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(54) Oxidation of flyash.

(57) A process for the partial combustion or oxidation of coal, the process being characterized by recovery of energy value in flyash and concomitant reduction of solids disposal requirements. In particular, the flyash is oxidized in a fluidized bed, preferably with other carbonaceous materials, and the heat recovered is used, e.g., to dry feed coal.

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OXIDATION OF FLYASH

The invention relates to a process for the gasification of coal to produce synthesis gas comprising the steps of
feeding particulate coal to a gasification zone, and partially oxidizing coal with oxygen in said gasification zone, producing a stream comprising synthesis gas and flyash;
quenching and cooling the stream, and separating flyash from the stream, producing a separated flyash.

Usually, in processes for the gasification of coal to produce synthesis gas, significant quantities of unreacted or impurity matter, known as flyash, are produced and entrained upon removal of the synthesis gas from the gasification zone. This matter must be eliminated from the synthesis gas before further purification or utilization of the gas.

Separation of the flyash from the synthesis gas creates a disposal problem, since the flyash has undesirable properties which limit options for its disposal. At the same time, the flyash contains, in addition to mineral matter or components, a residual carbon content that has substantial energy value. For example, the flyash may contain from about 3 per cent by weight to about 30 per cent by weight of residual carbon. If the flyash is disposed of, e.g. by land fill, this energy value is lost. Accordingly, a procedure which captured this energy value, at the same time reducing the volume of material to be disposed of, could have great economic importance. The invention provides such a procedure.

Additionally, if coal is dried to remove the bulk of the moisture therein before gasification, the removal of this moisture involves a significant energy expenditure. If coal is combusted to provide the heat necessary for the drying, from about 2 per cent to about 12 per cent by weight of the total coal supplied to the process may be utilized, thus lowering the efficiency of the process. The invention, in a further embodiment, is directed to reducing this energy expenditure.

Therefore, it is an object of the invention to provide a process for the partial oxidation or combustion of coal in which disposal problems for the flyash particulates are reduced, and energy costs for the process are reduced. The invention, further, integrates a procedure for reducing flyash disposal with a coal drying procedure, so that improvement in both techniques is achieved.

Therefore, the process of the invention is characterized by the steps of fluidizing separated flyash in a fluidized bed in a fluidization zone, and oxidizing said flyash in said fluidized bed with oxygen at a temperature below the fusion temperature of the mineral components of the flyash and the fluidized bed, producing a substantially carbon-free residue, and heated gases, and utilizing the heat in said heated gases. In an advantageous form, the invention comprises a process, as described, in which the partial oxidation or gasification is carried out in a gasification zone, the outlet temperature of which is from 1100 °C to 1800 °C, more advantageously 1200 °C to 1600 °C, the stream produced is quenched and cooled to a temperature of from 650 °C to 145 °C, and flyash separated is oxidized in a fluidized bed in a fluidization zone at a temperature of from 500 °C to 1150 °C, more advantageously 650 °C to about 1120 °C. Pressures in the gasification zone may be varied widely, but will for example, range from 10 to 100 atmospheres, more advantageously from 20 to 50 atmospheres, while pressures in the fluidization zone will range from atmospheric to 10 atmospheres or higher.

The heat liberated may be used to generate steam, or, may be used to dry feed coal to the process. That is, in this embodiment, the invention relates to a process for the gasification of coal to produce synthesis gas in which particulate coal is dried in at least one drying zone, the coal is fed from at least one drying zone to a gasification zone, and partially oxidized or combusted, as hereinbefore described, to produce synthesis gas and flyash, which is treated as described, and the heat generated by oxidizing the flyash is utilized in drying coal in at least one drying zone. As used herein, the term "flyash" refers to matter carried out of the gasification zone by the synthesis gas, including unconverted coal particles, partially converted particles, and molten matter which solidifies as discrete particles in the quench or cooling stages of the process. Unless otherwise evident from the context, the term oxygen is taken herein to include air, pure oxygen, air enriched with oxygen, and other oxygen-containing gases.

While the particular gasification or partial oxidation or combustion procedure employed is not per se part of the invention, the invention is particularly applicable to high pressure slagging coal gasification processes in which the coal is partially oxidized or combusted to produce, in addition to the synthesis gas and the flyash, a bottom materials variously known as char, fine slag, and coarse slag, which are removed separately from the gasification zone. The oxygen and coal flows are controlled so that little CO_2 is produced in the gaseous product. In general, these procedures are carried out by feeding coal, advantageously dry coal, e.g., coal having a moisture content of below ten percent by weight, entrained in a gas, such as an inert gas, into a gasification zone, and combusting or oxidizing the coal with oxygen. Flame temperatures may reach 3500 °C, with zone outlet temperatures ranging from 1100 °C to 1800 °C. Pressures in these processes may vary, but will advantageously range from 10 atmospheres to 100 atmospheres, more advantageously from 20 atmospheres to 50 atmospheres. In one such process, the synthesis gas and molten particles (which form flyash) are removed from the upper portion of the gasification zone, and the char, fine slag, and coarse slag are removed from the lower portion.

