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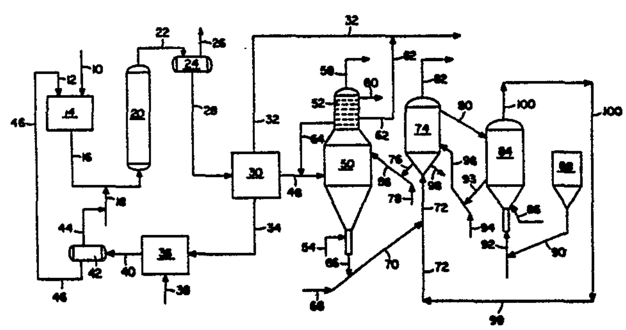
(54) An improved process for the gasification of coal and other mineral-containing carbonaceous solids.

(57) Agglomerate formation due to sintering is avoided in the nonslagging fluidized bed gasification of carbonaceous solids containing ash-forming, inorganic constituents by carrying out the gasification in the presence of an added hydrated aluminosilicate or an added hydrated magnesium silicate. In a preferred embodiment of the invention, the gasification zone is part of an integrated coking and gasification process wherein coal liquefaction bottoms are coked and the resultant coke is gasified.



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This invention relates to the processing of coal and other mineral-containing carbonaceous solids and is particularly concerned with an improved process for gasifying such materials, particularly the carbonaceous solids produced by coking liquefaction residues.

In most nonslagging, fluidized bed gasification processes, coal and other mineral-containing carbonaceous solids are reacted with steam to produce hydrogen, carbon monoxide and, in some cases, methane. Normally, the heat for this reaction is supplied by introducing air or oxygen into the gasifier to burn a portion of the organic material in the solids. Although these gasifiers are operated at temperatures below which slagging occurs, it has recently been found that sintering of the mineral matter in the feed solids may occur thereby resulting in the formation of agglomerates. It is believed that this sintering occurs mainly in the portion of the gasifier where heat is being generated by the introduction of air or oxygen into the reactor. It is further believed that localized combustion produces hot spots wherein portions of the mineral matter in the carbonaceous feed material are subjected to relatively high temperatures. The resulting agglomerates formed by sintering of the mineral matter constituents can plug distributors in the reactor and eventually become so large that they will inhibit fluidization of the solids during the gasification process.

It has been found that sintering is a major problem in the integrated coking and gasification process utilized to upgrade the carbonaceous residues produced by liquefying coal and other mineral-containing carbonaceous solids. Normally, this integrated coking and gasification process comprises subjecting the liquefaction residues to pyrolysis conditions to produce gases, hydrocarbon liquids and coke and then steam gasifying the coke to produce hydrogen and carbon monoxide for use as fuel. It has been found that during the gasification portion of the integrated process, the inorganic constituents of the coke tend to sinter thereby forming agglomerates which interfere with the fluidized bed gasification.

The present invention provides an improved process for the gasification of coal and other carbonaceous solids which contain ash-forming, inorganic constituents. In accordance with the invention it has now been found that agglomerate formation due to sintering in a nonslagging gasification zone can be substantially avoided by carrying out the gasification process in the presence of certain added inorganic solids which are hydrated aluminosilicate compounds or hydrated magnesium silicate compounds. The invention is based in part upon the discovery that the addition of such compounds will raise the sintering temperature of the mineral matter constituents in the carbonaceous feed material and thereby prevent agglomeration of the particles undergoing gasification. Preferred hydrated aluminosilicate compounds which are effective in the process of the invention include kaolinite, montmorillonite, pyrophyllite and illite. Preferred hydrated magnesium silicate compounds include talc, serpentine and hectorite. Normally, these inorganic compounds are added to the gasifier feed in an amount ranging from about 2 to about 20 percent by weight.

The process of the invention is preferably employed in an integrated coking and gasification system wherein carbonaceous solids containing inorganic constituents are pyrolyzed in a coking zone to form gases, hydrocarbon liquids, and mineral-containing coke. The coke is then gasified with steam in a nonslagging gasification zone in the presence of an added hydrated aluminosilicate or hydrated magnesium silicate compound to produce a synthesis gas composed primarily of hydrogen and carbon monoxide. In the preferred embodiment of this process, the feed to the coking zone is a heavy bottoms produced by liquefying coal or a similar carbonaceous feed material at an elevated temperature and pressure by treating it with a hydrocarbon solvent and gaseous hydrogen to produce coal liquids and a heavy bottoms stream, which normally boils above 1000°F, composed of carbonaceous material and inorganic constituents.

The drawing is a schematic flow diagram illustrating a preferred embodiment of the invention.

