CLEAN, PREMIUM-QUALITY CHARS:
DEMINERALIZED AND CARBON ENRICHED

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ABSTRACT

The overall objective of this two-year project is to evaluate methods of preparing
demineralized and carbon enriched chars from Illinois Basin coal. There are two processing
steps: physical cleaning of the coal and devolatilization of coal under different environ­
ments(He, H₂, He/O₂, CH₄, and CH₄/O₂) to form chars. Also, as-received and clean coal
samples were mixed with hectorite, Ca-montmorillonite, and kaolinite to evaluate the poten­
tial effects of these clays on chars yield and agglomeration during devolatilization processes.
Three different techniques were used: thermogravimetric analysis, differential thermogravi­
metric analysis, differential scanning calorimetry (DSC), and in-situ diffuse reflectance FTIR
(ISDR-FTIR). Thermogravimetric measurements showed that reactive gases (except He)
dissolve in the softened coal. Also, these gases convert some of the coal mineral matter into
catalyst by chemical reduction and oxidation. Coal reactivity increases by adding clays
because they may be catalyst for methane activation, may prevent coal agglomeration, and
may modify the geometric structure of the coal surface. DSC measurements show that clean
coil devolatilizes at a lower temperature than as-received sample and preoxidation lowers
the devolatilization temperature. Additionally, kaolinite addition increase yields of chars
from IBC-102 coal in He. In-situ diffuse reflectance FTIR experiments show that thermal
decomposition of coal either increases -CH₃ content in char or alters the physical structure of
-CH₄. Also, phenol groups of the coal play an important role in cross-linkage the coal struc­
ture when coal is thermally treated.

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shared program.
EXECUTIVE SUMMARY

The goal of this project is to develop a process that can produce a clean, desulfurized, premium-quality char from Illinois basin coal. This goal is achieved by utilizing the effective properties of smectites in combination with methane to manipulate char yields. The general objectives are to determine the optimum particle size of the coal for this process, to find the most reactive type of smectite and the method of its dispersion on the coal surface, to find the best conditions of removing sulfur from the char under the combination of methane/oxygen or helium/oxygen, and, finally, to identify the conditions for rejection of smectites from char by the gravitational separation technique.

Experiments were performed with IBC-102 coal using three different techniques: (1) thermogravimetric analysis (TGA) including differential thermogravimetric analysis (DTG), (2) differential scanning calorimetry (DSC), and (3) in-situ diffuse reflectance-FTIR (ISDR-FTIR).

The TGA experiments show that all reacting gases (methane, hydrogen, methane/oxygen, and oxygen) dissolves in the softened coal and/or react with the mineral matter of the coal, resulting in slower devolatilization than in helium between 370°C and 460°C for methane and hydrogen, and at 520°C for methane/oxygen and oxygen alone. Above these temperatures, the weight differences under these gases and helium start to decrease. Also, TGA results show that added clays change coal reactivity, possible by participating directly as a catalyst and by modifying the structure of the coal surface. Preoxidation of coal mixed with clays increases the reactivity and lowers the temperature at which maximum reactivity occurs. Optimum conditions for coal preoxidation are 80°C for 2 hrs. Since the role of coal weathering is not fully explained, we suggest that interaction of oxygen with coal structure at low temperature results in formation of weak ether bonds which may crack and form free radicals as the temperature is raised and before the coal structure becomes mobile. Thus, by increasing the quantity of free radical species, preoxidation will enhance the reactivity of coal. Also, oxygen may interact with the minerals present in the coal structure forming oxides which show catalytic activity for coal gasification processes. Similar experiments were performed with clean coal samples. In experiments with He, practically no difference occurs between preoxidized and not preoxidized samples. However, when methane was used, preoxidation increases coal reactivity and lowers the temperature at which maximum reactivity was occurs. A probable explanation is that the crude minerals fractions present on the coal surface are oxidized to form active catalysts for catalyzing the reaction of methane with coal.

Differential Scanning calorimetry (DSC) shows three thermal effects attributed to different processes during coal heating. These are dehydration of coal and clay (if present), cross linkage, and mild gasification. Clay addition shows substantial effects on the cross-linkage temperatures but does not change the maxima at mild gasification temperatures. Both preoxidation of the coal and removal of its mineral matter result in a 30°C lowering of the devolatilization temperature. Also, DSC experiments show that kaolinite with a layer charge of 3 to 15 meq/100 g is very effective in increasing the yields of chars from IBC-102 coal. The clean coal recovered from the selective-bitumen agglomeration shows enhanced weight loss during gasification under He. However, its preoxidation at 50°C prior to the reaction increases its char yields. Additionally, irrespective of the type of clay used in the gasification, the clay additive sharply retards the agglomeration tendency of coal during gasification.

Results of ISDR-FTIR experiments suggest that the carboxylic and phenolic groups present on the coal surface may play an important role in the cross-linking process, and therefore effect the yield of char. Additionally, these measurements show that condensation reactions
result in the formation of condensed aromatic sheet structures in char. Phenolic hydroxyl groups may facilitate condensation processes, and thermal decomposition of coal either increases -CH$_3$ content in char or alters the physical structure of methyl groups which are different from the starting coal.
OBJECTIVES

The goal of this project is to develop a bench-scale procedure to produce clean, desulfurized, premium-quality chars from the Illinois basin coals. This goal is achieved by utilizing the effective properties of smectites in combination with methane to manipulate the char yields. The major objectives are:

a. to determine the optimum water-ground particle size for the maximum reduction of pyrite and minerals by the selective-bitumen agglomeration process

b. to evaluate the type of smectite and its interlamellar cation which enhances the premium-quality char yields

c. to find the mode of dispersion of smectites in clean coal which retards the agglomeration of char during mild gasification

d. to probe the conditions that maximize the desulfurized clean-char yields under a combination of methane/oxygen or helium/oxygen

e. to characterize and accomplish a material balance of chars, liquids, and gases produced during mild gasification

f. to identify the conditions which reject dehydrated smectites from char by the gravitational separation technique

g. to determine the optimum seeding of chars with polymerized maltene for flammability and transportation

INTRODUCTION AND BACKGROUND

The carbonization process of coal is a well-established technology\(^1\,^2\), next only to the combustion utilization of coal, though its economic viability has considerably eroded due to the competition from other relatively cheap energy sources. Therefore, recent emphasis in the development of the carbonization process has been to recover liquids and gases from the coal, under mild gasification and gasification conditions, which can act as chemical feedstock\(^1\,^2\,^5\,^6\). Far less effort\(^17\,^21\) has been devoted in developing technology for producing enhanced yields of char or premium-quality char from coals. If the mild coal gasification process is to be commercially successful, then the production and utilization of clean, premium-quality chars are mandatory.

The high sulfur content, both inorganic and organic sulfur, of the Illinois bituminous coals in general and the high mineral content of some Illinois coals present significant hurdles for their effective, economical, and environmentally-acceptable utilization. This is especially true for the mild gasification of Illinois coals since it results in by-products, both liquids and solids, which have an environmentally unacceptable sulfur content. Additionally, the high ash content (for example, 10.4% in IBC-101 coal or 38.3% in IBC-104 coal) of Illinois coals may actually dilute the coal to such an extent that the coking properties of the coal are markedly diminished\(^4\). Also, chars rich in minerals foul the catalytic promoters via catalytic-material-mineral reactions in the gasification process\(^22\). Therefore, it is imperative that, prior to subjecting Illinois coals to the mild gasification process to produce chars and liquids, the
coals must be physically cleaned to reduce considerably the mineral and pyrite content.

The removal of pyrite and other minerals from Illinois bituminous coals have proven to be a vexing problem to coal preparation engineers. Most advanced, mechanical coal cleaning processes take advantage of the differences in the surface properties of minerals and organic coal in removing pyrite and other minerals. These processes (e.g., aggregate flotation, aglo-float process, static tube flotation, selective-froth flotation, microbubble flotation, air-sparked hydrocyclone, ultrasonically enhanced flotation, reverse coal-pyrite flotation, and the Otisca process) add surfactants, frothers, and surface-active polymers to separate minerals from coals\(^22,24\). Unfortunately, the mechanical-coal cleaning processes have had only limited success\(^24\) in rejecting pyrite from bituminous coal. In the aforementioned coal-cleaning processes, external additives are supplied to coal feed to selectively enhance the floatability of organic coal relative to minerals, and this results in the adsorption of additives on the surface of cleaned coal particles. The adsorption additives will have serious repercussion during mild gasification.

