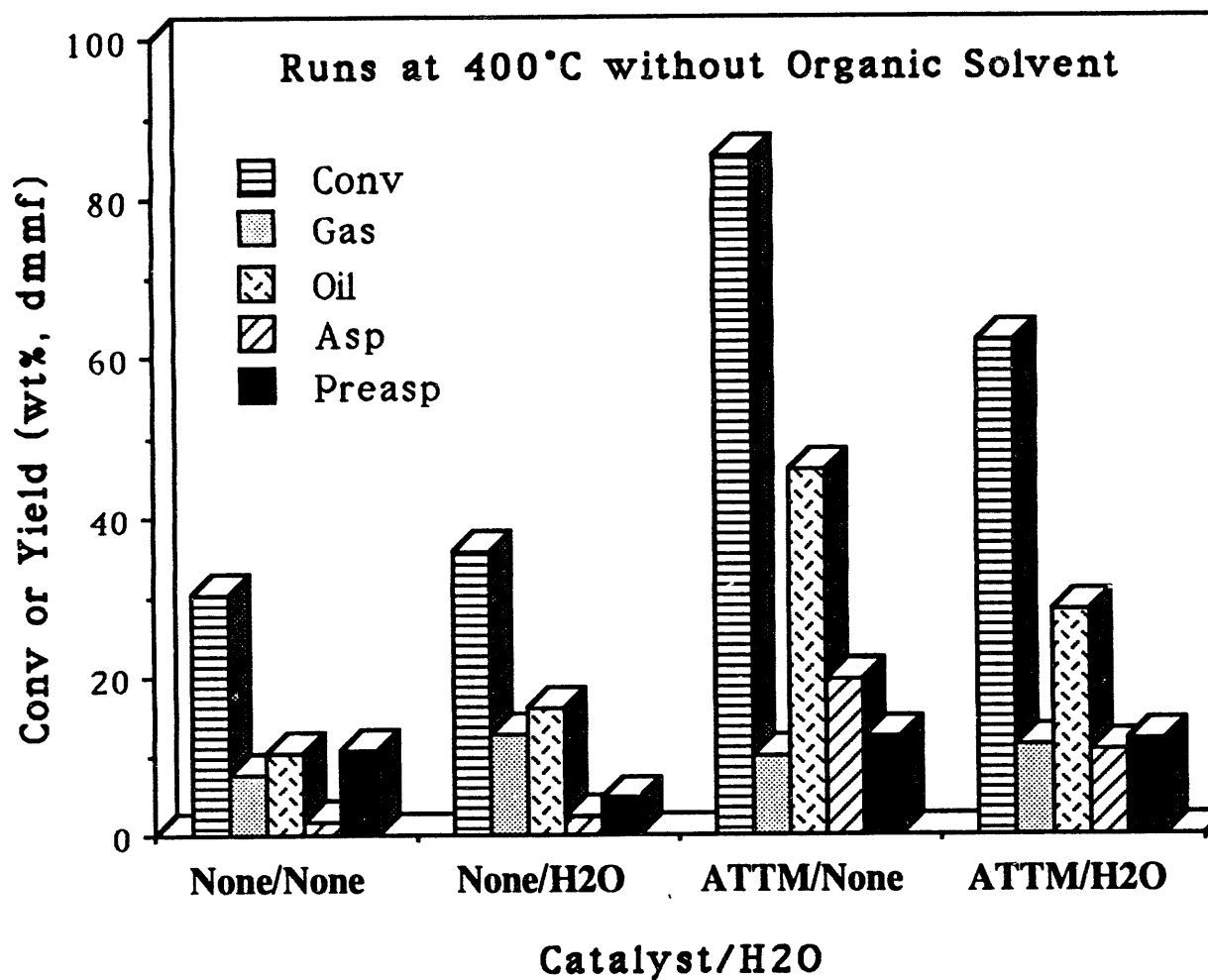Figure 13.

Effect of Water Addition in Catalytic Liquefaction at 400 °C

Title: THE EFFECTS OF DIFFERENT DRYING PROCESSES ON COAL
LIQUEFACTION YIELDS

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Organization: Western Research Institute, Box 3395, Laramie, WY 82071

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Objectives: The objectives of this project are to measure possible changes in coal
structure that occur during coal drying and to determine the effects of different drying
processes on coal liquefaction yields.

INTRODUCTION

One area for improvement in the economics of coal liquefaction is coal drying. This is
particularly true for subbituminous coals and lignites of which the US reserves are
huge. These coals contain significant amounts of water so that simply drying these
materials before transportation to their final destination can represent a sizable
reduction in cost. However, thermal drying makes these coals more reactive and
susceptible toward spontaneous combustion so that potential gains in reducing
transportation costs could be offset by generating coals that are more difficult to
process[1].

With regard to coal liquefaction, coal drying may be a viable preconversion step.
However, some studies have shown that drying has a detrimental effect on the
liquefaction behavior of coal[2-6]. As coals have both a physical and chemical structure, it
is conceivable that drying affects one, the other, or both of these structures.

Silver and Frazee[2,3] made a comprehensive study of the effect of drying coal on
liquefaction reactivity of Clovis Point subbituminous coal from Wyoming. Drying
methods included drying under different atmospheres, solvent drying, vacuum drying,
and microwave drying. The effect of artificially increasing the water partial pressure on
the reaction by adding distilled water to dried coal was also studied. The results of

drying in different atmospheres and using microwaves indicated that complete drying had an adverse effect on liquefaction reactivity. Microwave drying experiments showed that 75 % of the moisture could be removed without affecting conversions. In fact, conversions improved slightly by removing some of the moisture. However, removal of the remaining 25 % of the moisture caused the conversions to drop below that of the undried coal.

Different methods for coal drying are being investigated at Western Research Institute (WRI) to determine if drying can be accomplished without destroying coal reactivity toward liquefaction, thereby making coal drying a relatively economical and efficient method for coal pretreatment. Coal drying methods include conventional thermal and microwave drying at elevated temperatures, and chemical drying at low temperature. Solid-state nuclear magnetic resonance (NMR) techniques of cross polarization with magic-angle spinning (CP/MAS) are employed to measure changes in coal structure brought about by the different methods of drying and by low temperature oxidation. Most of the work on the project thus far has focused on development of standardized procedures for thermal, microwave, and chemical methods of coal drying. Results of this aspect of the project are reported in this paper.

EXPERIMENTAL

Coal Preparation

The coals selected for study consist of a lignite, three subbituminous, and two bituminous coals(Table 1). In order to study the effects of different methods for drying coal on coal structure and liquefaction yields, master batch samples (~500 g) of each coal were prepared by grinding and screening to -20, +100 mesh particle size. The samples were placed in a wide mouth jars and allowed to equilibrate in an oven in the presence of a beaker of water at 40°C for 24 hrs. The samples were then removed from the oven and placed in a humidifier until aliquots were taken for the different drying tests. The "moisture" values for all the coal drying tests were determined from the weight loss of the coals at 105°C for 24 hrs.

NMR Measurements

Solid-state ^{13}C NMR measurements were made using a Chemagnetics 100/200 solids NMR spectrometer. Carbon aromaticity measurements were made at 25 MHz using the

technique of cross polarization (CP) with magic-angle spinning (MAS) and high-power decoupling. These measurements were made using a large-volume sample spinner (2.1 mL) and a spinning rate of ~3.8 kHz. Between 3,600 and 7,200 transients were recorded.

Other instrument parameters were a pulse delay of 1 s, a contact time of 1 ms, a 6.2 μs pulse width, a sweep width of 16 kHz, and 1K data acquisition points. A 25 Hz exponential multiplier was applied to the free induction decay of each ^{13}C spectrum before integration.

Thermal Drying

Coal samples were heated to different final temperatures in order to determine at what temperature significant structural changes begin to occur that might affect the liquefaction behavior. These heating experiments are referred to as ballistic heating experiments. The ballistic heating experiments were performed with a small, vertically aligned furnace. The furnace has a 12-centimeter long heated section which accepts a 1.4-centimeter i.d. quartz liner. A stainless steel screen provides support for the coal and a steel wool pack heats the nitrogen sweep gas which is introduced at the bottom of the quartz liner. In a typical experiment, the furnace is preheated to about 10°C above the desired final coal temperature. A 2-gram coal sample is then poured into the quartz liner and a thermocouple is inserted into the coal sample bed. When this thermocouple reaches the desired temperature, the quartz liner is removed from the furnace and allowed to cool. Nitrogen flow is maintained at all times. When the sample temperature is below 50°C the coal is poured into a sample vial, capped with nitrogen, and sealed. Heatup times with this system are typically from 15 to 20 minutes. Samples were heated to final temperatures of (250°C. The percent "moisture" was determined by the weight loss.

Microwave Drying

Microwave drying experiments were conducted to determine the effects of microwave drying on liquefaction behavior. Experiments were conducted using a commercially available microwave oven. Microwave drying tests were conducting in the following manner: ~ 2 grams of coal were placed in 25 mL beakers, and the beakers placed at the center of the microwave oven. Samples were exposed to microwave radiation for different periods of time and at different power levels, after which the samples were

removed from the oven and a thermocouple inserted into the coal bed to determine an average temperature. The percent "moisture" was determined by the weight loss.

Chemical Drying

Chemical drying experiments were conducted on the six coals using 2,2-dimethoxypropane as a drying agent[7]. One-half gram of coal was weighed into a 10 mL centrifuge tube followed by 2 mL of 0.2 N CH_3SO_3H in CH_3OH and 1 mL of the reference standard cycloheptane. Four mL of dimethoxypropane were then added to the mixture. The total mixture was stirred, then centrifuged for 10 minutes. After 2, 4, 6, and 8 hours, one-half mL aliquots were removed, diluted with one-half mL $CDCl_3$, and the ^1H NMR spectrum recorded. The solution was stirred and centrifuged prior to removing the aliquots.

A ^1H NMR method was developed to measure the amount of water in coal. The ^1H NMR spectra of the reaction products, methanol and acetone, give single resonances for the methyl groups, which are easily identified. A known amount of cycloheptane was added as an internal standard. These resonances do not overlap the hydrogen NMR resonances of DMP. Integration of the methyl resonances from acetone is used to measure directly the moles of water reacted. The average relative error using the ^1H NMR method is < 3% for standard solutions with a known amount of water. A curve-fitting routine for determining the area of the peaks increases the precision and accuracy of the NMR method by eliminating instrumental and other artifacts which contribute to the peak shape. The amount of water is calculated from the signal intensity of the methyl groups in acetone to the signal intensity of the standard.

Coal liquefaction Experiments

Coal liquefaction experiments were conducted in a magnetically-stirred microautoclave reactor using a fluidized sandbath as a heating medium. The autoclave had a capacity of 75 cc with an inside diameter of 1.75 cm. This system was modified at Wilsonville to increase the volume and, as a result, improve material balances. The improved system, called VaSTeC for Variable Submergence Temperature Control because temperature excursions were controlled by varying submergence of the reactor in the heating medium, was used extensively and reliably to predict and augment test results from the Wilsonville thermal liquefaction unit[8]. The VaSTeC system is large enough to provide adequate materials for post-experiment analyses, yet is small enough to provide the rapid heating and cooling required for kinetic experiments.

Liquefaction experiments were carried out using a 1:1 weight ratio of tetralin to coal. The initial coal had a weight of 20 g, and was screened to a -20 +100 mesh size. The autoclave was pressured with hydrogen to 900 psig. Liquefaction experiments were carried out at 425 °C for 30 minutes. Coal conversion was based on conversion to THF solubles. We did not search for experimental conditions that would provide the greatest yields of any given product because our objectives were to determine the effects of different drying methods on coal structure and liquefaction behavior. Liquefaction experiments conducted under the same conditions were considered acceptable to meet the objectives of the project.

RESULTS AND DISCUSSION

Thermal Drying

Samples of the six coals were ballistically heated to final temperatures of 100, 150, 200, and 250 °C. Solid-state ^{13}C NMR measurements were made on the heated samples, and are shown in Figure 1 for the Eagle Butte coal heated to 150, and 250 °C. Overall, there were not any dramatic changes in the carbon structure as a result of ballistic heating to 250°C. The most noticeable change in the NMR spectra is in the carboxyl region (~180 ppm), where there is evidence of some decarboxylation having taken place during heating. There is also for some deterioration in resolution of branched aromatic carbons (~140 ppm), and phenolic carbons (~155 ppm), and there is some narrowing of the aliphatic band (0-60 ppm) in the spectrum of the heated coal. These results are all supportive of the data in Table 2 which shows that the weight losses, except for the Texas coal, are only slightly greater than the weight loss ascribed to moisture removal. The NMR spectra of the other ballistically-heated subbituminous coals showed similar features. NMR spectra of the ballistically-heated bituminous coals (Illinois #6 and Utah Blind Canyon), which had the smallest amounts of moisture, were virtually identical to the original coals.

Saini et al.[7] observed little change in coal structure under vacuum drying, and under thermal drying at 100 °C for up to 100 hrs. They did observe a decrease in the aliphatic carbons from extended drying at 150 °C for 20 hrs. In our experiments, because the sample was quenched immediately after temperature was reached, there was not sufficient time for devolatilization to have occurred in the coal resulting in any significant loss of aliphatic carbons.

Microwave Drying

Microwave drying is an alternative method to thermally dry coals. However, the mechanism of drying with microwaves is different from that of simply heating the coal. In order for a substance to absorb microwaves and become heated, it must have a permanent dipole moment. Therefore, the functional groups that are the most efficient absorbers of microwaves are those that are highly polar, such as the -OH group in water.

When a substance containing water molecules is exposed to microwaves of the proper frequency (2,450 MHz) the water molecules attempt to align and realign with the alternating electric field of the microwaves. This causes friction at the molecular level, which becomes manifested as heat. Because the water in coals can be distributed on the surface, in pores, or as part of the coal structure as in a gel, depending on rank, microwaves might be used to provide some selectivity for coal drying without appreciably affecting the overall coal structure and liquefaction behavior of the coal.

The objective of the microwave drying task is to determine whether microwave drying alters the structure and composition of the coal, and hence its behavior toward liquefaction. This work was prompted by earlier work of Silver and Frazee[2,3] that showed that drying coal with microwaves beyond ~75% moisture removal actually had a detrimental effect on the reactivity toward liquefaction. However, there has not yet been a systematic study of possible changes in coal structure induced by microwave drying.

At full power (600 watts), 75 % or greater of the moisture in coal is removed in ~2 min. Removal of the remaining moisture causes the temperatures to increase rapidly (Figure 2). Because of the rapid removal of moisture at full power, different levels of microwave power were used in order to obtain a more complete drying curve. At power levels of 300 watts, 25 -75 % moisture could be removed for irradiation times of up to 15 min.

The general features of the coal drying curves using microwave radiation are shown in Figure 2 for the subbituminous coals. The drying curves for the other coals were similar. In general, there is a very rapid temperature rise after ~10 % of the moisture is removed. This is followed by removal of the bulk of the moisture (10-80%) at temperatures approaching the boiling point of water, which is ~ 93 °C at the 7,200 ft elevation in Laramie, WY. The rapid increase in temperature after removal of about

80% of the moisture seems to be a general characteristic of microwave heating of subbituminous coals. This behavior was also observed by Silver and Frazee [2,3], who also noted a decreased reactivity toward liquefaction for greater than 75% moisture removal.

The moisture that is removed at higher temperatures could be from water in the gel or pore structure of the coal. These water molecules would have a more difficult time aligning and realigning with the radiation field, and thus would cause heating of the coal to higher temperatures, with possible disruption of part of the coal matrix enabling some retrograde reactions to take place that diminish the reactivity toward liquefaction. To test these ideas, a microwave drying curve was also measured for a Linde 13X molecular sieve containing 30.6 % moisture in its pores. The microwave drying curve for the molecular sieve is similar to those of the subbituminous coals (Figure 2).
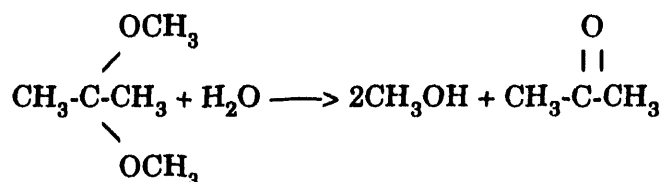
Weight losses greater than the weight of moisture determined by thermal drying were recorded by heating with microwaves for extended periods (180 min) at low power (300 watts)(Figure 3). The solid-state ^{13}C CP/MAS NMR spectra of Eagle Butte coal heated in this manner are shown in Figure 4. The spectra do not show any significant carbon structural changes as a result of moisture removal using microwaves, even though the temperatures were greater than 100 °C and greater than 100% of the moisture removable by thermal drying at 105°C (22.6 %wt loss) was observed. There is a decrease in the carboxyl carbons which would be manifested as CO_2 and could account for some of the weight loss. In general, there is a slight degradation in the resolution of some of the carbon functionality during heating, as evidenced by the smoothing of the resonance bands at ~140, 155, 180 ppm, similar to what was observed in the ballistically heated samples (Figure 1). The NMR spectra of the other coals heated similarly with microwaves exhibited similar features, i.e., there were no significant changes in carbon structure when drying with microwaves. Thus it appears that microwave drying curves (Figure 2) reflect mostly the drying behavior of water in different sized pores, and heating with microwaves under these conditions does not cause any major changes in carbon structure of the coals.

Chemical Drying

Chemical drying is a relatively unexplored technique for removing water from coals at low temperature. Thermal methods of drying can alter the physical structure of coal as well as promote undesirable chemical reactions. In contrast, low-temperature chemical drying of coal, on the other hand, should preserve the structural integrity, reduce

retrograde reactions, reduce thermal degradation, and provide information on nonbonded, chemisorbed, and physisorbed water. This method of dehydrating coal should provide a baseline for studying initial stages of retrograde/condensation reactions. That is, decarboxylation and low-temperature oxidation reactions can then be studied in the presence and absence of water and gases and as a function of temperature.

Several methods have been developed recently to determine the moisture content of coals [10-13]. We are investigating the use of the dehydrating agent 2,2-dimethoxy propane (DMP) to chemically dry coals according to the reaction,

$$CH_3\text{-}\underset{\underset{OCH_3}{\diagdown}}{\overset{\overset{OCH_3}{\diagup}}{C}}\text{-}CH_3 + H_2O \longrightarrow 2CH_3OH + CH_3\text{-}\overset{\overset{O}{\parallel}}{C}\text{-}CH_3$$

This reaction is rapid (<10 min) and endothermic. The use of DMP to dehydrate coal accomplishes two things: (1) the removal of water at ambient temperature by chemical means rather than by physically forcing exchange by mass action preserves the structural integrity of the coal components and (2) the reaction products can easily be measured quantitatively to determine the amount of water in coal.

The results of the chemical drying experiments are summarized in Figure 5. Four of the coals (Eagle Butte, Illinois No. 6,Utah, and Black Thunder) have average moisture contents determined by chemically drying that are slightly greater than those from determined by thermal drying. Presumably, the additional water is due to water that is more tightly bound in pores, which is not liberated during thermal drying at 105 °C. Finseth[14] also observed a greater moisture removal from different coals using an isotopic dilution method.

Coal Liquefaction Experiments on Eagle Butte Coal

Preliminary results of coal liquefaction experiments on partially dried Eagle Butte coal are shown in Figure 6. The partially dried coals were obtained using ballistic heating or microwaves to remove varying amounts of the moisture in the coal. Overall, the general trends in Figure 6 are similar to that reported by previously[2,3] for microwave dried Clovis Point subbituminous coal. Our results suggest that the conversion remains fairly constant until about 80 % of the moisture has been removed, after which the conversion

of the dried coal is less than the conversion of the undried coal. Sliver and Frazee[2,3] observed a slightly enhanced conversion upon removal of about 80 % of the moisture and a markedly decreased conversion for microwave dried coals.

Others have reported lower conversions for dried low rank coals. Saini et al.[5] observed similar conversion behavior with Wyodak coals that were dried in vacuum and in air for extended periods of time. The most severe drying (in vacuum for 2 hrs, 100 °C, or in air for 20 hrs at 150 °C) gave conversion that were lower than the undried coal. In solvent -free thermal liquefaction, however, partial drying had a detrimental effect on the liquefaction conversions. When the liquefaction was carried out without a catalyst, conversions were always lower for the dried coals.

SUMMARY AND FUTURE WORK

Experiments conducted so far indicate that ballistically heating Eagle Butte subbituminous coal to 250 °C does not cause any major changes in the carbon structure of the coal. Similarly, moisture removal using microwaves did not cause any major changes in coal structure.

The dehydration agent, 2,2 dimethoxypropane, can be used to chemically dry coals. In conjunction with ^{1}H NMR measurements on the reaction products, the moisture content of coal can be determined, simply, precisely, and accurately.

Removal of up to 80% of the moisture in subbituminous coals does not appear to affect the liquefaction yields. However, removal of the all the moisture in subbituminous coals has a detrimental effect on liquefaction yields.

Work will be continued to study the effects of different drying processes on coal structure and liquefaction yields. Chemical and microwave drying experiments will be conducted on coals of different rank. Liquefaction experiments will be conducted on partially dried coals to determine the minimum level of moisture that can be obtained without affecting conversion yields.

