ABSTRACT
Coal or other solid carbonaceous material is fed under a hydrogenation pressure of about 1,000 to 5,000 psi, in the absence of a pasting oil, to a closed, cyclic, high pressure system including a hydrogenation reactor and a reformer, and is contacted, preferably in the presence of a hydrogenation catalyst, with a stream of superheated steam, hydrogen and carbon monoxide-containing gases which have been produced by passing steam, oxygen and hydrocarbon-containing recycle gases, optionally with added solid carbonaceous material, through the reformer. The hot gaseous stream heats the coal to hydrogenation temperature and the coal is hydrogenated by hydrogen which to a large extent is produced in situ in contact with the coal through steam-carbon monoxide and steam-carbon reactions. The coal is effectively and economically hydrogenated to produce liquid hydrocarbon products and gases for recycling. Tars recovered from the product stream may be hydrogenated in like manner at system pressure with the products of tar hydrogenation being combined with the main product steam.

11 Claims, 2 Drawing Figures
HYDROGENATION OF COAL

COPENDING APPLICATION

This application is related to my copending application Ser. No. 268,201, filed June 30, 1972, now U.S. Pat. No. 3,823,084.

BACKGROUND OF THE INVENTION

The direct hydrogenation of coal to produce petroleum-like liquids was practiced in Germany and a few other countries prior to and during World War II. Since the end of the War, all commercial coal hydrogenation operations have ceased primarily because they could not produce gasoline and other hydrocarbons in competition with similar products from petroleum.

During the past 5 years world-wide concern has arisen over the rapid growth in oil consumption and the increasing danger of possible shortages. The United States has not been able to meet its internal oil requirements from domestic sources since 1948 and oil imports have increased until in the mid-summer of 1973 they supplied about 1/3 of the country's needs. These imports could be curtailed at any time.

The United States is believed to have the world's most extensive and easily mineable reserves of coal, which are sufficient to support all present uses for coal and to supply large amounts of oil and gas for a century or more. In spite of the serious petroleum supply situation, no commercial coal hydrogenation plants are presently under construction in the United States. The processes available from past technology, including such improvements as can now be incorporated, are still too expensive in terms of both capital and operating costs to be considered for large-scale commercial installations that could hope to compete with present petroleum production and processing costs as well as those anticipated for the next 5 to 10 years.

In the past, direct coal hydrogenation has been carried out by a complicated combination of at least 15 steps or processes as shown below along with the approximate percentage of capital cost which may be assigned to each step.

The percentages indicated have been estimated for liquid phase coal hydrogenation from studies by the Bureau of Mines and the Committee on Synthetic Fuels of the National Petroleum Council.

<table>
<thead>
<tr>
<th>Steps or Process</th>
<th>Percent of Total Capital Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Coal Pulverization</td>
<td>1.35</td>
</tr>
<tr>
<td>2. Paste Preparation</td>
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<tr>
<td>3. Liquid Phase Facilities</td>
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<td>4. Delayed Coking</td>
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<tr>
<td>5. Liquid Phase Distillation</td>
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<tr>
<td>6. Tar Acid Recovery</td>
<td>0.78</td>
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<tr>
<td>7. Low Temperature Gas Separation</td>
<td>3.14</td>
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<tr>
<td>8. Hydrogenation Steam Cracking</td>
<td>4.18</td>
</tr>
<tr>
<td>9. Coal Gasification</td>
<td>2.01</td>
</tr>
<tr>
<td>10. Oxygen Purification &amp; Compression</td>
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</tr>
<tr>
<td>11. Hydrogenation Purification &amp; Compression</td>
<td>17.70</td>
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<tr>
<td>12. Steam and Power</td>
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<td>13. Utilities</td>
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<tr>
<td>14. General Facilities</td>
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</tr>
<tr>
<td>15. Water Supply</td>
<td>1.88</td>
</tr>
<tr>
<td></td>
<td>100.00</td>
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</tbody>
</table>

SUMMARY OF THE INVENTION

This invention comprises a simplified coal hydrogenation process which substantially reduces capital and operating costs for the commercial production of oil, oil products, and gas from coal.