The thermal decomposition of coal is a complex sequence of events, which can be described in terms of several physicochemical changes, e.g., it has been suggested\(^13\) that weak tar formation appears at about 350°C from volatilization of low molecular weight coal constituents, and this event is followed by major tar yields at 400°C-450°C. It is also known\(^1\), that certain coals become soft and flow when heated to 400°C-600°C, where thermal depolymerization occurs with the release of liquids and gases. If surfactants and/or polymer additives are present on the surface of clean coal, then during the mild gasification process these additives will act as effective sites where cross-linking will agglomerate the coal particles and incorporate deleterious additives into the char, which may further retard the effective utilization of the chars. Consequently, the coal cleaning process employed to produce clean coal feedstock for mild gasification of coal must not include additives which can retard mass transport.

In order to remove pyrite and other minerals from coal it was found\(^25\) that coal must be ground with water prior to the cleaning process. This wet grinding results in the formation of hydrated-sulfate species on pyrite, irrespective of their location. Additionally, it was observed that grinding the coal under water inhibits the coal’s oxidation. This fact should further attenuate the cross-linking of coal under mild gasification\(^13\).

The chars produced from the clean coal can be upgraded by treatment with methane, which desulfurizes the char and deposits carbon on the coal surface. Desulfurization occurs chiefly from the interaction of methane with pyrite\(^36\):

\[
\text{CH}_4 + 2\text{FeS}_2 \rightarrow \text{CS}_2 + 2\text{Fe}^0 + 2\text{H}_2\text{S}
\]

However, considering the fairly ready transfer of sulfur between the inorganic (mineral) and organic phases\(^37\), desulfurization of the organic phases probably also occurs. In view of our previous study we strongly believe that when clean coal obtained from the selective bitumen agglomeration process is subjected to mild gasification under the mixture of CH\(_4\) with 2%O\(_2\), a further reduction of the sulfur in char will occur. This combination of methane and oxygen gas will not only reduce the sulfur content of the remaining pyrite but also will eliminate organically bound sulfur.

Deposition of carbon from methane decomposition on chars may occur in an amorphous from with extremely high surface area and in a filament form with high mechanical strength. These filaments grow from small crystallites of metals,\(^38,39\) which can be produced in the char.
Carbon may be deposited from methane by the action of high temperatures and/or metal catalysts as well as carbon. High temperature deposition of carbon leads to either amorphous (soot-like) or graphitic carbon depending on the presence and kind of surface available. These carbons, especially the amorphous carbons, have very high surface areas. On the other hand, filamentous carbons have moderate surface areas but high mechanical strength. A modification of carbon filaments, "cauliflower-like" graphitic structures, exhibit moderately high surface areas.

Graphitic filaments of carbon and "cauliflower" graphitic structures are formed from essentially the same process, that is, by the decomposition of methane on Fe, Co, or Ni surfaces. On small crystallites, which are called "growth" crystals, catalytic decomposition of methane to carbon and hydrogen occurs at one of the crystal faces. The carbon so formed then diffuses through the crystallite and re-emerges at the opposite surface to form a hollow graphitic filament with a diameter approximately the size of the metal crystallite. On larger crystallites "cauliflower-like" eruptions of graphitic carbon occur. The fibers possess high mechanical strength which they can impart to the char, and the "cauliflower" structures have fairly high surface areas. In this way methane treatment can upgrade char by desulfurizing it, by producing Fe "growth" crystallites, and by growing carbon filaments and/or graphitic "cauliflower" structures.

To determine the feasibility of decomposing methane on char a preliminary experiment was performed in the following way. In the microbalance reactor 61.945 mg of IBC-106 were devolatilized to constant weight (47.652 mg) under flowing helium at 600° C then the gas was switched to methane. Upon first contact with methane the char decreased in weight to 47.559 mg in 22 minutes and then increased to 49.250 mg in 19 hrs. We assume that the weight decrease upon initial contact with methane was due to reduction of residual iron pyrite; however, that has not been established. We know from ongoing research that methane reacts with coal char to produce chemicals, so the weight decrease could be a chemical reaction(s) between the char and methane to produce vaporizable organic molecules. Nevertheless, the subsequent weight increase can only be due to carbon deposition on the char.

With this knowledge in hand we tested desulfurization ability and BTU increase by preparing two more samples from IBC-106 in the plug flow reactor. One sample was treated with helium for 16 hrs at 500° C and the second sample was treated with methane for 19 hrs at 500° C. These samples were analyzed by Cephus Industries, Inc. of Marion, Illinois with the results shown in Table 1.

| Table 1 |
| BTU and S Contents of Chars from IBC-106 Treated with Helium and Methane at 500° C |
| after | after |
| He | CH₄ |
| BTU | 11738 | 14503 |
| %S | 3.49 | 1.39 |

BTU content is 23.5% larger for the methane-treated than the helium-treated sample. Moreover, since the original coal had a reported BTU value of 13226, the methane-treated sample has a 9.7% larger BTU value than the original coal. And sulfur content is substan-
tially smaller too. The original sulfur content of the coal was 3.77% (0.01% sulfatic, 1.86% pyritic, and 1.90% organic). Helium treatment reduces it by 7.4% while methane treatment reduces it by 63.1%. This latter substantial reduction in sulfur is large enough to account for all of the pyritic sulfur and 26.8% of the organic sulfur.

Since the formation of free radicals by the rupture of coal bonds during mild gasification is believed to be an important step in the production of liquids and chars, we have recently attempted to enhance the yields of chars from IBC-104 coal using free radical promoters. It is well known that pyrite plays a critical role in generating free radicals in coal at about 500°C. Though pyrite acts as a catalyst in promoting free radicals in coal, and thus may help in better polymerizing the coal, it unfortunately adds sulfur into the char. Also, pyrite does not retard agglomeration of the char during mild gasification. Therefore, any free radical promoter added to the clean coal should not only affect the free radical concentration but should also inhibit the agglomeration of the char.

It is well known that clay minerals display a number of catalytic activities including polymerization, desulfurization, cracking, and hydrogenation. Yet the role in mild gasification has been ignored. Granted that mineral matter in coal contains a significant amount of kaolinite and illinite clays; however, it is the naturally occurring smectites which display enhanced catalytic activities due to their very large surface areas and uncompensated edge structures. The EPR measurements performed under vacuum showed that montmorillonites are effective promoters of free radicals in coal at about 500°C. Our recent, preliminary mild gasification experiments on IBC-104 coal with various cation exchange smectite revealed that all smectites, when appropriately dispersed in coal, retard the agglomeration of the char at 500°C under CH₄/O₂ mixture, and, depending upon the exchanged cation of the smectite or type of smectite, the yields of liquids and chars are selectively enhanced.

**EXPERIMENTAL PROCEDURE**

**Materials**

Coal sample IBC-102 was obtained from the Illinois Basin Coal Sample Program. It contains 39.8% volatile matter, 6.9% ash, 14.2% moisture, and 3.3% sulfur. Before the experiments, the coal sample was first ground in a planetary ball-mill to reduce its particle size to < 75 μm. Then, this < 75 μm particle-sized coal was further ground under water in a micro-rapid Brinkman mill to reduce its particle size to < 37 μm. The water-ground coal was dried at 24°C under flowing nitrogen and then sieved to recover the < 37 μm particle-sized coal.

The methane (UHP grade), helium, hydrogen, and oxygen were obtained from MG Industries, Scientific Gas Division. The mixture of 2% oxygen in either methane or helium was prepared by mixing the proper amounts of the gases. The gases were dried over activated molecular sieve. Methane, helium, and hydrogen were further purified by flowing them through a Mn/SiO₂ trap to remove oxygen.

**Preparation of Clean Coal**

In an effort to produce clean, carbon-enriched chars from Illinois coals, we utilized the following procedure to prepare clean coals: (a) The as-received IBC-102 coal was first ground under water environment in a planetary ball mill to a particle size which could be accepted by the Brinkmann micro-rapid mill, i.e., < 740 micron. (b) The resultant coal paste from step 1 was transferred to the micro-rapid mill, and the coal samples were further ground in the micro-rapid mill under water for 15 minutes. (c) After the grinding procedure, the coal samples, which were in the form of a paste, were recovered and air dried. The air-dried
samples were sieved to produce < 38 micron-sized coal samples. (d) The < 38 micron-sized coal was magnetically stirred for 15 minutes in a vessel to prepare a water slurry. The slurry was stabilized. (e) The 13° API gravity, polymerized bitumen was added to the coal-water slurry in such a manner to establish a coal-to-bitumen ratio of 100:8 by weight. (f) The bitumen-coal-water slurry was further agitated at 1800 rpm for 15 minutes to enhance the bitumen-coal interactions. (g) After flocculation and agglomeration, the IBC-102 coal was separated into two fractions: one which floated and the other which settled on the bottom. (h) The floated, agglomerated fraction of IBC-102 coal, which henceforth will be called clean coal, was dried and was prepared for mild gasification experiments.