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Table 1. Elemental Composition of Coals

STATE	COAL	RANK	% H_2O	C	S	O(diff.)
N. Dakota	Beulah	Lig.	35.4	73.1	0.8	20.6
Texas	Freestone	subC	29.7	74.3	1.2	17.4
Wyoming	Black Thunder	subC	23.9	73.1	0.5	21.7
Wyoming	Eagle Butte	subC	20.8	72.2	0.6	20.7
Illinois	Ill. No.6	hvC	9.7	78.1	5.4	9.7
Utah	Blind Canyon	hvA	4.0	81.3	0.4	10.5

Table 2. Coal Weight Loss During Ballistic Heating to 250°C

Coal	% Moisture	% Weight Loss
N. Dak. DECS-11	34.46	35.38
Texas, DECS-1	28.73	26.88
Black Thunder	23.22	24.02
Eagle Butte	18.54	19.81
Ill. No. 6, DECS-2	9.79	11.63
Utah, DECS-6	3.99	5.85
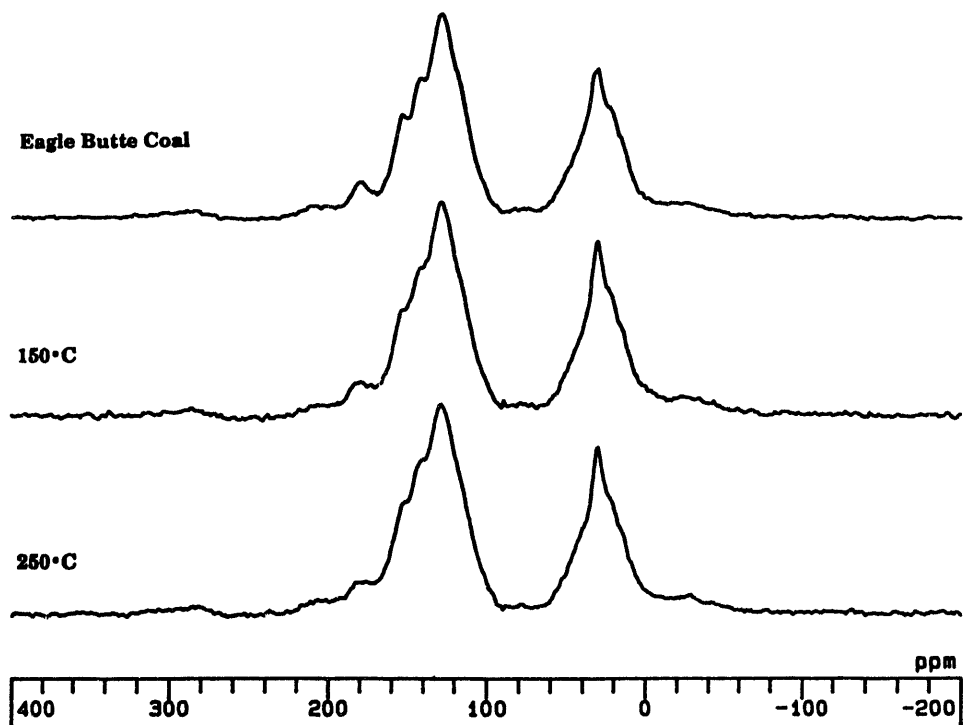
Figure 1. Solid-state ^{13}C NMR spectra of Eagle Butte coal ballistically heated to 250°C.
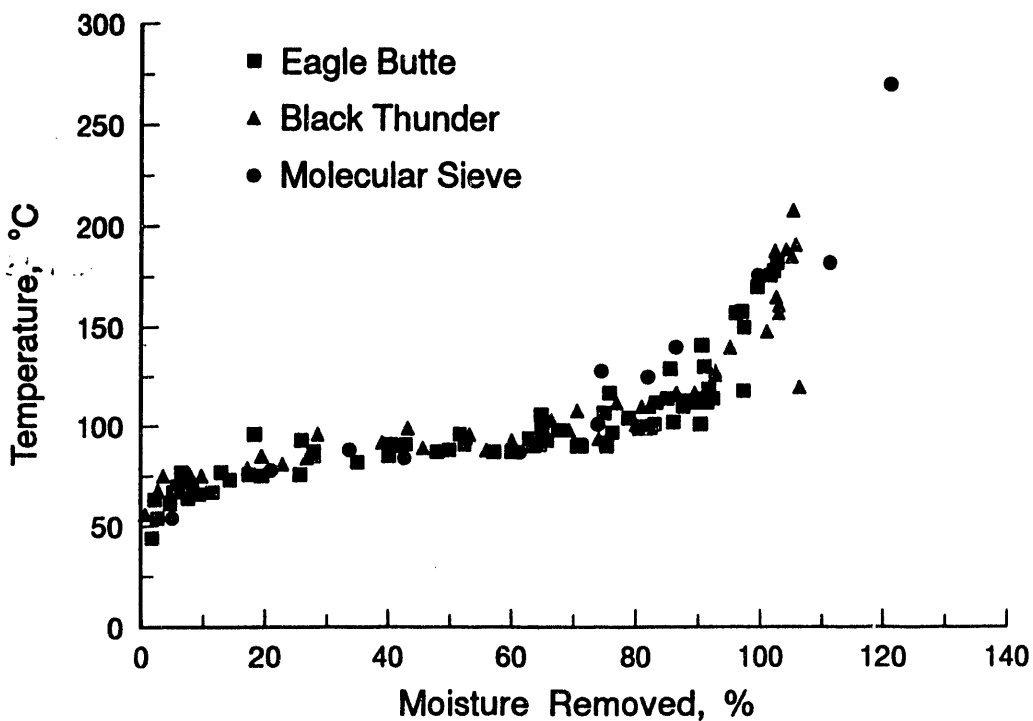

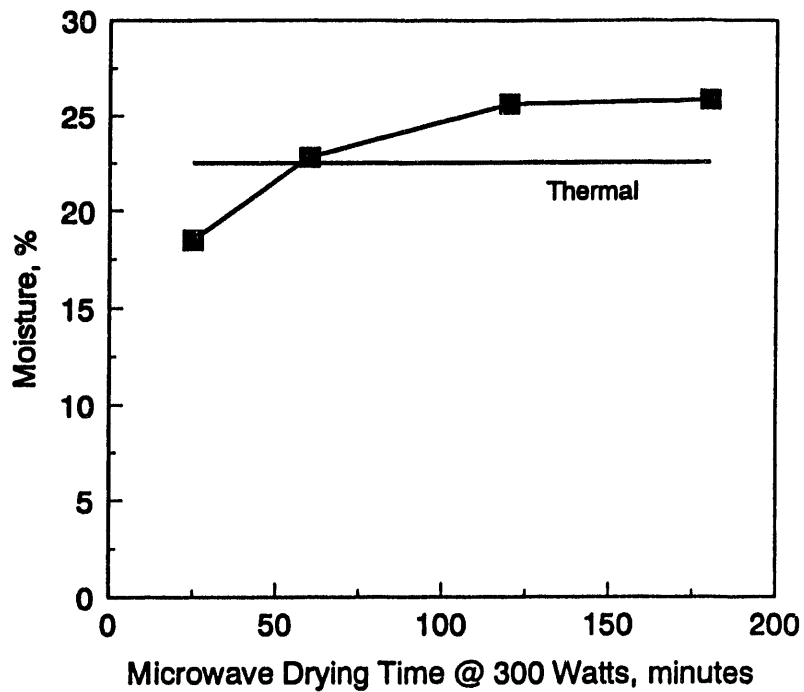**Figure 2. Microwave drying curve for Eagle Butte and Black Thunder coals.**

Figure 3. Moisture removed as a function of microwave drying time at 300 watts.
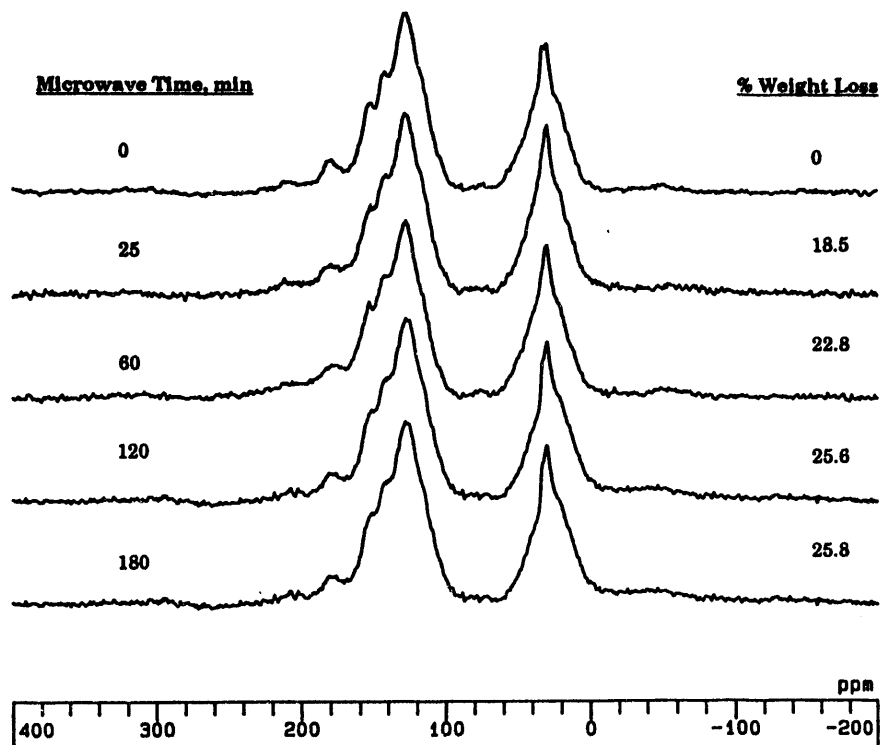

Figure 4. Solid-state ^{13}C NMR spectra of microwave-dried Eagle Butte coal.
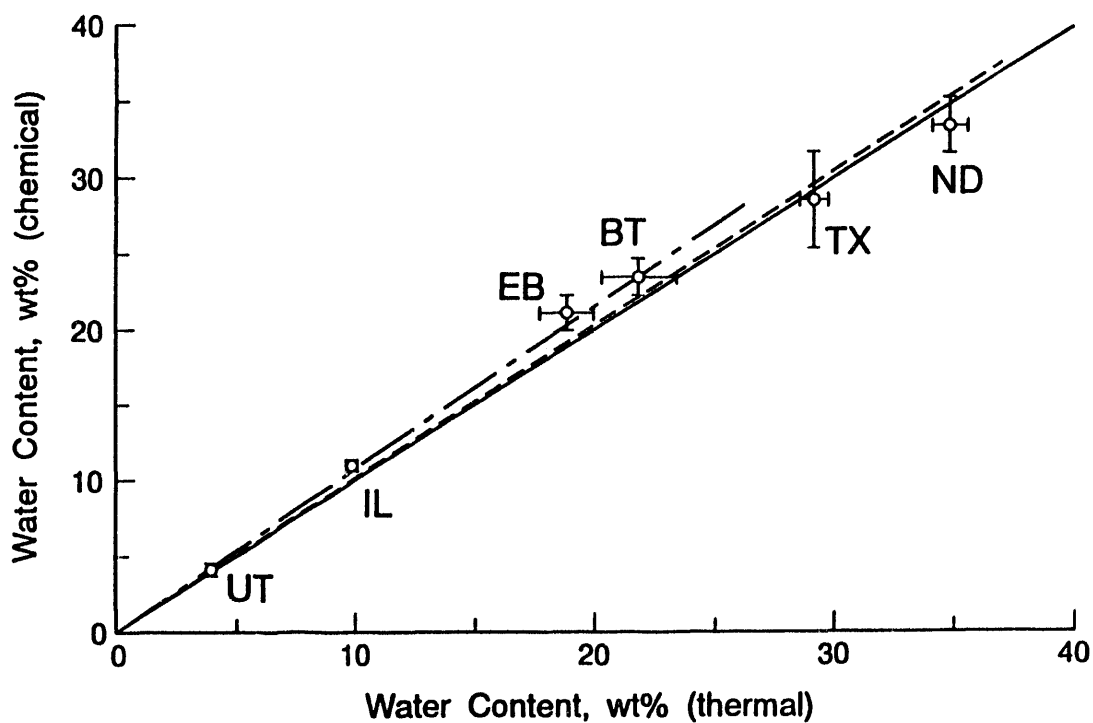
Figure 5. Plot of moisture determined by chemical drying vs. moisture determined thermally.
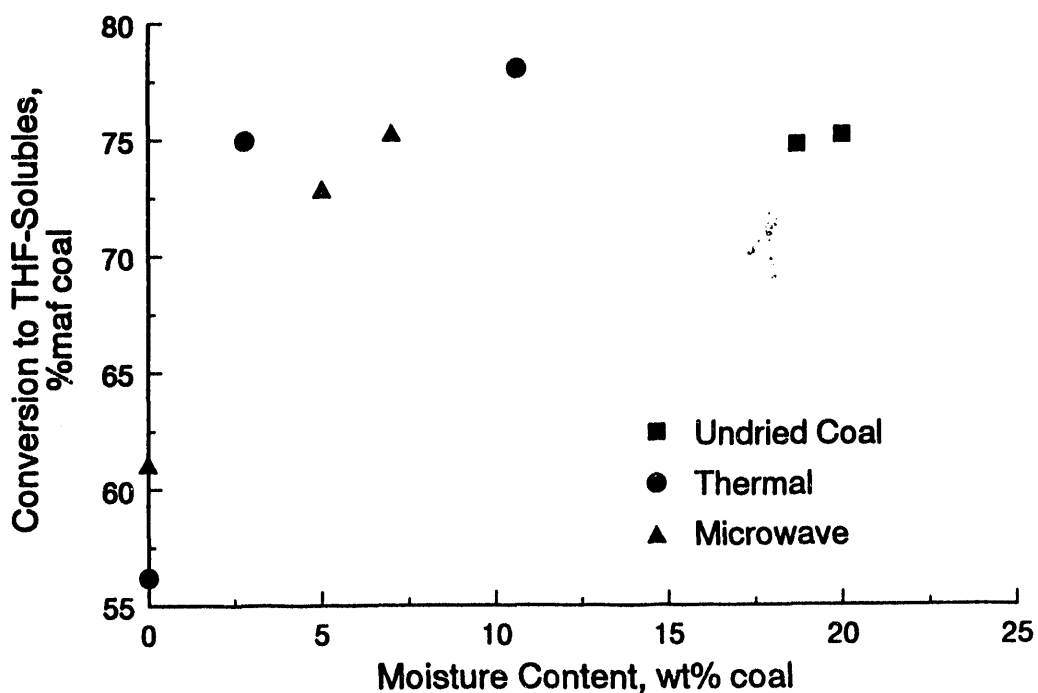

Figure 6. Coal liquefaction conversions for partially dried Eagle Butte coal.

INTRODUCTION

Liquefaction is generally achieved by heating coals with a donor solvent and, preferably, with a catalyst and hydrogen pressure at temperatures around 425°C. Attempts to achieve higher conversion by simply using higher temperatures often lead to coking and lower liquid yields. Furthermore, retrograde reactions can lead to crosslink formation (particularly in the case of low-rank coals) even before nominal liquefaction conditions are reached.[1] Thus, besides the bond cleavage reactions that lead to disintegration of the coal matrix, there are also retrogressive reactions that lead to the formation of new refractory linkages. In many instances, conversion appears to be limited by these retrogressive reactions more than by any inherent lack of reactivity of the coal.[2]

Oxygen functions in general, and specifically carboxylic acids and phenols, have been implicated as important in the retrograde reactions of coals.[1-4] Furthermore, phenols severely hamper the processability of coals both during liquefaction and during subsequent catalytic upgrading.[5-6] Thus, substantial benefits could be realized if coals were even partially deoxygenated before liquefaction. Ideally, this deoxygenation would be achieved in a preconversion step, before widespread retrogression occurs.

Deoxygenation of phenols is chemically the most difficult heteroatom removal to achieve,[7] particularly for heterogenous systems, where access of a solid catalyst (even if very finely divided) to the depth of an organic matrix is quite limited. Furthermore, some phenolic structures that deoxygenate readily also couple very readily during heatup, often before temperatures at which coals become fluid (and easily contactable by heterogeneous catalysts) and before temperature at which thermal hydrogen-transfer reactions lead to bond cleavage.[3,8] Carboxyl groups have also been associated with crosslinking. Solomon and coworkers have shown that decarboxylation, particularly in the low temperature regime of 200° to 250°C, correlates with crosslinking.[4] Thus, pretreatments that can effectively deoxygenate phenols or decarboxylate without the attendant crosslinking constitute a technical challenge whose resolution would greatly facilitate utilization of coal through direct liquefaction.

The combination of CO and water is well recognized as a thermodynamically powerful but kinetically limited reducing system. It has been extensively explored as a liquefaction system for low-rank coals by Appell[9] and by researchers in North Dakota,[10] following on much earlier work[11] in Germany. Since the utility of the system has been severely hampered by the requirement for high partial pressures of water, effective promoters must be found if it is to be effective under pretreatment conditions for removal of phenolic OH and for crosslink cleavage in low-rank coals. Since CO/water easily deoxygenates polycyclic phenols such as anthrone, and since the overall thermodynamic driving force for deoxygenation of monocyclic phenols is essentially identical to that for polycyclic phenols, the potential exists for greatly accelerating the reaction with promoters.

OBJECTIVES

The ultimate goal of this research is to help develop preconversion techniques that will mitigate crosslinking reactions and thereby substantially increase liquid yields during subsequent liquefaction. The immediate objective is to determine the potential for augmenting pretreatment of low-rank coals through the use of electron-transfer agents. This potential will be explored in laboratory studies through determination of the impact on the evolution of oxygen functions, crosslinking, and conversion. The pretreatments explored include several that hold promise for effecting deoxygenation (or other reduction), for example, treatment with CO/water/base and hydroquinones or other electron-transfer agents in various combinations. The effects of these pretreatments on functional group distribution, macromolecular structure, and liquefaction are to be compared with those that have shown promise in the past for improved conversions, such as simple hydrothermal pretreatment, mild hydrogenation with dispersed catalysts, and demineralization.

Additional objectives are to improve test procedures for assessing the effect of the pretreatment on subsequent liquefaction and achieve also some understanding of the chemical origins of the effects observed. These tests are: (1) proton magnetic resonance thermal analysis[12,13] (PMRTA) for determining the effect of pretreatment on fluidity as liquefaction conditions (temperature, pressure) are approached; and (2) a TGA-based simulated distillation for convenient measurement of product volatility following small scale batch liquefaction. The purpose of the PMRTA test is to gain additional insight into whether beneficial pretreatments primarily affect pre-existing crosslinks in the coals or whether they primarily limit additional crosslinking during liquefaction. The TGA-based simulated distillation test is being developed so that we can obtain conversion data and also assess the nature of the product (distillation profile) instead of only a single point measure of conversion such as wt % conversion to THF-solubles or the yield of 975°F- distillates.

ACCOMPLISHMENTS

We have conducted a range of batch-pretreatment conditions to determine how various additives affect the impact of pretreatment of the Argonne Wyodak and Zap lignite coals in near-critical, liquid water at ~350°C. The pretreated coals were subjected to batch liquefaction tests to assess the effectiveness of the pretreatment, which was judged primarily by the yield of hexane-solubles. The pretreated coals were also subjected to testing by the proton magnetic resonance thermal analysis technique (PMRTA) of Lynch and coworkers at CSIRO to determine how the pretreatment affects molecular mobility in the coal as it is subsequently heated to liquefaction temperatures.[12,13] The purpose here is to gain additional insight into whether beneficial pretreatments primarily affect pre-existing crosslinks in the coals or whether they primarily limit additional crosslinking during liquefaction. The increases in PMRTA-measured mobility correlate very well with batch liquefaction yields for Wyodak coal, which exhibits significant mobility during heating, but not for Zap coal for which there is much less mobility. We have also designed, constructed, and developed procedures for, a large-capacity thermogravimetric analysis (TGA) system in order to replace the traditional solvent solubility assessment of small scale batch liquefaction runs with an ASTM-related volatility measurement that is much more relevant to the normal processing criterion of distillability.

EXPERIMENTAL PROCEDURES

Pretreatment. The pretreatment experiments were performed in an unstirred, 90-ml 304 stainless steel reactor fitted with a quartz insert and heated in a fluidized sand bath. The basic pretreatment condition involved heating in liquid water at 350°C for 30 minutes, under a CO partial pressure of 500 psi (cold). Each pretreatment test used 10 grams (2 ampoules) of -100 mesh Argonne Premium Coal Sample Bank Wyodak or Zap Lignite, to which 15 mL of a 2 vol % solution of methanol (to facilitate wetting of coal) in deionized, de-oxygenated water. The reactor heat-up time was ~20 minutes, and the total reaction time was 50 minutes. After cooling in a cold sand bath, the excess water was removed with three stages of centrifuging and pipetting off the supernatant liquid. One third of the wet coal was stored under argon in a freezer for future analysis, and the remainder was subjected to liquefaction on the same day that the pretreatment was run.

Liquefaction. The liquefaction tests of the pretreated coals were run in 40-mL horizontally held, vertically shaken (ca. 500 cps, 5/8-in stroke) 316 stainless steel microautoclaves. The liquefaction tests were all run on about 6 grams of coal (as received basis) at 430°C for 50 minutes in tetralin (solvent:coal 2:1, on an as-received basis), under 1000 psi (cold) hydrogen. After cooling in sand- and dry-ice baths, the contents of the reactor were transferred to a beaker with 200 ml hexane, sonicated for 10 minutes, and filtered through a 0.45 μm PTFE membrane filter. The filter residue was dried at 76°C overnight in a vacuum oven at ~0.2 torr. The weight of the dried residue was determined and used to calculate the wt % conversion to hexane-soluble material.

We have relied on the residue-based conversion to hexane solubles as a rough measure (albeit generally an overestimate) of conversion to distillate material. The baseline pretreatment and liquefaction conditions seem to be appropriate for this conversion criterion: pretreatment in water at 350°C for 30 minutes, followed by liquefaction in tetralin at 420°C for one hour yields about 40% conversion (maf) to hexane solubles. We judged that this was a high enough conversion to secondary liquefaction products to have some relevance to high-severity two-stage liquefaction, but low enough to leave latitude for observing the benefits of improved pretreatment on the initial coal conversion reactions.

PMRTA Analyses of Pretreated Coals. Approximated 1.5 g of selected pretreated coals (which had been stored under argon in a freezer) were sent to Drs. Leo Lynch and Richard Sakurovs at CSIRO in Sydney, Australia, for analysis by the proton magnetic resonance thermal analysis (PMRTA) technique, which they have developed.[12,13] This programmed temperature method measures certain NMR relaxation parameters to obtain a measure of molecular mobility, or fluidity, as the coal is heated through the liquefaction temperature region. In the present case, the pretreated coals were dried under nitrogen at 105°C for 18 hours. The PMRTA test conditions involved heating at 4°C/min to 600°C, as described by Lynch et al.[12]

TGA-Based Simulated Distillation. Although this technique is based on and related to approaches that have been previously reported, and, in some cases, are now in use, there are significant differences between all of these and the approach we have taken here. Accordingly, our rationale and assembly of a large scale (up to 200 g) TGA system and the establishment of conditions for its used are described in the Results section.

RESULTS AND DISCUSSION

Pretreatment and Liquefaction of Wyodak and Zap Lignite Coals

Based upon recent studies at SRI and other laboratories, we used hydrothermal pretreatment under CO pressure at 350°C as a baseline for both Wyodak and Zap coals. These conditions provide modest improvement in subsequent liquefaction or coprocessing experiments. We compared the liquefaction yields obtained from baseline-pretreated coals with those obtained when base, electron-transfer agent, carbon disulfide, and ferrous sulfate are added to the pretreatment in various combinations. In brief, these experiments have shown moderate improvements in liquefaction yield resulting from pretreatment, including a further improvement when base, carbon disulfide, and electron-transfer agent are added to the aqueous pretreatment medium. These results are summarized in Tables 1 and 2 for Wyodak and Zap coals, respectively. As described under Experimental Procedures, the conversion diagnostic was the wt% (daf) of hexane-insoluble obtained after the pretreatment and subsequent liquefaction.

The results in Table 1 reflect a precision of 2-3 wt% hexane insolubles and a maximum total improvement of about 5 wt% daf in hexane-insolubles for pretreatment agents, *beyond* the

Table 1

EFFECT OF PRETREATMENT ON CONVERSION OF WYODAK COAL IN THERMAL BATCH LIQUEFACTION

| Expt No. | Pretreatment[a] | | | | Liquefaction Temp. (°C)[b] | Hexane Insolubles[c] |
| | Additives[d] | | | Gas | | |
	0.1 wt% Na_2CO_3[d]	5 wt% p-HQ[e,f]	2.5 wt% CS_2[e,g]	500 psi (cold)		
JC2				Ar	420	55.0
JC2A				Ar	430	50.2
JC3				CO	430	52.5
JC12		X		CO	430	53.8
JC14	X	X		CO	440[h]	41.3
JC14B	X	X		CO	430	48.0
JC14C	X	X		CO	430	47.8
JC14D	X	X		CO	430[h]	49.9
JC16	X	X	X	CO	430	49.9
JC17			X	CO	430	44.8
JC18	X	X	X	CO	430	50.5

a. 10.0 g coal; 15ml H_2O, mixed but unstirred; 53 min at 350°C.
b. 1 hr.; 1000 psi H_2 (cold)
c. Defined as %daf coal that was insoluble in 200 ml hexane.
d. As wt% of the added H_2O.
e. As wt% of raw coal.
f. p-HQ = p-hydroquinone
g. Calculated to produce H_2S at 13% the level of H_2 pressure.
h. Pretreated coal allowed to sit for 48 hrs (at room temperature, under CO pressure) after 350°C pretreatment.