The process depicted in the drawing is a preferred embodiment of the invention in which bituminous coal, subbituminous coal, lignitic coal, or similar solid carbonaceous feed material is first liquefied by contacting the solids with gaseous hydrogen in the presence of a hydrogen-donor solvent. Gases are separated from the liquefaction product and the remaining material is then fractionated to obtain liquids boiling normally up to about 1000°F and a heavy bottoms product normally boiling in excess of about 1000°F. A portion of the liquid stream is hydrogenated and recycled for use as solvent and the remaining liquids are withdrawn as product coal liquids. The heavy bottoms are then pyrolyzed to produce gases, additional liquid products and coke containing inorganic constituents. This coke is gasified with steam in the presence of an added hydrated aluminosilicate or hydrated magnesium silicate compound. It will be understood that the process of the invention is not restricted to the use of the added hydrated aluminosilicate or magnesium silicate compound in the gasifier of the coal liquefaction and integrated coking and gasification process illustrated in the drawing. To the contrary, the invention may be employed in any nonslagging gasification process in which carbonaceous solids containing between about 5 weight percent and about 40 weight percent inorganic constituents or mineral matter are gasified with steam, and in which oxygen or an oxygen-containing gas such as air is normally used to provide heat input into the gasifier. For example, the invention can be used in connection with the fluidized bed gasification of coal, liquefaction residues, coal char, solid organic wastes, and the like.

In the process depicted in the drawing, coal or similar solid, carbonaceous feed material is introduced into the system through line 10 from a coal storage or feed preparation zone, not shown in the drawing, and combined with a hydrogen-donor solvent introduced through line 12 to form a slurry in slurry preparation zone 14. The feed material employed will normally consist of solid particles of bituminous coal, subbituminous coal, lignitic coal, brown coal, or a mixture of two or more such materials. In lieu of coal, other solid carbonaceous materials may be introduced into the slurry preparation zone. Such materials include organic wastes, oil shale, coal char, coke, liquefaction bottoms and the like. The particle size of the feed material may be of the order of about one-quarter inch or smaller along the major dimension but it is generally preferred to use coal which has been crushed and screened to a particle size of about 8 mesh or smaller on the U. S. Sieve Series Scale. It is also generally preferred to dry the feed particles to remove excess water, either by conventional techniques before the feed solids are mixed with the solvent in the slurry preparation zone or by mixing wet solids with hot solvent at a temperature above the boiling point of water, preferably between about 250°F and about 350°F, to vaporize the water in the preparation zone. The moisture in the feed slurry is preferably reduced to less than about 2.0 weight percent.

The hydrogen donor solvent used in preparing the slurry in preparation zone 14 will normally be a coal-derived solvent, preferably a hydrogenated recycle solvent containing at least 20 weight percent of compounds that are recognized as hydrogen donors at the elevated temperatures of about 700°F to about 1000°F generally employed in coal liquefaction reactors. Solvents containing at least 50 weight percent of such compounds are preferred. Representative compounds of this type include C_{10}-C_{12} tetrahydronaphthalenes, C_{12} and C_{13} acenaphthenes, di, tetra- and octahydro anthracenes, tetrahydroacenaphthenes, and other derivatives of partially hydrogenated aromatic compounds. Normally, the solvent will contain above about 0.8 weight percent donatable hydrogen, preferably between about 1.2 and about 3.0 weight percent. Such solvents have been described in the literature and will therefore be familiar to those skilled in the art. The solvent composition resulting from the hydrogenation of a recycle solvent fraction will depend in part upon the particular coal used as the feedstock to the process, the process steps and operating conditions employed, and the conditions used in hydrogenating the solvent fractions selected for recycle following liquefaction. In slurry preparation zone 14, the incoming feed coal is normally mixed with solvent recycled through line 12 in a solvent-to-coal weight ratio of from about 1:1 to about 4:1, preferably from about 1.2:1 to about 1.8:1.

The coal-solvent slurry formed in slurry preparation zone 14 is withdrawn from the zone through line 16; mixed with a hydrogen-containing gas, preferably molecular hydrogen, introduced into line 16 via line 18; preheated to a temperature above about 670°F; and passed upward in plug flow through liquefaction reactor 20. The mixture of slurry and hydrogen-containing gas will contain from about 1 to about 8 weight percent, preferably from about 2 to about 5 weight percent, of hydrogen on a moisture-free coal basis. The liquefaction reactor is maintained at a temperature between about 700°F and about 900°F, preferably between 800°F and about 880°F, and at a pressure between about 300 psig and about 3000 psig, preferably between about 1500 psig and about 2500 psig. Although a single liquefaction reactor is shown in the drawing as comprising the liquefaction zone, a plurality of reactors arranged in parallel or series can also be used, provided that the temperature and pressure in each reactor remain approximately the same. Such will be the case if it is desirable to approximate a plug flow situation. The slurry residence time within reactor 20 will normally range between about 15 minutes and about 150 minutes, preferably between about 40 minutes and about 90 minutes.

