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[54] **PROCESS FOR THE HYDROGENATION OF COAL**
9 Claims, 1 Drawing Fig.

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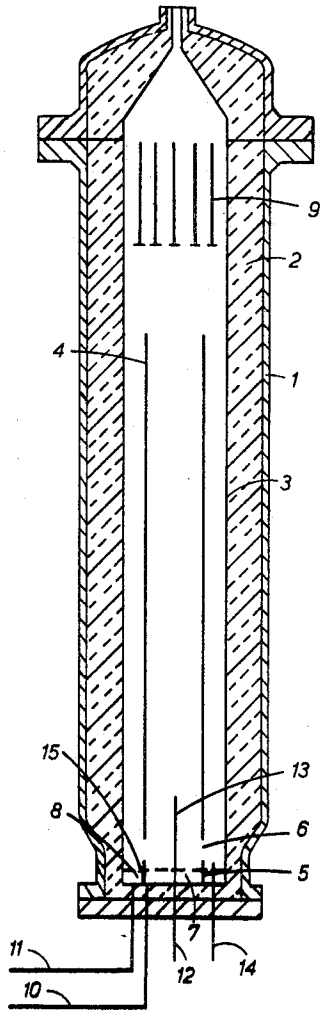
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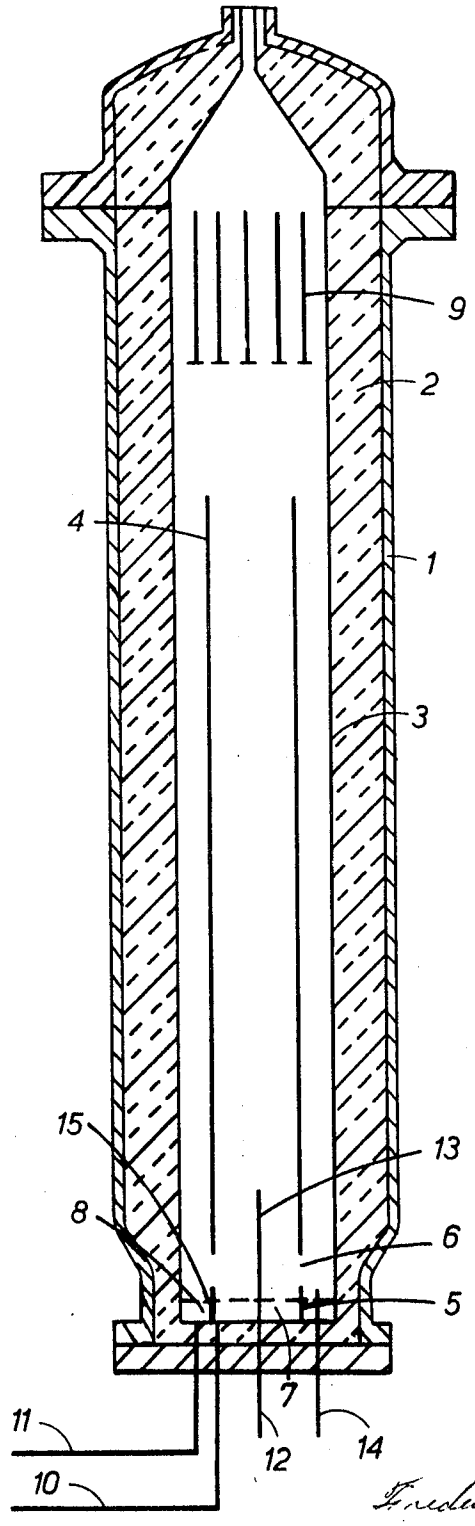
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ABSTRACT: A process for the hydrogenation of coal to produce a methane-containing gas is described. Powdered raw coal is introduced into a recycling fluidized bed of noncaking material. The coal is rapidly heated and at least partly hydrogenated, and converted into a noncaking powdered char. The process is generally operated at temperatures of 600° to 1,000° C. and pressures of 10 to 200 atmospheres.



