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PROCESS FOR THE HYDROGENATION OF COAL

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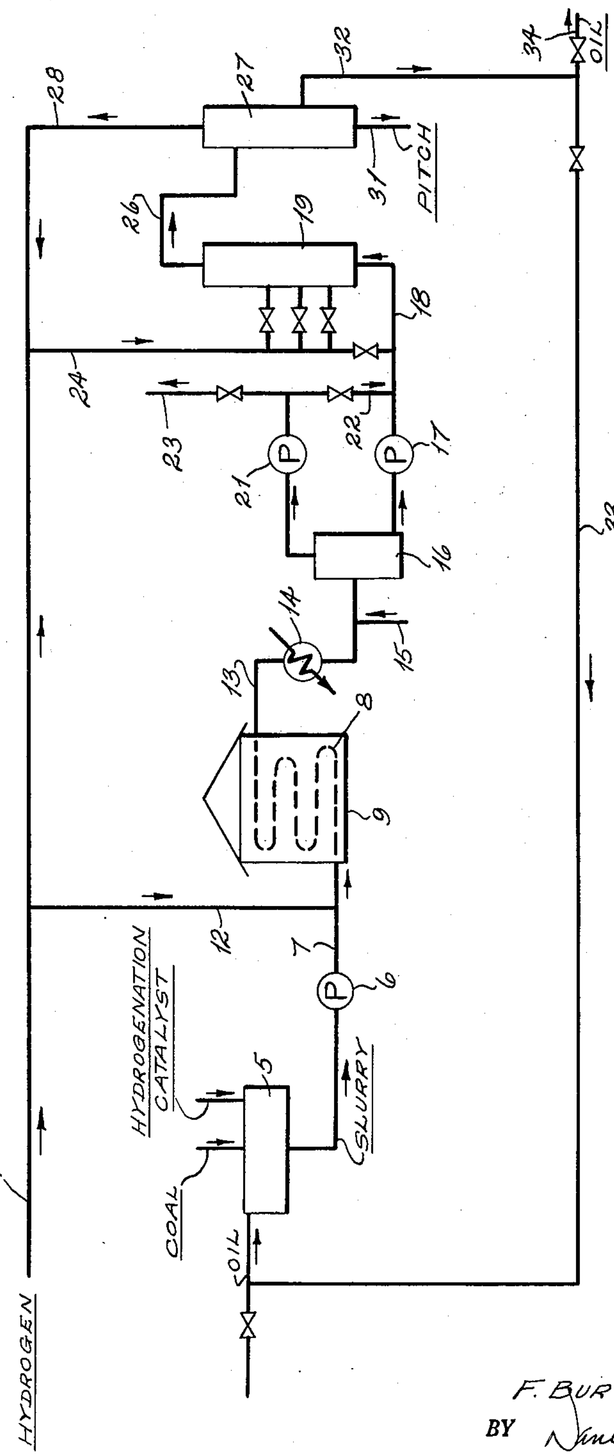

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PROCESS FOR THE HYDROGENATION OF COAL

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3 Claims. (Cl. 196—53)

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This invention relates to a process for the hydrogenation of solid carbonaceous material. The process of the present invention is particularly applicable to the treatment of coal and may be applied to hydrogenation of anthracite, bituminous coal, or lignite. In one of its more specific aspects, this invention relates to an improved process for the liquid phase hydrogenation of coal.

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

Another object is to provide an improved process for the production of oil from coal by reaction of powdered coal with hydrogen.

Other objects and advantages will be apparent to those skilled in the art from the following detailed description of the invention.

In a copending application of Du Bois Eastman and Leon P. Gaucher, Ser. No. 49,626, filed September 16, 1948, a novel process for pulverizing carbonaceous solids is disclosed. In accordance with the method disclosed in said application, particles of a solid carbonaceous material, particularly coal, are admixed with a fluid to form a suspension and the suspension passed as a confined stream in turbulent flow through a heating zone. The carbonaceous solid is heated in the heating zone to an elevated temperature. Heating of particles of coal under these conditions results in rapid disintegration of the particles to powder.

In accordance with the present invention, this novel step of heating and pulverizing solid carbonaceous material is employed in connection with hydrogenation of the resulting powder. Preferably, the hydrogenation step is carried out with a hydrogen concentrate, for example, hydrogen produced by a commercial process, containing 95 per cent or more hydrogen by volume. The hydrogenation reaction is carried out at an elevated temperature and pressure in the presence of a hydrocarbon oil. An important feature of the present invention is the novel procedure for preparation of the coal for hydrogenation.

In carrying out the process of the present invention, particles of coal are admixed with a sufficient quantity of oil to form a fluid suspension of the coal particles. This suspension is passed under conditions of turbulent flow through a tubular heating zone wherein it is heated to a temperature at least sufficient to vaporize a substantial portion of the oil. Preferably substantially all of the oil is vaporized in the heating zone. Hydrogen is added to the suspension prior

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to its introduction to the heating zone. Heated powdered coal is discharged from the heating zone in admixture with oil vapors and any residual unvaporized oil. Oil vapors are condensed forming a paste or slurry of powdered coal in oil. The paste or slurry is then passed to a liquid phase hydrogenation step wherein the coal is reacted with hydrogen at an elevated temperature and pressure. Oil produced as a result of the hydrogenation step is suitable as the source of oil used in making up the dispersion of coal fed to the heating zone.

The oil used in forming the suspension of coal as feed for the process preferably is a hydrogenated aromatic or an oil mixture comprising hydroaromatics which act as hydrogen transfer agents. Hydroaromatics which are suitable for use in the processes include tetralin and decalin. The heavy oil which is obtained from liquid phase hydrogenation of the coal is especially suited for the preparation of the feed mixture and contains hydroaromatics. If desired, a fraction separated from the heavy oil product or a suitable fraction of oil from another source may be used in the preparation of the feed suspension.

Cracking of the thermally less stable constituents of the oil may be effected in the heating zone. Also some volatile constituents may be distilled from the coal in the heating step. Hydrogenation and cracking of the volatile constituents of the coal generally take place during the heating step. Combined water need not be completely removed from the coal prior to or during the heating step. The heating step produces a gasiform dispersion of powdered solid in vapor.

Upon leaving the heating zone, the stream of oil and powdered coal is cooled by an amount at least sufficient to condense the more readily liquefiable vapors. Uncondensed vapors, comprising hydrogen and low boiling hydrocarbons, may be separately compressed and passed to the liquid phase hydrogenation step, or they may be processed separately in a more or less conventional vapor phase hydrogenation step.

The quantity of liquid admixed with the coal to form the suspension may vary considerably depending upon the process requirements and the type of coal and oil used in preparation of the suspension. A minimum of about 30 per cent oil by weight is ordinarily required to form a fluid suspension. Preferably at least 40 per cent oil by weight is used to form a suspension which may be readily pumped with suitable equipment, for example, with a diaphragm type pump of the type commonly used for handling similar suspensions of solids.

Anthracite silt may be advantageously used as a feed material for the present process. Anthracite silt is a term applied to the fine particles of coal and associated impurities obtained as a by-product in the mining, handling, and sizing of anthracite coal. It ranges in size from about 3/16 inch average diameter to about 300 mesh, the bulk of the material falling within the range of 3/32 inch to 100 mesh. Little, if any, preliminary grinding is required when using anthracite silt as feed for the present process.

The particle size of the coal fed to the heating step is not of especial importance. The particles should, however, be of a size such that they may be readily passed through the heating coil without difficulty due to plugging of the coil and associated piping. Those skilled in the art will recognize that the permissible particle size will depend, to some extent, upon the size of the piping, the density and viscosity of the oil, relative proportions of coal and oil in the suspension, and the velocity at which the suspension is passed through the piping. Generally, it is permissible to use particles having an effective diameter of less than about ¼ inch. Smaller sizes are even more readily handled.

Since the heating of the dispersion, under turbulent flow conditions, results in disintegration of coal, costly pulverization by mechanical means is eliminated. It is contemplated that in most applications of this process, the coal will be reduced only to a particle size such that it may be readily handled as a suspension or slurry. The coal may be crushed mechanically to about ¼ inch in average diameter with a relatively small expenditure of power. Further mechanical reduction in size becomes progressively more expensive, pulverization by conventional mechanical means requiring large expenditures of power. The heating step of the present invention successfully reduces the coal particles to powder, thus obviating the necessity of expensive mechanical pulverization. It is evident that the process of this invention possesses important advantages over conventional methods of hydrogenation which involve pulverization of the coal by mechanical means followed by admixing the coal with oil to form a paste prior to hydrogenation.

The linear velocity of the liquid suspension at the inlet to the heating coil should be within the range of from about 1 foot to about 10 feet per second. The velocity of the gasiform dispersion at the outlet of the coil should be within the range of from about 25 to about 200 feet per second.

The temperature at the outlet of the heating coil may range from about 250 to 1500° F. or higher. The temperature preferably is at least as high as the temperature at which hydrogenation is initiated, generally about 600° F., and preferably, also, it is at least sufficient to insure substantially complete vaporization of the oil present in the dispersion. A temperature within the range of 650° to 1400° F. is generally preferred as the temperature at the outlet of the heating coal. Higher temperatures within practical limits are often advantageous. At least a portion of the vapors are condensed after the dispersion is discharged from the heating zone. The pressure and temperature relationships may be so correlated that the desired condensation is attained at the temperature desired for hydrogenation.

Pressure, in itself, is not critical in the heating step. The temperature and pressure relationships affecting vaporization are well known. It is desirable to operate the heating step at a relatively low pressure as compared to the pressure in the hydrogenation step. A pressure within the range of from 50 to 500 pounds per square inch gauge at the outlet of the heating coil is usually adequate. A considerable reduction in pressure takes place in the heating coil due to resistance to flow. This pressure reduction may be on the order of, for example, 100 pounds per square inch. It may be desirable with some types of coal to reduce the pressure suddenly in the heating zone or at its outlet to improve the extent of disintegration of the coal.

Liquid phase hydrogenation of coal is a well-known procedure. A mixture of oil and powdered coal is supplied to a reactor operated at elevated temperatures and pressures. Pressures may range from 3,000 to 10,000 pounds per square inch gauge and temperatures from 600 to 900° F. Generally, the higher pressures and temperatures are preferred. Various metals or metal oxides may be admixed with the coal and oil as hydrogenation catalysts. Iron sulfate and tin oxalate are suitable catalysts. The hydrogenation step, per se, is not novel; conventional hydrogenation procedures may be used.

The invention will be more readily understood from the following detailed description and the accompanying drawing.

The figure is a diagrammatic elevational view illustrating a preferred mode of carrying out the process of the present invention.

Crushed coal is admixed with oil in a mixer 5 to form a slurry. A catalyst for the hydrogenation of coal is added and admixed with the coal and oil in the slurry. The slurry is forced by pump 6 through line 7 into a heating coil 8 disposed in furnace 9. Hydrogen from line 11 is introduced via line 12 into line 7 in admixture with the slurry prior to its introduction to the heating coil. The gasiform dispersion of powdered coal in oil vapors is discharged from the heating coil through line 13 and passed to a cooler 14 wherein it is cooled to a temperature sufficient to condense at least a portion of the vapors or the more readily condensible constituents. Additional oil, or catalyst, or both, may be admitted through line 15. The resulting condensed liquid admixed with solid particles from the coal is separated from the uncondensed vapor in separator 16.

The liquid oil and powdered solid are passed as a paste or slurry by pump 17 through line 18 into a hydrogenation zone 19. The vapors may be compressed by a compressor 21 and passed via line 22 into line 18 to the hydrogenation zone 19 or discharged through line 23. The vapors may be passed through line 23 and subjected to vapor phase hydrogenation or used for other purposes. Hydrogen is supplied to the hydrogenation zone from line 11 by line 24. The resulting products from the hydrogenation step, comprising residual carbonaceous solid, or pitch, and heavy oil resulting from the hydrogenation of the coal, is discharged through line 26 to separator 27. Recycle gas, comprising unreacted hydrogen is returned through lines 28 and 24 to the hydrogenation zone 19. Pitch, or residue, is discharged from the system through line 31. The heavy oil is drawn from the separator 27 through line 32 from which it may be passed through line 34 to storage for further processing. Heavy oil may be recycled through line 33 to the mixer 5 for preparation of the feed slurry.

In a typical operation of the process such as illustrated in the drawing, heavy oil produced by liquid phase hydrogenation of coal is admixed with particles of low ash bituminous coal having a size range of from about 3/32 inch to about 200 mesh. About 5 bbls. of oil is admixed with each ton of crushed coal to form a readily pumpable slurry. Ferrous sulfate is admixed with oil and supplied to the slurry at the rate of 4 pounds per ton of coal as catalyst for the hydrogenation reaction. The slurry is pumped at about 1 foot per second into a heating coil at a pressure of about 500 pounds per square inch. Hydrogen is supplied to the heating coil at the rate of 18,000 standard cubic feet per ton of coal. The temperature of the mixture at the outlet of the heating coil is about 1000° F. and the pressure is about 350 pounds per square inch. Approximately 95 per cent of the oil is converted to vapor on passing through the heating coil. The temperature of the mixture discharged from the heating coil is reduced to about 650° F. at 350 pounds per square inch. The condensed liquid, powdered coal, and uncondensed vapors are admixed with an additional 18,000 standard cubic feet of hydrogen and passed at a pressure of 10,000 pounds per square inch into a hydrogenation zone. The effluent of the hydrogenation step is separated without reduction in pressure into a gaseous fraction, predominantly hydrogen, which is recycled, a heavy oil fraction or crude product of the hydrogenation step, and residual solid or pitch. A portion of the heavy oil is returned to the mixing zone for admixture with the fresh coal. The heavy oil product amounts to about 1700 pounds per ton of coal fed to the process.

Obviously, many modifications and variations of the invention, as hereinbefore 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 coal wherein coal in finely divided form is admixed with oil and reacted with hydrogen at an elevated temperature and pressure, the improvement which comprises admixing particles of coal the bulk of which have a size range of from about 3/32 inch to about 200 mesh with a hydrocarbon oil to form a fluid suspension, passing said suspension at a pressure within the range of from about 50 to about 600 pounds per square inch gauge as a confined stream in turbulent flow through a heating zone wherein it is heated to a temperature above about 600° F. and at least sufficient to vaporize substantially all the oil thereby reducing the particle size of the coal, cooling the resulting mixture comprising hydrocarbon vapors and powdered solid from the coal by an amount sufficient to condense at least the more readily condensible components of said vapors in admixture with powdered solids from said coal and form a fluid mixture of powdered solid and liquid hydrocarbon, and subjecting the resulting mixture of liquid hydrocarbon and powdered solid to hydrogenation in liquid phase at an elevated temperature and pressure.

2. A process as defined in claim 1 wherein the suspension of coal and oil is heated in the heating zone to a temperature within the range of from about 650 to about 1200° F.

3. A process as defined in claim 1 wherein a coal hydrogenation catalyst is admixed with the suspension of coal and oil and passed through the heating zone.

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