

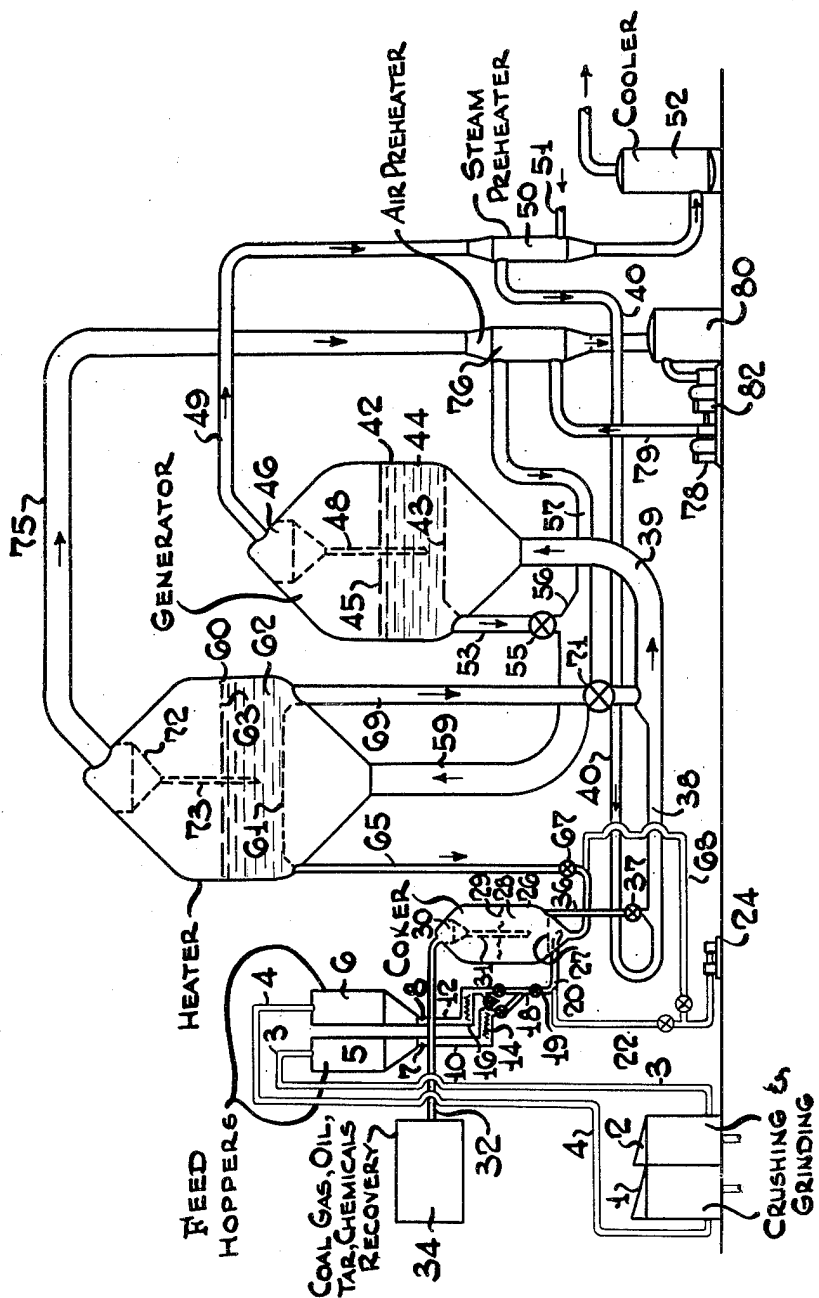
Dec. 23, 1952

F. T. BARR

2,622,973

METHOD FOR GASIFYING SOLID FUELS

Filed Oct. 2, 1945



Frank T. Barr Inventor

By P. J. Whelan Attorney

UNITED STATES PATENT OFFICE

2,622,973

METHOD FOR GASIFYING SOLID FUELS

Frank T. Barr, Summit, N. J., assignor to Standard Oil Development Company, a corporation of Delaware

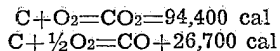
Application October 2, 1945, Serial No. 619,874

9 Claims. (Cl. 48-206)

1

The present invention relates to an improved process for the efficient utilization of solid carbonaceous fuels, such as coal, coke, peat, tar sands, oil shales, and the like, and more specifically to a process for the efficient generation of heat from said solid carbonaceous materials.