Within the liquefaction zone in reactor 20, the coal solids undergo liquefaction or chemical conversion into lower molecular weight constituents. The high molecular weight constituents of the coal are broken down and hydrogenated to form lower molecular weight gases and liquids. The hydrogen-donor solvent molecules react with organic radicals liberated from the coal to stabilize them and thereby prevent their recombination. The hydrogen in the gas introduced into line 16 via line 18 serves at least in part to stabilize organic radicals generated by the cracking of coal molecules. This hydrogen also serves as replacement hydrogen for depleted hydrogen-donor molecules in the solvent and its presence results in the formation of additional hydrogen-donor molecules by in situ hydrogenation to convert aromatics into hydroaromatics.

The effluent from liquefaction reactor 20, which contains gaseous liquefaction products such as carbon dioxide, carbon monoxide, ammonia, hydrogen, hydrogen sulfide, methane, ethane, ethlyene, propane, propylene and the like; unreacted hydrogen from the feed slurry, light liquids; and heavier liquefaction products including mineral matter, unconverted coal solids and high molecular weight liquids is withdrawn from the top of the reactor through line 22 and passed to separator 24. Here, the reactor effluent is separated, preferably at liquefaction pressure, into an overhead vapor stream which is withdrawn through line 26 and a liquid stream removed through line 28. The overhead vapor stream is passed to downstream units where the ammonia, hydrogen and acid gases are separated from the low molecular weight gaseous hydrocarbons, which are recovered as valuable byproducts. Some of these lighter hydrocarbons, such as methane and ethane, may be steam reformed to produce hydrogen that can be recycled where needed in the process.

The liquid stream removed from separator 24 through line 28 will normally contain low molecular weight liquids, high molecular weight liquids, mineral matter or ash, and unconverted coal. This stream is passed through line 28 into fractionation zone 30 where the separation of low molecular weight liquids from the high molecular weight liquids boiling above about 1000°F and solids is carried out. Normally, the fractionation zone will be comprised of an atmospheric distillation column in which the feed is fractionated into an overhead fraction composed primarily of gases and naphtha constituents boiling up to about 350°F and intermediate liquid fractions boiling within the range from about 350°F to about 700°F. The bottoms from the atmospheric distillation column is then passed to a vacuum distillation column in which it is further distilled under reduced pressure to permit the recovery of an overhead fraction of relatively light liquids and heavier intermediate fractions boiling below about 850°F and about 1000°F. Several of the distillate streams from both the atmospheric distillation column and the vacuum distillation columns are combined and withdrawn as product from the fractionation zone through line 32.

Another portion of the liquids produced in the fractionation zone are withdrawn through line 34 for use as feed to the solvent hydrogenation zone 36. This stream will normally include liquid hydrocarbons composed primarily of constituents boiling in the 350°F to 700°F range recovered from the atmospheric distillation column and heavier hydrocarbons in the 700°F to 850°F boiling range recovered from the vacuum distillation column. These liquids are introduced into solvent hydrogenation zone 36 where they contacted with molecular hydrogen introduced into the zone through line 38 in the presence of a hydrogenation catalyst. The solvent hydrogenation zone is operated at about the same pressure as that in liquefaction reactor 20 and at a somewhat lower temperature. In general, temperatures within the range between about 550°F and about 850°F, pressures between about 800 psig and about 3000 psig, and space velocities between about 0.3 and about 3.0 pounds of feed/hour/pound of hydrogenation catalyst are employed in the hydrogenation zone. It is generally preferred to maintain a mean hydrogenation temperature within the zone between about 620°F and about 750°F. Any of a variety of conventional hydrotreating catalyst may be employed in the zone. Such catalysts typically comprise an inert support carrying one or more iron group metals and one or more metals from Group VI-A of the Periodic Table of Elements in the form of an oxide or sulfide. Combinations of one or more Group VI-A metal oxide or sulfide with one or more Group VIII metal oxide or sulfide are generally preferred. Representative metal combinations which may be employed in such catalysts include oxides and sulfides of cobalt-molybdenum, nickel-molybdenum, and the like. The hydrogen treat rate will normally range from about 1000 to about 10,000 scf/bbl, preferably from about 2000 to about 5000 scf/bbl.

The hydrogenated effluent from solvent hydrogenation zone 36 is withdrawn through line 40 and passed into separator 42 from which an overhead stream containing hydrogen gas is withdrawn through line 44. This gas stream is at least partially recycled through lines 18 and 16 for reinjection with the feed slurry into liquefaction reactor 20. Hydrogenated liquid hydrocarbons are withdrawn from the separator through line 46 and recycled through line 12 for use as hydrogen-donor solvent in slurry preparation zone 14.

