 | 1.00 | 4.08 |
| Sr | 13.78 | 14.44 | 34 | 381 | 58 | 2.83 | .58 |
| Mo | 17.12 | 17.66 | 28 | 407 | 155 | 4.14 | 2.27 |

POINT 6

| MEM1: WINDOW LABEL | START keV | END keV | WIDTH CHANS | GROSS INTEGRAL | NET INTEGRAL | EFF. FACTOR | %AGE TOTAL |
|--------------------------|--------------|------------|----------------|-------------------|-----------------|----------------|---------------|
| O | .38 | .64 | 14 | 21066 | 15683 | .88 | 46.00 |
| Mg | 1.10 | 1.36 | 14 | 4683 | 2653 | .66 | 5.81 |
| Al | 1.38 | 1.60 | 12 | 12864 | 9960 | .57 | 18.83 |
| SiSr | 1.66 | 1.92 | 14 | 11617 | 8229 | .62 | 16.95 |
| P | 1.94 | 2.14 | 11 | 1022 | 148 | .64 | .31 |
| S | 2.18 | 2.48 | 16 | 2105 | 1009 | .60 | 2.01 |
| Cl | 2.50 | 2.76 | 14 | 673 | -20 | .65 | -.04 |
| Ca | 3.56 | 3.82 | 14 | 3161 | 2307 | .74 | 5.68 |
| BaTi | 4.32 | 4.62 | 16 | 798 | 398 | 1.00 | 1.33 |
| Fe | 6.20 | 6.56 | 19 | 653 | 321 | 1.00 | 1.07 |
| Sr | 13.78 | 14.44 | 34 | 188 | 35 | 2.83 | .33 |
| Mo | 17.12 | 17.66 | 28 | 208 | 124 | 4.14 | 1.71 |

POINT 8

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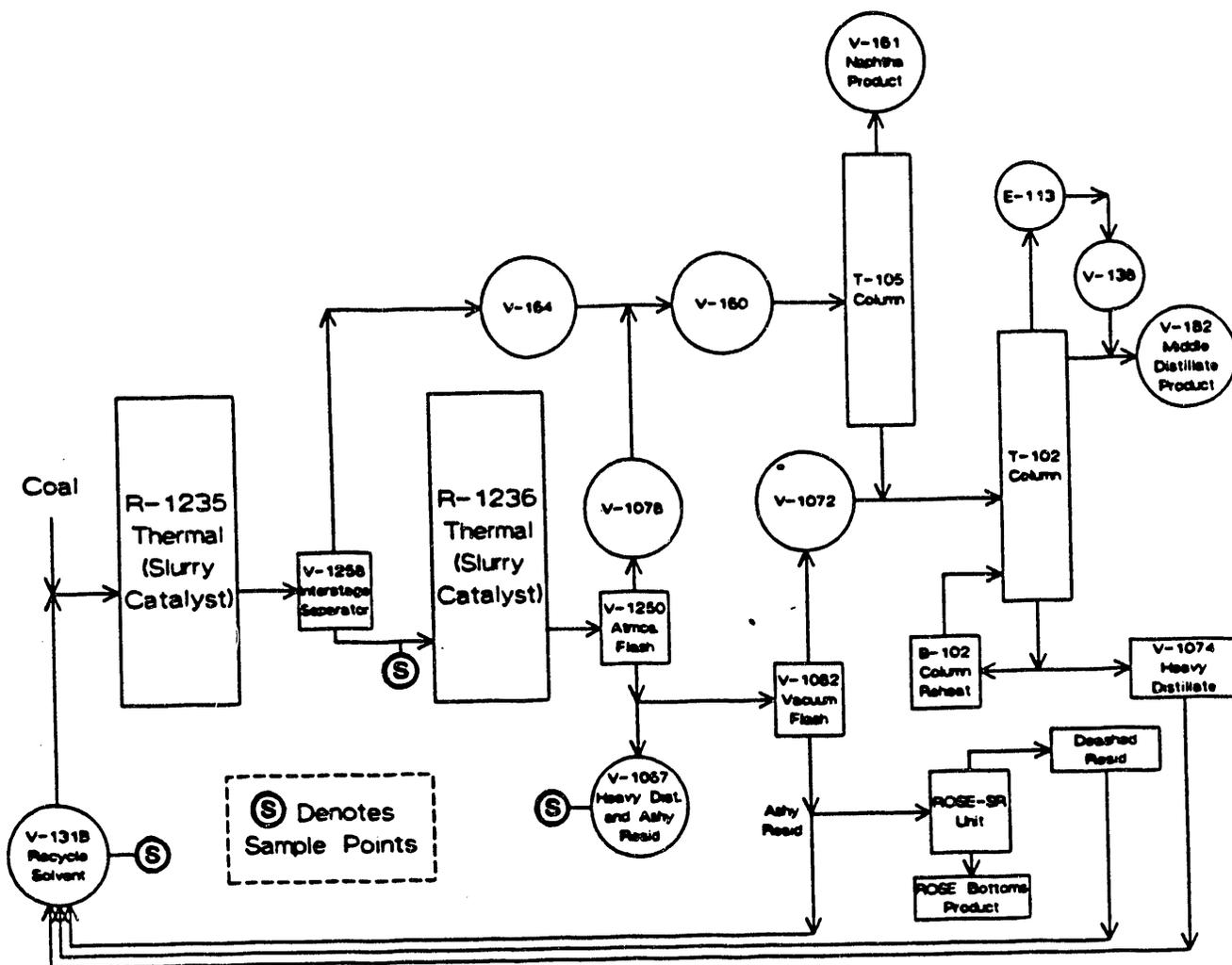
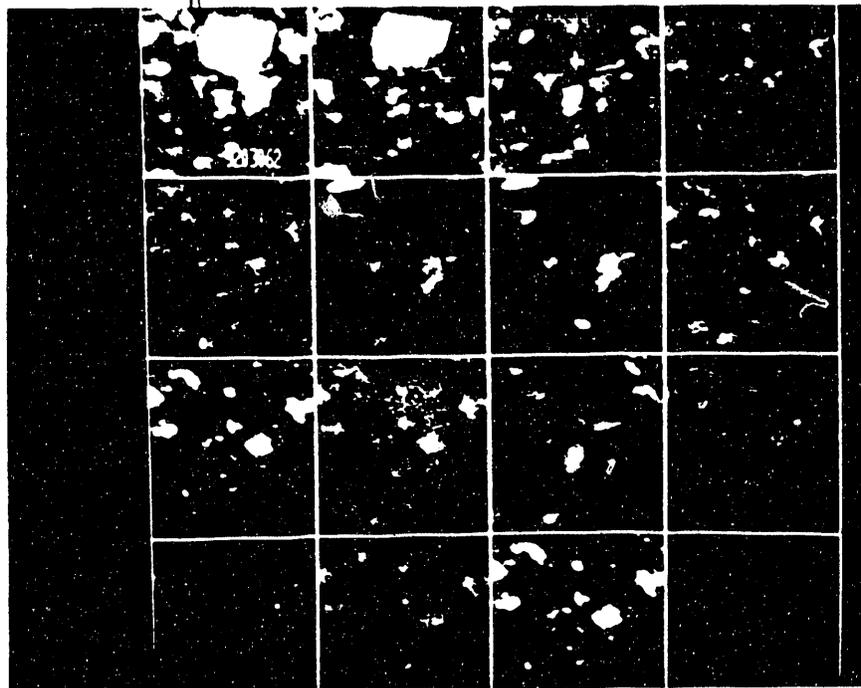


Figure 1. Partial CC-ITSL Process diagram for Wilsonville Run 263 Showing Major Distillate Streams.



10,000X

LEGEND

| | | | |
|-------|----|----|----|
| Image | C | O | Bk |
| Mg | Al | Si | P |
| S | Cl | Ca | Ti |
| V | Mn | Fe | Mo |

Figure 2: An Example of X-ray Maps from Sample No. 3: 262B, Recycle. In this legend "Bk" refers to background.

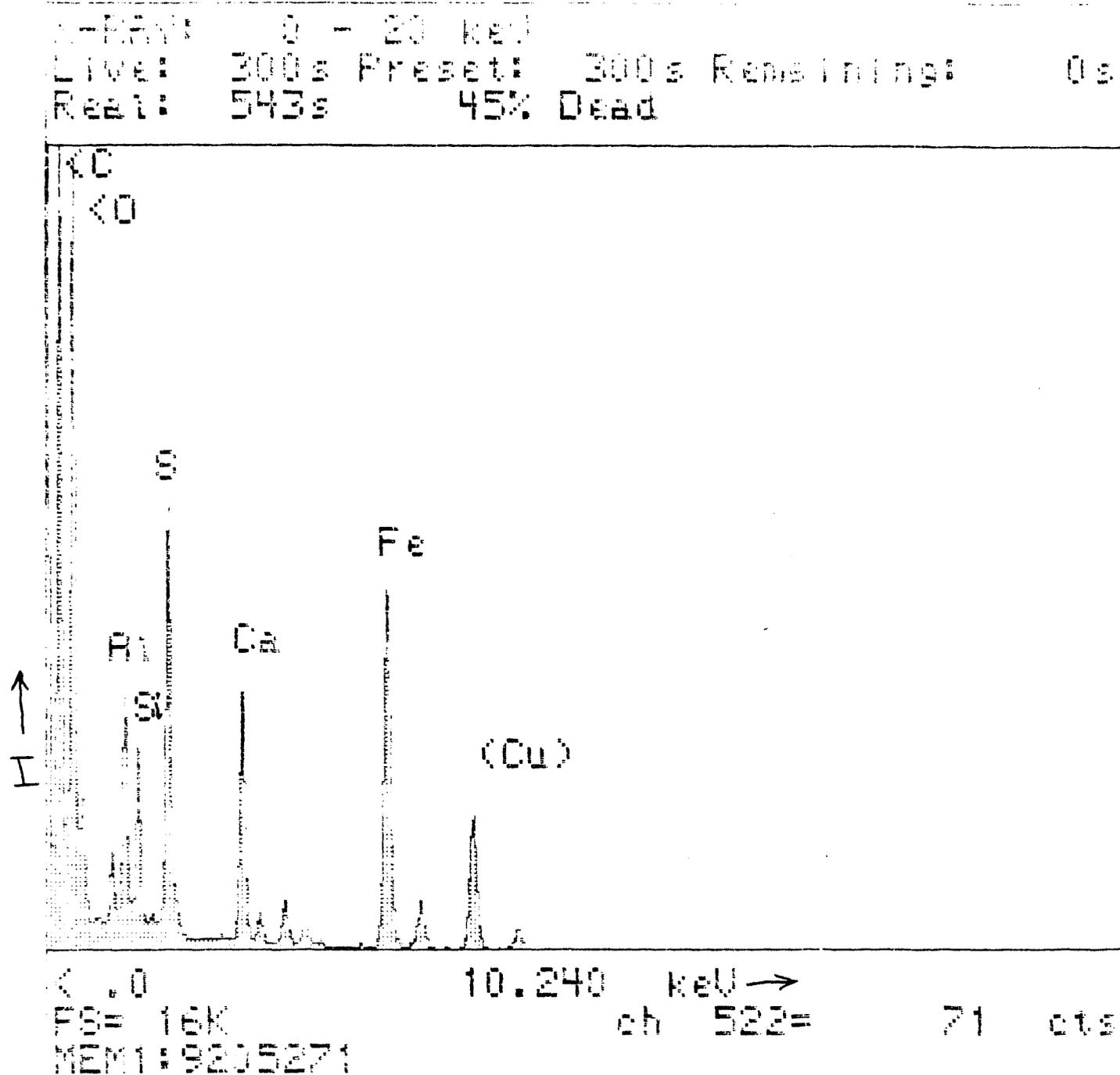
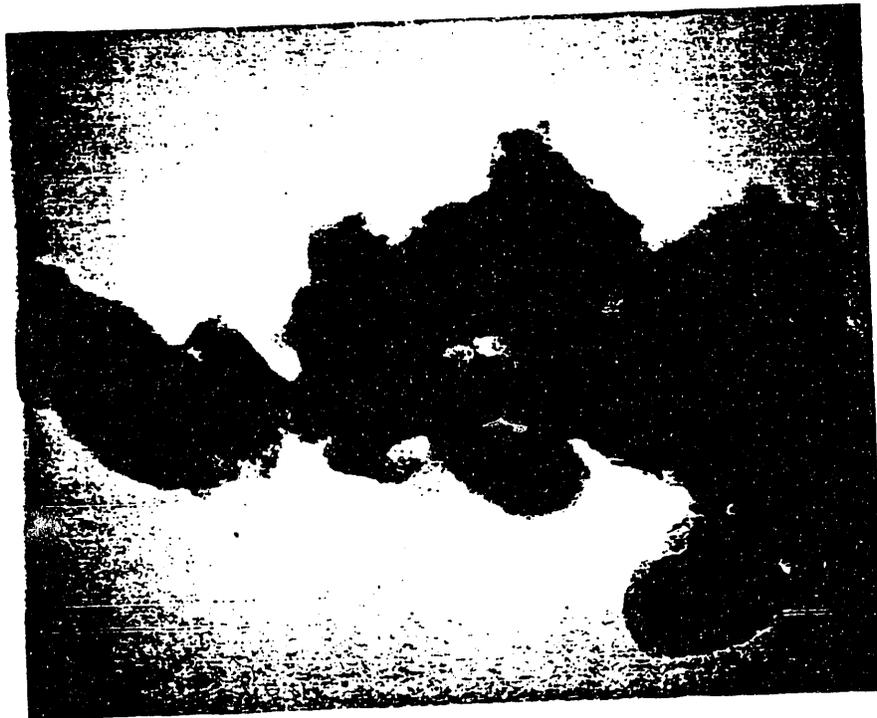


Figure 3. An Example of an Energy Dispersive X-ray Spectrum (X-ray Intensity, I, versus X-ray Energy, E).



