

Study of Solvent and Catalyst Interactions in Direct Coal Liquefaction

SEMIANNUAL REPORT

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Table of Contents

| | |
|------------------------------|----|
| Executive Summary | 3 |
| Introduction | 4 |
| Results and Discussion | 7 |
| Conclusions | 13 |
| Future Program | 14 |
| Publications | 14 |
| References | 14 |
| Appendix | 15 |

Executive Summary

There are several aspects of the Direct Coal Liquefaction process which are not fully understood and which if better understood might lead to improved yields and conversions. Among these questions are the roles of the catalyst and the solvent. While the solvent is known to act by transfer of hydrogen atoms to the free radicals formed by thermal breakdown of the coal in an uncatalyzed system, in the presence of a solid catalyst as is now currently practiced, the yields and conversions are higher than in an uncatalyzed system. The role of the catalyst in this case is not completely understood. DOE has funded many projects to produce ultrafine and more active catalysts in the expectation that better contact between catalyst and coal might result. This approach has met with limited success probably because mass transfer between two solids in a fluid medium i.e. the catalyst and the coal, is very poor. It is to develop an understanding of the role of the catalyst and solvent in Direct Liquefaction that this project was initiated. Specifically it was of interest to know whether direct contact between the coal and the catalyst was important.

By separating the solid catalyst in a stainless steel basket permeable to the solvent but not the coal in the liquefaction reactor, it was shown that the catalyst still maintains a catalytic effect on the liquefaction process. There is apparently transfer of hydrogen atoms from the catalyst through the basket wall to the coal via the solvent. Strong hydrogen donor solvents appear to be more effective in this respect than weak hydrogen donors. It therefore appears that intimate contact between catalyst and coal is not a requirement, and that the role of the catalyst may be to restore the hydrogen donor strength to the solvent as the reaction proceeds. A range of solvents of varying hydrogen donor strength was investigated.

Because of the extensive use of thermogravimetric analysis in this laboratory it was noted that the peak temperature for volatile evolution from coal was a reliable measure of coal rank. Because of this observation, a wide variety of coals of a wide range of ranks was investigated. It was shown in this work that measuring the peak temperature for volatile evolution was quite a precise indicator of rank and correlated closely with the rank values obtained by measuring vitrinite reflectance, a more difficult measurement to make. This prompted the desire to know the composition of the volatile materials evolved as a function of coal rank. This was then measured by coupling a TGA to a mass spectrometer using laser activation and photoionization detection TG-PI-MS. The predominant species in volatiles of low rank coal turned out to be phenols with some alkenes. As the rank increases, the relative amount of alkenes and aromatic hydrocarbons increases and the oxygenated species decrease. It was shown that these volatiles were actually pyrolytic products and not volatilization products of coal. Solvent extraction experiments coupled with TG-PI-MS indicates that the low boiling and more extractable material are essentially similar in chemical types to the non-extractable portions but apparently higher molecular weight and therefore less extractable.

Introduction

Despite many years of research on Direct Coal Liquefaction, there are some aspects of the process which are not fully understood and yet could have important implications for process improvement. Among these questions are the roles of the solid catalyst and the solvent. Neavel (1) has shown that the solvent in direct liquefaction in the absence of a catalyst is primarily a donor of hydrogen atoms to the free radicals formed as the coal is broken down thermally under coal liquefaction conditions. This minimizes degradative reactions of these radicals which tend to form insoluble and unreactive products. Much emphasis in modern coal liquefaction studies however have been on liquefaction in the presence of both a donor solvent and a solid catalyst such as nickel/molybdenum or cobalt/molybdenum on a alumina support. This results in higher conversion and yields of fuel grade product liquids (2). In this case, the role of the catalyst is not so clear. While sulfided molybdenum from sulfidation of soluble molybdenum naphthenate is a hydrogenation catalyst and is effective in coal liquefaction (3), mass transfer consideration would suggest that contact between solid coal and solid catalyst would be difficult and probably ineffective. Gorin (4) postulates that the role of the catalyst is primarily to rehydrogenate the spent hydrogen donor solvent. This is also supported by Tomlison et al. (5). This is an important question. If the role of the catalyst is more directly involved in the liquefaction process itself, an open question concerning the role of the solid catalyst is whether intimate contact between the catalyst and the coal particles is necessary.

Much research effort (6-8), some of it supported by DOE, has been devoted to producing ultrafine catalyst particles in order to get better contact between the catalyst and the coal with only limited success. Since producing ultrafine catalyst is a somewhat difficult and expensive process, it is important to avoid that step if possible. One objective of this project therefor is to determine whether intimate contact between catalyst and coal is necessary in the liquefaction process. If it is not, since catalyst have been shown to increase the liquefaction rate, what is the process of communication within the solvent between the catalyst and the coal? This raises the question of the actual role of the solvent in this system.

An additional objective of this project has been to identify the volatile matter in coals. Previous work under this project has shown that the amount of volatile matter evolved from coal increases as the temperature increases, goes through a maximum and then decreases. The temperature of this maximum turns out to be a rather precise measure of the rank of a coal. This temperature maximum can be rather precisely identified by thermogravimetric analysis using standard TGA equipment present in many laboratories, and represents a means of determining coal rank when the equipment and expertise of determining vitrinite reflectance is not available. The chemical identity of these volatiles however had not been determined. A technique for doing this has been developed and described and the various volatile products have been described as a function of coal rank.

Experimental section

Coal. In the study investigating the interaction of the coal and the catalyst in the liquefaction system we used a DECS 24 coal from the Penn State Coal Bank. This is an Illinois No 6 coal which has been used in the past in many liquefaction laboratory studies. The data on this coal is provided in Appendix 1. The coal was used as received and was stored under argon. Occasional TGA analysis were conducted on a sample of the coal to check for moisture content.

Catalyst. Two solid catalysts were used both obtained from Consol: Amocat 1C with 2.77 wt% Ni and 9.93 wt% Mo (unsulfided) and Shell 324 with 3.19 wt% Ni and 12.89 wt% Mo. The catalysts were in shape of pellets with a diameter of 2mm and length on the order of several mm.

The catalysts were presulfided in the reactor system prior to each experiment with 1 g of methyl disulfide.

Solvents. Several solvents were used for the liquefaction experiments. Tetralin, methyl-naphthalene, and decalin, were the primary solvents as examples of solvents of different donor strength. Other solvents use were 9,10-dihydrophenanthrene and 1,2-dihydronaphthalene which were reported in the literature as very strong donor solvents. Some of these stronger solvents were used in mixture with tetralin due to their high cost.

