ABSTRACT

Methane reacts with char and coal to produce gases and liquids. When a small amount of oxygen is introduced, yields of liquids increase. Several experiments were performed to establish reproducibility, mass balance, and chemical composition. Added ash increases liquid yields as does added MgO but the composition of products is different. The $^{13}$CH$_4$ experiments reveal that methane is not incorporated into the liquids in large quantities during the first hour of the experiment. Methane decomposes and deposits carbon on the char which exhibits increased BTUs and decreased sulfur content. The experiments with CD$_4$ show that deuterium may be incorporated into the liquids. Data obtained with model compounds reveal that when methylene bridges are present, a relatively high percentage of the compound reacts with methane, with methane/oxygen, and with hydrogen. These methylene bridges seem to be an important reactant in coal conversion by methane/oxygen treatment.
EXECUTIVE SUMMARY

The main objective of this project is to optimize the production of valuable chemicals from the treatment of coals and chars with methane and oxygen in a continuous flow pressure reactor. Additional objectives are to determine the mass balance of the process, characterize the chemicals formed, and, ultimately, to determine the chemical mechanism of the process.

Previously, we showed that under flowing nitrogen no significant products were formed when coal was heated. However, when methane with small amounts of oxygen are used as reactants, substantially more products were formed. Mixing ash with coal increases conversion of carbonaceous matter and produces more liquids. This finding indicates that coal ash or some of its components catalyzes methane dehydrogenation which produces CH₅⁻ and H⁻ radicals which react with coal.

Using 30 grams of IBCSP coal No. 4 and collecting and weighing the liquids resulting from the reaction of CH₄/O₂ at 120 psig and 500°C gave a mass balance consisting of 52.2% liquids (based on carbonaceous material) compared to 32.3% for hydrogen. Additional experiments with added ash disclosed that liquid yields increase with increasing ash concentrations (25% was maximum used). Added MgO also increases liquids but the product composition is different.

Several experiments were performed to establish reproducibility, mass balance, and chemical composition. Reproducibility is good when experimental conditions are rigidly maintained; however, deviations in method of condensation of liquids, gas flow rate (reactor residence time), and heat-up rate affect mass balance and liquid yield. Mass balance was improved by collecting gases in glass flasks over water, but yields of liquids are dependent on the method of collection. For example, higher yields of liquids are obtained when condensation is at reaction pressure rather than at atmospheric pressure. Chemical composition is rich in phenol, cresols, and xylenols (CTX) as well as benzene, toluene, and xylenes (BTX).

Additionally, we performed several experiments to establish reproducibility of mass balance and chemical composition. Reproducibility is good when experimental conditions are rigidly maintained; however, deviations in method of condensation of liquids, in gas flow rate (reactor residence time), and in heat-up rate affect mass balance and liquid yield.

A method was developed for measuring water composition of the liquids. Water composition was approximately that predicted from moisture content of the coal. The amount of water formed in the reaction is nearly independent of time, clearly indicating that water comes from the coal during the heat-up jump from room temperature to 500°C.

From experiments carried out at different times we found that the high molecular weight compounds are formed at the beginning of the experiments and the low molecular weight compounds are formed continuously during approximately the first 3 hrs of the run. In fact, the concentrations of naphthalenes, 2-naphthol, tetralin and methylnaphthalenes remain relatively constant, whereas the concentrations of toluene, ethylbenzene, xylenes and cresols increase during the first 3 hrs of the process.

Preliminary experiments with $^{13}$CH₄ show that $^{13}$C is not incorporated into the organic effluent in large quantities during the first hour. So the methane is not incorporated into the oils (at least in large quantities) at the early stages of the reaction. Possible explanations for the high yields of oils are that methane is incorporated at a later stage and/or it is decomposing to furnish hydrogen atoms for the organic effluents and depositing carbon and methane fragments in the char.

We obtained some evidence for the latter hypothesis by reacting methane with char in the microbalance. After initial devolatilization of a sample of coal no. 106 in flowing methane,
the resulting char increased in weight signaling carbon deposition. Moreover, the resulting char exhibited a 9.7\% larger BTU value than char from helium devolatilization of the original coal. And sulfur content is substantially smaller. 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.

Deuterium from CD₄ is incorporated into the liquids formed during the reaction. In ²H NMR spectra of these liquids two broad resonances are observed which can be attributed to deuterium. These signals indicate the presence of deuterium above natural abundance levels. Additionally, many of the signals in the ¹³C(¹H) spectrum show broad feet at their bases which suggest the presence of C-D multiplets.

Several experiments were performed with phenanthrene, diphenylmethane, diphenylethane and biphenyl. Those compounds were reacted with He, He/O₂, CH₄, CH₄/O₂ and H₂. In each case, the thermal cleavage of C-C bonds takes place. However, when methane alone or with oxygen is used, both the conversion and the total amount of detected compounds increase. This suggests that treatment with methane may promote cracking of some C-C bonds that are too strong for thermal cleavage.
OBJECTIVES

The main objective of this project is to optimize the production of valuable chemicals from the treatment of coals and chars with methane and oxygen in a continuous flow unit. Additional objectives are to determine the mass balance of the process, characterize the chemicals formed, and, ultimately, to determine the chemical mechanism of the process.

