AGGLOMERATION STUDIES IN THE LOW-PRESSURE HYDROGENATION OF COAL IN A FLUIDIZED BED

By Walter Kawa, Raymond W. Hiteshue, William A. Budd, Sam Friedman, and Robert B. Anderson
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by

Walter Kawa,1 Raymond W. Hiteshew,2 William A. Budd,3 Sam Friedman,2 and Robert B. Anderson4

Summary

AGGLOMERATION is one of the principal difficulties in the low-pressure dry-coal hydrogenation of bituminous coal in a fluidized system. Experiments with small batches of noncooking bituminous coal in a semicontinuous system have shown that agglomeration may be reduced or eliminated by employing a comparatively slow heating rate, by pretreatment at 400° C. with or without hydrogen, by impregnating with alkali carbonate or ammonium molybdate, or by dilution with material such as char. To obtain maximum yields of oil, residence time in the 400° to 500° C. temperature range must be sufficiently long.

No difficulties were experienced with agglomeration of a Texas lignite.

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INTRODUCTION

In Germany from 1927 to 1945 liquid fuels and lubricating oil were produced on an industrial scale by the Bergius-I. G. Farbenindustrie coal-hydrogenation process (9, 14)—similar to that practiced at Billingham, England, from 1935 to 1939 (8). Operating pressures were 3,500 to 10,000 pounds per square inch and temperatures 450° to 490° C., depending on the rank and composition of the coal and the catalyst used. Operating conditions favored high yields of liquids and maximum conversion of the coal to liquids and gases. One undesirable aspect of the process was that the recovered ash and coal residue (solids) were admixed with heavy oil. The mixture was difficult to handle, and a sizable quantity of oil was lost when the solids were being separated. More recent experiments in Germany (5) indicated that dry bituminous coal could be partly hydrogenated at pressures of 350 to 700 pounds per square inch gage (p.s.i.g.) and temperatures of 425° to 475° C., with appreciable yields of liquids and low yields of hydrocarbon gas. It appeared possible to separate the oil product in vapor form. The economic advantages of recovering the oil free of solids at comparatively low pressure suggested experimenting with the process potentialities of low-pressure dry-coal hydrogenation.

At low hydrogen pressures and temperatures above 400° C. coal undergoes simultaneous hydrogenation-carbonization reactions. Treatment under these conditions has been called "hydrocarbonization" (15). Hydrocarbonization of coal in a fluidized state has been studied, but little data have been published on the subject. An extensive hydrocarbonization program was pursued in England by Dent and coworkers for the Gas Research Board and the Gas Council (4). With the view of producing high B.t.u. gas, they investigated temperatures of 800° to 950° C. In experiments with weakly coking coals in a fluidized system, agglomeration difficulties were experienced.

Both hydrocarbonization and carbonization of coal in fluidized systems have been subjects of numerous patents, but fluidized carbonization systems have been more successful. A continuous low-temperature carbonization process for noncooking coal was developed at the Denver laboratories of the Bureau of Mines in cooperation with the Texas Power & Light Co. (12, 13). High-oxygen coals (over 12 percent) were carbonized at 800° F. in a fluidized bed.

In 1957 Lang and associates reported successful pilot-scale low-temperature carbonization of agglomerating coals in a fluidized bed (16).

Bench-scale hydrocarbonization studies were begun at the Bruceon laboratories of the Bureau of Mines in 1948 (3). Small batches (100 grams) of powdered coal were reacted in hydrogen flowing at a rate that provided some agitation of the particles. The effect of hydrogen velocity and reaction time on distribution of products from high-volatile bituminous C coal from Rock Springs, Wyo., was studied at 500° and 600° C. and pressures up to 1,000 p.s.i.g. The coal was heated at a rate of approximately 7° C. per minute. The residues were free flowing.

The encouraging bench-scale results prompted an effort to process Rock Springs coal continuously in a 3-inch reactor. The coal, at room temperature, was fed into a hot reactor and heated very rapidly to 600° C. in hydrogen at 500 p.s.i.g. Gas velocities of 1 foot per second and greater were used to cause fluidization and thereby transport coal through the reactor. Under these conditions the particles agglomerated, with consequent loss of fluidization and stoppage of flow.