Apparatus and Procedure. To determine whether close contact between catalyst and coal is necessary, a series of liquefaction runs were made using our short contact time batch reactor (8) but with the solid catalyst contained in a porous stainless steel basket in the reactor. The porosity of the basket was to be such that the coal could not contact the catalyst directly but the basket would be permeable to the solvent. Considerable effort was devoted to design and construction of the basket which had to fit into our liquefaction reactor (Fig 1) but also allowed free passage of solvent. Several baskets were constructed of stainless steel and were of different porosity: $0.5\mu\text{m}$, $2.0\mu\text{m}$, and one with holes which would not pass coal particles larger than 30 mesh. We found that the $2\mu\text{m}$ basket was the most appropriate one for our experiments.

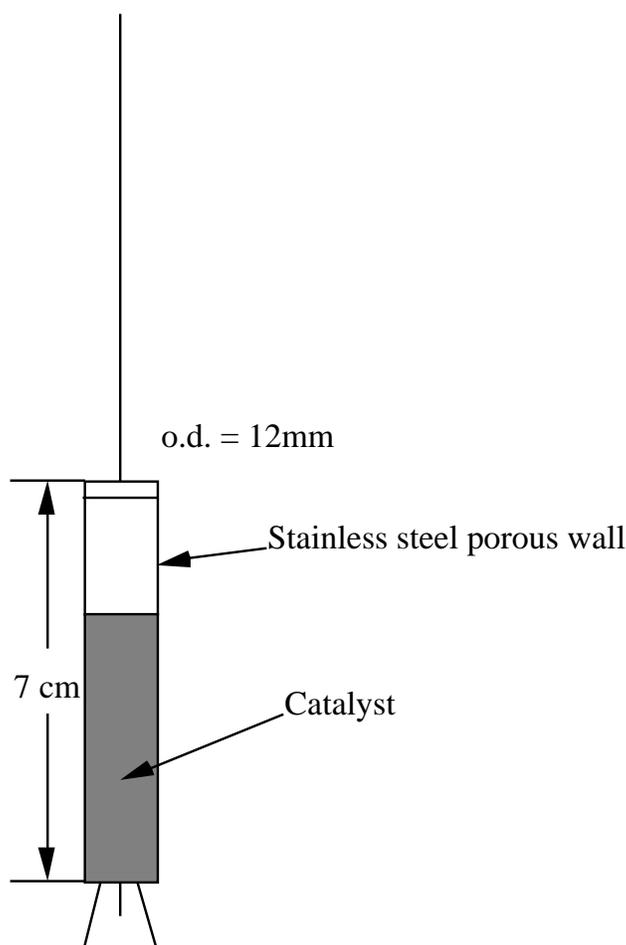


Figure 1. Stainless steel basket for solid catalyst.

For our experiments we used the short contact time reactor which was slightly modified. The schematic diagram of the reactor system is shown in Figure 2. The 50 cm³ reactor is connected through a preheater coil to a blow case which is charged with coal and solvent. A thermocouple is connected with a quick-connect to the top of the reactor. The quick-connect assembly was added especially so that the basket with the catalyst could be placed inside of the reactor. The porous stainless steel basket, loaded with 1 - 1.5g of fresh catalyst, is placed inside the reactor before each experiment. In operations, the preheater and reactor are brought up to the desired temperature by immersion in a Techne IFB-52 fluidized bath. High-pressure hydrogen or nitrogen is used to provide the driving force to deliver the reaction mixture from the blow case through the preheater into the reactor. Agitation of the reaction mixture is accomplished by bubbling hydrogen or nitrogen gas through the mixture from the bottom. At the end of the reaction, the high-pressure gas is again used to drive the content through the precooler into a receiver both of which are immersed in a water bath.

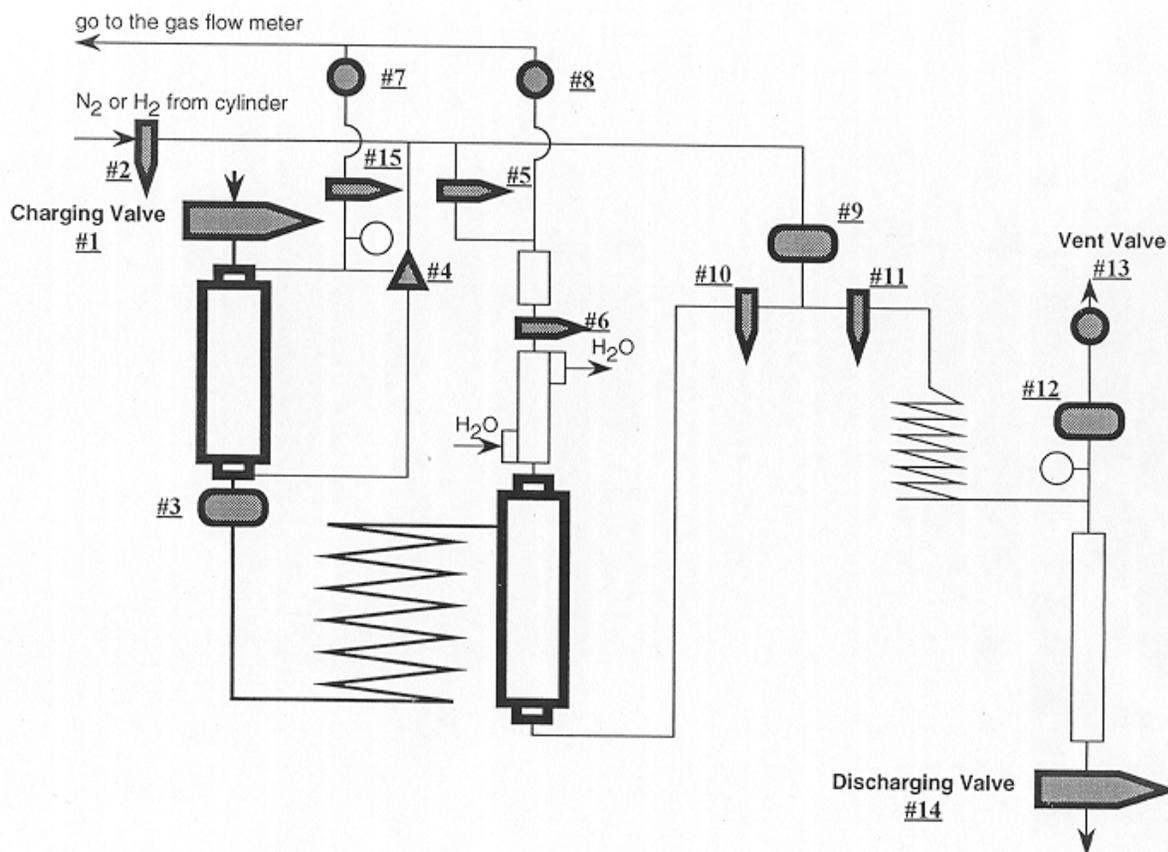


Figure 2. Valve Control Diagram of Short contact Time Reactor.

