DR-1788

FE-496-T4

R & D REPORT NO. 53

Interim Report No. 7

DEVELOPMENT OF A PROCESS FOR PRODUCING AN ASHLESS, LOW-SULFUR FUEL FROM COAL

Volume II - Laboratory Studies
Part 2 - Continuous Reactor Experiments Using Anthracene Oil Solvent

Period Covered: October 1970-November 1972

Contract E(49-18)-496

Date Published - September 1975

Prepared for

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
WASHINGTON, D.C. 20545

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Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161

Price: Paper Copy $7.60
Microfiche $2.25 (domestic)
$3.75 (foreign)

Printed in the United States of America
USERDA Technical Information Center, Oak Ridge, Tennessee

FE-496-4
Distribution Category UC-90d

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for

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Washington, D.C. 20545

This report is a summary of the work done to develop a continuous laboratory reactor system to study Solvent Refining of Coal. The report includes a description of the evolution of the continuous reactor system and of the analytical methods developed to support the studies done. As a result of this work apparatus and operating procedures were devised which allowed accurate closure of material balances and of most elemental balances involved in the study of this process. Studies were done with a bituminous coal, a lignite coal and a subbituminous coal, each chosen to represent a typical coal within the ranks represented. Pure hydrogen, carbon monoxide, and carbon monoxide-hydrogen mixtures were considered as reducing gases for each coal. Raw anthracene oil and two different lots of partly hydrogenated anthracene oil were used as solvent in these studies. The work was done under OCR Contract 14-01-0001-496 and covers laboratory activities in the period from October 1970 through November 1972.

(The data and conclusions presented in this report are essentially those of the contractor and are not necessarily endorsed by Fossil Energy, Energy Research and Development Administration.)

DEVELOPMENT OF A PROCESS FOR PRODUCING AN ASHLESS, LOW-SULFUR FUEL FROM COAL

OCR Research & Development Report No. 53
Contract No. 14-01-0001-496

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SUMMARY

It is the purpose of this report to present detailed descriptions of the continuous reactors which have been used to study the solvent refining of coal and to discuss the preparative procedures, the operating techniques, and the methods for product workup and evaluation which have been used. It is hoped that these details will facilitate similar studies or provide a sound basis for the beginning of related studies.

Methods have been developed for the preparation of carefully homogenized coal samples and for reducing the coal to well controlled particle size distributions which are necessary for reliable pump performance. This depends mostly on the elimination of the larger particle sizes, which tend to clog the ball checks of the positive displacement pump used to feed slurry into the high pressure reactors. An essential part of the feed system is a feed pot with a properly designed stirrer and a slurry recirculation pump which continually circulates the slurry from the feed pot to the head of the positive displacement pump and which returns the excess back to the feed pot. This arrangement has been shown to deliver a slurry uniform in composition with a precision of about 1%. This is confirmed by periodic analysis of the ash content of the coal slurry.

Methods have been developed for compressing and metering hydrogen or known composition mixtures of carbon monoxide and hydrogen which allow delivery of accurately predetermined quantities of reducing gas for reaction with the coal slurry.

The design of preheaters and reactors for continuously reacting coal slurries with hydrogen or synthesis gas mixtures is presented. This discussion includes methods for maintaining clean gage lines and control lines which operate dependably in contact with a reactor system containing solids, water, and potentially corrosive gases such as hydrogen sulfide and ammonia. Apparatus for collecting reliable samples of product liquids and gases is described. Careful use of this equipment allows closing of material balances better than 99%. Gradual improvement in these operations was experienced in the course of experiments reported here. The discussion of the continuing evolution of these techniques continues into the next report in this series, however most of the essential information for good materials handling is included in this report. 1/

The experiments were done with three different kinds of solvent, all related to anthracene oil. The least reactive solvent used was raw anthracene oil which had been redistilled to eliminate the low boiling fraction and the heavy end. The preferred boiling range of solvent is approximately 90°C to 230°C or 250°C in a vacuum distillation done at less than 3 mm Hg. A more reactive solvent was prepared by mild hydrogenation of the preferred distillation cut of anthracene oil. Raw anthracene oil contains about 5.75% of hydrogen. The hydrogenated anthracene oil first studied contained about 6.20% hydrogen. It is believed that most of this increase in hydrogen was active as transferrable hydrogen

in this case. A second hydrogenated solvent was prepared by mild hydrogenation of anthracene oil. In this case some solvent retained from pilot plant studies was also added, and this material probably contained a significant amount of coal derived oil. The hydrogen content of the second sample of solvent was only increased to about 6.04% and part of this hydrogen was involved in coal derived oil which may have had less hydrogen transfer reactivity.

Three different ranks of coal were studied. These were bituminous coal, represented by a sample of Kentucky No. 9 coal, subbituminous coal, represented by Elkol Coal from Wyoming, and lignite, represented by a sample of Baukol Noonan lignite from North Dakota. A complete analysis including the analysis of the minerals is reported for these samples. The Kentucky coal was studied with each of the three solvents and with hydrogen and carbon monoxide reducing gas mixtures. The lignite was studied with raw anthracene oil and the more hydrogenated anthracene oil solvent. Both hydrogen and carbon monoxide reducing gas mixtures were studied. Studies with the Elkol subbituminous coal used both of the hydrogenated anthracene oil samples and both hydrogen and carbon monoxide mixtures as reducing gas. Variables were temperature, pressure, and retention time. Most experiments were done with feed slurries made with one part of coal to two parts of solvent, although more dilute slurries were occasionally used.

Analytical methods have been developed for following the build up of coal products in the effluent stream from the reactor and which are useful in showing the time needed to establish well equilibrated samples. The most useful of these methods utilizes measurements made upon infrared spectra of the coal solutions. In addition it has been observed that the color of the solution is a sensitive and reproducible observation. Measurements made with a visible range spectrophotometer are helpful in showing the lineout characteristics of a reaction and for establishing the time needed for a fully equilibrated product to be prepared. Studies have shown that the ash minerals settle in the reactor, and that considerable time is required for the rate of exit of mineral from the reactor to match the rate of input to the reactor. This implies the existance of a settled (and somewhat more concentrated) burden of mineral matter in the dissolver reactor. This is a practical lineout problem and also creates sampling problems since the rate of emergence of mineral matter at equilibrium tends to oscillate both above and below the rate at which mineral matter is fed with the slurry. In early work many samples contained a non representative concentration of organic matter due to settling and it was necessary to develop methods of calculation which corrected for this sampling defect. The yield and material balance results presented are based on forced ash balance calculations, and in some cases have also been corrected by forced elemental balances as well.

A method for analysis of product solution has been developed which results in appropriate separations reported on a quantitative basis. The product is collected in a stainless steel flask which is weighed before and after filling with product solution. This flask is then placed on vacuum distillation apparatus to allow the removal of water and low boiling oil fractions.

These products are collected in tared flasks and cold traps to allow quantitative accounting of the materials removed at this stage. The stripped solution is then filtered with procedures which allow accurate weights to be recorded for each of the operations involved. Removal of the more volatile products in the stripping operation allows the use of vacuum filteration procedures with only minor losses of material in this operation. The filtrate is then distilled to finish the recovery of solvent and to obtain samples of the vacuum bottoms for subsequent analysis. The wet filter cake is further analyzed by a pyridine extraction method and the dry insoluble material which results from this procedure forms the basic sample used for determination of the conversion of coal in the reaction. Use of pyridine extraction is justified by a reasonably good match with the soluble material in the anthracene oil solvent used. Less active wash solvents fail to dissolve materials in the wet filter cake which are actually in solution in the imbibed anthracene oil derived solvent. It is felt that such extractions must use solvents appropriate for the process under investigation. The low conversion needed to allow coal to dissolve in heavy aromatic solvent used fails to render the vacuum bottoms fully soluble in benzene, for example.

Because of the difficulty of obtaining accurately balanced ash input-output relations in samples of reasonable size, it has been usual to calculate conversions from the relative concentrations of ash and unreacted organic matter in the insoluble residue from the pyridine extraction. Using a forced ash balance then allows an accurate statement of the weights of ash and of insoluble organic matter resulting in a reaction product. The results of all separations are then distributed on a loss-free basis to calculate the product distribution. These separations are made to rather arbitrary end points in the distillations involved, however cut points have been chosen to bear as close a relation to the plant operation as can be established prior to fully characterized equipment performance data from plant operations. Correction of cut points and end points will be needed to balance solvent requirements in the pilot plant with the distributions obtained and with the operating characteristics of the apparatus used. These experiments are therefore presented on a comparative basis which may relate more or less accurately to plant data depending on actual operating experience.

The yield and product distribution data are reduced to a loss-free basis referred to the MAF coal. This has been done to allow more direct comparisons of the reactivity of the organic matter in coals of different ranks and rather widely varying composition. The disadvantage in this method of reporting is that the lower concentration of carbonaceous material in the low rank coals tends to be neglected. The lower weights of product obtained per ton of wet coal processed at equal MAF conversions tends to be obscured but should not be overlooked in consideration of results.

The coal solution reactions appear to be complex, involving a hydrogen transfer reaction between the solvent and the coal followed by a catalytic or thermal hydrogenation reaction. To replace hydrogen in the solvent at a satisfactory rate appears to depend on the presence of mineral phases in the coal capable of some catalytic activity. The high volatile bituminous coals which contain appreciable amounts of pyrite are apparently well catalyzed naturally for hydrogenation reactions. These coals are therefore amenable to processing given the reaction time and hydrogen necessary to satisfy the demands for oxygen and sulfur removal and to cap the bonds broken as the coal molecules are decomposed. Many of the lignites investigated contain enough sodium in combination with minor amounts of iron to facilitate reaction of carbon monoxide and water to generate reactive hydrogen. This has been shown to dissolve lignite and to hydrogenate the solvent well in batch autoclave studies operated at pressures of about 4000 psig peak pressure. This reaction has been less effective in the continuous unit operated at 1000 psig and appears more satisfactory as the pressure increases. It is inferred that the reaction is pressure dependent as a consequence of reaction of the hydrogen formed with the organic matter present. Efficient use of this reaction therefore requires use of higher operating pressures, and probably the reaction should be run at higher pressures than were generally used in the experiments reported here. The high volatile bituminous coals containing an appreciable amount of iron also cause the water shift reaction to proceed in the coal dissolver. It is therefore practical to use mixtures of hydrogen and carbon monoxide in processing of properly chosen samples of lignite or bituminous coals. The sample of sub-bituminous coal investigated in this work appears to contain little reactive mineral matter useful for catalyzing rehydrogenation of the solvent or initial decomposition products of the coal. The organic matter can however be dissolved by suitable reactive solvents. The characteristics of the mineral matter in a coal therefore bear on the kind of processing scheme which may be needed for processing of a given coal. If the level of natural catalytic activity is not sufficient it will be necessary to supplement by means of an auxilliary catalytic step operating on the solvent or to add catalysis to the reactor system. This is a situation which could be encountered in coal of any rank, although limited experience suggests a more frequent occurrance of natural catalysis in bituminous and lignite coals. No attempt at a general survey of coals was planned as a part of the continuous reactor program and these opinions rely on correlation with the survey conducted with the batch autoclave. Much additional work remains before the comparative utility of pure hydrogen and of mixtures of hydrogen and carbon monoxide can be defined. It is expected that this will be studied in the Fort Lewis pilot plant and that the reaction will be extensively used in Project Lignite. 2/

The initial decomposition reaction appears to be comparatively rapid, particularly when supported by a reactive solvent. The reactions which rehydrogenate the solvent and which cause further conversion of the coal appear to be slower, and to be governed more by catalytic hydrogenation reactions. The initial decomposition causes rapid elimination of both oxygen and sulfur from the coal depending on the composition of the solvent and on the operating temperature in the preheater and dissolver.

Subsequent reactions continue at a slower rate but contribute to additional oxygen and sulfur removal. Nitrogen is not significantly attacked in the mild hydrogenation needed to produce filterable solutions. Higher temperature favors rapid removal of oxygen and sulfur and rapid production of some solvent range material. This is not effectively hydrogenated at the low pressures and low activity of catalyst available in studies of the kind reported here. Use of compromise conditions allows a suitable balance between these reactions, however, there are indications that a temperature profile from high initial conditions to low final conditions of temperature may facilitate both the cracking and the hydrogenation aspects of the reaction. Such an effect would most logically result from improvement in the initial decomposition step resulting from improved solvent compositions.

This in turn raises the question of the composition and inherent reactivity of the solvent in equilibrium with the process. An attempt to generate an equilibrium solvent by recycling solution with added coal is reported at the conclusion of this report. It is clear that the reaction can be driven further to completion in this way and that a much more hydrogenated solvent results. This procedure resulted in more sulfur removal and even appeared to result in enhanced ammonia formation. These studies were continued with petroleum derived starting solvent and are reported separately in a report to follow.

One objective of the experimental program was the development of appropriate analytical methods for following reactor operation and for evaluation of products. Many useful techniques have been evolved which have been discussed by example in appropriate places in the detailed discussion of experiments. These efforts have resulted in fairly detailed characterization of apparatus performance as well as in definition of sampling problems relative to obtaining valid sample sets. As is often the case, preparation of valid samples is more difficult than the analysis of the samples presented. Results commonly depend more on the skill of the sampler than on the skill of the analyst. There are however a few points of analytical technique which are unsettled. This is particularly true for the analysis of nitrogen in both input coals and the heavy products made in the process. It is difficult to select concordant results using either the Kjeldahl or the Dumas methods which will account for the nitrogen in these experiments. These problems have been discussed briefly in this report, and at greater length in a separate report prepared for the Environmental Protection Agency. It appears that the results of Kjeldahl analysis are influenced by the degree of reduction experienced for some of the heavy products. Amine type functions appear to be formed which result in better nitrogen recovery from products than from feed coal in some cases. Results from the Dumas method are often higher but involve more scatter. Elemental analysis results for carbon, hydrogen, and sulfur can be used to close elemental balances convincingly. This is not true for nitrogen, an observation which throws doubt on the accuracy of the commonly used methods for analysis. The validity of the samples and the weight relationships appears established by elemental balances for carbon, hydrogen, and sulfur. 3/

The results for each experiment are reported in a summary table presented in Appendix A of this report. An effort has been made to present these data in a uniform format and to correct deficiencies in the reporting of early samples which may have appeared in the monthly progress reports. Each experiment has also been discussed briefly in an attempt to add pertinent information. Selection of data for discussion and emphasis of particular points has been necessary to reduce the review to a manageable size. It is hoped that a balanced summary has resulted.

II Introduction

The results of batch autoclave studies in support of the Solvent Refined Coal Pilot Plant have recently been reported. 2/ This report discussed the need to continue laboratory studies using continuous laboratory scale equipment in order to develop more refined data for use in planning the experiments to be run in the Pilot Plant. One motivation for this program was the need to know more about the effect of partial pressures of carbon monoxide and hydrogen in reactions using synthesis gas or carbon monoxide plus water as reducing agent. A continuous unit also could match the retention time better than an autoclave which required a lot of time for heating and cooling. It was considered that the autoclave studies had outlined many reactions which should be followed in greater detail before the pilot plant was operated with such materials. Finally there was a need to know more about the reactivity of any solvent-coal-reducing gas system as the solvent was reclaimed and reused from pass to pass.

Another concern was the continuing need to develop better methods for the analysis of materials and for maintaining good control of reactions in the continuous plant. Operation of the continuous laboratory unit provided an opportunity to sample and analyze materials made under close control and to find by practical trials the points which needed to be sampled. In addition some of the analytical methods needed attention to improve the quality of the data from the Pilot Plant. About one third of the runs made with anthracene oil were used to develop operating procedures, sampling methods, analytical methods, or methods for the management of feed and product samples which were needed to arrive at a more sophisticated level of operation. These procedures will probably be used to guide the lineout of the Pilot Plant and will provide criteria for the attainment of steady state operation of that plant.

At the time these studies were started anthracene oil appeared to be the most reactive solvent available. No problem was anticipated in obtaining the quantity needed to start up the Pilot Plant. The review of work done at the Process Development Plant had established the general trend of data to be expected as the plant moved towards steady state operation. Thus data for anthracene oil startup in continuous equipment were better developed than data for other useable solvents. In these cases only a few autoclave runs could be called upon to indicate probable trends. This led to a preliminary decision to concentrate effort on anthracene oil as the startup solvent in the Pilot Plant. Later the availability of anthracene oil was questioned and the continuous laboratory unit was used to study the detailed chemistry for a startup using decanted oil or mixtures of decanted oil and anthracene oil. Because of the mass of data resulting from these programs it is expedient to make separate reports covering these subjects. This report will be limited to the studies done with anthracene oil.

This report will include a detailed discussion of apparatus and operating procedures and will introduce the studies done on reactor lineout and feed composition problems. Most of the working curves which were needed to define the behavior of coal solutions under different operating conditions were developed first with anthracene oil as the solvent. Except for extension and refinement of these to cope with other solvents the same curves are applied throughout work with the continuous reactor.

Much of the work with anthracene oil was exploratory and could be considered as an extension of some preliminary study in the autoclave or in the Process Development Plant. The range of exploration was somewhat more restricted than had been the case in the autoclave program. This reflects the study of a more carefully selected list of materials and the elimination of some of the cases which were thought to be less attractive for additional study. As studies become more detailed the effort required for critical evaluation of results increases. The number of cases which can be fully treated must become smaller. Thus as the time for operation of the Pilot Plant is approached studies have become restricted to detailed modeling of the startup with the coal and the solvent to be used. During the studies with anthracene oil time remained for some exploratory work. As a result some of the experiments may be at a tangent and may require that the Pilot Plant be modified if such leads are to be followed up. In any case it was felt that such studies could be justified by the basic analytical information which was developed. It is helpful to know the range over which working curves can be extended and to have at least seen samples which are qualitatively different from the typical products.

The studies with anthracene oil involve 49 continuous reaction studies. In the first dozen or so trials the experiments were of short duration and were mostly used to test equipment and develop preliminary operating procedures in the laboratory. Two separate reactor systems were used. The initial apparatus conducted the preheater-dissolver reaction in a single tube which was 1 inch O.D. X 11/16 inch I.D. and 7 feet long. Experiments done in this reactor are identified by the code letters CL. Later a second reactor system with a tubular preheater and a 450 cc dissolver vessel was substituted. Experiments in this reactor system are identified by the code letters CU. All of the experiments are numbered in sequence. Thus the tubular reactor was used from experiments CL 1 through CL 27. The CU reactor was used from CU 28 through CU 49 in the experimental program run with anthracene oil. Both units were slightly modified from time to time in order to improve performance. In describing apparatus an effort will be made to describe the best equipment and to indicate the nature of improvements which were needed to obtain good performance.

Installation of the CU unit was started in August 1970 and the first trial reactions were run in October 1970. This report overlaps the last few months of the autoclave report but is restricted to the work on the continuous unit. The last experiment with anthracene oil in the continuous unit was completed in November of 1972. Reevaluation of some of the experimental products has been continued whenever improvement in analytical technique or the need for better comparative data seemed to justify such added work. It is hoped that much of the discussion and reporting can be brought up to current levels of sophistication since retained samples are available from many of the experiments.

II

Emphasis in the laboratory program shifted in response to several circumstances. At one point efforts were directed to design of a new Process Development Unit to be installed at the University of North Dakota. The Pilot Plant which was built at Ft. Lewis, Washington, was not then slated for construction. During this time more emphasis was placed on work with lignite. After construction of the Pilot Plant was authorized the design and operation of the new Process Development Unit was assumed by the Chemical Engineering Department of the University of North Dakota. In this period laboratory work was done in close cooperation with the University of North Dakota group. This resulted in some work with lignite in the continuous unit and these experiments were continued until it was clear that the lignite work would be assumed at North Dakota. More recently the work at our laboratory has been concentrated on solvent problems and has been done with Kentucky No. 9 coal.

The continuous unit has a number of characteristics which required that new techniques be developed. First: the quantity of coal and solvent used in an experiment was greater. This required that procedures for preparing larger amounts of coal and solvent with good uniformity be developed. Second: experiments were continued for many hours. This required that operators and chemists be assigned to maintain the operation of the unit for several shifts and that procedures be worked out for passing along the information needed for continuity. An effort was made to do the laboratory work needed for reactor control as an experiment was in progress. Work up of samples was done after the experimental reaction was finished and the unit operators normally doubled as laboratory technicians during this phase of the experiment. Thus experiments normally required a period of intense effort during the operation of the continuous reactor and a period of routine work during the separation and analysis of product materials. It is evident that a complete workup and analysis of the products from an experiment consumes more time and labor than operation of the continuous unit. It is pointless to make more sample material than can be fully evaluated. A solution to this problem appears to be to conduct experiments in blocks of limited size and to use the same labor to operate the unit and to do the laboratory work needed for evaluation of the results. It will be found that each run contains a block of related experiments which are coded by letters.

The time needed to start up the continuous unit and to establish steady state compositions in the dissolver is a large part of the time needed for an experiment. It is not economical to start up the unit for a single sample. When an operating condition is changed more time must be allowed for the effect of the change to line out. Thus collection of a sample must be delayed until a suitable time has elapsed. There is therefore a minimum time schedule which must be satisfied if valid samples are to be obtained. The first experiments and the first laboratory studies were devoted to finding the time required for reactor lineout in order to establish suitable schedules. Naturally the first experiments were unsophisticated in this regard, and as experience has accumulated the lineout operation has been done with increasing attention to detail. Much of the technique now available has evolved from these inspections for uniformity of product as the reactor was lined out from start up or following a condition change.

II-A Definitions of Terms Used

MFPRS - Middle fraction of process reclaim solvent.

SRCP - Solvent refined coal product.

1/LHSV - Reciprocal/Liquid hourly space velocity. (Space Time)

GHSV - Gas hourly space velocity.

MFRAO - Middle fraction of raw anthracene oil.

PDU - Process development unit.

SHMFRAO - Stripped hydrogenated middle fraction of raw anthracene oil.

$\overline{\text{IR}}$ - The ratio of absorbance at 2920 wave numbers divided by the absorbance at 3040 wave numbers. Measured in infrared spectra to characterize coal solutions and solvents used in dissolving coal. See IVC4.

Solution Blackness - Determination of visible absorbance. This value is an empirical measure of the coal which is in solution.

Coal - A heterogeneous mixture of organic compounds from decayed vegetation that has been subjected to excessive pressures, restricted atmospheres over a prolonged time.

Coke - The char product resulting after pyrolysis of coal resulting in removal of gases and liquids from coal. Consists of converted carbonaceous material, or insoluble organic matter, and mineral matter (unignited ash) from coal.

Stripped Coal Solution - This solution is obtained by vacuum distilling the reaction product to the initial boiling point of the feed solvent. This material simulates the coal solution coming from the gas-liquid separator after disengaging volatile products. Materials boiling below 100°C. at 3 mm Hg should have been removed from the product to prepare a stripped coal solution.

Filtered Coal Solution - This is the liquid product obtained by filtering the stripped coal solution.

Aromatic Liquid - Aromatic hydrocarbons in solvent or derived from the reaction with coal. Substituted benzenes, indenes, naphthalenes, acenaphthalenes, phenanthrenes, anthracenes. The term includes phenols, anilines, quinolenes, and pyridenes.

Hydroaromatic Liquid - Typical compounds are reaction products of aromatic liquids and hydrogen :indanes, dihydronaphthalenes, tetralin, dihydrophenanthrenes, tetrahydrophenanthrene, dihyroquinoline. Normally this term implies a partly hydrogenated aromatic compound.

Saturates - Typical compounds are cyclohexane, decalin, and aliphatic hydrocarbons from ring openings or side chain removals.

Light Liquids (Cold Trap Oil) - During vacuum stripping of the reaction product, liquids are collected in a cold trap cooled with dry ice and acetone. When the material in the cold trap is thawed, a two phase product is obtained. The upper phase is a hydrocarbon mixture consisting of materials with an atmospheric pressure boiling range from room temperature to roughly 175°C. This product has an approximate density of 0.80. This material is a mixture of aliphatic and naphthenic hydrocarbons and is essentially a stabilized naphtha. The term light liquids applies to the oil phase. The lower phase is mostly water.

Water Phases - Water is collected in the cold trap along with cold trap oil. In addition water is collected with cut 1 oil. These are combined to obtain a consolidated value. This simulates the total yield of water from the coal process. The water originates as water fed with the coal or produced by reaction of hydrogen with oxygen containing functions in the coal. Water phases may contain variable amounts of ammonia, carbonate, sulfide, phenol, or other water soluble organic compounds available for extraction.

Solvent Cut No. 1 - This is the distillate obtained during the vacuum stripping of the reaction product. This is collected from room temperature to 100°C. at a nominal pressure of 3 mm. The oil fraction of this cut has a boiling range from about 175°C. to about 288°C. at atmospheric pressure. The oil has a density of 0.9 to 1.0. In the continuous plant this cut will be the source of material used to wash the filter cake. Any excess of this oil may be used as solvent or disposed of as product.

Solvent Cut No. 2 - After the stripped coal solution has been filtered, the filtrate is vacuum distilled to 230°C. at a nominal pressure of 3 mm. Usually this distillation cut had the boiling range 100°C. to 230°C in the vacuum distillation or 288°C. to about 425°C. at atmospheric pressure. When derived from anthracene oil this material has a density of 1.1. This solvent fraction is the principal component of the recycle solvent in the continuous plant. Cut points may be adjusted to obtain break even quantity of solvent if necessary in the plant.

Heavy Oil - Any distillate boiling from 230°C. to the end point (but not higher than 325°C.) at 3 mm nominal pressure which is recovered during the vacuum distillation of the filtered coal solution. This may have a theoretical atmospheric distillation range from 425°C. to about 560°C. with a density of about 1.2. This oil product is very viscous and is a solid at room temperature. It is probable that this material will not be isolated in the continuous plant. The cut 2 end point may be raised to utilize part of this material as solvent if necessary.

Total Reclaim Solvent - This is the summation of the light liquids, Cut No. 1 oil, Cut No. 2 oil, and heavy oil. For a successful process total reclaim solvent must exceed the amount of solvent used to prepare feed slurry. To obtain optimum reactivity the recycle solvent should be centered on Cut no. 2 oil with any additions required being obtained from the upper fractions of the Cut no. 1 oil and the lower fractions of the heavy oil.

Excess Solvent - Total liquid product less the weight of solvent used in the preparation of a coal solution.

Vacuum Bottoms - The residue from the vacuum distillation of the filtered coal solution. This product is actually the high molecular weight fraction of the coal that is dissolved in the process.

Solvent Refined Coal Product (SRCP)- This term is applied to fuels to be prepared from coal by solvent refining. It is intended to include vacuum bottoms and blends of vacuum bottoms with any excess of oil not needed to maintain the recycle solvent balance.

Wet Filter Cake - When the stripped coal solution is filtered, the insoluble materials present are retained on the filter as a cake of solids containing about 40% to 60% imbibed coal solution.

Washed Filter Cake - A wet filter cake may be washed with a suitable process solvent derived cut of oil to displace the imbibed coal solution. The wash solvent may originate as solvent cut 1 oil. As the insoluble materials will imbibe the wash solvent the washed filter cake must be passed through a heated dryer to reclaim the wash oil.

Pyridine Insolubles - In order to determine the amount of coal converted, the filter cake must be washed free of imbibed coal solution or any residual wash oil if the cake has been washed. A weighed portion of the filter cake is digested with hot pyridine, filtered and washed with hot pyridine until the washings come through colorless, then rinsed sequentially with benzene then acetone to remove the pyridine. The washed material is then dried and weighed. The residue consists of unconverted carbonaceous material (insoluble organic matter) and mineral matter (unignited ash) from the feed coal.

Percentage Coal Converted - The amount of coal converted (i.e. changed to gaseous, liquid, and solid products) in the process is determined from pyridine insolubles data. This result can be obtained in two different ways. The percentage of pyridine insolubles on a loss-free basis referred to feed coal is subtracted from 100. The result is the percentage of the feed coal converted. The alternative method for estimating the amount of coal converted was based on the increased concentration of ash observed in the pyridine-washed insolubles. This is called the Ash Enrichment Method for determining the percentage coal converted. The result is calculated as follows:

$$100\ (\%\ \text{Ash in Feed Coal}) = (100-X)\ (\%\ \text{Ash in Pyridine Insolubles})$$

Where X is the amount of feed coal converted

(Both of these methods are subject to some degree of error.) Since different coals may have different moisture and ash contents it is often desirable to reduce conversion to the moisture ash free basis.

$$\%\ \text{MAF Coal Converted} = \frac{\left\{[100 - (\%M + \%A)] - (\%PI - \%A)\right\}}{100 - (\%M + \%A)}$$

Where MAF is moisture-ash free (the organic fraction of the coal) and

%M = percentage moisture in the feed coal
%A = percentage ash in the feed coal
%PI = percentage of pyridine insolubles (feed coal basis)

III Reactions for Bituminous Coal - Hydrogen & Anthracene Oil

It is now possible to discuss several characteristic reactions which may be observed in this coal solution process based on observations reported for studies made with the batch autoclave and on observations made in the course of continuous reactor studies to be presented in this report. In addition it is possible to present estimates of the operating conditions at which different aspects of the complex of reactions may become dominant. In order to simplify the discussion these reactions have been placed on a diagram which shows the relationships which are thought to exist. The terms which are used in the reaction diagram will be defined and the characteristics of reactions which comprise various parts of the diagram will also be discussed.

The discussion which is to be presented is limited to a qualitative summary of experience with the coal solution process for bituminous coal using anthracene oil as solvent and hydrogen as the reducing gas. This system is the most studied and will serve as a basis for comparison throughout studies with other coals and other reducing gases or solvents. It has not been possible to develop a quantitative discussion in this detail because analytical techniques are not available to separate all of the materials of interest as independent results.

It is possible to identify the probable functions by watching data trends and/or relying on experience with several kinds of reactors to develop an intuition about the progress of the reaction.

Observations will be discussed briefly in order to justify the reaction diagram to be presented. The terms to be used in the reaction diagram will be defined and finally a discussion of the characteristics of the component reactions will be given.

III-A Observations

Observations which are available have been presented in a report detailing autoclave studies for the solution of coal in anthracene oil. 2/ Some of the most important observations will be repeated.

Additional work with the continuous reactor has extended the detailed observations of solvent behavior and the effect of reaction variables considerably. It is difficult to introduce all of the material needed to elucidate the mechanisms in a summary of reasonable length, particularly since some of the evidence is at best somewhat ambiguous. The reaction diagram is presented as a considered opinion and may be subjected to change.

When a high volatile bituminous coal is heated in a sealed autoclave with anthracene oil and hydrogen a reaction is observed at about 200-300°C which results in a great increase in the viscosity of the solution which is forming. As heating is continued to about 350°C the viscosity peaks then is rapidly reduced to values near that of the original solvent. During the gel or viscous period the temperature of the solution in the autoclave may remain constant or even fall slightly although the wall of the autoclave continues to heat up at a uniform rate. This is evidently an endothermic reaction which is part of the process. As heating is continued the viscosity falls to a minimum value which is only slightly greater than the original solvent value.

Heating for extended periods of time or at higher temperatures may result in an increase in the viscosity of the solution. This is evidence for eventual repolymerization of the materials in solution upon exposure to excessive heat.

As the reactor is heated the pressure of the hydrogen increases until the point is reached where the reaction consumes hydrogen fast enough to overcome the effect of heating the gas. At this point the viscous phase breaks up, hydrogen is consumed rapidly, and other gaseous products appear rapidly. This results in a series of rapid pressure drops and pressure rises. Following this hydrogen is consumed smoothly and the rate of hydrogen consumption gradually is reduced. The evolution of other gaseous products will overbalance the hydrogen consumption rate and pressure will stabilize and then increase slowly. The timing of this phase of the reaction depends on the final operating temperature since gas evolution increases rapidly as the temperature is increased. In the autoclave and continuous reactor studies which were terminated at low final temperatures the MAF conversion of the coal was low. As the final operating temperature was increased, the MAF conversion also increased. With higher final temperatures the MAF conversion was lowered. This is the result of repolymerization of coal derived material or solvent under the influence of excessive heat. One consequence of this effect is an optimum time for heating the reaction products and this time becomes shorter as the temperature is increased. As the partial pressure of hydrogen in contact with the solution is increased the exposure to heat can be prolonged without the repolymerization becoming a factor. Thermal attack on the coal can be achieved before reversion of products to polymeric material. The removal of sulfur and oxygen from the coal depends on exposure to heat.

In autoclave studies the amount of reactive hydrogen in the solvent was shown to have an important influence on the yield of liquid products and on the MAF conversion. Reactive solvent would dissolve coal with reasonable success even under conditions which did not work well with a less hydrogenated solvent. In studies with the continuous reactor ample evidence has accumulated to show that most of the initial solution reaction is accomplished by interaction of the coal and the solvent. This requires transfer of hydrogen from the solvent to the coal, particularly if the conversion is to be driven to high MAF yields. The solvent is reduced in hydrogen and is recovered in a dehydrogenated state. Prolonged exposure at moderate temperatures may facilitate rehydrogenation of the solvent and the coal derived liquids, and solvent reclaimed. Such reactions are promoted by use of higher partial pressures of hydrogen.

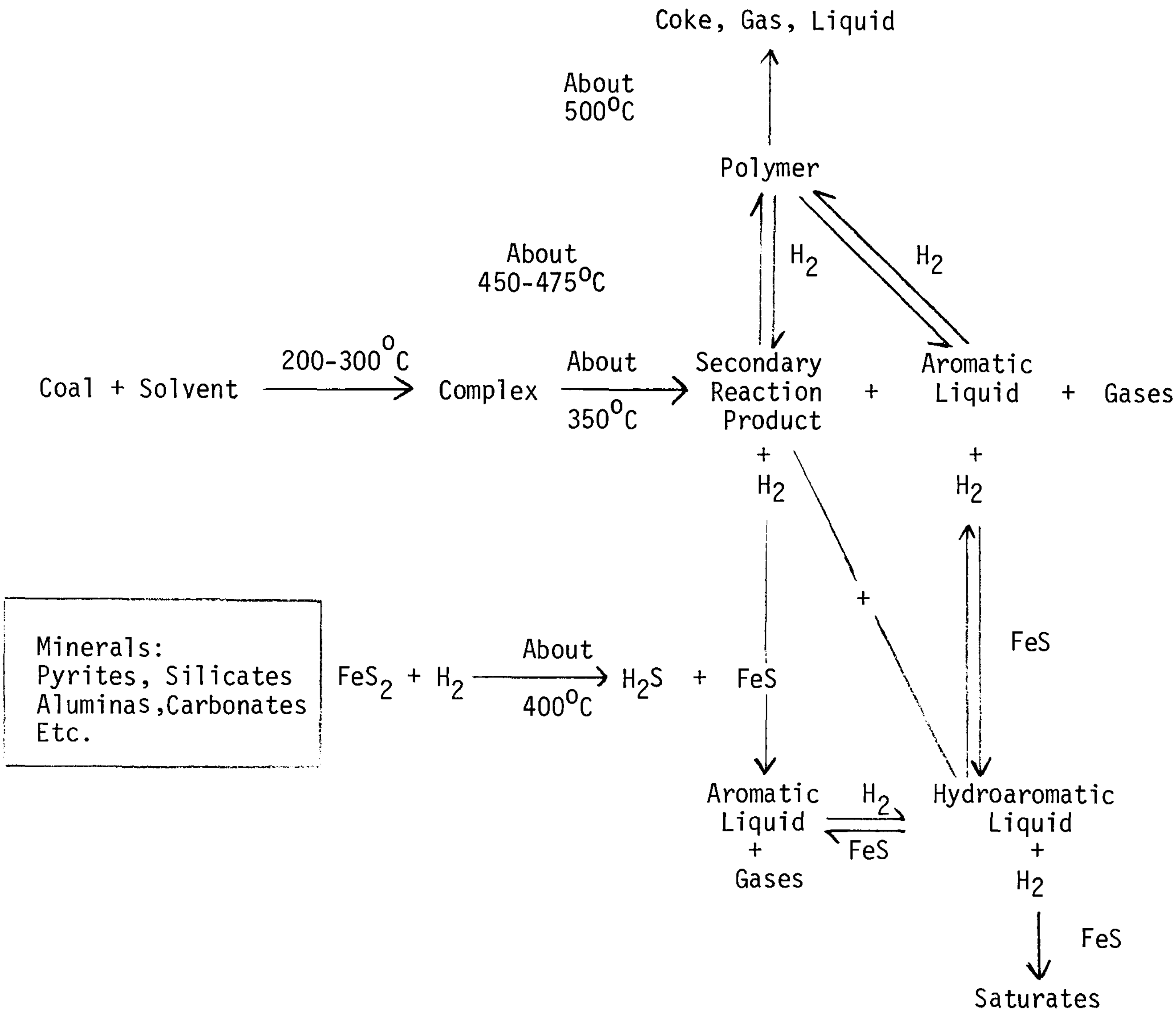
During the solution of coal,water, hydrogen sulfide, carbon dioxide, carbon monoxide, methane, ethane, propane, normal butane, and isobutane are observed in the gases from the reactor. Traces of ammonia may be observed. Water is recovered as a liquid which contains dissolved ammonium carbonate and ammonium sulfide. A light oil product is made which contains a high concentration of saturated aliphatic and naphtenic hydrocarbons. Higher boiling fractions tend to become more aromatic in character and contain variable amount of partially hydrogenated aromatic compounds such as tetralin for example.

III-A

The mineral phases present contain pyrite and at normal reaction temperatures the pyrite may be decomposed to form ferrous sulfide. Other minerals may be dehydrated at these temperatures and may or may not regain such water as the reaction products are recovered and cooled. The cooled products are full of water but this is well dispersed and droplets and mineral may not be in close contact to allow rehydration. Ferrous sulfide is thought to be active as a catalyst for the rehydrogenation of the solvent and its presence at reasonable concentrations in the reaction products from bituminous coal is the apparent cause for the smooth rehydrogenation of solvent in this case. It is not clear that other mineral phases normally present remain inert, it is possible that cracking reactions may be facilitated by the presence of certain clay, silicate or alumina containing minerals.

III-B Reaction Diagram

Estimated temperatures are given at which the indicated reaction becomes rapid enough to significantly influence the course of the reaction.



III-C Definition of Terms on Reaction Diagram

Coal For this discussion the coal is limited to a bituminous coal which contains a reasonable amount of pyrite as a part of the mineral phase.

Solvent A mixture of aromatic and hydroaromatic hydrocarbons with an approximate boiling range of $100^{\circ}C$ to about $230^{\circ}C$ at less than 3 mm Hg.

Complex Primary reaction product obtained when coal and solvent interact. This product is a gel obtained by heating coal and solvent in the range of $200^{\circ}C$ to $300^{\circ}C$. The gel is decomposed in the vicinity of $350^{\circ}C$ to product secondary reaction product, liquid and gaseous products.

Secondary Reaction Product Non volatile coal product insoluble in pyridine, and not distilled under vacuum at the end point of the distillation which is normally $250^{\circ}C$ to $270^{\circ}C$ maximum as limited by the decomposition of residue in the distillation flask.

Aromatic Liquid Aromatic hydrocarbons in solvent or derived from reaction of coal. These materials are typically substituted benzenes, indenes, naphthalenes, phenanthrenes and so on. Heterocyclic material may also be present such as pyridines or quinolines and so on.

Hydroaromatic Liquid Reaction products from reduction of aromatic liquids by hydrogen to produce partly hydrogenated products. Typical compounds are indanes, dihydronaphthalene, tetrahydronaphthalene, dihydrophenanthrene, tetrahydrophenanthrene, dihydroquinoline and so on.

Saturates Fully hydrogenated hydrocarbons such as cyclohexane, decalin, & aliphatic hydrocarbons derived from ring opening or side chain removal reactions, for example.

Polymer Condensation products from interaction of solvent and coal derived material or interaction of coal derived materials to form higher molecular weight less soluble and less reactive products. As molecular weight increases this material may be deposited as insoluble material and the MAF conversion declines as a consequence.

Coke Exposure of any of the carbonaceous materials in this process to excessive heat results first in polymer formation then carbonization of the material to form carbon cross linked insoluble material. Coke will not redissolve on exposure to solvent and continued heating results in a structure which becomes more graphitic in nature. The intermediate stage polymer may redissolve if exposed to solvent under proper conditions.

Gas Low boiling hydrocarbons, low molecular weight compounds which are normally in the vapor state or recovered as fixed gases in the reaction products. Methane, ethane, propane, normal butane, isobutane, hydrogen sulfide, carbon dioxide, carbon monoxide, ammonia, and water comprise the normal gaseous products.

III-D Characteristics of Various Reactions Shown on Diagram

A. $$\text{Coal} + \text{Solvent} \xrightarrow[200\text{-}300^{\circ}\text{C}]{\text{heat}} \text{Complex}$$

The rate of complex formation becomes very rapid as temperature is increased. At higher temperatures, the complex concentration reaches a maximum and declines rapidly as all of the coal is swelled and the formation of secondary reaction product removes complex from the system. This reaction involves solvent hydrogen transfer and molecular rearrangements of hydroaromatic functions already present in the coal. Gas evolution may be observed. If the reaction is stopped at this point the solvent appears to be bound to the coal in a complex which will not allow recovery of the solvent by extraction or distillation.

B. $$\text{Complex} \xrightarrow[\text{about } 350^{\circ}\text{C}]{\text{heat}} \text{Secondary Reaction Products} + \text{Aromatic Liquid} + \text{Gas}$$

At reactor temperatures the complex exists as a gel or a high viscosity fluid. It is decomposed on heating to form a dispersed soluble product plus some liquid which is probably aromatic. Water, hydrogen sulfide, carbon dioxide, carbon monoxide, and hydrocarbon gases are formed as this reaction takes place. Hydrogen transfer from the solvent and perhaps some reaction with gaseous hydrogen appear to be required for this step in the reaction. This reaction also is not thought to be reversible.

C. $$\text{Secondary Reaction Product} + H_2 \xrightarrow[\text{about } 400^{\circ}\text{C}]{\text{FeS}} \text{Aromatic Liquid} + \text{Gas}$$

Reduction of the secondary reaction products to liquid products in the solvent range produces first an aromatic liquid. The composition of the solvent and the products derived from this reaction depends on the partial pressure of hydrogen, the time allowed, and the temperature used. In general higher pressures and longer times favor increased hydrogen in the solvent while higher temperatures tend to lower the hydrogen in the liquid phase and to increase conversion to gas. In a single pass the anthracene oil type solvent is hydrogenated to about 6.1% hydrogen in the temperature range up to 450°C and to slightly higher values at about 425°C. This requires that enough reaction time be allowed for an equilibrium or a steady state to develop. Solvents containing more than this amount of hydrogen tend to lose hydrogen to this concentration and solvents which contain less tend to gain hydrogen to this concentration. In multiple pass experiments the observation of transferable hydrogen is obscured by the accumulation of oil which contains an increased concentration of saturated radicals associated with the aromatic rings. Presumably the hydrogen transfer functions remain mixed with these new species as solvent reactivity is not seriously reduced.

Hydrogen is required to allow the formation of gaseous products and the production of water, hydrogen sulfide, and the small amount of ammonia which is formed. Hydrogen may come from the solvent by transfer, or from the organic matter of the coal. In order to maintain the composition of the solvent constant and obtain liquid products from the coal, hydrogen must be taken from molecular form and used to reduce solvent and coal. It is assumed that this is facilitated by the iron in the coal and this seems to be mainly converted to ferrous sulfide in the mineral phases isolated at the end of the reaction.

D. $\text{Aromatic Liquid} + H_2 \xrightleftharpoons[400^\circ C \text{ to } 500^\circ C]{\text{FeS}} \text{Hydroaromatic Liquid}$

This appears to be a reversable system with the ultimate balance between the aromatic and the hydroaromatic species depending on the partial pressure of hydrogen and the operating temperature. In addition the hydroaromatic species concentration may be reduced by hydrogen transfer. The balance between aromatic and hydroaromatic species may therefore be influenced by the concentration of species which can accept reactive hydrogen from the hydroaromatic material present. Thus when the concentration of secondary reaction product is is high, the system will tend to build up a higher concentration of aromatic species. As time is allowed for reaction to consume secondary reaction product the rate at which hydrogenation can replenish hydroaromatic material brings this concentration up to the level allowed by the distribution of aromatic species present and capable of accepting this kind of hydrogen. Reaction time is therefore also a factor.

At high temperatures the transfer reactions are driven far toward completion leaving the solvent highly aromatic. The solvent will be subjected to cracking and gasification reactions if the temperature is high. At more moderate temperatures the aromatic species will tend to revert to hydroaromatic forms and these reactions are probably more frequent than direct hydrogenation of the larger more complex secondary reaction products. Thus the agent which moves hydrogen from the catalytic surface to the coal will most frequently be the hydroaromatic species since it is the more mobile material. This function is indicated by a line drawn to connect the hydroaromatic liquid with the secondary reaction product. It is also noted that the reclaim solvent which reacts with coal in the initial complex forming step must be rich enough in hydroaromatic material for this step to progress to a favorable level of completion.

E. $\text{Hydroaromatic Liquid} + H_2 \xrightarrow{\text{FeS}} \text{Saturates}$

The low molecular weight liquids formed in the coal solution reaction tend to become saturated. Apparently these are derived from the solvent by thermal cracking, which opens rings to produce aliphatic hydrocarbons, and by hydrogenation of the single ring compounds, which result from progressive ring opening reactions. The tendency for the low molecular weight hydrocarbons to become saturated may be the result of greater mobility of these molecules. Such compounds are chemically stable compared to the hydronaphthalenes for example and will have less tendency to revert to aromatic structures.

Thus once formed, this kind of material will tend to remain in the saturated condition.

F. $\text{Secondary Reaction Product} \xrightleftharpoons[\text{about } 450^{o}\text{C} - 475^{o}\text{C}]{\text{heat}} \text{Polymer}$

In the presence of higher temperatures the coal derived material tends to revert to more insoluble polymeric material. This may involve reaction with solvent range molecules as well. The temperature at which this reaction becomes a factor depends on the amount of hydrogen transfer capacity available for quenching free radicals formed by thermal bond rupture. At temperatures which produce frequent cracking reactions this quenching will use up the reagent available and the radicals will tend to initiate polymerization. The polymer first formed may be low molecular weight material and this may progressively increase in molecular weight until it is no longer soluble. Thermal bond rupture is necessary to remove sulfur, oxygen, and nitrogen from the coal and to reduce the molecular weight of the material derived from the coal. The source for the terminating agent which quenches the free radicals formed may be hydroaromatic hydrogen for the most part. Thus the preheater can be heated to comparatively high temperatures with a properly hydrogenated solvent but will plug with a poorly hydrogenated solvent under the same conditions. In some cases plugs formed in the preheater have been observed to dissolve spontaneously if the heat is cut off promptly and the heat in the sand bath used to heat the preheater is not excessive. On this basis the polymer formation reaction is reversible at least for the initial steps.

G. $\text{Polymer} \xrightarrow[\text{about } 500^{o}\text{C}]{\text{heat}} \text{Coke + Liquid + Gas}$

When temperatures are too high and retention time at such temperatures is too long the materials first polymerize then progressively decompose to form coke. Coke formation is regarded as an irreversible process, at least the effort required to return such material to the liquid condition would be excessive. Coke formation may be regarded as a disproportionation of the compounds involved. Carbon rich material is deposited as a solid while the hydrogen rich components are released as liquids and gaseous products. The temperature which may be used depends on the amount of readily available hydrogen and the retention time used. Thus high temperatures may be applied for short times or mild temperatures for extended times without polymer formation becoming a consideration. At higher temperatures however polymer formation may result in flow stoppage and lead to irreversible coke formation. In this system the temperature which can be used safely is not a fixed value but depends on flow rates and solvent composition.

IV Experimental

In this section of the report a detailed description of the reactors, the techniques used for coal and solvent preparation, and the general operating procedures for experimental runs will be reported. Following this a discussion of reactor control and lineout will be presented. All experimental data will be presented in appendixes. Data for special discussions will be abstracted and arranged in appropriate groupings.

IV-A Continuous Reactor Designs

The continuous reactors used in these experiments may be considered to consist of several subsystems connected together. These subsystems are the gas compression and metering system, the slurry pumping and metering system, the reaction section, and the sample letdown and collection system. The gas metering system has not been modified after its original installation and remains the same for both the CL and the CU reactor configurations. The slurry pumping and metering system has been modified several times. It will accordingly be discussed in detail in order to explain the nature of the improvements made. The main difference in the CL and the CU reactors is the result of changing from one preheater-dissolver configuration to another. These differences will also be discussed in detail. The sample letdown and collection system has remained the same for all of the experiments completed after the first few trial runs. A block diagram is presented below which shows the relationship of the subunits in the continuous reactor. When samples are not taken, the flow through the unit is directed to slop and product gas is vented.

IV-A-1 Gas Compression and Metering Subsystem

The gas compression and metering subsystem is designed to take gas from a standard gas storage bottle, compress and store a reserve of gas at operating pressure, and meter the gas from storage to the reactor system. In this system provision is made for calibrating the delivery of gas at operating pressure and for recording the delivery pressure and operation (reactor) pressure. The flow is adjusted to the desired value by maintaining a controlled differential pressure across a metering valve.

The system was originally designed with two rotameters to allow mixing of pure hydrogen and pure carbon monoxide from separate storage cylinders. It was found that it is difficult to reproduce such mixtures with the needed precision by this method. Therefore, when mixtures of gases are used it has been preferable to buy mixed gases from commercial sources. Such mixtures have been found to be more reproducible than continuously mixed gases.

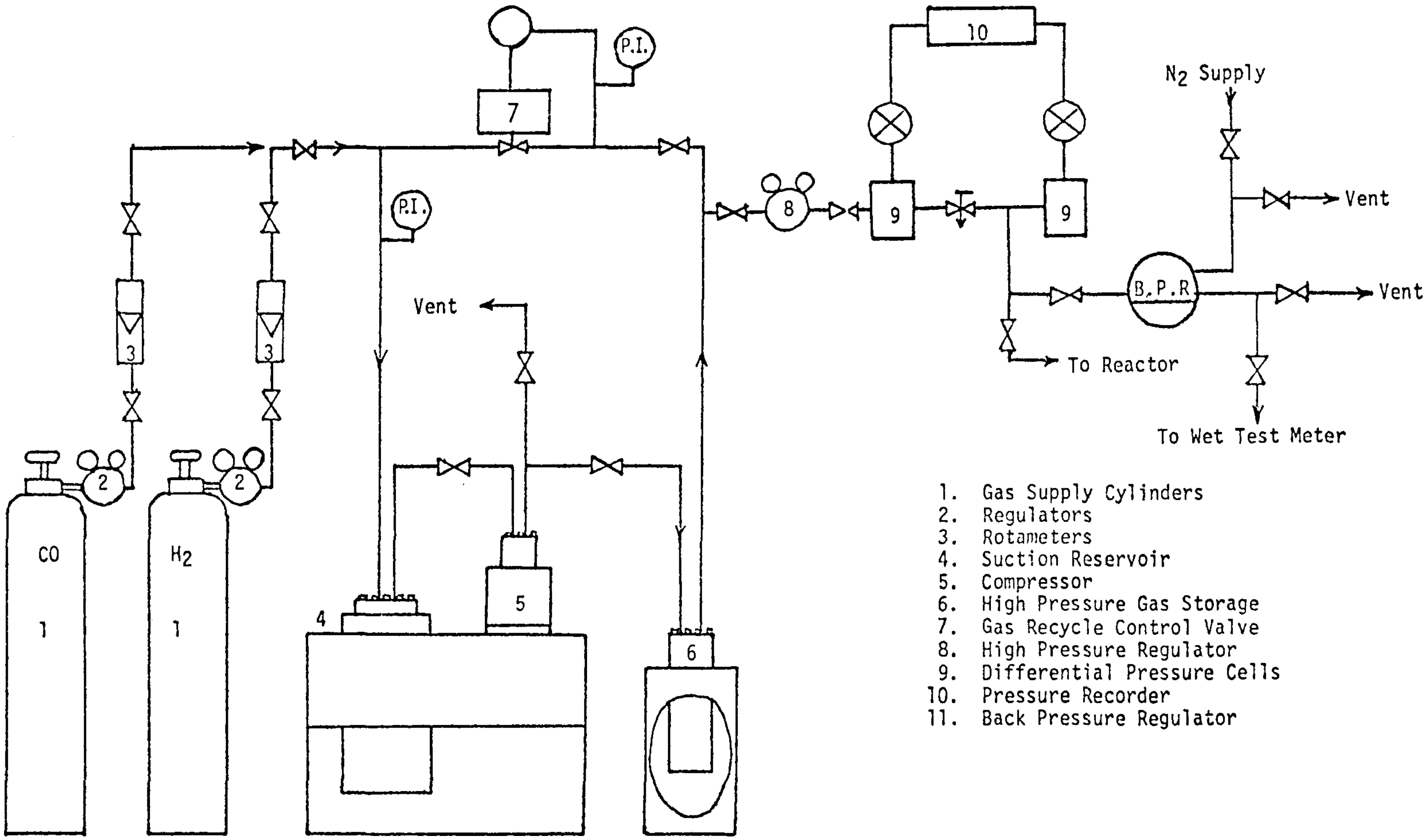
IV-A-1

A drawing of the gas compression and metering system is presented as Figure 1. Gas has been purchased in commercial size 1A cylinders. These are attached to the input fitting of the subsystem and deliver gas to the suction of the compressor through a high pressure regulator and a high pressure rotameter, Brooks type 1410-01D1B1A operable to 1900 psig at 100°F. The suction of the compressor (Aminco type 46-425SP) operates in the 800 to 1000 psig range therefore gas cannot be completely pumped from a cylinder by this apparatus.

The suction reservoir for the compressor is a one gallon Autoclave Engineers autoclave vessel. Gas in this vessel is maintained at the regulated input pressure set by the regulator on the supply cylinder. Normally this is in the 800 to 1000 psig range. Gas is taken from the suction reservoir and the pressure is boosted by means of an air operated compressor. The compressed gas is stored in a one liter autoclave at 2500 to 3000 psig. Delivery of gas to the reactor system is regulated to a specific pressure necessary to maintain the desired flow rate through a metering valve. Gas from the storage vessel can be recycled back to the suction reservoir of the compressor and this pressure and flow is controlled by an air operated Annin valve, type 5060. The pressure maintained in the one liter storage vessel is regulated by the setting of the pneumatic controller for the Annin valve.

The flow of gas to the reactor system is metered by means of a high pressure needle valve. A differential pressure is maintained across this valve in order to establish a controlled flow rate. The pressure on the low pressure side of the valve is set by the operating pressure maintained in the reactor system. The pressure of the high pressure side of the metering valve is controlled by the setting of the Marotta pressure regulator type RH-292GA-35-2222 which is in the line between the high pressure gas storage vessel and the metering valve. A Foxboro Consitrol model 5420 F-E pressure recorder is used to obtain a continuous record of the pressure on each side of the metering valve. This is a pneumatic instrument which operates through differential pressure cells installed in the gas line just before and just after the metering valve. The differential pressure cells are Foxboro type 11 GM Force Balance Pneumatic Pressure Transmitter units. In operation a pen in the recorder is actuated by the signal from each differential pressure cell and a chart is marked with the pressure on each side of the metering valve. The system also contains Bourden type indicating gages which allow separate checks on the performance of the pressure recording system.

In order to calibrate the flow through the metering valve, the flow to the reactor is shut off and the gas flow is diverted to an exit line through a back pressure regulator set at the operating pressure to be used in the reactor system. The flow of gas out of this line is then measured with a wet test meter using the usual differential pressure across the metering valve. Minor adjustments in the volume delivered per unit time may be made by making small changes in the differential pressure across the metering valve. Larger adjustments may require resetting the metering valve as well. Calibration to the desired gas delivery rate therefore requires that a valve setting and an operating pressure differential be established which causes the desired flow of gas through the metering valve while delivering this at the desired system pressure.



1. Gas Supply Cylinders
2. Regulators
3. Rotameters
4. Suction Reservoir
5. Compressor
6. High Pressure Gas Storage
7. Gas Recycle Control Valve
8. High Pressure Regulator
9. Differential Pressure Cells
10. Pressure Recorder
11. Back Pressure Regulator

Figure 1 Gas Compression & Metering Subsystem

IV-A-1

Figure 1 is a block diagram which indicates the direction of gas flow and the function of all of the important components of the gas compression and metering system. The system contains back pressure regulators which are adjusted by setting a gas pressure in the head of a pressure dome. Nitrogen supply lines are provided to pressurize these units allowing readjustment when necessary, and nitrogen supply lines are provided to allow purging of reducing gas from the reactor or gas compression system when necessary. In addition air supply lines for operation of the pressure sensing and pressure controlling devices are needed. These have been omitted from the diagram in order to avoid clutter. Gas from the gas compression and metering subsystem is mixed with feed slurry to complete the feed to the reaction section.

IV-A-2 Slurry Pumping and Metering Subsection

The apparatus in this subsection is designed to maintain a uniform slurry of coal in solvent, to pump this slurry into the reactor at a uniform rate, and to measure the pumping rate accurately. In addition a supply of solvent is maintained for use in start up and shut down operations.

Reliable performance of the equipment in this section has been found to be essential to the preparation of satisfactory coal solutions. Failure of one of the pumps in this section is the most common cause for subsequent difficulty in other sections of the apparatus. When flow is stopped in the preheater or the dissolver, repolymerization or even coke formation in the high temperature vessels will commonly result. When temperatures are mild settling of minerals may be observed. Either condition may result in a permanent plug in the reactor. This section of the apparatus has been modified several times in an effort to improve the uniformity of the feed and the reliability of performance of the equipment.

The coal slurry is mixed by weight separately and then is transferred to the slurry feed vessel. This vessel is a stainless steel beaker of about 8 liters capacity and is fitted with a stirrer which is operated continuously to keep the coal suspended in the solvent. In the original design, slurry was recirculated by means of a centrifugal pump. In order to allow the feed vessel to be weighed the slurry was drawn out through a tube located near the bottom of the beaker at one side, and this connection was made with a short length of flexible rubber tubing. The solvent tends to swell such tubing, particularly when the slurry becomes heated by repeated circulation through the centrifugal pump. This arrangement was altered to allow the slurry to be siphoned up through a dip tube which reached close to the bottom of the beaker but which allowed room for the scale to move. This tube was made of stainless steel tubing rigid enough to stand securely in place when connected to the feed line to the centrifugal pump. The return stream from the slurry recycle loop was made to run down the dip tube in order to reduce the tendency for bubbles of air to be injected below the surface of the slurry in the feed pot. The centrifugal pump was used throughout the work with anthracene oil but has been replaced by a gear pump. A properly trimmed gear pump appears to be the most reliable slurry recirculation pump. In this service the center pin should be made of tungsten carbide and the idler should be made of ceramic material. These changes will adapt a standard gear pump and produce satisfactory performance. No doubt special pumps designed for abrasive service should be specified.

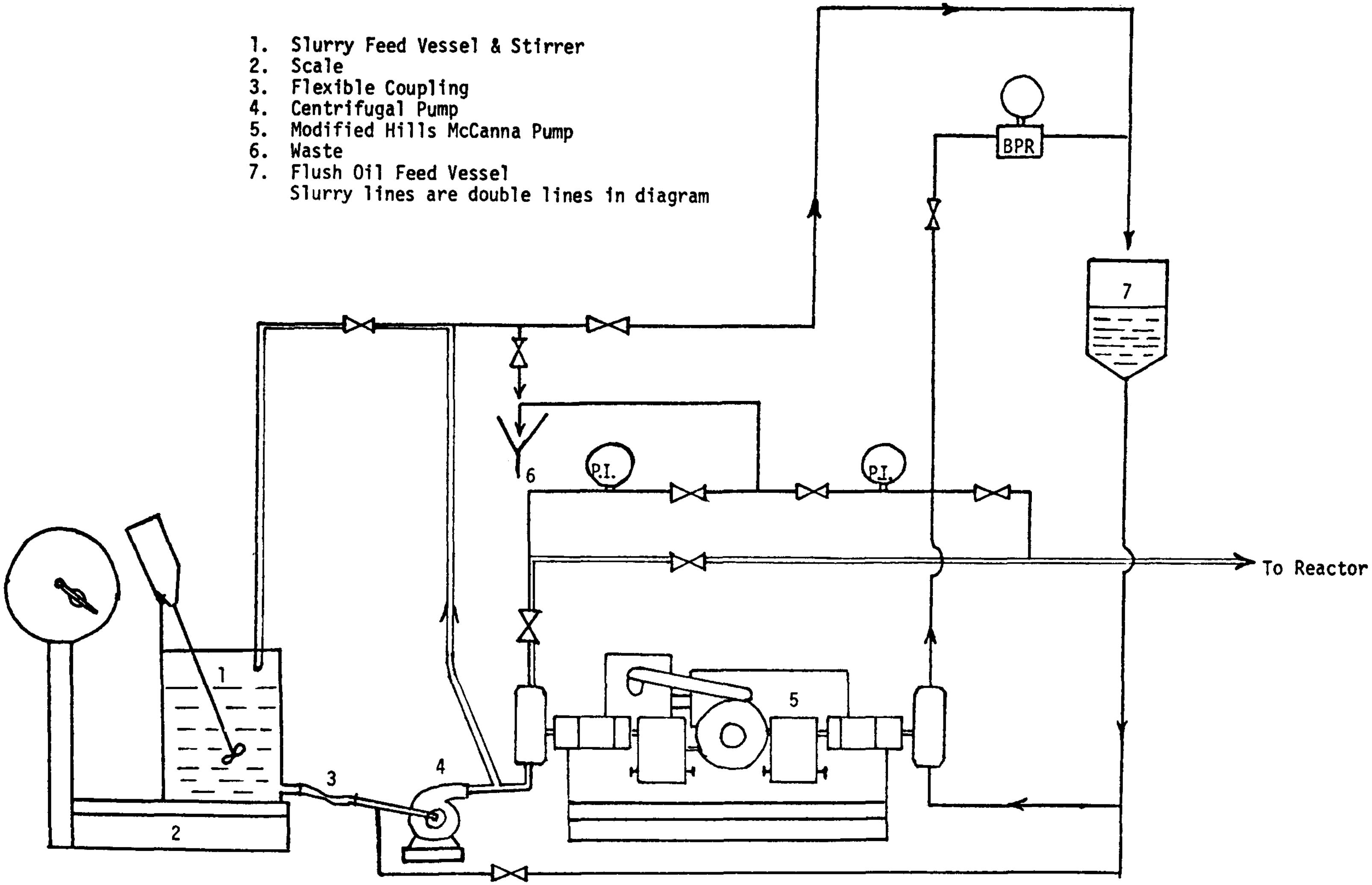


Figure 2A Slurry Pumping and Metering Subsystem, First Configuration

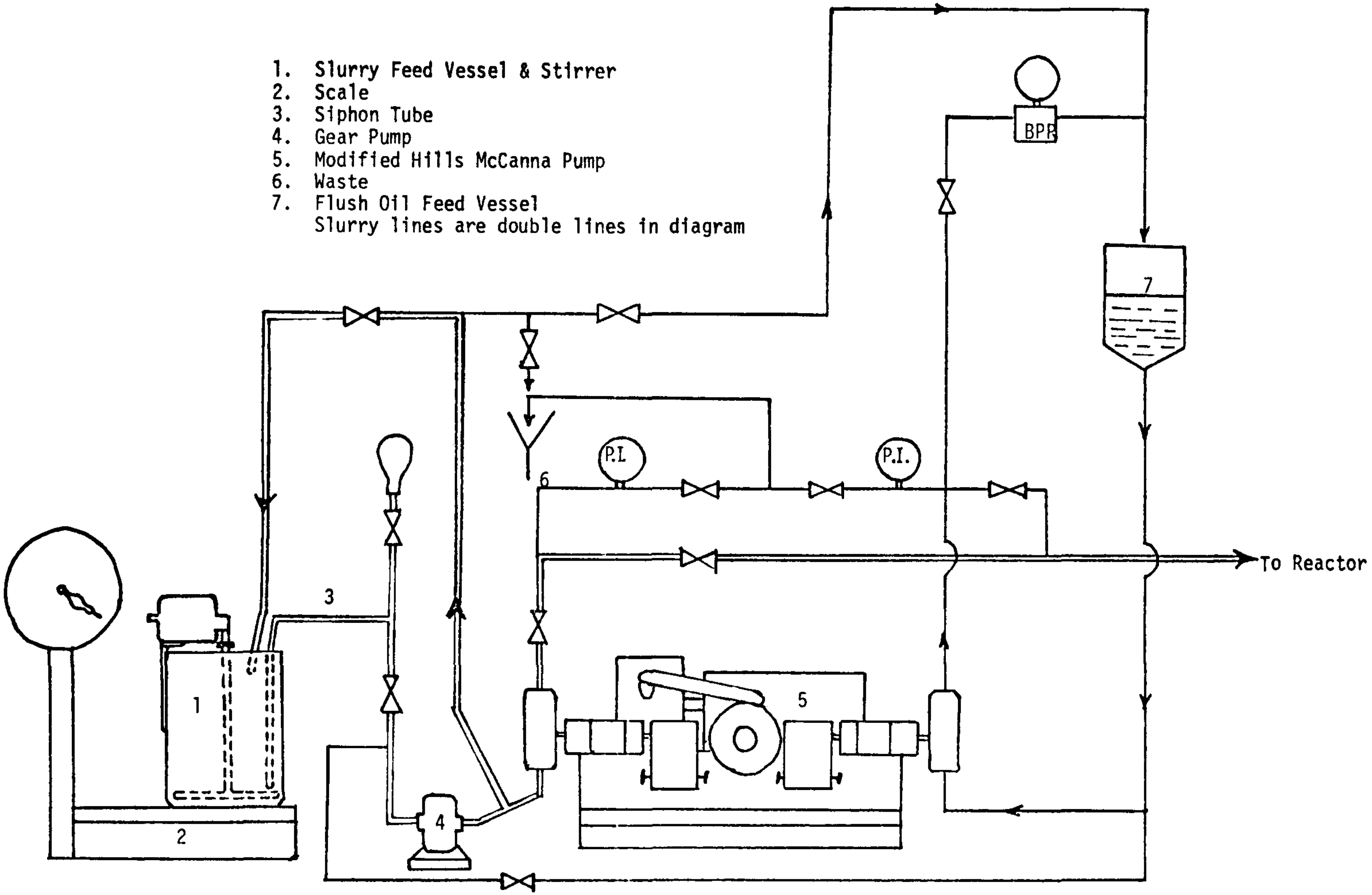


Figure 2B Slurry Pumping & Metering Subsystem, Final Configuration

IV-A-2

The slurry in the recirculating loop provides feed for the suction of the high pressure feed pump. The first experiments were completed using a Milton Roy pump. At the tenth experiment this pump was replaced with a Hills McCanna pump in order to substitute a drive unit with two pump heads. One pump head is used to pump flush oil when necessary. The slurry pump head on this unit was the standard Hills McCanna pump head. The internal volume of this pump head was too large for pumping slow feed rates of coal slurry, and coal would settle out in the pump head. The slurry pump head was then changed to adapt an Autoclave Engineers Speed Ranger pump head for the eleventh experiment. This combination of pump heads has been used for all subsequent experiments.

The slurry pumping and metering system thus contains a feed pot for coal slurry and a feed pot for flush oil. The piping is designed to allow pumping of flush oil with either of the pump heads and for pumping coal slurry only with the Speed Ranger head. This was done to allow flushing solids out of the slurry head when necessary. In normal operations the start up with flush solvent will be done with the Speed Ranger head and the flush oil will be recirculated by the centrifugal pump. At the start of an experiment the flow of flush oil is cut off and the feed slurry is substituted for the flush oil. The auxiliary pump head is normally kept working against a back pressure regulator in order to maintain the pump in condition to allow rapid switching from the pump head feeding slurry to the auxiliary feeding only flush oil.

Block diagrams of the slurry pumping and metering subsystem are presented as Figure 2A and 2B. The first configuration shows the installation using rubber tubing and the centrifugal pump in the recirculation loop. Figure 2B shows the preferred apparatus using the dip tube and gear pump.

IV-A-3 Reactors and Sampling Subsection

The reactors which are used have two functions. During the initial heating of the coal-solvent slurry most of the coal is dissolved by a hydrogen transfer reaction. This is usually completed in the preheater section of the reactor. Following this the solution must be kept hot and in contact with hydrogen for some time to hydrogenate the initial reaction product. In the first reactor system, the CL Unit, both reactions were done in a single tube. In the modified system, the CU Unit, the preheater was a separate coil of high pressure tubing heated in a sand bath and the dissolver was a 450 ml autoclave vessel. This modification allows operation of the preheater and dissolver at different temperatures and better matches the capability of the pilot plant.

Figure 3 is a block diagram of the dissolver and sampling subsection showing the configuration of the CL Unit. In this apparatus the feed slurry from the Slurry Pumping and Metering Subsystem was delivered to the bottom of the reactor through a length of high pressure tubing. This entered the reactor through a fitting in the side of a high pressure cross fitting. Hydrogen entered through a T in the feed slurry line near the reactor. The bottom entry was used for insertion of thermocouples which were in a thermowell.

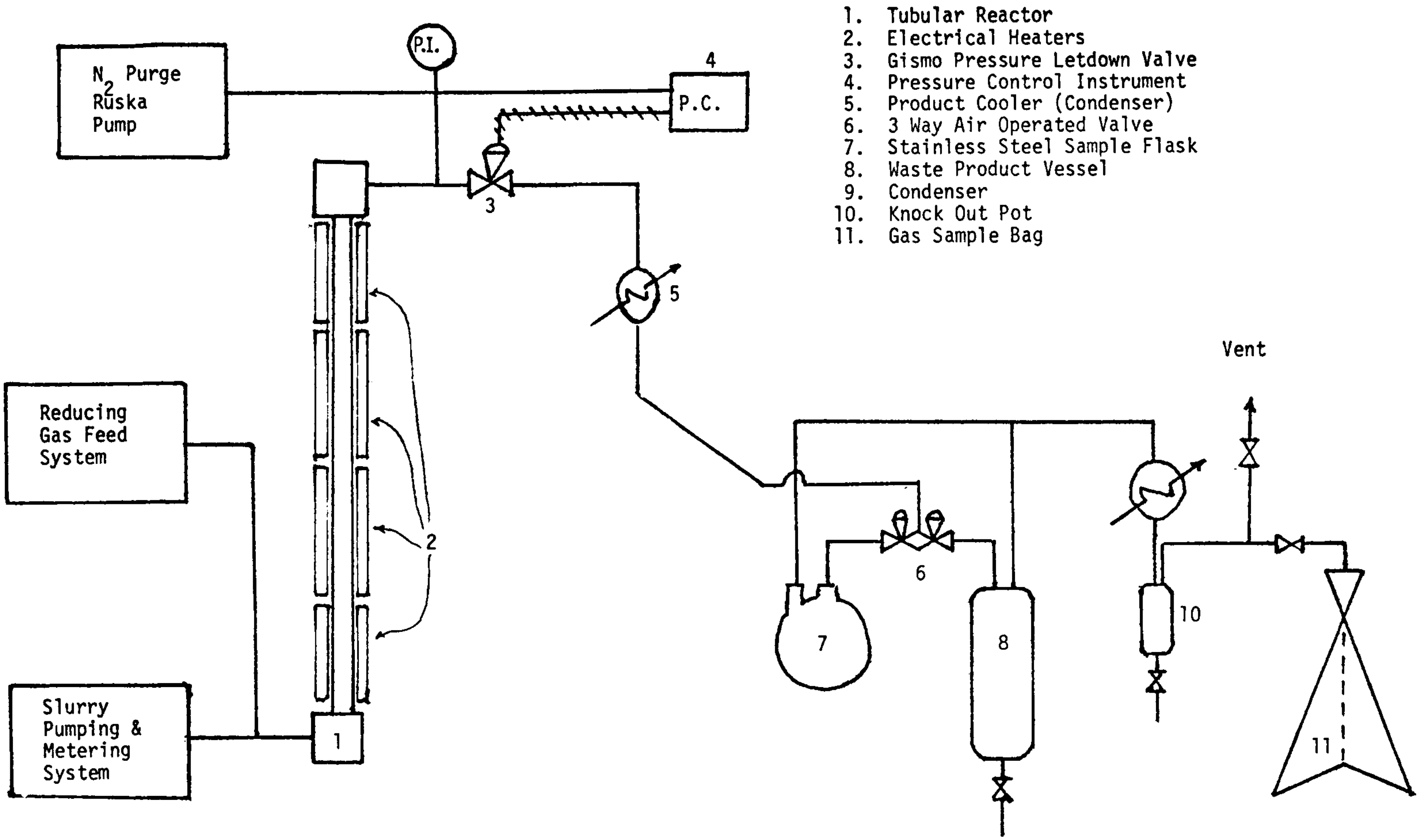


Figure 3 Diagram of the CL Unit

The top fitting in the cross was connected to the bottom of the one inch OD pressure tube used as a reactor by means of a standard high pressure cone and thread joint. The CL unit reactor was a 7 foot length of tubing. The top was closed by a second high pressure cross fitting. The top entry was used for insertion of a thermowell and thermocouples. The bottom was connected to the reactor tube by the cone and thread fitting. The reaction product was taken out of the port on the side of the upper cross. The fourth port on both the top and the bottom of the reactor cross fittings was closed by a rupture disc. The rupture disc fittings vented into suitable lines for collecting the liquid and gas which might leave the reactor upon opening of a rupture disc.

The reactor tube was heated by means of four pairs of electrical heaters. These were flat heaters which were rolled in a semicircular shape to fit the outer surface of the tube. These were clamped to the tube in pairs which enclosed a section of tube completely. Two thermocouples entered the reactor through the top thermowell fitting, and two thermocouples entered through the bottom thermowell fitting. One thermocouple was thus provided to measure the temperature in the center of each of the four pairs of heaters used. Each of the pairs of heaters was driven by a separate electrical circuit under the control of a variac. Additional thermocouples were placed between the heaters and the outer wall of the reactor tube. These allowed measurement of the outer wall temperature. One of these was used as the input signal for a temperature indicator controller for the lower heater bank. The second heater bank was controlled manually by variac adjustment. The third heater bank was controlled by a temperature indicator controller similar to the lower heater bank. The fourth heater bank was controlled manually by variac adjustment.

The product was removed from the system by allowing the gas and liquid to flow out through a Fisher Governor "Gismo" control valve. This device is an air operated valve which balances the operating pressure in the reactor against a bellows containing a controlled air pressure. The bellows moves the valve stem in and out to open or close the orifice in the pressure let down valve. All product made must flow through this orifice. Both the valve stem and the orifice in this valve are made from tungsten carbide in order to prevent rapid wear as the ash minerals flow through the pressure let down orifice.

The sample flows down from the pressure control valve and is directed to the collection flask by means of an air operated two way valve. If a sample is not being collected the product is directed to a slop receiver instead. The sample collection flask can be a standard glass laboratory distillation flask with a suitable standard taper joint. Generally samples have been collected in stainless steel flasks which are less likely to be broken accidentally. These are connected to the system by means of stainless steel standard taper fittings (Sample flasks are 3 liter stainless steel flasks with two necks each being a 29/42 metal standard taper joint). The gas which is disengaged from the liquid is allowed to flow out of the flask through a water cooled condenser. Condensate is collected and the gas is vented or collected in a rubberized fabric gas collection bag as desired. The standard taper joints are sealed with vacuum grease and are secured by clamps which are tightened with thumbscrews to prevent pressure surges from causing the joints to leak. Generally it is necessary to collect liquid and gas samples for different lengths of time in order to allow the air to be flushed out of the flask. The gas sample is taken for a times interval during the latter part of the liquid sampling period.

In order to prevent diffusion of vapors into the pressure gages the lines from the reactor to the gages are flushed with nitrogen. The nitrogen is pumped into the system by means of a Ruska pump at a constant rate. Thus pressure for the reactor is measured at this point by measuring the pressure in the nitrogen purge line which is at system pressure. This pressure is controlled by the setting of the Fisher Governor "Gismo" control valve.

Figure 4 is a block diagram which shows the configuration of the CU reactor system. This is substantially the same system as the CL unit except that the tubular reactor has been replaced by a more complex reactor assembly. The CU unit contains a preheater in a sand bath and a separate dissolver vessel which is heated separately. The preheater was constructed by coiling a suitable length of high pressure tubing and mounting it in the center of the sand bath heating vessel. The temperature of the sand bath is measured by means of thermocouples in the sand and between the heaters and the outer wall of the sand bath. The temperature of the fluid in the preheater coil can be estimated by means of thermocouples in blocks at the top of the coil. The effluent fluid from the preheater coil flows through a transfer line to the bottom of the dissolver vessel.

The dissolver vessel is a stainless steel bolted closure pressure vessel. It is cylindrical in shape, with an internal volume of 450 cubic centimeters. The internal volume is a cylinder 1½ inches in diameter and 15.1 inches deep with a hemispherical end 3/4 inches in radius in addition. The upper end of the cylinder is 1 3/4 inches in diameter for a distance of 1/2 inches and tapers down to the 1 1/2 inch diameter of the vessel. A thermocouple well is attached to the cover of the vessel and extends 12 inches below the cover into the cavity. Connections are provided at the bottom of the vessel and in the center of the cover for standard cone and thread high pressure fittings. In addition a hole is drilled through the body of the vessel near the top to allow the attachment of a rupture disc assembly. The outer diameter of the vessel is 2 9/16 inches which results in a wall thickness of 17/32 inches over most of the length of the vessel. The enlargement of the hole near the top is all within the flange provided for the bolted closure. The pressure vessel is heated by means of electrical heaters wound around the outside and covered by insulation. Product solution was delivered to a two liter stirred autoclave through an electrically heated transfer line. Product could be stored in this vessel or removed continuously through a dip tube which reached the bottom of the autoclave. It was

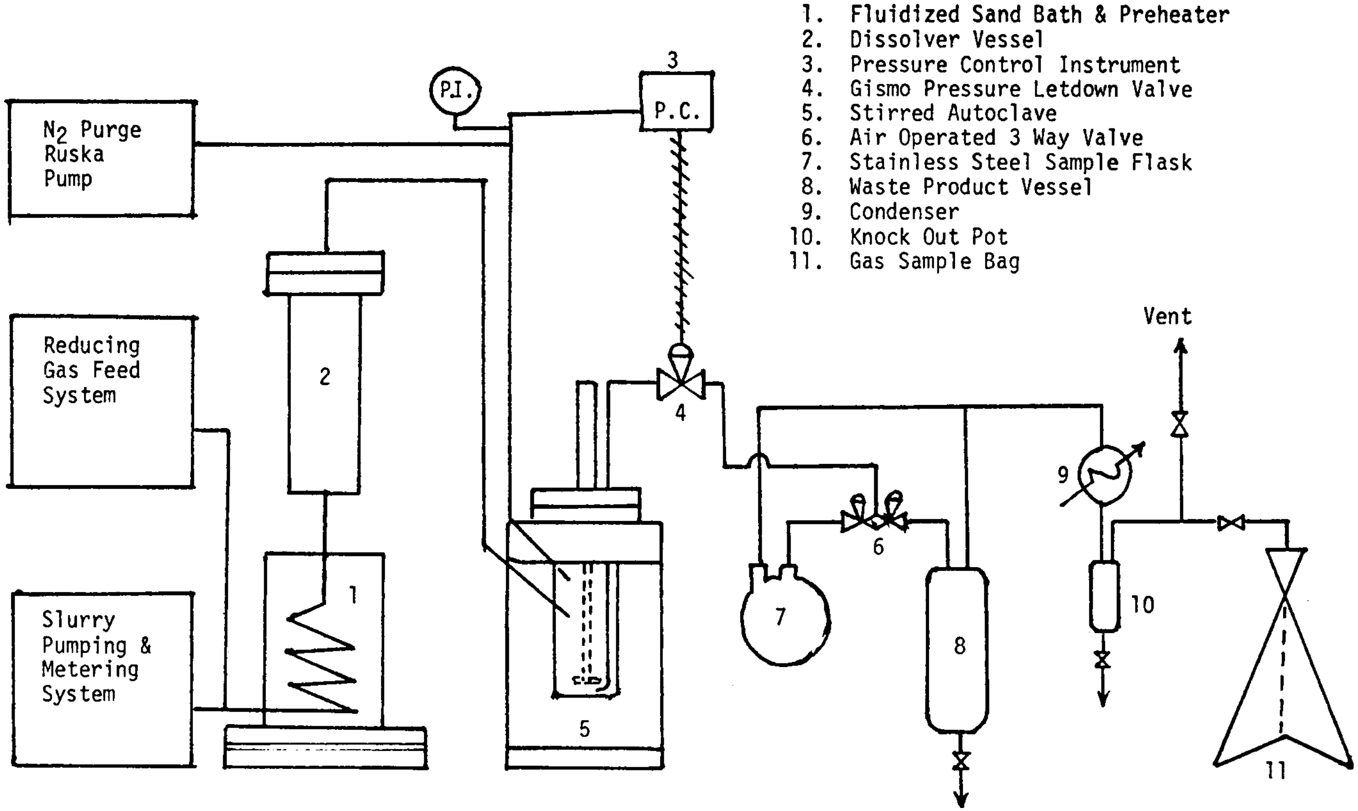

1. Fluidized Sand Bath & Preheater
2. Dissolver Vessel
3. Pressure Control Instrument
4. Gismo Pressure Letdown Valve
5. Stirred Autoclave
6. Air Operated 3 Way Valve
7. Stainless Steel Sample Flask
8. Waste Product Vessel
9. Condenser
10. Knock Out Pot
11. Gas Sample Bag

Figure 4 Diagram of the CU Unit

found that this latter mode of operation was normally the more convenient, therefore the main function of the autoclave was to provide a surge capacity which smoothed out pressure fluctuations.

The preheater tube used for the anthracene oil work was normally an 18 foot length of 7/64 ID pressure tubing. When allowance was made for all of the void space in the dissolver vessel and the volume of the thermowell the combined volume of the preheater and the dissolver was estimated to be 485 cubic centimeters. The volume of the preheater is about 33 cubic centimeters when constructed of 7/64 ID tubing. This has been the standard assembly for all of the anthracene oil experiments. A liquid space velocity of 1.0 requires the pumping of about 450 cc of cold slurry. This slurry has a nominal density of 1.15 grams /cc. By convention a liquid space velocity of 1.0 has been taken as a pumping rate of 520 grams of slurry per hour. It should be understood that the liquid expands when heated and that gas bubbles due to injected hydrogen or synthesis gas also displace the liquid. A further complication results from the absorption of the reducing gas by solution and reaction, and from the formation of various gaseous products. The "true retention time" is therefore less than the reciprocal of the LHSV by the factor which relates the relative volume of the gaseous and liquid phases actually present in the reactor. Unfortunately this is difficult to estimate with precision. As a result of this difficulty, it has been our practice to use a conventionalized value of 520 grams of slurry per hour as an LHSV of 1.0. The internal volume of the long tube used in the CL configuration also matches the internal volume of the bolted closure vessel used in the CU configuration with good accuracy. The same weight of slurry is therefore required to fill either vessel. The conventional LHSV is based on dissolver volume. For preheater studies the LHSV is based on preheater volume only.

The liquid plus the gas flows from the dissolver vessel through a transfer line to the two liter autoclave. Normally the liquid which accumulates will be removed from this vessel through a dip tube which reaches to the bottom of the autoclave. The retention of liquid in this vessel is therefore limited to the time required for liquid to drain to the bottom and be collected by the dip tube. This vessel is operated at a temperature well below reaction temperature and does not contribute reaction time for this reason. The nitrogen from the gage purge also enters this vessel and the gas sample therefore contains a fraction of nitrogen which is metered into the system as a consequence of the purge operation. In general the autoclave vessel provides a surge capacity which smooths out pressure surges resulting from the injection of feed slurry and in the case of a plug in the pressure let-down valve the system pressure increases gradually. This allows time for corrective action before the safety rupture discs in the system opens. The system can be operated by collecting samples in the two liter autoclave for timed intervals then drawing them off all at once, but this mode of operation has not been found to be advantageous.

In the usual mode of operation the Fisher Governor "Gismo" valve is set at the desired system pressure and all liquid and gas from the autoclave goes from the pressure of the reaction system to atmospheric pressure as the sample flows through this valve. Both liquid and gas from the reactor system flow down and enter either the slop vessel or the sample collection flask depending on the setting of an air operated valve. The slop vessel is used during lineout of the reactor or for intervals between samples. The sample vessel is a three liter two necked stainless steel flask which is clamped in place. The gas is disengaged from the liquid and flows from the flask through a condenser to a vent or to a gas sampling bag as required. Gas is also disengaged from the liquid in the slop receiver and this normally flows to the vent.

Satisfactory sampling of material from a reaction system of this kind requires that operating conditions and feed rates be brought to constant values which must be maintained for long enough to produce constant compositions in the product obtained. Some of the initial experiments were therefore used to establsih the time needed to change from flush oil, used in establishing the operating temperatures and pressures, to slurry and bring the product out without any residue of flush oil in the initial sample. After a change in operating conditions a further interval must elapse before the product can be considered to be lined out in equilibrium with the new operating conditions. In the usual startup the reactor can be brought to operating temperatures and pressures in about three hours. After this, slurry must be fed for an interval before the flush oil is completely displaced. This requires filling the reactor with about four volumes of slurry before the flush oil is reduced to a negligible concentration. After this has been accomplished a liquid product sample may be collected. Normally the sample flask will contain air which must be fully displaced before a representative gas sample can be collected. In the best sampling procedure the gas sample is collected during the last part of the liquid sampling interval. The time required to collect a satisfactory volume of liquid will vary with the feed rate, and may be reduced as the feed rate is increased. Many of the initial samples were taken for too small an interval, and the results from some of the preliminary experiments are of lower quality as a consequence. It has been found to be preferable to extend the sampling interval long enough to collect 1.5 to 2.0 Kg of liquid and to take the gas sample in the last half hour or last hour of the liquid sample interval. The liquid sample is then taken for a timed interval and the gas sample is taken for some fraction of this interval.

Gas samples are collected in rubberized fabric bags which are large enough to hold 100 to 150 liters of gas. It is therefore practical to collect samples for an hour or so without over filling a sample bag. The gas can be mixed by kneading the bag and well averaged compositions are produced. It has been found that hydrogen sulfide slowly escapes from such sample bags. This component is determined first immediately after the sample is removed from the system. Such results are accurate enough for satisfactory accounting of sulfur in most cases.

IV-B Preparation of Coal for Use

Three different types of coal have been studied in the continuous reactor system. Kentucky #9 coal has been taken as representative of the high volatile bituminous coals, Baukol-Noonan lignite from North Dakota has been taken as representative of the lignite coals, and Elkol subbituminous coal has been taken as representative of the subbituminous coals. Obviously these are examples which may not match other coals in the ranks represented with complete concordance. In order to apply the process to coal from a given mine the coal should first be tested in the laboratory. Experience has developed considerable correlative data which allows preliminary estimation of the effect of differences in the proximate analysis and the differences in the mineral matter present. Such comparisons are useful but can not be applied with complete assurance at this stage. It is also a consideration that the composition of coal from a given mine may change as mining moves from one location to another in the coal deposit. It is necessary to exercise care in sampling and in subsampling in order that the samples to be tested represent the current status of the coal being mined. Our experience in this regard illustrates the difficulties which are typical in this kind of sampling.