To study and possibly overcome the problem of agglomeration, an apparatus was constructed wherein small batches of coal could be charged into a hot reactor, simulating the continuous-unit method of feeding. The extent and severity of reactor-residue agglomeration were observed, and product-distribution data were obtained. The effects on agglomeration of temperature, heating rate, pretreatment, catalyst, diluents, and coal rank were studied briefly.

In this investigation the behavior of Rock Springs coal, which might be considered a typical western noncooking coal, was the primary concern. Western bituminous and subbituminous coals constitute 31 percent (590 billion tons) of the total United States reserves (1) and represent a large part of the synthetic-liquid-fuel potential of the United States (7). A few experiments were conducted with a lignite from Rockdale, Tex. Western lignite deposits represent about 24 percent (460 billion tons) of the United States proved reserves (1) and also represent a large potential source of synthetic liquid fuels (7).

ACKNOWLEDGMENTS

The authors are grateful to W. Kral, W. E. O'Neill, and R. Madden for their excellent assistance in obtaining the experimental data.
Figure 1 is a schematic diagram of the hydrocarbonization unit constructed for the agglomeration studies. The reactor is made of 2-inch schedule-80 pipe 44 inches long. First, coal is charged into the hopper. Cylinder hydrogen passes through a regulator that maintains pressure in the system at 500 p.s.i.g. The hydrogen is preheated in a coil of tubing wound around the electrically heated reactor and enters the reactor at the bottom. When the desired temperature and flow of hydrogen are attained, the plug valve below the hopper is opened to drop the coal charge into the reactor. The valve is then closed. The charge is heated at an average rate of about 75° C. per minute, requiring 5 to 10 minutes to reach reactor temperature. The gases and volatiles are withdrawn through a porous metallic filter near the top, then pass through a water-cooled condenser and a high-pressure receiver, where the liquids are collected. The gases are depressurized and sent through absorbers, which remove water vapor, carbon dioxide, and hydrogen sulfide. The scrubbed gas is metered, sampled, and vented. After 1 hour at temperature, the reactor is cooled at a rate of about 15° C. per minute. The flow of gas is stopped when 250° C. is reached. Agitation of the reactor contents is thereafter avoided to permit observation of the extent of agglomeration.

The recovered products are solids, oil, water, carbon dioxide, hydrogen sulfide, and hydrocarbon gas. The division between the solids and oil is arbitrarily based on solubility in benzene. The solids are materials of high molecular weight and are insoluble in benzene. The entire residue in the reactor is insoluble in benzene and contains the mineral matter of the coal. Solids and oil in the lines leading to the high-pressure receiver are recovered by washing with benzene. The washings (I) are freed of benzene on a steam bath. A two-phase mixture of organic material and water is recovered in the high-pressure receiver. After the water has been removed, the organic material (II) is combined with the washings, diluted with a large excess of benzene, and filtered. The benzene-insoluble material (III) thus separated is usually less than 0.5 percent of the coal charge. This material plus the reactor residue minus ash is reported as ash-free benzene insolubles. Conversion is 100-minus the percentage of the ash-free benzene insolubles. Benzene is separated from the benzene-soluble oil
on a steam bath, and the oil is diluted with a large excess of n-hexane. The precipitate obtained is washed with additional hexane and dried. This precipitate (IV) is reported as asphaltene. Oil soluble in hexane is determined by difference (I + II—III—IV). Water vapor present in the gases leaving the high-pressure receiver is absorbed by Drierite (anhdyrous calcium sulfate). The carbon dioxide and hydrogen sulfide are removed by Ascarite (sodium hydroxide on asbestos). The scrubbed gas, mainly hydrogen and hydrocarbon gas, is sampled and analyzed by a mass spectrometer.

The extent and severity of residue agglomeration were measured approximately. Gentle shaking on a 60-mesh sieve served to screen the residues. Material remaining on the sieve was weighed to obtain the percentage of agglomeration. An agglomerate was described as weak (crumbled when handled), mild (crumbled under firm finger pressure), or strong (withstood firm finger pressure). These criteria of agglomeration were sensitive enough to show trends and therefore sufficient for this investigation.

As in the earlier study of hydrocarbonization (8), 100- to 200-mesh coal was used, and the hydrogen velocity of 0.06 foot per second, nearly minimum for fluidization, was calculated on the open cross section of the reactor at operating conditions. Most of the tests were made at a pressure of 500 p.s.i.g. and at a reaction time of 1 hour. Previous data had indicated that appreciable reaction occurs at 500 p.s.i.g. and that in 1 hour the reaction nears completion. The hopper capacity was 450 grams, but the charge in most experiments was 100 grams. Larger charges made operations more difficult because the gas-exit filter became partly plugged. The bed depth with a 100-gram charge was 4½ inches. Volatiles were retained approximately 45 seconds.

