

COAL DESULFURIZATION IN THE P&M SOLVENT REFINING PROCESS

R. P. Anderson and C. H. Wright
The Pittsburg and Midway Coal Mining Co.
9009 W. 67th Street
Merriam, Kansas 66202

I. INTRODUCTION

In the P&M Solvent Refined Coal Process, coal is dissolved under moderate hydrogen pressure in an internally generated heavy aromatic solvent to produce a liquid from which mineral matter is removed by filtration. Solvent is recovered from the filtrate by vacuum distillation; the distillation residue which can be handled in either solid or liquid form is a very low ash, low sulfur material known as Solvent Refined Coal (SRC). An objective of the laboratory program in support of the Solvent Refined Coal Pilot Plant program is the development of procedures for improved desulfurization of high sulfur coals. Many of the high volatile bituminous coals in the eastern half of the United States contain an appreciable amount of pyrites which can be removed from the coal by filtration after the coal is dissolved in a suitable solvent. Normally this process is conducted in the presence of molecular hydrogen and a naturally catalyzed hydrogenation reaction is an important factor in the proper solution of the coal. This reaction also increases the removal of sulfur which is a component of the organic phase of the coal. The arguments and supporting evidence for the existence of natural catalytic effects in such coals have been reported previously. 1,2,3,4,5,6/

Current laboratory studies are directed to the development of suitable operating procedures to use the naturally catalyzed reactions more effectively. The general requirements for such reactions have been outlined by laboratory studies and are being tested in some pilot plant operations. 7,8/ It is now possible to dissolve a number of high volatile bituminous coals and to recover the organic material from the coal using these arts. The preferred reactor designs and the best operating conditions are not presently well defined.

A sound basis for commercial scale processing of these coals depends on better understanding of the chemistry of the coal solution reactions as well as on the solution of a number of practical engineering problems. To a considerable extent the engineering problems appear to be basic elements of coal processes utilizing either natural catalysts or synthetic catalysts. Therefore progress in solving these problems in the Solvent Refined Coal Process should contribute to advancing related processes as well. Evaluation of natural catalysts suggests that some coals will be suitable for processing without resort to synthetic catalysts but that others will need to be catalyzed additionally. The operating rules are not presently sharply defined; therefore the separation between suitable and unsuitable coals can not be made without resorting to a program of practical tests in the laboratory.

Accordingly the laboratory program is designed to improve the art by studies of reactor combinations and process variables and to demonstrate the suitability of various coals for processing. Emphasis is placed on the use of natural catalysis in the hope that such processing will prove to be the cheapest route to purified coal derived fuels in a significant number of cases. The effect of specifications, such as sulfur limits, which may be imposed may determine the applicability of alternative processes in the future. It is necessary to know the technical limits

for the process using natural catalysts and for alternative processes for this reason also. It is expected that various alternatives - catalysts, feedstocks, product quality requirements, and so on will be possible. An optimum plant design will require knowledgeable compromises between these alternatives. Sound data on the natural catalytic effects should comprise an essential component of the thinking which results in choosing a coal processing configuration.

The experimental section of this paper describes several recent experiments which were done to develop optimization procedures for the naturally catalyzed coal solution process. Such experiments must satisfy the constraint that a break-even amount of solvent be obtained and that the reactions be continued with solvent recycle until a steady state develops between the solvent, the coal, and the reaction conditions used. It is essential that the equilibrated solvent retain the capacity to donate hydrogen readily in the initial stages of the coal solution reaction. An additional constraint is that the product solution must remain filterable as the system is equilibrated. Several analytical procedures are used during reactor operation to follow the equilibration process. These produce data which allow the selection of representative samples for complete analysis and which can give advance warning in the event that unsuitable conditions or failing equipment are endangering the experiment. It is now occasionally possible to recognize problems in time to correct equipment or to select better operating conditions. Failure after a period of recycle operation may be observed if poor solvent reactivity results from the conditions in use, for example.

Although specific equipment and some detailed experimental data are to be presented, it is felt that the description of the operating methods may be of more general interest. Some of these procedures may be useful in related coal processing studies. The program of experiments involves changes in reactor combinations as well as the interplay of a number of variables. Rapid indications of trends facilitates decisions regarding the time to be spent in equilibration of the system before samples can be collected for analysis and give early indications of the utility of the conditions chosen for study in an experimental trial. Some rapid analytical methods have been developed which can be used to evaluate samples as the reactor is operated and which facilitate such studies. The results which are presented do represent some progress in improving sulfur removal from Kentucky coal. It is not expected that the conditions reported are optimized. Continued improvement should result from systematic explorations using these techniques. Applications to other coals are also planned as an extension of this program.

II. EXPERIMENTAL

A. Equipment

A simplified schematic diagram of the laboratory scale continuous reactor used in these experiments is shown as Figure 1. Excluded from the diagram are the slurry feed system and the hydrogen compression and metering system. A more complete description of the apparatus is presented in OCR Report No. 53 Interim Report No. 8. 4/ Coal dissolution and hydrogenation is accomplished in a two or three vessel reactor consisting of a preheater and one or two dissolvers operated in series. The preheater consists of an 18 foot coil of 13/64 ID high pressure tubing heated by a fluidized sand bath. The internal volume of this coil is about 110 ml. The first dissolver is an electrically heated autoclave of about 450 ml volume. This is a vessel 1½ inches ID X 15 inches tall. In control experiments reported in this paper the

reactor system consisted only of these two vessels. Reacted material passes from the first dissolver to a two liter autoclave, which may be used as a surge vessel only, or which may also serve as a second dissolver. In the control experiments, product was removed from the autoclave by means of a dip tube which reached the bottom of the vessel. The autoclave was kept cool enough to prevent additional reaction in this mode of operation. When the autoclave was used as a second dissolver it was heated sufficiently hot to allow reactions to proceed. Product was allowed to fill the vessel to a level established by an alternate dip tube ten centimeters from the bottom of the autoclave. This allowed the accumulation of about 565 ml of liquid in the autoclave. In the control experiments all liquid product was collected in the sample flask at near room temperature, and light oils in the product distribution were found by distillation of the sample. In the latter experiments under consideration a flash vessel was added to the reactor system to allow continuous separation of these fractions as the samples were made. This modification caused little variation in results except for a tendency for loss of some of the most volatile product which had previously been collected in a dry ice cold trap in the distillation of samples in the laboratory. In either mode of operation the gas is separated from the liquid stream as it is collected in the sample flask or in the flash vessel and is passed through a condenser before it is collected in a rubberized fabric bag. Samples are collected for timed intervals and when samples are not being collected the liquid is diverted to an alternate receiver while the gas which is disengaged flows to a vent line. Hydrogen is mixed at a Tee between the slurry feed pump and the preheater and has the chance to react in each of the heated vessels. Some additional hydrogen is metered into the system as a gage line purge and this contacts only the contents of the two liter autoclave. This is set to deliver one mole of hydrogen per hour, an amount which is small compared to the input before the preheater.

B. Materials Used

Kentucky coal from the Colonial Mine was used. An analysis is given in Table I. This coal is ranked as a high volatile B bituminous coal. Coal was ground to pass 150 mesh. The coal was sieved and air dried in the process to an average moisture content of 1.5% to 2.0%. Solvents were recycled in the process and after a number of passes the identity of the initial solvent is lost. In the control experiments the initial solvent was Gulf FS 120 Carbon Black Feedstock for the series which ended with CU 77, or a blend of FS 120 and crude anthracene oil for the series which ended with CU 90. The series of experiments, CU 91 through CU 93 was started with a partially hydrogenated anthracene oil. The properties of these starting solvents are summarized in Table II. One of the objectives of the experiments in this series was the demonstration that the initial solvent would be converted in the process and that the equilibrated solvent would have a composition determined by the operating conditions and the coal used. This was the reason for starting different experimental sequences with different initial solvents or with solvent mixtures.

C. Procedure and Product Workup

Although coal dissolution is accomplished in a continuous process, product workup is a batch process. Coal slurry and hydrogen are fed continuously to the reactor which is controlled at the desired pressure and temperatures. Product coal solution is accumulated in a product receiver over an interval of 3 or 4 hours. The coal product solution is taken to the laboratory for workup which may include the following

operations: stripping to remove water and light oils formed in the process, filtration to remove the ash and the small amount of undissolved organic matter, and distillation to recover solvent from the coal solution. The residue from this vacuum distillation is the principal Solvent Refined Coal Product. Some excess of light oil above the amount needed for recycle as solvent may also be obtained.

