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Coal Liquefaction Process Streams Characterization and Evaluation

The Preliminary Evaluation of the Kinetics of Coal Liquefaction Distillation Resid Conversion

Topical Report

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PROJECT ASSESSMENT

Introduction

Under subcontract from CONSOL Inc. (U.S. DOE Contract No. DE-AC22-89PC89883), The University of Delaware explored the use of a short contact-time batch reactor system to measure the kinetics of direct coal liquefaction resid reactivity. Products of the resid reaction were separated based on solubility and evaluated by thermogravimetric analysis (TGA), gas chromatography (GC), and gas chromatography/mass spectrometry (GC/MS). The full report authored by the University of Delaware is presented here. The following assessment briefly highlights the major findings of the project and evaluates the potential of the method for application to coal-derived resid materials. These results will be incorporated by CONSOL into a general overview of the application of novel analytical techniques to coal-derived materials at the conclusion of this contract.

Summary

This study evaluated the use of a novel laboratory-scale batch reactor, designed by the University of Delaware, to study the kinetics of coal liquefaction resid reactivity. The short time batch reactor (STBR) is capable of conducting reactions at temperatures up to 450 °C and pressures up to 2500 psi at well-defined reaction times from a few seconds to 30 min or longer. By the use of very rapid charging and preheating, this equipment avoids the problems of long heat-up and cool-down times associated with equipment traditionally used for such experiments. The small size, and batch nature of the reactor, also allows the running of many experiments over a range of conditions, in a relatively short time. Sixty experiments were conducted with the STBR in this project.

The products of the resid/tetralin/hydrogen reaction were separated by solubility, and several analytical procedures were used to evaluate the reaction products, including thermogravimetric analysis (TGA), gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). Changes were monitored in the boiling ranges of the products, as a function of process conditions (time, temperature, and tetralin donor

solvent-to-resid ratio), with and without catalysts. Two distillation resid samples were studied; Sample 1 is the resid of the second stage product stream from Wilsonville Run 259 which used Pittsburgh seam coal (Ireland mine) bituminous coal, and Sample 2 is the resid of the same stream from Wilsonville Run 260 which used Wyodak and Anderson (Black Thunder Mine) subbituminous coal. It was determined that the resid reactivity was different for the two samples studied. The results of this study demonstrate that further development of this experimental method is warranted to empirically assess resid reactivity and to provide data for use in the construction of an empirical model of coal conversion in the direct liquefaction process.

Program Description

This report describes the work performed at the University of Delaware under a subcontract from CONSOL Inc., Research and Development. CONSOL's prime contract to the U.S. Department of Energy (Contract No. DE-AC22-89PC89883, "Coal Liquefaction Process Streams Characterization and Evaluation") established a program for the analysis of direct coal liquefaction derived materials. The program involves a number of participating organizations whose analytical expertise is being applied to these materials. This Participants Program has two main objectives. The broad objective is to improve our understanding of fundamental coal liquefaction chemistry to facilitate process improvement and new process development. The specific approach to achieving this objective is to provide a bridge between direct coal liquefaction process development and analytical chemistry by demonstrating the application of various advanced analytical methods to coal liquefaction materials. The methodologies (or techniques) of interest are those which are novel in their application for the support of coal liquefaction and those which have not been fully demonstrated in this application. CONSOL is providing well-documented samples from different direct coal liquefaction production facilities to the program participants. The participants are required to interpret their analytical data in context to the processing conditions under which the samples were generated. The methodology employed is then evaluated for its usefulness in analyzing direct coal liquefaction derived materials.

Participant's Methodology

The University of Delaware employed two 850 °F distillation resids which contained ash and insoluble organic material (IOM) for this resid reactivity study. Both samples were distillation resids of material produced at the Wilsonville pilot plant and obtained from the atmospheric flash bottoms vessel (V-1067) after the second-stage reactor. The samples are composites of samples taken over long periods of individual processing runs. Two major processing parameters were varied among the Wilsonville runs: feed coal and reactor configuration. Run 259 used Pittsburgh seam, Ireland Mine, bituminous coal as feed, and was operated in the catalytic/catalytic reactor mode. Run 260 used Wyodak and Anderson seam coal, Black Thunder mine, subbituminous coal as feed and operated for approximately half the run in a thermal/catalytic reactor configuration (and high/low reactor temperature sequence), and for the remaining half of the run in a catalytic/thermal reactor configuration (and low/high reactor temperature sequence). The resids were reacted with tetralin and hydrogen and the products were analyzed. Reaction variables included time, temperature, solvent/resid ratio, and presence of catalyst. In total, sixty reactions were conducted. Reaction products were separated by solubility in tetralin. Both soluble and insoluble fractions were analyzed by TGA to determine volatile matter (VM), fixed carbon (FC), and ash content. Because ash contents of the products were used to determine the extent of conversion of the resid, it was necessary to correct the ash analyses for samples which contained catalyst. Details of the determination of the catalyst contribution to the ash analysis are given in the report (page 7). The short time batch reactor (STBR) apparatus, experimental procedures, and data analysis procedures used by the University of Delaware are described on pages 2 through 7 of the attached report.

Participant's Major Findings

The following principal observations were reported by the University of Delaware for the exploratory study of a method to determine direct coal liquefaction resid conversion kinetics. An expanded discussion can be found in the attached report, pages 7 through 14.

The tetralin-soluble portion of the products was found to contain no ash. This was key to the data analysis because conversion measurements are based on the relative ash contents of the unconverted resid and the conversion products. It was found that in the TGA analysis of the reaction products, slow heating rates resulted in conversion of unreacted resid. In order to avoid resid conversion during the TGA analysis, a relatively high heating rate (10 °C/min) was used.

The percent conversion for the two resid samples was found to be both time and temperature dependent. Lower temperature runs, performed for longer reaction time, approached the same conversions as higher temperature runs performed for shorter reaction times. In catalyzed and un-catalyzed runs, the increase in tetralin-soluble material, as reaction time increased from 0 to 30 min., was different for the two resids studied. For the un-catalyzed system, the difference found for the Run 259 resid (Sample 1) was 1 wt% at 412 °C to 6 wt% at 435 °C, and for the Run 260 resid (Sample 2) 2 wt% at 410 °C to 13 wt% at 434 °C. For the catalyzed case, the differences were found to be 10 wt% at 418 °C and 17 wt% at 435 °C for Sample 1, and 30 wt% at 421 °C and 32 wt% at 442 °C for Sample 2. The ordering of reactivity of the two samples was the same with and without catalyst present. Resid sample 2 was found to be more reactive than resid sample 1.

The TGA evolution pattern for un-catalyzed soluble reaction products showed a bi-modal distribution. The second (higher temperature) peak was not present in the products of the catalyzed runs. Based on the TGA evolution pattern, it was presumed that the average molecular weight of the products was lower in the catalyzed runs. Delaware estimated that as much as 20 wt % of the resid was cracked to compounds volatile enough for detection by GC. However, most of the material that dissolved in tetralin was too low in volatility to be detected by GC and GC/MS analysis; the material that was volatile enough could not be identified. Replication of experimental results by TGA was very good; characteristic values (volatile matter (VM), fixed carbon (FC), and Ash) were reproduced to within $\pm 0.5\%$, relative.

CONSOL Evaluation

The project goals in this limited study were: 1) to investigate the feasibility of using the STBR to determine the reactivity of coal-derived resids to forming lower boiling products; and 2) To develop and verify an experimental protocol for measuring relative resid reactivity for conversion to lower boiling products using tetralin solvent and a standardized catalyst and coal liquefaction conditions. Both goals were met. Experimental methods were adapted for the introduction of the resids to the reactor system and work-up procedures were altered to provide the best possible reaction monitoring system. An experimental protocol was developed to determine the relative amount of conversion of the resid, unhampered by the catalyst content of the reaction mixture. Reproducible data were obtained over a large matrix of reaction conditions, demonstrating the versatility of the technique.

The STBR was designed and built at the University of Delaware. It could be reproduced for about \$6000. The TGA used in this study costs about \$20,000. The GC and GC/MS systems cost \$25,000 and \$45,000, respectively.

Further Development

Some avenues for further development of this technique lie in improvement of the work-up procedures. In this study, solubility was used to measure the degree of resid conversion. As "resid" is defined by boiling point in plant operations, it is recommended that the resid conversion be monitored by analyzing the boiling point distribution of reaction products instead of solubility properties. This could be achieved by employing micro-distillation procedures or methods which can provide equivalent values such as TGA techniques.¹

Additionally, adding to the TGA, GC, and GC/MS analyses would enhance the potential for this method to provide chemical information that could be incorporated in an empirical model of resid conversion and reactivity. The following analytical procedures are suggested by the researchers at the University of Delaware for this purpose: 1) Thermogravimetric analysis followed by analysis of the effluent of the TGA by mass spectrometry and Fourier transform infrared spectrometry (TGA/MS/FTIR);

2) Vacuum TGA to analyze the volatile products of the reaction; 3) Vapor phase osmometry (VPO), gel permeation chromatography (GPC), or field ionization mass spectrometry (FIMS) for determination of the molecular weight distribution of the resid reaction products; or alternatively, 4) pyrolysis-mass spectrometry (PyMS) for the same purpose.

Participant's Statement of Work

Two different resid samples containing known ash contents will be selected by CONSOL. Reactions will be carried out in tetralin with hydrogen atmosphere at two selected concentrations (2:1 and 3:1 of tetralin-to-resid ratios) and run at 775 and 825 °F at least two reaction times (5 and 30 min). Hydrogen pressures of 1500 psi or, if possible, up to 2000 psi will be used. The same reactions will be run under the same conditions in the presence of catalyst supplied by CONSOL at a catalyst to resid ratio to be selected. In addition, a few selected runs will be made at other temperatures and concentrations to allow reasonable estimation of reaction order and the kinetic parameters (activation energy and frequency factor).

Reaction products will be evaluated according to the scheme shown in Figure 1. After each reaction is completed, a sample of the collected products will be analyzed by TGA with fast temperature ramp rates to determine the 975 °F resid and high temperature ash contents. Resid conversion will be calculated on the basis of the 975 °F resid content of the feedstock (as determined by TGA) and that of the reacted products. This conversion also will be compared with the resid-to-ash ratio of the feedstock and the reacted products.

The liquid reaction products will then be stripped of tetralin and other low boiling compounds in a Rotavapor. The low boilers removed in the Rotavapor will be analyzed by GC/MS for naphthalene, methylindan, benzene and other lower boiling products. The stripped product will be taken up in methylene chloride and again analyzed by TGA at a slow (5 °C/min) temperature ramp rate to determine the amount of resid which has been converted both to lower boiling products and to higher boiling retrograde products. The use of methylene chloride is an aid to transfer the liquid from the Rotavapor, since we have found that a slow temperature ramp rate

in the presence of tetralin results in further reaction during the TGA analysis, whereas there is no such effect of methylene chloride on the TGA analysis.

A kinetic analysis of the reactions may not be straightforward, since resid is a very complex mixture, both low and high boiling materials are likely to be formed and some gases and very low boiling products may also result. An effort will be made to develop a simple treatment of the data based on the reduction of the high boiling (over 524 °C or 975 °F) fraction based on TGA, with calculation of the kinetic parameters (activation energies and exponential factors).

Reference

Robbins, G. A.; Brandes, S. D.; Winschel, R. A.; Burke, F. P. "Coal Liquefaction Process Stream Characterization and Evaluation, Technical Progress Report, October 1, 1993 through December 31, 1993", DOE/PC 89883-86, February 1994.

**PRELIMINARY EVALUATION OF THE KINETICS OF COAL LIQUEFACTION
DISTILLATION RESID CONVERSION**

**Final Report
04/15/93 - 09/01/93**

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EXECUTIVE SUMMARY

By the use of a novel short-contact-time-batch reactor (STBR), a special product workup procedure, and thermogravimetric analysis (TGA), a method has been developed to measure the reactivity (kinetics) of coal derived vacuum resids toward conversion to low molecular weight more processible fuel materials. Gas chromatography and GC/MS were also used to examine the lower boiling products. This technique is designed to provide information concerning the behavior of these resids on recycling in a coal liquefaction process.

Only two resids from the Wilsonville plant derived from a bituminous and a subbituminous coal have been studied thus far, showing somewhat different conversion reactivities. Little conversion of these resids was observed under coal liquefaction conditions without a catalyst. With the use of a Ni/Mo on alumina catalyst, significant conversion is observed although only about 20 wt% of the resid was converted to gasoline and diesel boiling ranges under the times and conditions studied. The rest of the resid showed a breakdown into soluble and somewhat lower molecular weight materials, but ones requiring further processing to be useful liquid fuel materials.

The tetralin soluble portion of the unreacted resids studied showed a bimodal distribution of evolution rates (TGA). When reacted in the presence of the Ni/Mo on alumina catalyst, however, the high temperature peak disappears, and the low temperature peak shifts to still lower temperatures, indicating a breakdown of the resid structure.

INTRODUCTION

CONSOL Inc is performing an assessment of analytical and characterization methodologies relevant to the support of direct coal liquefaction process development. Much of the work has been concentrated on the analysis and characterization of the non-distillable portion of the liquefaction process stream because this "resid" usually constitutes a substantial portion of the liquefaction process stream(1-4). This material is typically recycled to the coal liquefaction process, since it is not suitable for processing in a conventional petroleum refinery. While the analyses obtained thus far provided analytical and structural information about the resids examined, they gave little indication of how these materials would break down to lower boiling materials during recycling to the liquefaction process. To complement more conventional analytical characterization methods, it is important to develop methods for assessing resid convertability under coal liquefaction conditions.

At the University of Delaware, we have developed a laboratory scale batch reactor(5) (Short Time Batch Reactor, STBR) capable of running reactions up to 450°C and 2500 psi at well defined reaction times from a few seconds to 30 minutes or longer. By the use of very rapid charging and preheating, this equipment avoids the problem of long heatup and cool down times associated with running reactions in the usual massive equipment required for such experiments. The small size and batch nature of the reactor also allows the running of many experiments over a range of conditions in a relatively short time.

In this project we have been making a preliminary study of the actual conversion of coal liquefaction non-distillable resids to lower boiling, lower molecular weight, material in this equipment (STBR) under conditions approximating the direct coal liquefaction process. Conversion of the resid has been determined primarily by TGA (Thermogravimetric Analysis), GC/MS (Gas Chromatography coupled with Mass spectrometry) and GC (Gas chromatography) on the reaction products. The objective of this work has been to determine whether such a method can be used to estimate the reactivity and convertability and therefore the recyclability of any such coal derived resid. Two coal derived resids from the Wilsonville Pilot Plant were examined, both with catalyzed and un-catalyzed reactions.

EXPERIMENTAL

Apparatus

An empty batch reactor, illustrated in Figure 1, is immersed in a sand bath and brought to the desired reaction temperature. Using high pressure gas, the reaction mixture under study is driven into the reactor from a small blow case through preheater tubing, which is also at reaction temperature. The reaction mixture is then agitated by gas bubbles injected through the slurry from the bottom of the reactor. The degree of agitation is controlled by the exit gas flow rate from the top of the reactor. At a selected time, the reactor contents are driven out of the reactor into a cold receiver through a precooler with

high pressure gas. Both the receiver and precooler are immersed in a water bath.

The details of the reactor system are shown in Figure 2. The heating bath used is a Techne IFB-52 industrial fluidized sand bath, which maintains a reaction temperature of $\pm 2^{\circ}\text{C}$. The 30 cm³ reactor is capable of containing up to 17 MPa (2500 psi) pressure at temperatures up to 550°C. The tubing used for preheater and precooler was 1/4" 316 stainless steel with wall thickness of 0.0035". The lengths of the preheater and precooler are both 21 feet. Since a gas (e.g. hydrogen) is bubbled through the reaction mixture under pressure and out through a let-down valve, a small water cooled condenser above the reactor and a disengaging space above it before the let-down valve have been added to avoid loss of solvent or other low boiling components and to improve operability.

Reaction Temperature Profile

A time-temperature profile for a mixture of 25% resid in tetralin is shown in Figure 3. At the time of injection, (less than 1 second) the reactor temperature dropped 5 - 8°C but it recovered to sand bath temperature within 30 seconds. This temperature drop can be reduced by longer preheater tubing.

The excellent time-temperature profile is due to the preheating of the comparatively massive empty reactor and the preheater tubing and fittings prior to $t = 0$. This allows the thermal transient to be focused only on the reaction mixture.

Sample Recovery

The amount of material recovered from the reactor when it is driven from the system depends on the surface area of the entire apparatus. This is because the surface holds up liquid by wetting. The surface areas of the preheater and precooler are the bulk of the surfaces involved and therefore there is a trade off between the reaction temperature drop on injection and the degree of material recovery. For that reason, the longer the preheater, the smaller the reaction temperature drop on injection, but the lower the recovery. The viscosity or fluidity of the sample stream also influences the recovery. For the very viscous resid samples examined in this project, recoveries have varied from about 65% to 89%, depending on the amount of solvent, such as tetralin which is used in this project in the reaction mixture. Because of the hold-up of some of the reaction mixture on the walls of the reactor and preheater and precooler tubings, 100% recovery of the reaction mixture is not practical. This means that analytical methods must be available to follow the course of the reaction with aliquots. This has not been a limitation for the reactions studied in this project. However, if better material balances are desired, the first sample can be supplemented with solvent washes of the system, and further quantities of the reactant recovered by solvent removal in a rotovapor.

For the resid conversion experiments to be meaningful, the products obtained in the receiver must be representative of the reactor contents, i.e., different components of the mixture are not held up preferentially on the walls of the reactor, preheater or precooler. This was shown to be the case by comparing the TGA parameters (such as ash content, VM,

and FC) of two resid-tetralin mixtures (Resid 1 and Resid 2) at room temperature without going through the reactor with the same mixture after processing through the reactor at room temperature (Table 1).

Cleaning the System

The reactor system is cleaned in place by a series of suitable solvent washes. In this research we have used tetralin which is a donor solvent used in the resid conversion.

Materials Studied

Analytical Data provided by CONSOL on the two coal derived resids studied are shown in Tables 2a and 2b. Both samples were obtained from the Wilsonville Pilot Plant, Runs 259 and 260. They are solid, 850°F distillation resids which were crushed to pass a fourteen mesh Tyler screen (1.17 mm). These materials were produced by CONSOL from whole process oils by distillation in a 1" x 3' jacket-heated Vigreux column to an end point of 320°C pot/270° column temperatures at 5 torr (850°F equivalent). The samples contain both ash and some tetrahydrofuran (THF) insoluble organic matter. They are composites of the resids of individual samples taken over long periods of each run.

Resid 1 was derived from Pittsburgh seam Coal from the Ireland Mine (Wilsonville Run 259). Resid 2 was derived from Wyodak and Anderson Seam Black Thunder mine (Wilsonville Run 260). Thus the two samples represent resids from a bituminous and a subbituminous coal liquefaction.

Catalyst

The catalyst used was a presulfided Ni/Mo on alumina catalyst (Shell 324). Its metal content was 10.5 wt % Mo ($\pm 2\%$ relative) and 2.08 wt % Ni ($\pm 2\%$ relative). The catalyst was presulfided in a distillate oil at the Wilsonville pilot plant. The conditions of presulfiding were as follows:

1. the catalyst was charged to a reactor with No. 6 fuel oil;
2. the reactor temperature was raised to 250 °F;
3. at 250 °F the reactor catalyst beds were ebullated;
4. at 250 °F the sulfiding agent dimethyldisulfide (DMDS) was added to the reactor;
5. the reactor temperature was ramped at 50 °F/hr until the temperature reached 400 °F, where it was held for one hour;
6. the reactor temperature was then raised at a rate of 50 °F/hr to intermediate temperatures of 500 °F and 600 °F, where the bed was held for one hour at each level;
7. the bed temperature was raised to a final temperature of 700 °F, and the catalyst was considered to be fully sulfided.

After sulfiding, the catalyst was removed from the reactor and stored in drums. The sample of the catalyst was received by CONSOL where 150 g batches were extracted in a Soxhlet extractor using freshly distilled tetrahydrofuran for 48-72 hr or until the extracting

fluid was colorless. This procedure was carried out under a nitrogen atmosphere. The catalyst was transferred, under nitrogen, to a nitrogen purged receiver and left to dry for 24 hours. The dried catalyst was ground under nitrogen to - 60 mesh. Batches of 100 - 150 g of ground catalyst were transferred to plastic-lined aluminum bags, flushed with nitrogen and vacuum sealed.

Instruments

The thermogravimetric analyzer (TGA) used in this research is a Model 51 thermogravimetric analyzer (TA Instruments, New Castle, DE).

The gas chromatography (GC) was done on a Hewlett Packard HP 5970 Series II GC using FID (Flame Ionization Detector). The packed column is HP Ultra 2 (Crosslinked 5% Ph Me Silicone), 50 m x 0.2 mm x 0.33 μ m film thickness. The helium elution conditions are: injector temperature, 275 °C; detector temperature, 275 °C; initial column temperature, 150 °C; ramp, 10 °C/min; and final column temperature, 275 °C.

The gas chromatography/Mass Spectrometry (GC/MS) was also performed on a Hewlett Packard HP 5970 Series II using HP 5970 Series Mass Selective Detector. The column and helium elution conditions are same as the above GC operation.

Resid Conversion Reactions

All reactions were run on mixtures of tetralin (T, the donor solvent) and resid (R) over the range of T/R ratios and temperatures with and without catalyst. Where catalyst was used an amount of catalyst equivalent to the amount of resid was added, simulating ebulating beds.

Reaction Product Workup Procedure

The product work up procedure planned originally was based on taking up the reaction mixture in methylene chloride in order to obtain a reasonably representative sample of the reaction product for analysis. This scheme had been based on preliminary experiments with a high boiling liquid distillate, and was satisfactory for that system. The resids we obtained for the project however contained substantial amounts of mineral matter as well as methylene chloride insoluble organics. Using coal washing experiments, we found that our proposed workup procedure was not satisfactory for these materials because there was a significant solubility of mineral matter in the methylene chloride (Table 3). Because we wanted a clear cut measure of the mineral content as a basis for determining the degree of conversion, a new workup system was therefore required.

It was also found that running the TGA analysis of the solid resid at slow ramp temperatures could not be performed if there was a significant amount of tetralin present, because conversion of the resid by the tetralin occurred during the TGA analysis itself (see Figure 4). As a result, a new reaction product workup procedure was developed, and is shown in Figure 5.

The new procedure required the filtration of the reaction mixture in a sintered glass filter. The liquid filtrate and the filtered solid resid, the solid remaining on the sintered glass filter, were analyzed separately. TGA analysis on the liquid filtrate which contained most of the tetralin showed that there is no mineral matter in the liquid sample. The filtered solid resid was dried in a vacuum oven at 100 °C for 48 hr, then ground in a mortar and pestle and dried again to remove residual tetralin.

As shown in Figure 6a, the tetralin content of the liquid filtrate as well as the amount of higher boiling materials which were soluble in the liquid could be determined by TGA in nitrogen. The liquid filtrate was also analyzed by GC/MS and GC to determine the number of compounds dissolved in the tetralin from the resid conversion and to determine, if possible, their identities. However, much of the resid material which dissolved in the tetralin, even after the liquefaction reaction under the conditions used, was still too low in volatility to be detected with GC or GC/MS. The soluble material in the liquid consisted of some conversion products of the tetralin, but also material in the original resid that was tetralin soluble as well as material formed by breakdown of the resid into tetralin soluble substances. The amount of the latter could also be estimated by comparison of the liquid reaction product under liquefaction reaction conditions at extremely short reaction times with that produced under the same conditions at longer times. In this project, the tetralin soluble resid plus that solubilized in the liquefaction process was estimated by comparison of the ash content of the solid filter cake with that of the unreacted resid. As shown in Figure 6a, no mineral matter (ash) is found in the liquid filtrate when oxygen is added at 600 °C in the TGA.