In the generation of heat by the combustion of solid fuels with air the principal products of combustion are carbon monoxide, carbon dioxide and water. It is known that most efficient utilization of both the carbon of fuels and the oxygen of the air is obtained in a heater burning solid fuels by conducting the combustion in such a manner as will produce carbon dioxide in preference to carbon monoxide. Formation of carbon monoxide instead of carbon dioxide in the combustion reaction consumes more carbon and requires more oxygen per unit of heat generated, as illustrated by the following equations:



In various processes involving the generation of heat by the combustion of solid carbonaceous material such as the manufacture of fuel gases, for instance water gas, in alternating make and blow periods, air-blown coking operations, and the like, the formation of carbon monoxide in the combustion stages cannot be avoided because hot carbon, which by the nature of these processes must be present in excess, has a strong tendency to reduce carbon dioxide to carbon monoxide by a reaction which consumes part of the heat generated by the original formation of carbon dioxide. These conditions exist no matter whether the combustion processes mentioned are carried out by blowing air or another oxidizing gas through a fixed bed of coarse pieces of solid fuels or the fluid solids technique is applied, that is to say the solid fuel is burned in the form of fine particles maintained by an aerating gas in the form of a dense, turbulent suspension having flow and heat transfer characteristics similar to those of a liquid.

The loss in calorific efficiency caused by the formation of substantial proportions of carbon monoxide in the generation of heat by the combustion of solid fuels is of particular importance in such processes as involve the utilization of the hot solid combustion residue to supply the heat required by various endothermic chemical reactions such as the manufacture of gases containing carbon monoxide and hydrogen, for instance water gas or synthesis gas for the synthetic production of hydrocarbons, the coking and cracking of solid and liquid carbonaceous

2

materials, and the like. Such processes contemplate, for instance, a continuous circulation of solid carbonaceous coking or gasification residue in a fluidized state from the conversion zones to a heater in which heat is generated by combustion of the carbonaceous constituents of the residue, and recirculation of the highly-heated solid fluidized combustion residue to the conversion zones to supply the heat required therein. This technique ordinarily involves circulation from the heater to the conversion zones of quantities of non-conversion materials considerably in excess of the amount of carbon used in the conversions, in order to supply the large amounts of heat required in the conversions. While for this purpose the non-conversion material might be unreacted conversion material, such as coke or coal, a circulation of the required large excess of coke or coal to the heater establishes in the latter conditions most favorable to the formation of carbon monoxide and conducive to the loss of calorific efficiency.

In these cases the ratio of fluidized solids to combustion air circulation rate is fixed by heat transport considerations; the rate of contact of carbon with air can be controlled only by maintaining carbon concentration in the circulating solids stream at the proper level. In the carbonization of coal and the manufacture of water gas, however, losses of solids from the fluid beds are often larger than the amount of ash charged to the system in the fresh coal. This tends to increase the carbon concentration in the fluid beds. For instance, if loss such as suspended material in the discharge gas or the like is twice as much as the amount of ash charged to the system, average concentration of process solids in the ash in the solids circulating stream must build up to about 50% of the total. Such concentration is conducive to CO formation in the combustion zone, as outlined above. One method of avoiding this increase in carbon concentration is to reduce losses to an amount equal to the ash to be rejected. This is often difficult and expensive, and control of the amount of loss is not as close and responsive as would be desired.

It has also been suggested to repress carbon monoxide formation by using thin fuel beds, thereby minimizing the opportunity for secondary reaction of carbon dioxide with additional carbonaceous material. However, this technique, while valuable, is not entirely satisfactory since it involves either incomplete conversion of the oxygen supplied or incomplete repression of the secondary reaction, depending on conditions employed; use of the thin bed also introduces a

number of operating difficulties, such as poor distribution of air flow, uneven charging in fixed bed sets, etc. Furthermore, in the conversion of coal or coke to gas or in the use of coal or coke as heating material, in a fluidized solids operation, the amounts of make- and flue-gas or -vapor are frequently so large that considerable useful process material is lost unless relatively expensive recovery equipment is installed. Thus, a coal with 5% ash may produce sufficient make- and flue-gas to carry out as much as 50% of the input solids instead of the 5% which would be desirable for rejection of the ash content.