In order to more rapidly attain a recycle solvent equilibrated with the coal and the reaction conditions, the filtration step may be eliminated, with solvent being recovered from stripped unfiltered coal solution. This is mixed with coal and returned to feed slurry until the system is judged to be equilibrated. An experiment is continued at one set of conditions with recycle of solvent until reaction control parameters indicate a stable reaction has been achieved. A product or products may be collected at this condition and subjected to the standard SRC workup including filtration for determination of product properties and distribution. A variable is then changed and solvent is again recycled until a new steady state appears to have been established. Typically an experiment will be continued for about 100 hours during which two condition sets may be equilibrated.

The stripping procedure provides two light oil cuts; "cold trap oil" which is not condensed by a water cooled condenser at the vacuum distillation pressure (nominally less than 3mm Hg) but is condensed in a dry ice trap, and "cut 1 oil" which is that distilling up to 90°C at less than 3mm Hg and condensed by the water cooled condenser. If needed, some of the cut 1 oil may be used to maintain a balance of recycle solvent.

Recycle solvent is that collected between the endpoint for cut 1 oil and an upper limit in the range of 250°C to 300°C at typical vacuum pump pressures. When distillations are carried out from unfiltered coal solutions some decomposition is noted and distillations are terminated when the evolution of gases becomes significant. This can be followed by use of a suitable vacuum gage or by noting the formation of light products which appear as a smoke like vapor in the condenser and solvent receiver. The decomposition point determines the maximum practical amount of solvent which can be reclaimed in this circumstance. In distillation of filtered solutions the solution appears more thermally stable, and the decomposition point is observed at a higher temperature than is the case with the mineral matter present. When several filtered samples are collected it is usual to stop the distillation at a standard temperature chosen to produce at least a break-even amount of solvent. Vacuum bottoms are evaluated by elemental analysis and by melting point determination. This information allows an estimation of the availability of more solvent from the vacuum bottoms if necessary. The melting point of vacuum bottoms is increased as solvent is removed, and break-even amounts of solvent usually are not obtained until the melting point is about 185°C to 200°C. The interplay between the degree of reaction with hydrogen, conversion to solvent, and depolymerization or repolymerization effects must be taken into account in obtaining a solvent balance, therefore it is difficult to use a standard temperature in all cases. The objective of the reclaim procedure is to obtain the necessary amount of solvent and remain within practical operating limits of vacuum flash equipment. If this can not be achieved the operating condition set must be abandoned as unsuitable for use.

In the equilibration procedure the reclaimed solvent is mixed with coal and returned to feed slurry. It is a simple matter to compare the weight of slurry fed in the preparation of a sample with the weight of slurry returned from the reformulated cut 2 oil. It is usually possible to establish a temperature at which a solvent

balance can be maintained, or to determine that no practical finish temperature will allow a balance, as the initial samples in the equilibration series are being distilled. As the equilibration process is continued a drift in yield or composition may be observed, as well as oscillation in these observations. Such adjustments from sample to sample are usually small. In the situation that more than a break-even amount of solvent is obtained, the weight of slurry in the feed vessel will increase. This is therefore an unambiguous indication that the conditions in use satisfy the constraint that at least a break-even quantity of solvent be obtained.

D. Discussion of Analytical Tools Used

One of the problems in working with the continuous reactor system has been the development of methods by which the reproducibility of the product could be established and which could be used to indicate when the product was equilibrated with feeds and the effect of reaction conditions. This problem is of particular importance in the current type of study in which the objective is preparation of well equilibrated samples. Two measurements which can be made rapidly on unfiltered coal solutions have been found to be particularly valuable in following the reaction while it is in progress. These are both based on spectrophotometric measurements. The methods are based on measurements taken from infrared spectra and measurements made in the visible region. Infrared spectra are obtained on thin films of unfiltered coal solution supported between polished rock salt plates. Of particular interest are bands in the CH stretching region. The ratio of the nonaromatic CH stretching band at about 2920 cm^{-1} to the aromatic CH stretching band at about 3050 cm^{-1} is determined and is reported as the term IR. This value increases as the hydrogenation of the coal solution increases and decreases as the hydrogenation decreases (and aromaticity increases). Plots of IR versus time indicate if the hydrogenation level of the product is increasing, decreasing, or has stabilized. Spectra can be obtained in a few minutes and use only a drop of sample. It is therefore easy to develop an observation rapidly and economically by this method and to make reliable estimates of the amount of hydrogen acquired or lost by the solution.

"Blackness" is a measure of absorbance of the coal solution in the visible region. It was found that colored material in the coal solution could be dissolved and measurements in the visible region could be used to follow the concentration of a fraction of dissolved coal in the reaction product stream. These solutions absorb throughout the visible region, therefore the absorbance is arbitrarily measured at 550 nanometers. Measurements are made in solution in pyridine in $\frac{1}{2}$ inch square cuvettes using a B&L Spectronic 20 spectrophotometer.

$$\text{Blackness} = \frac{(\text{Optical Density})(\text{Volume of Pyridine Soln. in ml})}{(\text{Sample size in grams}) 100}$$

The blackness of the solution should be accepted as an empirical observation of a solution property. The value reports on the net effect of competition between hydrogenation, depolymerization, and repolymerization reactions. It is one of the most sensitive indexes which can be used to investigate the state of the product solution from the reactor. Normally blackness increases as the concentration of coal in the feed is increased. Factors which increase the amount of hydrogen which is reacting tend to reduce the blackness of the solution while increased temperature-time stress on the system usually will cause an increase in the blackness of the solution. The responses are non linear and have not been fitted into a quantitative discussion despite the considerable reproducibility of the blackness observations. The blackness determination requires only a few drops of solution and can be completed in a few minutes time. The combined information from IR and blackness determinations therefore provides supporting indications related to the course of the reaction and its

probable extent of conversion. Also, it is readily determined if the same product is being obtained from sample to sample by use of these methods. Such results are available in a fraction of the time needed for an evaluation based on solution workup by distillation.

Gas analyses are also of value in monitoring the reaction. Concentrations of output gases including hydrocarbons, CO_2 , CO , H_2S , and small amounts of ammonia are determined by standard means including infrared spectra, molecular weight, gas solid chromatography, and volumetric determination of the hydrogen sulfide. Unreacted hydrogen is calculated from the composition and volume of the output gas. This is subtracted from the hydrogen input to calculate the amount of hydrogen reacted. The yield of hydrogen sulfide in the output gas is a good indication of the amount of desulfurization which is observed, although enough sulfide is dissolved in the water to cause some nonlinearity in this observation also. This is because the water dissolves ammonia which extracts both carbon dioxide and hydrogen sulfide from the gases until the ammonia is neutralized.

The above analyses are used in monitoring the continuous operation of the reactors. After product workup and solvent isolation, more detailed analyses of products are carried out. Recycle solvents are analyzed by infrared, nuclear magnetic resonance, and elemental and physical analysis methods. For Solvent Refined Coal-Product the elemental analysis, percentage ash, and the fusion point are determined. Product distribution is determined by performing all distillations and filtrations quantitatively. The insoluble residue is carefully pyridine washed and the MAF conversion of the coal is calculated from the relative proportions of ash and carbonaceous matter in the insoluble residue after careful drying of the washed residue. Liquid products may be further characterized by density determinations and by functional group analysis such as titration of amine or phenolic functions. These functions also tend to establish characteristic concentrations in the recycle solvent, for example, and provide additional inspection methods for lineout.

E. Range of Conditions Explored in These Experiments

The operating conditions and related information for the experiments under discussion are summarized in Table III. In this table each experiment is numbered and represents a continuous operation from a single startup of the reactor. A change in operating conditions is given a letter code and implies a lineout at a new condition.

F. Discussion of Experimental Results

Results of runs with the two vessel reactor system are presented for comparison purposes. The first of these, Run CU 77, may be considered as a base run from which modifications were made; first to simulate startup conditions at the Ft. Lewis pilot plant, and then modified to improve desulfurization, solvent recovery, and the reactivity of the recycle solvent for better long term operation.