1 μ m

Figure 4: Annular Dark-field Image of Sample No. 1.



0.1 μ m

Figure 5: A Bright-field Image of Sample No. 1.

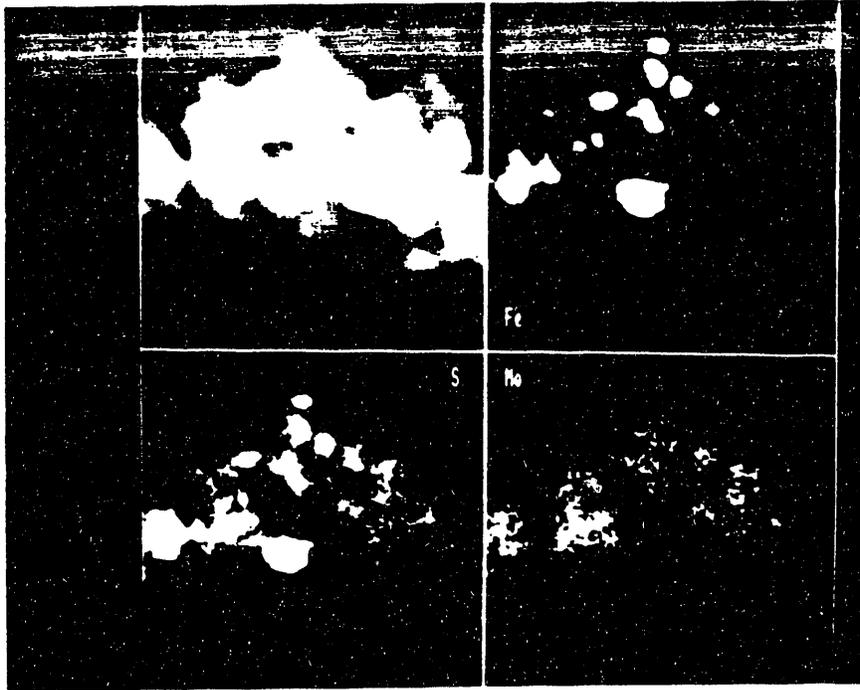


Figure 6: A Series of X-ray Maps for the Region of Sample No. 1 Shown in Figure 5.

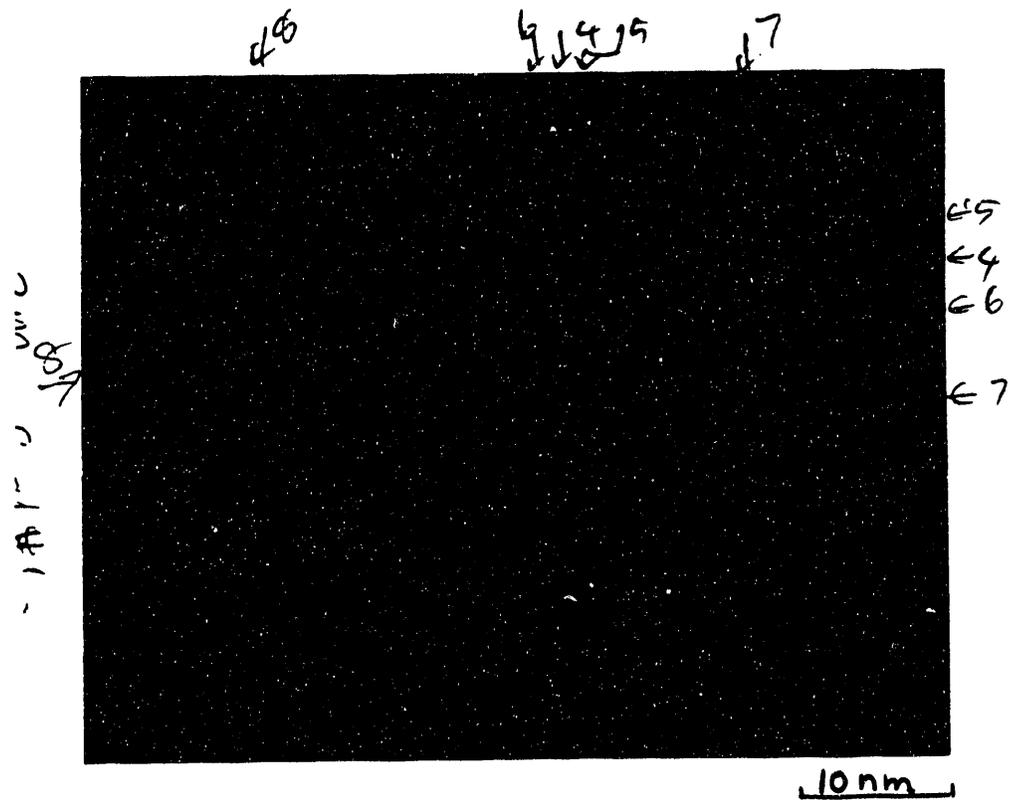


Figure 7: Annular Dark-Field Image of an Area in Sample No. 1 Showing the Location of X-ray Point Analyses Presented in Table 7.

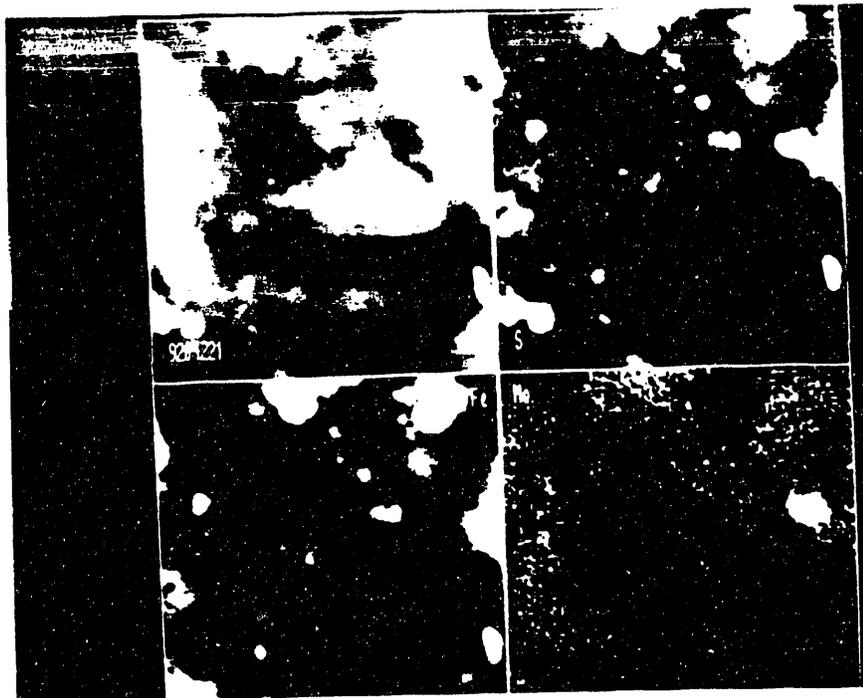
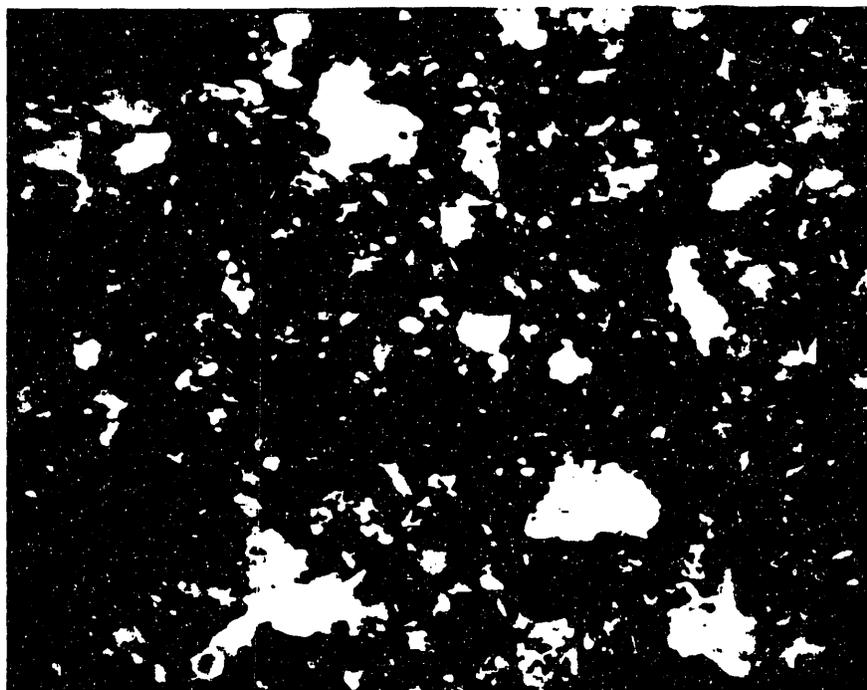


Figure 8: Annular Dark-Field Image of Sample No. 2.



Figure 9: X-ray Maps from the Region of Sample No. 2 Shown in Figure 8. Note Presence of Mo-rich Particle.



5 μm

Figure 10: Annular Dark-field Image of Sample No. 3.

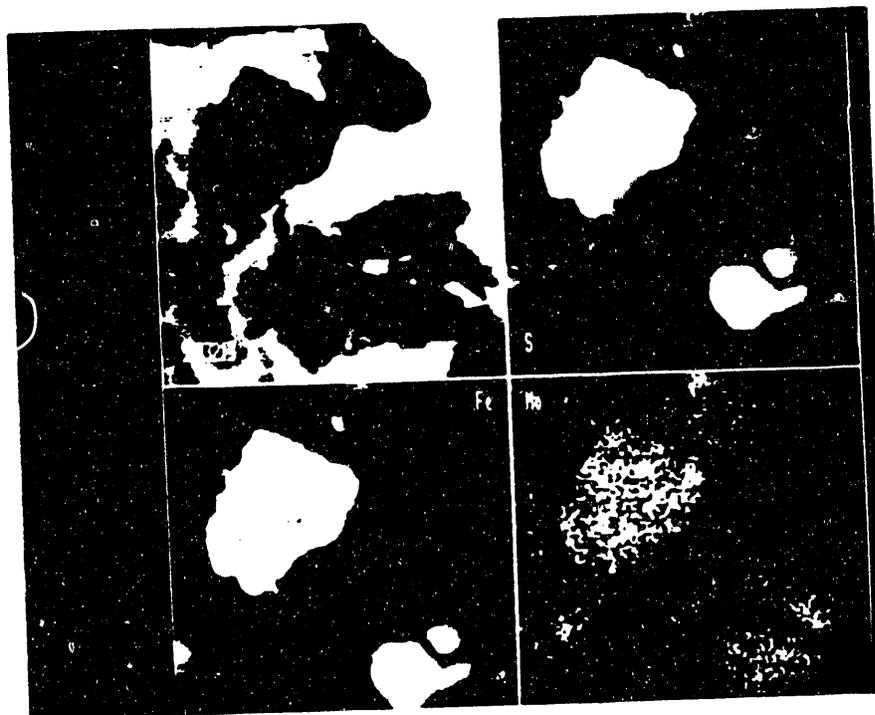
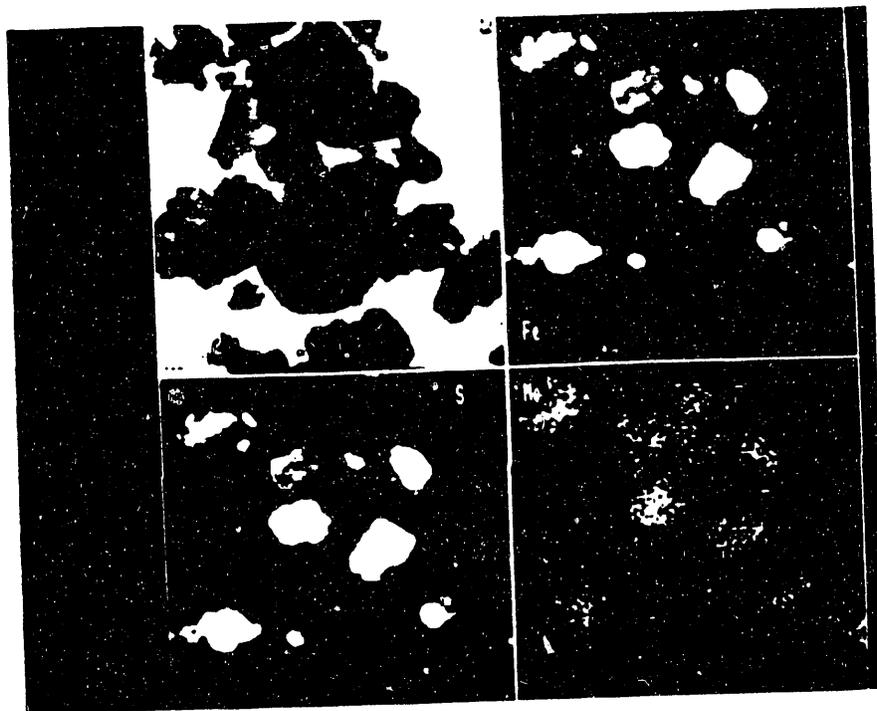
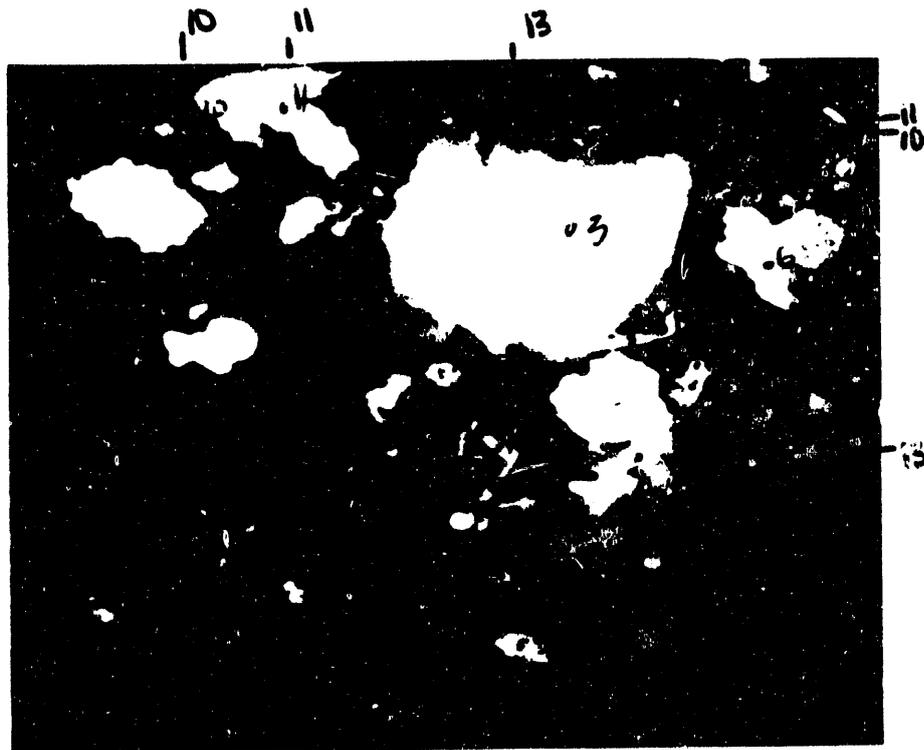