INTRODUCTIONS AND BACKGROUND

Methane reacts with char and coal to produce gases and liquids. The reaction may be radical in nature, with methane terminating (capping) the radicals generated by heating char or coal. Introducing small quantities of radical initiators enhances the reaction and possibly generates methyl radicals which directly attack the coal matrix causing cleavage and desulfurization.

Originally, methane was reported to be chemically inert during volatilization of coal.¹ Later, based on greatly increased C₂ and liquid yields, methane was reported to be very reactive in coal pyrolysis.² However, these increased yields were shown not to be due to coal conversion but, rather, due to methane conversion.³ In spite of these results, some work on the methane/coal interaction continued to appear,⁴ but generally, workers seem to believe that the use of methane in coal conversion has been thoroughly examined and there is nothing new to discover.

Generally, the authors of the forgoing work believed that methane serves as a reservoir of H atoms which can be generated in-situ to react with the free radicals from the liquefied coal during the initial stage of hydroliquefaction. According to Petrakis,⁵⁻⁷ in coal there are preexisting free radicals. But additional free radicals may be generated on various thermal treatments. These free radicals may be stabilized through hydrogen abstraction from hydrogen-donating compounds.

It appears that methane also has the ability to terminate radicals existing in the coal. And, additionally, the methane molecule serves not only as a reservoir of H⁻ atoms but also of CH₃ radicals which can play a role similar to hydrogen atoms. Support for the methyl radical mechanism recently comes from a related study by Vassalo et al.,⁸ who found that methyl iodide (generates CH₃ upon heating) increases yields of oil products from Australian coals.

In our previous reports we used a continuous pressure flow reactor and demonstrated a substantial increase in liquid yields for the treatment using methane/radical initiators compared to treatment using methane or nitrogen alone. Liquid yields in the effluent after 4 hrs treatment increased from lows of 17.5% in nitrogen and 21.8% in methane to highs of 46.9% in methane/O₂ and 45.3% in methane/NO. Total weight losses of the coal were 31% for nitrogen, 41% for methane, 49% for methane/O₂, and 42% for methane/NO.

EXPERIMENTAL PROCEDURE

Materials

Coal samples No. 4 and No. 5 were obtained from the Illinois Basin Coal Sample Program (IBCSP). They contain 30.56% and 40.38% volatile materials, 38.10% and 18.00% ash, and 1.76% and 2.08% inorganic sulfur, respectively. The methane, UHP grade, and mixture
of 3.0% oxygen in helium were obtained from MG Industries, Scientific Gas Division. These gases were used without further purification. Ashes were prepared by the oxidation of the coal sample in the air at 800°C for 12 hrs.

Apparatus

Continuous flow pressure reactor

Experiments were performed in a continuous flow pressure reactor. The construction of this reactor and diagram of the reaction system were in the previous report. At the beginning of our research, in the reactor there was one shelf for the coal located approximately 1/3 of the distance up from the bottom and the gases are introduced below the shelf such that they pass up through the coal bed to exit out the top. Later we mounted two shelves for the coal located approximately 1/3 and 1/2 of the distance up from the bottom. At the end of the system is a second autoclave which acts as a buffer for maintaining a constant pressure in the reactor and the liquids collector. Samples for analysis during the experiment were taken from the special port a short distance from the reactor exit which is heated to 200°C. In order to obtain the exact volume of gases on the outlet of the reactor they were collected in the bottles with known volume. The gases from each bottle were analyzed using gas chromatograph.

Plug flow reactor

Experiments with 12C labeled and deuterated methane were performed in a plug flow reactor consisting of a quartz tube 11 mm inside diameter and 14 cm long in a vertical position with gases entering from the bottom and exiting from the top. Three grams of coal no. 104 were positioned between glass wool plugs at the top of the reactor tube. The reactor was brought up to 500°C during a 45 min period and maintained at 500°C for one hour. The liquids were collected in an air cooled trap followed by an ice cooled trap. Most of the liquids condensed in the air trap. The ice trap was rinsed with perdeuterotetrahydrofurane (d₄-THF) and combined with the liquid in the air trap. The tube exiting from the reactor was found to contain 0.2 gms of liquid so the exit tubing was rinsed with d₄-THF and combined with the liquid in the air trap. A total of 1.0 cc of d₄-THF was used for rinsing. Before using 12CH₄, 21 preliminary experiments were performed with light methane in the reactor system to establish procedure and determine expected yields (total liquids, 0.52±0.03 gms; xylenes, 1.93±0.59%; phenol, 8.61±0.85%; cresols, 17.8±0.96%; xylenols 12.76±0.48%). Two experiments were performed with 12CH₄. The gas mixture in experiment 22 was approximately 32% 13CH₄, 67% 12CH₄ and 1% O₂ while in experiment 24 it was approximately 98% 13CH₄, 1% 12CH₄, and 1% O₂. The percentages are approximate because only flow meters were used to control the flows. One experiment was performed with 99% CD₄ and 1% O₂. The 13 enriched methane, a mixture of 99% 13CH₄ and 1% 12CH₄ and CD₄ were purchased from Cambridge Isotope Laboratories.

