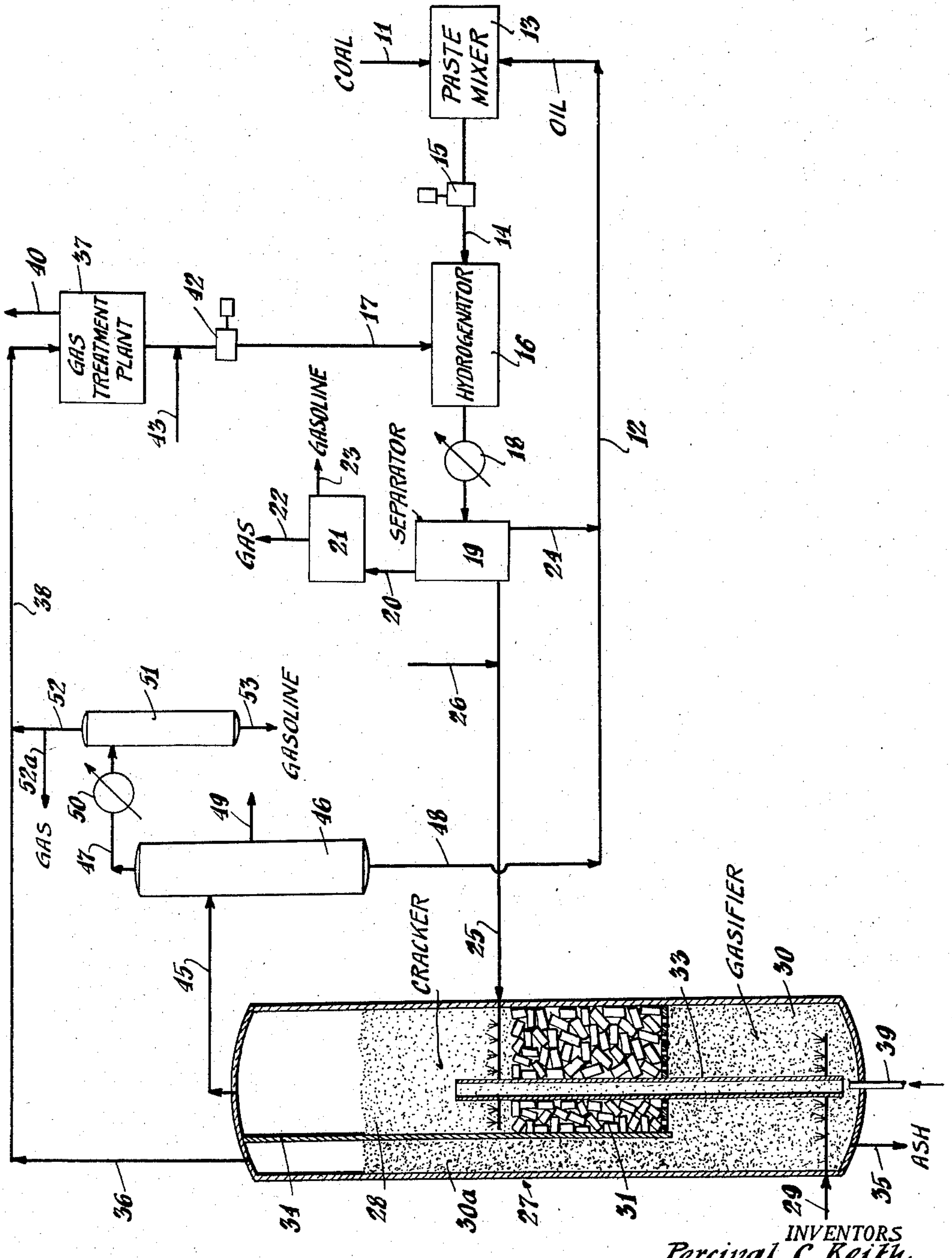
May 5, 1959

P. C. KEITH ET AL

2,885,337

COAL HYDROGENATION

Filed April 20, 1953



INVENTORS
Percival C. Keith
Friedrich Ringer
BY Paul W. Garbo
AGENT

United States Patent Office

2,885,337

Patented May 5, 1959

2,885,337

COAL HYDROGENATION

Percival C. Keith, Peapack, and Friedrich Ringer, Upper Montclair, N.J., assignors to Hydrocarbon Research, Inc., New York, N.Y., a corporation of New Jersey