Figure 11: (a) and (b) are X-ray Maps from Two Regions (See Images in Upper Left Hand Corner) in Sample No. 3.



2 μm

Figure 12: Annular Dark-field Image of Sample No. 3
Showing Position of X-ray Point Analysis
Presented as Table 8.

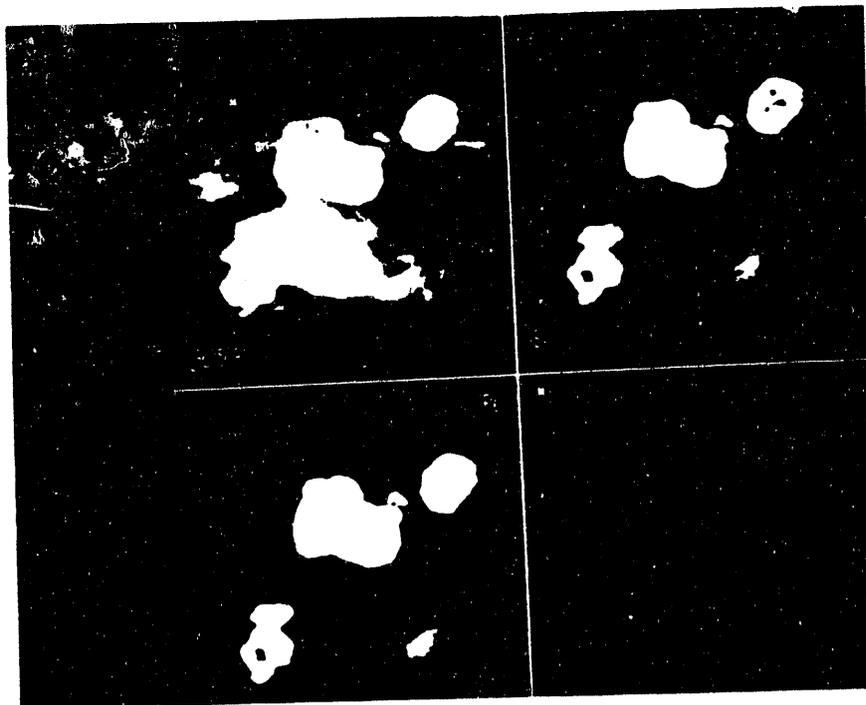
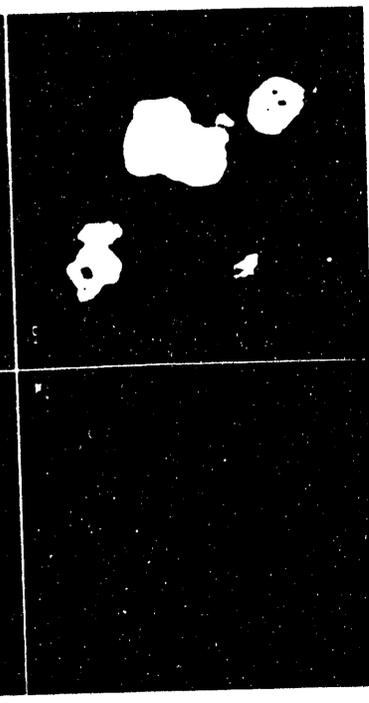
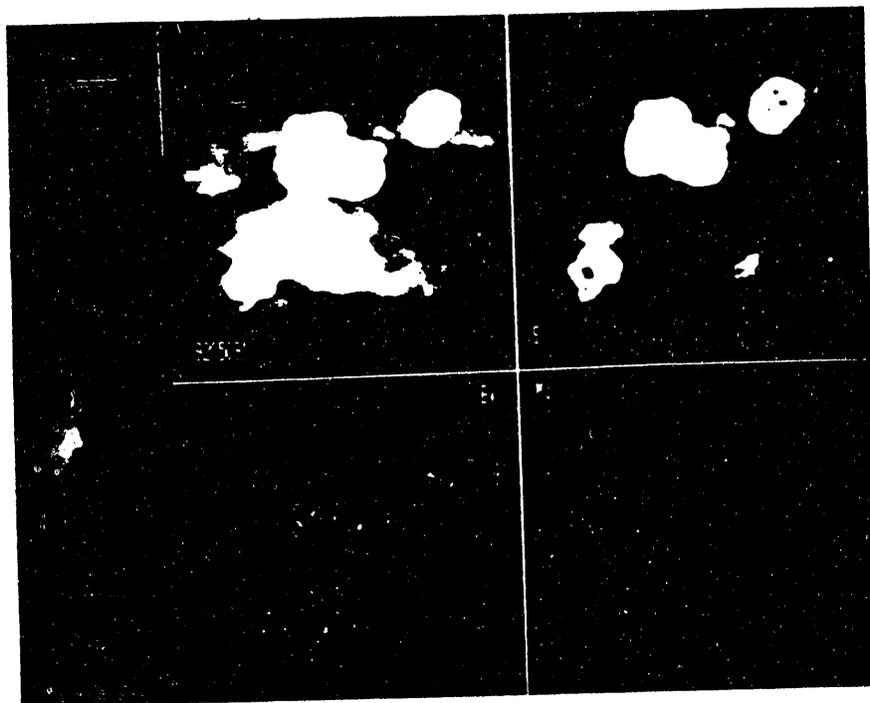


Figure 13. (a) and (b) X-ray Maps of a Region of Sample No. 4.

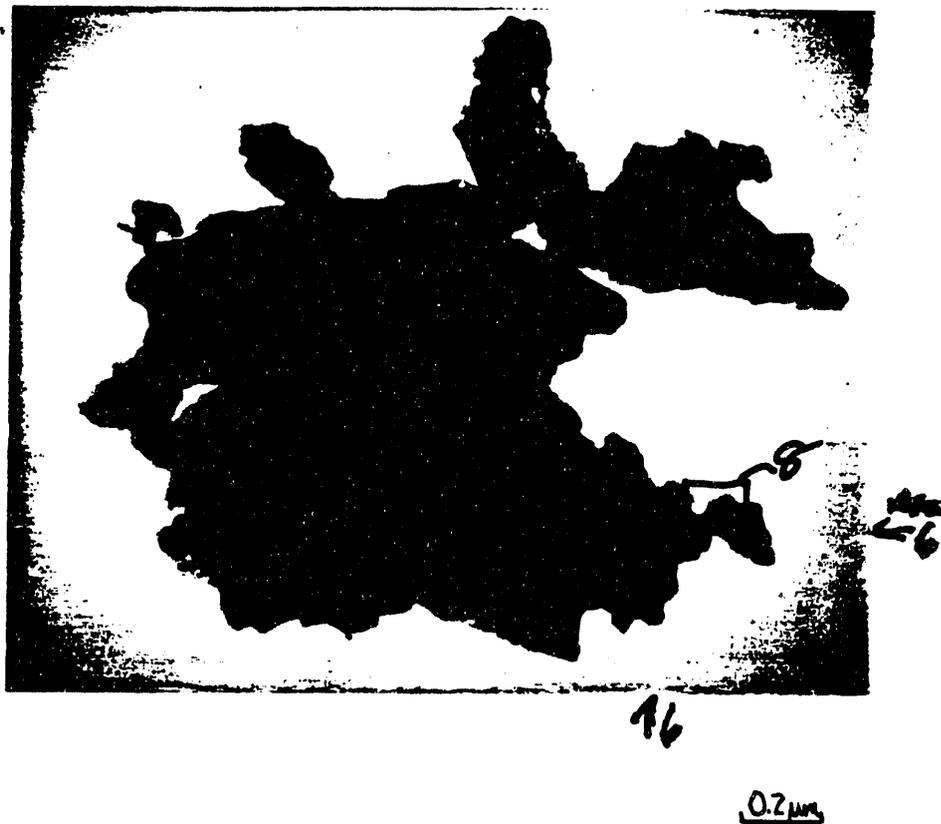
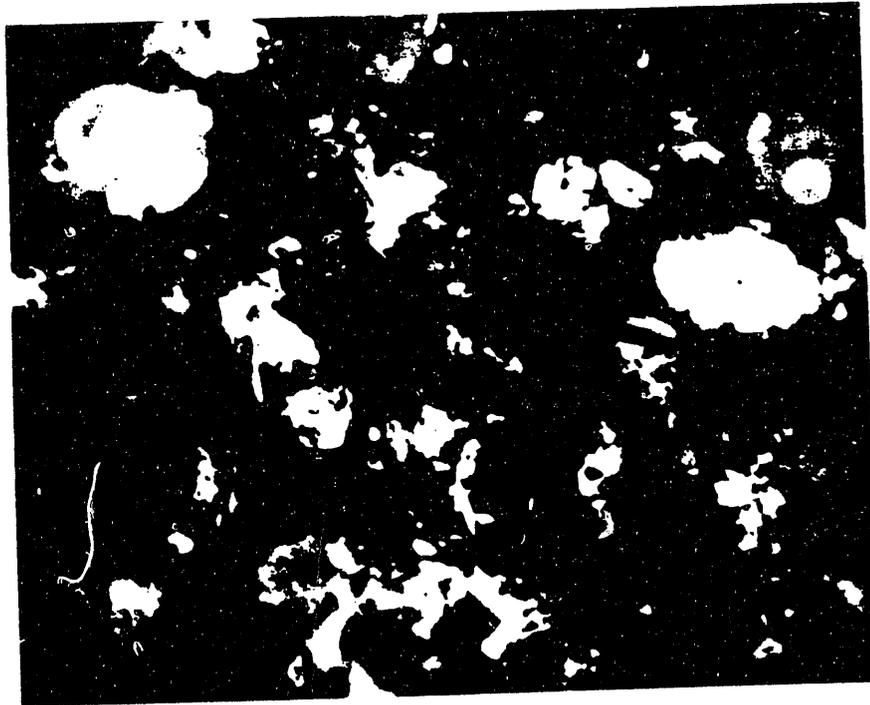
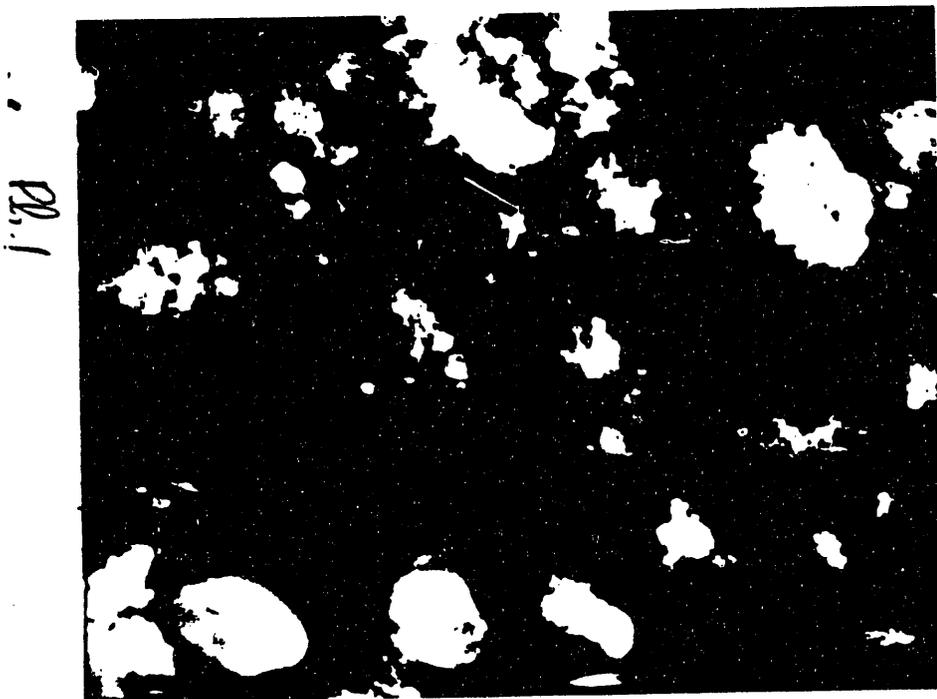


Figure 14: Bright Field Image of Sample No. 4 Showing the Positions of X-ray Point Analyses.