A TGA run on the filtered solid resid is shown in Figure 6b. TGA runs on the filtered solid resids give several characteristic parameters, such as VM (volatile matter), FC (fixed carbon), and ash for an un-catalyzed sample. By running in nitrogen at a ramp of 10°C/min to 600 °C, the amount of volatile matter (VM) can be determined(6). Then, by introducing oxygen at 600°C, the loss in weight was observed. It is due to the oxidation of the combustible materials in the resid, so called "fixed carbon (FC)", leaving the residue as mineral matter or ash. Thereafter, it is run at a ramp of 100 °C/min to 900 °C in oxygen to determine any further oxidation of the ash residue at higher temperatures. As shown in Figure 6b, there is no further loss in weight for un-catalyzed samples.

For a catalyzed sample, the 600 °C-oxidized residue includes the ash from the resid and partially oxidized catalyst. Since the mineral matter (ash) from the resid was used as a reference for determination of conversion, the amount of the residue must be corrected for the catalyst added. A TGA run on a solid resid with catalyzed sample is shown in Figure 6c. For this catalyzed sample, VM determined by TGA consists of VM from resid and weight loss of the catalyst; FC determined by TGA represents FC from resid and the first stage of catalyst oxidation; Ash₁ determined by TGA contains ash from the resid and partially oxidized catalyst; and Ash₂ determined by TGA includes ash from the resid and ash from the catalyst. During the second oxidation period, i.e., the interval of the temperature ramped at 100 °C/min to 1000 °C in oxygen and kept at 1000 °C for 120 min, an additional

loss in weight was obtained. It is due presumably to the oxidation of the sulfided catalyst to the oxides. This can be translated into catalyst concentration by comparison of the weight loss at 1000 °C with the weight losses obtained on catalyst alone and a calibration sample. The details about how to determine the amount of the catalyst and the content of the ash from the resid in a product stream are discussed in the following section.

Determination of the Amount of the Catalyst and the Content of the Ash from the Resid

A TGA run on the pure sulfided catalyst is demonstrated in Figure 7. Running in nitrogen at 10 °C/min to 600 °C, the first drop in weight loss was detected. As oxygen is added at 600 °C, the second drop in weight loss was obtained. This loss in weight is due to the partial oxidation of the catalyst, designated as the first stage of catalyst oxidation. When finally running in oxygen from 600 °C at 100 °C/min to 1000 °C and holding at 1000 °C for 120 min, the third drop in weight loss was observed. This loss in weight is due to the complete oxidation of the catalyst, designated as the second stage of catalyst oxidation, leaving the residue (so called "Ash₂") as the ash from the catalyst, i.e., metal oxides. As mentioned above, this third drop in weight loss is solely caused by the second stage of catalyst oxidation, because there is no such drop for the un-catalyzed resid sample alone (Figure 6b). Therefore, the amount of catalyst present in the resid-catalyst mixture is proportional to the third drop obtained by TGA, i.e.,

$$\text{Catalyst (wt\%)} = \alpha (\text{Ash}_1 (\text{wt\%}) - \text{Ash}_2 (\text{wt\%})) \quad (1)$$

where α is a scale constant which can be determined by a calibration sample, Ash₁ a 600 °C residue (wt%), and Ash₂ a 1000 °C residue (wt%).

The amount of ash from the resid can be estimated by the mass balance of the ash in the resid and that from the catalyst. Since the ash from the catalyst (Ash_{catalyst}) and the ash from the resid (Ash_{resid}) are unchanged throughout the reactor runs, their ratio should be a constant, i.e.,

$$k = \frac{\text{Ash}_{\text{catalyst}} (\text{wt\%})}{\text{Ash}_{\text{resid}} (\text{wt\%})} \quad (2)$$

The constant k can be determined by running a calibration sample. For a catalyst-resid mixture, the final residue (Ash₂) by TGA includes ash from the resid and ash from the catalyst. Therefore, we have another equation which can be used to solve simultaneously with Equation 2 for the amount of the ash from the resid,

$$\text{Ash}_{\text{catalyst}} (\text{wt\%}) + \text{Ash}_{\text{resid}} (\text{wt\%}) = \text{Ash}_2 (\text{wt\%}) \quad (3)$$

Determination of Percent Conversion of the Resid

Significant proportions of the resids are soluble in tetralin at room temperature (48 to 55 % for resid 1 and 35 to 40 % for resid 2, depending on the tetralin to resid ratio). During the liquefaction process, particularly in the presence of a catalyst, further solid resid becomes soluble in the tetralin. To the extent that this solubilization represents conversion of the resid, it can be estimated by comparing the amount of ash present in the solid filter cake with that of the unreacted resid. The total amount of resid dissolved in the tetralin, D, can be calculated using the equation:

$$D \text{ (wt\%)} = \left(1 - \frac{X_0}{X}\right) \times 100 \text{ (wt\%)} \quad (4)$$

D of course is the sum of the soluble resid and the resid which has become solubilized in the conversion process. Conversion can be estimated by subtracting the soluble portion of the resid D at time zero, from the D at time t.

Equation 4 is valid because no inorganic matter (ash) goes into the liquid (Figure 6a). When catalyst is used, the ash determined by TGA must be corrected for the ash from the catalyst added.

Degree of Breakdown of the Solubilized Resid

By TGA on the liquid filtrate, a change in material evolution temperature is an indication of the breakdown of the solubilized resid to more or less volatile and therefore lower boiling material.

Ultimately, it is important to know how the boiling range of the reacted resid changes in the liquefaction process so that changes in processability in a refinery or under recycling conditions can be estimated. The TGA provides a convenient way to measure the evolution pattern of a material at elevated temperatures. This evolution pattern is a combination of volatilization (boiling range) and pyrolysis (cracking). These components can be separated to some extent by running the TGA under vacuum. The boiling range is strongly influenced by the pressure and the evolution pattern of volatile materials is therefore shifted to lower temperature by vacuum. The pyrolysis or cracking reactions are strongly influenced by the temperature and are almost unaffected by vacuum (8). TGA under atmospheric pressure and vacuum therefore allows differentiation between volatilization and pyrolysis. The boiling range of the volatile components can be estimated, by calibration of the TGA with compounds of known boiling range. Unfortunately, there was insufficient time in this project to perform the vacuum TGA experiments.

Degree of Breakdown of the Solid Resid as indicated by the Ratio of Volatile Matter to Fixed Carbon Determined by TGA

In this study, we find that it is mainly the volatile matter (VM) component of the resid (by the TGA analysis) that dissolves in the tetralin (see Figures 8a and 8b). The ratio

of volatile matter (VM) to fixed carbon (FC) in the TGA curves for the solid (filtered) product is therefore another measure of the degree of breakdown of the heavy resid material in the liquefaction process.

Other Possible Measures of Resid Conversion

Although in principle the amount of conversion of the resid can be obtained from the GC and GC/MS on the liquid filtrate, much of the soluble material (at least 80 wt%) even after the liquefaction reaction under the most severe conditions used in this study was still too low in volatility to be detected by GC or GC/MS. Time did not permit the investigation of changes in molecular weight, such as Vapor Phase Osmometry, Gel Permeation Chromatography, and/or other analytical techniques.

Experimental Program

An outline of the experiments which were performed for this project are shown in Table 4. Resid conversion experiments were run with and without catalyst and over a range of conditions of temperature, and tetralin to resid ratios to learn whether such a test could be used to measure resid reactivity and convertability. The workup procedure and analytical systems were modified to be applicable to the resids studied. The experimental conditions of the reactor runs done on resids 1 and 2 combined with characteristic operating parameters are listed in Tables 5a and 5b.

RESULTS AND DISCUSSION

TGA, GC/MS, and GC Analysis

Results of the replicate TGA runs on unreacted resids are given in Table 6. The experimental error for determination of these characteristic variables is less than $\pm 0.5\%$ of the measured values.

A TGA run on a liquid filtrate shown in Figure 6a gives two fractions: a fraction boiling in the tetralin range and a higher-boiling tetralin soluble fraction. TGA measurements can not discriminate among the converted components whose boiling points are close to tetralin. Therefore, GC and GC/MS were used to detect them. Tests on both un-catalyzed and catalyzed samples by GC and GC/MS have shown that there is some (up to 0.5 wt% for un-catalyzed runs, and 2 wt% for catalyzed runs) of material in the liquid filtrate boiling close to tetralin, which is formed by breakdown of resid. This represents about 5% to 20% conversion of the resid which has been converted to low boiling material. These low boiling substances consist of more than 50 individual compounds detected by GC, each too low in concentration to be identified. The GC/MS used in this work is not sensitive enough to detect these many low boiling materials in the very low concentrations involved..

Un-catalyzed Conversion of Resids

Characteristic parameters of TGA runs on the filtered solid resids in un-catalyzed conversion are shown in Tables 7a and 7b. The WR-series samples (WR101, WR102,

WR103, WR104, WR201, WR202, WR203, and WR204) are calibration samples, which are treated by tetralin at room temperature. These samples are used as reference to the reactor run samples. (The best comparison basis would be the 0 min at the reaction temperature, which is obtained by extrapolation of finite reaction times at the reaction temperature. However, since the product workup is done at room temperature, comparison to a room temperature reference is a reasonable approximation.) The percent resid dissolved in tetralin (D) was calculated using Equation 4. (Assumes conversion of solid resid is to soluble material in the liquid fraction.) The calculation basis of D in Equation 4 is on 1 gram of resid. To convert it to an ash-free basis, we can use the equation:

$$D \text{ (wt\%)} = \frac{X - X_0}{X(1 - X_0)} \times 100 \text{ (wt\%)} . \quad (5)$$

The measured VM and FC by TGA were converted to a resid-normalized basis (i.e., taking 1 gram of charged resid as the calculation basis) by the formula:

$$\begin{aligned} VM_{(resid-normalized)} \text{ (wt\%)} &= (1 - D) VM_{(by TGA)} \text{ (wt\%)} \\ FC_{(resid-normalized)} \text{ (wt\%)} &= (1 - D) FC_{(by TGA)} \text{ (wt\%)} \end{aligned} \quad (6)$$

As shown in Tables 7a and 7b, a portion of the resid is tetralin soluble even at room temperature (WR-series samples). The percent resid dissolved in tetralin (D) for resid 1 at room temperature ranges from 48% to 55% depending on the ratio of tetralin to resid ($T/R = 2.0 - 5.0$), and that for resid 2 varies from 35% to 40%. To visualize the source of the dissolution portion in the resids under various conditions, resid-normalized VM, FC and D are plotted with various conditions in Figures 8a and 8b. From these figures, it is obvious that the majority of the dissolution portion (about 80 wt%) comes from the VM in the resids.

Plots of D vs. reaction times for resid 1 at different temperatures and T/R ratios are shown in Figures 9a, 9b, and 9c. The percent resid dissolved in tetralin (D) increases with reaction time and temperature. However, for un-catalyzed 30 min reactor runs, the percent resid dissolved in tetralin (D) increases only about 1 wt% at 412 °C, and only about 6 wt% at 435 °C for $T/R = 3.0$ samples. The same behavior was observed for the resid 2 conversion (Figures 10a, 10b and 10c). For un-catalyzed 30 min reactor runs, the percent resid dissolved in tetralin (D) increases about 2 wt% at 410 °C, and about 13 wt% at 434 °C for $T/R = 3.0$ samples, which shows about twice the reactivity as resid 1.

Evolution rate versus temperature of the liquid samples were determined on the liquid filtrate from the calibration sample WR103 (treated with tetralin at room temperature), and resid 1 reacted for 5 min at 434 °C, and for 30 min at 435 °C. The

results as plotted in Figure 11 indicate a bimodal distribution in the evolution pattern. There is no observable change in the evolution pattern through the reactor runs under the experimental conditions we have used in this project, although the material went into solution. A similar evolution rate vs. temperature of the liquid samples for the resid 2 conversion at 435 °C is shown in Figure 12. There is also no significant change in the molecular weight distribution (evolution temperature pattern) in the liquid filtrate.