The heavy bottoms produced in the vacuum distillation column which comprises a portion of fractionation zone 30 consists primarily of high molecular weight liquids boiling above about 1000°F, mineral matter or ash, and unconverted coal. This heavy bottoms contains a substantial amount of organic material and is normally further converted in an integrated coking and gasification system to recover additional hydrocarbon liquids and gases. The heavy bottoms stream is withdrawn from fractionation zone 30 through line 48, blended with heavy recycle material introduced into line 48 through line 64 and passed to fluidized bed coking unit 50. This unit will normally be provided with an upper scrubbing and fractionation section 52 from which liquid and gaseous products produced as a result of the coking reaction can be withdrawn. The unit will generally also include one or more internal cyclone separators or similar devices not shown in the drawing which serve to remove entrained particles from the upflowing gases and vapors entering the scrubbing and fractionation section and return them to the fluidized bed below.

The fluidized bed coking unit shown in the drawing contains a bed of coke particles which are maintained in the fluidized state by means of steam or other fluidizing gas introduced near the bottom of the unit through line 54. This fluidized bed is normally maintained at a temperature between about $850^{\circ}F$ and about $1600^{\circ}F$, preferably between above $900^{\circ}F$ and $1200^{\circ}F$, by means of hot char which is introduced into the upper part of the reaction section of the coker through line 56. The pressure within the reaction zone will generally range between about 10 and about 30 psig but higher pressures can be employed if desired. The optimum conditions in the reaction zone will depend in part upon the characteristics of the particular feed material employed and can be readily determined.

The hot liquefaction bottoms is fed into the reaction zone of the coking unit through line 48 and sprayed onto the surfaces of the coke particles in the fludized bed. Here it is rapidly heated to bed temperatures. As the temperature of the bottoms increases, lower boiling constituents are vaporized and the heavier portions undergo thermal cracking and other reactions to form lighter products and additional coke on the surfaces of the bed particles. The mineral or ash constituents present in the feed are retained by the coke as it forms. Vaporized products, unreacted steam, and entrained solids move upwardly through the fluidized bed and enter cyclone separators or similar devices, not shown in the drawing, where solids present in the fluids are rejected. The fluids then move into the scrubbing and fractionation section of the unit where refluxing takes place. An overhead gas stream is withdrawn from the coker through line 58 and may be employed as fuel gas or the like. A naphtha sidestream is withdrawn through line 60 and may be combined with naphtha produced at other stages in the process. A heavier liquids fraction having a nominal boiling range between about 400°F and about 1000°F is withdrawn as a sidestream through line 62 and combined with coal liquids removed from fractionation zone 30 through line 32 for withdrawal from the system. Heavy liquids boiling above 1000°F may be withdrawn through line 64 for recycle to the incoming feed as described earlier.

The coke particles in the fluidized bed of the reaction section tend to increase in size as additional coke is deposited. The particles, which contain inorganic constituents introduced with the feed, thus gradually move downward through the fluidized bed and are eventually discharged from the reaction section through line 66. This stream is entrained by steam or other carrier gas introduced through line 68 and transported upward through lines 70 and 72 into fluidized bed heater 74. Here the coke particles in the fluidized bed are heated to a temperature of from about 50°F to about 300°F above that in the reaction section of the coker. Hot solids are withdrawn from the bed of heater 74 through standpipe 76, entrained by steam or other carrier gas introduced through line 78, and returned to the reaction section of the coker through line 56. The circulation rate between the coker and the heater is maintained sufficiently high to provide the heat necessary to keep the coker at the required temperature. The solids within the heater are directly heated by the introduction of hot gases from the gasifier associated with the unit as described below.

Hot carbonaceous particles are continuously circulated from the fluidized bed in heater 74 through line 80 to fluidized bed gasifier 84. These particles will contain a significant concentration of inorganic constituent, normally between about 20 weight percent and about 40 weight percent. In the gasifier, these particles are contacted with steam in the presence of an added hydrated aluminosilicate compound or an added hydrated magnesium silicate compound. The phrase "added hydrated aluminosilicate compound" as used herein refers only to a hydrated aluminosilicate which is added to the gasifier and is not a naturally occurring part of the solids fed to the gasifier. Similarly, the phrase "added hydrated magnesium silicate compound" as used herein refers only to a hydrated magnesium silicate which is not a naturally occurring part of the solids fed to the gasifier. The steam is introduced into the bottom of the gasifier through line 86. Particles of the hydrated aluminosilicate or hydrated magnesium silicate compound, which are stored in vessel 88, are passed through line 90 into line 92 where they are entrained in air or an oxygen-containing gas and passed upward into the bottom of gasifier 84. The amount of air or oxygen-containing gas utilized is adjusted so that the temperature in the gasifier is maintained between about 1600°F and about 2000°F, preferably between about 1600°F and about 1850°F. The pressure in the gasifier is normally maintained between about 10 and about 60 psig, preferably between about 25 psig and about 45 psig. Under these conditions, the carbonaceous particles in the gasifier react with steam and the oxygen-containing gas to produce hydrogen, carbon monoxide, carbon dioxide, and some methane. The reaction of carbon with oxygen provides the heat necessary to drive the endothermic gasification reactions and the excess heat is absorbed by the particles in the gasifier. A stream of hot carbonaceous solids is continuously withdrawn from the gasifier through line 93, entrained in steam, flue gas, or other carrier gas introduced through line 94, and returned to heater 74 through line 96.