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PROCESS FOR THE HYDROGENATION OF COAL

This invention relates to a process for the hydrogenation of coal to provide a methane-containing gas.

The hydrogenation of coal to produce mainly gaseous hydrocarbons necessitates heating raw coal from cold to temperatures above at least 600° C., the coal being conveniently in the presence of hydrogen under elevated pressure while it is being heated. It is known that when bituminous coals are heated through a temperature range near and above about 400° C. their decomposition may be accompanied by partial fusion which can cause the pieces or particles of the coal to agglomerate or cake. The extent to which this occurs varies widely over a wide range of coal ranks, and in some circumstances it is possible to describe certain coals as noncaking. However, the treatment of coal with hydrogen under pressure while its temperature is being raised through the caking range increases the caking tendency and it is likely that there is no bituminous coal which is initially noncaking under the conditions used. If fluidized bed techniques are to be used in the hydrogenation process, care must be taken to operate so that the caking properties of the coal that are displayed as the coal is being heated do not lead to interference with the working of the process. Once the coal has been heated through the critical temperature range in such a way that its caking properties have been destroyed, difficulty with agglomeration is avoided for operation at any temperature.

We have found that it is possible to operate so as to avoid difficulty arising from the caking properties of the coal, and meanwhile to destroy these caking properties, by dispersing the coal into a hot recycling bed of fluidized noncaking material in the presence of hydrogen under pressure. The rapid heating experienced by the particles causes the rapid hydrogenation of at least their more reactive constituents and these are converted into a no-caking semicoke or char. At the same time the dispersion of the particles in the bed prevents any transistory caking tendency from causing buildup of agglomerates.

The invention provides a process for the hydrogenation of coal to provide a methane-containing gas, which process comprises introducing powdered raw coal into a recycling fluidized bed of noncaking material at a temperature of from 600° C. to 1,000° C. and in the presence of an hydrogenating gas, the rate of introduction of the coal into the bed and the temperature of the fluidized bed being such that the coal is rapidly heated and at least partly hydrogenated and converted to a noncaking condition.

The process may be carried out at pressures of, for example, from 10 to 200 atmospheres, preferably 25 to 100 atmospheres, with hydrogenating gas at reaction temperatures of from 600° C. to 1,000° C., preferably 700° C. to 900° C. The hydrogenation results in the production of gaseous hydrocarbons (arising mainly, and especially at the lower temperatures, from the hydrogenation of the volatile constituents of the coal) and of a residue of noncaking powdered char. This latter material may be hydrogenated under severer conditions in a later state of the overall process to produce more methane and a residue which may be used for hydrogen manufacture. Alternatively, but less advantageously, all the methane required from the overall process may be produced in the one hydrogenation stage and the solid residue from it may be used directly for hydrogen manufacture.

The use of a fluidized bed facilitates the temperature control of the reactions, which are exothermic. The level of temperature is controlled by adjustment of the preheat temperature of the reactants, including that of the raw coal particles, but as there is a limit to the temperature to which coal can be preheated, it may be necessary to provide heat from other sources. Preferably, this is done by carrying out other exothermic reactions in the fluidized bed along with the hydrogenation reaction, for example, an oxygen-containing gas can be introduced, or a light petroleum distillate can be fed and hydrogenated.

Preferably, the noncaking material constituting the fluidized bed is the noncaking char produced by the hydrogenation of the powdered raw coal which is fed in. Material is extracted from the bed as and when necessary. Preferably, the introduction of the coal and the extraction of treated char are both operated continuously. In starting up the process, the fluidized bed has to be initially noncaking and can suitably be high temperature coke; as the treatment proceeds this is progressively extracted and replaced by hydrogenated, noncaking char formed by the reaction. A stage is soon reached when the burden consists substantially completely of treated coal and the material extracted is of uniform composition suitable for the next stage of the complete process.

Suitable apparatus for carrying out the process of the invention is a modified version of the fluidized bed apparatus used for the hydrogenation of oil. The principal modifications required are the replacement of the oil atomizers by nozzles or injectors through which powdered coal, entrained in gas (which may be hydrogenating gas) is fed into the apparatus, and the provision of an offtake, by means of which the treated coal can be withdrawn by known means either continuously or intermittently.