Methods have been established by the ASTM for sampling ores to obtain well averaged samples.(See ASTM D346-35(1969)Ideally samples drawn for laboratory studies will be taken in accordance with these well established procedures. Unfortunately this may be done at a mine site with variable degrees of skill and care, and in reality the laboratory operation will be at the mercy of the sampler in this regard. About the only control of the quality of sample which can be exercised at the laboratory is to exercise reasonable care in drawing subsamples for study. It is necessary to empty the sample container completely, to break up large lumps, to mix and cone and quarter the sample or to use a suitable riffle to subdivide the sample. If the whole sample is to be ground it is helpful to take the coal from the original container and to make a long pile by spreading the coal along the length of the pile with a scoop or a shovel. Larger than average lumps should be broken up and distributed as this is being done. Coal from the long pile can then be ground in a suitable hammermill and stored in plastic bags or metal cans. Analytical results from individual bags of powdered coal made in this way tend to fall close to the average for the whole lot. Failure to exercise good control of this step in the operation will often result in a set of samples with variable ash contents and with corresponding risk of variability in the organic components as well.

The first sample of Kentucky #9 coal was received in a metal drum and weighed approximately 500 pounds. About half of this was removed from the drum and ground using a Mikro SH Bantam pulverizing mill. A subsample was taken from the ground coal and the analysis of this material was obtained by submitting the sample to the Industrial Testing Laboratory for analysis. The results for this sample are presented in Appendix B-1. The powdered coal was stored by placing portions in polyethylene bags which were taped shut and then placed in metal cans for storage. A five gallon pail will hold from 15 to 20 pounds of coal ground to -100 mesh. Samples stored in this way show little tendency to gain or lose moisture. As samples were used to prepare feed slurry, subsamples were taken to check the ash and moisture levels. It was found that the ash varied from the average value of the composite sample analyzed by Industrial Testing Laboratories over a range from about 9.4% to about 12.0%. The subsample of ground coal was used up by experiment CU 29 and the remaining coal in the drum was mixed and ground.

Upon analysis, the second subsample was found to contain 15.26% ash, which is significantly higher than the mean value for the first subsample ground. It became clear that mineral and organic phases in the coal had not been properly mixed before the first sample was removed. The second sample was well mixed and analysis for ash in this sample ranged from a low value of about 15.10% to a high value of about 15.30%. This coal sample was used for runs CU 31 through CU 49 in the anthracene oil series and for a single run in the FS 120 series which is to be reported separately. The analysis of this sample is presented in Appendix B-2.

Two additional lots of Kentucky #9 coal have been used in the later studies. Since difficulty had been encountered in subsampling the first large sample, greater effort was spent in mixing the coal and making a satisfactory preparation for grinding. The use of the long pile technique will allow the preparation of a series of bags of powdered coal with ash content constant within a percent relative.

Kentucky #9 coal will break into a fine powder when ground in a hammermill. Sieve analysis of typical ground coal samples indicate that over half of the coal reduces below 150 mesh in a single pass and that comparatively little material remains in particle sizes greater than 100 mesh. This is of course regulated to some extent by the size of the holes or slots in the screen in the mill but much of the coal is reduced to particle sizes well below the screen size. In the work with anthracene oil most slurries were prepared from the coal as ground and these were generally fed without particular difficulties. Ash analysis of coal slurries showed a tendency for the initial slurry to be below theoretical ash concentrations and for this to gradually increase as the level of liquid in the feed pot was lowered. Inspection of the residual slurry after a lengthy run disclosed that the largest mineral particles were systematically dropping to the bottom of the feed pot and were not being fed in the proper proportion.

An effort was made to correct this situation by improving the stirring in the feed pot. When this was accomplished the result was a dramatic increase in the number of stoppages caused by collection of larger mineral and coal particles in the ball checks of the high pressure pump head. It was found that very precise control of feed slurry composition could be maintained if the stirring was properly regulated but that the very small ball checks opened with a limited clearance. This forced sieving of the coal to a maximum particle size to avoid plugs in the pump head. For the pump head now in use this can be accomplished by sieving all coal to pass through a -150 mesh sieve. A single grinding with a hammermill will produce powdered Ky #9 coal which will pass about 80% by weight through this sieve and regrinding the oversize material will put most of the coal through the-150 mesh sieve in two or three additional sieving and regrinding operations. Operations were developed progressively throughout the experimental program with anthracene oil and coal was not routinely sieved for use until the studies with FS 120 were in progress. This higher viscosity oil improved the suspension of the larger particles; and the tendency for the larger troublesome particles to drop out of suspension, as was often the case in anthracene oil, often did not operate to the extent needed to avoid plugging the ball checks. Coal samples prepared recently have all been sieved to pass the-150 mesh sieve as one specification for useable samples. Normally at least 99% of the sample is made to pass through this sieve. Such work is expedited by the use of a mechanical sieve and a vibratory chemical feeder which will feed and sieve about 20 pounds of ground coal in a batch without much attention.

Preparation of Coal for Use (Current 8/74 Practice)

Pulverized stock is received which contains random size particles up to 1/4" to 0. This material is ground from a long pile and the ground product is transferred to a Syntron Vibrating Feeder, Model F 14TOC 3/4, which feeds into a Sweco Vibro-energy separator, Model 1518533. Equipment is intra-grounded to eliminate static electricity. The separator is composed of a -100 mesh scalping screen, which removes the larger flakes and a-150 mesh herring-bone type screen. That material which passes completely through is collected for use in the oil slurry mixture. Scalped material, that material not passing through the-100 mesh screen, along with that retained on the-150 mesh screen is then re-cycled several times. When it becomes apparent that re-cycling will no longer reduce the flake size, the remaining material is subjected to a Weber Brothers Laboratory Hammer Mill. This then is also processed. The final product is mixed and is then sampled for retain and laboratory assay. It is then properly labeled and packaged in polyethylene bags and stored in metal containers.

In working with the Kentucky #9 coal for several years the coal has been sampled about once a year to obtain new stock. In this interval the mining operation has moved from an area containing about 1.75% to 2.0% organic sulfur to an area containing about 1.3% organic sulfur. Such compositional drifts even within a single mine should not be surprising. All samples have contained substantial amounts of pyritic sulfur and the ash associated with the coal has consistently contained at least 15% to 20% of iron. A complete evaluation of a coal sample now requires a proximate analysis, an ultimate analysis, a mineral analysis to determine the composition of the ash, the determination of sulfur forms, and determination of the free swelling index of the coal. It has been determined experimentally that coals with high volatile matter content tend to dissolve more readily than coals with low volatile matter content. Coals which melt readily tend to be more reactive than coals which do not melt. The free swelling index is an indication of the reactivity. The use of these criteria has been discussed previously in OCR Report No. 53, Interim Report No. 6, page 99. Generally the presence of pyrite in the coal is not regarded as a problem since this is the source of the iron needed to catalyze the rehydrogenation of solvent used in the process. The decomposition products of pyrite are hydrogen sulfide, which is evolved in the product gases, and ferrous sulfide, which can be removed by filtration of the product solution. Accordingly there appears to be no reason to work with coals which have been processed to lower the sulfur content by removing pyrite. Routine washing procedures do not remove enough pyrite to produce low iron samples. Useful concentrations of iron have been routinely available in the bituminous coal, even after washing.

The Baukol Noonan lignite was received in a sealed drum and contained its normal bed moisture. It was possible to grind this material with the Mikro Pulverizer hammermill without greatly altering the amount of water retained by the lignite. The ground product was bagged in polyethylene and sealed to prevent loss of moisture. In experiments preformed with this material carbon monoxide, or mixtures of carbon monoxide and hydrogen were used as the reducing gas. In this reagent system the water shift reaction is utilized to generate hydrogen in situ and the presence of the natural bed moisture was expected to be beneficial. The ground coal tended to be a little larger in average particle size than the distribution produced from Kentucky #9 in the same mill. The ground coal was subsampled and submitted to the Industrial Testing Laboratory for analysis. The results obtained are presented in Appendix B-3.

Initial work with the Baukol Noonan lignite was attempted without sieving the ground coal. A slurry made with such coal tends to plug up the feed pump. The coal was sieved -100 mesh and this allowed preparation of feed slurry which could be pumped. Approximately 9.8% of the lignite was greater than 100 mesh particle size, while the Kentucky #9 coal had almost all been broken to particles less than 100 mesh using the Mirko Pulverizer and the same 013HB 3/64 B screen. The feed lignite was sieved to -100 mesh for succeeding experiments until the Speed Ranger pump head was installed. This apparatus allowed use of unsieved lignite in experiments after run C1-13. In retrospect, the probability exists that particle size classification in the feed pot prevented the feeding of particles which would otherwise have blocked the ball checks. In the light of current information on Kentucky #9 coal, sieving of any stock to control maximum particle size should materially improve the reliability of feed pump performance. The maximum allowable particle size depends on the design of the check valve and the clearance resulting from the flow of slurry through in response to the suction of the pump piston. Generally a viscous oil will open the ball check more than a low viscosity oil while increased operating pressure will tend to decrease the size of the opening. This is the probable cause for the observation that a slurry may pump well at a lower pressure but block the check valve when operating pressure is increased. The viscosity of the slurry can be altered by changing the temperature of the feed pot. This results in a condition in which slurry may pump well up to some critical temperature, and in which ball check performance becomes erratic above this temperature. Heating by the recirculation pump may cause the slurry to drift from good performance to poor performance characteristics. Most of these problems are the result of the attempt to use small pumps and to pump small volumes of material. As equipment size is increased the maximum allowable particle size should increase substantially and almost any reasonably efficient mill should be satisfactory and produce coal stock in acceptable particle size ranges.

IV-B

During work with lignite it became apparent that the mineral content of the coal materially influenced the course of the reaction between the coal and the reducing gas. Analytical procedures for evaluation of the coal ash are well standardized and will report the overall composition of the mineral phases accurately. It has become standard procedure to send samples to a testing laboratory for this analysis. With lignite some of the mineral matter can be removed from the coal by ion exchange with dilute hydrochloric acid and certain ions such as sodium can be removed by ion exchange with dilute calcium chloride solution. The sodium in lignite is mostly bound as the counter ion to a polymeric acid functional group and this tends to hydrolyze alkaline in contact with water. The iron in the lignite is partly pyritic and partly acid extractable with dilute hydrochloric acid. Presumably it may also function as a counter ion to polymeric acid functions. Other acid extractable ions include part of the calcium and magnesium present. Details have been discussed in a paper previously presented. 4/ The composition of typical mineral phases in each of the coals used for the continuous reactor work with anthracene oil is presented in Appendix B-5 to facilitate comparison. It has been established that Kentucky #9 coal is rich in iron (which originates mainly as pyrite) while the Baukol Noonan lignite is rich in sodium (which originates as an ion exchangeable species). The Elkol subbituminous coal has comparatively little iron or sodium.

Preparation of Elkol for use follows the general method applied to the lignite sample. The natural bed moisture in the coal is about 20% and it was possible to grind material containing this amount of moisture without much loss of the moisture present. The objective of much of the work with Elkol was to test the reactivity of the coal with carbon monoxide or with mixtures of carbon monoxide and hydrogen as the reducing gas. It was desirable to retain the natural bed moisture in the samples. This sample was ground -100 mesh and retained 18.97% moisture. The powdered coal was stored in polyethylene bags which were taped shut and placed in metal cans. The analysis of this material is presented in Appendix B-4.

IV-C Preparation of Solvent

IV-C-1 Distillation Procedures

The first distillation of raw anthracene oil resulted in three drums of middle fraction. Each drum was subsampled and the subsample was redistilled in the standard laboratory vacuum distillation to determine the boiling range under these conditions. Results are presented below.

Drum No.	Distillation Range (3 mm Hg Nominal)
1	69 - 216°C
2	72 - 244°C
3	70 - 215°C

IV-C-1

In previous experiments using the batch autoclave the solvent cut had been defined as distilling from 100°C to 230°C in the vacuum distillation done at a nominal pressure less than 3 mm. It was expected that some readjustment of cut point temperatures would be made in order to adjust the amount of solvent to balance input and recovery to break even quantities. The distilled solvent was considered to be acceptable. The first and third drum were scheduled for use first. The second drum and unused balance of material from drums No. 1 and 3 therefore comprised the feedstock used in the hydrogenation procedure, CL 18.

A second large lot of anthracene oil from the Cleveland works of the Reilly Tar and Chemicals Co. was distilled to prepare stock for hydrogenation in Run CU 40. Data from this distillation are presented for comparison.

Cut No.	% W/W
Cut No. 1 IBP - 450°F	3.4
Cut No. 2 450 - 550°F	5.4
Cut No. 3 550 - 800°F (Correct to 1 Atm.)	82.4
Distillation Residue	6.4
Loss	2.4

The motives for preparing hydrogenated solvent and the techniques used will be discussed later.

Three different kinds of solvent have been used in the continuous reactor studies with anthracene oil. They are the middle fraction of raw anthracene oil and two additional lots of solvent prepared by partially hydrogenating the middle fraction of raw anthracene oil. The raw material for any of these solvent preparations was weathered anthracene oil from the Cleveland works of the Reilly Tar and Chemicals Co.

Since the continuous reactor was expected to consume a few gallons of solvent for each experiment, it was necessary to obtain more solvent than had been used in the autoclave program. It was preferred to distill a single large lot rather than to make small preparations of solvent for each experiment in the laboratory as had been done previously.

The first lot was prepared by distillation of a batch of anthracene oil consisting of three 55 gallon drums of material. This was processed in a batch vacuum still available at the Gulf Research and Development Laboratory at Harmarville, Pa. The light fractions were removed by distillation at atmospheric pressure and the middle fraction was then taken under vacuum. The cuts which were made are listed below:

Cut	%W/W
No. 1 IBP - 450°F	2.4
No. 2 - 450°F - 550°F	13.8
No. 3 - 550°F - 800°F(corrected to 1 atmosphere)	75.9
Bottoms 800°F+	7.9

Distillation of the middle fraction (Cut No. 3 was done at 12 mm and temperatures reported are corrected to atmospheric pressure.

IV-C-1

This lot of anthracene oil was the source of the middle fraction of raw anthracene oil used as solvent in experiments CL 1 through CL 17. The remaining oil was catalytically hydrogenated in Run CL 18 to prepare solvent for subsequent use. This supply was used up by experiment CU 39. A second three drum lot of raw anthracene oil was obtained and distilled as described above. The middle fraction cut from this lot catalytically hydrogenated in Run CU 40 to prepare the solvent used in the remainder of the anthracene oil program.

As a rule, raw anthracene oil at room temperature will partly crystallize. This can be a problem even with well weathered oil after distillation to obtain the middle fraction needed for use as solvent. The large lots prepared by distillation were pooled in a container which could be heated and the oil was stirred until all crystalline material was melted and thoroughly mixed to make a uniform composite. The warm oil was then canned in clean one or five gallon cans which could be handled and stored conveniently. In preparing feed slurry it was standard procedure to warm the required number of cans of oil in an oven then to thoroughly mix the oil in each can before use. Subsamples drawn for analysis had been treated in the same manner to avoid use of segregated material for analysis.

Raw anthracene oil was used in the initial series of experiments (Runs CL-1 through CL 17). The results of infrared and elemental analysis on the cut 2 reclaim solvent from these experiments indicated that the solvent had gained hydrogen as a result of use in dissolving coal. It was reasoned that this gain in hydrogen could only be accomplished at the cost of competition between coal derived products and the solvent for the hydrogen. The hydrogen use or the reaction product distribution pattern could be expected to be influenced by the competition. In order to investigate this idea it was necessary to make a hydrogenated solvent and to use it as solvent. Ideally this should be made to contain the equilibrium concentration of reactive hydrogen, but the amount needed could not be estimated with precision for the first trial. Data from the single pass experiments available and data from the process development plant experiments were somewhat different. The range covered required the addition of from 0.25% to 0.50% hydrogen to raw anthracene oil, depending on the material taken as a reference for the equilibrium product.

IV-C-2 Preparation of Hydrogenated Anthracene Oil. Run CL - 18

The continuous preheater-dissolver tube of the CL unit was disassembled and packed with a nickel molybdate catalyst (HDS 3A as 1/16 x 1/8 extrudates). The reactor was then put back in place and pressure tested. The feed pump was modified to allow pumping rates up to one gallon per hour. The unit was lined out at 1000 psig with hydrogen at an oil rate of 2.4 kg per hour and the temperature was advanced until the reduction was running smoothly as observed by change in the infrared spectrum of the product. Pressure, temperature, and flow rate adjustments were made to produce a product with an $\overline{\text{IR}}$ value in the range from 1.0 to 1.1. (See Section IV C4) This resulted in hydrogenation of the raw anthracene oil at a rate of 2.4 kg per hour at 1000 psig and 425°C. After 5 hours of operation the catalyst bed began to plug and the flow rate became restricted to about 1 kg per hour while the $\overline{\text{IR}}$ increased to 1.4 to 1.6. At this point the trial was stopped and the reactor was taken apart for inspection. It was determined that some coking and accumulation of fines had been taking place at a point between thermocouples while the upper portion of the catalyst bed had remained active. At the lower flow rate the product became more hydrogenated than desired while the coke plug forming progressively throttled the pump rate.

With this experience the tube was repacked with a cobalt molybdate catalyst in 1/8 x 1/8 inch grain size. In packing the tube wire baskets were installed to retain the catalyst in the vicinity of thermocouples in the upper part of the reactor tube. Approximately 18 inches of the lower end of the reactor tube was left open to serve as a preheater space for the oil entering the reactor.

The tube was pressure tested after installation in the reactor system. The reaction was started with 1000 psig hydrogen and the $\overline{\text{IR}}$ ratio was checked as the temperature was advanced. The reaction started smoothly and the $\overline{\text{IR}}$ was adjusted by making minor adjustments in pressure and temperature. About 16 hours were needed to line out the reactor to make material which appeared to be the desired composition. At the end of this time the product was being made at a rate of 4.2 kg per hour. The operating temperature was 420-425°C at the top thermocouple, 400 - 410°C at the next lower thermocouple, and 395 - 398°C at the third thermocouple which was near the bottom of the catalyst bed. Hydrogen pressure was adjusted to 1050 psig. The product was made with an $\overline{\text{IR}}$ of 1.0 to 1.1. The unit operated smoothly and continuously for 3 days and produced about 70 gallons of hydrogenated product. Product composition could be readily determined by means of infrared spectra and control of composition could be maintained by small changes in pressure or temperature. The oil produced was blended and filtered to remove any catalyst fines which may have been present. Low boiling products that formed as a result of hydrocracking the oil were stripped out. A pilot study was done with the material made in the first trial run. Here the original sample had an $\overline{\text{IR}}$ of 0.96 which was reduced to 0.89 by stripping which removed 7-10% of the material. This oil analyzed carbon 92.00% and hydrogen 6.15%.

Following this pilot study the larger batch of oil was filtered with the addition of celite filter aid to assure complete removal of traces of catalyst fines. The filtered oil was stripped to remove any material boiling below 100°C at a nominal pressure of less than 3 mm Hg. This removed about 9% of light oil. The remaining material was the cut 2 solvent and had been hydrogenated slightly more than the material made in the first trial. The $\overline{\text{IR}}$ was 0.98 and the hydrogen content determined by combustion analysis was 6.20%.

IV-C-2

ELEMENTAL ANALYSIS OF RAW ANTHRACENE OIL AND CL 18 HYDROGENATION OIL

Determination	Middle Fraction of Raw Anthracene Oil	Stripped, Hydrogenated Middle Fraction of Raw Anthracene Oil
Carbon %	91.32	91.54
Hydrogen %	5.73	6.20
Nitrogen %	0.82	0.57
Sulfur %	0.54	0.24
Oxygen % (by difference)	1.56	1.45
H/C Atomic Ratio	0.75	0.81
$\overline{\text{IR}}$ Ratio	0.56	0.98

In addition to reactions which increase the percentage of hydrogen, reactions are observed which reduce the percentage of oxygen, nitrogen, and sulfur in the oil. The presence of a considerable percentage of low boiling product is apparently the result of hydrocracking to some extent. The cut 1 oil made and removed by the stripping procedure was still mostly aromatic in the sense that it was nearly all dissolved when put in contact with concentrated sulfuric acid. This mild reduction does not saturate even the light fractions of an aromatic material such as anthracene oil.

At the end of the hydrogenation procedure an attempt was made to hydrogenate some of the unchilled raw anthracene oil from the Granite City works of the Reilly Tar and Chemical Co. This material contains a comparatively large fraction of carbazole and exhibits a strong band at 2.92 microns which is largely due to this material. The presence of the crystalline material in the feed oil caused difficulties with the feed pump but it was possible to process about 8 kilograms of the oil before the pump was shut down by crystals in the feed line. The hydrogenation of this oil proceeded smoothly and the oil had an $\overline{\text{IR}}$ ratio of 0.98. The original sample of Granite City oil had an $\overline{\text{IR}}$ of 0.41. Qualitative spectra for the original sample and for the hydrogenation product are presented in Appendix C, items C-1 and C-2. The concentration of carbazole is considerably reduced by the hydrogenation procedure, and here at least is one ring structure which is opened readily by the mild hydrogenation used.

Spectra of the middle fraction of raw anthracene oil from the distilled sample and of the hydrogenation product CL 18 after stripping to produce the cut 2 solvent fraction are presented as items Appendix C-3 and C-4.

IV-C-3 Preparation of Hydrogenated Anthracene Oil. Run CU 40

The first lot of hydrogenated anthracene oil was used in Runs CL 19 through CU 39. At the end of this time it was used up. It was necessary to prepare additional solvent to continue the studies planned.

IV-C-3

In the course of experiments with the first lot of solvent it had been observed that the $\overline{\text{IR}}$ ratio of cut 2 reclaim solvent was normally reduced to a figure below the $\overline{\text{IR}}$ ratio of the input solvent. This was true at operating temperatures needed to achieve efficient removal of sulfur and even at the more moderate reaction temperatures in the vicinity of 425°C. In a single pass at 450°C the $\overline{\text{IR}}$ ratio of the reclaimed cut 2 solvent dropped to values in the 0.75 to 0.80 range from the initial value for the CL 18 solvent (0.98). At lower temperatures in the 425°C range the value for $\overline{\text{IR}}$ appeared to be about 0.90 at reaction times long enough to line out the product. The trend in the probable operating temperature range was for the CL 18 solvent to lose hydrogen slightly as the first pass through the reactor was made. From these results it appears that the first estimate for the proper hydrogen content of a solvent simulating the first pass reclaim had actually been slightly too high. It should be recalled that this estimate was also made for the 1000 psig operating pressure of hydrogen which was thought to be about the minimum practical operating pressure.

In preparing the next batch of solvent it was planned to try to produce a batch of solvent containing slightly less hydrogen than had been added in the CL 18 hydrogenation run. The reactor configuration had been changed by the addition of the preheater and by substituting a short tubular reactor for the long thin reactor previously used. Several changes in operating conditions and in operating procedure were also investigated.

For Run CU 40 the dissolver vessel of the CU unit was dismantled and cleaned out. A wire mesh basket about 1 1/2 inches in diameter and 14 inches long was made from fine mesh stainless steel screen. This just filled the volume of the dissolver vessel. The basket was filled with 150 grams of NALCOMO 471 Cobalt-Molybdenum-Alumina extruded catalyst (1/16 x 1/8 inch extrudates). The preheater was made double the normal length and the pumping heads were modified to allow pump rates of up to 10 kilograms of feed oil per hour. In order to simplify feeding of larger amounts of oil the slurry recycle pump was arranged to draw oil directly from a 55 gallon oil drum of material. The drum was heated electrically to allow maintaining a temperature over 73°C, the point at which all crystalline material appeared to melt in a laboratory test. Crystalline material was present in this lot of anthracene oil because it had not been fully weathered at the time it was needed for use. This material was less fluid and generally more difficult to process than the raw anthracene oil stock used in Run CL 18.

The unit was started with a hydrogen pressure of 1000 psig and the operating temperatures were slowly advanced to start the reaction. Samples were taken for measurement of infrared spectra to control the hydrogenation reaction. The sand bed for the preheater was advanced to 450°C (although at these flow rates it is likely that the fluid in the preheater did not reach this temperature). With catalyst bed temperatures ranging from 360°C upward to 430°C the reaction with hydrogen progressed at useful rates. Feed rates, temperatures, and hydrogen pressures were varied as required to produce product with an $\overline{\text{IR}}$ of about 0.77. Samples were taken about every two hours for inspection by infrared and the operating variables were adjusted as required to produce material with the desired composition. In several instances the reactor was upset and the off specification materials made

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in these time intervals were set aside for use in developing an infrared working curve for solvent analysis.

The materials which were considered useable were blended to make a composite sample. This material originally consisted of about 120 gallons of hydrogenated stock. About 30 gallons of Pilot Plant Process Reclaim Solvent which had been retained from previous work was then added to this stock. This material had an $\overline{IR}$ ratio of 0.83 and was considered suitable for this use. The resulting blend was then filtered through candle filters of about 30 to 40 micron retention to remove any insoluble materials present. Upon cooling it was found that excessive crystalline material was deposited and the filtration was repeated at room temperature to correct this problem.

A sample of the blended oil was then stripped to remove the fraction boiling below 100°C at a nominal pressure less than 3 mm Hg. Analytical data for the anthracene oil fraction processed and for the CU 40 final blend after stripping are as follows:

ELEMENTAL ANALYSIS OF RAW ANTHRACENE OIL AND CU 40 HYDROGENATION BLEND

Determination	Middle Fraction of Raw Anthracene Oil	Stripped, Hydrogenated Middle Fraction of Raw Anthracene Oil
Carbon %	91.68	90.58
Hydrogen %	5.77	6.04
Nitrogen %	0.99	0.60
Sulfur %	0.54	0.36
Oxygen % (by difference)	1.01	2.34
H/C Atomic Ratio	0.75	0.79
$\overline{IR}$ Ratio	0.51	0.75

IV-C-4 Solvent and Reclaim Solvent Analysis by Infrared

It has been observed that the relative intensity of the absorbance at 3.41 microns compared to the absorbance at 3.28 microns in the infrared spectrum of anthracene oil shifts as the anthracene oil is hydrogenated. Raw anthracene oil, as received, tends to be lean in hydrogen while the solvent reclaimed from coal solutions derived from raw anthracene oil tend to contain more hydrogen. When anthracene oil is catalytically hydrogenated, the ratio of the 3.41/3.28 micron band absorbance increases due to a considerable increase in the intensity of the 3.41 micron band with a small decrease in the intensity of the 3.28 micron band.

As experience and samples run under various conditions accumulated, it was possible to observe this ratio over a considerable range of hydrogen content. Representative samples were run on the Perkin Elmer 237 grating spectrophotometer at slow speed. Using the general techniques of infrared quantitative analysis as presented in ASTM E 168, a baseline was drawn from the vicinity of 2.6 microns to the vicinity of 4.8 microns. The absorbance at 3.28 microns and at 3.41 microns was calculated. In order to produce a function which increased as the hydrogen content of the solvent increased it was necessary to divide the absorbance at 3.41 microns by the absorbance at 3.28 microns. This ratio has been given the symbol $\overline{IR}$.

Precise values for total hydrogen were obtained for these samples by combustion analysis. The results were plotted on a chart as percentage hydrogen versus $\overline{IR}$ values determined from the spectra of the samples. A line was drawn to establish the preliminary working curve for the analysis of similar oils. The data used are presented in tabular form as follows:

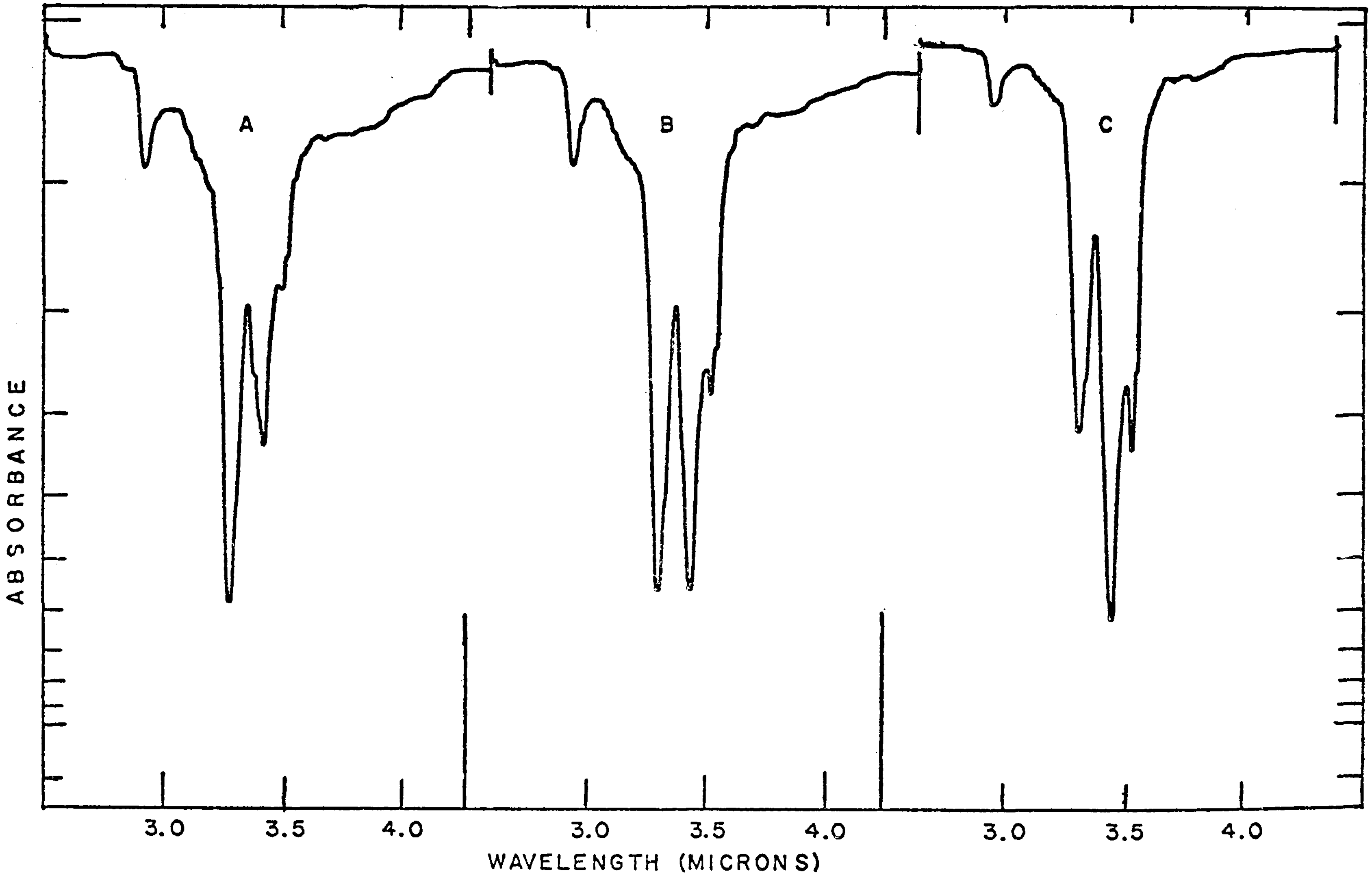
PRELIMINARY CALIBRATION DATA - WORKING CURVE FOR ANALYSIS OF SOLVENT

SUBSTANCE REPORTED	% CARBON	% HYDROGEN	IR RATIO
Middle fraction of hydrogenated reclaim solvent	91.42	6.901	2.32
Run PA 39 redistilled reclaim solvent	91.38	6.616	1.48
UND 373 reclaim solvent	90.64	6.412	1.26
UND 377 reclaim solvent	90.59	6.428	1.26
UND 376 reclaim solvent	90.85	6.407	1.22
Run PA 74 reclaim solvent	90.46	6.281	0.97
UND 277 reclaim solvent	90.33	6.132	0.94
Run PA 72 reclaim solvent	90.78	6.158	0.85
Continuous Run 2 reclaim solvent	90.65	6.092	0.78
Process Development Plant Run 66 reclaim solv.	90.41	5.987	0.77
Continuous Run 8 reclaim solvent	90.93	5.925	0.75
Run PA 73 reclaim solvent	90.90	6.151	0.74
Continuous Run 11 Sample 17 reclaim solvent	91.35	6.024	0.71
UND anthracene oil redistilled at atmos. press.	90.91	5.916	0.69
Continuous Run 7 reclaim solvent	91.05	5.895	0.65
Continuous Run 12 reclaim solvent	91.20	5.896	0.61
UND 357 reclaim solvent	91.09	5.828	0.57
Middle fraction of raw anthracene oil, sample 1	91.32	5.731	0.56
Middle fraction of raw anthracene oil, sample 2	91.01	5.741	0.56

Samples were analyzed to construct the preliminary working curve and were taken from several sources. PA runs are P&M batch autoclave materials. UND materials are samples taken from the batch autoclave experiments performed at the University of North Dakota. Continuous run samples were made in the first studies with the continuous reactor and are derived from MFRAO. Some materials were retained from the Process Development project. In order to visualize the extent of the change in the spectra which is covered in the preliminary working curve a comparative set of scans with about the same maximum absorbance for the strongest band has been prepared. These are presented as Figure 5.

These samples come from a variety of sources and in some cases the original solvent has been used to dissolve coal in more than one pass through the reactor. The scatter of the points is only partly due to experimental errors. Some of the scatter must be the consequence of variable amounts of hydroaromatic and saturated functional groups as substituents on the aromatic hydrocarbons which comprise the solvents. The working curve is presented as Figure 6.

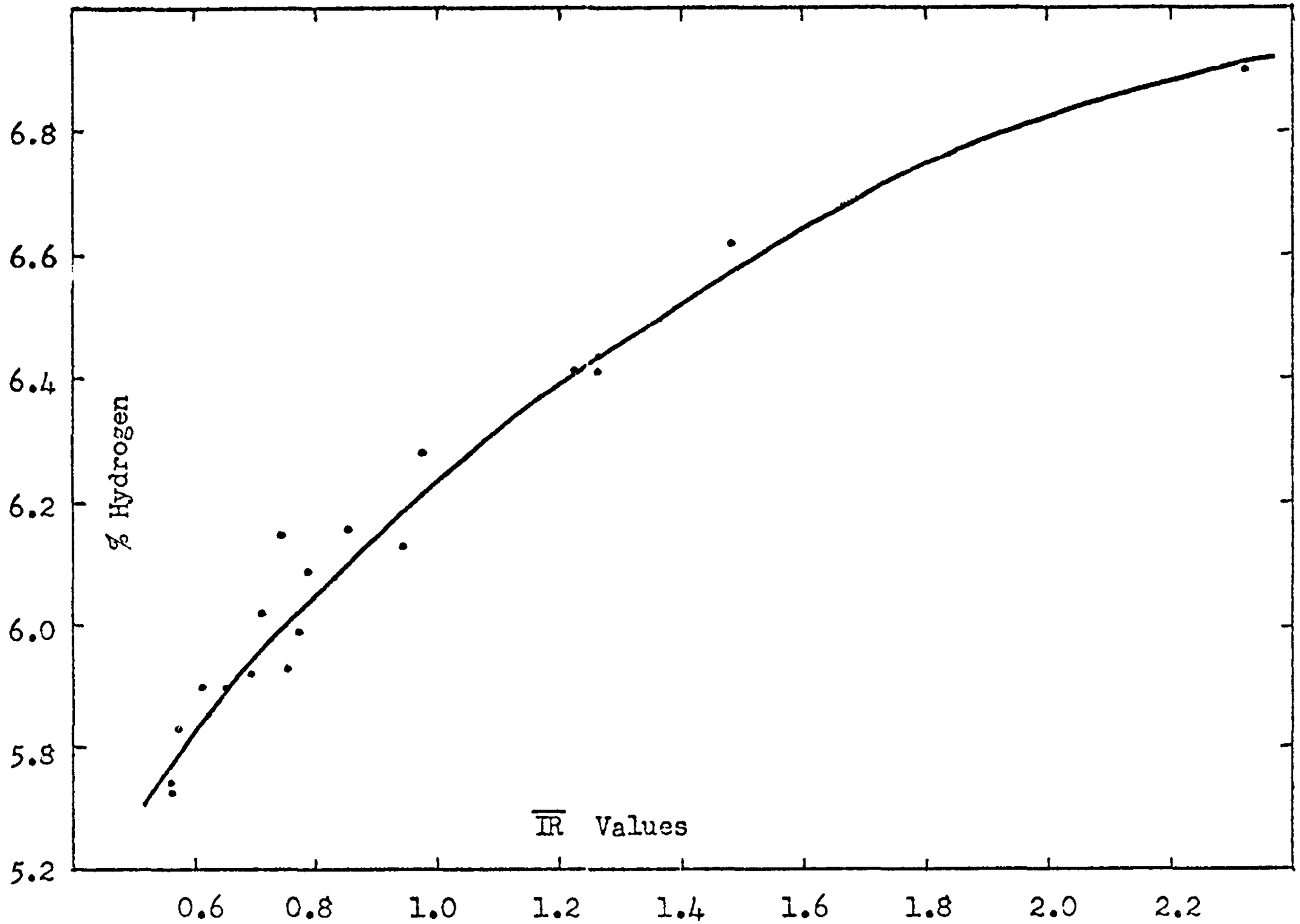
Spectra of Raw & Hydrogenated Anthracene Oil



A. MIDDLE FRACTION OF RAW ANTHRACENE OIL. B. MIDDLE FRACTION PARTLY HYDROGENATED.

C. MIDDLE FRACTION OF HYDROGENATED RECLAIM SOLVENT.

Figure 5



PRELIMINARY WORKING CURVE ON PERKIN ELMER 237 - % Hydrogen Versus $\overline{\text{IR}}$

Figure 6

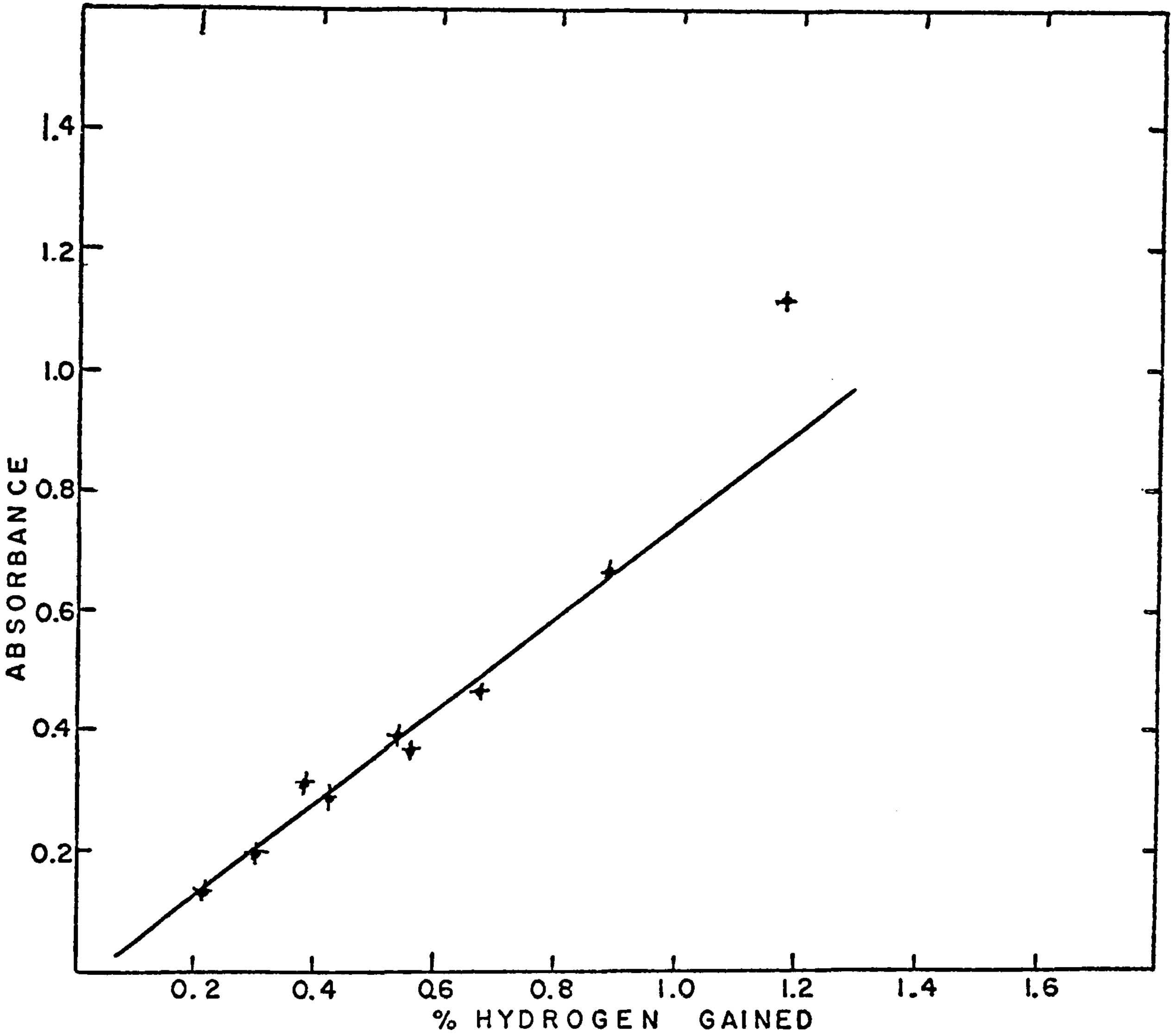
It is also possible to run spectra in solution to obtain quantitative results. Anthracene oil and reclaim solvent are soluble in carbon tetrachloride and spectra can be run using a solution in one cell and carbon tetrachloride in a matching cell in the reference beam. A more sophisticated differential measurement can be obtained by using the same concentration of raw solvent in the reference beam and reacted solvent in the measuring cell. In this system it is possible to relate the gain in hydrogen to a linear increase in the absorbance at 3.41 microns. Examples of this kind of data are as follows:

DIFFERENTIAL ABSORBANCE AND HYDROGEN GAIN DATA

SUBSTANCE REPORTED	% HYDROGEN	GAIN IN % HYDROGEN	DIFFERENTIAL ABSORBANCE
Continuous Run 14 Sample 11	5.736	-00-	Reference
Continuous Run 15 reclaim solvent	5.938	0.202	0.135
Continuous Run 11 Sample 17	6.024	0.288	0.195
UND Run 360 reclaim solvent	6.112	0.376	0.314
Continuous Run 18 Sample 7	6.148	0.413	0.298
Run PA 74 reclaim solvent	6.281	0.545	0.362
Continuous Run 19 Sample 40 reclaim solv.	6.267	0.531	0.396
UND Run 376 reclaim solvent	6.407	0.671	0.467
Run PA 39 reclaim solvent	6.616	0.880	0.670
Middle fraction of hydrogenated reclaim solvent	6.901	1.165	1.13

When results are plotted, most of the points fall on a straight line, as presented in Figure 7. It would be reasonable to assign most of the scatter observed to the errors inherent in the measurements made. This probably is not the case for the middle fraction of hydrogenated reclaim solvent. This observation deviates from the trend of the other data by an amount well outside the precisions of the elemental analysis and infrared measurement. The difficulty is no doubt qualitative. The result observed is an indication that more than one kind of structure can contribute to the absorbance at 3.41 microns and that new structures are being developed. The middle fraction of reclaim solvent, in question, was catalytically hydrogenated under severe conditions which resulted in removal of sulfur, oxygen, and nitrogen as well as hydrogenation of the oil. The formation of alkyl groups during this process could account for the difference observed. Problems of this kind are not serious enough to keep infrared measurements from being useful in the direct observation of hydrogen transfer reactions between anthracene oil and coal.

The data presented formed the basis for the evaluation of solvent and the coal solutions made through the first 40 runs in the continuous reactor. The reclaimed solvents obtained were plotted on a master chart and the results were checked by combustion analysis as a continuing program. It was found that the IR ratio applied to the coal solutions prepared give reasonable estimates of the percentage hydrogen in the dry ash free solution. The amount



DIFFERENTIAL IR WORKING CURVE

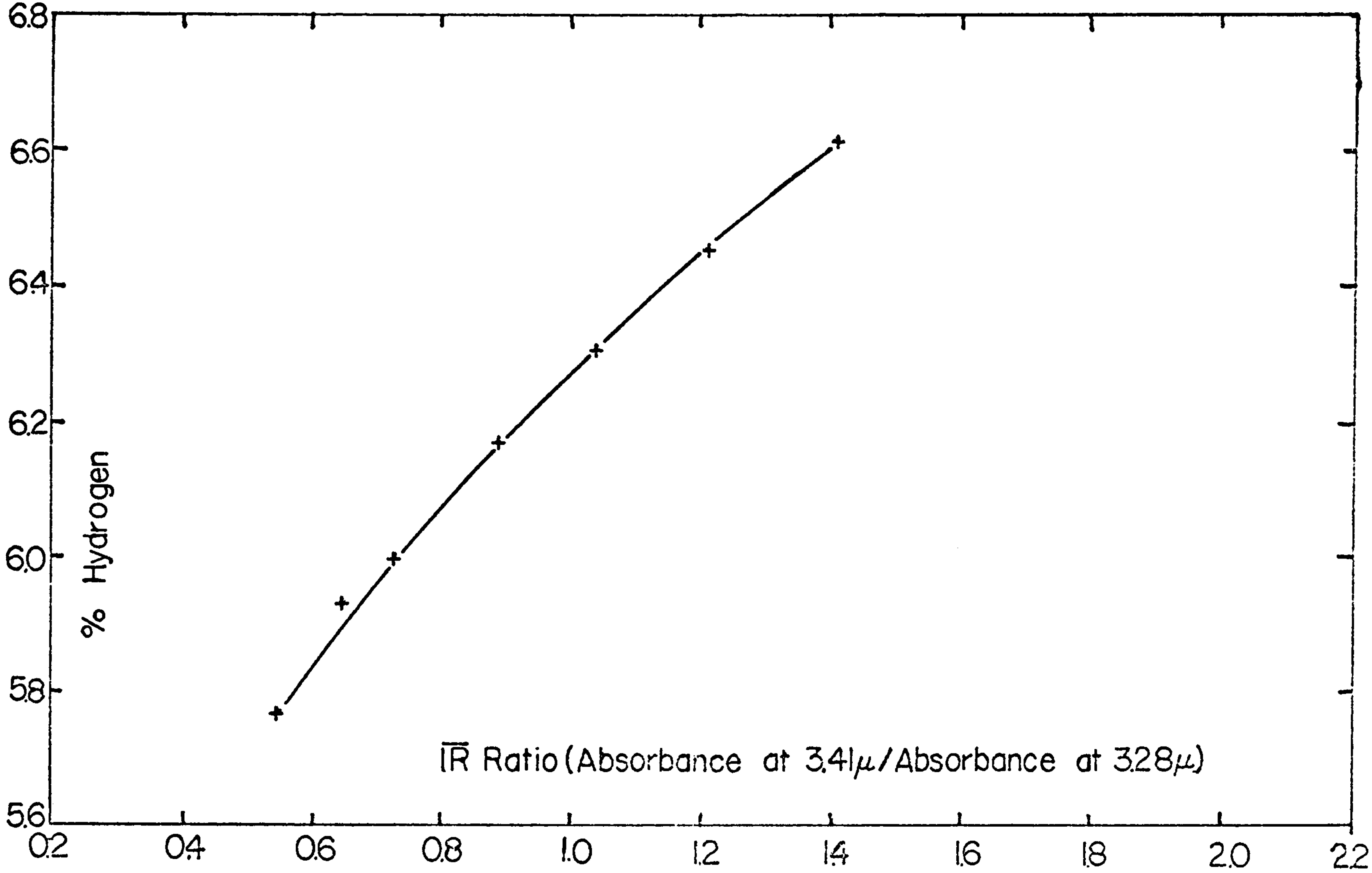
Figure 7

of solvent in a typical solution masks the contribution from the coal to a considerable extent. Results must be regarded as estimates of trends and are useful in rapidly evaluating the effect of a process variable change.

The ratio includes hydroaromatic hydrogen and hydrogen on any saturated radicals as substituents or any saturated hydrocarbons present as diluents in the solvent in the 3.41 micron region. The 3.28 micron region is predominantly due to the aromatic material present. In the anthracene oil derived materials little saturated diluent was ever observed, as most of the oil would readily dissolve in concentrated sulfuric acid. In cut 2 reclaim solvents the saturated oil present was less than a percent by volume and was usually too little to isolate from a sample of reasonable size. Although the increase in hydrogen can be readily observed by means of an $\overline{IR}$ ratio the difference between hydroaromatic and saturated structures was not resolved. In single pass experiments with anthracene oil the changes in ratio were predominantly due to changes in hydroaromatic content. As a solvent is recycled this becomes progressively obscured by saturated radicals derived from the coal. These charts have lately been extended to include solvents derived from petroleum sources and in these materials the population of saturated radicals obscures the hydroaromatic structures completely. It remains a problem to isolate this interesting function in general, though some progress can be made in the limited case of single pass studies with anthracene oil.

This working curve formed the basis for reactor control in the hydrogeneration of raw anthracene oil practiced in Run CL 18. Operating condition changes could be made to maintain about the ratio desired and when an upset produced material which was too far off the desired ratio it could easily be set aside. During the second hydrogenation procedure, conducted as Run CU 40, the same general procedure was used to control the reactor. In this case some operating intervals produced very hydrogenated anthracene oil and some produced a moderately hydrogenated product. These were set aside and were carefully analyzed by infrared and by combustion analysis to obtain reliable data. Two samples and some of the original raw anthracene oil stock were used to prepare blends of well established composition which were analyzed by infrared to obtain spectra for intermediate compositions.

Three samples were selected to be the basis for the new working curve. They were the original raw anthracene oil, a hydrogenated product selected from moderately hydrogenated stock, and a well hydrogenated sample selected from material set aside as over hydrogenated product. Each sample was carefully analyzed for carbon and hydrogen. Blends were then prepared using large sample weights to minimize blending errors. The infrared spectra were recorded for each sample or blend. The $\overline{IR}$ values were computed by dividing the measured absorbance at 3.41 microns by the measured absorbance at 3.28 microns. Data tabulated follows. The working curve is presented as Figure 8.



Working Curve On Perkin Elmer 267···% Hydrogen In Anthracene Oil Versus IR Ratio.

Figure 8

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Working Curve Data $\overline{\text{IR}}$ Values Versus Percentage Hydrogen

Basic Samples			$\overline{\text{IR}}$ Value
A	91.41 ± 0.16	6.341 ± 0.008	1.04
B	91.60 ± 0.08	5.770 ± 0.0001	0.55
C	91.69 ± 0.18	6.603 ± 0.076	1.41
Blend 1		Calculated 6.001	0.73
Blend 2		Calculated 5.933	0.66
Blend 3		Calculated 6.169	0.89
Blend 4		Calculated 6.450	1.21

Data when plotted fall on a smooth curve and this is reasonable because the only errors involved are the normal weighing and spectrophotometric errors. It is somewhat optimistic to expect this kind of procedure to solve reactor product compositions with equal precision, in the usual case the ratio of functional groups may not match exactly and small drifts from an averaged line must be expected. Despite these qualifications the curve has been helpful in inspection of reaction products and is often as accurate as a routine combustion analysis.

IV-D General Procedure for Experiments

Previous discussions have outlined the preparative work required to provide suitable stocks of coal and solvent. The reducing gas was either pure hydrogen, pure carbon monoxide, or mixtures of these two. The gas compression and metering subsystem made provision for preparing mixed gases continuously by compressing gas metered through two separate flow meters and provided by storage bottles of the pure gases. The purchase of mixed gases generally resulted in better controlled compositions than could be obtained by the continuous mixing apparatus. After preliminary experiments with syn gas this procedure was used. The initial step in preparation for an experiment was to fill the compressed gas reservoir with the gas or gas mixture to be used. The back pressure regulator for the calibration system was then adjusted to the desired operating pressure and the metering valve was set to deliver the desired volume of gas per unit of time. Since the adjustment had to be made by trial the gas metering adjustments were made the day before an experiment.

The reactor is normally left filled with flush oil between experiments as it was necessary to flush out the unit before it is cooled to room temperature. This is done to avoid prolonged exposure of coal or solvent to heat and to avoid situations in which the cooling reactor might become filled with partially processed coal or with minerals which might settle and plug the small diameter tubing used in the preheater.

In starting up the reactor for an experiment the heaters are turned on and the flow of liquid through the unit is established by pumping flush oil as the temperatures are adjusted to the values to be used. As the flow of liquid is being adjusted the flow of reducing gas through the unit is also started. Usually the unit can be brought to specified operating temperatures, flow rates, and operating pressures in approximately two to three hours.

Time is available during the initial condition lineout operation to prepare feed slurry. Cans of solvent are placed in a drying oven for use in preparation of solvent. The temperature varies with the kind of oil to be used. This temperature is usually 75 to 100 degrees centigrade. Raw anthracene oil contains crystalline material and must be heated to melt all solids before use. The oil in each can is thoroughly mixed before any material is removed, and partially used cans of oil are kept warm until used or reheated and remixed if allowed to cool to room temperature. Oil for use as flush solvent is taken from the same stock as solvent to be used in an experiment and is handled in the same way. In preparing slurry a stainless steel beaker is weighed and oil is added to the desired weight with a precision of about one gram in total weights of two to four kilograms. The charge of coal is weighed with similar precision, and is carefully scooped into the beaker containing the oil. A spatula is then used to stir the powdered coal into the oil and to work the air out of the wetted powder. Considerable air is mixed into the slurry as the coal is added, and this air must be eliminated before the high pressure pump can perform reliably. Air is partly removed by stirring the warm slurry for about half an hour using a motor driven stirrer at a moderate rate of stirring. Air is more fully eliminated by heating the slurry above operating temperature then allowing the slurry to cool to the desired temperature.

The temperature of the feed slurry has an important influence on the behaviour of the high pressure feed pump. This is because the viscosity of the oil determines the size of the opening between the ball check and the seat as the pump head operates. In working with raw anthracene oil the lower limit for slurry pot temperature is determined by the limit at which the oil may tend to crystallize. Otherwise the temperature is adjusted to obtain a viscosity which favors smooth operation of the ball checks in the pump head.

In long experiments it may be necessary to make several batches of slurry and to replenish the material in the feed pot when the remainder is reduced to a low level. This can be done without interruption of the high pressure pump or without upsetting the feed rate if the slurry is brought to a matching temperature. Additions must be made with reasonable care in order to avoid mixing air bubbles into the slurry. This is facilitated by making the addition before the level of the residual slurry is too low. Generally an effort is made to add makeup slurry with heels in the feed pot no smaller than two kilograms.

At the end of the condition lineout period the feed slurry is substituted for flush oil and the timed part of the experiment is started. It should be noted that considerable time may be required before the product taken from the reactor will be representative of equilibrium solution at the conditions used. Initially the product is mixed with flush oil and back mixing is evident,causing a progressive dilution of product by back mixed flush oil. Several reactor volumes of material are to be made before this flush oil is eliminated from the sample.

During the first experiments observations of product composition and physical properties were made in an effort to establish the time or the product volume which should be used before valid samples could be taken. As a result of these studies a rough rule was used, that four reactor volumes should be discarded before the timed sample for analysis was taken. Later studies on mineral equilibration suggested that perhaps this is not enough lineout for the most exacting work. In principle, the procedure followed required that material be made and discarded until a reasonable chance existed for obtaining a valid sample. This sample is then drawn for a timed interval and a gas sample is also taken for a timed interval during collection of the liquid sample. After completion of the sample the operating conditions are changed to the next set to be studied and a new lineout interval is started. In typical experiments a lineout interval of four or more hours should precede each sample interval. An effort should be made to study several operating condition sets before shutdown.

In a shutdown the feed slurry is replaced by flush oil and pumping of flush oil is continued as the unit is allowed to cool off. Gas flow is maintained until the unit is cooled below a temperature at which appreciable reaction could take place and then the gas flow is stopped. Pumping of flush oil is continued until the reactor temperature is below 200 degrees centigrade.

During the time that flush oil or reactor lineout slurry is pumped the product from the reactor is collected in the slop vessel. Liquid sample collection requires only that the air operated valve be activated in order that the flow of product be diverted from the slop vessel to the stainless steel flask used as a sample collector. After time has been allowed for the gas flow to flush the air out of the sample flask, the valve to the gas collection bag is opened and the valve to the vent line is closed.

At the end of a timed interval the line to the gas sample bag is closed and the vent line is opened. The gas sample bag is removed from the system and taken to the laboratory for the gas analysis procedures. The flow of liquid product is diverted from the sample flask to the slop vessel at the end of the sampling interval. In the preferred procedure the liquid sample is collected for several hours and the gas sample is collected for a half hour to one hour during the last portion of the liquid sampling interval.

During an experiment the unit operator is required to record certain data. The feed rate is measured by recording scale readings at 15 minute intervals and the rate is computed on an hourly rate basis. If necessary, minor adjustments of feed rate are made by changing the stroke length of the piston in the high pressure feed pump. The temperatures for the preheater and the dissolver are recorded continuously and may be adjusted by minor changes in variac or controller settings. Pressure readings across the metering valve are recorded continuously and the operator is required only to confirm that the values remain the same as those used to calibrate the gas flow. At the beginning of a timed sample interval the operator must confirm that temperature configuration, operating pressure and pressure differential across the metering valve, and slurry feed rates are all within tolerance and at the values specified for the experiment.

A feed slurry sample is taken from the recycle loop just before the timed interval. The pressure and volume reading for the nitrogen purge is recorded from observations made of the Ruska pump gage and scale readings. The weight of slurry in the feed pot is noted and the air operated valve is actuated at once to start slurry collection. The time for sample start is recorded. After an interval, allowed to flush air out of the sample collection flask, the gas sample is directed into the gas collection bag. This time is noted and recorded. After the desired interval, the valve to the gas bag is closed and gas from the sample flask is allowed to vent. The time at which gas sample collection ended is recorded in the log. The air operated valve is then actuated to stop liquid sample collection and the time is noted in the log. The readings for pressure and volume of nitrogen in the Ruska pump are noted. Finally, another slurry sample is taken from the slurry feed loop. The flask containing the liquid sample is removed from the system, stoppered, and taken to the laboratory for analysis. The water collected in the knock out vessel in the gas sampling line is drained into a weighed bottle. The bottle is weighed to determine the weight of knock out vessel product.

The input of material to the reactor is thus taken from the difference in slurry in the feed pot at the start and at the end of the timed interval. The input of reducing gas is calculated from the timed interval and gas calibration data generated just before the run was started. If operating pressures differ from those used in the calibration by readable amounts, the input gas must be calculated from these readings. The volume of purge nitrogen is measured at gage pressure from the initial and final readings of the scale on the Ruska pump. The sum of the weights of slurry and reducing gas plus nitrogen will be the total input.

The total output will consist of the liquid sample in the stainless steel flask. the gas sample in the rubber bag, and the knock out vessel liquid. The weight of gas can be determined from the molecular weight and volume of gas collected. This must be calculated to the weight which corresponds to the output over the same time interval as the liquid sample. These items should account for all of the slurry and gas fed to the system. These closures are presented for raw data in Appendix A. The data presented are gas volumes in moles and the molecular weight of the gas. The output of product includes any water or oil from the knockout pot.

IV-E Laboratory Procedures for Reactor Control

One of the objectives throughout the continuous reactor program has been the development of laboratory procedures which could be used to confirm that the feed slurry was the correct composition and that it could be fed into the reactor with uniform composition. The same problem existed for feed gas when mixtures of carbon monoxide and hydrogen were prepared from separate storage cylinders. It is considered essential to develop methods which can rapidly evaluate product solutions with regard to uniformity of composition and the effect of the solution reaction. This technology is needed to determine the time needed to produce lined out solutions in the laboratory, and the methods' are expected to find application in the pilot plant as well. These determinations, which are done rapidly while the reactor is being operated, have loosely been described as reactor control procedures. In most cases no correctionsof operating conditions have been based on such measurements although it is expected that with sufficient experience such results might become the basis for control decisions.

IV-E-1 Analysis of Feed Slurry

It is assumed that a feed slurry will be prepared from a well characterized solvent and from a coal which has been ground to a controlled particle size distribution. Each component should have been analyzed to establish the composition of the materials used. If each component is accurately weighed there is then no reason to suppose that the initial average composition should be in error. Unfortunately, there is still the problem of maintaining a uniform slurry for an extended period of time and to draw this suspension down to small residual volumes without affecting the average composition fed. If any component is systematically lost during this time the average composition will drift during the experiment. Three general problems have been investigated. They are settling of coal or coal and mineral phases in the feed vessel, evaporation of water from the feed vessel, and evaporation of solvent from the feed vessel. The following procedures have been used to study these questions.

IV-E-1-(a) Method for Determination of Ash in Feed Slurry

The simplest way to estimate the amount of coal in a slurry is to draw a weighed sample from the slurry recycle loop and to ash this to measure the mineral content of the slurry. A sample may be drawn conveniently by quickly passing a weighed platinum evaporating dish through the return stream to the slurry feed pot to collect about 5 to 10 grams of slurry. The dish and sample are then reweighed on an analytical balance to determine the exact weight of slurry taken. The dish is then placed on a sand bath which is heated by means of a low flame from a Fisher burner. The oil can be evaporated without being ignited if the flame is properly adjusted, burning the oil does not seem to introduce a significant error. After most of the volatile material has been removed the dish is placed just inside the door of a muffle furnace adjusted to operate at $750^{o}C$. In this location most of the residual oil and the organic matter in the coal will burn off without igniting. After a short time the dish can be moved to the back of the furnace to ignite the residual ash. If a deep ash layer is observed it is helpful to stir the ash with a platinum wire to bring any unburned carbonaceous matter to the surface. When ignition is complete the dish is removed from the furnace, cooled, and weighed. The percentage of ash in the feed slurry is reported. When the slurry is well suspended this result will be the percentage of ash in the feed coal times the fraction of coal in the slurry. Thus for a 2:1 solvent to coal ratio the ash should be 1/3 of the concentration in the feed coal.

Comment:

In cases where coal or mineral tends to settle out in the feed pot the first slurry samples taken tend to run below theory in ash. As the slurry is used up the slurry samples taken tend to increase in ash with the final samples running above the theoretical value. It should be noted that the slurry feed pot may have a layer or a cone of solids at some point where stirring is not sufficient to suspend the larger particles.

There is no reason why mineral matter and the organic matter in the coal must behave similarly. Inspection for ash is indirect evidence for discussion of the behavior of the organic phase in the coal. Attempts to measure the coal by filtering samples and washing the coal with reagents to remove the solvent have met with little success. No dependable reagent system has been devised, and it is less dubious to reason from the behavior of the ash than to try to cope with the rough data resulting from the attempts to recover, wash, and dry the coal. It is reasonable to assume that if the mineral suspension is uniform that the organic phases of the coal will be equally well suspended. The method has allowed mechanical improvements to be evaluated and uniform suspensions are now normally obtained.

IV-E-1-(b) Method for the Determination of Water in Feed Slurry

The Karl Fischer method for determination of water can be readily adapted for use in the analysis of water in feed slurry. The slurry is sampled by inserting a small bottle into the return stream from the slurry recycle loop. Samples should be from ten to twenty grams in size. The bottle is capped with a polyethylene lined cap and is reserved for analysis.

The whole sample taken must be used for the analysis since the water will usually be associated with the coal phase and this will settle out of the suspension rather quickly. The bottle may be weighed before filling or may be weighed back after complete wash out of the sample depending on the convenience of the operator. In either case the bottle plus sample must be weighed accurately on an analytical balance. A clean dry 200 ml volumetric flask is placed in the hood with a powder funnel or a suitable short stemmed funnel in the neck of the flask. The sample is transferred to the volumetric flask by use of a stream of dry pyridine from a wash bottle. When all coal particles and solvent have been transferred, the funnel is carefully rinsed and then is removed from the neck of the flask. The volume of the solution is then brought exactly to the line by adding dry pyridine. The flask is stoppered and the solution is mixed thoroughly and allowed to stand for an hour or so to extract the water from the coal. This procedure appears to effectively remove water from lignite or subbituminous coal as well as the water which may be added to solvent. If the bottle is to be weighed back after transfer of the sample it should be rinsed with acetone and air dried for a few minutes before weighing. Because of the large sample size taken these weighings need to be reproduced only within a few milligrams.

Reagent grade pyridine is available in several grades which may vary appreciably in water content. If a choice between lots is possible the material with the lowest water content is selected for this procedure. The Karl Fischer reagent should be diluted to a titre of one or two milligrams per milliliter. It is necessary to titrate a 25 ml portion of the pyridine to determine the water blank for the reagent. If this is larger than a few milliliters of reagent it is necessary to dry the pyridine. This can be done most conveniently by passing the pyridine through a column of molecular sieve. A suitable apparatus for this procedure consists of a 30 inch length of one inch ID. tubing sealed to a flask which will hold two liters of liquid. The lower end of the column should be closed by a Teflon stopcock. The tube should be filled with Linde type 4A molecular sieve. The reservoir is filled with reagent grade pyridine and the stopcock is adjusted to allow the pyridine to trickle through at 5 ml. per minute. The dry pyridine is collected in a clean dry reagent bottle. A column of well activiated molecular sieve of this size will process an eight pint reagent bottle of pyridine. The reagent blank for the dry material should be 2 to 3 ml. of Karl Fischer reagent for a 25 ml portion of the dry pyridine.

IV-E-1-(b)

The coal sample solutions to be titrated are dark colored, it is necessary to use an electrical device to locate the end point. A conventional dead stop indicator is satisfactory for this purpose. It is necessary to dilute the original sample in a volumetric flask, to mix thoroughly, and after a time to take an aliquot for dilution in a second volumetric flask. Obviously various combinations of aliquot and volumetric flask volumes may be used to obtain suitable samples for titration. It is difficult to draw samples within narrow weight ranges and variation in sample size must be compensated for in the dilution sequence or in variation in the amount finally taken for titration. There is a risk that the powdered coal will plug the tip of a small pipet and precision is improved by the use of larger volumes, consequently it is wise to plan dilution sequences to use 5 ml pipets or preferably 10 ml pipets as the smallest measuring apparatus in the dilution sequence.

The following paragraphs include details which may be used as a basis with this method. Changes in detail will be needed to adjust the method for different sample sizes or water concentrations.

Example of Detailed Procedure for Karl Fischer Analysis of Water in Feed Slurry

This method is an adaptation of the Karl Fischer method for titration of water. It uses a dead stop indicator and commercially available Karl Fischer Reagent. The reagent is put into an automatic buret (25 ml capacity) and the titration vessel is stirred by a magnetically driven stirring bar. Coal slurry is diluted with reagent grade pyridine. An aliquot of this solution is titrated. This procedure is scaled for slurries containing about 10% of water.

Reagents:
- a. Karl Fischer reagent (Fisher Scientific Co. SOK 3)
- b. Karl Fischer diluent (Fisher Scientific Co. SOK 5)
- c. Reagent grade Pyridine (low water content or dried over mol sieve)

Apparatus:
- Automatic Buret - 25 ml capacity with 1 liter reservoir
- Dead stop indicator and platinum electrodes
- Magnetic stirrer and Teflon coated stirring bars
- 3 neck standard taper flask - 200 ml round bottom or equivalent air tight titration vessel.

Procedure:

a. Weigh a clean dry sample bottle with cap which will contain 20 ml of liquid. Record the weight. With the slurry recycle pump running, collect about 10 to 20 grams of slurry. Cap the bottle and reweigh to determine the amount of sample taken.

b. Dilute the slurry with dry reagent grade pyridine and transfer quantitatively to a 200 ml volumetric flask. Fill to the mark with dry pyridine and stopper the flask. Mix the contents of the flask thoroughly and allow the flask to stand with occasional remixing for about an hour. Allow the powdered coal to settle out after the final mixing.

c. Put about 75 ml of the Karl Fischer diluent in the titration vessel and titrate until the microammeter of the dead stop indicator reads a constant 50-60 microampere current. Pipet 25 ml. of the dry pyridine into the titration vessel and titrate with the Karl Fisher reagent to establish a blank for the pyridine. The end point is taken when the same indicator current is obtained as originally used to pre-titrate the solvent.

d. Use a 10 ml pipet to transfer solution from the 200 ml volumetric flask to a 100 ml volumetric. Dilute with dry pyridine and adjust to the mark. Mix thoroughly.

e. Transfer 10 ml of the solution from the second flask to the titration vessel and titrate to the same indicator current used to pre-titrate the solvent. Depending on the exact water content the aliquot which can be titrated with one buret of reagent may allow the use of a larger pipet. With a titer of 1.0 mg of water per ml. the 10 ml pipet is a suitable volume assuming the original sample contained 10% water.

f. The reagent blank must be calculated in proportion to the sample taken for titration compared to the 25 ml. portion of dry pyridine used in the blank determination. Since the same pyridine is used for all dilutions its contribution to the water content remains constant in concentration. Thus the water content of the solvent is proportional to the sample taken.

Standardization of reagent:

Weigh a 200 ml volumetric flask on an analytical balance. Add about 250 milligrams of distilled water. Stopper the flask and reweigh to determine the exact weight of water taken. Dilute to the mark with dry pyridine and mix thoroughly. Titrate 10 or 15 ml aliquots of this solution, adding the solution to pretitrated solvent as described in the determination above. Calculate the titer in milligrams of water per ml of reagent.

$$\text{Titer} = \frac{\text{Weight of water taken}}{(\text{Ml of reagent - ml of blank})} = \frac{\dfrac{(\text{Total wt. of water})\ \text{Vol S}}{200}}{(\text{Vol Reagent - Vol of blank})}$$

Where Vol S - ml for titration

IV-E-1-(b)

Calculation of sample

$$\%H_2O = \frac{(\text{Vol of reagent - Vol of blank})(\text{Titer})(100)}{\text{Sample size in milligrams}}$$

Note: Sample size is $\dfrac{\text{Total Sample } (V_1)(V_2)}{(F_1)\ (F_2)}$

Where V_1 and V_2 are pipet volumes taken and F_1 and F_2 are the sizes of the volumetric flask used in the dilution sequence.

IV-E-1-(c) General Inspections of Feed Slurry

The density of feed slurry can be determined by drawing a sample from the slurry recycle loop into a volumetric flask and reweighing to determine the weight of slurry needed to fill the flask to the line. This has also been estimated by measuring the density of separate components by classical procedures and calculating the slurry density assuming no interaction between solvent and coal at the low operating temperatures which are used for feed slurry. Near room temperature this density is approximately 1.15 grams per cc. As the slurry temperature is increased the solvent becomes less dense. Expansion decreases the slurry feed density to about 1.14 at 50°C., with density decreasing to about 1.12 grams per cc at 90°C.

Another consideration in measuring feed slurry rates is the tendency for some of the lightest oil to evaporate from the feed pot during the extended periods of time needed to produce a sample. This oil is continually stirred and the recycle stream passes through air and is allowed to run back into the feed pot by trickling down the outside of the feed siphon line. Unfortunately, this procedure favors evaporation of the lightest fraction of the oil and removal of the most volatile fraction and has been standard practice in solvent preparation. It is obvious that some part of the weight loss recorded on the feed scale must be material which evaporates instead of being pumped through the unit. Solvent stocks have been tested for evaporation rates by placing a few grams of solvent in a weighed platinum evaporating dish and reweighing the dish and oil from time to time after exposure to air drafts or exposure in drying ovens at slurry feed temperatures. Such tests indicate that from 0.24% to 0.50% of the weight of slurry recorded as fed may in fact have been oil which evaporated from the feed pot. The rate of evaporation of water from the feed pot can be determined by means of the Karl Fischer method for water analysis. The means are available for estimating certain systematic errors in the slurry feed weights.

IV-F Methods for Reactor Lineout Control

One of the general 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 indicate when the product was equilibrated with feeds and the effect of reaction conditions. A general program of product inspection was initiated with the objective of selecting several measurable functions for use in such comparisons. The first procedure selected for study used the infrared spectra of the unfiltered product as the basis for evaluations. At the same time it was found that the colored material in the coal solution could be dissolved and that measurements in the visible region could be used to follow the build-up of dissolved coal in the reactor product stream. Studies were also based on the measurement of ash concentrations in the reactor product. It has been observed that some of the gaseous reaction products should be useful materials for such studies.

IV-F-1 Observations of Lineout by Means of Infrared

In early studies with the continuous reactor it was observed that the infrared spectrum of a coal solution contained several bands which were altered in relative intensity compared to the same bands in the initial solvent. The only band not present in the solvent but observed in the unfiltered solution was due to the presence of water in the raw product. It was observed that the absorbance ratio of bands at 3.28 and 3.42 microns changed in the product solution from the ratio of these same bands appearing in the solvent. It was observed that this change occurred progressively after the switch from flush solvent to feed slurry.

When a drop of unfiltered coal solution is placed between two rock salt plates it is possible to form a thin bubble-free film which is suitable for use as infrared specimen. Care must be taken that the film be of reasonably uniform thickness and that no water droplets or unusual amounts of mineral matter be present in the area in the sample beam. Mineral matter causes absorption of light in the 2.5 to 6.0 micron region of the infrared spectrum which causes an upward sloping baseline in this region. The presence of water introduces a broad absorbance which is centered on the 2.95 micron region. Despite these complications, the bands at 3.28 and 3.42 microns are resolved and can be measured with reasonable accuracy. By convention the absorbance has been measured from a baseline drawn from 2.6 microns to 4.8 to 5.0 microns. This includes some upward slope due to the presence of mineral matter but this factor is usually about the same from sample to sample. For comparison of samples the ratio of absorbance for the 3.42 micron band divided by the absorbance at the 3.28 wavelength is computed. In lineout studies the ratio (called $\overline{IR}$ hereafter) is plotted as a function of operating time.

IV-F-1

Generally in the work done with anthracene oil as solvent the experiments have been done in a single pass mode. The change observed corresponds to the effect of one pass of solvent through the reactor. Only in run CU 49 has any effort been made to extend the observations by recycling material through the reactor several times. However, even a single pass of solvent and coal through reaction results in an appreciable change in the composition of the solvent. The work done with anthracene oil has been useful in developing methods for observing these changes and for developing experience relating the effect of changing operating conditions.

In experiments starting with raw anthracene oil as solvent, the $\overline{IR}$ ratio is smaller in the initial flush oil than in the lined out sample. This results from the tendency for the raw solvent to become hydrogenated during the reaction. The material added to the solution from the dissolving coal also tends to add hydrogen components to the solution. During experiments of this kind the $\overline{IR}$ value for a coal solution will increase from an initial value of about 0.56 to a final value of approximately 0.75. The final value changes in response to operating conditions and is useful in evaluation of the effect of such variables. For this reason the lined out value has been recorded in Appendix A for each of the samples made.

In experiments with well hydrogenated solvents the initial value of $\overline{IR}$ may be higher in the flush oil than the value observed when the coal solution has been lined out at operating conditions. This is particularly true of those solutions made at higher temperatures or at short retention times. Initially it was hoped that the $\overline{IR}$ values could be related to transferable hydrogen functions in the solvent. For anthracene oil, and hydrogenated anthracene oil this is roughly the case for single pass experiments. It is apparent that as coal derived oil is added to the system that a significant amount of saturated structure is introduced. These quickly accumulate in amounts which interfere with the observation of the hydrogen transfer reactions. As a result it is not possible to resolve the hydroaromatic contributions from the contribution of the saturated functions present, given only infrared spectra as a basis for the analysis. This situation is less severe with anthracene oil as solvent and the results of the anthracene oil experiments are more useful in developing an intuition about the transfer reactions than is likely to be the case with other solvents.

With the observation that raw anthracene oil gained hydrogen as it was run through the process with coal it became evident that part of the hydrogen consumed must be spent in treating the solvent. It was reasoned that the reaction rates and the yields should be influenced on recycle as this hydrogen would not have to be replaced in the solvent for the second pass. When the CL 18 solvent batch was made it was necessary to estimate the amount of hydrogen that should be added in order to approximate the effect of a single pass through the coal dissolver. This was necessary as the techniques for evaluating samples from previous continuous pilot plant studies had not been perfected. Although retained samples were available with considerable information about the effect of solvent lineout and recycle, such information was not fully understood. The hydrogenation in CL 18 was adjusted to produce a composition with an $\overline{IR}$ value of approximately 1.0 for the product.

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During the series of experiments with this solvent it was determined that this was more transferable hydrogen than was likely to be reacted with the solvent, especially with short retention times and particularly if the temperature were high enough to facilitate efficient removal of oxygen and organic sulfur from the coal product.

The next hydrogenation was adjusted to a lower percent hydrogen in Run CU 40. The values chosen for publication were selected by plotting the trend of the $\overline{\text{IR}}$ as samples were made and only the final value or the lined out values averaged for several observations were accepted. This required that studies be made to determine the operating time needed to make these results reproducible. There were several limitations on reproducibility which should be mentioned. First, the feed slurry in early experiments tended to separate solids which may have caused misfeed of coal in the order of 5 to 10 percent relative through the course of an experiment. This has improved until the settling of solids is now virtually eliminated as a cause for variation in product composition or properties. Second, the effect of backmixing and retention time in flowing through the reactor was not known in early experiments and only accumulated experience allowed selection of data that should have been lined out. Third, as experience accumulated it became clear that the mineral phase in the coal exerted a catalytic influence on product composition, the settling of mineral in the reactor causes long swings in reactivity as minerals settle then classify by gravity separation processes. In this condition the reactivity oscillates periodically and a lined out reactor can be expected to produce slightly different composition product from time to time in response to this mechanism. This can be observed in the $\overline{\text{IR}}$ data derived from experiments. In studies in which the solvent has been returned to the reactor for repeated reuse, the composition of the solvent is progressively altered by the addition of oil from the coal and by the thermal decomposition of the original solvent. The observation of $\overline{\text{IR}}$ values has also been useful in recording these long term changes although little data of this kind were developed in the anthracene oil experiments. Only the slurry recycle experiment CU 49 has been operated in a mode which brings such considerations clearly into account.

IV-F-2 Observation of Lineout by Means of Visible Spectrophotometry

During the autoclave studies a procedure was investigated for estimating the amount of solution imbibed in a wet filter cake by measuring the color of a solution prepared by extracting the wet filter cake with pyridine. It was an extension of this work to investigate the absorbance of light by dilutions of coal solutions themselves in pyridine. This led to a systematic program in which coal solutions were sampled and weighed samples were dissolved in pyridine, diluted to known volumes, and the visible range spectrum of the filtered solution was recorded. It was determined that the absorbance at the 400 nanometer region was high while the absorbance declined along a smooth curve through the visible region, the absorbance at 700 nanometers being about 1/3 the absorbance at 400 nanometers. The relative intensity at various wavelengths does not change greatly from solution to solution. It was decided to make one point observations at 550 nanometers, the choice of wavelength being arbitrary. It was determined that the absorbance could be measured readily and that solutions obeyed Beer's law. This provides a rapid method for measuring a property of a coal solution which relates to the concentration of coal dissolved in the solution. The color can be related to the absorbance by a colorimetric factor to yield the concentration of coal in solution.

During lineout studies the color initially due to the solvent was very weak compared to the intense black color of the coal solution. Samples were taken during the period following the change from flush solvent to slurry and the color did increase in a smooth curve from the trace absorbance of the solvent to the intensely black color of the coal solution. The color was measured by making volumetric dilutions to produce optical densities within the range measurable with a Bausch & Lomb Spectronic 20 spectrophotometer. Results were then computed to the same basis by calculating the absorbance per gram of solution per 100 ml of pyridine. These units have been used since the initial series of measurements and the numerical values are convenient for comparison of coal solutions obtained in different ways.

Method for the Determination of Visible Absorbance

Apparatus and Reagents:

Analytical balance
Volumetric flasks 100 ml, 200 ml, 250 ml
Reagent grade pyridine
B&L Spectronic 20 Spectrophotometer and ½ inch square cuvettes or equivalent
Whatman GF/A glass fiber filter paper
Small beakers, 50 ml, 100 ml
Stirring rods, droppers and pipettes

Procedure:

a. Weigh a small clean dry beaker accurately on the analytical balance. Using an appropriate dropper or stirring rod, transfer a few small drops of the coal solution sample to the beaker. Determine the exact weight taken. The sample should be 0.050 to 0.075 grams for a lined out 2:1 solvent to coal solution. The sample should be diluted with pyridine.

b. Transfer the beaker and sample to the HOOD and add reagent grade pyridine (30-50 ml). Stir with a clean stirring rod to dissolve the sample. (A bright light source is helpful in observing the complete dispersal of the sample.)

c. Transfer quantitatively to a volumetric flask of suitable size. Allow about 100 ml for each 50 to 75 mg of sample solution taken. Rinse the beaker clean with fresh pyridine and add rinsing to the flask. Dilute the solution in the flask with pyridine until the solution is adjusted to the line. Stopper flask and mix thoroughly.

d. Filter a portion of the solution through a Whatman GF/A filter paper to remove any insoluble material. Fill a 1/2 inch square cuvette with this solution.

e. Set the spectrophotometer at 500 nanometers. Fill a ½ inch square cuvette with reagent grade pyridine. Adjust the instrument to read zero transmission with the shutter closed, then insert the cuvette of pyridine. Adjust the instrument to read zero absorbance with the pyridine in the light beam.

f. Replace the reference cell of pyridine with the solution to be measured. Record the absorbance reading.

g. Calculate the absorbance per gram of coal solution per 100 ml of pyridine. This value is defined as the BLACKNESS of a coal solution. The term results from the fact that these solutions absorb an appreciable amount of light at any wavelength in the visible region and appear black when inspected visually.

$$\text{BLACKNESS} = \frac{\text{Optical Density (flask size in ml)}}{\text{Sample size in grams (100)}}$$

COMMENTS:

The spectrophotometric studies (BLACKNESS measurements) were developed in an attempt to achieve a rapid analysis for the concentration of dissolved coal in a product solution. This can be done within carefully defined operating condition sets but is not practical as a general analytical procedure. The difficulty is the result of the color intensity reduction resulting from reaction with hydrogen and the tendency for exposure to high temperatures to cause the solution to become darker. 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 and depolymerization-repolymerization reactions. Within observation limits it is one of the most sensitive indexes which can be used to investigate the state of the product from the reactor. It has been useful in studies of lineout and product uniformity.

When vacuum bottoms are fractionated by the successive application of solvents, the colored fractions are found to be soluble in the more polar solvents such as acetone or the more effective solvents such as pyridine. The material which is insoluble even in acetone but is soluble in pyridine will be the most intensely colored. From observations freshly depolymerized coal fractions small enough in molecular weight to be soluble will be the source of most of the colored material. In the same fractions freshly repolymerized products may also be highly colored. Should this be the case, BLACKNESS could be expected to indicate optimum coal solutions at some intermediate values which have not been well established. In the initial stages of solution of coal the low color intensity is due to incomplete solution of the coal. After a time a value representing high levels of MAF conversion can be observed. As reaction times and temperatures are extended unduly and repolymerization becomes a factor BLACKNESS values will increase as a consequence. The analytical procedures or separation techniques needed to fully elucidate these conflicting reaction courses are not presently available. For a given set of materials and operating conditions the color of the solution is reproduced within narrow limits and changes in operating conditions results in systematic changes in color. Since this property is easily measurable it has been used as a routine observation for assessment of the effect of reaction parameters on the coal solutions.

IV -F-3 Observation of Lineout by Means of Ash Analysis

One criterion for a fully lined out product would be that the concentration of mineral in the product should account for all of the mineral fed into the reactor. Studies were conducted on several occasions to determine the time required for this condition to be established. Sampling is difficult since the mineral in the product solution normally settles out and resuspending the mineral well enough to obtain representative samples is questionable. It is considered reasonable to filter the whole of the product sample and to ignite the residue to determine the ash present. This also presents problems since the finest mineral matter may pass through a fine analytical filter paper. First samples out of the reactor have a larger proportion of such mineral matter and are difficult to process by filtration with reliability.

To date the best procedure is to collect a reasonable volume of sample which can then be warmed and properly stirred while subsamples are removed for ash analysis in the same manner used for feed slurry analysis. When precise duplicate values are obtained this is reasonable evidence for the reliability of the samples ashed.

Some runs were conducted by collecting small liquid samples at frequent intervals in order to follow the build-up of mineral matter in the product. This procedure allowed integration of the mineral matter fed, using the results of feed slurry analysis, and integration of the mineral in the product, using ash analysis of the reactor product. It became apparent that a significant amount of mineral settled in the dissolver vessel. and that the time required for equilibration of mineral could readily differ from time required for equilibration of the organic phases. This would be of little consequence if the mineral matter were free of catalytic effects. Tests indicate that iron concentrations in the feed coal are significant in influencing the reaction with hydrogen, and that mineral settling may build up concentrations of iron in the dissolver which do not reach final concentrations for appreciable periods of time. Several reaction characteristics can be explained if this is the case.

It is undetermined if the clay minerals or alumina containing minerals associated with coal have any influence on hydrocracking of solvent or coal products in the reactor. Observation of such activity in the minerals associated with coal probably would not be a surprising result. This area has not been properly investigated. In work with carbon monoxide it is clear that alkaline components of the lignites function as water shift catalysts. Such material is not present in Kentucky No. 11 or No. 9 coal tested, yet a water shift reaction is still observed. This activity may be due to the iron present. Since iron is also present in lignite the chance for mixed shift and hydrogenation catalyst activity in the mineral phase seems probable. These considerations, when qualified by the complications due to mineral classification in the dissolver, lead to some difficulty in defining the time needed to completely line out a reaction. Depending on the behavior of the mineral phases, and the amount of build-up of species which influence the course of the reaction, this classification may result in very long term changes in the reactivity of the system.

During the course of experiments with the continuous reactor the data for $\overline{\text{IR}}$, blackness, concentration of ash in the feed slurry, and selected gaseous components have been plotted routinely. It can be observed that the values for $\overline{\text{IR}}$ and blackness vary in a cyclic way after the time required for an approximate lineout of mineral has elapsed. Often the blackness will decline and the $\overline{\text{IR}}$ value will increase in syncronization and then the blackness will increase while $\overline{\text{IR}}$ will decrease. There are indications that these observations relate to the cyclic accumulation and overflow of minerals in the dissolver. It should be noted that cyclic variations often follow long term slopes which could be explained by the classification of some of the mineral phases. These suggestions have not been carefully worked out by analysis of minerals fed and minerals recovered. The discussion is based on the correlation of infrared and visible spectrophotometric results and may have other causes. Temperature control and feed rates were stable in the experiments and do not appear to be reasonable causes for the observations.

When the mineral phases behave as postulated the operating characteristics of a dissolver will depend somewhat on a complex set of variables which are not readily reduced to a model. The particle size of the mineral fed becomes one of these variables, while the viscosity and upward flow rate of the liquid in the dissolver become other variables which are also operating. Since the pyrite is converted it will likely break up to form smaller particles. Little is known about this parameter. The flow of gas through the dissolver will produce some turbulence or eddy current effects. It is doubtful that observations in the laboratory unit will scale up to larger vessels. The temptation to study long term behavior of mineral matter in the small unit has been tempered by the prospect that the detailed results would be academic rather than practical. It is sufficient to have methods available for use with the pilot plant if this observation is repeated with larger equipment.

