

2,944,807

PROCESS FOR SUPPLYING HEAT TO A BED OF FINELY DIVIDED REFRACTORY MATERIAL

Geert G. Kruijer, The Hague, Netherlands, assignor to Shell Oil Company, a corporation of Delaware

No Drawing. Filed Nov. 18, 1957, Ser. No. 696,968

Claims priority, application Netherlands Nov. 20, 1956

6 Claims. (Cl. 263—52)

This invention relates to the transmission of heat by means of finely divided refractory material and is more particularly concerned with a process wherein a gas stream is used to maintain the material in a fluidized state, namely, in a flowing state of a dense turbulent suspension and to heat the material at the same time.

It is known to heat particles of a bed of finely divided material which are fluidized by means of a gas stream by injecting therein and burning a fuel in direct contact therewith. During the combustion of the fuel the particles of the finely divided material should be retained in the fluidized state into which they were brought by the gas stream.

It has been found that the temperature at which the fuel is burnt in the fluidized bed of finely divided refractory material should be kept relatively low on account of the presence of solids which melt or flux at a relatively low temperature during the combustion of the fuel.

A method to overcome this difficulty has been suggested in which the combustion of the fuel and the fluidization of the finely divided material is effected in separate spaces separated from each other by a wall with which both the fuel and the finely divided material come into contact (see British patent specification 665,723).

Methods are also known for the preparation of a gas mixture substantially comprising carbon monoxide and hydrogen by partially burning liquid bituminous material such as heavy tars, heavy distillation residues of mineral oils or natural asphalts, in a bed of a finely divided refractory material, such as silica, which is maintained in the fluidized state of a dense turbulent suspension by an upward gas stream of a mixture of oxygen and steam. If the bitumen contains salts or other compounds of metals such as vanadium, which is usually the case, the powdered, refractory material is contaminated thereby. As the salts or metallic compounds occurring in the starting material generally do not melt at the relatively low temperature at which the partial combustion of the bituminous material is carried out, fresh powdered refractory material may be supplied continuously (see U.S. patent specification 2,605,178).

Tests have shown that in a fluidized bed of finely divided material such as sand, the particles thereof sinter when a fuel containing sodium, vanadium or both metals is burnt in this bed at a temperature in excess of that at which the ash formed during combustion melts or fluxes. Sintering phenomena do not occur in a sand bed at a temperature of 900° C. when the sodium content is lower than 0.03% calculated as sodium oxide. Under the same conditions, they do not occur either when the vanadium content in the sand bed is lower than 0.1%, calculated as vanadium pentoxide. The temperature above which sintering phenomena may occur in a sand bed is approximately 600° C.—900° C. Apparently a layer of molten ash is formed round the particles of the finely divided refractory material, as a result of which there is an interference of the fluidization. Lumps

may even be formed which entirely prevent fluidization of the bed.

It has been found that the addition of an admixture containing certain metals prevents sintering phenomena in the bed, e.g. of sand, even if fuels containing sodium and/or vanadium are burnt in the fluidized bed at a temperature higher than the melting or fluxing temperature of the ash formed during the combustion of these fuels in the absence of the admixture, and even if the bed contains a relatively high content of sodium, vanadium or both.

Accordingly, the invention relates to a process for the supply of heat to a bed finely divided refractory material maintained in a fluidized state by a gas stream by the combustion of a liquid fuel in direct contact with the finely divided refractory material.

According to the invention a liquid fuel containing sodium and/or vanadium is burnt in the bed of finely divided material in the presence of an admixture containing one or more metals of groups II and III of the periodic table.

This admixture may be added to the bed both continuously and discontinuously, either directly or indirectly. A simple method of supply is to spray the admixture in a finely divided form into the bed together with a gas, for instance the air with which the bed is fluidized and the fuel is burnt. However, it is also possible to dissolve or to suspend the admixture in a liquid and to spray the latter into the bed or add it thereto in another way. If the admixture has to be suspended in the liquid, a dispersant or a surface-active substance may also be added thereto. The liquid may be a gas oil or other petroleum hydrocarbon fuel.

The admixture may be a simple substance or a mixture of compounds each of which may contain one or more metals of groups II and III. The admixture may be wholly or partly inorganic or organic and may therefore consist of an inorganic or organic compound, or a mixture of inorganic or organic compounds. The most effective compounds are magnesium compounds such as magnesium oxide or magnesium naphthenate. Other types of suitable compounds are aluminum compounds such as alumina, zinc compounds such as zinc oxide, and calcium compounds such as calcium oxide. The compounds may be either of synthetic or natural origin. Thus dolomite or talc may also be used for the purpose of the invention.

The process according to the invention is illustrated by the following examples. All percentages are percentages by weight unless expressly stated otherwise.