Application April 20, 1953, Serial No. 349,589

10 Claims. (Cl. 208—8)

This invention relates to a process for hydrogenating coal to yield liquid products, and more particularly to a process for hydrogenating bituminous coal and for cracking the products of hydrogenation in a fluidized bed in the presence of hydrogen.

Numerous prior proposals have been made for the production of gasoline and other liquid products by hydrogenating coal. However, these proposals have been handicapped by technical complexity and high operating cost. For example, one of the difficult problems encountered in prior processes is the separation of the liquid hydrogenation products from the solid residue which remains after the coal has been hydrogenated. Another troublesome difficulty is that the last stages of coal hydrogenation proceed very slowly so that the hydrogenation apparatus has a low overall throughput when a high yield of liquid products is desired.

A principal object of this invention is to provide an improved process for recovering liquid products from coal, which comprises partial hydrogenation of the coal followed by cracking the mixture of liquid hydrogenation products and solid residue in a hydrogen atmosphere under elevated temperature and pressure conditions. Thus, by cracking the mixture of liquid products and solid residue, the problem of separating these components is greatly simplified and by using only partial hydrogenation of the coal, the throughput of the hydrogenation apparatus is materially increased, while a high yield of liquid products is still achieved with the aid of the subsequent cracking of the mixture of liquid products and solid residue in the presence of hydrogen.

Another important object is to provide a coal hydrogenation process in which the hydrogen is economically generated under elevated pressures from the carbonaceous residue formed in cracking the mixture of liquid hydrogenation products and solid residue resulting from the partial hydrogenation of coal.

Additional objects and advantages of the invention will be apparent from the description which follows.

Briefly, the invention comprises conducting the partial hydrogenation of coal while suspended in a hydrocarbon oil to convert a major portion of the carbon therein to liquid and gaseous products, and then introducing a mixture of liquid products and solid residue obtained from the partial hydrogenation of coal into a cracking zone wherein the mixture is converted at elevated temperature and pressure conditions and in the presence of hydrogen to lower-boiling products and a carbonaceous residue; the carbonaceous residue is gasified with oxygen and steam to produce the hydrogen utilized in both the cracking zone and the partial hydrogenation of coal.

More specifically, the invention comprises pasting powdered bituminous coal with an oil fraction and hydrogenating the coal paste or suspension to convert from about 60% to about 85% of the carbon content of the coal to liquid and gaseous products. In general, it is advisable to convert approximately 75% of the carbon content of the coal in this partial hydrogenation step. The conditions for hydrogenating coal while suspended in oil are well known and may be used in the partial hydrogenation step of this invention. For instance, a temperature of about 600 to 1000° F. and a pressure of about 1,000 to 12,000 p.s.i.g (pounds per square inch gauge) may be used. The reaction time is governed by the chosen conditions under which the coal hydrogenation is conducted but is limited to give the desired conversion in the range of about 60 to 85% of the carbon content of the coal. As is known, coal hydrogenation is advantageously carried out with the aid of catalysts such as iron oxide and tin compounds and such catalysts are contemplated for use in the partial coal hydrogenation step of this invention.

Desirably, a vapor product is removed from the partially hydrogenated mass, comprising unreacted hydrogen, product gases such as NH_3, H_2S, CH_4, and normally liquid lower boiling compounds. The remaining mixture of liquid hydrogenation products and solid residue is subjected to cracking in an atmosphere of hydrogen.