Each experiment used a nominal weight of 4 g of coal and of 32 g of (solvent (solvent to coal ratio 8:1). A nominal amount of 1 g of catalyst was loaded into the basket and placed in the reactor at the beginning of the heat-up period together with 1 g of methyl disulfide (a sulfiding agent). The sulfiding occurs during the heat-up time of the reactor to the desired temperature. Most reactions were conducted for 30 minutes unless otherwise indicated at a temperature of 410 or 420 °C.

The collected products mixture was filtered and the solid residue was washed with cold fresh tetralin thoroughly and dried in a vacuum oven for 24 hours. The dried solid residue was analyzed by thermogravimetric analyzed Model 2050 TGA (TA Instruments, New Castle, DE). The liquefaction residues were analyzed for ash and their ash content was compared to the initial content of ash (really mineral matter) in the coal. The coal conversion was calculated based on the ash contents using the following formula:

$$X(\text{dafwt}\%) = \frac{1}{1 - A_o} \times \left(1 - \frac{A_o}{A_s}\right) \times 100\%$$

where A_o and A_s are weight fractions of ash (derived from mineral matter) in a control sample of coal and the liquefaction residue, respectively.

Results and Discussion

A. Determination of the Role of the Solid Catalyst

A series of liquefaction runs were made using tetralin as the solvent, 30 minutes reaction times, ca. 420°C and 1000 psi hydrogen pressure. The catalyst basket was run without catalyst and with ~ 1.0 g of Shell 324 catalyst and with a similar weight of Amocat 1C catalyst. Results from similar experiments made with molybdenum naphthanate (MN) catalyst in this laboratory were used to compare with the current results. Table 1 lists the coal conversion for these experiments.

Table 1. Coal conversion with tetralin with and without catalyst in the basket.

| Sample | T, °C | t, min | P, psig | Catalyst | Basket | Conv, wt% |
|------------|-------|--------|---------------------|----------|---------|-----------|
| DOES-034 | 417 | 30 | 1000 H ₂ | no | no | 56.1 |
| DOES-035 | 419 | 32 | 1000 N ₂ | no | 0.5 μm | 57.9 |
| DOES-036 | 418 | 31 | 1000 H ₂ | no | 0.5 μm | 55.7 |
| DOES-052 | 421 | 30 | 1000 H ₂ | no | 2.0 μm | 55.4 |
| [previous] | 390 | 30 | N ₂ | no | no | 42.6 |
| [previous] | 390 | 30 | H ₂ | no | no | 46.3 |
| DOES-040 | 420 | 30 | 800 H ₂ | Shell | 2.0 μm | 61.3 |
| DOES-029 | 421 | 30 | 1000 H ₂ | Shell | 30 mesh | 59.7 |
| DOES-039 | 420 | 30 | 1000 H ₂ | Amocat | 2.0 μm | 65.2 |
| DOES-027 | 421 | 30 | 1000 H ₂ | Amocat | 30 mesh | 59.3 |
| DOES-060 | 411 | 30 | 750 H ₂ | Shell | 2.0 μm | 64.5 |
| DOES-062 | 417 | 30 | 1000 H ₂ | Shell | 2.0 μm | 57.2 |
| DOES-063 | 417 | 31 | 1000 N ₂ | Shell | 2.0 μm | 49.4 |
| [previous] | 402 | 30 | H ₂ | MN | no | 71.2 |
| [previous] | 418 | 30 | H ₂ | MN | no | 77.1 |

MN - molybdenum naphthanate catalyst

One can conclude from this table that significantly higher (ca 10% higher) conversions are obtained with sulfided catalyst in the basket than without the catalyst in the basket. This shows that direct contact between the coal and the catalyst is not necessary and that there must be transmission of active material between the catalyst and the coal presumably via the solvent. It should also be noted that conversion using sulfided MN catalyst, which is if not soluble is very

finely divided, is even more effective (gave somewhat higher conversion) than when the solid catalyst was used in the basket. This conversion may be due to the limited rate of mass transfer of solvent through the fine 2 μm basket wall when the solid catalyst is placed in the basket. This is not a limitation when a “soluble” catalyst is used.

It should be noted that a similar liquefaction run was made with sulfided Shell catalyst in the basket under the same set of conditions but with 1000 psig nitrogen instead of hydrogen. The conversion observed under these conditions was 49% which compares favorably with runs made without catalyst. This is an added indication that the catalyst plays no role in the system when gaseous hydrogen is absent. In this case, the hydrogen for liquefaction is supplied entirely by the donor solvent.

Similar runs were also made with the same two solid catalysts but finely powdered and fed together with the mixture of solvent and coal into the reactor under the same conditions. Conversions are listed in Table 2.

Table 2. Coal conversion with tetralin and powdered catalyst.

| Sample | T, °C | t, min | P, psig | Catalyst | Conv, wt% |
|----------|-------|--------|---------------------|----------|-----------|
| DOES-055 | 419 | 30 | 1000 H ₂ | Amocat | 53.8 |
| DOES-056 | 421 | 30 | 1000 H ₂ | Shell | 54.1 |
| DOES-053 | 417 | 30 | 1000 H ₂ | Shell | 57.4 |

It is interesting that conversion using powdered sulfided catalyst is not as effective as when the sulfided catalyst is placed in the basket although we expected that the conversions would be higher in this case due to smaller mass transfer limitations. One problem that occurs in the case of determining the coal conversion when powdered catalyst is used is the fact that the catalyst accumulates in the reaction residue and thus our coal conversion calculations based on the ash content are affected. This means that corrections are needed in order to subtract the amount of ash that originates from the catalyst and not from the coal. To correct for this amount we assumed that the all of the initial catalyst loaded accumulates in the solid residue and we subtracted that amount. It is possible however that some losses of the catalyst occur during the liquefaction and that by subtracting we “overcorrect” the final ash content and calculate lower conversions in this way.

B. The Role of Liquefaction Solvent

To better understand the role of the solvent in the presence and absence of the solid catalyst, a series of liquefaction runs were made with various solvents differing in hydrogen donor ability and using the 2 μm basket. It is interesting to note that the poorest of the hydrogen donor tested solvents (decalin) still gave appreciable conversion to liquid products and that in the presence of catalysts in the basket, significantly higher conversions were obtained than without the catalyst.

Methylnaphthalene on the other hand turns out to be a better hydrogen donor than decalin but shows little benefit from the presence of the catalyst in the basket. While methyl naphthalene appears to be a donor solvent, i.e. there is conversion of the coal, it does not appear to transmit hydrogen from the catalyst through the wall of the basket. The reason for this is not apparent.

Two presumably stronger donor solvents were tested: 1,2-dihydronaphthalene and 9,10-dihydrophenanthrene. In view of the cost of these two solvents they were used in combination with tetralin. The coal conversion results are listed in Table 4.

Table 3. Coal conversion with decalin and methylnaphthalene with and without catalyst in the basket.

| Sample | T, °C | t, min | P, psig | Solvent | Catalyst | Basket | Conv, wt% |
|------------|-------|--------|---------------------|---------|----------|--------|-----------|
| DOES-044 | 425 | 30 | 1000 H ₂ | Decalin | no | 2.0 μm | 42.2 |
| DOES-050 | 418 | 30 | 1000 H ₂ | Decalin | no | 2.0 μm | 40.4 |
| DOES-041 | 425 | 32 | 700 H ₂ | Decalin | Shell | 2.0 μm | 49.9 |
| DOES-048 | 417 | 16 | 1000 H ₂ | Decalin | Shell | 2.0 μm | 38.6 |
| DOES-045 | 420 | 30 | 1000 H ₂ | Decalin | Amocat | 2.0 μm | 50.0 |
| [previous] | 400 | 30 | H ₂ | Decalin | MN | no | 33.0 |
| DOES-043 | 424 | 30 | 1000 H ₂ | Me-Naph | no | 2.0 μm | 59.0 |
| DOES-049 | 420 | 32 | 1000 H ₂ | Me-Naph | no | 2.0 μm | 55.2 |
| DOES-0461 | 420 | 31 | 1000 H ₂ | Me-Naph | Shell | 2.0 μm | 54.8 |
| DOES-047 | 417 | 30 | 1000 H ₂ | Me-Naph | Shell | 2.0 μm | 54.8 |
| DOES-064 | 420 | 30 | 1000 H ₂ | Me-Naph | Shell | 2.0 μm | 45.9 |
| DOES-046 | 428 | 30 | 1000 H ₂ | Me-Naph | Amocat | 2.0 μm | 48.6 |
| [previous] | 412 | 30 | H ₂ | Me-Naph | no | no | 55.1 |
| [previous] | 412 | 30 | H ₂ | Me-Naph | MN | no | 66.4 |

Me-Naph – methylnaphthalene

MN – methylnaphthanate

Table 4. Coal conversion with 1,2 dihydronaphthalene and 9,10 dihydrophenanthrene added to tetralin.

| Sample | T, °C | t, min | Tetralin | Solvent | Amount | Catalyst | Conv., wt% |
|----------|-------|--------|----------|---------|--------|----------|------------|
| DOES-057 | 421 | 30 | 17.48 | 1,2-DHN | 14.5 | Shell | 52.9 |
| DOES-058 | 419 | 30 | 24.4 | 9,10-PH | 9.39 | Shell | 60.2 |

The 1,2-dihydronaphthalene showed little or no increase in conversion over tetralin itself in the presence of Shell catalyst in the basket. The 9,10-dihydrophenanthrene however did show increased conversion over the pure tetralin. The latter solvent is a known strong hydrogen donor and could be transferring hydrogen through the basket wall from the catalyst to the coal. The 1,2-dihydronaphthalene may have shown no advantage over tetralin itself because of isomerization of that compound to tetralin under the high temperature and long reaction times used.

C. Determination of Coal Rank by Thermogravimetric Analysis

Determination of the rank of coal by one parameter or set of parameters allows one to make a reasonable estimate of what the other properties of a particular coal will be. Parameters which have been used as indices of coal rank include volatile-matter yield, carbon content, the carbon/hydrogen atomic ratio, and the heats of combustion. One generally accepted and reliable measure of coal rank is mean maximum vitrinite reflectance. An advantage of this technique is that unlike most chemical methods, it is performed on a single maceral and so is largely independent of variations in petrographic composition. Not all laboratories are equipped to perform this precise optical measurement required for reflectance determinations, however and alternative techniques for rank estimation are always of interest. Because of the many

applications that have been developed for thermogravimetric analysis (TGA), this equipment is now available in many laboratories.

Another volatilization method also exists designed primarily for the study of kerogen in source rock as a means of determining their petroleum potential. This method, known as the Rock-Eval method employs special instrumentation to follow the evolution of hydrocarbons and other organic materials and CO₂ during the pyrolysis of kerogen. At the same time it measures the temperature maximum for volatiles evolution from kerogen. It does require special Rock-Eval equipment. Since this method does measure volatiles evolution from rocks, it has also been used in evaluating coal and determining coal rank.

A series of 28 coals whose elemental analysis, heat of combustion, vitrinite reflectance and vitrinite contents were known were analyzed by TGA. A model 51 TGA (TA instruments, New Castle, DE) was used. Approximately 30 mg sample of each coal was loaded in a quartz pan and mounted in the instrument. All TGA experiments were carried out in nitrogen at atmospheric pressure at a heating rate of 10°/min. Detailed procedure is given in reference (10) as well as a TG scan on Illinois No. 6. Figure 3 shows a plot of peak temperature vs peak height. Figure 4 shows a correlation between peak height and vitrinite reflectance (R_o). Figure 5 shows a correlation of the peak temperature with vitrinite reflectance. The correlation is very good with an R² value of 0.998, indicating that peak temperature is an excellent measure of coal rank.

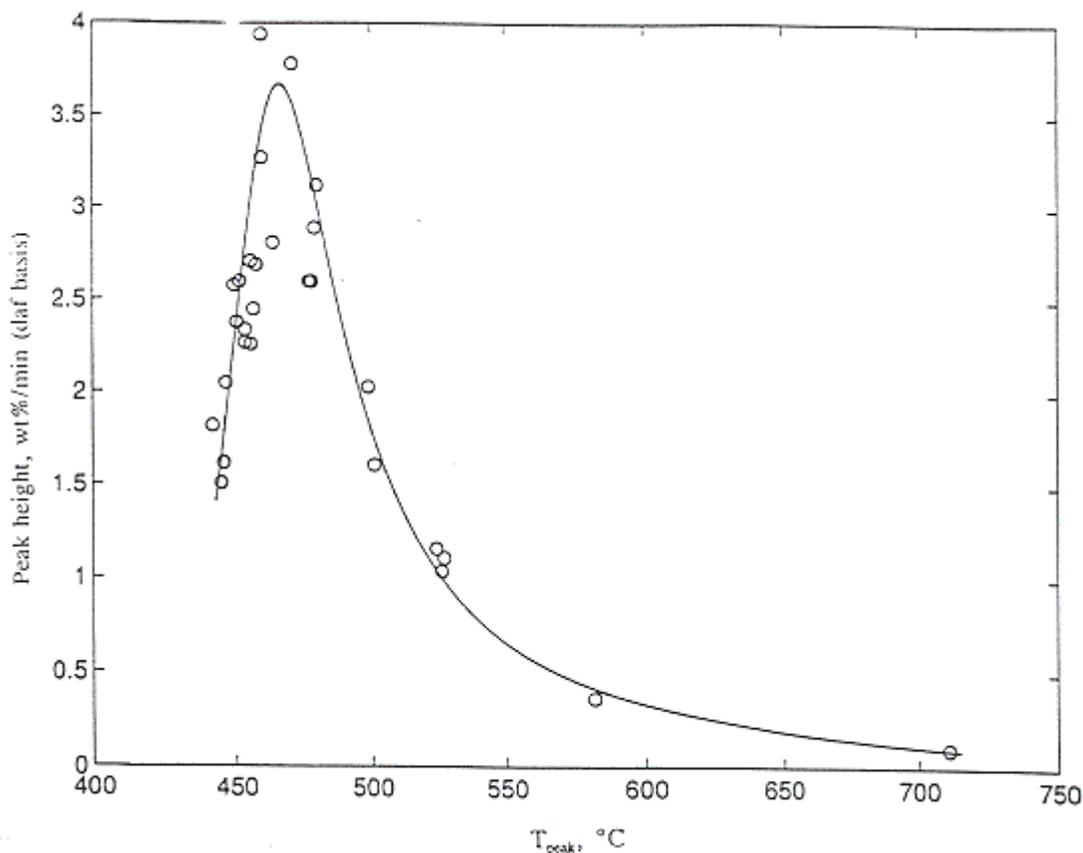


Figure 3. Correlation of the peak temperature (T_{peak}) with the peak height.

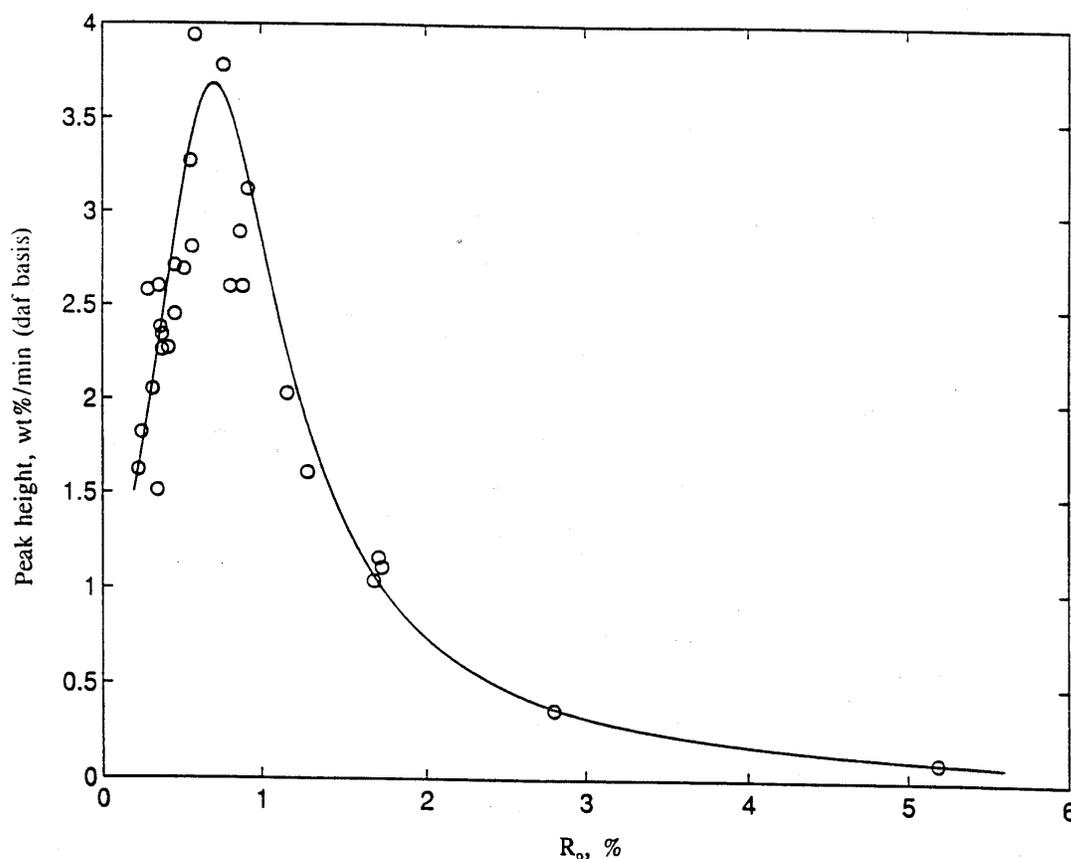


Figure 4. Correlation of the peak height with the vitrinite reflectance (R_o).

Similar experiments were performed comparing TGA measurements with Rock-Eval data on 18 coals from Penn State University coal Bank. Figure 6 shows both the correlation between peak temperatures by both the Rock-Eval method and the TGA procedure. While there is a reasonable correlation between vitrinite reflectance and the peak temperature by the Rock-Eval method, it is not nearly as good as the correlation with the TGA method.

Since an excellent correlation between the volatile matter of coal, and the coal rank, it was of interest to know how the composition of the volatile matter varied with coal rank. To do this, a TGA 2050 (TA Instruments, New Castle, DE) was attached to a mass spectrometer, a reflectron time of flight (RTOF) mass spectrometer (R.M. Jordan CO., Grass Valley, CA). All experiments were run in a stream of helium, maintained at 75 ml/min with a heating rate of 20°C/min. Because of the volume of the system, there was an average transfer time of 14 s. Further details of the TG/MS experiments are given in reference (11).

Experiments were run on 17 different coals ranging in rank from lignite to low volatile bituminous. In addition, TGA/MS scans were run on coals extracted with tetrahydrofuran or pyridine in a soxhlet extractor for 72 hours and then dried under vacuum at 60°C. The relative amounts of different compound classes (% of total ion current) are shown in Table 5.

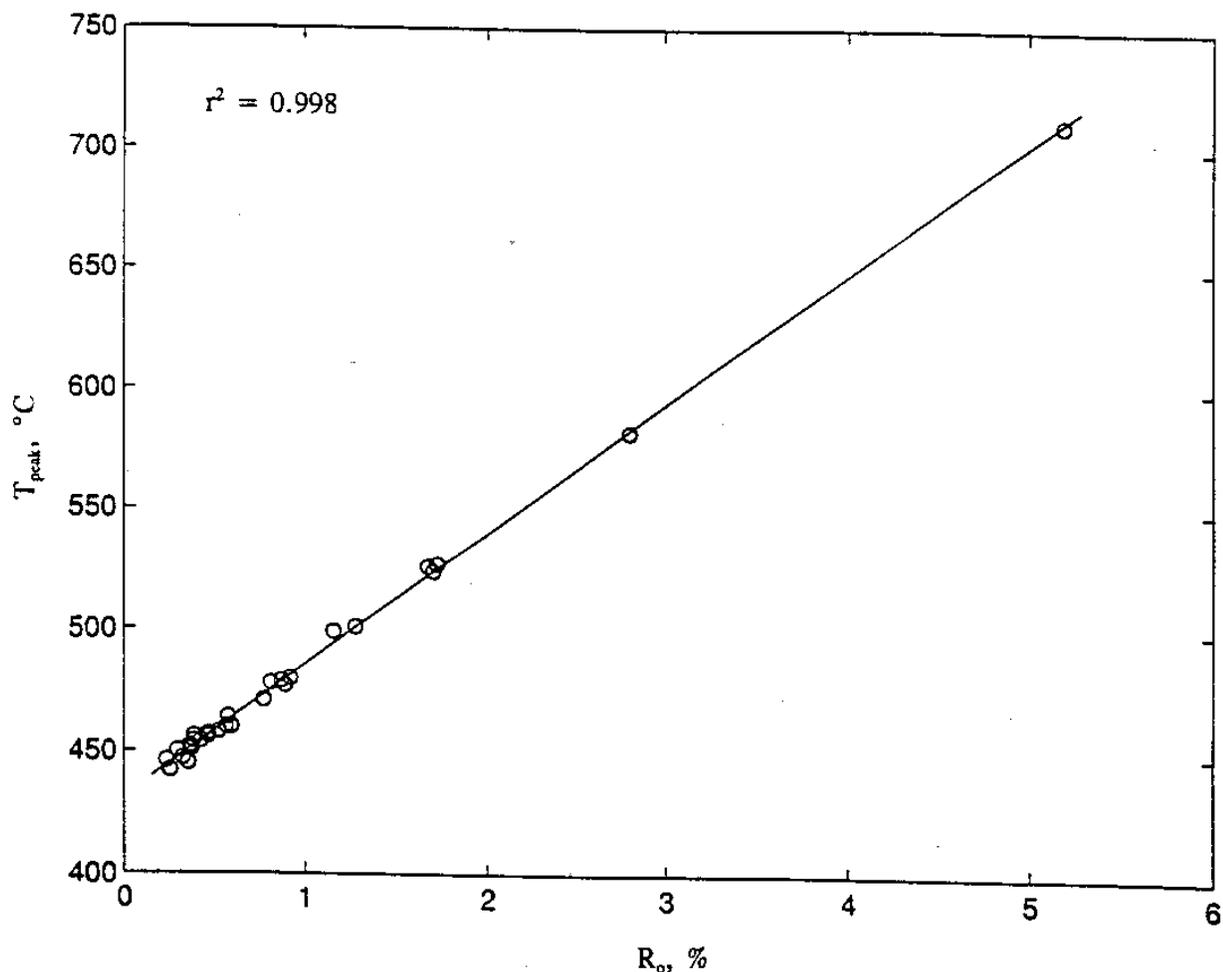


Figure 5. Correlation of the peak temperature (T_{peak}) with the vitrinite reflectance (R_o)

Overall, the relative amounts of oxygen containing compounds such as $C_nH_{2n}O$, phenols, and dihydroxybenzenes decrease with increasing coal rank. This decrease correlates well with the overall decrease in oxygen content of the coals with increasing rank. In addition, the relative amounts of aromatic hydrocarbons such as naphthalenes, phenathrenes and pyrenes increase with increasing coal rank. This increase in aromaticity of the evolved products correlates with an overall increase in the aromaticity of the coal.

Two separate experiments confirmed that the majority of compounds detected by TG-PI-MS were products of thermal bond cleavages and not thermal desorption products. First, it was determined that compounds spiked in coal evolved at much lower temperature than the same compounds evolved upon pyrolysis of the raw coal. In addition, laser desorption mass spectrometry of coal extracts revealed a higher molecular weight distribution of compounds than detected by TG-PI-MS. Therefore, these higher molecular weight compounds must pyrolyze in the TGA prior to detection by mass spectrometry.

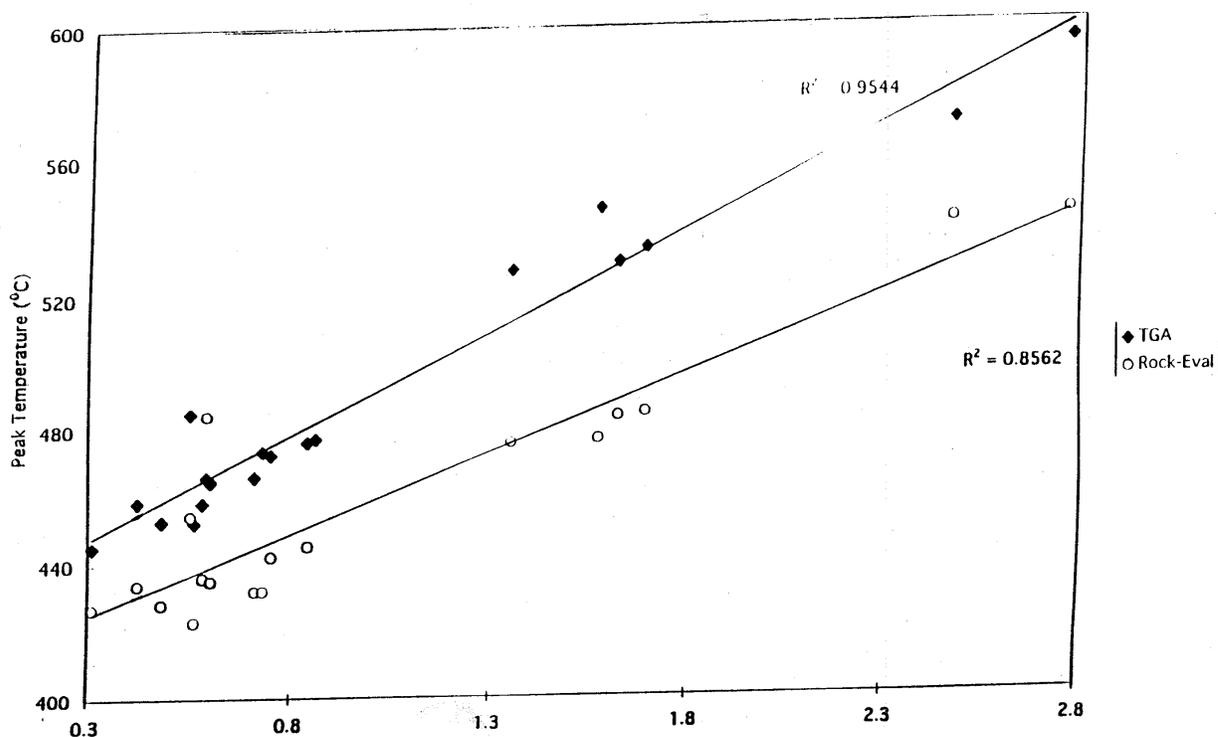


Figure 6. Peak Temperatures of TGA & Rock-Eval vs. Reflectance.

