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(54) **Method for preventing buildup of ash in a steam-gasification reactor.**

(57) A method for producing a combustible gas by gasifying coke containing between about 0.1 to about 5 weight % inorganic ash with steam and preventing ash buildup in excess of 30 weight % in the gasification reactor includes entraining the solids (coke and inorganic ash) in the gas product, separating the larger particles of such solids from the smaller and recycling only the larger particles to the reactor bed. It is found that these larger particles (say larger than about 200 US mesh) include substantially all the unreacted coke particles. An overall gasification efficiency of 90% by weight of the carbon in the coke is thereby achieved.

EP 0 019 487 A1

METHOD FOR PREVENTING THE BUILDUP OF ASH IN A STEAM-GASIFICATION REACTOR

It is known that various types of coke can be gasified to produce a combustible gas by the reaction between the carbon contained in the coke and steam. Sometimes the gasification reaction is conducted in the presence of a gasification catalyst such as an alkali metal salt in order to, inter alia, reduce the steam gasification temperature. Depending upon the temperature and pressures used the combustible gas produced from the gasification of carbon with steam will vary but in general the combustible gases will contain predominantly hydrogen, carbon dioxide, carbon monoxide and methane. Normally excess steam is utilized and the steam will be removed from the combustible gas by, for example, condensing the steam in any of a number of conventional ways.

One of the most desirable ways of gasifying coke with steam is in a fluidized bed. However, when utilizing a fluidized bed the combustible gas produced contains entrained solids which include inorganic ash from the coke as well as partially reacted coke particles. Inasmuch as processes involving the gasification of carbon with steam have gasification rates less than 50 weight % per hour based on the weight of the carbon in the reactor it is necessary to remove and recycle to the gasification reactor the entrained solid particles in the combustible gas if economical conversion rates of the carbon to combustible gas are to be achieved.

However, all coke contains inorganic elements (hereinafter inorganic ash) in varying amounts, for example, 0.1 weight % to 5 weight %, and since this ash is entrained in the combustible gas the recycling of the solid particles in the combustible gas causes ash buildup in the fluidized gasification reactor. After a period of time the inorganic ash will concentrate in the reactor to a sufficient level (for example in excess of 30 weight % of the solid material in the reactor may be inorganic ash) and slagging will occur. In addition, when the ash builds up to such excessive amounts in the gasification reactor the ash reacts with the alkali metal salt gasification catalyst, if such is used, rendering the catalyst inactive. Therefore, when reacting steam with carbon in a fluidized bed reactor it is necessary to purge a stream of partially gasified material from the reactor in an amount sufficient to prevent accumulation of the inorganic ash. This has many significant drawbacks; for example, it removes coke and catalyst from the reactor which reduces the overall efficiency of the process and makes the process more expensive because of the loss of catalyst.

Furthermore, the prior art generally teaches removal of ash by combusting and slagging a portion of material removed from the gasification reactor. The prior art also teaches the recombusting of the rejected solids to reduce the loss of thermal efficiency which would otherwise result if these carbon-containing particles are discarded without combustion.

The prior art does not teach any criteria to maximize the content of ash in the reject streams and to thereby minimiz the agglomeration and solids separation in the reactor. In fact, the recombustion and slagging disclosed by the prior art to prevent high losses of thermal efficiency implies that the techniques therein of separation of the finer and coarser solids are insufficient to concentrate the ash content of the fines to a level whereby the combustion and slagging of the fines would not be required. That is, as long as a separate combustion step is used to burn carbon and return that heat to the reactor almost any proportion of solids could be withdrawn and burned.

From the foregoing it is readily apparent that it would be very desirable if a process could be developed wherein coke is gasified with steam in a gasification reactor to convert at least about 90 weight % of the carbon to a combustible gas without having ash buildup in the gasification reactor.

It is therefore an object of the present invention to prevent ash buildup in a fluidized bed reactor during the steam gasification of carbon while allowing an overall conversion of approximately at least 90 weight % of the carbon to a combustible gas.

The present invention operates a gasification reactor under a specific set of conditions which separate and recycle only a certain portion of the entrained solids entrained in the combustible gas produced by the gasification of coke with steam. In general, depending upon the amount of inorganic ash in the starting coke, from about 85 weight % to 99 weight % of the coarser solid particles entrained in the combustible gas are removed therefrom and recycled for further gasification in the fluidized bed within the gasification reactor. Surprisingly, we have discovered that the coarser particles entrained in the combustible gas are substantially partially gasified coke whereas the finer particles are heavily concentrated with inorganic ash, which is substantially all of the inorganic ash formed in the reactor. This was very surprising to me since we initially expected that converting 90 weight % of the carbon in the coke to a combustible gas would inevitably lead to ash buildup in the bed within the reactor. However, no ash buildup was apparent if only the coarser particles of entrained solids were recycled to the reactor.