2 μm

Figure 15: Annular Dark-field Image of Sample No. 5.



2 μm

Figure 16: Annular Dark-field Image of Sample No. 6.

APPENDIX A

PROCESSING INFORMATION PACKAGE

WILSONVILLE RUN 262

RUN DESCRIPTION^{1,2}

Wilsonville Run 262 was operated with subbituminous coal from Black Thunder Mine and with slurry and supported catalysts in the first and second reactor stages, respectively. One run period (F) was made without the supported catalyst in the second stage. Run 262 was operated from July 10 through September 30, 1991, in the Close-Coupled Integrated Two-Stage Liquefaction (CC-ITSL) configuration with ash recycle. The high/low temperature sequence was used throughout the run, except for a one-day test during operation with slurry catalyst only. Molyvan L slurry catalyst precursor was fed to the first stage along with disposable iron oxide catalyst (and dimethyldisulfide, DMDS, as a sulfiding agent). In theory, the iron oxide promotes coal conversion; the Mo catalyst provides mild hydrogenation activity. Molyvan L is an oil-soluble lubricant additive (friction reducer, antioxidant, antiwear and extreme pressure agent) produced by R. T. Vanderbilt Company. It consists of the organometallic compound molybdenum di(2-ethylhexyl) phosphorodithioate in a petroleum oil. It contains 8.1% Mo, 12.3% S, and 6.4% P by weight. Presumably, under liquefaction conditions, the soluble Molyvan L turns into tiny, well-dispersed particles of MoS₂. The supported catalyst used in the second stage was Criterion 324 (Ni/Mo on 1/16" extrudate unimodal alumina support).

Run 262 was made using 50% of the available volume of each reactor. The interstage separator was in use throughout the run. The major operating variables were catalyst variables (concentration of slurry catalyst, presence or absence of supported catalyst), second-stage reactor temperature, coal feed rate (and consequently, space velocity), and resid concentration in the recycle solvent. The ashy recycle stream was V-1082 bottoms.

The resid injection system was used through period B, but its use was discontinued after that. This system, which provides a way to inject most of the resid directly without mixing it as a pasting solvent component, was designed to lower the recycle resid inventory requirements for the plant, and thereby to decrease the plant's equilibration time. Its use was discontinued because plugging occurred and because it introduced variability into the pasting solvent composition. The resid injection system was found not to improve resid conversion reactivity.

In the last run period (period F), the supported catalyst was withdrawn from the second reactor so that operability with only slurry catalyst could be tested. However, a small quantity of about 30 lb of supported catalyst (originally 170 lb) remained in the reactor during the test. Although yields were poor and the period was unstable, operability without supported catalyst (except for the 30 lb) was demonstrated.

The objectives for Run 262 were: 1) to evaluate the performance of a dispersed molybdenum catalyst processing a low-rank coal, and 2) to investigate and eliminate solids build-up processing a low-rank coal.

All-distillate product slates were obtained in periods A, B, C1, D and E. Resid yields were -4 to 3 wt % MAF coal. Wilsonville noted that Molyvan L dispersed catalyst improved resid and coal conversions, allowing operation at lower temperature and higher space velocity. Decreasing the Mo concentration from 1000 to 100 ppm appeared to have no effect on resid conversion, but did decrease coal conversion. Supported catalyst (Criterion 324) in the second stage allowed lower-temperature operation of the interstage heater, due to exothermic heat release in the second stage. Wilsonville reported the production of waxy product oils in this run. Gas chromatography was used to identify n-paraffins from C₁₆ to C₃₂ in the product. The product samples contained 2-7 wt % paraffins in periods A through D, and 8-9 wt % paraffins in periods E and F. There seemed to be a general increase in paraffin content in these streams throughout the run. Although it was not measured, a significant amount of the paraffinic material ended up in the recycle oil stream.

Operating conditions and yields¹ for material balance periods appear in Table 1. A simplified flow scheme³ of the Wilsonville plant, as configured for Run 262, appears in Figure 1. More detail on the part of the plant involving the major distillate streams is shown in Figure 2.

PLANT DESCRIPTION

During Run 262, the Wilsonville plant was operated in the thermal/catalytic (with regard to supported catalyst) CC-ITSL mode with ash recycle. The standard plant configuration, as used during most of the run, is described below. Exceptions to the standard configuration are described after that for operation with the resid injection system. For standard operation, coal was slurried with a mixture of second-stage vacuum-flashed bottoms (ashy resid, V-1082 bottoms), second-stage heavy distillate (V-1074), and deashed second-stage product resid (V-130). The pasting solvent stream is called V-131B. The slurry was mixed with hydrogen and passed through the preheater and first-stage backmixed reactor (R-1235). Run 262 was made with the interstage separator (V-1258) in place. The interstage separator removed the gas and light products from the first-stage products prior to processing in the second stage. The liquid portion of the separator overheads was sent to the product distillation system. The separator bottoms were sent to the second stage, along with make-up hydrogen. The second-stage ebullated-bed reactor was R-1236. Gases and light oils were separated from the second-stage product in an atmospheric flash (V-1250). The atmospheric flash bottoms (V-1067) were separated in a vacuum flash into distillate (V-1082 overheads) and resid (V-1082 bottoms). The V-1067 stream contains ash, IOM, resid and distillate-range material, and represents the recycled material prior to fractionation into distillate, ashy resid, and deashed resid components. A portion of the V-1082 bottoms stream was recycled to the first stage as a component of the pasting solvent. The remainder of the V-1082 bottoms stream was deashed in the Kerr-McGee ROSE-SR unit (formerly called Critical Solvent Deashing), which rejected an ash concentrate and produced a deashed resid product (V-130). The deashed resid was recycled back to V-131B as the second component of the pasting solvent. The atmospheric flash overhead liquids and the V-1082

overheads were sent to the distillation system (consisting of the T-105 atmospheric tower, followed by the T-102 vacuum tower), which produced naphtha (V-161, the T-105 overheads), middle-distillate (V-182, the T-102 overheads), and heavy distillate (V-1074, the T-102 bottoms). The heavy distillate was recycled as the third component of the pasting solvent.

In operations without resid injection (August 16 through the end of the run on September 30), all the components of the recycle oil (process or pasting solvent) were combined in V-131B to make the slurry oil. The slurry was prepared batchwise in V-101A by adding the coal. During resid injection (July 12 through August 16), the oil used for slurry preparation consisted of distillate only, or distillate plus some deashed resid. The remaining deashed and ashy resid required to achieve the target composition for the recycle material was injected separately. Slurry was still prepared batchwise in V-101A, but the oil used to prepare coal slurry contained no ashy resid (some batches may have contained no resid at all).

EFFECT OF OPERATING CONDITIONS ON OIL PROPERTIES

The following are observations about process oil properties during Run 262. Key differences in conditions of material balance periods are summarized here as a reference for comparison of oil properties.

- From period A (transitional) to period B, there was an increase in the resid concentration in the process solvent from 32.1 to 37.7 wt % and a decrease in the Mo concentration from 1000 to 500 ppm (MF coal basis). During part of period B, the vacuum tower T-102 was bypassed.
- From period B to period C1, the coal feed rate was increased from 247.7 to 301.4 MF lb/hr and the second-stage temperature was increased from 761 to 790°F. In addition, resid injection was discontinued after period B.

- From period C1 to period C2, the resid concentration was decreased from 39.1 to 35.8 wt %.
- From period C2 to period D, the Mo concentration was decreased from 500 to 200 ppm.
- From period D to period E, the coal feed rate was increased from 299.7 to 346.2 MF lb/hr, the second-stage temperature was increased from 790 to 810°F, and the Mo concentration was decreased from 200 to 100 ppm.
- From period E to period F (unstable), the supported catalyst was removed from the second stage (except for the residual 30 lb) and the added precursor Mo concentration was increased from 100 to 200 ppm.

Between periods, operational changes involved more than a single variable. Oil properties, however, did not change substantially during the run. Consequently, they will be discussed in a general way. During Run 262, there was an increase in 850°F⁺ resid concentration and a corresponding decrease in distillate concentration in all streams (i.e., feed, interstage, and product) from period A through period F. All three streams showed a general decrease in the concentration of the oils (hexane-solubles) in the THF-soluble 850°F⁺ resid through the run, with corresponding increases in the asphaltene (hexane-insoluble, benzene-solubles) and preasphaltene (hexane- and benzene-insoluble, pyridine-solubles) concentrations. Hydrogen aromaticity of the distillate and resid components of all streams generally decreased from period A to period B, but then increased from period B through the end of the run. Distillate hydrogen donor (hydroaromatic) content decreased throughout the run. Distillate paraffinic hydrogen content was generally lowest at the beginning and end of the run, and highest in periods B through D. The concentration of phenolic -OH in the distillate and resid portion of most streams stayed fairly constant through period D or E, and then increased. An exception was the interstage distillate, which increased in phenolic -OH concentration from period A through C2, dropped from period C2 to D, and increased from period D through F. Donor

solvent quality (coal conversion in a microautoclave solvent donor assay) generally decreased through period D or E, then increased. There were relative maxima in donor solvent quality during periods A, C2, and F. To some degree, these appear to be related to lower paraffinic hydrogen, especially in periods A and F. Past work at CONSOL has shown paraffins to be detrimental to donor quality. ^{4,5}

Most of the trends in process oil properties indicate decreasing distillate and resid quality as Run 262 progressed. In spite of confounding variables, changes in certain variables seemed to dominate the oil properties. There were concurrent increases in second-stage temperature and coal feed rate as the run progressed. There was a general decrease in slurry Mo concentration as the run progressed. In the last run period, most of the supported catalyst was removed from the second stage. These are changes that one might expect to worsen oil properties. There was also an increase in recycle resid concentration from period A through C1, a decrease from period C1 to C2, and then another increase from period C2 through F. Some of these recycle resid concentration changes were rather small, and their expected impact on oil properties is uncertain. Therefore, changes in recycle resid concentration did not play an obvious role in determining overall oil properties during the run.

GENERAL OBSERVATIONS - RUN HISTORY

Run 262 began on July 10, 1991, in the thermal/catalytic CC-ITSL mode feeding Black Thunder Mine subbituminous coal. Because of operating difficulties, July 12 was the first full day of operation. The first-stage reactor was R-1235 and the second-stage reactor was R-1236. Both reactors were configured to use 50% of the available reactor volume. The interstage separator (V-1258) was in use throughout the run. The second-stage reactor was charged with 145 lb (dry) of Criterion 324 1/16-inch (Ni/Mo) catalyst aged during Run 260. The catalyst age was initially 628 lb MF coal/lb cat, or 1470 lb resid + CI/lb cat. A subsequent addition of catalyst on July 14 brought the reactor catalyst charge to 170 lb. The start-up solvent was produced in Run 261 from Burning Star 2 mine

(Illinois 6 seam) bituminous coal. Start-up (target) conditions were: 250 MF lb/hr coal feed rate, 30 wt % coal in the slurry (2.33 solvent/coal ratio), 40 wt % resid and 12 wt % cresol insolubles (CI) in the recycle solvent, and 825/760°F reactor temperatures. Slurry catalysts and sulfiding agent were fed to the first-stage reactor as follows: iron oxide (2 wt % of the MF coal) was mixed with the coal slurry and Molyvan L (Mo was 1000 ppm of the MF coal) was mixed with dimethyl disulfide (DMDS) sulfiding agent and injected into the feed line before the first-stage preheater.

A chronological account of the run follows:

July 10, 1991: Run 262 started.

Jul 12: Resid injection was begun.

Jul 12-17: The best operation of resid injection occurred with 45 wt % coal in the slurry, which was lower than the target. This caused the coal concentration in the total feed to be lower than the target of 30 wt %.

Jul 12-22: Multiple operational problems occurred. Leaks were present in the V-1082 overheads condenser (E-1012), which resulted in a high solvent content in the ROSE-SR feed. The ROSE-SR unit was not deashing well and eventually plugged because of continued ash carryover. Poor deashing was attributed to the high solvent content of the feed, and perhaps unusual feed characteristics from dispersed Mo catalyst.

Jul 17-19: Increasing the coal concentration in the slurry to 46-48 wt % was attempted. After this, the coal slurry concentration was set to 45% due to circulation pump problems and other slurry preparation problems.