**COAL-CLAY MIXTURE PREPARATION**

One of the main objectives of this proposal is to elucidate the role of naturally occurring clay minerals, if any, in manipulating the yields of chars from Illinois basin coals. In addition, we are to evaluate whether clay additives inhibit the agglomeration of coal particles during the mild gasification process. To accomplish the aforementioned objectives, three different structural types of clays were tested, i.e., kaolinite, montmorillonite, and hectorite. The poorly crystallized kaolinite, Ca-montmorillonite, and hectorite clay sample were from Warren (Georgia), Cheto (Arizona), and San Bernardino (California), respectively.

In order to explore the effects of clay minerals on the mild gasification of coal, the following steps were used to prepare the coal-clay mixtures: (a) The < 38 micron particle-sized coal and the appropriate clay were accurately weighed in order to produce a mixture which had a coal-to-clay ratio of 2:1 (by weight). Methanol was added to the coal-clay mixture, and the mixture was vigorously stirred in an attempt to produce a homogeneous distribution of coal and clay within the mixture. After about one hour of agitation, the methanol was removed from the sample by subjecting it to a vacuum. The fact that methanol was removed from the sample by rotary-evaporation ensured the deposition of a thin layer of clay around the coal particles.

**RESULTS AND DISCUSSION**

**THERMOGRAVIMETRIC STUDIES**

**Experimental Procedures**

Temperature programmed reactions of coal under different environments were performed using a Cahn 113 microbalance reactor. It consists of a quartz-tube reactor with an inner diameter of 22 mm heated in a split-shell furnace, a quartz bucket for the coal sample, and auxiliary equipment for introduction and metering of gas flow. Flow of gases was maintained by micrometer valves and monitored by Sierra Top Trak model 821S2 mass flow meters. An auxiliary helium feed (10 mL/min) system was used for purging the "vacuum" bottle containing the motor assembly of the microbalance. The temperature control system utilizes a Micronic 823 computer connected to a thermocouple suspended just below the sample pan. The weight change signal is digitized by an IBM compatible computer using a locally developed data acquisition program/display and stored for further evaluation.

Normally, the coal samples were pretreated for 12 hrs at room temperature under flowing reaction gas to obtain a constant weight. Each experiment was performed at 20°C-650°C with a ramp of 10 deg/min and the data were normalized to account for differences in starting weights and to account for the effect of temperature on the volume flow of the gases. This was done in the following way. Several blank tests were performed with crushed glass
loaded in the microbalance under flowing helium at elevated temperatures. The average value of the blank values at every 10° ramp from 20°C - 650°C was subtracted from the experimental values collected at every 10° each experiment with coal. Therefore, the weight losses of coal samples are due only to the removal of the volatile materials because weight changes due to temperature effects and gas density changes are removed.

Non-isothermal reactivities of IBC-102 coal

The sample size used in this study was 2 mg or less. The gas flow rate of the reactants was 60 ml/min and the coal particle size was <38 μm. At these conditions, kinetically controlled reactivity results were obtained. The coal samples were heated in the flowing gas at a rate of 10 deg/min up to 650°C. The weight losses were continuously recorded and, at the end of each experiment, were calculated and normalized. The weight versus temperature data for IBC-102 coal reacted with different gases are shown in Figure 1. The weights were normalized to the same initial weight (1 mg).

To compare the reactivity of coal samples under different gases, the weight changes under helium were subtracted from the weight changes under CH₄, H₂, and CH₄/O₂. The resulting plots, which show the devolatilization relative to He, temperature programmed pyrolysis (TPP) curves, are in Figure 2. Essentially, no difference in devolatilization by hydrogen, methane, and methane/oxygen is observed until approximately 150°C. As the temperature increases up to 420°C, devolatilization rates decrease relative to the He devolatilization rate and for hydrogen and methane the rates go through minima at 360°C. In the temperature region 360°C - 420°C the devolatilization rate increases for these two gases. However, for the methane/oxygen mixture no minimum devolatilization rate is observed in the 360°C -420°C region. Additionally, below 360°C hydrogen devolatilizes slightly faster than methane or methane with oxygen. When the temperature reaches 420°C, the situation dramatically changes. The rates of devolatilization sharply decrease for all gases relative to He. This decrease in rates continues up to approximately 460°C for methane/oxygen, 480°C for methane, and 510°C for hydrogen. Above these temperatures, the weight differences between these gases and He start to decrease. We discussed the interpretation of these curves in the previous report. We hypothesized that the decrease of the rate of devolatilization relative to He may result from the reactive gases converting some of the mineral matter into catalysts through a chemical reaction which causes the observed increase in weight. Once the catalysts are formed, they enhance devolatilization processes. In fact, the mineral matter present in the coal may undergo oxidation or reduction (depends on the environment) resulting in the formation of catalysts that may not only activate methane but also crack the long chain compounds presents in the coal structure. Also, the observed decrease of the rate of devolatilization relative to He may be related to the solubility of the reacting gases (methane, methane/oxygen, and hydrogen) in the coal. This solubility depends on temperature and may cause weight increases in a certain temperature region.

Figure 3 shows the derivative thermogravimetric profiles (DTG) for IBC-102 samples treated with helium, methane, hydrogen, and methane/oxygen. As the temperature is raised, the weight of the coal decreases, however the rate of the weight loss for each gas is approximately constant till 250°C is reached. As the temperature continues to increase, the weight continues to decrease until the maximum weight loss rate is observed. The maximum reactivity is observed around 470°C for methane, methane/oxygen, and hydrogen, and at 460°C for helium. After that, the rate of the weight loss decreases. The higher maximum reaction rate is observed for methane/oxygen and hydrogen. By contrast, the lower reaction rate is observed for helium.
Experiments with coal mixed with kaolinite and Ca-montmorillonite

To explore the effect of clays on the devolatilization reaction, two IBC-102 coal samples were mixed with kaolinite and Ca-montmorillonite. The ratio of coal:clay was 1:2 for both samples. These samples were devolatilized in the microbalance reactor with He, CH₄, and CH₄/O₂ at the same conditions as described in the previous chapter. The rates of the weight losses (DTG) of IBC-102 mixed with kaolinite and Ca-montmorillonite under different gases are shown on Figures 4 and 5, respectively. A comparison of non-isothermal (DTG) plots for the raw IBC-102 coal and for the coal mixed with clays under different gases are presented in Figures 6, 7, and 8. Under flowing helium (Figure 6), practically no difference between raw coal and coal mixed with Ca-montmorillonite is observed. However, the IBC-102 coal mixed with kaolinite shows maximum reactivity at higher temperature (510°C) than the other samples. The effect of added clays on devolatilization is clearly seen in the reaction with CH₄ (Figure 7). Both clays increase the reactivity of the coal and, similar to devolatilization under He, the maximum of the rate of the weight loss of the sample mixed with kaolinite is shifted to a higher temperature. In the reaction with CH₄/O₂ (Figure 8) the maximum reactivity of the coal mixed with clays is greater than for the raw coal. However, the effect of clays is not so strong as in the reaction with pure methane.

The higher reactivity of the coal mixed with clays may be attributed to the clays serving as catalysts for the activation of methane. Also, clays may prevent coal agglomeration during gasification and increase amount of the coal surface which is reactive, a most significant parameter of the gas-solid reaction. There is also another explanation of the role of clays in coal devolatilization reactions. It is well known that coals are composed of pseudo-graphitic building blocks. The carbon crystallites are small in size and poorly aligned because of crosslinking. The edge sites and various imperfections in the carbon structure are thought to be the "active sites" during gasification reactions. Thus, the role of the added clays may be to modify the structure of the surface of the coal. The coal "active site" concept includes sites with a wide range of activities. From the gasification and liquefaction reactivity standpoint the sites that are both "available and active" under reaction conditions are the significant sites. Therefore, this modification of the structure of the coal surface by the clays will increase the number of available active sites present on the char surface.