In order to more fully illustrate the invention certain preferred embodiments will be described below in which all temperatures are in degrees centigrade all pressures are recited in kilograms per square centimetre guage kg/cm^2 and all mesh are in US standard size unless expressly stated otherwise.

The method of the present invention can be described, in general, as follows. Coke is introduced into a gasification reactor and a steam-containing gas is injected into the bottom of the reactor at a sufficient velocity to form a fluidized bed. The carbon contained in the coke is gasified by the reaction of the carbon with the steam, thereby producing a combustible gas. The coke containing between about 0.1 to about 5% by weight of inorganic matter. Because the velocity of the steam is sufficient to fluidize the coke, the combustible gas produced in the reactor contains entrained solids of inorganic ash originally contained in the coke as well as partially reacted coke particles. The entrainment rate in the reactor is maintained such that the rate of the solids leaving the bed is from 30 weight % to 50 weight % of the raw coke feed rate. From about 80 weight % to about 99 weight % of the larger or coarser particle size solids entrained within said combustible gas are separated with conventional separation means e.g. a cyclone (or cyclones) or venturi scrubber(s). The separated particles are then recycled to the reactor along with enough coke to allow overall about 90 weight % of the carbon in the coke to be gasified. The nonrecycled particles contain substantially all of the inorganic ash and their discarding thereby prevents any inorganic ash buildup in the reactor from exceeding about 1 weight % to 30 weight % of the total amount of solids in the reactor. Temperature and pressures do not appear to be critical, with the temperature needing to be kept only at a level such that the carbon is gasified.

As an alternative and equivalent description of the method of the present invention, the fluidized bed may comprise particles generally larger than 200 mesh. The gasification rate is then controlled to produce a combustible gas containing particles of varying size of the inorganic ash and coke, with from between 30 weight % and 50 weight % of the entrained particles being smaller than 200 mesh. At least 90% of the entrained particles larger than 200 mesh are then separated and recycled along with sufficient coke to gasify at least 90 weight % of the carbon, as before. The nonrecycled particles will then contain an ash concentration of at least ten times that of the feed coke, which will ensure an ash concentration in the reactor of from 1 weight % to 30 weight % of the total solids in the reactor.

The alternative and equivalent sets of reactor operating conditions produce the unexpected results of a very high concentration difference between ash in the reject material relative to the solids in the fluidized bed. These operating conditions are equivalent because the fluidized bed can be defined in terms of the weight percent of the entrainment, recycle, and reject streams, or by particle size analysis.

Furthermore, the particle size criteria are mathematically derivable from the other set of criteria because of such factors as the terminal settling velocities involved in the gasification process when the reactor is operated under the first set of criteria. Therefore, for a fluidized bed of particles generally larger than 200 mesh with an entrainment stream rate of 30 weight % to 50 weight % relative to the coke feed rate, a recycle stream of at least 80 weight % relative to the entrainment stream, and superficial fluidization velocities of the order of 0.6 metres per second, the terminal settling velocities for the particles will produce an entrainment stream containing particles of 30 weight % to 50 weight % smaller than 200 mesh, and a recycle stream of at least 90% of the particles greater than 200 mesh. Accordingly, the operation of the reactor under the first set of criteria for fluidized beds containing particles generally larger than 200 mesh produces the definition of the second set of operation criteria.

The gasification rate of the method may typically be in the range of 5 to 25 or 30 weight %/per hr, but this rate is not critical. The gasification rate, however, is interrelated with the entrainment rate, and a practical system will have its gasification rate within that range.

In the method of the present invention any type of coke may be used which contains from about 0.1 weight % to about 5 weight % inorganic constituents (i.e. inorganic ash). Coke which may be used to good effect in this invention is coke derived from coal as well as petroleum coke, either fluid or delayed. Generally speaking, petroleum coke will contain from about 0.5 weight % to as high as 3 or 4 weight % inorganic constituents but more generally such coke will contain from about 0.5 weight % to 1 or 2 weight % inorganic constituents, when, using the method of the invention, the buildup in the bed may be kept down to about 5%. Such inorganic constituents include, nickel, vanadium, calcium, silicon, aluminum, etc.