Apparatus which can be modified for the present purpose is described in British Pat. Nos. 830,960 and 873,832, but it is preferred to use in practicing this invention modified apparatus which is described in our copending U.S. Pat. application Ser. No. 566,947 U.S. Pat. No. 3,484,219, dated Dec. 16, 1969.

This latter-mentioned specification describes apparatus for performing a chemical reaction between a reactant gas and fluid material to produce a gaseous product, which apparatus comprises an elongated thermally insulated reaction vessel, to be held in a vertical position and to contain a fluidized bed, having mounted within it at least one dividing member which is shorter than the internal length of the vessel and which divides the interior of the vessel into at least two regions, at least one to act as a riser for the fluidized bed and a region surrounding the riser or risers to act as a downcomer therefor, all the regions being in communication with each other beyond the ends of the dividing member or members, means for supplying the reactant gas at the lower end of the reaction vessel so as to maintain at least one zone of ascending particles in the fluidized state in the riser or risers and a zone of descending particles in the fluidized state in the downcomer, at least one nozzle associated with each riser within the reaction vessel for injecting or atomizing the fluid material into the reactant gas and an outlet for a gaseous reaction product at the upper end of the reaction vessel. When this apparatus is used, an additional outlet or offtake (for solids) can be provided from the base of the downcomer.

The invention will now be described by way of example with reference to the accompanying drawing, which shows in diagrammatic form a sectional side elevation of a reaction vessel in which the process of the invention may suitably be carried out.

Within a pressure vessel **1** and separated from it by insulation **2** there is a cylindrical reaction vessel **3** within which is a coaxial cylinder **4** mounted so as to be spaced away from a shorter cylinder **5** by a gap **6**. There is a shallow compartment at the base of the vessel which is divided by the shorter cylinder **5** into a central cylindrical chamber **7** and an annular chamber **8**. These chambers, which are constructed according to British Pat. No. 1,036,890, provide means for obtaining uniformity of distribution of the reactants into the cylindrical and annular spaces above the top surface of the compartment, which is a perforated plate **15**. The insulating space **2** between the reaction vessel and pressure shell may be, but is not shown as, as in British Pat. No. 1,044,007. Baffles **9** may be located above the end of the cylinder **4**.

Pipe **10** is for the introduction of the large proportion of the hydrogenating gas into chamber **7** and thence into the base of the central tube **4**. Pipe **11** is for the introduction of a further quantity of hydrogenating gas into chamber **8** and thence into

the annulus between vessel 3 and cylinder 4 to ensure proper fluidization, when the apparatus is in operation, of descending solid particles. Pipe 12 is for the introduction of powdered coal, entrained in gas, the suspension entering the reaction vessel at the open end 13 of pipe 12. Pipe 14 is for the withdrawal of char.

The apparatus is charged with noncaking fluidizable solid, conveniently high temperature or medium temperature coke, and circulating fluidization (the solids circulate up cylinder 4 and down the annulus between cylinder 4 and vessel 3) is established by known means while the bed is being heated, say to 800° C., by known means which may include preheating the hydrogen introduced through the distributors (pipes 10 and 11) in the base and by introducing air. A suitable method for establishing the fluidized bed is described in our aforementioned U.S. Pat. No. 3,484,210. Meanwhile the pressure is being raised to say, 70 atmospheres. When the chosen operating temperature has been reached, the supply of powdered raw coal is started (through pipe 12), slowly at first, and is built up to a rate conveniently below that, ascertained by experience, at which agglomeration is first encountered. It may then be possible to stop or reduce the supply of air. The coal is rapidly heated and converted to a noncaking condition. The withdrawal of solids is begun at a corresponding rate so as to maintain the volume of the burden substantially constant. Temperatures are adjusted by control of the preheat temperature of the input materials and pressures by the rates of supply and withdrawal of gaseous reactants and products. As indicated hereinbefore, certain exothermic reactions may be conducted within the reactor if the heat liberated by the hydrogenation of the coal together with that supplied as preheat is insufficient to maintain the temperature. The powder withdrawn in the early stages consists predominantly of coke and is rejected, but as withdrawal proceeds the material contains an increasing proportion of the residue from coal that has been treated according to the invention. Eventually rejection of the solid product ceases and its retention for use in later stages of the overall process begins.