Effect of preoxidation on the mild gasification

In an effort to elucidate how preoxidation of coal will affect char production from IBC-102 coal, we conducted comparative experiments in the microbalance reactor. Prior to the reaction, coal samples were preoxidized with flowing oxygen at different temperatures and times. After preoxidation, the sample was cooled to room temperature (20°C) and the gas was switched from oxygen to CH₄ or He. Figure 9 presents the DTG profile for IBC-102 mixed with kaolinite unoxidized and oxidized at 80°C (2 and 12 hrs) and 150°C (4 hrs) and then reacted with methane. Figure 10 compares the DTG profiles from similar experiments performed with IBC-102 coal mixed with Ca-montmorillonite. For both samples, the higher reactivity of coal with methane was obtained after preoxidation at 80°C for 2 hrs. Figure 11 presents the DTG results from the experiment in which IBC-102 coal mixed with Ca-montmorillonite prior to reaction with methane was preoxidized at 80°C for different times. The highest reactivity was obtained for the samples preoxidized for 0.5 and 2 hrs; however, the sample preoxidized for 2 hrs shows the maximum point at lower temperature. The comparison of the DTG profiles for IBC-102 as received and mixed with Ca-montmorillonite samples preoxidized at 80°C for 2 hrs and then treated with methane at 20-650°C is shown in Figure 12. As can be seen from this figure, the sample containing clay exhibits higher reactivity than the as-received coal. Additionally, coal mixed with clay shows a maximum rate of devolatilization at lower temperature.
The observed increased coal reactivity after preoxidation at 80°C supports our previously reported DSC experiments\textsuperscript{51} in which we concluded that better yields of clean chars will be produced if IBC-102 coal is preoxidized prior to subjecting it to mild gasification. The role of preoxidation is still not well understood. Oxygen-related effects seem principally to involve cross-linking reactions. It has been claimed that cleavage of ether bonds (formed during low temperature preoxidation) may increase coal plasticity\textsuperscript{52,53}, the parameter which may play a key role in mild gasification. Wachowska \textit{et al.}\textsuperscript{54} reported the formation of weak ether links during low temperature preoxidation. When such materials crack in still nonmobile coal molecules, free radicals must be created and enhance the reactivity of the coal. Therefore, preoxidized coal should exhibit an increase reactivity even when no hydrogen sources are available. In fact, in the reaction with He alone (Figure 13), the preoxidized coal mixed with Ca-montmorillonite shows higher reactivity then the sample nonpreoxidized.

**Non-isothermal reactivities of clean IBC-102 coal**

The observed, comparative DTG profiles of as-received IBC-102 coal and clean IBC-102 coal obtained under flowing He are presented in Figure 14. These profiles were obtained under identical experimental conditions using a temperature ramp of 10 deg/min. The comparison of the DTG clearly shows that the sample in "clean" form devolatilizes faster than the sample "as-received". However, the maximum rate of devolatilization occurs at the same temperature - 460°C. Figures 15 and 16 show the DTG's for both clean and as received IBC-102 coal treated with methane and methane/oxygen, respectively.

As the temperature is raised, the weights of the coal samples decrease, however the rate of weight loss for each gas and sample is approximately constant till 250°C is reached. As the temperature continues to increase, the weight continues to decrease until a maximum rate of weight loss is observed. For methane, the maximum reactivity of 6.1 %/min at 480°C is observed for clean coal and 4.4 %/min at 430°C for as-received coal. When methane/oxygen is used, the maximum rate of weight loss (7 %/min) occurs at 425°C for the clean sample and at 450°C (5.2 %/min) for the as-received sample.

Significant results are represented in Figures 17 and 18. Prior to the devolatilization with He and CH\textsubscript{4}, IBC-102 clean coal was preoxidized at 80°C for 2 hrs. There is no difference in the DTG profiles under He between preoxidized and nonpreoxidized coal (Fig. 16). However, when reaction is performed under flowing CH\textsubscript{4}, there is a difference in DTG profile (Fig. 17) for preoxidized and nonpreoxidized samples.

The higher reactivity of clean coal may be attributed to this sample being devoid of minerals but having adsorbed crude oil fractions on its surface, including the surface of the pores. Since DSC of clean coal displays an exothermic behavior in the temperature range 100°C - 360°C\textsuperscript{51}, the possibility that the adsorbed crude fractions react with coal during thermal treatment can not be discounted. This interaction must somehow produce a resultant coal structure whose free energy is larger than the free energy of the corresponding un-cleaned (as-received) coal. If such is the case, clean coal should devolatilize faster and at lower temperatures. Therefore, crude species, adsorbed during coal cleaning, show catalytic properties during devolatilization.

**Thermogravimetric study of the char yields from IBC-102 coal under the different environments**

In order to determine the effects of clay additives and coal cleaning on the char formation, the following procedure was adopted. The initial weight (W\textsubscript{i}) of the coal sample, prior to the reaction, was determined, i.e.:
\[ W_{tp} = W_{cap} + W_{ap} + W_{clp} \]  \hspace{1cm} (1)

In eq. (1), \( W_{cap} \) is the initial weight of the organic fraction of the coal, \( W_{ap} \) is the initial weight of the ash in the coal, and \( W_{clp} \) is the initial weight of the clay additive. At the end of the TG run, the weight of the charred sample (\( W_{tf} \)) was obtained, and this weight in turn is composed of the final weights of the appropriate fractions, i.e.,

\[ W_{tf} = W_{caf} + W_{af} + W_{clf} \]  \hspace{1cm} (2)

where, \( W_{caf} \), \( W_{af} \), and \( W_{clf} \) are the final weights of the char, ash, and clay fractions, respectively. If it is assumed that no major loss in the ash weight occurs at \( T < 923 \) K, which is not an unreasonable assumption for IBC-102 coal, then the % organic fraction weight loss (OFWL) can be determined from

\[ \% \ OFWL = 100 \ \frac{[W_{tp} - W_{tf}] - (W_{clp} - W_{clf})}{[W_{tp} - W_{ap} - W_{clp}]} \]  \hspace{1cm} (3)

Once the % OFWL has been determined by substituting the normalized \( W_{ap} \) obtained from the thermogravimetric experiment with clay alone, into equation (3), then the char yields can be calculated. The effects of various additives on the char yields under the different environments and temperatures are shown in Figures 19, 20, and 21. The results of the thermogravimetric experiments performed under He (Fig. 19) show that at 550°C there is no difference in char production from ground coal and coal mixed with kaolinite. However, at 650°C kaolinite enhance the char formation, when compared with ground coal and mixed with Ca-montmorillonite. At both temperatures, Ca-montmorillonite is not effective in char production. The clean coal recovered by the selective-bitumen agglomeration shows enhanced weight loss when subjected to gasification under He. However, its oxidation at 80°C for 2 hrs prior to mild-gasification increases char production. A similar tendency is observed when coal was treated with \( \text{CH}_4/\text{O}_2 \) (Fig. 20). In this case kaolinite clay is most effective in increasing the char production from IBC-102 coal. The effect of methane on char yields from IBC-102 is shown in Figure 21. Here, unlike He and \( \text{CH}_4/\text{O}_2 \), Ca-montmorillonite greatly increases the char yields at both temperatures. From this observations we conclude that the coal sample mixed with Ca-montmorillonite catalyzes methane decomposition and carbon deposition on the char surface. Thus, this process should produce char with a high BTU value.

**DIFFERENTIAL SCANNING CALORIMETRY (DSC) EXPERIMENTS**

**Experimental Procedures:**

Calorimetric data under pyrolytic conditions were recorded on a Perkin-Elmer DSC7 system, interfaced with a Perkin-Elmer 7700 computer. The DSC was calibrated for temperature and enthalpy, applying the procedure reported in the literature.\(^{55,56,57}\) The temperature calibration was performed by the two-point method, using the melting transitions of indium (430 K or 157°C) and zinc (693 K or 420°C). The accuracy in temperature between 300 K and 693 K, based on our calibration procedure, was estimated to be +/- 1 K. The enthalpy calibration was performed using indium heat of fusion as the standard. After the enthalpy calibration, the DSC data on zinc metal were re-recorded, and the observed enthalpy of the melting transition of zinc was consistent with the values reported in the literature. The conditions under which the instrument calibration was performed exactly matched the experimental run conditions, namely the scan rate of 10 K/min, helium purge at 0.207 MPa pressure. Also, during both calibration and pyrolysis runs, the dry box assembly over the sample head was flushed with nitrogen gas to maintain thermodynamic equilibrium. Aluminum sample pans, in an
unsealed mode, generally were used to probe the pyrolytic behavior of coal. This was achieved by pushing down the top sample pan gently onto the bottom pan containing the coal. Typically 21 mg of sample were used for our DSC measurements.

As-Received Ground Coal:

Figure 22 presents the observed DSC thermograph obtained under helium purge at 313 K < T < 863 K of < 38 micron particle-sized IBC-102 coal. Six thermal events can be recognized from Fig. 22. The first thermal event, manifested as a very broad peak centered at around 361 K, can be associated with water loss from the coal. The broad peak at 361 K is asymmetric, starting at 321 K and ending at 413 K, and signifies the desorption of water from coal via a complex combination of desorption mechanisms. Above 470 K, the DSC curve shows a steady deflection downward, i.e., an exothermic response. The second thermal event occurs at around 530 K where a weak exothermic peak, marked as thermal event T1 in Fig. 22, is manifested in the DSC curve. A careful examination of the DSC curve around thermal event T1 indicates an endothermic response at T1 < T < 550 K. It should be noted that the endothermic deflection follows the exothermic thermal event at T1.