Some of the volatile matter detected by TG-PI-MS may be removed from coal by solvent extraction with THF or pyridine. Although differences in the absolute amount of compounds evolved from the solvent extract, the coal after extraction, and the raw coal exist, the relative intensities of compounds detected by photoionization mass spectrometry remain virtually identical. This suggests that the volatile matter consists of a range of molecular weights with similar molecular structures. The lower-molecular weight material is more soluble, leaving a significant fraction of higher molecular weight volatile matter in the coal after solvent extraction. The main thermal degradation products are alkenes and aromatic hydroxy aromatic compounds. The evolved products identified by TG-PI-MS suggest the generally postulated structure of the macromolecular network of coal which is believed to contain clusters of aromatic rings separated by aliphatic, thioethers and ether bridges.

Conclusions

Using a reactor in which the coal is physically separated from the solid catalyst by a porous wall permeable to the hydrogen donor solvent, it was shown that direct contact between the catalyst and the coal is not required for catalyzed coal liquefaction. This occurs however only when there is a hydrogen atmosphere, as liquefaction with catalyst participation does not occur in a nitrogen atmosphere. Liquefaction by hydrogen transfer from the donor solvent itself does occur. This suggests that there is transfer of hydrogen from the catalyst to the coal via the solvent. The character of the solvent makes a significant difference, the better solvents being good hydrogen donors. These results indicate that the role of the catalyst may be to regenerate the spent hydrogen donor solvent during the liquefaction process.

The peak temperature for volatiles evolution has been shown to be a reproducible measure of the coal rank. This was shown by an excellent correlation ($R^2 = 0.998$) between peak volatiles temperature (by TGA) and vitrinite reflectance. Using TG/MS, the volatiles contents of

colas of a wide range of ranks was determined. The low rank coals emit largely phenols and some other oxygen compounds and olefins. The higher rank coals emit largely aromatic hydrocarbons and some olefins.

Future Program

An effort will be made to demonstrate that the spent donor solvent is being regenerated and to determine the rate at which this occurs. The influence of catalyst type on this process will also be investigated. The behavior of other solvents including poor hydrogen donor solvents in this system will be studied as well as the mechanism of liquefaction of solid coals in the absence of solvents.

Publications

The following publications have been issued or are in the process of being written as a results of work on this project.

1. "Thermogravimetric and Rock-Eval Studies of Coal Properties and Coal Rank," H. Huang, S. Wang, K. Wang, M.T. Klein, W.H. Calkins and A. Davis *Energy Fuels*, **13**, 396-400, 1999.
2. "Thermogravimetry-Photoionization Mass Spectrometry of Different Rank Coals," D.L. Zoller, M.V. Johnston, J. Tomic, X.Wang and W.H. Calkins *Energy Fuels*, **13**, 1097-1104, 1999.
3. "Role of Solid Catalyst and Solvents in Direct Coal Liquefaction," J. Tomic, X.Wang and W.H. Calkins, to be submitted for publications.

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10. H. Huang, S. Wang, K. Wang, M.T. Klein, and W.H. Calkins, *Energy Fuels*, **13**, 396-400, 1999.
11. D.L. Zoller, M.V. Johnston, J. Tomic, X. Wang, and W.H. Calkins, *Energy Fuels*, **13**, 1097-1104, 1999.

Appendix

DECS 24 Coal Analysis

The Penn State Coal Sample Bank and Database

Sample DECS-24

Illinois #6 Seam (Herrin Seam)
Macoupin County, IL

hvCb rank

page 1 of 4
 printed 8/24/95
 sampled 6/02/94

SAMPLE LOCATION

Macoupin County, Illinois, USA
 Virden Township near Virden, Illinois
 Interior Coal Province
 Eastern Region

Farmersville (7.5') Topographic Quadrangle
 Latitude 39° 29' 06" North, Longitude 89° 44' 40" West

SAMPLE HISTORY

Whole-Seam Channel Sample collected June 2, 1994 by Penn State
 Mining method: underground

Coal Sample Bank reserve: 225 kg (497 lbs)

SAMPLE INFORMATION

Pennsylvanian
 Kewanee Group
 Carbondale Formation

Seam thickness at sample location: 229 cm (7 ft 6 in.)
 Sample thickness: 229 cm (7 ft 6 in.)

Seam profile:

| | |
|-------|-------------------------------|
| ROOF | black shale |
| 99 cm | dull clarain, pyrite partings |
| 58 cm | bright clarain with vitrain |
| 10 cm | dull clarain, partings |
| 61 cm | very dull clarain, pyrite |
| FLOOR | soft gray clay |

The Penn State Coal Sample Bank and Database

Sample DECS-24

Illinois #6 Seam (Herrin Seam)
Macoupin County, IL

hvCb rank

page 2 of 4
printed 8/24/95
sampled 6/02/94

PROXIMATE ANALYSIS

| | as rec'd | dry | daf | dmmf(Parr) |
|----------------|----------|-------|-------|------------|
| % Moisture | 13.20 | | | |
| % Ash | 11.62 | 13.39 | | |
| % Vol. Matter | 35.44 | 40.83 | 47.14 | 45.51 |
| % Fixed Carbon | 39.74 | 45.78 | 52.86 | 54.49 |

SULFUR FORMS

| | dry | daf |
|-----------|------|------|
| % Pyritic | 2.64 | 3.05 |
| % Sulfate | 0.25 | 0.29 |
| % Organic | 2.64 | 3.05 |
| % Total | 5.53 | 6.38 |

MOISTURE

| | |
|---------------|-------|
| % as received | 13.20 |
| % equilibrium | 11.59 |