In particular, it is the objective of the invention to eliminate or greatly reduce the capital cost of commercial coal hydrogenation equipment and facilities for steps 7 (low temperature gas separation), 9 (coal gasification), 11 (hydrogen purification and compression) and to greatly reduce 12 (steam and power), 13 (utilities), and 14 (general facilities). Further, as in my earlier U.S. Pat. Nos. 3,030,297 and 3,152,063, the present invention either eliminates or greatly reduces the capital costs of the equipment for carrying out steps 2 and 3.

This invention broadly comprises establishing a closed high pressure cyclic system through which a stream of hydrogen containing gases is continuously circulated, such system including a hydrogenation zone, a product separation zone, a gas-purification zone and a reforming and heating zone, adding steam, oxygen and coal (if necessary) at system pressure to the circulating gases in the reforming zone, adding coal at system pressure to the hydrogenation zone, withdrawing liquid hydrocarbon products from the circulating gases in the product separation zone and removing H2S and CO2 from the circulating gases in the gas purification zone.

Unlike the process of my copending application, Ser. No. 268,201 filed June 30, 1972, in which the gases introduced into the hydrogenation zone contain over about 90% hydrogen, the process of the present invention relies upon the inclusion of superheated steam in the H2CO-containing stream introduced into the hydrogenation zone whereby hydrogen is formed in said zone by steam-carbon monoxide and steam-carbon reactions. Heat is supplied to the gases by controlling the endothermic-exothermic ratio of the reactions in the reforming zone so that the overall reaction generates heat.

More particularly, the process of the invention comprises circulating hydrogen-containing gases continuously through a closed cyclic system which is maintained at hydrogenation pressure above about 1000 psi and which includes a reforming zone and a hydrogenation zone; introducing steam, oxygen and, if necessary, coal or other carbonaceous material, into the circulating hydrogen-containing gases in the reforming zone to cause reaction between part of the steam and the oxygen with hydrocarbons present in the circulating gases and with any added carbonaceous material, to form hydrogen and carbon monoxide, and to raise the temperature of the gaseous stream to that sufficient to provide heat necessary in the hydrogenation zone, introducing the hot gaseous stream from the reforming zone and coal into the hydrogenation zone, heating the coal to hydrogenation temperature (at least 750°F) in the hydrogenation zone by contact with said hot gaseous stream and hydrogenating the coal in said zone, preferably in the presence of a hydrogenation catalyst, by hydrogen produced in situ in contact with the coal by the reaction of steam with CO and carbon as well as with that present in the hot gases, to produce liquid and gaseous hydrocarbons in the circulating hydrogen-containing gaseous stream, recovering the liquid hydrocarbon products from said stream and recycling the hydro-
gen-containing gaseous stream including the gaseous hydrocarbons, after removal of H₂S and CO₂, without substantial loss of pressure, to the reformer.

Economies in operation of the process are accomplished by:
1. Elimination of hydrogen gas generation outside of the high pressure system:
2. Feeding the solid coal to be hydrogenated, and all other raw materials such as steam and oxygen, at the pressure of the hydrogenation system so that expensive and power-consuming gas compression steps are eliminated;
3. Use of heat resulting from the reaction of oxygen with gaseous hydrocarbons in the recycle stream and, if necessary, with added coal, in the reformer to preheat the incoming coal and to furnish heat for the endothermic reaction between carbon monoxide, carbon and steam to generate hydrogen for the hydrogenation process;
4. The production of liquid and gaseous products from coal by reaction between hydrogen, superheated steam and coal in the presence of a suitable hydrogenation catalyst and at suitable temperature and pressure;
5. Use of heat from the hydrogenation reaction zone and to promote the reaction of carbon monoxide with water to make hydrogen;
6. Hydrogenation of tars produced in the primary hydrogenation step by contacting them at system temperature with a part of the steam of superheated steam, and hydrogen containing recycle gases.

