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Hydrogenation of Coals and Chars to Gaseous Hydrocarbons

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INTRODUCTION

The hydrogenation of coal is being considered in this country and abroad for production of high B.t.u. gas for meeting peak-load demands of the gas industry and as a method for augmenting future supplies of natural gas. Experiments on the hydrogenation of coal and chars to gaseous products have been investigated by Dent,<sup>1</sup> Channabasappa,<sup>1</sup> and the Bureau of Mines<sup>2</sup> at 500 to 3000 pounds per square inch gauge, 500 to 750°C., with very long residence times. Recently the Bureau of Mines extended these studies<sup>4</sup> to 6000 pounds per square inch gauge and 800°C. with a coal from Rock Springs, Wyoming, using very short residence times. This paper discusses the amenability of other coals and chars to conversion to gaseous hydrocarbons at 6000 pounds per square inch gauge and 800°C.

EXPERIMENTAL PROCEDURE

A flow sheet of the apparatus is shown in figure 1. Hydrogen flowed from a storage vessel into the bottom of the reactor through a preheat zone and into the bed of coal or char. After a constant flow of hydrogen was established, the reactants were heated to 800°C. in 1-1/2 minutes by passing a high current through the tube at points E and E<sub>1</sub>. Hydrocarbon vapors and gases and excess hydrogen passed at pressure into a small condenser-receiver where the bulk of the oils were collected in a small glass vial. Noncondensable gases were reduced to atmospheric pressure, passed into a small gasholder, and after an appropriate storage period they were sampled, metered, and finally vented. At the end of an experiment, the reactor and its charge were cooled to room temperature by spraying with cold water. After the bulk of the unreacted solids were removed, the reactor was washed with benzene to remove the remainder of solids and high molecular weight oils. The unreacted solids and benzene washings were filtered and the solids were extracted with benzene in a Soxhlet apparatus. The percentage of coal reacted was then calculated by subtracting the weight percent of unreacted organic solids (organic benzene insolubles) from 100. The filtrate and extract were not analyzed.

Oils which were collected in the condenser-receiver were analyzed semi-quantitatively in a mass spectrometer using a low ionizing voltage technique. Gaseous hydrocarbons in the effluent gas stream were also analyzed by the mass spectrometer.

Yields of oils and hydrocarbon gases were expressed as weight percentages based on moisture- and ash-free coal or char. Total yields on this basis would be larger than 100 by an amount equal to the percentage of hydrogen absorbed based on moisture- and ash-free coal or char.

Studies were made with high-volatile bituminous coals from Pittsburgh, Pennsylvania and Rock Springs, Wyoming, a lignite from Rockdale, Texas, a medium-volatile anthracite from Luzerne County, Pennsylvania, and a char from Rock Springs, Wyoming coal. The char was prepared by heating the coal in helium for 2 hours at 600° C.; it represents the type of material which could be produced commercially by carbonization at low temperatures. Ultimate analyses of the substrates are shown in table 1. The coals and char were all pulverized and screened to 30 x 60 mesh. Ammonium molybdate was added to a weight of water 1.3 times the weight of coal or char to provide 1 percent molybdenum on the substrate. After standing for 5 minutes, the solution was added to the substrate and concentrated by evaporating on a hot plate with constant stirring at 100°C. The mixture was finally dried on a tray in air at 70° C. for 20 hours.

Experiments were conducted at 6000 pounds per square inch gauge and 800° C. and residence times of zero to 15 minutes. Zero residence time is defined as the time at which the coal attains reaction temperature. Flow of hydrogen was 100 standard cubic feet per hour, corresponding to a nominal linear velocity at pressure and temperature of 0.5 foot per second. In all cases, this rate of flow was sufficient to absorb the heat of reaction and thus maintain adequate control of temperatures.

## RESULTS

Conversions of coal and char to gases and liquids are shown in figure 2. Bituminous coal and lignite were more readily hydrogenated than the char and anthracite. This observation is reasonable because of the less condensed structures of lower rank coals. Increase in residence time from "0" to 15 minutes resulted in an increase in conversion for Texas lignite from 90 to 97 percent, based on moisture- and ash-free feed, and an increase in conversion with the bituminous coals from 75 to about 90 percent. Although conversions for char and anthracite were low at "0" time, they increased to 67 and 53 percent, respectively, during the first three minutes and at the end of 15 minutes the conversion of char and anthracite amounted to 84 and 65 percent, respectively.

The carbonaceous residues remaining in the reactor from bituminous coals and lignite were agglomerated, whereas, residues from char and anthracite were free-flowing. Agglomeration was less severe with Texas lignite than with bituminous coals.

