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PRODUCTION OF FUEL GAS FROM CARBONACEOUS SOLIDS

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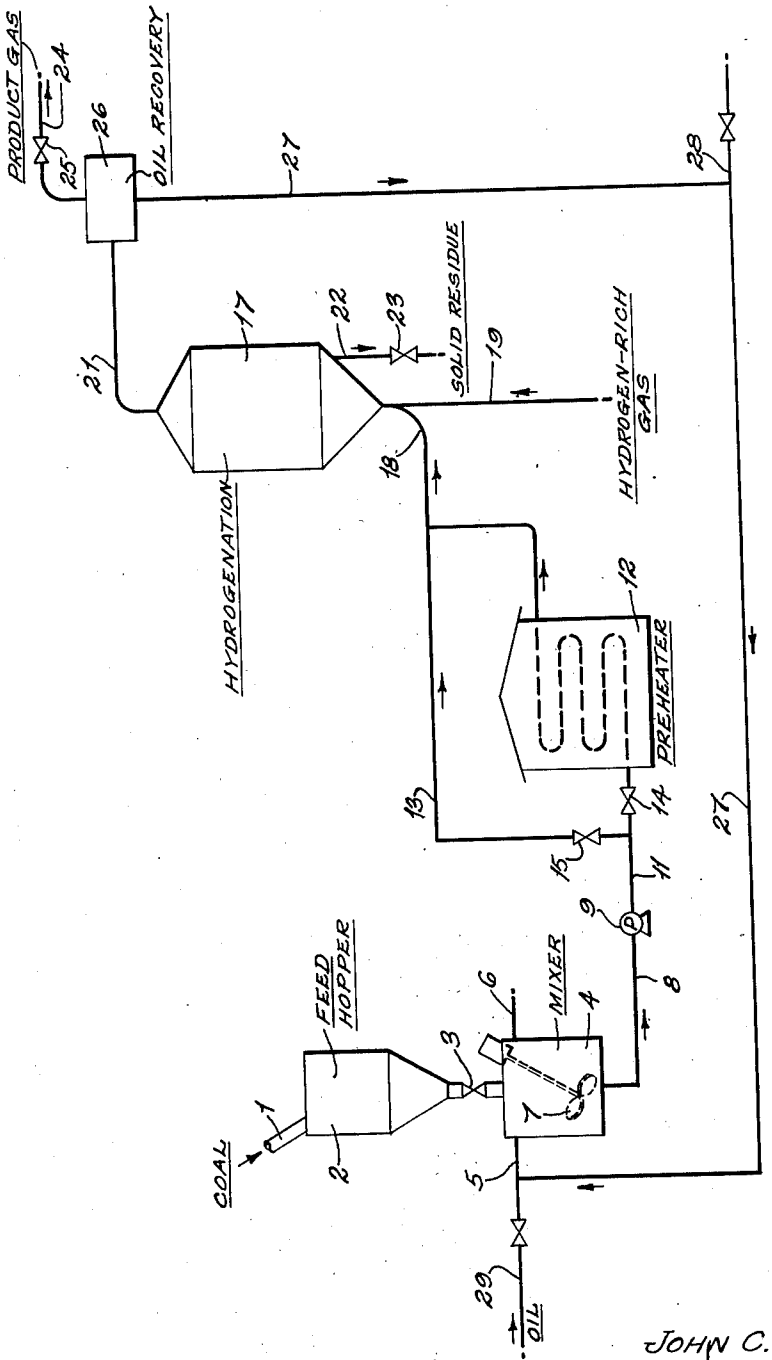

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PRODUCTION OF FUEL GAS FROM CARBONACEOUS SOLIDS

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This invention relates to a process for the generation of gas of high heating value from solid carbonaceous material. In one of its more specific aspects, it relates to the hydrogenation of coal in the presence of a hydrocarbon oil which is vaporized under reaction conditions to form a fuel gas of high heating value. An important feature of the present invention is the method of charging solid particles as a dispersion into a zone of elevated pressure.

The process of the present invention is especially useful as applied to the production of fuel gases from solid carbonaceous minerals. It is contemplated that the process will find particular application to the gasification of coal and similar fuels containing volatilizable constituents. Various grades of coal may be treated including anthracite, bituminous coals and lignite.

Waste coals, such as slack coal and the like, are suitable for use in the present process. The process is also applicable to the treatment of oil shale.

An object of this invention is to provide an improved process for the production of gas of high heating value from solid carbonaceous material.

Another object of this invention is to provide an improved process for the hydrogenation of solid carbonaceous material.

A further object is to provide an improved method for feeding solids to a fluidized hydrogenation system operating at a high pressure.

Still another object is to provide an improved method for forming a dispersion of solid particles in a vapor stream.

A further object of this invention is to provide an improved process for the treatment of coal and similar carbonaceous materials containing volatilizable constituents to produce a fuel gas of high heating value.

Other objects and advantages of this invention will be apparent from the following detailed description.

In accordance with this invention, solid carbonaceous material in particle form is admixed with a hydrocarbon oil to form a slurry. This slurry or suspension of coal in oil is pumped into a reaction zone where it is contacted with a hydrogen-rich gas under conditions of elevated temperature and pressure suitable for hydrogenation. The hydrocarbon liquid used for the preparation of the slurry is preferably derived from the solid carbonaceous material. The oil is vaporized and converted to the extent that a fluidized bed of substantially dry solids is maintained

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in the reaction zone. Vaporization of oil within the hydrogenation reaction zone is effective as a means for controlling the temperature at which the hydrogenation reaction is conducted.

In one embodiment of the invention, the slurry is passed through a heating zone under elevated pressure wherein it is preheated without substantial vaporization and the resulting preheated slurry injected into the hydrogenation zone. Unvaporized oil passing to the reaction zone is vaporized, aided by the exothermic heat of hydrogenation, and at the same time some of the oil may undergo destructive hydrogenation whereby it is converted to hydrocarbons of lower boiling point. In another embodiment of the present invention, substantially all of the oil is vaporized, forming a suspension of coal particles in oil vapor.

The hydrogenation step is carried out under fluid bed reaction conditions, the hydrogen-rich gas and hydrocarbon oil vapors serving as the fluidizing medium for the solid particles of carbonaceous material. Volatile constituents associated with the solid carbonaceous material, as well as the carbonaceous material and oil, are hydrogenated in the hydrogenation reactor. The resulting product comprises a large proportion of gaseous constituents of high heating value. Normally liquid products may be recovered from the product gas stream and part or all recycled to the process as the oil for preparation of the slurry. A solid residue or char is produced in the hydrogenation reaction which is suitable for use as a fuel, production of briquettes, production of hydrogen-containing gas, as by reaction with oxygen and steam, etc. The hydrogen for the hydrogenation reaction may be produced by gasification of the char with steam or a mixture of oxygen and steam, as is known in the art. The present process produces fuel gases of high heating value.

About equal parts of oil and carbonaceous solid by weight form a fluid slurry. Larger amounts of oil may be used if desired. The slurry may be readily pumped with conventional equipment and passed through pipe lines into the hydrogenation reactor. The slurry may be sprayed into the stream of hydrogen-rich gas entering the reactor.

The size of the particles used in making up the slurry is subject to considerable variation. The particles may range in size, for example, from a powder to particles of ¼" in average diameter. The smaller particle sizes are advantageous in that they facilitate handling and increase the rate of hydrogenation.

The slurry is preferably preheated before introduction into the reactor. This may be effectively accomplished by passing it through a pipe heater of conventional design. Part or all of the hydrocarbon oil may be vaporized in the heater. The temperature at the outlet of the heater should generally be approximately the temperature at which the reaction is carried out. Thus, the temperature may vary from about 550 to about 1000° F. for the hydrogenation of coal. The heater should generally be operated at a pressure at least the same as or higher than the pressure at which the reaction is carried out. The reaction pressure may range from about 750 to 1000 pounds per square inch gauge or higher.

It is not necessary to use pure hydrogen for the reaction. A mixture of hydrogen and carbon oxides, such as may be readily obtained by the gasification of carbonaceous solids with steam or a mixture of oxygen and steam is suitable for the present process. Preferably the hydrogen content of the hydrogen-containing gas is in excess of 65 percent by volume. In most applications of the process disclosed herein, it is contemplated that the char or residue from the hydrogenation reaction will be reacted with a mixture of steam and oxygen to produce a hydrogen-rich gas which may be fed directly to the hydrogenation zone.

More or less cracking of the hydrocarbon oil may take place within the heating zone. At the same time, some of the volatilizable constituents of the solid carbonaceous material may be released. The amount of cracking of hydrocarbons and distillation of the coal may be controlled by controlling the temperature and contact time of the slurry in the heating step.

A hydrogenation catalyst is preferably used to accelerate the hydrogenation reaction. Various metals and metal compounds are suitable as hydrogenation catalysts, as for example, nickel, nickel sulfide, tin oxalate and iron sulfate. The catalyst is preferably added to the slurry prior to passing the mixture through the preheater. Hydrogen may also be added to the slurry prior to the preheating step.

The figure is a diagrammatic elevational view illustrating a preferred method of carrying out the process of this invention. For simplicity in the detailed description of a preferred mode of operation of the process, to follow, coal is used as an example of the solid carbonaceous material. Other solid carbonaceous fuels may be substituted for coal.

With reference to the drawing, coal of suitable particle size is charged through line 1 to a feed hopper 2 from which it may be fed in regulated amounts through valve 3 into a mixer 4. Oil is supplied to the mixer through line 5. A suitable catalyst, such as nickel sulfide, may be introduced to the mixer through line 6, suitably in the form of a paste or slurry with oil. The mixer 4 is provided with a suitable stirring mechanism 7 for the preparation of a substantially uniform slurry of coal particles in the oil.

The slurry produced in the mixer 4 is withdrawn through line 8 to a pump 9 where it is subjected to increased pressure and discharged through line 11 to a preheater 12 which is of conventional design with the slurry passing through externally heated pipes. Part of the slurry may be passed through the preheater and part of the slurry passed through line 13, or all of the slurry may be passed through either, as determined by control valves 14 and 15. Generally, it is desirable to pass at least a portion of the slurry through the preheater 12. The slurry, under elevated pressure, is admitted to the hydrogenation reactor 17 through line 18 into admixture with hydrogen-rich gas supplied to the hydrogenation zone through line 19. The heat supplied to the hydrogenation reaction zone by lines 18 and 19, together with the exothermic energy of the hydrogenation reaction, insures substantially complete vaporization of the oil in the slurry. Vaporization of the oil may be accomplished in the preheater in which case the hydrogen-rich gas entering through line 19 need supply little, if any, of the heat requirements. On the other hand, the slurry may be supplied to the hydrogenation zone with substantially all of the oil in liquid phase whereupon sufficient heat is required from the hydrogen-rich gas stream supplemented by the heat of reaction to vaporize the oil in the hydrogenation zone. In this event, the slurry may be sprayed directly into the fluidized bed in the hydrogenation zone or into the hydrogen-rich gas stream flowing into the fluidized bed. In any event, the hydrogen-rich gas and the resultant oil vapors pass upwardly through the hydrogenation zone in contact with a fluidized bed of solid carbonaceous material, the vapors and gas providing the fluidizing medium for agitation of the bed of particles. Part of the oil may react with hydrogen or otherwise be converted to gaseous products during the process and some oil may be produced as a result of hydrogenation. The oil vapors are discharged from the hydrogenation zone with the product gas through line 21. Solid residue or char resulting from the hydrogenation is discharged from the reactor through line 22 as controlled by valve 23. This char may contain a considerable quantity of carbon and is suitable for use as fuel or for the generation of water gas, synthesis gas or the like by reaction with oxygen and steam.

The pressure at which the hydrogenation zone is operated is controlled by valve 25. The pressure and temperature within the reactor are generally kept within the range of from about 750 to about 1000 pounds per square inch gauge and 600 to 900° F. The oil is recovered from the product gas stream by a recovery unit 26. Product gases are discharged through line 24 as a fuel gas of high heating value while the oil is recycled through line 27 to a mixer 4. Excess oil produced by the process may be discharged from the system through line 28. Oil from any outside source may be supplied to the process through line 29. The amount of oil produced or consumed in the hydrogenation reactor is a function of the temperature and pressure at which the reaction is carried out. The quantity of liquid produced may be controlled by controlling the pressure and temperature and a balance may be reached whereby there is no net oil production or loss in the process and the process is self-sufficient. The quantity of oil recovered from the operation may be increased by decreasing the operating temperature or by increasing the operating pressure and may be decreased by increasing the temperature or by decreasing the pressure.