It has been proposed in Hoffman U.S. Pat. No. 3,505,204 to produce hydrocarbons from coal by contacting the coal in the presence of a two-component catalyst system with superheated steam. However, this process is essentially a low pressure Fischer-Tropsch type process requiring a large amount of catalyst and producing oxygenated hydrocarbons as well as hydrocarbon gases and liquids.

Coals ranging from bituminous through sub-bituminous to lignite are the preferred carbonaceous materials for use in the present invention. These coals normally contain 4 to 6 percent hydrogen. Other materials present in addition to ash and carbon are oxygen, sulfur, and nitrogen. Petroleum products on the other hand contain from about 10 to 15 percent hydrogen with the remainder being essentially carbon. To convert coal to a liquid hydrocarbon it must react with hydrogen to raise the hydrogen content to the range from 10 to 15 percent and at the same time oxygen, sulfur and nitrogen must be reduced or eliminated. The hydrogen does this by the formation of H₂O, H₂S and NH₃.

Coal for the hydrogenation process is usually washed to reduce the ash as much as possible and dried to 3 or 4 percent moisture although a greater amount of moisture can be left in the coal where it is desired for producing additional steam for the hydrogenation reaction. It is then crushed or pulverized, often to about 60 or 70 percent through 200 mesh which is about normal pulverizing for large size utility boilers. Pulverizing is not always a requirement for some coals have been found to disintegrate on introduction into the hot hydrogenation zone.

Past commercial practice for getting the coal into the high pressure hydrogenation zone was to mix it with about an equal amount of heavy oil and use "slurry pumps" to force it into the reaction zone.

It is no longer necessary to slurry oil and coal for solid pulverized coal can be fed into a very high pressure system by use of pulverized coal feeders, preferably such as described in my U.S. Pat. No. 3,762,773, issued Oct. 2, 1973.

The operating pressure for the coal hydrogenation process of this invention is between about 1000 and 10,000 psi, but with hydrogenation catalysts now commercially available pressures between about 1000 and 5000 psi are usually satisfactory.

The temperatures required for hydrogenation of coal to oil and gas cover a range from approximately 750° to 1500°F, depending on pressure, time, catalyst, type of coal, and products desired. The effect of various factors has been described in my aforementioned U.S. Pat. Nos. 3,030,297 and 3,152,063. At temperatures from about 750° to about 1050°F the products are largely liquid with relatively small amounts of gas. From 1000°F to 1300°F gas production increases and liquid decreases. The liquid that is produced at this temperature range is aromatic in nature. Above 1300°F the hydrocarbon products are largely gas and any liquids are essentially completely aromatic. The preferred temperature for producing liquid products for refining into gasoline and light oil fractions is in the range of about 800° to 1000°F.

At the lower temperatures, e.g. below 1000°F, it is important that a hydrogenation catalyst be present. These are usually compounds of heavy metals in the form of oxides or sulfides. These catalysts are well known to those skilled in the art and need no detailed description herein. They may, for example, comprise compounds of cobalt, molybdenum, iron, tin, nickel, other Th and mixtures thereof. The catalysts may be sprayed on the coal in a water soluble solution, or be present in the form of a fixed or fluidized bed. Where the catalyst is directly sprayed on the coal it may be applied in an amount of about 0.1 to 1% by weight of metal based on the weight of the coal.

DETAILED DESCRIPTION

This invention is illustrated in the accompanying drawing, wherein:

FIG. 1 is a part of a flow diagram of an improved coal liquefaction process embodying the principles of the invention.

FIG. 2 is the remainder of the flow diagram showing, in particular, the means for providing the hot gaseous stream for contacting the coal.

Referring to the flow diagram of the FIGS., the coal flows through line 1 into pressurized coal feeders 2 and 3. A preferred type of feeder is one which feeds pulverized coal at the full pressure of the system without loss of pressurized gas and without recovery steps that involve mechanically compressing dirty gas that may contain coal particles. Such a feeder is disclosed in my aforementioned U.S. Pat. No. 3,762,773. After the coal is in the feeder 2 and the feeder is closed, it is then pressurized by opening valve 4, which allows gas to flow through line 5 to equalize the pressure between the feeder and the hydrogenation system. Feeders 2 and 3 may be used alternately by proper manipulation of the valves and controls.