It has been found that because of the relatively large amount of inorganic or ash constituents in the material fed to the gasifier of the integrated coking and gasification system that forms part of the liquefaction process shown in the drawing, there may be a tendency for the inorganic constituents to sinter and form agglomerates that may interfere with fluidization in the gasifier. Sintering is particularly a problem in the lower portion of the gasifier where heat is generated by the introduction of the air or oxygen-containing gas into the gasifier. It has been found that the sintering in the gasifier and any associated operating problems can be substantially avoided by introducing an effective amount of a hydrated aluminosilicate compound or a hydrated magnesium silicate compound into the gasifier so that gasification of the mineral-containing carbonaceous solids fed to the gasifier can take place in the presence of these added materials. It is believed when such additives are introduced into the gasifier and subjected to gasification conditions, they are broken up into fine particles.

It is further believed that the small size of the resultant particles facilitates their interaction with the inorganic constituents comprising the carbonaceous feed materials thereby raising the sintering temperature of the inorganic constituents during gasification by increasing their fusion or melting temperature. Normally, aluminosilicate and magnesium silicate compounds that are not hydrated are not as effective in the process of the invention, evidently because they do not tend to break up into fine particles under normal gasification conditions.

Referring again to the drawing, the hydrated aluminosilicate or magnesium silicate additive is introduced through line 92 into the bottom of gasifier 84 with the oxygen-containing gas used to supply oxygen for supporting the combustion reactions which take place in the gasifier. These added solids are therefore present in the lower portion of the gasifier where sintering tends to take place because of the combustion heat generated as the oxygen-containing gas enters the reaction vessel. Although any hydrated aluminosilicate will normally be effective in increasing the sintering temperature of the inorganic constituents contained in the solids fed to the gasifier, the following compounds are preferred: kaolinite [$Al_2Si_2O_5(OH)_4$], montmorillonite [$Al_2Si_4O_{10}(OH)_2 \cdot xH_2O$], pyrophyllite [$Al_2Si_4O_{10}(OH)_2$] and illite [$KAl_2(AlSi_3O_{10})(OH)_2$]. Of these compounds, kaolinite tends to be most effective in preventing sinter formation and is more readily available and cheaper than other clay minerals. Other members of the kaolinite family of clays including halloysite, nacrite and dickite should be equally effective. As is the case with hydrated aluminosilicates, any hydrated magnesium silicate will normally be effective in increasing the sintering temperature. The preferred hydrated magnesium compounds include talc [$Mg_3Si_4O_{10}(OH)_2$] serpentine

$[Mg_3Si_2O_5(OH)_4]$, and hectorite $[Mg_3Si_4O_{10}(OH)_2 \cdot xH_2O]$. Normally, the hydrated aluminosilicate or magnesium silicate used is introduced into the gasifier at a rate such that between about 2 and about 20 weight percent of the material is present in the gasifier based upon the weight of the carbonaceous solids present, preferably between about 2 and about 10 weight percent. In general, it is desirable that the size of the particles comprising the hydrated aluminosilicate or magnesium silicate introduced in the gasifier be approximately the size of the particles of carbonaceous solids that are fed to the gasifier. Finely powdered materials may be used if they are not quickly elutriated from the fluidized bed in the gasifier.

The hot gases produced in gasifier 84 are removed overhead through line 100 and passed through lines 99 and 72 into heater 74. Here the hot gases transfer heat to the solid particles within the heater and maintain them at the required temperature level. The gas taken overhead from the heater will thus include the gasification products produced in gasifier 84. This gas stream, assuming that oxygen rather than air is injected into the lower end of the gasifier with the steam used for gasification purposes, will consist primarily of hydrogen, carbon monoxide, carbon dioxide, and some methane. The gases are taken overhead from the heater through line 82 and passed to downstream gas upgrading equipment not shown in the drawing. Here, the overhead gases are shifted, treated for the removal of acid gases, and the residual carbon monoxide is methanated by conventional procedures to produce a high purity hydrogen stream. A purge stream of ash-containing carbonaceous solids is continuously withdrawn from the heater through line 98 to prevent the inorganic constituents from building up within the integrated coking and gasification system.