- Jul 17-20:** Balance period A was transitional for several reasons. The actual resid concentration in the recycle solvent was much lower than the target value, there was ash carryover in the ROSE-SR unit, and there was inconsistency in hydrogen consumption during this period.
- Aug. 7:** The Mo concentration was decreased from 1000 to 500 ppm.
- Aug. 8-9, 14-15:** Balance period B
- Aug. 12:** The T-102 vacuum distillation column was by-passed. Atmospheric distillation column (T-105) bottoms were sent to V-178, the T-102 product vessel. The vacuum flash overheads (V-1072) were sent to the T-102 bottoms product vessel (V-1074) for recycle.
- Aug. 15:** Problems were encountered with the resid injection system. The T-102 vacuum distillation column was put back in service.
- Aug. 16:** Because of plugging of the resid injection system, resid injection was discontinued for the remainder of Run 262. The coal feed rate was increased from 250 to 300 MF lb/hr. The feed rate of DMDS and Molyvan L was inadvertently left set for the lower value, however.
- Aug. 16-18:** Ash in the recycle was low because of the transition from resid injection to the standard practice of blending slurry batchwise in V-101A. (Deashed and ashy resid inventories were low.) Because of this and the low DMDS/Molyvan L feed rate, coal conversion was low.
- Aug. 19:** The second-stage temperature was increased from 760 to 790°F. The DMDS and Molyvan L addition rate was

increased to the proper value for this coal feed rate (see entry for August 16).

- Aug. 22-23:** Balance period C1 (Period C was split into periods C1 and C2 to account for differences in recycle resid concentration.)
- Aug. 22:** The level control valve on V-1258 could not control the flow. Some gas blew through to the second stage. The V-1258 density/level gauge showed a high level, suggesting the presence of solids. These caused a run upset.
- Aug. 24-25:** Balance period C2
- Aug. 26-27:** The V-1258 mid-temperature reading was low. This is usually an indication of solids in the separator.
- Aug. 28:** The Mo concentration was decreased from 500 to 200 ppm.
- Sept. 3:** The viscosities of the contents of V-101A and B became high. T-102 overhead distillate was used to dilute the tank contents.
- Sept. 8-12:** Balance period D
- Sept. 8:** 27 lb of catalyst was added to the second-stage reactor (R-1236) to replace catalyst removed during the shutdown.
- Sept. 13:** The second-stage reactor temperature was increased from 790 to 810°F, since the interstage preheater outlet temperature was low enough to permit it. The coal feed rate was also increased from 300 to 350 MF lb/hr, so that resid inventory would not be depleted. The Mo concentration was decreased from 200 to 100 ppm.

Sept. 16: The target recycle solvent composition was increased from 40 to 42 wt % resid. Since Wilsonville consistently measured resid in the pasting solvent to be about 2 wt % lower than the target concentration, this would enable them to blend to 40% actual resid concentration.

Sep 18-22: Balance period E

Sept. 23: The Mo concentration was increased from 100 to 300 ppm for 1/2 day, then reduced back to 200 ppm. Most of the Criterion 324 supported catalyst was removed from the second-stage reactor (R-1236), according to the run plan. 92.2 lb dry catalyst was withdrawn and it was assumed that ca. 60 lb remained. At the end of the run, however only 29 lb dry catalyst was found. After withdrawal of the supported catalyst, reactor exotherms decreased and resid inventory increased rapidly.

Sep 24, 26-27, 29: Balance period F was considered unstable.

Sep 24-29: The first-stage distillate overheads (V-164) and the second-stage atmospheric flash overheads (V-1078) were reported to have a waxy gel-like consistency after September 24. This coincided with removal of catalyst from the second stage and with the onset of colder weather. Toward the end of the run, the line from V-105 (V-1258 overheads) to V-164 to V-160 had plugging problems from the waxy material. The waxy material also caused level control problems in V-1251 (atmospheric flash overheads separation vessel) September 25-29.

REFERENCES

1. Coal Liquefaction Process Streams Characterization and Evaluation, Quarterly Technical Progress Report, January 1 through March 31, 1992, G. A. Robbins, S. D. Brandes, R. A. Winschel, F. P. Burke.
2. Southern Clean Fuels, Wilsonville Advanced Coal Liquefaction R&D Facility, Handouts from Technical Meeting No. 112 (September 11-12, 1991), and No. 113 (November 13-14, 1991).
3. Adapted from various handouts from Wilsonville Technical Review Meetings.
4. Winschel, R. A.; Robbins, G. A.; Burke, F. P., *Fuel* 1986, 65, 526-532.
5. Winschel, R. A.; Robbins, G. A.; Burke, F. P., *Fuel* 1987, 66, 654-660.

TABLE 1

**OPERATING CONDITIONS AND YIELDS FOR MATERIAL BALANCE PERIODS
WILSONVILLE RUN 262**

| Operating Period Date, 1991 Operational Days | 262A (Transit.) 7/17-20 6-9 | 262B 8/8-9,14-15 14-15,18-19 | 262C 8/22-23 26-27 | 262C2 8/25-25 28-29 |
|--|-----------------------------------|------------------------------------|--------------------------|---------------------------|
| Coal | | | | |
| Feed rate, MF lb/hr | 242.0 | 247.7 | 301.4 | 295.9 |
| Ash, wt % MF | 6.4 | 6.3 | 6.5 | 6.5 |
| Conc. in slurry, wt % MF | 29.6 | 29.7 | 29.9 | 29.5 |
| Process Solvent, wt % | | | | |
| Resid | 32.1 | 37.7 | 39.1 | 35.8 |
| Cl | 19.3 | 18.7 | 18.6 | 19.2 |
| First Stage | | | | |
| Reactor temp, °F (avg) | 826 | 825 | 825 | 825 |
| Inlet H ₂ partial pressure, psia | 2740 ±12 | 2708 ±30 | 2722 ±70 | 2716 ±27 |
| Total gas flow, scfh | 5086 | 4814 | 4404 | 4480 |
| Recycle gas, scfh | 1024 | 820 | 542 | 568 |
| Space Vel., lb MF coal/hr/cu. ft | 63.9C | 65.4C | 79.6C | 78.1C |
| Iron Oxide, wt % MF coal | 2 | 2 | 2 | 2 |
| Moly Conc., ppm MF coal | 1000 | 500 | 500 | 500 |
| Second Stage | | | | |
| Reactor temp, °F (avg) | 780 | 781 | 790 | 790 |
| Inlet H ₂ Partial Pressure, psia | 2505 ±8 | 2500 ±5 | 2552 ±13 | 2580 ±5 |
| Total Gas Flow, scfh | 4570 | 4755 | 5125 | 5129 |
| Recycle gas, scfh | 3310 | 3367 | 2787 | 2984 |
| Space Velocity, lb feed/hr-lb cat | 4.7 | 4.5 | 5.8 | 5.8 |
| lb MF coal/hr-ft ³ cat | 76.9 | 78.7 | 95.7 | 94.0 |
| Catalyst Type | Crit. 324 | Crit. 324 | Crit. 324 | Crit. 324 |
| Catalyst Age, lb (R+Cl)/lb cat | 1545 ±37 | 1424 ±60 | 1350 ±47 | 1337 ±48 |
| lb MF coal/lb cat | 706 ±17 | 692 ±22 | 692 ±24 | 685 ±24 |
| Cat Replaces. Rate, lb cat/ton MF coal | 3 | 3 | 3 | 3 |
| ROSE-SRSM Unit | | | | |
| DAS Type | 2114 | 2164 | 2224 | 2274 |
| Yield, wt % MAF Coal | | | | |
| H ₂ | -4.4 ±0.2 | -5.4 ±0.1 | -5.8 ±0.2 | -5.4 ±0.1 |
| Water | 16.1 ±0.6 | 15.4 ±0.5 | 14.1 ±1.7 | 14.2 ±1.1 |
| H ₂ S | 0.5 ±0.1 | 0.1 ±0.3 | 0.6 ±0.0 | 0.2 ±0.3 |
| CO, CO ₂ | 5.0 ±0.7 | 7.3 ±0.2 | 6.8 ±0.2 | 6.7 ±0.0 |
| NH ₃ | 0.7 ±0.0 | 0.8 ±0.0 | 0.8 ±0.0 | 0.7 ±0.1 |
| C ₁ -C ₃ gas | 4.9 ±0.3 | 5.2 ±0.3 | 5.9 ±0.1 | 5.8 ±0.2 |
| C ₄ + distillate | 57.7 ±2.3 | 58.0 ±2.1 | 64.7 ±2.5 | 56.7 ±1.3 |
| C ₄ -C ₆ | 1.3 ±0.2 | 2.5 ±0.2 | 2.8 ±0.0 | 2.7 ±1.3 |
| IBP-350°F | 14.8 ±2.7 | 9.9 ±1.4 | 13.0 ±3.5 | 13.0 ±1.3 |
| 350-450°F | 8.2 ±1.1 | 7.2 ±1.2 | 8.3 ±0.8 | 7.8 ±0.3 |
| 450-EP | 34.4 ±3.0 | 38.4 ±3.4 | 40.6 ±6.9 | 33.2 ±0.4 |
| Resid | 2.3 ±3.0 | -0.1 ±2.3 | -3.0 ±0.6 | 6.0 ±0.3 |
| Intl Acc. UC | 0.7 ±0.6 | 1.7 ±0.9 | -1.1 ±0.5 | 0.1 ±0.7 |
| Solid Product (ash-free) | 16.4 ±1.8 | 17.0 ±0.7 | 18.9 ±1.3 | 15.0 ±0.3 |
| H ₂ Efficiency, % | 13.0 ±0.6 | 10.8 ±0.4 | 11.3 ±0.8 | 10.5 ±0.3 |
| C ₁ -C ₃ Selectivity, % | 8.5 ±0.6 | 9.0 ±0.3 | 9.1 ±0.5 | 10.2 ±0.1 |
| Coal Conv., wt % MAF | | | | |
| First stage | 89.9 ±2.6 | 87.0 ±2.1 | 90.6 ±1.4 | 88.0 ±1.8 |
| Second stage | 92.0 ±1.1 | 92.2 ±0.5 | 92.9 ±0.4 | 92.7 ±0.4 |
| Overall TSL | 92.8 ±1.3 | 91.1 ±0.9 | 91.7 ±0.5 | 92.2 ±0.3 |
| Resid + UC Conv., wt % feed | | | | |
| First stage | 29.7 ±1.5 | 28.9 ±0.9 | 23.8 ±1.5 | 20.9 ±2.8 |
| Second stage | 11.8 ±2.0 | 11.8 ±1.9 | 19.7 ±1.5 | 19.6 ±3.3 |
| Resid + UC Conv. wt % MAF coal | | | | |
| First stage | 61.9 ±1.5 | 62.8 ±1.3 | 53.8 ±4.1 | 45.4 ±5.9 |
| Second Stage | 18.7 ±1.8 | 18.7 ±2.6 | 33.4 ±2.9 | 33.5 ±6.1 |
| Overall | 80.6 ±2.6 | 81.4 ±2.0 | 87.1 ±1.2 | 78.9 ±0.2 |

TABLE 1 (Continued)

OPERATING CONDITIONS AND YIELDS FOR MATERIAL BALANCE PERIODS
WILSONVILLE RUN 262

| Operating Period Date, 1991 Operational Days | 262D 9/8-12 34-38 | 262E 9/18-22 44-48 | 262F Unstable 9/24,26,27,29 50-52-53-55 |
|--|-------------------------|--------------------------|---|
| Coal | | | |
| Feed rate, MF lb/hr | 299.7 | 346.2 | 342.8 |
| Ash, wt % MF | 6.4 | 6.3 | 6.5 |
| Conc. in slurry, wt % MF | 29.7 | 29.8 | 30.0 |
| Process Solvent, wt % | | | |
| Resid | 36.2 | 38.3 | 41.3 |
| Cl | 19.6 | 20.0 | 20.1 |
| First Stage | | | |
| Reactor temp, °F (avg) | 825 | 824 | 824 |
| Inlet H ₂ partial pressure, psia | 2795 +26 | 2840 +25 | 2862 +15 |
| Total gas flow, scfh | 4461 | 4900 | 4967 |
| Recycle gas, scfh | 187 | 672 | 784 |
| Space Vel., lb MF coal/hr/cu. ft | 79.2C | 91.5C | 90.6C |
| Iron Oxide, wt % MF coal | 2 | 2 | 2 |
| Moly Conc., ppm MF coal | 200 | 100 | 200 |
| Second Stage | | | |
| Reactor temp, °F (avg) | 790 | 810 | 809 |
| Inlet H ₂ Partial Pressure, psia | 2530 +9 | 2541 +23 | 2530 +24 |
| Total Gas Flow, scfh | 5125 | 5057 | 5165 |
| Recycle gas, scfh | 3054 | 2180 | 2663 |
| Space Velocity, | | | |
| lb feed/hr-lb cat | 5.8 | 6.6 | - |
| lb MF coal/hr-ft ³ cat | 95.2 | 110.0 | - |
| Catalyst Type | Crit. 324 | Crit. 324 | - |
| Catalyst Age, lb (R+Cl)/lb cat | 1404 +49 | 1315 +51 | - |
| lb MF coal/lb cat | 727 +25 | 674 +26 | - |
| Cat Replace. Rate, lb cat/ton MF coal | 3 | 3 | - |
| ROSE-SRSM Unit | | | |
| DAS Type | 2234 | 2294 | 2404 |
| Yield, wt % MAF Coal | | | |
| H ₂ | -5.5 +0.2 | -5.5 +0.4 | -4.2 +0.3 |
| Water | 13.9 +1.1 | 15.5 +0.7 | 13.1 ±0.6 |
| H ₂ S | 0.5 +0.1 | 0.5 +0.1 | 0.4 +0.1 |
| CO, CO ₂ | 5.5 +0.3 | 6.3 +0.4 | 6.9 ±0.6 |
| NH ₃ | 0.7 +0.0 | 0.6 +0.1 | 0.3 ±0.0 |
| C ₁ -C ₂ gas | 5.3 +0.3 | 6.0 +0.4 | 5.5 ±0.3 |
| C ₂ + distillate | 60.8 ±3.2 | 57.2 ±1.8 | 47.5 ±0.5 |
| C ₃ -C ₆ | 2.1 +0.1 | 2.3 +0.3 | 2.2 ±0.2 |
| IBP-350°F | 10.8 ±2.7 | 13.1 ±3.5 | 9.0 ±0.9 |
| 350-450°F | 7.7 +0.9 | 8.6 +1.3 | 8.9 ±0.9 |
| 450-EP | 40.1 ±6.2 | 33.2 ±3.2 | 27.4 ±1.1 |
| Resid | -0.3 +3.1 | -0.4 +2.5 | 11.0 ±2.0 |
| Intd Acc. UC | 0.6 ±0.6 | -0.1 ±1.1 | 0.4 ±1.2 |
| Solid Product (ash-free) | 19.0 ±0.8 | 19.8 ±1.3 | 19.1 ±2.6 |
| H ₂ Efficiency, % | 11.1 ±0.5 | 10.4 ±0.6 | 11.3 ±1.0 |
| C ₁ -C ₂ Selectivity, % | 8.8 ±0.8 | 10.5 ±0.6 | 11.6 ±0.7 |
| Coal Conv., wt % MAF | | | |
| First stage | 89.1 +2.6 | 86.7 +2.5 | 86.3 ±3.0 |
| Second stage | 91.9 ±0.5 | 92.3 ±0.8 | 92.3 ±0.3 |
| Overall TSL | 90.1 ±0.5 | 91.6 ±0.8 | 91.3 ±0.9 |
| Resid + UC Conv., wt % feed | | | |
| First stage | 24.7 ±1.3 | 21.4 ±1.6 | 22.9 ±2.7 |
| Second stage | 16.1 ±2.0 | 18.6 ±1.1 | 9.8 ±4.8 |
| Resid + UC Conv. wt % MAF coal | | | |
| First stage | 53.5 ±2.0 | 47.5 ±4.3 | 51.7 ±7.8 |
| Second Stage | 27.3 ±2.9 | 33.1 ±2.8 | 17.8 ±8.1 |
| Overall | 80.8 ±2.9 | 80.6 ±1.7 | 69.5 ±1.2 |