The cracking operation is conducted at an elevated temperature in the range of 900 to 1400° F., preferably 1200 to 1300° F., and at a pressure in the range of about 150 to 800 p.s.i.g., preferably 250 to 650 p.s.i.g. It has been found that the suppression of coke formation during cracking is achieved to a material extent when the partial pressure of hydrogen within the cracking zone is at least 35 p.s.i. and preferably in the range of about 75 to 150 p.s.i. It is curious to note that maximum benefits from the presence of hydrogen occur at hydrogen partial pressures not exceeding about 200 p.s.i. so that there is little justification in seeking a hydrogen partial pressure greater than about 200 p.s.i. As a preferred mode of operation, the cracking is carried out by injecting the mixture of liquid products and solid residue from the partial hydrogenating step into a fluidized mass of the solid residue from the coal used in the process. Where a hydrogenation catalyst like iron oxide is employed in the partial hydrogenation step, the fluidized mass in the cracking zone will also contain the hydrogenation catalyst. Other particulate solids such as bauxite may be added to the fluidized mass in the cracking zone to make the mass more easily fluidizable. With the aid of hydrogen flowing through the cracking zone, the injected hydrogenation mixture is converted to a gasiform effluent and a substantially dry carbonaceous residue. The gasiform effluent, which is readily separable from the dry carbonaceous residue, is removed for recovery of its constituents by conventional methods, such as rectification. The substantially dry carbonaceous residue in admixture with the contact material is withdrawn from the cracking zone and passed to a gasifying or regenerating zone where a regenerating gas consisting of a preponderance of steam and a minor proportion of high-purity oxygen gasifies the carbon under conditions favoring the production of hydrogen and carbon monoxide. Steam-to-oxygen molar ratios in the range of about 1.5:1 to 5:1 are generally satisfactory for maintaining the gasifying temperature in the desirable range of about 1600 to 2500° F. Steam-to-oxygen molar ratios of about 2:1 to 3:1 and gasifying temperatures of about 1700 to 2000° F. are preferred. The gasifying zone operates at substantially the same pressure maintained in the cracking zone. The high-purity oxygen may suitably be the product of air liquefaction and rectification containing at least 90% by volume of oxygen, preferably at least 95%.

Like the cracking operation, thte gasifying may be done under fluidizing conditions, the two preferably being conducted in the same vessel. The contact material circulates through the cracking and gasifying zones, and at least part of the hydrogen-containing products of the gasifying step, hereinafter termed "regeneration product gas," flows through the cracking zone. Large quantities of hydrogen are produced in the gasifying operation, and more hydrogen can be made from the carbon monoxide in the regeneration product gas and excess steam therein by the water-gas shift reaction: $CO+H_2O\rightarrow CO_2+H_2$. Thus, by suitable treatment, a stream of high-purity hydrogen may be recovered from the regeneration product gas and this recovery of hydrogen may be accomplished at substantially the pressure in the cracking and gasifying zones. The amount of hydrogen produced depends on the quantity of carbonaceous residue remaining from the cracking operation and this residue is in turn a function of the carbon conversion in the preceding step of partial hydrogenation. Large quantities of hydrogen are consumed in coal hydrogenation, but substantially all, i.e., over 80%, of the requisite hydrogen is supplied by the regeneration product gas even for a hydrogenation conversion of about 85% of the carbon content of the coal to liquid and gaseous products. A hydrogenation conversion of about 75 to 80% ultimately results in enough carbonaceous residue for the gasifying operation to allow recovery of 100% of the requisite hydrogen from the regeneration product gas.

For further clarification of the invention, reference is now made to the accompanying drawing which schematically illustrates an arrangement of apparatus suitable for carrying out the process of this invention.

Coal from a feed **11**, a pasting hydrocarbon oil from line **12** and a catalyst if desired enter mixer **13** wherein they are intermixed to form a paste which flows through line **14**. A pump **15** pressurizes the paste to the operating pressure of the partial hydrogenation step, e.g., 1000 to 12,000 p.s.i.g. Pressurized hydrogen from line **17** and paste from line **14** enter hydrogenator **16** wherein a temperature of about 600 to 1000° F. is maintained. The hydrogenation reaction per se and the equipment necessary for hydrogenation are known to the art, exemplary reference being made to the article "Liquid Fuel from Coal" in Industrial and Engineering Chemistry, May 1949 (vol. 41), pages 870 to 885. Suffice it to say that the hydrogenation reaction is carried out in hydrogenator **16** to convert between about 60 and 85% of the carbon content of the coal to liquid and gaseous products. A preferred set of hydrogenating conditions is approximately 10,000 p.s.i.g., 875° F. and 75% conversion.

