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Project Title: CLEAN, PREMIUM-QUALITY CHARS: DEMINERALIZED AND CARBON ENRICHED

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ABSTRACT

The interaction of methane, methane/oxygen, helium, and hydrogen with IBC-102 coal samples (≤2mg) has been investigated in a thermogravimetric reactor at 20°C-650°C. The results show that the reactive gases are converting some of the mineral matter of the coal into catalysts through chemical reactions (reduction or oxidation). Also, these gases (except He) dissolve in the softened coal. Added clays (kaolinite and Ca-montmorillonite) increase the reactivity of the coal. This higher reactivity may be attributed to the fact that clays may serve as catalysts for methane activation, may prevent the coal agglomeration, and/or may increase the number of active sites for the reaction by modification of the geometric structure of the coal surface. Differential Scanning Calorimetry (DSC) experiments show that clean coal (no mineral matter) devolatilizes at a lower temperature than raw coal. Also, preoxidation at 150°C for 50 minutes results in a 13°C lowering of the devolatilization temperature. ISDR-FTIR experiments suggest that phenol groups of the coal play an important role in the cross-linkage of the coal structure when thermally treated.

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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 capabilities 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 (DTA), (2) differential scanning calorimetry (DSC), and (3) in-situ diffuse reflectance-FTIR (ISDR-FTIR).

The TGA results show that methane, hydrogen, and methane/oxygen dissolve in the softened coal and/or react with the mineral matter in the coal to form catalysts which activate methane. TGA results show that coal mixed with kaolinite or Ca-montmorillonite has greater reactivity than raw coal. It was previously suggested that clays may serve as catalysts and inhibit agglomeration of the coal particles during the reaction. Now it is proposed that clays not only participate directly in the reaction as catalysts but also modify the geometric structure of the coal surface. This modification increases the number of available active sites on the coal surface and, therefore, increases the reactivity of the coal.

Differential scanning calorimetry (DSC) measurements show that both preoxidation of the coal (at 150°C for 50 minutes) and removal of the mineral matter from the coal result in a 30° lowering of the devolatilization temperature. Therefore, better yields of clean chars will be produced if clean IBC-102 is preoxidized prior to being subjected it to the gasification process. Results of ISDR-FTIR experiments of the as-received coal strongly suggest that the phenolic groups present in the coal play an important role in the cross-linking process during thermal treatment.

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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 capability of smectites in combination with methane to manipulate the char yields. The major objectives are:

- to determine the optimum water-ground particle size for the maximum reduction of pyrite and minerals by the selective-bitumen agglomeration process
- to evaluate the type of smectite and its interlamellar cation which enhances the premium-quality char yields
- to find the mode of dispersion of smectites in clean coal which retards the agglomeration of char during mild gasification
- to probe the conditions that maximize the desulfurized clean-char yields under a combination of methane/oxygen or helium/oxygen
- to characterize and accomplish a material balance of chars, liquids, and gases produced during mild gasification
- to identify the conditions which reject dehydrated smectites from char by the gravitational separation technique
- 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, 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. Far less effort 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. Also, chars rich in minerals foul the catalytic promoters via catalytic-material-mineral reactions in the gasification process. 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, agglomerate flotation, 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. Unfortunately, the mechanical-coal cleaning processes have had only limited success 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 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 400-450°C. It is also known, that certain coals become soft and flow when heated to 400-600°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 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.

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:

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

However, considering the fairly ready transfer of sulfur between the inorganic (mineral) and organic phases, 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 CH4 with 2%O2, 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 form with extremely high surface area and in a filament form with high mechanical strength. These filaments grow from small crystallites of metals, which can be produced in the char.

Carbon may be deposited from methane by the action of high temperatures and/or metal cata-
lys 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, exhibits 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 substantially 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 radicals 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 should also inhibit the agglomeration of the char. Promoter added to the clean coal should not only affect the free radicals but should also inhibit the agglomeration of the char.

**EXPERIMENTAL PROCEDURE**

**Materials**

Coal sample IBC-102 was obtained from the Illinois Basin Coal Sample Program. It contains 39.8% of volatile matter, 6.9% of ash, 14.2% of moisture, and 3.29% of 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.