Analysis

Analyses of light materials (gases) were performed on a conventional Gow Mac gas chromatograph equipped with a thermal conductivity detector. A stainless steel column packed with Porapak Q was used to separate the gases. The GC conditions were: carrier gas, helium; 30 mL/min; column, 70°C; injector and detector, 170°C.

The heavy materials (liquid products) were analyzed on a Shimadzu model 9A gas chromatograph equipped with a flame ionization detector. A fused silica capillary column (liquid phase 007 methyl phenyl silicone) was used to separate the liquids. The conditions of analysis
were: carrier gas, helium, 20 mL/min and then divided by a splitter; hydrogen flow, 30
mL/min; air flow, 600 mL/min; temperature program, 40°C for 4 min then ramp at 10°/min
to 140° and hold for 10 min. The peaks were integrated by a Hewlett-Packard model 3396A
reporting integrator.

As mentioned above, analyses were performed on two different gas chromatographs with
two different detectors. The GC with the thermal conductivity cell (TCD) was set up to
analyze the light materials while the GC with the flame ionization detector (FID) was set up
to analyze the heavier materials. So, on this latter GC all the light gases came through as a
single peak soon after injection. Because only one reporting integrator was available,
sample injections were alternated between the two GCs. Therefore, the percentages in Tables
1 and 2 shown for the TCD and FID detectors are not additive or relative, especially for the
earlier measurements. However, for the longest measurements the gaseous analysis (TCD)
probably represents the light materials portion of the heavier materials analysis (FID).
Consequently, the percentages shown for the TCD analyses (light materials) are only for the
light materials and not the percentages of those components in the total sample analyzed.
Likewise, the percentages shown for the FID analyses (light plus heavy materials) are only
for the heavy materials (liquids).

Estimates of the percentages of each component in the total sample can be made by using the
light material analyses to subtract out the carrier gas contributions to the FID analyses. This
calculation has been performed and is shown at the bottoms of Tables 1 and 2. Thus, the
percentages of light materials (gases) and of the heavy materials (liquids) are displayed.

A source of error in combining the two GC analyses is the difference in response of the two
detectors to the various components in the sample. For example, the TCD responds differen-
tly to different compounds whereas the FID does not respond to CO₂. The former prob-
lem can be overcome by multiplying the TCD peak area by the appropriate response factor,
but the latter can only be estimated. These problems have been taken into account in the
results shown in the tables.

Calculations were performed in the following way. First, the areas of methane as well as
nitrogen were subtracted from the total peak area of each integrated chromatogram. Then,
the percentages of selected products were recalculated using their TCD response factors to
minimize error. In the case of the FID analysis, in each analysis the area of the first peak
(light materials from TCD detector) was subtracted from the total area of the analysis and
again the new percentages were calculated. Since the FID analysis showed a number of
different compounds, focus was on selected products (benzene, toluene, xylenes, and naph-
thalenes), the retention times of which were carefully determined using pure compounds as
standards. The product samples were collected at the beginning of each run (time 0 was the
time at which 500°C was reached) and at times specified up to 4 hours. Analyses on the
TCD chromatograph were performed twice and the average is listed. Since FID analyses
required approximately 20 minutes, samples were injected only once.

We performed additional analysis of the water present in the liquid products. The procedure
of the water determination was as follow: first the liquid sample was dissolved in tetrahy-
drofuran (THF) to a volume of 25 mL. This was analyzed with TCD gas chromatograph.
The conditions of the analysis were the same as in the case of the analysis of the gases,
except the temperature of the column was 100°C. Another mixture of THF with a known
amount of water was prepared and injected into the gas chromatograph. Then, by compari-
on of the water peak area in the liquid sample and in the standard, we estimated the amount
of water present in the products.

To determine the mass balance of the reaction, we collected the liquids in the second (buffer)
autoclave which was kept in an ice bath. An insert made from aluminum foil was weighed before and after the experiment to determine the amount of liquids formed during the process. Some of the liquid remained in the lines between the reactor autoclave and the buffer autoclave (estimated at 10%), so the weight of liquid is low. Because the heat exchange was not perfect (thick walls of the second autoclave) we decided to increase the weight of collected liquids by starting with 30 grams of coal.