IV-F-4 Observation of Lineout of Gaseous Product Composition

During the work with anthracene oil the gas analysis was mostly by gas chromatography supplemented by a volumetric method for determination of hydrogen sulfide. Molecular weights were not usually determined separately but were calculated from the gas chromatographic analysis, which normally accounted for the sample presented reasonably well. In general the composition of the gas was not followed through lineout or for extended periods of time. Recently it has been observed that this is an excellent method for following lineout since the appearance of hydrogen sulfide and its change as a function of operating time follows a repeatable pattern. Other gaseous products also have characteristic yield patterns which may be the result of lineout parameters.

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The concentration of carbon dioxide appears to be sensitive to the cyclic behavior of the reactor. Yields of hydrocarbon products such as methane relate to operating temperatures and appear to be derived more from solvent than raw coal.

In the coal solution the conversion of nitrogen in the solvent of the coal to ammonia does not proceed very rapidly. The small amount of ammonia made is mostly dissolved in the water phases which accumulate with the liquid product or in the knockout vessel. The water which is recovered contains dissolved ammonium carbonate and ammonium sulfide and on standing will yellow as the result of polysulfide formation. When reduction conditions become more severe the gaseous products begin to show indications of ammonia, which is readily measurable in the infrared spectrum of the gas. This is the excess of NH_3 gas over the amount which dissolves in the aqueous phases. Since the yield of hydrogen sulfide tends to increase at the same time that ammonia tends to increase, the concentration of NH_4HS which dissolves in the water will also increase. The response in gas composition does not relate directly to pyrite fed, organic sulfur fed, or the amount of conversion produced. These observations account for some of the difficulty in making complete element by element balances since the time required to line out the composition of any given component needs to be satisfied in samples taken.

The concentration of gaseous products from the reactor will depend considerably on the behaviour of the product letdown apparatus. In this regard the compositions from the laboratory unit would be different from the pilot plant as the result of flashing product at different temperatures and separating product in different cooling and depressurization schedules. Continuous reactor experience with lineout will be helpful and its proper adaptation to the pilot plant may explain observations which would otherwise be confusing. If long term drifts in reactivity or yield are evident the result should not be discounted or innocently blamed on erratic controls or poor analytical results. For the most part these drifts have tended in the direction of product improvement. It has not been established that this will always be the case although in observations with the laboratory unit product quality has improved as time on reaction has been extended. The tendency has been for hydrogen sulfide concentrations in the gas to increase with reaction time and not to fully line out until considerably after the first approximation of mineral lineout. These long term upward drifts tend to correspond to gradual downward drifts in Blackness and upward drifts in $\overline{\text{IR}}$. Here again the result should be reasonable if mineral classification resulted in improved catalytic reactivity. The tendency for ammonia to appear in the gas after many hours of operation is also suggestive.

IV-G Gas Sampling and Analysis

The initial installation of the continuous reactor allowed the gas from the product letdown valve to flow continuously through a wet test meter. It was planned to draw gas samples through the sample loop of the gas chromatograph to measure the composition and for the major flow to be measured by the wet test meter. The product letdown valve operated intermittently producing a pulse of gas which overflowed the capacity of the wet test meter.

Then the gas flow was nearly stopped until the next release. As a result it was not possible to meter the volume accurately, and even sampling through the gas chromatograph loop was of doubtful reliability.

The method used to resolve this problem was the substitution of a large rubberized fabric gas sample bag for the wet test meter. In this system periodic release of gas posed no problem and the volume collected was large enough to average the composition over periods of time from one half an hour to an hour as needed. The whole of the gas sample passes through the sample collection vessel and the liquid and gas vapors are flashed to establish an equilibrium within the gas sample. The sample flask was initially full of air also. Because of this time was needed to flush the air and to equilibrate liquid and gas. This was not fully realized at first and the attempt was made to draw small liquid samples and gas samples with inadequate flush intervals with erroneous results being a consequence. The gas samples were analyzed for air content by determination of the oxygen content of the gas, and the results were then reduced to air free basis. The recommended procedure is to plan proper flush intervals rather than to attempt to collect samples prematurely.

It was determined that hydrogen sulfide would decline slowly in concentration in the rubberized sample bag. It is necessary to draw a subsample for titration promptly after the sample bag is removed from the system. The sample for infrared analysis is drawn at the same time and a qualitative inspection of the gas and a determination of the hydrogen sulfide content can be completed within a half hour. The samples for gas chromatographic analysis are drawn into 500 ml or 1000 ml gas tight syringes and the volume of the gas in the bag can be determined by venting the bag through a wet test meter. It has become standard procedure to include a gas density determination in the gas analysis. This gives an independent determination of its molecular weight.

As the result of accumulated experience it has been found that the molecular weight and composition of the product gas from experiments with hydrogen and Kentucky coal are reproduced well. Molecular weight data can be used to estimate the percentage of hydrogen in the gas with reasonable accuracy. This allows the use of short cut methods for estimating hydrogen consumption in those cases where the gas chromatographic analysis was not done for some reason. In work with carbon monoxide or with carbon monoxide-hydrogen mixtures the detailed gas chromatographic analysis was essential since the molecular weight did not allow estimation of composition.

Given proper lengths of gas cells the infrared analysis of the product gases can be substituted for the gas chromatographic analysis. This procedure was not normally expected to be used quantitatively but rather it was expected to supply an indication if an unusual reaction product were encountered. Qualitative results did not change for given coal, solvent, reducing systems. Changes in feed ratio or in operating conditions did alter concentrations of materials in the product gas but rarely changed the kind of material observed. When such change was observed it was commonly the increase of some material from trace levels to concentrations which could be observed in routine work.

IV-G-1 Method for the Determination of Hydrogen Sulfide in Product Gas

DETERMINATION OF HYDROGEN SULFIDE IN SRC PRODUCT GAS

Data: This method covers the determination of hydrogen sulfide in product gas from SRC lab unit. It is applicable on a concentration range of about 0.1 to 7% V/V H_2S. A measured volume of product gas is bubbled through ammonical zinc sulfate solution to remove hydrogen sulfide. The amount of hydrogen sulfide in the absorber is then determined iodometrically.

Special Apparatus:

(a) A 250 ml Erlenmeyer flask with a two-hole rubber stopper carrying (1) a 7-mm diameter glass tube, with a drawn down tip, extending nearly to the bottom of the flask and a (2) short 7-mm diameter glass tube, extending just a little ways on either end of stopper, for exit of excess unabsorbed gas. On the inlet end of the (1) inlet-tube, a 1-ft long rubber injection tube is attached. On the outer end of the (2) exit tube, a small rubber bulb having a small slit cut in it can be used as a 'flap' valve to restrict the rapid flow of gas and to exclude the entrace of air.

(b) Gas Syringes, 500 or 1000 ml - Hamilton Super Syringes No. S-0500 or S-1000.

Reagent Solutions:

(a) Ammoniacal Zinc Sulfate. Dissolve 50 grams of zinc sulfate heptahydrate in 250 ml of water, and then slowly add 250 ml of concentrated ammonium hydroxide while stirring. Filter off any precipitate that may form upon long standing.

(b) Hydrochloric Acid 1:1. Dilute concentrated HCl with an equal volume of water.

(c) Iodine Solution (0.05N). Weigh 12.8 gms of resublimed iodine crystals into a 250 ml beaker. Add 40 gms of potassium iodide (KI) and 100 ml of water. Stir until solution is complete, dilute to 200 ml, mix thoroughly, and store in a brown-glass reagent bottle. (No need to know iodine solution normality exactly if it does not change and the same exact volume (25.0 ml) is used in reagent blank and sample determinations).

(d) Sodium Thiosulfate Standard Solution (0.05N). Dissolve 25 gms of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in 500 ml water and add 0.01 gm sodium carbonate (Na_2CO_3) to stabilize the solution. Dilute to 2000 ml and mix thoroughly. Standardize versus potassium dichromate or potassium iodate by usual techniques to accuracy of ± 2 ppt.

(e) Starch Solution, 2%. To 250 ml of boiling water, add a cold suspension of 5 gms of soluble starch and 0.025 gms mercuric iodide. Boil for a few minutes to clear. Store in glass-stoppered bottle with undissolved mercuric iodide on bottom.

Sampling

The product gas must be analyzed for H_2S as soon as possible after receipt. Hydrogen sulfide can react with any condensed water vapor or ammonia and dissolve out of the gas mixture. It may also react with the sides of the bag and be lost. The effect of it possibly combining with carbon monoxide to form carbonyl sulfide (COS) is not known. It would be preferred if the gas could be sampled at the source.

Procedure:

Transfer 30 ml, by graduate, of the ammoniacal zinc sulfate solution to a 250 ml Erlenmeyer flask. Dilute with water to about 150 ml and add a 1½ inch stirring bar. Put in inlet tube-valved stopper. Attach filled gas syringe to injection tube by means of a short piece of glass or stainless steel tubing. While magnetically stirring, slowly inject 100 ml to 1000 ml of product gas depending on H_2S percentage. (Watch for heavy turbidity formation as guide to the volume of gas to use in first test.) (Caution: This part of test should be done in area free of open flames or sparks. Also if gas contains much carbon monoxide, it should be done in good fume hood.)

Remove syringe from injection tube and record volume of gas injected into flask. Raise rubber stopper just enough to bring end of inlet tube out of solution and wash down the injection tube with about 1 ml of 1:1 HCl and a little water from a wash bottle. Transfer the stirring bar, by means of a thief, from the 250 ml E flask to a 500 ml Erlenmeyer flask containing 25.0 ml of 0.05N iodine solution (by pipet) and 40 ml 1:1 HCl solution. While stirring continuously, very slowly pour the contents of the absorbing 250 ml flask into the 500 ml E. flask. Rinse the 250 ml flask with about 100 ml water into the 500 ml flask.

Quickly titrate the solution, while being stirred, with standardized 0.05N sodium thiosulfate solution until the solution is yellow. Then add 2 ml of 2% starch solution and continue titration to a permanent colorless end point. Record volume of sodium thiosulfate required for titration. (Sample solutions are usually turbid at end of titration, blanks are clear.)

Run through above procedure, leaving out gas sample, for reagent blank. The nature of this test is that the blanks are equal to or usually higher than the titration volumes obtained for samples.

The blank and sample tests should be run in duplicate. The blank values do not change very much, only a weekly check is necessary if there have not been any changes in reagents, room temperature, etc. If sample titration volume is less than half of the reagent blank, test should be rerun using less gas sample.

Calculations:

$$\frac{(V_b - V_s) \times N_t \times F \times 100}{V\ gas} = \%\ H_2S(\text{mole }\%)$$

where:

V_b = Volume(mls) of sodium thiosulfate used in blank.

V_s = Volume(mls) of sodium thiosulfate used in sample.

N_t = Normality of sodium thiosulfate

Vgas = Volume(mls) of product gas used in test.

F = Factor in milliliters of hydrogen sulfide per milliequivalent of sodium thiosulfate. It is one half of the reciprocal of the molar equivalent of one liter of gas(moles/liter) at temperature and pressure of product gas at time of testing. Consult standard texts for molar equivalent of one liter of gas at various temperatures and pressures.

STANDARDIZATION OF 0.05N SODIUM THIOSULFATE VERUS POTASSIUM IODATE

1. Weigh, to nearest 0.01 mgm, about 0.065 to 0.070 gms. of pure potassium iodate (KIO_3), dried at 180°C for 2 hours. Record weight as W. (see Note #1).
2. Transfer to a 250 ml Erlenmeyer flask. Add 2.0 g of potassium iodide(KI) and 50 ml water. Swirl to completely dissolve salts.
3. Add 10 ml of 1:10 Hydrochoric acid(HCl) solution. Solution will turn dark brown from liberated iodine.
4. Titrate immediately with sodium thiosulfate solution with constant swirling. When the yellow color of the iodine has almost disappeared, add 1 ml 2% starch solution. Continue the titration dropwise to disappearance of the blue color. (Run a blank determination, leaving out the KIO_3).
5. Calculation: $\frac{W}{V\ (0.03567)} = N$

   where: W = Weight, in grams, of KIO_3
   V = Volume, in mls, of sodium thiosulfate soln.
6. Do in triplicate. Widest difference should be ± 2 ppt.

Note #1. - Instead of weighing three small weighing, about 0.65 to 0.70 grams of KIO_3, weighed to nearest 0.1 mgms, may be transferred to a 250 ml volumetric flask. Add water to dissolve salt, then dilute to mark, and mix throughly. Take out 25.0 ml aliquots, by pipet, and transfer to 250 ml Erlenmeyer flasks. Add KI and only 25 ml water and continue above procedure. Use aliquot weight in calculations.

IV-G-2 Method for the Gas Chromatographic Analysis of Product Gas

Instrument: Hewlett-Packard Model 700-231 dual column Gas Chromatograph with dual gas sampling valves No. 1902A on each column.

Conditions	Column A	Column B
Column dimensions and packing	4M x ¼" SS tubing of Linde Molecular Sieve 5A 80-100 mesh	4M x ¼" SS tubing of Waters Associates Porasil A, 100-150 mesh
Gas Sample loops	1.0 cc	2.0 cc
Flow rates (Argon)	60 ml/minute	30 ml/minute
Carrier gas pressure	50 psig	
Detector	Thermal conductivity with WX filaments	
Bridge Detector Current	100 milliamperes	

Temperatures: Injection Port 125°C
Oven (isothermal) 100°C
Detector Block 110°C

Chart Speed: 0.5 inches per minute

Procedure:

a. Column A is used for the analysis of H_2, O_2, N_2, CH_4 and CO in product gas.

Column B is used for the analysis of Ethane, carbon dioxide, Propane Isobutane, and Normal butane in product gas. The sample is normally run on column B first. This column produces a peak for hydrogen which is merged with air and is not usually measured for this reason. A shoulder due to methane is observed on the side of this peak and is not usually measured. The remaining peaks emerge in the order: Ethane, Carbon dioxide, Propane, Isobutane, and Normal butane and are recorded for measurement.

The sample is then run on the A column. Peaks emerge in the order: Hydrogen, oxygen, nitrogen, methane and carbon monoxide and these are recorded for measurement. A peak for ethane is observed about one half hour after the injection of the sample but is not recorded for measurement.

Because of the long time required to observe the ethane peak on the A column it is possible to inject a second trial sample on this column just after the carbon monoxide peak from the first sample is observed and to observe all of the peaks of interest before the ethane peak from the first sample is observed. A second ethane must then be observed before another sample can be run.

b. Sampling

A gas syringe (500 ml or 1000 ml) is attached to the gas sample by means of a short length of rubber tubing. Care should be taken to see that the syringe is empty of air by pushing the plunger to the end as far as possible. Open the stopcock on the syringe and open the line to the gas bag. Fill the syringe and force the gas back into the gas bag several times to obtain an air free sample of gas. (This actually mixes the air in the tubing connection with the gas in the bag. The bag may contain 50 to 100 liters of sample while the tubing holds a few ml. This does no harm by diluting the sample in the bag but must not be mixed with the gas in the syringe by mistake.) Close the stopcock on the syringe and secure the clamp or stopcock on the gas bag.

Attach the syringe to the gas sample loop and open the valve and stopcock to allow gas to be injected through the loop selected. Slowly inject about 125 ml of gas. Start a stopwatch immediately and after 20 seconds inject the sample into the chromatograph by turning the sample injection valve. Start the recorder chart immediately. It is helpful to have the recorder pen on a major line at the start since this facilitates the accurate observation of elapsed time.

c. Attenuator Settings:

Hydrogen is observed first on either column. Usually this can be read at a 512 attenuator setting. After this most of the peaks will be read on x1 through x8 settings but optimum settings will need to be determined by trial. Preliminary settings may be established from observation of the infrared spectrum or knowledge of the molecular weight of the gas. If any peaks are not suitable for measurement in the chart from the first trial the attenuator setting is adjusted to improve the second chart.

d. Standards:

Standards are run to produce peaks of similar size to those in the samples analyzed using gas mixtures of known composition. These standard mixtures are purchased from commercial suppliers and are mixed to approximate the compositions of the samples to be run. Such gas mixtures are supplied with a certificate of analysis.

A list of standard mixtures used is presented below. As an example, for the analysis of product gas from a reaction using hydrogen and Kentucky coal: Run M4A on Columns A & B, Run M 7 on Column A only, Run M 2 on Column B only.

As a further example, for the analysis of product gas from a reaction run with carbon monoxide - hydrogen as reducing gas: Run M 1 or M 3 on Column A & B, Run M 7 on Column A only, & Run M 2 on Column B only.

IV-G-2

Gas Standards for G.C.

Column	Gas	M-1	M-2A	M-3	M-4A	M-5	M-6	M-7B
1. Mol. Sieve	H_2	37.3	70.0	48.6	77.5	46.4	38.2	-
	O_2	-	-	-	-	-	-	0.633
	N_2	0.966	6.98	0.49	12.7	12.2	6.56	5.97
	CH_y	2.89	8.14	2.05	6.34	10.0	4.89	-
	CO	29.9	0.941	47.3	0.338	12.1	32.6	-
2. Porasil A	Ethane	0.936	3.21	0.488	1.88	3.05	1.69	-
	CO_2	27.0	2.39	1.02	0.482	14.5	11.0	3.34
	Propane	-	1.70	-	0.726	1.25	1.07	-
	i-Butane	-	0.108	-	-	0.19	0.110	-
	n-Butane	-	0.444	-	-	0.30	0.226	-
	H_2S	0.964	-	-	-	-	-	-
	Helium	-	-	-	-	-	-	89.28
	Argon	-	6.08	-	-	-	3.66	-

IV-G-3 Method for the Determination of Molecular Weight of Product Gas

Gas is collected in a rubberized fabric sample bag and normally a volume of 50 to 100 liters will be available for use. It is practical to run replicate gas density determinations to improve the precision of the measurement. In this procedure a small bulb of about 250 ml capacity, fitted with an air tight stopcock is used. The bulb is evacuated, weighed then opened to the air and reweighed. The procedure is repeated several times to obtain precise results. Now the procedure is repeated except that the bulb is filled with gas instead of air to determine the density of the gas. The results are expressed molecular weight rather than gas density by comparison to air, at molecular weight of 28.95.

Procedure:

a. A drawing of a suitable gas density bulb is presented. It is essential that the stopcock be reliable and that a good vacuum be maintained in the bulb. Pump the air out of the bulb using a vacuum pump capable of reducing the final pressure in the bulb to a fraction of a millimeter. Use a small loop of wire to suspend the bulb on the pan of an analytical balance. Weigh accurately and record the weight of the evacuated bulb. Open the stopcock and allow air to flow into the bulb. Allow a minute for the bulb to equilibrate any temperature-pressure upsets then reweigh. Repeat for duplication of weights.

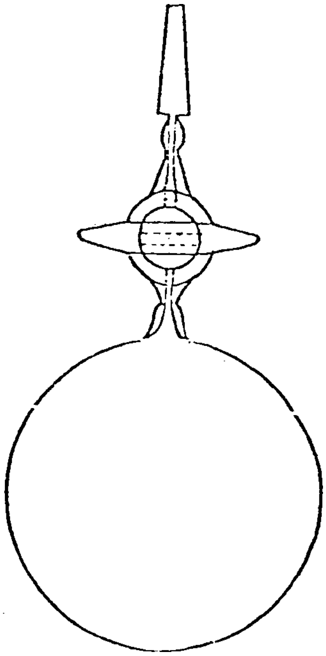
b. Evacuate the bulb and weigh. With full vacuum in the bulb, remove from the balance and obtain the gas sample. In order to manipulate the gas in the bag a small T is attached to the spout of the bag by means of tubing. A one liter gas sampling syringe is attached to one branch of the T and the evacuated gas density bulb is attached to the other branch of the T. The syringe plunger must be pushed to the end of the syringe as far as possible before it is attached. The valve on the syringe is opened and the valve to the gas sample bag is opened. The plunger of the syringe is moved back and forth several times to purge air out of the T and the tubing connections. (This introduces a few ml of air into the gas bag but it dilutes the large sample in the bag to a negligable extent.) Finally open the stopcock to the evacuated gas density bulb and allow sample to flow into the bulb. Close the

IV-G-3

stopcock to the bulb. Make sure all gas possible has been returned from the syringe to the gas bag and close the stopcock on the syringe and the valve on the bag. Remove the gas density bulb and weigh. Repeat to obtain duplicate values.

c. Calculation of Molecular Weight.

$$\text{Mol.Wt.} = \frac{(\text{Wt. of bulb and gas - Wt. of evacuated bulb})\ 28.95}{\text{Wt. of bulb and air - Wt. of evacuated bulb}}$$



IV-G-4 Measurement of the Volume of Product Gas Samples

When a gas sample is taken it is identified by the Run number and the time during the run that the sample was drawn. This information is necessary to allow calculation of the volume of gas which is produced during the time that the liquid sample is taken. As samples are taken from the gas sample bag for the several analytical procedures run the volumes withdrawn are noted. When all of the necessary work has been completed, or when subsamples of gas for the work are drawn in gas tight syringes, the final procedure is the measurement of the gas remaining in the sample bag. This is the major fraction of the gas sample. The subsamples usually involve drawing only a few liters of gas from the bag while the remainder is commonly 50 to 100 liters.

The gas bag is attached to a weighed cold trap by means of rubber tubing and the outlet from the cold trap is attached to a wet test meter by means of additional tubing. The pointers on meter dial are set to zero (or the reading may be recorded). The valve on the gas sample bag is opened to allow gas to flow through the cold trap into the meter. The cold trap is placed in a thermos of acetone cooled with dry ice and as the gas flows through the trap most of the water vapor in the gas freezes out. The gas flowing to the meter is then dry. A piece of plywood is placed on the gas bag and weights are added until the gas flows at a moderate rate through the wet test meter. This does not increase the pressure in the meter significantly above the atmospheric pressure, a water filled manometer on the top of the meter rarely deflects more than a few mm of water pressure. The bag is allowed to empty as completely as possible under the pressure from the weights, then any remaining gas is forced out by carefully folding and rolling the bag to force out all gas possible. The final reading of the wet test meter is recorded and any correction for initial dial reading is made.

Calculation of Gas Volumes and Weights

It is assumed that gas is dry after the cold trap and that it is measured in the wet test meter in equilibrium with water vapor from the water in the wet test meter. The measured volume is then corrected to standard conditions (271.1°K at 760 mm Hg). The observed barometric pressure is corrected for the water vapor in the wet test meter by subtracting the table value for the vapor tension of water from the barometric pressure. The observed temperature and barometric pressure must be recorded as part of the data relating to the volume measurement.

$$\text{Corrected volume} = \frac{(\text{measured Volume})\,(\text{Barometer reading} - \text{VP } H_2O)(273.1)}{(760)\,(\text{Temperature Centigrade} + 273.1)}$$

The corrected volume measured from the wet test meter should be added to the corrected volume of the gas samples withdrawn. This is the total sample volume. The total sample volume is then multiplied by the ratio of liquid sample time to gas sample time to calculate the volume of gas which relates to the liquid sample taken. The volume divided by 22.4 liters will be the number of moles of gas related to the liquid sample. The number of moles times the molecular weight will be the weight of gas associated with the liquid sample drawn. Usually the water vapor associated with the gas sample amounts to only a few grams. This should be added to the weight of gas, proper allowance being made to compute the weight related to the liquid sample drawn. Material balance calculations may be made on a per sample basis or on an hourly rate basis. If the latter procedure is used the weight of gas per hour is calculated by dividing by the hours the liquid sample collection ran.

IV-H Liquid Product Workup

Three samples were taken from the reactor to account for all of the feed slurry and gases fed to the reactor. Workup of the product gas has been discussed in the previous section. The other major sample was the liquid product collected in the stainless steel flask. A small amount of material, which was mostly water, was collected in the knock out vessel between the liquid sample flask and the gas sample bag. In calculation of the percentage recovery the sum of the weight of the liquid product plus the knock out vessel product plus the gaseous product must balance the total feed if 100% recovery is to be obtained. Accountability data for most runs are presented in Appendix A. In preparation of these tables the knock out vessel product weight has been included with the weight of liquid products. In the yield calculations the knock out vessel product is normally reported in the water yield. Actually traces of oil are present as well as ammonium carbonate, ammonium sulfide, and a small amount of phenol. They do not become concentrated enough to significantly change yield results as the weight of the sample is small. Further refinement by analysis of this fraction is possible but the influence on overall results would be small.

This section of the report will discuss the methods used for evaluation of the liquid product sample. Most of the data result from separation procedures, and handling losses had to be accounted in order to obtain a handling-loss-free product distribution within the sample. The basis for the first separation procedures used in the workup of these samples have been reported previously in the interim report concerned with batch autoclave studies. 2/

Modification of equipment and the increase in sample size available from the continuous unit led to an evolution of procedure and apparatus which virtually eliminated most of the serious handling losses which were considered to be unavoidable in previous work. The first experiments were worked up by procedures which required considerable mathematical treatment of results to develop a handling-loss-free product distribution and by the end of the anthracene oil studies the size of the corrections required had been substantially reduced. The improvement of data quality resulting from development of proper handling techniques, proper sampling techniques, the use of appropriate sample sizes, and accumulated experience is difficult to state explicitly. This is a real consideration in reporting results. The first fifteen experiments completed in this program show considerable influence from normal learning problems. As a result some have very poor accountability and some were off the desired properties to the extent that normal workup procedures could not be used. No doubt, the inclusion of raw material balance data in Appendix A will give indication of the gradual improvement in operating and analytical technique as it developed.

To obtain greater precision, attention had to be directed to a myriad of small details. It is impractical to attempt a comprehensive list of the small improvements and false starts involved in developing the data presented. As operating procedures are discussed it is hoped that some impression of the state of the art at different stages in the experimental program can be conveyed. It is usual for such art to be glossed over in reporting, but as a practical matter, material balances can not be closed with the best accuracy possible without attention to these techniques. In work with petroleum derived startup solvent, which will be reported separately, techniques have been developed for compensating most transfer and exclusion errors as well as for closing initial material balances accurately with the raw samples obtained. This eliminates much of the mathematical correction procedure involved in data such as that presented in the autoclave studies and which was still necessary for much of the data presented in this report.

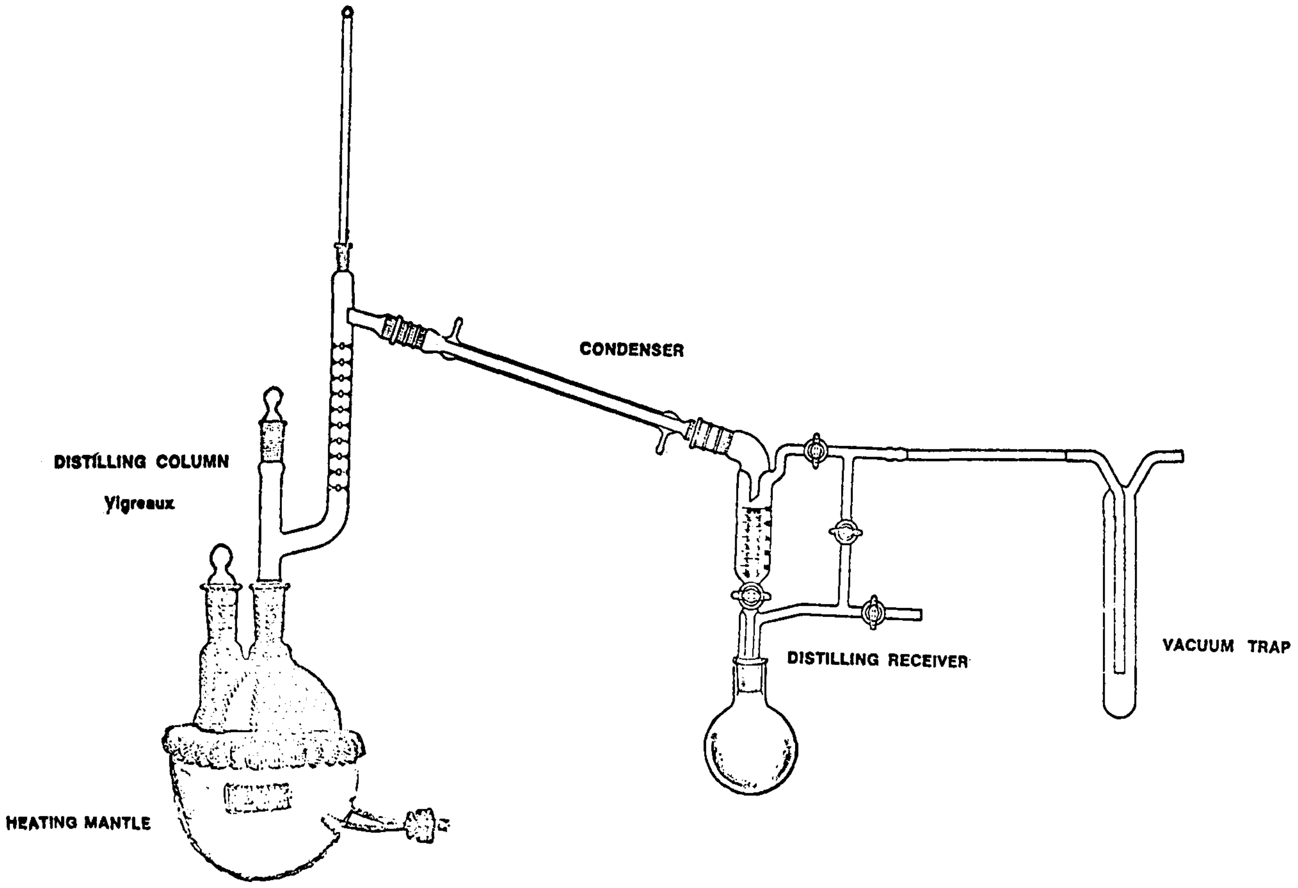
IV-H-1 Stripping to Recover Volatile Components of the Liquid Sample

The liquid sample was obtained in a previously weighted stainless steel flask. This was removed from the unit and delivered to the laboratory sealed by glass stoppers. The stainless steel flask has a 3000 ml capacity and often at least partly filled with hydrogen. This can introduce some bouyancy effects in cases where weighings are attempted with stoppers in place.

After weighing the stainless steel flask it may be necessary to draw samples for other work. The samples needed to obtain an infrared spectrum of the solution and to do the blackness determination remove only a few drops of material and do not change the sample weight within measurable limits. If an appreciable amount is needed for some other purpose the flask and liquid must be weighed after removal of the sample and proper correction for the material withdrawn must be done in the handling-loss-free accounting.

A sketch of the apparatus used for stripping the volatile products out of the liquid sample is presented as Figure 9. The stopper is replaced in one of the standard taper joints of the sample flask and an adapter is used to attach the flask to the glassware of the vacuum distillation equipment. The distillation equipment is attached to a rotary vacuum pump which will evacuate a vessel to a fraction of a millimeter of pressure. The pump is protected from water and light oil vapors by a cold trap. Because of the amount of dissolved gas and water in the sample the vacuum must be applied in increments and some warming of the product during the gas removal helps to eliminate foam-over which can cause problems. As a result the distillation usually starts as a low pressure steam distillation in which both oil and water co-distill. This is collected in the distillation receiver flask. As the vacuum improves and the temperature in the sample flask increases water is finally eliminated. During this interval the material in the receiving flask tends to reboil with the low boiling condensate transferring to the cold trap. The cold trap may freeze out such a large amount of material that it stops up. The cold trap is then replaced and the full trap is weighed. The cold trap material is weighed in several increments which are then composited after thawing. The oil phase is separated by using a pipet or a separatory funnel and weighed. These results account for the cold trap oil and part of the water in the product.

When the vapor temperature measured at the top of the Vigereaux column reaches the desired cut off point the heating mantle is turned off and lowered to allow the flask to cool slightly. The vacuum is reduced and distillation stops promptly. The distilling receiver flask is removed and weighed. The material in this flask is Cut 1 oil and a small layer of water normally remains at the bottom. The oil is separated from the water in order to determine its weight. The water layer accounts for the balance of the water removed as



APPARATUS FOR VACUUM STRIPPING OF COAL SOLUTIONS

Figure 9

reaction product except for the small amount previously indicated as a component of the product gas sample, or collected in the knock out vessel.

The flask containing the stripped solution is then quickly weighed in order to determine the residual liquid weight. This is the yield of stripped solution from the sample taken from the reactor. No handling loss needs to be encountered up to this point if unstripped solution samples are not taken.

IV-H-2 Filtration of Stripped Liquid Product Sample

The purpose of stripping the raw liquid product sample is to remove the volatile products which would be lost during the exposure to vacuum and to the atmosphere which would be necessary during filtration. It is evident that this cannot be completely controlled but the vapor pressure of the materials remaining has at least been materially reduced. The products from the stripping were available for study and their properties could be used to estimate the kinds of products which result from the corresponding operations in the pilot plant.

Filtrations were conducted by means of steam heated buchner funnels with suitable filter papers as the filter media. The filter papers were Whatman 42 or hardened papers such as Whatman 52. The performance of qualitative grade papers of similar retention is acceptable. In order to minimize handling loss the filtrate was collected in the round bottom flask to be used for the solvent reclaim distillation. This was facilitated by the use of a vacuum adapter. After the filtration was completed the hold-up on all surfaces was determined by reweighing all items. A sketch of the filtration apparatus is shown as Figure 10. The transfer from the stainless steel flask is done while the solution is still hot from the stripping procedure. It is necessary to swirl the flask in order to resuspend any mineral matter which may have settled during the stripping procedure, then transfer the solution rapidly onto the filter. Finally, the flask is clamped over the buchner for a time and allowed to drain as completely as possible. The flask is then reweighed in order to establish the hold up error from incomplete drainage.

It can be appreciated that the drainage errors for these moderately viscous liquids will depend on the surface wetted. It is important to use equipment well matched to the sample sizes to be handled, and it is advantageous to use as large a liquid sample as practical in order to minimize the proportion of the sample lost to such surfaces. Where single samples of a kind must be treated little can be done to correct the procedure. In studies in which a number of similar samples are to be processed, the first sample can be used to condition the surfaces of the apparatus and the drainage errors can be substantially cancelled in succeeding samples. In such work data can be made quite precise in the raw form. During the single point studies which were done in the anthracene oil program the accuracy of the data is dependent on proper accounting of all transfer and handling loss information. In the usual workup the major part of the sample was used in all separation procedures to avoid the problems encountered in preparing truly representative subsamples.

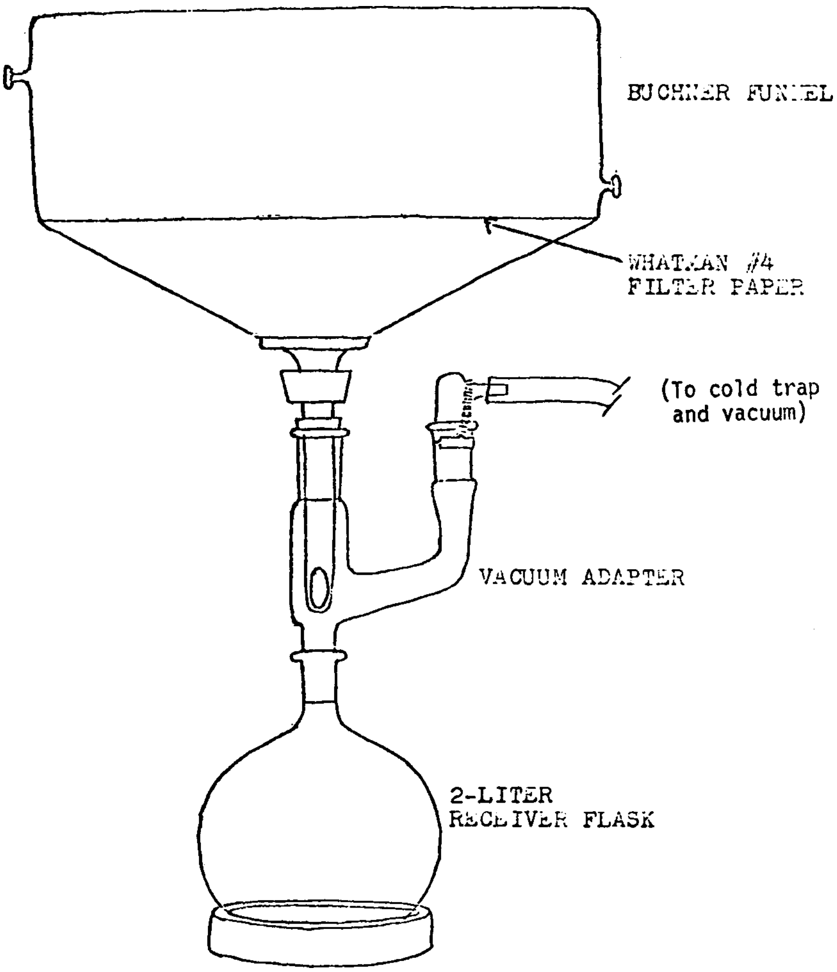

BUCHNER FUNNEL
WHATMAN #4
FILTER PAPER
(To cold trap
and vacuum)
VACUUM ADAPTER
2-LITER
RECEIVER FLASK

Figure 10

IV-H-2

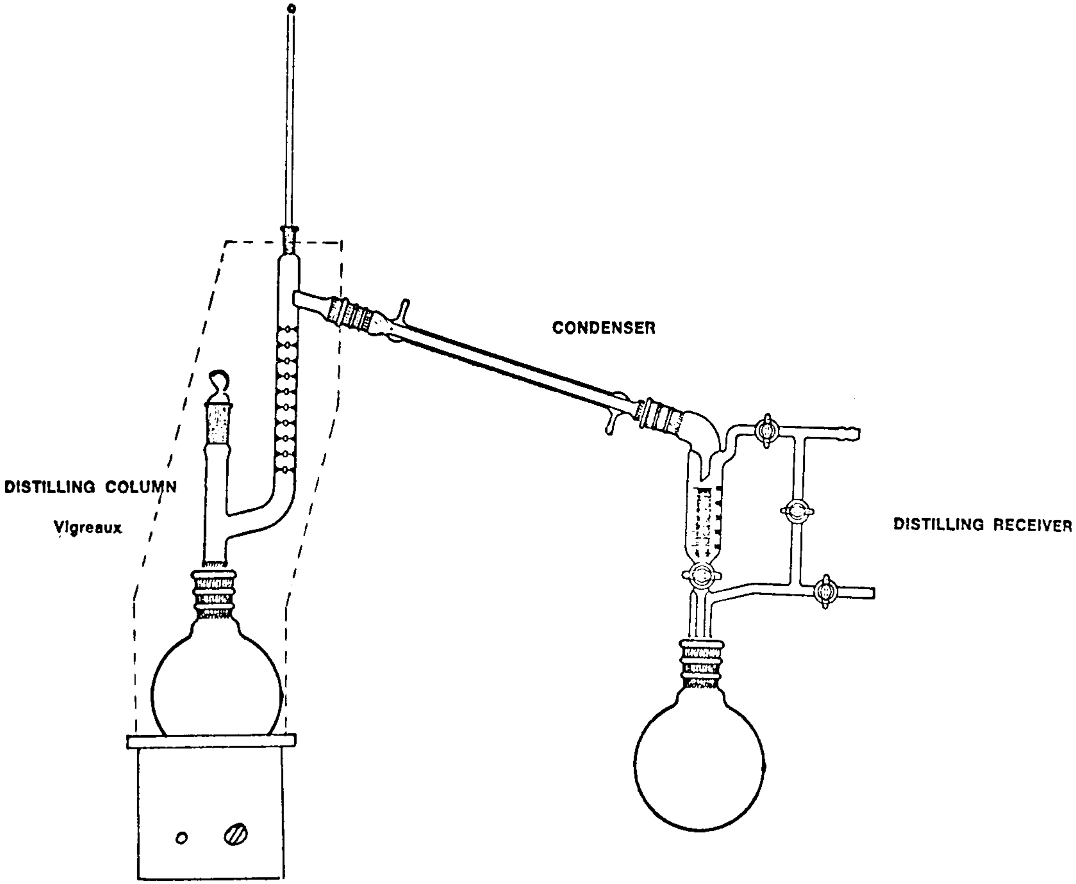
The filtration was conducted under vacuum supplied from a vacuum pump. A cold trap in this line prevented uncontrolled loss of material to the vacuum pump.

Some vapor loss to the air above the buchner was unavoidable. Such loss had to be accounted for in reweighing all of the equipment involved. Since several weighings are involved the sum had a limited precision which limited the accuracy of such estimates. In the case of a fluid readily filterable sample, the hold-up losses of material on surfaces would usually be three or four grams and the unaccounted material probably lost as vapor would be similar in weight. Such losses are not serious for filtrations of a kilogram of material but are relatively large for samples of a few hundred grams. Perhaps 20 to 25 grams of stripped solution may remain in the three liter flask from the transfer of liquid to the buchner funnel. Larger samples are preferred in order to reduce the size of the correction factors needed to make the calculation to handling-loss-free basis. At some of the longer retention times collection of an adequate sample would often require several hours, and the temptation to save time at the expense of sample size is strong. Collection of sufficiently large samples appears to be the best way to improve the results. There is at present no dependable substitute for actual filtration and actual distillation results. The products obtained from the filtration procedure were the filtrate, which was in a flask and ready for redistillation, and the wet filter cake which had to be analyzed for the percentage of insoluble material present. These procedures are described in the sections of the report which follow.

IV-H-3 Solvent Recovery

The relative amounts of solvent which could be reclaimed by distillation, and the vacuum bottoms remaining were determined by distillation of the filtrate. The stripping procedure removed material which boiled below 100°C under a nominal pressure less than 3 mm of mercury. When the filtrate was redistilled to obtain the higher boiling solvent cut only a small amount of additional material in the cut 1 solvent range was obtained. This would be collected in the cold trap which was used to protect the vacuum pump.

The filtrate was collected in a one neck round bottom flask and this was selected to contain the expected volume of liquid with the flask filled about two thirds full. Several small boiling chips were added to the empty flask before it was weighed. The filtrate weight was determined by reweighing the flask after the filtration was completed. This flask was placed on the distillation apparatus as shown in Figure 11. The distillation apparatus consists of a Vigereaux distillation column, a condenser, and a fraction collector and this glassware is a duplication of the glassware used in the stripping operation. In the anthracene oil studies the distillation flask was heated by means of a flask heater as shown in Figure 11 . The cut 2 solvent fraction was collected in a flask which was about the same size as the one containing the filtrate since this was usually 70% by volume of the filtrate sample. At times the distillation was conducted by taking several subsidiary fractions in smaller flasks in order to develop a rough distillation curve as the recovery of cut 2 was done.



APPARATUS FOR VACUUM DISTILLATION OF COAL SOLUTIONS

Figure 11

To maintain a uniform format such results have been consolidated in the appropriate category of boiling range for presentation in Appendix A.

The distillation was continued to collect the cut 2 fraction (nominal boiling range 100°C to 230°C at less than 3 mm Hg) and a heavy oil fraction (boiling from 230°C to an upper limit of 325°C at less than 3mm Hg). In many cases the upper limit for the heavy oil fraction was less than 325°C as the vacuum bottoms would begin to decompose before this temperature was obtained. In such cases the distillation was stopped at the decomposition point. All liquid fractions removed were collected in weighed flasks and were weighed to determine the size of the distillate fractions. The trap used to protect the pump was weighed before and after use.

In order to facilitate transfer of liquid the Vigereaux column and the sample flask were wrapped in glass fiber insulation. During collection of the light end of the cut 2 fraction water was run through the condenser. At some point the liquid will start to crystallize in the condenser. This can be corrected by stopping the flow of water to allow the condenser to be heated somewhat by the static volume of water remaining. Part of the water will boil away and as the vapor temperature becomes higher it may be necessary to empty the condenser of water completely to prevent crystal formation. During the final stages of the distillation it is necessary to warm the condenser and the fraction collector to prevent formation of solids and to cause the product to run into the collection flask. This was facilitated by use of an electrically heated stream of air from a heat gun. As an alternative, the glassware may be heated by infrared heat lamps or by heating tapes.

Filtrate samples in 500 ml or 1000 ml flasks have been distilled with heat from a flask heater. This apparatus has a coiled chromolox heating element and the flask was heated partly by convection of hot air but mostly by radiant heat from the heating element which does not touch the glass. For distillation of larger samples, heat has been supplied by means of suitable heating mantles controlled by variable transformers. The heat was applied to the flask by direct contact with the mantle. The operating temperature of the flask and the mantle were more nearly the same. No product properties appear to be materially different as a result of different heating methods. Since the objective is to predict yields which may result from the vacuum flash operation in the pilot plant, it may be necessary to develop correlation charts or to use other apparatus in time. These results are comparative values which are at least useful for relating the effect of changes in coal, solvent, or operating conditions. The results have correlated reasonably well with the vacuum flash unit used in the Process Development Studies done early in this project but may not correlate with other units. The vacuum flash leaves some material which can be removed by a batch vacuum distillation of the vacuum bottoms.

After the solvent is reclaimed, the flask containing the vacuum bottoms residue is allowed to cool and then weighed to determine the distillation residue obtained. An accounting of the filtrate was made by adding the weight of the vacuum bottoms to the weight of the liquid fractions and the small amount of material in the cold trap. The hold up in the distillation equipment was added to the weight of the heavy oil fraction. The distillation can be done without loss of material and the main correction required for product distribution data obtained results from the material held up in the buchner and the adapter as the filtrate sample is made.

The solidified vacuum bottoms are removed from the flask by breaking the solid into bits small enough to shake out the neck of the flask. This was sometimes difficult to accomplish without shattering the flask. The solid material was ground and sieved to remove any boiling chips (or bits of glass if the flask had to be broken). As an alternative the sample may be weighed while the flask is still hot and the melted product may then be poured into a suitable pan for cooling and recovery. This is especially useful for the larger size of flasks which are difficult to reach into in any case. Weighing of flasks is facilitated by use of a hard rubber ring placed on the balance pan of a top loading balance. Weighings can be made with the necessary precision even with a hot flask.

IV-H-4 Wet Filter Cake Evaluation

An accurate weight must be obtained for the wet filter cake. The cake is then subsampled and a weighed portion is extracted with hot pyridine to determine the amount of insoluble material in the cake. The pyridine insoluble residue is ignited to determine the amount of ash and insoluble organic matter in the pyridine insoluble residue. These determinations are the basis for calculation of the amount of coal converted in the solution process.

Several techniques have been used for weighing the wet filter cake obtained. If the sample to be filtered is not too large, the buchner funnel and the filter paper can be weighed before use and after the filtration has been completed. Wet filter cake is then removed and any material clinging to the sides of the funnel can be wiped off or picked up with a spatula. The holdup in the funnel and the weight of the wet filter cake plus the filter paper can then be determined by reweighing the buchner funnel. In working with steam heated buchner funnels it is necessary to drain the steam jacket and blow it out in order to obtain reasonably accurage weights.

Holdup and transfer losses are minimized by using larger samples and the preferred size of liquid samples are filtered in buchner funnels which are too large to weigh on the top loading balance available. In this case the filter paper is weighed together with a suitable beaker or metal can and after the filtration is completed the wet filter cake is transferred to this container by lifting the paper and wet cake from the funnel and placing it in the weighed container. This procedure is especially useful for filter cakes which cannot be completely dried. Most filtrations result in a solid residue which can be lifted on the filter paper without difficulty. Individual pieces of this kind of material are coherent and can be picked up without deforming or falling to bits. Subsampling such material is not difficult as the proportions of solution and mineral matter are reasonably reproducible. If the filter cake has moist spots it is more difficult to make a representative subsample and it may be necessary to remix the solids and work them into a putty like ball before a sample can be drawn.

IV-H-4

A subsample of the wet filter cake is used for the pyridine insolubles determination. A weighed sample of the material is placed in a beaker and heated with pyridine to dissolve the coal solution imbibed in the wet filter cake. The sample is filtered using a No. 42 Whatman filter paper which has previously been weighed. The filter paper is placed in a buchner funnel and the pyridine solution is poured into the funnel. All solids are rinsed out of the beaker and the insoluble residue is washed until the pyridine runs through the residue and remains colorless. The residue is dried by rinsing it with benzene then acetone while the funnel is still warm. Acetone is removed by drawing air through the filter. The filter paper is then removed from the funnel, cooled, and weighed to determine the amount of pyridine insoluble material present. This procedure is normally run on samples weighing ten grams and the amount of pyridine insoluble material in a filter cake is typically about 50%.

A portion of the dry insoluble residue is then transferred to a weighed platinum crucible and weighed. The crucible is then placed in a cool muffle furnace. As the furnace is turned on the normal heating rate causes the sample to ignite in a controlled way. The ignition is continued at 750°C until all carbonaceous material is burned away. The crucible is then removed from the muffle, cooled, and weighed. The percentage of ash present is reported.

IV-I Summary of Product Inspection Methods

The products from the reactor are separated into several fractions which need further characterization in order to develop a complete description of the effect of the reaction on the coal and the solvent used. Products which need inspection are listed below.

Product Gases	Gas Sample Bag	Fixed Gases & Some Water Vapor
Knock Out Vessel Liquid	Condenser in Gas Line	Water & minor fraction oil
Liquid Product	Liquid Sample Flask	Coal Solution
1. Light Liquid	Cold Trap from Stripping	Oil phase floating in C.T.
2. Cut 1	Oil Phase to 100°C	Oil phase floating in Flask of Stripping condensate
3. Water Phases	Separated from cold trap and condensate from stripping	Water containing dissolved ammonium carbonate & sulfide plus phenol
Stripped Coal Solution		
4. Cut 2 Oil	From distillation of filtered solution	Oil distilled from 100°C to 230°C at less than 3 mm Hg.
5. Heavy Oil	From distillation of filtered solution	Oil distilled from 230°C to the decomposition point or 325°C
6. Vacuum Bottoms	Distillation Residue	Black Pitchlike solid

IV-H

[illegible]ODUCT DISTRIBUTION AND ANALYTICAL METHODS AVAILABLE FOR CONTINUOUS REACTOR ANALYSIS

MATERIAL TYPE	FRACTIONS ISOLATED	RUN DATA REQUIRED*	ANALYSIS AVAILABLE*
Gaseous products	Timed interval gas sample	Temperature, pressure & volume	a. Percent H_2S from subsample by volumetric method b. Molecular weight c. Composition by IR and/or gas chromatography d. Percent H_2 can be estimated from MW correlation with reasonable accuracy
Liquid products (low molecular weight)	1. Cold trap water (water phases)	Weight of water phases	a. Total sulfur % b. Basic functions c. Acidic functions d. Waste water analyses
	2. Cold trap oil phase (light liquids)	Weight of oil phase	a. Density b. IR spectrum c. Elemental analysis d. Functional groups
Liquid products (moderate molecular weight)	1. Condensate IBP to 100°C @ 3 mm Hg (cut #1)	Weight of fraction	a. Density b. IR Spectrum c. Elemental analysis d. Functional groups
	2. Recycle solvent 100° to 230°C @ 3 mm Hg (cut #2)	Weight of fraction	a. Density b. IR spectrum c. Elemental analysis d. Functional groups
Liquid products (high molecular weight)	1. Heavy oil 230°C @ 3 mm Hg	Weight of fraction	a. IR Spectrum b. Elemental analysis
Solid products (not distilled)	1. Vacuum distillation residue (vacuum bottoms)	Weight of fraction	a. Fusion point (gradient bar) b. Elemental analysis c. Coking properties d. Ash % & composition e. Potential utility specifications
	2. Pyridine insolubles	Weight of fraction	a. Ash % b. Elemental analysis c. Potential utility specifications

* All fraction weights to be reported on handling loss-free basis.

7. <u>Wet Filter Cake</u>	From Filtration of stripped coal solution	Minerals and insoluble organic matter. Approximately 50% imbibed stripped coal solution
A. Pyridine Insolubles	From Analysis of wet filter cake by pyridine extraction	Minerals and insoluble organic matter
B. Ash	From Analysis of Pyridine Insolubles	Ignited mineral residue

Three samples are required to account for all of the products made in the reactor. Two of these can be analyzed directly as received from the reactor. The workup of the coal solution requires stripping, which produces three subsamples for analysis, and the stripped coal solution which must be filtered. The filtration produces two materials that must be further treated. The bulk of the material is the filtrate, which is evaluated by distillation to recover solvent and vacuum bottoms. The wet filter cake is extracted with pyridine to produce a sample of the unconverted material from the reaction product. This is analyzed to produce ash representing the mineral fraction of the reaction product.

Numberous inspections are possible on these samples. Usually sampling is restricted to the end products, and intermediate products from separations are only sampled for special purposes. Stripped coal solution or filtered coal solution is not usually sampled for further analysis but is all used to prepare recovered solvent and vacuum bottoms. Standard inspections for the final products from the separation procedures are indicated on the table on page 87. Most of the inspections for products have been described in sufficient detail in Interim Report No. 6. 2/ This discussion will be limited to a few items where additional experience has resulted in a changed procedure or shown a deficiency in the method previously reported.

In the section discussing special studies on wet filter cakes (Interim Report No. 6 III-F-1.) a method was suggested for measuring the amount of coal solution imbibed in a wet filter cake by measuring the blackness of an extract of the filter cake. It was suggested that the calibration could be based on the filtered solution made by weighing known portions of the filtrate and reading the color intensity of suitable dilutions of filtrate. It has since been found that a pyridine extract of the wet filter cake may be more colored than is accurately proportional to the concentration of colored material in the filtrate. The wet filter cake may contain a selected fraction of adsorbed or insoluble colored material which is pyridine soluble and the color related to the weight of imbibed solution is higher in concentration (or color intensity) than the color observed in the filtrate. While observations may not render the method useless it may require that calibration be based on wet filter cake analysis by correlation with the results of the usual extraction method rather than on the filtrate. This method has not been systematically investigated but initial results in the anthracene oil studies appeared to be less in error than results from samples made with decanted oil as the initial solvent. This procedure could be used to obtain more information about the marginally soluble fractions which may be produced in different amounts under different operating conditions. This has not been explored.

IV-I

In initial work with correlation of infrared analysis and elemental analysis the ratio resulting from dividing absorbance at 3.28 microns by the absorbance at 3.42 microns was plotted versus the total hydrogen in the cut 2 solvent. This procedure was described in a paper presented to the Fuels Division of the American Chemical Society. 4/ It has since been considered that the ratio should be calculated as the absorbance at 3.42 microns divided by the absorbance at 3.28 microns in order to obtain a plot in which the ratio increases as the percentage total hydrogen in the oil increases. As a result the data from all anthracene oil experiments have been converted to this format to allow a uniform style of charting for reporting the results of work with decanted oil and equilibrium solvents.

In presenting the results of spectral measurements in solution autoclave product solutions were made as a standard 3.00% weight/volume dilution in carbon disulfide. This is acceptable for anthracene oil samples and reclaim solvent from one pass anthracene oil samples. The concentration of oil may be too high for proper measurement of all bands at 3.00% W/V, particularly for lower molecular weight fractions such as cut 1 or cold trap oil. It is necessary to consider the spectra of a wider variety of oils in the work with petroleum derived solvent studies or in the studies which lead to the development of equilibrium solvent. No standard concentration can be chosen which is suitable for the comparison of all of these materials. In selecting spectra for presentation an effort will be made to facilitate comparisons from one report to another by presenting a few comparisons of the same material on different instruments and by adjusting concentrations where bands may be too strong at the usual concentration.

IV-J Discussion of Experiments

The results for all of the experiments done with anthracene oil derived solvents in the continuous reactor have been collected in a series of tables which are presented as Appendix A of this report. An effort has been made to reduce all of the data to a standard format. This has not been possible in all cases since a considerable variety of experiments and materials is included. There is the additional problem that reactor design and experimental procedures have evolved throughout the course of the program. The quality of the data presented for the first experiments is not as good as the quality of the data presented from the last experiments reported.

In order to place the data in context with regard to quality it has been considered reasonable to report the raw input and raw output material balance for each experiment. Thus the losses or other operating problems which produce poor recovery in some cases are evident in the percentage recovery. This result then gives an index for the probable reliability of the basic set of samples which are the source for the yield and product characterizations which follow in the report. As a general observation the initial experiments often resulted in percentage recovery of about 90% or so. By the middle of the program most of the obvious problems had been corrected and material balances of about 95% or so were usual. The equipment was then slowly improved and material balances accounting for 98% or so of the feed were common by the end of the program. An elemental balance for nitrogen and sulfur was requested by the Environmental Protection Agency near the end of the anthracene oil program. This resulted in a careful review of sampling procedures, remaining operating problems, and analytical techniques in use. As a result of this review the operating details have been further improved and the current program of experiments results in material balances closed better than 99.5% routinely.

The method of workup has been described previously. Generally the transfers from one piece of equipment to another have involved handling losses. In calculation of yields and product distributions these handling losses had to be accounted and materials were prorated on loss free basis by means of this accounting method. This depends heavily on the ability to sample and subsample without disproportionating materials in the sample. In a number of instances such sampling is actually quite difficult to do accurately and the tendency for error or lack of reproducibility in results depends on the quality of such sampling as must be done. It can be seen that the use of larger samples and the development of workup procedures which minimize transfers and which compensate handling losses have been the keys to obtaining the best possible accounting of materials.

It is thought that the variety of experiments and the amount of procedure development which is included in many of the trials will preclude a very systematic discussion of these experiments from the viewpoint of the reactivity of a particular coal, a particular solvent, a particular reducing gas, or so on. Accordingly the following section of the report is to discuss each sequence of experiments in numerical (chronological) order. Some emphasis will be given to technique studies and to the background work done to improve the quality of the experimental work. It is assumed that data for most of the comparisons which might be considered will appear in Appendix A and the discussions will attempt to include supplementary information which ought to be used to qualify or extend the information in Appendix A.

Most of the discussions to be presented will take only a few pages. In order to provide for rapid access to these discussions the pages of the report which discuss a series of experiments will be keyed with the code letters and numbers for the basic series involved. This should facilitate comparison of the data presented with other experiments involving similar materials or with additional results presented in Appendix A.

Evaluation of Experiment CL-1 and CL-2

This was the first attempt to run a continuous reactor laboratory study for the solution of Kentucky No. 9 coal in anthracene oil. The reducing gas was hydrogen at 1000 psig. The flow of the hydrogen was obtained by allowing the gas to flow from a regulated cylinder of hydrogen through a high pressure rotameter. The slurry was pumped by means of a Milton Roy positive displacement adjustable stroke pump. The CL reactor tube was used and the product letdown system utilized the Fisher Governor "Gismo" valve. An attempt to meter the product gas by allowing it to flow through a wet test meter was made in run CL-1. This was not successful since the gas was released in spurts which outran the capacity of the wet test meter at times. In Run CL-2 the wet test meter procedure was used for part of the gas collection interval and a gas collection bag was used for the remainder of the gas collection interval. The comparative volumes obtained indicated that about half of the gas sample was leaking through the wet test meter. The gas output for run CL-1 was corrected on this basis.

The solvent was the middle fraction of raw anthracene oil (which is indicated as MFRAO in Appendix A tables). The feed slurry was pumped at a rate of 512 grams per hour, which is near the LHSV value of 1.0 desired for the experiment. Since this was the first study the dissolver temperature was maintained at a mild temperature. The hydrogen flow rate was set at about 4.0 moles per hour. Exact figures are presented in Appendix A.

In run CL-1 the equipment was brought to operating temperature, pressure, and hydrogen flow rate while pumping MFRAO through the unit. This was accomplished in an hour and a half. At this point the feed pot was replaced with a similar vessel of 3:1 solvent to coal. An hour and a half was allowed for the product to reach a lined out composition. A liquid sample was collected for 3 1/2 hours. The gas was metered through the wet meter to determine the volume of effluent gas from the reactor. Small gas samples were taken from the reactor for determination of molecular weight, hydrogen sulfide, and the infrared spectrum of the gas. A qualitative gas chromatographic analysis was also done. This analysis was limited because standardization of the gas chromatograph was not completed at this time. Because of difficulty with measuring the volume of gas through the wet test meter the gas weight was not accurately known. Even so the raw material balance closes within 96.1%. The composition could be estimated reasonably well by correlation of molecular weights with similar gases from previous autoclave runs. This could be further detailed by comparison of infrared spectra from this experiment and for autoclave products. From the check done subsequently it would be fair to double the weight of gas obtained. This would result in a closure of 100% if this correction were applied.

The whole liquid sample obtained was taken for the workup procedure. This weighed 1721.9 grams. In addition 5.0 grams of material were collected in the knock out pot in the gas sampling line. This sum (1726.9) divided by 3.5 is then the liquid product weight which appears as the unstripped solution weight rate in grams per hour in Appendix A. This is a sufficiently large sample to allow a workup without handling losses becoming a significant problem. The yields were calculated to a % feed coal basis for the first monthly report and have been recalculated to a % MAF feed coal basis in order to fit them into the standard format that was developed later. The solvent reclaim distillation was continued to the apparent decomposition point and was stopped at 287^{o}C at a nominal vacuum of 3mm or less. This accounts for the high melting point of the vacuum bottoms product obtained. The solution was filterable and the product distribution obtained was the result of the standard work up which had been developed for autoclave samples. (See interim report No. 6) In general the operation of the unit was mechanically reasonably satisfactory with the exception of the gas sampling problem. The product distribution and the compositions obtained looked reasonable from the comparison with autoclave data with the same coal and solvent.

The gas yield on the MAF coal basis is large. This is probably the consequence of using a high ratio of solvent to coal, actually the gas is largely derived from decomposition of the solvent. One of the consequences of referring such yields to the MAF coal is that yields may look unreasonable if the source of the material is not actually the coal.

One other error is probable in the data presented. The time allowed for lineout and mineral equilibration in the reactor is probably too short. In this situation mineral is fed into the reactor and a part settles in the dissolver tube. The product which is taken as liquid sample is then rich in organic phases and deficient in mineral. When this subtle distortion of the sample is referred to the MAF coal fed the result is an abnormally high yield of organic products, that is the return of vacuum bottoms and reclaim solvent is too high by the proportion of mineral matter settled in the dissolver.

An objective in run CL-2 was to correct the gas sampling problem which had been encountered in the first run. The results from the collection of gas in the gas sampling bag were in accord with expectations based on the gas flow through the input rotameter. This was clearly the preferred sampling procedure. The experiment was done with a 2:1 solvent to coal slurry and all other conditions were the same as CL-1. Collection of liquid sample was stopped at the end of three hours. When the product workup was done it was discovered that the stripped solution could not be filtered. The product workup was then completed by distilling the unfiltered solution. Estimation of % MAF conversion was done by recovering the insolubles from the distillation residue by extraction of the soluble material with pyridine followed by ash analysis of the insoluble residue.

At this time no reason could be advanced for failure of the solution to filter. The original intention had been to run both CL-1 and CL-2 at 425°C. The data presented in Appendix A for operating temperatures are actually estimates of the probable operating temperature which were made later. The temperature recorder in use failed progressively and probably was inaccurate from the first use. The chances are good that the estimated temperatures are not particularly reliable. From the data patterns obtained, the CL-2 experiment probably was done at a lower operating temperature than CL-1. In addition the increased concentration of coal in the feed slurry should have resulted in a more difficult sample to filter.

The initial operation of the continuous reactor did not present any problems which seemed to require correction or mechanical work. The gas samples obtained were analyzed and compared to autoclave generated data. These results were used as a basis for ordering some analyzed gas mixtures for use in calibration of the gas chromatograph. The unit was then used to study the reaction of lignite in several following runs.

IV-J

Evaluation of Experiments CL-3, CL-4, and CL-5

Since the preliminary experiments with Kentucky No. 9 coal and hydrogen had shown the continuous unit to be operable, a series of experiments was planned to explore the operating problems associated with studies with lignite and carbon monoxide as the reducing gas. Several mechanical problems had to be solved in order to do these experiments. First, apparatus was installed to monitor the working area in the bay and at the operating control board for carbon monoxide in the air. Second, the lignite had to be ground and analyzed for content of water and ash after grinding. In preliminary trials it was found that the Milton Roy pump would not pump slurries of wet lignite in anthracene oil until the lignite was all sieved to pass through a 100 mesh sieve. Finally some new operating procedures had to be developed to line out the reactor. The desired flow rates for carbon monoxide and for hydrogen were therefore established by calibrating the rotameters for each gas before the experiment was attempted.

From autoclave studies and from the literature available, the utilization of carbon monoxide was thought to depend on a reaction with water which generated hydrogen for the reduction process. Autoclave data had indicated that the normal bed moisture in lignite should provide enough water to allow this kind of reaction to proceed efficiently. In addition it was reasonably well established that a lignite with an alkaline ash content would be reactive, the sodium in the lignite promoting the water shift reaction. See Appendix B for the analysis of the Baukol-Noonan lignite used in this work.

CL-3

The first trial in this series was done with a slurry mixed to contain a 3:1 ratio of the middle fraction of raw anthracene oil as solvent to wet lignite. The lignite was analyzed by oven drying and contained 29.3% of moisture and 10.56% of ash in the dry basis sample. These results are in reasonable agreement with the lot analysis for the coal as presented in the appendix.

The lineout was conducted by pumping MFRAO to bring the reactor to operating temperature with the desired flow rate of oil passing through the unit. During this time the reducing gas was hydrogen which was fed from a cylinder through a pressure regulator and a rotameter to measure the flow rate. The feed slurry was then substituted and at this point the flow of hydrogen was stopped and the flow of carbon monoxide was started. The carbon monoxide was taken from a cylinder at a regulated pressure and the flow rate was set by means of the previously calibrated rotameter. About an hour and a half was needed to bring the reactor to operating conditions, and then another hour and a half was used to line out the reactor after slurry feed was started. According to the operating log the sample was collected for a two hour period. Two gas samples were collected for analysis during this interval.

The liquid sample was stripped in the conventional procedure but the sample would not filter through an analytical filter paper in a buchner funnel.

The unfiltered solution was therefore returned to the flask and an estimate of the amount of reclaim solvent was obtained by distilling the unfiltered solution. A portion of the distillation residue was extracted with pyridine to obtain a sample of the insoluble material and the MAF conversion was calculated from the ash content of this residue.

Data for the run are reported in Appendix A. It can be seen that the recovery of product samples accounted for only 50% of the feed material. The slurry feed rate is 404 grams per hour and the gas feed rate is an additional 98 grams per hour of carbon monoxide. Thus in order to have a recovery of only 50% nearly a half kilogram of material would have to be misplaced. This seems to be completely unreasonable. The more probable cause for the bad accounting would be an operating error in which the collection of sample was stopped before the two hour period recorded. Another problem of a mechanical nature could be the cause, if the valve which switched the stream from the slop to the collection vessel failed to operate. Since this valve is air operated it is comparatively easy to improperly set the operating control by accident and the actual movement of the valve would not easily be observed. Low operating air pressure occasionally results in failure of the valve stem to move on signal from the control board. In any of these cases the real problem is an observational failure at the operating control board. Such problems are common in a new operation, and the control which results in closing the material balance is the application of properly designed instruction and data recording sheets.

Another more subtle operating error was later uncovered in this experiment. This was an improper temperature record from a potentiometric thermocouple recorder. The instrument was inaccurate because of the progressive failure of a reference battery, and the warning flag which should have signaled the failure of the battery did not operate. This resulted in operating the unit at lower than planned temperature. Temperatures recorded in Appendix A are estimates which were obtained after the recorder error had been detected and corrected. Failure of the solution to filter is most likely the consequence of operating at about 395°C instead of 425°C as had been intended, and as the bad recorder had reported.

CL-4

This was the second attempt to dissolve lignite in the middle fraction of raw anthracene oil using only carbon monoxide as the reducing gas. The feed slurry was made in the ratio of two parts of solvent to one part of wet lignite. The reactor was operated at 400°C according to the recorder which was later found to be defective. The actual temperature was later estimated to be 370°C. The reducing gas was pure carbon monoxide at 1000 psig pressure.

The lineout of operating conditions was conducted by pumping MFRAO through the unit with the gas flow of carbon monoxide established from the beginning of the procedure. After switching to feed slurry a two hour period was allowed for the reactor to reach steady operating conditions. The sample for workup was collected for 3.5 hours. A gas sample was collected in a rubberized fabric bag for a 30 minute interval beginning in the second hour of collection of the liquid sample.

Data obtained from this experiment are presented in Appendix A. It can be seen that considerable improvement in the management of the experiment had been obtained as the closure of the material balance accounted for 84.7% of the material fed. The liquid sample was stripped and as could be expected it could not be filtered. An estimate of the amount of reclaim solvent was then obtained by distillation of the unfiltered solution. The insoluble residue was then obtained by extraction of the distillation residue with pyridine. The MAF conversion was determined by ash analysis of the pyridine insoluble material.

CL-5

This was the third attempt to dissolve lignite in the middle fraction of raw anthracene oil using only carbon monoxide as the reducing gas. The feed slurry was again mixed in the ratio of 2 parts of MFRAO to 1 part of wet lignite. The operating pressure was 1000 psig and the experiment was done at 450°C according to the recorder which was later found to be defective. The actual temperature was later estimated to be 395°C.

The lineout was conducted by pumping MFRAO through the unit together with a flow of carbon monoxide to establish operating temperature and flow rates. A three hour period on feed slurry was used to establish compositional lineout and then a liquid sample was collected for one and a half hours. A gas sample was collected for the whole of the liquid sample collection period.

Data obtained from this experiment are presented in Appendix A. The percentage recovery increased and accounted for 89.2% of the feed materials. The liquid sample was stripped but again it was found to be unfilterable. The MAF conversion was determined from the analysis of the pyridine insoluble material as usual, and was only 59.2%. Conversions for the previous two runs had been low also. Values were 63.8% for CL-3 and 47.6% for CL-4.

In view of the low conversions and the several operating difficulties evident in poor material balance data obtained no effort was made to calculate yield and product distribution results. It was clear that the results in the several continuous reactor trials were much worse than had been obtained in the batch autoclave experiments. Because the temperature problem had not been recognized the major cause was thought to be use of 1000 psig operating pressures in contrast to the 4000 psig peak pressures commonly observed in the autoclave experiments. In addition the usual solvent in the batch autoclave experiment had been the middle fraction of process reclaim solvent retained from the previous process development program. This solvent was partly hydrogenated by use in coal processing and was known to be more reactive.

Discussion:

These experiments raised a number of questions regarding the control of input compositions and regarding the evaluation of product solutions and product gases. The need for careful regulation of operating procedures and data collection procedures was evident in the failure to make even a reasonable approximation of the material balance in experiment CL-3. It was also concluded that the operating pressure limit on the reactor should be changed, and the parts for the gas compression and metering system were accordingly requisitioned. The need for analysis of feed slurry compositions was fairly clear, since the chance for loss of water from the feed pot seemed to be the largest uncertainty in the material balance in run CL-5 for example.

This series of experiments was continued with the apparatus available using process reclaim solvent instead of the middle fraction of raw anthracene oil. It was hoped that this experiment would define the contribution of solvent reactivity and the need to operate at higher pressures.

IV-J

Evaluation of Experiment CL-6

The objective in this experiment was to repeat the previous run in all details substituting the middle fraction of process reclaim solvent for the middle fraction of raw anthracene oil used previously in CL-5. The process reclaim solvent was derived from anthracene oil. It had been used and recovered for recycle a number of times in the continuous solution studies done in the process development plant. The solvent contained a portion of fresh anthracene oil make up and contained a portion which had been partly hydrogenated by use in the process. (See interim report No. 6 for a detailed discussion of this material)

The feed slurry for this experiment was prepared by mixing two parts of the middle fraction of process reclaim solvent with one part of wet lignite. The lignite was from the same lot of Baukol-Noonan lignite used previously. Moisture and ash analysis confirmed that the material had retained its usual bed moisture reasonably well. The moisture was 26.76% and the ash was 7.14% on the moist sample. The operating pressure for the experiment was 1000 psig and the temperature was 450^{o}C using the recorder which was later found to be inaccurate. The true operating temperature was later estimated to be 390^{o}C.

The lineout was conducted by pumping the middle fraction of process reclaim solvent through the reactor with the desired flow rate of carbon monoxide in order to adjust flow rates and operating temperatures. The feed was then switched to the feed slurry. A two hour period was allowed for the composition of the reactor product to become established. A liquid sample was then collected for a three hour interval. Two gas samples were taken during the time the liquid sample was being collected.

Data obtained for this experiment are summarized in Appendix A. The percentage recovery was again improved, 95.3% of the feed to the reactor being accounted for by the samples taken. As had been expected the MAF conversion was improved since this increased from the 59.2% value observed in the previous run to 70.4%.

The solution was stripped but again the stripped product could not be filtered through an analytical filter paper in a buchner funnel. The solvent was therefore recovered by distillation of the unfiltered solution. The MAF conversion was determined by the ash analysis of the pyridine insoluble material isolated by extraction of the distillation residue.

Discussion:

At this time no rapid methods were available for inspection of product solutions or reclaimed solvent. The infrared spectra of reclaimed solvents were run routinely. From these it was possible to review the $\overline{\text{IR}}$ values and to deduce the extent to which the solvent may have gained or lost hydrogen as a result of use in an experiment. The reclaim solvent in experiments CL-3 and CL-4 were barely changed and tended to gain trace amounts of hydrogen. A small but significant increase in hydrogen was observed in experiment CL-5. In the last experiment the higher hydrogen content solvent lost a small but significant amount of hydrogen. (Compare the IR values presented in Appendix A) From this observation the gain in MAF conversion can be related to a measurable change in the solvent used in experiment CL-6. A small amount of hydrogen was transferred from the solvent in this case.

In all of these experiments the gas samples which were taken were analyzed carefully. The molecular weights were determined by the gas density method and the composition was determined by gas chromatographic analysis. These results are presented below for the gases as received.

PRODUCT GAS COMPOSITIONS

Component	CL-3	CL-4	CL-5	CL-6	CL-6
Mol %				bag 1	bag 2
Carbon Monoxide	73.80	58.90	65.50	60.00	48.5
Hydrogen	3.84	4.08	6.07	8.36	6.43
Methane	0.54	0.57	1.64	1.98	1.53
Ethane	0.16	0.15	0.58	0.90	0.76
Propane	0.08	0.11	0.30	0.41	0.32
Butanes	---	trace	trace	---	---
Nitrogen	9.51	15.20	11.20	10.30	28.6
Oxygen	2.19	1.11	1.11	0.64	1.68
Carbon Dioxide	10.90	22.20	16.40	18.59	13.8
Total	101.02	102.32	102.80	101.18	101.6
MW Calculated	29.2	31.1	29.7	29.8	29.2
MW by Gas Dens.	29.8	31.1	29.6	29.1	28.7

In general the molecular weight by the gas density method and the molecular weight from the gas analysis based on gas chromatography were similar. The amount of oxygen in the sample was taken as a measure of the amount of air which was introduced by improper flushing of the flask used for collection of the liquid sample before the gas sample was taken, or by the accidental addition of air by technique problems in drawing the samples used for analysis. Presumably the nitrogen in the sample was added in the same ratio in which it is present with oxygen in air and the balance above this figure was contributed by the nitrogen purge for the gage line and the pressure sensing tap of the "Gismo" valve used as the pressure let down device. According to the rotameter reading the flow of carbon monoxide to the reactor was not reproduced well from run to run, these differences being indicated in Appendix A by varying gas space velocity results.

Even though the temperature was not the desired value some conversion of carbon monoxide to hydrogen is indicated by the appearance of hydrogen in the product gases and by the accumulation of carbon dioxide in the product gases. Unfortunately carbon dioxide is normally made from lignite, even in hydrogen reductions, therefore the yield of carbon dioxide is not a direct indication of the extent of the reaction undergone by the carbon monoxide.

CL-6

IV-J

It was found that the cost of pure carbon monoxide was comparatively high, and that the use of pure carbon monoxide offered no advantage in cost over the cost of pure hydrogen. Therefore all subsequent experiments with carbon monoxide were done in mixtures with hydrogen which could be made by water gas reactions or by gas reform reactions. It is unfortunate that the temperature control for these reactions is of such dubious quality since only a small number of experiments have been done in this continuous reactor with pure carbon monoxide.* As a general observation the reproducibility of the gas metering system in use was poor and this end of the unit was clearly in need of improvement.

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* One other experiment using pure carbon monoxide and B.N. Lignite is available. This is Run CL 12, reported later.

IV-J

Evaluation of Experiment CL-7

Experiment CL-7 marked a return to the study of Kentucky No. 9 coal. The experiment was a continuation of the preliminary studies done in CL 1 & CL 2 and involved the use of a longer retention time and a reduction in the H_2 flow rate as well. Hydrogen at 1000 psig was used as the reducing gas. The middle fraction of raw anthracene oil was used as solvent. The retention time was increased to a 1/LHSV of 1.32. It was intended that the dissolver be operated at a temperature of 425°C. Because of failure of the temperature recorder the dissolver was actually operated at a lower temperature, later estimated to be 365°C. This is the probable cause for the low MAF conversion observed in this experiment. See Appendix A for the limited data available.

The lineout was accomplished by pumping the solvent while temperature and flow rate adjustments were made. When operating conditions were established, the feed slurry was substituted and one and a half hours of time were allowed to establish compositional lineout. The product sample was then collected for a two hour period. A gas sample was collected during the sampling interval.

Discussion of results

At the time this experiment was done little experience had been developed with the continuous unit. The solution which was made was found to be unfilterable and the work up of the sample was therefore not completed. The MAF conversion was estimated from the composition of the pyridine insoluble materials isolated from the unfiltered solution. In this case the MAF conversion was only 83.5%. These results appear reasonable in the light of corrected operating temperatures, but were not well understood at the time. Various mechanical studies were done to estimate the contact time with hydrogen and slurry. Most of these ideas can now be discounted since the temperature error is certainly the main cause of difficulty. Later work demonstrated that gas contact was adequate.

From later experience it is clear that the time allowed for reactor lineout was too short for an acceptable sample to be made. Thus the sample probably had some of the original flush solvent in it. These data are therefore of interest mostly for the indication that MAF conversion can be carried to a fairly high level even at low operating temperatures. This is an indication that the MAF conversion alone is not a key index for prediction of the utility of a coal solution for further processing. As such observations were accumulated in more detail it became clear that subsequent conversion of secondary products was a major consideration in the filterability of the solutions and the ultimate product distribution obtained.

The gas sample contained 89.9% hydrogen, 8.38% methane, 0.79% ethane, 0.40% propane, and 0.63% carbon dioxide. Thus, even at the mild conditions used, there was evolution of hydrocarbon gases. From this analysis and the volume of gas collected it can be computed that 3.6 grams of hydrogen were recovered while 5.2 grams of hydrogen were fed to the reactor. Thus, even at this temperature, a hydrogen consumption rate of significance is established.

The poor conversion was blamed on poor contact since the temperature error had not been located.

Evaluation of Experiment CL-8

This was the first experiment in which the lineout of the reaction was followed by infrared analysis of the product solution and by measurement of the absorbance of the solution in the visible region. Samples were taken for a 15 minute interval once each hour for these inspections. This was continued for the whole experimental run. During the final three hours the materials not collected in the 15 minute samples were composited to make a single large sample for the conventional workup. The reactor was operated on slurry for a total of ten hours.

Since low conversion was obtained in the previous experiment the reaction time was increased by pumping slurry at a slower rate. The 1/LHSV was 1.66 for this experiment. Hydrogen was fed at 1000 psig and the flow rate was 2.75 moles per hour, which is near the rate used in experiment CL-7. The feed slurry was made in the ratio of 2 parts of solvent to 1 part of Kentucky No. 9 coal. See Appendix A for a summary of the input and output for this experiment. These data apply to the composite sample collected at the end of the experiment. Because of the error in the temperature recorder the experiment was done at an estimated temperature of 350°C instead of 425°C as had been planned.

The apparatus was lined out at operating temperature, pressure, and flow rates while pumping solvent, in this case the middle fraction of raw anthracene oil. This required an hour of operating time. Slurry was then substituted and samples were collected for the study of lineout. The time of collection for each sample, and the results of measurements for each sample will be found on page 105. In addition to the product samples a slurry feed sample was collected to correspond to the time that product samples were collected. Collection of gas samples was also attempted for these short samples, and the samples were found to be badly contaminated with air. The lineout characteristics of the gaseous products therefore could not be studied with great reliability.

Discussion

The work done in this experiment placed emphasis on the development of methods for the analysis of feed slurry, and methods for observing the behavior of the products during reactor lineout. Samples of feed slurry were analyzed for coal content by filtering out the coal and rinsing the solvent away with acetone. These results are presented on page 105. The method was not considered to give satisfactory results. Errors are caused by extraction of the coal by the solvent and the acetone and by absorption of some solvent by the coal. This caused poor reproducibility of measurements by this method.

The 15 minute samples were collected in a series to tared glass flasks and the weight of each sample collected was determined by reweighing the sample plus flask. At the slow rate of feed the 15 minute samples weighed only about 70 grams each. The samples withdrawn for the blackness and $\overline{IR}$ measurements removed only a few drops of the material. In preliminary trials with samples #2 and #11 it was found that the samples could not be filtered. The solvent for other samples was therefore reclaimed by distillation of the unfiltered solutions. Conversion was determined from the amount of ash and carbonaceous material in the insoluble residue from pyridine extraction of the distillation residue. The composite sample taken for the standard workup was collected in a stainless steel flask. After stripping this sample was also found to be unfilterable, and the yield data presented are the result of distillation of the unfiltered solution. The MAF conversion was determined on insolubles which had been in contact with solvent throughout the heating time required to distill the solvent for reclaim. It is not thought that this kind of operation changes yields or MAF conversion results appreciably. For poorly converted material this point is hard to establish with reliability since the alternative extractions may also have some effect on the apparent conversion.

All of the gas samples taken during collection of the lineout samples were badly contaminated with air. This was the result of failure to flush the sample flasks properly. The whole sample period was only 15 minutes which does not allow time for this kind of gas sampling procedure to be done properly. In order to study lineout the results from the contaminated gas samples were reduced to the ratio of hydrogen to methane. These results are presented on page 105. It can be seen that the yield of methane increased as the concentration of coal built up in the reactor. It is premature to conclude that this is derived from the coal since mineral matter also builds up in the reactor at about the same rate as the coal. This material could just as well be increasing the concentration of a cracking catalyst, for example.

The more important observations made during this experiment were the infrared data for the product solutions and for the reclaimed solvent from these solutions. Here the $\overline{IR}$ for both the product solution and the reclaimed solvent increased as a function of operating time and tended to line out after a few hours of operation. These results are presented on page 105. In order to allow easy comparison of the trends the results are presented in graphic form as Figure 12. It is noteworthy that the hydrogen content of the reclaimed solvent, as indicated by the infrared spectra of the solvent, tends to increase during the experiment. At the same time the $\overline{IR}$ values for the raw coal solution samples trend higher and appear to line out after about 5 hours of operation. The difference between the values for the coal solution and the reclaimed solvent is due to a small amount of low molecular weight oil formed, but more importantly, it is also due to the presence of dissolved coal product. Spectra of vacuum bottoms have been presented previously and in all cases the strongest carbon-hydrogen band is observed at 2920 wavenumber. 2/ An example of this spectrum is presented as Appendix C-11 The infrared spectra for the input solvent and for the reclaimed solvent are presented in Appendix C items C3, C7, & C8.

The observations made with the visible range spectrophotometer were equally informative. It was found that the color of the solution increased systematically as the concentration of coal product in the reactor built up. Moreover the color intensity stabilized after about seven hours of operation. This was sufficient information to justify the use of this technique as a guide for lineout and product reproducibility studies. The results of blackness measurements are presented on page 105. and a graphic presentation of the data appears as Figure 13.

While the operating temperature used in this experiment is not known with precision, it is clear from the infrared spectra of the reclaimed solvent that a reasonable amount of hydrogen has been added to the solvent. This reaction can therefore be run at temperatures in the vicinity of 350°C. The coal is not rapidly depolymerized at this temperature therefore the product could not be filtered properly.

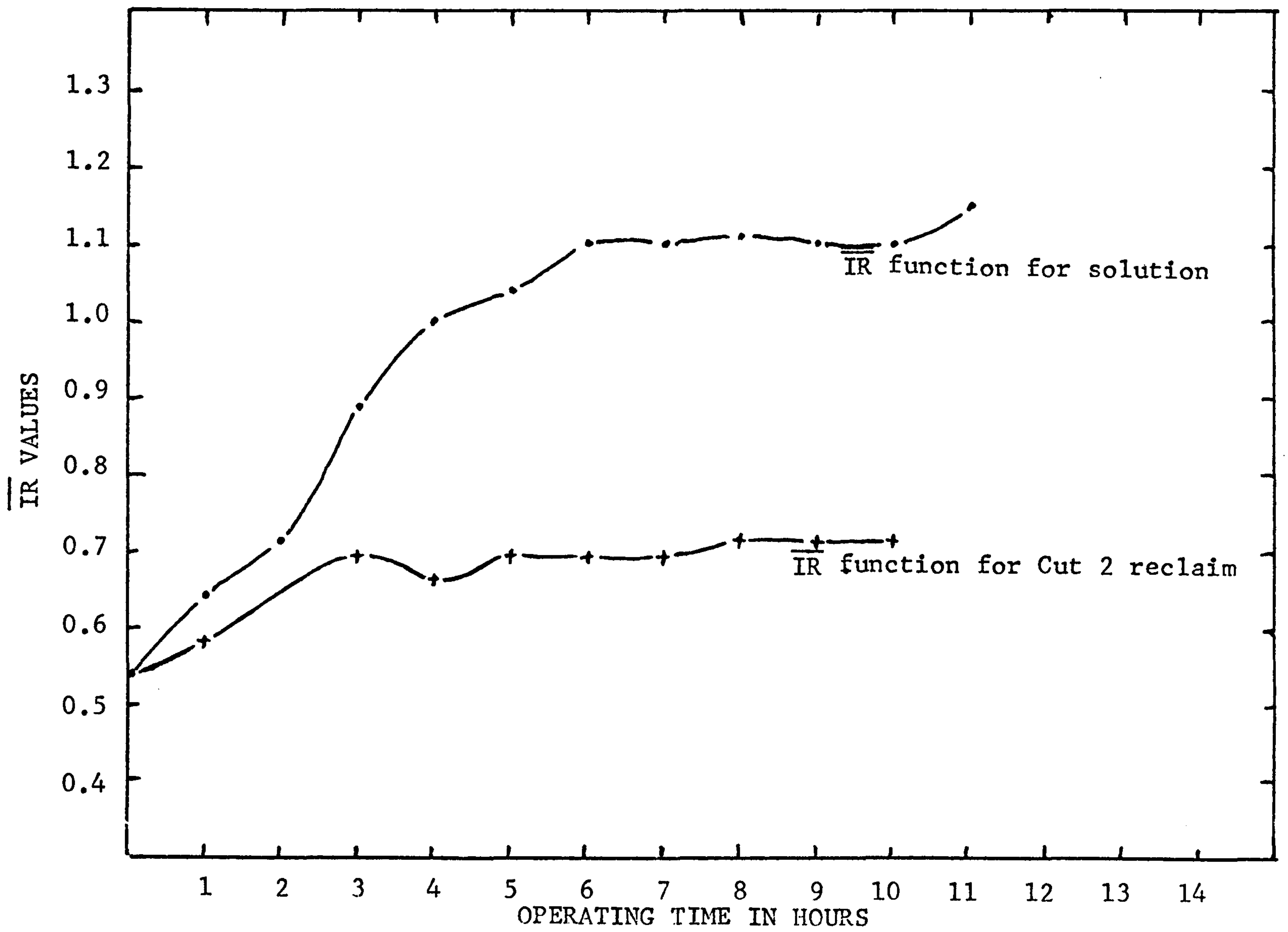
The results for the composite sample are presented in Appendix A. This sample also could not be filtered. The yield of reclaim solvent was therefore obtained by distillation of the unfiltered solution. The distillation residue was extracted with pyridine to obtain a sample of the insoluble material resulting from incomplete conversion of the coal. The pyridine insoluble material was analyzed to determine the proportions of ash and of insoluble organic material present. From this result it was calculated that 87.7% of the MAF organic matter of the coal had been converted. This was in good agreement with results obtained on the smaller lineout study samples.

