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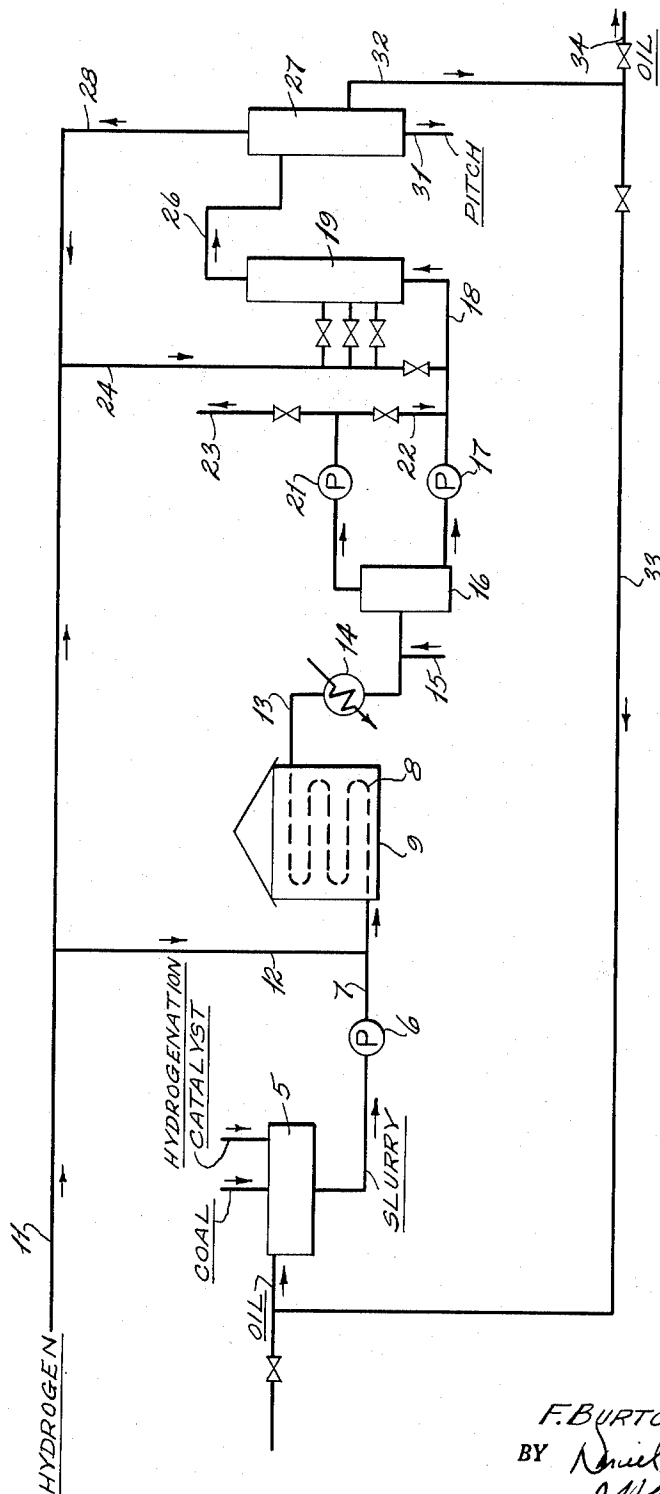
F. B. SELLERS

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PROCESS FOR THE HYDROGENATION OF COAL