Table 2

EFFECT OF PRETREATMENT ON CONVERSION OF ZAP LIGNITE IN THERMAL BATCH LIQUEFACTION

Exp.	Na$_2$CO$_3$[j]	p-HQ[e,f]	CS$_2$[e]	FeSO$_4$[g]	TAME[e,h]	Gas 500 psi (cold)	Liquefaction Temp. (°C)[b]	% Hexane Insolubles[c]
JC18A						CO	430	53.4
JC19	0.1	5				CO	≈ 410[i]	59.1
JC20	0.1					CO	430	51.5
JC22	0.1	5				CO	430	51.5
JC28	0.1	5				CO	430	51.1
JC24	0.1	5	2.5[j]			CO	430	44.5
JC26	0.1	5	2.5[j]			CO	430	45.1
JC25	0.1		2.5[j]			CO	430	47.5
JC27	0.1		2.5[j]			CO	430[k]	44.8
JC34	0.1		2.5[j]			CO	430	44.3
JC30	0.1				4.8	CO	430	49.7
JC29			6.3	2.5[l]		CO	430	43.6
JC32			6.3	2.5[l]		CO	430	45.2
JC33	m		6.3	2.5[l]		CO	430	44.2
JC31			6.3			CO	430	53.8

a. 10.0 g coal; 15ml H$_2$O, mixed but unstirred; 53 min at 350°C.
b. Unless noted, reaction times are 1 hr under 1000 psi H$_2$ (cold)
c. Defined as the percent of the organic portion of the coal that was insoluble in 200 ml hexane.
d. As wt% of the added H$_2$O.
e. As wt% of raw coal.
f. p-HQ = p-hydroquinone
g. As FeSO$_4$·7H$_2$O; weight percentages are on raw coal and refer to the nominal amount of unhydrated material.
h. TAME = tetrakis(dimethylamino)ethylene
i. Fluidized sand bath temperature set at 430 °C, but temperature did not recover after insertion of reactor, apparently due to excessive air flow through bath.
j. Calculated to produce H$_2$S at ≈ 13% the level of H$_2$ ostensibly available from the water gas shift reaction.
k. Fluidized sand bath temperature set at 430 °C, but temperature dropped to 381°C and recovered to 400°C only after 15 min. Total reaction time 75 min.
l. Washed with several aliquots of H$_2$O after pretreatment; calculated to remove > 99% of material freely soluble in pretreatment water. Initial ratio CS$_2$/FeSO$_4$ (mol/mol) = 5.
m. Final H$_2$O wash after pretreatment (note l) contained 0.1 wt% Na$_2$CO$_3$.

benefit provided by 350°C hydrothermal pretreatment. There appears to be little if any benefit provided by hydroquinone, once a very low level of base and/or CS_2 are present. The greatest limit to precision appears to be the steep dependence of conversion on temperature. In fact later experiments show that the high yield (low HI) observed in Run JC-14 (Na_2CO_3/HQ) is primarily due to the higher temperature, rather than to the combination of promoters and the 48-h "hold" time that the pretreated coal experienced in this run before the liquefaction test could be performed. Although the temperature of the fluidized sand bath is controlled to within ±2°C, the rate of reactor heat-up is dependent on the degree of fluidization and the location of the reactor in the sand bed. Notwithstanding these fluctuations in net reaction severity, the results in Table 1 give little indication that hydroquionone provides any added benefit over base and/or CS_2 under the pretreatment conditions employed here.

Carbon disulfide was tested (as a source of H_2S) as one of the promoters because these low-rank coals, being low in sulfur, are known to benefit, sometimes very substantially,[14] from addition of CS_2 or other sources of sulfur. We did not wish any benefits observed for hydroquinones or other added electron transfer agents to be misleadingly high because of the low sulfur content of these coals.

The results obtained for the Zap coal, shown in Table 2, indicate the following:

1)   The addition of 0.1 wt% Na_2CO_3 (on the added water) yields a small (~2 wt%) improvement in the amount of hexane insolubles.

2)   By itself, the addition of 6.3 wt% CS_2 (on the raw coal) does not lead to any improvement in the hexane insolubles.

3)   The addition of 2.5 wt% CS_2 (on the raw coal) together with base leads to a substantial (~9 wt%) improvement in the hexane insolubles.

4)   The addition of 2.5 wt% p-hydroquinone (p-HQ, on the raw coal) to a pretreatment system containing either base alone or a base/CS_2 mixture does *not* lead to improvement in the hexane insolubles when compared to the same system without added p-HQ.

5)   The addition of a mixture of 4.8 wt% TAME (on the raw coal) and 0.1 wt% base leads to a small (1.5 wt%) improvement in the hexane insolubles when compared to the base-only case. TAME is thus slightly more effective than p-HQ, but still less effective than the base/CS_2 mixture.

6)   The addition of 2.5 wt% $FeSO_4$ together with 6.3 wt% CS_2 yields a substantial (~9 wt%) improvement in the hexane insolubles.

7)   If the above $FeSO_4$/CS_2 system is washed with base prior to the liquefaction (after the pretreatment), there is no further improvement (or degradation) in the amount of hexane insolubles when compared with the unwashed system.

As detailed above, the two most promising systems involve pretreatment with a mixture of either base/CS_2 or $FeSO_4$/CS_2. Both of these treatments yield an improvement of about 9 wt% in the amount of hexane insolubles. In part, these results are at least qualitatively expected. The addition of iron and sulfur compounds, particularly to low rank coals poor in these two elements, is well known to be beneficial.

The electron transfer agents p-HQ and TAME (tetrakisdimethylaminoethylene) did not yield the same degree of improvement as $FeSO_4$ or CS_2. HQ addition did not help at all when either base or base/CS_2 were already present. TAME was somewhat more effective, but did not help as much as the already-known-to-be-useful additives CS_2 and $FeSO_4$. Thus, these electron transfer agents do not appear to offer great promise, *at least as pretreatment agents*. We are somewhat surprised to see essentially no additional benefit from hydroquinone, given that it and related hydroquinones have been shown[15] to be of significant benefit under liquefaction conditions, and that hydroquinone derivatives are used, in their oxidized forms, as hydrogen-transfer agents in synthetic procedures to promote low-temperature de-hydrogenation. Two possible reasons for the observed lack of benefit are (1) the added hydroquinone was largely removed when the excess water was removed after the pretreatment step, and was therefore not present during liquefaction, where it is known to be beneficial, and/or (2) the low-rank coals are themselves already indigenous sources of catechol and other hydroquinone species.

The removal of hydroquinone after the pretreatment step was intentional, since the purpose was to explore the benefits of these promoters under *pretreatment* conditions. But in fact, the removal of excess water after pretreatment could also remove some of the indigenous hydroquinones which are generated from the coal at about 300°C, and could thereby actually be detrimental to the subsequent liquefaction. In contrast with the probable removal of much of the added and indigenously generated hydroquinones, the added $FeSO_4$ and/or added CS_2, by virtue of conversion to iron sulfide, will be at least partially retained when the excess pretreatment water is removed. Therefore these latter additives may be positively impacting the liquefaction, having been favorably activated during the pretreatment.

Evolution of Oxygen Functional Groups. Although the deoxygenation of single-ring phenols under mild liquefaction conditions in general, or under CO/water conditions in particular, is not facile, it is thermodynamically just as favorable as the kinetically facile deoxygenation of polycyclic phenols. There was good reason to hope that the right combination of electron-transfer agents would substantially promote it. The monocyclic phenols have a more endothermic first step (reduction of keto-form) and a much more exothermic second step (water elimination) so as to have a net dexoygenation thermochemistry that is essentially identical to that for the easily reduced polycylic phenols. Successful promotion requires the chemical potential of the reducing system be increased in order to accomplish the first step. This may require not only a catalyst, but also an effective reservoir of reducing agent to keep the chemical potential high even after some reduction has taken place. However, direct oxygen analysis (as well as oxygen by difference) of pretreated coals shows that all of the pretreatments tested here, including baseline

conditions, reduce the O-content of Zap lignite from 20 wt% to about 15.5 wt% and for the Wyodak coal from 18 wt% to about 14 wt%. Similarly, very little difference with respect to hydrogen content was observed between the different pretreatments.** It is interesting that the pretreatment conditions employed did not accomplish the additional deoxygenation that was desired, but nevetheless did result in modest improvements in liquefaction yields.

The modest CO pressure used here (500 psi cold) evidently did not provide sufficient reduction potential to drive the deoxygenation. Since the reducing potential of the system is defined not merely by the CO partial pressure, but by the [CO]/[CO$_2$] ratio, the potential may also be increased by chemical or physical removal of CO$_2$. We had hoped that the high solubility of CO$_2$ in the near-critical aqueous pretreatment medium would provide for effective removal of the CO$_2$ from the vicinity of the reaction site. However, it was clearly not enough to bring about the desired reaction. An additional tactic that might be useful would involve generating a fluctuating density within the reaction medium. This fluctuation would produce a sort of "breathing" action that would repeatedly wash CO$_2$ and other reaction products out of the coal pores, and wash in fresh CO. In a static system where the medium in near critical, such density fluctuations could be produced by having a side-arm containing the near-critical fluid, and then imposing a cyclic temperature variation on this side arm (while the main reactor is held at constant temperature). Since the compressibility of liquids becomes very high near the critical point, only small variations in temperature would be necessary for substantial variations in density to result in the main reactor body.

Alternative modifications could involve addition to the pretreatment of some condensed-phase reservoir (e.g., a hydroaromatic), or perhaps the use of hydroquinones and other electron transfer agents under nominally non-aqueous (no added water) conditions. Such conditions are, after all, more representative of current liquefaction practice, and would avoid some of the experimental problems known to be associated with excessive water in liquefaction systems. We also believe that it would be helpful to the goal of enhanced oxygen removal during pretreatment (as well as of fundamental interest) to make some actual de-oxygenation rate measurements using some surrogate for the coal phenols (e.g., cresol and/or xylenol mixtures). However, all of these modifications are beyond the scope of this project, and there will be no opportunity to test them before completion of the project.

Lim et al.[17] have reported results from a similar effort to improve liquefaction yields by means of a CO/H$_2$O pretreatment. The have chosen to operate at slightly lower temperature and higher CO pressure, apparently projecting that more is to be gained by doubling CO pressure (e.g., from 400 to 800 psi cold) than is to be lost by decreasing the temperature 20 to 30°C and thereby lowering the vapor pressure of water by ~600 psi. In general terms their results appear to be similar to those described here: modest improvement in subsequent liquefaction yields, but no increase in pretreatment oxygen loss.

** The relative invariability of oxygen loss under various short-term pretreatment conditions observed here is consistent with the results reported by Loo and Ross.[16]

At this point, we can summarize our general conclusion for enhanced oxygen removal pretreatment using CO/H_2O. Without substantial improvement in the pretreatment benefits of added electron-transfer agents, we believe the prognosis for them being a practical pre-additive in an aqueous pretreatment scheme is not good. The improvements resulting from the pretreatment conditions we have tested thus far are significant, amounting to a 9 wt % (maf) increase in hexane-soluble material (a ~20% improvement on a base-case hexane-soluble yield of 46%). However, the 20% improvement noted above was not with the hydroquinone or TAME, but with promoters already known to be effective under liquefaction conditions (donor solvent) themselves, and already exploited in that context. Furthermore, even if the CO/H_2O/electron-transfer-agent had given this 9 wt % improvement in hexane solubles (and a corresponding) increase in distillate yield, it would remain to be seen whether this could provide any real process advantage, given that the pretreatment conditions are now not greatly lower in temperature/pressure severity than the liquefaction itself. We were well aware at the beginning of this project that the pressure and temperature requirements for straight CO-water systems severely limit their utility as liquefaction approaches per-se, and that significant catalysis would be necessary to overcome these limitations for a CO-water pretreatment. We had obviously hoped to overcome these limitations.

PMRTA Analyses of Pretreated Coals

Pretreated coal's were analyzed by the proton magnetic resonance thermal analysis (PMRTA) by Drs. Leo Lynch and Richard Sakurovs at CSIRO, Australia. For PMRTA, we selected a set of pretreated coals for which the subsequent liquefaction yields varied most widely. The objectives were to (1) determine the temperature-dependent molecular mobility of the pretreated coals to learn how this may correlate with their susceptibility to liquefaction, and (2) obtain information relevant to the question of whether the benefits observed arise because of pre-existing crosslinks that are broken by the pretreatment, or because crosslinking that takes place during liquefaction itself has been inhibited.

Figures 1 and 2 show the results of PMRTA analysis of variously pretreated Wyodak coal and Zap lignite. The figures show the variation of the $M_{2T}16$ parameter with temperature. For the Wyodak coal, the minimum impact ($\Delta M_{2T}16$) was provided by baseline pretreatment 350°C for 53 minutes in CO/H_2O only and the maximum impact was obtained from CO/H_2O with added sodium carbonate or ferrous sulfate and carbon disulfide. A larger number of samples of the pretreated Zap lignite were sent because control of the liquefaction conditions was more precise in that series of runs. In fact, included with the pretreated Wyodak coals were a pair of samples where the pretreatments were nominally identical but the hexane-insoluble yields of the subsequent liquefactions were substantially different. The purpose here was to use this pair as an additional test of how closely the liquefaction yields would be paralleled by the PMRTA mobility measurements. The pretreatment conditions, liquefaction yields, and PMRTA values are shown in Table 3.
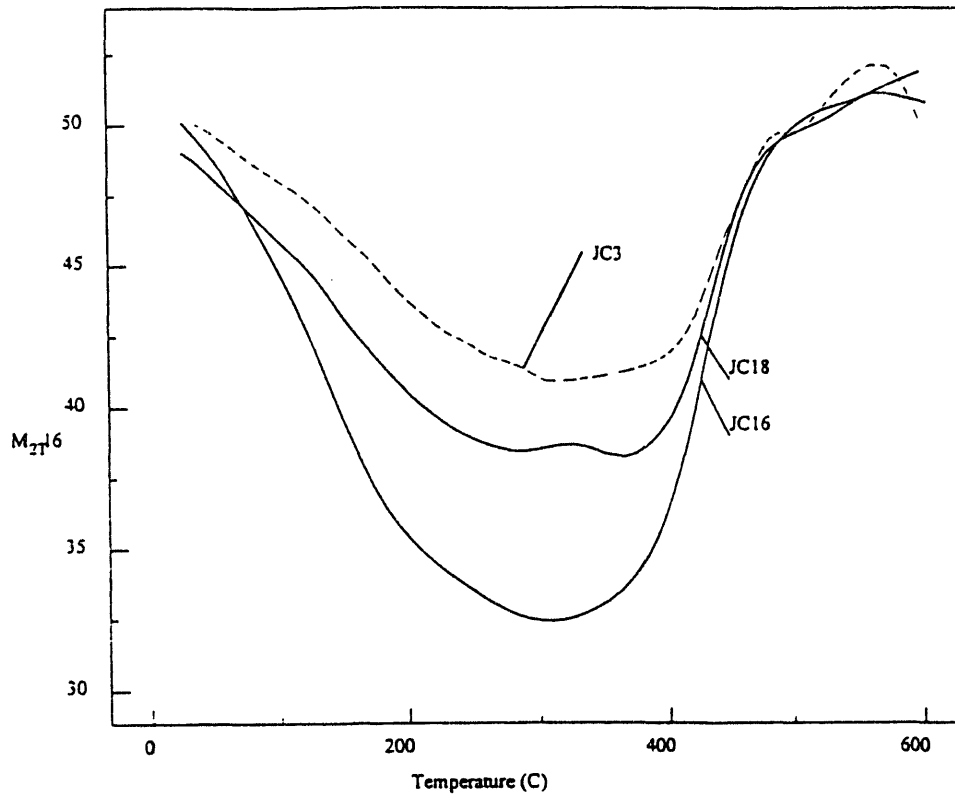
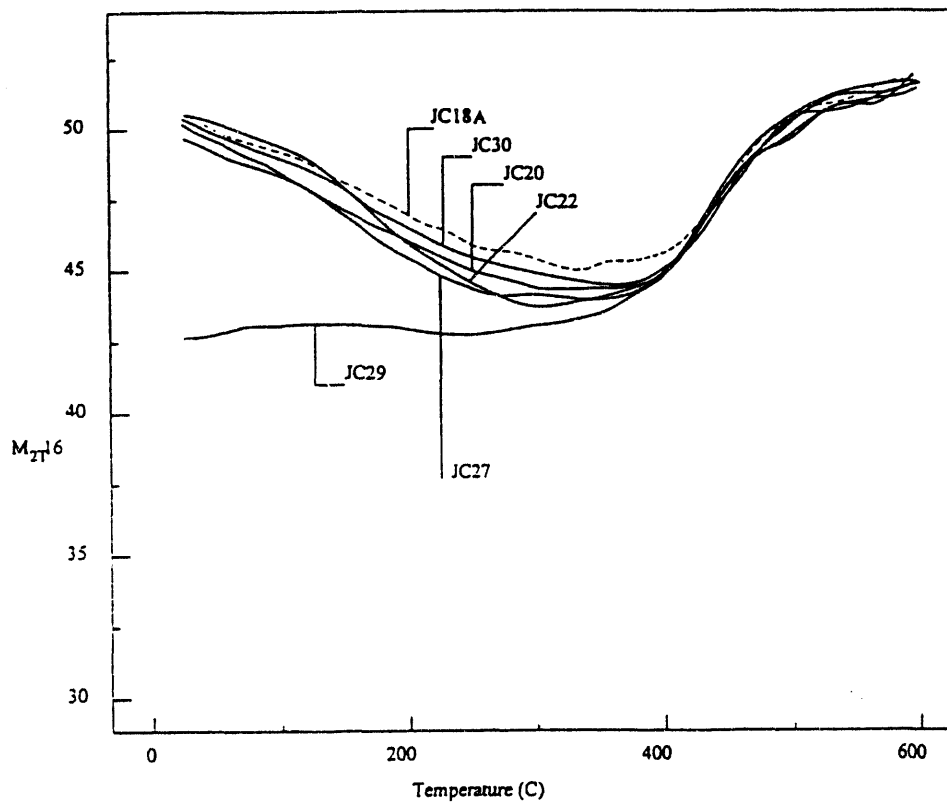Figure 1.   PMRTA analysis of variously pretreated Wyodak coals.

Figure 2.   PMRTA analysis of variously pretreated Zap lignites.

Table 3

Comparison of Wyodak and Zap Pretreatment Conditions, Liquefaction Yields, and Minimum PMRTA Values.

Sample No.	Pretreatment Conditions [a]	(100 - Hex Insol)[b]	Minimum M_{2T} Values	
Wyodak			$M_{2T}16(min)$ [c]	$M_{2T}40(380°C)$ [d]
	Untreated [a]	—	39.9	100.2
JC3 (blank)	CO/H2O only.	47.5	40.9	107.1
JC16	$Na_2CO_3/HQ/CS_2$	55.2	32.4	90.1
JC18	$Na_2CO_3/HQ/CS_2$	49.5	38.2	103.0
Zap Lignite				**$M_{2T}40$ (300°C)**
	Untreated	—	42.5	114.6
JC18A (blank)	CO/H2O only.	46.6	45.0	124.8
JC20	Na_2CO_3	48.5	44.4	121.3
JC22	Na_2CO_3/HQ	48.5	43.7	117.9
JC27	Na_2CO_3/CS_2	55.2	44.1	128.0
JC29	$CS_2/FeSO_4$	56.4	—[f]	—[f]
JC30	$Na_2CO_3/TAME$	50.3	44.7	124.8

a. "Untreated" coal was tested as received from the Argonne Premium Coal Sample Bank. The blank samples were pretreated at 350°C for 53 minutes in water with 500 psi (cold) CO pressure without any *additional* reagents. The other additional reagents used were sodium carbonate (Na_2CO_3, 0.1 wt% of raw coal), carbon disulfide.(CS_2, 2.5 wt% or 6..3 wt% of raw coal), ferrous sulfate ($FeSO_4$, 2.5 wt% of raw coal), hydroquinone (HQ, 5.0 wt% of raw coal), and tetrakis(dimethylamino)ethylene (TAME, 4.8 wt% of raw coal). No liquefaction tests were performed on the untreated coal: previous work had shown that pretreatment in water alone at 350°C has a beneficial impact on the subsequent coprocessing (i.e., liquefaction in a poor solvent) of the Argonne Wyodak and Zap coals.

b. 100 minus the wt fraction (maf) insoluble in a fixed volume of hexane was taken as the measure of liquefaction effectiveness, and as a rough indicator of the distillate yield.

c. $M_{2T}16$ and $M_{2T}40$ are relaxation parameters from broad-band solid state nmr signals. These parameters are indicators of molecular mobility in the coal structure that provide a measure of the degree of softening as the coal is heated in the spectrometer. $M_{2T}16$ values range from near 50 for a normal organic solid (or coal at room temperature) to near zero for a fully fused pitch.

d. The values of M_2T40 shown in this column are only local minima for the value of this parameter, achieved at about 380°C in the case of the pretreated Wyodak samples.

e. The Zap samples did not show even a consistent local minimum in the 300 to 400°C range, so the values at 300°C, where the most differentiation among the various pretreated samples was seen, have been included in this table.

f. Sample JC29, which was pretreated with carbon disulfide and ferrous sulfate, appeared to have ferromagnetic materials that completely blocked the ability to use the M_{2T} values as measures of molecular mobility.

The data in Table 3 show that there is a much larger range of mobility for the Wyodak than there is for the lignite, consistent with the general trend of greater softening with increasing rank. (*All* of the M_2T16_{min} values for Wyodak are lower than *all* of the M_2T16_{min} values for the Zap.) Furthermore, although the range of samples is limited, there is an excellent correlation between the liquefaction yields and both sets of minimum M_2T values for the Wyodak, as shown in Figures 3 and 4. The correlation was just as good with M_2T40 as it was with M_2T16, even though the interpretation of the M_2T40 results in terms of gross molecular mobility is less straightforward. We note that the pretreatment conditions are nominally identical for Wyodak samples JC16 and JC18, but the liquefaction yields are quite different. Figures 3 and 4 show that the difference in liquefaction yields is exactly paralleled by the difference in M_2T values, indicating (at least in this small set of samples) that both the batch liquefaction and the PMRTA measurements are more reliable as indicators of the impact of pretreatment than the pretreatment was reporducible. This was somewhat surprising: we had projected, that the differences in liquefaction yields between Samples JC-16 and JC-18 was most likely the result of differences in *liquefaction* reactor heating rate and therefore in net severity, but it seems that it was the pretreatment that was more variable. The factors determining the effectiveness of the pretreatment are evidently more ephemeral in nature. We also note that the minimum M_2T16 value for the pretreatment blank (CO/H_2O, no other added reagents) is actually *higher* than that for the untreated Argonne Wyodak, even though we have previously found that even this basic pretreatment condition improves subsequent liquefaction (albiet in a poorer liquefaction solvent, Maya atmospheric bottoms).