The reason that the coke used in the present invention will contain between 0.1 weight % to 5 weight % inorganic ash is because if the coke contains less than 0.1 weight % ash there is, in general, no problem with ash buildup in the reactor whereas if the coke contains more than about 5 weight % inorganic ash, it is very difficult to recycle the partially unreacted coke in amounts sufficient to gasify 90 weight % of the carbon in the coke and, at the same time, prevent ash buildup.

The particle size of the coke is also relatively unimportant provided that the coke can be readily fluidized. In general, it is preferred if the coke introduced to the reactor have a particle size range above about 100 or 200 mesh, up to about 2.5cm. Because of its particle size fluid petroleum coke is ideally suited for the fluidized gasification reaction since it is sufficiently fine to be easily fluidized.

If another type of coke, such as delayed coke, is utilized in the present invention it should be reduced to a particle size where it is readily fluidized, e.g. from about 100 or 200 mesh to about 2.5 cm.

The temperatures and pressures at which the gasification reaction is conducted are known in the art. The temperature will vary depending upon the particular gasification rate desired and also depending upon whether a gasification catalyst is used. In general, the temperature may vary anywhere from 535°C to 1075°C with a more preferred temperature being between about 535°C and 815°C and even a more preferred temperature between about 645°C and about 760°C, the latter temperatures being primarily used when a gasification catalyst is also used.

The pressures at which the gasification reaction is conducted may vary widely, which, in general, will be at least 0.7 kg/cm^2 and, more often, at least 1.4 kg/cm^2. There is no maximum pressure. In general, the pressures used will vary from 0.7 kg/cm^2 to 70 or 140 kg/cm^2 with the preferred pressure range being between 1.4 and 14 kg/cm^2 and the more preferred range being between 1.4 and 7 kg/cm^2.

It is not necessary to use a gasification catalyst in the process of the present invention; however, it is preferred to use such a catalyst because it lowers the temperature at which the reaction is operable, in general, such temperatures ranging from 535°C to 815°C.

Gasification catalysts are generally well known in the art and therefore no detailed description thereof will be given herein. Exemplary of gasification catalysts useful in the present invention are the alkali metal salts such as the carbonate salts, hydroxide salts, oxide salts, sulfate salts, and sulfide salts. The preferred alkali metals are potassium and sodium and the most preferred catalysts are potassium carbonate and sodium carbonate.

The concentration of the catalyst in the reactor may range from about 1 weight % to about 50 weight %, based on the combined weight of the coke and catalyst. The preferred concentration is from about 4 or 5 weight % to about 30 or 40 weight %.

The particle size of the catalyst should be such that it is readily fluidized but not less than the particle size of the coke in the reactor. In general, the particle size would range from about 100 to 200 mesh upwards to about 2.5 cm; in any case the particle size distribution in the reactor should be such that at least 90% is of a particle size greater than 100 mesh, more preferably greater than 200 mesh.

The amount of steam used in the gasification reaction is not important and in general will range from about 0.1 to about 1 part per weight of steam per hour per one part by weight of carbon in the reactor. The more preferred range is between 0.2 and about 0.6 parts by weight.

The temperature in the reactor may be maintained in a number of ways. For example, superheated steam may be utilized to maintain the temperature, the reactor may be heated by indirect means or, preferably, the temperature in the reactor is maintained by introducing oxygen into the reactor to oxidize a portion of the carbon in the coke thereby raising the temperature since the reaction is exothermic, the amount of oxygen introduced being sufficient to maintain the temperature at the desired level. The oxygen may be either inserted separate from the steam or as a mixture with the steam and preferably in the bottom of the reactor in order to fluidize the coke and, if present, the catalyst to form a fluidized mixture thereof.

Similarly, the catalyst may be added to the reactor in any convenient manner. The catalyst may be added to the coke prior to its introduction into the reactor, either as a solid or as a solution, and after introduction into the reactor there will be formed a fluidized mixture of coke and catalyst. The catalyst may also be introduced into the reactor separately from the coke.