The hydrogenated paste is removed from hydrogenator **16**, optionally cooled in heat exchanger **18** and passed to separator **19**. Unreacted hydrogen, H_2S, NH_3, water vapor, hydrocarbon gases and low boiling normally liquid organic compounds are removed in vapor phase through line **20**. The normally liquid components of the vapor are condensed out in stripper unit **21** for recovery of gas and liquid products which are withdrawn through lines **22** and **23**, respectively. If desired, a hydrogen-containing gas may be separated and recycled from unit **21** to hydrogenator **16**. The temperature at which vapors are separated from the hydrogenated paste may vary widely. In general, a separation temperature in the range of about 400 to 600° F. is preferred. Separation at below 400° F. will retain more of the lower boiling liquid products in the hydrogenated paste, advantageously increasing its fluidity but also increasing the volume of material which must subsequently pass through the cracking zone. Separation at above 600° F. will remove substantially all lower boiling liquid products from the hydrogenated paste as well as some of the higher boiling liquid products which should advantageously be converted to lower boiling products in the subsequent cracking step.

After the vapors are separated from the hydrogenated paste, the remaining mixture of liquid hydrogenation products and solid residue is charged through line **25** to the cracking zone **28** of vessel **27**. A transport gas or oil may be added from line **26** to facilitate the injection of the residual paste into zone **28**. Vessel **27** contains a fluidized bed of finely divided contact material which circulates from freely fluidized cracking zone **28** down through a thermal barrier **31**, which suitably may be a section packed with Raschig rings or the like, into freely fluidized gasifying zone **30**. A transport gas, such as steam, from line **39** carries contact material through upflow tube **33** back into cracking zone **28**. The mixture of liquid hydrogenation products and solid residue entering cracking zone **28** is converted therein to vapors and a substantially dry carbonaceous residue at a temperature in the range of about 900 to 1400° F., preferably 1200 to 1300° F., and in the presence of hydrogen-containing regeneration product gas. The carbonaceous residue becomes part of the fluidized bed of contact material passing down through thermal barrier **31** into gasifying zone **30** where it is gasified at a temperature in the range of 1600 to 2500° F. by oxygen and steam introduced near the bottom of zone **30** from line **29**. Ash having a carbon content of a few percent by weight or less is withdrawn through line **35** at a rate which maintains a substantially constant solids inventory in vessel **27**. The regeneration product gas consisting predominanely of hydrogen, carbon monoxide and excess steam fluidizes the contact material while passing up from zone **30** through thermal barrier **31** and cracking zone **28**, thus providing at the same time the desired hydrogen-containing atmosphere in cracking zone **28**. Regeneration product gas and the gasiform products of cracking are withdrawn overhead from cracking zone **28** through line **45** and passed into fractionating tower **46**. Tower **46** may be operated to pass overhead through line **47** all gases and liquid products, including gasoline hydrocarbons, boiling up to 400° F. Higher boiling liquids such as diesel oil may be withdrawn by way of line **49** while a heavy bottoms fraction discharged through line **48** is desirably recycled through line **12** to mixer **13** as pasting oil.

Advantageously, the pasting oil requirements are made up by taking all the bottoms fraction from tower **46** and supplementing it with sufficient oil drawn from separator **19** by line **24** to provide the necessary balance. It is to be understood, however, that an extraneous pasting hydrocarbon oil may be substituted for either or both of these products of the process. When oil is drawn from separator **19** through line **24**, it is preferable to decrease the content of solids suspended therein by settling, centrifuging or like operation; obviously, the portion of oil flowing through line **25** to cracking zone **28** will then have a higher concentration of solids.