Coal for the hydrogenation process flows, for example, from feeder 2 through line 6, valve 7 and line 8 into line 9 at the bottom of reactor 10. The rate of flow is controlled by a screw or vibratory feeder 11, or other suitable means.
A portion of the H₂ for hydrogenation is generated and coal is converted to hydrocarbon liquids and gases in reactor 10. This is a steel vessel capable of operating at the desired pressures and temperatures e.g., at a selected set of pressure and temperature conditions between about 1000 to 10,000 psi and about 750°F to 1500°F. Gas at high temperature containing hydrogen, carbon monoxide and steam enters reactor 10 through line 9 at the bottom of the reactor. The method for producing the hydrogen entering through line 9 will be described hereafter. At the temperatures and pressures involved (preferably in the presence of a catalyst) the coal structure disintegrates and the hydrogen present and produced in situ reacts with the resulting fragments to produce smaller molecules which are hydrocarbon liquids and gases. At the same time, the oxygen in the coal reacts with C or hydrogen to produce CO₂ or H₂O, the sulfur and nitrogen react with hydrogen to form H₂S and NH₃, respectively. These compounds (CO₂, H₂O, H₂S and NH₃) are all gaseous materials under the conditions in the reactor.

A substantial amount of CO₂ is formed in the reaction zone in reactor 10, which reduces the partial pressure of hydrogen. Lime (CaO) or other suitable solid alkaline material can be used to react with the CO₂ as follows: CaO + CO₂ \to CaCO₃. This will remove the CO₂ from the gas phase and increase the hydrogen partial pressure. Removal of the CO₂ also promotes the formation of additional H₂ from CO, as follows: CO + H₂O \to CO₂ + H₂. As the CO₂ is removed from the gas the reaction moves to the right. Pulverized lime may be fed with the coal into the pressurized coal feeders 2 and 3 by means not shown.

It has been noted that a catalyst is desired to promote the reaction between hydrogen and coal in vessel 10 at the lower temperatures. The catalyst e.g., molybdenum, may be applied by converting it to a water soluble compound such as ammonium molybdate, and spraying this solution on the coal in suitable known concentrations by well-known means not shown in the flow diagram. The catalyst may also be used in the form of pellets of such size that they form a fluidized or ebullating bed in reactor 10. In this case the pellets should be large enough so that they are not carried out of reactor 10 by the rising gas stream. Alternatively, a fixed bed of catalyst material may be placed in reactor 10.

With the fixed bed or ebullating bed, little catalyst is lost during operation. With catalyst sprayed on the coal it is carried out of the reactor and appears mainly in the coal ash. If appreciable concentrations of expensive catalysts are used it may be desirable to recover the catalyst from the ash. Again, means for doing this are known and are not shown in the flow diagram.

If the catalyst is sprayed on the coal, gas coming through line 9 may enter the reactor 10 at the bottom as shown, or it may enter at the top (not shown). Coal may be put in at the top, or it may enter at the bottom with the gas stream as shown. The coal may be entrained in the stream stream or it may be present as a fluidized bed in the reaction zone. The outlet line 12 leaving reactor 10 will be at the opposite end of the reactor from the point of gas entry.

Where the catalyst is present as a bed of fluidized pellets in the reaction zone, the gas must enter at the bottom. Coal may enter at the top or with the gas stream at the bottom. Outlet 12 leaving reactor 10 will then be near the top as shown.

For a fixed bed catalyst the gas and/or the coal may enter at the top or bottom of the reactor with the exit gases, liquids and solids leaving from the opposite end of the reactor.

Gases, oil and solids leave reactor 10 through line 12 and enter heat exchanger 14, where the temperature is reduced to about 400°F by indirect heat exchange with water and solids and some heavy tars separate out. This material is discharged through line 15 and is pumped by means of pump 16 into tar reactor 17 where it is hydrogenated by contact with hot steam and hydrogen containing gases entering through line 18. Alternate methods of separating and hydrogenating the tar within the closed cyclic system can be used.