A wide variety of coals are suitable for use in the invention. For example, anthracite, bituminous coal, lignite, and so-called brown coal may be used in the invention. A real advantage of the invention is the ability to use lower grade coals, such as lignite. As used herein, the term "coal" is taken to include these inferior grade carbonaceous fuels, as well as the higher quality coals. The coal can be fed to the gasification zone in a particle size suitable for boiler furnace operation, e.g., 80 to 90 microns in diameter, although those skilled in the art may select the appropriate particle size, as desired. In an advantageous embodiment, the invention employs "dry" coal, that is, coal having a moisture content of less than 10 per cent by weight, based on the weight of the moist coal.

The synthesis gas and particles entrained therein are then subjected to various quench and cooling procedures, producing a synthesis gas stream containing flyash, the temperature of the stream produced being from about 650 °C to 145 °C. If the flyash is removed at this stage, the sensible heat therein may also be recovered. This may be done, for example, by separating the flyash in cyclone separators. If the temperatures are sufficiently low, bag filters may be used. However, it is within the scope of the invention to separate the flyash differently, e.g. by scrubbing with an aqueous stream. If this approach, or a combination of a cyclone and a scrubbing system is employed, the flyash will be separated from the aqueous stream, e.g., by filtration, before the utilization thereof in the manner of the invention.

According to the invention, the separated flyash is oxidized in a fluidization zone, comprising at least one fluidized bed, to remove the carbonaceous matter therein, producing a denser, more easily disposed of material. The heat liberated during oxidation may be captured by generation of steam, or, as preferred, may be used either directly or indirectly to dry the coal to be fed to the gasifier. As will be appreciated by those skilled in the art, the amount of heat generated from the flyash will normally be insufficient to dry the large volume of coal needed for the process. To supplement the heat generated by the flyash, other combustible or partially combustible materials or fuels, such as coal or coal fines, may be added to the fluidized bed and oxidized. Obviously, a separate drying technique may also be used, but it is an advantage of the invention that an independent dryer or drying zone may be eliminated.

The type of fluidized bed or beds employed is a matter of choice. What is required, however, is that the bed or beds be operated at a temperature below the fusion temperature of the mineral matter in the flyash, and of any mineral matter in the bed, including that of a coal or fuel supplement. In general, the mineral content of flyash comprises silica, alumina, and other inorganic components in varying quantities, and the melting point of this mixture may be determined routinely. Since these temperatures are normally above about 1482 °C - (although some may be less), problems with clogging will normally not be encountered if the bed is operated below this temperature. As indicated, the fusion temperature or range of temperatures may be determined routinely for each flyash or coal fuel utilized, and the temperatures in the fluidized bed may be controlled accordingly. Advantageously, the temperatures are operated well below the fusion temperature, e.g., from 500 °C to 1150 °C, more advantageously from 650 °C to 1120 °C. Pressures in the fluidization zone may be varied, to the extent suitable for fluidized beds, but will for example range from atmospheric to 10 atmospheres, more advantageously from atmospheric to 5 atmospheres. The fluidized bed or beds may be jacketed, or may have coils to absorb the heat produced by the oxidation. The bed may contain other particulate matter, including catalysts. The combustion gases generated are removed from the fluidization zone, and transfer their heat, either directly or indirectly, as desired, advantageously to the coal feed. Advantageously, the coal is ground and dried in a combination procedure, and to allow conventional equipment to be used, a moderating gas, such as air or nitrogen, at a temperature of, for example, 15 °C to 40 °C, is added to the combustion gases to lower the temperature to about 200 °C to about 500 °C.

The invention will now be described by way of example in more detail with reference to the accompanying drawing, in which the figure is a - schematic illustration of the process flow type showing an embodiment wherein the heat generated by oxidation of the flyash is used to dry feed coal. All values are calculated or exemplary.