ULTIMATE ANALYSIS

| | as rec'd | dry | daf | dmmf(Parr) |
|------------------|----------|-------|-------|------------|
| % Ash | 11.62 | 13.39 | | (17.50%MM) |
| % Carbon | 57.33 | 66.05 | 76.26 | 80.06 |
| % Hydrogen | 3.98* | 4.59 | 5.30 | 5.56 |
| % Nitrogen | 0.99 | 1.14 | 1.32 | 1.38 |
| % Total Sulfur | 4.80 | 5.53 | 6.38 | |
| % Oxygen (diff.) | 8.07* | 9.30 | 10.74 | 12.99 |

* excluding H and O in moisture

Dry % Chlorine = 0.14 Dry % Carbon dioxide = 0.65

ELEMENTAL ANALYSIS

| | dry | dmmf(Mod.P) |
|---|-------|-------------|
| | | (16.44% MM) |
| % Carbon | 65.87 | 78.83 |
| % Hydrogen | 4.47 | 5.35 |
| % Nitrogen | 1.14 | 1.36 |
| % Organic Sulfur | 2.64 | 3.16 |
| % Oxygen (diff.) | 9.44 | 11.29 |
| % Mineral Matter (incl. 4.94% FeS ₂) | 16.44 | |

CALORIFIC VALUE (Gross) -

| | dry | | as rec'd moist | | equil. moist | |
|---------------------|--------|--------|----------------|--------|--------------|--------|
| | MJ/kg | Btu/lb | MJ/kg | Btu/lb | MJ/kg | Btu/lb |
| MM-containing | 28.287 | 12162 | 24.554 | 10557 | 25.007 | 10752 |
| MM-free (Parr) | 33.508 | 14407 | 28.294 | 12165 | 28.915 | 12432 |
| MM-free (mod. Parr) | 33.455 | 14384 | 28.305 | 12170 | 28.919 | 12434 |
| Net, dmmf Btu/lb | 32.271 | 13875 | | | | |

Mott-Spooner difference = 307 Btu/lb

ATOMIC RATIOS (dmmf)

| | Parr | mod. Parr |
|------------|-------|-----------|
| Atomic H/C | 0.835 | 0.815 |
| Atomic O/C | 0.122 | 0.108 |

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Sample DECS-24

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hvCb rank

page 3 of 4
printed 8/24/95
sampled 6/02/94

RANK CALCULATIONS

| ASTM Rank (equilibrium moist.) | hvCb | Reflectance Rank | hvCb |
|--------------------------------|------|------------------|------|
| (as rec'd moist.) | hvCb | | |

MACERAL COMPOSITION (white light, volume %)

| | mineral- free | mineral- containing |
|---------------------------------|------------------|------------------------|
| Vitrinite | 90.2 | 81.8 |
| TOTAL VITRINITE | 90.2 | 81.8 |
| Fusinite | 2.5 | 2.3 |
| Semifusinite | 3.4 | 3.1 |
| Macrinite | 0.0 | 0.0 |
| Micrinite | 0.9 | 0.8 |
| Sclerotinite | 0.0 | 0.0 |
| Inertodetrinite | 0.0 | 0.0 |
| TOTAL INERTINITE | 6.8 | 6.2 |
| Sporinite | 1.7 | 1.5 |
| Resinite | 0.2 | 0.2 |
| Alginite | 0.0 | 0.0 |
| Cutinite | 1.1 | 1.0 |
| Liptodetrinite | 0.0 | 0.0 |
| TOTAL LIPTINITE | 3.0 | 2.7 |
| Mineral matter (Parr, volume %) | | 9.28 |

REFLECTANCE DATA

| | | | | |
|------------|------------------------|------|------|-----|
| Vitrinite: | Mean-max R_D : 0.49% | | | |
| Vtypes: | V 3 | V 4 | V 5 | V 6 |
| percent: | 2.0 | 57.0 | 38.0 | 3.0 |

CAKING AND MECHANICAL PROPERTIES

| | | | |
|--------------------------------|------|----------------------------|---------|
| Free-swelling index | 3 | Gieseler Coal Plastometer: | |
| Hardgrove grindability index | 57.8 | Initial softening | 366°C |
| Vickers' microhardness index | n.d. | Maximum fluidity | 410°C |
| Washability data not available | | Solidification | 444°C |
| | | Fluid temp. range | 78°C |
| | | Maximum fluidity | 49 ddpm |

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Sample DECS-24

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page 4 of 4
printed 8/24/95
sampled 6/02/94

INORGANIC ELEMENT ANALYSIS

| Major Elements | | | | Trace Elements | |
|--------------------------------|-------------------|----|-----------------------------------|----------------|--------------------------|
| | oxide % of HTA | | element % of whole dry coal | ppm HTA | ppm whole dry coal |
| SiO ₂ | 41.3 | Si | 2.6 | Ag | < 0.3 |
| Al ₂ O ₃ | 14.8 | Al | 1.1 | As | 2 |
| TiO ₂ | 0.69 | Ti | 0.06 | Ba | 358 |
| Fe ₂ O ₃ | 29.4 | Fe | 2.8 | Be | 8.0 |
| MgO | 0.66 | Mg | 0.05 | Bi | |
| CaO | 5.47 | Ca | 0.53 | Cd | < 0.3 |
| Na ₂ O | 1.05 | Na | 0.11 | Ce | |
| K ₂ O | 1.58 | K | 0.18 | Cl | 1400 |
| P ₂ O ₅ | 0.28 | P | 0.017 | Co | |
| SO ₃ | 4.50 | | | Cr | 165 |
| | | | | Cu | 95 |
| | | | | Ga | |
| | | | | Ge | |
| | | | | Hg | 0.11 |
| | | | | La | |
| | | | | Mn | 387 |
| | | | | Nb | |
| | | | | Ni | 120 |
| | | | | Pb | 10 |
| | | | | Rb | 36 |
| | | | | Sc | |
| | | | | Se | 4 |
| | | | | Sn | |
| | | | | Sr | 254 |
| | | | | Th | |
| | | | | U | |
| | | | | V | 195 |
| | | | | Y | |
| | | | | Yb | |
| | | | | Zn | 240 |
| | | | | Zr | 125 |

High-temperature ash (HTA)
used for inorganic analysis
= 13.68 % of whole dry coal

ASH FUSION TEMPERATURES

| | Reducing atmosphere | | Oxidizing atmosphere | |
|---------------------|------------------------|--------|-------------------------|--------|
| Initial deformation | 1060°C | 1940°F | 1296°C | 2365°F |
| Softening | 1082°C | 1980°F | 1321°C | 2410°F |
| Hemispherical | 1149°C | 2100°F | 1354°C | 2470°F |
| Fluid | 1199°C | 2190°F | 1382°C | 2520°F |