Run CU 77 was the eleventh pass of solvent in a series, described earlier, designed to simulate startup of the Ft. Lewis pilot plant with a petroleum derived solvent. 9/ This series of experiments was started with FS 120 Carbon Black Feedstock and was designed to recycle the solvent recovered from pass to pass until an equilibrated

recycle solvent had been developed. From recent work it is now established that the eleventh pass solvent was not completely free of the influence of the startup solvent. The concentration of sulfur in the eleventh pass solvent was higher than the level observed in later equilibration products due to the presence of a fraction of stable sulfur containing compounds in FS 120. However, the bulk of the solvent hydrocarbon materials appears to have been equilibrated fairly well.

The CU 77 product distribution and SRC Product analysis are shown in Figure 2 and Table IV, respectively. A recycle solvent cut of 100-250°C at 3 mm Hg provided a 99% return of solvent in this experiment. A break-even solvent yield could be accomplished by addition of part of the cut 1 oil obtained. No attempt was made to optimize desulfurization in this series of experiments; vacuum bottoms contained 1.0% sulfur. The feed coal for CU 77 contained 1.50% organic sulfur which is somewhat higher than the 1.29% organic sulfur reported in Table I for the Kentucky No. 9 coal used in later experiments. This could be due to a mine run variation in composition or to the inclusion of some Kentucky No. 14 coal in the sample.

The next runs to be considered were made on the same equipment but operating conditions were changed to match the proposed startup conditions for the Ft. Lewis Pilot Plant. The initial solvent used was a blend of FS 120, crude anthracene oil, and some creosote oil. The laboratory operating procedure was modified by distilling the unfiltered product solution to recover solvent for recycle; this expedites attainment of equilibrated recycle solvent. Because the FS 120 component of the solvent was known to be low in reactivity, operating temperature for run CU 89 was 425°C in both the preheater and dissolver for the first few cycles; the temperature was then advanced in stages when the composition of the solvent had changed enough to justify a change in operating conditions. Final operating temperature was 445°C in both the preheater and dissolver. A plot showing the course of the $\bar{I}R$ and blackness functions for this experiment is presented as Figure 3. This plot also indicates the solvent recovery as a function of sample number in the experiment.

A gradual decline in hydrogen in the product solution is indicated by the $\bar{I}R$ function. Initial solvent recovery was low because of a high molecular weight fraction in the FS 120 which would not be distilled at the final temperature of the solvent reclaim distillation. Solvent recovery then improved rapidly but lined out at only 96% return on the average. Use of all available cut 1 oil would have allowed break-even operation. The operation could have been improved by the use of a higher distillation endpoint but distillations were finished near the temperature at which decomposition was a factor. The experiment was continued with the same solvent after a new startup (hence the designation experiment CU 90). By this time the Ft. Lewis Pilot Plant had been operated and an exotherm in the dissolver had been observed to raise the reactor to an average temperature of about 450°C with the preheater at 425°C. Experiment CU 90 was therefore initiated at a preheater temperature of 425°C and a dissolver temperature of 450°C. This experiment was conducted with great difficulty; flow through the reactor was interrupted by repeated plugging of the preheater. Somewhat better operation was achieved at a preheater temperature of 440°C rather than the planned 425°C but plugging was still severe. From the number of plugs encountered and subsequent inspection of the equipment it appeared that the solvent

obtained in the CU 89 experiment had been insufficiently reactive and that a slow deposition of carbon in the preheater had been in effect during the latter stages of the CU 89 experiment. This spalled off the tube later when the new startup was attempted and carbon deposition caused plugs to form at constrictions in fittings. This appears to be the main problem in recycling of a solvent which has not been well hydrogenated, since the slurry will tolerate only mild and carefully controlled heating in this circumstance. The uniformity of heating the preheater by the fluidized sand bath may not be sufficiently good for work near critical temperature limits, and this may have been a contributing factor in the difficulties observed. In any case the use of a high final temperature for desulfurization of product does not appear to be good procedure. The vacuum bottoms products which were made in experiment CU 89 contained an average of 0.83% of sulfur and in CU 90 the vacuum bottoms contained an average of 0.75% of sulfur. Thus use of hot reaction conditions had been effective in removal of sulfur, but at the cost of preparing a solvent of doubtful stability and reactivity on recycle. The concentration of coal was increased in experiment CU 90 to 30%. This may have been another factor in producing a less stable solution in the hot reactor but the concentration of coal is not thought to be the main problem.

It had been previously established that good performance in a coal dissolver could be obtained if the preheater were operated at a comparatively high temperature (450°C to 460°C for example) while the dissolver was operated at a milder temperature (about 425°C for example). This two temperature - two vessel system had been used routinely in the laboratory with good results. Experiment CU 77 typifies application of this strategy. In initial trials in the Ft. Lewis Pilot Plant it was found that the first dissolver heated spontaneously, as the result of the exothermic heat of hydrogenation, to a temperature of about 450°C. This is higher than the preferred final reactor temperature for preparation of a well hydrogenated recycle solvent. The preheater was operated at a maximum temperature of 425°C in order to minimize the temperature in the first dissolver. As a consequence the actual operation of the preheater and dissolver was not in the preferred temperature profile and not in the profile which had been used in most of the lineout study program done in the laboratory. Sulfur removal using this temperature profile had been good, resulting from exposure of the product solution to heat for relatively long time intervals. The problem therefore appeared to reduce to the question of obtaining and using good temperature controls in the reactors at hand. The Ft. Lewis Pilot Plant installation includes a second dissolver which can be operated in series with the first. It was therefore reasonable to investigate configurations in which the preheater temperature was mild (425°C), the first dissolver was allowed to heat under the influence of the exothermic reaction, and the last dissolver was presumed to be cooled to produce a solvent with a better hydrogen concentration in it. Such final temperatures were expected to fall in the 400°C to 425°C range with the best temperature not established. Experiments of this kind were simulated in runs CU 91 through CU 93.

Use of the second dissolver could be simulated in the laboratory by changing the location of the dip tube in the two liter autoclave to allow a volume of liquid product to accumulate in this vessel. In order to have a reaction in the autoclave it was necessary to heat it to normal reaction temperatures. Since a new heater and new equipment operations were involved it was decided to explore the use of the lower operating temperatures in the range of interest first. The autoclave has therefore been used only at 400°C in trials to be reported.

The initial investigation with the modified reactor system was done using the conditions shown for experiment CU 91A. The study was started with an initial solvent charge of lightly hydrogenated anthracene oil. As solvent was recycled in the process the concentration of hydrogen in the solution and in the reclaimed solvent was observed to increase. This was followed by means of infrared spectra for product solution and the reclaimed solvent. The course of the IR, blackness, and solvent recovery functions for this experiment is shown in Figure 4. In the initial series of samples made the recovery of solvent was improved for this operating mode. It was also observed that over half of the hydrogen added to the reactor was consumed. It was obvious that not as much hydrogen was being added as could be reacted under these conditions. The hydrogen flow rate was therefore increased without collecting a sample to represent the initial hydrogen starved portion of the experiment. The second portion of the experiment, after increasing the hydrogen flow, was designated experiment CU 91B.

The increased hydrogen addition rate caused an abrupt decline in the blackness of the solution and an abrupt increase in the IR values for the coal solution and for the reclaimed solvent obtained by redistillation of the coal solution. The increase in reacted hydrogen was confirmed by subsequent analysis for samples of the reclaimed solvent. The experiment was continued for a total of thirty samples, with return of the reclaimed solvent to the feed slurry in each case, in an effort to equilibrate the solvent as well as possible. Finally most of the feed slurry was run through the reactors to make two samples of solution for workup by filtration and preparation of the usual ash-free vacuum bottoms and reclaim solvent samples. Samples were analyzed. The reclaimed solvent was pooled for use in experiment CU 92. Vacuum bottoms properties are given in Table IV and reclaim solvent properties are given in Table V.

Observation of abrupt changes in the composition of these products in response to changes in the hydrogen input rate is convincing evidence that the material in the reactors is effectively catalyzed. Given suitable temperatures and hydrogen pressures, the coal can be reduced by hydrogen, and production of liquified material which accounts for most of the organic matter in the coal is possible. The MAF conversion in this case was 97.3% for the average of the two final samples in the series. Another convincing observation is the comparatively low sulfur content of the vacuum bottoms samples. In this case the vacuum bottoms contained 0.52% to 0.56% of sulfur.

The lightly hydrogenated anthracene oil which was used as the initial charge of solvent in this experiment contained 6.04% hydrogen. In the hydrogen starved portion of the experiment the reclaimed solvent had remained at substantially this composition. The analysis for several reclaim solvent samples is presented in Table V and it can be seen that the solvent had remained close to the composition of the initial solvent charge through sample 12. Sample 11 contained 6.00% hydrogen for example. Values for IR for the solution also indicate little change in the composition of the solution during this portion of the experiment. After the hydrogen flow was increased the IR values for solution samples and for the reclaimed solvent increased. The hydrogen content of the 14th sample increased to 6.58% for example. This composition remained established throughout the remaining samples with minor variations only. It should be remarked that IR values for the coal solutions contain a component contributed by the dissolved coal, and that the reclaimed solvent commonly will yield a different value. The volume of slurry required to maintain a safe level of material in the feed system while

solutions were being redistilled to obtain reclaim solvent was such that about 3 or 4 samples were needed to complete one pass of solvent through the reactor system. Experiment CU 91 therefore represents about 6 or 7 passes of solvent through the reactor.

Experiment CU 92 was started with the slurry heel retained from the previous experiment plus additional slurry formulated with the solvent reclaimed from the final samples prepared and worked up for analysis. In this sense experiment CU 92 is a continuation of the previous experiment. The initial operating temperatures were also the same as the final temperatures used in the previous experiment. The concentration of coal was increased from 30% used in the previous experiment to 35%. This change combined with a small adjustment in the hydrogen input rate resulted in reducing the hydrogen input rate from 8.0% in the CU 91B experiment to 5.6% based on the feed coal in the latter case. The CU 92A portion of the experiment was continued for 13 samples and an hour long sample was then taken for complete workup. After this sample was completed the temperature of the first dissolver was reduced from 450°C to 435°C.

This change resulted in an abrupt decline in the blackness of the solution and again a sharp increase in the IR values of the product solution and of the reclaimed solvent obtained from the solution. In addition a small exothermic reaction developed in the second dissolver which caused the temperature to increase from 400°C to the vicinity of 410°C. This persisted until the controller for the outer jacket was reset to allow a cooler jacket temperature. During this time the yield of solvent was well above the break-even amount. This situation prevailed throughout the remaining part of the experiment and would have averaged about 4% excess assuming the cut 1 oil were formulated also. The reactivity of the system appeared to oscillate throughout the remainder of the experiment.

The vacuum bottoms sample taken at the end of the CU 92A sequence contained only 0.54% sulfur. The samples taken at the end of the CU 92B sequence contained sulfur ranging from 0.60% to 0.70% and the values seemed to be under the influence of reactor oscillation. The reclaimed solvent obtained in the CU 92A sequence contained 6.64% hydrogen (from sample 14) while the reclaimed solvent made in the CU 92B part of the experiment contained an average of about 6.85% hydrogen. The control functions, IR and blackness, therefore reported this trend with apparent reliability. During this portion of the experiment the solvent accumulated another 6 or 7 cycles of use. Data for CU 92 are plotted in Figure 5.

Experiment CU 93 continued with the recycled solvent recovered from the previous experiment. The initial slurry contained 35% coal; operating changes were a reduction of the first dissolver from 435° to 425°C and an increase in the preheater from 425° to 450°C. This portion of the experiment was run with some difficulty since the temperature recorder failed at the end of the 5th sample. The continuous operation was sustained by moving a portable potentiometer from one thermocouple to another while the multipoint recorder was being repaired. Temperature control was upset during several samples and blackness, IR values, and the amount of recycle solvent obtained all show related effects during this portion of the experiment. The upset seemed to be well corrected by the 14th sample. A sample was therefore collected for complete workup at this time. The concentration of coal in the feed slurry was then increased to 40% to continue with the CU 93B sequence. This change resulted in an increase in the blackness of the solution but did not result in much effect on the IR values for the coal solution. Oscillation of the amount of reclaim solvent available for recycle developed following the increase in coal

concentration. Experiment CU 93 included the attempt to crowd three experiments into a week of continuous operation. A sample was taken to represent the equilibrated product at the 23rd sample. The temperature of the first dissolver was then increased to the 435°C level to investigate the prospect for better sulfur removal at this temperature. This change resulted in an increase in the blackness of the solution, little effect on the IR values for the coal solution, and a temporary drop in the amount of solvent which could be reclaimed from the unfiltered coal solution. This drop appears to have been mostly corrected five samples after the temperature change. Samples 29, 30, and 31 were taken for complete workup and analysis. It is questionable whether stable operation had been established at the time the reactor was shut down. The trend appeared established for a small yield of excess solvent in the usual solvent range, with some additional cut 1 oil available if needed. The vacuum bottoms sample representing CU 93A operations contained 0.59% sulfur. The vacuum bottoms representing CU 93B operations contained 0.73% sulfur. The experiment was terminated by the preparation of three samples for complete workup. The vacuum bottoms representing the CU 93C condition contained sulfur ranging from 0.62% to 0.69%. Data for CU 93 are plotted in Figure 6.

G. Reporting of Yield and Sulfur Balance Results

Methods have been developed for measuring the inputs and outputs in experiments in this continuous reactor system with precision. These are reported in detail in OCR Report 53, Interim Report 8. As a result of these studies material balances are commonly closed to account for 99.5% of the materials in each of the samples made. Distillations and filtrations are managed in a quantitative procedure which normally accounts for better than 99% of the materials in these subsidiary operations. Usually these results are summarized in the form of a yield table and a flow chart which consolidates several samples in a single average calculation. An example of such data is presented as Figure 7 which gives the detailed summary for experiment CU 92B and which reports the data based on three samples collected at the end of that experiment for complete analysis. The information on this chart can be combined with elemental analysis results to calculate the balance of sulfur in the process. The balance is presented in Table VI. Sulfur balance was closed with good accuracy. Sulfur is removed by the evolution of hydrogen sulfide and with the mineral phases removed by filtration. A small amount of sulfur is removed as ammonium sulfide dissolved in the water produced.

III SUMMARY

Measurements useful in studying the Solvent Refined Coal continuous reactor have been described. Several changes in operating conditions have been investigated with recycle of solvent at each condition so that the recycle solvent is in equilibrium with the process. Addition of a second dissolver vessel which is operated at a lower temperature than the preheater and the first dissolver had the following beneficial effects.

1. Improved desulfurization
2. Increased solvent recovery
3. Improved hydrogen transfer capacity of the recycle solvent.

Coal concentrations up to 40% in the feed slurry have been used without difficulty. Solvent Refined Coal Products with sulfur levels as low as 0.52% have been obtained. Conditions used are not known to be optimal but the stepwise investigation of variables described has brought about significant improvement in the sulfur content of the vacuum bottoms product.

Table I
Analysis of First Lot Pilot Plant Coal

Sample: First lot coal for Ft. Lewis Pilot Plant
 Six car composite; received May 7, 1974
 From Colonial Mine, Hopkins County, Kentucky

PROXIMATE ANALYSIS			ULTIMATE ANALYSIS		
	As received	Dry basis		As received	Dry basis
% Moisture	5.84	xxxxx	Moisture	5.84	xxxxx
% Ash	7.95	8.44	Carbon	69.15	73.44
% Volatile	39.89	42.36	Hydrogen	4.99	5.30
% Fixed Carbon	46.32	49.20	Nitrogen	1.53	1.62
	<u>100.00</u>	<u>100.00</u>	Chlorine	0.02	0.02
			Sulfur	3.14	3.33
Btu	12529	13306	Ash	7.95	8.44
% Sulfur	3.14	3.33	Oxygen (diff)	7.38	7.85
% Atk as Na ₂ O	xxxxx	0.12		<u>100.00</u>	<u>100.00</u>
				% Weight	
SULFUR FORMS			MINERAL ANALYSIS		
% Pyritic Sulfur	1.87	1.99	Phos. pentoxide, P ₂ O ₅	0.22	
% Sulfate Sulfur	0.05	0.05	Silica, SiO ₂	40.18	
% Organic Sulfur	1.22	1.29	Ferric oxide, Fe ₂ O ₃	31.28	
% Total Sulfur	3.14	3.33	Alumina, Al ₂ O ₃	22.00	
			Titania, TiO ₂	0.98	
			Lime, CaO	1.60	
			Magnesia, MgO	0.65	
			Sulfur trioxide, SO ₃	0.55	
			Potassium oxide, K ₂ O	1.88	
			Sodium oxide, Na ₂ O	0.23	
			Undetermined	0.43	
				<u>100.00</u>	

FREE SWELLING INDEX = 4
 SILICA VALUE = 54.51
 T250 = 2260^oF

Table II

Composition of Initial Solvents Used

Solvent	FS 120 Carbon Black Feedstock	CU40 Hydrogenated Anthracene Oil	Ft. Lewis Solvent Blend
Carbon	89.52	90.58	90.28
Hydrogen	7.72	6.04	6.76
Nitrogen		1.07	
Sulfur	2.20	0.36	1.62
Oxygen		1.95	
IR Value	4.47	0.98	1.81
Proton Distribution % by NMR*			
H _γ (30-60 Hz)	9.2	1.6	4.5
H _β (60-120 Hz)	31.4	8.6	14.7
H _α (120-200 Hz)	29.7	20.5	26.6
H _{Ar} (360-512 Hz)	29.7	69.3	54.2

* See reference 9

Table IV

Composition of Vacuum Bottoms

Experiment	Sample #	% C	% H	% S	% Ash	MP ^o C
CU 77	Average	87.88	5.33	1.03	0.079	207
CU 89	19	87.59	5.37	0.84	0.046	180
	20	87.77	5.46	0.83	0.058	198
CU 90	8	89.21	5.09	0.75	0.075	219
CU 91B	31	89.29	5.70	0.52	0.11	171
	32			0.56	0.16	226
CU 92A	14	88.19	5.16	0.54	0.11	223
CU 92B	31	87.84	5.43	0.60	0.10	212
	32	87.55	5.52	0.70	0.09	215
	33	86.83	5.11	0.64	0.11	220
CU 93A				0.59	0.21	243
93B		87.59	5.38	0.73	0.10	238
93C	29	88.24	5.34	0.69	0.10	225
	30	87.80	5.30	0.68	0.19	225
	31	88.09	5.22	0.62	0.11	235

Table III

Range of Conditions Explored

Run	Press. psig	Temperatures, °C		Coal Concentration in Slurry %	g slurry/ hr.	Feed Rates		Hydrogen Feed kgt. % Based on Coal
		Preheater	1st Dissolver			2nd Dissolver	lbs.slurry/ hr./cu.ft. ^a	
CU 77	1500	455	435	-	520	57.9	20.8	6.4
CU 89		425→445	425→445	-	610	68.0	17.0	4.9
CU 90		440	450	-	520	57.9	17.4	4.9
CU 91A		425	450	400	800	44.4	13.3	4.2
CU 91B		425	450	400	800	44.4	13.3	8.0
CU 92A		425	450	400	800	44.4	15.5	5.6
CU 92B		425	435	400	800	44.4	15.5	5.6
CU 93A		450	425	400	800	44.4	15.5	5.4
CU 93B		450	425	400	800	44.4	17.8	4.8
CU 93C		450	435	400	800	44.4	17.8	4.8

a) Includes combined volume of preheater and dissolver(s).

Table V
Properties of Recycle Solvents

Experiment	Sample #	% C	% H	% S	Density	IR in CS ₂ Solution	Proton Distribution by NMR*			
							H _γ 30-60	H _β 60-120	H _α 120-200	H _A 360-512
Started with FS 120										
CU 77	Average	88.66	6.99	1.98	1.071	2.19	4.9	18.3	28.9	48.0
Started with Ft. Lewis startup solvent blend										
CU 89	19	89.83	6.77	1.24	1.085	1.74	2.4	11.8	25.9	59.9
	20	89.79	6.54	1.31	1.087	1.30	2.1	10.5	25.3	62.1
CU 90	7	89.75	6.58	1.18	1.086	1.21	2.0	11.1	25.3	61.6
Started with partly hydrogenated anthracene oil										
CU 91A	7	90.40	6.08	0.41		0.92	1.3	8.8	21.7	68.7
	9	90.56	6.05		1.107					
	11	90.43	6.00	0.39	1.102	0.95	1.5	8.9	21.2	68.2
CU 91B	14	90.53	6.58	0.41	---	1.20	1.5	11.3	23.1	64.1
	30	89.63	6.57	0.41	---	1.40	2.4	13.0	24.5	60.1
	31	---	---	0.38	---	1.35	2.1	12.4	24.2	61.3
	32	89.65	6.68	0.42	1.092	1.45	2.2	13.2	24.9	59.7
CU 92A	14	89.59	6.64	0.51	1.093	1.45	2.3	14.2	25.3	58.2
CU 92B	31	89.05	6.82	0.51	---	1.81	2.7	15.1	27.4	54.8
	32	89.03	6.85	0.51	1.085	1.76	3.8	16.1	26.5	53.5
	33	---	---	0.49	---	1.74	3.3	16.0	27.2	53.5
CU 93A	A	88.34	7.18	0.48	1.091	1.95	2.4	16.3	28.4	52.4
CU 93B	B	88.51	6.98	0.49	1.076	2.13	3.3	17.3	29.9	49.5
CU 93C	29	88.30	7.22	0.48	---	2.10	5.0	17.3	28.2	49.5
	30	88.40	7.08	0.51	1.070	2.14	4.5	17.8	28.2	49.5
	31	88.03	7.17	0.49	---	2.17	4.6	17.9	28.3	49.2

* See reference 9

Table VI
Sulfur Balance Data for Run CU 92B
Composite samples 31, 32, & 33
Yields from Figure 7

Substance	Weight Grams	% Sulfur	Grams S
<u>Input</u>			
Coal	2527	3.33	84.15
Solvent	4649	0.49	22.78
Hydrogen	141		
Total	7317		106.93
<u>Output</u>			
Gas (raw) ^a	366		36.62
Water (Composite)	187.1	0.92	1.72
Cold Trap Oil	59.2	0.76	0.45
Cut 1 Oil	194.3	0.42	0.81
Cut 2 Oil	4607	0.50	23.03
Vacuum Bottoms	1514	0.65	9.84
Pyridine Insolubles	376.3	9.29	34.96
Not accounted for	12.7		
Total	7316.6		107.43
Accountability			100.5%

- a) Gas output = 42.39 moles at 2.70 mol % hydrogen sulfide. This accounts for 36.62 grams of sulfur.

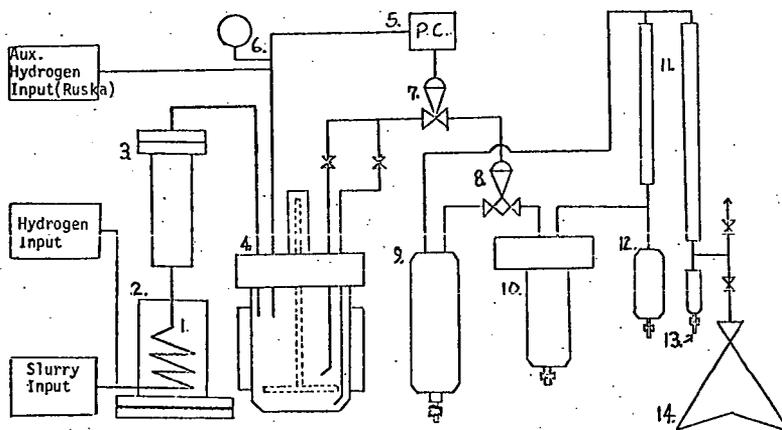
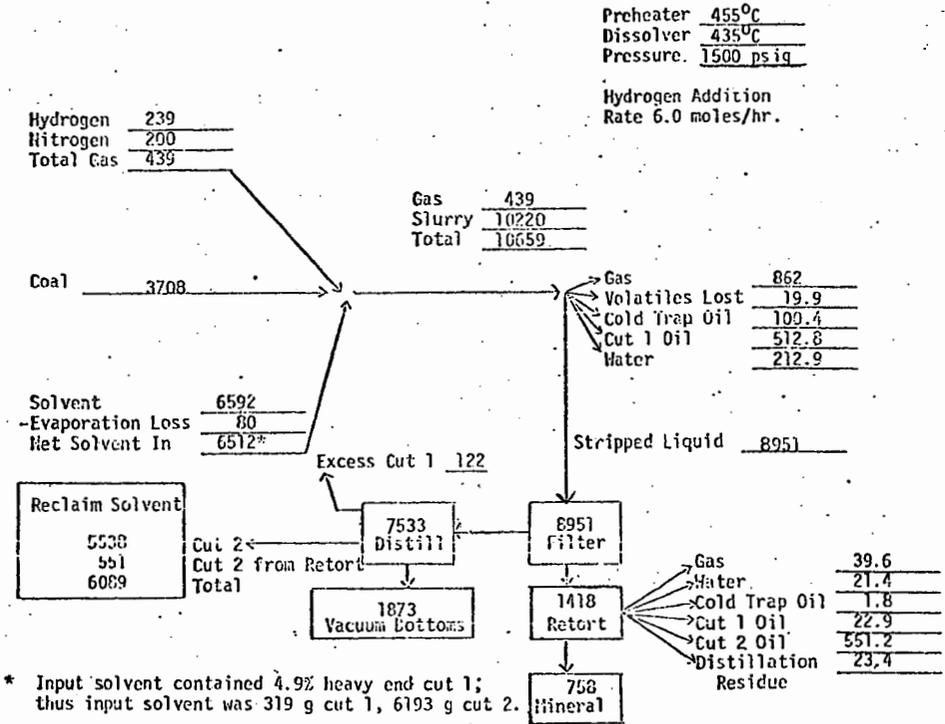


Figure 1. Simplified Schematic Continuous Reactor
(Not to scale)

Legend

1. Preheater Coil
2. Fluidized Sand Bath
3. 1st Dissolver (450ml Autoclave)
4. 2nd Dissolver (2 liter Autoclave, Volume used ca 565 ml)
5. Pressure Controller
6. Reactor Pressure Indicator
7. Gismo Valve
8. 3-Way Manifold Valve
9. Slop Vessel
10. Flash Vessel
11. Cold water condensers
12. Flash Condensate Receiver
13. Knockout Vessel
14. Gas Collection Bag

Figure 2 CU 77 Flow Diagram
11th Pass of Reclaim Solvent

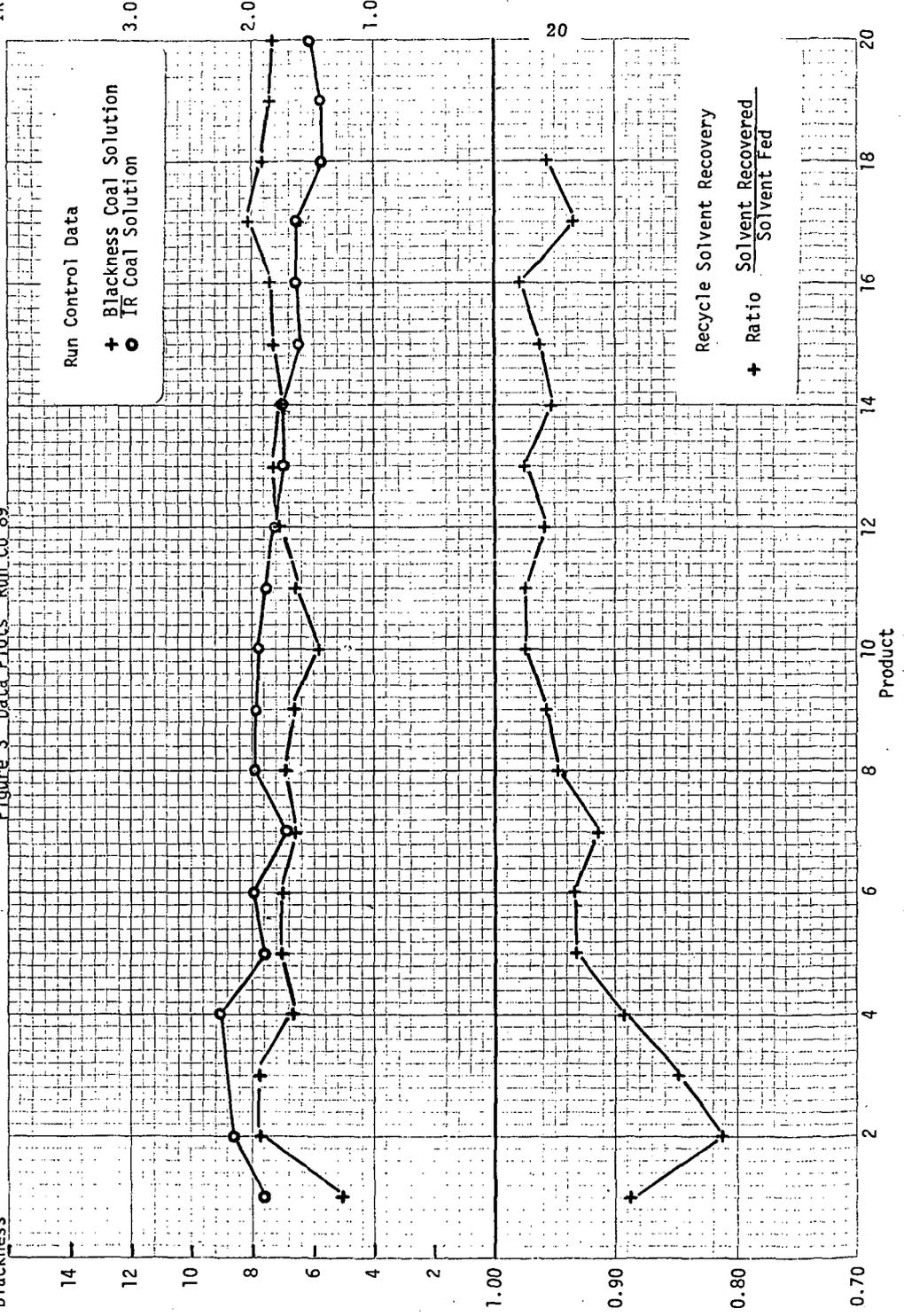


PRODUCT SUMMARY	Weight	% of Feed Slurry	% of Raw Coal
Gas	902		
H ₂	-161		
N ₂	-200		
Net Gas	541	5.29	14.58
Water	234.3	2.29	6.31
Volatiles Lost	19.9	0.19	0.52
Cold Trap Oil	102.2	1.00	2.76
Cut 1 Oil	657.7 ^a	6.44-3.12 ^c -1.02 ^d	6.34
Cut 2 Oil	6089.2	59.58+3.12 ^c +1.02 ^d	-
Heavy Residue (Retort)	23.4	0.23	0.63
Vacuum Bottoms	1873	18.33	50.52
Dry Mineral	758	7.42	20.45
		100.77% ^b	102.11 ^b

- a Includes excess cut 1 oil from distillation.
- b Greater than 100% due to addition of hydrogen.
- c Cut 1 oil in input slurry.
- d Additional cut 1 oil needed to reach breakeven reclaim solvent yield of 63.72%.

Blackness

Figure 3 Data Plots Run CU 89



Run Control Data

+ Blackness Coal Solution
o IR Coal Solution

Recycle Solvent Recovery

+ Ratio $\frac{\text{Solvent Recovered}}{\text{Solvent Fed}}$

IR

Figure 4 Data Plots Run CU 91

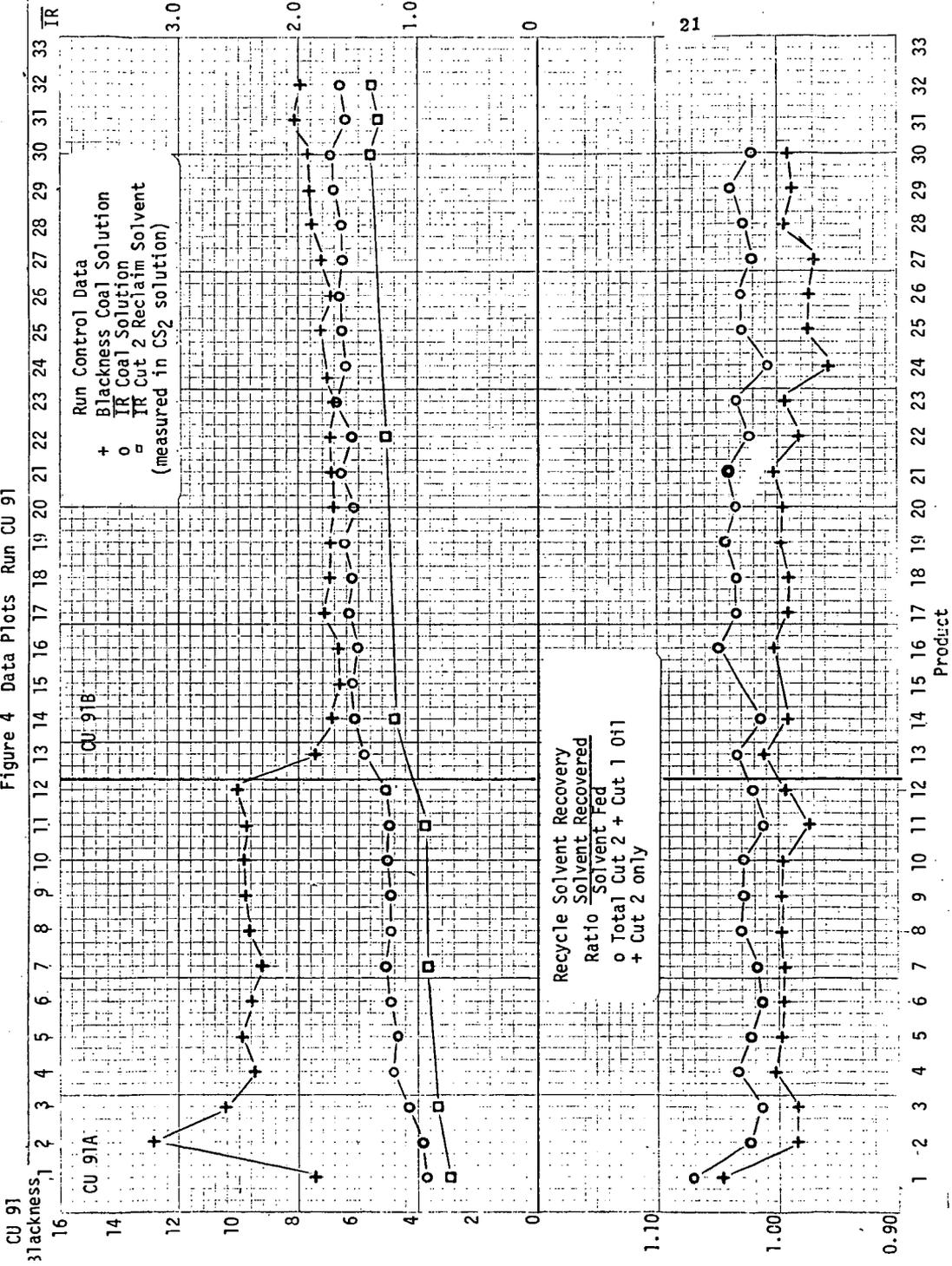


Figure 5 Data Plots Run CU 92

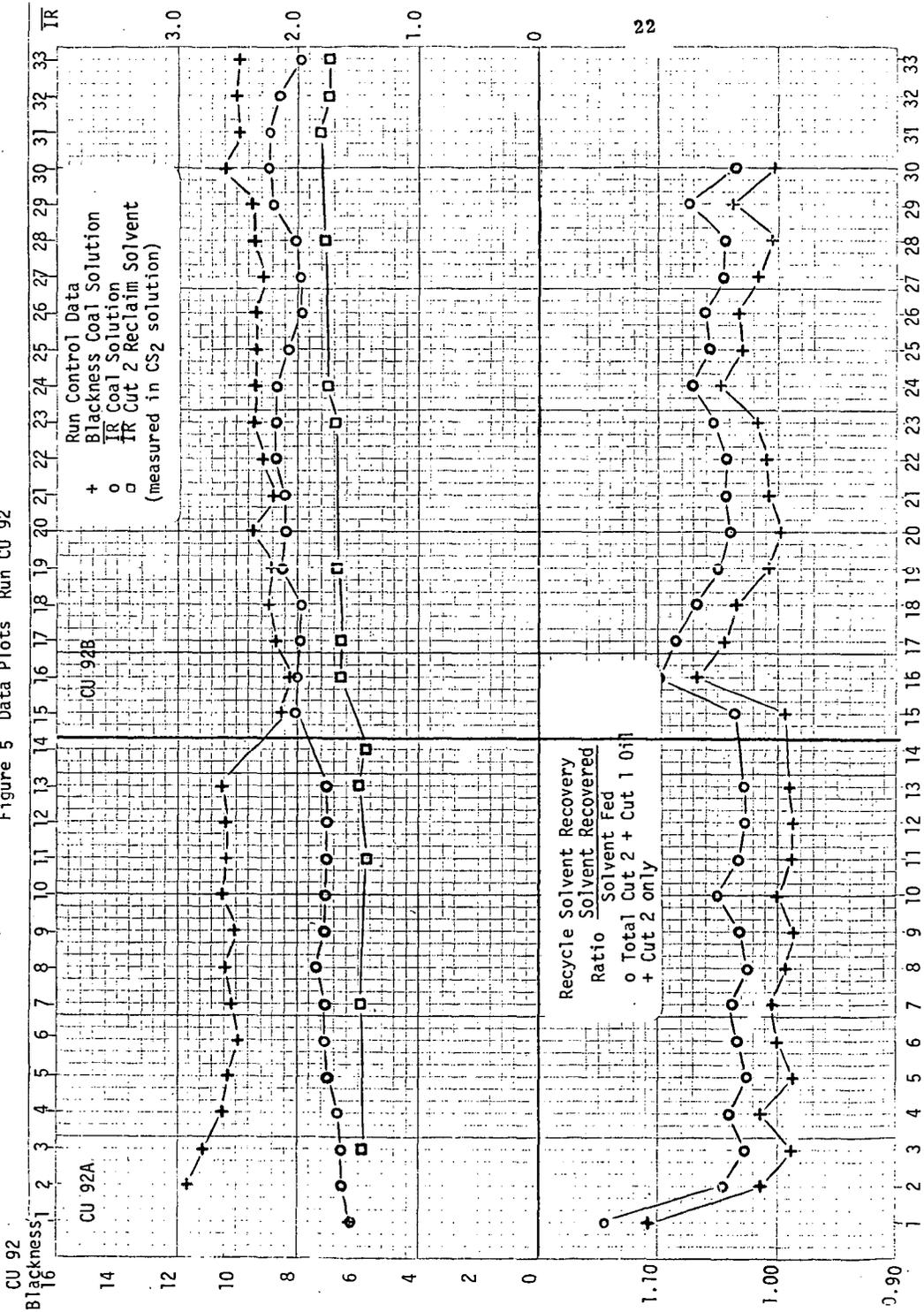


Figure 6 Data Plots Run CU 93

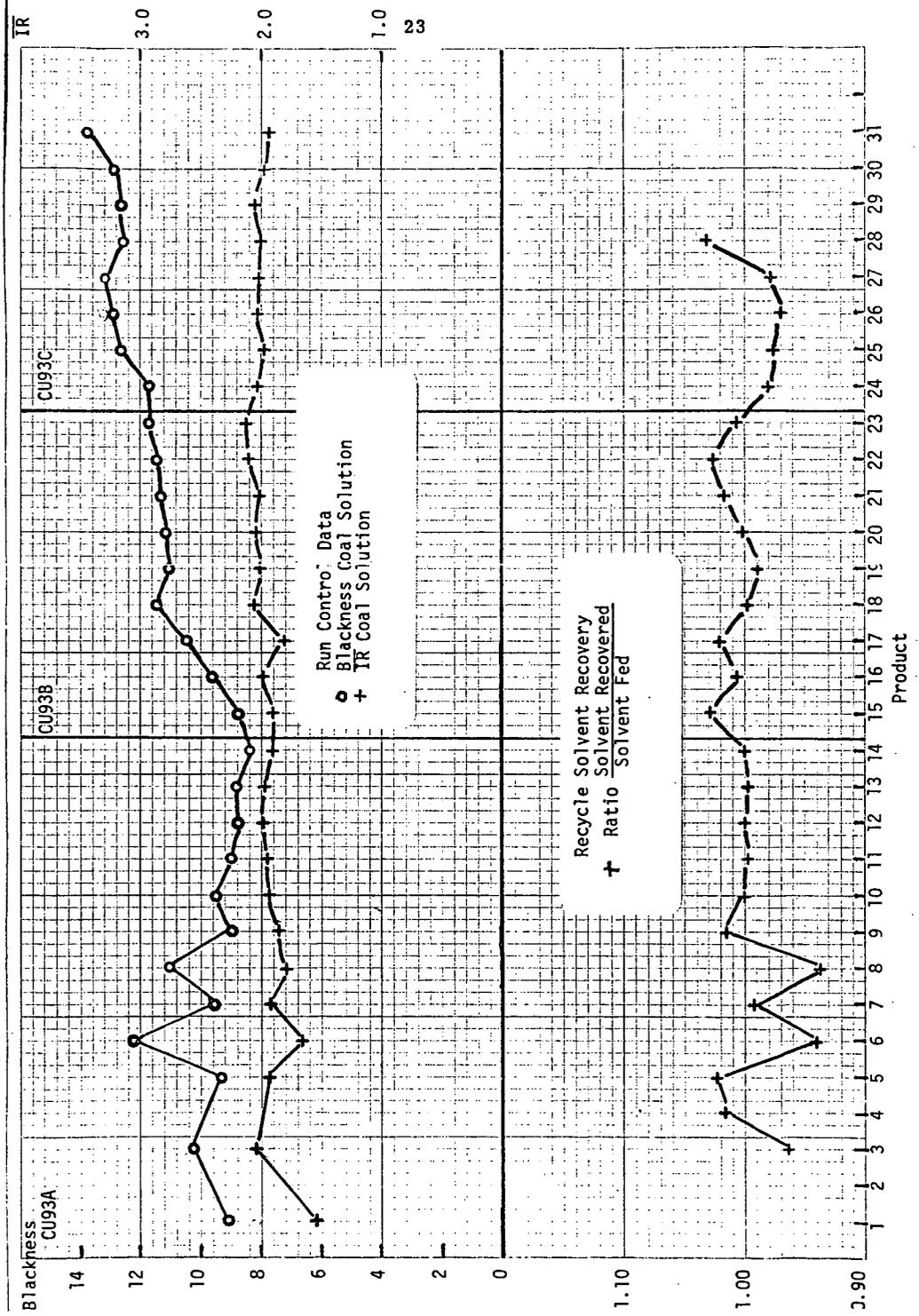
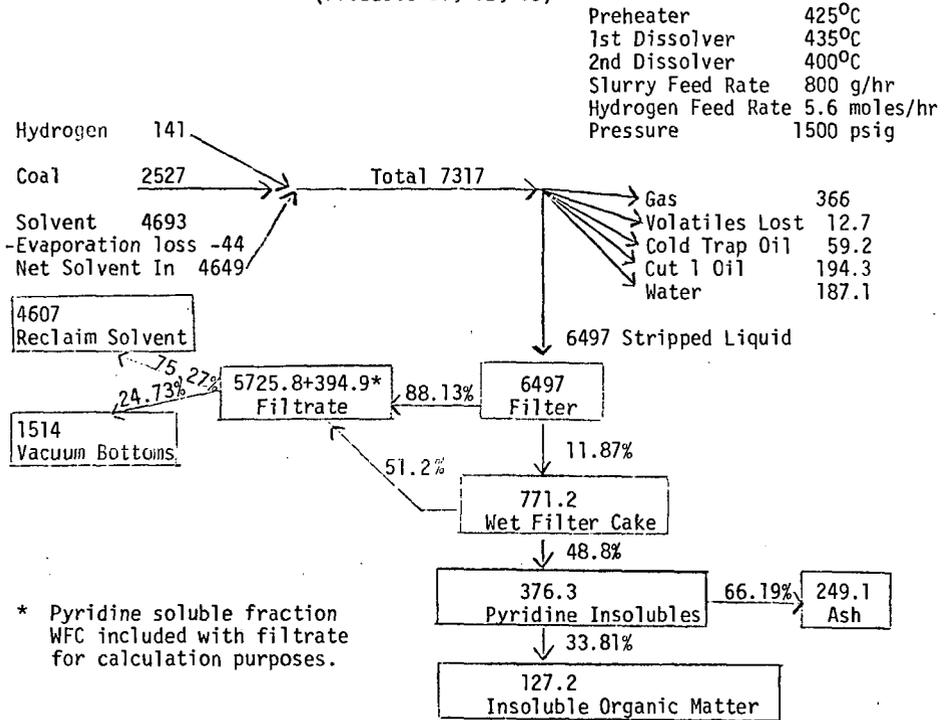


Figure 7 CU 92B Flow Diagram
(Products 31, 32, 33)

Product Summary	Weight	% of Feed Slurry	% of Raw Coal
Total Gas	366		
H ₂	- 87		
Net Gas	279	3.89	11.05
Water	187.1	2.61	7.41
Volatiles Lost	12.7	0.18	0.51
Cold Trap Oil	59.2	0.82	2.33
Cut 1 Oil	194.3	2.71 - 0.59 ^b	6.02
Cut 2 Oil	4607	64.20 ^a + 0.59 ^b	-
Vacuum Bottoms	1514	21.10	59.92
Ash	249.1	3.47	9.85
Insoluble Organic Matter	127.2	1.78	5.05
Total		100.76	102.14

a) Correct input cut 2 concentration is 64.79%.

b) Amount of cut 1 required to reach breakeven solvent yield.

REFERENCES

1. Kloepper, D. L., Rogers, T. F., Wright, C. H., and Bull, W. C., "Solvent Processing of Coal to Produce a De-Ashed Product". Report to Office of Coal Research, U. S. Department of Interior, by Spencer Chemical Division of Gulf Oil Corporation. Contract 14-01-0001-275, OCR R&D Report No. 9, (1965) Clearinghouse No. PB 167809.
2. Wright, C. H., Perrussel, R. E., and Pastor, G. R. "Development of a Process for Producing an Ashless, Low-Sulfur Fuel from Coal" R&D Report No. 53, Interim Report No. 6, Volume II Laboratory Studies Part 1 - Autoclave Experiments. OCR Contract 14-01-0001-496.