In order to obtain gasification of at least about 90 weight % of the carbon contained in the coke and in order to prevent ash buildup it is absolutely necessary to recycle only the coarser particles of the solid particles entrained in the combustion gas. We have unexpectedly found that ash buildup will not exceed from

1 weight % to 30 weight % of the total amount of solids in the reactor and a sufficient amount of partically reacted coke will be recycled to the reactor to convert 90% of the carbon to a combustible gas if the entrainment rate of 30 weight % to 50 weight % relative to the coke feed rate is maintained and if between about 80 weight % and about 99 weight % of the larger particle size solids entrained in the combustible gas are recycled to the reactor. The nonrecycled particle solids will contain substantially all of the inorganic ash initially present in the solids entrained in the combustible gas. More preferably, 90 to 97 or 98 weight % of the coarser particles entrained within the combustible gas should be separated from the finer particles entrained in the combustible gas and the coarser particles recycled to the reactor. These conditions will result in: (a) the ash buildup in the reactor being between 3 weight % and 20 weight % of the total solids in the reactor; (b) the concentrations of the inorganic ash in the nonrecycled particles being from 10 to 15 times greater than that of the feed coke; and (c) a carbon gasification efficiency of between 95% and 97%.

The means for separating the coarser particle sized particles from the finer solid particles entrained in the combustible gas is not important and may be any means well known in the art. For example, the coarser particles may be separated from the finer particles by particulate separation devices such as cyclones in a quantity of at least about 85 or 90 weight % of the total particles entrained in the combustible gas. If desired, the finer particles, which are heavily concentrated with inorganic ash, may be removed by a scrubber of the venturi-type which contacts the gas with a recirculating water stream which scrubs the fines from the gas.

In the preferred exemplary embodiments given below two cyclones were used wherein about 90 to about 95 weight % of the coarser particles were separated from the combustible gas.

In the preferred exemplary embodiments a gasification reactor was used which was 10 metres long and had an internal diameter of about 25 cm; however, it is emphasized that the particular type of reactor used is not important to obtain the desired results.

A mixture of steam and oxygen was injected into the reactor below the point where the fluid petroleum coke and catalyst are introduced into the reactor, the velocity at which the steam and oxygen were injected being sufficient to fluidize the coke and catalyst. Generally, the fluidized bed will have a fluidization velocity of between about 0.3 m per second to about 1 or 1.5 m per second. In the preferred exemplary embodiments the pressure in the reactor was between about 1.4 kg/cm^2 and 5.6 kg/cm^2 although higher pressures may be utilized without detrimental effect.

Also in the preferred exemplary embodiments a mixture of fluid coke containing approximately 0.5 weight % inorganic ash was used. This fluid coke was mixed with a potassium carbonate gasification catalyst, the concentration of catalyst in the reactor was about 4 to 8 weight % and was fed near the bottom of the reactor by a screw conveyor.

Example 1

This example was conducted for 30 days and the units given below were the average for the 30 day period.

A stream of fluid petroleum coke was fed to the fluidized bed reactor, described above, containing a fluidized bed of partially gasified petroleum coke and about 5 weight % solid potassium carbonate catalyst, the temperature of the fluidized bed being between about 730 to 760°C and a superficial fluidization velocity of 0.48 m per second. The reactor contained about 182 kg of the fluidized mixture of fluid petroleum coke and catalyst and the bed of this mixture was fluidized to a bed depth of about 5 metres. Coke containing about 0.6 weight % of potassium carbonate was fed to the reactor at a rate of about 23 kg per hour, the steam rate being about 50 kg per hour. The amount of oxygen to maintain the temperature at between about 730°C to about 760°C was about 23 kg per hour. The carbon gasification rate was about 12 weight % per hour.

It was found that about 95 weight % percent of the particles in the reactor were greater than about 200 mesh and between 30 weight % and 50 weight % of the particles entrained in the combustible gas were finer than about 200 mesh, the particles being entrained at a rate of about 50 weight % of the raw fluid coke feed rate.

The combustible gas containing the entrained solids was passed through two serially staged cyclones for particle removal. Approximately 95 weight % of the coarser entrained solids were removed by the cyclones and returned to the fluidized gasification zone. The remaining 5% of the particles were removed from the combustible gas by the wet venturi scrubber and were analyzed. It was found that the fines contained approximately 6.7 weight % of inorganic ash whereas the reactor contained approximately 3.2 weight % of inorganic ash.

This particular example was conducted over a period of 30 days and it was found that the ash buildup in the gasification zone remained constant at about 3.2 weight % and the amount of carbon converted to gas was about 95 weight %.