The gases and low boiling products removed from tower **46** through line **47** are cooled in heat exchanger **50** and passed into separator **51** from which the condensed liquid products rich in gasoline hydrocarbons are removed through line **53** and the gases through line **52**. These gases may be passed through line **38** into gas treatment plant **37** where such components as H_2S, NH_3, CO_2 and CH_4 are separated to leave a residual gas comprising essentially hydrogen and carbon monoxide. By the water-gas shift reaction, the carbon monoxide of the residual gas may be converted to additional hydrogen and carbon dioxide which may be readily eliminated to yield high-purity hydrogen, i.e., at least about 90% by volume of hydrogen.

A desirable expedient which allows a more facile recovery of high-purity hydrogen involves removing a side stream of regeneration product gas from gasifying zone **30** without becoming admixed with the cracked products in zone **28**. A partition or barrier **34** is placed in the upper portion of vessel **27**, extending from the top of vessel **27** to a level below packed section **31**. Barrier **34** splits the upflowing regeneration product gas so that part passes into cracking zone **28** to be removed with the products of cracking, while the rest simply passes up through zone **30***a* and discharges through line **36**, substantially undiluted with hydrocarbons. This side stream of regeneration product gas can be passed through line **38** into gas treatment plant **37**. Taking off a side stream through line **36** advantageously reduces the load on the effluent recovery system comprising tower **46** and separator **51**. Moreover, the treatment of side stream **36** to produce high-purity hydrogen is simpler than the treatment of the gas from line **52** because regeneration product gas contains substantially only H_2, CO, CO_2 and H_2O.

In any event, hydrogen of over about 90% by volume purity and at substantially the elevated pressure of the cracking operation is recovered from gas treatment plant **37**. This hydrogen is further pressurized by compressor **42** and fed by line **17** to hydrogenator **16**. Additional hydrogen, for instance, the hydrogen-containing gas in line **22**, may be added by way of line **43**, with or without any intervening treatment of the gas. While the gas from line **22** may be separately treated, it may be added to the gas in line **38** and passed through treatment plant **37**.

Gaseous products of the process may be withdrawn through line **52***a* and/or recovered as a by-product stream **40** from gas treatment plant **37**, as well as from line **22**. From these gas streams, an LPG (liquefied petroleum gas) product may be obtained. The gases also contain quantities of H_2S, NH_3 and CO_2 which may be removed to leave a valuable fuel gas of high heating value.

The primary liquid product of the process comprises gasoline hydrocarbons (boiling up to 400° F.). A minor portion of this gasoline is produced in the hydrogenation operation and removed from stripper **21** through line **23**. The major portion of the gasoline is produced in cracking zone **28**, recovered in separator **51** and removed through line **53**.

In a typical operation of the process, in which all quantities of materials are given on an hourly basis, 100 tons of coal having 40% by weight of volatile matter and 5% by weight of ash on a moisture-free basis is pasted with 150 tons of hydrocarbon oil in mixer **13**. The oil is made up of 26 tons of bottom fraction (line **48**) and 124 tons of recycle oil (line **24**). An additional 30 tons of solids contained in the recycle oil are returned to mixer **13**. The paste is hydrogenated at 10,000 p.s.i.g. and 875° F. and with a residence time of 30 minutes. The hydrogen gas input is 2.25 $\bar{M}$ s.c.f. (million standard cubic feet) of 91% by volume purity. Approximately 75% of the carbon in the coal is converted to liquid and gaseous hydrogenation products.

The hydrogenated paste is cooled to 500° F. and allowed to settle in separator **19**, vapors and gases being removed overhead through line **20**. The settled paste is split into the recycle stream of 124 tons of pasting oil containing 30 tons of solids and a thicker stream of 75 tons of liquid hydrogenation products containing 29 tons of solids. The gasiform effluent leaving separator **19** by way of line **20** is cooled and separated into:

6.4 tons gasoline (not including C_3 hydrocarbons)
4.0 tons H_2S and NH_3
10.0 tons water

After condensation of liquid products and removal of H_2S and NH_3, there remains 0.88 $\bar{M}$ s.c.f. of gas having the following composition (on volume basis):

	Percent
H_2	60
CO	10
CO_2	2
CH_4	19
C_2 hydrocarbons	5
C_3 hydrocarbons	4

The hydrogen actually consumed in the hydrogenation amounts to about 1.5 $\bar{M}$ s.c.f.

The thicker stream (line **25**) of hydrogenated paste totaling 104 tons of liquid and solids is fed into cracking zone **28** along with 0.23 $\bar{M}$ s.c.f. of transport gas. Vessel **27** operates at a pressure of 400 p.s.i.g. and with a temperature of 1200° F. in cracking zone **28**. Gasifying zone **30** is supplied with 46.5 tons of oxygen and 52 tons of steam suitably preheated. The temperature in gasifying zone **30** is about 1750° F.

The fluidized mass in vessel **27** is the finely divided ash of the coal undergoing treatment. About 5 tons of this ash is withdrawn through line **35** from gasifying zone **30** where the carbon content of the ash does not exceed about 1% by weight.

A hydrogen-rich (32% by volume of hydrogen) side stream of 3.88 $\bar{M}$ s.c.f. of regeneration product gas is removed through line **36** and scrubbed to remove steam and carbon dioxide. The previously mentioned transport gas (0.23 $\bar{M}$ s.c.f.) is taken from this scrubbed gas stream and the rest is shifted in the presence of added steam to convert its carbon monoxide content to additional hydrogen and carbon dioxide. After a further condensing and scrubbing operation, the shifted gas has 91% by volume of hydrogen and is compressed and fed to hydrogenator **16**.

The total gasiform effluent removed from cracking zone **28** through line **45** is separated into about 0.80 $\bar{M}$ s.c.f. (dry basis) of gas, 23.3 tons of gasoline (91–93 CFRR clear octane number) and 26 tons of hydrocarbons boiling above 400° F. All of the hydrocarbons boiling above 400° F. are recycled to hydrogenator **16** as pasting oil. The approximate composition of the gas product in $\bar{M}$ s.c.f. is:

H_2	0.21
CO	0.18
CO_2	0.06
CH_4	.18
C_2H_4	.06
C_2H_6	.04
C_3H_6	.04
C_3H_8	.01

and minor quantities of N_2, NH_3 and H_2S.

By depropanizing the gases leaving separator **51** and stripper **21**, an LPG product amounting to 4.3 tons is obtained. A total of 29.7 tons of gasoline is recovered from 100 tons of coal containing 5 tons of ash.

Various modifications of the invention will occur to those skilled in the art upon consideration of the disclosure herein. For instance, while in most cases the ash of the coal and the hydrogenation catalyst, if any is used, will suffice as the contact material maintained in a fluidized state in vessel **27**, extraneous materials like bauxite, alumina, and quartz may be used. Such extraneous contact material may be introduced with the fluid flowing through line **26** at a rate to compensate for the quantity removed from vessel **27** in admixture with the ash discharging by way of line **35**. Accordingly, in view of the modifications which may be made without departing from the spirit or scope of the invention, only such limitations should be imposed as are indicated by the appended claims.

What is claimed is:

1. In the hydrogenation of coal involving the treatment with hydrogen of said coal in powdered form while suspending in a hydrocarbon oil, the improvement which comprises terminating said treatment when a major portion not exceeding about 85% of the carbon content of said coal has been converted to liquid and gaseous hydrogenation products, subjecting a mixture of liquid hydrogenation products and solid residue resulting from said treatment to vapor-phase cracking by injecting said mixture into a fluidized mass of contact material maintained in the presence of hydrogen at elevated temperature and pressure whereby said mixture is converted to a substantially dry carbonaceous residue and a gasiform stream rich in gasoline hydrocarbons, and separating said gasi-

form stream from said dry residue by withdrawing said gasiform stream from the top of said fluidized mass.

2. In the hydrogenation of coal involving the treatment with hydrogen of said coal in powdered form while suspended in a hydrocarbon oil, the improvement which comprises subjecting a mixture of liquid hydrogenation products and solid residue resulting from said treatment to vapor-phase cracking by injecting said mixture into a fluidized mass of contact material maintained in the presence of hydrogen at elevated temperature whereby said mixture is converted to a gasiform effluent and a substantially dry carbonaceous residue, separating said gasiform effluent from said carbonaceous residue by withdrawing said gasiform effluent from the top of said fluidized mass, gasifying said carbonaceous residue with steam and oxygen to produce a hydrogen-rich gas, and supplying from said hydrogen-rich gas substantially all the hydrogen required in said treatment and in said vapor phase cracking.

3. A process for treating coal which comprises hydrogenating a mixture of hydrocarbon oil and coal at an elevated pressure and temperature until about 60 to 85% of the carbon content of said coal has been converted to liquid and gaseous hydrogenation products, converting the mixture of liquid hydrogenation products and solid residue resulting from the hydrogenation to gasiform products and substantially dry carbonaceous residue by injecting said mixture into a fluidized mass of contact material in a vapor-phase cracking zone at an elevated temperature and pressure and in the presence of hydrogen-containing gas exerting a hydrogen partial pressure of at least 35 p.s.i. in said cracking zone, gasifying said dry residue with steam and oxygen at a temperature of 1600 to 2500° F. to form said hydrogen-containing gas, separating said gasiform products in admixture with said hydrogen-containing gas from said dry residue by withdrawing the admixture from the top of said fluidized mass, separating high-purity hydrogen from the withdrawn admixture, and feeding said high-purity hydrogen to said hydrogenation.

4. The process of claim 3 in which a portion of the liquid hydrogenation products is mixed with coal and recycled to said hydrogenation.

5. The process of claim 4 in which said portion of the liquid hydrogenation products is supplemented with high boiling hydrocarbons recovered from the admixture withdrawn from the cracking zone.

6. The process of claim 3 in which the fluidized mass of contact material comprising said dry residue is maintained in circulation through said cracking zone and a lower zone wherein said dry residue is gasified, and hydrogen-containing gas formed in said lower zone discharges into said cracking zone.

7. The process of claim 3 in which hydrogen is recovered from the liquid and gaseous hydrogenation products and recycled to said hydrogenation.

8. A coal treating process comprising the steps of admixing coal with hydrocarbon oil to form a paste, hydrogenating said paste at a pressure in excess of 1000 p.s.i.g. and at a temperature in excess of 600° F. until about 60 to 85% of the carbon content of said coal is converted to liquid and gaseous hydrogenation products, removing from the hydrogenated paste a vapor phase of unreacted hydrogen and products of hydrogenation boiling below about 400° F., injecting the residual paste into the upper portion of a fluidized mass of contact material maintained at a pressure in excess of 200 p.s.i.g. and at a temperature of about 900 to 1300° F. thereby converting said residual paste to gasiform products rich in gasoline hydrocarbons and a substantially dry carbonaceous residue, gasifying said dry residue with oxygen and steam in the lower portion of said fluidized mass to produce hydrogen-containing gas, said hydrogen-containing gas exerting a hydrogen partial pressure of at least about 75 p.s.i. in said fluidized mass, withdrawing from the top of said fluidized mass said gasiform products in admixture with said hydrogen-containing gas, recovering high-purity hydrogen directly from the gasification of said dry residue, and utilizing said high-purity hydrogen in hydrogenating said paste.

9. The process of claim 8 in which said dry residue is gasified with steam and oxygen of at least 90% by volume purity supplied in a steam-to-oxygen molar ratio in the range of about 1.5:1 to 5:1.

10. The process of claim 8 in which said hydrocarbon oil is obtained in part from said liquid hydrogenation products and in part from said gasiform products.

References Cited in the file of this patent

UNITED STATES PATENTS

1,984,596	Pier et al.	Dec. 18, 1934
2,450,753	Guyer	Oct. 5, 1948
2,634,286	Elliott et al.	Apr. 7, 1953
2,658,861	Pevere et al.	Nov. 10, 1953
2,738,311	Frese et al.	Mar. 13, 1956
2,756,194	Mayland	July 24, 1956