Yields of oil from bituminous coals and lignite were independent of residence time. Virtually no oils were produced from char or anthracite. As shown in figure 3, yields from Texas lignite, Rock Springs, Wyoming and Pittsburgh coals were 32, 26, and 20 percent, based on moisture- and ash-free coal, respectively. As yields of oil

did not increase with increase in retention time, it appears that the bulk of the oils were formed during heating to 800° C. Past experiments have shown that the formation of oil begins at about 400° C., increases rapidly as the coal is heated to 525° C., and from there on decreases because of cracking reactions.

About 90 percent of the oil was collected as overhead material in the condenser-receiver, the remainder condensed in the connecting piping between the reactor and the receiver. Overhead oils produced from bituminous coals and lignite boiled below 300° C. and contained less than 4 percent asphaltenes. Table 2 shows the various compounds in the overhead product which were identified by mass spectrometer. It is believed that oils produced from Pittsburgh coal contained the highest quantity of alkyl benzenes and naphthalene.

Yields of gaseous products as a function of residence time are shown in figure 4. The highest yields of gases were obtained with char, followed by anthracite, Pittsburgh-seam coal, Rock Springs, Wyoming, coal, and Texas lignite. The yield of gaseous hydrocarbons at the end of 15 minutes from char was about 94 percent and the yield from Texas lignite or Rock Springs coal was about 67 to 70 percent, based on moisture- and ash-free feed. In all cases, the formation of gaseous hydrocarbons increased very rapidly during the first three minutes, and from there on the rate was smaller and approximately constant.

Methane in the gaseous products increased and C<sub>2</sub> and C<sub>3</sub> hydrocarbons decreased with increasing rank or carbon content of the substrates. Composition of gaseous products did not vary with residence time. Average compositions of the gases are shown below:

	Composition, volume-percent			Heating value, B.t.u.'s per standard cubic foot of hydrocarbons
	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	
Texas lignite	82	15	3	1170
Wyoming coal	88	10	2	1110
Pittsburgh coal	90	9	1	1085
Anthracite	92	7	1	1090
Char	92	8	-	1045

As the flow of hydrogen was high in these experiments, the concentration of hydrocarbon gases in the effluent stream was only 2 to 4 percent. If coal was hydrogenated in a continuous unit at high partial pressures of hydrogen, the effluent gases would be recycled and the gaseous products could be removed by scrubbing with an appropriate solvent. As some hydrogen would also be removed by scrubbing, it would probably be necessary to use a low-temperature fractionation system to enrich the product sufficiently to meet specifications for commercial fuels. In this apparatus, product distribution is affected by retention time of the volatile products as well as pressure, temperature, and residence time of the coal. The effect of increasing retention time of volatiles from 6 to 30 seconds by reducing flow of hydrogen from 100 standard cubic foot per hour to 20 standard cubic foot per hour is shown in figure 5

for Rock Springs, Wyoming coal. Increase in retention time of volatiles resulted in a significant increase in yield of gaseous products and a very substantial decrease in yields of liquid hydrocarbons. For example, an increase in retention time of the volatiles from 6 to 30 seconds resulted in increasing the yield of gaseous products from 70 to 82 percent and in decreasing the yield of oil from 26 to 4-1/2 percent, based on moisture- and ash-free coal. In addition, the oil was transformed from a relatively high molecular weight product to a low-boiling material very high in benzene and naphthalene. Similar results would probably be obtained with other ranks of coal. Further increase in retention time of volatiles would probably result in production of only gaseous hydrocarbons from coal.

It was not possible to hydrogenate char or anthracite at 800° C. and 6000 pounds per square inch gauge at the lower (20 standard cubic feet per hour) flow rates of hydrogen because of uncontrolled temperatures. Under these conditions, temperatures increased to over 1000° C. and as a result, the reactor ruptured. Uncontrolled temperatures did not occur with bituminous coals and lignite under identical conditions. This overheating may be related to the type of reactions which took place. It is believed that coal, when heated rapidly to 800° C., first undergoes thermal decomposition with simultaneous hydrogenation of reactive fragments to produce oil, gaseous hydrocarbons, and a carbonaceous residue. As temperatures increase, thermal cracking of oils takes place with production of additional hydrocarbon gases and residue. Residues remaining at 800° C. are then slowly hydrogenated to gaseous hydrocarbons. Reactions are much different with char or anthracite, as only hydrogenation to gaseous hydrocarbons occurs. Thus, reactions with bituminous coals or lignite are partly endothermic and exothermic, whereas, all of the reactions with char or anthracite are exothermic. With char or anthracite, the rate of heat release is sufficiently high to cause overheating. When char was mixed with equal weights of asphaltenes or heavy oil, overheating did not occur. In this case, endothermic reactions associated with thermal decomposition of these high molecular weight materials probably absorbed sufficient heat from the exothermic reactions to prevent overheating. Overheating with char or anthracite at the lower flow rates (20 standard cubic feet per hour) of hydrogen could also be prevented by dispersing the materials in a bed of sand. No overheating occurred with char or anthracite at high flow rates (100 standard cubic feet per hour) of hydrogen. It is of interest to point out that a natural graphite from Madagascar did not react at 800° C. and 6000 pounds per square inch gauge.

Literature Cited

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Table 1. Ultimate analyses of substrates

	<u>Moisture</u>	<u>Ash</u>	<u>Carbon</u>	<u>Hydrogen</u>	<u>Nitrogen</u>	<u>Sulfur</u>	<u>Oxygen*</u>
	As received, percent						
Texas lignite	2.3	17.4	54.8	4.4	1.2	1.9	18.0
Wyoming coal	0.6	1.9	75.1	5.4	1.8	0.7	14.5
Pittsburgh coal	0.6	8.6	73.9	5.0	1.7	1.5	8.7
Anthracite	0.1	9.3	83.6	2.4	0.3	0.9	3.4
Wyoming char	0.6	2.9	87.9	2.2	1.9	0.6	3.9

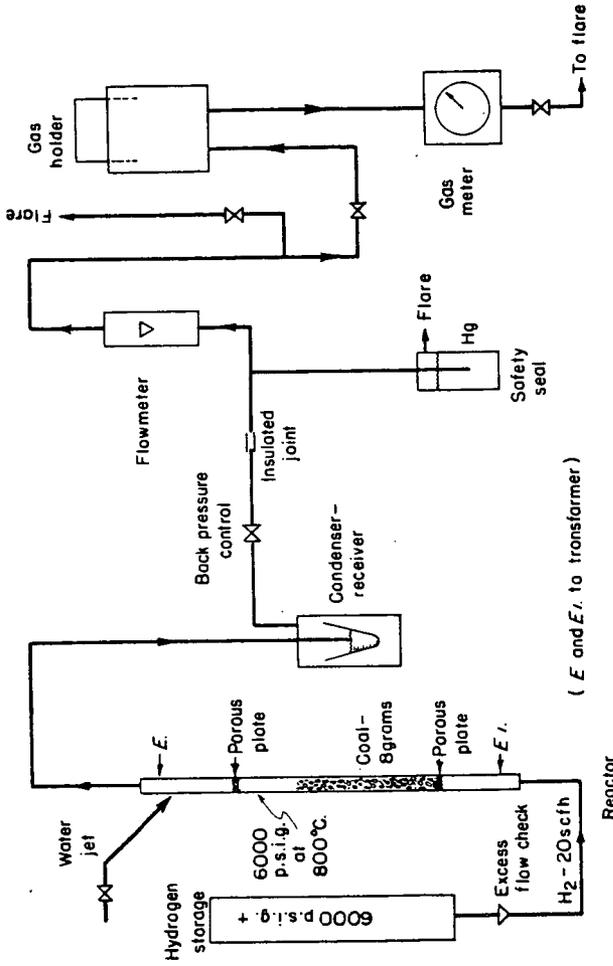
  

	<u>Moisture- and ash-free, percent</u>					
Texas lignite	68.2	5.5	1.5	2.4	22.4	
Wyoming coal	77.0	5.5	1.8	0.8	14.9	
Pittsburgh coal	81.4	5.5	1.9	1.6	9.6	
Anthracite	92.3	2.6	0.3	1.0	3.8	
Wyoming char	91.1	2.3	2.0	0.6	4.0	

\* By difference.

Table 2. Analyses of Overhead Oils

<u>Compound type</u>	<u>Molecular weight</u>
Alkyl benzenes	78-190
Phenylnaphthalenes	204-288
Phenols	94-164
Phenanthrenes-Anthracenes	178-290
Fluorenes	166-278
Acenaphthenes-Biphenyls	154-238
Benzopyrenes-Perylenes	252-294
Naphthalenes	128-240
Binaphthyls	254-296
Indenes	116-130
Naphthols	144-214
Chrysenes	228-298
Indans	118-188
Pyrenes	202-300



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Figure 1.-Semi-continuous unit for the hydrogenation of dry coal.

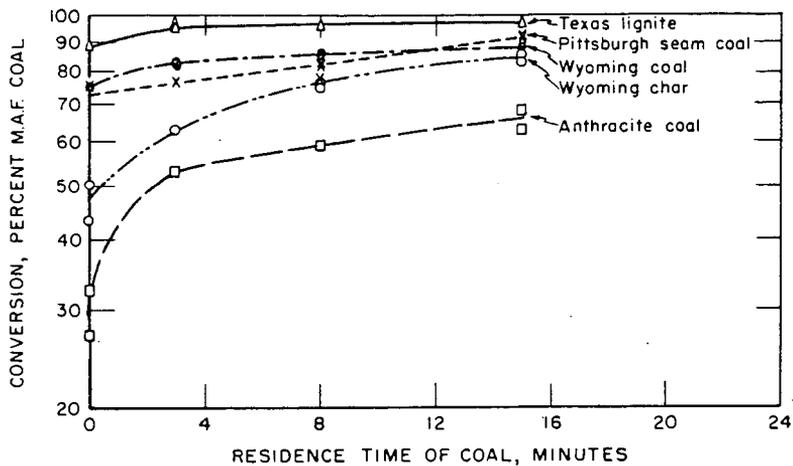


Figure 2. - Effect of residence time on conversion.