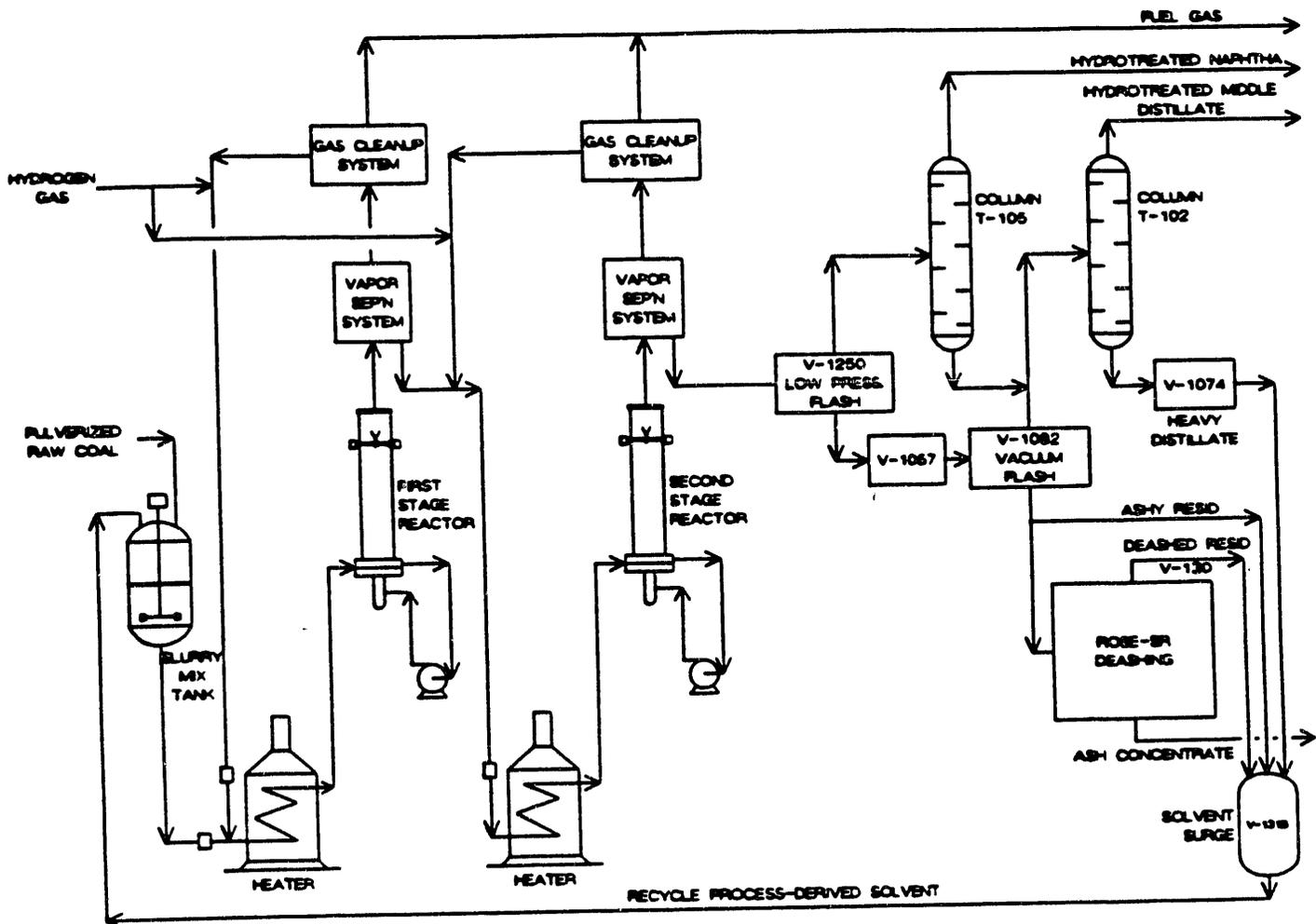


Figure 1. Simplified CC-ITSL Process Diagram for Wilsonville Run 262.
Resid injection system used in Periods A and B is not shown.

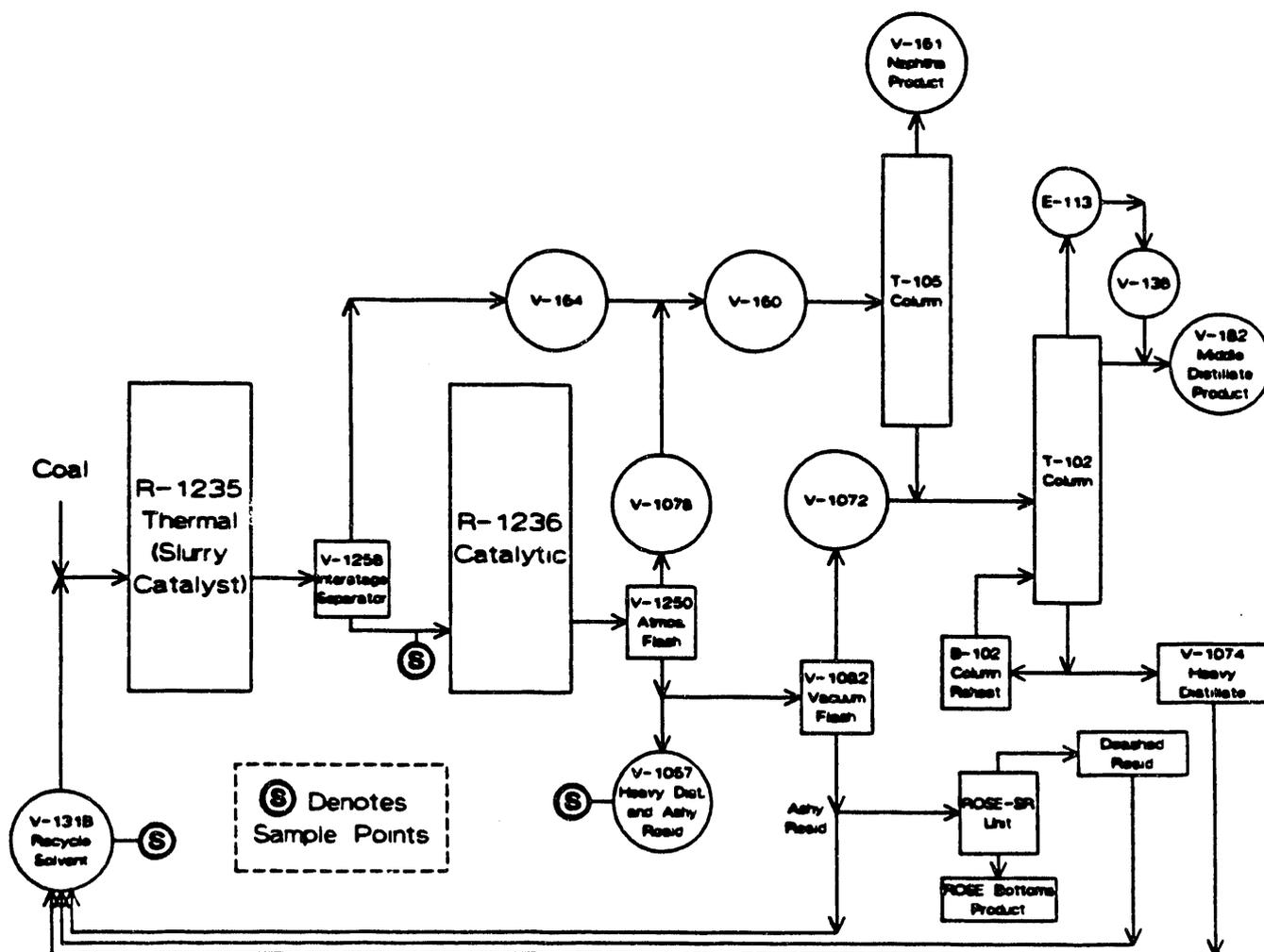


Figure 2. Partial CC-ITSL Process Diagram for Wilsonville Run 262 Showing Major Distillate Streams. Resid injection system used in Periods A and B is not shown.

APPENDIX B

PROCESSING INFORMATION PACKAGE

WILSONVILLE RUN 263 A-E¹**RUN CONDITIONS AND PROCESS PERFORMANCE**

Run 263 with Black Thunder Mine subbituminous coal (from Wyodak Anderson seam in the Powder River Basin in Wyoming) began (prior to Period A) on October 31, 1991. Period E ended on January 1, 1992. The thermal/thermal mode of operation of reactors with dispersed slurry catalysts and without the presence of a supported catalyst was used throughout periods A-E. The objectives for periods A-E of Run 263 were as follows:

- Evaluate the performance of a dispersed molybdenum catalyst while processing a low-rank coal, and
- Investigate and eliminate solids build-up while processing a low-rank coal.

The strategies to obtain the objectives for operating periods A-E were:

- Evaluate the performance of the Molyvan L slurry catalyst at a 200 ppm molybdenum addition rate in the absence of a supported catalyst.
- Evaluate the performance of the Molyvan L slurry catalyst at a 100 ppm molybdenum addition rate.
- Increase the first stage reaction temperature to 840°F in order to improve the resid conversion.
- Decrease the coal feed rate to 265 MF lb/hr in order to improve the process performance.

Reaction temperatures studied for periods A to E were 810-840°F in the first stage and 790-810°F in the second stage. Coal feed rates were 265-300 MF lb/hr, and targeted recycle resid and CI concentrations were 42-45 and 20 wt %, respectively, in the recycle process solvent. Molyvan L addition rate was at 100 and 200 ppm molybdenum. Iron-oxide addition was maintained at 2 wt % MF coal and dimethyl disulfide (DMDS) was used as a sulfiding agent. A summary of operating conditions and yields is given in Table 1.

The conclusions derived for periods A-E are summarized below.

- The lower molybdenum addition rate of 100 ppm did not reduce conversion performance compared to the 200 ppm addition rate.
- Operation at the higher first-stage temperature, 840°F, and lower coal space velocity with 265 MF lb/hr coal feed rate did not significantly affect distillate selectivity to conversion. The distillate selectivity to conversion was 69-70% (compared to 71% at 825°F and 300 MF lb/hr) without extensive production of gases.

GENERAL OBSERVATIONS FOR PERIODS A-E

- Apparent activation energy determined for the first stage thermal conversion with Molyvan L slurry catalyst addition was 30,400-40,600 Btu/lb-mol.
- Reduced backmixing flow rate seemed to affect significantly the first-stage reactor temperature profile, resulting in the increased reactor temperature spread from 25-30 to 55-65°F after December 22 (prior to period E).
- Overall and first-stage resid + UC conversion increased for 263°C as a result of increasing the first stage temperature from 825°F to 840°F on November 27. Overall and first stage resid + UC conversion

also increased in 263D due to a decrease in the coal feed rates to 265 lb/hr from 300 lb/hr.