The samples taken from the reactor for analysis accounted for 95.4% of the materials fed to the reactor in preparation of the composite sample. Product yields were calculated on the basis of the MAF organic matter fed as coal. On this basis the insoluble organic matter accounted for 12.3% of the feed coal. 82.9% of the feed coal was recovered as vacuum bottoms. An excess of solvent was obtained, 12.9% of the organic matter in the coal being recovered as liquid hydrocarbons or related compounds. At the comparatively low temperatures used, the conversion to hydrocarbon gases was quite low, accounting for only 0.46% of the MAF coal fed. These results may be compared to the results obtained in experiments CL-1 and CL-2, which were done with the same coal. It can be seen that the use of a mild temperature for an extended period of time resulted in fairly good conversion of the coal, but that the depolymerization of the secondary products had not progressed to the point of producing a readily filterable solution. These data are rational using the corrected

RUN CL-8 EXPERIMENTAL DATA SUMMARY
Kentucky No. 9 Coal: MFRAO
2/1 Ratio

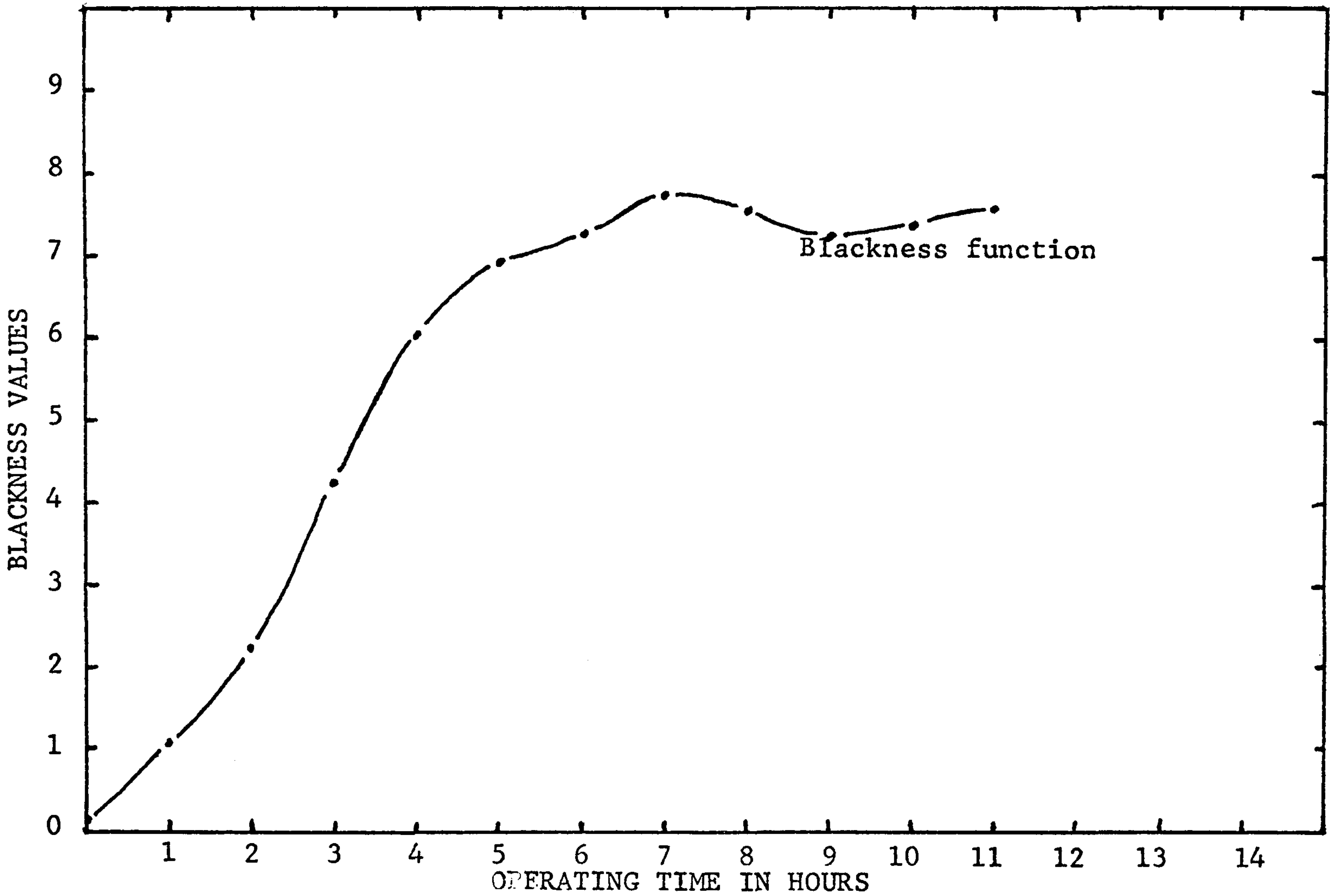
Sample No.	Time Hr	Slurry Rate Gm/Hr	Hydrogen Moles/Hr	Solvent to Coal Ratio (a)	Gas Analysis H_2 / CH_4	%MAF Conversion	Blackness	$\overline{\text{IR}}$ Solution	$\overline{\text{IR}}$ Cut 2
Solvent	0	----	----	----	--------	------	0.08	0.54	----
1	1	----	2.84	----	4674	87.0	1.08	0.64	0.58
2	2	332	2.76	2.5/1	2731	----	2.24	0.71	----
3	3	320	2.88	1.9/1	1685	87.1	4.23	0.89	0.69
4	4	344	2.60	2.6/1	881	87.6	6.03	1.00	0.66
5	5	324	2.72	1.8/1	744	86.6	6.93	1.04	0.69
6	6	200	----	1.9/1	759	87.2	7.28	1.10	0.69
7	7	332	2.48	2.8/1	710	88.0	7.75	1.10	0.69
8	8	316	2.60	1.9/1	781	89.3	7.59	1.11	0.71
9	9	364	2.72	1.9/1	933	91.6	7.25	1.10	0.71
10	10	320	2.76	2.0/1	723	88.3	7.36	1.10	0.71
11	11	288	2.72	1.9/1	880	----	7.55	1.15	----
Composite		312	2.72	-----	----	87.7	8.10	1.11	0.74

Notes: (a) determined by acetone washing procedure



RUN CL-8 LINEOUT STUDY BY $\overline{IR}$

Figure 12



RUN CL-8 LINEOUT STUDY BY BLACKNESS

Figure 13

values for operating temperature, but at the time caused considerable concern. The operating temperature was believed to be the same for all trials.

The solution had been allowed to stand for some time while the lineout samples were being analyzed. The blackness value obtained was higher for the composite sample than for the lineout samples taken at the same time. Apparently exposure of a solution to air for some time can result in some oxidation and a darker color is produced. This is a common observation with crude phenolic and amine compounds. For this reason it has been normal practice to make blackness determinations only on freshly prepared solutions.

Conclusions

Two separate methods which were rapid and simple to use had been outlined for observation of lineout characteristics of a coal solution. The infrared spectra were found to contain a lot of significant information which could be made quantitative in nature if necessary. The blackness function was thought to relate to the concentration of dissolved coal and it was expected that a colorimetric determination of dissolved coal could be developed on the basis of this measurement. The latter has not been fully realized but continued study of the blackness function has led to better understanding of this coal reduction process. These observations were the first reasonably successful attempts to estimate the amount of time needed for reactor product properties to become stabilized.

The solvent washing procedure used to estimate the concentration of coal in the feed slurry was found to give poor results. This procedure was therefore discarded in favor of ash analysis of the feed slurry. The gas sampling done on very short time interval samples was found to be afflicted by contamination with residual air, and such sampling was therefore not used in lineout studies.

IV-J

Evaluation of Experiment CL-9

In the series of experiments with lignite low conversion results were obtained and the need for operational capability at higher pressures was established. One of the changes required to develop this was substitution of a higher pressure rating feed pump for the Milton Roy pump originally installed in the CL unit. Experiment CL-9 was done to test the performance of a Hills McCanna pump which was capable of operation to 5000 psig.

The experiment was not completed because of repeated plugging of the Hills McCanna pump head. The pump head could be cleared by use of flush oil but upon return to slurry it would soon plug again. This behavior was reproduced several times in the attempt to line out an experiment. Finally the attempt to use this pump head was abandoned.

The Hills McCanna pump drive operates at 30 strokes per minute. At the lower feed rates used in typical experiments only about 4 1/3 cc per minute of slurry is pumped. The larger volume of the Hills McCanna pump head therefore has a slower liquid velocity in this service than the Milton Roy pump head which had operated reasonably well. It is not clear if the effect is due to settling of coal inside the pump head, or the failure of the small displacement of liquid to open the checks wide enough for the coal particles to pass through. An argument was developed based on the superficial liquid velocity in the pump head in order to compare the various pump heads available. The superficial liquid velocity was calculated from the following equation and has the units of length of flow per pump stroke.

$$V_S = \frac{\text{Slurry Volume / Minute}}{\text{(Head Volume / Head Length)(Strokes / Minute)}}$$

The dimensions and results for the various pump heads under consideration are presented in the table below. On the basis of these comparisons the Autoclave Engineers Speed Ranger pump head was selected for trial in experiment CL-10.

PUMP HEAD ASSEMBLY CHARACTERISTICS

Pump Head Assembly	Milton Roy	Hills McCanna	Autoclave Engineers
Head Volume, cc	0.5	13	3
Length, cm	4.0	15	8
Strokes / Minute	96	30	30
Liquid Rate, cc/min.	4.33	4.33	4.33
V_S cm / stroke	0.36	0.17	0.38
Remarks:	Adequate with Ky #9 & -100 mesh lignite	Would not pump with Ky #9	Good with Ky #9 and lignite on basis of later trials.

IV-J

Evaluation of Experiment CL-10

This experiment was done to test the use of the Autoclave Engineers Speed Ranger pump head with the Hills McCanna pump drive. The 1/LHSV was set at 1.31, which required pumping 6.6 grams of slurry per minute. The pump head performed well at this rate with a 2:1 slurry of Kentucky #9 coal in the middle fraction of raw anthracene oil and with the reactor operating at 1000 psig of hydrogen.

It was planned to operate the reactor at 425°C, but the faulty temperature recorder resulted in a misset temperature. The actual operating temperature was later estimated to be 325°C. The conversion was poor at this temperature but hydrogen was added to the solvent and evidence for coal in solution was obtained by means of infrared analysis of the solutions made. The experiment is of interest mostly for the evidence of reaction at 325°C which was obtained.

The experiment also involved a lineout study, although the time for the whole experiment was too short for a good lineout to be accomplished. The reactor was adjusted to operating conditions while flush oil was pumped. The feed was then switched to coal slurry and samples of product were collected for 15 minute intervals once each hour. In the last hour a sample was collected in a stainless steel flask for workup by the standard procedure. It was found that this sample could not be filtered, therefore the solvent was recovered by distillation of the unfiltered solution. The distillation residue was extracted with pyridine to isolate the insoluble material. Conversion was calculated from the ash analysis of the pyridine insoluble residue.

The infrared analysis of the product solutions and of the Cut 2 reclaim solvent is of particular interest because evidence for a reasonable concentration of partly dissolved coal as well as evidence for hydrogenation of the solvent at 325°C was obtained. These data are presented in the following table:

CL-10 EXPERIMENTAL RESULTS

Sample	Time	$\overline{\text{IR}}$ of Solution	$\overline{\text{IR}}$ of Cut 2
1	1 Hr	0.83	
2	2 Hr	0.92	
3	3 Hr	0.99	
4	4 Hr	1.05	
5	5 Hr	1.08	
SS Flask	6 Hr	1.06	0.68

The data obtained from workup of the final sample are presented in Appendix A. The MAF conversion was only 15% with a low yield of vacuum bottoms and a loss of recoverable solvent indicated. These results are hypothetical of course since the solution actually could not be filtered. They do indicate a slow depolymerization rate and swelling of the coal to produce a stable interaction product between the coal and the solvent. Compare also the results for CL-11A done at substantially the same temperature but at a slower feed rate. This temperature is high enough to cause the solvent to swell the coal but the complete breakup of the swelled material is not accomplished at a useful rate at 325°C.

CL-11A and CL 11B

IV-J

Experimental Data and Discussion:

This was the second experiment in which the infrared spectra and the visible spectra of the coal solutions were used to study lineout characteristics of the reactor. In the initial part of the run it was discovered that the temperature recorder was in error. The unit was operating at an estimated temperature of 325°C while operation at 425°C had been intended. The temperature was then corrected to 425°C after switching the thermocouple to a recorder which was in good working order. This correction was made between the seventh and eighth hour of the experiment. As a result the experiment which was done as CL-11A shows the progress of a lineout from flush oil to coal solution with a reactor at about 325°C followed by a lineout on coal solution, in CL-11B, at normal concentration in which the temperature was advanced from 325°C to 425°C.

The reactor product was sampled each hour throughout the experiment in order to follow the lineout characteristics of the product being made. The low temperature part of the experiment lasted seven hours and resulted in seven samples for spectral analysis. The temperature was corrected between samples seven and eight. Samples were again taken each hour to continue the spectral study and at the end of the experiment a large sample was taken for the standard workup to determine filterability and yields. The experiment was ended after 16 hours of operation.

During the low temperature part of the experiment the blackness in the solution increased, from an initial value which was the same as the solvent, along a smooth curve which finally leveled out in 5 to 6 hours. After the temperature was increased the blackness of the solution became more intense and again the concentration of colored material in the solution required 5 to 6 hours to establish a steady concentration. These observations were supported by measuring the ratio of absorbance at 3.41 microns to the absorbance at 3.28 microns in the infrared spectrum of the unfiltered coal solution samples. This ratio increased systematically as the first (concentration) lineout was achieved then stabilized in the 5th to the 6th hours. After the temperature was corrected the ratio dropped and reached a new stable value in an additional 5 to 6 hours. From these observations it was concluded that both the infrared method and the blackness measurement method would show responses to changes in product concentration and to the reactor operating conditions. Data from the spectral observations are as follows:

CL-11A and CL-11B

IV-J

Lineout Observations for Experiments CL-11A & CL-11B

(Kentucky #9 Coal, MFRAO, 1000 psig Hydrogen)

Elapsed Time Hours	Temperature °C	$\overline{IR}$ Values	Blackness Values
0	325	0.55	---
1	325	0.80	3.16
2	325	0.90	5.85
3	325	1.01	6.97
4	325	1.05	7.13
5	325	1.05	7.40
6	325	1.05	7.54
7	325	1.10	7.42
8	425	1.07	8.61
9	425	0.97	10.22
10	425	0.93	10.41
11	425	0.85	12.67
12	425	0.86	13.21
13	425	0.86	12.50
14	425	0.89	12.96
15	425	0.82	12.57
16	425	0.86	12.99
CL-11B Workup Sample	425	0.83	12.89

It was found that the samples made at 325°C could not be filtered, while the large CL 11B sample could be filtered. A standard workup of the CL 11B was therefore possible. The CL 11A sample was distilled without filtration to obtain the reclaim solvent data. Conversion was determined by isolating the pyridine insolubles in the distillation residue from the CL 11A sample and then determining the relative amounts of carbonaceous material and ash in the insoluble material. The MAF conversion was determined for the CL 11B sample by the analysis of the insolubles from washing the wet filter cake with pyridine in the standard procedure. The MAF conversion for the CL 11A sample was 47.5% and for the CL 11B sample it was 88.9%.

These results have been presented in graphic form in order to facilitate a visual comprehension of the relationships between the two lined out solutions made and to show the shape of the transition intervals between the lined out segments of the experiment. These curves are fairly representative of the time delays which must be observed in order to produce valid samples. These observations influenced planning of subsequent runs and the timing of the intervals allowed for lineout between samples or following a condition change.

It can be seen that the empirical function "Blackness" responds to changes both in coal concentration and to operating conditions. In addition the $\overline{IR}$ function has already been correlated with the amount of hydrogen in the solvent and with the coal solution. It was noticed that conditions which improved the solution of the coal tended to increase the blackness of the solution so long as an appreciable amount of undissolved coal remained available. Higher temperatures obviously increased the transfer of hydrogen from the solvent to the coal ($\overline{IR}$ values decreased between CL 11A & CL 11B). It is equally interesting to observe that the solvent acquired considerable hydrogen at the colder operating temperature. If the $\overline{IR}$ value is accepted at face value the solvent was hydrogenated rapidly even though the coal was not vigorously attacked at 325°C. ($\overline{IR}$ values increased from 0.55 for the raw anthracene oil to 1.05 by the end of the lineout at this condition.)

It was concluded that these functions taken together had the potential for following the coal solution mechanism in more detail than was possible from the standard distillation, filtration, and solvent extraction workup used previously. Correlation of such functions with operating conditions and the results of the standard workup could lead to rapid methods of analysis for coal solutions. These measurements were made routinely in subsequent experiments.

LINEOUT STUDY FUNCTIONS RUNS CL 11 A & CL 11 B

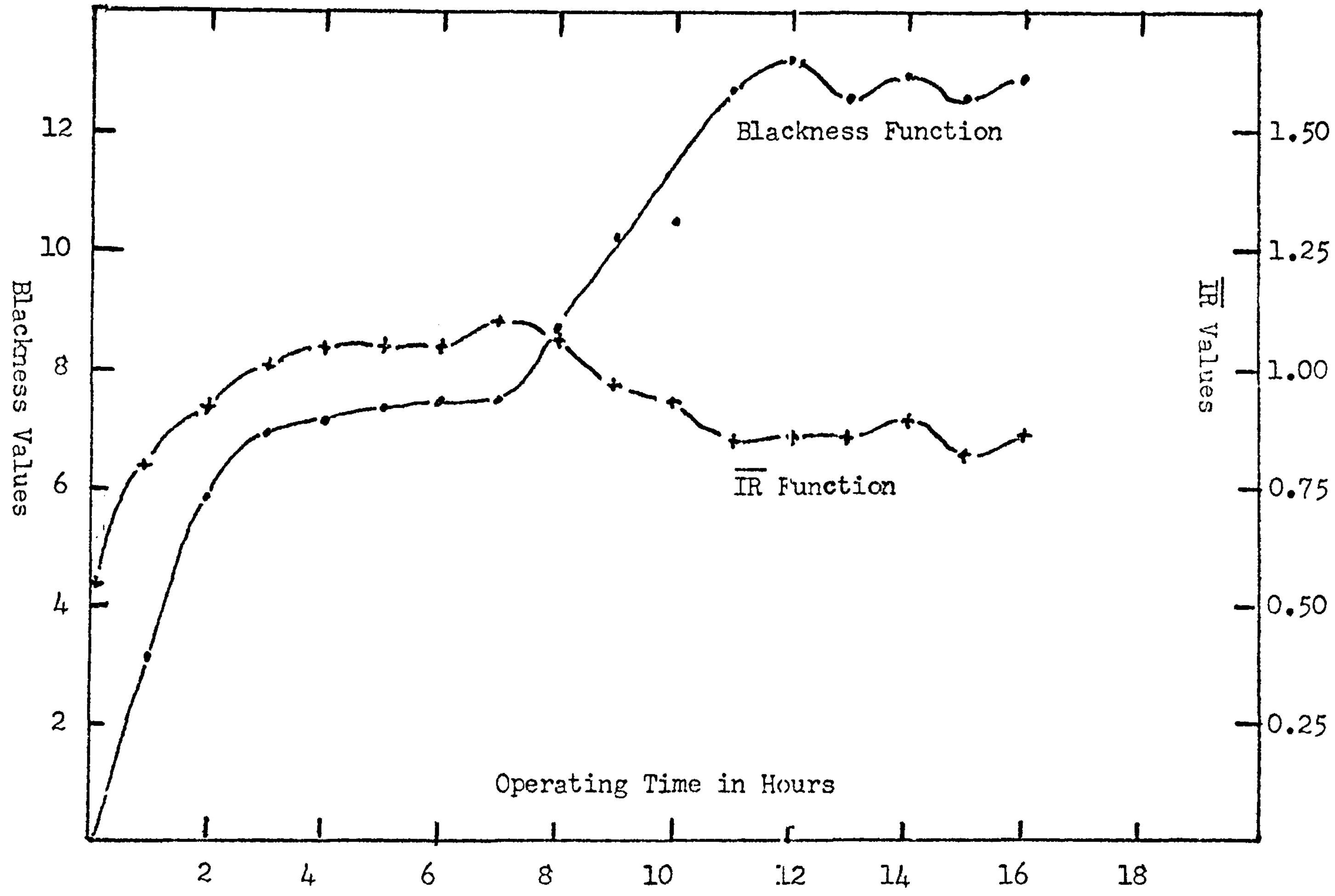


Figure 14

IV-J

Lignite Studies with the Middle Fraction of Raw Anthracene Oil

Runs CL 12, CL 13, CL 15 & CL 16. These comprise a short study in which the solvent was always the MFRAO and the reducing gas and operating conditions were varied to explore the application of the continuous reactor to Lignite processing. These are the first lignite studies done with the CL reactor configuration in which mechanical problems and temperature control problems do not have a material influence on the results obtained. The data for the experiments are summarized in Appendix A Part 2. In order to facilitate discussion selected information is repeated here.

Run No.	Reducing Gas	Pressure, Psig	Temperature	1/LHSV	MAF Conversion
CL 12	CO	1000	425°C	1.35	42.0%
CL 13	H_2	1000	425°C	1.33	72.0%
CL 15	CO-H_2	2000	425°C	1.79	82.2%
CL 16	CO-H_2	1000	425°C	1.62	62.2%

It can be seen that none of these experiments resulted in a particularly high MAF conversion. The result with pure carbon monoxide was especially interesting since carbon monoxide had produced superior results in batch autoclave studies. It is evident that some difference between the operation of the continuous unit and the autoclave had resulted in considerably less conversion of the lignite in the continuous unit. Since the same lignite was used this had to be the result of a difference in solvent, or a difference in operating conditions. The most likely cause appeared to be the use of a controlled 1000 psig reactor pressure in the continuous unit as compared to a peak pressure of about 4000 psig in a typical autoclave experiment in which the same proportions of material were heated together in a sealed autoclave. If this is the cause for the difference in conversion observed, the conclusion is forced that the reaction of carbon monoxide plus water in the presence of coal is pressure dependent. This is reasonable since the hydrogen which is liberated by the water shift reaction reacts promptly with the coal.

In Run CL 12 the MFRAO used as solvent had an $\overline{IR}$ = 0.56. The $\overline{IR}$ of the unfiltered solution was 0.71 and the $\overline{IR}$ of the Cut 2 reclaim solvent was 0.61. The increased value for the solvent reclaimed can be taken as an indication that the solvent was slightly hydrogenated. The higher figure observed in the unfiltered solution is due to the presence of coal product in solution. This is a normal pattern. The implication of the differences between the solution and the reclaimed solvent was not fully appreciated for some time. Indications are that the coal in solution will generally be less aromatic than anthracene oil and that coal in solution or the vacuum bottoms to be recovered will tend to add to the absorbance at the 3.41 micron band more than to the absorbance at the 3.28 micron band. The shift from the $\overline{IR}$ of the MFRAO to the $\overline{IR}$ of the reclaim solvent is small and indicates marginal hydrogenation in this reaction.

CL-12, CL-13, CL-15, & CL-16

IV-J

It should be noted that a higher MAF conversion was obtained in PA-74 (Interim Report #6). Further studies using carbon monoxide were not pursued in the Continuous Reactor Series, economics of pure CO vs. H_2 deemed it more feasible to pursue other sources of hydrogen.

In Run CL 13 hydrogen at 1000 psig was used and here again the lignite was fed with its natural bed moisture. The MAF conversion in this case was improved by comparison to the results in CL 12. Here 72.0% of the carbonaceous material in the lignite dissolved. This is a significant improvement over the 42.0% conversion obtained under the same conditions using pure carbon monxoide as the reducing gas. The $\overline{IR}$ of the Cut 2 reclaim solvent was increased to 0.64 which shows some increase in the amount of hydrogenation of the solvent. Neither solution CL 12 or CL 13 could be filtered in the laboratory using a filter paper and a buchner funnel. The estimates for reclaim solvent yield were made by distilling the unfiltered product. Normally any solution which fails to be converted sufficiently by reaction with reducing gas or solvent will not be filterable. No exact rule can be given for the amount of MAF conversion required for good filterability, but MAF conversions below 80% or so usually result in solutions with difficult filterability characteristics. Here, although the reaction using hydrogen did improve the conversion and the amount of hydrogen reacted, the solution was not really suitable for completion of the process.

In Run CL 15 a synthesis gas mixture in the ratio of 1.26/1 hydrogen to carbon monoxide was used as the reducing gas. The operating pressure was increased to 2000 psig and the pumping rate was reduced to obtain a longer retention time in the reactor. The 1/LHSV value was 1.79 and is an indication of the relative increase in retention time compared to the 1.33 value used in run CL 13. The lignite for this experiment was fed with its natural bed moisture and the water content of the feed slurry was the same as that used in run CL 13. This reaction produced a solution which was filtered through a filter paper using a buchner funnel. Thus it met the first criterion for an acceptable solution, and the data which are presented in Appendix A, part 2, are the result of the standard separations and analytical procedures. In this experiment the $\overline{IR}$ values for the unfiltered solution and for the Cut 2 reclaim solvent are 0.85 and 0.71 respectively. Both results indicate increased hydrogenation of the solvent and the materials in the solution. The MAF conversion increased to 82.2% which is probably near the lower limit for a solution which can be processed normally.

In Run CL 16 the experiment was designed to duplicate Run CL 15 except for the use of 1000 psig pressure. The retention time was only approximately matched since the 1/LHSV was 1.62 compared to 1.79 in the previous experiment. It can be seen that mechanical details still cause problems since the 1/LHSV did not match with the precision which would be preferred. The MAF conversion dropped to 62.2% and as might be expected the solution obtained could not be filtered in the laboratory. The $\overline{IR}$ values for the unfiltered solution and for the reclaimed cut 2 solvent were 0.75 and 0.63 respectively. Both values show less reduction of the lignite and less hydrogenation of the solvent phase had been obtained. Results from this experiment are reasonable evidence that the reaction with carbon monoxide or with synthesis gas mixtures is indeed pressure dependent.

CL-12, CL-13, CL-15, & CL-16

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An operating problem in the synthesis gas work became evident in these experiments. The ratio of hydrogen/carbon monoxide was obtained by mixing pure gases, using rotometers to measure the amount of each gas which continuously entered the compression system. In Run CL 16 the GHSV ratio was 1.14 and in Run CL 15 the ratio was 1.26. This presents problems in the comparison of results since the limits of reproducibility are too wide in these feed gas mixtures. This problem was solved by switching to preblended feed gases later in the program.

In these experiments the reclaimed Cut 2 solvent had gained hydrogen when compared to the MFRAO used to prepare the feed slurry. This led to the conclusion that the raw solvent did not simulate a realistic case for the plant since the recycle solvent would be used there. The amount of hydrogen consumed by the solvent was actually more than the amount of hydrogen consumed by the coal in experiments with the MFRAO. This raised the question about reaction rates and yields in the process using recycle solvent since the demand for hydrogen in the solvent should have been satisfied after a few passes through the reactor. It was hoped that adjustment of the solvent composition to an approximation of the steady state composition would allow the hydrogenation to be directed to conversion of the coal and that this would improve the conversion appreciably. In order to evaluate this idea the use of MFRAO was discontinued and hydrogenated anthracene oil was used for most subsequent experiments.

The overall quality of the data obtained in this series of experiments was better than that obtained in the first attempts with lignite. The recovery of material in these runs averaged 95.3% while the previous attempts in Runs CL 3 through CL 6 averaged only 80% recovery. It is evident that improvement in the management of materials and the reliability of the sampling techniques had been accomplished. One of the contributing factors here was the use of the Karl Fischer procedure which was used in CL 15 and CL 16 for the determination of the water content of the feed slurry. The ratio of MAF coal to water in the feed was known for the specific sample used rather than from the original quantities mixed in preparing the feed slurry. In cases where water evaporates from the feed slurry this can cause significant losses. This loss is included in the difference in weights of the feed pot and enters the material balance as material fed.

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Evaluation of Experiment CL 14

This experiment was designed to study the mixing behavior of materials in the CL dissolver tube. The unit was flushed with MFRAO while operating conditions were established and flushing was continued for an extended period of time. Samples were analyzed from time to time to establish the reactivity of anthracene oil with hydrogen in the absence of any mineral matter. Thus if thermal reactions or reactions catalyzed by reactor wall surfaces were evident a base observation would be available. Following this a slurry of washed coal minerals was fed to the unit and samples of product were taken at frequent intervals for analysis. An infrared spectrum was obtained for selected product samples and the mineral content in each sample was determined. These data allowed a measurement of the rate at which mineral matter passed through the unit and also allowed investigation of chemical reactions which might result from the presence of the mineral matter.

The coal insolubles were recovered from the solution made in Process Development Plant Run 66 which has been reported previously. 5/ These insolubles had been carefully pyridine washed, followed by benzene and acetone rinses before being dried in a vacuum oven. The oven was cooled before removing the dried insolubles. Finally, the insolubles were ground to pass a 100 mesh sieve before use. The ash content of this material was 46.14%. This lot of Kentucky No. 11 hvBb coal yields an ash which contains about 15% iron. Typical insolubles contain about 40% carbon and 2% hydrogen. The 5.5% total sulfur present was distributed: 0.1% pyritic sulfur, 0.5% sulfate sulfur, 1.9% organic sulfur, and 3.0% sulfide sulfur. Most of the iron is present as FeS although the presence of some oxide is not precluded. The organic material present is the most refractory carbonaceous part of the coal and has almost no tendency to react to further processing.

Experimental Procedure:

The reactor was lined out using MFRAO as feed. This solvent has an average hydrogen of 5.736% and IR Ratio of 0.56. Operating conditions were: 1000 psig hydrogen, temperature 425^{o}C., liquid hourly space velocity 0.60, gas hourly space velocity 266. The effluent liquid was sampled at half hour intervals and an infrared spectrum was run to measure the IR ratio. At the end of 5 hours a sample was collected for a period of one hour and this sample had an IR ratio of 0.56.

During this period, the weighed slurry feed vessel was filled with 3800 grams of MFRAO and 200 grams of washed coal insolubles. This slurry was switched into the feed loop at the end of the 6 hour line out period. Immediately samples were taken at 5 minute intervals (samples being collected for 4 minutes of each interval) for the first hour. During the second hour, samples were taken 15 minutes apart (for 5 minutes intervals). During the third hour, samples were taken 30 minutes apart (for 5 minutes intervals). Samples were taken hourly thereafter until the IR ratio appeared to be nearly constant. A sample was collected for a full hour to conclude the experiment. The slurry was pumped for a total of seven hours. All material not collected as samples was accumulated in a waste vessel. The infrared spectrum of selected samples was recorded. The samples were then analyzed for insoluble material by filtration followed by ashing the filter paper. In some cases the minerals were so fine that part of the material passed through the filter paper. In these cases the results were corrected by ashing the filtrate as well. The results were expressed as weight percent coal insolubles by using the previously determined ash content of the insoluble material.

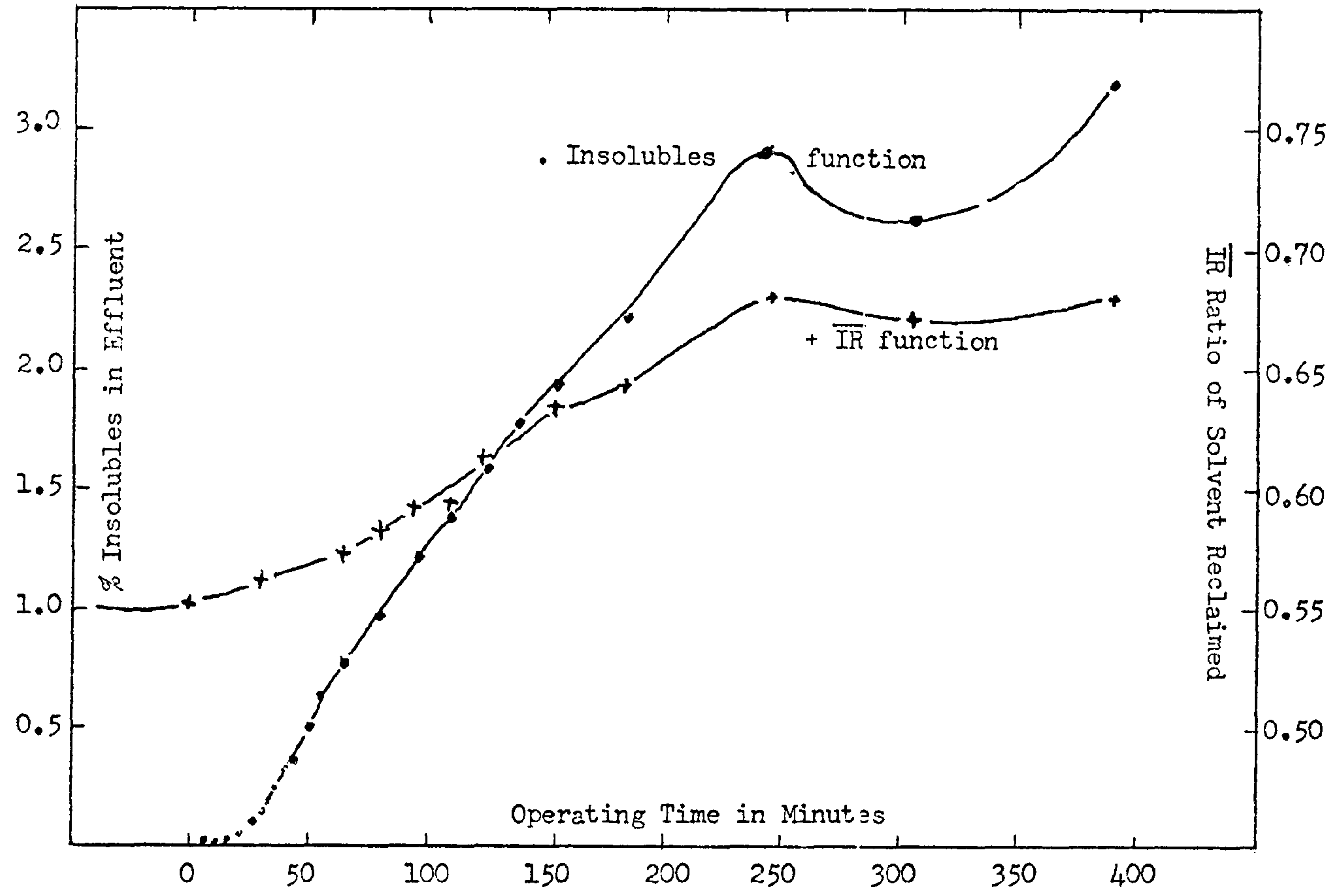
Discussion:

The experiment generated a total of 33 samples. Eleven of these were used to line out the reactor and were only analyzed by infrared. An ash analysis was done on all of the samples made with coal-insolubles slurry feed. The infrared spectrum was run on selected samples as required to develop a smooth curve showing the change in solvent composition. The results are as follows:

DATA FOR HYDROGEN CONTENT OF EFFLUENT SOLVENT VS PERCENT INSOLUBLES

SAMPLE NUMBER	TIME FROM SLURRY START	$\overline{IR}$ RATIO OF SAMPLE	% HYDROGEN FROM WORKING CURVE	GAIN IN % HYDROGEN	% INSOLUBLES IN EFFLUENT
11	Last Lineout	0.55	5.725	Reference	None
12	5 min.				Nil
13	10 min.				Nil
14	15 min.				0.001
15	20 min.				0.035
16	25 min.				0.093
17	30 min.				0.133
18	35 min.	0.56	5.733	0.008	0.234
19	40 min.				0.305
20	45 min.				0.339
21	50 min.				0.475
22	55 min.				0.614
23	60 min.				0.641
24	65 min.	0.57	5.750	0.025	0.747
25	80 min.	0.58	5.770	0.045	0.949
26	95 min.	0.59	5.790	0.065	1.19
27	110 min.	0.59	5.800	0.075	1.37
28	125 min.	0.62	5.845	0.120	1.61
29	155 min.	0.63	5.863	0.138	1.89
30	185 min.	0.64	5.875	0.150	2.19
31	245 min.	0.68	5.935	0.210	2.90
32	305 min.	0.67	5.921	0.196	2.60
33	360 to 420	0.68	5.940	0.215	3.16

Figure 15 is a graphical presentation of the course of the $\overline{IR}$ ratio of the reclaimed solvent and the percentage of insolubles in the effluent product as a function of operating time. It can be seen that the $\overline{IR}$ ratio increases as the concentration of insolubles increases. The original slurry fed to the reactor contained an average of 5.0% of insolubles. At the time the experiment was discontinued it was believed that sufficient time had been allowed to line out the mineral concentration. Actually the concentration of mineral matter in the effluent had only reached a figure of 3.16% in the final effluent sample. The last samples indicate that the mineral concentration in the effluent fluctuated.



$\overline{IR}$ Ratio and % Insolubles Versus Operating Time

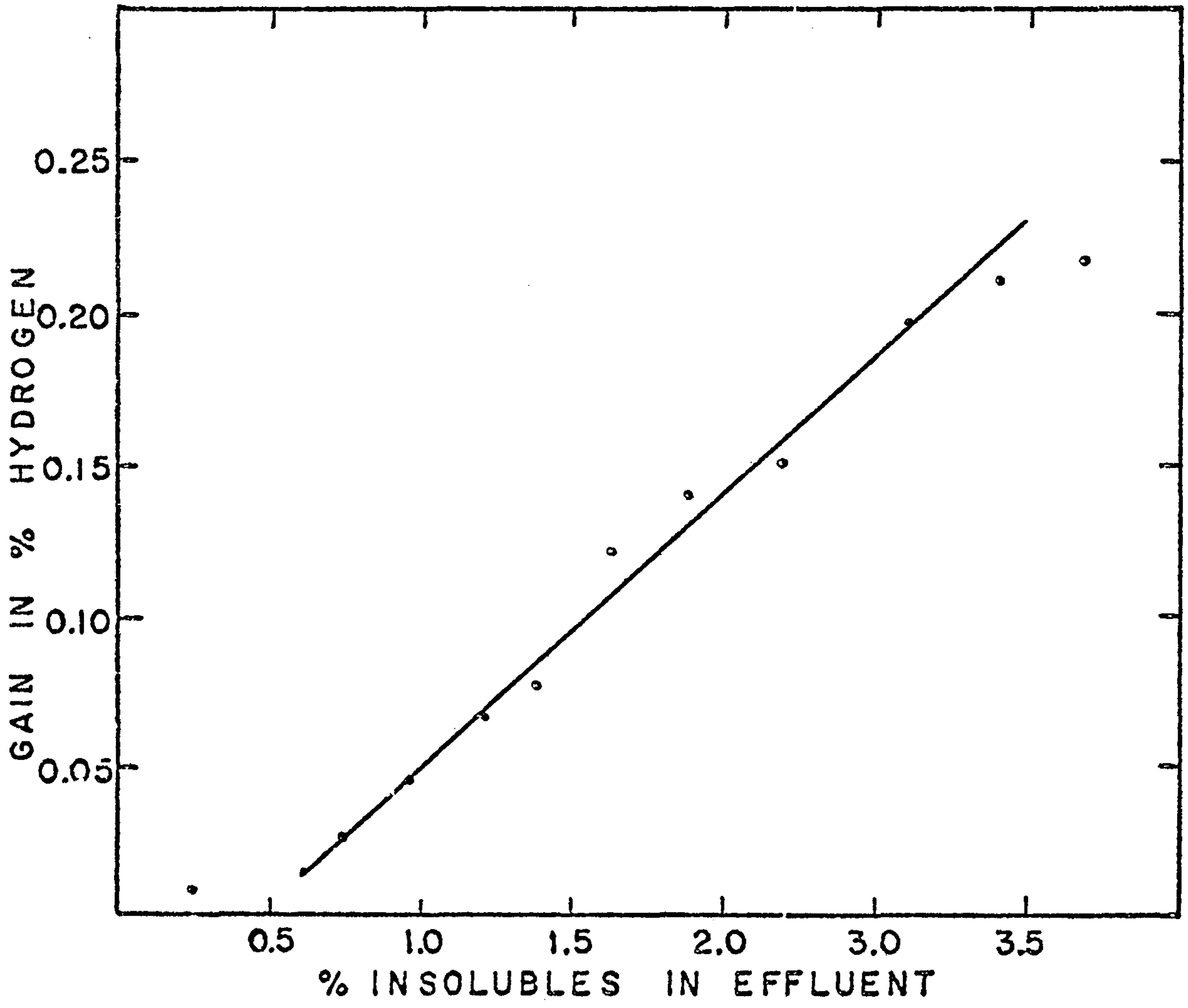
Figure 15

In order to check on the accuracy of these results the residual slurry in the feed pot was filtered to reclaim the insolubles. The concentration of insolubles in the feed pot had increased to 6.03%. The insolubles not found in the feed pot or in the samples taken were assumed to be in the dissolver. The estimated concentration in the dissolver was then 5.02%.

This experiment yielded the following information. First: it was clear that the stirring mechanism in the feed pot did not effectively mix the minerals with the solvent to produce a uniform slurry. Second: The delay between the injection of minerals into the reactor and the first evidence for minerals appearing in the effluent was about 15 minutes. At the flow rate used the 1/LHSV was 1.67. For plug flow the delay in mineral would be 1.67 hours for a liquid full reactor or some fraction of this time depending on the relative volume occupied by liquid and by gas bubbles. The short retention time observed is the result of back mixing from convection currents and the stirring effect of gas bubbles passing through the liquid in the reactor. Since the time delay is a significant fraction of the plug flow delay time it is clear that back mixing is not complete. The reactor is best described as a partially back mixed vessel. The third significant observation is that the insolubles settled in the dissolver vessel and that the concentration was higher than the concentration in the effluent product.

In order to better understand the results of the experiment a plot of the gain in hydrogen, as determined by infrared analysis of the reclaim solvent, versus the percentage of insolubles in the effluent solution was prepared. Despite oscillations in the concentration of minerals in the effluent, the IR values and the gain in hydrogen derived from the IR values related well to the mineral concentrations observed. See Figure 16.

Since no change in the infrared spectrum of the anthracene oil was observed during the flush period it is reasonable to assume that the catalytic effects which may be attributed to the walls of the reactor are not significant. After the coal insolubles were added a response was obtained which increased in proportion to the concentration of insolubles in the effluent from the reactor. This has been taken as direct evidence for catalytic activity associated with the coal minerals. Iron sulfide is the most probable material present to account for these observations.



%H GAINED VS % INSOLUBLES

Figure 16

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Evaluation of Run CL 17

Mechanical Considerations:

It was originally planned to react Kentucky No. 9 coal in MFRAO solvent with hydrogen at 2000 psig. The reactor was flushed with MFRAO to line out operating conditions. The feed slurry was a 2:1 ratio of MFRAO and Kentucky No. 9. The feed slurry was pumped successfully for approximately one hour. At this time the ball checks in the Speed Ranger pump head choked with coal particles. Efforts to clear the pump head with flush oil failed. The pump head was removed, cleaned out, and replaced. It was found that the slurry could be pumped at 1000 psig but that the pump head would choke up when the pressure was advanced to 2000 psig. Efforts to continue with the experiment at 2000 psig were discontinued.

The attempt to start up at 2000 psig had produced two samples. The first covered the time from the first injection of slurry to the end on the first half hour of operation. The second contained the product collected from the first half hour to the end of the first hour of operation.

Since the unit could not be operated properly at 2000 psig an alternative experiment was substituted. Run CL 17,as reported, is a preheater simulation done with Kentucky No. 9 coal and MFRAO at 1000 psig hydrogen pressure. This experiment was conducted by pumping slurry for seven hours to produce a lined out sample. The pump head performed well throughout this experiment.

Failure of the pump head to operate properly at higher operating pressures coupled with normal performance at lower pressures has been observed on several occasions. This is more likely to happen at low flow rates when the suction stroke of the pump is small. It is now believed that this is the consequence of the opening of the space between the ball and the seat on the suction stroke becoming smaller than the diameter of some of the largest coal particles. Thus the larger particles tend to wedge between the ball and the seat and this strains coal out of the solvent until the seat area is plugged up. To obtain good performance it is necessary to screen the feed coal to eliminate oversize particles. There are relationships between the stroke volume, the viscosity of the slurry, and the maximum particle size allowed in the coal. The viscosity is a function of operating temperature and this at times becomes a factor in pump performance.

Lineout Studies

It was possible to obtain some information about mineral lineout by analysis of the two samples from the 2000 psig startup, and the final sample taken at the end of the preheater study. The reactor had been pumped full of flush oil at the end of Run CL 16, which was done with lignite. Nevertheless the first one half hour sample contained a significant concentration of mineral derived from lignite. By analyzing for the concentration of iron in the ash from the samples taken in Run CL 17 it was shown that residual lignite ash had remained in the reactor and that this was gradually replaced by ash from the Kentucky No. 9 coal during the preheater study. These results are as follows:

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Sample	Time Taken	Percentage Ash in Sample	Percentage Iron in Sample Ash	Blackness of Solution
CL 17-1	0 - ½ hour	0.549%	6.06%	2.40
CL 17-2	½ - 1 hour	1.03%	12.78%	4.53
CL 17 Final	7 hours	3.55%	20.92%	11.93

The iron content of the lignite ash was 5.5% and the iron content of the Kentucky No. 9 coal ash was 21.14%. The Kentucky No. 9 coal contained 9.33% ash. The feed slurry should have contained 3.11% ash and a product should line out slightly higher as the result of some gas formation.

These observations define another reason for using extended lineout times in experiments with this kind of reactor. Here the time required to replace the minerals of one composition with minerals of another composition must become a consideration. This would not be as consequential if the mineral matter could be regarded merely as an inert diluent. From the observations reported in CL 14 some level of catalytic activity associated with ash minerals seems established. If this is accepted, the catalytic activity in the dissolver should follow changes in mineral concentration and composition and lineout should depend on reaching a steady state for the mineral phases also.

Run CL 17 Preheater Simulation Study:

To simulate the performance of a preheater the temperature profile along the CL unit reactor was adjusted to obtain progressive heating of fluid flowing along a tube. The reactor was seven feet long and the following temperature profile was established: temperature one foot from the bottom of the tube 145^{o}C, temperature three feet up the tube 290^{o}C, temperature four and one half feet up the tube 410^{o}C, and temperature six feet up the tube 445^{o}C. The 1/LHSV value for the slurry feed rate was 0.65, which would correspond to filling the reactor liquid full in 39 minutes. After making allowance for the volume occupied by the gas bubbles and for expansion resulting from heating the liquid, a theoretical hot liquid residence time of 24 minutes was estimated. If this estimate is used as a basis, the liquid in the tube was heated to 145^{o}C in 3.4 minutes, to 290^{o}C at the end of 10.2 minutes, to 410^{o}C at the end of 15.4 minutes, and to 445^{o}C at the end of 20.5 minutes. Such figures are expected to approximate the heating schedule in a plant scale preheater furnace. The products recovered accounted for 98.2% of the materials fed to the reactor. Although the liquid sample was reasonably fluid it was not filterable through a Whatman No. 42 filter paper using a steam heated buchner filter funnel. The product solution was therefore distilled without filtration to determine the amount of solvent which could be reclaimed. Insoluble material was recovered by dissolving the distillation residue in pyridine and filtering out unreacted insoluble material. From the ratio of carbonaceous material to ash in the washed insoluble residue the MAF conversion of the coal was determined to be 85.5%.

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The product solution and the recovered cut 2 oil were analyzed by infrared. The $\overline{\text{IR}}$ value for the unfiltered solution was 0.94 and for the cut 2 oil it was 0.84. The $\overline{\text{IR}}$ of the original solvent was 0.56 and the increase observed in the unfiltered solution and the cut 2 oil indicates appreciable reaction with hydrogen even in the short average reaction time allowed in the preheater. From the analysis of the gases recovered and the moles of hydrogen fed to the reactor, it was calculated that 1.06% of hydrogen based on the MAF coal had reacted. The solution had a blackness of 11.93 which is an indication that an appreciable concentration of dissolved coal had been produced. Poor filterability is the consequence of a residual concentration of gelatinous coal which has not had sufficient time to be broken down to a fluid condition.

This experiment was useful in obtaining an estimate of the minimum amount of time required to decompose coal and produce a reasonably fluid product. It is apparent that a major part of the reaction is completed during the initial heating of the reaction mixture. Conversion alone is not a sophisticated measure of the effect of the process, since the secondary products must in turn react before the desired chemical and physical properties can be produced. This requires additional thermal treatment and hydrogenation. It is the rate of these secondary and tertiary reactions which establish the time required to produce a satisfactory product.

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Evaluation of Run CL 19

Preparation of hydrogenated solvent in Run CL 18 required that the reactor be dismantled for loading catalyst. At the end of the procedure the reactor was again dismantled to allow removal of the catalyst and cleaning of the reactor. Run CL 19 was started with a clean empty reactor. This provided opportunity to study mineral lineout with a reactor known to be mineral free.

The experiment was run with Kentucky No. 9 coal and the hydrogenated solvent prepared in the previous run was used to prepare the feed slurry. The slurry was 2 parts CL 18 solvent and 1 part coal. This coal contained 10.68% ash. The theoretical value for ash in the feed slurry was then 3.56%. As the experiment was run feed slurry samples were taken at intervals and the ash content of the material in the sample loop was determined by ignition of the samples. This gives an independent check on the uniformity of the feed slurry for the mineral phase present.

The general objective of the experiment was to obtain well lined out samples which represented products made with Kentucky No. 9 coal and a solvent which corresponded to a recycle solvent in reactive hydrogen content. The feed rate for the slurry was kept constant and the operating pressure was changed to produce lined out samples at 1000 psig, at 1500 psig, and at 2000 psig. Samples were taken at frequent intervals and lineout was judged by observation of the infrared spectra of the product solutions and by observation of the blackness of the product solutions.

During the first 2 hours of the experiment, samples were taken for 5 minute time intervals every 15 minutes. During the second 2 hours of the experiment samples were taken for 5 minute time intervals each half hour. After that samples were taken for 5 minute time intervals each hour. These samples were collected in glass flasks and were used to obtain IR values and blackness values for the product solution. They were also distilled to obtain samples of reclaim solvent for further analysis. The residue in the flask was then transferred to a platinum dish with the aid of pyridine and the residue was ashed to determine the mineral matter present. The ash residue was dissolved in hydrochloric acid to extract the iron present and the iron was determined volumetrically.

At those times that the system was believed to be lined out, samples of 40 minute duration were taken in stainless steel flasks. These were worked up by the standard method of analysis to obtain filterability and product yield data.

A total of 40 samples were produced during the 21 1/4 hours the unit was on feed slurry. Mechanical operation was satisfactory at 1000 psig and at 1500 psig. Here the feed rate was reproduced accurately. At 2000 psig the slurry was fed at 1/LHSV = 1.39 while the desired value was 1.33 as used for the previous sections of the experiment. This was an improvement in performance, however, since previous attempts to work at 2000 psig had resulted in plugging of the feed pump. The reason for this improvement remains obscure but the viscosity of the hydrogenated oil, tending to be

LINEOUT STUDY DATA RUN CL 19

Sample No.	Time Hours	% Ash in Feed	% Ash in Product	% Iron in Product Ash	IR Value in Solution	IR Value in Cut 2 Solv.	Blackness of Solution
A. Run at 1000 psig 1/LHSV = 1.33							
1	0	3.66	0.012		1.03	0.87	0.04
2	1/4		0.037		1.01	0.91	0.12
3	1/2		0.224	25.1	1.01	0.85	0.80
4	3/4		0.595	16.9	1.02	0.82	1.80
5	1		0.935	18.3	1.00	0.76	2.80
6	1-1/4		1.44	19.5	1.05	0.79	3.85
7	1-1/2		(2.09)	(15.3)	1.07	0.80	4.53
8	1-3/4		1.81	19.1	1.07	0.85	5.09
9	2	3.34	1.93	19.5	1.05	0.80	5.62
10	2-1/2		2.29	19.9	1.12	0.81	6.26
11	3		2.36	19.9	1.18	0.87	6.74
12	3-1/2		2.55	19.5	1.18	0.87	6.81
13	4	3.43	2.57	20.0	1.25	0.85	7.05
14	5				1.22		6.88
15	6	2.97	2.39	20.5	1.19	0.83	6.97
16	7				1.22		6.98
17	8	2.92	2.72	19.1	1.23	0.90	7.08
18*	8-1/4					0.89	7.14
19	9		2.79	18.8	1.26	0.87	7.25
20*	9-1/4	**				0.88	**
21	10	3.57			1.25		7.12
22*	10-1/4						
23	11		3.08		1.19		
B. Run at 1500 psig 1/LHSV = 1.33							
24	11-1/2	3.64	2.99	20.8	1.23	0.93	6.60
25	12-1/2		3.16	21.5	1.25	0.97	5.80
26	13		3.14	21.6	1.31	0.95	5.66
27	13-1/2	3.59	2.65	20.0	1.36	0.95	5.76
28	14		2.78	20.6	1.42	1.03	5.92
29	15				1.32		
30	16		3.12	21.7	1.40	1.03	5.57
31*	16-1/4	3.41			1.40	1.06	5.70
32*	17				1.42		
33	18		2.89	20.0	1.42	1.02	5.51
C. Run at 2000 psig 1/LHSV = 1.39							
34	18-1/2	3.25	3.15		1.45		5.47
35	19				1.47		5.78
36	19-1/2		3.00	20.2	1.50	1.07	5.82
37	20				1.50		5.74
38	20-1/2	3.52	3.12	20.0	1.42	1.11	5.71
39	21		3.49		1.49		5.77
40*	21-1/4	3.32	3.43		1.48	1.20	5.69

* Sample taken for 40 minute interval, others at 5 minute duration.

** Feed slurry tank refilled with new slurry mix.

(Doubtful results in parentheses)

lower than the viscosity of the MFRAO, may have been decreased enough to allow troublesome particles to settle out better. The results from the lineout study are presented on page 127. Since the reactor had been cleaned thoroughly the only traces of mineral in the first sample would have to be from traces in the sample letdown system. The initial concentration was small. At the start, the product was also substantially the same color as the feed solvent. The $\overline{IR}$ value of the first solution sample was 1.03 compared to the 0.98 value for the feed solvent. Upon distillation the fraction corresponding to the cut 2 solvent had an $\overline{IR}$ value of 0.87. This pattern may be the result of a small amount of hydrocracking since the light fraction tends to be more hydrogen rich and the cut 2 fraction tends to be somewhat reduced in hydrogen content. It can be seen that the ash in the product samples and the color of the solution both increase for about 5 to 6 hours. As coal in solution builds up in the product samples the $\overline{IR}$ value of the solution increases from 1.03 initially observed to about 1.25. The system would appear to be lined out based on solution blackness and infrared spectra. Three 40 minute samples were taken for a complete workup in order to complete the study at 1000 psig. The A part of the experiment covered eleven hours.

The hydrogen pressure was then advanced to 1500 psig and the pumping rate was kept constant. This change resulted in a decrease in the color of the product solution, the blackness dropping from about 7.15 to about 5.50 in the seven hours this set of operating conditions was maintained. The $\overline{IR}$ value of the product solution increased from about 1.25 to about 1.40 in this interval.

Finally the hydrogen pressure was advanced to 2000 psig while the feed rate was kept as nearly constant as could be managed. At the higher pressure the feed rate obtained was slightly reduced. This part of the experiment was continued only for 3 1/4 hours. The blackness of the solution remained about the same as had been observed at 1500 psig. The $\overline{IR}$ value of the product solution may have increased slightly as the final samples read about 1.50. In retrospect the time allowed for the 2000 psig experiment to line out was too short and the final result may not be at steady state.

The ash analysis of the feed slurry gave results which tended to be below theory for almost all samples. This is evidence that the stirring mechanism was not satisfactory. This has been improved by producing uniform particle size distribution in the powdered coal. The necessary experience had not yet been acquired to show that these changes were required. Although the feed slurry analysis result was somewhat below theory, the mineral matter in the product samples can be seen to be substantially lower than the concentration in the feed loop. This situation prevails throughout the whole experiment and only after 20 hours does the concentration in the product sample begin to account for the mineral being fed. These results were somewhat surprising since the previous methods based on blackness or infrared analysis had led to the conclusion that the reactor would be lined out in 5 or 6 hours. It is apparent that mineral was settling in the reactor system throughout this experiment. Product composition may be influenced by the concentration of minerals as the catalytic effect should have increased throughout the run. The change in composition of the solution as measured by $\overline{\text{IR}}$ values of the solution and the cut 2 reclaimed should then be attributed not only to the increase in pressure but may have been influenced by a variable catalytic effect as well.

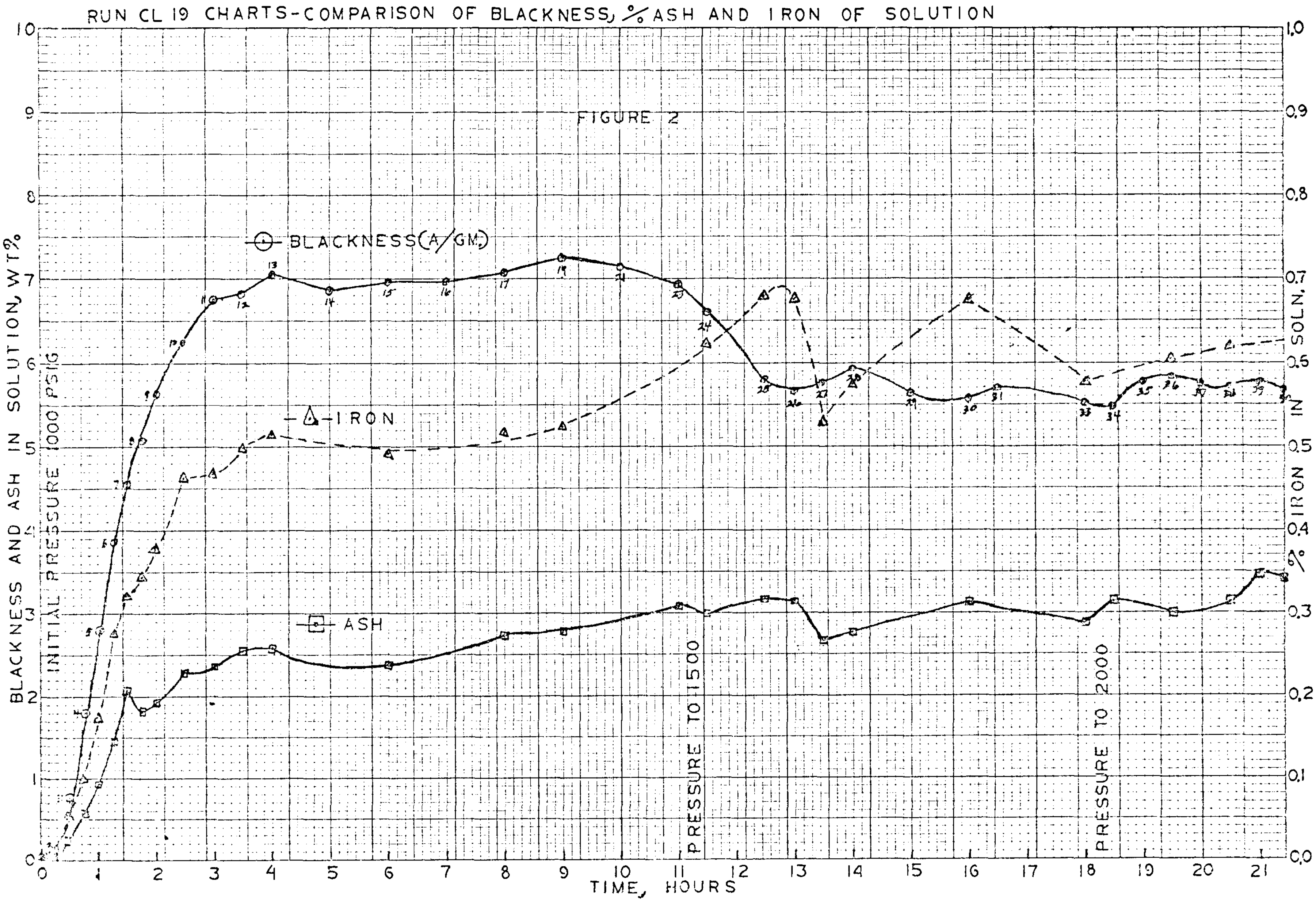
Despite questions regarding how well experimental samples may represent fully lined out products, it is certain that a number of clear cut responses were observed as operating pressure was changed. At 1000 psig the solution returned a cut 2 reclaim solvent which was slightly depleted in hydrogen based on the $\overline{\text{IR}}$ value of 0.89. When the pressure was increased to 1500 psig the cut 2 reclaim solvent had an $\overline{\text{IR}}$ value of 1.06 which indicates that the solvent was slightly hydrogenated by the process. At 2000 psig the $\overline{\text{IR}}$ value increased again to 1.20, assuming that the final sample is at least approximately lined out. These observations were subsequently checked by analysis of the cut 2 reclaim solvent and the percentage of hydrogen found was in agreement with the spectral data. See Appendix A part 2 for these results.

Yield data are also presented in Appendix A. An excess of oil was realized at each pressure used. Since all samples were taken after reasonably long time from startup it is unlikely that these could be "salted" with solvent from the initial reactor flush. The yield of excess liquid hydrocarbons is 27.57% based on the MAF coal fed for the 1000 psig experiment, 29.92% based on the MAF coal fed for the 1500 psig experiment, and 46.73% on the same basis at 2000 psig. The increase observed at 2000 psig has come at the expense of a reduction of the yield of vacuum bottoms residue. Between 1000 and 1500 psig the difference in yield is apparently due to an increase in the MAF conversion of the coal.

The reclaimed solvent is reported as a percentage yield referred to the quantity of solvent initially charged. In all cases the total hydrocarbon yield represents an increase in weight. The boiling range of materials has been altered and generally the amount of cut 2 oil has been somewhat diminished while a considerable yield of cut 1 oil has been obtained. These results indicate only that the arbitrary cut points used would have to be changed to obtain the solvent needed for recycle. It is noteworthy that the gain in hydrogen at 1500 or 2000 psig would suggest that a more reactive solvent could be obtained for the next cycle. This may not be entirely true since some of the hydrogen is substituted as saturated functional groups and not readily available, although it does appear in the total hydrogen value.

The vacuum bottoms products were analyzed also. These results are also presented in Appendix A, part 2. It can be seen that the concentration of sulfur in the vacuum bottoms declined as the operating pressure increased. The vacuum bottoms also tend to contain more hydrogen than resulted with MFRAO solvent at similar operating conditions. The distillation was reasonably reproducible since the melting point of each of the samples is approximately the same. The gain in hydrogen may be partly due to retained solvent for the 2000 psig sample since it is somewhat lower melting. This difference is not great. A most interesting trend is the tendency for the nitrogen content of the vacuum bottoms to increase as the conversion to oil increases. The more refractory compounds appear to be nitrogen rich and the mild catalysis available does not attack such functions as effectively as sulfur or oxygen functions. Refer to Appendix A, part 2 for summary of data discussed.

Figure 17


RUN CL 19 CHARTS-COMPARISON OF BLACKNESS, % ASH AND IRON OF SOLUTION
FIGURE 2
BLACKNESS (A/GM.)
IRON
ASH
BLACKNESS AND ASH IN SOLUTION, WT%
INITIAL PRESSURE 1000 PSIG
IRON IN SOLN, WT%
PRESSURE TO 1500
PRESSURE TO 2000
TIME, HOURS
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

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Evaluation of Experiment CL 20

This was the first experiment done with synthesis gas as the reducing agent reacting with Kentucky No. 9 coal and hydrogenated anthracene oil as solvent. The experiment produced three samples and time was allowed to provide a reasonable first approximation lineout before samples were collected for workup. Water was added to the coal slurry to provide reagent for the water shift reaction with the carbon monoxide present in the synthesis gas. In this case the synthesis gas was made by mixing carbon monoxide and hydrogen in a 1:1 ratio. This gas was analyzed by GSC at the time of use and the mixing ratio was accurately accomplished. It was originally planned to duplicate the series done with hydrogen in experiment CL 19. Pumping problems were encountered at 1500 psig and the sample made at this pressure did not have a matching retention time to compare to CL 19B with accuracy. It was not possible to operate the pump at 2000 psig with this feed slurry. An alternate experiment was substituted to explore for the effect of operating at 450°C using a 1000 psig operating pressure.

The experiments which were accomplished were:

CL 20A Kentucky No. 9 coal (CL-18 solvent) 1000 psig syn gas 1/LHSV = 1.27 at 425°C.

CL 20B Kentucky No. 9 coal (CL-18 solvent) 1500 psig syn gas 1/LHSV = 2.08 at 425°C.

CL 20C Kentucky No. 9 coal (CL-18 solvent) 1000 psig syn gas 1/LHSV = 1.27 at 450°C.

Mechanical considerations:

It was planned to obtain data at 1000 psig, 1500 psig, and 2000 psig in order to compare results directly with run CL 19 results. This plan was frustrated by failure to obtain the necessary pumping rate at the 1500 psig pressure and by complete failure to pump the feed slurry at 2000 psig. The ball checks in the speed ranger pump head were removed for inspection and cleaning and were found to be plugged up with powdered coal. Since previous operation had been successful at the pressures used here the cause for the plugging was investigated.

It was necessary to prepare a new grinding of the Kentucky No. 9 coal. Water had to be added to the slurry in order to supply reagent for the reaction to be studied. It was not known which of these changes may have caused the mechanical problem. The particle size distribution of the two samples of Kentucky No. 9 coal was determined by sieve analysis of retained samples. A sample of the Baukol-Noonan lignite was also checked since this had been successfully pumped at 2000 psig in experiment CL 15.

SCREEN ANALYSES ON FEED COALS

Coal:	Baukol-Noonan Lignite	Kentucky #9 (Run CL-19)	Kentucky #9 (Run CL-20)
U.S. Standard Screen	Weight Percent Retained		
+60	0.69	0.08	0.18
-60/+100	6.30	0.74	0.99
-100/+200	57,76	11.61	9.18
-200/+400	27.43	65.94	66.78
-400	7.82	21.63	22.87

The screen analysis did not give a clear indication of the cause for the pumping problems. The amount of coal over sixty mesh was 0.08% in the original sample which had been pumped successfully. The amount in the troublesome sample was only 0.18%. The difference was not considered to be significant at the time since the Baukol-Noonan lignite contained 0.69% of material over 60 mesh. From these results it was concluded that the addition of water to the slurry probably caused some clumping of the coal powder in the slurry.

Current practice now requires that all coal be sieved to less than 150 mesh in order to assure reliable pump performance. The particle size which was obtained in either of the Kentucky No. 9 grindings would now be regarded as unsuitable and the oversize particles would be sieved out, reground to pass 150 mesh and returned to the sample. Such material has not been tested with added water. Lignite contains water within its structure and would be less likely to be clumped by surface tension effects. This question remains somewhat unsettled.

Experimental data

The experimental plan included provision for lineout intervals before each analytical sample was collected. These times were as follows: Flush the reactor with oil as the temperature and flow rate settings were adjusted, switch to feed slurry and allow 5 hours operating time for lineout. Collect sample CL 20A. Change operating conditions and allow 5 hours of lineout time. Collect analytical sample CL 20B. Change operating conditions and allow 5 hours of lineout time. Collect analytical sample CL 20C.

In reviewing previous experiments it was concluded that the raw material balances for all experiments in which the feed slurry contained much water had been closed poorly. It was a special project in this experiment to use the Karl Fischer method for water analysis to analyze the feed slurry and to use these results to attempt a better closure of the material and elemental balances. As a general rule the accounting for oxygen in experiments had been in error because of the fugitive nature of water both in the feed and in the product samples.

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The original feed slurry prepared was made up accurately to contain 10.3% of water. This was checked by analysis and the result obtained was within reasonable precision of the expected value. As the initial slurry was used a sample was drawn just before analytical sample CL 20A was started and a second sample was drawn just after this sample was completed. It was necessary to replenish the supply of slurry at this point. The same procedure was followed for the CL 20B sample. A third addition was necessary before the CL 20C sample was started. In this case the initial samples were not taken close to the start of the analytical sample. A final sample was taken at the end of the sample interval and the water in the feed was determined by allowing for the evaporation rate determined for the final slurry.

The usual slurry ash determinations were also done with samples taken for water analysis. As a result the actual ash analysis for the slurry containing water and the dry basis results for ash are available for comparison. The dry basis results show that the mineral component in the slurry was maintained with reasonable precision in this experiment, until the final sample in the set. In this case the mineral declined in concentration to about 90% of theory.

Calculation of MAF conversion from the amount of insolubles isolated from a sample would appear to be the most direct method. It can be seen that misfeeding of minerals or settling of minerals in the dissolver would both invalidate such results. This has resulted in reliance on the ash enrichment method. It is helpful in treating results to know the feed data from an independent analysis since this allows for correction of the input data for mechanical errors and increases the chance that the samples obtained may indeed match the materials fed. It can be seen that the amount of water which evaporated from the feed pot would be recorded as weight of slurry fed. This may explain the relatively lower material balance in the CL 20 series by comparison to the results obtained in the CL 19 series.

Slurry analysis results are as follows:

RESULTS OF WATER AND ASH ANALYSIS OF RUN CL-20 FEED SLURRIES

Slurry Sample Number	Time of Run (hours)	% H_2O		% Ash in Slurry (as rec'd basis)	% Ash in Slurry (H_2O-free basis)
Theory	--	10.30		3.567	3.98
A. (Initial conditions: 1000 psig, 425°C.)					
1	0	10.56		3.435	3.84
2	5¼	7.99	A Sample	3.553	3.86
3*	7½	6.16		3.594	3.83
B. (Conditions changed to: 1500 psig, 425°C.)					
4	9 3/4	8.17		3.608	3.93
5	12	7.27	B Sample	3.472	3.74
6	14	5.93		3.359	3.57
C. (Conditions changed to: 1000 psig, 450°C.)					
8*	15½	4.53		3.502	3.67
9	22	2.43	C Sample	3.437	3.52

Notes:

* Makeup slurry was added just after sample No. 3 and in between samples No. 8 and 9. These were made to the original weight ratio of: 2(SHMFRAO solvent)/ 1(Ky#9 coal - 4.04% H_2O and 11.77% ash)/ 0.3(water) and added to residual material in feed slurry tank.

Gas Analysis Results

In the discussion of experiments previously presented, little emphasis has been placed on the composition of the gaseous products obtained. This is a necessary consideration in complete reporting for an experiment and a discussion is in order. The weight of gaseous products can be obtained by measurement of the molecular weight and the volume of the gas which relates to a sample. This is sufficient information for use in closing the raw material balance.

The amount of hydrogen sulfide in the gas can be determined volumetrically by precipitating the sulfide from a known volume of gas and then reacting the sulfide with a measured excess of standard iodine solution. The unreacted iodine is then back titrated with standard thiosulfate solution. This does not determine all of the sulfur liberated from the reaction, since a significant amount dissolves in the various water phases removed by distillation or in the knock out vessel.

A more complete analysis of the gas was normally obtained by means of gas chromatography. This was necessary for the products from synthesis gas experiments since the composition of the mixtures could not be estimated from molecular weight correlations. The detailed gas analysis together with the volume of gas related to a sample could be used to compute the conversion of carbon monoxide, the utilization of hydrogen, and the production of hydrocarbon gases. These were of course broken down to specific compounds such as methane, ethane, propane, and so on. In preparation of Appendix A these were added together in order to save space in the table and appear as a single entry.

The gas analysis results for experiment CL 20 are presented as an example of the data collected for a synthesis gas experiment. It is clear from these results that the reaction in the dissolver has shifted the carbon monoxide to produce some carbon dioxide.

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GAS ANALYSIS OF RUN CL-20A, B, & C

	Feed Gases		Process Gases		
Gas (Mol %)	CL-20A	CL-20C	CL-20A	CL-20B	CL-20C
Hydrogen	49.7	48.5	40.4	38.5	33.8
Nitrogen			6.26	8.27	9.14
Methane			3.12	3.50	6.01
Ethane			1.06	1.07	2.04
Propane			0.50	0.53	0.89
n-Butane			0.16	0.14	0.19
iso-Butane			0.04	0.05	0.07
Carbon Dioxide			10.3	9.64	11.3
Carbon Dioxide	50.3	51.5	37.2	37.7	35.8
Hydrogen sulfide			1.02	0.65	0.77
H_2/CO Ratio	0.988	0.942	1.086	1.021	0.940
Moles per hour in product			4.646	4.062	4.458

Discussion of Results

Most of the information for comparison of results has been included in Appendix A part 2. The effect of the declining concentration of water in the feed pot is indicated by a declining ratio of water in the ratio of solvent/MAF coal/H_2O, which is presented in the Appendix data.

It can be seen that the operating conditions for CL 19A and CL 20A match reasonably well. On this basis it is reasonable to compare entries on a line for line basis between these two experiments. For example the MAF conversion with the synthesis gas was not as high as with hydrogen. The difference of about 3% of carbonaceous material is significant. The lower hydrogenation potential of the synthesis gas system is also reflected in the change in the $\overline{IR}$ values in the cut 2 reclaim solvent. The hydrogen reaction at 1000 psig had resulted in a minor transfer of hydrogen from the solvent in run CL 19A. This tendency is greater in the synthesis gas case since the $\overline{IR}$ value drops down to 0.81 from the initial solvent value of 0.98. As might be expected in this situation, the yield of excess reclaim solvent is lower for the synthesis gas case than for the hydrogen case.

Direct comparisons with CL 20B results are complicated by the different retention time which was the consequence of pump performance limitations in this experiment. In comparing results it must be remembered that reactions run at different retention times are involved. With this qualification established, it is possible to compare experiment CL 19B and CL 20B results and to obtain some idea of the differences in using synthesis gas and hydrogen. As a general rule increased retention time at moderate temperatures tends to increase conversions and yields and to improve the hydrogen content of reclaimed solvents. The decline in MAF conversion between CL 19B and CL 20B might have been a little larger at matching retention times. It is clear that the increase in pressure between CL 20A and CL 20B did improve the conversion. The increased hydrogenation potential is also reflected in the $\overline{\text{IR}}$ value of the cut 2 reclaim which is only slightly below the value for the initial solvent in this case. The yield of excess solvent improved also which is additional support for the conclusion that the reaction should operate better at higher pressures.

When the synthesis gas was used at 450°C the MAF conversion was slightly improved compared to operation at 425°C. This was not reflected in an equivalent improvement in the yield of liquid products. In this case a small solvent loss was observed. In addition the cut 2 solvent reclaimed had experienced a substantial dehydrogenation during its exposure to heat and coal in the reactor. The yield of vacuum bottoms increased substantially and it is clear that the depolymerization had been superseded by a repolymerization reaction.

Taken at face value, the infrared data show a tendency for loss of hydrogen from the solvent available for recycle at any condition used in experiment CL 20. Further study would be needed to establish a suitable operating condition. From the trend observed this could be accomplished by use of higher operating pressures.

One desirable property was observed in the products obtained. The amount of sulfur and oxygen in the vacuum bottoms was significantly lower for the products made with synthesis gas. This would seem to require a difference in mechanism in this case and this observation alone would justify continuing interest in the use of synthesis gas.

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Evaluation of Experiment CL 21 (Samples A through F)

This experiment was designed to study time temperature effects on the solution of Kentucky No. 9 coal using 1000 psig hydrogen as the reducing gas and the hydrogenated anthracene oil (CL 18 Prep.) as solvent. A provision was made for a first approximation lineout following startup and following each operating condition change. This schedule is as follows:

Operating Schedule	1/LHSV	Temperature °C
Lineout on flush oil		
Lineout on slurry for 3 hours		
Collect sample 21A 1 hour	0.75	450
Lineout on slurry for 3 hours		
Collect sample 21B 1 hour	0.73	425
Lineout on slurry for 3 hours		
Collect sample 21C 1 hour	0.90	425
Lineout on slurry for 3 hours		
Collect sample 21D for 1 hour	0.92	450
Lineout on slurry for 3 hours		
Collect sample 21E for 1 hour	0.92	400
Lineout on slurry for 4 hours		
Collect sample 21F for 1 1/2 hours	1.35	450

It was reasoned that the time needed to line out the reactor was a function of the quantity of material which was flushed through it. Lineout was conducted at the 1/LHSV to be used at sample collection time in order to properly equilibrate the contents of the reactor. At the higher flow rates the lineout time could be shortened slightly while at the low flow rates the lineout time had to be extended in order to pump an equivalent amount of material through the unit. The table given above is an example of the application of this procedure in an experiment which was run without complications.

Discussion of Results

The data which are available for this series of experiments are summarized in Appendix A part 3. Many of the operating and sampling problems were under reasonably good control and as a consequence the raw material balance closed to about 97% of the material fed on the average. The feed slurry was analyzed at the start of the experiment and again at the end of the experiment. Ash in the first sample was 3.84% and in the final sample ash was 3.99%. The feed coal contained 12.01% ash from which the theoretical ash in the feed should have been 4.00%. These data are taken as evidence that the feed slurry was maintained under good control throughout the length of the experimental series.

Since the correlation between $\overline{\text{IR}}$ and the percentage hydrogen in the feed solvent and the cut 2 reclaim solvent had been reasonably well established, it was a project in this experiment to investigate the correlation between

$\overline{IR}$ measured for the unfiltered coal solution and the percentage of hydrogen in the solution. Small samples of unfiltered solution were reserved for elemental analysis to accomplish this study. As a practical consideration it is quite difficult to sample and subsample such materials and to acquire samples with a representative amount of ash and insoluble material in them. If the weight of feed slurry for a sample is compared to the weight of unstripped raw product obtained, it will be observed that the unstripped product commonly weighs less than the slurry originally fed. This is the consequence of the evolution of gaseous products, and it can be seen that as operating temperatures are increased the shrinkage is normally greater. The theoretical value for ash in an unfiltered solution is then the ash in the feed slurry increased by the ratio of feed slurry/unstripped solution. The analytical results for the unfiltered solutions are given at the bottom of Appendix A part 3 for these samples. If this procedure is applied for the data in experiments in CL 21 it will be found that no sample analyzed contained exactly the theoretical amount of ash. The expected values range from 4.00% to 4.43% while the observed values range from 3.57% to 8.89%. In order to reduce observations to a uniform basis the combustion analysis results and the ash residues obtained were used to calculate hydrogen on ash free basis. These results follow the $\overline{IR}$ values for the unfiltered solution with satisfactory regularity. One sample, CL 21F, appears to have been reported in error. It should be added in this discussion that drawing samples for sulfur or nitrogen determinations is no more reliable than the operation for drawing samples of unfiltered material for combustion analysis. This will be found to introduce a few percent of error in such results and correction for ash variation is not possible in these cases.

It is observed that the $\overline{IR}$ values for unfiltered solutions are normally significantly larger than the $\overline{IR}$ values for the cut 2 solvent reclaimed from the solution. This is because the raw solution contains some lower molecular weight hydrocarbons which tend to be richer in hydrogen and because the dissolved coal derived material is normally less aromatic than the hydrogenated anthracene oil solvent reclaimed. Possibly this difference could be used for a quantitative analysis of these solutions if the necessary detailed work were done. A qualitative inspection of the coal solution is now the application which is established. In this regard the differences in the $\overline{IR}$ values for the input solvent, the unfiltered solution, and the reclaimed cut 2 solvent are generally informative. In run CL 21E the solution $\overline{IR}$ is high, 1.41, and the hydrogen consumed is higher than normal, 2.47%. In run CL 21F the hydrogen consumed is 3.17% and the $\overline{IR}$ is 1.09. The operating temperature in CL 21E was 400°C and the gas output at these mild conditions was low. On the other hand the CL 21F experiment was run at 450°C at a longer retention time and the gas yield was high. It can be seen that the hydrogen appears in the gaseous products rather than in the coal solution produced. It is clear that the reclaimed cut 2 solvent has been depleted in hydrogen compared to the initial solvent charged. There would be no incentive to operate the reactor at high temperatures if this were not necessary to remove sulfur to the lowest practical levels.

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Such detailed data have been used to develop a general picture of the normal operation of the reactor with a bituminous coal and a solvent containing a moderate amount of hydrogen transfer capacity. The experiments with raw anthracene oil indicate that the solvent will tend to gain hydrogen with use. The experiments with the CL 18 solvent have given some indication of the probable concentration of hydrogen to be expected after a limited exposure to reaction conditions, as an example after two or three recycles through the reactor. It can be seen that such composition is influenced by reactor conditions and not all choices may be suitable for continued use. Hopefully the discussions presented in reviewing these experiments will allow inspection of the data in Appendix A for various relationships of interest without detailed discussion in every case.

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Evaluation of Experiment CL 22 (Samples A through E)

This experimental series was done to study the reaction of Baukol-Noonan lignite with 1:1 carbon monoxide to hydrogen synthesis gas as reducing agent. All studies were done at 1500 psig. The CL 18 hydrogenated anthracene oil was used as solvent in all cases. Operating temperature and retention time were variables in the studies. The feed slurry was analyzed for ash and for water content to establish compositional control of the feed to the reactor. A long lineout time was used before collection of the first sample in an effort to assure flushing out any residual Kentucky No. 9 coal residues which may have been retained from previous experiments. The standard lineout procedure was used for the remaining samples. A study of minerals in the products made was conducted to evaluate the efficiency of the long flushing procedure in unloading the residues from a previously used coal. It is preferable to do this without dismantling the reactor for cleanout if this can be done dependably. The operating schedule is given below.

Operation	1/LHSV	Temperature
Solvent flush for condition lineout		
Pump slurry for composition lineout 8 hours		
Collect sample CL 22A for 1 hour	0.77	425
Pump slurry for composition lineout 3 hours		
Collect sample CL 22B for 1 hour	0.91	425
Pump slurry for composition lineout 3 hours		
Collect sample CL 22C for 1 hour	0.93	450
Pump slurry for composition lineout 3 hours		
Collect sample CL 22D for 1 hour	0.92	400
Pump slurry for composition lineout 4 hours		
Collect sample CL 22E for 1 1/2 hours	1.35	425

Discussion of Results

The composition of the feed slurry was established by systematically sampling and analyzing the slurry. Results of this study are presented below. The experiment was started at 04:00 hours with slurry feed started at 05:13 hours. A preliminary sample was taken at 08:00 hours and a check sample after the first makeup at 11:00 hours. Samples were then taken to bracket each sub-experiment. The whole data set describe the control of the feed pot for a period of about 28 hours.

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Time	Sample	$\%H_2O$ in Slurry(1)	% Ash in Slurry(2)	% Iron in Ash from Slurry(3)
8:00	Preliminary	10.37		
11:00	First Check	10.09		
12:55	A-1	9.93	2.185	3.90
14:00	A-2	10.15		
17:03	B-1	9.68	2.236	4.31
18:00	B-2	9.46		
20:56	C-1	8.92	2.282	3.94
22:02	C-2	8.44		
0:55	D-1	9.66	2.260	4.33
2:10	D-2	9.53		
5:58	E-1	8.48	2.313	4.51
7:31	E-2	7:83		

Notes: (1) Feed Lignite: 31.45-31.67% H_2O. With 1:2 coal-to-solvent ratio, the slurry contains 10.48% H_2O.
(2) Feed Lignite: 6.893% Ash. With 1:2 coal-to-solvent ratio, the slurry contains 2.298% ash.
(3) Iron in lignite ash = 4.352%.

The reactor had been used for runs with Kentucky No. 9 coal which is rich in iron. The value obtained in a number of cases (discussed previously) was about 20% Fe on the ash in the coal. We analyzed the filter cakes from Run CL 22A, B, C, D and E in an effort to find the extent to which settled minerals in the dissolver would be a problem in a lignite run following a Kentucky No. 9 run. Samples of the filter cakes were ignited and the resulting ash was dissolved in concentrated hydrochloric acid to extract the acid soluble iron for titration. Results are as follows:

IRON CONTENT OF FEED AND ASHED FILTER CAKES

Sample	% Fe in Feed	% Fe in Ash from Filter Cake
A-1 A-2	3.90	4.833
B-1 B-2	4.31	4.525
C-1 C-2	3.94	5.287
D-1 D-2	4.33	5.803
E-1 E-2	4.51	5.888

At first inspection it is gratifying that the concentration of the iron in the ash recovered from the filter cake samples is near the value established for the lignite fed. In experiment CL-17 we had studied the reverse case in which lignite minerals were replaced by Kentucky No. 9 coal minerals. In CL 17 the concentration of iron in the ash increased from 6.06% to 20.92% in about 8½ hours of operation.

The average input iron concentration in the feed slurry ash was 4.19% while the average concentration of iron in the product ash was 5.27%. Since the ash concentration was about 2.3% in the output slurry the increased concentration of iron in the slurry was approximately 0.02%, an increase which is insignificant. It appears that the flushing procedure did an acceptable job of unloading any serious level of contaminant which may have remained from the runs made previously.

Analytical results for the composition of the feed and product gases are presented below. From these results it can be seen that the concentration of carbon monoxide in the product gas is reduced and that carbon dioxide has increased substantially. This is attributed to the reaction of carbon monoxide with water to produce hydrogen and carbon dioxide. From the number of moles of synthesis gas fed and the results presented in the table it can be shown that both hydrogen and carbon monoxide have been consumed in the reaction.

ANALYSIS OF FEED AND PROCESS GASES FOR RUN CL 22A to E
(normalized, air and water free basis)

GAS (Mol %)	Feed Gases			Product Gases				
	CL 22A	CL 22C	CL 22E	CL 22A	CL 22B	CL 22C	CL 22D	CL 22E
Hydrogen	50.7	52.6	51.8	34.7	40.3	37.4	40.1	36.3
Nitrogen				7.77	8.87	8.85	10.8	12.0
Methane				5.91	3.02	5.42	0.95	2.65
Ethane				2.15	1.18	1.93	0.41	0.98
Propane				0.87	0.50	0.82	0.23	0.40
n-Butane				0.16	0.09	0.16	0.05	0.12
Isobutane				0.05	0.03	0.05	0.02	0.04
Carbon Dioxide				18.6	15.3	17.4	16.3	14.5
Carbon Monoxide	49.3	47.4	48.2	29.7	30.7	28.0	31.0	32.9
Hydrogen Sulfide				0.07	0.06	Nil	0.11	0.07
H_2/CO Ratio	1.028	1.110	1.075	1.168	1.313	1.336	1.294	1.103
Moles per hour				5.185	4.965	4.646	4.062	4.458

From the input data presented it can be seen that the materials were fed into the reactor under good compositional control. Lineout time was provided to obtain samples which were at least a first approximation of a steady state.