Accordingly, reference numeral (1) designates a supply line from, for example, a storage vessel, not shown, in which coal having an average particle size diameter of 1.3 cm is fed to a drying zone (2) which contains a combination pulverizer-dryer wherein the coal is crushed to an average particle size of from 80 to 90 microns and dried by the gas stream in a line (3) to a moisture content of about 10 per cent by weight, based on the weight of the moisture and the coal. In this illustration, the gas stream in the line (3) has a temperature of about 250 °C, contacts the coal directly in the combination pulverizer-dryer, and exits the drying zone (2) via a line (4). The exit gas may be treated for control of pollutants, or utilized (not shown). Concomitantly, dried particulate coal is removed from the drying zone (2) through a line (5) and forwarded to a gasifier (6). Means may be provided (not illustrated) for raising the pressure of the coal and entraining gas up to the level employed in the gasification zone. In the gasification zone (6), the coal is injected in an entraining gas, e.g., nitrogen, through nozzles and combusted in a reducing atmosphere or partially oxidized with pure oxygen at 25 atmospheres and at a flame temperature of about 3400 °C to about 3500 °C. Synthesis gas and impurity particles are removed overhead from the gasification zone at a temperature of about 1400 °C, and sent to a quenching and cooling zone (7). Char and slag, which are heavier impurity materials, fall downward into the gasifier, and are removed from the lower portion thereof through a line A. The quench and cooling zone (7) can be connected directly to the outlet of the gasifier (6). The synthesis gas can first be quenched and cooled with cold recycle gas, if desirable. The temperature of the synthesis gas is advantageously lowered to about 900 °C, and molten impurities in the gas are solidified to what is known as flyash. The quenching and cooling sequence can be carried out in more than one stage, the final temperature before separation of the flyash being from about 235 °C to about 320 °C.

In order to separate the flyash from the synthesis gas, the stream is forwarded via a line (8) to a cyclone (9) (or the cooling zone may discharge directly thereto). The great bulk of the flyash is separated in the cyclone (9), and the flyash is removed from the cyclone (9) via a line (10). The gas stream is removed from the cyclone (9) via a line (11) and sent for further processing, such as for H_2S removal, and for product use. Because the cyclone is not totally effective, a final solids cleanup stage (12), e.g., bag filters, is provided in the line (11). Solids are removed from the unit (12) via a line (13). Solids from the cyclone (9) and the solids removal stage (12) are utilized for energy recovery according to the invention.

Accordingly, solids in the lines (10) and (13) are injected into a fluidized bed (14), and are reacted with oxygen in excess from a line (15) at a temperature of about 800 °C to about 900 °C, which is well below the fusion temperature of the mineral components of the bed. The oxygen may serve as the fluidizing gas, or a separate fluidizing gas may be provided. The substantially carbon-free residue may be removed via a line (16). Residence times of the solids will depend on the operating conditions, such as the temperatures, pressures, and specific equipment, and may be adjusted suitably by those skilled in the art. The combustion gas is removed from the bed (14) via the line (3), and is utilized as described previously. Should the total carbon present in the flyash be insufficient for complete drying of the coal, as is normally the case, additional carbon-containing materials, such as coal fines, may be added to the fluidized bed - (14) via a line (17).

In order to determine if the bulk of density of flyash remaining from the gasification of coal might be increased, a sample was heated in a quartz dish for at least one hour in air at 750 °C in a muffle furnace. The sample weighed 23.43 grams and had a volume of about 92 ml, thus having a bulk density of about 0.255 g/ml. After the heat treatment, the sample weighed 17.72 grams, had a volume of about 40 ml., and a bulk density of about 0.443 g/ml. The loss on ignition was 24.38 per cent by weight, based on the weight of the original sample.

While the invention has been illustrated with particular apparatus, those skilled in the art will recognize that, except where indicated as material herein, other equivalent or analogous equipment may be employed. For example, crushing and drying equipment may be separate, and the gasifier need not have the specific configuration shown. Means other than a cyclone may be provided for flyash removal.

Again, as used herein, the term "zone", as employed in the specification and claims, includes, where suitable, the use of segmented equipment operated in series, or the division of one unit into multiple units to improve efficiency or overcome size constraints, etc. For example, multiple gasification reactors may be employed, and only one or more need supply flyash to the fluidization zone described herein, a series of cyclones may be employed, and the quench and cooling operations are preferably carried out in multiple units, utilizing different techniques. Parallel operation of units, is, of course, well within the scope of the invention, and all equipment, such as pumps, valves, control units, etc., has not been illustrated.

Claims

1. A process for the gasification of coal to produce synthesis gas comprising the steps of feeding particulate coal to a gasification zone, and partially oxidizing coal with oxygen in said gasifica-