- There was a slight decrease in the resid hydrogen in the process solvent and interstage sample in 263C compared to 263B when increasing the first-stage temperature to 840°F.
- The first-stage reactor in-bed temperature change increased beginning with period 263C as a result of increasing the first-stage temperature to 840°F.
- Solids deposit was observed in the interstage separator, V-1258, about 20 days after the first-stage temperature was increased to 840°F. Upon cleaning, 100 lb of deposits in V-1258, composed mostly of gummy material, was obtained. This includes about 20 lb (estimated) of hard dry solids which were deposited on the walls opposite to the point where the feed enters the vessel. In comparison, about 20 lb of deposit was observed in Run 262 which mainly contained hard, chunky material.
- Organic rejection, resid recovery, and ash content in ROSE-SRSM bottoms product all showed a slight improvement over Run 262. One contributing factor to this improved performance is the increased coal conversion starting November 27 resulting from the increase in the first-stage reactor temperature to 840°F. The deashing solvent strength was maintained at a high level without the ash carry-over that was experienced in Run 262.
- The GC cut point (obtained from GC simulated distillation and by the equal weight percent overlap method) for periods 263A, 263B, 263C and 263D were 804, 797, 795 and 776 with an overlap of 8-12 wt %.
- Preliminary data from periods 263A and 263B total oils indicate that they have less hydrogen content and more heteroatoms, sulfur, nitrogen and oxygen, when compared to Run 262 oils.

- Based on the unusually high nitrogen contents (above 1 wt %), there is very little tendency for denitrogenation using the dispersed slurry system. Still persisting are the usual trends of increasing nitrogen content by boiling point and sulfur being more prevalent in the naphtha fraction.

PLANT DESCRIPTION

During Run 263 periods A-E, the Wilsonville plant was operated in the thermal/thermal CC-ITSL mode with ash recycle. The standard plant configuration (Figure 1) is described below. For standard operation, coal was slurried with a mixture of second-stage vacuum-flashed bottoms (ashy resid, V-1082 bottoms), second-stage heavy distillate (V-1074), and deashed second-stage product resid (V-130). The pasting solvent stream is called V-131B. The slurry was mixed with hydrogen and passed through the preheater and first-stage backmixed reactor (R-1235). Run 263 periods A-E were made with the interstage separator (V-1258) in place. The interstage separator removed the gas and light products from the first-stage products prior to processing in the second stage. The liquid portion of the separator overheads was sent to the product distillation system. The separator bottoms were sent to the second stage, along with make-up hydrogen. The second-stage backmixed reactor was R-1236. Gases and light oils were separated from the second-stage product in an atmospheric flash (V-1250). The atmospheric flash bottoms (V-1067) were separated in a vacuum flash into distillate (V-1082 overheads) and resid (V-1082 bottoms). The V-1067 stream contains ash, IOM, resid and distillate-range material, and represents the recycled material prior to fractionation into distillate, ashy resid, and deashed resid components. A portion of the V-1082 bottoms stream was recycled to the first stage as a component of the pasting solvent. The remainder of the V-1082 bottoms stream was deashed in the Kerr-McGee ROSE-SR unit, which rejected an ash concentrate and produced a deashed resid product (V-130). The deashed resid was recycled to V-131B as the second component of the pasting solvent. The atmospheric flash overhead liquids and the V-1082 overheads were sent to the distillation system (consisting of the T-105 atmospheric tower, followed by the T-102 vacuum tower), which produced

naphtha (V-161, the T-105 overheads), middle-distillate (V-182, the T-102 overheads), and heavy distillate (V-1074, the T-102 bottoms). The heavy distillate was recycled as the third component of the pasting solvent.

REFERENCES

1. Southern Clean Fuels, Wilsonville Advanced Coal Liquefaction R&D Facility, Handouts from Technical Meeting No. 114 (January 15-16, 1992), and No. 115 (March 18-19, 1992).

TABLE 1

OPERATING CONDITIONS AND YIELDS FOR MATERIAL BALANCE PERIODS A-E
WILSONVILLE RUN 263

| Operating Period Date, 1991 | 263A 11/10-14 | 263B 11/17,18,20-22 | 263C 12/3, 6-9 | 263D 12/13-17 | 263E 12/26-28,31, 1/1 |
|--|------------------|------------------------|-------------------|------------------|--------------------------|
| Operational Days | 10-14 | 17,18,20-22 | 26, 29-32 | 36-40 | 46-48, 51,52 |
| Coal | | | | | |
| Feed rate, MF lb/hr | 299.0 | 298.8 | 293.6 | 259.7 | 260.9 |
| Ash, wt % MF | 7.7 | 7.0 | 7.6 | 7.2 | 7.1 |
| Conc. in slurry, wt % MF | 24.8 | 25.0 | 24.4 | 24.6 | 24.5 |
| Process Solvent, wt % | | | | | |
| Resid | 45.2 | 44.1 | 43.3 | 41.1 | 44.0 |
| Cl | 20.0 | 20.0 | 20.2 | 19.6 | 20.1 |
| Recycle Cls from First Stage | | | | | Vac. Fl. |
| Reactor temp, °F (avg) | 826 | 825 | 840 | 840 | 840 |
| Inlet H ₂ partial pressure, psia | 2756 | 2797 | 2707 | 2759 | 2724 |
| Total gas flow, scfh | 4886 | 5014 | 4684 | 5044 | 4614 |
| Recycle gas, scfh | 1534 | 1449 | 1196 | 1528 | 1234 |
| Space Vel., lb MF coal/hr/cu. ft | 79.0C | 78.6C | 77.6C | 68.6C | 68.9C |
| Iron Oxide, wt % MF coal | 2 | 2 | 2 | 2 | 2 |
| Moly Conc., ppm MF coal | 200 | 100 | 100 | 100 | 100 |
| Moly Precursor | | | | | MV L |
| Second Stage | | | | | |
| Reactor temp, °F (avg) | 810 | 809 | 810 | 810 | 809 |
| Inlet H ₂ Partial Pressure, psia | 2436 | 2420 | 2415 | 2477 | 2546 |
| Total Gas Flow, scfh | 4765 | 4872 | 4757 | 5094 | 4850 |
| Recycle gas, scfh | 2570 | 2775 | 2628 | 3115 | 3021 |
| Space Vel., lb MF coal/hr-ft ³ cat | 79.0C | 78.6C | 77.6C | 68.6C | 68.9C |
| Catalyst Type | - | - | - | - | - |
| Catalyst Age | | | | | |
| lb (R+Cl)/lb cat | - | - | - | - | - |
| lb MF coal/lb cat | - | - | - | - | - |
| Cat Replace. Rate, lb cat/ton MF coal | - | - | - | - | - |
| ROSE-SRSM Unit | | | | | |
| DAS Type | 2334 | 2304 | 2394 | 2404 | 2414 |
| Yield, wt % MAF Coal | | | | | |
| H ₂ | -4.3 ±0.3 | -4.9 ±0.5 | -4.6 ±0.6 | -5.2 ±0.2 | -5.5 ±0.2 |
| Water | 11.6 ±1.8 | 13.4 ±1.8 | 13.7 ±0.7 | 13.0 ±0.7 | 13.2 ±1.3 |
| H ₂ S | 0.3 ±0.2 | 0.4 ±0.4 | 0.2 ±0.0 | 0.4 ±0.2 | 5.7 ±0.2 |
| CO, CO ₂ | 6.2 ±1.3 | 6.0 ±0.7 | 5.8 ±0.3 | 6.3 ±0.3 | 0.3 ±0.2 |
| NH ₃ | 0.4 ±0.1 | 0.3 ±0.0 | 0.3 ±0.2 | 0.5 ±0.1 | 0.4 ±0.1 |
| C ₁ -C ₃ gas | 6.7 ±0.5 | 6.3 ±0.2 | 7.8 ±1.1 | 9.1 ±1.2 | 9.0 ±0.3 |
| C ₄ + distillate | 47.9 ±4.8 | 51.8 ±1.8 | 52.1 ±0.6 | 54.6 ±4.3 | 60.7 ±2.0 |
| C ₄ -C ₆ | 2.4 ±0.3 | 2.7 ±0.6 | 3.0 ±0.3 | 3.0 ±0.3 | 3.3 ±0.5 |
| IBP-350°F | 7.9 ±2.0 | 8.0 ±1.2 | 8.9 ±0.9 | 9.1 ±1.2 | 8.0 ±0.6 |
| 350-450°F | 8.4 ±1.5 | 9.3 ±1.0 | 11.3 ±0.9 | 10.3 ±1.3 | 10.5 ±0.7 |
| 450-EP | 29.1 ±6.7 | 31.9 ±1.4 | 28.8 ±1.2 | 32.1 ±6.5 | 39.0 ±2.4 |
| Resid | 9.4 ±5.3 | 8.6 ±2.8 | 6.6 ±2.4 | 5.5 ±3.3 | 2.4 ±0.9 |
| Int. Acc. UC | 0.7 ±1.2 | 1.0 ±0.9 | 0.4 ±0.3 | 0.3 ±1.0 | -0.3 ±0.1 |
| ROSE-SR SM bottoms Product (ash-free) | 21.3 ±1.5 | 17.0 ±0.9 | 17.5 ±0.6 | 15.8 ±0.7 | 14.1 ±0.4 |
| H ₂ Efficiency, % | 11.1 ±0.9 | 10.8 ±1.2 | 11.6 ±1.4 | 10.4 ±0.9 | 11.0 ±0.4 |
| C ₁ -C ₃ Selectivity, % | 14.1 ±2.3 | 12.3 ±0.7 | 14.9 ±2.1 | 16.7 ±2.5 | 14.9 ±0.4 |
| Coal Conv., wt % MAF | | | | | |
| First stage | 80.4 ±5.9 | 82.2 ±3.2 | 86.1 ±3.9 | 87.0 ±1.4 | 90.2 ±1.3 |
| Second stage | 92.7 ±0.9 | 93.4 ±0.3 | 93.7 ±0.1 | 94.5 ±0.2 | 94.7 ±0.4 |
| Overall TSL | 92.8 ±1.4 | 92.5 ±1.4 | 92.9 ±0.5 | 93.1 ±0.5 | 94.1 ±0.8 |
| Resid + UC Conv., wt % feed | | | | | |
| First stage | 17.9 ±3.0 | 16.6 ±1.3 | 19.9 ±1.0 | 20.1 ±1.2 | 22.7 ±0.6 |
| Second stage | 8.4 ±4.2 | 13.7 ±1.4 | 9.6 ±1.5 | 12.7 ±1.5 | 9.7 ±1.0 |
| Resid + UC Conv. wt % MAF coal | | | | | |
| First stage | 48.7 ±9.7 | 41.8 ±5.2 | 53.4 ±2.7 | 51.9 ±3.3 | 62.1 ±2.4 |
| Second Stage | 19.9 ±8.5 | 31.6 ±5.1 | 22.0 ±3.2 | 26.6 ±2.7 | 21.7 ±1.8 |
| Overall | 68.7 ±4.0 | 73.5 ±2.2 | 75.4 ±1.7 | 78.5 ±3.9 | 83.8 ±0.7 |

Note: MV L - Molyvan L (263A-E, I-M)

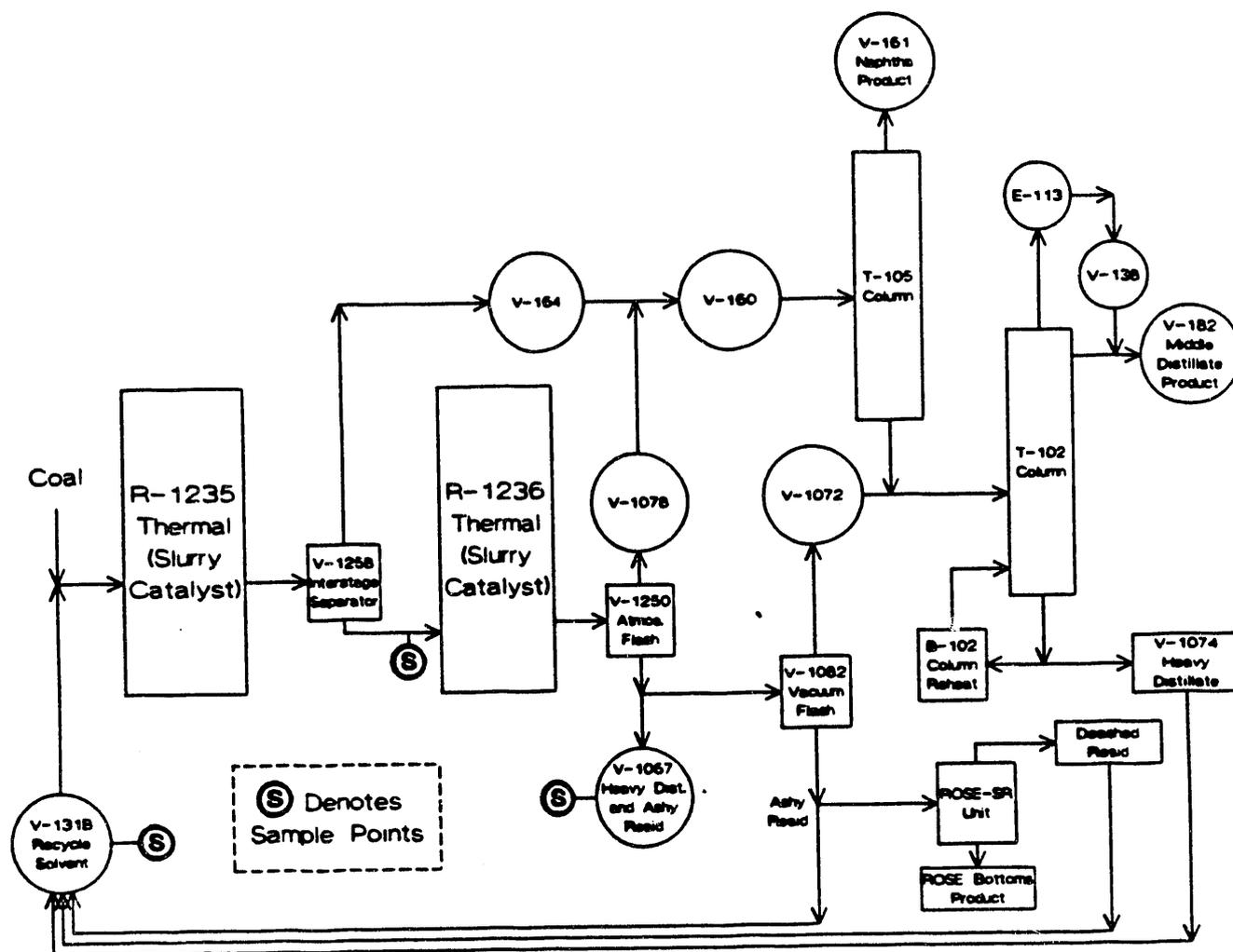


Figure 1. Partial CC-ITSL Process diagram for Wilsonville Run 263 Showing Major Distillate Streams.