Filed Sept. 4, 1951

2 Sheets-Sheet 1



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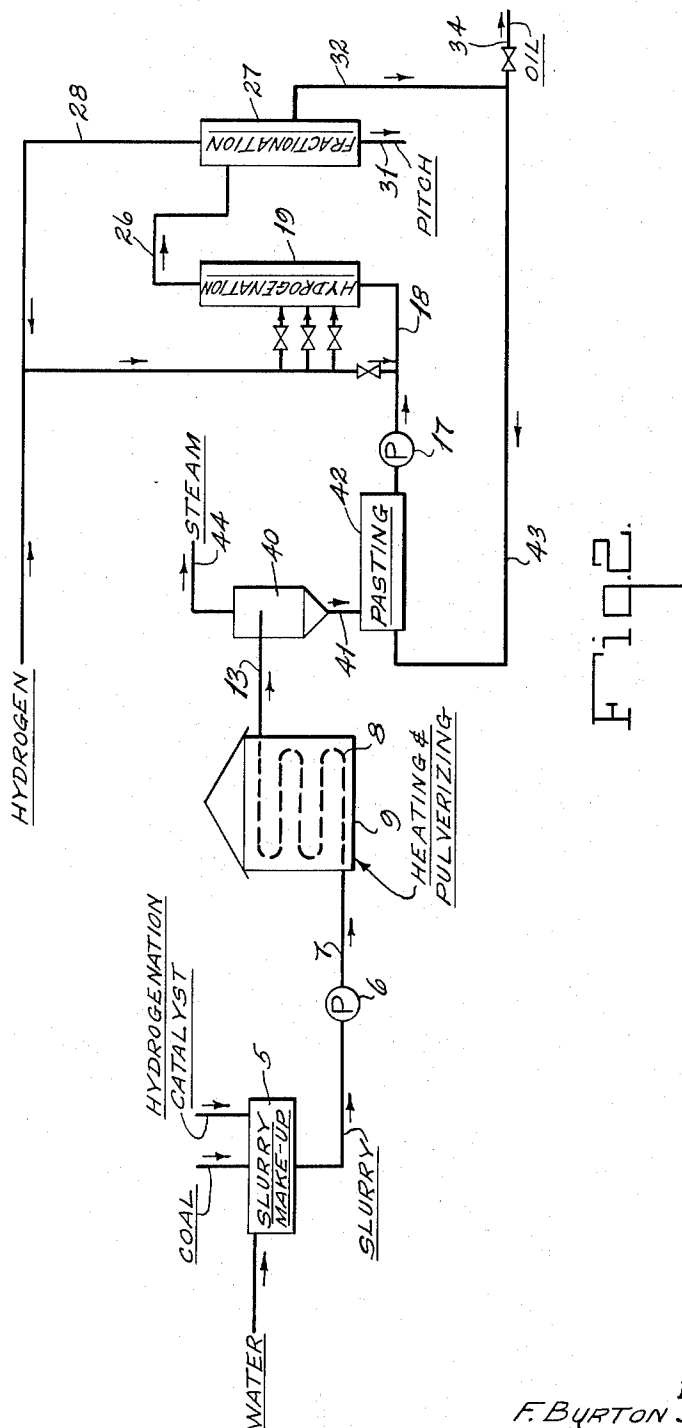


Fig. 2

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PROCESS FOR THE HYDROGENATION OF COAL

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2 Claims. (Cl. 196—53)

This invention relates to a process for the hydrogenation of a 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.

This application is a continuation-in-part of my copending application, Serial Number 49,583, filed September 16, 1948, now Patent No. 2,572,061.

In a copending application of duBois Eastman and Leon P. Gaucher, Ser. No. 490,214, filed February 24, 1955, 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 the process of the invention disclosed in my above-identified copending application, 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 may be added to the suspension prior 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

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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.

In carrying out the process of this invention, an intimate association between finely powdered coal and hydrogenation catalyst is obtained by bringing them together in the heating zone. Accordingly, a slurry is made up of coal, vaporizable carrier liquid, and catalyst and the resulting slurry passed as a confined stream in turbulent flow through a heating zone wherein the slurry is heated to at least a temperature sufficient to vaporize substantially all of the carrier liquid. The heating zone preferably comprises an externally heated tubular coil. Vaporization of liquid in the coil results in a considerable increase in volume which, in turn, results in forming a dispersion of the solid particles in vapor moving through the coil at high velocity. Very effective pulverization of the coal results. At the same time, the catalyst is most intimately associated with the pulverized particles of coal. The catalyst may be added to the slurry in the form of solid particles, suitably having a comparable size range as the coal, or it may be dissolved in the carrier liquid. In either case, the catalyst appears to be more active than when mixed with powdered coal in the usual manner, probably because of the more uniform and more intimate combining of the two by the process of this invention. Water and liquid hydrocarbons are preferred as the carrier liquid. When water is used as the carrier liquid, it is separated from the powdered coal following pulverization in the heating coil, and the powdered coal mixed with oil in the usual manner to form a paste for hydrogenation.

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 liquid used in preparation of the suspension. A minimum of about 30 per cent oil or about 35 percent water, by weight, is ordinarily required to form a fluid suspension. Preferably at least 40 per cent oil or 45 per cent water, 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. The quantity of liquid required to form a fluid slurry is readily determined by trial.

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 $\frac{3}{16}$ inch average diameter to about 300 mesh, the bulk of the material falling within the range of $\frac{3}{32}$ 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 plugging 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 carrier liquid, relative proportions of coal and liquid 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 $\frac{1}{4}$ inch. Smaller sizes are even more readily handled. Preferably the bulk of the particles charged have a size range of from about $\frac{3}{32}$ to about 200

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mesh. The vaporization of liquid in the slurry and the resulting high velocity fluid flow in the coil readily reduces the coal to a particle size substantially all of which are smaller than 200 mesh. 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 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 will vary within the range of from about 25 to about 3000 feet per second, depending upon the pressure at which it is discharged.

The temperature at the outlet of the heating coil may range from about 250 to 1500° F. or higher. The temperature is at least sufficient to insure substantially complete vaporization of the oil present in the dispersion. When a liquid hydrocarbon is used as the carrier fluid, the temperature preferably is at least as high as the temperature at which hydrogenation is initiated, generally about 600° F. A temperature within the range of 650° to 1400° F. is generally preferred as the temperature at the outlet of the heating coil. Higher temperatures within practical limits are often advantageous.