The Rock Springs coal as received from the mine contained about 5 percent ash. The coal was washed in a dense-medium plant to reduce the ash content to 2 percent; this practice was established in other investigations at this laboratory. The low-ash fraction amounted to approximately 85 percent of the as-received coal. This fraction was pulverized in a continuous ball mill; then, the 100- to 200-mesh fraction was separated. The 100- to 200-mesh fraction amounted to about 13 percent of the clean coal or about 11 percent of the as-received coal. The results probably do not differ significantly from those with unwashed coal for this fraction.

As charged to the unit, the Rock Springs coal contained 1.2 percent moisture. Its moisture- and ash-free ultimate analysis was:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>5.4</td>
</tr>
<tr>
<td>Carbon</td>
<td>77.7</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.6</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.8</td>
</tr>
<tr>
<td>Oxygen</td>
<td>14.5</td>
</tr>
</tbody>
</table>

The pulverized low-ash coal (the 85-percent fraction) contained 40 percent volatile matter; its heating value was 13,000 B.t.u. per pound; and its free-swelling index was 1. In this test the residue was a powder (8). The coal showed no plastic properties in a Gieseler plastometer test (2).

The lignite from Rockdale, Tex., was pulverized in a ball mill, and the 100- to 200-mesh portion (about 15 percent of the total) was separated. It contained 15.2 percent moisture and 13.9 percent ash. The moisture- and ash-free ultimate analysis was as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>5.4</td>
</tr>
<tr>
<td>Carbon</td>
<td>73.7</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.4</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2.5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>17.0</td>
</tr>
</tbody>
</table>

RESULTS

EFFECTS OF HEATING RATE AND TEMPERATURE

The experiments conducted with Rock Springs coal in hydrogen at 500 p.s.i.g. at heating rates of 6° and 75° C. per minute approximated earlier bench-scale and continuous operations. The reaction time was 1 hour. Agglomeration results are presented in table 1. The slow heating rate (6° C. per minute) was achieved by charging coal into the cold reactor, then heating the coal and reactor at the same time. In tests with slow heating to 400°, 500°, 600°, and 700° C., residues were free flowing. Rapid heating (75° C. per minute) to 400° and 450° C. also produced free-flowing residues, but heating rapidly to 500° C. produced a residue that was 10 percent weakly agglomerated. The percentage of agglomerates is based on the total weight of the residue. With rapid heating to higher temperatures, agglomeration was more severe. The residue produced at 600° C. was 70 percent mildly agglomerated, while residue produced at 750° C. was 80 percent strongly agglomerated. In tests employing rapid heating to 500°, 600°, and 750° C. exothermic temperature rises of 20° to 200° C. above the nominal were recorded. The maximum temperatures were momentary. The periods of overtren-
TABLE 1.—Effect of heating rate, temperature, and hydrogen pressure on agglomeration 1

<table>
<thead>
<tr>
<th>Temperature, °C.</th>
<th>Slow heating rate 2</th>
<th>Rapid heating rate 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pressure, 500 p.s.i.g.</td>
<td>Pressure, 1 atm. abs.</td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>N₂</td>
</tr>
<tr>
<td>400</td>
<td>None</td>
<td>No determination</td>
</tr>
<tr>
<td>450</td>
<td>None</td>
<td>No determination</td>
</tr>
<tr>
<td>500</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>600</td>
<td>Do</td>
<td>No determination</td>
</tr>
<tr>
<td>675</td>
<td>Do</td>
<td>No determination</td>
</tr>
<tr>
<td>700</td>
<td>Do</td>
<td>No determination</td>
</tr>
</tbody>
</table>

1 Agglomerations are expressed as weight-percent of residue. Time at nominal temperature was 1 hour. Gas velocity was 0.06 foot per second.
2 °C. per minute.
3 275 °C. per minute.

temperature lasted 5 to 10 minutes and undoubtedly influenced both agglomeration and yield data. The maximum temperature rise in the tests reported in table 1 was 80° C.