2

PETROLEUM DEPARTMENT

APPENDIX C

MVL-1
 8901(8201)

MOLYVAN^o L

EXTREME PRESSURE/ANTIWEAR AGENT

ANTIOXIDANT

FRICTION REDUCER

Typical Properties

| | |
|--------------------------------------|---|
| Composition: | Organic molybdenum compound |
| Physical State: | Liquid |
| Color: | Dark green |
| Density at 25°C, Mg/m ³ : | 1.08 |
| Viscosity at 100°C, cSt (SUS): | 9.07 (56) |
| Molybdenum Content, %: | 8.1 |
| Phosphorus Content, %: | 6.4 |
| Sulfur Content, %: | 12.3 |
| Flash Point, COC, °C (°F): | 165.6 (330) |
| Solubility: | Soluble in petroleum oils and greases, aliphatic and aromatic solvents and in various synthetic lubricant bases. Insoluble in water. |

MOLYVAN L is a stable organic liquid additive containing molybdenum, sulfur, and phosphorus. It is completely oil soluble and is an excellent friction reducer with antiwear and extreme pressure properties. It can be used in a wide range of automotive and industrial applications.

MOLYVAN L mixes easily in greases and oils, eliminating the problems associated with the use of solid molybdenum additives.

MOLYVAN L is effective in low concentrations in automotive crankcase oils to reduce friction, to lower operating temperatures and to reduce oil consumption. It can also be an extreme pressure and antiwear additive in lubricating oils and greases operating under high loads.

Note: Whenever top treating a finished oil formulation with **MOLYVAN L** it is recommended that the finished product be tested to confirm original test results.

In some formulations, the presence of **MOLYVAN L** may contribute to copper corrosion which would be detrimental to some diesel engines. Its use in such lubricants is therefore not recommended.

Information presented herein has been compiled from sources considered to be dependable and is accurate and reliable to the best of our knowledge and belief but is not guaranteed to be so. Nothing herein is to be construed as recommending any practice or any product in violation of any patent or in violation of any law or regulation. It is the user's responsibility to determine for himself the suitability of any material for a specific purpose and to adopt such safety precautions as may be necessary. We make no warranty as to the results to be obtained in using any material and, since conditions of use are not under our control, we must necessarily disclaim all liability with respect to the use of any material supplied by us.

PROPERTIES

Trade Name

MOLYVAN® A

MOLYVAN® L

MOLYVAN® 807

Function

Antiwear agent, extreme pressure agent, antioxidant.

Antiwear agent, antioxidant, friction reducer, extreme pressure agent.

Non-phosphorus friction reducer, antioxidant.

Formula



Chemical Composition

Molybdenum oxysulfide dithiocarbamate

Sulfurized oxymolybdenum organophosphorodithioate

Molybdenum-sulfur compound
Molybdenum content 4.6%

Physical State

Powder

Liquid

Liquid

Color

Yellow

Dark green

Dark green

Density at 25°C
Mg/m³ (lbs./gal.)

1.58

1.08 (8.0)

0.98 (8.2)

Viscosity at 100°C
cSt (SUS)

—

9.0 (56)

12.74 (69.2)

Flash Point,
COC, °C (°F)

—

168 (330)

168 (336)

Pour Point, °C (°F)

—

-37 (-38)

—

Melting Point, °C (°F)

281 (484)

—

—

Solubility

Slightly soluble in aromatic hydrocarbons.
Insoluble in water.

Soluble in petroleum and synthetic lubricant bases.
Insoluble in water.

Soluble in petroleum and synthetic lubricant bases.
Insoluble in water.

Use Conc., % mass

0.5 to 3.0

0.25 to 1.0

0.25 to 0.5

Typical Uses

Used in long life chassis greases for ball joints, steering linkages and other lubricating greases requiring good antioxidant and antiwear at high temperatures for long periods of time. MOLYVAN A is an organic molybdenum E.P. and antiwear additive for petroleum and synthetic lubricants. It has good high temperature stability and a light yellow color. In lubricating greases it is superior to inorganic molybdenum additives in both antiwear and antioxidant properties. MOLYVAN A is slightly basic and does not promote rusting. It has a low specific gravity which makes it easy to disperse with simple equipment. It is used in non-petroleum base valve lubricants.

MOLYVAN L is the first commercial oil-soluble organic molybdenum additive containing sulfur and phosphorus. Functions as friction reducer, antioxidant, antiwear, and E.P. agent. Its oil solubility permits formulation of attractive single-phase oils containing molybdenum. Used in hypoid oils, engine oils, metalworking compositions and in a variety of industrial and automotive lubricating oils, greases and specialties. MOLYVAN L is an outstanding antiwear agent of low toxicity. It is quite useful in automotive and industrial gear oils and greases which operate under heavy load conditions.

MOLYVAN 807 presents the unique properties of the molybdenum-sulfur combination in an oil-soluble form which is easy to blend into lubricants. MOLYVAN 807 can be used to maintain the anti-rust properties of an engine oil while reducing the phosphorus content. To obtain significant increases in extreme pressure properties and impart improved antiwear performance, MOLYVAN 807 can be used in combination with VANLUBE 7723, a run-in metallic dithiocarbamate which functions as antioxidant and extreme pressure agent.

Note: Since oil formulations vary it is recommended that upon the incorporation of any additive the finished product be tested to confirm original test results. In some formulations, the presence of MOLYVAN L may contribute to copper corrosion which would be detrimental to some diesel engines. Therefore, its use in such lubricants is not recommended.

Note: Since oil formulations vary it is recommended that upon the incorporation of any additive the finished product be tested to confirm original test results. In some formulations, the presence of MOLYVAN 807 may contribute to copper corrosion which would be detrimental to some diesel engines. Therefore, its use in such lubricants is not recommended.

EXPERIMENTAL METHODS

Descriptions are given below for most of the analytical techniques used to generate the data in the preceding tables. The references provide additional details on the methods.

Sample Handling and Preparation¹

Samples are stored, as received, at ambient temperature until analysis. Full-range samples, i.e., samples that contain both distillate and resid, are distilled in a 1" x 3' jacket-heated Vigreux column to an end-point of 320°C pot/270°C column/5 torr (850°F equivalent). Small samples, such as the HRI samples provided, are distilled at similar conditions in a microstill. The distillate and resid fractions may be further analyzed.

Determination of Insoluble Organic Matter (IOM) and Ash¹

The distillation residue is ground with a mortar and pestle and a 5 g sample is pressure-filtered with freshly distilled tetrahydrofuran (THF) through Whatman No. 42 paper at ambient temperature. The filter cake is washed with THF until the filtrate is colorless. The solids are weighed to determine the insolubles (IOM and mineral matter), then combusted for one hour at 800°C in an electric muffle furnace to convert the mineral matter to oxidized ash. IOM is determined as the insolubles less the ash. The THF is removed from the filtrate by distillation or rotary vacuum evaporation. The resultant THF-soluble resid may be further analyzed.

Solubility Fractionation^{2,3}

Liquid column fractionation (LCF) is the solubility fractionation method we use. It separates THF-soluble coal extracts into the following categories: oils (hexane solubles), asphaltenes (benzene soluble/hexane insoluble, and preasphaltenes (pyridine soluble/benzene insoluble). The LCF procedure consists of injecting a THF-dissolved sample onto a 2 x 1000 mm glass column packed with glass beads (Analab, 70/80 mesh).

The solvents then are pumped through the column sequentially at a flow rate of 1.5 mL/min: hexane (6 min), benzene (8 min) and pyridine (10 min) to elute oils, asphaltenes, and preasphaltenes, respectively. Sample

size is 20 μm and the sample concentration is approximately 5 g/L in THF. Peak areas (vida infra) are measured with an HP-3388 integrator. Response factors are applied to the peak areas to obtain weight percentages of the three fractions.

The LCF method is not expected to reproduce the more conventional Soxhlet methods. However, it is rapid, reproducible, and of acceptable analytical precision. Its rapidity (~20 min) makes it much more suitable for process monitoring than the Soxhlet methods which have turn-around times of several days.

The apparatus used for this procedure consists of a Milton-Roy Laboratory Mini-Pump, a Rheodyne 7010 loop-type on-line injector, and a Pye Unicam LCM2 flame ionization detector (FID). The Pye FID response is quantitative for the detection of carbon. It is, therefore, well-suited for coal-liquids work since it will respond equally well to alkyl groups and aromatic compounds. An ultra-violet detector, for example, would not respond to alkanes or unconjugated alkenes.

The Pye detector operates by passing a moving stainless steel wire of fine gauge through the effluent stream from the column. A small amount of column effluent is carried by the wire into an evaporator oven where the solvent is stripped, leaving the sample deposited on the wire. Since some volatiles can be lost at this point, the detector response can be sensitive to sample volatility. However, all the materials analyzed by this technique are non-volatile (850°F or greater).

Upon leaving the evaporator oven, the coated wire passes into a heated (800°C) quartz tube where the deposited sample is quantitatively burned in an air stream. The resultant CO_2 passes into a molecular entrainer, where H_2 is mixed with the stream. This mixture is carried into a Ni catalyst chamber. The CO_2 is quantitatively reduced to methane, to which the FID responds.

Detector response is dependent upon the chromatographic solvent, presumably because of the thickness of coating on the wire. Therefore, response factors are determined by making preparative runs on large-scale

columns (9 x 1000 mm), with proportional increases in solvent flow (4 mL/min) and sample size (735 μ m, 200 g/L). Fractions obtained are rotary evaporated, vacuum dried and weighed. Response factors are calculated as the ratio of detector response (area from an analytical run) to fraction weight (from a preparative run). Given the relatively minor variations in residuum composition for a given run, it is assumed that one set of response factors is adequate for all samples from that run. A separate set of response factors is determined for each coal feed.

¹H-Nuclear Magnetic Resonance Spectroscopy^{4,5}

¹H-NMR spectra are recorded on a Varian EM-360L 60 MHz instrument. Homogenized distillate samples are dissolved in chloroform-d, to make a 12% v/v solution, then filtered. Homogenized residue samples, either THF-soluble or whole, are dissolved in pyridine -d₅ (99.96%D) to ~190 g/L, then filtered. An internal tetramethylsilane (TMS) reference is used to lock the RF field. Samples are spun at -50 rps in 5 mm OD precision sample tubes. Spectra are scanned from 10.5 to 0 ppm over 5 min at 0.05 mG RF power.

We investigated the use of elevated sample temperatures for the residue samples, but determined there to be no significant improvement. All samples, therefore, are run at ambient temperature.

Integrations are performed in duplicate on the instrument using a sweep rate of 1 min. The integrations are divided into seven regions generally corresponding to seven proton types.

| Chem Shift (TMS), ppm | Proton Type | Description |
|-----------------------|-------------------|--|
| 10.5-7.15 | Cond. Aromatics | Proton attached to a condensed aromatic ring. |
| 7.25-4.7 | Uncond. Aromatics | Proton attached to an uncondensed aromatic ring. |
| 4.7-2.5 | Cyclic Alpha | Proton on naphthenic carbon adjacent to fused aromatic ring of naphtheno-aromatic. |
| 2.5-2.0 | Alkyl Alpha | Methyl or non-cyclic methylene or methyldene proton adjacent to aromatic ring. |
| 2.0-1.4 | Cyclic Beta | Naphthenic protons. Naphthenic protons two positions from the aromatic ring of naphtheno-aromatics. |
| 1.4-1.0 | Alkyl Beta | Interior protons of paraffins. Methyl protons two positions from an aromatic ring. Non-cyclic methylene protons two or more positions from an aromatic ring. |
| 1.0-0.5 | Gamma | Terminal methyl protons of paraffins or alkyl sidechains three or more positions from an aromatic ring. |

Hydroxyl peaks are disregarded during integration and normalization.

Analysis of Molybdenum in THF-Insoluble Distillation Resid Samples

The tetrahydrofuran-insoluble distillation resid samples were ashed at 750°C following ASTM procedure D-3682. The ash then was digested in HNO₃ and HF/HCl aqua regia, complexed with H₃BO₃. The resultant solution was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Thermo Jarrell Ash JA61 instrument.

Elemental Analyses and Heating Value

Carbon, hydrogen and nitrogen are determined with a Leco CHN-600 instrument. Sulfur is determined with a Leco SC-32 instrument. Gross calorific values are determined with a Parr 1261 Calorimeter. The ten

major ash elements are determined with a Thermo Jarrel-Ash JA-61 inductively coupled plasma atomic emission spectrometer.

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END

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