**NMR Analysis**

The $^{13}$C-NMR spectra were obtained on a Varian VXR-300 wide-bore spectrometer operating at 75 MHz. No relaxation delay was used and the data acquisition period was 0.911 s following an approximate 45 degree pulse. Proton decoupling was achieved with the WALTZ method and was on throughout. The number of transients recorded varied according to sample concentration to provide sufficient signal-to-noise. No reagent was added to samples to stimulate relaxation of the quaternary carbons. Deuterium spectra were recorded on the same instrument operating at 46.045 MHz with the field-frequency lock disabled. The spectral width was 1000 Hz, the cycle time was 1.0 seconds, and the pulse angle was approximately 70 degrees. Depending on the sample, 1000 to 6000 transients were recorded.

**RESULTS AND DISCUSSION**

Earlier, we reported that ashes exhibit catalytic properties for coal conversion. Those results exhibited this effect when 13% ashes were mixed with coals. For comparison we prepared 5% and 25% mixtures of ash from coal No. 5 with coal No. 5. Tables 1 and 2 and Figure 1 present the results obtained from these mixtures. It can be seen that CO$_2$, C$_2$, and C$_3$ formation increase when ash is used. However, xylenes formation increases with increasing ash content up to 13%, but decreases with the 25% ash mixture. A similar effect is observed in benzene formation. Toluene formation decreases when 5% of ash is in the mixture, then slightly increases with more ash, but generally, formation of this compound is slightly lower with ash present in the coal.

These experiments show that ash plays a catalytic role in the mild gasification process. Ash also plays a role in C2 and C3 formation, which increase with added ash. This means that ashes activate the methane molecule to produce CH$_3^+$ radicals. These radicals may be responsible for breaking the coal structure.

A recent coal structure described by several researchers and presented by J. Haggin$^9$ consists of two phases -- one phase of smaller molecules which are occluded in a second phase composed of a macromolecular network. The essential feature of this model is that there is a large amount of mobile, low molecular weight molecules trapped within regions of the higher molecular weight network phase. It appears, however, that just by heating the coal in an inert atmosphere, more polymers are formed and those low and mobile phases are trapped by the polymers. By using CH$_3^+$ radicals we can depolymerize the large molecules as well as reduce polymerization. The data presented above shows that probably more CH$_3^+$ is produced when ash is mixed with coal and, therefore, more chemicals are formed in the process.

In contrast to the usual mild gasification results, we find that a large fraction of the coal can be removed as light liquids by the action of methane and a small amount of oxygen. In fact, it appears that the complex coal matrix is being broken down into small molecules. But another possible explanation is that the pristine coal structure is composed of relatively small molecules linked by labile bonds and that these bonds are easily ruptured. In the absence of a capping material these bonds recombine to form the complex coal matrix usually observed.
### Table 1
Yields of selected products obtained from IBCSP No. 5 with 5% addition of ash from IBCSP No. 4 in Continuous Flow Pressure Reactor at 500°C and 120 psig

<table>
<thead>
<tr>
<th>time /hrs/#</th>
<th>0</th>
<th>1</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>28.49</td>
<td>30.10</td>
<td>31.70</td>
</tr>
<tr>
<td>C₂</td>
<td>21.63</td>
<td>22.14</td>
<td>13.56</td>
</tr>
<tr>
<td>C₃</td>
<td>14.11</td>
<td>15.22</td>
<td>10.92</td>
</tr>
<tr>
<td>H₂S</td>
<td>19.70</td>
<td>12.76</td>
<td>10.88</td>
</tr>
<tr>
<td>H₂O</td>
<td>10.85</td>
<td>15.21</td>
<td>32.94</td>
</tr>
<tr>
<td>méthanol</td>
<td>0.66</td>
<td>1.08</td>
<td>0.00</td>
</tr>
<tr>
<td>acetaldehyde</td>
<td>4.56</td>
<td>3.49</td>
<td>0.00</td>
</tr>
<tr>
<td>benzene</td>
<td>4.52</td>
<td>7.07</td>
<td>4.09</td>
</tr>
<tr>
<td>toluene</td>
<td>8.47</td>
<td>19.82</td>
<td>9.93</td>
</tr>
<tr>
<td>xylenes</td>
<td>7.89</td>
<td>19.38</td>
<td>9.06</td>
</tr>
<tr>
<td>naphthalene</td>
<td>1.24</td>
<td>4.00</td>
<td>2.56</td>
</tr>
<tr>
<td>MTNPTH</td>
<td>1.00</td>
<td>3.25</td>
<td>2.01</td>
</tr>
<tr>
<td>phenol+cresol</td>
<td>3.68</td>
<td>8.21</td>
<td>9.14</td>
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</tbody>
</table>

<table>
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<tr>
<th>gases</th>
<th>63.58</th>
</tr>
</thead>
<tbody>
<tr>
<td>liquids</td>
<td>36.42</td>
</tr>
</tbody>
</table>

### Table 2
Yields of selected products obtained from IBCSP No. 5 with 25% addition of ash from IBCSP No. 4 in Continuous Flow Pressure Reactor at 500°C and 120 psig