INFLUENCE OF HYDROGEN

In addition to the tests with hydrogen at 500 p.s.i.g., experiments were conducted with hydrogen and nitrogen at atmospheric pressure and with helium at 500 p.s.i.g. to determine the role of hydrogen in the agglomeration process. The results of these tests are also listed in table 1. As in previous tests, the linear velocity of the fluidizing gas was 0.06 foot per second, and reaction time was 1 hour. Calculations based on correlations developed by Leva and co-workers (11) indicated that slightly more agitation of the coal bed was attained with nitrogen at atmospheric pressure and with helium at 500 p.s.i.g. than with hydrogen at 500 p.s.i.g. In hydrogen at atmospheric pressure agitation was slightly less. No agglomeration resulted when Rock Springs coal was heated slowly to 600° and 675° C. in hydrogen or nitrogen at atmospheric pressure, or when heated rapidly to 400° C. in helium at 500 p.s.i.g. These results were the same as those obtained in similar tests with hydrogen at 500 p.s.i.g. However, rapid heating in helium at 500 p.s.i.g. to 500°, 600°, and 700° C. produced greater agglomeration than in corresponding tests with hydrogen at 500 p.s.i.g. No exothermic temperature rises were experienced with helium; therefore, the results are not entirely comparable. However, the results at 500° C. are comparable, and hydrogen clearly reduced both the extent and severity of agglomeration. In hydrogen, the exothermic rise was only about 20° C. in the 500° C. test.

STEPWISE TREATMENT

Data in the previous section demonstrated that Rock Springs coal could be heated rapidly to 400° C. in either hydrogen or a carbonizing atmosphere without agglomerating; hence, stepwise treatment was investigated. Nonagglomerated residue produced in experiments with hydrogen at 400° and 450° C. was heated rapidly to 500° C. in hydrogen at 500 p.s.i.g. No agglomeration occurred. A similar experiment to 600° C. gave the same result. In a single experiment coal was heated rapidly to 400° C., then successively to 500°, 600°, and 700° C. Each temperature was maintained for 1 hour. About 12 minutes was required to increase the temperature to successive levels. The residue was free flowing. In another experiment, after 1 hour at 400° C., the temperature was raised to 700° C. and held there 1 hour. No agglomeration resulted.

Thermal treatment at 400° C. was less effective in nitrogen than in hydrogen. Free-flowing residue produced in atmospheric nitrogen at 400° C. was heated rapidly to 600° C. in hydrogen at 500 p.s.i.g. The residue was 10 percent weakly agglomerated.

RANK AND PARTICLE SIZE OF COAL

To observe the behavior of a lignite in the apparatus, 100- to 200-mesh lignite from Rockdale, Tex., was treated in hydrogen at 500 p.s.i.g. by rapid heating to 400°, 500°, and 600° C. No agglomeration occurred. Rapid-heating experiments were also made at 500° and 600° C. with 4- to 6-mesh Texas lignite without incurring agglomeration. Heating 4- to 6-mesh Rock Springs coal rapidly to 400° C. at the same hydrogen pressure caused agglomeration.
It should be noted that, in hydrogen flowing at 0.06 foot per second, the bed of 4- to 6-mesh coal was static. In one experiment, when finer than 325-mesh Rock Springs coal was heated rapidly to 600° C., the resulting agglomeration was more severe than that obtained with 100- to 200-mesh coal under similar test conditions.

**EFFECT OF MIXING CHAR OR LIGNITE WITH ROCK SPRINGS COAL**

When coal is fed continuously into a well-fluidized reactor, the coal is diluted with partly reacted material in the reactor. This condition was simulated by charging coal mixed with residues derived from previous experiments. The extent of agglomeration reported in these experiments is the ratio of the weight of agglomerated residue over the weight of residue produced at the same temperature from coal alone expressed as percent. A mixture of 2 parts coal and 1 part residue heated rapidly in hydrogen at 500 p.s.i.g. to 675° C. produced a residue 70 percent mildly agglomerated. This was less severe than the 80-percent strong agglomeration obtained from whole coal under similar conditions. Mixing coal with Texas lignite in ratios of either 2:1 or 1:1 and heating rapidly to 675° C. produced a residue about 20 percent weakly agglomerated. The greater reduction of agglomeration obtained with lignite than with char is not explained readily.

**ALKALI CARBONATES**

In the work reported by Dent (4), alcalies and alkaline earths were found to be catalytic in the coal-hydrogen reaction. Their influence was explained as possibly being due to adsorption on the reacting surface and consequent inhibition of a competing reaction—graphitization. The net result was a marked increase in the rate of methane formation. The effect of sodium and potassium carbonates on agglomeration and product distribution was studied briefly at this point. Rock Springs coal was always tested by heating rapidly in hydrogen at 500 p.s.i.g.