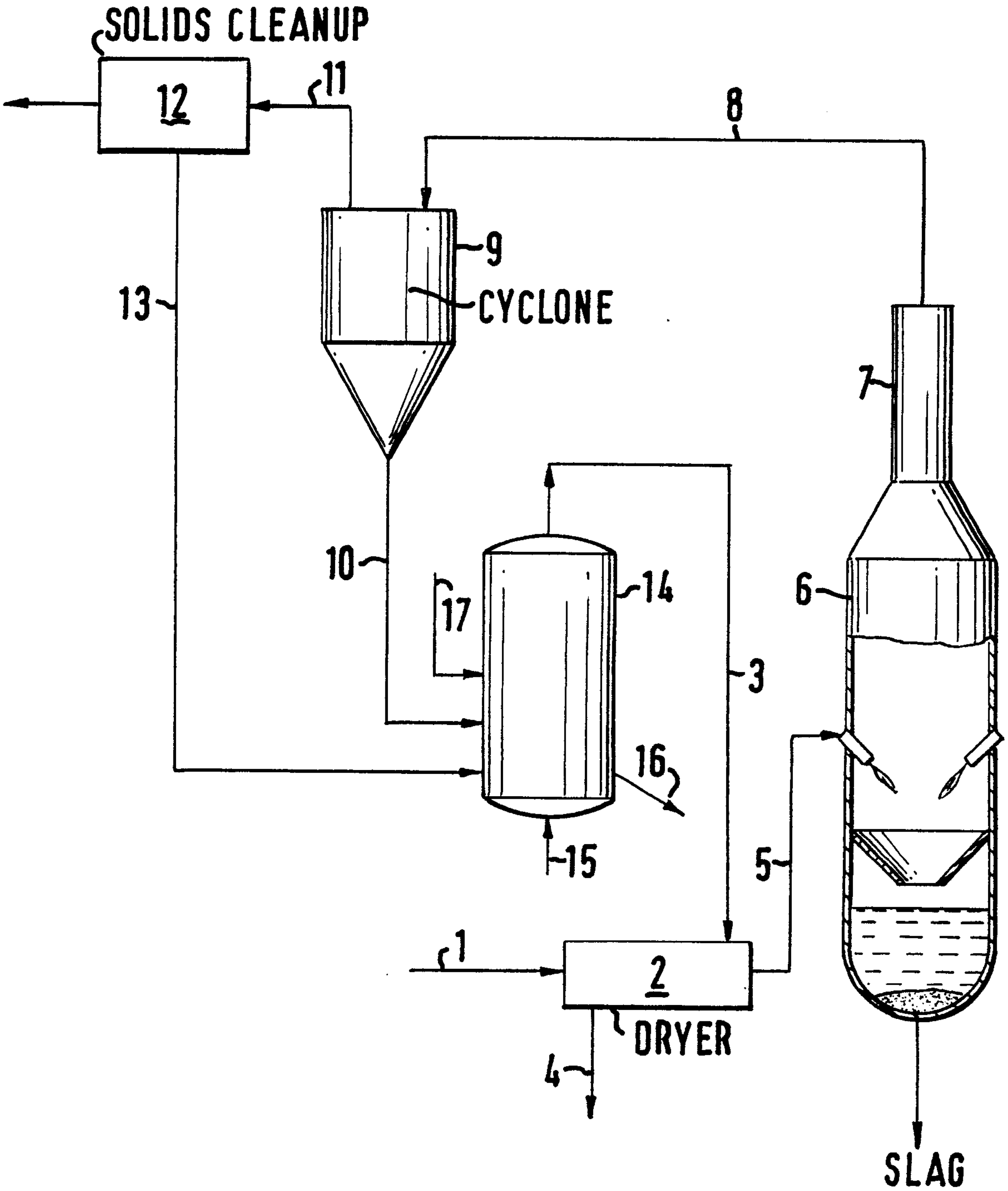
tion zone, producing a stream comprising synthesis gas and flyash;
quenching and cooling the stream, and separating flyash from the stream, producing a separated flyash; characterized by the steps of
fluidizing separated flyash in a fluidized bed in a fluidization zone, and oxidizing said flyash in said fluidized bed with oxygen at a temperature below the fusion temperature of the mineral components of the flyash and the fluidized bed, producing a substantially carbon-free residue and heated gases, and utilizing the heat in said heated gases.

2. The process as claimed in claim 1 characterized in that the heat from the heated gases is used to generate steam.

3. The process as claimed in claim 1 characterized in that the heat is utilized by contacting the heated gases directly with moist coal to remove the moisture from the coal.

4.The process as claimed in claim 1 characterized in that the heat is utilized by contacting the moist coal with a solid or gas heated directly or indirectly by said heated gases.

5. The process as claimed in any one of claims 1-4 comprising the steps of
partially oxidizing coal with oxygen in said gasification zone at a pressure of from 10 atmospheres to 100 atmospheres, the gasification zone outlet temperature being from 1100 °C to 1800 °C; and
quenching and cooling the stream to a temperature of from 650 °C to 145 °C, characterized by the steps of oxidizing said flyash in said fluidized bed with oxygen at a temperature of from 500 °C to 1150 °C, and a pressure of about atmospheric or higher.


SOLIDS CLEANUP
12
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DRYER
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SLAG