<table>
<thead>
<tr>
<th>time /hrs/#</th>
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<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
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<td>32.46</td>
<td>47.32</td>
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<tr>
<td>C₂</td>
<td>26.94</td>
<td>28.08</td>
<td>11.94</td>
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<tr>
<td>C₃</td>
<td>16.58</td>
<td>14.64</td>
<td>6.62</td>
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<tr>
<td>H₂S</td>
<td>20.00</td>
<td>12.91</td>
<td>2.42</td>
</tr>
<tr>
<td>H₂O</td>
<td>11.85</td>
<td>9.62</td>
<td>31.28</td>
</tr>
<tr>
<td>méthanol</td>
<td>0.99</td>
<td>1.12</td>
<td>0.42</td>
</tr>
<tr>
<td>acetaldehyde</td>
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<td>1.17</td>
<td>0.00</td>
</tr>
<tr>
<td>benzene</td>
<td>4.34</td>
<td>10.10</td>
<td>15.20</td>
</tr>
<tr>
<td>toluene</td>
<td>21.54</td>
<td>24.11</td>
<td>23.39</td>
</tr>
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<td>xylenes</td>
<td>7.80</td>
<td>7.96</td>
<td>10.07</td>
</tr>
<tr>
<td>naphthalene</td>
<td>0.34</td>
<td>0.36</td>
<td>0.73</td>
</tr>
<tr>
<td>MTNPTH</td>
<td>0.24</td>
<td>0.32</td>
<td>2.46</td>
</tr>
<tr>
<td>phenol+cresol</td>
<td>7.12</td>
<td>7.02</td>
<td>14.76</td>
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</table>

<table>
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<tr>
<th>gases</th>
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</tr>
</thead>
<tbody>
<tr>
<td>liquids</td>
<td>47.79</td>
</tr>
</tbody>
</table>

# - time after reactor reaches 500°C
* - methylnaphthalene
by most workers. However, in the presence of the methane/oxygen mixture the bonds do not form but are capped by methyl groups. If the coal matrix is composed of complex high molecular weight molecules, then they must be of relatively simple and frequently repeating units to give the simple low molecular weight mixtures obtained in our experiments.

We performed several experiments in which the liquid products were trapped in the ice bath and then weighed to obtain the mass balance of the process. The mass balance of the reaction with IBCSP No.4 is presented below:

**Substrates:**

- coal: 30.00 g (-11.4 g ash = 18.6 g carbonaceous material)
- liquids: 0.00 g
- gases: 3.76 g (CH₄/O₂)
- total: 33.76 g

**Products:**

- coal/char/ash: 16.2 g
- liquids: 9.7 g (18.6 x 9.7 x 100 = 52.2%)
- gases: 7.71 g
- total: 33.61 g

Liquids contain approximately 3.9 - 5.5% of water. Therefore, we subtracted 0.53 g and the total amount of chemicals is now 9.17 g.

The same coal sample was treated with hydrogen to compare the reaction with the mixture of methane and oxygen. The mass balance is:

**Substrates**

- coal: 30.00 g (-11.4 g ash = 18.6 g carbonaceous material)
- liquids: 0.00 g
- gases: 0.35 g
- total: 30.35 g

**Products**

- coal/char/ash: 21.7 g
- liquids: 6.0 g (6.0 x 18.6 x 100 = 32.3 %)
- gases: 3.87 g
- total: 31.57 g

For the experiment with IBCSP No.5 the mass balance is presented below:

**Substrates**

- coal: 30.00 g (-5.4 g ash = 24.6 g carbonaceous material)
- liquids: 0.00g
- gases: 3.76 g
- total: 33.76 g
coal/char/ash  20.5 g
liquids    8.33 g ($8.33 \div 24.6 \times 100 = 33.9 \%$)
gases      6.85 g
total      35.68 g

Additionally, we performed an experiment in which we used MgO mixed with IBCSP No. 5 in the reaction with methane at 500°C and 120 psig. The results are presented in Table 3. For comparison, in the parentheses the results with coal and ash are presented.

**Table 3**

| Yields of selected products obtained from IBCSP No. 5 with 13% addition of MgO in Continuous Flow Pressure Reactor at 500°C and 120 psig |
|---|---|---|---|
| time /hrs/# | 0 | 1 | 4 |
| CO₂ | 35.24(26.11) | 35.94(33.04) | 37.77(32.28) |
| C₂ | 25.04(24.59) | 21.64(25.06) | 10.28(10.97) |
| C₃ | 15.13(14.94) | 11.35(12.00) | 2.61(3.21) |
| H₂S | 9.98(8.92) | 10.68(11.24) | 9.21(14.02) |
| H₂O | 14.16(14.63) | 20.00(17.98) | 40.13(39.52) |
| methanol | 0.45(0.49) | 0.92(0.68) | 0.00(0.00) |
| benzene | 2.67(3.04) | 7.85(3.74) | 13.64(7.31) |
| toluene | 15.49(17.36) | 29.13(16.67) | 23.64(15.18) |
| xylene | 11.79(15.51) | 16.81(23.78) | 23.86(16.89) |
| naphthalene | 0.13(0.00) | 0.19(0.45) | 0.55(0.00) |
| MTNPHT | 0.16(0.00) | 0.00(0.00) | 0.75(0.00) |
| gases | 60.44(65.01) | | |
| liquids | 39.56(34.99) | | |

Both magnesium oxide and coal ash have a similar effect on coal liquefaction. MgO is one of the minor components of coal ash and MgO doped with lithium can activate the methane molecule.¹⁰ Of course, coal ash contains several other oxides which can play a significant role in the methane activation reaction. Therefore, determining the role of these oxides may lead to improvements in coal conversion and methane activation processes.

In order to evaluate the reproducibility of our experiments we performed several experiments with the IBCSP coal No. 104 and CH₄/O₂ at 500°C and 120 psi, in which both liquids and gases were collected and analyzed. The reproducibility of these experiments is shown in Table 1. In experiment 4 the gases coming from the reactor were vented at atmospheric pressure to a test tube immersed in ice; whereas the effluents in experiments 1, 2, and 3 were condensed in the second buffer autoclave immersed in ice before releasing the pressure to the atmosphere.
Table 4

REPRODUCIBILITY EXPERIMENTS WITH IBCSP NO. 4 COAL

<table>
<thead>
<tr>
<th>EXPT No.</th>
<th>Coal in</th>
<th>Coal out</th>
<th>Total liquids</th>
<th>Water</th>
<th>Organic liquids</th>
<th>Gases</th>
<th>Mass Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30.0</td>
<td>21.2</td>
<td>7.2</td>
<td>1.9</td>
<td>5.3</td>
<td>2.8</td>
<td>31.2</td>
</tr>
<tr>
<td>2</td>
<td>30.0</td>
<td>20.8</td>
<td>7.8</td>
<td>2.1</td>
<td>5.9</td>
<td>2.9</td>
<td>31.52</td>
</tr>
<tr>
<td>3</td>
<td>30.0</td>
<td>21.3</td>
<td>8.0</td>
<td>2.6</td>
<td>5.4</td>
<td>3.0</td>
<td>32.3</td>
</tr>
<tr>
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<td>23.1</td>
<td>5.8</td>
<td>2.8</td>
<td>3.0</td>
<td>2.2</td>
<td>31.1</td>
</tr>
</tbody>
</table>

In this case we observed the loss of organics due to evaporation when they are not condensed under pressure. The average percentages of organic compounds from experiments 1 - 3 is 29.7±1.3%, corrected for water but not for entrained and occluded organics. The concentrations of the various compounds identified are shown in Table 2. These percentages are estimated from the integrator values and have not been normalized to take into account differences in detector responses to the different compounds. Benzene is not reported, since it is obscured by the large THF solvent peak used to homogenize the liquid products.

Table 5.

ORGANIC COMPOUNDS IN LIQUIDS FROM EXPERIMENTS WITH IBCSP NO. 4 COAL (WT% OF TOTAL LIQUIDS)

<table>
<thead>
<tr>
<th></th>
<th>Exp.1</th>
<th>Exp.2</th>
<th>Exp.3</th>
<th>avg.±</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>9.18</td>
<td>8.23</td>
<td>9.67</td>
<td>9.03 ± 0.56</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>1.48</td>
<td>1.54</td>
<td>1.65</td>
<td>1.57 ± 0.07</td>
</tr>
<tr>
<td>xylenes</td>
<td>11.12</td>
<td>10.90</td>
<td>11.56</td>
<td>11.19 ± 0.24</td>
</tr>
<tr>
<td>mesitylene</td>
<td>2.19</td>
<td>2.25</td>
<td>2.32</td>
<td>2.25 ± 0.06</td>
</tr>
<tr>
<td>phenol</td>
<td>12.45</td>
<td>11.45</td>
<td>13.21</td>
<td>12.35 ± 0.82</td>
</tr>
<tr>
<td>indene</td>
<td>2.95</td>
<td>2.90</td>
<td>3.02</td>
<td>2.9 ± 0.04</td>
</tr>
<tr>
<td>cresols</td>
<td>16.53</td>
<td>14.34</td>
<td>16.92</td>
<td>15.93 ± 1.19</td>
</tr>
<tr>
<td>tetralin</td>
<td>5.17</td>
<td>5.21</td>
<td>4.97</td>
<td>5.12 ± 0.09</td>
</tr>
<tr>
<td>naphthalene</td>
<td>6.02</td>
<td>5.98</td>
<td>6.21</td>
<td>6.06 ± 0.09</td>
</tr>
<tr>
<td>methyl-naphthalenes</td>
<td>3.13</td>
<td>3.25</td>
<td>3.42</td>
<td>3.27 ± 0.08</td>
</tr>
<tr>
<td>2-naphthol</td>
<td>2.27</td>
<td>2.34</td>
<td>2.19</td>
<td>2.17 ± 0.10</td>
</tr>
</tbody>
</table>

In addition to these experiments, the char after run No. 3 was treated with THF at room temperature overnight. After that, the solution was injected into the FID gas chromatograph. The analysis showed the presence of several compounds (e.g. approximately 3.4% of cresols). This means that under the conditions of this experiment the char still contains chemicals adsorbed on its surface.

Yields at different times at 500° C and 120 psig

Figure 2 shows the plot of weights of total liquid products and water obtained in the reaction of IBCSP coal No. 104 with methane and oxygen versus time. For "0" reaction time, only
4.95 g of liquids are formed. These liquids contain 2.3 g of water. Weights of the total liquids gradually increase with time of the reaction; however, little difference exists between the amount of liquids formed after 3 hrs (7.15 g) and 7 hrs (7.50 g). The amount of water formed in the reaction is nearly independent of time, clearly indicating that water comes from the coal during the heat-up step from room temperature to 500°C.

Table 6 presents the concentrations of the various compounds identified in the liquids after different reaction times. These percentages are estimated from the integrator values and have not been normalized to take into account differences in detector responses to the different compounds (especially light molecular weight compounds). Benzene is not reported, since it is obscured by the large THF solvent peak used to homogenize the liquid products.

### Table 6

**ORGANIC COMPOUNDS IN LIQUIDS FROM EXPERIMENTS WITH IBCSP COAL NO. 104 (WT% OF TOTAL LIQUIDS) AFTER DIFFERENT REACTION TIMES**

<table>
<thead>
<tr>
<th></th>
<th>0</th>
<th>1</th>
<th>3</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>3.21</td>
<td>7.28</td>
<td>8.15</td>
<td>9.03</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>0.00</td>
<td>0.46</td>
<td>1.44</td>
<td>1.57</td>
</tr>
<tr>
<td>xylenes</td>
<td>8.23</td>
<td>10.29</td>
<td>10.99</td>
<td>11.19</td>
</tr>
<tr>
<td>mesitylene</td>
<td>1.89</td>
<td>2.01</td>
<td>2.20</td>
<td>2.25</td>
</tr>
<tr>
<td>phenol</td>
<td>10.21</td>
<td>11.45</td>
<td>12.23</td>
<td>12.35</td>
</tr>
<tr>
<td>indene</td>
<td>1.56</td>
<td>2.87</td>
<td>2.99</td>
<td>2.90</td>
</tr>
<tr>
<td>cresols</td>
<td>12.98</td>
<td>15.97</td>
<td>16.90</td>
<td>15.93</td>
</tr>
<tr>
<td>tetralin</td>
<td>4.76</td>
<td>5.02</td>
<td>5.21</td>
<td>5.32</td>
</tr>
<tr>
<td>naphthalene</td>
<td>5.87</td>
<td>5.99</td>
<td>5.56</td>
<td>5.82</td>
</tr>
<tr>
<td>methylnaphthalenes</td>
<td>2.34</td>
<td>3.00</td>
<td>3.21</td>
<td>3.19</td>
</tr>
<tr>
<td>2-naphthol</td>
<td>1.98</td>
<td>2.00</td>
<td>2.02</td>
<td>2.19</td>
</tr>
</tbody>
</table>

The above results show that the high molecular weight compounds are formed at the beginning of the experiments and the low molecular weight compounds are formed continuously during approximately the first 3 hrs of the run. Indeed, the concentrations of naphthalenes, 2-naphthol, tetralin and methylnaphthalenes remain relatively constant, whereas the concentrations of toluene, ethylbenzene, xylenes or cresols increase during the first 3 hrs of the process.

**Experiments with $^{13}$CH$_4$**

Experiments with IBCSP coal No. 104 and labelled methane were described in the experimental section. All peaks in the $^{13}$C-NMR spectra of the liquids from these experiments have not been identified and full analysis is incomplete; however, preliminary findings are clear — $^{13}$C is not going into the organic effluents in large quantities during the first hour. Therefore, methane from the reactant gas is not incorporated into the oils (at least in large quantities) at the early stages of the reaction. Other possible explanations for the high yields of oils from the methane/oxygen treatment are that methane is incorporated in the oils at a later stage and/or it is decomposed to hydrogen atoms, which are incorporated into the organic effluents, and carbon or methane fragments, which are incorporated into the char.
The latter hypothesis obtains some support from the following experiments. In the microbalance reactor 61.945 mg of coal No. 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. It could be a reaction between the methane and coal to make vaporizable organic molecules (which does not seem too likely since 13C is not going into the oils). 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 coal No. 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 2.

| Table 7 |
| BTU and S Contents of Chars from IBCSP Coal No. 106 |
| Treated with Helium and Methane at 500°C |
|after He|after 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 value of 13226, the methane-treated sample has a 9.7% larger BTU value than the original coal. And sulfur content is substantially smaller also. 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.

Experiments with CD₄

The ²H spectrum (Figure 2) of a fraction of liquids contains two sharp signals from the natural abundance for deuterium in the THF solvent. In addition, two broad resonances are observed which can be attributed to deuterium in the solute liquids from coal. These signals may be strong enough to indicate the presence of deuterium above natural abundance levels. If deuterium were indeed incorporated into the liquids derived from coal, the ¹H-decoupled ¹³C spectra could show splitting of some signals from deuterium. This would likely appear as small multiplets at the bases of the signals for the main non-deuterated sites. Many of the signals in the ¹³C(¹H) spectrum (Figure 3) show broad feet at their bases which suggest the presence of these C-D multiplets.
Experiments with model compounds

We performed several experiments with model compounds thought to be representative of coal structure. The reactions of phenanthrene, diphenylmethane, and diphenylethane with CH₄/O₂, CH₄, He/O₂, and He were performed in the autoclave reactor. The conditions of the reactions were: temperature-500°C, pressure-120 psig, time-1 hr. When the reaction was completed, the products were released from the autoclave at 500°C and collected in the test tube which was kept in an ice bath. Liquids were dissolved in 1 ml of THF and analyzed using FID gas chromatograph. Table 8 presents the results.

Table 8

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Conversion</th>
<th>Total number of compounds detected (GC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenanthrene + He</td>
<td>2.0</td>
<td>7</td>
</tr>
<tr>
<td>phenanthrene + He/O₂</td>
<td>3.9</td>
<td>10</td>
</tr>
<tr>
<td>phenanthrene + CH₄</td>
<td>3.6</td>
<td>15</td>
</tr>
<tr>
<td>phenanthrene + CH₄/O₂</td>
<td>4.6</td>
<td>19</td>
</tr>
<tr>
<td>phenanthrene + H₂</td>
<td>3.8</td>
<td>13</td>
</tr>
<tr>
<td>diphenylmethane + He</td>
<td>1.6</td>
<td>25</td>
</tr>
<tr>
<td>diphenylmethane + He/O₂</td>
<td>2.5</td>
<td>30</td>
</tr>
<tr>
<td>diphenylmethane + CH₄</td>
<td>1.8</td>
<td>45</td>
</tr>
<tr>
<td>diphenylmethane + CH₄/O₂</td>
<td>26.0</td>
<td>75</td>
</tr>
<tr>
<td>diphenylmethane + H₂</td>
<td>6.2</td>
<td>30</td>
</tr>
<tr>
<td>diphenylethane + He</td>
<td>55.0</td>
<td>25</td>
</tr>
<tr>
<td>diphenylethane + He/O₂</td>
<td>62.0</td>
<td>29</td>
</tr>
<tr>
<td>diphenylethane + CH₄</td>
<td>83.0</td>
<td>40</td>
</tr>
<tr>
<td>diphenylethane + CH₄/O₂</td>
<td>96.0</td>
<td>55</td>
</tr>
<tr>
<td>diphenylethane + H₂</td>
<td>88.0</td>
<td>42</td>
</tr>
<tr>
<td>biphenyl + He</td>
<td>0.3</td>
<td>5</td>
</tr>
<tr>
<td>biphenyl + He/O₂</td>
<td>0.9</td>
<td>8</td>
</tr>
<tr>
<td>biphenyl + CH₄</td>
<td>0.7</td>
<td>8</td>
</tr>
<tr>
<td>biphenyl + CH₄/O₂</td>
<td>1.0</td>
<td>9</td>
</tr>
<tr>
<td>biphenyl + H₂</td>
<td>0.9</td>
<td>8</td>
</tr>
</tbody>
</table>

The above data reveal that when methylene bridges are present in the model compound, a relatively high percentage of the compound reacts with methane, with methane/oxygen, and with hydrogen. The conversion of 55% diphenylethane in helium suggests much of the reaction is due to simple pyrolysis processes. However, in the presence of methane, methane/oxygen, or hydrogen the conversion and the number of products increases substantially. So methylene bridges seem to be an important reactant in coal conversion by methane/oxygen treatment.

Apparently, the synergistic effect of methane and oxygen is to attack methylene bridges and stabilize the resulting radicals before they can react further. When only one methylene
forms the bridge between two phenyls, the weak carbon-hydrogen bond is attacked, but when a weak carbon-carbon bond exists also (as in 1,2-diphenylethane), extensive rupturing, rearrangement, and recombination occur.
REFERENCES


Figure 1. Yields of selected products from IBCSP No. 5 reaction with CH$_4$/O$_2$ at 500°C for different percentages of added ash No. 5.
Fig. 2 $^2$H NMR Spectrum of the Liquids Obtained in the Reaction of IBCSP
Coal No. 104 with CD$_4$/O$_2$ at 500°C
Fig. 3 $^{13}$C[$^1$H] NMR Spectrum of the Liquids Obtained in the Reaction of IBCSP Coal No.104 with CD$_4$ / O$_2$ at 5000°C