In the embodiment of the invention depicted in the drawing and discussed above, the hydrated alumino-silicate or magnesium silicate compound is introduced into the gasifier with the oxygen-containing gas. It will be understood that the invention is not limited to this method of adding these materials to the gasifier. For example, the hydrated aluminosilicate or magnesium silicate compound can be mixed with the liquefaction bottoms leaving fractionation zone 30 through line 48 and the resultant mixture fed to coker 50. When this molten mixture is then sprayed onto the coke in the fluidized bed reaction zone, the hydrated alumino-silicate or magnesium silicate compound will be distributed on the individual particles that eventually pass through the heater into the gasifier where the compound interacts with the mineral matter constituents originally in the coke particles to increase their sintering temperature. The hydrated aluminosilicate or magnesium silicate can be mixed with the liquefaction bottoms in several ways. In one method, the additive is powdered and fed into a mixing tank located in line 48 where it is stirred with the bottoms stream to obtain uniform distribution of the additive throughout the bottoms. Alternatively, the recycle coker liquids in line 64 can first be mixed with particles of the additive and the resultant slurry blended into the bottoms in line 48. When the molten mixture of the slurry and the bottoms is sprayed onto the coke in the coker, the hydrated aluminosilicate or magnesium silicate will then be distributed on the individual coke particles. Either of these two methods of introducing the hydrated aluminosilicate or magnesium silicate into the gasifier is normally more effective in preventing sintering than is the method of introducing the additive directly into the gasifier with the oxygen-containing gas because better distribution of the additive on the carbonaceous particles fed to the gasifier is obtained.

In the embodiment of the invention depicted in the drawing and discussed above, the hydrated aluminosilicate or magnesium silicate is introduced into a gasifier that forms part of an integrated coking and gasification system that is in turn part of a coal liquefaction process. It will be understood that the process of the invention can be used in connection with any fluidized bed gasification reactor regardless of whether it is integrated with a coker or other reactor, or operates independently. The hydrated aluminosilicate or magnesium silicate compound will normally be added to an independently operated gasifier in the same amount and manner that it is added to the gasifier shown in the drawing. In general, the compounds are only added to a gasifier if it is operating at a temperature where sintering problems are encountered, temperatures normally above about 1600°F.

The nature and objects of the invention are further illustrated by the results of laboratory tests which indicate that the sintering temperature of mineral-containing carbonaceous solids is significantly increased when the solids are gasified in the presence of an added hydrated aluminosilicate compound or an added hydrated magnesium silicate compound.

In the first series of tests, a predetermined amount of ground liquefaction bottoms produced by liquefying Illinois No. 6 coal in a pilot plant generally similar to the one depicted in the portion of the drawing to the left of line 48 was mixed thoroughly with a predetermined quantity of a powdered hydrated aluminosilicate or talc (a hydrated magnesium silicate) having a particle size less than 200 mesh on the U.S. Sieve Series Scale. The particle size of the ground liquefaction bottoms was normally less than about 70 mesh on the U.S. Sieve Series Scale. The powdered mixture was then coked at about 1000°F for about 15 minutes in a laboratory bench scale coking unit. Normally, batches of 20 grams of the mixture were processed at a time. The resultant coke from each batch was recombined and uniformly ground to between 40 and 100 mesh on the U.S. Sieve Series Scale. The ground coke was then heated in a tube furnace under a nitrogen atmosphere at about 1300°F for about 30 minutes to remove residual volatile materials. In addition to the "additive" cokes prepared by coking a mixture of liquefaction bottoms and a hydrated aluminosilicate or talc, a coke was prepared in the same general manner as set forth above except that it was not mixed with an additive. A 20 gram sample of this "nonadditive" coke and of each "additive" coke was then placed in a laboratory scale fluidized bed unit designed to measure the sintering temperature of the mineral-containing coke particles. The unit consisted of a one-inch diameter quartz tube mounted vertically in a tube furnace. The 20 gram sample was fluidized with air and steam above a fritted quartz cone. The temperature in the unit was controlled and monitored by a pair of thermocouples located near the bottom of the fluidized bed. Sintering occurred when a temperature delta was shown to exist across the thermocouples. The fluidizing gas contained 30 volume percent steam and 70 volume percent air and was passed through the fluidized bed at a rate of about 0.5 feet per second. The results of these tests are set forth below in Table 1.

TABLE 1

EFFECT OF VARIOUS ADDITIVES ON SINTERING

Run Number	Additive	Amount of Additive (wt% prior to coking)	Maximum Non-Sintering Temperature (^{o}F)
1	None	--	1750
2	Kaolinite ($Al_2Si_2O_5(OH)_4$)	5	1820
3	Kaolinite ($Al_2Si_2O_5(OH)_4$)	10	1825
4	Kaolinite ($Al_2Si_2O_5(OH)_4$)	20	1850
5	Montmorillonite ($Al_2Si_4O_{10}(OH)_2 \cdot xH_2O$)	20	1830
6	Pyrophyllite ($Al_2Si_4O_{10}(OH)_2$)	20	1820
7	Illite ($KAl_2(AlSi_3O_{10})(OH)_2$)	20	1810
8	Talc ($Mg_3Si_4O_{10}(OH)_2$)	20	1845
9*	Kaolinite* ($Al_2Si_2O_5(OH)_4$)	20*	1810

*Kaolinite added directly to coke instead of to liquefaction bottoms prior to coking as in runs 1 through 8.