For the pretreated Zap samples, the degree of mobility was much less, and the correlations between liquefaction yields and M_2T values was very poor. Figure 5 shows the essential absence of any correlation with M_2T16 values (although elimination of the point at 43.7 and 48.5 provides a correlation coefficient of 0.7). Figure 6 shows what appears to be a modest correlation between hexane-soluble liquefaction yield and M_2T40 (correlation coefficient 0.7), but actualy depicts a trend opposite to that observed for the pretreated Wyodak samples; that is, the liquefaction yield increases with *increasing* M_2T values. We suspect that this latter correlation is simply spurious, resulting from the very small extent of fluidity development exhibited by either the raw or the pretreated lignite. While it is *possible* that since liquefaction of this lignite normally takes place without benefit of very much thermal relaxation (i.e., melting or other phase change) that whatever small amount of thermal relaxation does occur is not large enough to dominate a correlation, we believe that in fact the apparent inverse correlation between molecular mobility and liquefaction yield shown in Figure 6 for pretreated lignite is accidental.

The temperature dependence of increased molecular mobility allows us to answer, at least provisonally, whether pretreatments are beneficial to liquefaction primarily because they decrease crosslinking in the starting coal, or because they inhibit crosslinking during liquefaction. The PMRTA data in Figure 3 for the Wyodak coal reveal that the mobility of all of the pretreated samples is similar at room temperature, but by the time 200°C is reached, the sample that shows
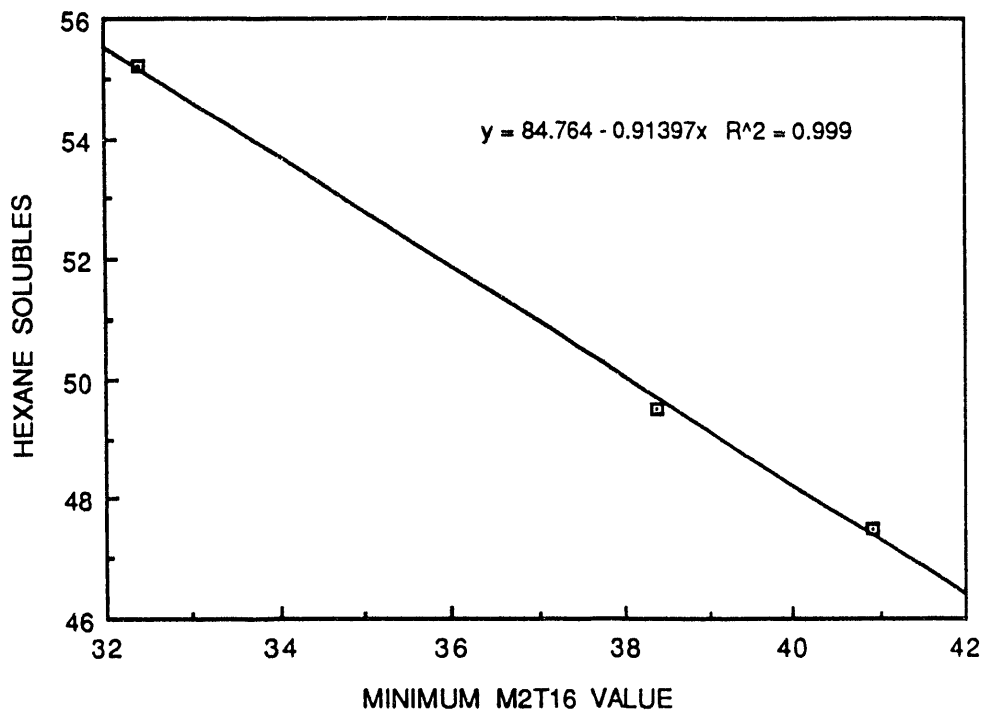
Figure 3. Correlation of conversion of Wyodak coal with minimum M2T16 values.
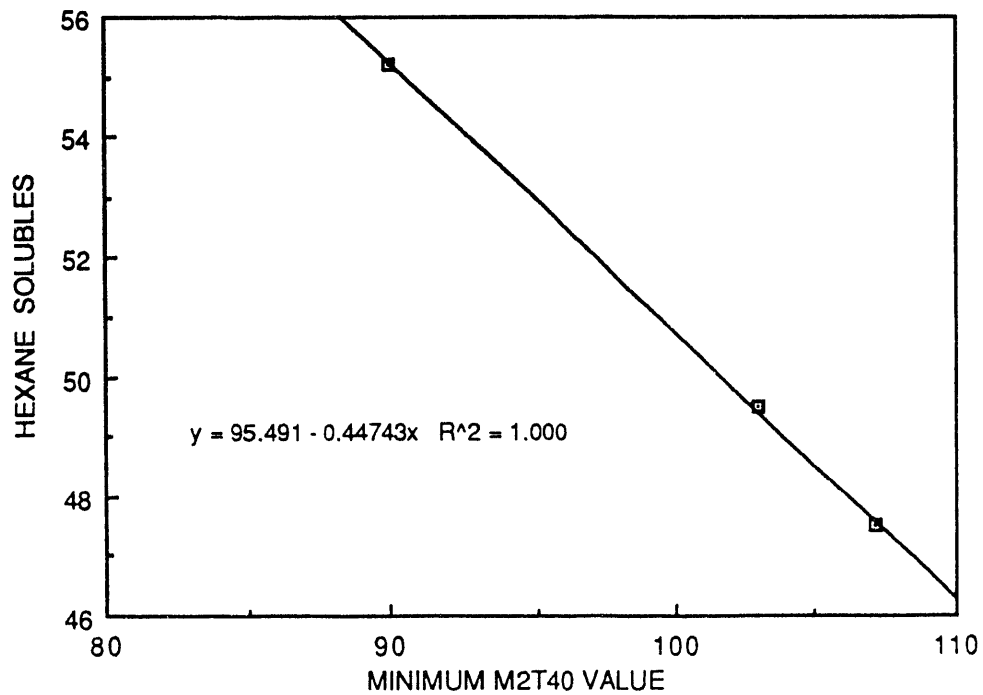

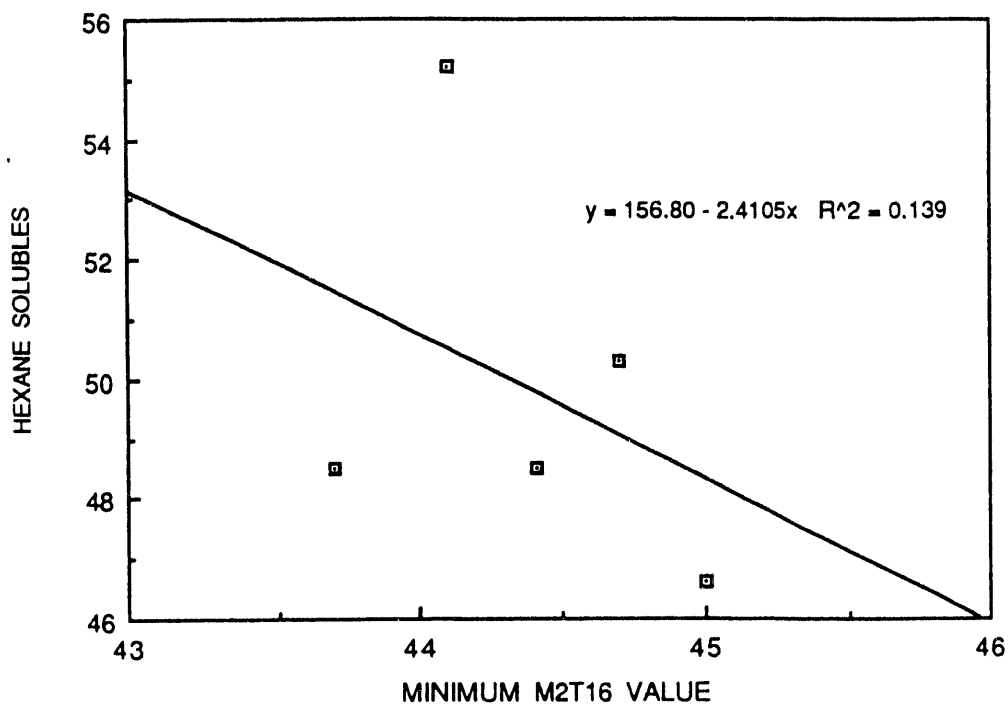Figure 4. Correlation of conversion of Wyodak coal with minimum M2T40 Values.

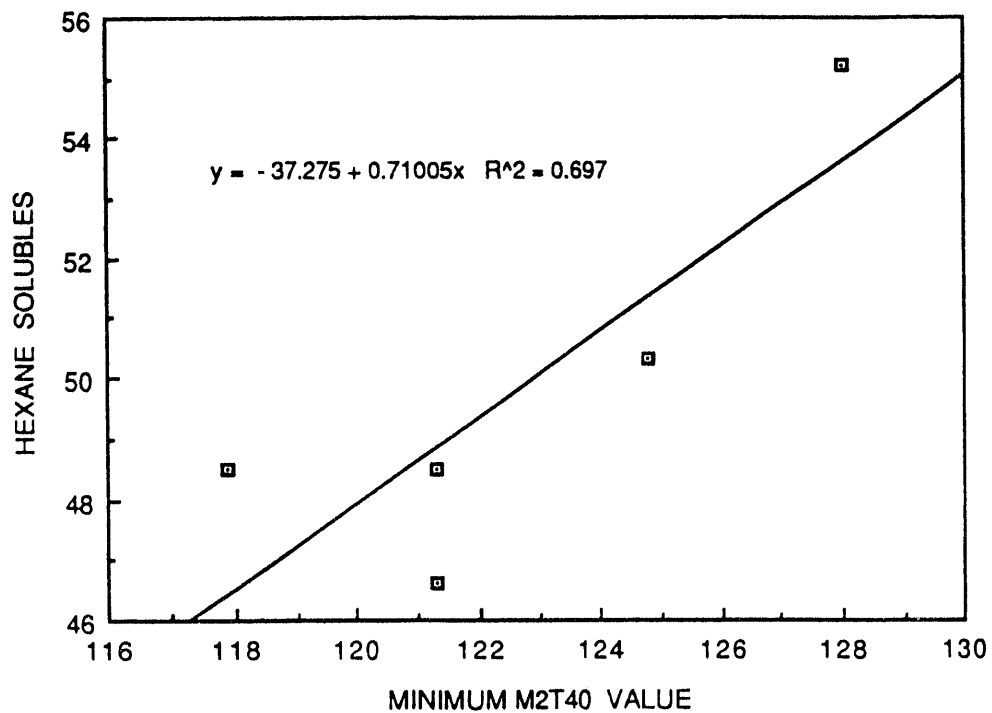Figure 5. Correlation of conversion of Zap lignite with minimum M2T16 values.

$y = 156.80 - 2.4105x \quad R^2 = 0.139$

Figure 6. Correlation of conversion of Zap lignite with minimum M2T40 values.

$y = -37.275 + 0.71005x \quad R^2 = 0.697$

the best liquefaction yield is already showing substantially higher mobility. In contrast, by ca. 400°C, when the mobility is rapidly decreasing, there is little differentiation among the samples. Differentiation that is seen already at 200°C, when little hydrogenolysis (or homolysis) of coal linkages is thought to take place, suggests that the pretreatment has removed some of the original crosslinks either covalent or hydrogen-bonded in the coal. Similarly, confluence of the curves at about a temperature of 400°C suggests that pretreatment has rather little impact on the high-temperature crosslinking that dominates in the absence of a good liquefaction solvent.

Development of a TGA-Based Simulated Distillation Technique

The impetus to develop an improved technique for assessing small-scale batch liquefaction products came principally from three observations. First, the solvent solubility criteria commonly used in batch liquefaction studies are experimentally cumbersome, somewhat operator sensitive, and not exactly relatable to volatility, the main criterion that defines process streams in liquefaction itself. Second, substantial care is typically required to minimize physical losses of material during transfer following the liquefaction test iteslf, and this problem becomes more severe as the scale of the test decreases. Third, mass transport limitations (inadequate mixing and hydrogen starvation) tend to become more severe as the size of the microautoclaves decreases. A test that would be rapid and realiable and address these conversion and assessment limitations would be very useful as a screening tool in this and other studies.

Our initial goal for this TGA was to achieve an automated, convient, and process-relevant volatility measure of small scale batch liquefaction yields. The design of our apparatus was guided by the following considerations.

(1) In order to make the analysis more convenient and to eliminate the problem of non-representative sampling in the transfer of small-scale heterogeneous product mixtures, it was desirable to have the apparatus large enough so that the entire sample could be subjected to the "distillation," *prefereably in the original liquefaction reactor*.

(2) So as to provide a reasonable match to ASTM distillation data and also minimize analysis time, provision shold be made for ability to tailor the heating rate, gas flow rate, vessel shape, and sample size.
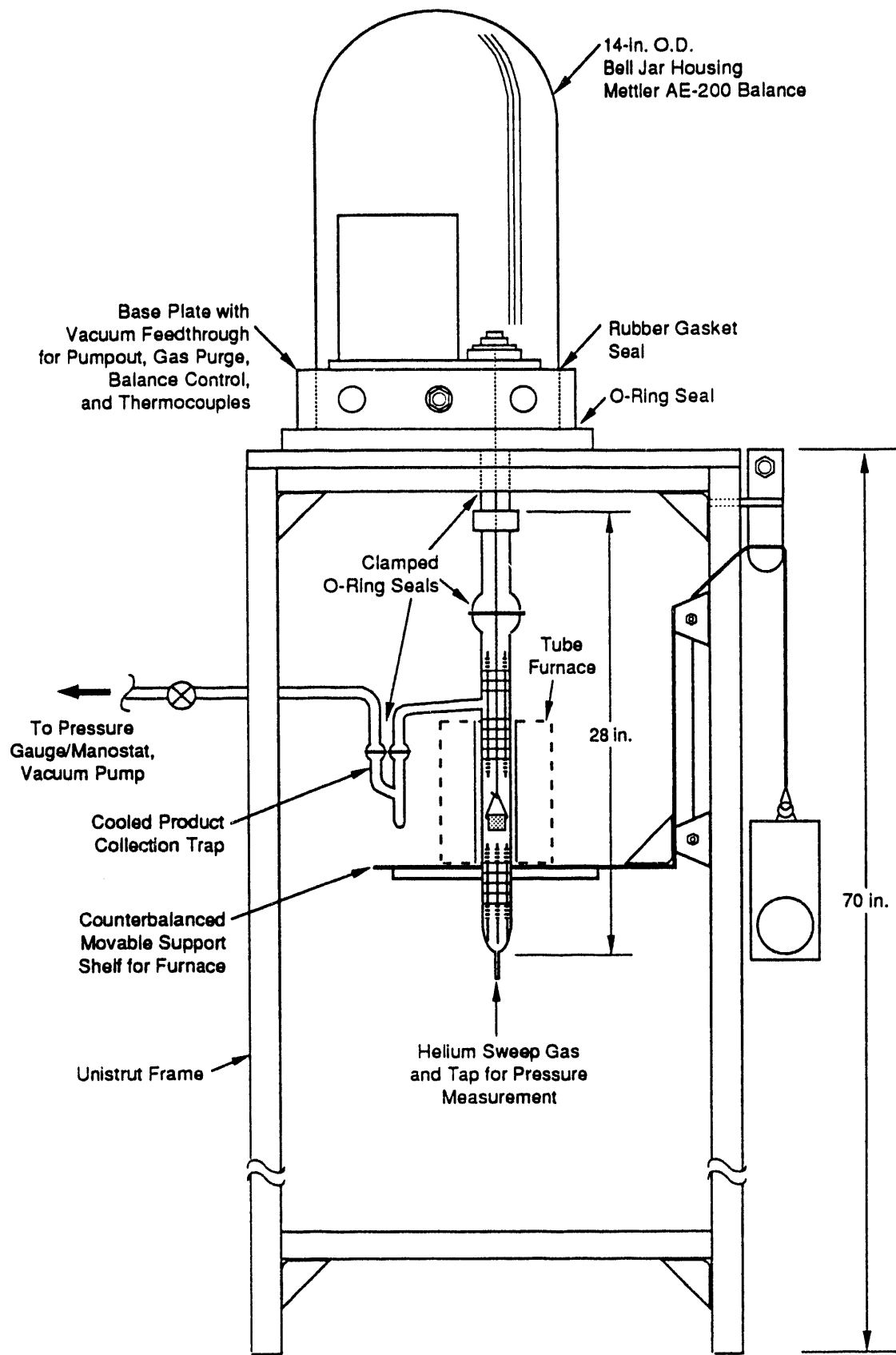
Mondragon and Ouchi published detailed test results in 1984 showing that for materials in the boiling range up to vacuum gas oils, a TGA sample holder (designed for use with small-scale commercial instruments and a ~15-mg sample size) with a restricted outlet provides TGA weight-loss curves that closely simulate an ASTM distillation.[18] For vacuum gas oils and higher boiling materials, an open pan at reduced pressure (~1 torr) was found to work best. We presume that this work of Ouchi's was also part of the basis for the TGA simulated distillation approaches now being used or explored at HRI, Consol, and University of Kentucky. All of these approaches apparently use a limited sample size (~10-20 mg), and are therefore subject to difficulties if representative sampling is a problem; they are best suited for analysis of homogeneous products

(i.e., filtered liquids). Because our interest was in finding a more convenient and process-relevant diagnostic for small scale batch liquefaction products, we decided to use an approach where *all* (or at least a large fraction) of the product can be subjected to the analysis, minimizing problems with non-representative sampling.

The TGA apparatus we have assembled incorporates a Mettler force-cell balance (200 gram capacity and 0.1 mg sensitivity, model AE-200-SE) to provide a high capacity TGA capability. The general construction of the TGA apparatus is shown in Figures 7 and 8, which are roughly to scale. The bell jar housing the Mettler AE-200-SE balance is supported by a six-foot unistrut frame which rests on the laboratory floor and is bolted to the wall via shock-absorbing connections. The temperature controller (Eurotherm Model 808) and computer (MacIntosh Mac Plus) and balance control are located on a separate bench. Flow control is provided by Tylan mass flow controllers. The furnace is raised and lowered by means of a counterweighted, tracked shelf. Full disassembly of the furnace tube, heat shields, and thermocouple is painstaking, requiring one to two hours, however the system has proved quite convenient for normal use; loading of a sample and pumpdown requires only 5 to 10 minutes.
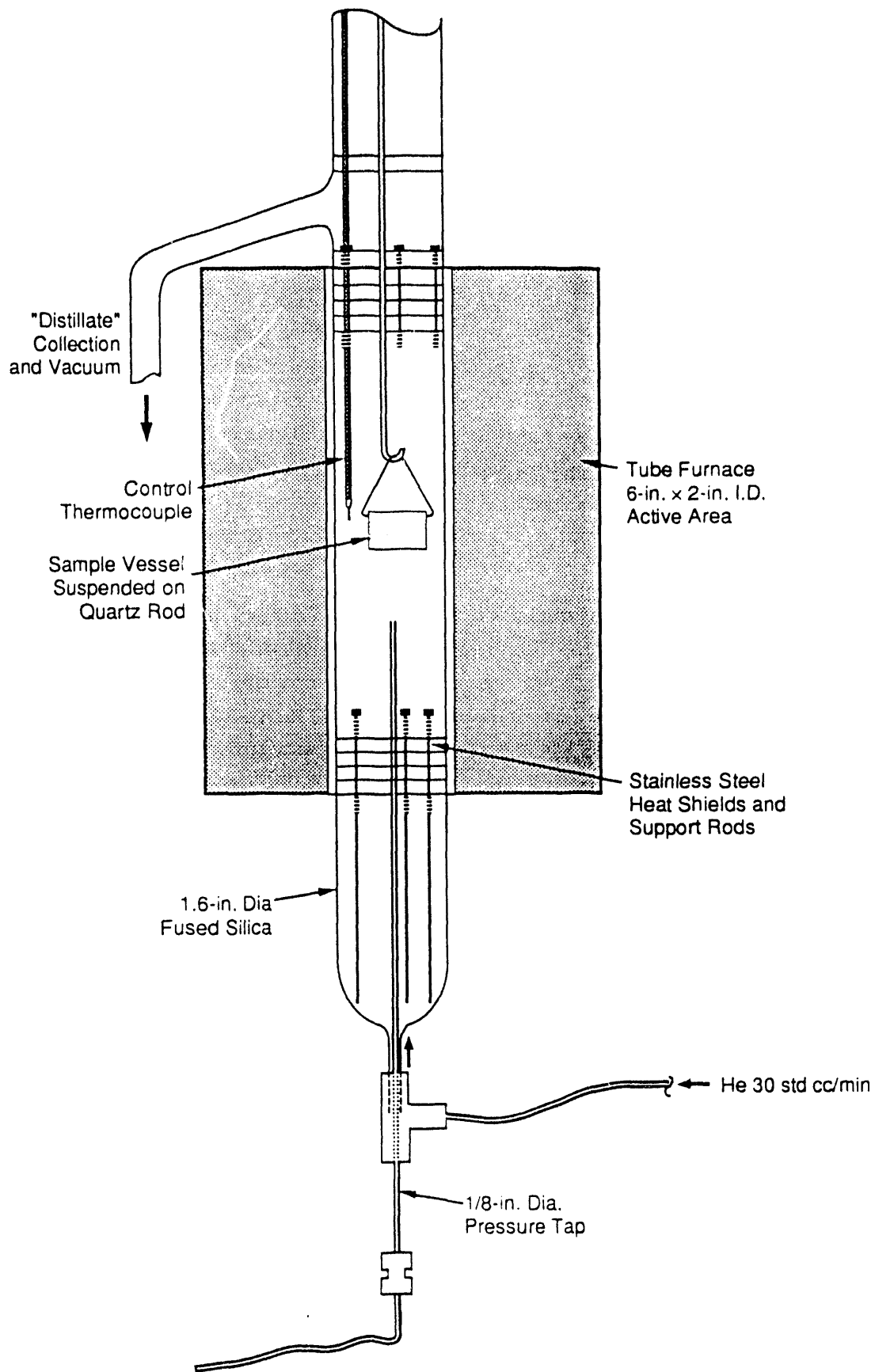
As can be seen in Figures 7 and 8, the control thermocouple is located outside the distillation vessel, about 3 mm away from its outside wall. Although the heated section of the tube is well heat-shielded, one expects a significant temperature differential between the inside and outside of the vessel. The size of this temperature differential depends on the size and mass of the distillation vessel, the thermal conductivity of the sweep gas, the heating rate, and the temperature. The location of the thermocouple is a compromise between easing control by being close to the heat source, and minimizing the temperature differential by being closer to the vaporizing liquid. Use of separate control and measurement thermocouples is a possible future modification that would allow us to effectively eliminate this temperature differential. However, at present we have chosen to impose linear temperature ramps on a single control thermocouple and to determine, in "blank" experiments in which no weight-loss measurements are made, the temperature lag between the control thermocouple and an extra thermocouple inside the distillation vessel (in the liquid layer and touching the inner wall of the vessel). The experiments show, as one would expect, a variable lag, large at first, when heating is begun, and smaller and fairly constant as a temperature of about 150°C is passed. This variable temperature lag is then used to adjust the control thermocouple readings during the actual run to reflect the actual temperature within the liquid inside the distillation vessel. Thus the establishment of conditions that suitably mimic the ASTM distillation can be a painstaking procedure, requiring the recording of a "blank" for every temperature program that is tested. However, once a suitable heating regimen is established, all of this adjustment can be automated.