An especially important application of the process of this invention is the production of fuel gases from solid carbonaceous materials, such as coal, by hydrogenation at elevated pressures where hydrocarbon oils are not readily available and are not desired as products. In such a case, by means of the present process all

of the oils derived from the coal are converted to gases simultaneously with conversion of the coal. Sufficient oil is recycled within the system to form a slurry of the coal feed with the quantity of process oil controlled as described hereinabove.

Obviously many modifications and variations of the invention, as hereinabove set forth, may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. In a process for the hydrogenation of a solid carbonaceous material at an elevated temperature and pressure, the improvement which comprises forming a slurry of said solid carbonaceous material in particle form with a liquid hydrocarbon which is substantially completely vaporizable under reaction conditions, passing said slurry into admixture with a hydrogen-rich gas in a hydrogenation zone, vaporizing said liquid hydrocarbon within said hydrogenation zone, maintaining a dense-phase fluidized bed of said carbonaceous material in said hydrogenation zone, passing said hydrocarbon vapors and hydrogen-rich gas upwardly through said bed thereby effecting fluidization and reaction of said carbonaceous material with hydrogen, and recovering from the reaction zone the products of hydrogenation and vaporized liquid hydrocarbon.

2. A process as defined in claim 1 wherein the hydrogenation reaction is carried out at a pressure within the range of from about 750 to about 1,000 pounds per square inch gauge and at a temperature within the range of from about 600° F. to about 900° F.

3. A process as defined in claim 2 wherein said solid carbonaceous material is coal.

4. A process as defined in claim 1 wherein a hydrogenation catalyst is admixed with said slurry.

5. In a process for the production of a fuel gas of high heating value, the improvement which comprises admixing coal in particle form with a vaporizable liquid hydrocarbon to form a slurry, passing said slurry through a heating zone wherein a substantial portion of the hydrocarbon is vaporized, passing said coal particles dispersed in hydrocarbon vapors into a reaction zone into admixture with a hydrogen-rich gas at a temperature within the range of from about 600° F. to about 900° F. and at a pressure within the range of from about 750 to 1,000 pounds per square inch gauge, maintaining a dense-phase fluidized bed of solid particles from said coal in said reaction zone, passing said hydrocarbon vapors and hydrogen-rich gas upwardly through said bed thereby effecting fluidization thereof and reaction of said solid particles with hydrogen, discharging the resulting products of hydrogenation and hydrocarbon vapors from the reaction zone, and separating normally liquid hydrocarbons from normally gaseous hydrocarbons to produce said fuel gas.

6. In a process for the production of a fuel gas of high heating value from a solid carbonaceous material containing volatilizable constituents by hydrogenation of said solid carbonaceous material at an elevated temperature and pressure, the improvement which comprises forming a slurry of said carbonaceous material in particle form with liquid hydrocarbons, passing said slurry into admixture with a hydrogen-rich gas in a reaction zone maintained at an elevated temperature and pressure such that said carbonaceous material is hydrogenated, maintaining a dense-phase fluidized bed of said carbonaceous material undergoing reaction within said reaction zone, effecting vaporization of said liquid hydrocarbons within said reaction zone, passing the hydrocarbon vapors and hydrogen-rich gas upwardly through said bed to effect fluidization thereof and reaction of said carbonaceous material with hydrogen, discharging from the reaction zone the products of hydrogenation and vaporization comprising normally gaseous and normally liquid hydrocarbons, separating normally liquid hydrocarbons from the normally gaseous hydrocarbons discharged from said reaction zone to produce said fuel gas, forming additional slurry of carbonaceous material with said normally liquid hydrocarbons, and maintaining the pressure and temperature within said reaction zone such that the quantity of liquid hydrocarbons recovered therefrom is just sufficient for the preparation of slurry feed to said reaction zone.

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