It can be seen by comparing runs 2 to 8 with run 1 in Table 1 that the addition of talc and hydrated aluminosilicates including kaolinite, montmorillonite, pyrophyllite, and illite to liquefaction bottoms prior to subjecting them to an integrated coking and gasification process will result in increasing the temperature at which sintering occurs in the gasifier of the integrated process. The increases in the maximum non-sintering temperature range between 60°F for 20 weight percent pyrophyllite to 100°F for 20 weight percent kaolinite. The data for runs 2 to 4 indicate that the maximum non-sintering temperature increases as the concentration of the additive increases. Runs 4 and 8 indicate that kaolinite and talc are the most effective of the additives in increasing the maximum non-sintering temperature. The data for runs 1 to 8 in Table 1 clearly show that the addition of hydrated aluminosilicates or hydrated magnesium silicates to liquefaction bottoms prior to subjecting the bottoms to an integrated coking and gasification process will result in a significant increase in the temperature at which the gasifier can be operated without sintering of mineral matter consituents taking place.

The second series of tests was carried out to determine if the maximum non-sintering temperature of the mineral constituents in the coke could be increased by adding the hydrated aluminosilicate or talc to the liquefaction bottoms after they had been coked instead of prior to coking. In this series of tests, coke was prepared in a manner similar to that described for the first series of tests except that no additives were mixed with the bottoms prior to the coking procedure. A sample of this "nonadditive" coke composed of particles between 40 mesh and 100 mesh on the U.S. Sieve Series Scale was placed in the laboratory bench scale fluidized bed unit used to determine the sintering in the first series of tests. Kaolinite particles ranging in size between 40 and 80 mesh on the U.S. Sieve Series Scale were then added to the coke in the fluidized bed reactor in amounts sufficient to yield 20 percent by weight. A mixture comprising 30 volume percent steam and 70 volume percent air was then fed into the fluidized bed at a rate of about 0.5 feet per second and the maximum non-sintering temperature was determined. The results of this series of tests are set forth as run 9 in Table 1.

As can be seen by comparing run 9 in Table 1 with run 1, the addition of the kaolinite directly to the coke increases the maximum non-sintering temperature 60°F over the case where no additive is utilized. A comparison of runs 2 to 4 with run 9 indicates that adding the kaolinite directly to the coke is not as effective as adding it to the liquefaction bottoms prior to coking and then subjecting the resultant coke to gasification. It is believed that the reason for this difference is the fact that when the kaolinite or other hydrated aluminosilicate or hydrated magnesium silicate is added to the liquefaction bottoms prior to coking, it is more uniformly distributed on the coke particles subsequently formed thereby making it easier for the additive to interact with the mineral constituents of the coke during gasification than would be the case if the additive was introduced into the gasifier with the fluidizing gas.

It will be apparent from the foregoing that the invention provides a process which is effective in preventing sintering and resultant agglomeration in a fluidized bed gasifier during the gasification of carbonaceous solids containing a substantial amount of inorganic constituents. Since the process results in an increase in the maximum non-sintering temperature in the gasifier, it ensures that gasification can take place at relatively high temperatures without significantly affecting the operation of the fluidized bed gasifier.

CLAIMS:

1. A process for gasifying carbonaceous solids containing ash-forming, inorganic constitutents in a nonslagging fluidized bed gasification zone without a significant amount of agglomerate formation due to sintering of said inorganic constituents which comprises gasifying said carbonaceous solids in said nonslagging fluidized bed gasification zone in the presence of an added hydrated aluminosilicate compound or an added hydrated magnesium silicate compound.

2. A process according to claim 1 wherein said carbonaceous solids containing ash-forming inorganic constituents are first converted into liquids, gases and coke by pyrolyzing said carbonaceous solids in a fluidized bed coking zone under coking conditions to form liquids, gases and coke containing inorganic constituents and at least a portion of said coke is passed from said fluidized bed coking zone to said fluidized bed gasification zone.

3. A process according to claim 1 or claim 2 wherein said carbonaceous solids comprise the heavy bottoms produced by liquefying coal.

4. A process according to claim 1 or claim 2 wherein said carbonaceous solids comprise coal.

5. A process according to any one of claims 1-4 wherein said carbonaceous solids are gasified with steam in the presence of an added oxygen-containing gas.