Recently Yun and Suuberg, from their DSC and solvent-swelling measurements on Pittsburgh No. 8 coal, have argued that bituminous coals undergo physical transition between temperature range 523 K to 573 K when subjected to a pyrolytic heating under an inert environment. They attributed the observed change in the DSC curve at around 523 K to physical relaxation of the coal. Since changes observed in the DSC curve of bituminous coal in the vicinity of 523 K were irreversible, Yun and Suuberg discounted the observed thermal event between 523 K to 573 K as being a glass transition. It should be noted that the thermal event T1 for as-received IBC-102 coal falls in the same temperature range where Yun and Suuberg reported a physical transition for Pittsburgh No. 8 bituminous coal. Therefore, it is logical to ask whether thermal event T1 is somehow also related to a physical transition in IBC-102 coal. To answer this question, we recall that the DSC curve, reproduced in Fig. 22, is in fact the differential heat supplied (with respect to the reference pan) to the coal sample as its temperature is raised, i.e.,

\[ H = \text{(heat supplied to the sample)} = \text{Differential Power} \cdot \left( \frac{dQ}{dt} \right) \]

where \( \left( \frac{dQ}{dt} \right) \) and \( \left( \frac{dQ}{dt} \right)_r \) are the heat flow to the sample and reference pans, respectively. The specific heat capacity \( (C_p) \) of the sample at any given temperature, \( T \), is defined as

\[ C_p = \left( \frac{1}{m} \right) \left( \frac{dQ}{dT} \right). \]

In Eq. (5), \( m \) is the mass of the sample. By combining Eqs. (4) and (5), the heat flow to the sample in a DSC experiment can be ascertained, i.e.,

\[ (dQ/dt) = m C_p (dT/dt). \]

Since we employed a heating rate of 10 K/min in the present DSC experiments, Eq. (6) can be further simplified, i.e.,
\[
\frac{dQ}{dt} = 10 \ m \ C_p
\]  

Equation (7) predicts that if the mass of the coal sample remains constant then the differential heat flow to the sample will be proportional to \( C_p \). Yun and Suuberg have argued that the physical transition of coal at 523 - 573 K is devoid of any weight loss. If such is the case, then the observed DSC curve, reproduced in Fig. 22, should show an endothermic peak associated with the physical transition. Clearly, our DSC experiments on IBC-102 coal show no such endothermic peak and consequently, no physical transition at 523 - 573 K. The TGA and DTG data on as-received IBC-102 coal under helium purge, presented in an earlier section, clearly indicate that the rate of weight loss increases at around 518 K. Above 518 K, the rate of weight loss steadily increases, and the maximum weight loss for the IBC-102 coal occurs at 743 K. If such is the case, then Eq. (4) predicts an exothermic response. This is precisely what is observed in Fig. 22. Therefore, it is argued that there is no physical transition in IBC-102 coal at 523 - 573 K. However, it is worth pointing out that the thermal event T1 for the IBC-102 coal is not an experimental/instrumental odd effect since it persists when the measurement is repeated.

A second thermal event (marked T2), in the form of a broad peak at around 627 K can clearly be seen in Fig. 22. Lucht et al.61, from their DSC data on fresh coals, argued that the thermal process at 630 K suggests the existence of a glass-to-rubber transition for coal. However, their reported DSC thermograph is not consistent with a typical glass-to-rubber transition behavior. It is well known that when glass transforms to rubber, molecular chain mobility increases. The molecular chains are free to vibrate and, therefore, will absorb more heat. Consequently, in a DSC experiment, increased heat will be supplied to maintain a constant heating rate. This will result in a displacement in the DSC curve opposite to that reported by Lucht et al.61 In view of the above, we discount their conclusion that the thermal event observed at 627 K for IBC-102 coal is associated with a typical glass-to-rubber transition. If the exothermic thermal event at 627 K does not result from a glass-to-rubber transition, then it may result from first cross-linking reactions in coal. However, additional DSC and spectroscopic measurements will be required to confirm or discount this speculation.

The major thermal event for IBC-102 coal is observed at around 720 K (marked Tp). Two strong, superimposed exothermic peaks are observed at 714 K and 726 K as depicted in Fig. 22. Based on published work, these peaks can be assigned to major mild gasification reactions61,62. It is generally believed that the carbonization process starts at approximately 623 K, initially with the release of carbon dioxide and hydrogen. As the temperature is increased beyond 623 K, methane and other lower aliphatics are evolved along with hydrogen and carbon monoxide. The rupture of hydrogen bonded cross-links and the breaking of aliphatic and hydroaromatic bonds provide sufficient energy for the competing endothermic devolatilization of condensable liquids and tars. This process effectively produces an exothermic curve at about 720 K in the DSC thermograph.

**Effect of Clean Coal on Mild Gasification Characteristics:**

The comparative DSC profiles of as-received and clean IBC-102 coal are reproduced in Fig. 23. These profiles were recorded under identical experimental conditions using a temperature ramp of 10 K/min. Careful examination of the as-received coal DSC profile reveals the following: (a) The DSC curve abruptly starts to deviate downward at 500 K indicating this event is exothermic in nature. This is followed by a very weak but broad exothermic peak at around 526 K. (b) Between 526 K and 640 K, the exothermic rate of reaction continues to gradually increase but no major exothermic peak is observed in this temperature range. (c) At T > 640 K, a strong exothermic reaction begins which effectively produces a broad, strong exothermic peak centered at 713 K. Comparison of the DSC profiles, presented in Fig. 23, clearly shows major alterations in the thermal characteristics of the coal when the
coal is in "clean" form. Unlike the as-received coal, the clean coal's DSC profile suggests an exothermic reaction at the beginning of the measurement, i.e., at 383 K. The rate of exothermic reaction increases gradually but continuously at 383 K < T < 633 K. A series of small, sharp endothermic peaks at 542, 544, 546, and 551 K, which are superimposed on the overall exothermic profile of the coal, are observed for the clean coal and can be attributed to the volatilization of the crude oil fraction from the clean coal. The major exothermic peak for clean coal occurs at 706 K. It is important to note that the main exothermic event for clean coal is about 17 K lower than that for unprocessed coal.

Recently, Miura et al.\textsuperscript{63} reported DSC profiles of nine coals of different rank. They recorded their DSC profiles on dried coals under nitrogen gas at 323 K < T < 473 K. Based on their profiles, Miura et al. assert that the endothermic rates of all coals, except the highest rank coal, manifest an abrupt change at around 373 K. They attribute abrupt discontinuity in the endothermic rates to the breakage of hydrogen bonds in coal. However, our DSC profiles of as-received and clean IBC-102 coal, measured under He gas, exhibit no endothermic changes around the aforementioned temperature. It is possible that the breakage of hydrogen bond is a more significant for low rank coals than for relatively higher rank coals like our IBC-102 coal.

As pointed out earlier, the major thermal event for as-received coal is observed at 723 K, while for clean coal the event is 17 K lower. To understand why this major thermal event, which signifies the rupture of hydrogen bonded cross-links and the breaking of aliphatic and hydroaromatic bonds, is lower for clean coal than for un-cleaned coal, we need to recall the differences between the two samples. The clean coal is devoid of minerals but has some adsorbed crude oil fractions on its surface, as well as in the pores. Since for the clean coal the DSC displays an exothermic behavior at 373 K < T < 633 K, the possibility that the adsorbed crude fractions react with coal, when subjected to thermal energy, cannot be discounted. This interaction must somehow produce a resultant coal structure at T < 633 K whose free energy is larger than the free energy of the corresponding un-cleaned coal. If such is the case, then the clean coal will display its major thermal event at a lower kT. It is worth mentioning here that when the samples were subjected to thermal treatment under He at 373 K < T < 853 K, the organic mass loss for clean coal was 33 wt%, while for the unprocessed coal it was 21 wt%. This observation, along with the above-described thermal effects, raises the speculation that the adsorbed crude oil fraction may have catalytic properties.

Effect of Pre-oxidation on the Mild Gasification:

In an effort to elucidate how pre-oxidation of coal at 423 K will affect char production from the clean IBC-102 coal, we conducted comparative thermal measurements on an oxidized and un-oxidized coal sample. For these measurements, the clean coal was first dried \textit{in-situ} in DSC at 423 K, and then gas was switched from He to O\textsubscript{2} for one of the samples. The sample was oxidized for 35 minutes. After 35 minutes, the gas was again switched from O\textsubscript{2} to He, and the sample was cooled under He to 373 K. Figure 24 reproduces the comparative DSC profiles observed for the un-oxidized and for the oxidized clean coal at 373 K < T < 853 K. It can be clearly seen from Fig. 24 that the oxidation of coal profoundly affects the resultant DSC thermal profile. The changes incorporated in the thermal behavior of clean coal due to oxidation can be better understood by generating the difference curve between un-oxidized and oxidized coal's DSC profiles, as depicted in Fig. 24. The oxidation of coal affects the thermal behavior of coal in three distinct temperature regions, i.e., a broad positive peak at 451 K, a broad negative peak at 595 K, and a broad positive peak at 735 K. The positive peaks at 451 and 735 K imply that more exothermic reactions result in the un-oxidized clean coal relative to the oxidized coal in the positive peak regions. The strong, broad negative peak at 595 K in Fig. 24 suggests additional exothermic reactions in the oxidized
coal relative to the un-oxidized coal result in the negative peak temperature region. It should also be noted that the major thermal event for the oxidized clean coal occurs at 698 K, about 25 K less than the unprocessed coal. The total organic mass loss on subjecting the oxidized coal to mild gasification was 22 wt%. Therefore, it is argued that better yields of clean chars will be produced if clean IBC-102 coal is pre-oxidized prior to subjecting it to the mild gasification process.

**Effects of Clay Mineral Additives on the Charring Behavior of Coal:**

**Phyllosilicate structures:** As pointed out in the experimental section, one of the main objectives of the project is to evaluate the effects of clay mineral additives on the charring behavior of coal. All phyllosilicates (clay minerals) contain silicate or aluminosilicate layers in which sheets of tetrahedrally coordinated cations are linked through shared oxygens to sheets of cations octahedrally coordinated to oxygen and hydroxyls. Depending upon whether one or two tetrahedral sheets are linked to the octahedral sheet, various phyllosilicate structures are produced. If one octahedral sheet is linked to one tetrahedral sheet a 1:1 layer is formed. A typical structure of 1:1 layer phyllosilicate is kaolinite with a chemical composition $\text{Al}_3\text{Si}_2\text{O}_5(\text{OH})_4$. When one octahedral sheet is linked to two tetrahedral sheets, one on each side of the octahedral sheet, a 2:1 layer is produced as, for example, in montmorillonite with composition $\text{Al}_{2.33}\text{Mg}_{0.67}\text{Si}_{4.29}\text{O}_{10}(\text{OH})_8\cdot n\text{H}_2\text{O}$. If divalent cations are the major impurities in the octahedral sheet of the 2:1 layer clay mineral, then the resultant mineral is classified as dioctahedral smectite. However, if divalent Mg cations substitute for the trivalent Al cations in the octahedral sheet of 2:1 layer mineral, then smectite is termed trioctahedral smectite. The typical example of a trioctahedral smectite is hectorite with chemical composition $(\text{Mg}_{0.33}\text{Li}_{0.47})\text{Si}_4\text{O}_{10}(\text{OH})_8\cdot n\text{H}_2\text{O}^{64,65,66}$. Since various cations can be doped in phyllosilicates, both in the tetrahedral sheet and the octahedral sheet, in principle it is possible to selectively alter the structural and chemical activity of clay minerals.

The cation impurities and/or vacancies in phyllosilicates produce a charge distribution on the surface of the clay mineral. Whether this charge distribution is on the octahedral sheet or the tetrahedral sheet depends on where the vacancies or doped cations are located. Generally, kaolinite has a charge layer which is between 3 to 15 meq/100 g, hectorite has a charge 80 meq/100 g, and montmorillonite has a charge between 90 to 100 meq/100 g. Therefore, it is reasonable to expect that the maximum catalytic activity will be displayed by montmorillonite.

**Effects of clay mineral additives:**

In the first set of experiments on IBC-102 coal, the effect of purge gas on the pyrolytic behavior, as determined by DSC, was examined. Figure 25 depicts the observed DSC thermographs for "clean" IBC-102 coal (the cleaned coal was recovered by selective bitumen agglomeration process) under He and $N_2$ purge. The observed differences in the pyrolytic behavior are dramatic. Under He purge, the main exothermic reaction initiates at around 667 K with an exothermic peak at 710 K. On the other hand, the observed pyrolytic behavior under $N_2$ suggests the exothermic reaction initiates at around 619 K with an exothermic peak at 657 K. Moreover, under a nitrogen environment three additional endothermic peaks are observed at 717 K, 773 K, and 823 K. It should be noted from figure 22 that when coal is pyrolyzed under He no endothermic peaks are observed. Whether the additional endothermic peaks observed, under $N_2$ purge, are indicative of a reaction between the coal matrix and nitrogen or are due to thermal diffusivity and thermal conductivity of $N_2$ at high temperature is not clear to us at present. Also, why the main exothermic peak for $N_2$ purge is lower by 53 K remains unanswered at present. Additional experiments are under way to answer these surprising experimental observations.
Figures 26 and 27 reproduce the effects of clay additives on the DSC thermographs of IBC-102 coal obtained under He purge. The important pyrolytic parameters, as defined by DSC experiments, are depicted in Fig. 22. The parameters listed in Fig. 22, i.e., T1 or T2, the onset temperature T3, the peak temperature Tp, and ΔH were determined for the data presented in Figs. 26 and 27. To calculate the heat of the exothermic reaction, ΔH, the area under the exothermic peak was obtained, i.e.,

\[
\Delta H = \left[ \frac{60/m}{(dt/dT)} \right] \int_{T_1}^{T_2} \left[ (dQ/dt) - (dQ_r/dt) \right] dT.
\]

(8)

In Eq. (8), m is the mass of the coal or clay sample prior to the charring reaction, (dt/dT) is the scanning rate, Q is the heat energy supplied to the sample pan, and Q_r is the heat energy supplied to the reference pan. The results are summarized in Table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Clay Additive</th>
<th>T1 (K)</th>
<th>T2 (K)</th>
<th>H (J/g)</th>
<th>Agglomeration after charring</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received ground coal</td>
<td>none</td>
<td>515</td>
<td>724</td>
<td>743</td>
<td>yes</td>
</tr>
<tr>
<td>Ground coal</td>
<td>Ca-montmorillonite</td>
<td>-</td>
<td>721</td>
<td>304</td>
<td>no</td>
</tr>
<tr>
<td>Ground coal</td>
<td>Hectorite</td>
<td>-</td>
<td>730</td>
<td>256</td>
<td>no</td>
</tr>
<tr>
<td>Ground coal</td>
<td>Kaolinite</td>
<td>-</td>
<td>628</td>
<td>98</td>
<td>no</td>
</tr>
<tr>
<td>Clean coal (recovered by selective-bitumen agglomeration)</td>
<td>none</td>
<td>526</td>
<td>710</td>
<td>246</td>
<td>yes</td>
</tr>
<tr>
<td>Clean coal (oxidized at 423 K prior to DSC run)</td>
<td>none</td>
<td>-</td>
<td>699</td>
<td>171</td>
<td>yes</td>
</tr>
</tbody>
</table>

In order to determine the effects of coal cleaning and clay mineral additives on the yields of chars, the similar as described in "Thermogravimetric study of the char yields from IBC-102 coal under the different environments" chapter was adopted. The effects of various additives on the char yields of IBC-102 coal are graphed in Fig. 28. They DSC results presented in Figs. 22 to 28 and table 2 can be summarized as follows:

(1) The kaolinite clay mineral with a layer charge of 3 to 15 meq/100 g is most effective in increasing the yields of chars from IBC-102 coal. It should be noted from table 2 that the maximum char yield is accompanied by the least H observed for IBC-102 coal + kaolinite sample.
(2) The Ca-montmorillonite clay mineral with a layer charge of 90 to 100 meq/100 g is least effective among the clays tested in increasing the yields of chars from IBC-102 coal.

(3) The clean coal recovered by the selective-bitumen agglomeration process shows enhanced weight loss when subjected to mild gasification at 300 K < T < 860 K under He. However, its oxidation at 423 K prior to mild gasification increases its char yields.

(4) Irrespective of the type of clay used in the mild gasification experiments, the clay additive employed sharply retarded the agglomeration tendency of coal during pyrolysis.

**IN-SITU DIFFUSE REFLECTANCE FOURIER TRANSFORM INFRARED (ISDR-FTIR) MEASUREMENTS**

**High-Temperature (T < 773 K) ISDR-FTIR Setup:**

For ISDR-FTIR measurements at 300 K < T < 773 K, < 38 micron particle-sized IBC-102 coal was placed in a DRIFT cup mounted in a diffuse reflectance center-focused accessory in the optical compartment of a Nicolet 740 FTIR spectrometer. The spectrometer was linked to a Nicolet 620 computer and was fitted with a fast response, high sensitivity MCT detector. The heating chamber was connected via a flexible, stainless steel tube to a He gas cylinder. The He gas, which flows through our heating chamber mounted in the optical beam path, was forced into the chamber via a liquid nitrogen trap. A positive pressure of He gas was maintained in the heating chamber to ensure that no back-streaming of air would occur at the He outlet of the chamber. Two hundred scans at a resolution of 4 cm\(^{-1}\) were collected at each desired temperature. The heater assembly, mounted underneath the sample cup containing the coal, was used to alter and control the sample temperature to +/- 2 K. Tap water was circulated through the heating chamber in such a way that while the heater and the sample were held at the desired high temperature the rest of the chamber was at the tap water temperature.

**High-Temperature (T < 1100 K) Catalytic ISDR-FTIR Setup:**

To understand the heat induced cross-linking process in coal and the role of cross-linking in dictating the char yields from coal, ISDR-FTIR measurements were conducted on the IBC-102 coal at 300 K < T < 1100 K. These measurements were accomplished with the help of a Spectra-Tech high-temperature high-pressure catalytic chamber. The design and the experimental arrangement of the catalytic chamber are very similar to those of the high-temperature ISDR-FTIR setup, except the sample cell and the heater assembly in the catalytic chamber are isolated from the rest of the cell by ceramic construction.

**Charring Behavior of IBC-102 Coal at 300 K < T < 750 K:**

Figures 29 and 30 reproduce the changes incorporated in the ISDR-FTIR spectra of the as-received IBC-102 coal when subjected to thermal processing under He at 300 K < T < 700 K. The changes in the vibrational properties of the coal, induced because of thermal energy kT, can be best described by generating the difference spectrum, i.e., the observed ISDR-FTIR spectrum at T minus the observed ISDR-FTIR spectrum at 373 K. We chose to generate the difference spectra at T relative to the spectrum observed at 373 K to ensure that water’s vibrational modes would not interfere with our analysis.

As can be seen from the difference spectra, depicted in Figs. 29 and 30, the major changes in
the vibrational modes occur in two regions, i.e., 3700 - 2500 cm⁻¹ and 1800 - 1000 cm⁻¹. A sharp, strong negative band at 3642 cm⁻¹ appears in the difference spectrum at 423 K. The intensity of this vibration steadily increases as the temperature of the thermal treatment is increased. It should also be observed that the change in the intensity of the negative band at 3642 cm⁻¹ is accompanied by a change at 1280 cm⁻¹. The negative intensity at 1280 cm⁻¹ in the difference spectrum is also sharp, like 3642 cm⁻¹. The changes induced in the intensity of the 3642 and 1280 cm⁻¹ bands, as a function of thermal treatment temperature, are graphed in Figs. 31 and 32, respectively. The vibrations at 3642 and 1280 cm⁻¹, because of their sharp characteristics, can be assigned to O-H stretch and O-H bend of phenolic groups in coal. Because the width of 3642 and 1280 cm⁻¹ modes is very small, it is reasonable to argue that the hydroxyl groups of phenols are free, i.e., they are not hydrogen bonded to the other functional groups in coal. The change in intensity, in the form of negative bands at 3642 and 1280 cm⁻¹, implies that as the coal is heated the free OH groups are either lost from the coal or they get hydrogen bonded to other groups in coal. If on heating the coal the coal's structure attains considerable mobility, then it may be argued that the free OH groups of phenols may get involved in hydrogen bonds in the coal. This apparently is not the case because the hydrogen bonding of OH groups will shift their stretching frequency to about 3300 cm⁻¹. However, we do not observe a positive band at 3300 cm⁻¹ in the difference spectra depicted in Figs. 29 and 30.

As the intensity is lost at 3642 and 1280 cm⁻¹ on heating the coal, the intensity is gained at 1093 cm⁻¹ (see figure 33). The vibration at 1093 cm⁻¹ can be assigned to C - O - C stretch of benzyl ethers. The fact that the loss of intensity at 3642 cm⁻¹ almost mirrors the gain in intensity at 1093 cm⁻¹ raises the possibility that cross-linking in IBC-102 coal occurs via condensation of two phenol groups, i.e.,

\[ \text{O-H} + \text{H-O} \xrightarrow{-\text{H}_2\text{O}} \text{O} \]

In addition to the intensity gain at 1093 cm⁻¹, the intensity of vibrations at 1768 and 1690 cm⁻¹ also increases as the pyrolysis temperature increases. The effect of temperature on the intensity gain at 1768 and 1690 cm⁻¹ is graphed in Figs. 31 and 32, respectively. The positive bands at 1768 cm⁻¹ can be assigned to C = O stretching mode due to the esters, while the positive 1690 cm⁻¹ band can be due to C = O stretch of ketones and/or aldehydes. Our preliminary conclusion based on ISDR-FTIR measurements is that phenols play an important role in the cross-linkage of the coal structure when thermally treated. Additional measurements are planned in the coming year to ascertain what role the formation of ester and ketonic groups has on the cross-linking of coal, thus, the char yields.

**Char Structure:**

Efforts were also made to ascertain the structure of char produced when IBC-102 coal was subjected to mild gasification under He. The changes induced in the coal structure when charred at 748 K can be best manifested by generating a difference spectrum, i.e.,

\[ \text{ISDR-FTIR (difference spectrum)} = \text{ISDR-FTIR (char, after gasification)} - \text{ISDR-FTIR (coal, prior to gasification)} \]

The absorbance changes observed in the difference ISDR-FTIR spectrum are summarized in table 3.
<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Absorbance Change</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3643</td>
<td>-0.010</td>
<td>-O-H stretch (phenolic)</td>
</tr>
<tr>
<td>3151</td>
<td>-0.003</td>
<td>-O-H stretch (strongly hydrogen bonded)</td>
</tr>
<tr>
<td>2942</td>
<td>+0.002</td>
<td>C-H ((-\text{CH}_3))</td>
</tr>
<tr>
<td>2896</td>
<td>+0.002</td>
<td>C-H</td>
</tr>
<tr>
<td>2852</td>
<td>+0.002</td>
<td>C-H ((-\text{CH}_3))</td>
</tr>
<tr>
<td>1763</td>
<td>+0.005</td>
<td>-C=O</td>
</tr>
<tr>
<td>1697</td>
<td>+0.004</td>
<td>-C=O</td>
</tr>
<tr>
<td>1279</td>
<td>-0.003</td>
<td>-O-H bend</td>
</tr>
<tr>
<td>1124</td>
<td>-0.002</td>
<td>-C-O- stretch</td>
</tr>
<tr>
<td>1074</td>
<td>-0.001</td>
<td>-C-O- stretch</td>
</tr>
<tr>
<td>883</td>
<td>+0.001</td>
<td>isolated aromatic C-H</td>
</tr>
<tr>
<td>820</td>
<td>+0.001</td>
<td>isolated aromatic C-H and/or 2 neighboring aromatics</td>
</tr>
<tr>
<td>770</td>
<td>+0.001</td>
<td>four adjacent aromatic C-H</td>
</tr>
</tbody>
</table>

The data presented in table 3 suggest: (1) the condensation reactions result in the formation of condensed aromatic sheet structures in char, (2) the phenolic hydroxyl groups facilitate condensation reactions, and (3) thermal decomposition of coal either effectively increases -CH₃ content in char or alters the physical structure of -CH₃ groups which is different from the starting coal.

**ISDR-FTIR Monitoring of Tar Yields**

The acceptance of a process which produces clean, carbon- enriched chars from Illinois coals will require the process to be economically competitive and viable. The economics of the process will demand that we recover and enhance the liquid yields from coal without compromising the quality of the chars produced. It is known that the thermally induced cross-linking in coal retards liquid yields under mild- gasification conditions. However, the mechanism(s) of cross-linking and the condition under which extensive cross- linking in coal occurs is not well established. As an initial strategy to optimize the yields of chars and liquids from Illinois coals, we undertook ISDR-FTIR measurements on IBC-102 coal at 300 K < T < 1100 K in a Spectra-Tech high-temperature high-pressure catalytic chamber. It is hoped the such measurements will provide enough information not only to understand the mechanisms of cross-linking in coal but also to provide information to enhance the yields of chars and liquids.