The present invention overcomes the aforementioned difficulties and affords various additional advantages. These advantages, the nature of the invention and the manner in which it is carried out will be fully understood from the following description thereof read with reference to the drawing which shows a semi-diagrammatic view of apparatus particularly adapted to carry out the invention.

It is the main object of my invention to provide a process for the efficient generation of heat from solid carbonaceous materials.

Another object of my invention is to provide a process for conducting the combustion of solid carbonaceous materials in such a manner as will produce CO₂ in preference to CO as gaseous combustion product.

A further object of my invention is to promote the combustion of solid carbonaceous materials to CO₂ in preference to CO in a combustion zone operated by the fluid solids technique.

Another object of my invention is to promote the combustion of solid carbonaceous materials to CO₂ in preference to CO in a combustion zone which is operated by the fluid solids technique and from which solid highly-heated residues are used to maintain the reaction in at least one zone for converting solid into fluid fuel and which receives a solids supply from at least one of these conversion zones.

A still further object of my invention is to reduce the blow-out of solid carbonaceous material from combustion zones operated by the fluid solids technique.

Other objects and advantages of my invention will appear hereinafter.

I have found that these objects may be accomplished quite generally when the carbon concentration in the combustion zone is maintained at a sufficiently low level to reduce the formation of carbon monoxide. More specifically, these objects may be accomplished by adding to the solid carbonaceous material subjected to combustion an amount of solid non-combustible material.

In accordance with one embodiment of my invention, the extraneous non-combustible material is inert and comprises such low-cost materials as sand, clay, ordinary furnace ash, and the like. In this operation reduction of carbon concentration in the combustion zone, and thus reduced carbon monoxide formation, is accomplished by increasing the proportion of inert material charged. Conversely, if the carbon concentration in the combustion zone is to be raised, the proportion of inert material charged is decreased. Closely responsive control of carbon concentration and CO formation is thereby achieved.

When applied to conversion zones operated by the fluid solids technique, the extraneous non-combustible material may be fed to the conver-

sion zones together with the solid carbonaceous material or, when a cycle of solid material between several such conversion zones is involved, the non-combustible material may be added at any convenient point to the circulating stream of solids. In any case, the extraneous material introduced not only serves to adjust the carbon concentration in the combustion zones to the proper level but, in addition, reduces to a minimum the content of valuable carbonaceous substances lost or undesirably conveyed to other zones by blow-out. Since the amount of material entrained in gases discharged from fluid contact vessels is strongly influenced by the state of subdivision of the solid, an additional recovery effect is accomplished by careful sizing of the added extraneous material. This is of particular advantage when the carbonaceous material itself does not permit suitable sizing.

In general, satisfactory results are obtained by adding 0.001 lb. to 0.25 lb., preferably 0.10 lb., of preferably coarse extraneous inert material per lb. of solid carbonaceous material in fixed bed operation applying downdraft combustion and about 0.001 lb. to 0.50 lb., preferably 0.10 lb., of extraneous inert material having a particle size varying from 25 to 300 mesh, per lb. of solid carbonaceous material in the case of fluid operation. Carbon concentrations in the combustion zone vary within the approximate limits of 0.1% and 25%, depending upon the proportion of extraneous material added and the characteristics of the carbonaceous materials used. Optimum results with respect to combustion to CO₂ are obtained at carbon concentrations of about 0.5% to 5%.