At 500° C. the addition of 20 percent anhydrous sodium carbonate produced a 75 percent mildly agglomerated residue. When 20 percent sodium carbonate was added by impregnation from aqueous solution, the residue in a 500° C. test was 30 percent mildly agglomerated. It appeared that addition by impregnation was more effective than dry mixing. In succeeding tests carbones were added by impregnation. The drying temperature during impregnation was 70° C.

Agglomeration of coal impregnated with 20 percent sodium carbonate was slightly more severe than for raw coal at 500° C., but at 600° and 675° C., 10- and 20-percent additions produced 5- to 10-percent weak agglomeration—much less than with raw coal at the same temperatures. Two percent sodium carbonate reduced agglomeration at 600° and 675° C. but was less effective than the higher concentrations. Sodium and potassium carbonates were equally effective. Residues in these experiments were pyrophoric and had to be collected under inert atmospheres. Exothermic temperature rises were 50° to 100° C. higher in experiments with carbonates. Overtemperatures were prevented in three experiments by increasing the rate of hydrogen flow as the specified temperature was approached. The further lessening of agglomeration thus achieved may have been due to the greater agitation afforded by the higher hydrogen rate.

**COAL-HYDROGENATION CATALYSTS**

Molybdenum and tin are effective catalysts for high-pressure hydrogenation of coal in the liquid phase. The influence of these catalysts on agglomeration during the hydrocarbonization of Rock Springs coal in hydrogen at 500 p.s.i.g. was studied. Coal impregnated with 1 percent molybdenum in the form of heptammonium molybdate was heated rapidly to 450°, 600°, and 675° C. About 50-percent mild agglomeration occurred at each temperature. Compared with raw-coal tests, agglomeration was much more severe at 450° C. but less severe at 600° and 675° C. Rock Springs coal impregnated with stannous chloride (1 percent tin) produced 70-percent mild agglomeration when heated rapidly to 675° C. When the tin-impregnated coal was heated slowly to 675° C., the agglomeration was 100 percent strong. By contrast, slow heating of raw coal to 675° C. yields a free-flowing residue.

**PRODUCTS**

Complete distribution of the product for tests at 500 p.s.i.g., with slow and rapid heating in hydrogen and rapid heating in helium, are shown in table 2. Some results are averages of 2 or 3 tests. The total yield indicates the extent of recovery. Complete recovery would be 100 plus the percentage of hydrogen consumed. Ash balances provided checks on the recovery of solids and indicated that the benzene insolubles were the most accurate of the yields.

There was little hydrogenation at 400° C., as shown by the similarity of yields in hydrogen and in helium (carbonization) at this temperature. However, hydrogenation was appreciable at 450° C. In both gases, conversion increased with rising temperature.
The yield of benzene-soluble oil (asphaltene plus hexane-soluble oil) obtained in helium was 6.8 percent at 500°C, 5.3 percent at 600°C, and 2.9 percent at 700°C. These values are considerably less than the 10-percent yield obtained by slow heating in helium to 600°C. (3). In the carbonization tests at 500°C and higher about 80 percent of the oxygen was removed as water and carbon dioxide.

In hydrogen, the distribution of products was independent of heating rate up to 500°C. When heating at 75°C per minute, the yield of benzene-soluble oil was a maximum at 500°C. It decreased sharply at higher temperatures with a corresponding increase in the yield of hydrocarbon gas. In the tests employing a heating rate of 6°C per minute, the yield of oil reached a maximum at 600°C and then remained constant. Greater conversion was obtained at 675°C than at 600°C because additional hydrocarbon gas was produced. The highest conversion and the highest yield of oil were obtained when the slow heating rate was employed. At 500°C, about 70 percent of oxygen was removed; at 600°C, about 80 percent of oxygen was removed. The ultimate analyses of the residues produced by heating Rock Springs coal rapidly in hydrogen at 500 p.s.i.g. are presented in Table 3. The residue from the experiment at 600°C contained 19 percent of the sulfur and 48 percent of the nitrogen that were initially in the coal.

Very little, if any, hydrogenation occurred at a hydrogen pressure of 1 atmosphere. Slow heating to 600°C and 675°C gave conversions of 37 and 39 percent. Corresponding conversions in nitrogen were 33 and 36 percent.