Example I

Sand already containing ash formed by the combustion of a liquid fuel containing sodium and having a sodium content of 0.1%, calculated as sodium oxide, was heated without an admixture for 5 hours at 900° C. The sand sintered. When the sand also contained 0.5% magnesium oxide (MgO), alumina (Al₂O₃) or zinc oxide (ZnO), sintering was prevented.

Example II

Sand already containing ash formed by the combustion of a liquid fuel containing sodium and having a sodium content of 1.06%, calculated as sodium oxide, was heated without an admixture at 900° C. for 5 hours. The sand sintered. Sintering phenomena did not occur, however, when the sand also contained at least 3% magnesium oxide, at least 10% alumina or at least 10% zinc oxide.

Example III

Results similar to those given in Examples I and II were obtained with sand already containing ash formed

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by the combustion of a liquid fuel containing sodium and vanadium. This sand had a vanadium content of 0.312%, calculated as vanadium pentoxide, and a sodium content of 0.069%, calculated as sodium oxide. When heated for 5 hours at a temperature of 900° C. sintering occurred in the sand, but when at least 0.5% magnesium oxide, at least 3% alumina or at least 5% zinc oxide were added to the sand no sintering phenomena were observed.

Example IV

A substance containing sodium was added to a liquid fuel, so that the percentage of sodium in the fuel was 0.4%, calculated as sodium oxide. This fuel containing sodium was burnt in a fluidized sand bed at a temperature of 900 to 950° C. The quantity of liquid supplied daily was 500 kg., while the quantity of admixture consisting of magnesium oxide supplied daily to the sand bed was gradually reduced from 7½ kg. to 2 kg. per diem. Towards the end of the test, which lasted for 760 hours, the sand contained 4.5-5% Mg, calculated as MgO, to slightly more than 3% sodium, calculated as sodium oxide, viz. in the approximate ratio of 1.5:1. Difficulties on account of sintering in the sand bed were not experienced.

Example V

A fuel oil with a specific gravity of 0.96, an ash content of 0.096% and a V_2O_5 content of the ash of 67% was burnt in a fluidized sand bed at a temperature of 900-950° C. The quantity of fuel supplied daily to the sand was 500 kg., while the quantity of admixture consisting of magnesium oxide supplied to the sand bed was gradually reduced from 8 kg. per diem to 2 kg. per diem. Difficulties on account of sintering in the sand bed were not experienced in this test either which lasted longer than 2,000 hours.

Example VI

A fuel oil with a specific gravity of 0.96, an ash content of 0.2%, a V_2O_5 content of the ash of 42% and an Na_2C content of 42% was burnt in a fluidized sand bed at a temperature of 900° C. The quantity of fuel supplied daily to the sand was 500 kg., while the quantity of admixture consisting of magnesium oxide supplied to the sand bed was gradually reduced from 8 kg. per diem to 2 kg. per diem. The test lasted 2,000 hours. There were no difficulties on account of sintering in the sand bed.

Example VII

This experiment was carried out with a sand sample which already contained ash formed by the combustion of a liquid fuel containing sodium. This sample, having a sodium content of 3.0%, calculated as sodium

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oxide, was heated without an additive for 5 hours at 900° C. The sand sintered. When the sand sample also contained 1%, 5%, 10% or 20% by weight of calcium oxide (CaO), sintering was prevented. The degree of sintering decreased as the sand sample contained more calcium oxide.

Example VII

This experiment was carried out with a sand sample which already contained ash formed by the combustion of a liquid fuel containing vanadium and sodium. This sample, having a vanadium content of 0.3%, calculated as vanadium pentoxide, and a sodium content of 0.068%, calculated as sodium oxide, was heated without an additive for 5 hours at 900° C. The sand sintered. When the sand sample also contained 0.1%, 1.0% or 2.0% by weight of calcium oxide (CaO), its degree of sintering was lower in comparison with that of the sample without calcium oxide.

I claim as my invention:

1. In a process for preventing the sintering of a bed of sand particles directly heated by the combustion with air of a liquid hydrocarbon fuel containing amounts of a metal of the group consisting of vanadium and sodium sufficient to cause sintering of said bed, the steps of adding to a bed of sand particles amounts of a material selected from the group consisting of magnesium oxide, aluminum oxide, zinc oxide and calcium oxide to a bed of sand sufficient to prevent the sintering of said bed and passing hot gases resulting from the combustion of the liquid hydrocarbon fuel with the air through the resulting mixed bed at sufficient velocity to cause fluidization of said mixed bed.

2. A process as defined in claim 1 wherein the temperature of the mixed bed is maintained at about 900° C.

3. A process as defined in claim 1 in which the material added to the bed of sand particles is magnesium oxide.

4. A process as defined in claim 1 in which the material added to the bed of sand particles is aluminum oxide.

5. A process as defined in claim 1 in which the material added to the bed of sand particles is zinc oxide.

6. A process as defined in claim 1 in which the material added to the bed of sand particles is calcium oxide.

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