We performed extensive tests on the TGA apparatus in order to define operating parameters that would allow us to satisfactorily mimic an ASTM vacuum distillation of a heavy-oil/resid mixture as a test for providing process relevant distillation data for microautoclave products. These

14-in. O.D.
Bell Jar Housing
Mettler AE-200 Balance

Base Plate with
Vacuum Feedthrough
for Pumpout, Gas Purge,
Balance Control,
and Thermocouples

Rubber Gasket
Seal

O-Ring Seal

Clamped
O-Ring Seals

Tube
Furnace

To Pressure
Gauge/Manostat,
Vacuum Pump

28 in.

Cooled Product
Collection Trap

70 in.

Counterbalanced
Movable Support
Shelf for Furnace

Helium Sweep Gas
and Tap for Pressure
Measurement

Unistrut Frame

CM-2869-1

Figure 7.   Large capacity vacuum TGA apparatus.

"Distillate" Collection and Vacuum

Control Thermocouple

Sample Vessel Suspended on Quartz Rod

Tube Furnace 6-in. × 2-in. I.D. Active Area

Stainless Steel Heat Shields and Support Rods

1.6-in. Dia Fused Silica

He 30 std cc/min

1/8-in. Dia. Pressure Tap

CM-2869-2

Figure 8. Heated portion of vacuum TGA apparatus.

tests involved varying the heating rate, sweep gas and sweep-gas flowrate, pressure, thermocouple location, pressure sensor location, and reactor- or distillation pot geometry. Our goal was first to be able to reproduce the yield of material that is non-distillable at 1050°F AEBP (as HRI does with its 15-mg scale TGA), and second, to reproduce as much of the D-1160 distillation curve for the vacuum gas oil fraction as convenient. We feel this latter goal is worthwhile, since it will provide a diagnostic of liquefaction chemistry that has more information than a single-point parameter (i.e., the 1050°F+ fraction). It is also desirable, in order to meaningfully assess (i.e., discriminate among) materials that are high in materials that are normally considered non-distillables (i.e., 1050°F+), to provide sufficiently good mass transfer through the sample layer and out of the distillation pot that the technique can distill deeply into the "resid" fraction. This will provide maximum additional information about the volatility of material still heavier than a 1050°F end point.

Tests to establish a suitable heating regimen have involved the use of a heavy gas oil (635°F to 977°F), which we obtained, together with D-1160 data and simulated distillation data, through the courtesy of the CANMET Ottawa laboratory. All of our initial tests showed the fractional weight loss at any adjusted (i.e., "true") temperature to be substantially less than estimated from ASTM correlation. As Ouchi and coworkers have previously demonstrated,[18] two readily available parameters that can be used to change the weight loss at a given temperature are the heating rate and the length of the neck of the distillation vessel. Accordingly, we first decreased the heating rate from our initially chosen 10°C/min to 5°C/min (the slowest heating rate we find convenient). When this decrease in heating rate proved insufficient, we changed the sweep gas from argon to helium, in order that the increased diffusivity of helium would increase that mass transport of sample vapors out of the neck of the distillation vessel. When these measures did not easily lead us to a substantially better match of the D-1160 curve, we shortened the distillation vessel from an aspect ratio of about 6.7 to a ratio of 0.7, using a stainless steel vessel (shown in Figures 7 and 8) machined to have inside dimensions 1.5-cm. height × 1.9-cm. id.(total volume 3.2 cc). We had wished to avoid this change in order that we could suspend the entire high pressure reactor [3.7-in. height × 0.75-in. od × 0.125-in. wall (9.4 cm × 2.1 × 0.32 cm, ~150 grams, ~12 cc volume)] in the TGA and distill directly from it. However, in the face of having to arrange for a more complicated gas flow path in order to meet the original goal, we have for the present opted to use these low aspect ratio vessels, which are still large enough to accommodate the entire reaction mixture from 0.5 g of coal and 1g solvent. [Note that the increased diameter of these low aspect ratio vessels means that the cross section area is increased 2.25 fold. Thus a given weight of product will have a total depth in the pot that is decreased by a factor of 2.25 (to ~0.5 cm for a 1.8-g sample) and a characteristic diffusion time (should vapor transport through the liquid layer be primarily diffusion limited) that is decreased about 5 times.]

An additional difficulty that had to be overcome with a "liquid" layer in the distillation pot that is fairly thick is that of bumping, or splattering. The use of marble boiling chips was, by itself, not sufficient to prevent splattering. We achieved a satisfactory solution to this problem by

placing a 16-mesh screen, formed into the shape of a shallow inverted cone, over the top of the pot. This screen prevented any significant splatters from leaving the distillation pot, without substantially inhibiting vapor transport. When all of the above modifications had been made and the TGA parameters adjusted, we obtained the test results described below.

Figure 9 shows the weight-loss curve for a 2:1 mixture of tetralin and heavy oil (1.3, 0.65 grams), simulating a whole-product mixture of a liquefaction experiment. At this heating rate and pressure (heat rapidly to 80°C, hold for 30 min., ramp to 500°C (1336°F AET at 2.5 torr of He) at 10°C/min), and with the HGO having an IBP of 635°F, a distinct plateau separates the tetralin loss from the heavy oil distillation. The lower portion of this curve matches very closely with the CANMET ASTM correlation curve. (Note that with the shortened distillation vessel described above, the slower heating rate is not necessary; 10°C/min also provides quite satisfactory results.)

The final test mixture we used was a mixture of tetralin and a very heavy Wilsonville recycle vehicle (Black Thunder, Run 263, 63% non-volatile at 1050°F AEBP). The purpose of performing these additional tests was to determine whether the same set of parameters that worked for a heavy but fully distillable liquid, also allow us, for a material containing a substantial amount of non-distillables, to match ASTM data *and* distill deeply into the 1050°F+ fraction. Figure 10 shows in fact that at a TGA temperature corresponding to an AEBP of 1050°F, namely 353°C, we observed about 65% weight loss, almost 30 wt % greater than the Wilsonville data. Subsequent conversation with Charles Cantrell of Southern Company Services revealed that in fact the 0.1 torr distillation regimen used at Wilsonville involved cutting the heat to the distillation vessel shortly after reaching 600°F (316°C) because of concern that the weight loss after that point would have an excessive contribution from pyrolysis), but that substantial weight loss would be observed at their end-point if that temperature was simply held for a longer time.

To address this concern about possible pyrolysis in our TGA simulated distillation, we obtained a field ionization mass spectrum (FIMS) analysis of the Run 263 sample. The series of spectra obtained during the 4°C/min heating from 29 to 446°C shows that no significant intensity at masses lower than 300 Daltons was observed at probe temperatures above 300°C, all the way up to the maximum temperatures used in the analysis (446°C), which is well beyond the 353°C TGA vessel temperature that corresponds to an AET of 1050°F. The absence of any small fragments at temperatures above 400°C in the FIMS probe is all but conclusive evidence that there was essentially no thermal decomposition during the vacuum evaporation of this sample, and strongly indicates there was also very little decomposition during TGA simulated distillation *at least* up to ca. 350°C. (Note that in the TGA method, 353°C is the actual pan temperature: there is no differential between a distillation vessel temperature and a refluxing vapor temperature as there is in a normal distillation.) In any case, it is clear that not all 1050°F+ fractions are equal in terms of actual cut point, and that the use of any particular heavy fraction as an absolute standard for testing this method may not be a completely definitive test. Therefore, it will be very useful to obtain from researchers at Consol a sample of the distillation standard they are now preparing and to use it at least as a *relative* standard.
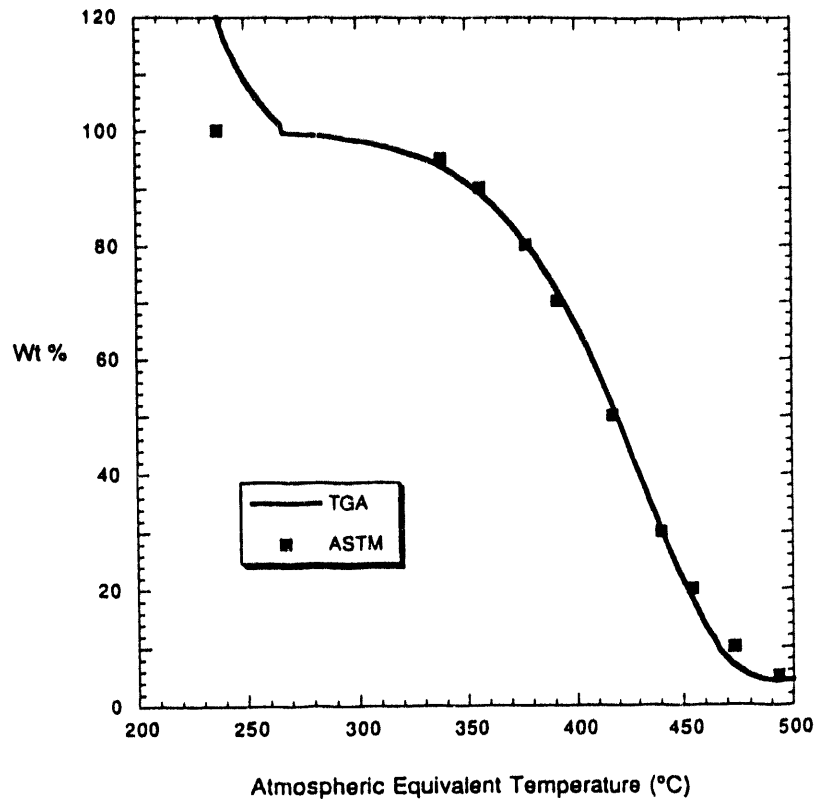
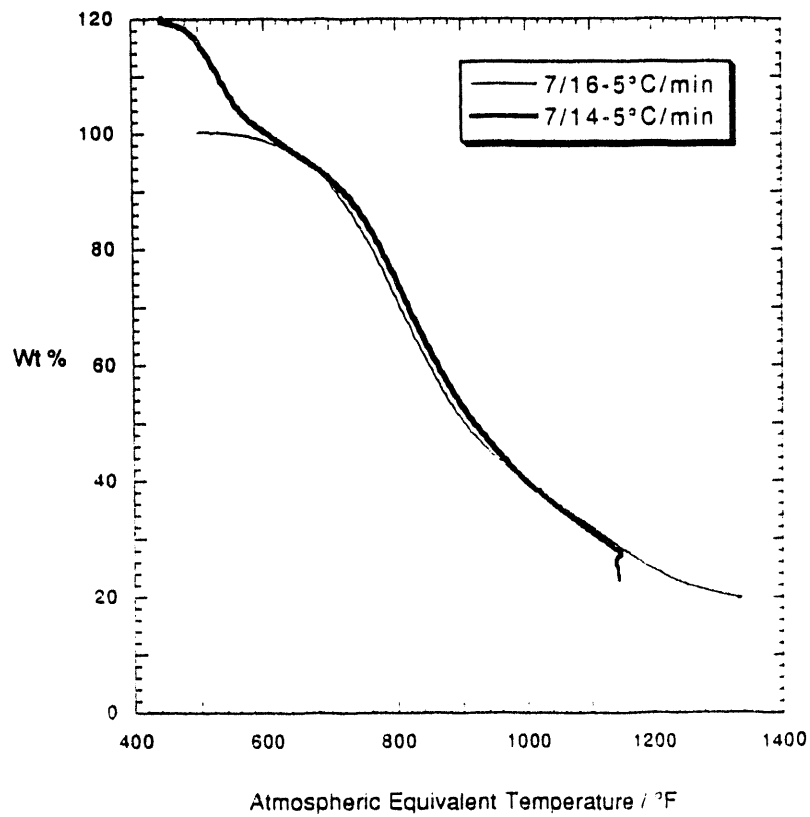Figure 9. Comparison of TGA of CANMET HGO 313 at 10°C/min with ASTM correlation.

Figure 10. Two TGA simulated distillation runs of a mixture of tetralin and a Wilsonville Run 263 recycle vehicle containing 63 wt% of nominal 1050°F+ material.

The questions of comparison with a "true" ASTM heavy-liquid/resid mixture aside, it seems clear that the version of a TGA-simulated distillation method we have developed here will be very useful, particularly for measuring the volatility distribution of small-scale, *unfiltered*, batch liquefaction products. We have established conditions where a simulated whole products (that is, mixtures of the liquefied coal, the liquefaction solvent tetralin, and the insoluble mineral and organic matter) reliably show a clean break in the weight-loss curves at a weight corresponding to 100% removal of the solvent, and at higher temperatures match the ASTM distillation of the remaining heavy gas oil product within 2 to 3%. Under exactly the same conditions, tests using mixtures of tetralin and a still heavier coal product (Wilsonville recycle vehicle Run 263 B-C) containing 30-60 1050°F+ material were also successful. However, because of some arbitrariness in the end-point definintion for the Run 263 material, it was not possible to determine whether we could also match, with the same set of TGA parameters, the true "ASTM" volatility of the heavier coal product. In fact, Mondragon and Ouchi's earlier work[18] has already illustrated that a TGA weight loss method needs to have somewhat different distillation vessel dimensions and/or TGA parameters (temperature ramp rate, etc.) to *exactly* match ASTM data for different boiling range materials. What we have shown here is that this TGA method can accept sample sizes of at least 1-2 g and provide volatility data that can match ASTM data very closely over a substantial part of the heavy distillate range and is *relatable* to ASTM distillation over the entire range. We believe, therefore, that it will be a valuable supplement to, if not replacement for, the solvent solubility tests normally used as the sole measure of product yield and quality for small scale batch liquefaction products.

SUMMARY AND CONCLUSIONS

Pretreatment of Wyodak and Zap Coals

Pretreatment and liquefaction tests of promoters for CO/H2O pretreatment of low-rank coals provide the following results.

- The addition of 0.1 wt% Na_2CO_3 (on the added water) yields a small (~2 wt%) improvement in the amount of hexane insolubles.

- By itself, the addition of 6.3 wt% CS_2 (on the raw coal) does not lead to any improvement in the hexane insolubles.

- The addition of 2.5 wt% CS_2 (on the raw coal) together with base leads to a substantial (~9 wt%) improvement in the hexane insolubles.

- The addition of 2.5 wt% p-hydroquinone (p-HQ, on the raw coal) to a pretreatment system containing either base alone or a base/CS_2 mixture does *not* lead to improvement in the hexane insolubles when compared to the same system without added p-HQ.

- The addition of a mixture of 4.8 wt% TAME (on the raw coal) and 0.1 wt% base leads to a small (1.5 wt%) improvement in the hexane insolubles when compared to the base-only case. TAME is thus slightly more effective than p-HQ, but still less effective than the base/CS_2 mixture.

- All pretreatments tested remove about 25% of organic oxygen.

- We conclude that the benefits of near-critical hydrothermal pretreatment can be augmented by additives such as base, CS_2, and $FeSO_4$, but the specific benefits of hydroquinones are not significant under the conditions tested here. The benefits of CO/H_2O pretreatment can presumably be enhanced further by increasing CO pressure, but the total CO and H_2O pressure, even if the temperature is reduced to 320°C, is still uncomfortably close to that necessary for liquefaction itself.

PMRTA Measurements of Pretreated Coals

Proton magnetic resonance thermal analysis was performed on selected samples of pretreated Wyodak and Zap coals. For Wyodak, a very good correlation was observed between the temperature-dependent molecular mobility and the convertibility of the pretreated coals to hexane-soluble material under subsequent donor solvent liquefaction. For Zap lignite, the degree of molecular mobility developed during heating of the pretreated coals was much lower and there was poor correlation with the liquefaction tests. The increased molecular mobility shown by the Wyodak pretreated coals began appearing at about 200°C, well below temperatures at which significant thermal cleavage of covalent bonds is significant, and also before the temperatures at which the early crosslinking in low-rank coals has been observed. We therefore conclude that the benefits of pretreatment result primarily from the cleavage or disruption of pre-existing crosslinks, either covalent or hydrogen-bonded.

Development of a TGA Simumulated Distillation Technique

At this point all objectives in this portion of the effort have been achieved, except that we are not distilling from the liquefaction reactor itself. We anticipate that the technique will be very useful even with the added step of transferring the contents of a liquefaction reactor ; the potential problem of non-representative sampling should be substantially minimized as long as we use the majority (ca 95%) of the liquefaction sample. We have shown that this technique is suitable for application to heterogeneous samples up to at least 1.5 g, and have established condtions that give weight-loss vs temperature curves that agree within about ±3 % (across the entire boiling range) with true ASTM correlations for heavy distillate material (635 - 975°F) and are relatable to ASTM distillation for heavier materials.

FUTURE PLANS

The project is essentially complete. We have covered most of the range of aqueous pretreatment conditions originally outlined, have demonstrated the utility of an NMR-based molecular mobility measurement for predicting liquefaction yields, and have assembled and developed conditions for operation of a TGA-based simulated distillation technique for sample sizes of 1.5-3.0 grams. A few additional analyses of pretreated coals and the writing of the final report will complete the project.

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Title: Surfactant Studies for Bench Scale Operation

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Contract No.:   DE-AI22-92PC92150

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I.   Abstract

A study has been carried out to examine the effect of a surfactant, sodium lignosulfonate, on the coal liquefaction process to increase coal conversions. A series of coal liquefaction experiments with surfactant addition were conducted in a stirred batch autoclave with 1:2 coal-solvent mixtures with Illinois # 6 coal at temperatures from 300 to 400 $^\circ$C and hydrogen pressures from 1500 to 1800 psig. The treated products were analyzed for overall conversion and the distribution of the converted products into lighter and heavy oil fractions, respectively. The batch autoclave results indicate an increase in coal conversions due to surfactant addition at all processing conditions. The analysis also indicates an upgrading of the product slate for temperatures not exceeding 350 $^\circ$C. An investigation into the mechanism indicates that the surfactant promotes access of hydrogen to coal, and assists in the breakage of crosslinks of the associated coal molecules, which increases the hydrogenation rate and the overall conversion. A continuous flow bench scale test was conducted at HRI utilizing their CTSL process and Shell 317 catalyst at second stage reactor temperature of 430 °C. However, this particular test showed no improvement over the baseline case possibly due to the high activity of the catalyst. or surfactant deactivation at temperatures above 400 °C.

II.   Introduction

The liquefaction of coal is a promising technology for producing alternate fuels that may eventually replace petroleum based fuels. This technology has the implication toward the goal of attaining self-sufficiency in the Nations energy needs. However, in order to make coal liquefaction technology competitive with existing energy sources, high carbon conversion without extensive processing of the coal is desired. It has long been known that the operating conditions (such as solvent type and structure, the hydrogen to carbon (H/C) ratio, temperature, etc.) play a significant role in the dissolution and reaction of the organic matter in the coal. The possible effects of lowering the viscosity and surface tension of the liquid phase in the reactor have mostly been speculated upon but not systematically investigated. Further, the research emphasis in coal liquefaction has recently shifted away from intensive processing to maximize liquid yields toward milder processing to obtain a more economically attractive slate of products. This present work studies the effect of adding a surfactant to the coal liquefaction process in order to explore the possibility of designing an efficient process operable under less intensive conditions and improve distillate quality yields.

A Phase I study[1] using the surfactant approach for milder processing in liquefaction was completed at the Jet Propulsion Laboratory (JPL) in December 1990. This study, though preliminary and of a limited scope, identified sodium lignosulfonate as the surfactant additive which appeared most promising based upon viscosity tests. A few coal liquefaction autoclave test runs carried out with a small amount of the lignosulfonate additive showed an increase in light soluble solids. These preliminary tests also indicated a possible increase in the liquid yields. The present work effort relates to an investigation of surfactant-assisted coal liquefaction with the objective of quantifying the enhancement in liquid yields and the product quality.

The structure of coal has been investigated by many researchers and it is generally agreed to consider coal as a highly crosslinked polymer, which consists of a large number of stable aggregates connected by relatively weak hydrogen bond crosslinks. Coal fragments typically disperse poorly in nonpolar and mildly polar solvents, and tend to agglomerate into aggregates of high molecular weights. The approach was to add a surfactant with an "asphaltene-like" structure to better disperse the particles and prevent them from aggregating. Sodium lignosulfonate surfactant was chosen because it is an oil-compatible colloidal surfactant that is commercially available as an inexpensive by-product from waste paper and pulp processing. At mild processing temperatures it readily disperses in hydrocarbon solvents as molecular units. It is typically used in industry as a dispersion agent for solids, and as an oil-water emulsion stabilizer with free aromatic, cyclic, primary and secondary alcoholic carboxylate groupings. Other researchers[2,3,4,5] have investigated the coprocessing of lignin with coal at high lignin concentrations (lignin to coal ratios from 0.25 to 2.0) at mild processing conditions and have found an improvement in the liquid product and conversion. This work uses a surfactant with structural similarities to lignin at low concentrations, where its addition is intended to modify the coal particle agglomeration.

II.   Experimental

The effect of surfactant addition on coal liquefaction was studied in a series of batch autoclave reactor experiments. The surfactant-assisted coal liquefaction experimental reactor system consists of a Parr series 4500 autoclave and accessories. The reactor consists of a one liter stainless steel pressure vessel with a maximum operation pressure of 1900 psig at 375 °C, or 1750 at 400 °C. The reactor contents are mixed by a belt driven stirrer with a six blade turbine-type impeller. The reactor system has gas lines and flow valves for nitrogen and hydrogen, and a vent line with a burst reservoir. Temperature is controlled by an automatic temperature controller.

The coal being used in this study is Illinois # 6 obtained from the Penn State Coal Data Bank (PSCD) with PSCD designation DECS-2. The coal particle size is -60 mesh and is stored in a sealed, dry container. The coal is used in as-received condition. The solvent used is SRC-2 recycle solvent obtained from Hydrocarbon Research Inc. (HRI). The surfactant is sodium lignosulfonate obtained from Pfaltz and Bauer (Catalogue No. S05950).

The sodium lignosulfonate surfactant was added in concentrations of 0.0, 0.5, 1.0 and 2.0 Wt % additions based on total slurry. The processing temperatures were from 300 to 375°C, with hydrogen pressure at 1800 psig, or 400 °C at 1700 psig. A processing time of 1 hour was used on the majority of runs. Selected experiments were conducted with time as a variable and at a lower pressure. Conversions are reported on a moisture and ash free (MAF) basis and were determined by a mass balance of the amount of coal derived liquid produced and coal slurry filter cake that could be extracted by tetrahydrofuran (THF) after processing. The experimental run procedures and analysis scheme have been presented in detail previously[6,7]. The procedures have been developed over the last year to produce consistent and reproducible experimental results.