6. A process according to any one of claims 1-5 wherein the added hydrated aluminosilicate compound is kaolinite, montmorillonite, illite, pyrophyllite, halloysite, nacrite, dickite or a mixture thereof.

7. A process according to any one of claims 1-5 wherein the added hydrated magnesium silicate compound is talc, serpentine, hectorite or a mixture thereof.

8. A process according to any one of claims 1-7 wherein the added hydrated aluminosilicate or the added hydrated magnesium silicate is introduced into said gasification zone in amounts sufficient to yield a concentration in said zone of between about 2 weight percent and about 20 weight percent based on the weight of the carbonaceous solids or coke present in said zone.

9. A process according to any one of claims 1-8 wherein the added hydrated aluminosilicate or the added hydrated magnesium silicate is introduced into said gasification zone with said oxygen-containing gas.

10. A process according to any one of claims 1-8 wherein the added hydrated aluminosilicate or the added hydrated magnesium silicate is mixed with said carbonaceous solids and the resultant mixture is introduced into said gasification zone.

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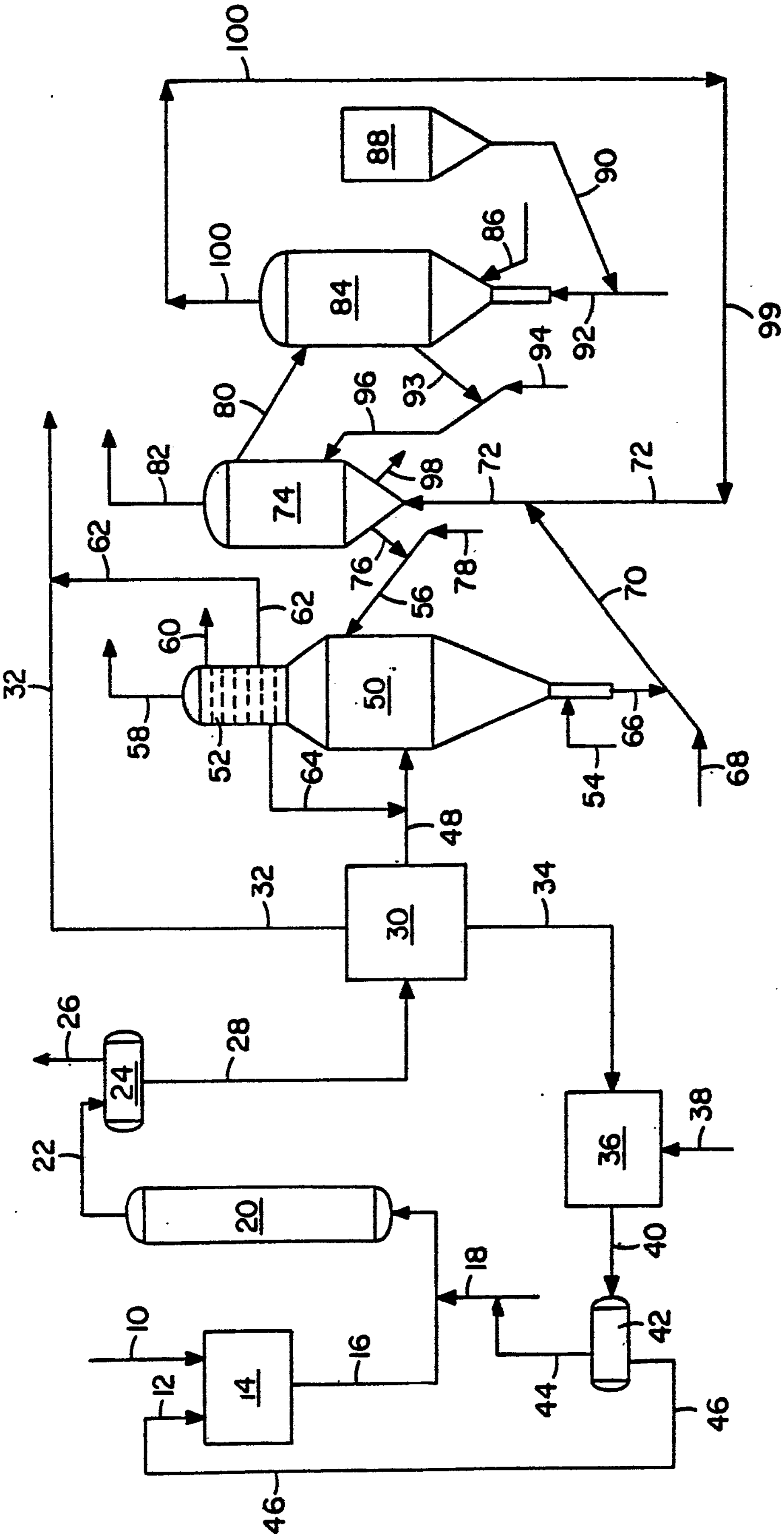
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