The temperature of the steam and hydrogen containing gases in lines 9 and 18 may be, for example about 1300°F. This is usually sufficient to maintain a hydrogenation temperature of about 875°F in reactors 10 and 17.

The effluent from the tar reactor 17 leaves the reactor through line 19 and enters cyclone separator 20 where solids are separated from the oils and gases. The solids are removed through pressure reduction device 21 and line 22.

Gases and oils leave cyclone separator 20 through line 23 and join the product in stream 24 from heat exchanger 14. The combined streams in line 25 enter heat exchanger 26 where further cooling by indirect heat exchange with water reduces the temperature to about 100°F. The oils are taken from this heat exchanger through line 27 and pressure reduction device 28 and enter oil-gas separator 29. Oils go to refining through line 30. Recovered gases, which were dissolved in the oil, are recycled to the hydrogenation system through line 31 and compressor 32. These gases are primarily hydrogen and methane.

The gases from heat exchanger 26, which comprise hydrogen, methane, carbon monoxide, carbon dioxide, hydrogen sulfide and ammonia, pass through line 33 at system pressure into water wash tower 34. The water is in direct contact with the gases in tower 34. At these high pressures (above about 1000 psi) the water will remove H₂S from the gas to below 0.1 volume percent and will remove most of the CO₂. The gas leaving through line 35 is primarily H₂ with small amounts of CH₄ and CO. Typically, the hydrogen concentration will be above about 70% and the methane concentration will be from about 5 to 15%.

The gases in line 35 may be partially vented through line 35a to other uses as desired. This will prevent build-up of inert gases in the recycle stream and serve to control the volume of recycle gas. Wash water leaving through line 36 goes through pressure reducer 37 and line 38 to gas stripper 39. The gases leaving the stripper through line 40 are H₂S and CO₂. These are treated in a Claus plant 41 to convert the H₂S to solid or liquid sulfur. The CO₂ is vented. The degassed water leaves stripper 39 through line 42 and may be recycled, after cooling and filtering, to the wash tower 34.

It has been noted that the gases leaving water tower 34 through line 35 are largely H₂ with some CH₄ and CO. It is most important to note that while this gas has been cooled it is still at almost full system pressure. It is estimated that the pressure drop through the apparatus elements 10, 17, 20, 26, 14 and 34 is less than 150 psi.
Gas from line 35 is returned to the system through recycle compressor 43 where the initial operating pressure is restored. Relatively little energy is required for this operation.

The gases from the recycle compressor 43 through line 44 and a small amount then flows through line 5 to maintain pressure in the coal feeders 2 and 3.

Referring now to FIG. 2, the remainder of the recycle gas from line 44 may be passed through line 45 and valve 46 to join the recycle gases from compressor 32. The combined recycle gases are passed through line 47 into heat exchanger 48 where they are heated to a temperature of from about 800°F - 900°F. The hot recycle gases then pass through line 49 into reformer 50.

This is a refractory lined, water jacketed vessel operating at a temperature above about 1800°F, and preferably near 2600°F, in which the gas is required to pass with oxygen coming through line 51 and superheated steam (at a maximum temperature of about 1200°F) coming through line 52. It is important that the amount of steam in the reformer 50 be in excess of that required to produce CO and H2 from all the carbon or hydrocarbon materials in the gasification zone. At least twice the stoichiometric amount of steam required for hydrogen make-up in the closed cyclic system is introduced at this point. Coal for supplying heat and make-up hydrogen may be introduced into the reformer 50 through line 53 from a pressurized feeder such as those shown at 2 and 3.