The product slurry usually separates into two fractions, the top fraction being mostly liquid, while the bottom fraction contains the major part of the solids. The top fraction is decanted, filtered and put in a collection vessel, and the remaining wet solids are vacuum filtered for 15 minutes to remove the filterable liquids from the filter cake. The filtration is conducted with a buchner funnel with 5 micron pore size filter paper. The filtered liquid is added to the original filtrate. The filtrate and the filter cake are weighed and the mass balance closure during the filtration step is verified.

The filter cake is subjected to a series of extractions to determine the light oil, asphaltenes and preasphaltenes fractions The solvents used for successive extractions are hexanes, toluene and tetrahydrofuran (THF), respectively. All solvents are reagent grade. For the extraction, 10 grams of filter cake are added to 30 ml of hexanes, stirred, and allowed to sit overnight. The slurry is then vacuum filtered using a conical funnel and 2.5 micron pore size filter paper (Whatman 42). The mixture is washed with solvent until the filtrate is clear. The remaining solvent is removed by heating the filter cake in an oven maintained at a temperature of about 100 °C for 4 to 8 hours. The dried filter cake is weighed and then mixed with 30 ml of toluene for the toluene extraction and the extraction procedure is repeated and the sample is dried at 125 °C for 4 to 8 hrs. The final filter cake is then extracted with THF. At the completion of the THF extraction, the THF insoluble solids are dried 16 hrs at 100 °C in air to drive off any residual solvent before a final weight is determined.

Coal conversions were obtained based on the conversion of the moisture and ash free (MAF) carbonaceous material to either the coal-derived liquid directly or the fraction that is soluble in solvents used in the extractions with the filter cake. The conversion was obtained using the relationship:

MAF Conversion $= (W_{init} - W_{fin})/W_{init}$

where W_{init} is the initial weight of the coal on moisture and ash-free basis subjected to liquefaction and W_{fin} is the final weight of the carbonaceous residue obtained from the treated slurry that is not soluble in hexanes, toluene or THF. Note that W_{fin} is to be corrected by subtracting the ash in the initial sample as well as subtracting the insoluble part of the surfactant in the runs where surfactant was added.

To validate that this extraction procedure extracts only reacted coal, the extraction sequence was performed on as-received Illinois #6 coal. The pseudo-

conversion for raw coal (after successive washes with hexane, toluene, and THF) was similarly determined and was found to be only about 2.0 percent. Careful attention was paid to minimize material losses at each processing and analysis step, and as a result, the mass balances closed to within 3 percent.

In order to characterize the liquid obtained as the filtrate, 50 ml of the filtrate are removed for atmospheric distillation using the procedure outlined in ASTM D 246-89[8]. Distillation fractions are taken for the following cuts: room temperature to 210 °C, 210 to 270 °C, 270 to 300 °C, and residual bottoms. This distillation gives a measurement of the lower-temperature boiling point fractions.

Results

Table 1 shows overall conversion results for processing runs that were completed with 1 hour processing time with Illinois #6 coal and varying amounts of sodium lignosulfonate surfactant. The pressures were 1800 psig hydrogen unless noted. The uncertainty in the conversion values is estimated to be less than 3 percent. From an examination of the data presented in Table 1, some noteworthy trends are apparent. One trend is the dependence of the conversion upon operating temperature with and without the surfactant. This dependence is illustrated in Figure 1. Note that the surfactant addition increases the coal conversions by about 10 to 20 percent, generally increasing with temperature with the largest absolute increase occurring at the temperature of 350 °C. As seen in Figure 2, only a small amount of surfactant is required to increase conversion.

Detailed results of the distillation cuts are presented elsewhere[7,9], so only general trends will be discussed here. One important trend is that the addition of the surfactant increases the amount of the light distillates at processing temperatures up to 375 °C. Light boiling fractions are defined as having a boiling point less than 300 °C. This trend is illustrated in Figure 3, which compares the 2.0 % surfactant addition versus the 0 % case.

It was also noted that the production of preasphaltenes increases with processing temperature. The production of preasphaltenes was determined from the THF extraction that succeeded the hexane and toluene washes. This is illustrated in Figure 4. There is a greater increase in the amount of preasphaltenes with the addition of the surfactant. This would appear to be due to high molecular weight fragments (preasphaltenes) from the coal entering the liquid product.

As expected, the conversion of the coal showed a strong dependence on processing time. This trend is illustrated in Figure 5. The addition of the surfactant increases the rate of conversion at shorter processing times compared to the case without surfactant. At longer processing times, the coal processed without surfactant approached the conversion of the surfactant-added processing runs. The maximum MAF conversion for Illinois #6 coal in a catalytic reactor with long processing times approaches 95 %. Complete conversion is not achieved due to nonreactive carbon in the coal macerals.

A detailed analysis of the coal filtercake and filtrate products was conducted to help determine the possible mechanism associated with the surfactant on improving the liquefaction of the coal in this study. To date, only samples processed up to 375 °C have been characterized. The same trends are expected at 400 °C. The analysis is presented elsewhere[9,10], so only the highlights will be reviewed. The analysis included FTIR analysis of the filtercakes, filtrates and residues, proton and ^{13}C NMR of selected filtrates and GC/MS of filtercake extracts to determine the chemical composition of the liquefaction products in reaction runs with and without the surfactant. The primary results show that the addition of the surfactant increases both the amount and constituent species of light oils, asphaltenes, and preasphaltenes, as compared to equivalent processing runs without surfactant. Physical examination of the processed coal suggests that the addition of the surfactant opens up the crosslinked structure of the coal, allowing more surface area to be available for reaction.

Discussion

The batch autoclave tests indicate a significant increase in overall coal conversions due to the surfactant addition at all operating temperatures in the range from 300 to 400°C. Coal liquefaction conversion has a strong dependence on temperature. Below 350 °C there is only a small amount of conversion. As expected, increasing temperature increased the rate of conversion. Within the pressure range evaluated in this study, there was a weak dependence on hydrogen pressure. This work was conducted at 1800 psig hydrogen as the maximum pressure due to equipment limitations, whereas Industrial processes have operated at 2200 psig hydrogen. There is a need for only a small amount of surfactant to show a significant increase in conversion. Adding additional surfactant from 0.5 to 2.0% concentration produced only a small additional increase in conversion.

The results in Table 1 have been corrected for the amount of lignosulfonate that is retained in the filtrate during processing. The surfactant is either hydrogenated and becomes liquid product, or it may decompose to smaller organic species. Separate experiments were conducted on processing the surfactant in the recycle solvent without coal to determine the fraction that is either retained in the filtercake or transferred into the liquid phase. At temperatures of 350 to 375 °C, approximately 50 % surfactant is transferred into the liquid phase while at 400 °C, approximately 70 % of the surfactant ends up in the liquid phase.

The increase in light boiling fractions of the filtrate was found to be significant only up to 350°C. Analytical test results on the structure and functional groups of organic compounds in the filtrate, filtercake and extracted residues show only minor differences in the samples processed with and without surfactant. The same is also true of the structure and functional groups for the successive extracts obtained by washing the filtercakes with hexane, toluene, and THF. The most significant differences obtained for the hexane and THF extracts are in the average molecular weights, which were higher in the 375°C processing run with 2.0 % surfactant than for the case with no surfactant added.

The above results suggest that this surfactant appears to speed up the breakage of the crosslinks in the coal. If this process was rate controlling, the reaction of the hydrogen with coal fragments and the rehydrogenation of the solvent, would also speed up. The following discussion will help visualize how the surfactant may help in the breakage of the crosslinks of the coal. Let the coal be represented by R-O-H. Without the surfactant, coal molecules (represented as R-O-H and R'-O-H in Figure 6) are associated by hydrogen bonding between the H-atom of one coal molecule and the O-atom of the other (dashed line). Due to its anionic polar nature, the surfactant attaches itself to the acid site (H atom) on the coal. Thus it breaks the association with the O-atom between different coal molecules, increasing the favorable hydrogenation reactions. Because the lignosulfonate is a Lewis acid and a partially hydrogenated aromatic compound, it is possible that it could act as a hydrogen donor in the reaction. This is a possible additional avenue of increase in favorable liquefaction processes due to the surfactant.

The addition of the surfactant at 375 °C processing temperature increased coal conversion from 83% to about 86 %, at 400 °C the increase is from 84 % to 93 %. Analysis of the 375 °C filter cake showed that the increase was primarily related to the increase in the THF extracted species from the filtercakes. This is in agreement with the results in Figure 4. As the THF extracted species are expected to be preasphaltenes and analysis of the 375 °C THF filtercake extracts by GC/MS indicates these species to be polyaromatic compounds, the increase in the average molecular weight of the THF extract was not surprising. The species that converted to a THF soluble product due to the surfactant are expected to be bigger (hence, higher molecular weight) than those that did not require the surfactant.

The effects of the surfactant on the quality of the filtrate (i.e. the fraction of light boiling distillates) are clearly dependent on processing temperature. The surfactant increases the straight chain (lower boiling) hydrocarbons as well the molecular weight of the polyaromatics. At 350°C, the increase in straight chain hydrocarbons based on FTIR, appears to dominate, resulting in an increase of lighter fractions. At 375 °C, the production of aromatics appears to counter the production of aliphatic hydrocarbons. Hence, a significantly smaller increase in lighter fractions is observed.

The observed increase in the overall coal conversion due to the addition of the surfactant, sodium lignosulfonate, appears to result mainly from the breakage of crosslinks of the associated coal molecules. This, in turn, appears to lead to greater access of hydrogen to the coal fragments and thus a significant increase in the hydrogenation rate and subsequent solubilization rate. Table 1 shows that overall conversions are relatively independent of surfactant concentrations from 0.5 to 2.0 %. The observation that overall coal conversions are relatively independent of surfactant concentration is consistent with a recent study on the kinetics of adsorption of surfactants on mineral matter. Marbrel and Somasundaran[11] have reported a study of the surfactant adsorption on a mineral at the solid-liquid interface by electron spin resonance spectroscopy. This study showed that 40% of the total ultimate surfactant adsorption occurred during the first 5 seconds of contact, independent of the initial surfactant concentration (provided sufficient surfactant was present). The second stage of adsorption was much slower and occurred on the order of one to three hours. In our case, where the coal is a mineral-containing solid with preferential acid sites for

the surfactant, close to 100% of the total surfactant adsorption may take place during the first minute of contact, even with very low surfactant concentrations.

It is clear from the analysis of the test runs where only the surfactant was processed with the recycle solvent (without coal), that a part of the surfactant is converted to liquid products. These liquid products are likely to cause some enhancement in coal conversions due to lignin generated intermediate species formation as discussed by Coughlin[4,5]. However, such enhancement in conversions in this work will be very small as the amount of surfactant used is small. Further, the overall conversions observed here are relatively independent of the surfactant concentration, whereas, the lignin induced improvement in conversion seen by Coughlin is strongly dependent upon the lignin concentration. Hence, the improvement due to addition of sodium lignosulfonate would appear to be uniquely due to the surfactant effect and relatively free of the artifacts of its decomposition to lignin type products.

IV.   BENCH SCALE TEST

All previous work completed under this research program has evaluated the effect that surfactant addition would have on thermal liquefaction processes. With the objective of pursuing a rapid technology transfer to industry, it was deemed useful to test out the surfactant addition in an industrial bench-scale liquefaction facility.

Hydrocarbon Research, Inc. (HRI) has been under contract to conduct bench-scale test of coal liquefaction by PETC utilizing their Catalytic Two Stage Liquefaction (CTSL) process. During May 1993, they had a scheduled operation (Run 227-78 (CMSL-2)) to evaluate the impact of lower solvent/coal ratios (0.9 - 1.1) on Illinois #6 coal. This was a 17 $2/3$ day operation, of which the last 4 $2/3$ days were devoted to evaluating the effect of sodium lignosulfonate surfactant addition on operation and process performance.

Run 227-78 was carried out using Illinois #6 Burning Star mine No. 2 coal and Shell-317 (NI-Mo/Al$_2$O$_3$) catalyst (1/32" extrudates) in both reactors. The startup oil was L-769. The first three and $1/3$ days of operation were at high stage temperatures (first stage 775 °F and second stage 810 °F) and the remaining one and $1/3$ days of operation at reduced temperatures (first stage 750 °F and second stage 800 °F). The lignosulfonate surfactant was added to the feed slurry at 2 weight % (relative to the coal).   A summary of the operation conditions are given in Table 2.   In this table, periods 10, 12, and 13 represent operating conditions and performance before adding the surfactant while periods 16 and 18A/B represent operating conditions and performance after adding the surfactant.

By a comparison of period 16 to period 13, it is seen that the overall coal conversion increased by only 1 percent. Other performance parameters were somewhat lower. This degradation in these performance parameters was the same as would be expected due to the aging of the catalyst. Thus, it appears that no improvement in the process run due to surfactant addition was seen. Reducing the temperature in period 18 A/B showed a decline in performance.   While the

temperature was stabilized, it is indeterminate if the reactor system reached full equilibrium. Results for this period are presented in Reference 9.

There may be several reasons for the absence of a process performance improvement due to the surfactant addition in the bench scale test. It is possible that the baseline overall conversion for this coal was already close to the maximum before adding the surfactant. The non-reactive carbon macerals in the coal are not expected to liquefy. Also, the surfactant may decompose appreciably at the high operating temperatures used in the bench-scale run, thus losing most of its effectiveness. It is also possible one or more of the decomposition products from the surfactant may interfere with the supported Ni-Mo catalyst and thus degrade its performance.

HRI also conducted six batch microreactor tests to determine coal conversions at temperatures of 750, 800, and 825 °F with and without surfactant addition. There was a modest increase observed in coal conversion in HRI's microreactor experiments due to the surfactant addition at temperatures of 750 and 800 °F, respectively. HRI's results on the coal conversion and the percent increase in coal conversion (due to the surfactant) as a function of processing temperature are plotted in Figure 7 along with JPL's results (at lower processing temperatures) with 1% surfactant (based on total slurry) addition. The left part of Figure 7 shows the JPL data while the right part shows the HRI data. It is seen that the HRI results fit the trend established by the JPL results on overall coal conversions. The conversions appear to saturate when they approach 92 percent. Further, at temperatures higher than 400 °C, the increase in conversion due to surfactant addition gradually decreases to zero due to saturation of the conversion.

It is understood that the differences in conversions measured at HRI in their microreactor tests compared to JPL, are due to differences in the amount of coal and analysis procedures used . For these reasons, batch autoclave tests were conducted at 400 °C with the HRI catalyst alone and with the catalyst and the surfactant together to determine the synergistic effects. Figure 8 shows a comparison at 400 °C between the a) baseline case of thermal processing of coal alone, b) coal with 1% surfactant, c) coal with 1% HRI catalyst, and d) coal with 1% HRI catalyst and 1% surfactant. It is seen that the addition of either the surfactant or the HRI catalyst improves the conversion significantly over the base case, but the HRI catalyst is somewhat more effective. However, when both the catalyst and the surfactant are added together at 400 °C, the conversion diminishes somewhat compared to the catalyst alone.

The filter cake analysis for these cases showed that the yield of light oils was nearly the same for the runs where the additives were HRI catalyst alone (case c) and HRI catalyst mixed with the surfactant (case d), respectively. However, the yield of asphaltenes was higher and preasphaltenes lower for case d compared to case c. This indicates that at 400 °C, even though surfactant addition to HRI catalyst lowered the conversion by a small amount, it still improved the product slate due to generation of increased amounts of lighter components.

A mass spectrometric analysis of the decomposition products of sodium lignosulfonate in the 350 to 420 °C range showed persistent peaks of species corresponding to the sulfonate group. These species appear not to aid the catalyst

operation. A thermally more stable surfactant may be likely to have a positive synergistic effect.

V.   Conclusions

The addition of sodium lignosulfonate surfactant has been shown to increase the conversion of coal in batch coal liquefaction experiments in the temperature range from 300 to 400 °C. This increase in conversion was associated with an increase in less than 300 °C boiling point distillate over process runs without surfactant. The improvement in conversion by the addition of surfactant is believed to result from decreasing the agglomeration of the coal and increasing the rate of breaking crosslinks in the coal into smaller molecular units. These results imply the possibility of improved process economics for coal liquefaction by being able to have liquefaction unit operations at lower temperature and pressures than the conventional catalytic process and eliminating the need for a costly catalyst. The use of surfactant in a catalytic process may also be beneficial if the surfactant or its thermal decomposition products do not interfere with the catalyst.

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Table 1: Test matrix results of Illinois #6 coal conversion (MAF basis) processed for one hour with varying amount of sodium lignosulfonate surfactant.

Temperature	H$_2$ Pressure (Psig)	Surfactant Concentration			
		0%	0.5%	1.0%	2.0%
300 °C	1800	21.4 %	24.7 %	24.6 %	24.5 %
325 °C	<1800				24.2 % (A)
325 °C	1800	25.4 %	29.8 %	36.5 %	29.2%
350 °C	<1800		65.9 % (B)		60.0 % (C)
350 °C	1800	54.4 %		62.5 %	63.1 %
375 °C	<1800	77.0 % (B)			82.5 % (C)
375 °C	1800	83.1 %	86.0 %	85.9 %	87.4 %
400 °C	1700	84.1 %		92.9	

Notes: A: 1050 Psig, B: 1300 Psig, C: 1500 Psig

TABLE 2
RUN 227-78 (CMSL-2) OPERATING SUMMARY
EVALUATION OF LOW SOLVENT-TO-COAL RATIOS

COAL   : ILLINOIS NO. 6   HRI-6107
CATALYST : SHELL-317   HRI-5394 (BOTH STAGES)

Period Number	9	10	11	12	13	14	15	16
Date (Start of Period)	4/27/93	04/28/93	04/29/93	04/30/93	05/01/93	05/02/93	05/03/93	05/04/93
Hours of Run (End of Period)	208.	232.	256.	280.	304.	328.	352.	376.
Stage 2 Catalyst Age,Lb Dry Coal/Lb Cat	270.	295.	333.	376.	422.	458.	495.	535.
1st Stage Temperature (°F)	751.	751.	767.	775.	777.	776.	776.	776.
2nd Stage Temperature (°F)	801.	802.	811.	812.	812.	811.	812.	811.
Unit Back Pressure (PSIG)	2502.	2503.	2503.	2503.	2500.	2501.	2501.	2502.
Space Velocity, Lb Coal/Hr/Ft³ Catalyst (per stage)	42.3	41.0	60.2	66.7	74.2	56.7	57.5	63.5
W% OF DRY COAL								
PFL Recycle	90.1	90.1	90.1	90.1	90.2	90.1	90.0	88.5
PFL to Buffer to Stage 1	4.9	4.5	3.3	2.6	2.6	4.7	3.2	3.0
PFL to Buffer to Stage 2	4.8	4.4	3.4	2.9	2.6	4.5	3.1	3.5
Make-up Oil	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
SOLVENT-TO-COAL (DRY) RATIO	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
MATERIAL BALANCE (%) (GROSS)	95.46	99.25	95.63	97.91	97.28	95.81	99.3	97.69

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TABLE 2 contd.

Period No.	12	13	16
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED			
C_1-C_3 in Gases	5.89	4.73	5.21
C_4-C_7 in Gases	3.46	3.36	3.25
IBP-390°F in Liquids	15.83	14.75	11.12
390-500°F in Liquids	8.61	8.09	8.78
500-650°F in Liquids	21.14	20.52	20.01
650-850°F in Liquids	10.60	12.34	14.37
850-975°F in Liquids	2.41	3.36	3.73
Toluene Soluble 975°F° Oil	3.73	5.66	8.15
Toluene Insoluble 975°F° Oil	0.06	0.12	0.17
Unconverted Coal	6.28	6.69	5.98
Ash	12.04	12.04	12.04
Water	10.16	10.14	8.66
CO	0.17	0.15	0.16
CO_2	1.72	0.12	0.15
NH_3	1.34	1.31	1.23
H_2S	3.29	3.29	3.21
Total (100 + H_2 Reacted)	106.74	106.67	106.21

PROCESS PERFORMANCE
====================

	12	13	16
C4-975°F Distillates, W% of MAF Coal	70.6	71.0	69.6
975°F° Conversion, W% MAF	88.6	85.8	83.7
Coal Conversion, W% MAF	92.9	92.4	93.2
HDS, W%	77.3	77.5	75.6
HDN, W%	87.5	85.8	80.1

Overall Coal Conversion
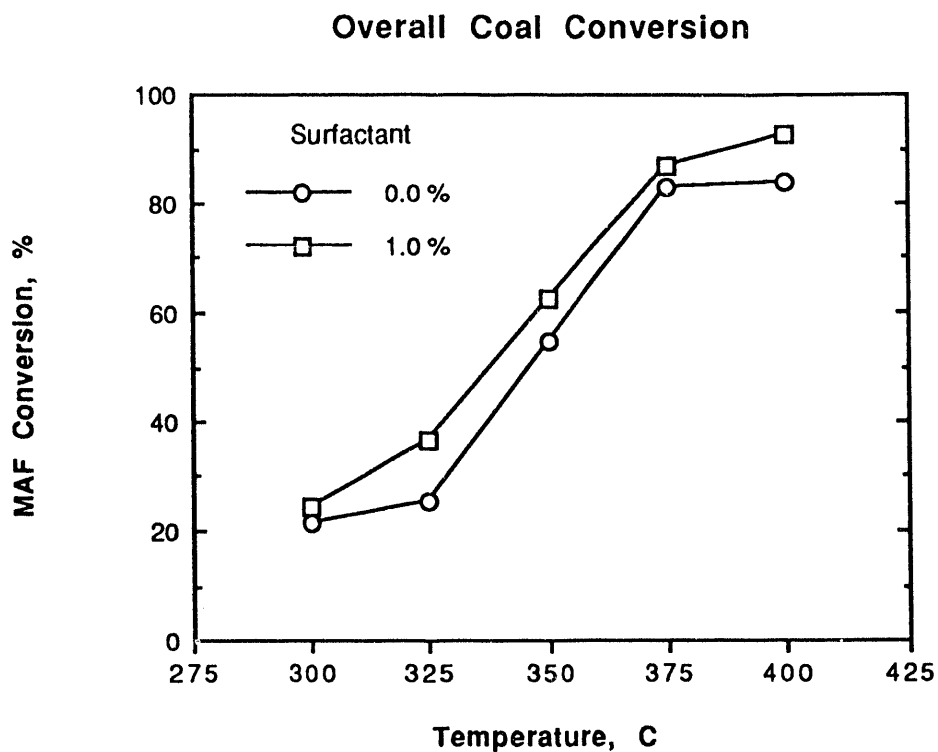
Figure 1: Temperature dependence of conversion with and without surfactant.