Product distributions for experiments in which carbonates were added were not entirely comparable with those obtained with raw coal because of the differences in maximum temperatures reached. At the same nominal temperatures, yields of benzene-soluble oil were approximately equal. Conversions and yields of hydrocarbons were considerably higher with the carbonates. It is not clear whether the carbonates functioned as contact catalysts of exothermic hydrogenation reactions or as inhibitors of endothermic reactions.

Product distributions for experiments with molybdenum and tin are listed in Table 4. Some catalysis was evident by the increased conversions and yields of oil at 450°C with 1 percent molybdenum and at 500°C with 0.1 percent molybdenum. This is the approximate temperature range normally used in high-pressure hydrogenation of coal in the liquid phase. At higher temperatures conversions with both molybdenum and tin were the same as with raw coal.
Table 3.—Ultimate analyses of residues from Rock Springs coal
[Rapid heating; 500 p.s.i.g.; hydrogen velocity, 0.06 ft. per sec.; 1 hour at temperature]

<table>
<thead>
<tr>
<th>Temperature, °C.</th>
<th>Conversion, percent</th>
<th>Ash, percent</th>
<th>Ash-free analysis, percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>H</td>
</tr>
<tr>
<td>400</td>
<td>15.4</td>
<td>2.2</td>
<td>4.3</td>
</tr>
<tr>
<td>500</td>
<td>36.2</td>
<td>2.6</td>
<td>3.7</td>
</tr>
<tr>
<td>600</td>
<td>49.2</td>
<td>3.2</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Whole coal, moisture- and ash-free

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th>H</th>
<th>C</th>
<th>N</th>
<th>S</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.4</td>
<td>77.7</td>
<td>1.6</td>
<td>.8</td>
<td>14.5</td>
</tr>
</tbody>
</table>

1 Oxygen by difference.
2 Temperature reached 700° C. momentarily.

Table 4.—Distribution of products from hydrocarbonization of Rock Springs coal in the presence of molybdenum and tin
[Rapid heating; 500 p.s.i.g.; hydrogen velocity, 0.06 ft. per sec.; 1 hour at temperature]

<table>
<thead>
<tr>
<th>Temperature, °C.</th>
<th>Catalyst, percent</th>
<th>Yields, weight-percent of coal 1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ash-free benzene insolubles</td>
</tr>
<tr>
<td>MOLYBDENUM, IMPREGNATED AS AMMONIUM MOLYBDATE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>1.0</td>
<td>60.1</td>
</tr>
<tr>
<td>500</td>
<td>.02</td>
<td>62.9</td>
</tr>
<tr>
<td>500</td>
<td>.1</td>
<td>58.7</td>
</tr>
<tr>
<td>600</td>
<td>.04</td>
<td>48.5</td>
</tr>
<tr>
<td>675</td>
<td>1.0</td>
<td>47.8</td>
</tr>
</tbody>
</table>

TIN, IMPREGNATED AS STANNOUS CHLORIDE

| 675               | 1.0               | 46.2 | 1.5 | 9.0  | 33.2 | 17.0 | 106.9 |

1 Moisture- and ash-free.
2 Percent of coal.

Table 5.—Distribution of products from hydrocarbonization of 100- to 200-mesh Texas lignite
[Rapid heating; 500 p.s.i.g.; hydrogen velocity, 0.06 ft. per sec.; 1 hour at temperature]

<table>
<thead>
<tr>
<th>Temperature, °C.</th>
<th>Yields, weight-percent of coal 1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ash-free benzene insolubles</td>
</tr>
<tr>
<td>400</td>
<td>79.5</td>
</tr>
<tr>
<td>500</td>
<td>49.0</td>
</tr>
<tr>
<td>600</td>
<td>42.3</td>
</tr>
</tbody>
</table>

1 Moisture- and ash-free.
A continuous proportional gas sample was taken for each 15-minute interval during the 1 hour at temperature. Analyses of these samples gave some indication of reaction rates. Either with or without molybdenum or tin about 60 weight-percent of the hydrocarbon gas (methane, ethane, and propane) was produced in the first 15 minutes. A typical analysis of the hydrocarbon gas showed 77 volume-percent methane, 18 percent ethane, and 5 percent propane. In experiments with carbonates, 80 to 85 weight-percent of the hydrocarbon gas was produced in the first 15 minutes. It was about 90 volume-percent methane, 8 percent ethane, and 2 percent propane.