The following is an example of the process of the invention as carried out in the above-described apparatus.

Example

A weakly caking British (Nottinghamshire Arkwright) coal was treated by hydrogenation under pressure, using as the hydrogenating gas a gas that was made by the gasification and hydrogenation of char resulting from the present process. The hydrogenation of the char produces a gas of higher calorific value than that of the gas used to hydrogenate the char and further char from which more hydrogenating gas can be made.

In the apparatus the reaction vessel had an internal diameter of 16 inches and the inner coaxial cylinder had an internal diameter of 11 ⅝ inch and was 18 feet long. A charge of powdered char, formed by the replacement of an initial charge of coke by the product of hydrogenation of raw coal, was kept in circulation up the central tube and down the annulus by the supply of the fluidizing hydrogenating gas at the base. The average linear velocity of solids flow up the central tube was 1 foot per second. The temperature of the circulating bed was 800° C. and the operating pressure 1,000 p.s.i.g.

The hydrogenating gas had the volumetric percentage composition

CO	CO_2	CH_4	H_2
3.65	2.45	27.95	65.95

percent by volume, and it was supplied at a rate of 37,670 s.c.f. per hour.

2,000 pounds per hour of the raw coal, of composition (percent by weight)

C	H	O	S	N	H_2O	Mineral matter
73.77	4.95	9.00	1.38	0.90	2.00	8.00

and graded 25–300 B.S.S., were introduced as described into the circulating burden of char. It underwent hydrogenation, with destruction of its caking properties, and there were produced 49,120 s.c.f./hour of gas (dried and freed from ammonia and hydrogen sulfide) having the composition

CO	CO_2	CH_4	H_2
13.25	0.9	43.0	42.85

percent by volume. Its calorific value was 606 B.t.u./s.c.f., that of the initial hydrogenating gas being 500 B.t.u./s.c.f.

There was withdrawn from the reaction vessel 1,167 lb./hr. of hydrogenated, noncaking char, of composition

C	H_2	Mineral matter
85.24	1.07	13.69

percent by weight. 35.7 lb./hr. of tar were also produced by condensation from the cooled product gas.

We claim:

1. A process for the hydrogenation of coal to provide a methane-containing gas, which process comprises introducing powdered raw coal into a recycling fluidized bed of noncaking material at a temperature of from 600° C. to 1,000° C. and at a pressure of from 10 to 200 atmospheres in the presence of an hydrogenating gas, the rate of introduction of the coal into the bed and the temperature of the fluidized bed being such that the coal is rapidly heated and at least partly hydrogenated and converted to a noncaking condition.

2. A process as claimed in claim 1 wherein the process is carried out at a pressure of from 25 to 100 atmospheres.

3. A process as claimed in claim 1 wherein the process is carried out at a reaction temperature of from 700° to 900° C.

4. A process as claimed in claim 1 wherein additional heat is supplied to the fluidized bed by carrying out another exothermic reaction in the bed.

5. A process as claimed in claim 4 wherein the other exothermic reaction is established in the fluidized bed by introducing into the bed a material selected from the group comprising an oxygen-containing gas and a light petroleum distillate.

6. A process as claimed in claim 1 wherein the powdered raw coal is continuously fed to the fluidized bed, and the treated noncaking material produced from the powdered material continuously withdrawn from it.

7. A process as claimed in claim 1 wherein the process is operated such that the powdered raw coal is only partially hydrogenated, the hydrogenation being subsequently completed in a separate stage.

8. A process as claimed in claim 1 wherein the powdered raw coal is introduced into the fluidized bed entrained in hydrogenating gas.

9. A process as claimed in claim 1 wherein the powdered raw coal is preheated prior to being introduced into the fluidized bed.