In the gas reformer the equilibrium for the reactions:

1. \( C + H_2O \rightarrow CO + H_2 \)
2. \( 2C + H_2O + 1/2O_2 \rightarrow 2CO + H_2 \)
3. \( C + CO_2 \rightarrow 2CO \)
4. \( 2CH_4 + H_2O + 1/2O_2 \rightarrow 2CO + 5H_2 \)

is strongly to the right (favors the existence of CO and H2) the higher the temperature. Reactions 2 and 4 are exothermic and reactions 1 and 3 are endothermic. The added reactants are balanced to reach the equilibrium and to provide a temperature about 1800°F. Therefore, the CO and H2 are the recycle gases not consumed by the oxygen; instead, the reaction is largely between CH4 (and any other hydrocarbons), CO2 and steam, to give more CO and H2. No catalyst is required in the reformer at these high temperatures.

The high temperature gases, containing H2 and CO and including the excess steam, leave gas reformer 50 through line 54 and enter the heat exchanger 48. The gases at this point may have a temperature of about 2200°F. In the heat exchanger 48 the temperature of the gases is reduced to that which is just sufficient to maintain the necessary hydrogenation temperature in reactor 10. For example, the steam and hydrogen containing gases in line 55 which supplies lines 9 and 18 respectively, may be about 1300°F. A portion of the recycle gases from line 44 may be introduced into the gases in line 54 through line 56 and valve 57, provided the amount of methane in the gases to be introduced into the reactor 10 is below about 10%. This is a further means for control of temperature and gaseous components in the stream to the reactor 10.

In reactor 10, the large amount of coal present reacts with any remaining high-temperature steam to give H2 and CO or CO2. This is a strongly exothermic reaction which lowers the temperature of the incoming gases rapidly. The coal flow and the temperature and flow of gases into the reactor must be so adjusted that the temperature in the reaction zone in reactor 10 is above 750°F, for example, between 800° and 1000°F. Under these conditions, in addition to the H2 entering through line 9, hydrogen will be formed by the reaction of coal with steam and the reaction of CO with steam. The reactions taking place in the reformer 50 and in reactor 10 generate the hydrogen needed for hydrogenation of the coal. It is to be noted that there is always a large volume of excess hydrogen circulating in the closed high pressure system.

It is also important to note that some of the reactions generating hydrogen are occurring at the coal-gas interface in vessel 10 and that elemental or nascent hydrogen is present. Elemental hydrogen is substantially more effective than molecular hydrogen in hydrogenating the coal.

Superheated steam necessary for the system is supplied by steam boiler 58 which may burn coal as shown. This steam may readily be produced at pressures above 1000 psi and at a maximum temperature of about 1200°F as known in the art. Desirably it is supplied to the system at a temperature above 800°F. Part of the steam is supplied to line 52 and is further heated and partially reacted in reformer 50. Another part of the steam may be supplied through line 59 to supply power for oxygen plant 60. The oxygen is also delivered at system pressure.

The process of the invention may now be examined to determine the steps or items of capital cost of the conventional process which have been eliminated or reduced.

First, there is no low pressure gas separation because the gas from the process is recycled at system pressure to make hydrogen.

The coal gasifier is virtually eliminated by the generation of most of the hydrogen from very high temperature steam and recycle gases in the hydrogenation reactor and reformer.

Hydrogen compression is eliminated by feeding coal, steam, oxygen, and recycle gas at the full system pressure so that very little gas compression is needed. The production of pure hydrogen (for production of liquid hydrocarbons) is eliminated by using both H2 and CO in the hydrogenation reactor. The CO generates additional hydrogen by reacting with steam, as follows:

\[ CO + H_2O \rightarrow CO_2 + H_2 \]

This reaction is favored at temperatures between 800°-1100°F.

Hydrogen compression required about 77 percent of the total power used in the former commercial processes. Since hydrogen compression is eliminated in the present process, the power plant is reduced to about 1/5 of its former size.

Utilities and general facilities are reduced since fewer and simpler process steps are required, and are estimated at about half their former size.

The process will require pressurized coal feeders and oxygen must be delivered to the process at high pressure. Oxygen compression may be carried out while the oxygen is in the form of a liquid and the equipment will be comparatively small. The pressurized coal feeders are estimated to add 3 or 4 percent to the capital costs and oxygen compression about 1 percent. The net capital savings are estimated to amount to at least 65-75 percent.