In the first set of experiments, > 38 micron-sized coal particles were systematically heated under He in the catalytic chamber while their diffuse reflectance spectra were continuously
monitored. Figure 34 reproduces the effect of thermal energy on the ISDR-FTIR spectra of IBC-102 coal in the C - H stretching region. As can be seen from the figure, when the pyrolysis temperature exceeds 623 K there is a dramatic change in the ISDR-FTIR spectra. Not only the intensity of the aliphatic C - H stretch modes rapidly increases as the pyrolysis temperature increases but also additional new vibrations appear at around 3660 and 3560 cm⁻¹. Since the vibrations at 3660 and 3560 cm⁻¹ are typically assigned to O - H stretch, their appearance under He pyrolysis conditions seems very surprising. However, the dome, containing ZnSe optical flats, above the ceramic sample holder is maintained at tap water temperature, effectively becoming a cold temperature trap for the liquids evolved under pyrolysis. Therefore, based on the data presented in Fig. 34, it is argued that liquids suddenly appear as the pyrolysis temperature equals 673 K. As is depicted in Fig. 35, the yields of liquids from the coal continue to increase as the pyrolysis temperature increases to 773 K. The intensity of the aliphatic C - H stretch vibrations then decreases as the pyrolysis temperature exceeds 773 K. Two possible explanations for the decrease of intensity above 773 K can be offered: (1) the volatiles are swept away from the chamber by the He gas over time, or (2) the liquids which are released above 773 K somehow react with the liquids which were released below 773 K, thus forming condensed aromatics. Additional ISDR-FTIR measurements are in progress which will answer this, as well as above-mentioned questions.

CONCLUSIONS AND RECOMMENDATIONS

1. A new technique was developed in which the weight losses were compared under different environments. This method has the advantage that under the same experimental conditions, the direct differences between the experiments are obtained.

2. The mineral matter present in the coal may undergo oxidation or reduction (depends on the environment) resulting in the formation of active catalysts that may not only activate methane but also crack the long chain compounds present in the coal structure.

3. The higher reactivity of the coal mixed with clays suggest that clays (a) may serve as catalysts activating the methane molecule, (b) may prevent coal agglomeration during the reaction, and (c) may modify the structure of the coal surface resulting in increasing number of active sites.

4. In the case of clean coal, the devolatilization reaction is shifted to a lower temperature when compared with raw coal. Also, this coal shows higher reactivity with CH₄ than as-received coal.

5. Preoxidation of the coal prior to the mild-gasification results in a 13° lowering of the devolatilization temperature and increases the rate of devolatilization.

6. Preoxidation of clean coal results in an increased rate of devolatilization under CH₄, but no difference is observed under He.

7. The kaolinite clay, with a layer charge of 3 to 15 meq/100 g is highly effective in increasing the yields of chars from IBC-102 coal.

8. Among the clays tested, the Ca-montmorillonite clay with a layer charge of 90 to 100 meq/100 g is the least effective in increasing the yields of chars under He and CH₄/O₂ environments.

9. The clean coal recovered by the selective-bitumen agglomeration process shows greater weight loss than as-received coal when subjected to mild gasification under He.
10. Phenols and carboxylic groups are important in the cross-linking process of the coal. Therefore, they may play a very important role in the fabrication of premium quality chars.

11. The condensation reactions result in the formation of condensed aromatic sheet structures.

12. Phenolic hydroxyl groups facilitate condensation reactions, and thermal decomposition of coal either increases -CH₃ content or alters the physical structure of -CH₃ groups.

13. In order to compare the thermal effects of coal interaction with methane and methane/oxygen, additional experiments with these gases will be performed using differential scanning calorimetry.

14. Additional ISDR-FTIR experiments will be done in order to ascertain what roles the formation of ester and ketonic groups have on cross-linking of coal, thus, and the resulting char yields.
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Figure 1. Plot of the weight loss versus temperature for IBC-102 coal sample treated with different gases.

Figure 2. Plot of weight differences from collecting data of weight losses of IBC-102 coal samples treated with different gases.
Figure 3. Comparison of DTG curves for the IBC-102 coal samples treated with different gases.

Figure 4. Plots of DTG curves versus temperature for the IBC-102 coal samples mixed with kaolinite treated with helium, methane, and methane/oxygen mixture.
Figure 5. Plots of DTG curves versus temperature for the IBC-102 coal samples mixed with Ca-montmorillonite treated with helium, methane, and methane/oxygen mixture.

Figure 6. Comparison of DTG curves for IBC-102 raw coal and mixed with kaolinite and Ca-montmorillonite in the reaction with helium.
Figure 7. Comparison of DTG curves for IBC-102 raw coal and mixed with kaolinite and Ca-montmorillonite in the reaction with methane.

Figure 8. Comparison of DTG curves for IBC-102 raw coal and mixed with kaolinite and Ca-montmorillonite in the reaction with methane/oxygen.
Figure 9. DTG profiles of IBC-102 coal mixed with kaolinite, preoxidized at different temperatures, and then reacted with methane.

Figure 10. DTG profiles of IBC-102 coal mixed with Ca-montmorillonite, preoxidized at different temperatures, and then reacted with methane.
Figure 11. DTG profiles of IBC-102 coal mixed with Ca-montmorillonite, preoxidized at 80°C for different time and then reacted with methane

Figure 12. Effect of preoxidation on DTG profiles of IBC-102 as received and mixed with Ca-montmorillonite in the reaction with methane
Figure 13. Effect of preoxidation on DTG profiles of IBC-102 coal mixed with Ca-montmorillonite in the reaction with He

Figure 14. Comparison of DTG profiles of IBC-102 coal as received and clean in the reaction with He
Figure 15. Comparison of the DTG profiles of IBC-102 coals as received and clean in the reaction with methane.

Figure 16. Comparison of the DTG profiles of IBC-102 coal as received and clean in the reaction with CH₄/O₂.
Figure 17. Effect of preoxidation on DTG profiles of clean IBC-102 coal in the reaction with He.

Figure 18. Effect of preoxidation on DTG profile of clean IBC-102 coal in the reaction with methane.
Figure 19. The effect of various additives on the char yields of IBC-102 coal (microbalance study) in the reaction with He.

Figure 20. The effect of various additives on the char yields of IBC-102 coal in the reaction with CH₄/O₂ (microbalance study).
Mild-Gasification of IBC-102 Coal/Microbalance Study
Gas: CH₄; Heating Rate: 10°C/min

Figure 21. The effect of various additives on the char yields of IBC-102 in the reaction with methane (microbalance study).

MILD-GASIFICATION OF IBC-102 COAL
DSC RESULTS

Gas: He, Heating Rate: 10 K/min

Figure 22. Thermograph of IBC-102 coal sample under helium.
MILD–GASIFICATION OF IBC–102 COAL
DSC RESULTS

Gas: He, Heating Rate: 10 K/min

As–received Coal
Clean Coal

Figure 23. Comparison of DSC results of clean and as-received IBC-102 coals under He.

MILD–GASIFICATION OF IBC–102 COAL
DSC RESULTS

Gas: He, Heating Rate: 10 K/min

A: Clean Coal
B: Oxidized
Clean Coal
(T=423 K,
t=35 min)

Difference Curve A – B

Figure 24. Effect of preoxidation on the DSC results of clean IBC-102 coal.
MILD-GASIFICATION OF ILLINOIS COAL: DSC RESULTS
SAMPLE: Clean Floated IBC102 Coal (Selective-bitumen)

Heating Rate = 10 K/min.

Gas: Helium

Gas: Nitrogen

Figure 25. Comparison of DSC results of IBC-102 clean coal treated with helium and nitrogen

MILD-GASIFICATION: DSC Experiments on IBC-102 Coal

IBC-102 Coal
GAS: He
Heating Rate: 10K/min.

IBC-102 Coal + Kaolinite

Figure 26. Effect of kaolinite addition on DSC results of IBC-102 coal in the reaction with helium
Figure 27. Comparison of DSC results of IBC-102 coal alone, mixed with hectorite, and Ca-montmorillonite.

Figure 28. Effect of various additives on the char yields of IBC-102 coal treated with He.
Figure 29. ISDR-FTIR spectra of as-received IBC-102 coal sample during thermal treatment in He

Figure 30. ISDR-FTIR spectra of as-received IBC-102 coal sample during thermal treatment in He
Figure 31. Changes in the intensity of the 3642 cm\(^{-1}\) bands for IBC-102 coal during thermal treatment.

Figure 32. Changes of the intensity of the 1280 cm\(^{-1}\) band for IBC-102 coal during thermal treatment.
Figure 33. Variation of intensity of 2886 cm\(^{-1}\) and 1147+1093 cm\(^{-1}\) bands during IBC-102 coal gasification under He.

Figure 34. ISDR-FTIR monitoring of the charring process of IBC-102 coal sample.
Figure 35. The effect of temperature on the aliphatic concentration in IBC-102 coal sample.