Atmospheric distillation in an American Society for Testing Materials type apparatus was made of the composite of the benzene-soluble oils produced in several experiments at 600° C.

As shown in table 5, Texas lignite was converted to higher yields of benzene-soluble oil than Rock Springs coal under comparable conditions. The yields of oil decreased from 18.3 percent at 500° C. to 15.6 percent at 600° C. A lignite from Sandoz, Tex., of approximately the same ultimate composition as the lignite in these experiments, gave a yield of tar plus light oil of 13.2 percent in a carbonization assay at 500° C. (12). The residue produced by hydrocarbonization at 600° C. contained 31 percent ash. The yields of carbon dioxide and water at 600° C. indicated nearly complete elimination of oxygen.

**DISCUSSION**

The results of this investigation show that agglomeration of Rock Springs coal during hydrocarbonization in a fluidized system can be decreased or eliminated by slow heating, by pretreatment at 400° C. with or without hydrogen, by impregnating with alkali carbonates or ammonium molybdate, or by mixing with material such as char. Other investigators (4, 10) have reported that preoxidation also decreases the tendency of coals to agglomerate. Although a hydrogen velocity of 0.06 foot per second and a 45-inch bed were used exclusively in this investigation, gas velocity and bed depth are important variables. Deepening the bed probably would have an adverse effect, but the agglomeration described as weak probably would not occur at higher gas velocities.

Agglomeration appears to be controlled by the concentration of liquid of high molecular weight on the surface of the coal particles. As the reactions progress, some of this liquid is reduced further in molecular weight and becomes volatile enough to be removed in the stream of hydrogen. The remaining liquid carbonizes. The carbonized liquid is probably the binding agent in the agglomeration process. Agglomeration does not occur when the rate of removal of the liquid of high molecular weight approaches its rate of formation. This condition probably is achieved when a slow heating rate is employed. Pretreatment at 400° C. probably reduces the later concentration of liquid. When a char is mixed with coal, the liquid concentration probably is reduced by absorption. In preventing agglomeration, carbonates may act in the same manner as char.

Some evidence indicates that, with heating to temperatures of 600° C. or higher at rates much greater than 75° C. per minute the concentration of liquids on coal particles is kept low enough to avoid agglomeration, probably because of very rapid carbonization rates above 600° C. Dent (4) reported that heating rates of hundreds of degrees per minute produced powdery residues. In the present investigation, when carbonates and ammonium molybdate were used, the exothermic heat of reaction caused increases in heating rates and reduced agglomeration at high temperature.

In a fluidized hydrocarbonization process, selection of an operating technique would depend on the products desired and on economic considerations. The probable objectives are: (1) maximum oil production and a high yield of char (suitable for use as a fuel in powerplants); (2) maximum oil production, followed by complete hydrogenation of the solids to methane; or (3) complete hydrogenation without regard to yield of oil. To maximize the yield of oil, residence time in the 400° to 500° C. range must be sufficiently long. Additional oil is produced between 500° and 600° C., but the effect of heating rate on agglomeration and yield of oil from 500° to 600° C. was not determined. Slow heating to 600° C. is not practical in a continuous, fluidized single-reactor system. Such processing would be achieved most readily by stepwise treatment in a multi-reactor system. Up to 500° C. ammonium molybdate not only increases the yield of oil but also the agglomerating tendency. However, it may be possible to use ammonium molybdate in a stepwise treatment. Adding char to the feed decreases the agglomerating tendency and also throughputs. Once the oil product has been removed from the system,
further processing at higher temperatures requires no special precautions.

In a process directed toward complete hydrogenation without concern for the yield of oil, heating directly to 700° C. or higher would be desirable—it is possible with thermal pre-treatment, after impregnation with alkali carbonates, or by dilution. A process directed toward complete hydrogenation might also employ stepwise treatment.

Preoxidation would be one of the less desired techniques because of reduced thermal efficiency. In addition, Lang (12) reported that preoxidation caused a 47-percent decrease in the yield of tar obtained from low-temperature carbonization.

Texas lignite can be hydrocarbonized in a fluidized system with no careful temperature schedule; however, as observed with Rock Springs coal, maximum yields of oil are obtained only with adequate processing time between 400° and 500° C.
BIBLIOGRAPHY


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