Operating costs are also reduced. Reduction in power requirements reduces the amount of coal needed. Labor and maintenance costs are reduced by
EXAMPLE

As an example of one application of this invention, 120 tons of bituminous coal (moisture and ash free) per hour is converted to hydrocarbon products at 4000 psi and 850°F. An additional 30 tons of coal per hour is required to generate electric power and raise steam. The ultimate analysis of the coal is 5.3% H, 80.6% C, 2.0% N, 10.0% O, and 2.1% S. As received, the coal contains 8% moisture and 6.2% ash. The heating value on a moisture and ash free basis (MAF) is 29 million Btu per ton.

The coal is first washed and separated into a high and low ash fraction. The high ash fraction is used in the electric power plant and for steam raising, while the low ash fraction goes to the hydrogenation process.

The coal for hydrogenation is dried to about 3 to 4% moisture and pulverized to about 70% through 200 mesh. High pressure coal feeders supply coal continuously to the coal hydrogenation reactor. The hydrogen content of the coal in the reactor increases from 5.3% to 13 or 14%, which gives a product yield of about 528 barrels per hour of middle and light oils.

It should be noted that hydrogen requirements are greater than the difference between the hydrogen in the product (about 14%) and the hydrogen in the coal (5.3%). In addition, hydrogen must be supplied to convert the sulfur to H₂S and the nitrogen to NH₃. The oxygen in the coal is partly removed as CO₂ and the rest as H₂O.

Coal for hydrogenation is contacted by the hot gas stream from the gas reformer which contains hydrogen, carbon monoxide and steam in some excess of that required for production of the necessary hydrogen for the coal hydrogenation reaction. Total steam requirements are about 170 tons per hour. The temperature of the combined gas and steam flow from the reformer is adjusted to about 1300°F. These gases heat the coal and furnish heat to produce hydrogen from the carbon monoxide, carbon and steam. This lowers the gas and steam temperature and raises the coal temperature to about 850°F. If necessary, the temperature of the incoming gas stream may be increased or decreased to maintain this temperature in the reactor. The result of the reactions in the hydrogenator provide the hydrocarbon liquid product.

The cooling and separation of the oil from the gases follows the remainder of the flow diagram shown in FIG. 1 of the drawing. The oil is largely removed in heat exchanger 26 and oil separator 29. The oil product is ready for further refining.

Oil produced is approximately 3.5 barrels per ton of coal. Thermal efficiency of the process, is above 65 percent based on heat in the products divided by the heating value of the total MAF coal fed. (120 + 30 tons).

The steps set forth in this example are illustrative of one representative process. It is to be understood that these steps may be combined in other ways. It is not intended that the application of the various steps be limited only to the representative process set forth herein.

I claim:

1. A process for hydrogenating coal comprising: continuously circulating a stream of hydrogen-containing gases including CO and steam at coal hydrogenation pressure between about 1000 to 5000 psi through a closed cyclic system including a hydrogenation zone and an oxygen-steam reforming zone, adding coal in the substantial absence of a pasting medium under system pressure to the hydrogenation zone and hydrogenating the coal in said zone at a temperature in the range of about 750°F to 1250°F by contacting with said gases to produce liquid and gaseous hydrocarbons in the circulating stream, removing liquid hydrocarbons from the circulating stream without substantially reducing the pressure of such stream, introducing the resulting gaseous stream containing gaseous hydrocarbons and hydrogen into the reforming zone, introducing oxygen and steam at system pressure into said reforming zone for reaction with the gaseous hydrocarbon components of the gaseous stream to produce carbon monoxide and hydrogen and to raise the temperature of the gaseous stream sufficiently to bring the coal to coal hydrogenation temperature in said range, the amount of steam introduced into the reforming zone being in excess of that required for the reforming reaction, and introducing the hot gaseous stream from the reforming zone into the hydrogenation zone to complete the closed cycle, heat the coal, and provide steam, carbon monoxide and hydrogen for reaction in the hydrogenation zone.

2. The process of claim 1 wherein the hydrogenation of the coal is carried out in the presence of a hydrogenation catalyst.