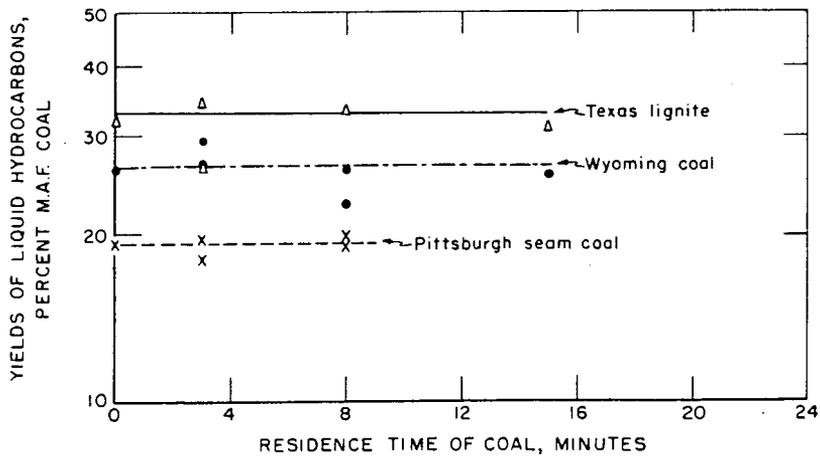


Figure 3.-Effect of residence time on yield of liquid hydrocarbons.

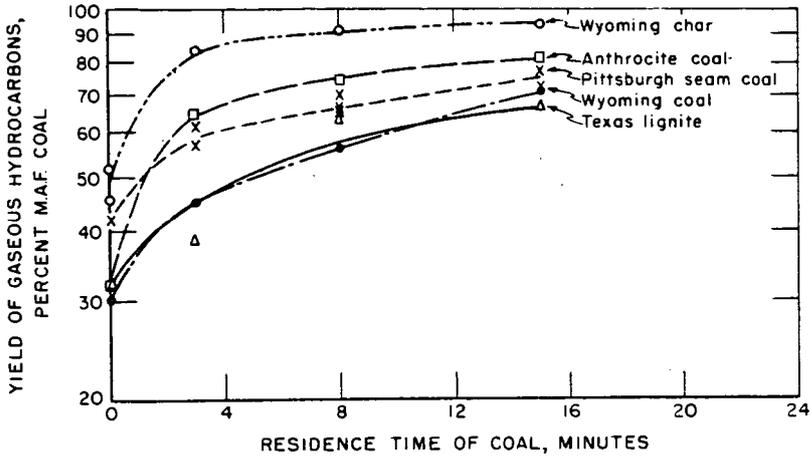


Figure 4. - Effect of residence time on yield of gaseous hydrocarbons.

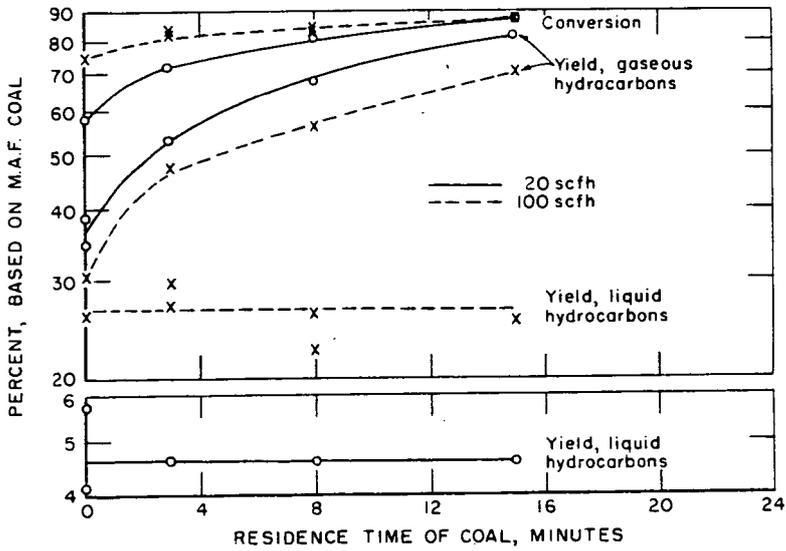


Figure 5. - Effect of residence time on product distribution for Wyoming coal at two gas rates.