According to another embodiment of my invention, the solid non-combustible material added comprises or consists of catalytic materials capable of increasing oxidation reaction rates. Such catalytic materials include iron oxide, iron ore, rusty scrap iron, high-iron clays, red mud, spent cracking catalysts and numerous other substances known to promote oxidation reactions. The use of these catalytic materials is of particular advantage for the operation of combustion zones at low temperatures of about 1000° to 1500° F. where the rate of reaction, rather than equilibrium conditions, controls the combustion process. I have found that by the addition of my catalytic materials the rate of the reaction to form CO₂ may be increased to such an extent that combustion is practically completely to CO₂.

The catalytic materials may be added either alone or together with the inert materials mentioned above in various proportions according to the degree of conversion of CO₂ desired, the activity of the catalytic material and the extent of blow-out control desired. Good results are obtained by maintaining, for instance, 10% concentration of iron oxide in the fluid solids mass. This may be added as a fairly coarse material, say 25 to 100 mesh, in order to reduce its rate of loss, but should not, of course, be so coarse as to interfere with satisfactory fluidization.

When the solid carbonaceous raw material contains in itself catalyzing constituents of the type mentioned, the addition of extraneous catalytic material may be limited accordingly, that is, the desired effect may, in part or completely, be accomplished by a proper choice of the raw materials for the process.

A more specific modification of a preferred procedure employing the fluid solids technique and circulation of solids between fluid carbonization,

5

gasification and combustion zones is illustrated diagrammatically in the accompanying drawing. As may be seen in this drawing, a solid carbonaceous fuel and a solid non-combustible material are crushed or pulverized in crushers 1 and 2, respectively, to a finely-divided form, for example, of the order of 50% having a size of less than 100 mesh, though small lumps of up to $\frac{1}{4}$ or $\frac{1}{2}$ inch size may be used. For the purposes of the following description, the carbonaceous material will be referred to as carbonization coal and the non-combustible material as a clay of high iron content, but other materials can be used. The properly sized materials are hoisted or conveyed in any manner known per se through lines 3 and 4 to feed hoppers 5 and 6, respectively. From here they are fed through control valves 7 and 8 and lines 10 and 12 provided with screw feeders 14 and 16 into mixing pipe 18 provided with control valve 19 and then into a dispersing chamber 20. Valves 7 and 8 and screw feeders 14 and 16 are so controlled that a mixture of about 100 parts by weight of carbonization coal and 10 parts by weight of clay is supplied to dispersing chamber 20. It will be understood, however, that this proportion may vary widely, depending on the type of solid materials used. The solid materials may also be mixed in a single crusher of the type shown at 1 and supplied in the proper proportions to a single feed hopper 5 from which the mixture may reach dispersing chamber 20 in the manner outlined above. The mixture of solids in dispersing chamber 20 is dispersed in a stream of "fluidizing" gas, such as superheated steam, nitrogen, combustion gases or the like, supplied through line 22 by compressor 24. The solids in the dispersion are now in the so-called fluidized state in which they are capable of flowing through pipes, valves, etc., similar to a liquid and exhibiting static and dynamic heads. Pressure of the system may be essentially atmospheric, but is preferably kept within the approximate limits of 25 to 75 lbs. per sq. in. gauge to save compression on the gas manufactured. Higher pressures may be used as feasibility and economy of construction techniques allow. The fluidized mixed solids enter the conical lower portion of the enlarged cylindrical carbonization chamber 26 and pass through a distributing grid 27 into the carbonization zone 28 where the carbonization coal is subjected in the form of a dense, ebullient, fluidized mass forming a well-defined upper lever 29 to coking temperatures of between about 1000° and 2000° F., preferably around 1200° F. A pressure of about 40 lbs. per sq. in. gauge will ordinarily be required to provide water gas at 25 lbs. The heat required for the carbonization reaction is supplied by highly-heated solids recirculated from combustion chamber 60 through line 65, as will appear more clearly hereinafter. Product vapors containing small amounts of solids fines are passed through a gas-solids separator 30 which may be a centrifugal or electrical type precipitator, and through line 32 to any conventional system 34 for the recovery of such volatile carbonization products as coal gas, oil, tar, chemicals, etc. Solids separated in 30 are recycled through pipe 31 to the dense phase in 28.

A fluidized mixture of coke and clay is withdrawn from carbonization chamber 26 at a point above grid 27 through pipe 36. This mixture, which may now consist of about 75 parts by weight of coke and 300 parts by weight of clay plus ash due to the loss of volatile products and

6

the addition of inert combustion residue from zone 60, is then passed through control valve 37 to dispersing chamber 38 where it is taken up by highly-heated steam supplied from steam preheater 50 through line 40. From dispersing chamber 38 the fluidized mixture is passed through line 39 into the lower conical portion of a cylindrical gas generator 42 provided with distributing grid 43 in an arrangement similar to that of carbonization chamber 26. The gas generator is maintained at a temperature of between about 1400° and 2400° F., preferably about 1600° to 1800° F., at a pressure of about 30 lbs. per sq. in. gauge to permit the water gas reaction to take place between the steam and the carbon of the fluidized solids mixture maintained in a dense, ebullient mass 44 forming a level 45 in generator 42. The heat required for the water gas reaction is supplied by highly-heated solid residues recirculated from combustion zone 60 through line 69 at the desired temperature, as will appear more clearly hereinafter.

A gas consisting mainly of CO and H₂ is taken overhead from generator 42 and freed in gas-solids separator 46 from entrained fines which may be returned through pipe 48 to the dense phase 44. It should be noted, however, that as a result of the high concentration of non-combustible solids which I maintain in generator 42 the carbon content of the fines reaching separator 46 is negligible and these fines may either be removed from the system or added at any other point to the circulating solids without incurring significant loss of process materials. The gas leaves separator 46 through line 49 and passes through steam preheater 50 in heat exchange with steam admitted through line 51, to a cooling system 52 from which it may be withdrawn for any desired use as a fuel gas, for hydrocarbon synthesis, and others. Tower 52 may also be a scrubber for removal of any traces of suspended solids not separated in 46. The steam preheated in 50 passes through line 40 to dispersing chamber 38, as outlined above.

The solid gasification residue is withdrawn through vertical pipe 53 from a point above grid 43 and passed through control valve 55 to dispersing chamber 56 where it is taken up by hot air, oxygen or other oxidizing gas supplied through line 57, as will appear more clearly below. The mixture of solid gasification residue and oxidizing gas passes at about the temperature of the gasification zone through line 59 into the conical lower portion of the cylindrical combustion chamber 60 which has a construction similar to that of chambers 26 and 42 and serves as a heater for zones 26 and 42. The solids-gas mixture enters the cylindrical portion of heater 60 through a distributing grid 61 and forms thereabove a fluidized, dense, ebullient phase 62 having a well-defined upper level 63.

The carbon concentration of the solids supplied to heater 60 has dropped below 5% and may be as low as 0.1 to 1%, as a result of the gasification reaction in 42 and the recycle of non-combustible solids from heater 60 through line 69. At these low carbon concentrations the danger of CO₂ being reduced to CO by excess carbon is practically non-existing and combustion to CO₂ takes place at a most efficient rate. This effect is further enhanced by the catalytic activity of the iron oxide constituents of the clay with the result that practically complete combustion to CO₂ is accomplished in heater 60 with the theoretical or a

moderate excess of O₂ which may amount to about 5 to 10% of theoretical.

The temperature for zone 62 is maintained between 1600° and 2500° F., preferably at about 1800° to 1900° F., at a pressure of about 30 lbs. per sq. in. gauge. Solid combustion residues, now consisting essentially of clay and coal ash, are returned from a point above grid 61 at about the temperature of the combustion zone 62 through vertical pipe 65 provided with control valve 67 to the lower conical portion of carbonization chamber 26 in amounts sufficient to supply the heat required for carbonization. This amount may vary between 70% and 1500% of the solids charged through line 20, depending on the temperature difference between combustion zone 62 and carbonization zone 28, good results being in general obtained at a solids recycle ratio of about 150% to 300%. A fluidizing gas may be supplied by compressor 24 through line 68 to facilitate the transport of the solids through pipe 65.

Another considerably larger amount of solid combustion residue is withdrawn from above grid 61 through vertical pipe 69 provided with control valve 71 to be returned through line 39 to gas generator 42 to supply the heat required in gasification zone 44. In accordance with the considerably higher temperature and the normally large dimensions of gas generator 42, the amount of solids recycled to 42 is a high multiple of that recycled to carbonization chamber 26 and may vary between the approximate limits of 30 to 300 times the carbon content of the solids charged through line 36 or may be about 20 to 100 times the amount of solids returned through line 65.

Flue gases are withdrawn overhead from heater 60 through gas-solids separator 72 where they are freed from solid fines. The fines may be returned through vertical pipe 73 to the dense phase 62 or withdrawn from the system. Hot flue gas substantially free of solids is passed through line 74 to air preheater 76 where it preheats the air supplied by compressor 78 through line 79. The preheated air passes through line 57 into dispersing chamber 56, as shown above. The flue gas, if desired after further dust removal in 80, may then be applied to any desired use, such as the operation of a flue gas turbine 82, or discarded.

The addition of non-combustible solids, in accordance with my invention, to systems of the type described in the above example, which involve the use of fluidized solids beds, has particular advantages during the starting period when it is necessary to establish a fluid bed from the materials charged. If coal or coke only were charged in the example mentioned above, the amount of ash remaining after combustion of the fuel in an excess of air (which will ordinarily be used in order to avoid temperature building up too high before the process operation is started) would in many cases be less than the amount of material suspended in the flue gas and thus lost to the system. In this case it is of particular advantage for the establishment of the fluid bed if extraneous non-combustible material is charged to the system as described above.

It will be understood that my invention is applicable to any fluidized solids operation whether the valuable substance charged is raw process material, catalyst, or otherwise. It is merely necessary that the added material does not interfere to an undesirable extent with the process

operations. Its addition in many cases will have further advantages. For instance, the inert material, if chosen for its high fusion point, may assist in preventing clinkering of the ash in the coke. Also, in the system described above any one or two of the conversion chambers may be omitted; thus the heater 60 may be omitted and chambers 26 and 42 be operated on the basis of the make- and blow-principle involving alternating combustion and production cycles, both of which will be benefitted either by the low carbon concentration or the reduced blow-out, or both, resulting from the addition of my extraneous non-combustible material. Similarly, the invention may be applied to full advantage in the operation of pure carbonization or pure gasification reactions with separate heater or on a make-and-blow-basis. It should also be understood that whenever the gasification of solid carbonaceous material is mentioned herein, this is meant to comprise the production of any gas of practical heat value, including water gas, producer gas, etc. My invention is likewise applicable to any type of fixed bed operation requiring an efficient combustion of solid carbonaceous material, particularly in combination with downdraft combustion.

My invention will be further illustrated by the following specific examples comparing the materials and equipment requirements for supplying 1,000,000 B. t. u.'s per hour of heat to circulating fluid solids by combustion of carbon in air, flue gas leaving the heater at 2000° F., air being charged at 1000° F. and fuel at 100° F.

	Example I— Conventional Operation	Example II— Improved Operation
Proportion of Carbon converted to CO ₂percent.....	50	100
Proportion of Carbon converted to CO.....percent.....	50	0
Pounds of Carbon required per hr.	145	90
C. F. M. Air Compressed	265	225
C. F. S. Flue Gas Handled (30 lbs. per sq. in. gauge)	7.7	5.9
Heater Vessel Diameter (Ft.)	2.6	2.2
Air Preheater Duty (B.t.u. per hr.).....	280,000	230,000

In general, the ratio of increase of requirements shown above for incomplete conversion of CO₂ will be followed for all equipment in the heater circuit and is of significant magnitude. For combustion to still smaller proportions of CO₂, material and equipment requirements rise even more rapidly.

It should be understood that for the purpose of starting up the process illustrated by the drawing the feed gases supplied by compressors 24 and 78, the steam supplied through line 51 and/or the solids feed may be preheated to the desired temperatures by any conventional heating means (not shown).

While the foregoing description and exemplary operations have served to illustrate specific applications and results of my invention, other modifications obvious to those skilled in the art are within the scope of my invention. Only such limitations should be imposed on my invention as are indicated in the appended claims.