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A summary of experimental results for these experiments is presented in Appendix A part 3. The raw data indicate a recovery of about 91% on the average. As a general trend the loss is proportionately larger as the sample size is reduced. Between feed and sampling errors this loss amounts to roughly 50 grams of material. There is no doubt that the water rich system is more difficult to study with precision. Depending on the sample chosen the evaporation of water from the feed pot could account for about a third or up to about a half of the missing material. The difference in water determined at the beginning and the end of the sample period is applied to feed pot weights averaging from a low of about 4 Kg to an upper weight of about 6 Kg.

The composition of the reclaimed cut 2 solvent was reported by means of $\overline{IR}$ data. These results indicate that hydrogen was lost from the solvent in all experiments in this series. This loss is greater at short retention times and at higher operating temperatures. As retention time is increased the $\overline{IR}$ values increased but did not return to the value observed in the feed solvent. Between the CL 22B and the CL 22E samples the hydrogen concentration did not improve. A small reversion may even be indicated, even at 425^{o}C. A yield of excess solvent was obtained in every case but it must be remembered that this has been obtained at the cost of hydrogen transfer from the solvent. In order to evaluate the result of this change in composition it would be necessary to repeat the reaction with the reclaimed solvent.

Reporting solvent yield to MAF basis tends to amplify the result since the concentration of organic matter in the lignite is lower. (After removal of water and ash only 61.6% of organic matter is obtained.) A fairer impression of the excess solvent term is obtained by looking at the increase based on the weight of feed solvent. Here the increase ranges from about 3% to about 9% of the original charge of solvent. During redistillation a fair amount is found to be shifted into cut 1 boiling range material. In order to obtain a balanced return of solvent some of the cut 1 would be returned to the solvent volume, which could be conveniently done by an adjustment in the cut point temperature.

All solutions were filtered without difficulty except CL 22D which was made at 400^{o}C. Here the conversion to filterable material was marginal and the sample was only partly filtered. The results are based on the material that did pass through the filter. It is unlikely that this operating condition could be used in a plant since filterability is a requirement. Of course the agreement between the laboratory operation and the performance of plant scale equipment is actually a consideration. It is the limitations of the plant scale equipment which are the final constraint.

As a practical consideration the reaction does produce a high BTU product from lignite which also contains a low percentage of sulfur. This observation is the justification for interest in processing this grade of coal.

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Evaluation of Run CL 23 (Samples A through F)

This experiment was a continuation of the variable study for reaction of Baukol-Noonan lignite. The reducing gas was 1:1 carbon monoxide to hydrogen mixture. The solvent was CL 18 hydrogenated anthracene oil. Variables in the study were retention time, temperature, and pressure.

The program of water and ash analysis for control of feed slurry composition was continued. The feed pot was operated in the temperature range 36-45°C which is an average of about 10 degrees cooler than the temperatures used in run CL 22. Water retention by the feed slurry was improved slightly by this small change in operating procedure. The concentration of iron in the ash from filtercake was determined for comparison to the concentration of iron in the ash from the feed slurry samples. The composition of the feed gas mixture was determined by gas chromatography.

The reactor lineout was done according to the procedure which had evolved in the preceding experiments. Lineout times were based on the time required to pump four volumes of slurry through the reactor. The schedule for the experiment follows:

Operation	1/LHSV	Temp. °C	Pressure, psig
Condition lineout, pump flush oil			
Composition lineout, on slurry 3 hr. Collect sample CL 23A for 1 hour.	0.58	450	1500
Composition lineout, on slurry 2 hr. Collect sample CL 23B for 1 hour.	0.76	450	1500
Composition lineout, on slurry 4 hr. Collect sample CL 23C for 1½ hours.	1.35	450	1500
Composition lineout, on slurry 4 hr. Collect sample CL 23D for 1½ hours.	1.30	400	1500
Composition lineout, on slurry 4 hr. Collect sample CL 23E for 1 hour.	1.39	425	1000
Composition lineout, on slurry 3 hr. Collect sample CL 23F for 1 hour.	0.92	425	1000

Discussion of Results:

Results from studies of feed slurry composition and the composition of the ash from the wet filter cakes are consolidated in the table which follows.

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ANALYSIS OF FEED SLURRY & WET FILTER CAKE

Sample	%Ash in Slurry	%H_2O in Slurry	% Fe in Slurry Ash	% Fe in Wet Filter Cake Ash
CL-23A Start	2.259	10.61	5.06	
CL-23A Final	2.276	10.16	4.33	3.79
CL-23B Start	2.376	10.94	4.39	
CL-23B Final	2.487	11.14	4.30	3.49
CL-23C Start	2.454	10.58	4.42	
CL-23C Final	2.428	9.95	4.33	4.67
CL-23D Start	2.355	10.08	4.50	
CL-23D Final	2.336	9.80	(3.06)	3.95
CL-23E Start	(2.101)	9.65	4.56	
CL-23E Final	2.409	9.49	4.67	3.47
CL-23F Start	2.334	10.00	4.68	
CL-23F Final	2.389	9.80	4.63	3.34
mean	2.373 ± 0.055	10.18 ± 0.42	4.53 ± .17	3.78 ± 0.35

Notes: The Baukol-Noonan Lignite used contained 6.96% ash and 29.50% water by oven drying. The ash content of 1:2 coal-to-solvent slurry should be 2.32% and the water should be 9.83%. The Karl Fischer method gives slightly higher results than oven drying.

As a general observation, the feed slurry components checked appear to have maintained the average composition with good precision. The average water content of the slurry is definitely higher at the cooler operating temperature. The trend is for the iron content of the ash from the wet filter cakes to be a little lower than the iron content of the mineral in the feed slurry. This is in contrast to the trend in the CL 22 experiment which may have been slightly under the influence of residual mineral from Kentucky No. 9 coal. In both cases the deviations result in quite small changes in the concentration of iron in the product solution.

Gas analysis results are presented in the table below. The composition of the feed gas remained constant within reasonable precision throughout the course of the experiment. The composition of the product gases obtained is also presented in this table. Carbon monoxide was reacted and a good conversion to carbon dioxide is indicated by the concentration of this material in the product gas. These results together with the information in Appendix A part 4 can be used to show that both carbon monoxide and hydrogen were consumed in the reactions studied.

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ANALYSES OF FEED AND PRODUCT GASES OF RUN CL-23 A TO F
(Normalized, air-and water-free basis)

General Conditions: Solvent-to-coal: 2/1 CL 18/Lignite; 1:1 H_2/CO; GSV=230/hr.

Specific Condition	PRODUCT GASES						FEED GASES		
	CL-23A	CL-23B	CL-23C	CL-23D	CL-23E	CL-23F	CL-23A	CL-23C	CL-23E
GAS (MOL %)									
Hydrogen	33.8	35.2	36.9	40.9	38.8	37.8	52.0	51.0	50.6
Nitrogen	8.34	9.32	10.8	10.6	6.66	7.76			
Methane	8.45	6.66	5.22	1.16	2.40	2.26			
Ethane	2.98	2.41	1.78	0.46	0.88	0.93			
Propane	1.19	0.97	0.72	0.20	0.42	0.46			
n-Butane	0.22	0.17	0.14	0.04	0.17	0.10			
Isobutane	0.13	0.13	0.09	0.02	0.09	0.06			
Carbon Dioxide	24.1	22.6	18.0	13.7	13.6	16.1			
Carbon Monoxide	20.7	22.4	26.3	32.9	37.0	34.5	48.0	49.0	49.4
Hydrogen Sulfide	0.16	0.21	0.09	0.06	0.09	0.12			
H_2/CO Ratio	1.63	1.57	1.40	1.24	1.05	1.10	1.08	1.04	1.02
Moles per hour	5.707	4.912	4.345	4.518	3.794	3.314			

The percent recovery based on raw data is given in Appendix A for each sample in the series. The average for this set is 91.7% recovery which is not much different from the previous experimental set. As usual the balances were closed better on the larger samples than on the smaller ones. In this regard the use of the cooler feed pot may have been helpful but no major improvement resulted from this change.

Temperature has a strong influence on the rate of formation of the hydrocarbon gases taken from the process. This is approximately doubled by a 25° temperature increase based on a few comparisons which are made with these data and the data from experiment CL 22. At a given operating condition the amount of carbon dioxide observed in a product gas increases with retention time.

At the 450°C operating temperature and the shorter retention times, CL 23A and CL 23B, the solvent yield was less than the amount needed for recycle. This improved as retention time increased with the longer retention time used in CL 23C resulting in an excess of solvent over the amount needed for recycle. Extending the reaction time at 400°C resulted in a filterable solution and a modest increase in solvent yield. (Compare results for CL 22D and CL 23D.) These data are taken at 1500 psig and in comparison the results at 1000 psig seem to follow a different pattern. Extending the reaction time at 425°C and at 1000 psig produced less solvent at the longer retention time. (Compare results from CL 23E and CL 23F.) This may be an indication of an optimum reaction time at 1000 psig with continued heating resulting in reversion of the product.

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From the infrared analysis data none of the cut 2 reclaim solvents contained as much hydrogen as the hydrogenated anthracene oil used as the initial solvent. The transfer of hydrogen was greater at high temperatures and shorter retention times at 1500 psig. As retention time increased the cut 2 solvent fraction had a slight tendency to regain hydrogen based on an increasing IR. It is improbable that this is reactive hydrogen however at 450°C. The distillation data suggest that cracking reactions are operating to produce enough cut 1 oil to lower the average molecular weight of the solvent and to introduce more saturated functional groups.

The cut 2 reclaim solvent had the most hydrogen in it at the low temperature long retention time condition used in CL 23D. This kind of solvent might be the most likely to recycle without complications since it is the least depleted in hydrogen and the volume recovered is also favorable. These operating conditions do not allow maximum sulfur removal.

The vacuum bottoms which resulted from these studies were all low in sulfur content. The effect of high operating temperatures was especially well demonstrated in this set of samples. Both sulfur and oxygen removal are shown to depend on operating temperatures and the rules for lignite are similar to the rules for bituminous coal in this regard. Nitrogen is not converted effectively and remains at about the same concentration in all of the vacuum bottoms.

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Evaluation of Experiments CL 24 & CL 25 (CL 24A & CL 25A to F)

These experiments were a continuation of the study of the reaction of Baukol-Noonan lignite with carbon monoxide-hydrogen mixtures as reducing gas. In this case the reducing gas mixture was intended to be 1:3 carbon monoxide to hydrogen. CL 18 hydrogenated anthracene oil was used as solvent.

The program of water and ash analysis for feed slurry was continued. Results of analytical studies on feed slurry showed that composition of the feed slurry was maintained with excellent precision and accuracy. The feed gas was analyzed by gas chromatography. It was found that this gas composition was poorly reproduced. The intended mixing ratio was not obtained in either CL 24 or CL 25. In the longer experiment the ratio wandered well away from the original mixture. This is different from experience with the 1:1 mixtures which had been made with reasonable accuracy.

The usual extended sequence of experiments had been planned for Run CL 24. This was cut short during preparation of the second sample by formation of a plug in the reactor. This required that the reactor be taken apart and cleaned out.

The CL 25 sequence was then run starting with a clean empty reactor. This experiment was also terminated by a plug in the reactor. In both cases the stoppage developed during an attempt to run an experiment at 450°C using only 1000 psig pressure and using retention time characterized by a 1/LHSV of 0.74. This experiment was completed without difficulty in experiment CL 25D. It appears that 1000 psig operation is marginal from the aspect of chemical stability of the reacting materials. Plug formation was induced by malfunction of the feed pump which stopped flow completely in the attempted experiment CL 25G and which was pumping a much reduced flow rate in the CL 24B attempt. Both experiments were stopped during the lineout period.

All experiments were conducted with the standard lineout procedures which have been discussed previously. Details are presented below.

Operation	1/LHSV	Temp. °C	Pressure
Condition lineout on flush oil			
Composition lineout on slurry 4 hours			
Collect sample CL 24A for 1 hour	0.72	425	1000
Composition lineout to plug formation three hours	0.72	450	1000
Condition lineout on flush oil			
Composition lineout on slurry 3 hours	0.56	425	1500
Collect sample CL 25A for 1 hour			
Composition lineout on slurry 3 hours	0.74	425	1500
Collect sample CL 25B 1 hour			
Composition lineout on slurry 3 hours	0.74	450	1500
Collect sample CL 25C 1 hour			

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table continued

Operation	1/LHSV	Temp. °C	Pressure
Composition lineout on slurry 3 hours Collect sample CL 25D 1 hour	0.72	450	1000
Condition lineout on slurry 2 hours Collect sample CL 25E for 1 hour	0.56	450	1000
Condition lineout on slurry 2 hours Collect sample CL 25F for 1 hour	0.56	425	1000
Condition lineout to plug 2 hours	0.56	450	1000

Note: a gas flow adjustment was necessary to obtain normal flow before CL 25F was started on lineout. From this observation it is possible that some deposit had been formed on the reactor wall during the 450°C operation. If this was the case the hot liquid retention time may have been reduced proportionately to the volume of solids deposited relative to the volume of the reactor.

Discussion of Results:

The results of work done to establish the composition of feed slurry, the minerals in the products from the reactor, and the composition of the plugs formed in the reactor are presented below:

ANALYSIS OF FEED SLURRY, WET FILTER CAKES & COKE PLUGS

Sample	% Ash in Slurry	%H_2O in Slurry	% Fe in Slurry Ash	% Fe in Wet Filter Cake Ash(or coke)
CL-24A Start	2.272	10.51		
CL-24A Final	2.272	10.05		3.41
Coke CL-24B	2.277			(10.26)(9.02)
Mean	2.273 ± .008	10.27		
CL-25A Start	2.234	9.66	4.66	No wet filter cake
CL-25A Final	2.234	9.46	(5.56)	
CL-25B Start	2.294	10.54	4.54	
CL-25B Final	2.289	9.99	4.57	3.99
CL-25C Start	2.252	10.78	4.65	
CL-25C Final	2.317	9.89	4.44	3.84
CL-25D Start	2.242	10.38	4.51	
CL-25D Final	2.262	10.43	4.41	3.96
CL-25E Start	2.295	9.84	4.47	
CL-25E Final	2.221	9.84	4.41	4.28

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table continued

Sample	% Ash in Slurry	%H_2O in Slurry	% Fe in Slurry Ash	% Fe in Wet Filter Cake Ash(or coke)
CL-25F Start	2.279	10.34	4.58	
CL-25F Final	2.278	10.13	4.50	4.52
Mean	2.266 ± 0.026	10.10 ± 0.39	4.52 ± 0.07	4.12 ± .23
Coke CL-25G				

Notes: The Baukol-Noonan lignite sample contained 6.965% ash and 25.50% water (by oven drying loss). The ash content of 1:2 coal to solvent slurry should be 2.32% and the water should be 9.83%. The Karl Fischer method used for slurry analysis gives slightly higher results for water than oven drying the lignite.

The analysis of feed gases for CL 24 and CL 25 is given below:

Gas	CL 24A	CL 25A	CL 25C	CL 25E	CL 25G
Hydrogen	76.4%	80.0%	78.5%	73.5%	84.1%
Carbon Monoxide	23.6%	20.0%	21.5%	26.5%	15.9%
H_2/CO Ratio	3.24	4.00	3.65	2.77	5.29

The composition of the product gas samples is presented below:

Gas (Mol%)	CL 24A	CL 25A	CL 25B	CL 25C	CL 25D	CL 25E	CL 25F
Hydrogen	59.9	67.9	70.9	55.2	47.8	44.0	74.6
Nitrogen	6.89	4.90	2.27	8.56	4.35	4.20	1.79
Methane	1.98	1.83	1.99	5.51	9.10	9.30	1.19
Ethane	0.79	0.90	0.87	2.28	3.30	3.58	0.59
Propane	0.40	0.41	0.41	0.98	1.26	1.34	0.23
n-Butane	0.10	0.08	0.07	0.15	0.19	0.21	0.04
Isobutane	0.06	0.05	0.04	0.08	0.11	0.11	0.01
Carbon Dioxide	13.0	12.8	11.2	16.6	20.0	23.9	8.55
Carbon Monoxide	16.8	11.0	12.1	10.5	13.8	13.2	12.9
Hydrogen Sulfide	0.11	0.13	0.11	0.14	0.02	0.23	0.16
H_2/CO Ratio	3.57	6.17	5.86	5.26	3.46	3.33	5.78
Moles per hour out	4.458	5.540	5.211	3.324	2.536	2.513	6.828

There is some evidence in the gas output data that the flow through the reactor may have been progressively constricted during samples CL 25C, D, & E. It is possible from the volumes of gas recovered that the input values may have been less than the amounts calculated. Despite this problem the material balances closed reasonably well. The average recovery was 94.6% of the materials fed in this series.

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Coke plugs were formed for runs CL 24B and CL 25G. In both instances an attempt to operate at 450°C with syn gas at 1000 psig was being made. In both cases the feed rate was high to obtain retention times which were short. 1/LHSV = 0.75 approx. External temperatures of the reactor tube wall were advanced to try to maintain a normal temperature profile at these flow rates. This may be the main factor in causing the reactor tube to plug although the stability of the solution at 1000 psig is probably marginal also. Estimated temperature profiles across the reactor tube wall are given below:

Temperature Data for Runs CL 24B, CL 25D, & CL 25G

Run No.	CL 24B	CL 25D	CL 25G
Maximum at tube wall	535°C	505°C	500°C
Average tube wall	500	500	485
Maximum internal	510	450	475
Average internal	450	450	450

The general objective of the operating conditions explored would be to increase through put and to operate at minimum pressures. It appears that these trials generally skirt the boundary of useable conditions. Although no difficulty was experienced in the operation of the reactor, the product made in experiment CL 25A could not be filtered. The solvent was recovered by distillation of the unfiltered product and not enough total hydrocarbons were returned to replace the solvent initially charged. As might be expected the infrared data indicate that the hydrogen transfer capacity of the solvent has been spent and not replenished. The quality of the reclaim solvent as well as the amount returned will therefore tend to exclude operating with these conditions.

At the higher flow rates the MAF conversions (or the amount of insoluble organic matter obtained) will also be seen to be unfavorable. The conversion of the input coal must be driven at least to the point at which the yield of liquid balances the output of hydrocarbon gases. In the latter part of CL 25 the insoluble organic matter remained as high as 31% of the organic matter fed. (See CL 25D, E & F)

General Conclusions from Lignite Studies

No lignite studies have been done in the continuous reactor after run CL 25. It is worthwhile to comment on some of the general tendencies which have been observed. Previous studies with the batch autoclave have been more encouraging than have the results from the continuous reactor studies. This seems to be the consequence of pressure dependence for the reaction. Autoclave runs all used higher pressures than were used in the continuous reactor.

At the end of this block of studies with lignite a rough idea of operating boundary limits and practical operating problems had been developed. Variables had been changed to produce both unfilterable low conversion products, and products which resulted from exposure to too much heat and too low an operating pressure. These conditions resulted in polymerization or decompositions which resulted in plug formation in the reactor. Here lower operating pressure may have been a factor also.

1. It seems established that carbon monoxide will react with water in the presence of the mineral phases in lignite to produce carbon dioxide and hydrogen. In addition it is fairly well established that the nascent hydrogen which is formed is more reactive than molecular hydrogen in contact with the organic matter present in the coal and solvent. The reaction is apparently pressure dependent (probably as a consequence of the disappearance of the nascent hydrogen) and higher pressures at least increase the reaction rate. This reaction is facilitated by alkaline material, such as Na^+.

2. In the Baukol-Noonan lignite experiments some reaction with hydrogen in the molecular form is also observed. This reaction is also facilitated by the mineral phases present in the lignite. This reaction may be due to the presence of iron in the lignite. The quantity is small but is apparently sufficient for inducing measurable reactions.

3. In all experiments with CL 18 hydrogenated anthracene oil solvent the results from infrared analysis of the reclaim solvent indicate a transfer of reactive hydrogen from the solvent as a result of solution of the lignite. None of the operating conditions used have resulted in replenishment of the original concentration of hydrogen in solvent used. Some of the conditions may produce solvent which could be recycled, since the reclaim solvent did not return to the composition of raw anthracene oil in most instances. The question of behavior on recycle has not been studied experimentally. It is clear that a part of the reactivity observed must be credited to the chemical reactivity of the CL 18 solvent.

4. The initial studies done with raw anthracene oil and carbon monoxide are generally defective since the operating temperature may have been too low. (See CL 3 to CL 6) In other studies with carbon monoxide-hydrogen mixtures and raw anthracene oil the product made at 1000 psig using 425°C operating temperature and a retention time characterized by 1/LHSV = 1.62 was found to be unfilterable in the laboratory test. (See run CL 16) Using the same temperatures and retention times with 2000 psig reducing gas produced a filterable solution. (See run CL 15) There are technique questions in these early runs which would perhaps result in some changes in the data on repeating the experiments but these should not alter numerical values extensively. More importantly, the infrared spectrum of the cut 2 reclaim solvent in run CL 15 indicates that the solvent gained hydrogen compared to the raw anthracene oil originally used. This is good evidence that the solvent should recycle without complication.

5. Analytical procedures for control of feed slurry composition, feed gas composition, product recovery and analysis and for inspection of feed lignite for minerals of interest have been developed. These are available for use in a more critical review of these reactions.

6. The impression gained from the limited study done with lignite remains that no particular advantage lies with the use of pure hydrogen in lignite reduction, and that mixtures of carbon monoxide and hydrogen should be sufficiently reactive for the preparation of solutions with lignite. It is believed that there are reasonable prospects for improvement in the efficiency of these reactions.

Recommendations:

Before pilot plant studies with lignite can be conducted additional work is needed to establish the effect of higher operating pressures and to demonstrate that the reclaim solvent can be kept in balance and recycled properly. In selecting a coal for this work the ion exchangeable sodium content of the lignite and the total iron as pyrite or acid leachable material should be considered. These appear to be the materials which are present naturally that are instrumental in facilitating the utilization of carbon monoxide and hydrogen. These materials should be present in useful amounts in order to obtain the desired reactions. 4 /

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Evaluation of Experiment CL 26 (Samples A to G)

These experiments were done to obtain data at short retention times and higher operating temperatures, using Kentucky No. 9 coal and mixtures of carbon monoxide and hydrogen as the reducing gas. The solvent was CL 18 hydrogenated anthracene oil. The gas mixture was prepared by continually blending gas from cylinders of pure hydrogen and pure carbon monoxide. Water was added to the feed slurry to maintain a concentration of reagent for reaction with the carbon monoxide. All experiments were done at 1000 psig pressure. The reactor had been dismantled and cleaned out at the end of the previous experiment. The tube was therefore clean and empty at the beginning of this procedure.

The feed slurry was analyzed for ash and water content in order to monitor the precision of the feed. The ash from the feed slurry samples and the ash from the wet filter cake samples was analyzed for iron content to follow the input and output of iron to the reactor and from the reactor as the experiment progressed. The gas mixture was sampled and analysis by gas chromatography for the initial samples was completed while the experiment was in progress. These results were used to correct rotometer readings in an effort to maintain better control of the gas mixture in use. Time was allowed for initial condition and compositional lineouts and intervals between samples to lineout after changes in operating variables. This schedule follows:

Operation	1/LHSV	Temp. °C	Pressure
Condition lineout on flush oil			
Composition lineout on slurry 5 hours	0.57	450°C	1000
Collect sample CL 26A for 1 hour			
Composition lineout on slurry 2½ hours	0.57	425	1000
Collect sample CL 26B for 1 hour			
Composition lineout on slurry 3 hours	0.73	425	1000
Collect sample CL 26C for 1 hour			
Composition lineout on slurry 3 hours	0.71	475	1000
Collect sample CL 26D for 1 hour			
Composition lineout on slurry 2½ hours	0.57	475	1000
Collect sample CL 26E for 1 hour			
Composition lineout on slurry 2½ hours	0.42	475	1000
Collect sample CL 26F for 1 hour			
Composition lineout on slurry 3 hours	0.72	450	1000
Collect sample CL 26G for 1 hour			

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Discussion of Results

The results of slurry analysis and studies on wet filter cake composition are presented in the table which follows. Water was added to the feed slurry to produce 5.0% water content in the initial mixture. The feed loop was cooled to maintain a slurry temperature of about 45°C. Water was kept at a more uniform concentration in the slurry as a consequence of these changes.

CL-26 FEED SLURRY ANALYSIS VS FILTER CAKE COMPOSITION

Sample	% Ash In Slurry	% H_2O In Slurry	% Fe In Slurry Ash	% Fe in Filter Cake Ash
26-A Start	3.893	5.30	25.98	
26-A Final	3.872	5.03	24.56	24.08
26-B Start	4.039	4.05	25.20	
26-B Final	3.897	4.81	23.43	23.99
26-C Start	3.898	4.52	24.33	
26-C Final	3.952	4.19	24.58	23.61
26-D Start	3.886	4.50	26.08	
26-D Final	3.877	4.47	25.60	23.32
26-E Start	3.979	4.22	25.81	
26-E Final	3.851	3.84	21.57	22.03
26-F Start	3.927	4.07	24.92	
26-F Final	3.771	4.11	23.38	23.22
26-G Start	4.075	3.96	26.21	
26-G Final	3.838	3.45	24.33	23.90
Mean	3.911 ± 0.059	4.32 ± 0.38	24.71 ± 0.96	23.45 ± 51
Variance	± 1.5% Relative	8.8%	3.9%	2.2%

CL-26 feed coal is Kentucky No. 9 with 11.65% ash and 4.58% water content. The ash content should be 3.75% for 2:1 slurry containing a total of 5.00% water. During condition lineout the feed slurry was observed to deposit a little mineral and coal in the stirred feed pot. This resulted in slightly higher mineral level after stirring efficiency was increased and make up slurry batches were added.

The analysis of feed gases for run 26 is presented below:

Gas (Mol%)	CL 26A	CL 26C	CL 26E	CL 26G
Hydrogen	75.6	73.5	73.3	77.3
Carbon Monoxide	24.4	26.5	26.7	22.7
H_2/CO Ratio	3.10	2.77	2.75	3.41

Adjustments were made after the analysis of the first two samples were reported. This reduced the wandering of the composition but did not result in precise control.

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Analytical results for the composition of the output gases are as follows:

ANALYSIS OF PRODUCT GASES OF RUN CL 26A to G

Gas (MOL %)	CL-26A	CL 26B	CL 26C	CL 26D	CL 26E	CL 26F	CL 26G
Hydrogen	54.8	57.6	59.8	36.1	32.5	35.3	46.0
Nitrogen	4.84	7.19	5.54	7.45	8.72	8.64	9.11
Methane	7.24	3.07	3.73	23.3	25.7	22.8	13.1
Ethane	2.73	1.21	1.37	6.57	7.48	7.08	4.11
Propane	1.14	0.57	0.59	2.38	2.75	2.70	1.46
n-Butane	0.25	0.18	0.11	0.42	0.54	0.57	0.17
Isobutane	0.08	0.05	0.04	0.17	0.17	0.20	0.09
Carbon Dioxide	11.1	10.7	11.2	15.2	14.2	13.2	11.4
Carbon Monoxide	14.5	16.7	17.0	7.09	4.62	4.80	10.3
Hydrogen Sulfide	3.27	2.72	0.56	1.39	3.35	4.75	4.36
H_2/CO Ratio	3.78	3.45	3.52	5.09	7.03	7.35	4.47
Moles per hour out	3.858	3.270	2.467	2.237	2.223	2.613	1.834

Data for comparison of the results of these experiments is presented in Appendix A part 5. The raw recovery of product samples accounted for 91.3% to 96.7% of the materials fed to the reactor. The average for all experiments was 93.4%. It is difficult to point out an area of the procedure which is so far from expectation that the error can be located mostly in one place. The down trend in gas yield is suspicious and suggests that the metering of gas into the reactor trailed off during the run, it is not obvious how this could happen. None of the gas weights are large enough to cause the material balance to be off more than a few percent even if they are not entered into the calculation at all. Persistent failure to improve on recovery of the material above about 95% probably is the result of the mechanics of the weighing of the feed pot which was coupled to the pump by flexible tubing and stirred with an air driven stirrer coupled to an airline by a flexible hose. This may be added to the effect of evaporation of water and solvent and perhaps other fairly systematic errors in recovery of vapors which may have eluded sampling. It is suggestive that more difficulty in closing material balances has been encountered with water added to the system than in studies without added water.

These experiments were planned to explore limits for high feed rates and high operating temperatures. It can be seen that the MAF conversion gradually declined as feed rates were increased and as reaction times became progressively shorter. Higher processing rates were attempted by compensating for short reaction times by the use of higher reactor temperatures. One price for this choice is the return of cut 2 reclaim solvent which is substantially depleted in hydrogen. Thus IR values for reclaim cut 2 solvent fell to low figures similar to those previously obtained with raw anthracene oil. These results would imply virtual depletion of reactive hydrogen and prospects for recycle of such material are dim. (See data for CL 26D, E, & F at 475°C)

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The advantage in use of high reaction temperatures is the efficient removal of sulfur and oxygen which can be accomplished under these conditions. The vacuum bottoms fraction comprises the bulk of the fuel available from the coal solution process. It is important to be able to reduce the sulfur concentration in the vacuum bottoms to the lowest practical value. From the results at 475°C it is clear that the lowest concentrations derived from Kentucky No. 9 coal have been obtained at the highest temperatures.

The combination of high operating temperature and short retention times removes sulfur to the lowest concentration observed. By comparing results at the same retention time (CL 26B & CL 26E at 1/LHSV = 0.57) several curious observations can be made. First the MAF conversion is higher at 425°C than at 475°C. This seems to be unambiguious evidence for a repolymerization reaction which results in lowered conversion. Taken at face value the MAF conversion would decline at 450°C compared to the conversion at 425°C, all comparisons being made at 1/LHSV values of 0.57.

At 475°C the hydrogen, which had been catalytically added to the CL 18 solvent, appears to have been stripped out by 1/LHSV = 0.42. Extending the reaction time fails to lower the IR value of the cut 2 reclaim solvent even though a gradual increase in the yield of total reclaim solvent is observed. (See CL 26D, E, & F.) At this temperature the hydrogen transfer function of the solvent is used up and a slow hydrogenation reaction continues to produce some further conversion in competition with repolymerization reactions. This IR value is similar to the ratio observed for raw anthracene oil used to make the CL 18 solvent and the raw anthracene oil must then have little transfer capacity as made. The high temperature pyrolysis process which is the genesis of the oil probably results in thoroughly dehydrogenated material.

For a number of experiments little comment has been made regarding the behaviour of blackness in response to changes in operating conditions. In these experiments the operating conditions impose the most severe thermal stress on the system which has yet been used. In response to this stress the blackness of the solutions increased to values of 17.60 in the case of CL 26F. At the other extreme the lowest blackness value in this set was 7.79 at 425°C in the case of CL 26C.

It has been hoped that the blackness function would provide a simple method for estimating the concentration of dissolved coal in a solution. As observations have accumulated the prospect for using this measurement for this purpose has diminished. Unexpectedly, it now appears that the blackness function is more nearly a measure of the difference of the rates of free radical formation and the rate of termination by hydrogen. Thus at high temperatures and low hydrogenation activities the solution becomes darker in color. At lower temperatures and higher hydrogenation activities the solution becomes lighter in color. As an empirical observation, removal of sulfur and oxygen to the lowest levels has generally been done only when enough thermal stress is present to produce a dark colored solution. On the other hand considerable liquid yield can be obtained without producing either dark colored solutions or particularly well desulfurized material.

CL-26

IV-J

The forces which must be applied to remove sulfur are not compatible with the desire to make excess solvent. Heat causes an increase in the rate of gas formation as well as a tendency to repolymerize as temperatures are increased. These tendencies are countered by the activity of the reducing gas, and in this regard the partial pressure of hydrogen, the catalytic activity present, and the donor capacity of the solvent become considerations. Unless the carbon monoxide is at least as reactive as hydrogen its addition would not be helpful.

IV-J

Evaluation of Experiment CL 27 (Samples A to F)

The experiments in this set were done to obtain data at short retention times and higher temperatures using Kentucky No. 9 coal and using only hydrogen as the reducing gas. The solvent was CL 18 hydrogenated anthracene oil. These experiments were intended to cover comparable conditions to those used in the synthesis gas study done as run CL 26. The reactor had been flushed with solvent at the end of run CL 26 and any mineral residue which was left may have been observed in the initial samples of CL 27. Normal lineout intervals were used to cope with such effects.

The feed slurry was analyzed only for ash content in order to obtain data on feed uniformity and the composition of the minerals fed. The slurry had no added water and only the moisture in the ground coal sample should have been present. Water analysis was not done on the slurry for this reason. The ash from the input slurry was analyzed for iron content. The ash from the wet filter cake samples was analyzed for iron content in order to find if the iron concentration in the reactor had stabilized. The detailed operating schedule is given below.

Operation	1/LHSV	Temp. ^{o}C	Pressure
Condition lineout on flush oil			
Composition lineout on slurry 3 hours Collect sample CL 27A for 1 hour	0.53	425^{o}C	1000 psig
Composition lineout on slurry 3 hours Collect sample CL 27B for 1 hour	0.52	450	1000
Composition lineout on slurry (6 hours) Collect sample CL 27C for 3/4 hour*	0.49	475	1000
Composition lineout on slurry 3 hours Collect sample CL 27D for 1 hour	0.73	475	1000
Composition lineout on slurry 2 3/4 hr. Collect sample CL 27E for 3/4 hour	0.42	475	1000
Composition lineout on slurry 2 1/2 hr. Collect sample CL 27F for 3/4 hour	0.41	450	1000

* Difficulty with circulating pump caused rejection of the first sample CL 27C and additional lineout time was needed to prepare for running the sample made.

Discussion of Results

The results for feed slurry analysis and for the analysis of the wet filter cakes are presented in the following table. Some difficulty with the feed slurry recycle pump was encountered. As a result the slurry seems to be fed with a little less precision than normal. The iron content of the wet filter cakes from analysis of the ash for iron is substantially the same as the input. At least the variation of the two sets of numbers would include the means of both sets.

IV-J

CL-27 FEED SLURRY ANALYSIS VS FILTER CAKE COMPOSITION

	% Ash In Slurry	% Fe in Ash	Fe In Filter Cake Ash
27-A Start	3.549	23.01	
27-A Final	3.527	22.22	24.21
27-B Start	3.797	23.70	
27-B Final	3.554	22.89	24.93
27-C Start	3.803	24.14	
27-C Final	3.911	25.12	
27-C 3rd Sample	4.387	26.02	25.86
27-D Start	4.127	26.74	
27-D Final	4.051	25.87	25.54
27-E Start	3.925	24.84	
27-E Final	4.037	26.20	24.80
27-F Start	4.237	25.77	
27-F Final	4.538	27.55	26.13
Mean	3.950±.268	24.92±1.35	25.24±0.60
Variance % Relative	±6.8%	5.4%	2.4%

The gas feed system was vented and the system was repressurized with pure hydrogen to start this experiment. The feed gas therefore did not need to be analyzed. Analytical results for the product gases are presented below.

ANALYSIS OF PRODUCT GASES RUNS CL 27A to F

Gas (MOL %)	CL 27A	CL 27B	CL 27C	CL 27D	CL 27E	CL 27F
Hydrogen	82.6	78.5	61.4	67.6		78.1
Nitrogen	8.56	5.26	5.31	7.08		5.49
Methane	2.44	6.63	17.0	13.0	NO	5.81
Ethane	0.94	2.52	5.13	4.00		2.38
Propane	0.45	1.14	2.17	1.64	GAS	1.10
n-Butane	0.20	0.32	0.58	0.43		0.32
Isobutane	0.04	0.10	0.18	0.14	SAMPLE	0.09
Carbon Dioxide	1.17	1.66	2.51	1.69		2.07
Carbon Monoxide	0.32	0.42	0.68	0.62		0.47
Hydrogen Sulfide	3.23	3.47	5.05	3.72		4.20
Moles per hour	4.421	4.239	4.332	4.489		4.099

Sample CL 27E was lost by a leak in the sampling system. The yield of gaseous products for this experiment was estimated using the CL 27F gas volume and the CL 27C gas composition data.

CL 27

IV-J

In order to determine the comparative efficiency of pure hydrogen and the 1:3 carbon monoxide to hydrogen mixture as reducing agent for this Kentucky No. 9 coal it is necessary to compare results from materials made at matching operating conditions. For example Sample CL 27A and Sample 26B are made at nearly the same conditions. Pressures are the same, temperatures are the same, and 1/LHSV values are 0.53 and 0.57, values which are closely comparable. When the results are compared on a line for line basis it is difficult to find any entry in which one reducing gas mixture is clearly superior to the other. On the basis of a slightly larger yield of excess solvent the slight edge would be in favor of the synthesis gas mixture. In addition the relative yield of Cut 2 oil is a little larger fraction of the total oil reclaimed. Thus at 425°C and a short retention time the weight of solvent obtained is more favorable in the synthesis gas case. Desulfurization and yield of vacuum bottoms figures are reproduced to near the limits of precision of the measurements.

A similar close comparison can be made at 450°C and a 1/LHSV of 0.52 - 0.57 by comparing CL 27B and CL 26A results. Here again the differences are slight with the over all trend to increased yield of solvent and sulfur removal being a little better in the synthesis gas case.

A third close comparison of results can be made at 475°C and 1/LHSV of 0.71-0.73 by comparing CL 26D and CL 27D results. At the higher temperature the MAF conversion was higher in the hydrogen reduction. The $\overline{IR}$ of the reclaimed cut 2 oil was also higher for the material made in contact with pure hydrogen. The yield of excess reclaim solvent was higher and the yield of vacuum bottoms was somewhat less. The vacuum bottoms contained a significantly larger amount of hydrogen and melted a little lower. This could be the result of failure to reclaim solvent from the CL 27D vacuum bottoms as completely as from the CL 26D material. Hence more solvent or a higher heat of combustion vacuum bottoms would be obtained. The trend is therefore for pure hydrogen to be the more effective reducing gas at higher operating temperatures.

In all of the reclaim solvents resulting from the high temperature and short retention time cases, the hydrogen has been reduced from the concentration in the CL 18 hydrogenated anthracene oil used as input solvent. Thus the question of utility of the reclaim solvent for recycle is raised for both hydrogen and synthesis gas reductions at these conditions.

The unfiltered solutions were sampled for elemental and ash analysis. As has been reported previously, the sampling for ash was difficult to do accurately and the percentage ash obtained is generally off the theoretical result based on the ash content of the feed slurry and the relative yield of liquid sample compared to feed slurry used. The analysis of unfiltered solution is also complicated by the presence of small water droplets since the solutions are collected near room temperature. The hydrogen results follow the $\overline{IR}$ values roughly and even when corrected to ash free basis are still not as systematic as would be expected. Probably a correlation could be developed on stripped filtered solutions which could be used with reasonable precision. This project therefore mostly shows that the unfiltered samples are unsatisfactory.

CL-27

IV-J

When the results from hydrogen analysis are reduced to ash free basis and this result is in turn corrected for water on the basis of the yield observed, a more orderly array of results is obtained. Thus CL 27A $\overline{IR}$ = 1.21 %H = 6.39, for CL 27B $\overline{IR}$ = 1.05 %H = 6.19, for CL 27C $\overline{IR}$ = 0.79 %H = 5.83, for CL 27D $\overline{IR}$ = 0.90 %H = 6.03, for CL 27E $\overline{IR}$ = 0.87 %H = 5.79, and for CL 27F $\overline{IR}$ = 1.05 %H = %0.88. The last point does not fit the trend well.

IV-J

Evaluation of Experiment CU 28 (Samples A-1, A-2, and B)

This was the first experiment done using the CU reactor configuration. See section IV A3 for the details of construction of this reactor. The objective of this experiment was to test the unit by repeating an experiment done previously and comparing the products from the two experiments as carefully as possible. The first test was done in duplicate to obtain reproducibility data on the new unit also. The results which may be compared are experiment CL 27A and CU 28B which compare reactions done at 425°C with a 1/LHSV of 0.53 - 0.51, and experiments CL 27B and CU 28A-1 & CU 28 A-2 done at 450°C with a 1/LHSV of 0.52 - 0.51. All experiments were done with 1000 psig hydrogen and with the CL 18 hydrogenated anthracene oil as solvent. The same lot of Kentucky No. 9 coal was used throughout.

In the CU 28 series the lineout characteristics of the new unit were also studied. Small samples were taken at regular intervals to observe the changes in blackness, infrared spectra, and mineral content of the reactor product as the concentration of coal built up in the reactor. Feed slurry was analyzed for ash and for iron content. Product samples taken for lineout studies were collected for 5 minute periods every half hour for the first two hours then for 5 minute periods each hour thereafter until the end of the experiment. These samples were analyzed for blackness, $\overline{IR}$ values, ash content, and iron content.

Larger samples were taken for a complete workup. The CU 28 A-1 sample was collected for a half hour period starting 6 1/2 hours after the slurry feed was started. The CU 28 A-2 sample was collected for a half hour period starting 7 1/2 hours after the slurry feed was started. The dissolver temperature was then reduced to 425°C and the CU 28 B sample was collected for a half hour starting at the 11th hour after slurry feed was started. This allowed three hours for the effect of the temperature change to line out before sample collection was started. Gas samples were taken during the sampling period for each of the samples which were taken for complete workup.

Discussion of Results

Two experiments had been followed by sampling the product frequently to follow lineout of blackness, $\overline{IR}$ values, and the mineral content of the effluent product. These are experiment CL 19 and experiment CU 28. The CL 19 experiment was done at a 1/LHSV of 1.33 and the CU 28 experiment was done at a 1/LHSV of 0.51. Because of the difference in the dimensions of the tubes the CL 19 experiment was done with an upward flow velocity of 5.6 ft/hr while the CU 28 experiment was done with an upward flow velocity of 2.9 ft/hr. These differences are the result of using a long thin tube in the CL experiment and a short tube in the CU experiment. The tubes of both reactors had the same volume. The ratio of length to diameter for the CL reactor was 120/1. The ratio of length to diameter for the CU reactor was 10/1.

CU 28

IV-J

Feed slurry samples were taken to measure the uniformity of the feed slurry. The Kentucky No. 9 coal used for this experiment contained 11.66% ash and 4.58% moisture. The ash contained 25.0% iron. Since the slurry was mixed in a 2/1 ratio of solvent to coal the slurry should have contained 3.887% ash. The following table presents the results for the analysis of feed slurry and also presents the results of measurements on the solution samples taken to study lineout characteristics.

Data for Lineout Studies

Sample	Time	%Ash in Slurry	%Iron in Ash	%Ash in Solution	% Iron in Solution Ash	$\overline{IR}$ Value for Solution	Solution Blackness
0	0	3.901	25.62				
1	½ hr	3.901	25.39	1.494	21.63	1.01	5.53
2	1 hr	3.876	24.85	2.721	24.91	0.93	9.14
3	1½ hr	3.592	25.03	3.262	25.02	0.97	9.92
4	2 hr	3.690	24.17	3.252	24.55	1.00	10.73
5	3 hr	3.554	23.55	3.394	24.23	1.02	10.48
6	4 hr	4.008	26.06	3.532	24.73	0.96	10.90
7	5 hr	4.017	25.77	3.573	25.75	0.96	10.63
8	6 hr	3.938	24.88	3.669	25.66	0.96	10.79
9	7 hr	3.656	23.66	3.719	25.05	0.99	10.99
10	8 hr	4.073	26.36	4.132	26.52	1.06	9.70
11	9 hr	3.981	25.30	3.863	26.17	1.09	8.56
12	10 hr	3.872	23.95	3.796	25.64	1.15	9.00
13	11½ hr	3.730	23.37	3.518	24.34	1.18	8.37
Mean value		3.846	24.85	3.378	24.94		

The concentration of minerals fed to the reactor in the slurry and the concentration of minerals recovered in the samples of product solution was plotted versus operating time. See Figure 18. From this plot it is clear that in the initial stages of the lineout minerals are deposited in the reactor on the average. An estimate of the weight which has settled out can be made by calculating from sample compositions and weights represented to obtain the weight of ash fed and the weight of ash recovered. Appendix A gives the weight per hour of slurry fed and the weight per hour of liquid product obtained. When these rates are applied to the data tabulated above the input ash weight is estimated to be 455 grams. The ash output was estimated to be 402 grams. The difference of 52 grams is then the amount of ash which was retained by the dissolver. From the data above the iron did not tend to classify in this experiment. The mineral was deposited from a liquid moving upward with a linear velocity of 2.45 feet per hour.

Similar detail has been developed for the CL reactor in run CL 19. The data have been presented in the discussion of that experiment. When the mineral input and the mineral outputs are estimated as above the total input is 284 grams of ash in and 222 grams of ash out. The difference,

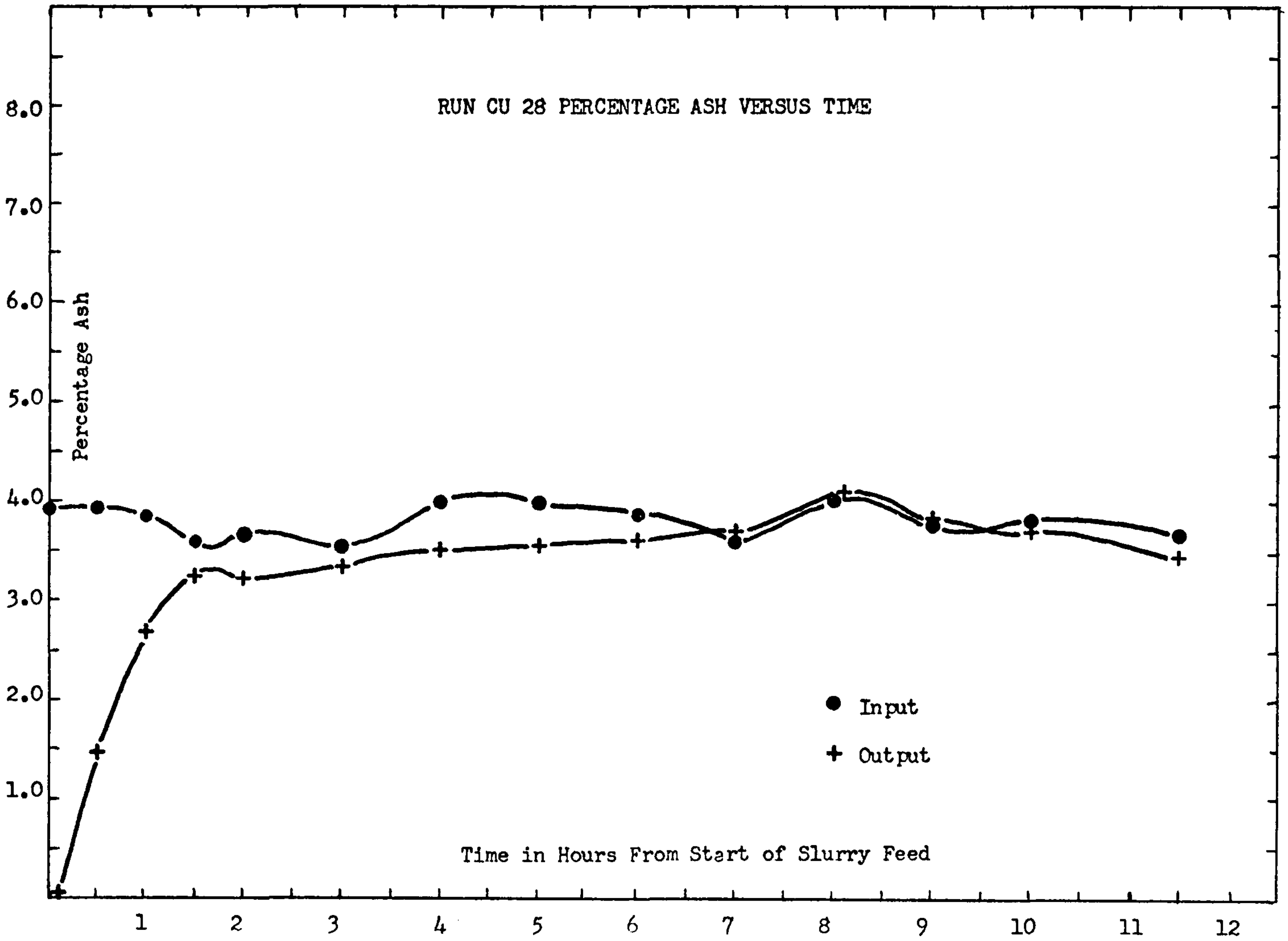

RUN CU 28 PERCENTAGE ASH VERSUS TIME
Percentage Ash
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
● Input
+ Output
Time in Hours From Start of Slurry Feed
1
2
3
4
5
6
7
8
9
10
11
12

Figure 18

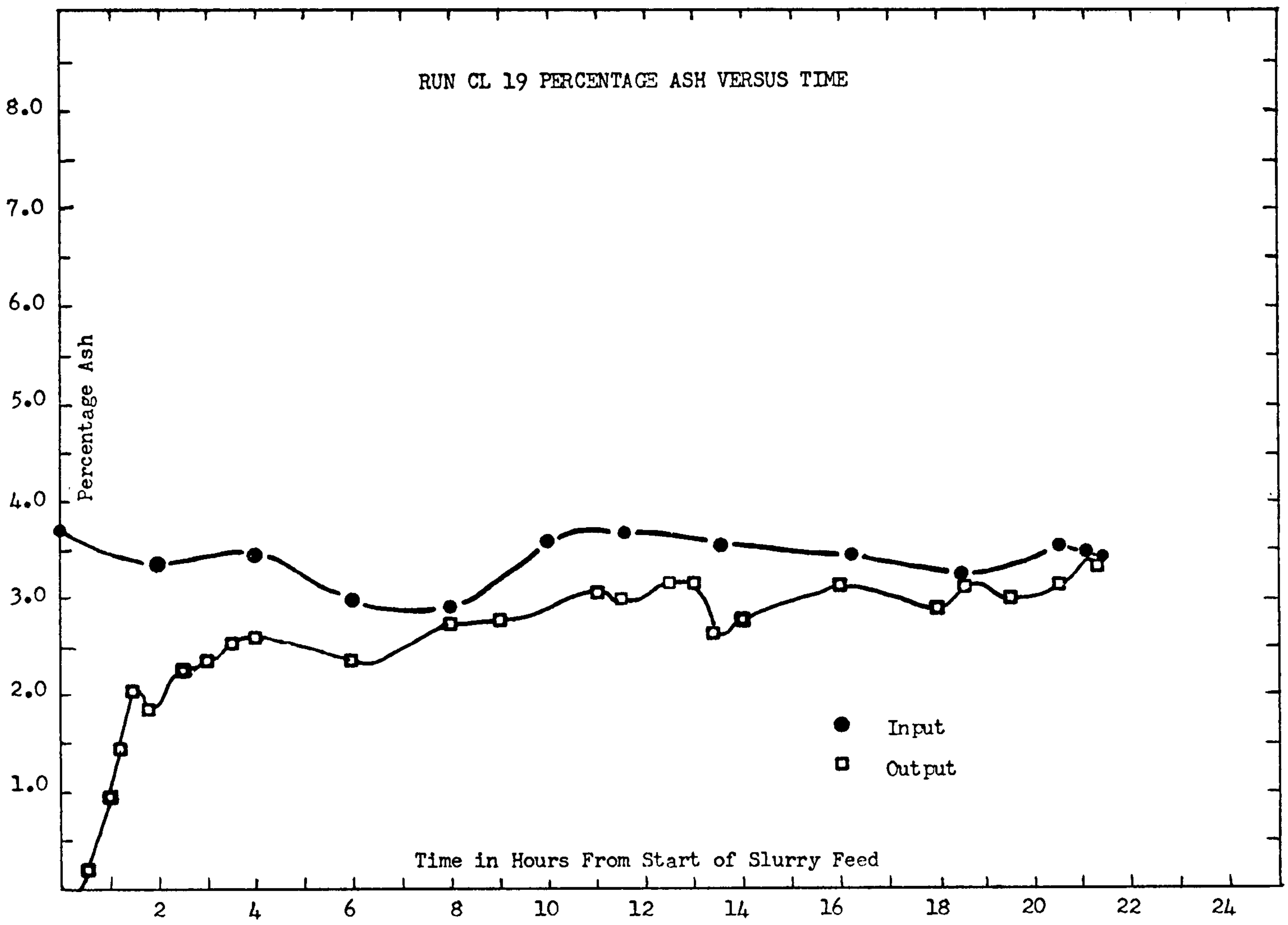

RUN CL 19 PERCENTAGE ASH VERSUS TIME
Percentage Ash
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Input
Output
Time in Hours From Start of Slurry Feed
2
4
6
8
10
12
14
16
18
20
22
24

Figure 19

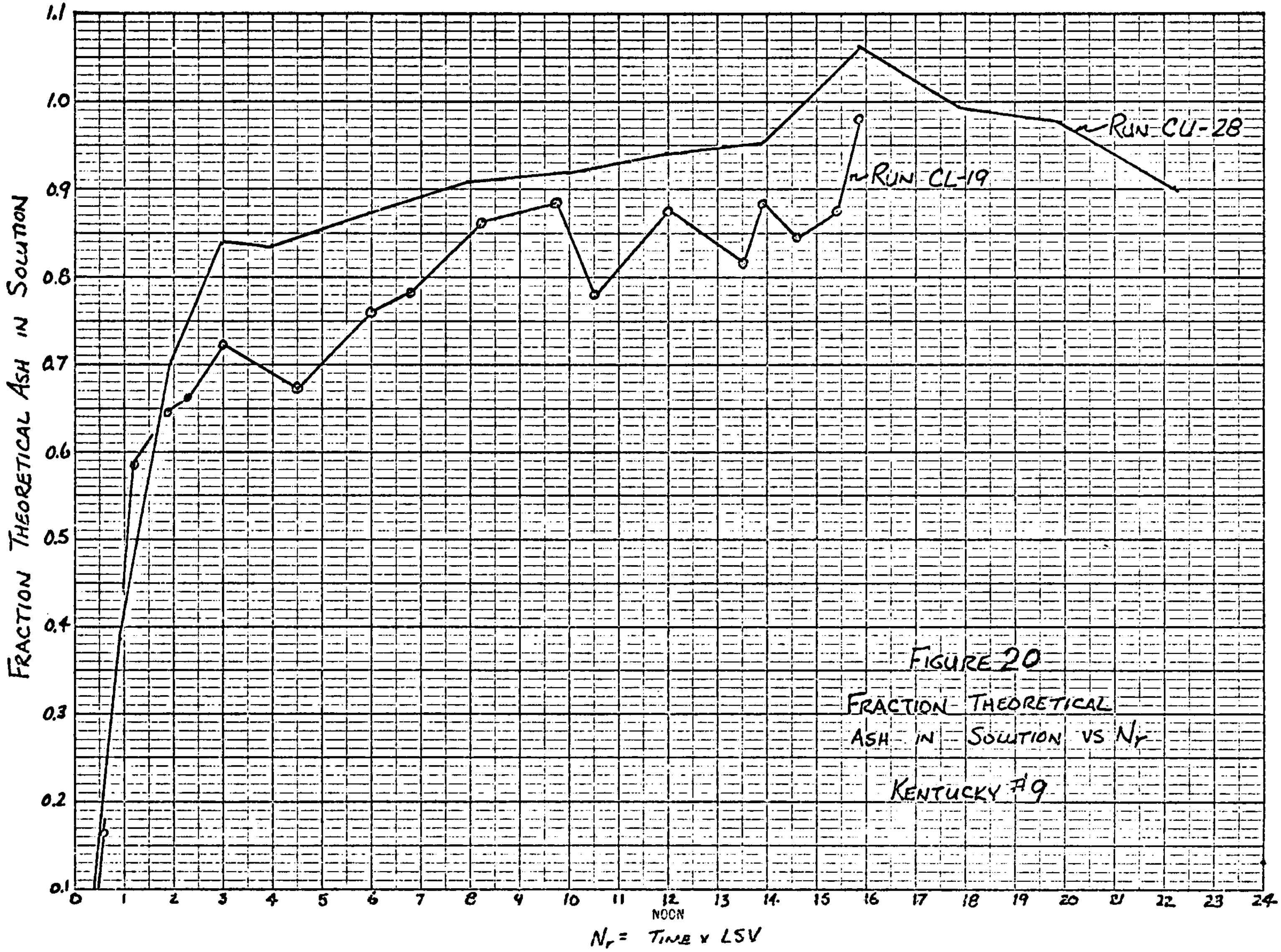

Fraction Theoretical Ash in Solution
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1
2
3
4
5
6
7
8
9
10
11
12
NOON
13
14
15
16
17
18
19
20
21
22
23
24
N_r = Time x LSV
Run CU-28
Run CL-19
Figure 20
Fraction Theoretical
Ash in Solution vs N_r
Kentucky #9

Figure 20

62.0 grams, would have been deposited from the solution during the course of the CL 19 experimental sequence. This liquid had an upward linear velocity of 5.3 feet per hour. In this case the mineral matter also seems to have deposited iron with a little selectivity. See Figure 19 for a plot of mineral input and recovery data.

Since an effort was made to obtain the same reactor volume in both the CL and the CU units the relative weights of mineral deposited should be proportional to the concentration in each reactor. In all probability the mineral is in the form of a concentration gradient from the bottom to the top in either vessel except for the upsetting effect of random convection currents or stirring by the ascending hydrogen stream. From these data it appears probable that a long thin reactor of the CL design will tend to back mix the contents less and to settle and classify minerals more than a fat reactor of the CU design. It is uncertain that such effects would extrapolate to larger vessels in the same proportions.

If iron is catalytic in a reaction of this kind, it would appear to be an advantage for the mineral matter to settle. This must be qualified by the realization that it is probably only the surface area which is effective. Thus a large weight of ash mineral in the form of large particles could be of no particular value and could even reduce average retention time by reducing the space available for reactive slurry. In the same vein, the mineral could readily be rendered inactive by a coating of polymer, carbon, or undissolved coal. It can be seen that utilization of this kind of material presents some problems and that inappropriate heating schedules or flow rates could render the mineral inactive or lift it out of the reactor. This argument also applies to the differences which might result from grinding the coal to different particle sizes initially or to coals with pyrites of different inherent particle size as mined. The effect of thermal shock on these particles is not established by systematic observations, but the impressions gained from inspection of filter cake materials suggest that spalling of large particles is a factor. In time any large particle may tend to break up and lift out. If this is not the case for some mineral phase which is inert the build up of this kind of material could result in a reduced reactivity.

When the estimates for the concentration of mineral settled in the CL 19 experiment and in the CU 28 experiment are compared one clear cut difference in reactor behaviour is evident. Even though the upward flow velocity was greater in experiment CL 19, more mineral settled in this reactor. This can be illustrated graphically when the results are plotted as fraction of theoretical ash recovered in product as a function of the number of reactor volumes pumped through the unit. See Figure 20.

When product properties are compared,as in experiment CL 27A and CU 28B, for example, the differences are small and it is hard to conclude from these data that significant differences have resulted from the different reactor shapes. There are some practical differences in the operation of the units which ought to be reviewed however before such comparisons are accepted. For example the CL unit had no preheater and a portion of the reactor volume therefore had to serve this purpose. The time remaining for reaction was then a little less than was the case for the CU reactor which did receive heated feed slurry at reactive temperatures. This may account for the tendency for the blackness values for the CU reactor products to be a little larger than observed for matching reaction conditions in the CL unit. This could also be a result of increased hydrogenation potential in the CL unit. The blackness of the CL 27B solution was 9.76 and the Blackness of the CU 28A solutions averaged 11.07. The differences in $\overline{\text{IR}}$ values for the product solutions and for the reclaim cut 2 solvent fractions in these cases may be significant. In addition the conversion to produce excess solvent seems to have been more efficient for the CL reactor if such small differences can be taken at face value. CL 27B yield of excess solvent was 11.73% and CU 28A average yield of excess solvent was 8.00%.

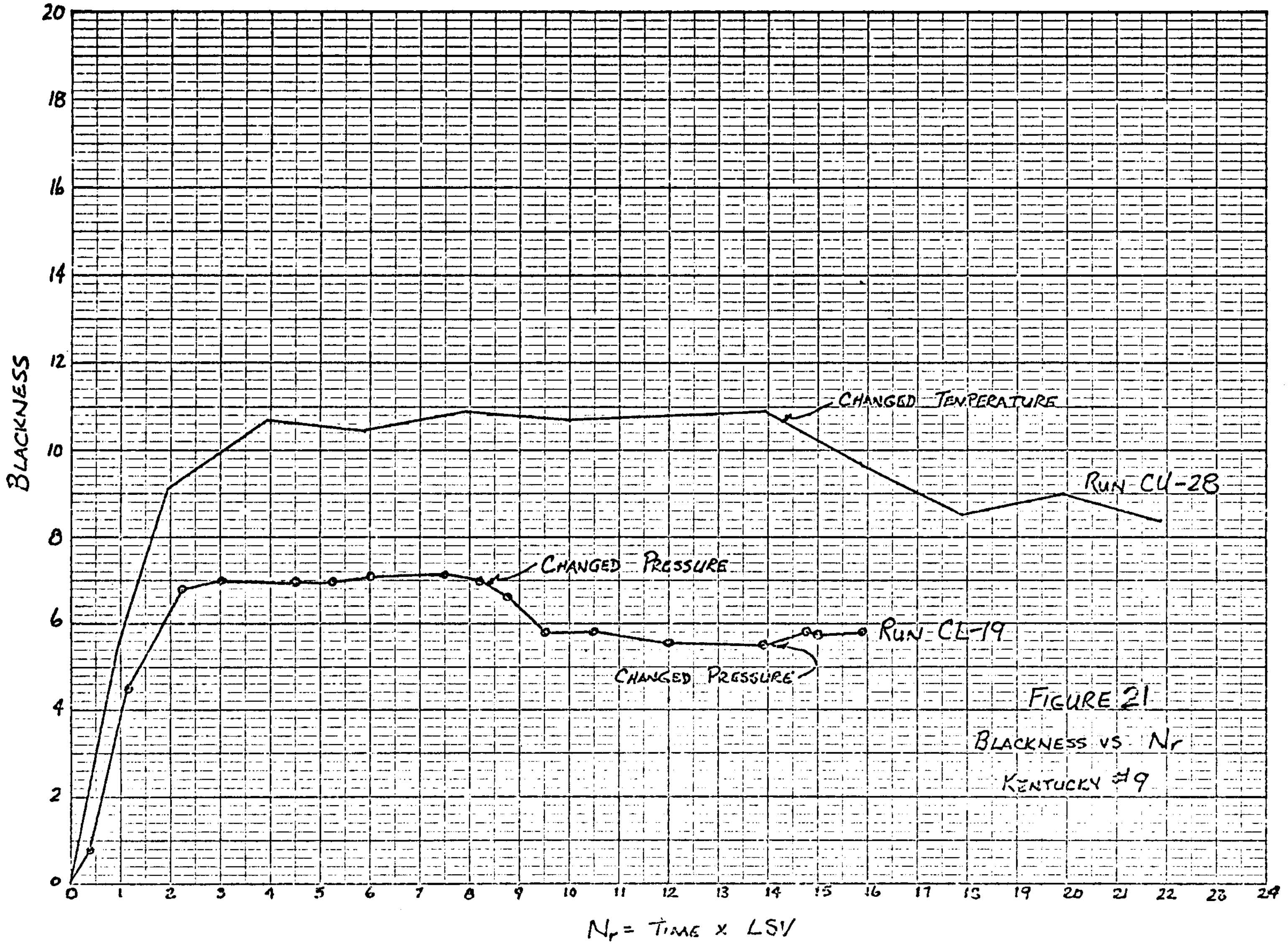
These comparisons can be extended by using the materials processed at 425°C also, although in this case the preheater of the CU unit was operated at a temperature which may have exposed the solution to 450°C operating temperature briefly. The Blackness value for the CL 27A solution was 7.46 and the value for the CU 28B solution was 8.52. The $\overline{\text{IR}}$ value for the unfiltered solution was 1.21 for the CL 27A solution and 1.18 for the CU 28B solution. These results could readily be caused by different heating schedules in the different reactors.

A unique observation which relates to the appearance of the organic matter derived from coal in the solution can be made by measuring the color of the solution. When this is done it is found that the lineout based on the color of the solution is obtained in about four fillings of the reactor. When a change in operating conditions is imposed, which results in a change in the blackness of the solution, the time required for the effect of the change to stabilize is again the time needed to pump four reactor volumes. This kind of result is shown in Figure 21 which presents the blackness measurements for runs CL 19 and CU 28 for comparison.

In addition the $\overline{\text{IR}}$ values for the solution take about the same length of time to line out. This is not clearly demonstrated for the CU 28A portion of the experiment because the choice of operating conditions results in a solution with $\overline{\text{IR}}$ values which are nearly the same as those for the initial solvent used. After the dissolver temperature was reduced in the CU 28B portion of the experiment a response is observed and the ratio increases from about 0.99 to 1.18 in the three hour period allowed for lineout.

Thus two of the functions commonly used to follow lineout appeared to stabilize in about four reactor volumes of material. The mineral lineout

Figure 21



20
18
16
14
12
10
8
6
4
2
0
BLACKNESS
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
Nr = TIME x LSV
CHANGED TEMPERATURE
RUN CU-28
CHANGED PRESSURE
RUN CL-19
CHANGED PRESSURE
FIGURE 21
BLACKNESS VS Nr
KENTUCKY #9

certainly took longer and the concentration at lineout appeared to differ appreciably at the lined out condition in different reactors (and presumably with different flow rates and so on in a given reactor). Since no great difference in product properties appeared to result from differences in the mineral lineout parameters subsequent experiments were designed to allow blackness and $\overline{IR}$ values to line out and little emphasis was placed on the mineral lineout. This had the additional virtue of reducing the operating time needed for a first approximation lineout. This is probably a reasonable compromise since the single pass data neglects the possibly significant change in reactivity which could result from continued recycle of the Cut 2 reclaim solvent in any case.

Line for line comparisons can be made between material made in either the CL or the CU reactor under conditions which are matched with reasonable care. These data are available in Appendix A and need not be presented in detail here. Within the limitations of the observations available at the time no great differences in products made could be observed. In retrospect the time needed to critically evaluate the two units was not spent. The effect of mineral lineout and classification will develop slowly if this is indeed a consideration. There are small hints in the data that the reactors may not match exactly if experiments are done with great care. As a practical matter the experience is not available to predict the effect of increasing reactor size and until some correlation with the pilot plant is established there is little basis for such studies.

IV-J

Evaluation of Experiment CU 29 (Samples A through E)

In the series of experiments following the hydrogenation of anthracene oil, considerable progress had been made in the establishment of improved lineout and operating procedures. All of this work had been done with hydrogenated anthracene oil. It was therefore the objective of this experimental series to acquire additional data with raw anthracene oil to extend the range of information available, and to check a few points at similar conditions to compare the reactivity of raw anthracene oil and the hydrogenated derivative. Kentucky No. 9 coal was used in a 2/1 solvent to coal ratio.

This was the second use of the new CU reactor configuration. The lineout times used were longer than had been previously used in order to better line out the minerals in the reactor. The feed slurry was sampled before each sample collection period and after each sampling period. This allowed a study of the uniformity of the feed and of the recovery of mineral matter in the samples made. The operating schedules for the experiment are presented below.

Operation	1/LHSV	Temperature°C	Pressure
Establish operating conditions on flush oil			
Composition lineout on slurry 3 hours			
Collect sample CU 29A for ½ hour	0.51	450	1000
Composition lineout on slurry 5 hours			
Collect sample CU 29B for 1 hour	0.84	450	1000
Composition lineout on slurry 6 hours			
Collect sample CU 29C for 1 hour	0.96	450	1000
Composition lineout on slurry 6 hours			
Collect sample CU 29D for 1 hour	1.26	450	1000
Composition lineout on slurry 4½ hours			
Collect sample CU 29E for 1 hour	0.85	450	750

Gas samples were collected for half hour intervals. Except for the first sample this allowed fifteen minutes for the flask to flush before the collection of the sample was started. Because of the shoft time interval used for collection of the liquid sample in experiment CU 29, the gas sample had to be started at the same time that collection of the liquid sample was started. Gas samples all contained some air. The oxygen present was determined to allow calculation of the air present. A proportional amount of nitrogen was removed in the mathematical treatment of the gas analysis results to obtain air-free results.

IV-J

Discussion of Results

The results for the analysis of feed slurry and for the analysis of wet filter cakes are presented in tables which follow. The results for gas analysis are also presented. Most of the results useful for comparative purposes are to be found in Appendix A (Part 6).

ASH ANALYSIS OF FEED SLURRY AND WET FILTER CAKES CU-29

	Feed Slurry			Wet Filter Cakes	
Samples	% Ash	% Iron in Ash	% Iron in Slurry	% Ash	% Iron in Ash
CU 29A-1	3.749	24.15	0.9053		
CU 29A-2	3.775	24.23	0.9146	21.49	24.48
CU 29B-1	3.784	24.50	0.9271		
CU 29B-2	---	---	---	25.19	24.85
CU 29C-1	3.922	24.91	0.9770		
CU 29C-2	3.850	24.54	0.9448	24.13	24.25
CU 29D-1	4.184	26.48	1.108		
CU 29D-2	4.207	26.36	1.109	29.95	25.57
CU 29E-1	4.186	25.39	1.063		
CU 29E-2	4.114	24.90	1.024	21.56	26.20
Mean	3.975	25.05			25.06

Notes:
1. The Kentucky No. 9 coal contained 11.65% ash and the iron in the ash was 25.79%. A 2/1 solvent to coal slurry should contain 3.883% ash.
2. The reactor tube was cleaned out at the end of experiment CU 29 and the material in the tube averaged 5.16% ash with an iron content of 25.30%.

ANALYSIS OF PRODUCT GASES FROM RUN CU 29 SAMPLES
(Normalized, air and water free basis)

GAS (MOL %)	CU 29-A	CU 29-B	CU 29-C	CU 29-D
Hydrogen	69.4	70.5	73.4	76.6
Nitrogen	6.84	6.71	7.23	6.46
Methane	10.7	10.8	9.47	8.29
Ethane	3.58	3.58	3.00	2.74
Propane	1.49	1.49	1.26	1.21
n-Butane	0.35	0.35	0.36	0.31
Iso-butane	0.10	0.12	0.11	0.09
Carbon Dioxide	2.62	1.96	1.39	1.00
Carbon Monoxide	0.53	0.48	0.53	0.47
Hydrogen Sulfide	4.41	3.96	3.23	2.83
Moles per hour	3.699	2.991	3.584	3.321

CU 29

No results are presented for CU 29-E because a leak in the gas sampling system caused this sample to be lost. It was necessary to estimate the yield of gaseous products by using the CU 29 C gas volume and composition results.

A summary of experimental results is presented in Appendix A part 6. The gas analysis results presented above can be checked by calculating the nitrogen recovery and comparing this to the weight of material injected through the Ruska to purge the gage system. The recovery of nitrogen is 6.0 grams for 7.0 grams from the Ruska readings. This procedure therefore provides a standard for validation of the reliability of the gas sampling system.

The analysis of input and reclaim cut 2 solvent by infrared is summarized by means of $\overline{\text{IR}}$ values as reported in Appendix A. The input solvent had an $\overline{\text{IR}}$ value of 0.58. The reclaim cut 2 solvent from all experiments in the CU 29 series had slightly higher values. As the 1/LHSV was increased the $\overline{\text{IR}}$ values increased from 0.66 in experiment CU 29A to a maximum of 0.82 in experiment CU 29D. These experiments involve retention times characterized by 1/LHSV values ranging from 0.51 to 1.26. These experiments, which were done at 450^{o}C and using only 1000 psig hydrogen, resulted in comparatively small gains in the hydrogen content of the reclaim cut 2 solvent. At the temperature used it is likely that the small increases in $\overline{\text{IR}}$ values is the result of the accumulation of coal derived oil in the solvent rather than to an increase in the hydroaromatic hydrogen of the reclaimed solvent. In experiment CU 29E, which was run using only 750 psig hydrogen, a small increase in the $\overline{\text{IR}}$ of the reclaim cut 2 was observed also. (The initial solvent had a value of 0.58 and the reclaimed cut 2 had a value of 0.61.) This change is quite small, and the increase is near the limit of reliable measurement. From this it is inferred that pressures as low as 750 psig are too low to be practical.

The vacuum bottoms made in this series of experiments show a systematic decrease in the concentration of residual sulfur as the retention time at high temperatures is increased. This is a way to obtain lower sulfur content products provided that the yield and reactivity of the reclaimed solvent can be maintained within the requirements for recycle.

From the data available it is clear that the yield of reclaim solvent is too small at the shorter retention times using raw anthracene oil as a solvent. As the retention time is increased both the yield and the hydrogen content of the reclaim cut 2 solvent improves somewhat. At 450^{o}C the increase in the amount of solvent is marginal until reaction times well in excess of an hour are used. The gain in the concentration of hydrogen in the reclaimed solvent is also very small. There is a marked contrast in the reactivity of the raw anthracene oil and its hydrogenated derivatives. This can be shown by comparing the yield of total reclaim solvent from experiments done at similar reaction conditions using the raw anthracene oil and using the CL 18 solvent preparation product.

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YIELDS OF EXCESS SOLVENT AT 1000 psig and 450^oC

1/LHSV	Compare Experiments	Yield With Raw A.O.	Yield With CL 18
0.51	CU 29A & CU 28A	0.21%	9.98%
0.96	CU 29C & CU 21D	4.48%	16.98%
1.26 - 1.35	CU 29D & CL 21F	8.21%	18.97%

Such comparisons can be extended somewhat by comparisons at other operating temperatures and retention times. Unfortunately the data available do not match retention times and temperatures closely enough to allow line for line comparisons as above. Matching requires plotting of the data on correlation charts which make allowance for differences of this kind. Generally such comparisons show that the hydrogenated solvent has produced more excess solvent. When similar comparisons are done with the percentage of sulfur in the vacuum bottoms made, it is found that the hydrogenated solvent is also more effective in lowering the sulfur content of the vacuum bottoms. This effect is however smaller than the effect of increasing the temperature 25^oC.

When the reactions with raw anthracene oil at milder operating temperatures are considered it is observed that more hydrogen is gained by the reclaimed cut 2 solvent obtained. Thus the quality and reactivity of the solvent available for recycle can be improved but only at the cost of removing less sulfur from the vacuum bottoms product. There are single point compromise conditions of temperature and retention time which do allow a fair amount of progress toward both objectives. It is not practical to attempt to optimize both functions in a single reactor at a single operating condition set however. In all cases the use of higher operating pressures of hydrogen tend to favor higher conversions and more effective hydrogenation of the reclaimed solvent. These conclusions are derived from comparisons of $\overline{IR}$ values and the elemental analysis correlation work which allows translation into percentage hydrogen values. The reliability of the correlation depends on working with similar molecular weight distributions in the hydrocarbon mixtures under consideration. As could be expected, there are many circumstances in which the correlation should be used with care or not at all. This does not reduce the utility of the $\overline{IR}$ correlation in following reaction product compositions, but it does impose a requirement for checking such results with elemental analysis of the materials until a dependable working curve is established. The curve has in it an implicit molecular weight distribution function which should be reproduced with some reliability to maintain acceptable accuracy in the estimates.

It is evident that the hydrogenated anthracene oil is superior in reactivity. It is less evident how the reactor should be managed to take advantage of this reactivity on repeated recycle of the solvent. This depends on the ability to derive replacement solvent from the coal in sufficient amounts and with sufficient inherent reactivity. In the long run the opportunity to use this information depends on the kind of oil which is made from coal by hydrogenation under reaction conditions and on the ability to manage operating condition profiles to optimize desirable properties in the reclaim solvent.

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Evaluation of Experiment CU 30 (Samples A through H)

This experiment was the first attempt to study a subbituminous coal in the continuous laboratory reactor. The coal chosen to represent the subbituminous rank was taken from a sample supplied from the Elkol Mine located near Kemmerer, Wyoming. The analysis of this coal is presented as Appendix B item 4. The mineral analysis is presented as Appendix B item 5.

The experiment was done with a 2/1 ratio of CU 18 hydrogenated anthracene oil to Elkol containing the natural bed moisture retained by the coal after grinding. The first sample was prepared using pure hydrogen as the reducing gas. The gas system was then switched to a cylinder which supplied a mixture of 75% hydrogen and 25% carbon monoxide. The remaining samples were prepared using this as the reducing gas.

After the preceding run, which was done with Kentucky No. 9 coal, the reactor was drained to remove as much of the mineral residue remaining in the dissolver tube as possible without dismantling the reactor. This was done by disconnecting the preheater tube and transfer line at the bottom of the dissolver vessel. In order to improve on the mineral lineout the lineout times were kept long on the first samples made. The feed slurry was sampled both for ash analysis and for water analysis. The wet filter cake was analyzed for ash content and the ash was analyzed for iron content to check for the possible presence of Kentucky No. 9 coal minerals which may have remained in the system. The operating schedule which was used is given below.

Operation	Reducing Gas	1/LHSV	Temp. ^{o}C	Pressure psig
Establish operating conditions				
Composition lineout on slurry 6 hours	H_2			
Collect sample CU 30A for 1 hour		1.02	425	1000
Composition lineout on slurry 5 hours	CO:H_2			
Collect sample CU 30B for 1 hour	1:3	0.98	425	1000
Composition lineout on slurry 4½ hours	CO:H_2			
Collect sample CU 30C for 1 hour	1:3	0.71	425	1000
Composition lineout on slurry 5 hours	CO:H_2			
Collect sample CU 30D for 1 hour	1:3	1.30	425	1000
Composition lineout on slurry 5½ hours	CO:H_2			
Collect sample CU 30E for 1 hour	1:3	1.22	400	1000

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Operation (continued)	Reducing Gas	1/LHSV	Temp. °C	Pressure psig
Composition lineout on slurry 6 hours Collect sample CU 30F for 1 hour	$CO:H_2$ 1:3	1.20	450	1000
Composition lineout on slurry 4 hours Collect sample CU 30G for 1 hour	$CO:H_2$ 1:3	0.71	450	1000
Composition lineout on slurry 4 hours Collect sample CU 30H for 1 hour	$CO:H_2$ 1:3	1.06	450	1000

Discussion of Results

The results of control checks on the feed slurry are presented in the table which follows. Both ash and water concentrations were maintained throughout the experiment with reasonable precision. Water loss was about 21% relative.

Sample	% Ash in Slurry	% Water in Slurry	% Iron in Ash from Wet Filter Cake
A-1	0.9486	5.81	
A-2	0.9712	5.80	6.77
B-1	0.9634	4.81	
B-2	0.9535	4.41	4.72
C-1	0.9925	4.98	
C-2	0.9827	4.85	4.39
D-1	0.9720	4.63	
D-2	0.9620	4.30	4.21
E-1	1.020	5.01	
E-2	1.024	4.64	3.60
F-1	1.019	5.30	
F-2	1.029	5.19	3.54
G-1	1.020	5.52	
G-2	1.048	5.53	3.66
H-1	1.033	4.61	
H-2	1.022	4.45	3.44
Mean	0.9975	4.99	
Variation	± 2.94% Rel. + 4.3% Rel.	± 8.12% Rel. - 21% Rel.	

CU 30

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Notes: Ash in feed coal 2.87%. For a 2/1 solvent to coal slurry the ash should be 0.9566%. The water in the feed coal was 18.87%. For a 2/1 solvent to coal slurry the water should be 6.29%.

The iron in the ash of the feed coal was 3.29%. The ash of all wet filter cake samples inspected therefore contains iron in excess of the concentration fed. This is an indication that draining the reactor failed to completely unload minerals from the reactor system.

At the end of the experiment a coke deposit was removed from the dissolver. This coke contained 11.82% ash which contained 26.2% iron. This deposit is presumed to have been formed during previous reactions with Kentucky No. 9 coal based on the iron found in the ash.

ANALYSIS OF PRODUCT GASES OF RUN CU 30 SAMPLES
(Normalized air and water free basis)

GAS (MOL%)	CU 30A	CU 30B	CU 30C	CU 30D	CU 30E	CU 30F	CU 30G	CU 30H
Hydrogen	87.4	64.0	62.5	64.2	66.8	61.1	58.7	61.1
Nitrogen	4.81	5.66	5.82	5.39	5.77	5.59	5.04	4.25
Methane	2.09	2.46	2.23	2.18	0.76	4.66	4.95	4.73
Ethane	0.81	1.02	1.00	0.87	0.33	1.56	1.80	1.55
Propane	0.42	0.55	0.50	0.42	0.17	0.67	0.77	0.63
n-Butane	0.32	0.41	0.41	0.36	0.15	0.54	0.62	0.36
Isobutane	0.04	0.06	0.06	0.03	0.03	0.08	0.06	0.06
Carbon Dioxide	3.03	4.44	5.26	3.29	2.51	3.79	5.39	3.82
Carbon Monoxide	0.74	20.9	21.6	23.0	23.2	21.6	22.2	23.1
Hydrogen Sulfide	0.34	0.41	0.52	0.33	0.29	0.42	0.47	0.40
Moles per hour	5.109	4.619	3.143	4.565	4.584	4.441	4.753	4.659

The amount of carbon monoxide and hydrogen fed to the reactor for each sample is listed in Appendix A part 7. These values are 29.7 grams of carbon monoxide and 6.6 grams of hydrogen. The gas output data above can be used to investigate the amount of hydrogen and the amount of carbon monoxide recovered and by difference to calculate the amount which may have reacted. These results are tabulated below.

WEIGHTS OF HYDROGEN AND CARBON MONOXIDE RECOVERED

Sample No.	CU 30A	CU 30B	CU 30C	CU 30D	CU 30E	CU 30F	CU 30G	CU 30H
Grams Hydrogen	8.92	5.91	3.93	5.86	6.12	5.43	5.58	5.69
Grams CO	1.06	27.0	19.0	29.4	29.8	26.8	29.5	30.1

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There is an indication that a small amount of hydrogen may have reacted in an average trial. There is no convincing evidence that carbon monoxide was used at all. The recoveries for sample CU 30C are low and the suspicion that a gas loss is the cause is unavoidable. Reference to the IR data presented in Appendix A will disclose that the cut 2 reclaim solvent has been reduced in IR value below the values observed in the input solvent. The Elkol thus appears to be ill catalyzed and the solution of organic matter observed must be the result of the transfer of reactive hydrogen from the solvent used.

The recovery of solvent is found to be less than the amount of solvent invested in the preparation of the feed slurry. It is a matter of some interest that this reaction did produce filterable solutions which could be worked up by the standard procedures. The problem in processing a material such as Elkol is then to develop a catalyzed system for replenishing the solvent or to develop a catalyst which can be added with the coal slurry or inserted into the reactor. It is doubtful that the solvent reclaimed could be recycled successfully in a second or third use.

Because of these difficulties Elkol was studied with hydrogen as reducing gas in experiments CU 41 through CU 47. None of these trials were particularly encouraging either. Further comment is reserved until the conclusion of those experiments.

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Evaluation of Experiment CU 31 (Samples A through G)

This experimental series was done to test the use of 1:1 carbon monoxide to hydrogen mixtures at 1000 psig as the reducing gas for processing Kentucky No. 9 coal. The solvent used in this series was the CL 18 hydrogenated anthracene oil. Water was added to the feed slurry to provide reagent for the reaction of the carbon monoxide.

After the preceding experiment the dissolver was dismantled to allow removal of an accumulation of coke. The reactor was therefore clean and empty at the beginning of this series.

A new grinding of Kentucky No. 9 coal was used for this series. This was taken from the second half of the drum of coal used for previous experiments. This material had been segregated as the result of improper mixing of the coal in the drum. The ash content was found to have been increased to 15.27% in the first sample used from the new grinding. The ash had an average of 23.06% of iron. Since the coal was the same as previously analyzed, the previous analysis was corrected to allow for the changed ash content. The organic matter was assumed to have the same composition in either subsample.

The operating details for lineout times and reaction conditions are presented in the table below. Slurry samples were taken for ash and water analysis before and after the collection of each liquid sample. For liquid samples collected for one hour intervals, a 20 minute flush period was allowed before collection of the gas sample was started. Such samples were collected for half hour intervals. For half hour liquid samples only a 5 minute flush period was allowed and the gas sample was collected for 25 minutes.

Operation	1/LHSV	Temp. ^{0}C	Pressure psig
Establish condition lineout on flush oil			
Composition lineout on slurry 5 hours			
Collect sample CU 31A for ½ hour	0.505	425	1000
Composition lineout on slurry 6 hours			
Collect sample CU 31B for 1 hour	0.763	425	1000
Composition lineout on slurry 4 hours			
Collect sample CU 31C for 1 hour	0.813	450	1000
Composition lineout on slurry 4½ hours			
Collect sample CU 31D for 1 hour	0.592	450	1000
Composition lineout on slurry 3½ hours			
Collect sample CU 31E for ½ hour	0.409	452	1000

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Operation (continued)	1/LHSV	Temp. °C	Pressure psig
Composition lineout on slurry 3½ hours Collect sample CU 31E for ½ hour	0.409	452	1000
Composition lineout on slurry 4½ hours Collect sample CU 31F for ½ hour	0.461	475	1000
Composition lineout on slurry 6 hours Collect sample CU 31G for 1 hour	0.662	475	1000

During an attempt to continue with CU 31H also at 475°C the unit coked.

Discussion of Results

The results of control checks on feed slurry are presented in the table below. The slurry ash appears to have been fed with good precision throughout the experiment. This reflects the effect of more care in mixing the coal as it is ground for use and the effect of more attention to stirring of the feed pot. The target value for water added should have resulted in about 6.25% water in the feed slurry. Systematic loss of water is evident in these results.

Sample	% Ash in Slurry	% Iron in Slurry Ash	% Water in Slurry	% Iron in Ash From Wet Filter Cake
A-1	5.017	23.14	6.25	
A-2	5.028	22.88	5.99	21.12
B-1	5.121	23.19	5.61	
B-2	5.155	23.04	5.34	21.87
C-1	5.179	21.40	3.81	
C-2	5.275	21.19	3.27	21.19
D-1	5.333	22.77	4.42	
D-2	5.251	21.90	3.96	22.03
E-1	5.094	21.88	4.69	
E-2	5.087	21.30	4.33	21.92
F-1	5.201	23.62	5.66	
F-2	5.255	23.41	5.21	22.43
G-1	5.181	23.13	5.12	
G-2	5.408	23.33	4.70	22.67
Mean	5.184%	22.58%	4.88%	21.89%

Mean Deviation 1.7% Rel.

Notes: This is a new grinding of Kentucky No. 9 coal. Ash is 15.27% for this material. The ash contains 23.06% iron. The moisture content of the coal is 5.16% by oven drying loss.

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The analysis of product gases is given below. The reducing gas was from commercially prepared cylinders and contained 52.5% hydrogen and 47.5% CO.

Analysis of Gas Samples for Experiment CU 31
(Normalized Air & Water Free Basis)

Gas (Mol %)	CU 31A	CU 31B	CU 31C	CU 31D	CU 31E	CU 31F	CU 31G*
Hydrogen	41.3	41.5	34.6	36.0	37.7	33.9	40.5
Nitrogen	3.91	4.53	5.04	5.19	4.10	3.81	1.38
Methane	2.85	2.56	6.40	5.89	6.02	13.0	5.74
Ethane	0.94	0.90	2.03	1.97	2.00	3.55	1.73
Propane	0.44	0.44	0.91	0.84	0.80	1.38	0.66
n-Butane	0.12	0.12	0.24	0.27	0.18	0.31	0.13
Isobutane	0.04	0.04	0.06	0.07	0.07	0.11	0.04
Carbon Monoxide	37.3	37.6	36.9	34.3	33.8	29.2	38.3
Carbon Dioxide	10.95	10.5	11.7	12.9	12.6	12.1	9.21
Hydrogen Sulfide	2.15	1.10	2.07	2.56	2.69	1.16	1.06
Moles per Hour	5.276	4.837	5.044	5.028	4.862	6.060	4.765

*CU 31G gas compositions are influenced by coke deposition and consequent reduction of reactor volume and retention time.