Catalyzed Conversion of Resids

Characteristic parameters of TGA runs on the filtered solid resids in catalyzed conversion are tabulated in Tables 8a and 8b. As discussed in the previous section, for the catalyzed samples interpretation of the TGA results are much more complicated than those of un-catalyzed samples. For examples, "VM" determined by TGA is not VM only of resid for a catalyzed sample. In fact, the loss in weight during this TGA process for a catalyzed sample included the weight loss of the catalyst ($VM_{catalyst}$). The same problem is involved for the measurements of "FC" by TGA for a catalyzed sample. This is because during the 600 °C-ashing process, not only fixed carbon in resid is oxidized, but also the first stage of catalyst oxidation takes place ($FC_{catalyst}$). Therefore, the "VM" and "FC" determined by TGA have to be corrected to a catalyst-free basis, i.e.,

$$\begin{aligned} VM_{resid}(wt\%) &= VM_{by\ TGA}(wt\%) - VM_{catalyst}(wt\%) \\ FC_{resid}(wt\%) &= FC_{by\ TGA}(wt\%) - VM_{catalyst}(wt\%) . \end{aligned} \quad (7)$$

The values of $VM_{catalyst}$ and $FC_{catalyst}$ were estimated from the TGA runs on the catalyst alone, the catalyst through the reactor at reaction conditions, and calibration samples.

The amount of the catalyst in the final product stream was estimated by Equation 1. Running calibration samples (WCR101 and WCR201) on TGA, we obtained: $\alpha_1 = 7.55$ for resid 1 and $\alpha_2 = 10.35$ for resid 2.

The amount of the ash from the resid in the final product stream was estimated by Equations 2 and 3. Running calibration samples (WCR101 and WCR201) on TGA, we obtained: $k_1 = 5.87$ for resid 1, and $k_2 = 3.79$ for resid 2.

To correct the amount of ash from the resid-catalyst mixture basis to a catalyst-free basis, we used the formula:

$$Ash_{catalyst-free}(wt\%) = \frac{Ash(wt\%)}{1 - Catalyst(wt\%)} . \quad (8)$$

Then, Equation 4 was used to calculate the D from the values of resid $Ash_{catalyst-free}$ obtained by Equation 8.

Using the same method mentioned in the previous section, we can estimate the resid-normalized VM and FC.

Plots of the D vs. reaction times for resid 1 at different temperatures and at T:R:Cat. (Tetralin:Resid:Catalyst) = 3:1:1 are shown in Figure 13. For reaction temperature around 415 °C, the percent resid dissolved in tetralin (D) increases with reaction time up to about 10% for 30 min (ten times higher than un-catalyzed run). For a reaction temperature around 434 °C, the percent resid dissolved in tetralin (D) increases with reaction time up to 20 min, then it levels off. In 20 min, it increases to about 17% (four times higher than un-catalyzed runs).

Plots of the D vs. reaction times for resid 2 at different temperatures and at T:R:Cat. = 3:1:1 are shown in Figure 14. For a reaction temperature around 415 °C, the percent resid dissolved in tetralin (D) increases with reaction time up to about 31.6% for 30 min (fifteen times higher than un-catalyzed runs). For a reaction temperature around 440 °C, it increases with reaction time up to 10 min, then it levels off. In 10 min, it increases to about 33.2% (eight times higher than un-catalyzed runs). It is interesting to point out that:

1. in the lower temperature runs, they approached the same value of D in high temperature runs at longer reaction time (Figure 14);
2. at reaction time 30 min, the percent resid dissolved in tetralin (D) on an ash-free basis for 421 °C approaches about 87% and that for 442 °C to about 91%;
3. the reactivity of the resid 2 in catalyzed conversion is higher than that of the resid 1, the similar order which is observed in un-catalyzed conversion.

To examine the evolution pattern (a function of the molecular weight distribution) of the converted materials in the liquid filtrate, slow ramp TGA (1 °C/min) was run on selected liquid samples. Evolution rate vs. temperature of the liquid samples from the catalyzed resid 1 conversion: 0 min (the liquid filtrate from calibration sample WCR101, which is treated with tetralin at room temperature), 5 min at 434 °C, and 30 min at 435 °C for resid 1 was plotted in Figure 15. This shows that the evolution rate for reactor runs significantly shifted to lower temperature. In other words, there is a notable reduction in the average molecular weight by the catalyst. This can be quantitatively described by two characteristic variables: peak evolution temperature (T_{peak}) and mean evolution temperature (T_{mean}). T_{peak} is defined as the evolution temperature at maximum evolution rate. T_{mean} is defined as the mean evolution temperature weighted by the evolution rate. Mathematically,

$$T_{mean} = \frac{\sum_i (Evolution Rate)_i T_i}{\sum_i (Evolution Rate)_i} \quad (9)$$

The calculated T_{peak} and T_{mean} for the catalyzed runs and reference sample (at 0 min) are listed in Table 9. For longer reaction time, not only T_{mean} decreases by about 60 °C, but also T_{peak} shifted to lower temperature direction by about 50 °C.

The same behavior was observed in the resid 2 catalyzed conversion (Figure 16). The calculated T_{peak} and T_{mean} for this resid are shown in Table 9.

It is interesting to note from Figures 11, 12, 15 and 16 that the soluble fraction of the resids shows a bimodal distribution of differential evolution peaks in the TGA. The higher temperature peak disappears after catalytic reactions, but is unchanged in reactions without catalyst.

SUMMARY AND CONCLUSIONS

1. The combination of reaction in the STBR (Short Time Batch Reactor) with TGA analysis of the liquid filtrates and the "un-converted" filtered solid resids provides a direct and reproducible means of indicating the breakdown of coal-derived liquefaction resids under liquefaction conditions.
2. The conversion of resid to tetralin soluble material is determined by relating the inorganic matter (ash) in the reacted resid with that of the un-reacted resid. Conversion of un-catalyzed tetralin-insoluble resids to tetralin soluble products in this study was very low (< 10 wt%) under coal liquefaction conditions, however, up to 50 wt% of the resid is tetralin-soluble at room temperature.
3. Up to 80% (ash-free basis) of the room temperature tetralin insoluble resid is solubilized in tetralin using sulfided Ni/Mo on alumina catalyst at 434 °C for 10 min.
4. A method has been devised for determining the catalyst concentration and the ash from the resid by TGA.
5. The two resids examined showed somewhat different reactivities.
6. In the catalyzed experiments, a progressive decrease in the temperature evolution range (as measured by TGA) of the solubilized materials with time under liquefaction conditions is observed by TGA. In the un-catalyzed experiments, no change in the evolution range of the solubilized materials with time up to 30 min is

observed by TGA.

7. The majority of tetralin soluble or solubilized materials come from the volatile matter in the resids.
8. While liquefaction conditions, particularly in the presence of Ni/Mo on alumina catalyst are effective in converting tetralin insoluble to tetralin soluble material and to reducing the average molecular weight (as shown by TGA), only a small fraction (perhaps 20 percent) of this material is converted to the boiling range of gasoline or diesel fuel under the liquefactions conditions studied (30 minutes at 434°C) as shown by GC.

SUGGESTIONS FOR FUTURE RESEARCH

While the combination of liquefaction in the STBR followed by analysis by TGA is effective and convenient for measuring resid conversion reactivity, a more sensitive method for following the changes in molecular parameters in the higher molecular weight ranges (molecular weight, molecular weight distribution, molecular species formed etc) is needed to adequately follow the resid conversion and the pathways involved. This need may be addressed by use of TGA/MS/FTIR or a combination of vapor phase osmometry, gel permeation chromatography, FIMS, and pyrolysis into a high resolution mass spectrometer.

The use of vacuum TGA along with the conventional atmospheric TGA should provide insights into the degree of volatilization of the resids in the liquefaction process.

The use of the STBR reactor system together with TGA and a combination of other analytical methods can shed a great deal of light on the coal liquefaction process particularly as it relates to recycling of the high boiling resid materials. It also provides a means for determining the relative reactivities of various resids and of determining what catalysts are most effective in resid conversion.

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List of Tables

Table 1 Characteristic Parameters of TGA Runs on the Filtered Solid Resid Treated by Tetralin at Room Temperature with and without the Reactor

Table 2a Analysis of Distillation Resid 1

Table 2b Analysis of Distillation Resid 2

Table 3 Effect of Methylene Chloride Washing on Coal Sample

Table 4 Overview of Experimental Program

Table 5a Reactor Runs of Resid 1

Table 5b Reactor Runs of Resid 2

Table 6 Replicate TGA Runs on Resids

Table 7a Characteristic Parameters of TGA Runs on the Filtered Solid Resid 1 in Uncatalyzed Conversion

Table 7b Characteristic Parameters of TGA Runs on the Filtered Solid Resid 2 in Uncatalyzed Conversion

Table 8a Characteristic Parameters of TGA Runs on the Filtered Solid Resid 1 in Catalyzed Conversion

Table 8b Characteristic Parameters of TGA Runs on the Filtered Solid Resid 2 in Catalyzed Conversion

Table 9 Peak Evolution Temperatures (T_{peak}) and Mean Evolution Temperatures (T_{mean}) of the Liquid Filtrates from the Catalyzed Resids Conversion

List of Figures

Figure 1 Batch Reactor (STBR) for Resid Conversion

Figure 2 Apparatus for Short Contact Time Coal-derived Resid Conversion

Figure 3 Time-Temperature Profile for a Typical Resid Conversion ($T/R = 3:1$)

Figure 4 Effect of tetralin on TGA Analysis

Figure 5 Schematic Diagram of the Experimental Procedure

Figure 6a Typical TGA Curves for a Liquid Filtrate of Catalyzed Conversion

Figure 6b Typical TGA Curves for a Filtered Solid Resid of Un-catalyzed Conversion

Figure 6c Typical TGA Curves for a Filtered Solid Resid of Catalyzed Conversion

Figure 7 TGA Curves of the Pure Sulfided Catalyst of Mo-Ni on Alumina

Figure 8a Resid-normalized VM, FC and D in the Resid 2 Treated or Reacted with Tetralin under Various Conditions ($T/R = 3.0$)

Figure 8b Resid-normalized VM, FC and D in the Resid 2 Treated or Reacted with Tetralin in the Present of Catalyst (sulfided Mo-Ni on alumina) under Various Conditions ($T:R:Catalyst = 3:1:1$)

Figure 9 Percent Resid Dissolved in Tetralin (D) Versus Reaction Time of Un-catalyzed Resid 1 Conversion at Two Temperatures: (a) $T/R = 2.0$; (b) $T/R = 3.0$; and (c) $T/R = 5.0$

Figure 10 Percent Resid Dissolved in Tetralin (D) Versus Reaction Time of Un-catalyzed Resid 2 Conversion at Two Temperatures: (a) $T/R = 2.0$; (b) $T/R = 3.0$; and (c) $T/R = 5.0$

Figure 11 Evolution Rate Versus Temperature Determined by Slow Ramp TGA ($5^\circ\text{C}/\text{min}$) for the Liquid Filtrates of Un-catalyzed Resid 1 Conversion: 0 min (Sample: WR103), 5 min at 434°C (Sample: C1011), and 30 min at 435°C (Sample: C1014)

Figure 12 Evolution Rate Versus Temperature Determined by Slow Ramp TGA ($5^\circ\text{C}/\text{min}$) for the Liquid Filtrates of Un-catalyzed Resid 2 Conversion: 0 min (Sample: WR203) and 30 min at 434°C (Sample: C2024)

Figure 13 Percent Resid Dissolved in Tetralin (D) Versus Reaction Time of Catalyzed Resid 1 Conversion at Two Temperatures ($T:R:Catalyst = 3:1:1$)

Figure 14 Percent Resid Dissolved in Tetralin (D) Versus Reaction Time of Catalyzed Resid 2 Conversion at Two Temperatures ($T:R:Catalyst = 3:1:1$)

Figure 15 Evolution Rate Versus Temperature Determined by Slow Ramp TGA (1 °C/min) for the Liquid Filtrates of Catalyzed Resid 1 Conversion: 0 min (Sample: WCR101), 5 min at 434 °C (Sample: CC1001), and 30 min at 435 °C (Sample: CC1004)

Figure 16 Evolution Rate Versus Temperature Determined by Slow Ramp TGA (1 °C/min) for the Liquid Filtrates of Catalyzed Resid 2 Conversion: 0 min (Sample: WCR201) and 30 min at 442 °C (Sample: CC2006)

Table 1 Characteristic Parameters of TGA Runs on the Filtered Solid Resid Treated by Tetralin at Room Temperature with and without the Reactor

Sample	T/R	Time, min	T, °C	TGA Results		
				VM	FC	Ash
WR103*	3	N/A	25	23.9%	53.9%	22.2%
WR103RS**	3	30	25	23.8%	54.2%	22.0%
WR203*	3	N/A	25	19.2%	49.5%	31.3%
WR203RS**	3	30	25	19.2%	49.3%	31.5%

* the filtered solid residue treated with tetralin at room temperature without going through the reactor;

** the filtered solid residue treated with tetralin at room temperature processing through the reactor.

Table 2a Analysis of Distillation Resid 1

Ref. No. 1

Plant: Wilsonville

Run Number: 259

Sample Designator: V1067

Sampling Point: 2nd Stage Product

Feed Coal: Pittsburgh Seam
Ireland Mine

Ultimate:

Ash, wt% as det.	10.21
C, wt % MAF	90.24
H, wt % MAF	6.39
N, wt % MAF	1.05
S, wt % MAF	1.49
O (dif), wt % MAF	0.83

Ash Elementals (%):

Na ₂ O	0.51
K ₂ O	1.60
CaO	2.72
MgO	0.84
Fe ₂ O ₃	21.83
TiO ₂	0.91
P ₂ O ₅	0.15
SiO ₂	43.89
Al ₂ O ₃	24.30
SO ₃	1.37
Unaccounted	1.88

Proton Distribution (% pyridine-soluble Basis)

Condensed Aromatics	27.8
Uncondensed Aromatics	3.8
Cyclic Alpha	21.2
Alkyl Alpha	9.6
Cyclic Beta	15.5
Alkyl Beta	13.4
Gamma	8.7

Phenolic -OH Concentration

(meq/g, THF Soluble Basis): 0.70

Phenolic Peak Location (cm⁻¹): 3296

Insoluble Organic Matter (wt%, as det.): 6.28

Table 2b Analysis of Distillation Resid 2

Ref. No. 2

Plant: Wilsonville

Run Number: 260

Sample Designator: V1067

Sampling Point: Second Stage Product

Feed Coal: Wyodak and Anderson seam
Black Thunder mine

Ultimate:

Ash, wt% as det.	18.30
C, wt % MAF	91.03
H, wt % MAF	6.56
N, wt % MAF	1.15
S, wt % MAF	0.09
O (dif), wt % MAF	1.17

Ash Elementals (%):

Na ₂ O	0.66
K ₂ O	0.27
CaO	15.99
MgO	3.56
Fe ₂ O ₃	21.77
TiO ₂	0.86
P ₂ O ₅	0.76
SiO ₂	21.23
Al ₂ O ₃	11.50
SO ₃	21.98
Unaccounted	1.42

Proton Distribution (% pyridine-soluble Basis)

Condensed Aromatics	27.2
Uncondensed Aromatics	6.8
Cyclic Alpha	18.3
Alkyl Alpha	8.8
Cyclic Beta	13.6
Alkyl Beta	16.6
Gamma	8.7

Phenolic -OH Concentration

(meq/g, THF Soluble Basis): 0.69

Phenolic Peak Location (cm⁻¹): 3297

Insoluble Organic Matter (wt%, as det.): 13.9

Table 3 Effect of Methylene Chloride Washing on Coal Sample

Sample	VM wt%	FC wt%	Ash wt%
Illinois #6	34.7	49.1	16.2
3 hr Methylene Chloride Washing of Illinois #6	34.5	52.3	13.2

Table 4 Overview of Experimental Program^a

<u>Variables</u>	
Contact Time, min	5, 10 ^b , 20 ^b , 30
Temperature, °C (°F)	413 (775), 441 (825)
H ₂ Pressure, psig	1500
Resid ^c	Resid A and B
Solvent ratio	2:1 ^b , 3:1, 5:1 ^b (Tetralin:Resid)
Catalyst	None, Criterion (Shell) 324 catalyst ^c

a: Arranging experiments by combination of the reaction conditions given in this table;

b: Running a few experiments at selected conditions;

c: Samples provided by CONSOL.

Table 5a Reactor Runs of Resid 1*

Run No.	Feed, g				Temp °C	Time min.	Recovery	
	Resid	Tetralin	Catalyst	T/R			g	%
<u>Un-catalyzed Runs</u>								
Calibration								
WR101	5.4	28.0	0	5.2	25	N/A		
WR102	6.7	26.7	0	4.0	25	N/A		
WR103	9.2	27.5	0	3.0	25	N/A		
WR104	12.8	25.5	0	2.0	25	N/A		
Reactor Runs								
C1002	5.4	27.1	0	5.0	413	30	23.5	72.3%
C1003	9.1	27.2	0	3.0	412	5	23.2	64.0%
C1004	9.2	27.5	0	3.0	411	10	23.7	64.6%
C1005	9.0	27.0	0	3.0	412	20	24.1	66.9%
C1006	9.3	28.0	0	3.0	412	30	24.7	66.3%
C1007	13.9	27.7	0	2.0	411	5	25.6	61.5%
C1008	13.7	27.4	0	2.0	412	30	26.3	64.0%
C1009	5.3	26.2	0	5.0	437	5	20.8	66.1%
C1010	5.7	28.2	0	5.0	436	30	30.1	88.9%
C1011	9.3	28.0	0	3.0	434	5	25.1	67.3%
C1012	9.6	28.6	0	3.0	435	10	27.1	71.0%
C1013	9.3	27.7	0	3.0	435	20	23.9	64.6%
C1014	9.3	27.7	0	3.0	435	30	24.5	66.3%
C1015	14.0	27.8	0	2.0	432	5	30.4	72.7%
C1016	13.4	26.8	0	2.0	434	30	28.4	70.5%
C1020	5.8	29.0	0	5.0	411	5	23.8	68.4%
<u>Catalyzed Runs</u>								
Calibration								
WCR101	8.79	26.38	8.80	3.0	25	N/A		
Reactor Runs								
CC1001	9.55	28.60	9.55	3.0	434	5	34.5	72.3%
CC1002	9.28	27.80	9.28	3.0	435	10	33.7	72.6%
CC1003	9.37	27.95	9.37	3.0	434	20	35.5	76.1%
CC1004	8.43	25.29	8.41	3.0	435	30	35.2	83.5%
CC1005	9.21	27.56	9.28	3.0	412	5	32.4	70.4%
CC1006	8.50	25.51	8.54	3.0	413	10	35.5	83.5%
CC1007	9.24	27.73	9.24	3.0	415	20	35.9	77.7%
CC1008	8.44	25.29	8.44	3.0	418	30	36.5	86.4%

* Resid from Wilsonville Run No.: 259 of Pittsburgh Coal Liquefaction

Table 5b Reactor Runs of Resid 2*

Run No.	Feed, g				Temp °C	Time min.	Recovery	
	Resid	Tetralin	Catalyst	T/R			g	%
<u>Un-catalyzed Runs</u>								
Calibration								
WR201	5.5	27.5	0	5.0	25	N/A		
WR202	6.5	26.0	0	4.0	25	N/A		
WR203	8.9	26.6	0	3.0	25	N/A		
WR204	13.6	27.1	0	2.0	25	N/A		
Reactor Runs								
C2008	8.1	24.7	0	3.0	410	5	21.5	65.5%
C2009	8.1	25.3	0	3.1	410	30	22.1	66.2%
C2010	8.2	26.0	0	3.2	411	20	24.3	71.1%
C2011	8.5	26.5	0	3.1	410	10	23.8	68.0%
C2012	6.5	26.3	0	4.0	409	5	20.7	63.1%
C2013	6.6	26.7	0	4.0	413	30	23.4	70.3%
C2014	5.4	26.6	0	4.9	409	5	22.8	71.3%
C2015	5.5	27.3	0	5.0	413	30	21.8	66.5%
C2016	13.5	26.7	0	2.0	412	30	24.3	60.4%
C2017	5.6	27.8	0	5.0	433	5	20.5	61.4%
C2018	5.6	27.3	0	4.8	434	30	21.6	65.6%
C2019	9.7	29.1	0	3.0	431	5	24.1	62.0%
C2020	8.4	25.0	0	3.0	435	10	21.2	63.7%
C2022	12.8	25.3	0	2.0	411	5	24.6	64.6%
C2023	9.1	26.9	0	3.0	433	20	23.9	66.5%
C2024	8.7	26.0	0	3.0	434	30	22.4	64.6%
C2025	12.7	25.3	0	2.0	429	5	23.8	62.7%
C2026	12.9	25.3	0	2.0	434	30	24.1	63.1%
<u>Catalyzed Runs</u>								
Calibration								
WCR201	8.8	26.5	8.9	3.0	25	N/A		
Reactor Runs								
CC2003	8.7	26.0	8.7	3.0	438	5	26.8	61.9%
CC2004	8.9	26.7	8.9	3.0	438	10	28.7	64.4%
CC2005	9.1	27.2	9.1	3.0	441	20	27.4	60.3%
CC2006	9.0	27.0	9.0	3.0	442	30	28.1	62.4%
CC2007	9.4	28.1	9.4	3.0	411	5	35.1	74.9%
CC2008	8.5	25.3	8.5	3.0	414	10	29.2	68.9%
CC2009	9.1	27.2	9.1	3.0	415	20	30.9	68.2%
CC2010	9.1	27.2	9.1	3.0	421	30	30.5	67.2%

* Resid from Wilsonville Run No.: 260 of Wyodak and Anderson Coal Liquefaction

Table 6 Replicate TGA Runs on Resids

Run No.	Sample	VM	FC	Ash
1	Resid 1	54.0%	35.0%	10.9%
2	Resid 1	53.9%	35.2%	10.8%
3	Resid 1	54.4%	34.7%	10.9%
4	Resid 1	54.2%	35.0%	10.9%
5	Resid 1	54.2%	35.2%	10.6%
6	Resid 1	53.9%	35.2%	10.9%
	Mean	54.1%	35.1%	10.8%
	Std	0.2%	0.2%	0.1%
1	Resid 2	44.3%	37.5%	18.2%
2	Resid 2	44.5%	37.1%	18.4%
3	Resid 2	44.4%	37.3%	18.3%
	Mean	44.4%	37.3%	18.3%
	Std	0.0%	0.2%	0.1%

Table 7a Characteristic Parameters of TGA Runs on the Filtered Solid Resid of Un-catalyzed Conversion

Sample	T/R*	Time, min	T, °C	TGA Results			Normalization (Resid 1)			
				VM	FC	Ash	D	VM	FC	Ash
Resid 1	N/A	N/A	N/A	54.1%	35.0%	10.9%	N/A	54.1%	35.0%	10.9%
<u>Calibration</u>										
WR101	5	N/A	25	22.2%	53.7%	24.1%	54.8%	10.0%	24.3%	10.9%
WR102	4	N/A	25	23.8%	52.9%	23.3%	53.2%	11.1%	24.8%	10.9%
WR103	3	N/A	25	23.9%	53.9%	22.2%	50.9%	11.7%	26.5%	10.9%
WR104	2	N/A	25	29.9%	49.2%	20.9%	47.8%	15.6%	25.7%	10.9%
<u>Reactor Runs</u>										
C1020	5	5	411	18.6%	57.4%	24.0%	54.6%	8.4%	26.1%	10.9%
C1002	5	30	413	17.4%	59.4%	24.2%	55.0%	7.8%	26.7%	10.9%
C1003	3	5	412	20.6%	56.9%	22.5%	51.6%	10.0%	27.5%	10.9%
C1004	3	10	411	22.9%	54.5%	22.6%	51.8%	11.0%	26.3%	10.9%
C1005	3	20	412	23.3%	54.0%	22.7%	52.0%	11.2%	25.9%	10.9%
C1006	3	30	412	23.0%	54.5%	22.5%	51.6%	11.1%	26.4%	10.9%
C1007	2	5	411	26.8%	51.6%	21.6%	49.5%	13.5%	26.1%	10.9%
C1008	2	30	412	27.3%	49.8%	22.9%	52.4%	13.0%	23.7%	10.9%
C1009	5	5	437	14.6%	60.3%	25.1%	56.6%	6.3%	26.2%	10.9%
C1010	5	30	436	9.9%	64.2%	25.9%	57.9%	4.2%	27.0%	10.9%
C1011	3	5	434	19.1%	57.3%	23.6%	53.8%	8.8%	26.5%	10.9%
C1012	3	10	435	21.3%	54.9%	23.8%	54.2%	9.8%	25.1%	10.9%
C1013	3	20	435	20.0%	55.9%	24.1%	54.8%	9.0%	25.3%	10.9%
C1014	3	30	435	20.1%	54.6%	25.3%	56.9%	8.7%	23.5%	10.9%
C1015	2	5	432	22.1%	53.9%	24.0%	54.6%	10.0%	24.5%	10.9%
C1016	2	30	434	20.1%	53.5%	26.4%	58.7%	8.3%	22.1%	10.9%

* T/R: ratio of Tetralin to Resid.