I claim:

1. The process of converting solid carbonaceous materials into valuable volatile fuels by means of heat generated by partial combustion of said carbonaceous materials in a fluidized bed of solids, which comprises passing finely-divided solid carbonaceous material through a circuit compris-

ing at least two conversion zones, maintaining said material as a mass of fluidized solids in said conversion zones at elevated temperatures suitable for the production of volatile conversion products, maintaining substantial temperature gradients between said conversion zones, subjecting a portion of said material to combustion in at least one of said conversion zones at a temperature of about 1600°-2500° F., subjecting said material to a gasification reaction in one of said conversion zones, supplying heat required in said conversion zone wherein the gasification reaction is effected by circulating finely-divided solids highly heated by the heat generated by said combustion thereto adding fluidizable extraneous solid particles produced outside said combustion-conversion zone and consisting of solid non-combustible materials to said combustion conversion zone to maintain the concentration of carbon therein at 0.1-1% of the fluidized solids in said combustion conversion zone and circulating said non-combustible materials together with said highly heated solids through said conversion zones.

2. The process of claim 1 wherein the conversion of the solid carbonaceous material into volatile fuels is carried out in a fluidized bed of solids under an elevated pressure substantially exceeding the pseudo-hydrostatic pressure of said bed.

3. The process as claimed in claim 1 in which said non-combustible materials comprise substances promoting the combustion reaction.

4. The process of generating heat by the combustion of solid carbonaceous materials with oxidizing gases which comprises contacting said gases and solid materials within a zone of combustion for a time sufficient substantially completely to convert the oxygen content of said gases into carbon oxides and adding extraneous solid particles produced outside said combustion zone and consisting of non-combustible solid materials to said carbonaceous solids in amounts sufficient to reduce the concentration of carbon in the zone of combustion to 0.1-1% of the solids mixture obtained.

5. The process as claimed in claim 4 in which said non-combustible materials comprise substances promoting the combustion reaction.

6. The process of generating heat by the combustion of solid carbonaceous materials with oxidizing gases which comprises maintaining the carbonaceous solids in the zone of combustion in the form of a fluidized, dense, ebullient mass, contacting said gases with said bed for a time

sufficient substantially completely to convert the oxygen content of said gases into carbon oxides and adding extraneous fluidizable solid particles produced outside said combustion zone and consisting of non-combustible, fluidizable solid materials to said bed in amounts sufficient to reduce the concentration of carbon in the zone of combustion to 0.1-1% of the fluidized solids.

7. The process as claimed in claim 6 in which said non-combustible material comprises substances promoting the combustion reaction.

8. The process as claimed in claim 6 in which said non-combustible material has a particle size suitable to reduce blow-out of solids from said mass.

9. The process of generating heat by the combustion of solid carbonaceous materials with oxidizing gases which comprises maintaining the carbonaceous solids in the zone of combustion at a temperature of about 1600°-2500° F. in the form of a fluidized, dense, ebullient mass, contacting said gases with said bed for a time sufficient substantially completely to convert the oxygen content of said gases into carbon oxides and adding extraneous fluidizable solid particles produced outside said combustion zone and consisting of non-combustible solid materials to said bed in amounts sufficient to reduce the concentration of carbon in the zone of combustion to 0.1-1% of the fluidized solids.

FRANK T. BARR.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,747,676	Kerr -----	Feb. 18, 1930
1,840,649	Winkler et al. -----	Jan. 12, 1932
1,857,799	Winkler -----	May 10, 1932
1,947,460	Contant -----	Feb. 20, 1934
1,977,684	Lucke -----	Oct. 23, 1934
2,436,938	Scharmann et al. -----	Mar. 2, 1948
2,446,221	Ferguson -----	Aug. 3, 1948
2,480,670	Peck -----	Aug. 30, 1949
2,482,187	Johnson -----	Sept. 20, 1949
2,509,866	Hemminger -----	May 30, 1950

FOREIGN PATENTS

Number	Country	Date
632,466	France -----	Oct. 10, 1927

OTHER REFERENCES

"Industrial and Engineering Chemistry," vol. 28, pp. 564-567, (1936).