In order to examine the catalytic effect, if any, of smectite minerals on the cross-linkage process of coal, the following procedure was adopted to prepare the coal-smectite mixtures:

(i) The < 37 µm particle-sized coal and Ca-montmorillonite (Cheto, Arizona) were accurately weighed in order to produce a mixture which had a coal-to-montmorillonite ration of 2:1 (by weight). Then methanol was added to the coal-montmorillonite mixture, and the mixture was vigorously stirred in an attempt to produce a homogeneous distribution of coal and smectite within the mixture. After about one hour of agitation, the methanol was removed from the sample by subjecting it to a vacuum.

The methane (UHP grade), helium, hydrogen, and oxygen were obtained from MG Industries, Scientific Gas Division. The mixture of 2% of oxygen in methane or in helium was prepared by mixing the proper amounts of the gases. The gases were dried over an activated molecular sieve trap. Methane, helium, and hydrogen were further purified by flowing them through a Mn/SiO$_2$ trap in order to remove oxygen.
Preparation of Clean Coal

We adopted the following procedure to prepare clean coals: (1) The as-received IBC-102 coal was first ground under water in a planetary ball mill to a particle size which could be accepted by the Brinkmann micro-rapid mill, i.e., < 740 micron. (2) 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. (3) 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 samples containing < 38 micron-sized coal particles. (4) The < 38 micron-sized coal was magnetically stirred for 15 minutes in a vessel to prepare a water slurry. The slurry was stabilized. (5) Polymerized bitumen, 13° API gravity was added to the coal-water slurry in enough quantity to establish a coal-to-bitumen ratio of 100:8 by weight. (6) The bitumen-coal-water slurry was further agitated at 1800 rpm for 15 minutes to enhance the bitumen-coal interactions. (7) After flocculation and agglomeration, the IBC-102 coal was separated into two fractions: one which floated and the other which settled on the bottom. (8) The floated, agglomerated fraction of IBC-102 coal, which henceforth will be called clean coal, was dried and prepared for mild gasification experiments.

Apparatus

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 flowmeters. 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 Micricon 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 at every 10°) ramp from 20°C - 650°C was subtracted from the data collected at every 10° of 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 and gas density changes are removed.

Differential Scanning Calorimetry (DSC) Measurements

Calorimetric data under mild gasification conditions were recorded on a Perkin-Elmer DSC7 system, interfaced with a Perkin-Elmer 7700 computer. Two sets of experiments were conducted. In the first set, the DSC profiles were recorded at 40°C (313 K) < T < 577°C (850 K) under He purge on ground (< 38 micron), but unprocessed, IBC-102 coal and processed clean IBC-102 coal. In the second set of experiments, the ground IBC-102 coal was first held at 150°C under He for 10 minutes, then the gas was switched to oxygen, and the coal was oxidized at the aforementioned temperature for 30 minutes. After oxidation, the DSC mild gasification profile was recorded under He purge at 100°C < T < 580°C. It is
worth mentioning that the pre-thermal treatment, oxidation, and mild gasification experiments were conducted in-situ, i.e., without removing the coal sample from the DSC sample holder.

In-situ Diffuse Reflectance-FTIR (ISDR-FTIR) Measurements:

For ISDR-FTIR measurements, < 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 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. At present our ISDR-FTIR system is capable of operating at 300 K (or 27 °C) < T < 773 K (or 500 °C).

RESULTS AND DISCUSSION

Non-isothermal reactivities of the small samples (< 2 mg) of IBC-102 coal

In our previous report we presented the results from microbalance experiments in which approximately 60 mg of the sample was used in each run. In the present study, the sample size 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 weight 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 temperature programmed pyrolysis (TPP) curves in the previous report. There we hypothesized that the decrease of the rate of devolatilization relative to He may be related to the fact that the reactive gases are 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 present 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 which depends on the temperature, may cause the weight increase in the 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 was 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 fact that clays may serve as catalysts for the activation of methane. Also, clays may prevent coal agglomeration during gasification and increase the coal active surface area, 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 geometric 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 geometric structure of the coal surface by the clays will increase the number of available active sites present on the char surface.
Differential Scanning Calorimetry (DSC) Experiments:

Effect of Clean Coal on Mild Gasification Characteristics

The observed, comparative DSC profiles of as-received IBC-102 coal and clean IBC-102 coal are reproduced in Fig. 9. These profiles were recorded under identical experimental conditions using a temperature ramp of 10 deg/min. A careful examination of the as-received coal's DSC profile reveals the following: (a) The DSC curve abruptly starts to deviate downward at 227°C indicating this event is exothermic in nature. This is followed by a very weak but broad exothermic peak at around 253°C. (b) Between 253°C and 367°C, the exothermic rate of reaction continues to gradually increase but no major exothermic peak is observed in the DSC profile at this temperature range. (c) At T > 367°C, a strong exothermic reaction begins which effectively produces a broad, strong exothermic peak centered at 540°C. The comparison of the DSC profiles, presented in Fig. 9, 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°C. The rate of exothermic reaction increases gradually but continuously at 110°C < T < 360°C. A series of small, sharp endothermic peaks at 269, 271, 273, and 278°C, 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 fraction from the clean coal. The major exothermic peak for clean coal occurs at 433°C. It is important to note that the main exothermic event for clean coal is about 17°C lower than that for unprocessed coal.

Recently, Miura et al.55 reported the DSC profiles of nine coals of different rank. They recorded their DSC profiles on dried coals under nitrogen gas at 50°C < T < 200°C. Based on the observed profiles, Miura et al.55 assert that the endothermic rates of all coals, except the highest rank coal, manifest an abrupt change at around 100°C. They attribute the reported discontinuity in the endothermic rates to the breakage of the 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 breakage of the hydrogen bond is a more significant effect for low rank coals than for relatively higher rank coals like IBC-102 coal.

As pointed out earlier, the major thermal event for as-received coal is observed at 450°C, while for the clean coal the event is 17°C lower. To understand why clean coal's major thermal event, which signifies the rupture of hydrogen bonded cross-links and the breaking of aliphatic and hydroaromatic bonds56,57, is lower than the un-cleaned coal's, we need to recall the differences between the two samples. The clean coal is devoid of minerals but has some adsorbed crude fractions on its surface, including the pore surface. Since for the clean coal the DSC displays an exothermic behavior at 100°C < T < 360°C, the possibility that the adsorbed crude fractions react with coal, when subjected to thermal energy, can not be discounted. This interaction must somehow produce a resultant coal structure at T < 360°C 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 the major thermal event at a lower kT. It is worth mentioning here that when the samples were subjected to thermal treatment under He at 100°C < T < 580°C, 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 fraction may have catalytic properties.

Effect of Pre-oxidation on the Mild Gasification

In an effort to elucidate how pre-oxidation of coal at 150°C 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 150°C, and then gas was switched from He to O$_2$ for one of the samples. The sample was oxidized for 50 minutes. After 50 minutes, the gas was again switched from O$_2$ to He, and the sample was cooled under He to 100°C. Figure 10 reproduces the comparative DSC profiles observed for the un-oxidized and for the oxidized clean coal at 100°C < T < 580°C. It can be clearly seen from Fig. 10 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. 11. The oxidation of coal affects the thermal behavior of coal in three distinct temperature regions, i.e., a broad negative peak at 178°C, a broad positive peak at 322°C, and a broad negative peak at 462°C. The negative peaks at 178 and 462°C imply that more exothermic reactions result in the un-oxidized clean coal relative to the oxidized coal in the negative peak regions. The strong, broad positive peak at 322°C in Fig. 11 suggests additional exothermic reactions in the oxidized coal relative to the un-oxidized coal result in the positive peak temperature region. It should also be noted that the major thermal event for the oxidized clean coal occurs at 425°C, about 25°C 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.

\textbf{in-situ Diffuse Reflectance-FTIR (ISDR-FTIR) Experiments}

Figures 12 and 13 reproduce the changes incorporated in the ISDR-FTIR spectra of the as-received IBC-102 coal when subjected to thermal processing under He at 20°C < T < 500°C. 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 100°C. We chose to generate the difference spectra at T relative to the spectrum observed at 100°C to ensure that water's vibrational modes would not interfere with our analysis.