Vaporization of the carrier liquid takes place in the first portion of the coil, forming a dispersion of solid particles in vapor flowing at a velocity many times the velocity of the slurry. This vaporous dispersion may be passed through a heated or unheated section of coil to effect further pulverization and, if desired, heating of the solid particles. No distinction is made herein between heated and unheated portions of the coil, the entire coil being referred to as the heating zone or heating coil. It will generally be found desirable to employ a tubular heating and grinding coil having an internal diameter within the range of from about one half to about two inches and a length within the range of from about 100 to about 500 feet.

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. With oil, a pressure within the range of from 50 to 500 pounds per square inch gauge at the outlet of the heating coil is generally desirable; this aids in subsequent condensation of the vapor. 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 to 1,000 pounds per square inch in order to produce a flow rate of slurry of 1 to 10 feet per second.

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. An alternative procedure for the hydrogenation of coal is dry hydrogenation, or direct hydrogenation of the powdered coal. This may be carried out under the same temperature and pressure conditions and with the same catalysts as liquid-phase hydrogenation. Generally somewhat lower pressures are used for dry hydrogenation than for liquid phase hydrogenation. In dry hydrogenation it is preferable to conduct the hydrogenation of the coal in the form of very small particles in a dense phase fluidized bed. Hydrogen passes upward through the particles imparting turbulent motion characteristic of the fluidized bed. The hydrogenation step, per se, is not novel; conventional hydrogenation procedures may be used.

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Catalysts suitable for the hydrogenation of coal are known in the art. Among the numerous catalysts are various compounds, particularly the oxides, sulfides or nitrides, of titanium, tin, copper, lead, zinc, chromium, cobalt, iron, various alkali metals, and rare earths. Of the many catalysts mentioned in the art, stannous oxalate and ferrous sulfate have shown the most promise for commercial operations. Stannous oxalate is insoluble in water, whereas ferrous sulfate is water soluble.

The invention will be more fully understood from the following detailed description and the accompanying drawings, wherein like parts are designated by the same numerals.

Figure 1 is a diagrammatic elevational view illustrating a preferred mode of carrying out the process of the present invention.

Figure 2 is a diagrammatic elevational view illustrating an alternative procedure.

With reference to Figure 1, 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 condensable constituents. Additional oil, or catalysts, 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 29 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 Figure 1 of the drawings, 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 $\frac{3}{32}$ 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 1,000° F. and the pressure is about 300 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

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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 1,700 pounds per ton of coal fed to the process.

With reference to Figure 2 of the drawings, a slurry of coal and a hydrogenation catalyst is made up in mixer 5 using water as the carrier fluid. The slurry is pumped through line 7 into heating coil 8 in heater 9, corresponding to the apparatus of Figure 1. The resulting dispersion of powdered coal and catalyst in steam is discharged through line 13 into a separator 40, suitably a cyclone separator, in which the powder is separated from the steam. The powdered coal, together with the associated catalyst, is passed through line 41 into a mixer 42 in which it is mixed with oil to form a paste. The oil is supplied to mixer 42 through line 43 from separator 27. The paste of powdered coal, catalyst, and oil from the mixer 42 is charged by pump 17 through line 18 into a liquid phase hydrogenation step 19 corresponding to that described in Figure 1. The operation of the heating step, hydrogenation step, and separation step are the same as previously described in connection with Figure 1.

An alternative procedure, previously mentioned, is dry hydrogenation of the powdered coal and catalyst formed in the heating and pulverizing coil 8. By this procedure, the powdered coal and catalyst separated from the steam is subjected directly to the action of hydrogen at an elevated temperature and pressure, preferably in a fluidized bed. The specific procedure for dry hydrogenation does not, per se, form a part of the present invention and is, therefore, not illustrated in the drawings.

A light hydrocarbon oil may be used in place of water in the modification of the process illustrated in Figure 2. A relatively stable light oil, i. e., one having a relatively

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low boiling point, for example, kerosene, may be used instead of water to make up the slurry. The resulting vapors separated in separator 40 may be condensed and the condensate returned to mixer 5 for the preparation of additional slurry.

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 $\frac{3}{32}$ inch to about 200 mesh, and a hydrogenation catalyst with water substantially free from oil to form a fluid suspension; passing said suspension through a heating zone wherein the water is vaporized thereby forming a dispersion of solid particles in steam moving as a confined stream in turbulent flow reducing the particle size of the coal to less than 200 mesh and simultaneously intimately associating the catalyst with the resulting powdered coal; separating the powdered coal and the associated catalyst from said steam; and subjecting said coal in said mixture to reaction with hydrogen in the absence of steam at an elevated temperature and pressure.

2. A process as defined in claim 1 wherein said catalyst is dissolved in said water.

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