The amount of carbon monoxide, hydrogen, and nitrogen fed to the reactor during each experiment in the series is given in Appendix A (parts 7 & 8). For convenient reference these results will be repeated in the table below. In addition the weights of each of these materials recovered in the product gases has been calculated using the gas analysis results and the number of moles of gas collected. These results may then be compared to the weights of each of the gases fed.

Comparisons of Gas Inputs and Outputs for Experiment CU 31

Material	CU 31A	CU 31B	CU 31C	CU 31D	CU 31E	CU 31F	CU 31G
Gm H_2 In	4.8	4.8	4.8	4.6	4.6	4.7	4.9
GM CO In	60.7	60.7	60.5	58.7	58.7	59.6	61.9
Gm N_2 In	5.7	2.4	2.4	7.0	4.8	5.4	5.4
Gm H_2 Out	4.4	4.0	3.5	3.6	3.7	4.1	3.9
Gm CO Out	55.1	50.9	52.1	48.3	46.0	49.5	51.0
Gm N_2 Out	5.8	6.1	7.1	7.3	5.6	6.5	1.8

CU 31

In these results a clear cut trend for conversion of carbon monoxide and for consumption of hydrogen appears. Some of the input nitrogen values must be erroneous, particularly the values for CU 31B and CU 31C. If these values are discarded the trend for input and output checks reasonably well. In the case of CU 31G the nitrogen in the output gas appears a little low. From the hydrogen input and output results it appears that roughly a half mol of hydrogen has been consumed in each case. In addition roughly ten grams of carbon monoxide has been used up. This would be about 0.35 moles of carbon monoxide and presumably this much hydrogen must have been formed. The total gas useage is then equivalent to about 0.85 moles of hydrogen. This is in contrast to the behavior of Elkol which exhibited little tendency to convert any monoxide or to react with hydrogen.

Inspection of the $\overline{\mathrm{IR}}$ values for the cut 2 reclaim solvent will disclose that thaere is a general tendency for these values to be lower than for the $\overline{\mathrm{IR}}$ values of the original solvent. It therefore appears that an appreciable amount of the reaction observed has been supported by hydrogen transfer from the solvent. The hydrogen reacted from the gas phase (including any contribution from the reaction of carbon monoxide and water) appears to be rather too small an amount to effectively dissolve coal. The yield of excess solvent ranges from a slight gain to a small loss and when allowance is made for the cold trap oil, the amount available for recycle may exceed break even weights only by a percent or two.

It appears that the conditions used in this experimental series skirt the minimum operating pressure, and may exceed prudent operating temperatures. Under such conditions the materials tend to repolymerize as retention time is increased. One consequence of this situation is the tendency for total reclaim solvent to decrease as the retention time increases. Recycle with a less hydrogenated solvent would tend to increase the vulnerability of the coal to repolymerization under such conditions. The use of 1:1 carbon monoxide to hydrogen ratio gas appears to reduce the partial pressure of hydrogen too much for satisfactory operation at 1000 psig. The main problem would be the composition of the recycle solvent.

Evaluation of Experiment CU 32 (Samples A through D)

The objective of experimental series CU 32 was to operate with Kentucky No. 9 coal and hydrogen with high temperature short retention time conditions. Some of these were comparable to conditions used in the previous experiment with 1:1 syn gas and others extended the study to shorter retention times in combination with high temperatures.

The experiment was done with the standard procedures designed to allow adequate lineout times between condition changes and to follow the composition of the feed slurry by sampling for analysis at the time liquid samples were collected. At these short retention times the feed rate is sufficient to fill the reactor two or three times an hour. Thus the lineout time needed could be reduced to two hours while maintaining the requirement that the reactor ought to be flushed with four to six volumes to lineout a condition change. The reaction products were followed by the usual measurements of IR, blackness, and output gas compositions.

The operating details are given in the table below. This was the second experiment done with the newly ground Kentucky No. 9 coal sample. The solvent was the CL 18 hydrogenated anthracene oil, as usual.

Operation	1/LHSV	Temp. °C	Pressure psig
Establish condition lineout on flush oil			
Composition lineout on slurry 5 hours Collect sample CU 32A for ½ hour	0.333	450	1000
Composition lineout on slurry 3 hours Collect sample CU 32B for ½ hour	0.495	450	1000
Composition lineout on slurry 2 hours Collect sample CU 32C for ½ hour	0.338	475	1000
Composition lineout on slurry 2 hours Collect sample CU 32D for ½ hour	0.267	475	1000

Discussion of Results:

The results of control checks on the feed slurry are presented in the table which follows. The average values for ash fed and for iron in the ash fed are reasonably close to the values for the feed coal. It can be seen that variations in stirring efficiency are present since ash in some of the early samples falls below theory and this material is picked up in the feed later in the experiment. These variations also result in variations in the concentration of iron in the feed samples, hence it is likely that some of the variation in the ash content is the result of preferential settling of pyrities from the coal.

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The coal originally formulated into slurry contained 4.95% of moisture and 15.12% ash. The average ash content of the slurry should then have been one third of the ash content of the coal, or 5.038%. The average value observed was 5.113% which may be the result of evaporation of some of this water.

Sample	% Ash In Slurry	% Iron In Ash from Slurry
A-1	4.597	23.54
A-2	5.333	23.39
B-1	4.840	20.99
B-2	4.676	20.58
C-1	5.389	23.03
C-2	5.233	24.05
D-1	5.396	22.80
D-2	5.447	22.18
Mean	5.113	22.56

The results for gas analysis of each product gas are presented in the table below.

ANALYSIS OF PRODUCT GASES FOR EXPERIMENT CU 32
(Normalized air and water free basis)

GAS (MOL %)	CU 32A	CU 32B	CU 32C	CU 32D
Hydrogen	66.3	71.8	55.8	49.7
Nitrogen	7.08	6.17	6.04	6.35
Methane	11.7	10.3	19.8	21.8
Ethane	3.99	3.47	6.00	6.77
Propane	1.95	1.29	2.77	3.14
n-Butane	0.44	0.38	0.64	0.79
Isobutane	0.15	0.11	0.18	0.24
Carbon Dioxide	2.74	1.97	2.88	3.92
Carbon Monoxide	0.70	0.64	0.80	0.87
Hydrogen Sulfide	4.95	3.83	5.05	6.39
Moles per Hour	3.199	3.462	4.611	4.369

The hydrogen input in these experiments was nominally 4.4 moles per hour. At the flow rates of slurry used the amount of hydrogen available was too small for an effective excess of hydrogen to be present. The weight percentage of hydrogen available ranged from 2.5% in experiment CU 32B to only 1.4% in experiment CU 32D. The ratio of hydrogen to slurry resulted in utilization of unusually large fractions of the gas available. In this case the gaseous products were concentrated in the effluent gas from the reactor. This accounts for the abnormally high concentrations of methane and other hydrocarbon gases and for the concentration of hydrogen sulfide observed.

It is clear that an appreciable fraction of the coal was reacted. This could be done only because reactive hydrogen was also present in the solvent. The amount of hydrogen removed from the solvent can be estimated from the decline in the $\overline{\text{IR}}$ value from the input solvent to the reclaimed cut 2 solvent. At the higher temperatures this value corresponds to reversion of the solvent to about the same composition as the raw anthracene oil used in the preparation of the CL 18 hydrogenated anthracene oil. The experiment is then of particular interest as an indication of the rate of conversion which is possible given a reactive solvent and a high operating temperature.

Values are presented in Appendix A showing the hydrogen reacted as calculated from the amount of hydrogen fed to the reactor less the hydrogen recovered in the gaseous reactor products. These results are presented as a weight percentage based on the MAF organic matter in the coal fed. It is clear that this amount of hydrogen reacted, but it should be borne in mind that a substantial transfer of hydrogen from the solvent has also been observed. The solvent to MAF coal ratio for experiment CU 32A is given in the operating conditions for this experiment as 2.50/1. The $\overline{\text{IR}}$ of the solvent was 0.98 which corresponds to 6.20% hydrogen. (See section IV-C-2.) The reclaimed cut 2 solvent had an $\overline{\text{IR}}$ value of 0.74 which would correspond to a material containing about 5.95% hydrogen. This would amount to the transfer of 0.25% hydrogen from the solvent to the coal and allowing for the 2.5/1 solvent to MAF coal ratio this would be equivalent to the addition of 0.62% of hydrogen in addition to the amount from the gaseous phase. Thus the MAF conversion, 87.59%, must be attributed not to the 1.10% hydrogen reacted from the gaseous phase, but to the larger value of 1.72% estimated by adding the change in solvent composition into the result. At 450°C extension of the reaction time caused the gaseous hydrogen consumption to increase while the transfer from the solvent remained about the same. Compare $\overline{\text{IR}}$ values for CU 32A and CU 32B reclaim cut 2. Despite this increase the MAF conversion was not improved and a small decrease in conversion is evident. This implies some repolymerization of material and increased evolution of gases which used up the extra hydrogen.

At 475°C the transfer of hydrogen from the solvent has been completed at least to the extent that the solvent reclaimed had substantially the composition of raw anthracene oil. Moreover the amount of gaseous hydrogen which has reacted is a little less than the amount reacted at 450°C. There is some tendency for the amount reacted to decline with increasing reaction time. In this case the tendency for MAF conversion to decrease with increasing reaction time appears clearly established. The general tendency for the MAF conversion to decline under the influence of extended reaction times at 450°C and generally as the temperatures increase to 475°C would lead to the conclusion that such temperatures are near the practical upper limit. This situation could be modified by availability of more reactive solvent or by use of higher partial pressures of hydrogen but limits are not well defined. Higher temperatures also caused loss of solvent which became larger as the reaction time increased.

The solutions which were obtained could be filtered and products were obtained from standard workup procedures. At the higher temperatures the vacuum bottoms made were effectively deoxygenated and desulfurized. Both desulfurization and deoxygenation were increased as reaction time increased. There were therefore favorable aspects to the higher temperature reactions as well as the difficulties in control of MAF conversion and liquid yield previously discussed. Additional work with temperatures in this area was needed to better define the limits of applicability.

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Evaluation of Experiment CU 33 (Samples A through G)

A series of experiments with Kentucky No. 9 coal, CL 18 hydrogenated anthracene oil, and hydrogen was designed to study only the preheater. These experiments consist primarily of a temperature variable study at constant reaction time. Solvent and coal were mixed in a 2:1 ratio to prepare the feed slurry. The experiments were designed to determine and to obtain estimates of the heat of reaction for materials passing through the preheater.

For these experiments the CU reactor was modified by disconnecting the dissolver vessel and providing a transfer line for delivery of product directly from the preheater to the two liter autoclave used as a buffer vessel. The slurry feed system, the gas feed system, and the sample collection system remained as drawn in figure 4. (See section IV-A of this report.) The two liter autoclave was operated at a temperature low enough to prevent further reaction of materials as they passed through this vessel. Usually the product could be kept fluid enough to allow normal product removal through the Gismo product let down valve.

The preheater coil was 18 feet of 1/4" x 7/64" high pressure tubing with approximately six feet of interconnecting tubing to the 2 liter surge reservoir. The liquid space velocity and the gas space velocity reported for experiments in this mode is calculated using the volume of the 18 foot coil of tubing only. The preheater exit temperature was measured by means of a thermocouple inserted into a specially fabricated Autoclave Engineers tee. A thermowell is drilled within 5/32" of the process fluid on the branch side of the tee. This tee is wrapped with several layers of asbestos tape and is located in the fluidized bed preheater such that it is below the level of the sand. Precise measurement of the preheater effluent in this configuration is questionable, but it is estimated that the temperature is known within about ten degrees centigrade. This may be less accurate at higher flow rates since the apparatus measures tube wall temperatures rather than true fluid temperatures.

Product yields were determined by distillation of the unfiltered coal solution as most of the solutions would not filter. The quantity of vacuum bottoms was then calculated by subtracting the amount of pyridine insoluble material in the distillation residue. Operation at the lower temperatures was difficult as viscous material accumulated in the 2 liter surge reservoir. (Note the erratic percentage recovery values reported for these experiments in Appendix A.) Difficulties with recovery of material are evident from about 300°C to about 400°C as the result of unreliable transport of material out of the surge reservoir.

Because of the small volume of the preheater the need for lineout was mostly the result of time needed to readjust temperatures between samples and to allow for flushing of the surge reservoir. At the 200°C operating temperature this presented no problem because the product was not yet viscous as the result of coal reacting. At 300°C to 400°C the viscous behavior of the product caused loss of material, by retention of viscous product in the surge vessel, and the probability of poorly representative samples is high. The data presented for CU 33B through CU 33D should be regarded as indicative of trends, the problem of sample removal from the two liter autoclave used as surge reservoir and the risk of mixing back with old viscous product in this vessel would justify some caution in accepting the numerical results from these samples. Qualitatively they are quite interesting and are presented for the purpose of describing the coal solution process in greater detail.

The operating schedule for the experiments in the CU 33 series is given below.

Operation	1/LHSV hr.	Temp. °C	Pressure psig
Establish condition lineout on flush oil			
Composition lineout on slurry 1 hour Collect sample CU 33A for 40 minutes*	0.035	200	1000
Composition lineout on slurry 1 hour* Collect sample CU 33B for 40 minutes*	0.035	300	1000
Composition lineout on slurry 1 hour Collect sample CU 33C for 40 minutes*	0.036	350	1000
Composition lineout on slurry 1 hour Collect sample CU 33D for 40 minutes*	0.035	400	1000
Composition lineout on slurry 1 hour Collect sample CU 33E for 40 minutes*	0.035	450	1000
Composition lineout on slurry 1 hour Collect sample CU 33F for 1 hour	0.066	450	1000
Composition lineout on slurry 1 hour Collect sample CU 33E-2 for 25 minutes*	0.035	450	1000
Composition lineout on slurry 1 hour Collect sample CU 33G for 25 minutes*	0.035	500	1000

*Sample collection 30 minutes in stainless steel flask for material balance determination and distillation workup. A ten minute sample was collected for elemental analysis procedures and calorimetric studies on unfiltered coal solutions.

The sample preparation sequence given above includes the return to a previously used operating condition for preparation of a second sample. This is indicated by use of the same run number in combination with an identifying number. In Appendix A only the results from CU 33E-2 have been reported. These results were selected for presentation in the appendix in the belief that more representative sampling should have been done on the second attempt.

Discussion of Results

The low operating temperatures and the short retention times which are encountered in the preheater result in samples which are only partially converted. The solution process has not reached the point at which it is reasonable to expect the products to filter normally. It is therefore necessary to place more reliance on the infra red spectra and on the blackness measurements as indications of the amount of conversion which has been experienced. As usual the composition of the feed slurry was valiadated by analysis of the feed slurry for ash content. The results for ash analysis, blackness measurements, and IR measurements are presented in the table which follows. IR values for the reclaim cut 2 solvent are included for comparison.

Comparative Results for Preheater Studies

Sample	Temp. °C	1/LHSV	% Ash in Feed Slurry	Blackness of Solu.	IR Value Solution	IR Value Cut 2
CU 33A	200	0.035	4.512	1.61	1.23	1.41
CU 33B	300	0.035	5.251	2.71	1.20	1.39
CU 33C	350	0.036	5.236	3.20	1.20	1.30
CU 33D	400	0.035	5.363	6.75	1.28	1.06
CU 33E	450	0.035	4.595	7.11	1.24	0.78
CU 33F	450	0.066	5.365	6.99	1.22	0.88
CU 33G	500	0.035	5.370	8.33	1.05	0.71
CU 33E-2	450	0.045	4.766	7.19	1.25	0.88
mean			5.057			

Note: The ash in the feed coal was 15.24%. The feed was 2:1 hence the ash should have been 5.08% of the slurry. The average is accurate but feed precision is poor.

The blackness of the product solution increased in a systematic way as the operating temperature increased. This increase shows the progressive attack on the coal as the result of exposure to heat and solvent. The blackness for CU 33E and CU 33E-2 check reasonably well and show that return to a similar heat and reaction time will produce a reasonably reproducible result. The $\overline{\text{IR}}$ values for these solutions also check well. The MAF conversions and the recovery of solvent are variable, which may well be the result of mixing of solution with material retained in the two liter autoclave in either case. The difference in the amount of solvent recoverable may influence the $\overline{\text{IR}}$ values for the reclaimed cut 2 solvent. It will be observed that the reclaimed cut 2 solvent appears more hydrogenated than the solution (see $\overline{\text{IR}}$ values for CU 33A through CU 33C) for the lower temperature samples. No doubt this is an artifact resulting from retention of the high molecular weight fractions of the solvent by the partly reacted coal. The boiling range of the solvent was narrowed by failure to reclaim the high boiling components in this case.

As the temperature was increased the $\overline{\text{IR}}$ for the solution and for the reclaimed cut 2 solvent both declined. This is believed to be unambiguous evidence for the hydrogen transfer reaction, and this is completed very rapidly at the higher temperature conditions. There may well be qualifications regarding these times, since the length of the tube used in heating the slurry and the relative volume occupied by gas are both conjectural in this apparatus. These data should be understood to be a comparative set of results and absolute values should not be taken seriously.

Another index for conversion can be obtained by study of the composition and value of gas recovered during each experiment. These data are presented in the table which follows.

ANALYSIS OF PRODUCT GASES FOR EXPERIMENT CU 33
(Normalized air and water free basis)

Gas (Mol %)	CU 33A	CU 33B	CU 33C	CU 33D	CU 33E	CU 33F	CU 33G	CU 33E-2
Hydrogen	97.8	98.5	98.7	92.3	90.4	91.3	82.7	91.2
Nitrogen	2.03	1.04	0.63	5.57	5.81	5.39	7.03	4.92
Methane	Nil	Nil	Nil	0.09	0.59	0.74	3.33	0.64
Ethane	Nil	Nil	Nil	0.03	0.24	0.28	1.26	0.26
Propane	Nil	Nil	Nil	0.01	0.01	0.12	0.55	0.12
n-Butane	Nil	Nil	Nil	Nil	Nil	Nil	0.13	Nil
Isobutane	Nil	Nil	Nil	Nil	Nil	Nil	0.03	Nil
Carbon Dioxide	0.12	0.26	0.27	0.45	0.58	0.41	1.03	0.60
Carbon Monoxide	Nil	Nil	Nil	0.07	0.13	0.10	0.43	0.14
Hydrogen Sulfide	0.07	0.14	0.37	1.45	2.09	1.66	3.53	2.12
Moles Per Hour	3.806	3.818	3.812	3.812	3.841	4.143	4.226	3.816

From the moles of hydrogen fed and from the moles of hydrogen recovered in the product gases it would appear that some hydrogen reacted at even the coolest temperature used. This may perhaps be true, though it would be reasonable to suspect that this is more likely a measure of the hydrogen dissolved in the oil under product letdown conditions. At the higher temperatures the color of the solution indicates that a reaction dissolving coal has progressed appreciably. The increased amounts of hydrogen consumed for these samples may be reasonably accurate values. As is usually the case, much of the rapidly available hydrogen has been taken from the solvent rather than from the gas phase.

The MAF conversion increased as the reaction temperature increased. It is characteristic of low conversions that the solvent interacts with the coal and forms a product which retains the solvent tenaciously. The solvent can not be reclaimed by distillation of such products. Better separation can be obtained by pyridine extraction of the product but, for the most obdurate complexes formed, the pyridine is unable to recover all of the solvent originally used. Thus there are instances in which the insoluble organic matter may be greater than the organic matter originally present in the coal. In such cases the MAF conversion is a negative value. Data are presented in tabular form below.

Sample	Temp.	% MAF Conversion	% Insoluble Organic Matter	% Solvent Recovery	% Vacuum Bottoms	Moles H_2S Out
CU 33A	200	- 6.84	106.84	38.53	147.91	0.0026
CU 33B	300	21.48	78.52	31.16	193.61	0.053
CU 33C	350	32.97	67.03	46.10	167.60	0.014
CU 33D	400	59.70	40.21	48.27	187.58	0.055
CU 33E2	450	76.80	23.20	76.31	136.21	0.0808
CU 33F	450	86.79	13.21	103.12	75.78	0.0688
CU 33G	500	87.17	12.83	105.37	71.17	0.149

An indication of the rate of decomposition of the swelled gel phase can be obtained by noting the decrease in the amount of MAF vacuum bottoms from CU 33E2 to CU 33F. The space time was increased from 0.035 to 0.066 hours. (or from 2.1 to 3.96 minutes.) This resulted in reduction of the vacuum bottoms from 136.3 to 75.78 percent of the MAF coal. A corresponding increase in the solvent recovery as well as a decrease in the amount of insoluble organic matter was observed. The reaction rate is very rapid for both reactions which are required to be nearly completed before good yields of reclaim solvent can be obtained.

From these results it is clear that coal can be put into solution with great speed at high temperatures, given a solvent of suitable reactivity. The rate limiting step therefore is not the decomposition of the coal, but rather the ability to recover a solvent of suitable reactivity for recycle. It is clear that the solvent recovered from these solutions has lost an appreciable fraction of the hydrogen added in the CL 18 hydrogenation procedure. Presumably this must be the source for most of the hydrogen used in these rapid reactions. The rate at which hydrogen is being removed from the gas phase does not seem sufficient for this purpose. It appears that only a rearrangement of material in a coal-solvent complex which resulted in formation of soluble and lower molecular weight products could account for the observations made in the preheater study.

The requirements for energy to produce such reactions were not well established. Observations in the Process Development plant had led to the conclusion that this portion of the solution mechanism was endothermic. One of the objectives in the preheater studies was to determine the heat of reaction at various stages in the process to correct previous estimates and attempt a more detailed description of heat requirements along a preheater tube. Subsamples for this work were drawn in glass flasks. The material in a sample flask was stirred by means of a magnetic stirring bar while samples were taken for elemental analysis and for determination of the heat of combustion.

Heats of combustion for the solvent, the Kentucky No. 9 coal, and for the unfiltered coal solutions were measured in the laboratory with a Parr Series 1221 Adiabatic Calorimeter using a Hewlett-Packard Model 2801A quartz thermometer. Heats of combustion of the gases were taken from the 1966 Edition of the NGPSA Data Book. Heats of reaction were then calculated for most of the runs with Kentucky No. 9 coal. Two methods were used in calculating the heats of reaction. In one method the heat of reaction was calculated from a loss free material balance on the products and reactants, and in the other method the heat of reaction was calculated using an elemental material balance on the products and reactants. The elemental material balance corrects the loss free material balance for sulfur loss as hydrogen sulfide and oxygen loss as water. Representative sampling of the unfiltered solution for either elemental analysis or for determination of heat of combustion in the calorimeter is a difficult problem. Water droplets condense on the side of the flask and water vapor loss during subsampling is also likely. Usually some water loss is inevitable and the heat of combustion determined is too high as a result. Moreover a tendency for non representative sampling of ash is also observed. Again the determined heat of combustion will be high as a result. By correcting with an elemental balance to allow for these sampling problems the calculated heats of reaction should be more accurate than the results calculated from raw samples.

Data are presented in Appendix A giving the composition of the unfiltered coal solutions used for these studies. A number of practical problems can be illustrated with these raw data. First: the ash content of the feed coal was 15.24% and for a 2/1 solvent to coal ratio the ash content of the product should be one third of this value, as increased by the effect of gas and volatile oil removal. If good material balances are obtained the concentration of ash should be determined by the ratio of feed slurry/unstripped solution obtained multiplied by 5.08% for these samples. The ash in the raw samples is generally low compared to such estimates. Second: the series includes several cases in which hold up in the two liter autoclave buffer vessel caused large loss of product. It was necessary in these cases to analyze such product as could be removed from the autoclave and to correct the results by forcing ash and elemental balances. At the peak concentration of gel phase the product is not manageable and the methods which are satisfactory with well converted coal in solution fail to cope with the gel. Results for product made at 300°C and 350°C are influenced by this effect.

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Heat of reaction results for the preheater studies are presented below. The heat of reaction as calculated by the two methods varys considerably as a result of sampling problems. The heat of reaction is given in BTU per pound of feed coal.

Sample	Heat of Reaction from loss free material balance	Heat of Reaction from Elemental Material Bal.
CU 33A	303	155
CU 33B	194	-129
CU 33C	850	119
CU 33D	206	-537
CU 33E2	459	47
CU 33F	913	154
CU 33G	540	30

Perhaps an average of the values given above would be a reasonable estimate for the heat of reaction in the preheater. The heat of reaction at 0.035 hour space time increases with preheat temperature. Apparently the endothermic solution-depolymerization is not fully completed in this short time even at the highest temperature studied. Hydrogenation reactions, which should be exothermic, are not yet evident and their contribution is not sufficient to generate a net release of heat at this early stage in the reaction.

Additional preheater studies were done in experiments CU 34, CU 35, and CU 36. These were done at temperatures and with space times which resulted in good recoveries and in some cases in samples which could be filtered and worked up by standard procedures. Discussions of these experiments follow.

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Evaluation of Experiments CU 34 & CU 35 (Samples A through E)

Preheater studies with Kentucky No. 9 coal and hydrogen were continued in this series of experiments. The objectives were to repeat some points, which may have been doubtful because of hold up of viscous material in the buffer vessel, and to obtain data at high temperatures and longer space times. The buffer vessel was opened and the viscous material which had accumulated was removed before this series of experiments was started.

The experiments were done with the same apparatus used for experiment CU 33. The lineout and sampling procedures were generally the same as used for that set of experiments also. Details are presented below.

Operation	1/LHSV hr.	Temp. °C	Pressure psig
Establish condition lineout on flush oil			
Composition lineout on slurry 5 hours			
Collect sample CU 34A for ½ hour	0.035	450	1000
Establish condition lineout on flush oil			
Composition lineout on slurry 3 hours			
Collect sample CU 35A for 2 hours	0.129	450	1000
Composition lineout on slurry 3 hours			
Collect sample CU 35B for 2 hours	0.128	475	1000
Composition lineout on slurry 6 hours			
Collect sample CU 35C for 1 hour	0.073	475	1000
Composition lineout on slurry 1 hour			
Collect sample CU 35D for ½ hour	0.036	475	1000
Composition lineout on slurry 3 hours			
Collect sample CU 35E for 2 hours	0.13	500	1000

Samples for elemental analysis and for determination of heats of combustion were taken separately at the end of each sampling period by collecting additional material in clean glass flasks. These extended the sampling time long enough to allow collection of 75 to 100 grams of sample for this work.

Discussion of Results:

The usual samples were taken to validate the composition of the feed slurry and for determination of blackness and infrared spectra of product solutions. Gas samples were also taken for analysis by gas chromatographic and infrared methods. Results are presented in the following tables.

Comparative Results for Preheater Studies

Sample	Temp. °C	1/LHSV	% Ash in Feed Slurry	Blackness of Solution	$\overline{\text{IR}}$ Value Solution	$\overline{\text{IR}}$ Value CUT 2
CU 34A	450	0.035	4.830	7.00	1.25	0.83
CU 35A	450	0.129	4.872	6.87	1.23	0.87
CU 35B	475	0.128	5.357	7.11	1.15	0.84
CU 35C	475	0.073	4.663	7.91	1.14	0.78
CU 35D	475	0.036	5.208	7.84	1.19	0.75
CU 35E	500	0.130	5.175	11.42	1.02	0.74
Mean			5.017			

Note: The ash content of the feed coal was 15.12% which would yield a slurry with an average ash of 5.04% at 2/1 solvent to coal ratio. The average is accurate but the precision is poor indicating improper stirring of the feed slurry.

In these product solutions the MAF conversion increased with increased exposure to heat and with increased time at reaction conditions, except for the last sample, CU 35E. In this case a decline in MAF conversion was observed even though the solution blackness increased. This combination of observations would be reasonably explained by initially high conversion of the coal followed by repolymerization. The blackness of the solution may increase with increased coal in solution or in response to the accumulation of polymeric material in the solution. Observation of blackness is then apparently an observation of a small, but relatively important component of the solution. The numerical value is only useful in conjunction with information relating to input coal concentrations and reduction potentials. Blackness thus indicates the concentration of intermediate molecular weight, highly colored, material in transition from coal to dissolved product or in transition from dissolved material to polymer.

Further insight into the relationships between temperature, reaction time, and conversion to various species can be gained by study of excess solvent, vacuum bottoms, and insoluble organic matter yields in these experiments. (See Appendix A part 9) At the high temperatures used, these values are redistributed very rapidly and show clearly the tendency for solvent to become tied up in the initial reaction product which must be further decomposed by heat to release solvent and lower molecular weight coal derived material. $\overline{\text{IR}}$ values have declined as these conversions were accomplished leading to the conclusion that these rapid reactions are essentially the result of hydrogen transfer from solvent.

The amount of gas and the composition of the gas made can be used as additional measures of the conversion of the coal. These results must, of course, be related to the amount of material fed in order to obtain proper comparisons. The necessary information is presented in Appendix A and in the table of gas analysis results which follows.

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ANALYSIS OF PRODUCT GASES - RUNS 34 & 35
(Normalized Air and Moisture Free Basis)

GAS (MOL %)	CU 34A	CU 35A	CU 35B	CU 35C	CU 35D	CU 35E
Hydrogen	91.2	93.4	89.9	89.2	88.6	88.6
Nitrogen	5.59	4.70	6.30	6.78	6.22	5.71
Methane	0.41	0.49	1.20	0.75	1.15	2.78
Ethane	0.17	0.18	0.82	0.56	0.38	0.78
Propane	0.08	0.08	0.18	0.22	0.16	0.37
n-Butane	Nil	Nil	0.04	0.06	0.04	0.11
Isobutane	Nil	Nil	0.02	0.01	Trace	0.04
Carbon Dioxide	0.54	0.20	0.25	0.43	0.68	0.29
Carbon Monoxide	0.13	0.16	0.18	0.40	0.33	0.11
Hydrogen Sulfide	1.85	0.79	1.11	1.59	2.46	1.24
Moles per Hour	4.267	4.405	4.431	4.245	4.317	4.351

The raw input data presented in Appendix A show the weights of slurry per hour for each experiment. The high concentration of hydrogen sulfide observed in the product gas for CU 34A is the result of a moderate conversion of coal at a slurry feed rate of 1080 grams per hour. This solution was not converted well enough to be filterable. At the lower slurry feed rates used in experiments CU 35A through CU 35C the product solutions were filterable. The increasing concentration of hydrogen sulfide in the product gas from CU 35A to CU 35B is a direct measure of increasing sulfur removal as the operating temperature was increased. Experiment CU 35C involved an increase in the amount of slurry used. Thus the increase in the concentration of hydrogen sulfide in the gas could not be taken as an indication of better sulfur removal. Compare the composition of the vacuum bottoms for each of these samples. Variability in the concentration of ash in the unfiltered coal solutions is large enough to obscure the comparison which is made in this case. Continued improvement in sulfur removal can be seen in experiment CU 35E. This was made at the same feed rate as CU 35A and CU 35B. The effect of increasing temperature at a constant feed rate can be studied by direct comparisons for these three cases.

Efforts were continued to determine the heats of reaction of materials in these preheater studies. Most of the samples could be filtered, and were therefore more fluid than previous preheater products. Difficulty in sampling ash is evident in all cases despite presumed improvement in the properties of the solutions obtained. Heats of reaction were calculated from the loss free material balance data, and after correction to force elemental balances. These results are presented below. Results are given in BTU per pound of feed Coal.

Sample	Heat of Reaction from Loss Free Material Balance	Heat of Reaction from Elemental Material Balance
CU 34A	564	-433
CU 35A	643	-180
CU 35B	202	-666
CU 35C	808	- 64
CU 35D	1727	1286
CU 35E	527	168

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The heat of reaction determined by these methods has not been obtained with the accuracy needed to follow the course of the reaction or to estimate the heat requirements for operating equipment. Because of the sampling problems this procedure will generally be difficult to use with precision. Use of an alternative method would be desirable, perhaps differential thermal analysis apparatus could be developed to operate with suitable pressures of hydrogen present.

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Evaluation of Experiment CU 36 (Samples A through E)

The objective of the experiments in this set was to test the use of a 1:1 mixture of carbon monoxide and hydrogen as reducing gas in the preheater reaction studies. With some operating experience established using hydrogen it was possible to select conditions which gave filterable solutions for the most part. The apparatus and the operating procedures used were the same for this series of experiments as for the previous set of experiments. Studies on heats of reaction were discontinued. The operating details are presented in the table below:

Operation	1/LHSV hr.	Temp. °C	Pressure psig
Establish condition lineout on flush oil			
Composition lineout on slurry 4 hours Collect sample CU 36A for 2 hours	0.123	425	1000
Composition lineout on slurry 2 hours Collect sample CU 36B for 2 hours	0.125	450	1000
Composition lineout on slurry 1½ hours Collect sample CU 36C for 2 hours	0.072	450	1000
Composition lineout on slurry 3 hours Collect sample CU 36D for 1 hour	0.070	475	1000
Composition lineout on slurry 1½ hours Collect sample CU 36E for 2 hours	0.123	475	1000

An attempt to continue at the same feed rate with temperature increased to 500°C resulted in the formation of a coke plug in the preheater.

Discussion of Results:

In all experiments using mixtures of hydrogen and carbon monoxide it was usual procedure to add water to the feed slurry in order to assure presence of reagent for reaction with the monoxide. From previous experience it was known that reasonably well controlled compositions could be maintained with about 5% of water added to Kentucky No. 9 coal slurries. These studies were done at rates which required addition of makeup slurry from time to time and water loss had been corrected by this procedure. In this experiment the amount of slurry used had been less and as a result the original charge was only replenished once. Results of water analysis on the feed slurry are presented below. Solution blackness and IR data are included.

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Sample	% Water in Feed Slurry Initial	Final	Solution Blackness	$\overline{\text{IR}}$ of Solution	$\overline{\text{IR}}$ of Cut 2
CU 36A	5.46	4.67	7.08	1.18	0.81
CU 36B	3.55	2.43	7.85	1.16	0.79
CU 36C	4.77	4.43	7.52	1.14	0.79
CU 36D	3.33	2.93	8.69	1.05	0.76
CU 36E	2.42	1.84	9.86	1.02	0.75

The effect of progressive evaporation of water from the feed slurry can be seen clearly in these data. Because the concentration declined throughout preparation of samples, it was necessary to use the average value for calculation of results. It can be seen that the blackness of the product solution increased as the time at temperature increased. Since the amount of insoluble organic matter tends to increase in syncronization with the blackness this colored material is likely to be due mainly to repolymerizing material. The changes in the $\overline{\text{IR}}$ values for the coal solution and for the reclaimed cut 2 solvent indicate progressive loss of hydrogen from the solvent. These data are therefore in accord with a mechanism in which most of the reaction observed is the result of rapid hydrogen transfer from the solvent to the coal. At the low activities of hydrogen present, the tendency for repolymerization reactions to progress more extensively seems evident also. It is a question why the CU 36A solution did not filter well. Apparently the concentration of partly depolymerized coal had not been reduced sufficiently in the time allowed at 425°C. At 450°C this material had been well converted, but reversion to insoluble material had already become a factor. (See Appendix A Part 10.)

The results for gas analysis of samples obtained are presented below. It can be seen that in the very short times available little conversion of the carbon monoxide had been obtained. This is not surprising if one assumes that such conversion will depend on first decomposing the pyrites and exposing a comparatively clean mineral residue surface to the gas.

ANALYSIS OF PRODUCT GASES FROM RUN CU 36
(Normalized air and water free basis)

GAS (MOL %)	CU 36A	CU 36B	CU 36C	CU 36D	CU 36E
Hydrogen	46.9	46.6	46.1	43.2	45.5
Nitrogen	5.91	5.57	6.41	6.42	6.20
Methane	0.31	0.56	0.58	0.87	1.09
Ethane	0.09	0.19	0.20	0.33	0.40
Propane	0.05	0.08	0.09	0.15	0.18
n-Butane	Nil	Nil	Nil	Nil	Nil
Isobutane	Nil	Nil	Nil	Nil	Nil
Carbon Dioxide	0.79	0.93	1.87	1.91	1.42
Carbon Monoxide	45.5	45.5	43.7	54.9	44.4
Hydrogen Sulfide	0.51	0.62	1.04	1.14	0.84
Moles per Hour	4.457	4.461	4.603	4.561	4.477

The feed gas used was a prepared mixture containing 52.5% hydrogen and 47.5% carbon monoxide.

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In those experiments producing filterable solutions, enough solvent was obtained to provide a sufficient volume for recycle. This had been done at the cost of transfer of hydrogen from the solvent, and it is necessary to correct the solvent composition before an equivalent effect could be expected in the next pass. The vacuum bottoms compositions are not materially different from the materials made at matching conditions in experiment CU 35.

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Evaluation of Experiment CU 37 (Samples A through C)

This series of experiments was done with the CU reactor in its normal configuration. The objective of the experiments was to acquire additional data for the reaction of Kentucky No. 9 coal with synthesis gas using hydrogenated anthracene oil as solvent. The reducing gas in this instance was a 3:1 mixture of hydrogen to carbon monoxide. Water was added to the coal slurry to provide reagent for reaction of the carbon monoxide. The slurry was analyzed for water content but no ash analysis was done. The usual checks for blackness and $\overline{\text{IR}}$ values of product solutions were done. Gas samples were taken for analysis as usual. The experiment was done with conventional lineout intervals between changes in operating conditions. Details follow.

Operation	1/LHSV hr.	Temp. °C	Pressure psig
Condition lineout on flush oil			
Composition lineout on slurry 6 hours Collect sample CU 37A for 1 hour	1.25	425	1000
Composition lineout on slurry 3 hours Collect sample CU 37B for 3/4 hr	1.11	450	1000
Composition lineout on slurry 2 hours Collect sample CU 37C for ½ hour	0.40	450	1000

Discussion of Results:

Results for water analysis of the feed slurry and for blackness and infrared analysis of product solution and reclaim cut 2 are presented in tabular form below.

Sample	Average % Water in Feed Slurry	Solution Blackness	$\overline{\text{IR}}$ Value of Solution	$\overline{\text{IR}}$ Value Cut 2
CU 37A	2.96	6.98	1.15	0.93
CU 37B	3.68	10.54	0.92	0.79
CU 37C	4.11	10.78	0.93	0.74

The operating temperature in this experimental set was the same in both the preheater and the dissolver vessels. The space times used were substantially longer than had been used in the preheater and as a result both hydrogen and carbon monoxide were more extensively reacted. The yield data and the data for reducing gas usage are presented in Appendix A Part 10. It can be seen that the longer reaction time did not improve the MAF conversion or the amount of excess solvent obtained. In this series the general rule that higher temperatures and shorter retention times are roughly equivalent to lower temperatures and longer retention times is demonstrated clearly. The removal of hydrogen from the reclaimed cut 2 solvent also shows that this conversion has been accomplished largely by hydrogen transfer. Despite the yield of an excess of total reclaim solvent, it is clear that an additional adjustment is needed to obtain a recycle solvent which is equivalent to the original solvent used.

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Some differences in the reaction products appear in the gas, where the yield of hydrocarbon gases is increased, and in the vacuum bottoms, where the concentration of sulfur has been reduced. By comparing the results in CU 37B with similar results in CU 37C it is clear that these reactions continue as a function of time and that desulfurization can be improved in this way. There is evidence for different amounts of conversion of coal to distillable liquid and for different amounts of hydrocracking of the solvent or coal derived products. This appears in the distribution presented for the reclaimed solvent, and shows that attention to details other than gross yields is needed in the selection of operating conditions. One of the effects of temperature-time profiles appears to be the redistribution of products within the solvent array. While total solvent yields match well, the distribution is different in each case.

One of the complications in planning experiments results from the ease with which liquid flow rates can be adjusted compared to the amount of effort needed to establish a calibrated gas input. In order to maintain well known gas inputs the gas flow was not normally changed within a series of trials. This means that as pump rates were changed the relative amounts of coal and reducing gas also changed. The accumulation of products in the gas is then influenced greatly by flow rates of the slurry fed and simple observation of concentrations of hydrocarbons, hydrogen sulfide, or so on does not lead to directly useful comparisons. In chemical terms the activities of the reagents and products are influenced in complex ways by even simple adjustment in the pumping rate. This change influences both the reaction time, and the relative amounts of reagent and charge. Assuming that a change in the amount of gases and light liquid results, the vapor pressures in the reactor will in turn change resulting in a further adjustment in the partial pressures of the components. It is not easy to make a change in only one variable in a system of this complexity since even simple adjustments may lead to a chain of consequences. This is further complicated by the requirement that the reclaimed solvent be returned at a later time for reuse. There are therefore mechanical lineout problems which result in chemical effects that must in turn be lined out in the process. It takes some time and considerable attention to detail to develop a chemical intuition for such systems. Care is needed to avoid blunders in experimental design which result in starving reactions for lack of reagents or so on.

CU 37

ANALYSIS OF PRODUCT GASES FOR RUN CU 37
(Normalized air and moisture free basis)

GAS (MOL %)	CU 37A	CU 37B	CU 37C
Hydrogen	59.7	51.0	47.8
Nitrogen	6.54	10.4	6.65
Methane	3.65	7.53	9.87
Ethane	1.18	2.48	3.64
Propane	0.56	1.05	1.56
n-Butane	0.29	0.28	0.45
Isobutane	0.05	0.07	0.13
Carbon Dioxide	5.19	6.27	11.18
Carbon Monoxide	21.5	19.4	14.4
Hydrogen Sulfide	1.37	1.48	3.72
Moles per Hour	4.266	4.009	4.515

The interaction of slurry flow rate and gas sample composition can be illustrated by examples from the data presented for experiments in the CU 37 sequence. The concentration of hydrogen in the gas declines from the initial sample to the final sample. In addition the concentration of hydrocarbons in the gas samples increases progressively in the series. The data presented in Appendix A show that a shorter retention time was used for the last sample. The higher utilization of hydrogen is then accomplished by exposure of the standard amount of feed gas to a greater weight of slurry. It is then also observed that greater conversion of the carbon monoxide in the input gas has been obtained by exposure of the standard amount of reducing gas to more slurry. Despite the more effective utilization of reducing gas, small penalties in MAF conversion, sulfur removal and solvent yield have resulted. It can be seen that process optimization involves compromises and that gains in one area frequently coincide with losses in another.

The greater utilization of carbon monoxide in the CU 37 series by comparison to the small effect observed in the preheater series tends to confirm the idea that some time is required for effective conversion of the mineral to catalytically active material. Hydrogenation either with molecular hydrogen or by reaction of carbon monoxide with water and subsequent reaction of the nascent hydrogen produced appears to be a rate process. Conversion increases with time in either process. The tendency for MAF conversions to level off at about 85% in many of the synthesis gas trials, (CU 36 and CU 37), probably is the result of use of too low an operating pressure. Neither high temperature short residence time conditions nor milder temperatures at longer residence times have materially altered the amount of organic matter which remained insoluble. It appears that conversion by the hydrogen transfer reaction may be initially high, but that the reduction potential of the reagent system may not be sufficiently high to maintain this distribution of products. Some reversion by repolymerization is likely.

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Evaluation of Experiments CU 38A & CU 38B

In previous experiments the preheater and the dissolver had been operated at the same temperature. The objective in this set of experiments was to explore the effect of operating the preheater and the dissolver at different temperatures. The choice of the temperature was influenced by current interest in high temperature short retention time reactions. The study was done with Kentucky No. 9 coal using hydrogenated anthracene oil as solvent, and with hydrogen as the reducing gas. The usual intervals were used for reactor lineout at startup and between samples.

Operation	1/LHSV hr.	Temp. PH/Diss.	Pressure psig
Condition lineout on flush oil			
Composition lineout on slurry 3 hours			
Collect sample CU 38A for 1 hour	0.98	500/450	1000
Composition lineout on slurry 5 hours			
Collect sample CU 38B for ½ hour	0.41	450/500	1000

Discussion of Results:

The products from the reactor were analyzed by blackness and IR measurements as usual. Because no water was added to the slurry and the experiments were of comparatively short duration the usual control procedures for slurry composition were not used. The gaseous products were sampled for analysis as usual. The results for IR and blackness measurements are reported in Appendix A. The results for analysis of product gases will be presented below.

ANALYSIS OF PRODUCT GASES FOR RUN CU 38
(Normalized air and moisture free basis)

GAS (MOL %)	CU 38A	CU 38B
Hydrogen	73.8	74.1
Nitrogen	6.64	5.91
Methane	10.1	9.74
Ethane	3.35	2.64
Propane	1.44	0.99
n-Butane	0.32	0.23
Isobutane	0.10	0.06
Carbon Dioxide	1.11	1.84
Carbon Monoxide	0.62	0.55
Hydrogen Sulfide	2.53	3.89
Moles per Hour	3.570	4.499

In both trials the hydrogen input was nominally 4.4 moles per hour. This is 4.98% by weight of the feed coal in experiment CU 38A or 1.66% by weight of the slurry used. Probably this is an adequate amount of hydrogen to prepare a filterable solution. The same amount of hydrogen was used for experiment CU 38B. The increased amount of slurry used reduced the relative amount of hydrogen to only 2.07% of the feed coal, or only 0.69% of the slurry. All of the hydrogen supplied can not be used because the reaction rate slows down as the partial pressure of the residual hydrogen declines. The amount of hydrogen which remains unreacted can be determined from the gas analysis results. From these results it can be calculated that 3.53 grams per hour of hydrogen were reacted in experiment CU 38A. This is only 0.666% based on the feed slurry or 2.47% based on the MAF coal. At the greater slurry feed rate used in CU 38B, only 2.03 grams of hydrogen were used. This is 0.161% of the slurry fed, or 0.59% based on the MAF coal. Preparation of filterable solutions has depended on the utilization of reactive hydrogen from the solvent in both cases, but especially in the second case has this been an essential factor. The IR values for the reclaimed cut 2 solvent have been reduced from the 0.98 value of the input solvent to 0.80 in both cases.

The yield of total reclaim solvent in experiment CU 38A is quite favorable and the vacuum bottoms are reasonably well desulfurized as well. From these considerations the temperature profile and the retention time used appear to be reasonably satisfactory. The hydrogen content of the reclaimed solvent is still lower than the hydrogen content of the initial solvent and some adjustment of conditions would be needed to correct this compositional problem. The conditions used in experiment CU 38B are unsatisfactory since some loss of solvent as well as poor sulfur removal was observed.

In some previous experiments it had been observed that exposure of the reducing gas to more slurry had increased the utilization of the reducing gas even though the percentage on the slurry basis declined. In experiment CU 38B even the net weight of hydrogen reacted declined as the amount of slurry was increased. The MAF conversion was materially less than had been seen in some of the preceding preheater studies. This leads to the conclusion that the initial solution reaction has been followed by considerable reversion of the solution to form polymer. The low utilization of hydrogen may well be the consequence of coating the minerals with polymeric shells derived from the coal solution. This is a common problem in catalysis and the minerals in the coal are as subject to this kind of activity reduction as any other supported catalyst. When this is considered, the use of certain extreme conditions becomes clearly unwarranted. In conditions in which the MAF conversion has been shown to reach a minimum then increase as more severe conditions are imposed, coating of the active surfaces of the catalyst becomes a risk.

CU 38

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Experiment CU 38A was the second time that a temperature profile had been used. One previous trial, experiment CU 28B, had been run. In that experiment the preheater was operated at 450°C and the dissolver was operated at 425°C. At a slurry feed rate of 1030 grams per hour the reaction had produced a 91.36% MAF conversion. Evidently these temperatures are better suited for the initial depolymerization step than the higher temperatures and longer retention times used in either CU 38A or CU 38B. The removal of sulfur was appreciably less in CU 28B however. The results of the two different series taken together suggest that the optimum time and temperature for depolymerization could be established in the preheater leaving the dissolver for further processing of the raw solution. One of the main functions of the dissolver would be the rehydrogenation of the product solution. In this system the benefit of producing a reactive solvent would appear when the reactive solvent was returned in new slurry.

GENERAL DISCUSSION

General Discussion:

After experiment CU 38 was completed an attempt was made to continue the study of preheater conditions with high temperatures and slightly longer retention times. This attempt was run CU 39 which used Kentucky No. 9 coal, CL 18 hydrogenated anthracene oil as solvent, and hydrogen at 1000 psig as reducing gas. The retention time was increased to 1/LHSV = 0.243. At this operating condition the preheater tube was plugged in about two hours of operation. It is clear from these observations that the cracking reactions which depolymerize the coal will progress satisfactorily until the hydrogen transfer rate to the coal declines as the result of depletion of these functions in the solvent. The presence of hydrogen and catalytic minerals tends to lengthen the time of exposure allowed at lower temperatures and adds to the effectiveness of the solvent available. As the temperature is increased the solvent may be depleted to the extent that the system in the preheater begins to form polymer. At a hot surface the polymer may coat out as a film and eventually form a carbon rich deposit which will no longer dissolve. The tube will eventually plug with a coke like deposit under such conditions.

There are limits in a vessel which relate the temperature, the time, and the composition of the feed slurry which may not be exceeded without formation of excessive amounts of polymer. At lower temperatures polymer may redissolve in the dissolver as reaction time and exposure to hydrogen work on the preheater product. At higher preheater temperatures the tendency will be for the reaction to continue in the direction of producing coke. The time effect and the temperature effect interchange so long as the product does not come too close to the polymer formation boundary. At this boundary the wall temperature must not be too high or progressive deposition of carbon on the tube wall will be observed. In addition carbon (or more likely polymer) will also deposit on the mineral phases present. This will tend to reduce the catalysis available from the minerals. Such conditions also result in increasing amounts of insoluble organic matter and reduced MAF conversion. Generally such conditions are also observed to produce high blackness solutions. These experiments have not been done with equipment which is known to simulate the behavior of plant equipment. The temperatures and the times which produce coke deposits in the laboratory may not be predictive for other equipment. It will therefore be necessary to work out limits for time, temperature, and compositional parameters by progressive testing, and perhaps by eventual risk of pilot plant scale vessels. One laboratory test may be helpful in identifying risk regions, since the blackness will normally be high as risk regions are approached. The limit for solution blackness is also not well established, although values in the vicinity of 15 probably should be considered high with conventional feeds (as with a 2:1 slurry for example).

After experiment CU 39 it was necessary to dismantle the equipment and modify it for the solvent preparation run, CU 40. This work has been previously reported in section IV-C-3 of this report.

Work was then continued with Elkol subbituminous coal using the new lot of solvent. One preliminary study has already been reported using the CL 18 hydrogenated anthracene oil solvent. Evaluation of subsequent experiments will be reported in the following section of the report.

CU 41 through CU 47

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Evaluation of Experiments with Elkol Subbituminous Coal

A preliminary series of studies with the Elkol coal has been reported. (See the discussion of experiment CU 30A through CU 30H) These trials were done with CL 18 hydrogenated anthracene oil as solvent. The reducing gas was hydrogen for CU 30A and was a 1:3 mixture of carbon monoxide and hydrogen for the remaining trials. The results with pure hydrogen had been better than the results with the synthesis gas mixture at similar conditions. In all cases the MAF conversions had been marginal with conversions tending to decline with increasing exposure to heat in the process. It appeared that most of the solution observed was the result of the hydrogen transfer process, and that the solution had little tendency to become rehydrogenated by continued exposure to hydrogen or to the synthesis gas mixture and heat.

The experiments with Elkol were interrupted by frequent stoppages caused by plugging of the preheater and by failures of the feed pump. The experiments were planned to produce long series of samples at different operating conditions, an objective never realized in the course of these studies. Some of the stoppages are clearly the result of formation of plugs in the preheater, while others appear to be the result of plugging of the ball checks in the Speed Ranger pump head. In retrospect, improved reliability could have been obtained by sieving the coal to meet the particle size requirements of the pump head. The study would still have encountered chemical reaction problems which are the consequence of the coal and solvent compositions used.

The ratio of solvent to raw coal was made 1.5 to 1 for experiment CU 41. This was done in the hope that the coal rich ratio would compensate for the water burden in the feed coal and result in MAF coal concentrations similar to the concentrations used in the Kentucky No. 9 coal reactions. The operating details for experiment CU 41 follow.

Operation	1/LHSV Hr.	Temp. °C	Pressure psig
Condition lineout on flush oil			
Composition lineout on slurry for 7 hours* Collect sample CU 41A for ½ hour	0.32	425	1000
Composition lineout on slurry for 2 hours Collect sample CU 41B for ½ hour	0.52	425	1000
Composition lineout on slurry for approx. 3/4 hour to preheater plug	1.0	425	1000

* Preliminary lineout interrupted by rupture disc failure at feed pump at 5th hour. After replacement of rupture disc the pump head had to be removed and cleaned before the experiment could be restarted.

CU 41 through CU 47

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Discussion of Results

The attempt to work up the CU 41 product samples by filtration failed. It was therefore necessary to estimate the amount of solvent which could be reclaimed by distillation of the unfiltered sample. Pyridine washed insolubles were prepared from residues of insoluble material resulting from attempts to filter the solutions. MAF conversions are reported from the ash enrichment results.

Slurry samples were taken for analysis before the collection of the product sample was started and after collection of the product sample was completed. The main interest was the retention of water by the feed slurry. Ash analysis was not done for these trials. The composition of the feed coal is reported in Appendix B item 4. As received, the coal contained 18.97% moisture which should have resulted in 7.6% of water in the feed slurry. The samples were drawn into bottles which were sealed with polyethylene lined lids and saved for subsequent analysis. The samples for all of the Elkol experiments were run as a block. Retention of water by the slurry was reasonably good and results for the initial samples are close to theoretical values. This is a consequence of the tendency for the water in the subbituminous coal to be a hydrate or absorbed in the coal particle rather than to be present as a film of free water. In this situation better retention of water by the slurry is observed than is usual with water added to a Kentucky No. 9 coal, for example.

The difficult filterability of the solutions made in experiment CU 41 forced a return to a more dilute coal slurry in subsequent experiments. These were all formulated with 2 parts of solvent to 1 part of raw coal. At 18.97% water in the coal, the slurry should have contained 6.32% of water. Adjustment of the concentration of coal in the feed slurry resulted in solutions which could be filtered. Results of subsequent trials are therefore more satisfactory since the standard workup procedure could be used.

Results for water analysis of the feed slurry and for blackness and $\overline{IR}$ values for product solutions are presented below. The new solvent had an $\overline{IR}$ of 0.75.

Sample	% Water in Feed Slurry	Solution Blackness	$\overline{IR}$ Value of Solution	$\overline{IR}$ Value of Cut 2
CU 41A-1	7.05			
CU 41A-2	6.48	10.51	0.97	0.65
CU 41B-1	6.14			
CU 41B-2	6.09	10.93	0.93	0.65
CU 41C*		9.72	0.81	

* Slop vessel sample representing lineout material made before preheater plug formed.

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ANALYSIS OF PRODUCT GASES FOR RUN CU 41
(Normalized air and moisture free basis)

GAS (MOL %)	CU 41A	CU 41B
Hydrogen	81.4	83.9
Nitrogen	4.31	4.34
Methane	2.28	2.03
Ethane	0.92	1.04
Propane	0.68	0.62
n-Butane	0.19	0.15
Isobutane	0.12	0.10
Carbon Dioxide	8.14	5.84
Carbon Monoxide	1.20	1.33
Hydrogen Sulfide	0.81	0.61
Moles per hour	6.225	5.744

Hydrogen was fed to the reactor at the rate of 4.5 moles per hour. These gas analysis results indicate that more hydrogen was in the gaseous products than was fed into the reactor.

The CU 40 hydrogenated anthracene oil had been processed with a limited amount of hydrogen and the amount of reactive hydrogen present was reduced to about half the concentration present in the CL 18 solvent used previously. The $\overline{IR}$ Value for a typical raw anthracene oil will be about 0.5 to 0.6 depending on the source. The $\overline{IR}$ for CU 40 solvent product was 0.75 while the $\overline{IR}$ for the CL 18 solvent was 0.98. As could be expected the decrease in the hydrogen content of the solvent resulted in a less reactive material and the increase in the concentration of Elkol in experiment CU 41 feed slurry would have required more hydrogen transfer for proper decomposition of the coal. The consequence was that the conversion dropped off compared to conversions in the CU 30 series and the solutions obtained were unfilterable as well. The reaction was not well completed, and the failure to recover break even amounts of solvent from the solution is a good indication of the extent of the shortage of reagent in this case. Since solvent recovery is far short of break even, the molecular weight distribution of the reclaimed solvent will be skewed to the lower end of the solvent array. The $\overline{IR}$ values obtained for the reclaimed cut 2 will then be higher than would be the case for a complete cut 2 distribution, and the fact that the value is higher than the value for a raw anthracene oil can not be construed to mean that the transfer capacity of the solvent has not been exhausted. The distillation range for the CU 41A reclaim was 54° to 175°C and for the CU 41B reclaim was 67°C to 145°C. The use of longer reaction time therefore resulted in more interaction product derived from solvent and coal. Note that the blackness of the solution increased from CU 41A to CU 41B.

Experiments CU 42 and CU 43 were done with a reduced concentration of feed coal in the slurry. Operating procedures are summarized below.

CU 41 through CU 47

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Operation	1/LHSV Hr.	Temp. °C	Pressure psig
Condition lineout on flush oil			
Composition lineout on slurry 2 hours Collect sample CU 42A for ½ hour	0.34	450	1000
Composition lineout on slurry 2 hours Collect sample CU 42B for ½ hour	0.49	450	1000
Composition lineout on slurry for approx. 1½ hours to preheater plug	1.0	450	1000
Condition lineout on flush oil			
Composition lineout on slurry 5 hours* Collect sample CU 43A for 1 hour	0.67	425	1000
Composition lineout on slurry 3 hours Collect sample CU 43B for 1 hour	0.98	425	1000
Composition lineout on slurry approx. 2½ hours to plug in preheater	1.33	425	1000

* Composition lineout interrupted by coal plugs in the Speed Ranger pump head after ½ hour of operation and again after 1½ hours of operation. Coal for experiment CU 43 had been sieved to -100 mesh. From subsequent experience and the plugging observed here this was not fine enough to allow reliable feeding of the coal with this pump head.

The results for water analysis of the feed slurry and for blackness and $\overline{IR}$ values for product solutions are presented below. These slurries were formulated with 2:1 solvent to coal ratios, therefore the water content of a freshly formulated slurry should be 6.32%.

Sample	% Water in Feed Slurry	Solution Blackness	$\overline{IR}$ Value of Solution	$\overline{IR}$ Value of Cut 2
CU 42A-1	6.78%			
CU 42A-2	5.99	14.40	0.74	0.54
CU 42B-1	5.56			
CU 42B-2	5.29	14.19	0.77	0.55
CU 43A-1	5.33			
CU 43A-2	5.27	13.01	0.86	0.65
CU 43B-1	3.41			
CU 43B-2	3.39	12.83	0.83	0.65

CU 41 through CU 47

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In these experiments more difficulty was observed in maintaining the concentration of water in the feed slurry. The temperature recorded for the feed slurry was 40°C and readings were not taken with great frequency. The stirring and pumping through the slurry feed loop tends to heat the slurry and the probability of higher temperatures than this as the feed volume is reduced is real. The temperatures often have been noted to rise to 50°C in this apparatus.

The decrease in the concentration of feed coal resulted in a higher MAF conversion, and solution of the more refractory fractions of the coal was observed to produce a darker colored solution. This change was due to the use of higher temperatures or longer retention times as well, therefore it is difficult to compare results from these experiments directly with previous experimental results. The more striking improvement was in the recovery of reclaimed solvent as well as the preparation of filterable solutions in this set of experiments. However none of the solutions allowed the recovery of a break even quantity of solvent.

ANALYSIS OF PRODUCT GASES FOR RUNS CU 42 & CU 43
(Normalized air and moisture free basis)

GAS (MOL %)	CU 42A	CU 42B	CU 43A	CU 43B
Hydrogen	75.9	78.6	86.7	88.7
Nitrogen	4.20	4.40	4.54	4.33
Methane	6.61	6.00	2.41	2.07
Ethane	2.56	2.24	0.70	0.60
Propane	1.11	1.04	0.38	0.32
n-Butane	0.20	0.16	0.12	0.13
Isobutane	0.09	0.08	0.06	0.05
Carbon Dioxide	7.06	5.67	3.82	2.66
Carbon Monoxide	1.49	1.25	0.90	0.69
Hydrogen Sulfide	0.84	0.63	0.41	0.41
Moles per Hour	6.669	6.309	5.677	5.521

The hydrogen input in these experiments was nominally 4.5 moles per hour. Here again the amount of hydrogen observed in the product gases exceeded the amount fed to the reactor originally. The decline in the IR value for the reclaimed solvent indicates substantial dehydrogenation of the solvent, a change sufficient to produce material equivalent to raw anthracene oil in composition for the material used at 450°C and to reduce the concentration of hydrogen appreciably in the material used at 425°C. The CU 40 solvent contained 6.04% hydrogen and the raw anthracene oil which was hydrogenated to make this solvent contained 5.77% hydrogen. Reversion to the raw anthracene oil composition would then liberate about 0.3% hydrogen from the solvent. The slurry used in CU 42A weighed 1510 grams, 2/3 of which was solvent. This would supply 1.5 moles of hydrogen to the system in addition to the 4.5 moles fed as molecular hydrogen. The output gas contains 5.05 moles of hydrogen in this case, which indicates that about 0.55 moles of molecular hydrogen were released in the course of the coal solution reaction. Some hydrogen was used to form methane and other hydrocarbon gases, hydrogen sulfide, and water. These observations were repeated throughout the work with Elkol and indicate that catalytic effects which tend to induce hydrogenation of the products are minimal for this coal.

It is noteworthy that as retention time is extended the amount of reclaim solvent declines, and that the MAF conversion also declines. This observation can be checked with data at 425°C in CU 41A and CU 41B at the higher concentration of coal in the slurry, and again at 450°C in CU 42A and CU 42B at the 2:1 ratio of solvent to coal. This behaviour appears at 425°C with the 2:1 ratio of solvent to coal in the results reported for CU 43A and CU 43B. Thus continued exposure to heat and hydrogen does not increase the conversion or the yield of useful material.

As a consequence of this observation the following experiments were done at shorter retention times to determine if any condition would produce useful solutions. Pumping difficulties and preheater tube plugging continued to prevent the completion of experimental sequences planned. Each new startup is given a new experiment number, and it can be seen that completion of only one or two points per startup was the rule in the Elkol series. The operations for the remaining experiments are summarized below.

Operation	1/LHSV Hr.	Temp. °C	Pressure psig
Condition lineout on flush oil			
Composition lineout on slurry 3 hours Collect sample CU 44 for 50 minutes*	0.42	450	1000
Condition lineout on flush oil			
Composition lineout on slurry 3 hours Collect sample CU 45A for ½ hour	0.25	450	1000
Composition lineout on slurry 2 hours Collect sample CU 45B for ½ hour **	0.26	475	1000
Condition lineout on flush oil			
Composition lineout on slurry 5 hours Collect sample CU 46A for ½ hour***	0.17	450	1000
Condition lineout on flush oil			
Composition lineout on slurry 1½ hours Collect sample CU 47A****	0.037	450	1000

* Stopped by plug in preheater resulting from progressive deposition of carbon in preheater.

** Stopped by plug in preheater during condition lineout for CU 45C.

*** Stopped by plug in preheater during condition lineout for CU 46B.

****Stopped by plug in preheater during condition lineout for CU 47B.

At the higher temperatures the preheater plugged frequently. This may have been clearly the result of carbon deposition, as was the case in experiment CU 44, or may have been precipitated by flow stoppages resulting from plugging of the pump head by oversize coal particles. At these temperatures the solution is thermally unstable and too slow a feed rate or a stoppage of flow will either one result in plugs of carbon in the preheater. Most of the plugs formed as the result of increasing the temperature to line out for a new sample at 475°C or at 500°C. Such temperatures are not suitable with a solvent such as CU 40 hydrogenated anthracene oil even at quite short exposure times. In the case of Elkol coal little contribution from catalytic hydrogen mechanisms is evident and the tendency for the system to deposit carbon is observed at lower temperatures and shorter retention times than would likely be the case with Kentucky No. 9 coal. As a general observation more hydrogen appears in the product gases from the reaction than should be fed into the reactor initially.

The usual observations of blackness, infrared spectral results, and composition of feed slurry were made in these experiments. Data are tabulated below.

Sample	% Water in Feed Slurry	Solution Blackness	$\overline{\text{IR}}$ Value of Solution	$\overline{\text{IR}}$ Value of Cut 2
CU 44A-1	6.09			
CU 44A-2	5.95	16.80	0.75	0.57
CU 45A-1	5.17			
CU 45A-2	5.40	13.11	0.77	0.56
CU 45B-1	5.37			
CU 45B-2	5.02	16.75	0.69	0.53
CU 46A-1	5.97			
CU 46A-2	5.64	14.30	0.92	0.60
CU 47A-1	6.16			
CU 47A-2	5.45	8.67	0.99	0.67

It can be seen that the water content of the feed slurry declines as time of exposure to air and heat from stirring increases. The initial sample is usually close to the theoretical result based on the composition and the water content of the coal. As make up slurry additions are made the downward drift in water concentration is partially corrected but long experiments usually have been completed with less water in the slurry than planned. In these short trials this has not been a problem.

The blackness of the solution increases with time and with temperature and some of the highest values observed were obtained with Elkol coal. Since the preheater plugged frequently during these experiments it may be supposed that such color intensity indicates the accumulation of a high concentration of repolymerizing material in the solution. The values of 15 or more obtained here must be near the limit at which carbon deposition will be observed at bothersome rates. This is also observed by the tendency for the $\overline{\text{IR}}$ values of the product solution to decline and for the Cut 2 solvent to be dehydrogenated to compositions similar to raw anthracene oil. Loss of solvent was observed in all experiments except CU 47A. Here the preheater only was used as the reaction vessel and the high temperature short retention time condition limited the reaction to the initial hydrogen transfer step effectively. The preheater experiment would appear conclusive in showing that Elkol is dissolved by the hydrogen transfer mechanism while it contains very little of the material which causes the hydrogenation to operate to rejuvinate the solvent or continue with decomposition of the initial depolymerization products in the case of Kentucky No. 9 coal.

It is therefore instructive to return to the information in Appendix B item 5. The reactivity of the Kentucky No. 9 coal appears to be well established and the outstanding difference between this coal mineral analysis and the analysis for the Elkol is the difference in the amount of pyritic iron present. The Kentucky No. 9 coal contains 9.0% or 10.0% of ash and this ash may be 15% to 20% iron derived mostly from pyrite. The Elkol contains less than 3% ash and this is in turn only about 3% iron.

Lignite used in these studies contains about 7% to 8% ash. Nearly 10% of this ash is iron and the iron is derived partly from pyrite and is partly bound in the lignite as an ion exchangable metallic ion. This can be extracted from the coal by means of dilute hydrochloric acid for example. In addition the lignite contains a significant amount of sodium which can be removed from the coal by ion exchange with calcium choloride or by dilute hydrochloric acid extraction. Lignite therefore shows some tendency to react with pure hydrogen because the iron which is present is sufficient to sustain a modest reaction rate. In addition the alkaline ions as well as iron appear to facilitate the reaction of carbon monoxide with water to produce hydrogenation by a nascent hydrogen mechanism. It is therefore practical to process lignite with hydrogen or with mixtures of hydrogen and carbon monoxide if partial pressures and reaction times are adjusted to meet the compositional requirements. It is not clear that sodium ion will be effective in the complete absence of iron since it is difficult to extract all iron from lignite. It is established that removal of sodium from the lignite does reduce the reaction of lignite in the presence of carbon monoxide and water. The difficulties in processing the Elkol sample are best explained by the low concentration of iron or alkaline ions such as sodium or potassium which are present. This is a common observation with subbituminous coals and may extend into certain lignites as well.

It seems to be established that the hydrogen transfer reaction can be used alone to dissolve the subbituminous coals, the lignite coals, or the bituminous coals. This is a rapid reaction and the ratio of solvent to coal as well as the time and temperatures will have considerable influence on the amount of depolymerization which can be obtained. The composition of the solvent can be modified by a catalytic hydrogenation which is designed to add a limited amount of hydrogen to a highly aromatic stock. In this regard anthracene oil is well suited for use as a solvent stock.

The mineral phases in certain coals can be used as catalysts which will facilitate rehydrogenation of the solvent. In this case the initial depolymerization may be due to hydrogen transfer or if a raw solvent is used the process may be largely under the control of the catalytic effect of the minerals throughout. It is therefore possible to use mixed mechanisms with the Kentucky No. 9 coal or to operate under conditions dominated either by hydrogen transfer, or by the catalytic mechanism. It is not clearly established that any of these modes is superior to the others nor is it easy to estimate the contribution of each in the usual experimental study. It seems well established that enough high sulfur bituminous coal, in which a large part of the sulfur is due to the presence of pyrite, exists to make it worth while to better define the utility of iron sulfide as a hydrogenation catalyst.

Ultimately the reactivity of a coal will need to be defined in terms of its inherent catalytic mineral content and the recycle solvent which can be made from the coal by manipulation of reactor variables. If the coal is not itself reactive enough, the material will need to be supplemented by the addition of a catalyst to the coal, or inserted into the reaction as a supported catalyst in the dissolver loop or in a solvent treatment loop. Probably none of these alternatives can be effectively managed without first defining the base activity of the coal.

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Evaluation of Experiment CU 48 (Samples CU 48A-1 & CU 48A-2)

This experiment was done with several objectives in mind. The CU 40 hydrogenated anthracene oil solvent preparation had been used only with Elkol subbituminous coal. Results in this series of experiments had been disappointing and it was considered necessary to demonstrate that the CU 40 solvent would perform normally with a reactive coal. A run with Kentucky No. 9 coal was used to verify the quality of the CU 40 solvent for use in subsequent experiments. A long reaction study was planned to show that reaction conditions and product compositions could be maintained for an extended period of time. Samples were taken after an initial lineout period and again after a day of operation to study reproducibility. These samples were carefully prepared and were used for an elemental balance study and for related analytical technique studies which were done at the request of the Environmental Protection Agency. Finally it was planned to use the coal solution made in the long intervals between the collection of analytical samples for exploratory work aimed at developing methods for using coal solution instead of redistilled solvent in the solvent refining process.

Reaction conditions were chosen from previous experimental data to give a break even amount of total reclaim solvent together with reasonably effective removal of sulfur from the vacuum bottoms obtained. The preheater and the dissolver were both operated at 450°C. The slurry feed rate was adjusted to give a cold slurry retention time of about a half hour. The hydrogen input was set at 5.6 moles per hour. This corresponds to only 1.1% hydrogen based on the weight of feed slurry or only 3.3% based on the weight of coal fed. The reactor was operated at 1000 psig total pressure.

The experiment was conducted in the usual way to obtain lined out samples. The desired operating conditions were established using flush oil as the fluid phase in the reactors. The feed was then switched to slurry and the reactors were operated for nine hours to establish compositional lineout before the first analytical sample was collected. Sample CU 48A-1 was collected for a one hour period, and the gas sample was collected for the last 45 minutes of the sampling interval. The reaction was maintained for a 24 hour period and then the CU 48A-2 sample was collected. Slurry samples were taken for water analysis before and after each of the hour long samples were collected. The product made during the lineout and between the samples collected for evaluation was delivered to the slop vessel and was saved for use in subsequent exploratory work.

Discussion of Results

The two samples taken for analysis were worked up by standard procedures, including filtration of the stripped solution and distillation of the filtered solution to determine the amount of solvent and vacuum bottoms in the solution. The results obtained from the routine workup of these samples are presented in Appendix A part 12. The operating conditions which were used in CU 48 match the conditions used in CU 28A-1 and CU 28A-2, in which the CL 18 hydrogenated anthracene oil was used as solvent, and

CU 29A, in which the middle fraction of raw anthracene oil was used as solvent. Comparison of results for these three sets of experiments allows estimation of the effect of three different levels of hydrogen transfer on the reaction. The raw anthracene oil has the lowest amount of reactive hydrogen, the CU 40 solvent used in the CU 48 experiment has an intermediate concentration of hydrogen transfer capacity, and the CL 18 solvent has the highest concentration of reactive hydrogen in the sets compared. None of the solvents have been extensively reacted and the level of reactive hydrogen in CL 18 solvent is probably less than half of the reactive hydrogen which could be put into the solvent if this reaction were run to completion. Results selected from Appendix A are presented below. Although a change in the concentration of reactive hydrogen is the main variable in the comparison the results are slightly irregular, an observation which suggests that this may not be the only factor involved. The operating conditions were matched well from trial to trial and this should not be a factor.

Comparison of Solvent Reactivity at Different Total Hydrogen Concentrations

Sample	Solvent	% Total Hydrogen	Solution Blackness	$\overline{\text{IR}}$ Value Cut 2	% Excess Solvent	& MAF Conversion	% Sulfur in V.B.
CU 29A	MFRAO	5.77	14.44	0.66	0.21	87.14	1.05
CU 48A-1	CU 40	6.04	11.65	0.74	2.88	82.85	0.88
CU 48A-2	CU 40	6.04	12.26	0.76	5.36	85.09	0.94
CU 28A-1	CL 18	6.20	11.04	0.74	9.98	89.18	0.97
CU 28A-2	CL 18	6.20	11.11	0.77	6.00	99.90	1.04

In the comparison of results the total hydrogen content of the solvent was expected to relate closely to the increase in transferable hydrogen available. This is probably true for comparisons between MFRAO and the CL 18 hydrogenated anthracene oil, since the CL 18 product was made by hydrogenation of the raw anthracene oil. In preparing the CU 40 solvent some oil retained from the process development plant was added to the hydrogenation product. This added a small amount of oxygen containing material as well as some coal derived hydrocarbons. The increase in hydrogen compared to raw anthracene oil may not all be due to reactive hydrogen in this case. This may be the explanation for the slightly lower MAF conversion in the CU 48 experiments.

The MFRAO, which contained the least hydrogen, produced no excess solvent and also produced the blackest solution. This condition must run the reaction to the brink of repolymerization onset. A great deal of repolymerization is unlikely since the MAF conversion is comparatively high. The reclaimed cut 2 solvent has gained a small amount of hydrogen compared to the original raw anthracene oil used. In the runs with higher concentrations of hydrogen in the solvent the hydrogen in the cut 2 reclaim solvent was adjusted to about 6.03%. For the CU 40 solvent this resulted in substantially no change in the hydrogen output compared to the hydrogen input of the solvent. The CL 18 solvent lost hydrogen, the input value of 6.20% in the solvent being reduced to about 6.03% based on the infrared spectra of the input and output solvents. The more reactive solvent produced a less colored solution, but the big difference is the increase in solvent range material in the solution. A minor change in the MAF conversion was also observed.

It appears from these results that at 450°C the hydrogen content of the solvent will become adjusted to about 6.03%. This may be compared to a value of about 5.75% in the raw anthracene oil used initially. Some of the hydrogen in the reclaimed solvent is in coal derived hydrocarbons and this may not be all reactive. However, the greater part of the hydrogen should be capable of hydrogen transfer activity. Thus it can be estimated that about 0.3% of reactive hydrogen may be available in the solvent at 450°C. This could be considered as potentially in transit from a catalytic surface to the coal being reacted. The transfer reaction is rapid, therefore an excess of reactive hydrogen in the solvent may be rapidly consumed. This is the apparent cause for the increase in liquid product yield using CL 18 solvent. Once the excess of reagent is consumed the reaction rate declines to that rate allowed by the transfer of hydrogen gas to the solvent. This depends on the partial pressure of hydrogen present and the catalytic effect of the coal minerals. Solvent compositions at lower operating temperatures are richer in hydrogen. This may be due to the slower transfer rate of hydrogen from the solvent, or to a faster hydrogenation rate at the lower temperature. It should be borne in mind that the numerical values used here are only applicable for a solvent that is mostly anthracene oil. As coal derived oil builds up in the solvent more hydrogen in the substituent radicals on the aromatic rings derived from the coal will be evident. Here estimates of hydrogen with potential transfer reactivity become difficult and estimates of the reactivity of the solvent can no longer be made directly from measurements of the total hydrogen present.

At the time the CU 40 solvent was made this kind of problem had not been defined. The relation of reactivity to total hydrogen content had been assumed to be more direct than now appears likely. As the composition of reclaimed solvent made in the Process Development Plant was more fully understood it became increasingly clear that the addition of this fraction to the solvent blend in CU 40 had slightly skewed the compositional relationships and that the hydrogen functional group distribution was not the same as in CL 18. A greater fraction of the increase in total hydrogen is likely to be invested in inert functions in the CU 40 solvent than in the CL 18 solvent.

On the basis of these data the tie between desulfurization and solvent yields does not appear to be very direct. Effective sulfur removal appears to depend on breaking many bonds. Solvent production depends more on the effective capping of free radicals while molecules are still small. It may be that rapid capping of radicals interferes with reactions removing sulfur. At least sulfur is eliminated more effectively by increasing temperature than by improving solvent quality. Thus conditions which favor sulfur removal tend to generate more gas and do not favor the production of solvent or the preparation of reactive solvent, which on recycle would favor production of more solvent.

The tendency for the yield of liquid in the solvent range to increase in the long duration run suggests that some classification of mineral matter on a long time schedule may be expected. This could slowly build up the reactivity for some time. The observation made in run CU 48 has been repeated in later work and the data here would be of doubtful significance if no confirming evidence were available from other experience.

At the time the CU 48 experiments were done it was considered sufficient that the input and reclaim solvent maintained constant composition for percentage hydrogen and that a sufficient total reclaim solvent be obtained for recycle. Since then it has become apparent that the functional group distribution could change during recycle. To stabilize reactivity therefore would require that the hydrogen functional group distribution be stabilized and reproduced well from pass to pass of the solvent. Observation of long term drifts in the reactor then adds a complication to this kind of stabilization study.

Such observations led to consideration of methods for establishing the composition and reactivity of solvent recycled to equilibrium. This was one of the motives for interest in using the coal solution as solvent instead of redistilled solvent. This kind of procedure appeared capable of building up the concentration of coal derived oil at a faster rate and with less labor than would be required in the conventional mode of operation. The material saved between sample collection periods was reserved for exploratory work in an effort to develop practical methods for using coal solution as solvent. It was found that filtered solution could be mixed with fresh coal and that such material could be pumped through the reactor without particular difficulty. None of the conditions used produced filterable solutions and at the higher temperatures this kind of material was observed to polymerize and plug the preheater with coke more readily than standard reaction feeds. These efforts were generally unsuccessful since the solutions were either unfilterable in the laboratory, or coked the preheater. All experiments were done with 1000 psig hydrogen and with temperatures which were comparatively high.

As a result of these explorations it was concluded that the operating procedures needed to be substantially modified in order to use the solution as solvent in the process. The further discussion of this aspect of the experiment will be reserved for later, since a more successful trial was run in experiment CU 49.

ELEMENTAL BALANCES AND ANALYTICAL METHODS STUDIES

A detailed report concerned with elemental balances in the Solvent Refined Coal process has been prepared for the Environmental Protection Agency, (Sulfur and Nitrogen Balances in the Solvent Refined Coal Process, EPA-650/2-75-011).

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This describes the operating procedures, the apparatus, sample preparation, and analysis in great detail. It does not seem worthwhile to repeat such detail in this summary. Comments will therefore be limited to the presentation of some of the summary tables and to the presentation of the conclusions resulting from the elemental balance studies.

The attempt to develop an accurate elemental balance required that operating procedures be refined as much as possible in order to obtain an accurate material balance. Some systematic errors resulting from loss of water and possibly loss of some light oil from the feed vessel appear to preclude complete closure of the material balance. The problem is further complicated by settling of minerals from the feed slurry, and by settling of minerals in the reactor vessels. In initial samples the mineral settling results in samples too rich in organic matter and deficient in ash minerals. After an extended reaction time the mineral concentration of the reactor effluent begins to oscillate and may be either higher or lower than the equilibrium concentration expected from feed slurry composition.

Thus even when long lineout times are used it is not likely that a sample taken over a short time interval (an hour for example) will contain exactly the theoretical amount of ash. The ash contains an appreciable concentration of sulfur therefore a sulfur balance can not be obtained in practice without forcing an ash balance. The bomb combustion method is suitable for sulfur analysis for most of the normal products from the reaction. Complete combustion of the mineral rich samples, such as pyridine insolubles, or filter cakes is difficult in the oxygen bomb since the samples are often too lean in organic matter to burn properly. The preferred method for analysis for such samples is the Eschka fusion method to decompose the sample followed by the usual gravimetric finish. Hydrogen sulfide is determined volumetrically in the gaseous products with sufficient accuracy by bubbling the gas through ammoniacal zinc or cadmium sulfate solution and then titrating the sulfide iodimetrically. By using these methods the sulfur balance can be closed to account for 98% or so of the sulfur in the system. The validity of the samples is further substantiated by accountability of carbon and hydrogen with similar accuracy. A forced ash balance is necessary to obtain a good sulfur balance.

In preliminary trials the nitrogen balance was obtained using analytical results by Kjeldahl determination methods. These balances were peculiar in showing the presence of more nitrogen in the reaction products than had been determined for the feed materials. It was assumed that this was due to incomplete determination of nitrogen in the feed coal and perhaps also to incomplete determination of nitrogen in the feed solvent. This is not an uncommon problem with nitrogen contained in heterocyclic structures.

Another attempt was therefore made to improve the balance by using nitrogen results from the Dumas method. This work was done by the Schwarzkopff Microanalytical Laboratory. It was observed that many of the samples gave variable results, in which the percentage of nitrogen determined appeared to increase as the sample size was reduced. This was consistent with previous observations, using the Coleman Nitrogen Analyzer, in our laboratory. It was hoped that this was an indication that this effect was caused by formation of coke with this coke formation becoming more of a problem as the sample size increased. The nitrogen was then estimated by extrapolation of the results to zero sample size. Unfortunately it is difficult to obtain data with sufficient precision to perform the extrapolation with reliability in all cases. The nitrogen balance calculated from the extrapolated data has the property of showing more nitrogen in the feed materials than is recovered in the products. This is perhaps a more reasonable result since loss of ammonia in the workup of the low boiling product fractions could be a problem.

In considering the accuracy of alternative methods it was found that one comparatively little used method for determination of nitrogen in coal had not yet been tested. This is the German Standard Method published as DIN 51722. 6/This method is based on the gasification of coal samples in the presence of a catalyst mixture and superheated steam. The ammonia in the condensate is trapped in standard acid and then purified by redistillation to standard acid or boric acid solution. The excess of acid is then titrated to determine the ammonia formed by gasification of the sample. This method has not been used with Kentucky coal or with solvent refined coal products long enough to establish a nitrogen balance with such results. Preliminary trials have tended to show more nitrogen in the coal and in the vacuum bottoms than determined by the Kjeldahl method. It is less clear whether such results are reliable at this stage.

The results for nitrogen balances are presented in the tables which follow and are substantially the tables presented in the Environmental Protection Agency report, (Sulfur and Nitrogen Balances in the Solvent Refined Coal Process, EPA-650/2-75-011). At this time it is considered that preferred methods for accurate determination of nitrogen in coal and Solvent Refined Coal Products remain an open question. It is possible to select combinations of data which give an apparent balance, it is less easy to defend a combination of such methods as being accurate.

FIRST TRIAL ELEMENTAL BALANCE, CU 48A1

MATERIAL	Wt. GRAMS	% C	% H	% N	% S	% ASH	GRAMS C	GRAMS H	GRAMS N	GRAMS S	GRAMS ASH
INPUT											
Feed Coal	322.3	66.34	4.57	1.29	5.12	16.04	213.8	14.72	4.157	16.501	51.70
Feed Solvent	676.8	90.58	6.04	0.60	0.36		613.0	40.90	4.061	2.436	
Feed Water	20.9		11.19					2.34			
Feed Hydrogen	11.2		100.					11.20			
TOTAL	1031.2						826.8	69.16	8.212	18.937	51.70
OUTPUT - PRIMARY SEPARATION - CORRECTED TO 100% RECOVERY OF FEED											
Gas	37.03	See table 9					15.27	11.83		5.908	
Knock Out Pot	1.1				0.547			0.123		0.006	
Cold Trap H_2O	24.2			0.38	0.821			2.707	0.092	0.199	
Cold Trap Oil	8.0	82.68	12.04	0.212	0.65		5.78	0.843	0.017	0.052	
Filtrate	768.0	90.36	6.25	0.981	0.45		693.96	48.00	7.535	3.456	
Wet Filter Cake	192.9	62.32	3.89	0.895	4.66	27.51	120.21	7.50	1.726	8.989	53.10
TOTAL	1031.2						835.22	71.00	9.370	18.61	53.10
% RECOVERY	100						101	102.6	114	98.3	102.7
OUTPUT - SECONDARY SEPARATION - CORRECTED TO 100% RECOVERY OF FEED											
Gas	37.03	See table 9					15.27	11.83		5.908	
Knock Out Pot	1.1				0.547			0.123		0.006	
Cold Trap H_2O	24.7			0.38	0.821			2.707	0.092	0.199	
Cold Trap Oil	8.0	82.63	12.04	0.212	0.65		5.78	0.843	0.017	0.052	
Cut 1 Oil	29.9	87.47	7.99	0.566	0.20		26.33	2.405	0.169	0.060	
Cut 2 Oil	631.6	91.31	6.02	0.765	0.40		576.53	38.010	4.830	2.526	
Heavy Oil	15.3	86.35	5.15	1.611	0.815		15.19	0.906	0.246	0.125	
Vacuum Bottoms	185.5	87.50	5.23	2.040	0.882	0.179	159.07	9.508	3.782	1.635	0.331
Pyridine Insol.	97.8	33.61	1.67	0.644	8.128	52.88	30.52	1.516	0.632	7.973	51.875
TOTAL	1030.9						828.78	67.90	9.770	18.542	52.206
% RECOVERY	100						100.2	98.2	118.9	97.9	101

FIRST TRIAL ELEMENTAL BALANCE, CU 48A2

MATERIAL	Wt. GRAMS	% C	% H	% N	% S	% ASH	GRAMS C	GRAMS H	GRAMS N	GRAMS S	GRAMS ASH
INPUT											
Feed Coal	317.9	66.34	4.57	1.29	5.12	16.04	210.9	14.53	4.100	16.21	50.99
Feed Solvent	667.5	90.58	6.04	0.60	0.36		604.6	40.317	4.005	2.403	
Feed Water	14.6		11.19					1.633			
Feed Hydrogen	11.2		100.					11.2			
TOTAL	1011.2						815.5	67.68	8.105	18.61	50.99
OUTPUT - PRIMARY SEPARATION - CORRECTED TO 100% RECOVERY OF FEED											
Gas	34.23	See table 10					12.136	12.60		5.515	
Knock Out Pot	1.6				1.25			0.176		0.020	
Cold Trap H_2O	20.0			0.485	0.841			2.238	0.097	0.168	
Cold Trap Oil	7.0	86.41	11.28	0.219	0.886		6.03	0.789	0.015	0.062	
Filtrate	780.6	89.68	5.94	0.979	0.46		700.0	46.37	7.642	3.590	
Wet.Filter Cake	168.2	59.27	3.54	0.868	(4.772)	30.16	99.60	5.95	1.459	(8.026)	50.73
TOTAL	1011.2						817.87	68.12	9.244	17.40	50.73
% RECOVERY	100						100.3	100.6	114	93.5	99.7
		(Probable Error - Difficult Decomposition of W.F.C. Minerals)									
OUTPUT - SECONDARY SEPARATION - CORRECTED TO 100% RECOVERY OF FEED											
Gas	34.23	See table 10					12.136	12.60		5.515	
Knock Out Pot	1.6				1.25			0.176		0.020	
Cold Trap H_2O	20.6			0.485	0.841			2.238	0.099	0.173	
Cold Trap Oil	7.0	86.41	11.28	0.219	0.886		6.05	0.789	0.015	0.062	
Cut 1 Oil	30.1	88.05	7.71	0.560	0.244		26.50	2.321	0.168	0.073	
Cut 2 Oil	627.3	91.73	6.03	0.734	0.377		575.42	37.82	4.603	2.364	
Heavy Oil	17.6	87.26	6.24	1.627	0.842		15.36	1.10	0.286	0.148	
Vacuum Bottoms	181.8	87.32	5.11	1.909	0.944	0.133	158.74	9.289	3.470	1.716	0.24
Pyridine Insol.	90.8	32.02	1.73	0.590	8.930	56.07	29.07	1.57	0.536	8.108	50.91
TOTAL	1011.2						823.3	67.90	9.177	18.179	51.15
% RECOVERY	100						100.9	100.3	113	97.7	100.4

REPRODUCIBILITY IN FEED COAL NITROGEN RESULTS (KJELDAHL)

SAMPLE WEIGHT (g)	ml H_2SO_4 (0.10034)	% N[b]	DEVIATION d	d^2	$\sqrt{\frac{\Sigma d^2}{n-1}}$
Set 1[a]					
1.0373	10.30	1.369	+0.022	0.00048	
1.0235	9.90	1.332	-0.015	0.00023	
1.0572	10.55	1.376	+0.019	0.00036	1.347±0.03
1.0245	10.12	1.361	+0.014	0.00020	
1.0908	10.25	1.295	-0.052	0.00270	
Blank	0.20	(1.347) average			
Set 2[a]					
1.0722	10.35	1.350	-0.011	1.21×10^{-4}	
1.0341	10.10	1.366	+0.0005	2.5×10^{-7}	
1.0083	6.55	0.806 lost			1.366±0.0064
1.0673	10.40	1.363	+0.0002	0.8×10^{-3}	
1.0453	10.20	1.365	+0.004	1.6×10^{-7}	
Blank	0.05	(1.366) average			
Set 3[a]					
1.0040	9.80	1.358	+0.006	3.6×10^{-5}	
1.0108	9.75	1.342	-0.010	1×10^{-4}	
1.0064	9.75	1.348	-0.004	1.6×10^{-5}	1.352±0.0512
1.0687	10.15	1.322	-0.030	0.9×10^{-3}	
1.0499	10.48	1.390	+0.038	1.488×10^{-3}	
Blank	0.60	(1.352) average			

[a] Samples in set 1 were allowed 2 hours digestion after the green color appeared; set 2 allowed 3 hours; and set 3 allowed 4 hours. Regents were 0.7 g mercuric oxide (red) selenium and kelpack plus 30 g H_2SO_4 (concentrated).