Table 7b Characteristic Parameters of TGA Runs on the Filtered Solid Resid of Un-catalyzed Conversion

Sample	T/R	Time, min	T, °C	TGA Results			Normalization (Resid 2)			
				VM	FC	Ash	D	VM	FC	Ash
Resid 2	N/A	N/A	N/A	44.4%	37.3%	18.3%	N/A	44.4%	37.3%	18.3%
<u>Calibration</u>										
WR201	5	N/A	25	15.7%	52.6%	31.7%	42.3%	9.0%	30.3%	18.3%
WR202	4	N/A	25	18.2%	50.4%	31.4%	41.7%	10.6%	29.4%	18.3%
WR203	3	N/A	25	19.2%	49.5%	31.3%	41.6%	11.2%	28.9%	18.3%
WR204	2	N/A	25	22.6%	48.1%	29.4%	37.6%	14.1%	30.0%	18.3%
<u>Reactor Runs</u>										
C2008	3	5	410	19.1%	49.3%	31.6%	42.1%	11.0%	28.6%	18.3%
C2011	3	10	410	21.0%	47.2%	31.8%	42.5%	12.1%	27.1%	18.3%
C2010	3	20	411	19.4%	48.5%	32.2%	43.1%	11.0%	27.6%	18.3%
C2009	3	30	410	20.4%	47.3%	32.3%	43.4%	11.6%	26.8%	18.3%
C2012	4	5	409	16.9%	51.0%	32.1%	43.0%	9.6%	29.1%	18.3%
C2013	4	30	413	17.7%	49.5%	32.8%	44.2%	9.9%	27.6%	18.3%
C2014	5	5	409	15.8%	52.1%	32.1%	43.0%	9.0%	29.7%	18.3%
C2015	5	30	413	15.9%	51.3%	32.8%	44.2%	8.9%	28.6%	18.3%
C2022	2	5	411	18.0%	50.2%	31.8%	42.5%	10.4%	28.9%	18.3%
C2016	2	30	412	18.3%	48.1%	33.5%	45.4%	10.0%	26.3%	18.3%
C2017	5	5	433	13.4%	53.3%	33.3%	45.0%	7.4%	29.3%	18.3%
C2018	5	30	434	15.9%	46.3%	37.9%	51.7%	7.7%	22.4%	18.3%
C2019	3	5	431	16.6%	51.1%	32.3%	43.4%	9.4%	28.9%	18.3%
C2020	3	10	435	13.6%	53.0%	33.4%	45.3%	7.4%	29.0%	18.3%
C2023	3	20	433	16.3%	45.2%	38.5%	52.5%	7.7%	21.5%	18.3%
C2024	3	30	434	13.6%	46.4%	40.0%	54.3%	6.2%	21.2%	18.3%
C2025	2	5	429	19.4%	46.9%	33.7%	45.6%	10.6%	25.5%	18.3%
C2026	2	30	434	19.9%	42.0%	38.1%	52.0%	9.5%	20.2%	18.3%

Table 8a Characteristic Parameters of TGA Runs on the Filtered Solid Resid 1 in Catalyzed Conversion

Sample	Time, min	T,°C	TGA Results				Cat.(ash)	Ash	Composition in PS		Normalization (Resid 1)			
			VM	FC	Ash1	Ash2			Catalyst	Resid	D	VM	FC	Ash
Catalyst														
Cat00	N/A	N/A	11.7%	4.0%	84.2%	70.0%	N/A	N/A	100.0%	0.0%	N/A	N/A	N/A	N/A
Cat01	5	415	7.5%	8.5%	84.1%	71.0%	N/A	N/A	100.0%	0.0%	N/A	N/A	N/A	N/A
Cat02	30	415	7.2%	6.3%	86.6%	73.8%	N/A	N/A	100.0%	0.0%	N/A	N/A	N/A	N/A
Calibration														
WCR101	N/A	25	10.1%	29.7%	60.3%	51.5%	44.0%	7.5%	66.4%	33.6%	51.1%	11.2%	26.8%	10.9%
Reactor Runs														
CC1001	5	434	6.5%	25.1%	68.4%	59.8%	51.1%	8.7%	65.2%	34.8%	56.3%	5.2%	27.6%	10.9%
CC1002	10	435	5.8%	26.5%	67.7%	58.4%	49.9%	8.5%	70.5%	29.5%	62.1%	4.2%	22.8%	10.9%
CC1003	20	434	5.4%	25.7%	68.9%	59.0%	50.4%	8.6%	75.0%	25.0%	68.2%	3.4%	17.5%	10.9%
CC1004	30	435	5.4%	25.3%	69.3%	59.4%	50.8%	8.6%	75.0%	25.0%	68.4%	3.4%	17.3%	10.9%
CC1005	5	412	6.1%	26.9%	67.0%	58.7%	50.2%	8.5%	62.9%	37.1%	52.6%	4.9%	31.6%	10.9%
CC1006	10	413	6.0%	26.2%	67.8%	59.0%	50.4%	8.6%	66.7%	33.3%	57.6%	4.6%	26.9%	10.9%
CC1007	20	415	6.3%	26.5%	67.2%	58.1%	49.7%	8.4%	68.9%	31.1%	59.9%	4.9%	24.3%	10.9%
CC1008	30	418	6.3%	26.3%	67.4%	58.2%	49.7%	8.5%	69.7%	30.3%	61.0%	4.9%	23.2%	10.9%

Abbreviation: SEF/SSF, Solvent-Extractable/Solvent-Soluble Fraction;
Cat.(ash), ash from catalyst;
PS, product stream;
N/A, not applicable.

Table 8b Characteristic Parameters of TGA Runs on the Filtered Solid Resid 2 of Catalyzed Conversion

Sample	Time, min	T, °C	TGA Results				Cat.(Ash)	Ash	Composition in PS		Normalization (Resid 2)			
			VM	FC	Ash1	Ash2			Catalyst	Resid	D	VM	FC	Ash
<u>Catalyst</u>														
Cat00	N/A	N/A	11.7%	4.0%	84.2%	70.0%	N/A	N/A	100.0%	0.0%	N/A	N/A	N/A	N/A
Cat01	5	415	7.5%	8.5%	84.1%	71.0%	N/A	N/A	100.0%	0.0%	N/A	N/A	N/A	N/A
Cat02	30	415	7.2%	6.3%	86.6%	73.8%	N/A	N/A	100.0%	0.0%	N/A	N/A	N/A	N/A
<u>Calibration</u>														
WCR201	N/A	25	9.4%	27.5%	63.0%	57.0%	45.1%	11.9%	62.1%	37.9%	41.7%	11.7%	27.4%	19.2%
<u>Reactor Runs</u>														
CC2003	5	438	8.0%	24.8%	68.4%	61.8%	48.9%	12.9%	68.0%	32.0%	54.7%	8.4%	18.6%	18.3%
CC2004	10	438	6.8%	21.9%	71.2%	63.4%	50.2%	13.2%	80.7%	19.3%	73.3%	2.3%	6.1%	18.3%
CC2005	20	441	6.8%	20.5%	72.7%	64.9%	51.4%	13.6%	80.2%	19.8%	73.3%	3.2%	5.2%	18.3%
CC2006	30	442	6.4%	21.5%	72.9%	65.0%	51.4%	13.6%	81.4%	18.6%	75.0%	1.5%	5.2%	18.3%
CC2007	5	411	6.5%	28.6%	67.2%	60.7%	48.0%	12.7%	67.0%	33.0%	52.4%	6.3%	23.0%	18.3%
CC2008	10	414	7.0%	24.0%	69.0%	62.3%	49.3%	13.0%	69.3%	30.7%	56.8%	6.8%	18.1%	18.3%
CC2009	20	415	6.6%	22.9%	70.5%	63.0%	49.8%	13.1%	77.8%	22.2%	69.2%	5.6%	6.9%	18.3%
CC2010	30	421	6.5%	22.9%	70.6%	62.8%	49.7%	13.1%	79.8%	20.2%	71.8%	4.9%	5.0%	18.3%

Abbreviation: See Table 6a.

Table 9 Peak Evolution Temperatures (T_{peak}) and Mean Evolution Temperatures (T_{mean}) of the Liquid Filtrates from the Catalyzed Resids Conversion

Sample	T_{peak}, °C	T_{mean}, °C
<u>Resid 1 + Catalyst</u>		
0 min	320	349
5 min at 434 °C	318	322
30 min at 435 °C	273	291
<u>Resid 2 + Catalyst</u>		
0 min	307	321
30 min at 442 °C	274	282

Figure 1 Batch Reactor (STBR) for Resid Conversion

Figure 2 Apparatus for Short Contact Time Coal-derived Resid Conversion

Figure 3 Time-Temperature Profile for a Typical Resid Conversion (T/R = 3:1)

Figure 4 Effect of tetralin on TGA Analysis

Figure 5 Schematic Diagram of the Experimental Procedure

Sample: CC2006, Liquid Filtrate

Size: 44.3420 mg

Method: Resid Conversion II

Comment: Reactor Run CC2006, Catalyzed Resid 2 Conversion, 30 min, 442 °C

TGA

File: C: CC2006L.01

Operator: Dr. Huang, He

Run Date: 4-Oct-93 07:06

Figure 6a Typical TGA Curves for a Liquid Filtrate of Catalyzed Conversion

Sample: C2024, Filtered Solid Resid

Size: 41.0520 mg

Method: Resid Conversion

Comment: Reactor Run C2024, Resid 2 Conversion, 30 min, 434 °C

TGA

File: C: C2024S.001

Operator: Dr. Huang, He

Run Date: 8-Sep-93 12:52

Figure 6b Typical TGA Curves for a Filtered Solid Resid of Un-catalyzed Conversion

Sample: CC2004, Filtered Solid Resid

Size: 49.1590 mg

Method: Resid Conversion - Cat

Comment: Reactor Run CC2004, Catalyzed Resid 2, 10 min, 438 °C

TGA

File: C: CC2004S.001

Operator: Dr. Huang, He

Run Date: 20-Sep-93 09:14

Figure 6c Typical TGA Curves for a Filtered Solid Resid of Catalyzed Conversion

Sample: Pure Sulfided Catalyst

Size: 36.7200 mg

Method: Resid Conversion

Comment: Catalyst: Sulfided Mo-Ni on Alumina (Shell 324)

TGA

File: C: CAT.002

Operator: Dr. Huang. He

Run Date: 13-Aug-93 15:37

Figure 7 TGA Curves of the Pure Sulfided Catalyst of Mo-Ni on Alumina

Figure 8a Resid-normalized VM, FC and D in the Resid 2 Treated or Reacted with Tetralin under Various Conditions ($T/R = 3.0$)

Figure 8b Resid-normalized VM, FC and D in the Resid 2 Treated or Reacted with Tetralin in the Present of Catalyst (sulfided Mo-Ni on alumina) under Various Conditions (T:R:Catalyst = 3:1:1)

Figure 9 Percent Resid Dissolved in Tetralin (D) Versus Reaction Time of Un-catalyzed Resid 1 Conversion at Two Temperatures: (a) T/R = 2.0; (b) T/R = 3.0; and (c) T/R = 5.0

Figure 10 Percent Resid Dissolved in Tetralin (D) Versus Reaction Time of Un-catalyzed Resid 2 Conversion at Two Temperatures: (a) T/R = 2.0; (b) T/R = 3.0; and (c) T/R = 5.0

Figure 11 Evolution Rate Versus Temperature Determined by Slow Ramp TGA (5 °C/min) for the Liquid Filtrates of Un-catalyzed Resid 1 Conversion: 0 min (Sample: WR103), 5 min at 434 °C (Sample: C1011), and 30 min at 435 °C (Sample: C1014)

Figure 12 Evolution Rate Versus Temperature Determined by Slow Ramp TGA (5 °C/min) for the Liquid Filtrates of Un-catalyzed Resid 2 Conversion: 0 min (Sample: WR203) and 30 min at 434 °C (Sample: C2024)

Figure 13 Percent Resid Dissolved in Tetralin (D) Versus Reaction Time of Catalyzed Resid 1 Conversion at Two Temperatures (T:R:Catalyst = 3:1:1)

Figure 14 Percent Resid Dissolved in Tetralin (D) Versus Reaction Time of Catalyzed Resid 2 Conversion at Two Temperatures (T:R:Catalyst = 3:1:1)

Figure 15 Evolution Rate Versus Temperature Determined by Slow Ramp TGA (1 °C/min) for the Liquid Filtrates of Catalyzed Resid 1 Conversion: 0 min (Sample: WCR101), 5 min at 434 °C (Sample: CC1001), and 30 min at 435 °C (Sample: CC1004)

Figure 16 Evolution Rate Versus Temperature Determined by Slow Ramp TGA (1 $^{\circ}\text{C}/\text{min}$) for the Liquid Filtrates of Catalyzed Resid 2 Conversion: 0 min (Sample: WCR201) and 30 min at 442 $^{\circ}\text{C}$ (Sample: CC2006)

APPENDIX
TGA SCANS

Sample: Resid 1
Size: 38.6520 mg
Method: Resid Conversion
Comment: Original Sample of Resid 1

TGA

File: C:R1.001
Operator: Dr. Huang, He
Run Date: 6-Aug-93 10:29

TGA V5.1A DuPont 2000

Sample: Resid 1
Size: 43.2660 mg
Method: Resid Conversion
Comment: Original Sample of Resid 1

TGA

File: C:R1.002
Operator: Dr. Huang. He
Run Date: 6-Aug-93 13:23

Sample: Resid 1
Size: 43.2220 mg
Method: Resid Conversion
Comment: Original Sample of Resid 1

TGA

File: C: R1.003
Operator: Dr. Huang, He
Run Date: 6-Aug-93 16:18

Sample: WR101, Solid
Size: 26.7260 mg
Method: Resid Conversion
Comment: Work-up Sample: Resid 1, No. 1

TGA

File: A: WR101S.001
Operator: Dr. Huang, He
Run Date: 13-Aug-93 09:32

Sample: WR102, Solid
Size: 40.7970 mg
Method: Resid Conversion
Comment: Work-up Sample: Resid 1, No. 2

TGA

File: A: WR102S.001
Operator: Dr. Huang, He
Run Date: 7-Aug-93 09:56

Sample: WR103, Solid
Size: 33.8470 mg
Method: Resid Conversion
Comment: Work-up Sample: Resid 1, No. 3

TGA

File: C:WR103S.001
Operator: Dr. Huang. He
Run Date: 2-Aug-93 07:35

Sample: WR103RS

Size: 37.1260 mg

Method: Resid Conversion

Comment: Work-up Sample WR103 Run through Reactor under Room Temperature

TGA

File: C: WR103RS.001

Operator: Dr. Huang, He

Run Date: 2-Aug-93 12:10

Sample: WR104, Solid

Size: 40.9530 mg

Method: Resid Conversion

Comment: Work-up Sample: Resid 1, No. 4

TGA

File: A: WR104S.002

Operator: Dr. Huang, He

Run Date: 16-Aug-93 15:20

Sample: C1002, Solid
Size: 28.2250 mg
Method: Resid Conversion
Comment: Reactor Run: C1002

TGA

File: C:\C1002S.002
Operator: Dr. Huang, He
Run Date: 30-Aug-93 23:02

Sample: C1003, Solid
Size: 42.7540 mg
Method: Resid Conversion
Comment: Reactor Run: C1003 Solid

TGA

File: C: C1003S.001
Operator: Dr. Huang, He
Run Date: 7-Aug-93 15:29

Sample: C1004, Solid
Size: 27.2610 mg
Method: Resid Conversion
Comment: Reactor Run: C1004

TGA

File: C: C1004S.001
Operator: Dr. Huang, He
Run Date: 10-Aug-93 14: 13

Sample: C1005, Solid
Size: 22.3250 mg
Method: Resid Conversion
Comment: Reactor Run: C1005

TGA

File: C: C1005S.001
Operator: Dr. Huang, He
Run Date: 9-Aug-93 16:44

Sample: C1006, Solid
Size: 23.4260 mg
Method: Resid Conversion
Comment: Reactor Run: C1006

TGA

File: C: C1006S.001
Operator: Dr. Huang, He
Run Date: 8-Aug-93 21:04

Sample: C1007, Solid
Size: 37.4180 mg
Method: Resid Conversion
Comment: Reactor Run: C1007

TGA

File: C: C1007S.001
Operator: Dr. Huang, He
Run Date: 31-Aug-93 14: 51

Sample: C1008, Solid
Size: 38.8290 mg
Method: Resid Conversion
Comment: Reactor Run: C1008

TGA

File: C: C1008S.001
Operator: Dr. Huang, He
Run Date: 19-Aug-93 15: 02

Sample: C1009, Solid
Size: 44.1440 mg
Method: Resid Conversion
Comment: Reactor Run: C1009

TGA

File: C: C1009S.001
Operator: Dr. Huang, He
Run Date: 7-Sep-93 19:17

Sample: C1010, Solid
Size: 39.0200 mg
Method: Resid Conversion
Comment: Reactor Run: C1010

TGA

File: C: C1010S.001
Operator: Dr. Huang, He
Run Date: 7-Sep-93 16:29

Sample: C1011, Solid
Size: 39.6330 mg
Method: Resid Conversion
Comment: Reactor Run: C1011

TGA

File: C: C1011S.001
Operator: Dr. Huang, He
Run Date: 18-Aug-93 13:58

Sample: C1012, Solid
Size: 33.6710 mg
Method: Resid Conversion
Comment: Reactor Run: C1012

TGA

File: C:\C1012S.001
Operator: Dr. Huang, He
Run Date: 18-Aug-93 11:25

Sample: C1013, Solid
Size: 38.3910 mg
Method: Resid Conversion
Comment: Reactor Run: C1013

TGA

File: C: C1013S.001
Operator: Dr. Huang. He
Run Date: 18-Aug-93 08:46

Sample: C1014, Solid
Size: 36.7540 mg
Method: Resid Conversion
Comment: Reactor Run: C1014

TGA

File: C:\C1014S.001
Operator: Dr. Huang, He
Run Date: 17-Aug-93 14:30

Sample: C1015, Solid
Size: 36.1540 mg
Method: Resid Conversion
Comment: Reactor Run: C1015

TGA

File: C: C1015S.001
Operator: Dr. Huang, He
Run Date: 17-Aug-93 11: 07

Sample: C1016, Solid
Size: 39.7070 mg
Method: Resid Conversion
Comment: Reactor Run: C1016

TGA

File: C: C1016S.001
Operator: Dr. Huang. He
Run Date: 16-Aug-93 17: 45

Sample: C1020, Solid
Size: 36.6340 mg
Method: Resid Conversion
Comment: Reactor Run: C1020

TGA

File: C: C1020S.001
Operator: Dr. Huang, He
Run Date: 13-Aug-93 19:32

Sample: Resid 2
Size: 34.2720 mg
Method: Resid Conversion
Comment: Original Sample of Resid 2

TGA

File: C:\R2.006
Operator: Dr. Huang, He
Run Date: 12-Nov-93 16:16

Sample: Resid 2
Size: 37.0470 mg
Method: Resid Conversion
Comment: Original Sample of Resid 2

TGA

File: C:R2.007
Operator: Dr. Huang, He
Run Date: 13-Nov-93 04:13

Sample: Resid 2
Size: 23.7730 mg
Method: Resid Conversion
Comment: Original Sample of Resid 2

TGA

File: C:R2.008
Operator: Dr. Huang, He
Run Date: 14-Nov-93 03:16

Sample: WA201, Solid
Size: 50.5000 mg
Method: Resid Conversion
Comment: Work-up Sample: Resid 2, No. 1

TGA

File: C:WA201S.001
Operator: Dr. Huang, He
Run Date: 28-Sep-93 08:22

Sample: WR202, Solid

Size: 41.2980 mg

Method: Resid Conversion

Comment: Work-up Sample: Resid 2, No. 2

TGA

File: C:WR202S.001

Operator: Dr. Huang, He

Run Date: 28-Sep-93 12:28

TGA V5.1A DuPont 2000

Sample: WR203, Solid
Size: 37.2280 mg
Method: Resid Conversion
Comment: Work-up Sample: Resid 2, No. 3

TGA

File: C:WR203S.001
Operator: Dr. Huang. He
Run Date: 28-Sep-93 15:57

Sample: WR203RS

Size: 31.7480 mg

Method: Resid Conversion

Comment: Work-up Sample WR203 Run through Reactor under Room Temperature

TGA

File: C: WR203RS.001

Operator: Dr. Huang, He

Run Date: 11-Aug-93 14: 22

Sample: WR204, Solid
Size: 43.9520 mg
Method: Resid Conversion
Comment: Work-up Sample: Resid 2, No. 4

TGA

File: C:WR204S.001
Operator: Dr. Huang, He
Run Date: 29-Sep-93 07:02

Sample: C2008, Solid
Size: 29.1190 mg
Method: Resid Conversion
Comment: Reactor Run: C2008

TGA

File: C: C2008S.004
Operator: Dr. Huang, He
Run Date: 2-Aug-93 14:18

Sample: C2009, Solid
Size: 30.8750 mg
Method: Resid Conversion
Comment: Reactor Run: C2009

TGA

File: C: C2009S.002
Operator: Dr. Huang. He
Run Date: 27-Sep-93 16: 03

Sample: C2010, Solid
Size: 43.3340 mg
Method: Resid Conversion
Comment: Reactor Run: C2010

TGA

File: C: C2010S.002
Operator: Dr. Huang, He
Run Date: 26-Sep-93 21: 00

Sample: C2011. Solid
Size: 44.6450 mg
Method: Resid Conversion
Comment: Reactor Run: C2011

TGA

File: C: C2011S.002
Operator: Dr. Huang. He
Run Date: 25-Sep-93 19: 25

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Sample: C2012, Solid
Size: 32.0210 mg
Method: Resid Conversion
Comment: Reactor Run: C2012

TGA

File: C: C2012S.001
Operator: Dr. Huang, He
Run Date: 25-Sep-93 14: 19

Sample: C2013, Solid
Size: 40.9190 mg
Method: Resid Conversion
Comment: Reactor Run: C2013

TGA

File: C: C2013S.002
Operator: Dr. Huang, He
Run Date: 24-Sep-93 21: 43

Sample: C2014, Solid
Size: 29.8400 mg
Method: Resid Conversion
Comment: Reactor Run: C2014

TGA

File: C: C2014S.002
Operator: Dr. Huang, He
Run Date: 24-Sep-93 16: 59

Sample: C2015, Solid
Size: 38.3120 mg
Method: Resid Conversion
Comment: Reactor Run: C2015

TGA

File: C: C2015S.002
Operator: Dr. Huang, He
Run Date: 24-Sep-93 21:51

Sample: C2016, Solid
Size: 45.8520 mg
Method: Resid Conversion
Comment: Reactor Run: C2016

TGA

File: C: C2016S.001
Operator: Dr. Huang, He
Run Date: 24-Sep-93 08: 41

Sample: C2017, Solid
Size: 30.1830 mg
Method: Resid Conversion
Comment: Reactor Run: C2017

TGA

File: C: C2017S.002
Operator: Dr. Huang, He
Run Date: 24-Sep-93 16:06

Sample: C2018, Solid
Size: 26.8540 mg
Method: Resid Conversion
Comment: Reactor Run: C2018

TGA

File: C: C2018S.002
Operator: Dr. Huang, He
Run Date: 23-Sep-93 23:05

Sample: C2019, Solid
Size: 43.9290 mg
Method: Resid Conversion
Comment: Reactor Run: C2019

TGA

File: C: C2019S.002
Operator: Dr. Huang, He
Run Date: 23-Sep-93 21: 44

Sample: C2020, Solid
Size: 40.4130 mg
Method: Resid Conversion
Comment: Reactor Run: C2020

TGA

File: C: C2020S.002
Operator: Dr. Huang, He
Run Date: 23-Sep-93 18:46

Sample: C2022, Solid
Size: 34.5070 mg
Method: Resid Conversion
Comment: Reactor Run: C2022

TGA

File: C: C2022S.003
Operator: Dr. Huang, He
Run Date: 4-Aug-93 08:40

Sample: C2023, Solid
Size: 39.2390 mg
Method: Resid Conversion
Comment: Reactor Run: C2023

TGA

File: C: C2023S.002
Operator: Dr. Huang, He
Run Date: 8-Sep-93 19:42

Sample: C2024, Solid
Size: 41.0520 mg
Method: Resid Conversion
Comment: Reactor Run: C2024

TGA

File: C: C2024S.001
Operator: Dr. Huang, He
Run Date: 8-Sep-93 12:52

Sample: C2025, Solid
Size: 46.7170 mg
Method: Resid Conversion
Comment: Reactor Run: C2025

TGA

File: C: C2025S.002
Operator: Dr. Huang, He
Run Date: 8-Sep-93 20:10

Sample: C2026, Solid
Size: 46.9370 mg
Method: Resid Conversion
Comment: Reactor Run: C2026

TGA

File: C: C2026S.001
Operator: Dr. Huang, He
Run Date: 8-Sep-93 07:46

Sample: Catalyst
Size: 45.9660 mg
Method: Resid Conversion - Cat
Comment: Pure Catalyst

TGA

File: C: CAT.004
Operator: Dr. Huang, He
Run Date: 1-Sep-93 12:14

Sample: Catalyst Run 001

Size: 40.2410 mg

Method: Resid Conversion - Cat

Comment: Catalyst Run 001, 5 min in tetralin at 415 °C

TGA

File: C: CAT01.001

Operator: Dr. Huang, He

Run Date: 29-Sep-93 16:23

Sample: Catalyst Run 002

Size: 43.7530 mg

Method: Resid Conversion - Cat

Comment: Catalyst Run 002, 30 min in tetralin at 415 °C

TGA

File: C: CAT02.001

Operator: Dr. Huang. He

Run Date: 29-Sep-93 10:34

TGA V5.1A DuPont 2000

Sample: WCR101, Solid

Size: 56.3930 mg

Method: Resid Conversion - Cat

Comment: Work-up Sample: Catalyst, Resid 1, No. 1

TGA

File: C:\WCR101S.001

Operator: Dr. Huang, He

Run Date: 6-Sep-93 10:13

Sample: CC1001, Solid
Size: 47.3020 mg
Method: Resid Conversion - Cat
Comment: Reactor Run: CC1001

TGA

File: C: CC1001S.001
Operator: Dr. Huang, He
Run Date: 4-Sep-93 02:05

Sample: CC1002, Solid
Size: 52.8370 mg
Method: Resid Conversion - Cat
Comment: Reactor Run: CC1002

TGA

File: C: CC1002S.001
Operator: Dr. Huang. He
Run Date: 4-Sep-93 10:22

Sample: CC1003, Solid
Size: 58.0260 mg
Method: Resid Conversion - Cat
Comment: Reactor Run: CC1003

TGA

File: C: CC1003S.001
Operator: Dr. Huang, He
Run Date: 4-Sep-93 16:28

Sample: CC1004, Solid
Size: 59.2070 mg
Method: Resid Conversion - Cat
Comment: Reactor Run: CC1004

TGA

File: C: CC1004S.001
Operator: Dr. Huang, He
Run Date: 4-Sep-93 21:35

Sample: CC1005, Solid
Size: 56.2520 mg
Method: Resid Conversion - Cat
Comment: Reactor Run: CC1005

TGA

File: C: CC1005S.001
Operator: Dr. Huang. He
Run Date: 5-Sep-93 10:01

Sample: CC1006, Solid
Size: 47.4780 mg
Method: Resid Conversion - Cat
Comment: Reactor Run: CC1006

TGA

File: C: CC1006S.001
Operator: Dr. Huang, He
Run Date: 9-Aug-93 03:29

Sample: CC1007, Solid
Size: 52.3890 mg
Method: Resid Conversion - Cat
Comment: Reactor Run: CC1007

TGA

File: C: CC1007S.001
Operator: Dr. Huang, He
Run Date: 3-Sep-93 13:25

Sample: CC1008, Solid
Size: 42.4530 mg
Method: Resid Conversion - Cat
Comment: Reactor Run: CC1008

TGA

File: C: CC1008S.001
Operator: Dr. Huang, He
Run Date: 3-Sep-93 07:57

Sample: WCR201, Solid

Size: 46.7950 mg

Method: Resid Conversion - Cat

Comment: Work-up Sample: Catalyst, Resid 2, No. 1

TGA

File: C:WCR201S.001

Operator: Dr. Huang, He

Run Date: 6-Sep-93 15:43

Sample: CC2003, Solid
Size: 50.6430 mg
Method: Resid Conversion - Cat
Comment: Reactor Run: CC2003

TGA

File: C: CC2003S.001
Operator: Dr. Huang, He
Run Date: 21-Sep-93 13:25

Sample: CC2004, Solid
Size: 49.1590 mg
Method: Resid Conversion - Cat
Comment: Reactor Run: CC2004

TGA

File: C: CC2004S.001
Operator: Dr. Huang, He
Run Date: 20-Sep-93 09:14

TGA V5.1A DuPont 2000

Sample: CC2005, Solid
Size: 55.8400 mg
Method: Resid Conversion - Cat
Comment: Reactor Run: CC2005

TGA

File: C: CC2005S.001
Operator: Dr. Huang, He
Run Date: 18-Sep-93 11:13

Sample: CC2006, Solid
Size: 54.6130 mg
Method: Resid Conversion - Cat
Comment: Reactor Run: CC2006

TGA

File: C: CC2006S.001
Operator: Dr. Huang, He
Run Date: 10-Sep-93 12:33

Sample: CC2007. Solid
Size: 49.4920 mg
Method: Resid Conversion - Cat
Comment: Reactor Run: CC2007

TGA

File: C: CC2007S.001
Operator: Dr. Huang. He
Run Date: 20-Sep-93 13:56

Sample: CC2008, Solid
Size: 55.1400 mg
Method: Resid Conversion - Cat
Comment: Reactor Run: CC2008

TGA

File: C: CC2008S.001
Operator: Dr. Huang, He
Run Date: 9-Sep-93 13:11

Sample: CC2009, Solid
Size: 57.0260 mg
Method: Resid Conversion - Cat
Comment: Reactor Run: CC2009

TGA

File: C: CC2009S.001
Operator: Dr. Huang. He
Run Date: 8-Sep-93 20:29

Sample: CC2010, Solid
Size: 54.6770 mg
Method: Resid Conversion - Cat
Comment: Reactor Run: CC2010

TGA

File: C: CC2010S.001
Operator: Dr. Huang, He
Run Date: 6-Sep-93 20:03

Sample: WR103. Liquid Filtrate

Size: 53.7860 mg

Method: Resid Conversion I

Comment: Work-up Sample: Resid 1, No. 3 (T/R = 3.0), 5 °C/min

TGA

File: C:WR103L.001

Operator: Dr. Huang. He

Run Date: 29-Jul-93 20:30

Sample: C1011, Liquid Filtrate

Size: 53.5250 mg

Method: Resid Conversion I

Comment: Reactor Run: C1011 (Liquid), 5 °C/min

TGA

File: C:\C1011L.001

Operator: Dr. Huang. He

Run Date: 26-Jul-93 04:12

Sample: C1014, Liquid Filtrate

Size: 53.0910 mg

Method: Resid Conversion I

Comment: Reactor Run: C1014 (Liquid), 5 °C/min

TGA

File: C:\C1014L.001

Operator: Dr. Huang, He

Run Date: 27-Jul-93 03:11

Sample: WR203, Liquid Filtrate

Size: 51.4280 mg

Method: Resid Conversion I

Comment: Work-upSample: Resid 2, No. 3 (T/R = 3.0), 5 °C/min

TGA

File: C:WR203L.001

Operator: Dr. Huang, He

Run Date: 30-Jul-93 22:54

Sample: C2024, Liquid Filtrate

Size: 59.3950 mg

Method: Resid Conversion I

Comment: Reactor Run: C2024 (Liquid), 5 °C/min

TGA

File: C: C2024L.001

Operator: Dr. Huang, He

Run Date: 1-Aug-93 14:13

Sample: WCR101, Liquid Filtrate

Size: 55.6990 mg

Method: Resid Conversion II

Comment: Work-up Sample: WCR101 (liquid), 1 °C/min

TGA

File: C: WCR101L.001

Operator: Dr. Huang, He

Run Date: 5-Aug-93 21:15

Sample: CC1001, Liquid Filtrate

Size: 56.0830 mg

Method: Resid Conversion II

Comment: Reactor Run: CC1001 (liquid), 1 °C/min

TGA

File: C:CC1001L.001

Operator: Dr. Huang, He

Run Date: 16-Aug-93 20:43

Sample: CC1004, Liquid Filtrate
Size: 59.6810 mg

Method: Resid Conversion II

Comment: Reactor Run: CC1004 (liquid), 1 °C/min

File: C:CC1004L.001
Operator: Dr. Huang, He
Run Date: 29-Aug-93 17:06

TGA

Sample: WCR201, Liquid Filtrate

Size: 48.4590 mg

Method: Resid Conversion II

Comment: Work-up Sample: WCR201 (liquid), 1 °C/min

TGA

File: C: WCR201L.001

Operator: Dr. Huang, He

Run Date: 30-Sep-93 17:11

Sample: CC2006, Liquid Filtrate

Size: 53.6830 mg

Method: Resid Conversion II

Comment: Reactor Run: CC2006, 1 °C/min

TGA

File: C:CC2006L.001

Operator: Dr. Huang, He

Run Date: 2-Oct-93 06:20

Sample: Argonne Coal: Illinois #6
Size: 30.2630 mg
Method: DOE Coal Liquefaction
Comment: Dry Coal

TGA

File: A: ARGN301.003
Operator: Dr. Huang, He
Run Date: 25-Oct-93 10:38

Sample: 3hr CH₂Cl₂ Washing - Illinois #6
Size: 29.7210 mg
Method: DOE Coal Liquefaction
Comment: 3 hr CH₂Cl₂ Washing of Illinois #6 Coal

TGA

File: A: S301W03.002
Operator: Dr. Huang. He
Run Date: 9-Nov-93 11:26

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END