3. The process of claim 1 wherein the temperature in the hydrogenation zone is maintained in the range of about 800°F to 1000°F to produce primarily liquid hydrocarbon products from the coal.

4. The process of claim 1 in which the excess steam and gases are heated in the reforming zone to a temperature in excess of about 1800°F to thereby provide heat for use in the hydrogenation zone.

5. The process of claim 1 in which steam in an amount at least twice that required for the reforming reaction is supplied to the reforming zone at a pressure above about 1000 psi and at a temperature above 800°F.

6. The process of claim 1 in which a small amount of coal at system pressure is introduced to the closed cyclic system in the reforming zone for reaction therein with steam and oxygen to produce carbon monoxide and hydrogen as well as to provide heat for raising the temperature of the gases.

7. The process of claim 1 wherein the product stream from the hydrogenation zone is cooled by indirect heat exchange to condense tars and solids, the tars and solids are introduced at system pressure into a tar reactor along with a portion of the steam, hydrogen and carbon monoxide containing gases from the reforming zone, the tars are hydrogenated to produce liquid and gaseous hydrocarbons, solids are removed from the product stream from the tar reactor without pressure reduction on this stream and the resulting product stream from the tar reactor is combined with the main product stream.

8. The process of claim 1 wherein the circulating stream of gases after removal of liquid hydrocarbons is contacted with water at system pressure to remove H₂S and CO₂ prior to introduction to the reforming zone.

9. The process of claim 1 wherein coal is added to the system through feeders pressurized by a portion of the continuously circulating hydrogen containing gases in the closed cyclic system.

10. The process of claim 1 wherein hydrogenation of the coal is carried out in the presence of lime to remove...
CO₂ from the gases produced in the hydrogenation zone.

11. A hydrogenating for hydrogenating coal comprising introducing said coal at a hydrogenation pressure of from 1000 to 5000 psi into a hydrogenation zone, contacting said coal in said zone with a hot gaseous stream containing hydrogen, steam, and carbon monoxide at a temperature sufficient to raise the temperature of the coal in the zone to about 750°F to 1250°F, hydrogenating the coal in said zone with hydrogen present in the hot gaseous stream and produced in situ in contact with the coal by steam-carbon monoxide and steam-carbon reactions to produce liquid and gaseous hydrocarbons, separating the liquid hydrocarbons from the product stream without substantial pressure reduction on the gases in such stream, washing the resulting gaseous stream with water without substantial pressure reduction to remove H₂S and CO₂, and passing at least a portion of the purified gaseous product stream at hydrogenation pressure through a reformer along with superheated steam, oxygen and additional coal also supplied at hydrogenation pressure to provide the hot gaseous stream for introduction into the hydrogenation reactor.

* * * * *
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,926,775

Inventor(s): Wilburn C. Schroeder

Dated December 16, 1975

Patent No. 3,926,775

Page 1 of 2

It is certified that error appears in the above-identified patent and that said letters Patent are hereby corrected as shown below:

IN THE ABSTRACT:

The last word, before the period (.), change "steam"

to ---stream---.

IN THE SPECIFICATION:

Column 1, line 50, change "steps" to ---step---;

line 59, change "hydrogenation" to ---hydrogen---;

line 61, change "hydrogenation" to ---hydrogen---.

Column 2, line 36, change "H₂CO" to ---H₂, CO---;

line 57, change "steam" to ---stream---.

Column 4, line 34, change "The" to ---metals---;

change second "the" to ---The---;

change "catalysts" to ---catalyst---;

line 43, change "drawing" to ---drawings---.

Column 5, line 60, after "the" insert ---gas---;

delete "strem".

Column 6, line 52, change "build-upp" to ---build-up---.
UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,926,775

Dated December 16, 1975

Inventor(s) Wilburn C. Schroeder

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 7, line 39, change "about" to ---above---;

line 40, change "is" to ---in---.

Column 11, line 3, delete first "hydrogenating" and insert ---process---;

change "hydrogenationg" to ---hydrogenating---.

Signed and Sealed this

sixth Day of April 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks