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PRODUCTION OF HYDROCARBON SYNTHESIS GAS FROM COAL

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1

The invention herein described and claimed may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of royalties thereon or therefor.

This invention relates to the production of synthesis gas and more particularly to the production of a low-sulfur content mixture of carbon monoxide and hydrogen by gasifying the finely-divided low-sulfur content char obtained as a byproduct of the direct hydrogenation of coal in the dry fluidized state.

In copending application Serial No. 120,584 filed October 10, 1949, on the Hydrogenation of Coal by Clark, Pelipetz, and Storch, a process is described for the hydrogenation of coal in the dry state by passing a stream of heated hydrogen-containing gas upwardly through a reaction zone containing a mass of substantially dry coal particles at a velocity sufficient to fluidize the mass. The reaction zone is maintained under an elevated temperature and pressure and the hydrogen reacts with the coal to produce gaseous and liquid products which are volatilized at reaction temperatures and carried out of the reactor as overhead products. There is no accumulation of liquid products in the reaction zone since all of the liquid products of the reaction, including the ordinarily non-distillable asphaltic products, are carried out of the reactor. Substantially the only product of the reaction not carried out of the reaction zone as an overhead product is a dry, solid, finely-divided char which apparently is the result of partial reaction of the coal with hydrogen. This char is formed in substantial amounts during the course of the reaction and remains suspended in the upwardly flowing stream of hydrogen-containing gas until it is removed from the reaction zone.

It has now been found that this char may be obtained from the hydrogenation reaction zone in a condition which renders it eminently suited for the production of a low-sulfur content synthesis gas (mixture of hydrogen and carbon monoxide) particularly when the char is utilized immediately after withdrawal from the hydrogenation zone. It has been found that the byproduct char may contain as little as 10 percent of the sulfur of the original coal and that the hydrogen-carbon monoxide mixture produced by gasification of this char with steam according to the usual water gas process contains a correspondingly small amount of sulfur compounds. It has further been found that by operating the gasification unit directly in conjunction with the coal hydrogenation unit, so that the char withdrawn from the hydrogenation zone is passed

2

directly into the gasification zone, all the special properties possessed by the char as it leaves the hydrogenation zone are taken advantage of, and substantial savings in energy and operational costs are achieved. As will appear more in detail from the subsequent description, the char may be continuously withdrawn from the hydrogenation zone under pressure and in a dry, finely-divided, fluent condition, by virtue of which it may be easily passed directly to a gasification zone without any appreciable loss of the substantial quantities of heat and pressure energy which is gained by the char in the hydrogenation zone.

The low-sulfur content synthesis gas produced by gasification of this low-sulfur content char will find one of its most advantageous uses in processes such as the Fischer-Tropsch which employ catalysts which are sensitive to poisoning by sulfur compounds. As is well known, the iron and cobalt catalysts ordinarily used in the Fischer-Tropsch process for the hydrogenation of carbon monoxide to form liquid and gaseous hydrocarbon, are very sensitive to sulfur poisons particularly to organic sulfur compounds such as carbon oxysulfide, CS₂, mercaptans, thiophene, and other ring sulfur compounds. In the production of synthesis gas from raw coal, one of the important items of cost has been the removal of such organic sulfur compounds from the gas prior to its use in the synthesis. By means of the present invention it is possible to minimize the cost of the synthesis gas needed for such processes as the Fischer-Tropsch by utilizing the low-sulfur content char produced as a byproduct of the direct hydrogenation of coal in the dry fluidized state and particularly by operating the unit for gasifying the char in immediate conjunction with the hydrogenation unit.

It is an object of the invention to provide a process for production of a low-sulfur content mixture of carbon monoxide and hydrogen by employing the low-sulfur content residue char obtained by the direct hydrogenation of coal in the dry fluidized state.

It is a further object of the invention to provide a process for the production of a low-sulfur content synthesis gas which takes advantage of all the special properties of the residue char resulting from the direct hydrogenation of coal in the fluidized state by passing the residue char from the hydrogenation zone directly into a gasification zone, thus reducing handling costs, and avoiding losses in energy which would normally attend discharge of the char from the hydrogenation zone to atmospheric temperature and pressure.

Other objects of the invention will become

3

apparent from consideration of the description and the drawing which is to be read in connection with the description below and in which the single figure is a schematic diagram of a plant layout suitable for carrying out the process of the present invention.

Referring now to the figure, numerals 1 and 1a refer to hoppers into which essentially dry powdered coal is fed by line 2 and header 3 controlled by valves 4 and 4a. Hydrogen gas under pressure is fed to manifold 6 by compressor 7. Line 8 taking off from manifold 6 feeds compressed hydrogen through header 9 which connects at either end to standpipes 10 and 10a, respectively. Powdered coal in standpipes 10 and 10a is kept in an agitated state by compressed hydrogen entering the bottom of the standpipe through header 9. As will be explained in more detail below, each hopper 1 and 1a is used intermittently to insure continuous feed of powdered coal to the process. Line 11 taking off from manifold 6, feeds compressed hydrogen through heat exchanger 11a. Hot hydrogen leaving heater 11a is led through line 12 where it picks up a mixture of powdered coal and hydrogen flowing down standpipe 10 or 10a. The resultant mixture then flows into the bottom of reactor 13. In reactor 13, the inflowing preheated stream of hydrogen passes upwardly through a confined mass of substantially dry coal particles at a velocity sufficient to fluidize, that is to suspend but not entrain, the mass of coal particles in the stream of hydrogen. Reaction takes place between the hydrogen and the coal and the reaction products, volatile at reaction temperatures, leave the reactor by line 14. The gaseous products are led through cyclone 15 and solids are removed and returned to the reactor by line 16. Products leaving cyclone 15 are conducted by line 17 into waste heat boiler 18 where steam may be produced by utilizing the heat content of the products. Partially condensed products are then led by line 19 into separator 20 where heavy oil products, condensed in waste heat boiler 18, may be removed through line 21. Uncondensed oil and gas leave the separator 20 by line 22 and pass through cooler 23 into separator 24 via line 25. Light oil product is removed from separator 24 by line 26, while uncondensed hydrocarbon gases and hydrogen leave separator 24 via line 27 and pass into a conventional absorber stripper tower system designated by block 28. Hydrocarbon gases are led out of the stripper through line 29 while hydrogen gas containing minor quantities of impurities leaves gas separation plant 28 via line 30, and is returned to the manifold 6 by means of recirculating compressor 31.

Reactor 13 is provided with a standpipe 32. Residue char resulting from the reaction of hydrogen with the coal is carried over into standpipe 32 from the reactor 13. Char separated in cyclone 15 is returned to standpipe 32 by line 16. Char, settling in standpipe 32, flows downwardly into line 33. Line 33 is fed with steam from a source (not shown). The steam flowing in line 33 at a suitable velocity picks up the char flowing down from standpipe 32 and carries it into a water gas reactor 35. Line 34 injects steam into the bottom portion of standpipe 32 in order to strip the down flowing char of the adsorbed oil and other products, and in order to maintain the contents of the standpipe in a fluidized state.

In reactor 35, the incoming mixture of steam and char, with enough oxygen fed by line 36

4

to provide heat through combustion of the char, react to produce a mixture of carbon monoxide and hydrogen with small amounts of carbon dioxide and other impurities. Solid residue, such as ash mixed with small quantities of unreacted char is removed from water gas reactor 35 through line 35a. The gas mixture is led out of the water gas reactor by line 37 and passed to waste heat boiler 38, to cooler 39, and to separator 40. Condensed liquids, consisting mostly of water, are led out of separator 40 through line 41, while the gas mixture is led out through line 42. All or part of the gas mixture carried in line 42 may be passed to a Fischer-Tropsch reactor via line 43. In this case the mixture may be first purified by scrubbing out the carbon dioxide in scrubber 44 and removing small amounts of sulfur compounds in scrubber 45, and then passed to a gas synthesis reactor 47 by line 46 where the carbon monoxide-hydrogen mixture may be passed over suitable catalysts to produce a mixture of hydrocarbons and oxygenated organic compounds by the so-called Fischer-Tropsch process. The products of this reaction leave reactor 47 by means of line 48, are condensed in condenser 49 and separated into a gas, oil and aqueous fraction in separator 50.

Instead of using all of the water gas produced in water gas reactor 35 in a Fischer-Tropsch plant, a portion of this gas may be withdrawn from line 42 by means of line 51 and led to a water gas shift reactor 54. At a suitable point in line 51, steam may be added to the water gas mixture by means of line 57. Hydrogen and carbon dioxide leaving the water-gas shift reactor is then led to carbon dioxide scrubber 55 and the substantially pure hydrogen is then led to compressor 7 by line 56 where it is utilized to supply hydrogen for the coal hydrogenation plant.

The operation of the above schematic layout in connection with the process of the present invention will now be described in more detail. Attention is directed first to the coal hydrogenation system, wherein powdered coal is reacted with hydrogen while in a fluidized state to produce the solid, finely divided, low-sulfur content char which is later converted into synthesis (water) gas. A batch of powdered coal is fed to hopper 1 through line 2 and header 3, after which valve 4 is closed, sealing hopper 1 from the batch coal feed line 2. Valve 9a is opened and powdered coal in the hopper is kept agitated and in a fluent condition by cool compressed hydrogen fed to the bottom of standpipe 10 and flowing upwardly through the powdered coal in the standpipe and the hopper. Suitable means for insuring continuous flow of hydrogen through the powdered coal in the standpipe and hopper may be provided, such as a hydrogen bleed line at the top of the hopper which would allow a small volume of hydrogen to flow out of the hopper back into manifold 6. Valve 101 is opened and a mixture of coal and hydrogen is allowed to flow into line 12 where it joins a stream of hot compressed hydrogen from preheater 11a and is carried into the bottom of reactor 13. A venturi may be inserted at the junction of line 12 with standpipes 10 and 10a to prevent hot hydrogen from passing into the hoppers. When the coal supply in hopper 1 is exhausted, valves 9a and 101 are closed and valves 9b and 102 are opened and powdered coal is then supplied to line 12 by means of hopper 1a. The hydrogen-coal mixture passing through line 12 is heated to a temperature in the vicinity of reaction tem-

5

perature but the mixture is carried through line 12 quickly enough so that very little reaction takes place while the mixture is on its way to reactor 13. The mixture enters the bottom of reactor 13 and flows upwardly through a mass of coal particles already present in the reactor. In order to initiate the reaction, the reactor is initially charged with enough powdered coal to provide the proper bed depth when the coal is in a fluidized state.

After the reaction has begun, coal consumed in the reaction is replaced by way of line 12 at a rate selected to insure the desired coal-hydrogen contact time. The more rapidly coal is fed to the reactor, the more rapidly will solids be withdrawn through standpipe 32 due to the increased static pressure at the bottom of the standpipe. Thus, other conditions being equal, a higher rate of coal feed to the reaction zone will result in a shorter average residence time of the coal particles in the reactor and consequently a shorter coal-hydrogen contact time.

The coal supplied by way of line 12 is entrained in the stream of hydrogen flowing through this line. Due to the difference in cross-sectional area of line 12 and reactor 13, the velocity of the gas flowing in line 12 will be greater than the velocity in the reactor. When the coal-hydrogen mixture reaches the reactor, the velocity of the stream diminishes to the point where the coal will no longer be entrained. The velocity of the stream of hydrogen in the reactor is so adjusted in relation to the size of the coal particles that the coal particles are suspended but not entrained in the hydrogen stream. In other words, the velocity of the hydrogen stream is so adjusted that the coal mass becomes fluidized, that is, takes on the appearance and properties of a boiling liquid wherein the mass as a whole remains substantially stationary in the reactor but the individual particles are maintained in a state of constant turbulent motion and circulate freely throughout the body of the mass much the same way as convection currents pass through the body of a heated liquid.

The temperature of the hydrogen stream flowing into the bottom of reactor 13 through line 12 is so adjusted that the internal temperature of the fluidized bed, is maintained at a temperature most advantageously between 450° to 650° C.; and the pressure in the feed lines so adjusted that the pressure in the reactor lies in the range between 250 to 1500 pounds per square inch. Under these conditions, all of the liquid products of reaction including the ordinarily non-distillable asphaltic products are carried out of the reactor as overhead products by line 14. The solid products of reaction, mainly a solid, finely-divided char are carried over into standpipe 32 and are removed from the reactor for subsequent gasification. If desired or necessary a portion of the char may be recycled back into the hydrogenation reactor.

In carrying out the dry coal hydrogenation process which produces the finely-divided, solid low sulfur content char of the present invention, it is essential that the reacting coal be maintained in a fluidized state by a stream of hydrogen containing gas during the hydrogenation step. If hydrogenation of the coal is attempted using a stationary bed of coal or a merely expanded (as distinguished from fluidized) bed, the hydrogenation will not proceed properly and the residue will not be suitable for subsequent gasification. If the velocity of the hydrogen containing gas

6

flowing upwardly through the coal bed is less than the minimum velocity required to truly fluidize the bed, coking and agglomeration of the coal bed will soon take place. The hydrogenation reaction itself will become uncontrollable due to local over-heating and runaway reactions. In many cases the bed will become entirely plugged and at best the product yields will be greatly reduced. The coking and agglomeration that occurs in the non-fluidized bed renders the solid residue unsuitable for entrainment for subsequent gasification. The coked and agglomerated residue is caked and non-fluent and is difficult to remove from the reactor. In such a form the residue cannot be passed directly into a gasification unit without loss of the energy gained in the hydrogenation zone. Furthermore, the coked and agglomerated residue from the hydrogenation of coal employing a non-fluidized bed is not reduced in sulfur content to the extent that sulfur is removed from the char obtained employing a fluidized bed. A velocity of hydrogenating gas which merely expands and somewhat agitates the bed without rendering it truly fluid is not sufficient to avoid these difficulties.

As more fully set out in the above-mentioned application for the Hydrogenation of Coal by Clark et al., the fluidization is preferably carried out with the velocity of the hydrogenation gas slightly above the minimum required to maintain the bed in a truly fluidized state. The particle size of the coal employed may vary from 4 to 250 mesh but is preferably in the range of from 100 to 200 mesh. The hydrogenation is most advantageously operated at temperatures within the range of 450° C. to 650° C., preferably in the range of from 500° to 600° C.; and at pressures from 250 to 1500 pounds per square inch, preferably from 500 to 1000 pounds per square inch. As explained more fully in copending application Serial No. 120,584, filed October 10, 1949, on the Direct Hydrogenation of Coal, above referred to, these ranges of temperatures and pressures are most advantageous from the standpoint of obtaining good yields of oil, while keeping operating pressures to a minimum and minimizing the production of large quantities of hydrocarbon gas.

Directing attention now to the gasification portion of the system, particularly to the manner in which char is transferred from the hydrogenation zone to the gasification zone, it will be noted that hydrogenation reactor 13 is provided with standpipe 32, the top of which is submerged slightly below the surface of the fluidized bed of coal particles. Coal particles entering the bottom of the reactor, circulate in a random course throughout the reactor, and after remaining for the desired residence period are withdrawn by way of standpipe 32. As previously explained, the average residence period of coal particles in the reaction zone depends chiefly on the rate of feed of new coal to the reactor. Various precautions may be taken to insure that the solids withdrawn by way of standpipe 32 are relatively free from large quantities of unreacted or only partially reacted coal. Thus, various baffles may be inserted in the reactor, or the coal inlet may be more widely separated from the char outlet, or other well known means may be employed to secure a low concentration of unreacted coal particles at the top portion of the reactor where the standpipe opening is located.

The char, as it passes over into the standpipe, is in a dry, highly fluent condition due to the fluidized action of the hydrogenating gas. In

order to maintain the char in this fluent condition so that it may be continuously withdrawn from the hydrogenation reactor and passed into the gasification zone, a flow of steam is injected into the bottom of the standpipe by means of line 34 at a velocity sufficient to fluidize the char in the standpipe. In addition to maintaining the standpipe char in a fluidized condition, the steam flowing upwardly through the standpipe strips the char of oil and hydrocarbon gases which may be carried down with it and at the same time prevents hydrogen from leaving the reactor by way of the bottom of the standpipe.

The char being thus maintained in a highly fluent state, when valve 32a at the bottom of the standpipe is open, the char will flow down into the gasification zone which begins with feed line 33. Line 33 is fed with steam, which may be at atmospheric but is preferably under super-atmospheric pressure, flowing at a velocity (e. g. 10 to 40 feet per second) sufficient to carry the char in suspension.

The char flowing through valve 32a is under an elevated pressure due to the gas pressure (usually 250-1500 p. s. i.) under which the hydrogenation zone is maintained and due to the static pressure which the fluidized column of char in the standpipe exerts on the bottom of the standpipe. In order for the char to flow from the hydrogenation zone into the gasification zone, it is, of course, necessary that the steam pressure in the gasification zone be less than the pressure in the hydrogenation zone at the point where the char is withdrawn. Thus, the steam pressure in line 33 must be less than the total static pressure at the bottom of the standpipe 32. Most advantageously, the steam pressure in line 33, is maintained in the vicinity of the hydrogenating gas pressure in the hydrogenation reactor. When this is the case, the steam pressure in line 33 and the gas pressure in the hydrogenation reactor will substantially balance one another and the char will flow into the line 33 by virtue of the static pressure which the column of char in the standpipe exerts on the bottom of the standpipe. In this way the flow of undesirable quantities of steam into the hydrogenation reactor by way of valve 32a, or the flow of hydrogenating gas from the hydrogenation reactor into line 33 may be avoided. If the steam pressure in line 33 is substantially lower than the gas pressure in the hydrogenation reactor, valve 32a may be designed to serve as a reducing valve and any desired pressure drop across valve 32a may be created to prevent the escape of hydrogenating gas into line 33.

The char let down from standpipe 32 is entrained in a flow of high temperature steam, preferably about 2000° F. and preferably at an elevated pressure and is carried into the gasification reactor 35. The char entering the gasification zone is at elevated temperature, usually between 450° to 650° C. and substantially all the heat energy gained by the char in the hydrogenation zone may be carried over into the gasification zone without loss. Oxygen is fed into gasification reactor 35 through line 36 to provide heat for the gasification process by combustion of a portion of the char. The gasification reactor 35 may be of any desired construction and the gasification of the char may be carried out by any suitable known process which ordinarily utilizes pulverized coal. The gasification step itself is not a feature of the present invention since the gasification is carried out in known manner, but the invention

resides rather in the discovery that the low-sulfur content byproduct char from the hydrogenation of coal in the dry fluidized state may be very advantageously employed for the production of a high grade synthesis gas particularly when passed directly from the hydrogenation zone to the gasification zone.

One process suitable for gasifying the finely divided char leaving the hydrogenation reactor is the so-called Koppers dust gasification process described in an article by L. L. Newman appearing in *Industrial and Engineering Chemistry*, vol. 40, pp. 559-82 (1948). This process as applied to the present invention involves blowing a mixture of finely divided char and oxygen into both ends of a cylindrical vessel. The char-oxygen mixture is ignited as it enters the vessel and combustion of a portion of the char provides heat for reaction of the remainder of the char with high temperature steam which is blown into the vessel from annular nozzles surrounding the char-oxygen input nozzles at both ends of the vessel. A mixture of carbon monoxide and hydrogen is produced which is withdrawn from a duct at the top of the vessel. Steam is injected at temperatures from about 1800-2000° F. while the gasification temperature ranges from about 1800° to 2500° F. Usually, the upper limit of the gasification temperature is determined by the softening point of the ash content of the char.

Another suitable process for gasifying the finely-divided low sulfur content char of the present invention is the so-called Winkler process which ordinarily employs a fluidized bed of pulverized coal. This process is also described in the above article by L. L. Newman and in various U. S. patents such U. S. Patents 1,687,118 and 1,840,649. Besides these two processes, any of other known processes for gasifying a finely-divided carbonaceous material may be used operating at atmospheric or super-atmospheric pressures.

While the char leaving the hydrogenation zone may be let down and gasified with steam at atmospheric pressure, in order to take full advantage of the properties of the char as it leaves the hydrogenation reactor, it is preferable to operate the gasification unit at an elevated pressure. By operating under pressure, the water gas produced leaves the gasification zone under pressure and may be used, without further compression in such processes as the Fischer-Tropsch requiring water gas under pressures from 100 to 600 pounds per square inch. The pressure in the gasification zone is adjusted in accordance with the pressure in the hydrogenation reactor and the pressure at which it is desired to deliver the synthesis gas. For example, if the synthesis gas produced is intended for use in a Fischer-Tropsch reactor which is to be operated at 450 pounds per square inch, the steam pressure in line 33 will be adjusted so that the synthesis gas delivered from the gasification unit will be at a pressure of 450 pounds per square inch after taking into account pressure drops in the gasification system from feed line 33 to delivery line 42. If line 33 is to be in the neighborhood of 450 pounds per square inch, the gas pressure in the hydrogenation reactor must be at least as great or somewhat greater than this pressure as explained above.

Operation of the gasification unit under pressure besides giving greater outputs of water gas per unit of reactor volume results in a substantial

savings in the cost of compressing water gas after production. The only material supplied to the process which is not obtainable under pressure without compression is the relatively small amount of oxygen supplied to provide heat by combustion of char. The steam used in the process being at high temperatures may be supplied at any desired pressure without compression, and the char may be supplied directly from the hydrogenation reactor under pressure and easily injected into the gasification zone by the method, for example, outlined above. The direct let down of the char from the high pressure hydrogenation zone into the gasification zone is a solution for the otherwise difficult problem of continuously injecting solid coal into a high pressure zone. Where high pressure gasification is carried on today, the usual practice is to admit the coal by the batch from a lock hopper which is sealed from the atmosphere when open to the gasification zone. This procedure is cumbersome and expensive, however, and reduces the economic advantage gained by using high pressure gasification.

The hydrogen-carbon monoxide mixture produced by gasification of the char obtained in the fluidized hydrogenation process may be most advantageously employed in processes such as the Fischer-Tropsch where advantage is taken of its low sulfur and of the fact that it may be obtained without compression at the pressures required in the Fischer-Tropsch process. Most Fischer-Tropsch plants employing iron catalysts operate under pressures of from 300 to 600 p. s. i. Synthesis gas can easily be supplied to the Fischer-Tropsch reactor 47 at these pressures without compression since these pressures are well within the upper limit of 1500 pounds per square inch at which it is advantageous to operate the fluidized bed coal hydrogenation process. However, any other desired use may be made of the hydrogen-carbon monoxide mixture produced by gasification of the byproduct char. Thus it may be employed in the so-called methanol synthesis involving condensation of mixtures of carbon-monoxide and hydrogen in the presence of suitable catalysts to produce methanol and small amounts of higher alcohols, or it may be employed in the so-called Oxo process involving the condensation of olefins with carbon monoxide and hydrogen to produce carbonyl compounds.

If desired, a portion of the water gas produced by gasification of the char may be passed to water gas shift reactor 54 where the carbon monoxide content of the water gas is reacted with steam to produce hydrogen and carbon dioxide by the well-known water gas shift process preferably operated under pressure. The carbon dioxide can be scrubbed out of the mixture and substantially pure hydrogen delivered to com-

pressor 7 for use in the hydrogenation zone. Valves 52 and 53 may be used to control the relative amounts of water gas passed to the water gas shift system and the Fischer-Tropsch system respectively. Since high pressure water gas may be supplied from the gasification reactor to the water gas shift reactor, the hydrogen produced by the water gas shift is supplied to the hydrogenation zone under pressure with consequent saving in the cost of hydrogen compression. If desired, a portion of the hydrogen produced in the water gas shift reactor may be passed to the Fischer-Tropsch reactor to enrich with hydrogen the carbon-monoxide hydrogen mixture obtained from the gasification reactor wherein the molar ratio of carbon monoxide to hydrogen will be in the neighborhood of 1:1.

The following examples are intended to illustrate the invention.

Examples 1 to 5

Examples 1 to 5 illustrate the type of char that is obtained upon hydrogenation of a bituminous coal particularly the difference in sulfur content between the starting coal and the byproduct char and the difference in sulfur content between the synthesis gas produced by gasifying the starting coal and by gasifying the byproduct char.

The bituminous coal employed was a Rock Springs, Wyoming, coal from the D. O. Clark mine and as charged to the hydrogenation reactor had the following average composition:

Element	Percent by weight, Based on starting coal	Percent by weight, Based on moisture free coal
Hydrogen.....	5.0	5.2
Carbon.....	72.4	74.7
Nitrogen.....	1.5	1.5
Sulfur.....	0.8	0.8
Oxygen.....	11.9	12.3
Ash.....	5.3	5.5
Water.....	3.1	-----

The weight ratio of carbon to sulfur for this coal, on a moisture-free basis is 91. This coal was crushed to a particle size of from 100 to 200 mesh and then submitted to the action of a stream of hydrogen at the temperature and under the pressure listed in Table I below passing upwardly through a reactor containing a bed of this coal at a linear velocity of 0.01 foot per second. This velocity was sufficient to fluidize the coal bed. Conditions in the reactor were adjusted so that the coal was in contact with hydrogen at reaction temperatures for a reaction time equivalent to about 75 minutes. No catalyst was used. In Table I, analyses of the char obtained by hydrogenation at various temperatures and pressures are tabulated.

TABLE I

Example	Temp., ° C.	Pressure, p. s. i. g.	Total Product Analysis, Percent by Weight, Based on Starting Coal				Residue Analysis, Percent by Weight, Based on Weight of Residue						Weight Ratio of Carbon to Sulfur in Residue
			Residue, Percent	Oil, Percent	Hydro-carbon Gas, Percent	H ₂ O+CO ₂ +CO, Percent	H	C	N	S	O	Ash	
1 (42).....	600	250	55.9	16.8	12.4	15.1	2.7	84.6	1.6	0.3	1.3	9.5	282
2 (57).....	600	1,000	37.5	24.6	25.1	14.6	2.6	81.9	1.3	0.1	0.0	14.1	819
3 (39).....	500	500	61.8	17.1	7.6	14.3	3.4	83.0	1.9	0.5	2.6	8.6	166
4 (70).....	600	500	47.3	22.2	17.3	15.5	3.0	84.2	1.6	0.1	2.1	9.0	842
5 (67).....	500	1,000	56.4	20.2	10.2	14.6	3.7	83.9	1.8	0.3	2.8	7.5	279

It will be noted in the above examples that while the sulfur content of the starting coal on a moisture-free basis is about 0.8 percent, the sulfur content of the residue char on a moisture-free basis ranges from about 0.1 percent to about 0.5 percent, indicating a substantial reduction in the total amount of sulfur present in the residue char as compared to the starting coal. More significant than the total amount of sulfur in the material to be gasified is the ratio of sulfur to carbon since this ratio will indicate the percentage concentration of sulfur compounds to be expected in the gasification mixture. The higher the ratio of carbon to sulfur, the lower the concentration of sulfur in the gasification mixture. It will be noted that the weight ratio of carbon to sulfur in the starting coal on a moisture-free basis is 91 while the weight ratio of carbon to sulfur in the residue ranges from 842 to 166. In general higher temperatures and higher pressures of operation result in greater reduction in the sulfur content in the residue char. It will be noted that in Example 1 where a pressure of 250 pounds per square inch gage was employed, the reduction of sulfur is not so great as where larger pressures were employed as in Example 2. Similarly, in Examples 3 and 5, where a temperature of 500° C. was employed the reduction in the sulfur content is less than in Examples 2 and 4 where a temperature of 600° C. was employed. In all cases however, under varying conditions of operation, the amount of sulfur will be reduced to some extent. In the examples above, the lowest reduction of sulfur (Example 3) resulted in nearly doubling the weight ratio of carbon to sulfur, which increased from 91 to 166.

Using the Koppers dust gasification process described above and fully set out in the article by L. L. Newman in Ind. and Eng. Chem. above referred to, the raw coal used as a starting material in the above examples was gasified under the following conditions. A mixture of oxygen and coal (oxygen to coal ratio equals 9.23 cubic feet of oxygen per pound of coal), was injected into both ends of the cylindrical gasification reactor, while steam at 1725° F. (steam to coal ratio equals 1.1 pounds of steam per pound of coal) was in-

pounds which may be removed with comparative ease.

Examples 6 and 7

Examples 6 and 7 illustrate the type of char obtained upon hydrogenation of a lignitic coal, particularly the difference in sulfur content between the starting lignite and the by-product char and the difference in sulfur content between the synthesis gas produced by gasifying the starting lignite and by gasifying the by-product char.

The lignite employed was a Velva lignite, representative of North Dakota lignite deposits containing about 16 to 25 percent by weight of moisture. Before feeding to the hydrogenation reactor, the lignite was air dried to approximately 10 percent moisture and showed the following average composition in percent by weight:

Ingredient	Percent by Weight of Coal Actually Charged to the Reactor	Percent by Weight on a Moisture-free basis
Hydrogen.....	3.8	4.2
Carbon.....	59.2	65.6
Nitrogen.....	1.0	1.1
Sulfur.....	0.4	0.5
Oxygen.....	19.2	21.4
Ash.....	6.4	7.2
Water.....	10.0	-----

For the above lignite the weight ratio of carbon to sulfur on a moisture-free basis is equal to 131. The lignite was crushed to a particle size of from 100 to 200 mesh. A stream of purified hydrogen was passed upwardly through a reactor containing a bed of this crushed lignite at a linear velocity of 0.01 foot per second and at the temperature and pressure listed in Table II. This velocity was sufficient to maintain the lignite in a fluidized state. Conditions in the reactor were so adjusted that the coal was in contact with hydrogen at reaction temperature for a reaction time equivalent to about 75 minutes. No catalyst was used. In Table II, analyses of the char obtained by hydrogenation at various temperatures and pressures are listed.

TABLE II

Example	Temp., ° C.	Pressure, p. s. i. g.	Total Product Analysis, Percent by Weight, Based on Starting Coal				Residue Analysis, Percent by Weight, Based on Weight of Residue						Weight Ratio of Carbon to Sulfur in Residue
			Residue, Percent	Oil, Percent	Hydrocarbon Gas, Percent	H ₂ O+CO ₂ +CO, Percent	H	C	N	S	O	Ash	
6 (73).....	500	500	47.3	18.0	7.2	27.8	3.7	75.7	1.1	0.3	7.2	12.0	252
7 (84).....	500	1,000	44.4	15.9	23.0	27.8	3.7	76.8	1.2	0.3	6.0	12.0	

jected into the vessel from annular nozzles concentric with the coal-oxygen inlet nozzles. The gasification temperature was 2400° F. The hydrogen, carbon monoxide, carbon dioxide mixture obtained contained 133 grains of H₂S per 100 cubic feet of gas at 60° F. and 29.9 inches of mercury, and 14 grains of sulfur (as sulfur present in organic sulfur compounds) per 100 cubic feet of gas at 60° F. and 29.9 inches of mercury.

Gasification of the char obtained in Examples 2 and 4, under the same conditions as the raw starting coal was gasified would produce a synthesis gas containing only 18.5 grains of H₂S per 100 cubic feet of gas at 60° F. and 29.9 inches of mercury, with only traces of organic sulfur com-

In the above examples it will be noted that the sulfur content of the original lignite on a moisture-free basis was about 0.5 percent while the residue char also on a moisture-free basis was reduced to a sulfur content of about 0.3 percent. The weight ratio of the carbon to sulfur in the residue is about double the ratio of carbon to sulfur in the original lignite on a moisture-free basis. In general the amount of sulfur removed from the lignite during the fluidized hydrogenation process to produce the residue char is not as great as the amount of sulfur removed from bituminous coal. However a substantial improvement in the sulfur content of the residue char as compared to starting lignite is obtained

which greatly facilitates the problem of removal of the sulfur compounds from the water gas produced by gasification of the residue char.

Gasification of the starting lignite under the same conditions at which the Rock Springs bituminous coal was gasified in Examples 1 to 5, would produce a synthesis gas containing 85 grains of H₂S per 100 cubic feet of gas at 60° F. and 29.9 inches of mercury and 10 grains of sulfur (as sulfur present in organic sulfur compounds) per 100 cubic feet of gas at 60° F. and 29.9 inches of mercury. Gasification of the char obtained in Examples 6 and 7 under the same conditions as the starting lignite was gasified would produce a synthesis gas containing 48 grains of H₂S with only traces of organic sulfur compounds.

As used in specification and in the claims which follow, the word coal is intended to include carbonaceous material suitable for conversion into hydrocarbons by direction reaction with hydrogen. In particular, the term is intended to include such materials as bituminous and sub-bituminous coals and lignite or lignitic coals, which are particularly suitable for direct hydrogenation into hydrocarbons. Other materials such as anthracite coals and peats are not as amenable to direct hydrogenation, but these materials are also intended to be included within the meaning of the term coal when such materials are utilized in the process of the present invention.

The term dry coal as used in the specification and claims is intended to define coal in the absence of a liquid vehicle.

The above description and drawings are intended merely to illustrate the invention and it is not intended that the invention be limited thereby nor in any way except by the scope of the appended claims.

We claim:

1. An integrated continuous process for the production of liquid hydrocarbon fuels from coal as a starting material, involving substantial savings in compressional energy and in gas purification costs comprising the steps of passing a stream of hydrogen containing gas upwardly through a hydrogenation reaction zone containing a mass of coal particles at a velocity sufficient to fluidize said mass, maintaining said hydrogenation reaction zone at an elevated temperature of from 450° to 650° C. and under a pressure of from 250 to 1500 lbs. per sq. in., reacting said hydrogen with said coal to produce a major proportion of liquid hydrocarbons and a minor proportion of gaseous hydrocarbons together with a finely-divided, solid, low-sulfur content char, continuously withdrawing said char from said fluidized mass and passing said char directly into a gasification zone maintained at elevated temperature and under a pressure less than that in said hydrogenation reaction zone and ranging from 300 to 600 lbs. per sq. in., whereby said char flows from said hydrogenation reaction zone into said gasification zone by virtue of the differential pressure between said zones, reacting said char in said gasification zone with steam to produce a mixture of hydrogen and carbon monoxide at a pressure of from 300 to 600 lbs. per sq. in., said mixture being substantially free from organic sulfur and containing only small amounts of inorganic sulfur, without substantial reduction in pressure, passing said compressed low-sulfur content hydrogen-carbon monoxide mixture to a Fischer-Tropsch reaction zone, and therein act-

ing said hydrogen carbon monoxide mixture in the presence of a catalyst to produce predominantly liquid hydrocarbons, passing another portion of said compressed low sulfur content hydrogen-carbon monoxide mixture to a water gas shift reaction zone wherein the carbon monoxide content of said mixture is converted to hydrogen and carbon dioxide, scrubbing out said carbon dioxide from said hydrogen-carbon dioxide mixture, and then passing the compressed hydrogen to said hydrogenation reaction zone.

2. An integrated continuous process for the production of liquid hydrocarbon fuels from coal as a starting material, involving substantial savings in compressional energy and in gas purification costs, comprising the steps of passing a stream of hydrogen-containing gas upwardly through a hydrogenation reaction zone containing a mass of coal particles at a velocity sufficient to fluidize said mass, maintaining said hydrogenation reaction zone at a temperature of from 450° to 650° C. and under a pressure of from 250 to 1500 pounds per square inch, reacting said coal with said hydrogen to produce a major proportion of liquid hydrocarbons and a minor proportion of gaseous hydrocarbons together with a finely-divided, solid, low-sulfur content char, continuously withdrawing said char from said fluidized mass and passing said char from said hydrogenation reaction zone into a gasification zone maintained at elevated temperature and under a pressure less than that in said hydrogenation reaction zone and ranging from 300 to 600 pounds per square inch, whereby said char flows from said hydrogenation reaction zone into said gasification zone by virtue of the differential pressure between said zones, reacting said char in said gasification zone with steam to produce a mixture of hydrogen and carbon monoxide at a pressure of from 300 to 600 pounds per square inch, said mixture being substantially free from organic sulfur and containing only small amounts of inorganic sulfur, without substantial reduction in pressure, passing said compressed low-sulfur content hydrogen-carbon monoxide mixture to a Fischer-Tropsch reaction zone maintained at a pressure of from 300 to 600 pounds per square inch and therein reacting said hydrogen-carbon monoxide mixture in the presence of a catalyst to produce predominantly liquid hydrocarbons.

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