[b] The same coal was analyzed by the Dumas method in various milligram sample sizes, with these results:

42.780 mg 1.09 %N
33.930 mg 1.11 %N
24.830 mg 1.30 %N
23.080 mg 1.21 %N
13.220 mg 1.58 %N
13.138 mg 1.58 %N

ALTERNATE NITROGEN DETERMINATIONS

SAMPLE	CU 48A1[a]		CU 48A2[a]	
	SAMPLE SIZE (mg)	%N	SAMPLE SIZE (mg)	%N
Feed coal	40.345	1.25		
	34.828	1.30		
	30.460	1.37	(Same Coal)	
	20.290	1.39		
	13.461	1.64		
	13.772	1.51		
Cut 1 Oil	25.110	0.67	30.315	0.58
	21.100	0.68	26.643	0.61
	15.100	0.65	21.869	0.63
	11.005	0.66	16.790	0.55
	C 7.878	0.54	C 14.563	0.55
	C 7.706	0.54	C 8.015	0.53
	C 4.704	0.59	C 5.039	0.54
Cut 2 Oil	24.928	1.06	22.792	0.84
	18.440	0.99	16.820	0.80
	13.665	1.01	12.570	0.91
	C 11.858	0.76	C 11.201	0.75
	C 10.451	0.76	C 10.782	0.74
	9.427	1.14	8.310	0.77
	C 6.760	0.81	C 5.340	0.76
Filtrate	25.810	1.03	24.580	1.06
	21.760	1.01	19.492	1.11
	14.120	1.05	14.610	1.03
	9.390	1.15	9.820	1.19
Heavy Oil	20.645	1.54	17.580	1.56
	16.060	1.63	12.115	1.69
	12.035	1.70	9.343	1.77
	8.510	1.75	7.705	1.78
Vacuum bottoms	21.855	1.84	20.551	1.91
	17.812	1.86	16.370	1.97
	12.365	2.13	11.553	2.17
	8.885	2.03	8.740	2.20
Wet filter cake	26.834	0.905	24.565	0.994
	19.828	0.978	19.510	1.07
	14.611	1.02	15.070	1.03
	10.585	1.04	8.840	1.12
Pyridine insolubles	39.330	0.701	40.452	0.704
	31.710	0.724	30.665	0.663
	20.062	0.734	22.048	0.800
	15.180	0.756	16.048	0.783

[a] All determinations were by Dumas except as noted: C indicates colorimetric determination. Analyses were made between 23 and 25°C at 760-778 mm Hg, at Schwarzkopf Microanalytical Laboratory.

COMPARATIVE NITROGEN ANALYSES (%)

MATERIAL	KJELDAHL		EXTRAPOLATED DUMAS		OTHER	
	CU 48A1	CU 48A2	CU 48A1	CU 48A2	CU 48A1	CU 48A2
Coal (dry basis)	1.30		1.85			
Solvent	0.60		1.07-1.11		0.77[b]	
Knockout H_2O					0.24[c]	0.55[c]
Cold trap H_2O	0.38[a]	0.485			0.38[a]	0.485[a]
Cold trap oil	0.212	0.219				
Filtrate	0.981	0.979	1.17	1.28		
Cut 1 oil	0.566	0.560	0.665	0.69-0.74	0.56[b]	0.54[b]
Cut 2 oil	0.765	0.734	1.14-1.19	0.91-1.00	0.74[b]	0.75[b]
Heavy oil	1.611	1.627	1.87	1.92		
Vacuum bottoms	2.04	1.909	2.20	2.27		
Wet filter cake	0.895	0.868	1.08-1.10	1.10		
Pyridine insolubles	0.644	0.590	0.775	0.90		

a Ammonia in H_2O phase, distilled over MgO

b Colorimetric N (Schwarzkopf)

c H_2O in the knockout vessel was used up by the analysis for sulfur (as NH_4SH), from which N values are taken.

ELEMENTAL BALANCE, CU 48A1

MATERIAL	WEIGHT (g)	% C	% H	% N	% S	% ASH	% O	C (g)	H (g)	N (g)	S (g)	O (g)	ASH (g)
INPUT - Coal assumed to have 3.25% H_2O; slurry assumed dry when fed													
Coal	332.5	64.76	4.36	1.85	4.94	15.76	8.33	215.3	14.50	6.15	16.43	27.70	52.4
Solvent	687.5	90.58	6.04	1.07	0.36	-	1.95	622.7	41.53	7.36	2.48	13.41	-
Hydrogen	11.2								11.20				
Total	1031.2							838.0	67.23	13.51	18.91	41.1	52.4
PRIMARY SEPARATION - Loss free basis, ash balance forced													
Dry gas	35.9		See table 9					15.14	11.68		5.88	3.13	
H_2O (knockout)	2.6[a]			0.24	0.547		88.9		0.29	0.01	0.01	2.31	
H_2O (cold trap)	23.9[b]	0.57		0.38	0.821		88.0	0.14	2.35	0.09	0.20	21.03	
Cold trap oil	8.0	82.68	12.04	0.212	0.65		4.42	6.61	0.96	0.02	0.05	0.35	
Filtrate	770.3	90.36	6.25	1.17	0.45		1.77	696.04	48.14	9.01	3.47	13.63	
Wet filter cake	190.5	62.32	3.89	1.08	4.70	27.51	0.50	118.72	7.41	2.06	8.95	0.95	52.4
Total	1031.2							836.6	70.83	11.19	18.56	41.40	52.4
% Recovery								99.8	105.3	82.8	98.1	100.7	
SECONDARY SEPARATION - Loss free basis, ash balance forced													
Dry gas	35.9		See table 9					15.14	11.68		5.88	3.13	
H_2O (knockout)	2.6[a]			0.24	0.547		88.9		0.29	0.01	0.01	2.31	
H_2O (cold trap)	23.9[b]	0.57		0.38	0.821		88.0	0.14	2.35	0.09	0.20	21.03	
Cold trap oil	8.0	82.68	12.04	0.212	0.65		4.42	6.61	0.96	0.02	0.05	0.35	
Cut 1 oil	29.9	87.47	7.99	0.0665	0.20		3.67	26.15	2.39	0.20	0.06	1.10	
Cut 2 oil	631.6	91.31	6.02	1.14	0.40		1.13	576.7	38.02	7.20	2.53	7.14	
Heavy oil	15.3	86.35	5.15	1.87	0.815		5.82	3.21	0.79	0.29	0.13	0.89	
Vacuum bottoms	185.5	87.50	5.23	2.20	0.882	0.179	4.01	162.31	9.70	4.08	1.64	7.44	0.33
Pyridine insolubles	98.5	33.61	1.67	0.775	8.68	52.88	2.39	33.10	1.64	0.76	8.54	2.35	52.07
Total	1031.2							833.4	67.82	12.65	19.04	45.74	52.4
% Recovery								99.4	100.9	93.6	100.7	111.3	

a 99% H_2O
b 98% H_2O

ELEMENTAL BALANCE, CU 48A2

MATERIAL	WEIGHT (g)	% C	% H	% N	% S	% ASH	% O	C (g)	H (g)	N (g)	S (g)	O (g)	ASH (g)
INPUT - Coal assumed to have 3.25% H_2O; slurry assumed dry when fed													
Coal	324.9	64.76	4.36	1.85	4.94	15.76	8.33	210.4	14.17	6.01	16.05	27.06	51.20
Solvent	675.1	90.58	6.04	1.07	0.36		1.95	611.5	40.78	7.22	2.43	13.16	
Hydrogen	11.2								11.20				
Total	1011.2							821.9	66.15	13.23	18.48	40.22	51.20
PRIMARY SEPARATION - Loss free basis, ash balance forced													
Dry gas	32.2		See table 10					12.08	11.39		5.50	2.52	
H_2O (knockout)	3.6[a]			0.55	1.25		88.0		0.39	0.02	0.05	3.16	
H_2O (cold trap)	19.4[a]	0.57		0.485	0.841		88.0	0.11	2.13	0.09	0.16	17.07	
Cold trap oil	6.8	86.41	11.28	0.219	0.886		1.21	5.88	0.77	0.01	0.06	0.08	
Filtrate	779.4	89.68	5.94	1.28	0.46		2.64	699.00	46.29	9.98	3.58	20.57	
Wet filter cake	169.8	59.27	3.54	1.10	5.14	30.16	0.79	100.64	6.01	1.37	8.73	1.34	51.20
Total	1011.2							817.7	66.98	11.97	18.08	44.74	51.20
% Recovery								99.5	101.2	90.5	97.8	111.2	
SECONDARY SEPARATION - Loss free basis, ash balance forced													
Dry gas	32.2		See table 10					12.08	11.39		5.50	2.52	
H_2O (knockout)	3.6[a]			0.55	1.25		88.0		0.39	0.02	0.05	3.16	
H_2O (cold trap)	19.4[a]	0.57		0.485	0.841		88.0	0.11	2.13	0.09	0.16	17.07	
Cold trap oil	6.8	86.41	11.28	0.219	0.886		1.21	5.88	0.71	0.01	0.06	0.08	
Cut 1 oil	30.9	88.05	7.71	0.69	0.244		3.36	27.21	2.38	0.21	0.08	1.04	
Cut 2 oil	627.6	91.73	6.03	0.91	0.377		0.95	575.7	37.84	5.71	2.37	5.96	
Heavy oil	17.7	87.26	6.24	1.92	0.842		3.74	15.45	1.10	0.34	0.15	0.66	
Vacuum bottoms	182.1	87.32	5.11	2.27	0.944	0.133	4.22	159.00	9.31	4.13	1.72	7.68	0.24
Pyridine insolubles	90.9	32.03	1.73	0.90	9.14	56.07	0.13	29.11	1.57	0.82	8.31	0.12	50.96
Total	1011.2							824.5	66.85	10.71	18.40	38.29	51.20
% Recovery								100.3	101.0	80.9	99.6	95.2	

[a] 98% H_2O

CONCLUSIONS

The elemental balance study revealed shortcomings in the handling of feed coal, a need for better suspension of mineral matter in feed slurry, a need for larger samples for analysis, a need for changes in sampling techniques, and a need for a better analytical method for nitrogen in feed coal and SRC products.

Material recovery, 98% at the time of the study, is currently 99% or better as a result of subsequent improvements. This is significant because reactor behavior permits a preferential segregation of mineral, which is rich in sulfur; laboratory-size, short-interval samples reveal variations in ash content, forcing a prorating of lost sulfur to the product distribution. The loss of water from the slurry feed vessel has similarly been controlled.

The balances for carbon and hydrogen are accurate, for sulfur good. Accounting for nitrogen from raw data is awkward because output exceeds input, especially by conventional Kjeldahl analyses; the effect of sample size on Dumas analysis of feed coal is demonstrable; and other analytical methods for products have special limitations.

It is clear that the SRC process removes from coal nearly all of the ash, much of the sulfur, and less of the nitrogen. To remove an appreciable fraction of the nitrogen might require liquefaction under conditions that convert all material to hydrocarbons of appreciably lower molecular weight than is usual now in the SRC process.

RECOMMENDATIONS

Insofar as they would apply to the laboratory reactor operation, many of the recommendations arising from the study have already been adopted: Details are presented in Interim Report #8 of OCR R&D 53.

1. The uniformity of feed coal composition was achieved by adopting the ASTM long pile sampling method for handling initial lots, by improved methods for homogenizing the ground sublots, and other procedures.

2. The uniformity of feed slurry has been greatly improved by modified grinding and sieving equipment for the coal, modified stirring of slurry in the feed vessel for suspension of mineral, and by avoidance of the need to warm slurry and hence lose contained water from the input.

3. The effect of holdup of material in sample flasks has been significantly reduced by taking larger samples and, when appropriate, leaving flasks uncleaned for a relatively constant holdup of mineral-rich material between runs; so that raw material recovery is good, mass balances are regularly closed above 99%, and exact elemental balances are facilitated.

For exact nitrogen balances, analytical methods other than Kjeldahl and Dumas should be investigated. This is particularly true for feed coal, solids, and high molecular weight products.

In any scaled up operation of the SRC process, an exact element-by-element balance will require good understanding of mineral behavior in the dissolver and its operating characteristics. Initially recovery of either 100% raw material or 100% ash is unlikely. Therefore, a preliminary elemental balance study should be undertaken for the purpose of discovery and procedure development some months before the final study.

IV-J

Evaluation of Experiment CU 49 (Samples A through E)

Experiment CU 49 was an exploratory experiment which was done to investigate the use of unfiltered coal solution as solvent for the process as a replacement for distilled solvent. In the previous experiment use of filtered solution for this purpose had been found to be difficult or perhaps impossible to accomplish. The results of these trials were reviewed and a new set of conditions was established designed to expose the reactants to more hydrogen and to use a longer reaction time. The use of the split temperature profile, in which the preheater was operated at a higher temperature than the dissolver, was also added to the procedure. It was reasoned that if the minerals in the coal were catalytic the use of unfiltered solution as recycle solvent should cause an accumulation of active material and facilitate reaction of the coal. The reaction was started with a conventional lineout procedure and collection of a sample to measure the properties of the single pass product made with initial conditions. Coal was then added to the solution and the material was put through the reactor again. Samples were collected from time to time as the accumulation of material allowed products to become available for removal from the system.

In a procedure of this kind it is difficult to maintain exact accounting of feed composition, since gas and light liquid formation removes material from the system and some unaccounted handling losses are encountered which tend to accumulate as the experiment progresses. Methods for closing material balances had not been developed to cope with experiments of the complexity of CU 49, therefore the results to be presented will contain some error which is difficult to state with precision. The results are therefore presented as carefully considered estimates. Some difficulty was encountered in the analysis of the product gases, which may have contained an unusually large amount of hydrocarbon vapors, not determined by the gas chromatographic procedure in use, or which may have caused difficulty with the instruments detector or column packing. These errors have been accumulated in a term reported as gas not accounted and this term may not be completely reliable. Some water was present in the feed coal and probably was lost from the feed. This is an additional cause for failure to close the material balance. The use of slow feed rates and use of rather small samples for analysis also contribute to the difficulty in fully closing material balances.

A detailed listing of the procedure followed for making samples for recycle and for analysis will be presented in an effort to show exactly how each sample was obtained. The accumulation of coal or of coal derived material in the recycle slurry was followed by ash analysis of the feed slurry. These results allow quite accurate values for coal derived material concentrations in the feed, and on this basis it appears most reasonable to calculate yields on the basis of feed slurry composition only. The feed coal contained 15.18% ash and a completely lined out slurry would contain this concentration of ash increased by the ratio of slurry fed to liquid products recovered. Removal of gaseous products and low boiling liquids during stripping increases the concentration of ash at complete steady state by about 12% by the end of the experiment, requiring an ash concentration of about 17% in the slurry. The experiment was therefore stopped at a point representing only about 2/3 of the mineral concentration needed for a steady state resulting from the addition of only coal to the feed slurry being recycled.

Listing of Feed and Recycle Operations

Operation	Time	Comment
Start up on flush oil	3 hours	To establish conditions
Operate on feed slurry	4 hours	For composition lineout
Collect product #1	7 hours	To use for recycle slurry
Collect sample CU 49A	2 hr. 50 min.	For analysis
Return product #1 + coal		
Collect product #3	5 hours	To use for recycle slurry
Collect product #4	5 hours	To use for recycle slurry
Return product #3 + coal		
Collect sample CU 49B	3 hours	For analysis
Return product #4 + coal		
Collect product #6	5 hours	To use for recycle slurry
Collect product #7	5 hours	To use for recycle slurry
Return product #6 + coal		
Collect product #8	2 hours	To use for recycle slurry
Return product #7 + coal		
Continue product #8	3 hours	To use for recycle slurry
Collect sample CU 49C	3 hours	For analysis
Return product #8 + coal		
Collect Product #10	3 hours	To use for recycle slurry
Collect sample CU 49D	3 hours	For analysis
Return product #10 + coal	1½ hours	Allowed to lineout at 475°C
Collect sample CU 49E	2 hours	For analysis

Coal was mixed with the CU 40 partially hydrogenated anthracene oil in the ratio of one part coal to two parts of solvent to prepare the slurry used to start the experiment. Coal was mixed with unfiltered product solution in the same proportion to prepare material for recycle. Control chart data are presented in the table which follows.

It was planned to maintain a constant feed rate throughout the experiment. Because the viscosity of the solution used for recycle increased throughout the experiment, adjustment in the pump stroke was required from time to time. The slurry feed rates actually realized were slightly variable. This was also due to the use of slow feed rates which were near the lower limit of stroke needed to make the ball checks in the feed pump operate properly. The feed rates obtained produced retention times ranging from 1.73 to 1.94 hours (1/LHSV).

Hydrogen was fed at the rate of 6 moles per hour nominal and this rate was reproduced well throughout the experiment. This is also confirmed by the

CU 49

CONTROL CHART DATA

Reaction Time	Sample or Event	$\overline{\text{IR}}$	Blackness	% Ash
3 hours	Lineout operating conditions			
4 hours	Solution at end of lineout	1.368	6.35	
11 hours	Feed Slurry Sample			5.285
11 hours	Product #1 Solution off	1.410	7.45	
14 hours	Analytical Sample CU 49A off	1.460	7.00	
14-1/12 hrs.	Add Product 1 + coal makeup			
17 hours	Feed Slurry Sample			6.80
19 hours	Product #3 Solution off	1.540	7.65	
24 hours	Product #4 Solution off	1.610	9.63	
24-1/12 hrs.	Add Product 3 + coal makeup			
25 hours	Feed Slurry Sample			7.42
27 hours	Analytical Sample CU 48B	1.653	12.17	
27-1/12 hrs.	Add Product 4 + coal makeup			
29-1/2 hrs.	Feed Slurry Sample			8.33
32 hours	Product #6 Solution off	1.661	14.16	
34-1/2 hrs.	Add Product #6 + coal makeup			

Note: Recirculation Pump off 25 min. at 35 hrs. - Feed is only solvent for 25 min.

36 hours	Feed Slurry Sample			8.58
37-1/2 hrs.	Product #7 Solution off	1.686	14.17	
39-1/2 hrs.	Add Product #7 + coal makeup			
40 hours	Feed Slurry Sample			9.25
42 hours	Product #8 Solution off	1.748	12.30	
45 hours	Analytical Sample CU 49C	1.786	14.11	
45-1/20 hrs	Add Product #8 + coal makeup			
47 hours	Feed Slurry Sample			10.08
48 hours	Product #10 Solution off	1.838	15.13	
50 hours	Analytical Sample CU 49D	1.754	18.27	
50-1/6 hrs.	Add Product #10 + coal makeup			
50-7/12 hrs.	Slurry Sample			10.65
54-1/2 hrs.	Analytical Sample CU 49E	1.825	19.77	

volumes of gas recovered from the reactor. These data are presented in Appendix A (Part 12). It can be seen that the volume recovered is significantly less than the volume of hydrogen fed into the reactor, and that hydrogen has been reacted in greater amounts than in most previous trials. The CU 49A sample has been reported on the MAF coal basis and again on the slurry basis. 4.97% of hydrogen was reacted on the MAF coal basis and 1.33% on the slurry basis. It is certainly misleading to report reaction of this much hydrogen as though it were reacted only with the coal. The infrared spectra of the input solvent and of the reclaimed solvent show clearly that much of the hydrogen reacted with solvent. The $\overline{\text{IR}}$ of the feed solvent was 0.75 and was increased to 1.21 by one pass of the solvent through the reactor. This can be evaluated by reference to Appendix C Spectrum C9 of this report. This change in $\overline{\text{IR}}$ value would indicate that the solvent gained about 0.5% of hydrogen in the initial pass through the reactor under the conditions used. At the end of the experiment the $\overline{\text{IR}}$ was increased to 1.89.

As the slurry recycle procedure was continued the $\overline{\text{IR}}$ for the make up solution was entered as the value for the solvent. It can then be seen that in recycle the hydrogen gained by the product solution is less per pass than was the case for the original charge of anthracene oil. This is also reflected in the relatively small rate of increase in the hydrogen content of distilled solvent reclaimed from these product solutions. See the $\overline{\text{IR}}$ values for the Cut 2 reclaim solvents reported. This can be further studied by reference to actual elemental analysis results for filtered solutions which are reported at the bottom of the tables in Appendix A. It is clear from the composition of the reclaimed solvent that an appreciable amount of hydrogen has been added to the solvent, the final $\overline{\text{IR}}$ value observed being greater than the $\overline{\text{IR}}$ value of the most hydrogenated material used in preparation of the working curve on the Perkin Elmer 267.

As the concentration of coal derived material increased in the recycling system, the blackness of the solution increased. In this regard the data from the analytical samples appears more systematic than the data from all solutions used for recycle. These results show that the blackness followed an oscillating upward course rather than increasing in direct response to changes in ash or accumulated coal feed concentrations. Blackness is a fair indication of the increasing concentration of middle molecular weight materials which will be found in vacuum bottoms rather than in distillable fractions. It is also clear that even this is a nonlinear relationship. The first two samples taken for analysis were filtered without difficulty. The following two samples could be only partly filtered using a filter paper and a buchner funnel. As a result of this observation and as a result of the increasing viscosity of the solution being recycled it was decided to increase the preheater temperature for the final sample. This resulted in an apparent increase in the amount of hydrocracking of the solution and the coal materials and the final solution could be filtered completely. These temperatures should be treated with some caution, the preheater was a small volume tube through which the fluid passed rapidly. It is not certain that the liquid reached the temperature of the tube wall or of the surrounding sand, or that it was exposed to such temperatures for much of the time in the preheater.

Such results should be taken as indications of the kind of responses to be expected from increasing heat stress with the realization that temperature and time parameters are poorly established in this preheater.

The hydrogen content of the Cut 2 solvent reclaimed at the end of the experiment was found by combustion analysis to have been increased to 6.87%. The sulfur in the vacuum bottoms being made at this time was 0.49%. The reclaimed solvent had then been increased nearly one percentage above the hydrogen in a typical raw anthracene oil. The sulfur in the vacuum bottoms was reduced to 0.49% from an organic sulfur concentration of about 1.9%, MAF basis.

The main point of interest in this experiment lies in the demonstration that unfiltered product solution recycle can be used to reduce or perhaps eliminate the need for redistilled solvent to operate the process. This experiment also shows that reactivity can be improved by allowing the mineral phases to build up in concentration, assuming of course that suitable minerals are present. There are problems in bringing such systems to complete steady state while maintaining an acceptable balance of properties, feeds and conversion rates. This experiment has probably been terminated shortly before serious mechanical or reaction rate problems are to develop.

In subsequent work similar recycle studies have been initiated with petroleum derived solvent as the starting material for slurry preparation. With this material, which is less reactive than anthracene oil, it is necessary to start the reactions with milder conditions and to maintain better control of reaction conditions than is necessary with anthracene oil as the starting solvent. In the long run the reactivity of the steady state solvent determines the reaction conditions which are allowed. This results from the interaction of the solvent, the catalytic effects associated with the coal, and the polymeric nature of the coal in question. There are indications that a reactive coal such as the Kentucky No. 9 coal can be processed by recycle of unfiltered solution as solvent without excessive difficulty. This may not be generally true of bituminous coals since both the concentration of iron and the degree of polymerization of the coal may be considerations. Additional studies to perfect operating conditions then to scan other coals would be necessary to establish the range of materials which is suitable for such processing.

V Comments on Infrared Spectra Presented in Appendix C

In this report use of infrared spectra for characterization of coal solutions and for the solvents used to make coal solutions has been discussed. Working curves for conversion of $\overline{\text{IR}}$ values to corresponding percentages of hydrogen in solvents derived from anthracene oil have been presented. It is noteworthy that considerable additional information is contained in such spectra and some additional discussion can be presented to indicate some of these details.

One of the first considerations in this project has been the analysis of raw anthracene oil and the preparation of solvents from this kind of material. It has been observed that anthracene oil is quite variable in composition, and depending on the source of the oil and the treatment which it may have received, it may have been either a liquid or a slush which was nearly solid at room temperature. The liquid varieties are usually prepared by allowing the oil to weather, a process in which the oil is allowed to stand in a tank during cold weather until the materials which may crystallize have all been precipitated. The oil remaining tends to be somewhat more hydrogen rich and the crystalline phases precipitated tend to include the less soluble carbazole rich materials. Oil which has not been weathered may be a waxy slush and usually contains considerable carbazole. Spectrum C1 was prepared from an oil of the latter type, and the presence of a substantial fraction of carbazole is indicated by the band at 2.91 microns. The oil is more aromatic in character than a weathered oil as indicated by the low $\overline{\text{IR}}$ value.

An example of a weathered oil which has been redistilled to prepare the middle fraction which was used as solvent is presented as Spectrum C3. In this case the sample was actually used as the feed solvent in experiment CL 8. The carbazole content was low and a more favorable concentration of hydrogen is indicated by an $\overline{\text{IR}}$ value of 0.56. This was also the feedstock which was catalytically hydrogenated to prepare the CL 18 hydrogenated anthracene solvent. The spectrum of the hydrogenated product is presented as Spectrum C4. At the end of the hydrogenation procedure a portion of the Granite City anthracene oil was hydrogenated in order to investigate the reactivity of this kind of oil. The spectrum of the hydrogenation product is presented as Spectrum C2. It can be seen that the hydrogenation was successful and produced a material which nearly matched the material made from the weathered and redistilled oil. The reduction had removed an appreciable part of the carbazole function, although the residual was still a little greater in concentration than was present in the corresponding sample made from the weathered oil. This procedure also removed most of the tendency for formation of crystalline substances which was an objectionable factor in the use of the raw oil.

Spectrum C5 shows the middle fraction of raw anthracene oil which was the stock used in the second hydrogenation procedure, which prepared the CU 40 solvent lot. It was usual procedure during these hydrogenations to sample the product stream from time to time and to run infrared spectra of the product for control analysis. The operating conditions for the reactor were adjusted as necessary to maintain approximately the desired $\overline{IR}$ value. The lots which were occasionally found to be off the desired composition could readily be set aside and the main blend was thus kept close to the desired composition. The scan presented shows the kind of information which was used to maintain control of the operation.

Spectrum C3 presents the data for an experimental lineout solvent, in this case Experiment CL 8. Spectrum C7 shows an example of the small change in composition which may be observed in the oil from the reactor during the initial flushing period used to line out the reactor on the desired operating conditions. It can be seen that the flush oil was becoming slightly hydrogenated as a consequence of this operation. The $\overline{IR}$ value increased from the initial value of 0.56 to a value of 0.64. While this is a small increase in hydrogen the effect is certainly real and has been observed repeatedly. Based on the rather careful observations described in experiment CL 14, the hydrogenation is most probably caused by the presence of residual minerals which are difficult to flush completely out of the reactor during a shut down procedure. In experiment CL 14 the flow of flush oil was observed for 5 hours before the output oil and the input flush oil were found to have substantially the same composition based on infrared spectra. The ability of the unit to produce an oil with only minimal change in the oil shows that reactor wall effects are of little consequence in this apparatus. The apparatus does commonly retain some mineral from one trial to another and this often results in some kind of deflection of the product during the lineout operation.

Spectrum C8 shows the appearance of the oil reclaimed from sample number 10 of experiment CL 8. The oil had become hydrogenated during use and the $\overline{IR}$ value had increased to 0.72. Thus even is an experiment in which many things went wrong it was still possible to obtain an indication that a reaction was proceeding. It was later found that the temperature recorder was in substantial error, and from later estimates of temperature the reaction observed here took place at about 350°C. The data presented in Appendix A are taken from the last sample in the experiment.

Spectrum C9 shows a typical example of the improved dispersion available in the new Perkin Elmer 267 instrument. Part of the difference in appearance of the spectrum is due to the presentation, which is linear in wavenumber, while the older Perkin Elmer 237 instrument was linear in wavelength. It was found that only minor differences in the ratio of absorbance at 3.3 and 3.4 wavelength resulted and that working curves were comparable without serious error from one instrument to the other. In this report all spectral data after experiment CU 40 are taken from the new instrument and should be referred to the CU 40 working curve data. Practically little error would result from use of the older curve however. The example which is presented is taken from experiment CU 49 Sample A. This was the first pass of the material through the reactor and the Cut 2 oil which was reclaimed increased in hydrogen in readily observable amounts. Compare Spectrum C6, for the input solvent, to spectrum C9, for the Cut 2 reclaim solvent. This increase in ratio from 0.75 to 1.21 is an unambiguous demonstration of an "uncatalyzed" hydrogenation effect.

V

This effect was enlarged as the unfiltered solution was recycled together with additional coal. Spectrum C10 shows the appearance of the spectrum at the end of Experiment CU 49. The Cut 2 oil reclaimed from sample E was found to have an $\overline{\text{IR}}$ value of 1.89 an increase of 1.14 in the ratio. This oil was analyzed by combustion analysis and was found to contain 6.87% hydrogen compared to the initial solvent which was analyzed and found to contain only 6.04% hydrogen. It can be seen that the $\overline{\text{IR}}$ value is a sensitive measurement for percentage hydrogen. Its accuracy does depend on the distribution of functional groups on the aromatic rings which are present. In cases where these distributions may vary widely some drift from the calibration line would be reasonable. In addition the use of a calibration line implies using the curve with about the same molecular weight distribution of material. These qualifications have not limited application of the method seriously in this work.

The spectrum for the CU 49 E Cut 2 oil is representative of a material which has been moved appreciably towards the composition of an equilibrated oil. This can be seen by the growth of two characteristic bands at 3420 and 3540 wavenumber. These bands are due to phenolic and amine functions which are added to the oil as reaction products derived from coal and always appear in the spectrum of oil which has been used in the process. In addition the coal derived oil which is added to the solvent always introduces some aliphatic substituents which result in a characteristic triple band centered at 2920 wavenumber. One shoulder appears at about 2950 wavenumber and the other at about 2850 wavenumber.

The spectrum of vacuum bottoms prepared in the Solvent Refined Coal Process is presented as item C 11. In this material the ratio of the aromatic band to the aliphatic band region shows that the high molecular weight material derived from the coal has an appreciable amount of aliphatic character. Apparently this is retained as the material is decomposed to make molecules in the solvent range.

Studies of this kind have been continued and are reported at greater length in the Interim Report No. 8 which follows in this series. In this work the working curve which correlates $\overline{\text{IR}}$ values and percentage hydrogen in the reclaim solvent has been extended to oils containing over eight percent hydrogen. This is more hydrogen than is normal for coal derived oils made under typical solvent refined coal process conditions. It is therefore usual for the hydrogen content of solvents started with petroleum derived solvents to decrease as the solvent is reused. Final compositions depend on exact operating conditions and perhaps on other less well established variables. The CU 49 E oil sample is at least indicative of a first approximation of an equilibrated sample of solvent.

VI STATUS OF THE LABORATORY PROGRAM-DECEMBER 1972

At the end of December in 1972 a total of 49 experiments, some consisting of operation at a number of conditions, had been completed using continuous reactor techniques. The laboratory unit originally installed had been modified and improved in a number of ways. As a result it was possible to conduct experiments with an average material accountability of about 98%. The probable cause for the remaining losses was generally known. In later work these problems have been substantially eliminated. The methods which were developed to complete the closure of material balances have been included in this report, particularly in those sections describing apparatus, materials preparation procedures, and methods for the workup and analysis of reactor products.

Anthracene oil had been shown to be a suitable startup solvent for processing each of the samples representing the three coal ranks which were considered as probably useful feedstocks. It had been demonstrated that hydrogenated anthracene oil was far superior to raw anthracene oil for this purpose. In the case of bituminous coal containing an appreciable fraction of pyritic sulfur, the presence of the iron was shown to be sufficient to catalyze hydrogenation of raw anthracene oil as the coal was dissolved. Thus prospects for improving reaction rates on reuse of the solvent seemed good. In the case of lignite enough iron and sodium was often present to allow reduction of the coal and hydrogenation of the solvent by use of carbon monoxide, provided that suitable reactor pressures were established. The subbituminous coal sample studied was not effective in causing the solvent to become hydrogenated at the end of the solution procedure. Such coals can be dissolved by reactive solvents but tend to remove hydrogen from the solvent. Replacement of this hydrogen would require a separate catalytic operation or the addition of catalyst to facilitate the solution process. The ability of coal to operate without added catalyst is thought to depend on the presence of suitable amounts of naturally catalytic minerals. These are identified as pyrite, sodium ion, or iron salts of organic acids naturally occurring in the coal together with sufficient sulfur to convert the iron to ferrous sulfide. Iron may act as a hydrogenation catalyst or as a water shift catalyst. Sodium is identified as a water shift catalyst. Other active species are possible but have not been identified in coals studied. Use of pure hydrogen is not required provided that the partial pressure is increased to compensate for dilution with inert material, or if the diluent is carbon monoxide, that the catalyst be active as a water shift and as a hydrogenation catalyst also.

At the end of 1972 the availability of the amounts of anthracene oil or related coal tar products needed to start up a full scale coal processing plant appeared to be questionable. It was therefore recommended that studies be done to evaluate available petroleum derived materials as start up solvent for the pilot plant. A number of samples of petroleum products were acquired and inspected to select a readily available aromatic rich product. Considerations of boiling range, density, reactivity, viscosity, and prior experience with materials in the batch autoclave led to selection of the catalytic cracker recycle stream material, typified as decanted oil. This is available commercially as Gulf FS 120 Carbon Black Feedstock. A number of similar materials were very kindly provided for testing by several other companies and from several samples tested the interchangability of the more aromatic varieties seems assured. The aromatic petroleum oils are generally much more substituted than the coal tar products by radicals, such as methyl,ethyl, or larger aliphatic groups. Thus although they contain more hydrogen than the coal tar derived products, they tend to be less reactive and to contain less transferable hydrogen after hydrogenation.

Some trial and error studies were done in an effort to develop a coal derived solvent using recycle techniques similar to those described in experiment CU 49 as discussed at the end of this report. Although this could be accomplished in the laboratory the procedure was not considered appropriate for pilot plant startup. Accordingly the development of a coal derived solvent was demonstrated using the conventional SRC operating mode, in which a solution is made, the solution is filtered, and solvent is reclaimed for reuse by distillation. The development of procedures for using petroleum derived solvent as a starting solvent and for continuing with reclaimed solvent from this step until the solvent appeared to be in steady state equilibrium with the coal and the operating conditions will comprise the main topic to be discussed in the next report in this series.

Bibliography

1/. Anderson, R. P., and Wright, C. H., Office of Coal Research R&D Report No. 53, Interim Report No. 8. Volume II Part 3 Continuous Reactor Studies Using Petroleum Derived Solvents.

2/. Wright, C. H., Perrussel, R. E., and Pastor, G. R., Office of Coal Research R&D Report No. 53. Interim Report No. 6 Volume II Part I Autoclave Experiments.

3/. Wright, C. H., Sulfur and Nitrogen Balances in the Solvent Refined Coal Process. Report No. EPA-650/2-75-011.

4/. 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).

5/. 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.

6/. Radmacher, W., "Brennstoffe, feste flüssige," Ullmans Encyklopädie der technischen Chemie, dritte auflage. (München: Urban und Schwarzenberg, 1953). Band 4, P. 701.

APPENDIX A (PART 1)

SUMMARY OF EXPERIMENTAL RESULTS FOR CONTINUOUS REACTOR STUDIES

RUN NO.	CL-1	CL-2	CL-3	CL-4	CL-5	CL-6	CL-7	CL-8	* CL-10	CL-11A	CL-11B
CONDITIONS											
Coal	KY#9	KY#9	BN Lignite	BN Lignite	BN Lignite	BN Lignite	KY#9	KY#9	KY#9	KY#9	KY#9
Solvent	MFRAO	MFRAO	MFRAO	MFRAO	MFRAO	MFPRS	MFRAO	MFRAO	MFRAO	MFRAO	MFRAO
Ratio Solvent/MAF Coal/H_2O	3.56/1/0.06	2.37/1/0.06	4.74/1/0.46	3.04/1/0.40	3.09/1/0.43	3.05/1/0.40	2.37/1/0.06	2.37/1/0.06	2.37/1/0.06	2.37/1/0.06	2.37/1/0.06
Pressure PSIG	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Dissolver Temperature °C	410	410	395	370	395	390	365	350	335	325	425
1/LHSV	1.02	0.99	1.28	1.56	1.72	1.66	1.32	1.66	1.31	1.72	1.55
GHSV	212	239	190	114	152	122	109	122	255	223	223
Reducing Gas	H_2	H_2	CO	CO	CO	CO	H_2	H_2	H_2	H_2	H_2
INPUT DATA-RAW											
H_2 Grams/Hr.	7.8	8.8	-	-	-	-	5.2	5.55	9.3	15.3	15.3
CO Grams/Hr.	-	-	98	58.8	78.4	70.0	-	-	-	-	-
N_2 Purge Grams/Hr.	6.5	6.5	3.8	5.8	5.2	16[e]	5.6	4.84	4.8	7.2	7.2
Feed Slurry Gm/Hr.	512.0	527.0	404.0	332.0	302	312	393	312	396	302	359.3
Total Feed Gm/Hr.	526.3	542.3	505.8	396.6	385.6	398.	403.8	322.4	410.1	324.5	381.8
OUTPUT DATA-RAW											
Gas Moles/Hr.	(1.92)[a]	3.94	2.05	0.934	2.46	2.16	2.00	1.2	(4.2)	(3.69)	3.69
MW of Gas	6.53	6.08	29.8	31.1	29.6	29.5	8.34	6.0	5.0	7.0	8.85
Gas Output Gm/Hr.	12.5	23.9	60.8	29.1	72.8	106.8	16.7	7.2	(20.1)	(25.9)	32.7
Unstripped Soln. Gm/Hr.	493.4	500.9	195.3	306.7	271.5	273.2	338.9	300.4	364.8	168.8	331.4
Recovery Gm/Hr.	505.9	524.8	256.1	835.8	344.3	380.0	355.6	307.6	(384.9)	(194.7)	364.1
% Recovery	96.1	96.8	50.6	84.7	89.2	95.3	88.0	95.4	(93.9)	60[h]	95.4
OBSERVATIONS											
% Ash in Feed Slurry	2.72 [c]	3.62 [c]	1.81 [c]	2.41 [c]	2.41 [c]	2.41[c]	3.62[c]	3.62[c]	3.62[c]	3.62[c]	3.62[c]
Solution Blackness	-	-	-	-	-	-	-	8.10	7.41	7.42	12.87
Solution IR Ratio	-	-	-	-	-	-	-	1.11	1.06	1.11	0.62
Cut 2 Reclaim IR Ratio	0.66	0.75	0.58	0.57	0.62	0.71		0.74	0.68	0.47	0.71
Feed Solvent IR Ratio	0.56	0.56	0.56	0.56	0.56	0.77	0.56	0.56	0.56	0.56	0.56
% H_2 Reacted MAF Coal Basis	(1.7)	1.43	-	-	-	-	-	(1.5)	0.51	0.40	2.64
% CO Reacted MAF Coal Basis	-	-	-	-	-	-	-	-	-	-	-
% Water Reacted MAF Coal Basis	-	-	-	-	-	-	-	-	-	-	-
% MAF Conversion	92.7	89.1	63.8	47.6	59.2	70.4	83.5	87.7	15.0	47.53	88.97
YIELDS ON LOSS FREE MAF COAL BASIS		g	b	d	d	f	d	g	g		
H_2	-		-	-	-	-	-	-	-	-	-
CO	21.6	9.7	-	-	-	-	-	-	-	-	0.46
CO_2			-	-	-	-	-	0.05	0.38	0.40	1.32
H_2S			-	-	-	-	-	-	1.0	1.09	2.18
Hydrocarbon Gas			-	-	-	-	-	0.46	0.13	0.10	10.43
H_2O	3.3	3.7	-	-	-	-	-	3.1	5.4	2.18	7.07
Excess Solvent	4.8	6.7	-	-	-	-	-	12.9	-12.5	-30.99	8.85
Vacuum Bottoms	72.0	78.7	-	-	-	-	-	82.9	34.1	75.15	61.30
Insoluble Organic Matter	7.3	10.9	-	-	-	-	-	12.3	85.0	52.47	11.03
Total	109.0	109.7	-	-	-	-	-	111.7	113.8	100.40	102.64
VACUUM BOTTOMS COMPOSITION											
% Carbon	84.80	Not Filtered	Not Filtered	Not Filtered	Not Filtered	Not Filtered	Not Filtered	Not Filtered	Not Filtered	Not Filtered	90.04
% Hydrogen	5.52										4.55
% Nitrogen	1.95										1.92
% Sulfur	1.29										0.56
% Oxygen	5.97										2.93
% Ash	0.47										0.07
Fusion Point °C	>270	210									2.05

a = Low due to gas loss.
b = Yields not calculated. Poor material balance.
c = Calculated value.
d = Yields not calculated, poor conversion.
e = From gas analysis.
f = Yields not calculated. Gas samples variable in composition and soln. not filterable.
g = Product distribution by distillation of unfiltered solution.
h = Based on 15 minute sample, too small for an accurate balance. Product distribution from distillation of unfiltered soln.
i = Ky #9 coal 10.88% ash--4.83% moisture.

* CL-9 not finished - pump failure.

APPENDIX A (PART 2)

SUMMARY OF EXPERIMENTAL RESULTS FOR CONTINUOUS REACTOR STUDIES

RUN NO.	CL-12	CL-13[a]	CL-15	CL-16	CL-17[b]	CL-19A	CL-19B	CL-19C	CL-20A	CL-20B	CL-20C
CONDITIONS											
Coal	BN Lignite	BN Lignite	BN Lignite	BN Lignite	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9
Solvent	MFRAO	MFRAO	MFRAO	MFRAO	MFRAO	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18
Ratio Solvent/MAF Coal/H_2O	2.22/1/0.83	3.25/1/0.57	3.20/1/0.49	3.17/1/0.47	2.37/1/0.06	2.34/1/0.04	2.34/1/0.04	2.34/1/0.04	2.38/1/0.27	2.38/1/0.25	2.38/1/0.10
Pressure PSIG	1000	1000	2000	1000	1000	1000	1500	2000	1000	1000	1000
Dissolver Temperature	425	425	425	425	425[c]	425	425	425	425	425	450
1/LHSV	1.35	1.33	1.79	1.62	0.65	1.33	1.33	1.39	1.27	2.08[h]	1.27
GHSV	239	239	362	282	232	225	239	239	228	229	228
Reducing Gas	CO	H_2	CO-H_2	CO-H_2	H_2	H_2	H_2	H_2	CO-H_2	CO-H_2	CO-H_2
INPUT DATA-RAW											
H_2 Grams/Hr.	-	8.8	7.4	4.5	8.6	8.35	8.77	8.82	4.2	4.2	4.2
CO Grams/Hr.	134.4	-	82.5	55.6	-	-	-	-	59.1	59.4	59.0
N_2 Grams/Hr.	5.6	5.2	8.7	5.2	4.0	6.0	6.0	6.0	8.0	10.7	8.2
Feed Slurry Grams/Hr.	385.0	388.8	292	320.6	804	389.3	397.3	372.0	415	247.5	424
Total Feed Grams/Hr.	525.0	402.8	390.6	385.9	816.6	403.7	412.0	386.8	486.3	321.8	495.4
OUTPUT DATA-RAW											
Gas Moles/Hr.	5.678	4.717	7.062	3.56	3.336	2.66	2.50	(2.50)	4.548	4.601	3.440
MW of Gas	28.85	8.51	18.2	19.8	3.3	7.9 [g]	7.9 [g]	7.9 [g]	19.15	18.92	20.42
Gas Output Gm/Hr.	163.8	40.2	128.5	70.5	11.0	21.0	19.8	19.8	87.1	87.1	70.2
Unstripped Solution Gm/Hr.	331.2	351.2	250.7	286.3	790.8	359.3	373.5	355.8	323.5	180.1	369.8
Recovery Gm/Hr.	495.0	391.4	379.2	356.8	801.8	380.3	393.3	375.6	410.6	267.2	440.0
% Recovery	94.5	97.2	97.1	92.5	98.2	94.4	95.4	97.1	84.4	83.0	88.8
OBSERVATIONS											
% Ash in Feed Slurry	2.41	2.41	2.41	2.23[f]	3.29	2.92	3.41	3.32	3.59	3.36	3.44
Solution Blackness	13.85	12.07	9.11		11.93	7.14	5.70	5.69	10.57	7.13	13.57
Solution $\overline{IR}$ Ratio	0.71	0.69	0.85	0.75	0.94	1.25	1.40	1.49	0.99	1.29	0.94
Cut 2 Reclaim $\overline{IR}$ Ratio	0.61	0.64	0.71	0.63	0.84	0.89	1.06	1.20	0.81	0.94	0.74
Feed Solvent $\overline{IR}$ Ratio	0.56	0.56	0.56	0.56	0.56	0.98	0.98	0.98	0.98	0.98	0.98
% H_2 Reacted MAF Coal Basis	-	0.46	0.54		1.06	1.62	2.29	2.88	0.46	0.99	0.85
% CO Reacted MAF Coal Basis	30.63	-	29.12		-	-	-	-	10.75	16.50	12.44
% H_2O Reacted MAF Coal Basis	14.10	-	19.41	11.18	-	-	-	-	6.92	10.57	2.44
% MAF Conversion	42.0	72.0	82.2	62.2	85.5	90.14	92.18	92.09	87.27	90.64	89.46
YIELDS ON LOSS FREE MAF COAL BASIS				e							
H_2	0.87	-	-		-	-	-	-	-	-	-
CO	-	0.63	-	-	-	0.14	0.13	0.50	-	-	-
CO_2	50.99	8.78	60.63	-	0.80	0.81	0.94	1.26	19.00	29.66	19.43
H_2S	-	-	-	-	1.33	2.43	1.89	2.26	1.48	1.52	1.02
Hydrocarbon Gas	4.94	4.68	4.91	-	0.79	3.38	3.50	5.27	4.85	8.52	8.25
H_2O	-14.10	11.04	-19.41	-11.18	5.93	1.62	2.29	7.04	-6.92	-10.57	-2.44
Excess Solvent	-37.59	4.68	16.79	7.32	0.71	27.57	29.92	46.73	14.94	25.85	-3.51
Vacuum Bottoms	71.33	58.28	38.94	54.19	77.0	55.81	55.80	31.91	65.13	53.15	80.00
Insoluble Organic Matter	51.12	38.0	27.80	37.80	14.5	9.86	7.82	7.91	12.73	9.36	10.54
Total	127.56	126.09	129.66	-	101.06	101.62	102.29	102.88	111.21	117.49	113.29
VACUUM BOTTOMS COMPOSITION	d										
%Carbon			88.59			86.63	86.77	86.76	89.48	88.17	90.82
%Hydrogen	Not Filtered		5.01	Not Filtered	Not Filtered	5.70	5.58	5.83	5.38	5.75	5.36
%Nitrogen			1.58			1.63	1.80	1.95	2.04	2.03	1.96
%Sulfur			0.28			1.03	0.91	0.84	0.80	0.72	0.67
%Oxygen			4.34			4.77	4.67	4.63	2.30	3.33	1.19
%Ash		1.25	0.20			0.28	0.27	0.53	i	i	i
Fusion Point °C						237	237	224	216	212	152
SOLVENT YIELDS (% of Feed Solvent) [d]				d	d						
Cold Trap Oil	-	0.51	0.37	-	0.56	1.27	1.50	1.56	1.28	1.57	0.77
Cut 1 Oil < 100°C Vac.	4.28	5.49	9.44	6.05	11.60	22.85	17.36	16.72	9.75	17.99	8.46
Cut 2 Oil 100°C - 230°C Vac.	77.95	92.95	91.55	96.23	88.13	82.65	90.43	97.90	93.42	88.80	89.29
Heavy Oil > 230°C Vac.	-	2.78	3.87	-	-	5.03	3.52	3.82	1.65	2.53	-
Total	82.23	101.73	105.23	102.28	100.29				106.10	110.89	98.52
CUT 2 RECLAIM COMPOSITION											
%Carbon						91.69	91.28	90.98			
%Hydrogen						6.092	6.235	6.527			
%Nitrogen						0.56	0.59	0.68			
%Sulfur						0.30	0.27	0.62			
%Oxygen (By Difference)						1.36	1.62	1.19			

a-Run CL-14 was a retention time study with mineral tracer.
b-CL-18 was a solvent hydrogenation study-Solvent prep. CL18.
c-Dissolver tube heated with a profile 410-445°C mean 425°C to simulate preheater operation.
d- Yields from distillation of unfiltered solution.
e- Gas analysis incomplete GLC failure.
f- By slurry analysis.
g- By MW correlation.
h- Feed rate not steady. Rate dropped during sample period
i- Calculated ash free.

APPENDIX A (PART 3)

SUMMARY OF EXPERIMENTAL RESULTS FOR CONTINUOUS REACTOR STUDIES

RUN NO.	CL 21A	CL 21B	CL 21 C	CL 21 D	CL 21 E	CL 21 F	CL 22A	CL 22B	CL 22C	CL 22D	CL 22E
CONDITIONS											
Coal	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	BN Lignite	BN Lignite	BN Lignite	BN Lignite	BN Lignite
Solvent	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 22B	CL 18	CL 18	CL 18
Ratio/Solvent/MAF Coal/H_2O	2.40/1/0.06	2.40/1/0.06	2.40/1/0.06	2.40/1/0.06	2.40/1/0.06	2.40/1/0.06	3.24/1/0.49	3.25/1/0.46	3.24/1/0.41	3.24/1/0.46	3.24/1/0.39
Pressure PSIG	1000	1000	1000	1000	1000	1000	1500	1500	1500	1500	1500
Dissolver Temperature	450	425	425	450	400	450	425	425	450	400	425
1/LHSV	0.75	0.73	0.90	0.92	0.93	1.35	0.77	0.91	0.93	0.92	1.35
GHSV	231	220	217	228	231	235	236	239	228	235	239
Reducing Gas	H_2	H_2	H_2	H_2	H_2	H_2	CO-H_2 1:1	CO-H_2 1:1	CO-H_2 1:1	CO-H_2 1:1	CO-H_2 1:1
INPUT DATA-RAW											
H_2 Grams/Hr.	8.5	8.1	8.0	8.4	8.5	8.7	4.4	4.6	4.4	4.5	4.6
CO Grams/Hr.	-	-	-	-	-	-	60.5	59.6	55.8	58.0	59.2
N_2 Grams/Hr.	9.8	10.6	11.4	11.0	10.6	10.7	14.0	14.0	14.0	14.0	14.0
Feed Slurry Grams/Hr.	696.0	724.0	579.0	566.0	554.0	398.0	677.0	572.0	562.0	565.0	385.0
Total Feed Grams/Hr.	714.3	742.7	598.4	585.4	573.1	417.4	755.9	650.0	636.2	641.5	462.8
OUTPUT DATA-RAW											
Gas Moles/Hr.	3.907	(3.9)	2.875	2.875	2.719	3.745	5.185	4.965	4.646	4.062	4.458
M.W. of Gas	8.57	7.34	7.02	8.58	5.12	7.48	21.3	19.7	21.1	20.1	20.3
Gas Output Gm/Hr.	33.5	28.6	20.2	24.6	13.9	28.0	110.4	97.8	98.0	81.6	90.5
Unstripped Soln. Gm/Hr.	697.8	685.1	559.9	535.5	544.1	358.8	593.6	512.2	474.7	486.0	321.1
Recovery Gm/Hr.	731.3	713.5	580.1	560.1	558.0	386.8	704.0	610.0	572.7	567.6	411.6
% Recovery	102.4	96.0	96.9	95.6	97.4	92.7	93.1	93.9	90.0	88.5	88.9
OBSERVATIONS											
% Ash in Feed Slurry	3.84					3.99	2.185	2.236	2.282	2.260	2.313
Solution Blackness	10.02	7.19	6.67	7.76	6.44	8.69	9.41	6.25	8.46	4.65	6.16
Solution IR Ratio	1.07	1.23	1.28	1.09	1.41	1.09	0.74	0.85	0.76	1.06	0.95
Cut 2 Reclaim IR Ratio	0.80	0.92	0.92	0.82	0.96	0.85	0.67	0.82	0.69	0.80	0.78
Feed Solvent IR Ratio	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98
%H_2 Reacted-MAF Coal Basis	1.24	1.16	1.43	1.20	2.47	3.17	0.64	0.67	0.85	1.10	1.80
%CO Reacted-MAF Coal Basis	-	-	-	-	-	-	13.45	16.18	17.40	20.19	23.79
%H_2O Reacted-MAF Coal Basis	-	-	-	-	-	-	8.65	10.36	8.23	11.28	11.65
%MAF Conversion	89.40	88.65	88.00	89.88	89.73	90.37	86.34	87.45	89.90	77.10	89.42
YIELDS-LOSS FREE MAF COAL BASIS											
H_2	-	-	-	-	-	-					
CO	0.47	0.25	0.19	0.25	0.13	0.37					
CO_2	1.45	1.21	0.99	1.02	0.58	1.37	29.33	26.71	29.29	24.00	33.96
H_2S	1.50	2.52	2.11	2.42	1.04	2.86	0.07	0.08	Trace	0.09	0.16
Hydrocarbon Gas	6.31	3.07	2.50	5.34	1.17	8.83	7.44	4.55	7.39	1.45	5.34
H_2O	1.81	3.13	2.92	3.75	7.60	2.30	-8.65	-10.36	-8.23	-11.28	-11.65
Excess Solvent	14.74	12.46	13.68	16.98	4.94	18.97	10.59	25.86	19.86	23.49	29.86
Vacuum Bottoms	64.36	67.17	67.04	61.32	76.74	58.53	61.65	57.46	59.84	60.64	57.34
Insoluble Organic Matter	10.60	11.35	12.00	10.12	10.27	9.64	13.66	12.55	10.10	22.90	10.58
Total	101.24	101.16	101.43	101.20	102.47	102.87	114.09	116.85	118.25	121.29	125.59
VACUUM BOTTOMS COMPOSITION											
%Carbon	87.59	85.43	86.07	87.57		88.57	88.79	87.91	90.10	85.97	88.20
%Hydrogen	5.44	5.77	5.90	5.37	Not	5.24	4.93	5.59	4.92	5.83	5.23
%Nitrogen	1.96	1.80	2.04	2.01	Filtered	2.01	1.44	1.59	1.49	1.53	1.58
%Sulfur	0.85	1.15	1.12	0.80		0.70	0.18	0.21	0.14	0.23	0.16
%Oxygen	4.04	5.64	4.74	4.00		3.36	4.53	4.49	3.22	6.10	4.64
%Ash	0.13	0.22	0.14	0.25		0.12					
Fusion Point °C	208	212	215	204	235	200	205	204	217	263	217
SOLVENT YIELDS(% OF FEED SOLVENT)											
Cold Trap Oil	1.19	0.95	1.04	1.72	0.79	1.53	1.19	1.14	1.57	1.28	1.37
Cut 1 Oil< 100°C Vacuum	10.54	8.78	15.13	14.74	13.73	16.24	13.60	3.66	14.18	17.76	15.81
Cut 2 Oil 100-230°C Vacuum	93.56	94.08	88.37	88.58	87.55	87.72	86.99	100.55	88.25	88.21	89.98
Heavy Oil> 230°C Vacuum	0.86	1.39	1.17	2.04	-	2.41	1.48	2.62	2.12	0.00	2.05
Total	106.15	105.20	105.71	107.08	102.07	107.90	103.26	107.97	106.12	107.25	109.21
UNFILTERED SOLUTION COMPOSITION											
%Carbon	85.28	85.87	85.33	80.43	86.14	88.64					
%Hydrogen	5.838	5.941	6.056	5.58	6.288	6.458[b]					
%Nitrogen	0.97	0.97	0.91	0.94	0.99	0.90					
%Sulfur	0.99	0.71	0.81	0.73	1.12	0.62					
%Oxygen(By Difference)	1.45	0.64	3.24	3.43	0.51	(-1.24)					
%Ash[a]	5.47	5.87	3.57	8.89	4.95	4.62					
%H Ash Free	6.18	6.31	6.28	6.12	6.61	6.77[b]					

[a] Sampling of unfiltered solution for ash analysis not satisfactory. Oxygen by difference not accurate.

[b] Doubtful.

APPENDIX A (PART 4)

SUMMARY OF EXPERIMENTAL RESULTS FOR CONTINUOUS REACTOR STUDIES

RUN NO.	CL 23A	CL 23B	CL 23C	CL 23D	CL 23E	CL 23F	CL 24A	[b] CL 25A	CL 25B	CL 25C	CL 25D
CONDITIONS											
Coal	BN Lignite	BN Lignite	BN Lignite	BN Lignite	BN Lignite	BN Lignite	BN Lignite	BN Lignite	BN Lignite	BN Lignite	BN Lignite
Solvent	CU 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18
Ratio/Solvent/MAF Coal/H_2O	3.15/1/0.49	3.15/1/0.53	3.14/1/0.49	3.15/1/0.47	3.15/1/0.45	3.15/1/0.47	3.15/1/0.49	3.15/1/0.45	3.15/1/0.49	3.15/1/0.49	3.15/1/0.49
Pressure PSIG	1500	1500	1500	1500	1000	1000	1000	1500	1500	1500	1000
Dissolver Temperature	450	450	450	400	425	425	425	425	425	450	450
1/LHSV;Hr.	0.58	0.76	1.35	1.30	1.39	0.92	0.72	0.56	0.74	0.74	0.72
GHSV	232	228	233	236	212	220	238	242	233	230	216
Reducing Gas	CO-H_2 1:1	CO-H_2 1:1	CO-H_2 1:1	CO-H_2 1:1	CO-H_2 1:1	CO-H_2 1:1	CO-H_2 1:3.24	CO-H_2 1:4	CO-H_2 1:3.8	CO-H_2 1:36	CO-H_2 1:3.2
INPUT DATA-RAW											
H_2 Grams/Hr.	4.4	4.3	4.3	4.3	3.9	4.1	6.7	7.1	6.8	6.6	6.0
CO Grams/Hr.	57.6	57.1	57.1	57.1	53.9	56.0	28.9	25.0	24.9	25.5	26.8
H_2 Grams/Hr.	15.4	16.4	14.8	14.8	9.8	10.3	9.8	11.9	3.0	9.6	5.2
Feed Slurry Grams/Hr.	898.0	689.0	384.0	402.6	377.3	569.0	722	929	705	701	719
Total Feed Grams/Hr.	975.4	766.8	460.2	478.8	444.9	639.4	767.4	973.0	739.7	742.7	757
OUTPUT DATA-RAW											
Gas Moles/Hr.	5.707	4.912	4.345	4.518	3.794	3.314	4.458	5.540	5.211	3.324	2.536
M.W. of Gas	22.24	21.99	20.81	20.00	20.00	20.65	14.43	13.32	11.24	15.47	18.07
Gas Output Gm/Hr.	126.9	108.0	90.4	90.4	75.9	68.4	64.3	73.8	58.6	51.4	45.8
Unstripped Solution Gm/Hr.	797.6	606.2	320.9	321.8	345.5	521.9	665.7	851.3	648.2	637.1	668.9
Recovery Gm/Hr.	924.5	714.2	411.3	412.2	421.4	590.3	730.0	925.1	706.8	688.5	714.7
%Recovery	94.78	93.14	89.37	86.09	94.72	92.32	95.12	95.07	95.54	92.70	94.4
OBSERVATIONS											
%Ash in Feed Slurry	2.267	2.431	2.441	2.345	2.409	2.361	2.272	2.234	2.291	2.284	2.251
Solution Blackness	10.86	9.86	9.61	4.44	8.81	7.80	6.92	7.84	9.24	9.61	10.93
Solution $\overline{IR}$ Ratio	0.63	0.69	0.78	1.01	0.89	0.77	0.80	0.80	0.80	0.73	0.60
Cut 2 Reclaim $\overline{IR}$ Ratio	0.54	0.60	0.63	0.87	0.73	0.68	0.73	0.65	0.69	0.64	0.57
Feed Solvent $\overline{IR}$ Ratio	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98
%H_2 Reacted-MAF Coal Basis	0.32	0.62	1.48	0.86	1.16	1.33	0.92	-0.20	-0.40	1.96	2.38
%CO Reacted-MAF Coal Basis	12.96	18.26	33.00	21.36	18.14	19.93	5.20	4.00	4.91	10.64	11.43
%H_2O Reacted-MAF Coal Basis	8.36[a]	5.97	12.23	6.50	8.07	8.47	3.36	2.58	3.16	3.73	1.52
%MAF Conversion	80.27	83.83	88.42	83.96	80.45	78.16	75.33	79.23	80.69	80.90	71.78
YIELDS-LOSS FREE MAF COAL BASIS											
H_2	-	-	-	-	-	-	-	0.20	0.40	-	-
CO	-	-	-	-	-	-	-	-	-	-	-
CO_2	32.01	33.96	42.36	32.00	28.37	19.52	16.78	15.80	17.29	16.46	14.74
H_2S	0.16	0.28	0.16	0.08	0.17	0.08	0.13	0.10	0.14	0.14	Trace
Hydrocarbon Gas	9.00	8.13	9.85	2.35	4.66	2.58	2.24	2.28	2.90	4.75	5.28
H_2O	-8.36	-5.97	-12.23	-6.50	-8.07	-8.47	-3.36	-2.58	-3.16	-3.73	-0.13
Excess Solvent	-6.98	-0.49	11.41	26.76	14.06	27.57	11.38	-2.63	12.11	15.92	1.52
Vacuum Bottoms	67.72	66.80	71.35	51.49	60.56	58.14	54.28	70.06	55.92	59.96	64.18
Insoluble Organic Matter	19.73	16.17	11.58	16.04	19.55	21.84	24.67	20.77	19.31	19.10	28.22
Total	113.28	118.88	134.48	122.22	119.30	121.26	106.12	104.00	104.91	112.60	113.81
VACUUM BOTTOMS COMPOSITION											
%Carbon	91.05	90.40	90.96	86.35	89.08	88.43	88.00		88.42	89.95	90.12
%Hydrogen	5.05	5.03	4.88	5.79	5.14	5.19	5.36	Not	5.85	5.09	5.00
%Nitrogen	1.26	1.43	1.39	1.63	1.48	1.47	1.49		1.47	1.43	1.32
%Sulfur	0.16	0.14	0.12	0.20	0.16	0.18	0.22	Filtered	0.20	0.15	0.16
%Oxygen	2.48	2.91	2.63	5.69	3.97	4.49	4.34		3.97	3.28	3.31
%Ash	0.23	0.09	0.021	0.347	0.168	0.24	0.29		0.19	0.10	0.09
Fusion Point °C	195°C	195°C	183°C	226°C	219°C	243°C	223°C		280°C	255°C	235°C
SOLVENT YIELDS (% OF FEED SOLVENT)											
Cold Trap Oil	1.29	1.81	2.01	1.84	1.69	2.14	1.94	1.68	1.73	3.03	2.20
Cut 1 Oil< 100°C Vacuum	15.29	13.04	15.81	13.20	6.77	7.49	4.16	9.00	7.68	7.42	6.59
Cut 2 Oil 100-230°C Vacuum	81.20	85.00	85.81	92.39	93.90	97.65	95.86	88.49	92.86	92.25	89.92
Heavy Oil> 230°C Vacuum	-	-	-	1.07	2.12	1.48	1.65	0.00	1.58	2.34	1.76
Total	97.78	99.85	103.63	108.5	104.48	108.76	103.61	99.17	103.85	105.04	100.47
UNFILTERED SOLUTION COMPOSITION											
%Carbon			83.64				81.32				
%Hydrogen			6.16				6.29				
%Nitrogen			0.83				0.82				
%Sulfur			0.25				2.42				
%Oxygen							6.83				
%Ash			2.27				2.32				

a - Calculated from CO used.

b - Run CL 24B at 1000 PSIG 1/LHSV=0.74 resulted in a plug in dissolver.

APPENDIX A (PART 5)

SUMMARY OF EXPERIMENTAL RESULTS FOR CONTINUOUS REACTOR STUDIES

RUN NO.	CL 25 E	CL 25F	CL 26A	CL 26B	CL 26C	CL 26D	CL 26E	CL 26F	CL 26G	CL 27A	CL 27B
CONDITIONS											
Coal	BN Lignite	BN Lignite	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9
Solvent	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18
Ratio Solvent/MAF Coal/H_2O	3.15/1/0.46	3.15/1/0.48	2.38/1/0.11	2.38/1/0.16	2.38/1/0.16	2.38/1/0.16	2.38/1/0.15	2.38/1/0.15	2.38/1/0.14	2.37/1/0.06	2.37/1/0.06
Pressure PSIG	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Dissolver Temperature	450	425	450	425	425	475	475	475	450	425	450
1/LHSV;Hr.	0.56	0.56	0.57	0.57	0.73	0.71	0.57	0.42	0.72	0.53	0.52
GHSV	209	306	226	216	217	224	223	234	238	236	225
Reducing Gas	CO-H_2 1:2.8	CO-H_2 1:5.3	CO-H_2 1:3	CO-H_2 1:3	CO-H_2 1:3	CO-H_2 1:3	CO-H_2 1:3	CO-H_2 1:3	CO-H_2 1:3	H_2	H_2
INPUT DATA-RAW											
H_2 Grams/Hr.	5.6	9.5	6.3	5.9	5.9	6.0	6.0	6.5	6.8	8.7	8.3
CO Grams/Hr.	28.6	25.0	28.3	28.3	29.6	30.7	30.8	29.7	27.8	-	-
N_2 Grams/Hr.	5.6	3.4	5.8	7.1	6.5	6.2	8.8	6.9	6.6	7.2	7.0
Feed Slurry Grams/Hr.	926.0	930.0	908.0	914.0	715.0	727.0	915.0	1234.0	720.0	955.0	965.0
Total Feed Grams/Hr.	965.8	967.9	948.4	955.3	757.0	769.9	960.6	1277.1	761.2	970.9	980.3
OUTPUT DATA-RAW											
Gas Moles/Hr.	2.513	6.828	3.858	3.270	2.467	2.231	2.223	2.613	1.834	4.421	4.239
M.W. of Gas	19.70	9.92	15.12	14.65	13.98	18.58	19.62	19.30	16.97	6.76	7.61
Gas Output Gm/Hr.	49.50	67.7	58.3	47.9	34.5	41.5	43.6	50.4	31.1	29.9	32.3
Unstripped Solution Gm/Hr.	858.30	865.4	833.5	875.5	671.3	661.7	839.7	1144.4	674.4	900.2	896.4
Recovery Gm/Hr.	902.80	833.1	891.8	923.4	705.8	703.2	883.3	1194.8	705.5	930.1	928.7
%Recovery	93.48	96.41	94.05	96.66	93.24	91.34	91.95	93.59	92.70	95.79	94.72
OBSERVATIONS											
%Ash in Feed Slurry	2.258	2.278	3.882	3.968	3.925	3.881	3.965	3.848	3.956	3.538	3.672
Solution Blackness	9.78	6.81	11.43	8.02	7.79	16.63	17.17	17.60	13.43	7.46	9.76
Solution $\overline{IR}$ Ratio	0.61	0.80	1.00	1.23	1.14	0.68	0.64	0.71	0.89	1.21	1.05
Cut 2 Reclaim $\overline{IR}$ Ratio	0.58	0.66	0.75	0.85	0.86	0.52	0.54	0.54	0.68	0.84	0.82
Feed Solvent $\overline{IR}$ Ratio	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98
%H_2 Reacted - MAF Coal Basis	1.73	-0.36	0.84	0.85	1.49	2.23	1.84	1.40	2.59	2.17	2.18
%CO Reacted - MAF Coal Basis	9.84	0.15	5.04	5.24	9.21	13.33	11.18	7.79	11.42	-	-
%H_2O Reacted - MAF Coal Basis	1.89	0.10	-	3.10	3.91	1.22	1.56	1.90	-	-	-
%MAF Conversion	68.44	68.79	88.15	89.52	89.25	77.75	73.43	76.59	85.89	89.09	89.38
YIELDS - LOSS FREE MAF COAL BASIS											
H_2	-	0.36	-	-	-	-	-	-	-	-	-
CO	-	-	-	-	-	-	-	-	-	0.15	0.18
CO_2	13.46	13.10	7.53	6.21	6.28	7.55	5.57	4.52	4.67	0.83	1.11
H_2S	0.10	0.20	1.72	1.21	0.26	0.56	1.00	1.25	1.37	2.10	2.58
Hydrocarbon Gas	4.28	1.73	4.12	1.60	1.69	8.01	7.13	5.77	3.86	1.59	3.86
H_2O	-1.89	-0.10	0.24	-3.10	-3.91	-1.22	-1.56	-1.90	0.41	4.84	7.08
Excess Solvent	1.84	-0.76	14.21	17.82	22.70	2.69	-3.45	-0.06	18.58	11.57	11.73
Vacuum Bottoms	62.22	54.41	66.21	71.78	72.93	75.72	77.76	76.20	71.01	70.18	65.02
Insoluble Organic Matter	31.56	31.21	11.85	10.48	10.75	22.25	26.57	23.41	14.11	10.91	10.62
Total	111.58	100.15	105.88	106.00	110.70	115.56	113.02	109.19	114.01	102.17	102.18
VACUUM BOTTOMS COMPOSITION											
%Carbon	89.72	87.72	87.63	85.20	85.22	90.28	90.13	89.65	87.66	84.88	86.85
%Hydrogen	5.02	5.36	5.18	5.61	5.60	4.48	4.64	4.62	4.99	5.79	5.47
%Nitrogen	1.25	1.32	2.08	2.02	1.95	1.71	1.73	1.79	2.03	2.04	2.07
%Sulfur	0.18	0.20	0.96	1.28	1.29	0.67	0.68	0.78	0.97	1.29	1.01
%Oxygen	3.59	5.08	4.06	5.72	5.76	2.73	2.75	3.12	4.29	5.87	4.46
%Ash	0.24	0.32	0.082	0.18	0.18	0.13	0.17	0.06	0.06	0.136	0.135
Fusion Point °C	230°C	270°C	230°C	235°C	235°C	235°C	235°C	260°C	260°C	255°C	227°C
SOLVENT YIELDS (% of Feed Solvent)											
Cold Trap Oil	1.90	2.71	1.87	1.13	1.58	2.19	2.16	1.52	1.77	0.85	1.69
Cut 1 Oil < 100°C Vacuum	9.57	8.72	8.27	6.58	8.35	9.14	7.61	5.60	9.60	10.84	7.58
Cut 2 Oil 100-230°C Vacuum	87.64	86.91	93.05	97.44	97.51	86.37	86.60	90.14	93.77	91.47	93.29
Heavy Oil > 230°C Vacuum	1.47	1.43	2.77	2.32	2.10	3.43	2.19	2.71	2.66	1.71	2.38
Total	100.58	99.77	105.96	107.47	109.54	101.13	98.56	99.97	107.80	104.87	104.94
UNFILTERED SOLUTION COMPOSITION											
%Carbon										86.78	87.18
%Hydrogen										6.31	6.14
%Nitrogen										0.98	0.96
%Sulfur										0.84	0.70
%Ash										3.11	3.70
Difference (0)										1.98	1.32

CL 26 Feed Coal 11.65% Ash and 4.58% H_2O.

APPENDIX A (PART 6)

SUMMARY OF EXPERIMENTAL RESULTS FOR CONTINUOUS REACTOR STUDIES

RUN NO.	CL 27C	CL 27D	CL 27E	CL 27F	CU 28A-1	CL 28A-2	CU 28B	CU 29A	CU 29B	CU 29C	CU 29D
CONDITIONS											
Coal	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9
Solvent	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	MFRAO	MFRAO	MFRAO	MFRAO
Ratio Solvent/MAF Coal/H_2O	2.37/1/0.06	2.37/1/0.06	2.37/1/0.06	2.37/1/0.06	2.37/1/0.03	2.37/1/0.03	2.37/1/0.03	2.37/1/0.05	2.39/1/0.05	2.39/1/0.05	2.39/1/0.05
Pressure PSIG	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Preheater Temperature °C	-	-	-	-	450	450	450	450	450	450	450
Dissolver Temperature °C	475	475	475	450	450	450	425	450	450	450	450
1/LHSV;Hr.	0.49	0.73	0.42	0.41	0.51	0.51	0.51	0.51	0.84	0.96	1.26
GHSV	225	231	236	234	204	208	204	229	208	233	233
Reducing Gas	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2
INPUT DATA-RAW											
H_2 Grams/Hr.	8.3	8.5	8.7	8.6	7.6	7.6	7.4	8.4	7.7	8.6	8.6
CO Grams/Hr.	-	-	-	-	-	-	-	-	-	-	-
N_2 Grams/Hr.	8.3	7.1	5.8	7.1	7.4	7.4	7.8	8.4	7.0	7.0	7.0
Feed Slurry Grams/Hr.	1053.0	715.0	1233.0	1266.6	1020.0	1020.0	1030.0	1030.0	618.0	540.0	410.0
Total Feed Grams/Hr.	1069.6	730.6	1247.5	1282.3	1035.0	1035.0	1045.2	1046.8	632.7	555.6	425.6
OUTPUT DATA-RAW											
Gas Moles/Hr.	4.332	4.489	(5.099)[a]	4.099	3.566	3.468	2.918	3.699	2.991	3.584	3.321
M.W. of Gas	11.38	9.83	(11.38)	7.92	9.59	9.84	9.21	9.81	9.40	8.81	7.78
Gas Output Gm/Hr.	49.3	44.1	58.0	40.4	34.2	34.2	26.9	36.3	28.1	31.6	25.8
Unstripped Solution Gm/Hr.	953.9	725.7	1198.6	1241.3	978.6	996.0	995.2	1011.0	591.4	489.3	375.9
Recovery Gm/Hr.	1003.2	769.8	1256.8	1281.7	1012.8	1030.2	1022.1	1047.3	619.5	520.9	401.7
%Recovery	93.79	105.3	100.7	99.95	97.85	99.53	97.78	100.04	97.92	93.75	94.38
OBSERVATIONS											
%Ash in Feed Slurry	3.857	4.089	3.481	4.387	3.669	3.719	3.651	3.762	3.784	3.886	4.195
Solution Blackness	14.71	12.81	13.22	10.13	11.04	11.11	8.52	14.44	14.65	13.16	11.05
Solution IR Ratio	0.79	0.90	0.87	1.05	0.96	0.97	1.18	0.84	0.88	0.91	0.95
Cut 2 Reclaim IR Ratio	0.61	0.70	0.67	0.82	0.74	0.77	0.83	0.66	0.70	0.76	0.82
Feed Solvent IR Ratio	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.58	0.58	0.58	0.58
%H_2 Reacted-MAF Coal Basis	1.04	2.20	0.81	0.33	0.91	0.98	0.98	1.11	2.01	2.25	3.06
%CO Reacted-MAF Coal Basis	-	-	-	-	-	-	-	-	-	-	-
%H_2O Reacted-MAF Coal Basis	-	-	-	-	-	-	-	-	-	-	-
%MAF Conversion	86.29	87.77	86.97	89.27	89.18	88.90	91.36	87.14	83.31	86.41	89.17
YIELDS-LOSS FREE MAF COAL BASIS											
H_2	-	-	b	-	-	-	-	-	-	-	-
CO	0.29	0.38	0.28	0.19	0.14	0.21	0.14	0.21	0.16	0.33	0.35
CO_2	1.56	1.58	1.57	1.25	1.19	1.26	0.97	1.46	1.13	1.46	1.31
H_2S	2.41	2.68	2.44	1.96	1.60	1.74	1.38	1.95	1.74	2.59	2.79
Hydrocarbon Gas	7.92	9.27	8.01	3.24	4.51	4.89	2.00	4.80	4.77	7.69	8.47
H_2O	4.62	5.30	2.94	2.82	4.39	6.00	4.22	5.01	4.94	4.64	4.37
Excess Solvent	1.14	5.78	5.60	11.57	9.98	6.00	10.51	0.21	1.44	4.58	8.21
Vacuum Bottoms	69.39	64.98	66.94	68.57	68.32	69.78	73.12	74.61	71.14	67.37	66.73
Insoluble Organic Matter	13.71	12.23	13.03	10.73	10.82	11.10	8.64	12.86	16.69	13.59	10.83
Total	101.04	102.20	100.81	100.33	100.95	100.98	100.98	101.11	102.01	102.25	103.06
VACUUM BOTTOMS COMPOSITION											
%Carbon	89.23	89.13	85.72	86.11	88.04	87.94	85.73	87.81	87.49	87.92	87.65
%Hydrogen	4.78	5.03	4.85	5.33	5.15	5.07	5.58	4.71	5.34	4.98	4.86
%Nitrogen	1.95	2.01	1.99	2.10	2.04	2.02	2.02	1.98	2.04	2.09	2.13
%Sulfur	0.70	0.71	0.87	1.14	0.97	1.04	1.33	1.05	0.96	0.85	0.77
%Oxygen	3.29	2.95	6.48	5.16	3.67	3.82	5.17	4.25	4.00	4.05	4.66
%Ash	0.05	0.17	0.09	0.16	0.13	0.11	0.17	0.21	0.17	0.12	0.12
Fusion Point °C	215	210	232	230							
SOLVENT YIELDS (% of Feed Solvent)											
Cold Trap Oil	1.85	2.07	1.55	1.49	1.91	2.06	1.37	2.27	2.18	2.44	3.29
Cut 1 Oil< 100°C Vacuum	12.13	11.05	8.56	7.11	5.82	6.12	4.72	5.01	6.41	6.94	4.65
Cut 2 Oil 100-230°C Vacuum	83.73	86.27	89.84	94.39	92.76	91.15	96.07	89.25	86.98	87.25	91.69
Heavy Oil> 230°C Vacuum	2.77	3.04	2.41	1.89	3.71	3.20	2.27	3.55	3.87	5.28	3.81
Total	100.48	102.43	102.36	104.88	104.20	102.53	104.43	100.08	99.44	101.91	103.44
COMPOSITION ON UNFILTERED SOLUTION											
% Carbon	86.48	86.81	86.17	85.61							
% Hydrogen	5.77	5.93	5.63	5.69							
% Nitrogen	0.95	0.96	0.97	0.93							
% Sulfur	0.92	0.77	0.93	1.00							
% Ash	3.04	3.79	3.96	4.34							
Difference (0)	2.84	1.74	2.34	2.43							

a - Gas sample lost calculated with CL 27C gas composition and CL 27F volume.
b - Gas yields estimated only.

APPENDIX A (PART 7)

SUMMARY OF EXPERIMENTAL RESULTS FOR CONTINUOUS REACTOR STUDIES

RUN. NO.	CU 29E	CU 30A	CU 30B	CU 30C	CU 30D	CU 30E	CU 30F	CU 30G	CU 30H	CU 31A	CU 31B
CONDITIONS											
Coal	KY#9	ELKOL	ELKOL	ELKOL	ELKOL	ELKOL	ELKOL	ELKOL	ELKOL	KY#9	KY#9
Solvent	MFRAO	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18
Ratio Solvent/MAF Coal/H_2O	2.39/1/0.05	2.58/1/0.22	2.56/1/0.17	2.56/1/0.19	2.56/1/0.17	2.56/1/0.18	2.56/1/0.20	2.56/1/0.21	2.56/1/0.17	2.51/1/0.21	2.51/1/0.14
Pressure PSIG	750	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Preheater Temperature °C	450	425	425	425	425	400	450	450	450	425	425
Dissolver Temperature °C	450	425	425	425	425	400	450	450	450	425	425
1/LHSV;Hr.	0.85	1.02	0.98	0.71	1.30	1.22	1.20	0.71	1.06	0.505	0.763
GHSV	242	228	235	235	235	235	235	235	235	248	248
Reducing Gas	H_2	H_2	CO-H_2 1:3	CO-H_2 1:3	CO-H_2 1:3	CO-H_2 1:3	CO-H_2 1:3	CO-H_2 1:3	CO-H_2 1:3	CO-H_2 1:1	CO-H_2 1:1
INPUT DATA-RAW											
H_2 Grams/Hr.	8.9	8.4	6.6	6.6	6.6	6.6	6.6	6.6	6.6	4.8	4.8
CO Grams/Hr.	-	-	29.5	29.5	29.5	29.5	29.5	29.5	29.5	60.7	60.7
N_2 Grams/Hr.	4.8	9.6	7.4	6.8	7.2	7.2	7.0	7.0	7.2	5.7	2.4
Feed Slurry Grams/Hr.	615.0	510.0	530.0	730.0	400.0	425.0	430.0	730.0	490.0	1030.0	680.0
Total Feed Grams/Hr.	628.7	528.0	573.5	772.9	443.3	468.3	473.1	773.1	533.3	1101.2	747.9
OUTPUT DATA-RAW	a										
Gas Moles/Hr.	(3.584)	5.109	4.619	3.143	4.565	4.584	4.441	4.753	4.659	5.276	4.837
M.W. of Gas	(8.81)	5.70	12.01	12.57	11.80	11.04	12.50	13.34	14.38	18.93	18.81
Gas Output Gm/Hr.	(31.6)	29.1	55.5	39.5	53.9	50.6	55.5	63.4	70.0	99.8	91.0
Unstripped Solution Gm/Hr.	562.5	463.0	516.1	691.5	387.4	412.5	407.6	689.2	466.7	960.0	633.7
Recovery Gm/Hr.	594.1	492.1	571.6	731.0	441.3	463.1	463.1	752.6	533.7	1059.8	724.7
% Recovery	94.49	93.20	99.66	99.58	99.54	98.89	97.84	97.41	100.01	96.24	96.89
OBSERVATIONS											
% Ash in Feed Slurry	4.150	0.9599	0.9635	0.9876	0.9670	1.022	1.024	1.034	1.027	5.022	5.139
Solution Blackness	14.62	11.88	12.86	11.84	13.50	10.48	16.72	14.47	15.58	7.09	7.10
Solution IR Ratio	0.89	0.92	0.93	0.95	0.89	1.09	0.78	0.79	0.79	1.07	1.07
Cut 2 Reclaim IR Ratio	0.73	0.72	0.71	0.72	0.71	0.71	0.66	0.65	0.65	0.86	0.88
Feed Solvent IR Ratio	0.58	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98
% H_2 Reacted-MAF Coal Basis	2.10	2.94	0.50	1.40	0.66	0.44	1.06	0.52	0.69	0.19	0.46
% CO Reacted-MAF Coal Basis	-	-	1.78	5.34	-0.09	-0.18	2.29	0.00	-0.61	2.30	5.71
% H_2O Reacted-MAF Coal Basis	-	-	-	-	-	-	-	-	-	1.49	3.00
% MAF Conversion	84.56	83.92	68.35	64.35	79.68	72.71	76.79	67.41	65.03	86.90	87.55
YIELDS-LOSS FREE MAF COAL BASIS	a										
H_2	-	-	-	-	-	-	-	-	-	-	-
CO	0.29	0.83	-	-	0.09	0.18	-	-	0.61	-	-
CO_2	1.28	5.13	6.40	3.78	6.21	4.44	6.53	5.84	6.00	9.69	13.09
H_2S	2.27	0.45	0.43	0.31	0.47	0.36	0.53	0.42	0.46	1.46	1.67
Hydrocarbon Gas	6.75	3.69	3.99	1.87	4.33	1.68	7.32	5.11	6.09	2.06	2.65
H_2O	4.02	4.83	6.90	6.48	6.59	5.69	8.83	7.40	6.84	-1.49	-3.00
Excess Solvent	-0.46	4.68	-12.52	-4.92	-5.46	0.80	-14.83	-16.06	-22.52	9.66	11.99
Vacuum Bottoms	72.51	67.25	65.43	63.57	68.11	60.00	71.76	65.22	68.10	68.01	67.32
Insoluble Organic Matter	15.44	16.08	31.65	35.65	20.32	27.29	23.21	32.59	34.97	13.10	12.45
Total	102.10	102.94	102.28	106.74	100.66	100.44	103.35	100.52	100.55	102.49	106.17
VACUUM BOTTOMS COMPOSITION											
%Carbon	87.89	87.39	87.90	86.91	88.33	86.05	89.79	88.78	89.55	85.67	85.95
%Hydrogen	4.88	4.93	5.01	5.19	4.98	5.10	4.64	4.75	4.64	5.62	5.61
%Nitrogen	2.07	1.50	1.47	1.45	1.46	1.45	1.40	1.35	1.38	1.99	2.03
%Sulfur	0.95	0.14	0.15	0.16	0.16	0.17	0.17	0.12	0.12	1.27	1.18
%Oxygen	4.01	5.81	5.23	6.18	4.88	6.99	3.61	4.87	4.07	5.10	5.09
%Ash	0.20	0.24	0.25	0.20	0.18	0.25	0.39	0.12	0.24	0.35	0.15
Fusion Point °C											
SOLVENT YIELDS (% OF FEED SOLVENT)											
Cold Trap Oil	2.20	1.67	1.75	2.65	2.35	1.46	2.38	1.98	2.37	1.25	1.61
Cut 1 Oil < 100°C Vacuum	3.80	3.51	3.59	2.35	4.34	4.79	3.28	2.81	2.37	2.68	2.18
Cut 2 Oil 100-230°C Vacuum	90.37	92.19	85.83	88.85	85.29	88.64	84.21	85.50	82.25	96.68	96.22
Heavy Oil > 230°C Vacuum	3.44	4.45	3.95	4.23	5.88	5.42	4.34	3.44	4.21	3.23	4.77
Total	99.81	101.82	95.12	98.08	97.86	100.31	94.21	93.73	91.20	103.84	104.78

a - Based on CU 29C gas volume and composition. CU 29E gas sample lost.

b - Run CU 30 started after a KY#9 coal series. Normal flushing procedures tend to leave some mineral in the reactor. See text for discussion. Ref: Table VI, page 14, February 1972.

APPENDIX A (PART 8)

SUMMARY OF EXPERIMENTAL RESULTS FOR CONTINUOUS REACTOR STUDIES

RUN NO.	CU 31C	CU 31D	CU 31E	CU 31F	CU 31G	CU 32A	CU 32B	CU 32C	CU 32D	CU 33A*	CU 33B*
CONDITIONS											
Coal	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9
Solvent	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18
Ratio Solvent/MAF Coal/H_2O	2.51/1/0.14	2.51/1/0.16	2.51/1/0.18	2.51/1/0.21	2.51/1/0.19	2.50/1/0.06	2.50/1/0.06	2.50/1/0.06	2.50/1/0.06	2.50/1/0.06	2.50/1/0.06
Pressure PSIG	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Preheater Temperature °C	450	450	452	475	475	450	450	475	475	200	300
Dissolver Temperature °C	450	450	452	474	468	450	450	475	475	-	-
1/LHSV;Hr.	0.813	0.592	0.409	0.461	0.662	0.333	0.495	0.338	0.267	0.035	0.035
GHSV	247	240	240	244	253	239	236	239	239	2978	2978
Reducing Gas	CO-H_2 1:1	CO-H_2 1:1	CO-H_2 1:1	CO-H_2 1:1	CO-H_2 1:1	H_2	H_2	H_2	H_2	H_2	H_2
INPUT DATA-RAW											
H_2 Grams/Hr.	4.8	4.6	4.6	4.7	4.9	8.8	8.7	8.8	8.8	8.1	8.1
CO Grams/Hr.	60.5	58.7	58.7	59.6	61.9	-	-	-	-	-	-
N_2 Grams/Hr.	2.4	7.0	4.8	5.4	5.4	8.4	8.7	7.5	1.8	-	-
Feed Slurry Grams/Hr.	640.0	880.0	1270.0	1130.0	785.0	1560.0	1050.0	1540.0	1950.0	1070	1070
Total Feed Grams/Hr.	707.7	949.3	1338.1	1199.7	857.2	1577.2	1067.4	1556.3	1960.6	1078.1	1078.1
OUTPUT DATA-RAW											
Gas Moles/Hr.	5.044	5.028	4.862	6.060	4.765	3.199	3.462	4.611	4.369	3.806	3.818
M.W. of Gas	20.51	20.42	19.89	20.14	18.59	10.67	9.05	12.68	14.40	2.54	2.42
Gas Output Gm/Hr.	103.5	102.7	96.7	122.0	88.6	34.1	31.3	58.5	62.9	9.7	9.2
Unstripped Solution Gm/Hr.	578.7	819.2	1248.6	1056.8	734.4	1473.5	1004.6	1537.5	1902.7	1016.6	1269.2
Recovery Gm/Hr.	682.2	921.9	1345.3	1178.8	822.9	1507.6	1036.9	1596.0	1965.6	1026.3	1278.4
%Recovery	96.39	97.11	100.5	98.26	96.01	95.59	97.05	102.54	100.25	95.19	118.5
OBSERVATIONS											
Ash in Feed Slurry	5.227	5.292	5.091	5.228	5.295	4.965	4.758	5.311	5.422	4.512	5.251
Solution Blackness	11.12	9.13	9.62	14.58	10.27	10.27	9.30	14.54	15.19	1.61	2.71
Solution IR Ratio	0.96	1.02	0.99	0.68	0.92	0.94	0.97	0.74	0.78	1.23	1.20
Cut 2 Reclaim IR Ratio	0.79	0.81	0.77	0.60	0.76	0.74	0.78	0.60	0.61	1.41	1.39
Feed Solvent IR Ratio	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98
% H_2 Reacted - MAF Coal Basis	0.78	0.44	0.27	0.21	0.49	1.10	1.32	0.87	0.91	0.24	0.21
% CO Reacted - MAF Coal Basis	5.22	4.70	3.88	3.50	5.31	-	-	-	-	-	-
% H_2O Reacted - MAF Coal Basis	1.80	1.05	0.37	0.07	-	-	-	-	-	-	-
% MAF Conversion	85.78	86.86	87.23	81.14	87.34	87.59	86.95	80.49	82.99	-6.84	21.48
YIELDS-LOSS FREE MAF COAL BASIS											
H_2	-	-	-	-	-	-	-			-	-
CO	-	-	-	-	-	0.14	0.21	0.25	0.21	0.00	0.00
CO_2	15.49	12.48	8.22	11.27	9.53	0.94	1.07	1.41	1.44	0.07	0.14
H_2S	2.10	1.93	1.34	1.91	1.84	1.30	1.61	1.93	1.83	0.04	0.07
Hydrocarbon Gas	6.66	4.62	3.06	8.39	4.27	3.28	4.40	7.50	6.29	0.00	0.00
H_2O	-1.80	-1.05	-0.37	-0.07	2.48	3.62	4.18	4.36	4.37	-0.95	0.25
Excess Solvent	0.72	5.10	9.53	-9.85	5.76	10.49	8.61	-5.68	-9.76	-153.91	-172.38
Vacuum Bottoms	68.61	68.92	69.60	73.20	69.17	68.92	68.09	74.19	76.93	147.91	193.61
Insoluble Organic Matter	14.22	13.14	12.77	18.86	12.66	12.41	13.05	17.01	19.51	106.84	78.52
Total	106.00	105.14	104.15	103.71	105.71	101.10	101.22	100.97	100.82	100.00	100.21
VACUUM BOTTOMS COMPOSITION											
%Carbon	86.88	86.88	87.08	89.54	87.36	89.39	88.08	90.57	89.43	Not Filtered	Not Filtered
%Hydrogen	5.13	5.31	5.42	4.74	5.11	5.38	5.33	4.97	5.07		
%Nitrogen	1.99	2.04	2.02	1.86	2.02	2.06	2.04	1.89	1.95		
%Sulfur	0.98	1.02	1.10	0.79	1.00	1.05	1.08	0.78	0.92		
%Oxygen	3.70	4.46	4.26	2.92	4.34	1.96	2.70	1.50	2.50		
%Ash	1.32	0.29	0.13	0.14	0.18	0.16	0.77	0.29	0.13		
Fusion Point °C											
SOLVENT YIELDS (% OF FEED SOLVENT)											
Cold Trap Oil	1.43	1.31	1.20	1.57	1.15	1.21	1.34	1.38	1.28	0.86	1.49
Cut 1 Oil< 100°C Vacuum	3.27	2.40	2.84	4.59	2.74	4.26	3.30	3.48	4.07	0.94	6.65
Cut 2 Oil 100-230°C Vacuum	91.23	93.40	94.97	86.23	93.66	93.12	93.46	88.35	87.08	36.73	23.02
Heavy Oil> 230°C Vacuum	4.35	5.28	4.78	3.68	4.74	5.60	5.34	4.52	3.68	-	-
Total	100.28	102.39	103.79	96.07	102.29	104.19	103.44	97.73	96.11	38.53	31.16
COMPOSITION OF UNFILTERED SOLUTION											
%Carbon						85.46	85.17	86.41	84.91	83.59	82.82
%Hydrogen						5.95	5.88	5.80	5.65	5.82	5.74
%Nitrogen						0.99	1.02	0.99	1.02	0.94	0.97
%Sulfur						1.19	1.23	1.16	1.30	1.69	1.68
%Ash						3.521	4.068	2.605	3.966	3.956	4.908

* Preheater is the only reactor used. Run CU 33 is a preheater study.

Ash in CU 31 feed coal = 15.27%.
Ash in CU 32 feed coal = 15.12%.
Ash in CU 33 feed coal = 15.24%.

APPENDIX A (PART 9)

SUMMARY OF EXPERIMENTAL RESULTS FOR CONTINUOUS REACTOR STUDIES

PREHEATER STUDIES

RUN NO.	CU 33C	CU 33D	CU 33E-2	CU 33F	CU 33G	CU 34A	CU 35A	CU 35B	CU 35C	CU 35D	CU 35E
CONDITIONS											
Coal	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9
Solvent	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18
Ratio Solvent/MAF Coal/H_2O	2.50/1/0.06	2.50/1/0.06	2.50/1/0.06	2.50/1/0.06	2.50/1/0.06	2.50/1/0.06	2.50/1/0.06	2.50/1/0.06	2.50/1/0.06	2.50/1/0.06	2.50/1/0.06
Pressure PSIG	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Preheater Temperature	350	400	450	450	500	450	450	475	475	475	500
Dissolver Temperature	-	-	-	-	-	-	-	-	-	-	-
1/LHSV;Hr.	0.036	0.035	0.035	0.066	0.035	0.035	0.129	0.128	0.073	0.036	0.13
GHSV	2978	2987	2964	3012	2988	2953	3083	3095	3126	3102	3066
Reducing Gas	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2
INPUT DATA-RAW											
H_2 Grams/Hr.	8.1	8.1	8.0	8.2	8.1	8.0	8.4	8.4	8.5	8.4	8.3
CO Grams/Hr.	-	-	-	-	-	-	-	-	-	-	-
N_2 Grams/Hr.	-	9.3	6.9	7.8	5.0	7.2	7.2	7.8	6.8	7.8	7.8
Feed Slurry Grams/Hr.	1065	1080	1080	580.0	1080.0	1080	295.0	297.5	520.0	1050.0	292.5
Total Feed Grams/Hr.	1073.1	1097.4	1094.9	596.0	1093.1	1095.2	310.6	313.7	535.3	1066.2	308.6
OUTPUT DATA-RAW											
Gas Moles/Hr.	3.812	3.812	3.816	4.143	4.226	4.267	4.405	4.431	4.245	4.317	4.351
M.W. of Gas	2.40	4.14	6.83	4.35	6.63	4.52	3.77	4.64	4.95	5.12	4.87
Gas Output Grams/Hr.	14.6	15.8	26.1	18.0	28.0	19.3	16.6	20.6	21.0	22.1	21.2
Unstripped Solution Gm/Hr.	279.0	995.3	1028.1	522.7	1047.3	1041.2	281.6	282.7	505.1	1042.5	277.5
Recovery Gm/Hr.	293.6	1011.1	1054.2	540.7	1075.3	1060.5	298.2	303.3	526.1	1064.6	298.7
%Recovery	27.3	92.13	96.28	90.72	98.37	96.83	96.01	96.68	98.28	99.84	96.79
OBSERVATIONS											
Ash in Feed Slurry	5.236	5.368	5.370	5.365	4.766	4.830	4.872	5.357	4.663	5.208	5.175
Solution Blackness	3.20	6.75	7.19	6.99	8.33	7.00	6.87	7.11	7.91	7.84	11.42
Solution IR Ratio	1.20	1.28	1.25	1.22	1.05	1.25	1.23	1.15	1.14	1.19	1.02
Cut 2 Reclaim IR Ratio	1.30	1.06	0.88	0.88	0.71	0.83	0.87	0.84	0.78	0.76	0.74
Feed Solvent IR Ratio	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98
%H_2 Reacted-MAF Coal Basis	0.21	0.38	0.35	0.39	0.38	0.28	0.25	0.50	0.65	0.29	0.77
%CO Reacted-MAF Coal Basis	-	-	-	-	-	-	-	-	-		
%H_2O Reacted-MAF Coal Basis	-	-	-	-	-	-	-	-	-		
%MAF Conversion	32.97	59.79	76.80	86.79	87.17	68.66	84.77	85.79	86.62	90.91	86.83
YIELDS-LOSS FREE MAF COAL BASIS											
H_2	-	-	-	-	-	-	-	-	-	-	-
CO	-	0.24	0.03	0.06	0.17	0.07	0.25	0.25	0.36	0.14	0.13
CO_2	0.11	0.28	0.35	0.45	0.66	0.35	0.51	0.63	0.58	0.46	0.77
H_2S	0.07	0.66	0.97	1.49	1.77	1.73	2.66	2.01	2.59	1.57	2.94
Hydrocarbon Gas	0.00	0.03	0.31	0.65	1.85	0.21	0.76	3.27	1.29	0.62	5.11
H_2O	0.35	0.87	-1.42	0.91	-1.50	1.11	-0.12	0.63	0.29	-2.43	0.64
Excess Solvent	-134.95	-129.56	-59.30	7.84	13.43	-39.61	11.80	17.11	13.09	-11.13	25.45
Vacuum Bottoms	167.60	187.58	136.21	75.78	71.17	105.31	69.93	63.15	69.57	101.97	52.56
Insoluble Organic Matter	67.03	40.21	23.20	13.21	12.83	31.34	15.23	14.21	13.38	9.09	13.17
Total	100.21	100.31	100.35	100.39	100.38	100.55	101.02	101.26	101.15	100.29	100.77
VACUUM BOTTOMS COMPOSITION											
%Carbon					86.67		84.00	84.87	84.62		88.30
%Hydrogen					5.33		5.71	5.42	5.56		4.96
%Nitrogen	Not	Not	Not	Not	1.78	Not	1.93	2.04	1.90	Not	2.10
%Sulfur	Filtered	Filtered	Filtered	Filtered	1.21	Filtered	1.38	1.29	1.34	Filtered	0.80
%Oxygen					4.90		6.59	5.42	6.23		4.19
%Ash					0.11		0.39	0.96	0.35		0.15
Fusion Point °C											
SOLVENT YIELDS (% of Feed Solvent)											
Cold Trap Oil	1.45	1.68	1.19	1.47	1.88	0.67	1.02	1.31	1.27	0.83	1.74
Cut 1 Oil < 100°C Vacuum	0.52	13.49	3.69	2.09	10.63	10.17	7.93	9.02	15.46	15.43	18.51
Cut 2 Oil 100-230°C Vacuum	44.13	33.10	71.43	99.56	92.86	73.33	95.78	94.35	88.52	79.30	87.64
Heavy Oil > 230°C Vacuum	-	-	-	-	-	-	-	2.17	-	-	2.31
Total	46.10	48.27	76.31	103.12	105.37	84.17	104.73	106.85	105.25	95.56	110.20
COMPOSITION OF UNFILTERED SOLUTION											
%Carbon	84.05	83.48	83.99	84.67	84.45	84.62	85.20	82.99	85.94	83.54	79.71
%Hydrogen	5.92	5.80	5.74	5.81	5.73	5.87	6.05	5.83	6.06	5.73	5.44
%Nitrogen	0.86	0.96	0.86	0.93	0.96	0.92	0.83	0.96	0.96	0.89	0.96
%Sulfur	1.47	1.52	1.42	1.22	1.07	1.36	1.15	1.31	1.20	1.43	1.11
%Ash	4.542	5.260	4.319	4.462	4.295	4.48	3.524	5.921	3.554	4.801	9.805

Ash in CU 35 feed coal = 15.12%. Slurry Ash = 5.04% theory.

APPENDIX A (PART 10)

EXPERIMENTAL RESULTS FOR CONTINUOUS REACTOR STUDIES

	CU 36 PREHEATER STUDY										
RUN NO.	CU 36A	CU 36B	CU 36C	CU 36D	CU 36E	CU 37A	CU 37B	CU 37C	CU 38A	CU 38B	* CU 41A
CONDITIONS											
Coal	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	KY#9	ELKOL
Solvent	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CL 18	CU 40B
Ratio Solvent/MAF Coal/H_2O	2.49/1/0.20	2.49/1/0.11	2.49/1/0.18	2.49/1/0.12	2.49/1/0.08	2.49/1/0.11	2.49/1/0.14	2.49/1/0.16	2.49/1/0.06	2.49/1/0.06	1.93/1/0.21
Pressure PSIG	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Preheater Temperature °C	425	450	450	475	475	425	450	450	500	450	425
Dissolver Temperature °C	-	-	-	-	-	425	450	450	450	500	425
1/LHSV;Hr.	0.123	0.125	0.072	0.070	0.123	1.25	1.11	0.40	0.98	0.41	0.32
GHSV	3203	3203	3210	3220	3220	222	221	218	239	236	244.5
Reducing Gas	CO-H_2 1:1.1	CO-H_2 1:1.1	CO-H_2 1:1.1	CO-H_2 1:1.1	CO-H_2 1:1.1	CO-H_2 1:3	CO-H_2 1:3	CO-H_2 1:3	H_2	H_2	H_2
INPUT DATA-RAW											
H_2 Grams/Hr.	4.6	4.6	4.6	4.6	4.6	6.1	6.1	6.0	8.8	8.7	9.0
CO Grams/Hr.	57.7	57.7	57.8	58.0	58.0	28.6	28.4	28.2	-	-	-
N_2 Grams/Hr.	6.0	7.1	7.4	8.0	7.9	9.0	8.2	8.0	7.0	7.5	4.8
Feed Slurry Grams/Hr.	310.0	305.0	530.0	540.0	310.0	415.0	466.7	1290.0	530.0	1260.0	1610.0
Total Feed Grams/Hr.	378.3	374.4	599.8	610.6	380.5	458.7	509.4	1332.2	545.8	1276.2	1623.8
OUTPUT DATA-RAW											
Gas Moles/Hr.	4.457	4.461	4.603	4.561	4.477	4.266	4.009	4.515	3.570	4.499	6.225
M.W. of Gas	15.95	16.04	16.31	17.05	16.36	13.17	15.22	17.00	8.36	8.38	7.97
Gas Output Grams/Hr.	71.1	71.6	75.1	77.8	73.2	56.2	61.0	76.8	29.8	37.7	49.6
Unstripped Solution Gm/Hr.	284.6	285.3	501.6	502.4	291.0	378.0	323.9	1214.0	497.4	1246.8	1498.0
Recovery Gm/Hr.	355.7	356.9	576.7	580.2	364.2	434.2	384.9	1290.8	527.2	1284.5	1547.6
% Recovery	94.03	95.32	96.14	95.02	95.72	94.66	75.55[a]	96.89	96.59	100.65	95.31
OBSERVATIONS											
%H_2O in Feed Slurry	5.06	2.99	4.60	3.13	2.13	2.96	3.68	4.11	-	-	6.76
Solution Blackness	7.08	7.85	7.52	8.69	9.86	6.98	10.54	10.78	9.15	9.65	10.51
Solution IR Ratio	1.18	1.16	1.14	1.05	1.02	1.15	0.92	0.93	0.92	1.03	0.97
Cut 2 Reclaim IR Ratio	0.81	0.79	0.79	0.76	0.75	0.93	0.79	0.74	0.80	0.80	0.65
Feed Solvent IR Ratio	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.75
%H_2 Reacted-MAF Coal Basis	0.50	0.50	0.29	0.49	0.61	0.91	1.64	0.51	2.47	0.59	-0.22
%CO Reacted-MAF Coal Basis	1.12	1.12	1.09	-0.42	2.79	2.65	5.41	2.97	-	-	-
%H_2O Reacted-MAF Coal Basis	0.00	-	0.07	-	-	-	2.21	1.90	-	-	-
%MAF Conversion	94.37	88.56	89.44	89.79	85.07	86.20	85.91	84.97	86.17	85.34	47.16
YIELDS-LOSS FREE MAF COAL BASIS											
H_2	-	-	-	-	-	-	-	-	-	-	0.22
CO	-	-	-	-	-	-	-	-	0.42	0.21	0.41
CO_2	1.88	2.24	2.77	2.68	3.40	8.87	9.09	6.96	1.20	1.10	4.40
H_2S	1.00	1.12	1.17	1.27	1.58	1.83	1.64	1.70	2.12	1.78	0.34
Hydrocarbon Gas	0.49	1.12	0.65	0.98	2.06	5.39	8.60	4.94	8.89	3.98	1.38
H_2O	0.00	1.00	-0.07	0.56	1.09	0.00	-2.21	-1.90	4.10	2.23	-2.07
Excess Solvent	-0.50	15.92	3.42	10.13	16.02	11.88	11.30	10.86	15.10	-1.93	-73.78
Vacuum Bottoms	93.12	68.78	82.88	74.24	64.32	61.79	64.54	65.89	56.81	78.56	116.26
Insoluble Organic Matter	5.63	11.44	10.56	10.21	14.93	13.80	14.09	15.03	13.83	14.66	52.84
Total	101.62	101.62	101.38	100.07	103.40	103.56	107.05	103.48	102.47	100.59	100.00
VACUUM BOTTOMS COMPOSITION											
%Carbon		84.89	83.99	84.73	85.74	84.09	89.14	87.54	89.03	85.72	
%Hydrogen		5.54	5.33	5.44	5.24	5.40	5.40	5.16	5.12	5.47	
%Nitrogen	Not	2.00	1.95	1.99	2.08	2.09	2.04	1.99	2.02	1.77	Not
%Sulfur	Filtered	1.37	1.41	1.38	1.22	0.91	0.62	0.95	0.72	1.32	Filtered
%Oxygen		5.91	6.87	6.19	5.47	7.40	2.95	4.22	3.04	5.51	
%Ash		0.29	0.45	0.27	0.25	0.108	0.127	0.133	0.067	0.205	
Fusion Point °C											
SOLVENT YIELDS (% of Feed Solvent)											
Cold Trap Oil	1.00	2.25	2.22	1.19	1.65	1.28	1.90	0.45	1.87	0.87	1.07
Cut 1 Oil < 100°C Vacuum	10.63	10.68	21.23	11.94	8.71	3.12	8.21	9.34	6.79	11.99	3.16
Cut 2 Oil 100-230°C Vacuum	88.15	91.12	77.93	90.94	91.00	94.35	86.77	91.99	90.69	86.37	31.50
Heavy Oil>230°C Vacuum	-	2.35	-	-	5.06	6.01	7.65	2.57	6.71	-	-
Total	99.78	106.40	101.38	104.07	106.42	104.76	104.53	104.35	106.06	99.23	35.73

* Run CU 40 was a solvent preparation.

Run CU 36F not reported. Preheater plugged at 500°C LHSV = 8.14 KY#9 coal and 33.3% slurry.

Run CU 39 not reported. Preheater plugged at 475°C LHSV = 4.1.

a- Experimental sample taken at time rupture disc in feed line opened. Probable error in feed slurry entry. Part should have vented through rupture disc.

Feed Coal for CU 36 15.06% ash H_2O added to slurry. H_2O analysis of slurry shows loss by evaporation.

APPENDIX A (PART 11)

SUMMARY OF EXPERIMENTAL RESULTS FOR CONTINUOUS REACTOR STUDIES

RUN NO.	CU 41B	CU 42A	CU 42B	CU 43A	CU 43B	CU 44	CU 45A	CU 45B	CU 46A	CU 47A**
CONDITIONS										
Coal	ELKOL	ELKOL	ELKOL	ELKOL*	ELKOL*	ELKOL	ELKOL	ELKOL	ELKOL	ELKOL
Solvent	CU 40B	CU 40B	CU 40B	CU 40B	CU 40B	CU 40B	CU 40B	CU 40B	CU 40B	CU 40B
Ratio Solvent/MAF Coal/H_2O	1.93/1/0.19	2.51/1/0.24	2.51/1/0.20	2.48/1/0.20	2.48/1/0.12	2.51/1/0.23	2.55/1/0.20	2.55/1/0.20	2.56/1/0.22	2.56/1/0.22
Pressure PSIG	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Preheater Temperature °C	425	450	450	425	425	450	450	475	450	450
Dissolver Temperature °C	425	450	450	425	425	450	450	475	450	-
1/LHSV;Hr.	0.52	0.34	0.49	0.67	0.98	0.42	0.25	0.26	0.17	0.037
GHSV	244.5	244.5	244.5	247	247	249	241	235	244.5	
Reducing Gas	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2
INPUT DATA-RAW										
H_2 Grams/Hr.	9.0	9.0	9.0	9.1	9.1	9.0	8.9	8.6	9.0	9.2
CO Grams/Hr.	-	-	-	-	-	-	-	-	-	-
N_2 Grams/Hr.	6.4	6.5	6.0	6.9	6.5	6.0	6.8	4.8	7.8	9.6
Feed Slurry Grams/Hr.	1000.0	1510.0	1070.0	780.0	530.0	1250.0	2080.0	2020.0	2980.0	920.0
Total Feed Grams/Hr.	1015.4	1525.5	1085.0	796.0	545.6	1265.0	2095.7	2033.4	2996.8	938.8
OUTPUT DATA-RAW										
Gas Moles/Hr.	5.744	6.669	6.309	5.677	5.521	5.875	6.451	7.250	6.276	4.864
M.W. of Gas	8.40	9.01	8.08	7.18	5.23	9.19	11.05	13.36	14.30	5.73
Gas Output Grams/Hr.	48.5	60.1	51.0	40.8	28.9	54.0	71.3	96.9	89.7	27.9
Unstripped Solution Gm/Hr.	927.0	1394.8	1003.3	705.1	490.1	1175.1	1898.0	1885.6	2748.7	867.7
Recovery Gm/Hr.	975.5	1454.9	1054.3	745.9	519.0	1229.1	1969.3	1982.5	2838.4	895.6
%Recovery	96.07	95.37	97.17	93.70	95.12	97.16	93.96	97.50	94.71	95.39
OBSERVATIONS										
%H_2O in Feed Slurry	6.11	6.39	5.43	5.30	3.40	6.02	5.28	5.20	5.81	5.81
Solution Blackness	10.93	14.40	14.19	13.01	12.83	16.80	13.11	16.75	13.19	8.67
Solution $\overline{IR}$ Ratio	0.93	0.74	0.77	0.86	0.83	0.75	0.77	0.69	0.92	0.99
Cut 2 Reclaim $\overline{IR}$ Ratio	0.65	0.54	0.55	0.65	0.65	0.57	0.56	0.53	0.60	0.67
Feed Solvent $\overline{IR}$ Ratio	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
%H_2 Reacted-MAF Coal Basis	-0.19	-0.27	-0.31	-0.33	-0.48	-0.09	-0.02	0.04	-0.13	-0.29
%CO Reacted-MAF Coal Basis	-	-	-	-	-	-	-	-	-	-
%H_2O Reacted-MAF Coal Basis	-	-	-	-	-	-	-	-	-	-
%MAF Conversion	41.07	55.94	48.60	54.83	60.92	60.40	64.88	65.65	58.80	79.23
YIELDS-LOSS FREE MAF COAL BASIS										
H_2	0.19	0.27	0.31	0.33	0.48	0.09	0.02	-	0.13	0.29
CO	0.66	0.70	0.77	0.67	0.76	1.12	1.02	1.51	0.18	0.13
CO_2	4.67	5.19	5.50	4.52	4.46	4.70	4.78	5.55	4.99	2.57
H_2S	0.35	0.43	0.42	0.33	0.55	0.51	0.42	0.49	0.35	0.33
Hydrocarbon Gas	2.04	4.42	5.26	2.42	2.89	4.79	3.63	6.78	2.88	1.04
H_2O	2.15	2.13	3.96	3.95	9.07	1.63	0.34	-7.77	0.99	3.48
Excess Solvent	-90.00	-25.04	-38.17	-25.17	-43.96	-21.74	-16.18	-12.83	-9.12	21.02
Vacuum Bottoms	121.01	67.84	70.55	67.78	86.67	69.48	70.85	71.96	58.66	50.95
Insoluble Organic Matter	58.93	44.06	51.40	45.17	39.08	39.60	35.12	34.35	41.20	20.77
Total	100.00	100.00	100.00	100.00	100.00	100.18	100.00	100.04	100.26	100.58
VACUUM BOTTOMS COMPOSITION										
%Carbon		88.62	89.37	87.28	87.43	88.96	87.54	90.21	87.60	83.62
%Hydrogen		4.70	6.16	5.11	5.21	4.56	4.97	4.82	5.13	5.62
%Nitrogen	Not	1.37	1.38	1.42	1.38	1.37	1.36	1.27	1.26	1.10
%Sulfur	Filtered	0.28	0.21	0.403	0.37	0.36	0.32	0.28	0.30	0.39
%Oxygen		4.83	2.60	5.62	4.75	4.60	5.25	3.28	5.60	9.16
%Ash		0.20	0.28	0.16	0.86	0.15	0.56	0.13	0.11	0.12
Fusion Point °C										
SOLVENT YIELDS (% OF FEED SOLVENT)										
Cold Trap Oil	1.07	1.77	1.95	1.19	1.30	1.56	1,20	0.80	1.20	
Cut 1 Oil< 100°C Vacuum	3.16	6.54	4.51	4.28	3.13	6.20	5.12	6.61	3.35	
Cut 2 Oil 100°-230°C Vacuum	31.50	80.09	78.33	83.18	77.86	80.56	86.91	85.41	88.97	
Heavy Oil> 230°C Vacuum	-	1.62	-	1.21	-	3.00	0.42	2.15	2.91	
Total	35.63	90.02	84.79	89.86	82.29	91.32	93.65	94.97	96.43	

* Screened - 100 mesh used to make feed slurry.

**Preheater only.

APPENDIX A (PART 12)

SUMMARY OF EXPERIMENTAL RESULTS FOR CONTINUOUS REACTOR STUDIES

RUN NO.	SINGLE PASS DATA MAF COAL BASIS		
	CU 48A-1	CU 48A-2	CU 49A
CONDITIONS			
Coal	KY#9	KY#9	KY#9
Solvent	CU 40B	CU 40B	CU 40B
Ratio Solvent/MAF Coal/H_2O	2.50/1/0.08	2.50/1/0.05	2.49/1/0.05
Pressure PSIG	1000	1000	1000
Preheater Temperature °C	450	450	450
Dissolver Temperature °C	450	450	425
1/LHSV;Hr.	0.510	0.510	1.77
GHSV	304	304	342
Reducing Gas	H_2	H_2	H_2
INPUT DATA-RAW			
H_2 Grams/Hr.	11.2	11.2	12.6
N_2 Grams/Hr.	10.4	11.0	9.6
Feed Slurry Grams/Hr.	1020.0	1000.0	292.9
Total Feed Grams/Hr.	1041.6	1022.2	315.1
OUTPUT DATA-RAW			
Gas Moles/Hr.	5.039	5.566	4.789
M.W. of Gas	8.70	8.04	4.99
Gas Output Grams/Hr.	43.8	44.8	23.9
Unstripped Solution Gm/Hr.	979.7	957.3	281.6
Recovery Gm/Hr.	1023.5	1002.1	305.5
%Recovery	98.26	98.03	96.95
OBSERVATIONS			
%Ash in Feed Slurry			5.285
%H_2O in Feed Slurry	2.05	1.46	
Solution Blackness	11.65	12.26	7.00
Solution IR Ratio	0.94	0.94	1.46
Cut 2 Reclaim IR Ratio	0.74	0.76	1.22
Feed Solvent IR Ratio	0.75	0.75	0.75
%H_2 Reacted-MAF Coal Basis	1.37	0.94	4.97
%MAF Conversion	82.85	85.09	88.41
YIELDS-LOSS FREE MAF COAL BASIS			
CO	0.26	0.23	0.51
CO_2	1.37	1.12	0.64
H_2S	2.33	2.32	2.04
Hydrocarbon Gas	6.54	5.28	5.73
H_2O	2.33	3.60	3.82
Excess Solvent	2.88	5.36	31.98
Vacuum Bottoms	68.51	68.12	48.66
Insoluble Organic Matter	17.15	14.91	11.49
Total	101.37	100.94	104.87
VACUUM BOTTOMS COMPOSITION			
%Carbon	87.50	87.32	88.54
%Hydrogen	5.23	5.11	4.74
%Nitrogen	2.04	1.91	2.22
%Sulfur	0.88	0.94	0.68
%Oxygen	4.17	4.58	3.62
%Ash	0.18	0.13	0.21
SOLVENT YIELDS (% OF FEED SOLVENT)			
Cold Trap Oil	1.18	1.05	0.92
Cut 1 Oil < 100°C Vacuum	4.42	4.51	5.99
Cut 2 Oil 100-230°C Vacuum	93.32	93.95	101.79
Heavy Oil > 230°C Vacuum	2.26	2.64	4.15
Total	101.18	102.15	112.85
COMPOSITION OF CUT 2 RECLAIM			
%Carbon	91.31	91.73	
%Hydrogen	6.02	6.03	
%Nitrogen	0.765	0.734	
%Sulfur	0.40	0.377	
%Oxygen	1.51	1.13	
COMPOSITION OF FILTERED SOLUTION			
%Carbon	90.36	89.68	89.40
%Hydrogen	6.25	5.94	5.93
%Nitrogen	0.981	0.979	1.06
%Sulfur	0.45	0.46	0.41
%Oxygen	1.96	2.94	5.00

			SLURRY RECYCLE DATA FEED SLURRY BASIS		
	CU 49A	CU 49B	CU 49C	CU 49D	CU 49E
CONDITIONS					
Coal	KY#9	KY#9	KY#9	KY#9	KY#9
Solvent (a)	CU 40B	CU 49A Soln.	CU 49B Soln.	CU 49C Soln	CU 49D Soln.
Ratio Solvent/Coal	2:1	2:1	2:1	2:1	2:1
Pressure PSIG	1000	1000	1000	1000	1000
Preheater Temperature °C	450	450	450	450	475
Dissolver Temperature °C	425	425	425	425	425
1/LHSV;Hr.	1.77	1.88	1.73	1.79	1.94
GHSV	342	342	342	342	342
Reducing Gas	H_2	H_2	H_2	H_2	H_2
INPUT DATA-RAW					
H_2 Grams/Hr.	12.6	12.6	12.7	12.7	12.8
N_2 Grams/Hr.	9.6	10.4	10.5	10.9	10.1
Feed Slurry Grams/Hr.	292.9	276.6	300.0	288.9	267.5
Total Feed Grams/Hr.	315.1	299.6	323.2	312.5	290.4
OUTPUT DATA-RAW					
Gas Moles/Hr.	4.789	4.142	5.173	4.114	5.647
Molecular Wt. of Gas[c]	4.99	5.77	5.63	6.03	5.47
Gas Output Gm/Hr.	23.9	24.0	29.1	24.8	30.9
Unstripped Solution Gm/Hr.	281.6	255.5	270.8	276.8	240.3
Recovery Gm/Hr.	305.5	279.5	299.9	301.6	271.2
%Recovery	96.95	93.29	92.79	96.51	93.38
OBSERVATIONS					
%Ash in Feed Slurry	5.285	7.42	9.25	10.08	10.65
%H_2O in Feed Slurry[d]	(1.48)	(1.48)	(1.48)	(1.48)	(1.48)
Solution Blackness	7.00	12.17	14.11	18.27	19.77
Solution IR Ratio	1.46	1.65	1.78	1.75	1.83
Cut 2 Reclaim IR Ratio	1.22	1.47	1.62	1.62	1.69
Feed Solvent IR Ratio	0.75	1.61	1.75	1.83	1.75
%H_2 Reacted Feed Slurry Basis	1.33	1.88	1.13	1.76	0.86
%Conversion (100-IOM)	96.89	95.99	95.99	95.35	93.99
YIELDS-LOSS FREE FEED SLURRY BASIS					
CO	0.14	0.07	0.10	-	0.07
CO_2	0.17	0.18	0.17	0.14	0.07
H_2S	0.55	0.43	0.50	0.35	0.52
Hydrocarbon Gas	1.54	1.55	1.60	1.25	1.91
Not Accounted (Gas)	0.18		1.76	2.49	3.29
H_2O	2.49	1.80	1.43	1.93	1.98
Total Distilled Oils	76.75	68.01	56.46	54.03	53.22
Vacuum Bottoms	13.04	18.75	25.76	26.47	23.25
Insoluble Organic Matter	3.11	4.01	4.07	4.84	6.01
Ash	5.05	7.04	9.26	9.65	10.50
Total	103.02	101.84	101.11	101.15	100.82
VACUUM BOTTOMS COMPOSITION					
%Carbon	88.54	88.51			91.12
%Hydrogen	4.74	5.35	Partly	Partly	5.10
%Nitrogen	2.22	2.10	Filtered	Filtered	2.22
%Sulfur	0.68	0.61			0.49
%Oxygen	3.62	3.16			1.00
%Ash	0.21	0.08			0.08
DISTRIBUTION OF TOTAL DISTILLED OILS					
Cold Trap Oil	0.61	0.90	0.70	1.04	1.04
Cut 1 Oil < 100°C Vacuum	5.50	4.63	7.13	6.47	3.51
Cut 2 Oil 100-230°C Vac.	67.87	60.46	47.33	44.72	46.05
Heavy Oil > 230°C Vacuum	2.77	2.02	1.30	1.80	2.62
Total	76.75	68.01	56.46	54.03	53.22
COMPOSITION OF CUT 2 RECLAIM					
%Carbon					90.38
%Hydrogen					6.87
%Nitrogen					0.91
%Sulfur					0.40
%Oxygen					1.43
COMPOSITION OF FILTERED SOLN.			b	b	
%Carbon	89.40	89.72	91.40	90.98	90.65
%Hydrogen	5.93	6.20	6.70	6.59	6.54
%Nitrogen	1.06	1.15	1.21	1.33	1.31
%Sulfur	0.41	0.42	0.36	0.34	0.44
%Oxygen	5.00	2.51	0.76	0.76	1.06

(a) Composition of recycle solvent (unfiltered coal solution) changed progressively. See Text for details, slurry mixed with recycle of approximately the composition indicated.

(b) Sample partly filtered. Filtrate used for elemental analysis. QNS for distillation.

(c) Molecular weight by gas density method used. GLC method failed to check M.W. due to progressive failure of detector. Gas not accounted probably should be distributed pro rata to gas identified.

(d) Ky#9 coal used 15.18% ash and 4.44% H_2O. Loss of water from feed slurry by evaporation probable value is initial H_2O only.

APPENDIX B-1

SUMMARY SHEET -- PROXIMATE AND ULTIMATE ANALYSIS OF COAL

COAL SAMPLE INFORMATION: KENTUCKY Coal - Colonial Mine - Bed: No. 9. (hvAb).
Jan. 19, 1970 sample. Madisonville (Hopkins County), Kentucky.
Run-of-mine, 8-inch by 0.(The Pittsburg & Midway Coal Mining Co.) -100 mesh.

Proximate Analysis

Determination	As Received	Moisture Free	Moisture & Ash Free
% Moisture	4.83	**************	***********
% Ash	10.88	11.43	***********
% Volatile Matter	36.19	38.02	42.93
% Fixed Carbon	48.10	50.55	57.07
Btu Determined	12,506	13,140	14,836
% Sulfur	3.58	3.76	1.95*

Ultimate Analysis

Determination	As Received	Moisture Free	Moisture & Ash Free
% Moisture	4.83	**************	***********
% Ash	10.88	11.43	***********
% Carbon	67.67	71.10	80.28
% Hydrogen(corrected)	4.71	4.95	5.59**
% Nitrogen	1.28	1.35	1.52
% Sulfur	3.58	3.76	1.95*
% Oxygen(by difference)	7.05	7.41	10.66
Free-Swelling Index - 4.5.			
% Air Drying Moisture			
% Sulfate Sulfur	0.18	0.19	**********
% Pyritic Sulfur	1.76	1.84	***********
% Organic Sulfur	1.65	1.73	1.95*
Total:	3.58	3.76	
Btu Calculated(Dulong)	12,362		

* organic sulfur only

** H/C atomic ratio: 0.82

Industrial Testing Lab., 804 Woodswether Road, Kansas City, MO. 64105.
No. 132-896. and GR&DC KCL No. 108578.

APPENDIX B-2

SUMMARY SHEET -- PROXIMATE AND ULTIMATE ANALYSIS OF COAL

COAL SAMPLE INFORMATION:	KENTUCKY COAL - Bed: No. 9 Colonial Mine (HvAb).
Jan. 19, 1970 sample.	Madisonville (Hopkins County), Kentucky
Second portion of drum.	Ground - 100 mesh from run of mine 8 inch by 0 inch lumps.

Determination	As Received	Moisture Free	Moisture & Ash Free
	Proximate Analysis		
% Moisture	3.25	*****	*****
% Volatile Matter	34.17	35.31	41.92
% Fixed Carbon	47.33	48.91	60.01
% Sulfur	4.63	4.78	5.86*
	Ultimate Analysis		
% Moisture	3.25	****	****
% Ash	15.25	15.75	****
% Carbon	62.66	64.78	76.88
% Hydrogen (corrected)	4.22	4.36	5.17
% Sulfur	4.63	4.78	5.68
% Nitrogen	1.26	1.30	1.54
% Oxygen (by difference)	8.73	9.02	10.71

*Note: Sulfur forms distribution was not determined on this subsample. From the previous sample the organic sulfur in the sample as received should be approximately 1.7%. The estimate for pyrite sulfur is about 2.7%.

APPENDIX B-3

SUMMARY SHEET -- PROXIMATE AND ULTIMATE ANALYSIS OF COAL

COAL SAMPLE INFORMATION:
Jan. 9, 1970 sample.
Run-of-mine, 1½" x 0.
(From coal car delivered at University North Dakota power plant).

LIGNITE - Baukol Nooan Mine, Noonan bed. (ligA).
Larson (Burke County), North Dakota.
(Baukol-Noonan Mining Co.) Ground to -65 mesh.

Proximate Analysis

Determination	As Received	Moisture Free	Moisture & Ash Free
% Moisture	31.37	*************	**********
% Ash	7.24	10.55	**********
% Volatile Matter	28.38	41.36	46.24
% Fixed Carbon	33.00	48.09	53.76
Btu Determined /lb.	7,682	11,193	12,513
% Sulfur	0.44	0.65	0.52*

Ultimate Analysis

Determination	As Received	Moisture Free	Moisture & Ash Free
% Moisture	31.37	*************	**********
% Ash	7.24	10.55	**********
% Carbon	45.12	65.74	73.49
% Hydrogen(corrected)	3.25	4.74	5.30**
% Nitrogen	0.73	1.06	1.18
% Sulfur	0.44	0.65	0.52*
% Oxygen(by difference)	11.85	17.26	19.51***
Total:	100.00%	100.00%	100.00%
% Air Drying Moisture			
% Sulfate Sulfur	0.01	0.02	**********
% Pyritic Sulfur	0.11	0.16	**********
% Organic Sulfur	0.32	0.47	0.52*
Total:	0.44	0.65	
Btu Calculated(Dulong) /lb.	7,678	11,187	12,483

* organic sulfur only, ** H/C atomic ratio: 0.859, *** O/C atomic ratio 0.198

Industrial Testing Lab., 804 Woodswether Road, Kansas City, Mo. 64105
No. 132-361 on dried sample. Ash value corrected

APPENDIX B-4

SUMMARY SHEET -- PROXIMATE AND ULTIMATE ANALYSIS OF COAL

COAL SAMPLE INFORMATION: WYOMING Coal - Elkol Mine - Bed: Adaville(subB)
Feb. 27, 1970 sample. Frontier (Lincoln County), Wyoming.
Run-of-mine, 1-5/8"x 0. (The Kemmerer Coal Co.) Ground to -100 mesh.

Proximate Analysis

Determination	As Received	Moisture Free	Moisture & Ash Free
% Moisture	18.97	*************	**********
% Ash	2.88	3.55	**********
% Volatile Matter	36.17	44.64	46.28
% Fixed Carbon	41.98	51.81	53.72
Btu Determined/lb	10,272	12,677	13,144
% Sulfur	0.69	0.85	0.65 *

Ultimate Analysis**

Determination	As Received	Moisture Free	Moisture & Ash Free
% Moisture	18.97	*************	**********
% Ash	2.88	3.55	**********
% Carbon	58.58	72.30	74.96
% Hydrogen(corrected)	4.16	5.13	5.32
% Nitrogen	0.92	1.14	1.18
% Sulfur	0.69	0.85	0.65 *
% Oxygen (by difference)	13.80	17.03	17.89
Total:	100.00%	100.00%	100.00%
% Natural Bed Moisture	20.2	Free-Swelling Index 0 (N.A.)	
% Sulfate Sulfur	0.03	0.04	**********
% Pyritic Sulfur	0.15	0.18	**********
% Organic Sulfur	0.51	+ 0.63	0.65 *
Total:	0.69%	0.85%	0.65%
Btu Calculated/lb.(Dulong)		12,411	

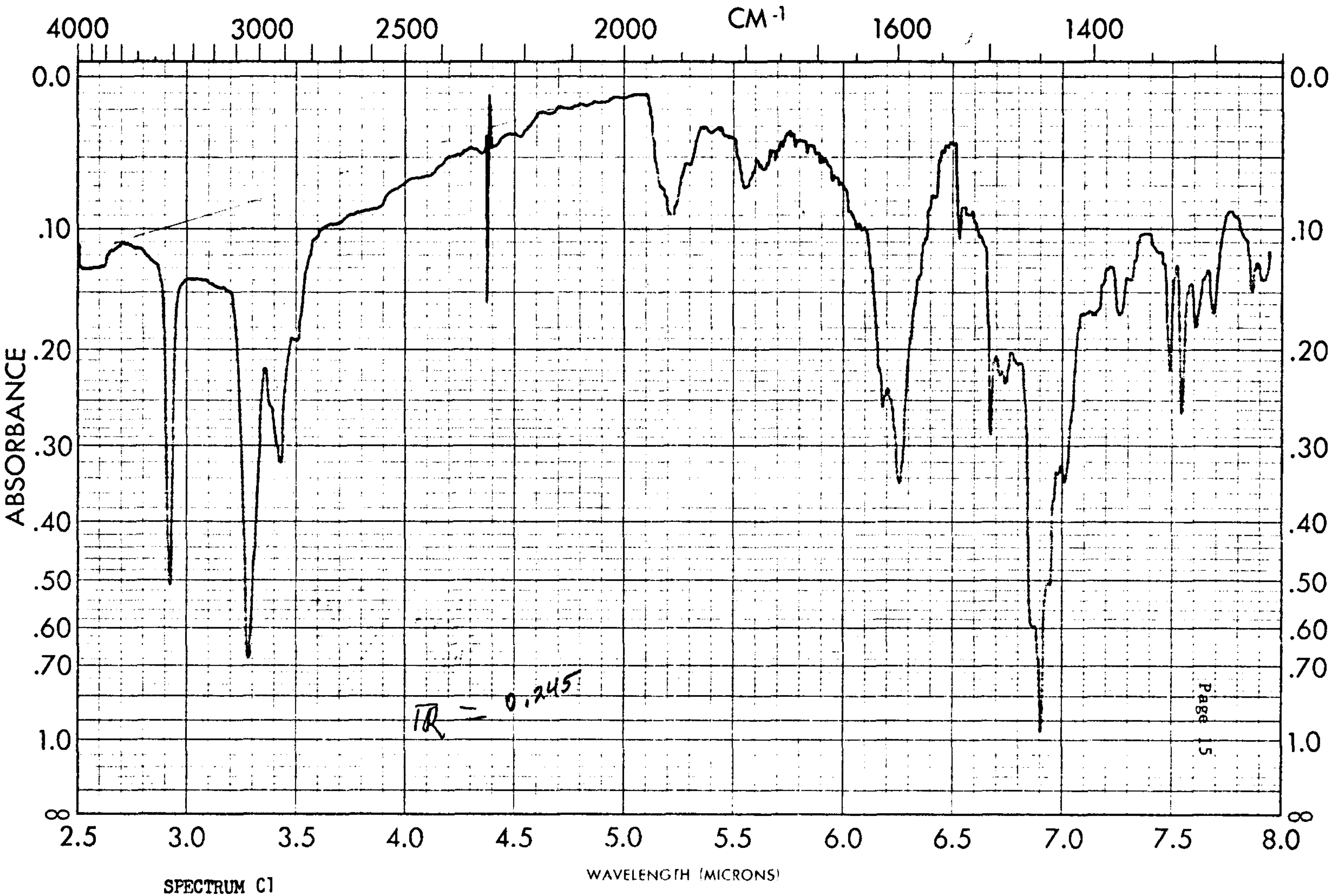
* organic sulfur only

Industrial Testing Lab., 804 Woodswether Road, Kansas City, MO. 64105.
No. 132-360. May 20,

APPENDIX B-5

Typical Mineral Analyses

Substance	Ky #9	BN Lignite	Elkol
P_2O_5	0.12	0.1	0.33
Silica SiO_3	42.86	27.2	52.71
Ferric Oxide Fe_2O_3	27.30	15.9	4.70
Alumina Al_2O_3	17.73	7.1	29.70
Titania TiO_2	0.81	0.3	0.76
Lime CaO	3.80	16.7	4.08
Magnesia MgO	0.80	4.3	1.34
Sulfur Trioxide SO_3	3.60	13.3	5.15
Potassium Oxide K_2O	1.98	0.5	0.25
Sodium Oxide Na_2O	0.23	13.5	0.40
Undetermined	0.77	0.6	0.57
	100.00	100.00	100.00
Na_2O by ion exchange	nil	13.5	

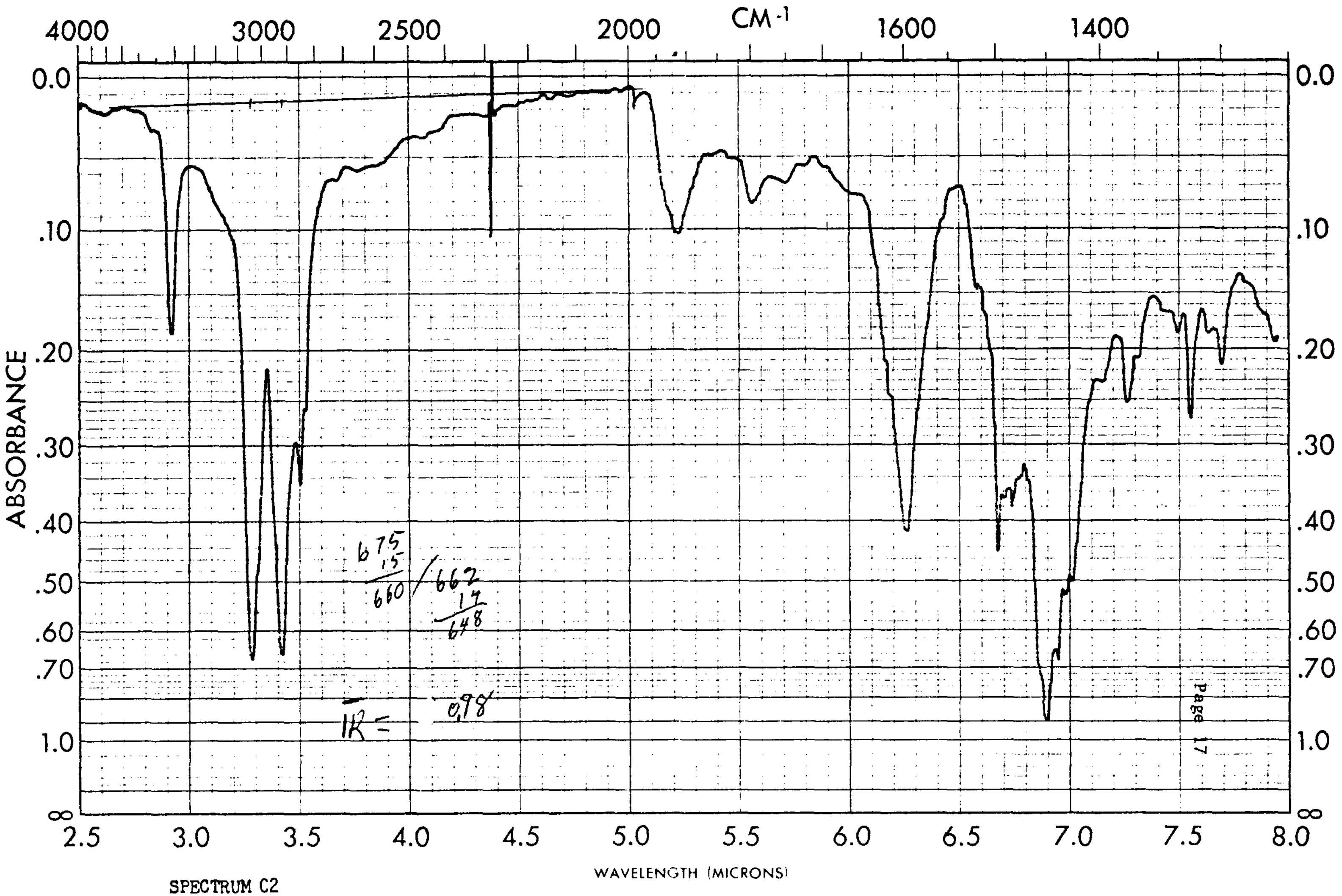


SPECTRUM C1

SAMPLE Anthracene Oil As Received Granite City	CURVE NO.	SCAN SPEED sf	OPERATOR CHW
	CONC.	SLIT	DATE 4/30/71
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE		

PART NO. 237-1028

PERKIN-ELMER

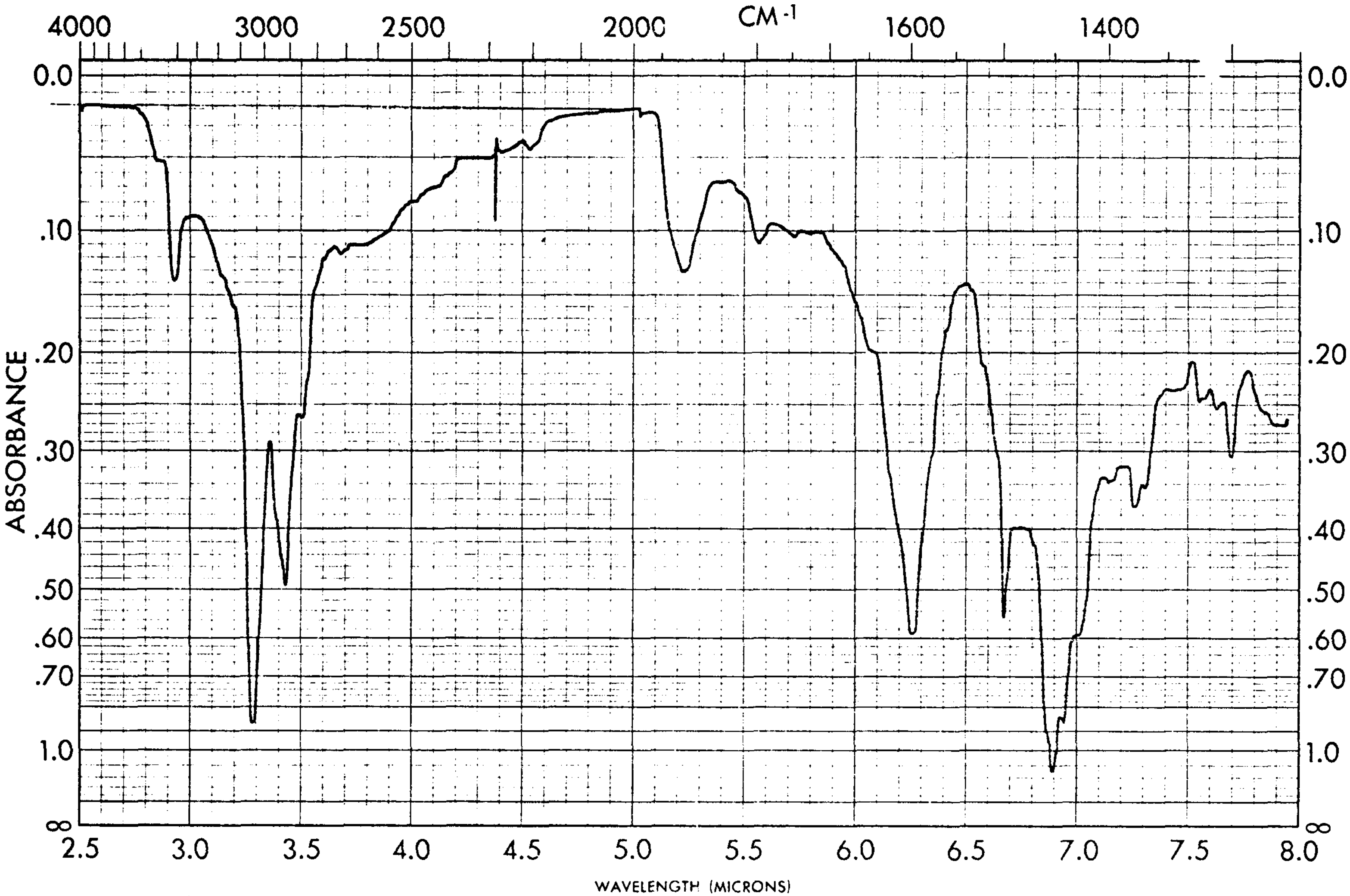


SPECTRUM C2

SAMPLE Hydrogenated Anthracene Oil Granite City	CURVE NO.	SCAN SPEED SF	OPERATOR CHW
	CONC.	SLIT	DATE 4/30/71
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE		

PART NO. 237-1028

PERKIN-ELMER

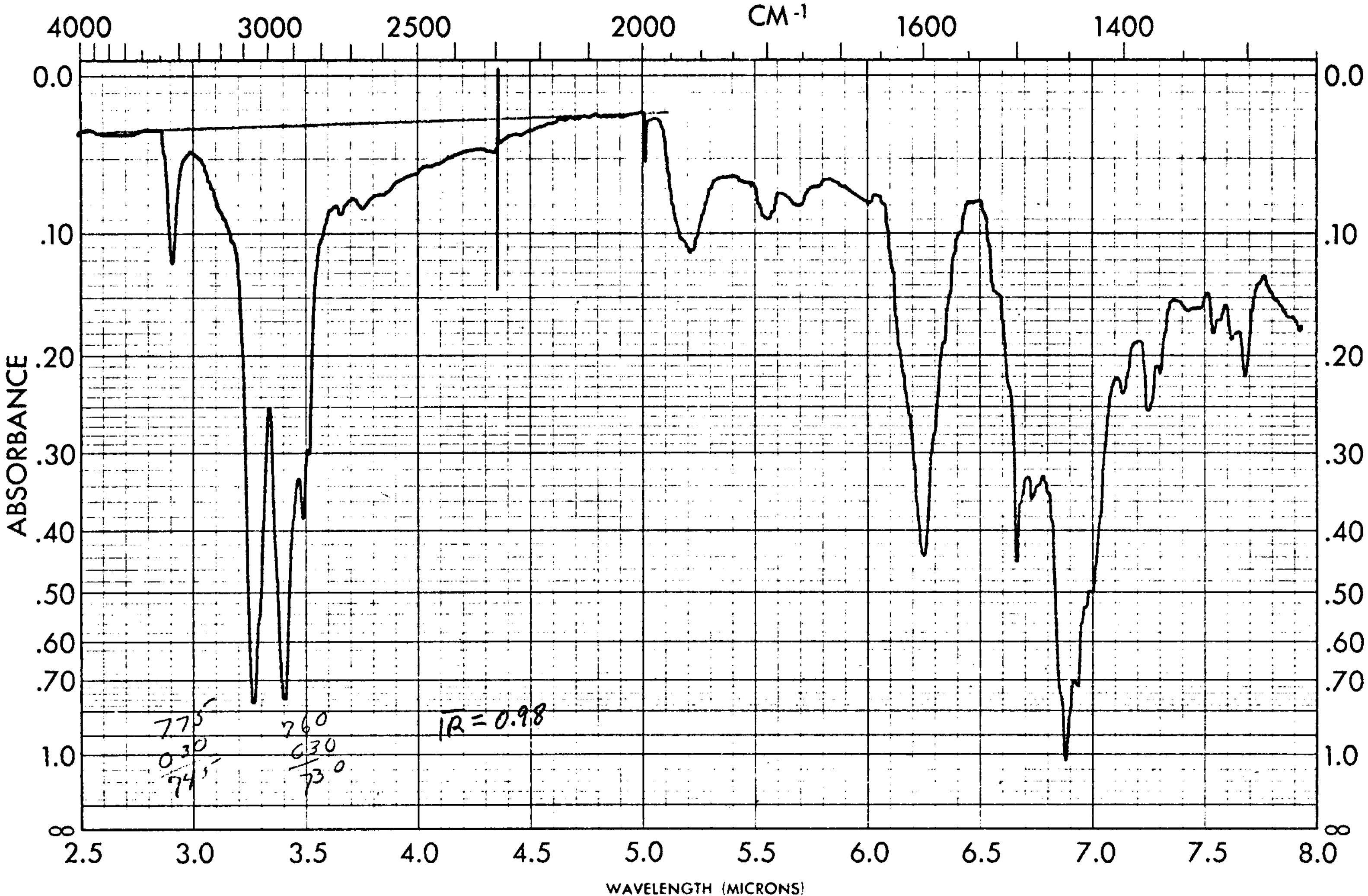


SPECTRUM C3

SAMPLE Feed Solvent For Run CL 18	CURVE NO.	SCAN SPEED SF	OPERATOR CHW
	CONC.	SLIT	DATE Jan 13, 1971
ORIGIN	CELL PATH Smear Between Salts	REMARKS Ratio 3.3 to 3.4 = 1.732	
SOLVENT	REFERENCE		

PART NO. 237-1028

PERKIN-ELMER

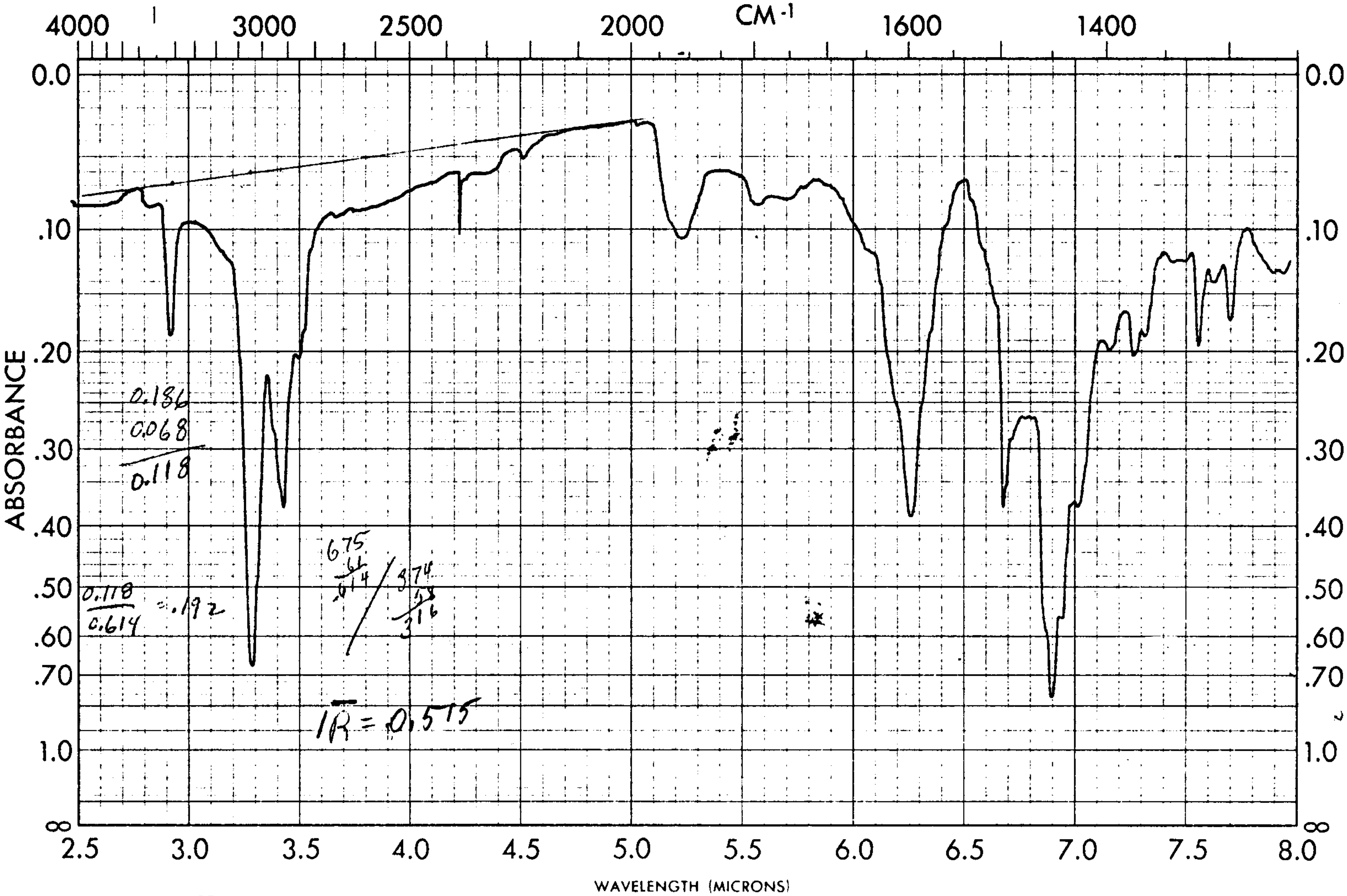


SPECTRUM C4

SAMPLE Run CL-18B, Hydrogenated MFRAO	CURVE NO.	SCAN SPEED SF	OPERATOR REM
Filtered and Stripped, 100-214° C @	CONC.	SLIT	DATE May 7, 1971
ORIGIN 3mm Hg	CELL PATH One 0.015 mm Teflon Spacer	REMARKS Ratio 3.3/3.4 = 1.021	
SOLVENT	REFERENCE 263839		

PART NO. 237-1028

PERKIN-ELMER

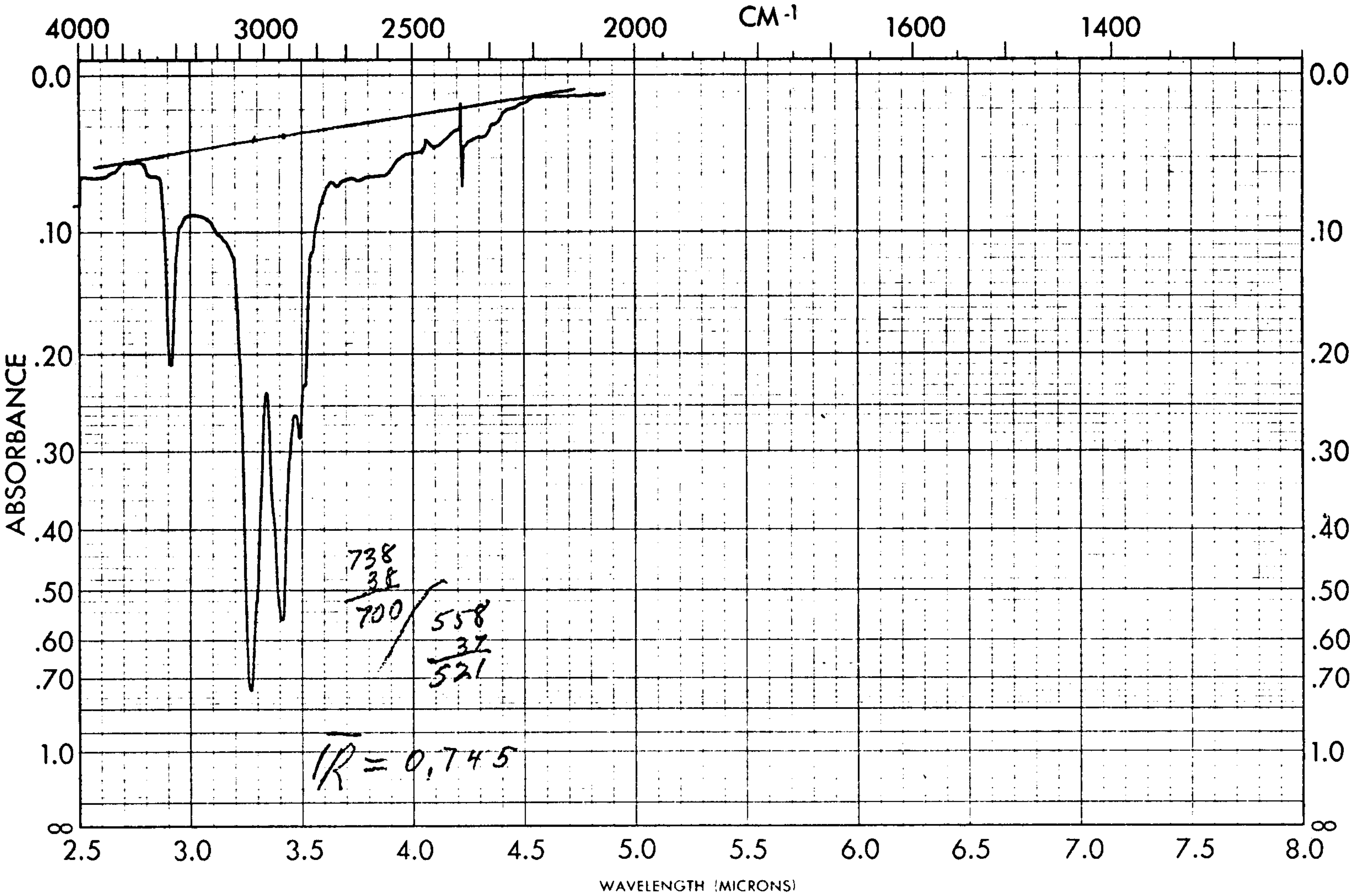


SPECTRUM C5

SAMPLE Middle fraction of Raw Anthracene Oil.. From Harmarville 2nd Batch	CURVE NO.	SCAN SPEED SF	OPERATOR CHW
	CONC.	SLIT	DATE 5/12/72
ORIGIN Sample taken at end of blending Feed for Run CuU 40	CELL PATH	REMARKS	
SOLVENT	REFERENCE		

PART NO. 237-1028

PERKIN-ELMER

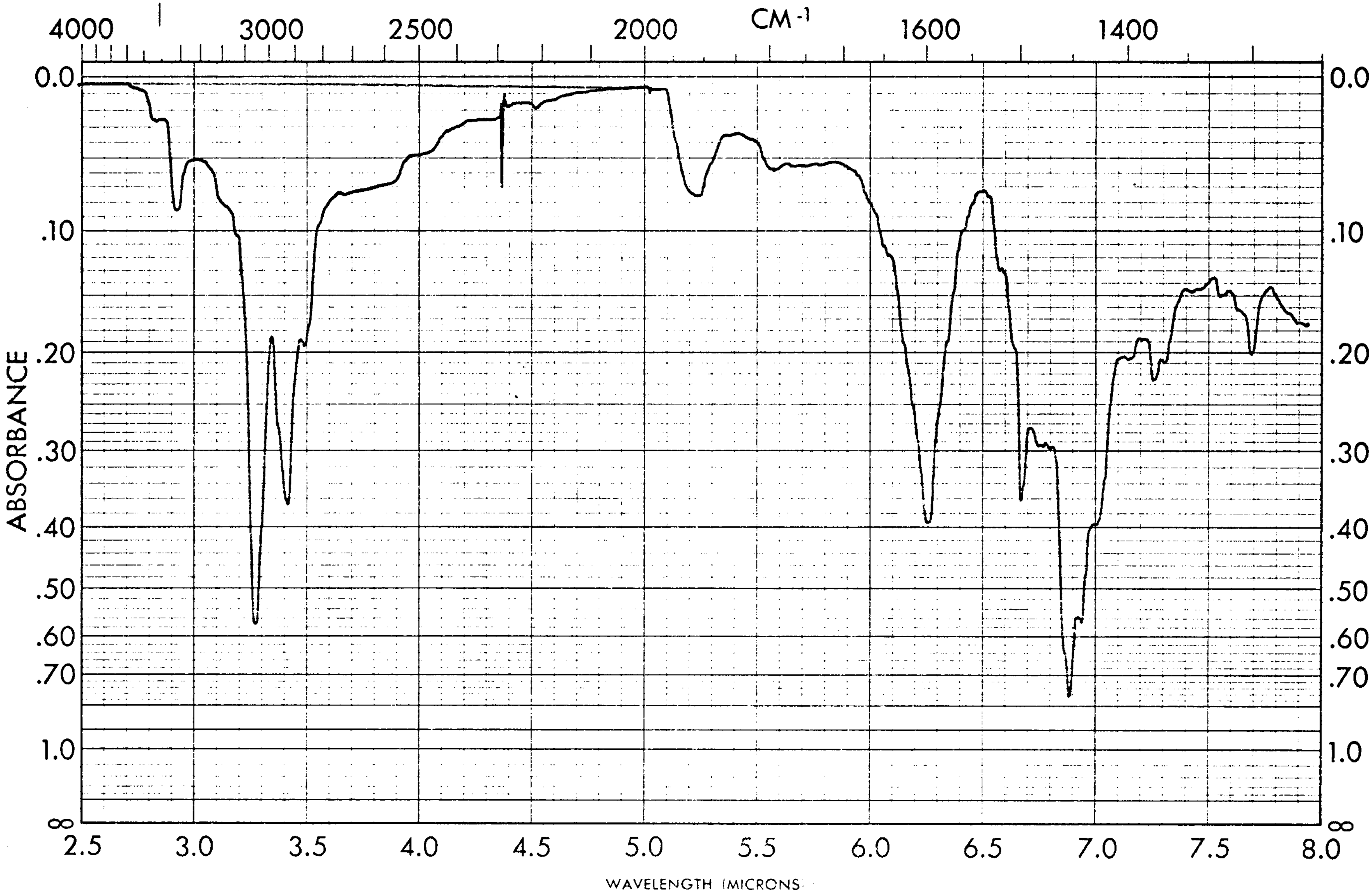


SPECTRUM C6

SAMPLE CV 40 POT 18 - 2nd SAMPLE @ $10^{\underline{00}}$	CURVE NO.	SCAN SPEED SF	OPERATOR CHW
	CONC.	SLIT	DATE 5/16/72
ORIGIN	CELL PATH	REMARKS Feed Rate 7600 gm/hr @ 04 - 64 on pump	
SOLVENT	REFERENCE		

PART NO. 237-1028

PERKIN-ELMER

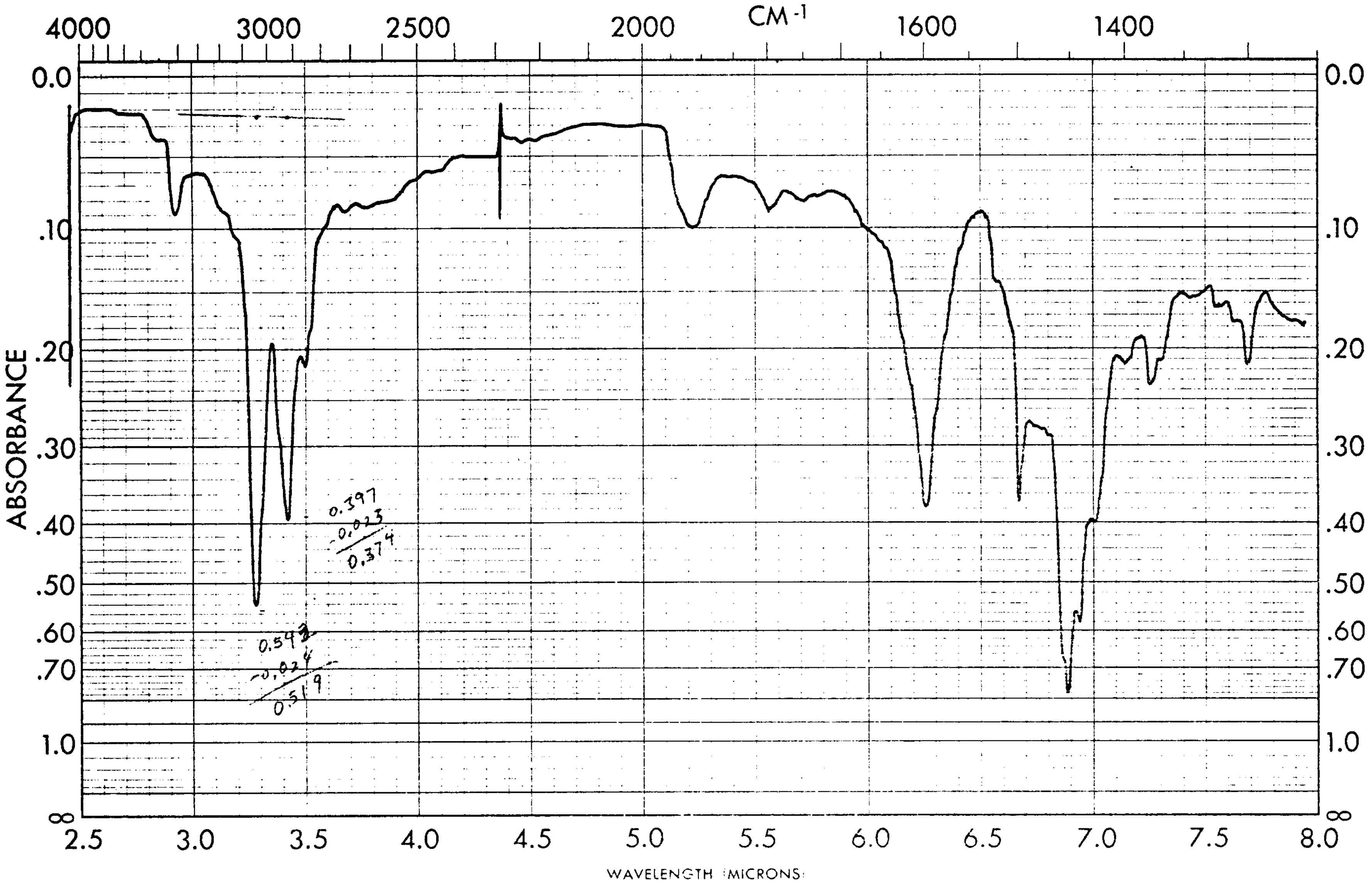


SPECTRUM C7

SAMPLE. Sample #1 From Run CL-8, Solvent Only, Exposed to H_2, 0840 CST to 0855 CST	CURVE NO.	SCAN SPEED SF	OPERATOR CHW
	NC.	SLIT	DATE Jan 13, 1971
ORIGIN	CELL PATH One 0.015 mm Teflon Spacer	REMARKS Ratio 3.3 to 3.4 = 1.571	
SOLVENT	REFERENCE		

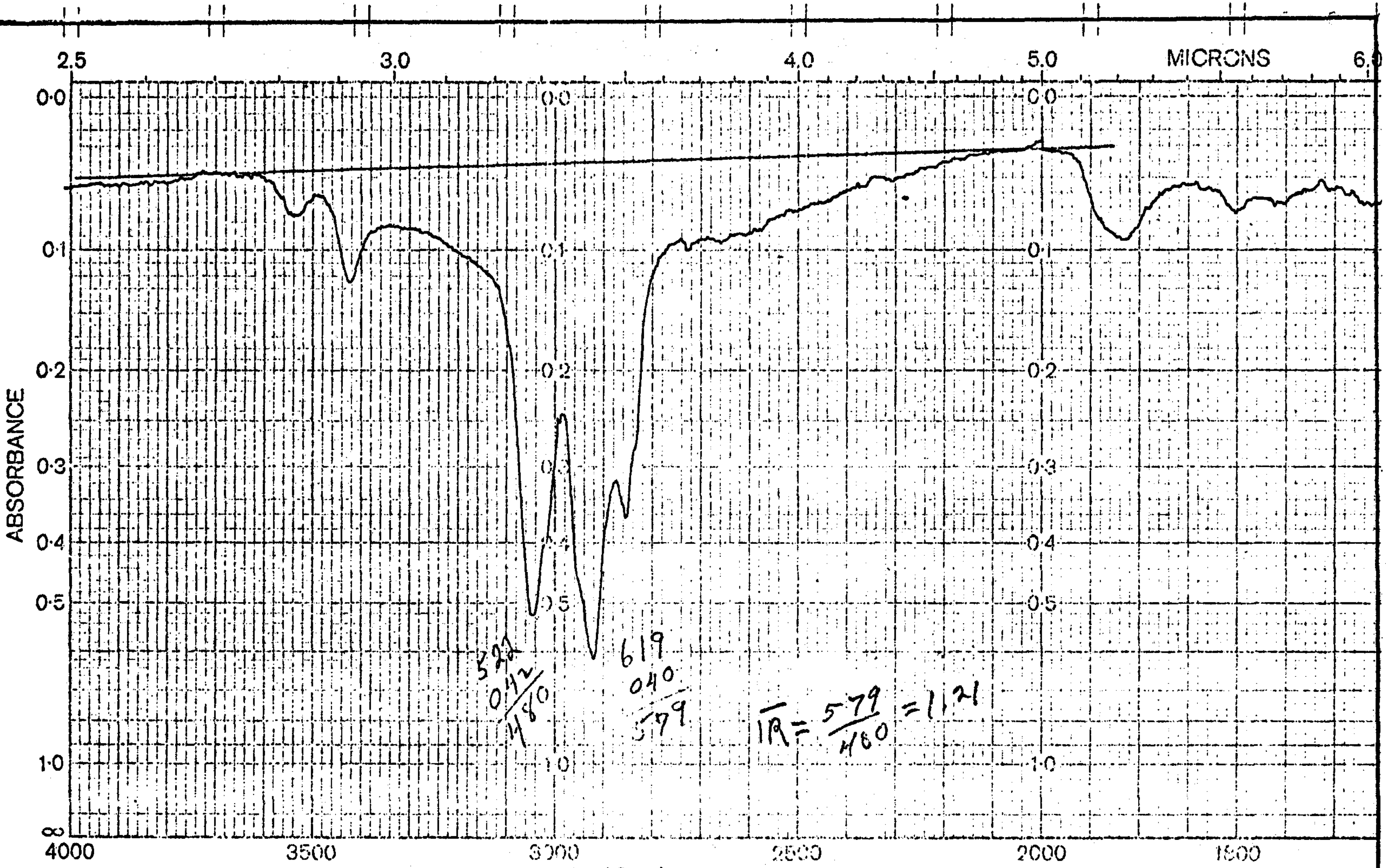
PART NO. 237-1028

PERKIN-ELMER



SPECTRUM C8

SAMPLE Distillate from Sample #10 of Run CL-8 (1745-1800 CST)	CURVE NO. CONC.	SCAN SPEED SF SLIT	OPERATOR REP DATE Feb. 2, 1971
ORIGIN 100-195°C @ 3 mm Hg SOLVENT	CELL PATH One 0.015mm Teflon spacer REFERENCE	REMARKS Ratio 3.3/3.4 = 1.39	



522
042
480

619
040
579

$\overline{IR} = \frac{579}{480} = 1.21$

SPECTRUM C9

SAMPLE CU49A, Cut #2
100-230°c @ 3mm Hg

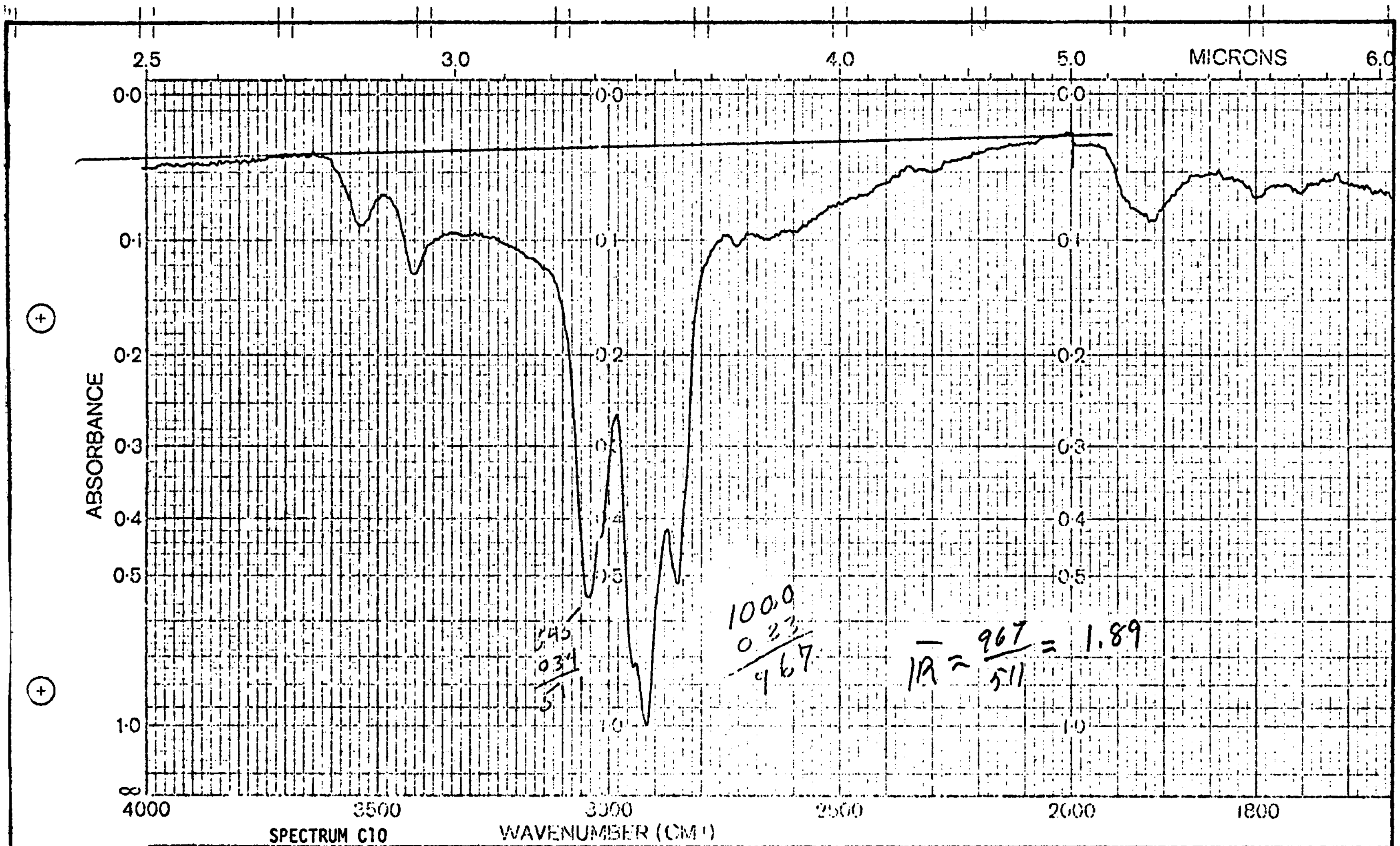
ORIGIN

SOLVENT

CONCENTRATION

CELL PATH

REFERENCE



SPECTRUM C10

SAMPLE CU49E, Cut#2
100-230°C @ 3mm Hg
ORIGIN

SOLVENT
CONCENTRATION
CELL PATH One 0.015 mm Teflon spacer
REFERENCE