Effect of Surfactant Co.   ation
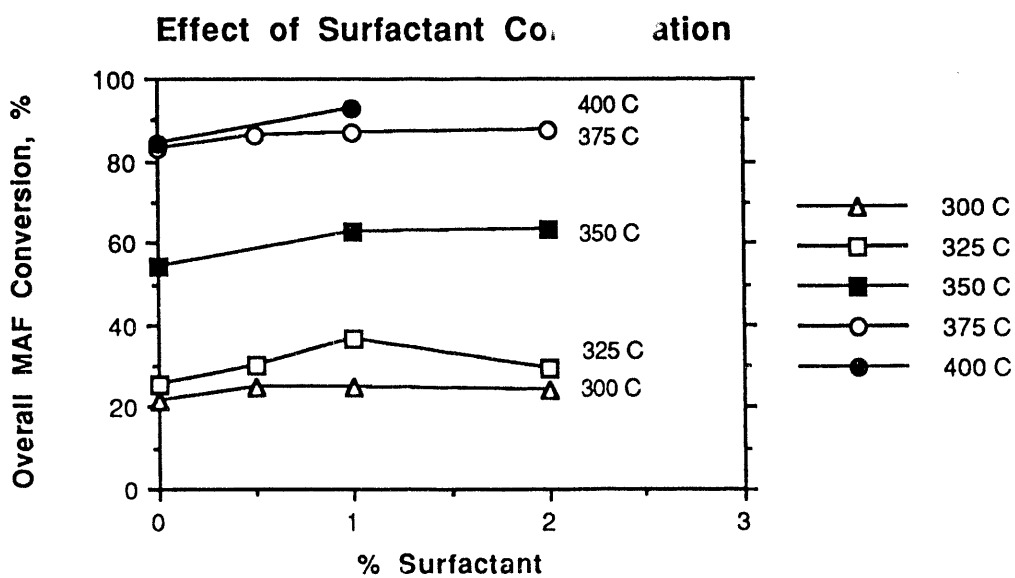
Figure 2: Effect of surfactant concentration on MAF conversion.

1800 psig Distillation Cuts
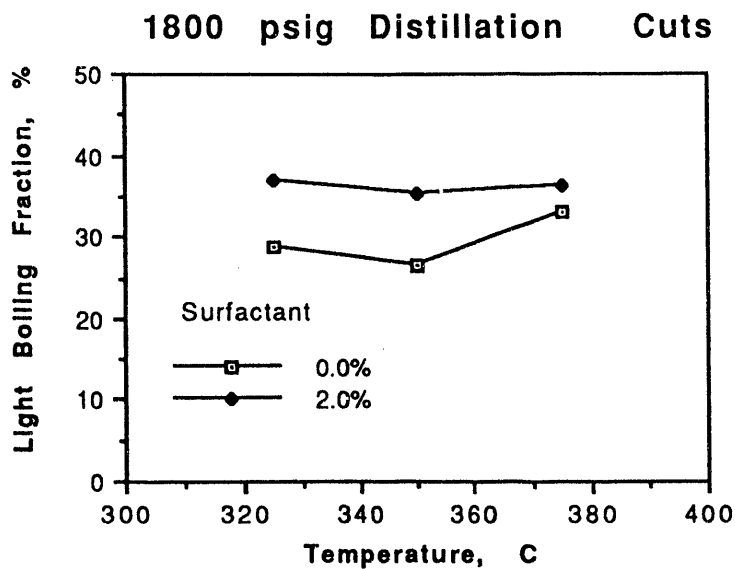
Figure 3: Temperature dependence of light boiling fractions with and without surfactant.
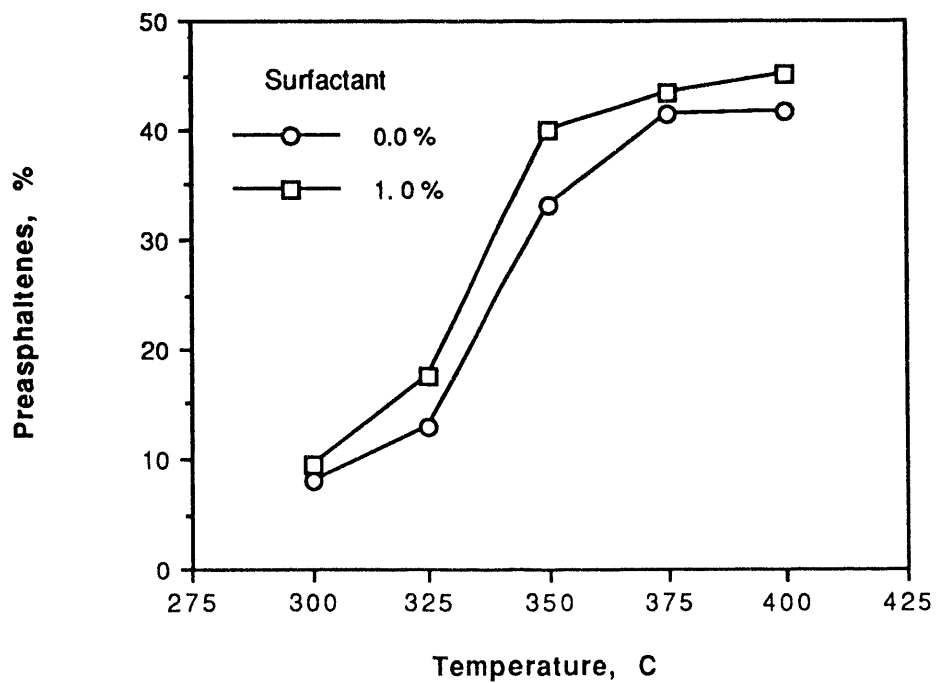
Figure 4: Yield of preasphaltenes (as determined from THF extraction) as a function of temperature with and without surfactant.

Conversion Dependence On Time
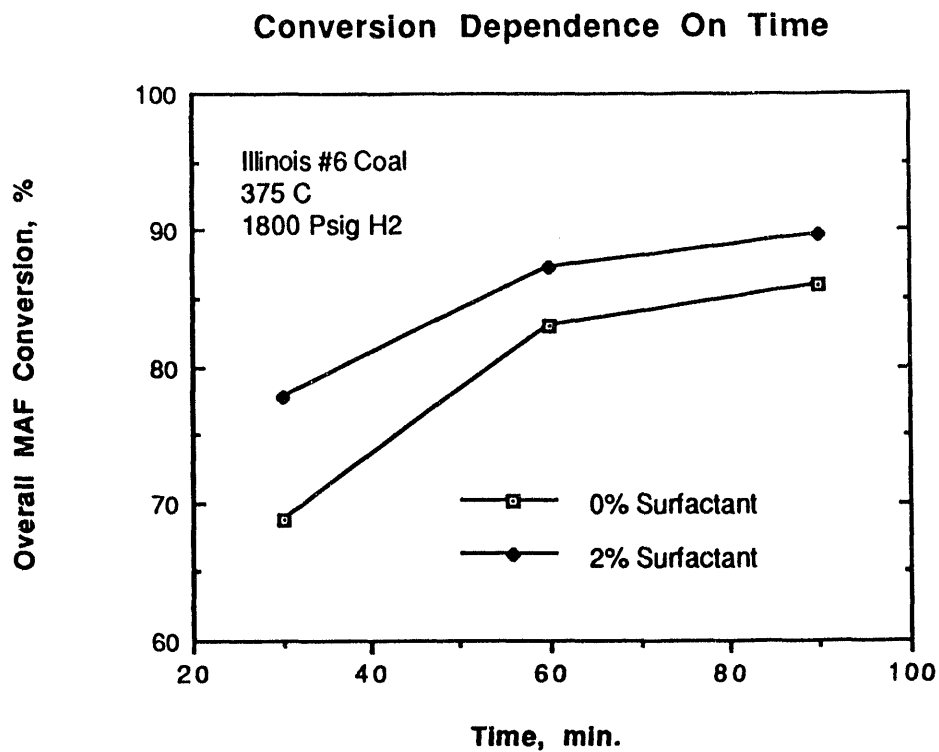
Figure 5: Conversion dependence on time, with and without the addition of surfactant.
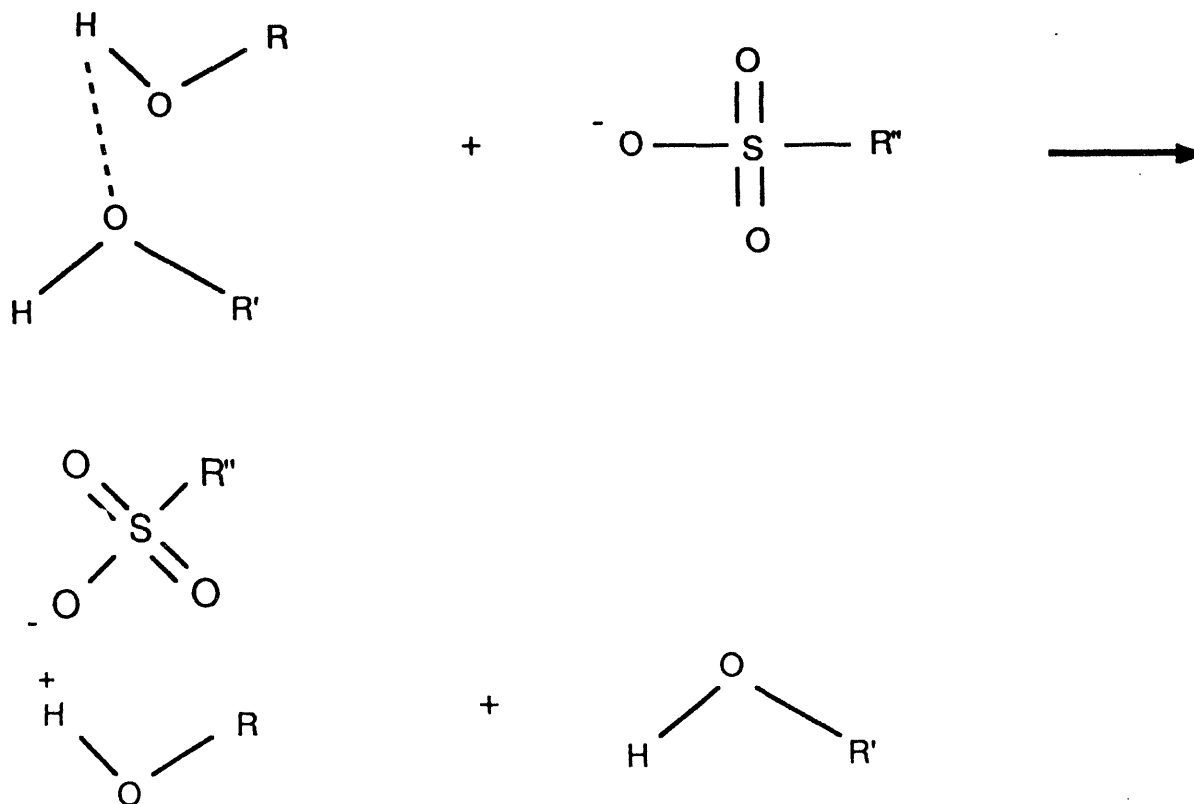
Figure 6: Representative mechanism for the role of the surfactant.

Figure 7: Comparison of JPL and HRI autoclave data.
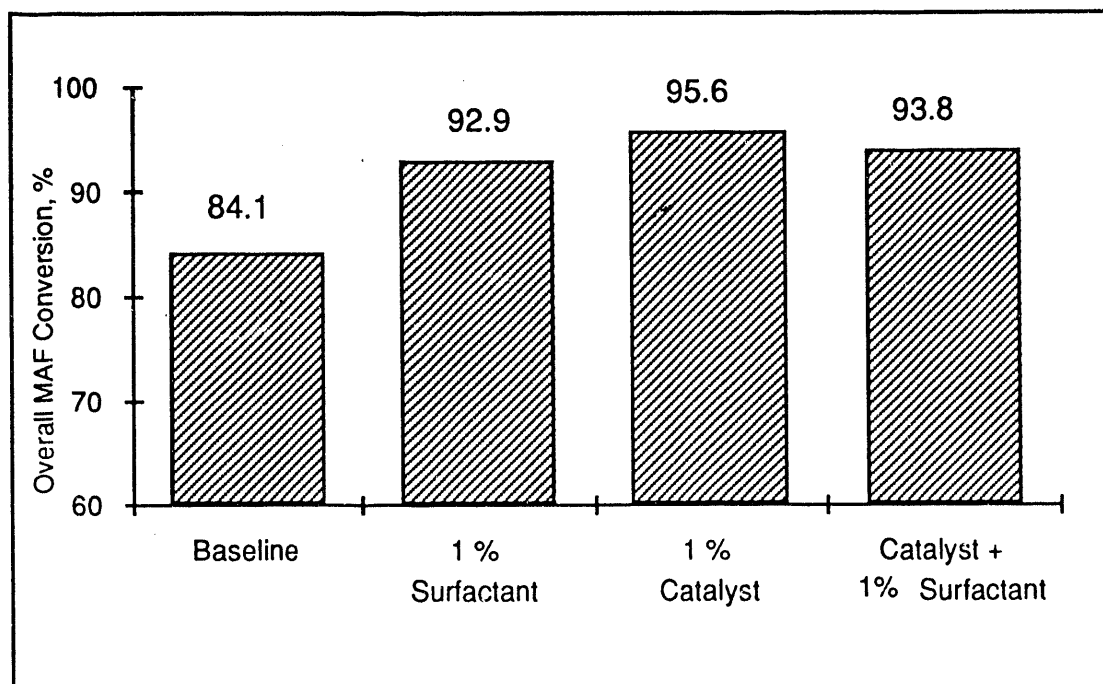
Figure 8: Comparison of MAF conversion of catalyst and surfactant interactions at 400 °C.

New Direction to Preconversion Processing of Coal

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Objective:

1.   Reinvestigation of coal liquefaction based on the new coal structural model
2.   Evaluation of the optimum coal dissolution by high temperature soaking
3.   Investigation of radical initiators on coal conversion
4.   Investigation of the effect of coal dissolution on liquefaction
5.   Estimation of possible cost reduction

Accomplishment & Conclusions:

1.   Two-step soaking at 350°C and 400°C in a recycle oil is a very effective coal solubilization procedure.
2.   Dissolution by high-temperature soaking is primarily controlled by a physical process rather than chemical reactions.
3.   The addition of radical initiators is positive on coal conversion at <430°C, but negative at >430°C. The negative effect is not as significant as expected by the conventional reaction mechanism.
4.   Selective molecules such as weakly acidics (phenol etc.) and weakly basics (nitrogen-containing compounds) are strongly adsorbed on coal during high-temperature soaking.
5.   After dissolution, different reactivity of components with various molecular weights should be considered for coal conversion.
6.   New directions for coal preconversion are suggested as follows: (1) dissolution of coal with two-step high-temperature soaking, (2) separation of dissolved coal into oil and heavy fractions with vacuum distillation, and (3) liquefaction of the separated heavy fraction.
7.   Tests of the proposed procedure resulted in a 30% increase in the oil yield and a 15-20% decrease in the gas yield on a small autoclave scale.

Plan:

The project has been completed on schedule. It is expected that the proposed procedure will lead to a substantial reduction in the cost of coal liquefaction. The effectiveness of the proposed procedure was confirmed with batchwise reactions. A test of the proposed procedure with a continuous operation is highly recommended.

Introduction

A comprehensive knowledge of basic coal structure must be acquired for the effective development of coal liquefaction. The cross-linked, macromolecular model has been widely accepted by most researchers, and current coal liquefaction studies are proceeding under this assumption. Recent studies, however, show that significant portions (far more than generally believed) of coal molecules appear to be physically associated[1]. This new structural model has gained the credibility from our latest work[2-5]. Therefore, the development of any coal liquefaction processes should consider this possibility. If physical association is dominant for cross-links, all properties and reactivities in the liquefaction process must be specific functions of intra- and intermolecular (secondary) interactions as well as molecular weight.

Recent work[6-11] showed the significance and importance of relatively strong secondary interactions for all ranks of coal. These interactions include ionic forces, the charge-transfer interaction, and the so-called π-π interaction[14]. Dissolution of these interactions is believed to be an essential step required before breaking the covalent bonds in coal liquefaction. Some portions of these specific associations, however, are not solvated under normal extraction conditions, even with good solvents such as pyridine[6,7]. Therefore, dissolution becomes a very difficult task.

It is known from the literature[1], that a substantial amount of high-volatile bituminous coal can be disintegrated in coal-derived liquids and polycyclic aromatic hydrocarbons at 300-400°C (high temperature soaking). These temperatures are well below those maintained during coal liquefaction or other coal decomposition processes. It is proposed that electron donors and acceptors with low molecular weight substitute coal-coal complexes with charge-transfer interactions (physical dissolution), understanding that some chemical bond cleavage may occur concurrently at these temperatures[1].

High-volatile bituminous coal molecules may associate when soaked at temperatures <300°C[6,7]. This mechanism probably involves the severance of relatively weak secondary interactions concurrent with the formation of stronger secondary interactions (solvent-induced associations)[7]. The reduction in dissolution observed when soaking coal in a coal liquid at 200-300°C has been regarded as a retrograde reaction[15,16]. These temperatures, however, are used in many processes[17] for the mixing and preconversion of coal in recycle oils. Hydroaromatics and hydrogenated solvents have been used in the past to prevent retrograde reactions[18]. Bond cleavage and stabilization of labile intermediates during preconversion based on the network model are major concerns for current liquefaction processes. Because of the associated nature of coal[1], it is important to carefully select optimal temperatures during pretreatment operations.

One of the main goals in coal liquefaction is to decrease gas yields to reduce hydrogen consumption. Costly hydrogen is lost in the production of gases such as methane and ethane. More gases are generated from severe reactions with undissolved coal which is not as reactive as coal in solution. Therefore, higher reactivity will result in a decrease in gas yield under mild conditions. Since high-temperature soaking in a coal liquid is an

effective method for the physical dissolution of coal in the absence of additional chemicals and hydrogen, the subsequent generation of gases should be minimized.

Based on the associated molecular nature of coal, another important factor is suggested to decrease the gas yield. While severe conditions are obviously required for the decomposition of higher-molecular-weight fractions, a larger amount of gas will be produced from associated lower-molecular-weight fractions under these conditions. To optimize the process, coal fractions with different molecular weights should, if possible, be liquefied separately.

Treatment of coal under mild conditions has been studied for years[19,20]. Pretreatment procedures involving chemical reactions such as alkylation, oxidation, and hydrolysis have been attempted[19]. Other methods include treatments in the presence of CO/H_2O[21-24], CH_3OH[31], nitrogen-containing compounds[25,26], etc. at temperatures of 300-350°C. From an economic point of view, process conditions involving high pressures of H_2, H_2O and CO and the addition of chemicals are not recommended.

In this paper, an improved pretreatment procedure for coal liquefaction is investigated on the basis of the associated molecular nature of coal. Activities are focused on two issues mentioned above: (1) maximizing the dissolution of associated coal and (2) step-wise conversion of associated coal with a wide molecular weight distribution. An improved preconversion concept is proposed and tested with autoclave reactors.

Experimental

Coal samples were obtained from the DOE Coal Bank at the Pennsylvania State University. Elemental analyses are presented as *Table 1*. The Illinois coal (DECS-2) was used as received while the Smith Roland coal (DECS-8) was washed with 2N HCl[9] and dried before use. Two coal liquids derived from the Illinois No. 6 coal (Liquid A) and Pittsburgh No. 8 coal (Liquid B) were obtained from the Wilsonville pilot plant[27]. Elemental analyses of these coal liquids are also shown in *Table 1*. Reagents and solvents (HPLC-grade) were obtained from Aldrich Chemical Co. (Milwaukee, WI) and Fisher Scientific (Pittsburgh, PA) and used without further purification.

A 250 ml autoclave (Model 4576; Parr Instrument Co., Moleine, IL) and 27 ml microreactors fabricated[28] were used. These reactors were evacuated and purged with nitrogen five times after charging coals and solvents. The autoclave samples were heated at ~ 8°C min^{-1} to the required temperature, then controlled to ± 3°C while being agitated with the autoclave stirrer (500 rev min^{-1}). The microreactor was heated in a fluidized sand bath (Model SBL-2; Techne Corp., Princeton, NJ) which was controlled to ± 1.0°C of the set point. A shaker (Model 75; Burrell Corp., Pittsburgh, PA) was modified to agitate the microreactor samples in a horizontal plane at 320 rev min^{-1}. Mixtures in the microreactor attained the set point within 5 min from the time of immersion into the sand bath. Conditions for all experimental runs are summarized in *Table 2*. Liquid A from the Illinois No. 6 coal was generally used, but Liquid B was used for Runs 5-9.

After reactions, the mixtures were filtered and Soxhlet-extracted with cyclohexane, toluene and tetrahydrofuran (THF) for 24 h at each stage. The individual fractions were then dried under vacuum at 95°C overnight. Amounts of cyclohexane solubles (CyS), toluene solubles (ToS), THF solubles (TS), and pyridine solubles (PS) were determined from the weights of their respective insolubles. Gas yields were generally included in CyS yields.

Gases were collected for analysis in a sample bag after cooling the autoclave, then analyzed using gas chromatography by the University of Pittsburgh Applied Research Center (Pittsburgh, PA). Approximate gas yields were calculated assuming no change in the amount of nitrogen before and after the reactions.

Results and Discussion

1 Coal Dissolution and Liquefaction

Weakening secondary interactions in coal may aid in increasing its conversion. In this study, the effect of solvation on liquefaction due to soaking was evaluated. Illinois No. 6 coal was liquefied at 430°C for 1 h after soaking at 200°C and 350°C (Runs 1 and 2 in *Figure 1*). The yields of TS were the same for both tests, but the yields of ToS and CyS were ~5% higher for the sample soaked at 350°C. For Run 4, the coal was refluxed in pyridine (~115°C) for 24 h instead of undergoing high-temperature soaking. After removal of the pyridine, the sample was liquefied at 430°C. Comparing the total conversion to the conversion of the raw coal liquefied under the same conditions (Run 3), showed the yield of CyS increased ~10% after refluxing in pyridine. These results indicate that solvated coal can be readily converted, and that higher temperatures are needed to solvate coal when soaking in poorer solvents. Alternatively, even low temperatures are effective for solvating coal when soaking in better solvents. Reported results support this interpretation. In one case, an increase in conversion at 427°C was observed when a coal/coal liquid mixture was soaked at 277-322°C for 10 min[29]. In another case, swelling with THF and tetraammonium-hydroxide at room temperature, followed by removal of the solvents, was shown to enhance hydroliquefaction yields at 400°C[30,31].

As reported in our recent paper[28], the optimum range for high-temperature soaking in coal liquids was ~350°C (Runs 5-9 in *Figure 2*). The CyS (or oil) yield, however, was low (35%) even at optimum temperatures. A second soaking on the product from the 350°C treatment (two-step soaking) was tested to determine any differences in oil yield. Two-step soaking at 350°C and 400°C generated a 50% oil yield (Run 10 in *Figure 3*)[33]. Soaking at 200°C, however, followed by soaking at 400°C, produced an apparent yield in excess of 100% due to incorporation of the coal liquid into the product (Run 11). Therefore, two-step high-temperature soaking is proven effective for dissolving coal, but temperatures > 200°C are required for the first step.