As can be seen from the difference spectra, depicted in Figs. 12 and 13, 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 150°C. 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 3642 and 1280 cm$^{-1}$ bands, as a function of thermal treatment temperature, are graphed in Figs. 14 and 15, 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 hydrogen bonded 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. 12 and 13.
As the intensity is lost at 3642 and 1280 cm\(^{-1}\) on heating the coal, the intensity is gained at 1768 and 1690 cm\(^{-1}\). The effect of temperature on the intensity gain at 1768 and 1690 cm\(^{-1}\) is graphed in Figs. 14 and 15, 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 and analysis on the ISDR-FTIR of coals are in progress.

CONCLUSIONS AND RECOMMENDATIONS

1. 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.

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

3. In the case of clean coal, the devolatilization reaction is shifted to a lower temperature when compared with raw coal.

4. Preoxidation at 150\(^\circ\)C for 50 minutes results in a 13\(^\circ\) lowering of the temperature devolatilization.

5. Phenol groups are most important in the cross-linking process. Therefore, they may play a very important role in the fabrication of premium quality chars.

6. Temperature programmed pyrolysis experiments with prior preoxidation at different temperatures will be performed with Cahn microbalance reactor.
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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. Comparison of DSC profiles of as-received and clean IBC-102 coal samples.
IBC-102 CLEAN COAL (Float, 8% crude): DSC Measurements

A: Dry Coal (Under He, 150°C)

B: Dry Coal
(Dried He at 150°C, then oxidized at 150°C for 50 min.)

Figure 10. Comparison of DSC profiles of clean IBC-102 and preoxidized IBC-102 coal samples.
Figure 11. Difference DSC curve of un-oxidized and oxidized IBC-102 coal samples
CHARING OF IBC-102 COAL UNDER He: in-situ FTIR Measurements

Difference spectrum at $T = \text{Spectrum } (T) - \text{Spectrum } (100^\circ \text{C})$

$T=300 \degree \text{C}$

$T=250 \degree \text{C}$

$T=200 \degree \text{C}$

$T=150 \degree \text{C}$

Change in intensity (arb. units)

FREQUENCY ($\text{cm}^{-1}$)

Figure 12. ISDR-FTIR spectra of the as-received IBC-102 coal sample during thermal treatment
CHARING OF IBC-102 COAL UNDER He: in-situ FTIR Measurements

Difference spectrum at $T = \text{Spectrum (} T \text{)} - \text{Spectrum (} 100^\circ \text{C)}$

- $T = 475^\circ \text{C}$
- $T = 450^\circ \text{C}$
- $T = 400^\circ \text{C}$
- $T = 350^\circ \text{C}$

Figure 13. ISDR-FTIR spectra of the as-received IBC-102 coal sample during thermal treatment.
Figure 14. Changes in the intensity of the 3642 cm⁻¹ bands for IBC-102 coal during thermal treatment.
Figure 15. Changes of the intensity of the $1280^{-1}$ band for IBC-102 coal during thermal treatment.
PROJECT MANAGEMENT REPORT
December 1, 1991 through February 29, 1992

Project Title: CLEAN, PREMIUM-QUALITY CHARS: DEMINERALIZED AND CARBON ENRICHED

Principal Investigator: Gerard V. Smith
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Tomasz Wiltowski
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Project Monitor: Frank Honea, CRSC

This project is funded by the U. S. Department of Energy (METC) and by the Illinois Department of Energy and Natural Resources as part of their cost-shared program.
SCHEDULE OF PROJECT MILESTONES

A. Clean Coal From Selective-Bitumen Agglomeration
B. Catalytic Effects of Smectites  
   (Reactor-Based Measurements)
C. Mild Gasification  
   (Methane + Oxygen and Helium + Oxygen)
D. ISDR-FTIR and DSC Measurements
E. Analyses
F. Rejection of Smectite and Seeding of Char
G. Quarterly Technical Progress Reports
H. Quarterly Project Management Reports

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Sept. 1, 1991
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*Quarter: Projected, Estimated, Actual*
COSTS BY QUARTER - EXHIBIT C
Clean, Premium-QualityChars

Cumulative $ (thousands)

Sept 1
Nov 30
Febr 29
May 31
Aug 31

Months and Quarters

Proj. Expen
Actual Expen

Total CRSC Award $149,025