3. Wright, C. H. Pastor, G. R., and Perrussel, R. E., "Development of a Process for Producing an Ashless, Low-Sulfur Fuel from Coal" R&D Report No. 53, Interim Report No. 7, Volume II Laboratory Studies Part 2 "Continuous Reactor Studies." OCR Contract No. 14-01-0001-496.
4. Anderson, R. P., and Wright, C. H., "Development of a Process for Producing an Ashless, Low-Sulfur Fuel from Coal" R&D Report No. 53, Interim Report No. 8, Volume II Laboratory Studies Part 3 "Continuous Reactor Studies Using Petroleum Derived Solvent" OCR Contract No. 14-01-0001-496.
5. Wright, C. H., and Severson, D. E., Experimental Evidence for Catalytic Activity in Coal Minerals, PREPRINTS, Division of Fuel Chemistry ACS, 16 No. 2, 68 - 92 (1972)
6. Severson, D. E. Souby, A.M., and Kube, W. R., Laboratory Studies on Solution - Hydrogenation of Lignite. Bureau of Mines Symposium, May 1973 - Grand Forks N.D., Available from Bureau of Mines, Circular #8650
7. Schmid, B. K., The Solvent Refined Coal Process, Symposium on Coal Gasification and Liquefaction, University of Pittsburgh, Pittsburgh, PA, August 6-8, 1974.
8. Harrison, W. B., and Huffman, E. L., Solvent Refining of Coal - A Progress Report, 167th ACS Meeting, Los Angeles, California, March 31 - April 5, 1974.
9. Anderson, R. P., Evolution of Steady State Process Solvent in the Pittsburg & Midway Solvent Refined Coal Process, Abstracts 78th National Meeting, American Institute of Chemical Engineers, Salt Lake City, Utah August 18-21, 1974.

ACKNOWLEDGMENT

This paper is based on work carried out by The Pittsburg & Midway Coal Mining Co. with support from The Office of Coal Research, U.S. Department of the Interior, under OCR Contract No. 14-01-0001-496.