Since two-step high-temperature soaking at 350°C and 400°C generated 50% cyclohexane solubles, slow or programmed heating seems more efficient than fast heating for enhancing coal conversion. In practice, the autoclave was slowly heated with the

autoclave heater. The effect of variable heating rates was investigated using the microreactor, which was controlled with the sand bath. For Run 12, the reactor was rapidly heated in one step from room temperature to 430°C in 0.5 h and held at 430°C for 2 h. For Run 13, the mixture was liquefied under the same conditions, but heated in two steps (350°C for 0.5 h and 400°C for 0.5 h) then held at 430°C for 1 h. The total heatup time from room temperature to 350°C, from 350°C to 400°C, and from 400°C to 430°C was 0.5 h. Therefore, the total residence time including heatup was 2.5 h. In Run 14, the mixture was slowly heated from 130°C to 430°C and held at 430°C for 1 h. Total duration of heatup and reaction times was maintained at 2.5 h. The lowest coal conversion resulted from conditions set forth in Run 12, which reacted the coal for the longest time but used one-step heating. In comparison, oil yields were enhanced ~10% using the programmed heating methods. These results infer that programmed heating and step-wise high-temperature soaking are important factors for increasing coal conversion. Song et al.[35] recently reported the effect of temperature-programmed liquefaction for low rank coals. In their work, Montana subbituminous coal produced 5-10% more THF solubles by slow heating than rapid heating. These results support the present work.

2 Coal Fractions and Liquefaction

A wide molecular weight distribution is another feature of associated coal[1]. Realizing that a higher gas yield should be obtained by pyrolysis from a fraction with low molecular weight, the dissolved coal may be fractionated into light and heavy fractions and the heavy fraction with high molecular weight selectively liquefied. In this study, pyridine solubles and insolubles were liquefied to compare conversions under similar conditions (Runs 15 and 16). Approximately the same oil yield was obtained from both fractions (Figure 4). Liquefaction of cyclohexane insolubles from Run 10 was also examined. Even from this heavy fraction, a 50% oil yield was obtained.

Dissolution and hydrogen consumption rates of PI and coal were found to be similar using West Kentucky coal (80% carbon, daf)[33]; however, a significant decrease in conversion was observed when Illinois No. 6 coal was extracted with pyridine[34]. Warzinski and Holder[35] also observed this retrogressive behavior in conversion using pyridine as a characteristic of Illinois No. 6 coal. Although the effect of the soluble and insoluble components on coal conversion is difficult to conclude from these results, it appears that the reactivity of residues or high molecular weight components is better than previously thought when compared with that of the low molecular weight components.

3 The Associated Molecular Nature and Liquefaction

It has been shown that a significant portion of coal can be dissolved by high-temperature soaking in coal liquids and, that programmed or step-wise heating is preferred to enhance oil yields. Highly dissolved coal has also produced greater liquefaction yields. Test results further suggested that coals, which have a wide molecular weight distribution, should be separated into light and heavy fractions after dissolution with only the heavy fraction liquefied in the next step. From these results, a procedure designed to increase the oil yield and decrease the gas yield is presented in a block diagram as Figure 5. As described, coal is soaked in a recycle oil at 350°C and 400°C. Gas and oil fractions are isolated using vacuum distillation, and the heavy fraction liquefied under low hydrogen

pressure at relatively low operating temperatures.

This procedure was bench tested in the autoclave. The DECS-2 coal was soaked in the coal liquid under nitrogen at 350°C and 400°C, respectively. The oil fraction was extracted with cyclohexane and the cyclohexane insoluble portion liquefied under low hydrogen pressures (400 psi) at 430°C for 1 h (Run 19). For comparison, the coal was soaked in the coal liquid at 200°C for 1 h and the mixture liquefied under the same conditions for 2 h (Run 18). Gas yields from these tests were determined (*Figure 6*). *Scheme 1* presents the mass balance for Run 19, which shows that the CyS (or oil) yield increased 30% and the gas yield decreased 15% when compared with yields from Run 18.

DECS-8 (subbituminous) coal was tested using the same procedure. As ionic forces are more significant in lower rank coals[9], these forces must be weakened prior to high-temperature soaking. Although acid washing has been known to enhance the conversion of lower rank coal[36-39], details of this treatment have not been clearly explained. Washing in 2N HCl was used to weaken the ionic forces in the coal before high-temperature soaking. The sample was soaked in the coal liquid at 350°C and 400°C for 1 h, respectively. Cyclohexane insolubles from the soaked coal were similarly liquefied at 430°C for 1 h (Run 21). Since the dried acid-washed coal was used, the dried DECS-8 coal was soaked at 200°C for 1 h then liquefied at 430°C for 2 h (Run 20). Results showed more than 30% increase in the oil yield and 20% decrease in the gas yield (*Figure 6* and *Scheme 1*).

In a controlled experiment made without using coal, about 2% of the gas was produced from the coal liquid under conditions existing at 430°C; therefore, total gas yields in the previous Runs were compensated by this amount. Since the change in the amount of gas produced from the coal liquid was greater than that of gas produced in the liquefaction step (CyI at 430°C), only semi-quantitative yields were obtained. *Table 3* shows the composition of the gases generated at 430°C. The residue (CyI) from high-temperature soaking produced a small amount of CO, CO_2, and methane with a large amount of olefin gases.

Conclusions

Suggested improvements in the coal liquefaction process were tested using the current two-stage process assuming an associated molecular structure for coal. Considering that significant portions of coal molecules are physically associated, it is suggested that physical dissolution should be carried out prior to liquefaction. Step-wise high-temperature soaking is a simple and effective method for coal dissolution in the absence of additional chemicals and hydrogen. A greater degree of dissolution requires less severe conditions during liquefaction. A wide molecular weight distribution of the associated coal is another important factor to be considered for coal conversion. Liquefaction of high-molecular-weight fractions isolated after high-temperature soaking produced higher oil yields and lower gas yields. Tests made using autoclave reactors tend to verify the concept proposed in *Figure 5* and show it to be a superior coal conversion procedure. Use of this concept resulted in 30% more oil and 15-20% less gas, which projects a substantial reduction in the ultimate cost of coal liquefaction.

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Table 1 Elemental Analyses of Coals and Coal Liquids Used (wt%)

symbol	sample	H_2O	Ash	element (daf)			
				C	H	N	S
DECS-2	Illinois No. 6 (hvb)	10.4	14.5	78.1	5.4	1.3	5.4
DECS-8	Smith-Roland (subb)	28.4	9.9	74.4	5.2	1.0	0.9
Liquid A	coal liquid derived from Illinois No. 6 coal	--	--	88.4	11.4	0.2	< 0.1
Liquid B	coal liquid derived from Pittsburgh No. 8 coal	--	--	87.1	9.6	0.2	< 0.1

Table 2 Run Numbers and Experimental Conditions

run no.	condition					
	coal (g)	temp. (°C)	time (h)	solvent (ml)	atmosphere (psi)	cat. (mg)
1	DECS-2 (5)	200/430	1.0/1.0	Liquid A (50)	N_2 (200)	
2	"	350/430	"	"	"	
3	"	430	1.0	" (100/400)	N_2/H_2 (50)	MoS_2
4[a]	"	"	"	"	"	"
5[b,c]	"	275	1.5 (15)	Liquid B (50)	N_2	
6[b,c]	"	300	"	"	"	
7[b,c]	"	325	"	"	"	
8[b,c]	"	350	"	"	"	
9[b,c]	"	375	"	"	"	
10	"	350/400	1.0/1.0	Liquid A (50)	N_2 (200)	
11	"	200/400	"	"	"	
12[b]	DECS-2 (3.5)	430	2.0	Liquid A (14)	N_2 (50)	
13[b]	"	350/400 /430	0.5/0.5 /1.0	"	"	
14[b]	"	d	d	"	"	
15	DECS-2/PS[e] (5)	430	1.0	Liquid A (50)	N_2/H_2 (100/400)	MoS_2 (50)
16	DECS-2/PI[e] (5)	"	"	"	"	"
17	DECS-2/CyI[f] (5)	"	"	"	"	"
18	DECS-2 (5)	200/430	1.0/2.0	"	"	"
19	(Run 10 + Run 17)					
20	DECS-8[g] (5)	200/430	1.0/2.0	Liquid A	N_2/H_2 (100/400)	MoS_2 (50)
21	" → 430	350/400[h] → 1.0	1.0/1.0[h] → 1.0	"	"	"

[a]Coal refluxed in pyridine, followed by the removal of pyridine
[b]Microreactor (27 ml) was used
[c]Ref. 28
[d]Programmed heating: 130°C —— 240°C —— 350°C —— 400°C —— 430°C (1 h)
　　　　　　　　　(28 min)　(30 min)　(21 min)　(11 min)
[e]PS: pyridine solubles, PI: pyridine insolubles
[f]Cyclohexane insolubles from Run 10
[g]2N HCl-washed and dried coal
[h]Cyclohexane insolubles was liquefied after soaking at 350/400°C
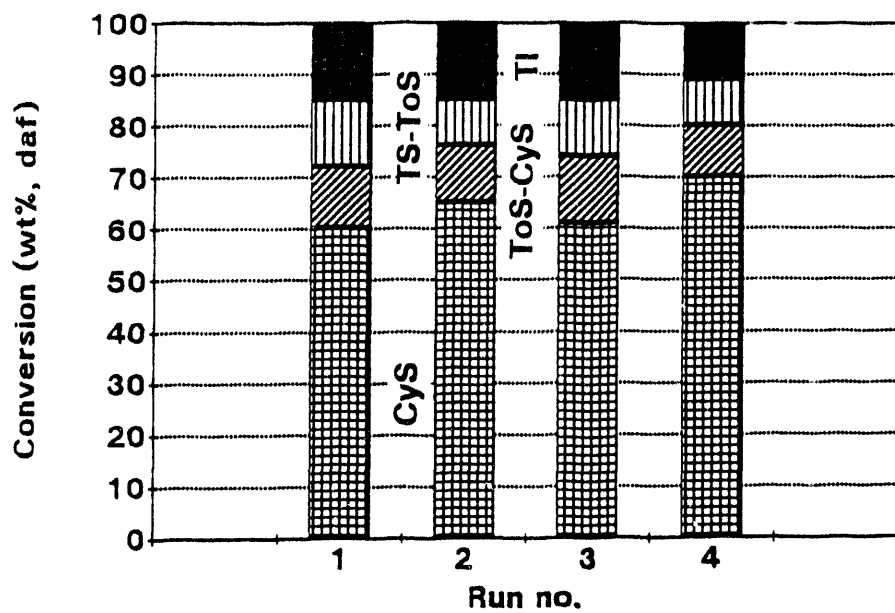
Figure 1 Effect of soaking before liquefaction on coal conversion
(Conditions are listed in *Table 2*)
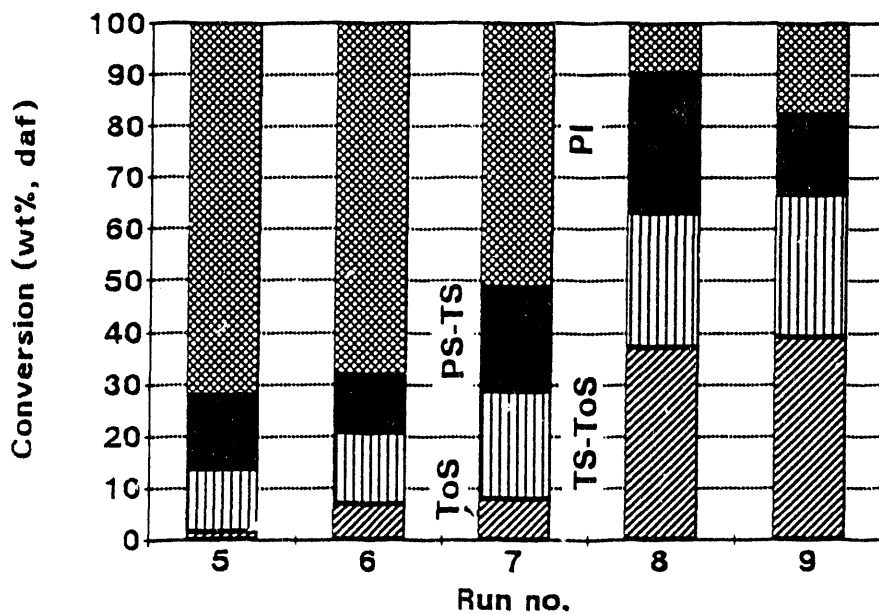
Figure 2 Effect of soaking temperature on extractability[22]
(Conditions are listed in *Table 2*)
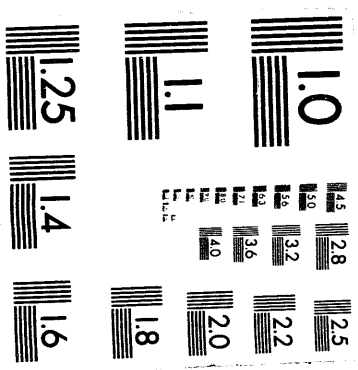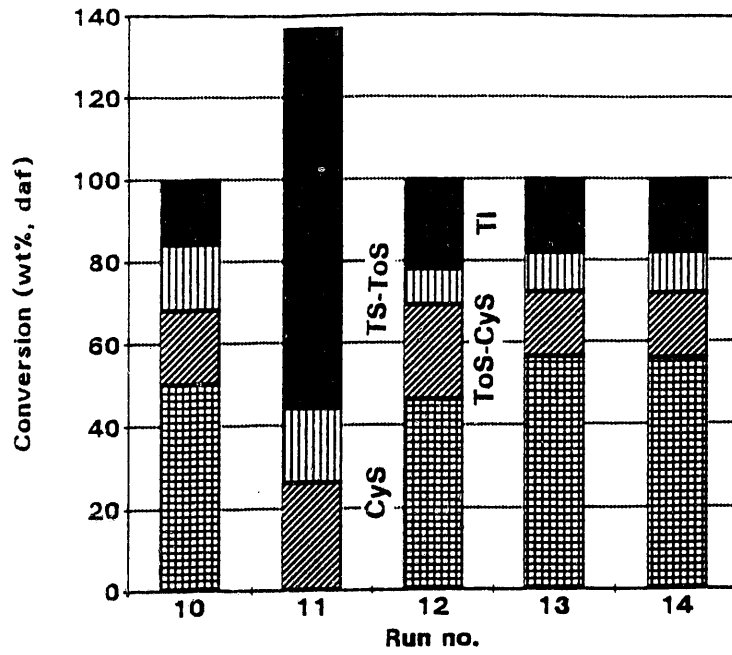
Figure 3 Effect of step-wise soaking on extractability
(Conditions are listed in *Table 2*)
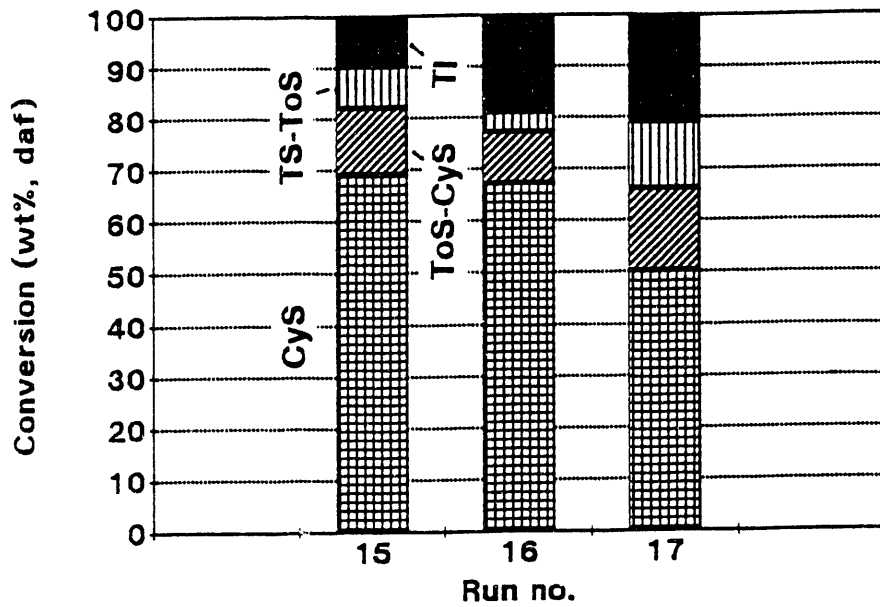
Figure 4 Coal fractions and their conversion
(Conditions are listed in *Table 2*)
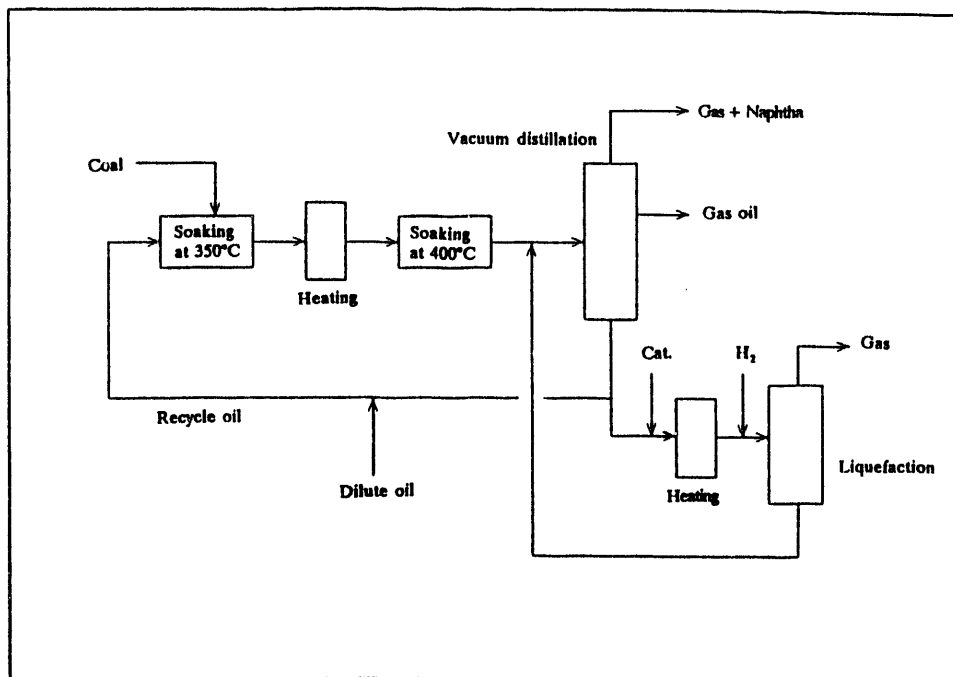
Figure 5 Block diagram of the proposed coal liquefaction procedure
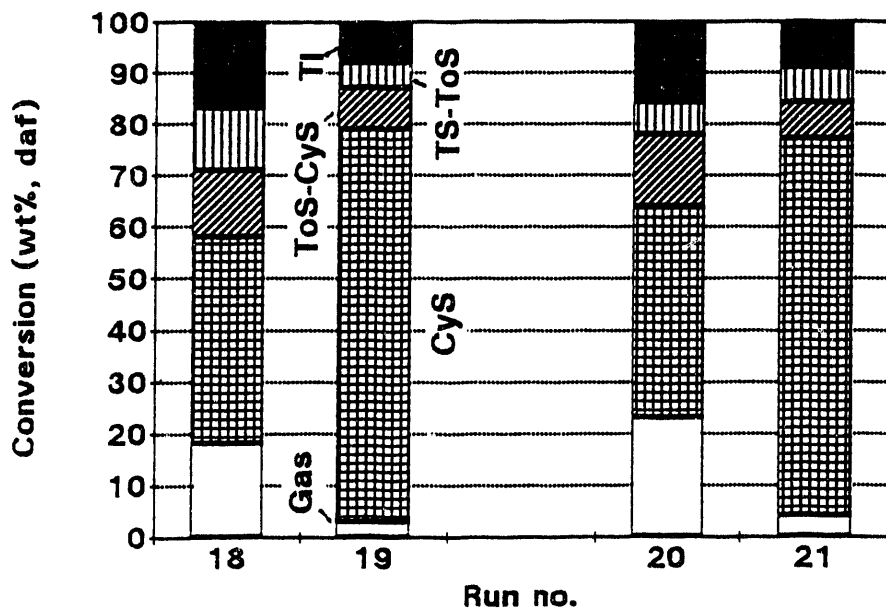
Figure 6 Coal conversion by the proposed procedure for a high-volatile bituminous coal and a subbituminous coal (Conditions are listed in *Table 2*)

Run 19 (DECS-2 Coal) (wt%)

```
                        3 (Gas)
Coal (100) 350/400°C   36 (CyS)              < 1 (Gas)        Total yield (daf)
   75 (daf) (1h/1h)    35 (CyI)  430°C       18 (CyS)          Gas       4
   15 (ash)            15 (ash)  (1h)         5 (ToS-CyS)       CyS      73
   10 (water)                                 5 (TS-ToS)        ToS-CyS   7
                                              7 (TI)            TS-ToS    7
                                             15 (ash)           TI        9
```

Run 21 (DECS-8 Coal) (wt%)

```
                        3 (Gas)
Coal (100) 350/400°C   44 (CyS)              < 1 (Gas)        Total yield (daf)
   86 (daf) (1h/1h)    39 (CyI)  430°C       21 (CyS)          Gas       3
   14 (ash)            14 (ash)  (1h)         7 (ToS-CyS)       CyS      76
                                              4 (TS-ToS)        ToS-CyS   8
                                              7 (TI)            TS-ToS    5
                                             14 (ash)           TI        8
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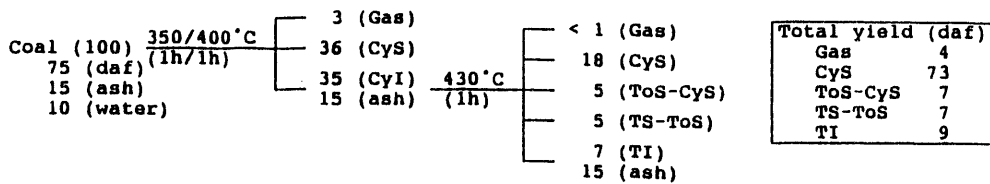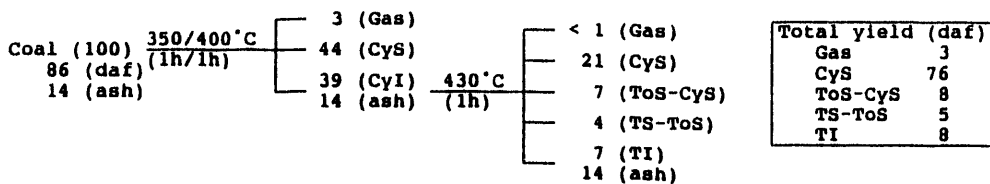
Scheme 1 Mass balance for Runs 19 and 21

Table 3 Gas Composition Obtained from Liquefaction[a]

gas	run 18	run 19[b]	run 20 (CyI)	Run 21[b] (CyI)
			(Vol %)	
Hydrogen	61.53	68.05	62.61	70.76
CO	0.15	0.09	0.45	0.14
CO_2	0.21	0.07	1.41	0.14
Methane	9.32	5.03	9.23	4.84
Ethane	4.19	2.55	4.15	2.44
Ethylene	0.04	0.05	0.04	0.05
Propane	2.21	1.44	2.15	1.38
Propylene	0.09	0.11	neg	0.10
n-Butane	0.51	0.40	0.48	0.36
i-Butane	0.16	0.12	0.16	0.11
Butene	0.02	0.04	neg	0.02

[a]Gas samples include gas produced from coal liquid,
Coal/coal liquid = 5 g/50 ml
[b]Gas obtained after the second step at 430°C

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