Example 2

The foregoing example was repeated changing the temperature (about 645^{o}C), and changing the concentration of catalyst so that the catalyst was about 40 weight % of the mixture of coke and catalyst in the reactor. Under such conditions it was found that recycling approximately 90 to 95 weight % of the of the coarser particles entrained in the combustible gas prevented ash buildup in excess of 5 % by weight.

Example 3

In this example, sodium carbonate was used as the catalyst and under conditions similar to Example 1 substantially identical results were obtained.

CLAIMS:

1. A continuous method for producing a combustible gas from coke by fluidizing said coke with steam-containing gas to form a fluidized bed and to gasify the carbon contained in said coke, thereby producing a combustible gas containing entrained solid particles of varying size of inorganic ash and of coke, characterized in:

(a) maintaining an entrainment rate of the solids leaving the fluidized bed of from 30 weight % to 50 weight % of the coke feed rate;

(b) passing the combustible gas through a means for separating the larger entrained solid particles from it; and

(c) recycling only the larger separated solids to said reactor, the nonrecycled particles containing substantially all the inorganic ash, to prevent inorganic ash buildup in said reactor from exceeding about 30 weight % based on the total amount of solids in said reactor.

2. A continuous method for producing a combustible gas from coke containing between about 0.1 weight % to about 5 weight % inorganic ash by introducing coke and a steam containing gas into a gasification reactor; fluidizing bed of particles larger than about 200 mesh; and gasifying the carbon contained in said coke with said steam containing gas, characterized by:

(a) controlling said gasification of said carbon to produce a combustible gas containing entrained solid particles of varying size of said inorganic ash and said coke, with from between 30 weight % and 50 weight % of said entrained particles being smaller than 200 mesh;

(b) separating at least 90% of the entrained particles larger than 200 mesh from said combustible gas;

(c) recycling substantially all of said separated particles larger than 200 mesh to said reactor, the non-recycled particles containing an ash concentration of at least ten times that in said feed coke and ensuring an ash concentration in said reactor of from 1 weight % to 30 weight % based upon the total amount of solids in said reactor; and

(d) recycling a sufficient amount of coke to said reactor to gasify at least about 90 weight % of said carbon in said coke based upon the total weight of said coke introduced into said reactor.

3. A method according to claims 1 or 2 wherein said separating means removes between about 95 weight % and 97 weight % of said larger entrained solids from said gas, said separated particles then being recycled to said reactor, whereby said ash buildup in said reactor is between 3 weight % and 20 weight % based on the total amount of solids in said reactor, the concentration of said inorganic ash in said nonrecycled particles is from 10 to 15 times greater than that of the feed coke, and said carbon

gasification is between 95% to 97% relative to said weight of said coke introduced into said reactor.

4. A method according to claim 1, claim 2 or claim 3 wherein an alkali metal salt gasification catalyst is present in the bed.

5. A method according to claim 4 wherein the catalyst is a member selected from the group consisting of potassium carbonate, sodium carbonate and mixtures thereof.

6. A method according to claim 4 or claim 5 wherein the concentration of catalyst is between about 4 weight % and 40 weight %.

7. A method according to any one of the preceding claims wherein the temperature within said reactor is between about 535°C and 815°C.

8. A method according to any one of the preceding claims wherein said coke contains between about 0.5 weight % and 1 weight % inorganic ash whereby inorganic ash build-up in said reactor is prevented from exceeding about 5 weight % based on the total of solids in the bed.

9. A method according to any one of the preceding claims wherein the superficial fluidization velocity in said reactor is between about 0.3 m per second and 1 m per second.

10. A method according to any one of the preceding claims wherein the carbon gasification rate is between about 5 weight % and about 25 weight % per hour based on the weight of said carbon contained within said reactor.

11. A method according to claim 1 wherein at least about 90 weight % of the solid particles contained within said reactor have a particle size larger than about 100 mesh.

12. A method according to claim 11 wherein between 30 weight % and 50 weight % of the solid particles entrained within said combustible gas have a particle size less than about 200 mesh.

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Application number

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EUROPEAN SEARCH REPORT

EP 80 30 1656

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	US - A - 3 993 583 (SEGLIN)	
A	US - A - 3 957 459 (MITCHELL)	
A	US - A - 2 654 665 (PHINNEY)	
A	US - A - 2 652 319 (SWEETSER)	

CLASSIFICATION OF THE APPLICATION (Int Cl. 3)

C 10 J 3/54
C 10 J 3/84

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

C 10 J 3/54
3/56
3/84

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	04-08-1980	WENDLING

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