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Luckenbach

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[54] **GASEOUS PRODUCTS OF GASIFIER USED TO CONVEY COKE TO HEATER**

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[51] **Int. Cl.**..**C10j 3/16**

[58] **Field of Search**............................201/21–23, 31, 201/15, 16, 28, 38; 208/127, 11, 8; 48/202, 197, 203, 206

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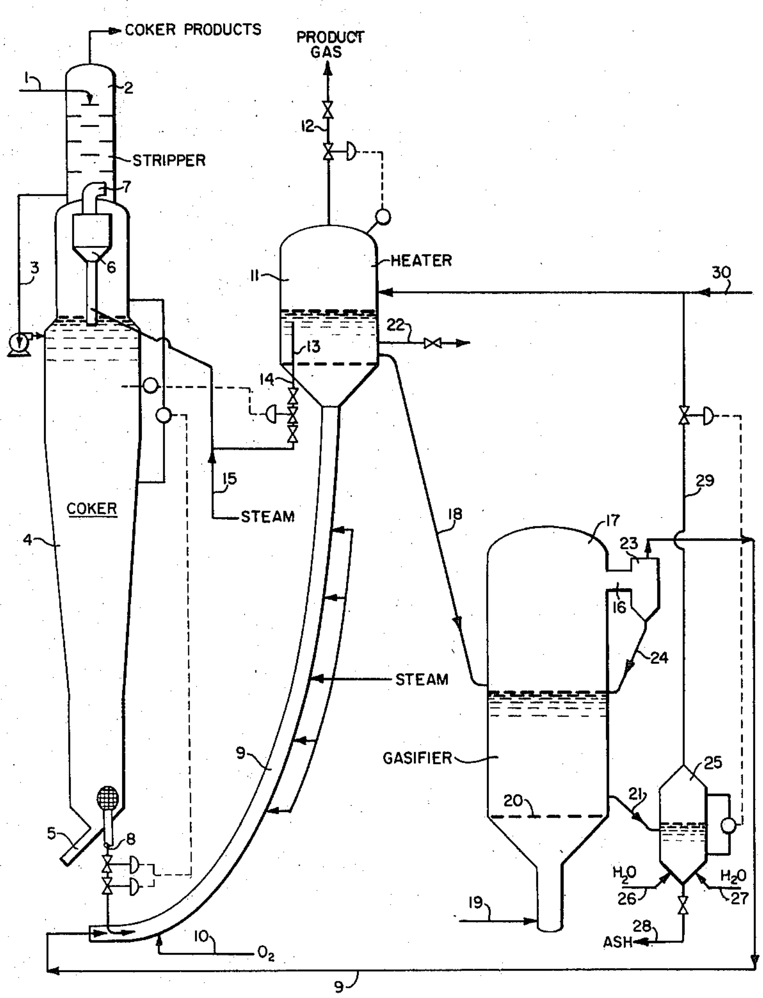
[57] **ABSTRACT**

In a fluid coking process in which the coke is substantially completely gasified, solids are conveyed from the coker to the heater, supplying both the coker and gasifier, by means of the fuel gas produced in the gasifier. The solids may be inert or the coke produced by the process.

4 Claims, 1 Drawing Figure



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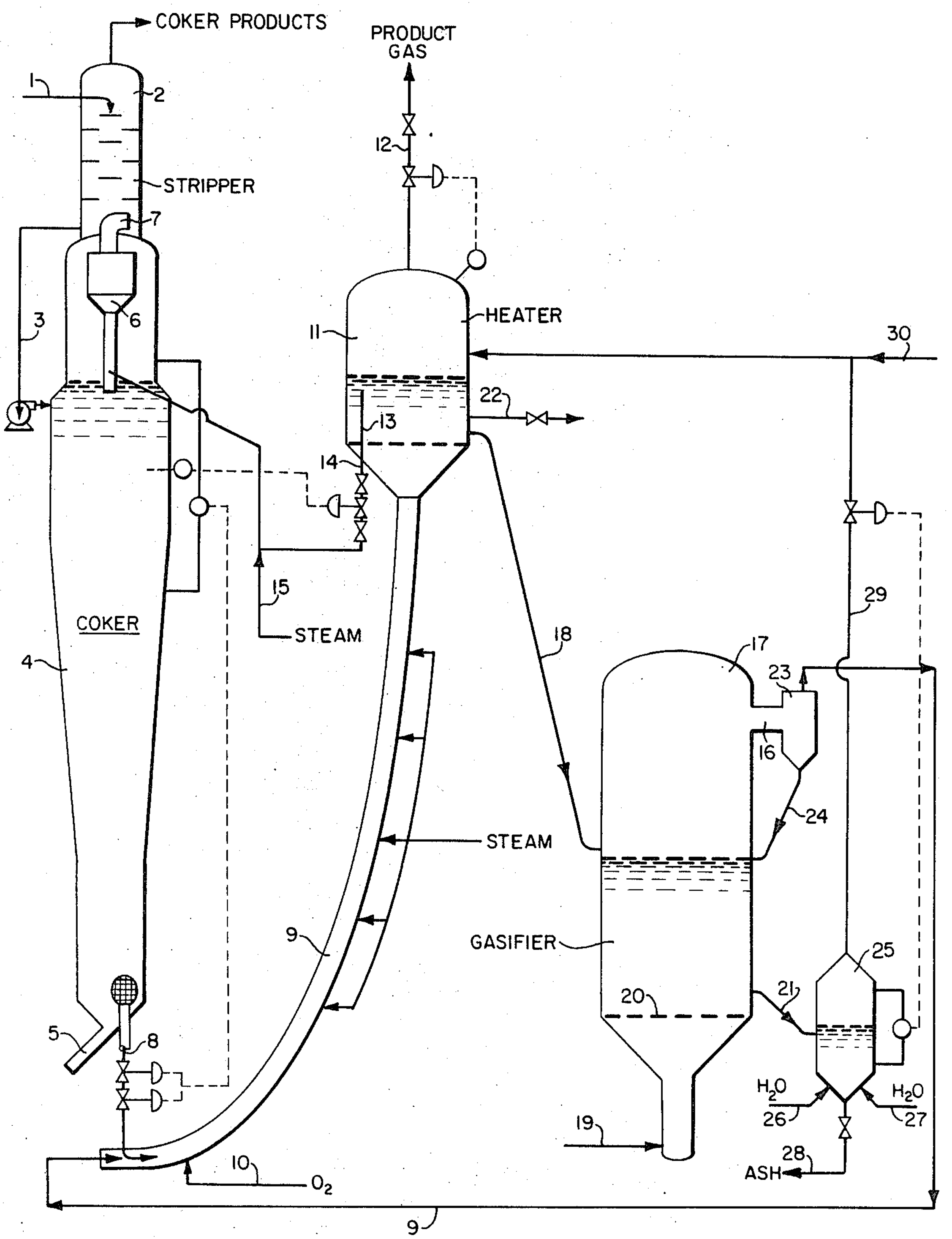

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GASEOUS PRODUCTS OF GASIFIER USED TO CONVEY COKE TO HEATER

This invention relates to the fluid coking of carbonaceous feed, and more particularly it relates to a fluid coking process in which there is no substantial net production of coke but substantially all the coke is converted to gases having high concentration of H_2 and CO.

In conventional fluid coking, the carbonaceous feed is injected into a bed of fluid coke where it is cracked to vapors and coke. The vapors pass through a cyclone to a scrubber/fractionator where they are fractionated to gas, naphtha and oil products, and a heavy stream which is recycled to the coking reactor. A circulating stream of coke is stripped in the bottom zone of the reactor and transferred to a coke burner where sufficient air is injected for burning part of the coke and heating the remainder sufficiently to satisfy the heat requirements of the coking reactor when the unburned hot coke is recycled thereto. Net coke above that consumed in the burner is withdrawn as product coke.

Unfortunately, the market for this coke has been limited with the result that attempts have been made to increase its value by subsequent treatment such as high temperature calcining and briquetting. Alternatively, the coke can be converted to an H_2 and CO rich gas in a subsequent processing step by reaction with steam and an oxygen-containing gas. None of these subsequent coke processing steps has been found to be economically attractive for general use.

Furthermore, when processing typical petroleum residuum in a conventional fluid coker, the combustion products from the burner have and undesirably high SO_2 content which is an atmospheric pollutant.

The above two problems—low market value of the product coke, and atmospheric pollution from the burner—have limited the use of fluid coking which is otherwise a superior residuum conversion process.

An attempt has been made to overcome the above difficulties by replacing the conventional coker burner with an integrated coke gasifier and heater as described and claimed in Ser. No. 880,219, filed Nov. 26, 1969 for A. L. Saxton. In this system hot gas from the gasifier is distributed to the heater through a gas distributor made of high alloy or ceramic material. This distributor adds to the cost and complexity of the process. Furthermore, excessively large quantities of steam must be provided to lift the coke solids for the coker to the gasifier-heater unit.

In accordance with the present invention, these difficulties are overcome by supplying the heat for the coking by cooling the very hot gas from the gasifier from its generation temperature of around 1,800°F. or so to the coking temperature of 1,050° to 1,100°F. and using this gas to replace the steam for lifting the coke from the bottom of the coking zone to the heating zone supplying heat to the coking zone. Additional heat can be provided by adding heated air or gas in the riser from the coking zone to the zone supplying heat to the coking zone or by providing a heated air distributor and bed in the heating zone.

The invention will be better understood by reference to the accompanying drawing which shows in diagrammatic form suitable apparatus for carrying out a preferred embodiment of the invention.

Referring now to the drawing, a carbonaceous material having a Conradson carbon of at least 15 percent, such as heavy residuum boiling 1,050°F.+, or a coal char slurry, or tar sands oil is passed by line 1 into the top of scrubber 2 where it flows downwardly countercurrent to vaporous reaction products and collects in the bottom from where it is passed by line 3 to the upper portion of coking zone 4 onto a fluidized bed of solid particles, e.g., coke of 40–1,000 microns in size, maintained at a temperature of 950°–1,050°F. The contact of the heavy hydrocarbons in the feed and hot contact material results in the heavy hydrocarbons being converted to coke and light hydrocarbons and gases which are removed overhead through cyclone 6 and exit line 7 into scrubber 2 where they are scrubbed by incoming feed. The coke is removed in the dense phase through line 8. The coke from line 8 is picked up by gasification gases produced in the process as described below and flowing in line 9. These gases may be supplemented, if desired, by air or oxygen introduced through line 10. The resulting fluidized mass of particles and coke is carried by line 9 to separator-heater 11. The particles and gas may introduced into separator-heater 11 either through a rough cut cyclone (not shown) or into a bed of coke deposited on solids. Additional air or oxygen can be introduced into this bed by the distributor which fluidizes the bed. The gas from the fluidized particles so introduced is removed through cyclones (not shown) and exit line 12. Solid coke particles fall to the bottom of separator 11 and are withdrawn from the bed through well 13 into standpipe 14. Solids may be withdrawn from separator heater vessel 11 through line 22 for particle size control. The particles in standpipe 14 are lifted by steam or other inert gas or vaporized feed introduced through line 15 and carried to the top of the fluid bed in coker 4. Solids are also fed from separator-heater 11 to a fluidized bed in gasifier zone 17 by a conventional standpipe slide valve system 18. The coke thus introduced is contacted with steam and air or oxygen introduced through line 19 and grid 20. The temperature of the bed is maintained at a level of about 1,400°–2,800°F. by preheating the inlet air, steam, oxygen stream, and/or varying the steam and air ratio according to well-known equilibrium relationships. In the gasifier 17 the following reactions take place:

$$(n+1)C + (0.5+n)O_2 \rightarrow CO + nCO_2 \quad (1)$$

$$CO + O_2/2 \rightarrow CO_2 \quad (2)$$

$$CO_2 + C \rightleftarrows 2CO \quad (3)$$

$$H_2O + C \rightleftarrows H_2 + CO \quad (4)$$

$$H_2O + CO \rightleftarrows CO_2 + H_2 \quad (5)$$

When coke is oxidized, the initial product is a mixture of CO and CO_2 as shown in Equation (1). At temperatures of 1,600°F.+ in the presence of oxygen, CO is rapidly oxidized to CO_2 according to Equation (2). After oxygen has been exhausted, CO_2 reacts with carbon to form CO. At high temperatures, equilibrium favors drawing Equation (3) to the right to form CO. Low pressure also favors this reaction. Reaction (3) is slower than reaction (2). Thus, equilibrium would favor very high CO/CO_2 ratios at conditions of 1,600°–2,800°F. and pressures of 2.7 atmospheres or lower in the gasifier. Steam will also gasify coke as represented by Equation (4). The reaction is slightly endothermic and when steam is substituted for some of the oxygen, the gasification zone temperature drops at a constant quantity of coke gasified. Finally, water reacts with CO to produce CO_2 and hydrogen in the water gas shift represented by Equation (5). Most of the sulfur in the coke will be converted to H_2S with a very small amount of COS being formed.

The gases formed by the above reactions pass upwardly through the gasifier and are removed by line **16** and passed to cyclone **23** where they are separated from entrained solids. The gases leave the cyclone **23** by line **9** and have the typical composition shown below when air is used for gasification:

	Mol % Including H_2O+H_2	Mol % Excluding H_2O+H_2S
H_2	6.5	6.8
H_2O	2.9	
CO	19.9	20.6
CO_2	7.9	8.2
N_2	61.9	64.4
H_2S	0.9	
Total	100.0	100.0

Net heating value on a dry basis is 84.6 BTU/SCF. When oxygen is used for gasification, a typical composition of the gas is:

	Mol % Including H_2O+H_2	Mol % Excluding H_2O+H_2S
H_2	24.2	30.9
H_2O	20.0	
CO	34.2	43.6
CO_2	19.8	25.3
N_2	0.1	0.2
H_2S	1.7	
Total	100.0	100.0

Net heating value on a dry basis is 224 BTU/SCF.

These gases are used to pick up solids coming from the reactor as described above. The quantity of gas is large and can easily carry twice the solids circulation that would be used in a conventional fluid coker. The superficial density is only 0.7 lbs./CF. This high rate reduces the temperature of solids gas mixture to about 1,050°F. (if the gasifier is at 1,800°F.).

Solids from cyclone **23** are passed by line **24** and returned to the dense bed in the gasifier **17**.

Solid particles leave gasifier vessel **17** by line **21** and are introduced into stripper **25** where they are stripped of occluded gases by steam introduced by lines **26** and **27**.

Ash is removed by line **28** and gases containing suspended ash are removed by line **29** and returned to separator-heater **11**.

From the foregoing it is evident that the integration of the use of solids as heat carrier and surface for coke laydown and the use of the product gases to circulate reactor effluent coke permits high solids rates and smaller coke reactors and eliminates need for high temperature grid between the gasifier and heat exchange vessel **11**.

While the process has been described with respect to the circulation of coke as the fluidizing medium used in the process, it is to be understood that a captive bed of fluidized inert particles, such as silica, alumina, zirconia, magnesia, alundum or mullite, or combinations thereof may be used. They may also be particles built up of vanadium, nickel or other contaminants in the feed. The materials may be synthetically prepared or may be naturally occurring material such as pumice, clay kieselguhr, diatomaceous earth, bauxite and the like. This can be advantageous for systems in which substantial quantities of very fine ($<$ about 10μ) particles of foreign solids are released in the gasifier such that very low velocities would be required in order to maintain a stable fluidized bed. Such a captive bed can be fluidized readily without significant entrainment of the captive bed particles at superficial velocities substantially higher than the entrainment velocity of fine particles released from the coke. A captive bed of this type provides a well-mixed reaction zone in the gasifier in which the carbon can be burned and the foreign solids released without causing severe fluidization problems. Some equilibrium concentration of the fine particles are retained in the gasifier bed, thus providing sufficient residence time for complete gasification of the carbon before the bulk of the particles are entrained by the exit gases. The hot gasifier products, including entrained solid particles, pass through a heat exchange bed similar to the bed described in connection with separator-heater **11**. In this heat exchange bed the coke from the reactor would be heated as required to satisfy the reactor heat balance. This type of process would be preferable when processing feeds containing much higher solids than are normally present in petroleum residua, e.g., bitumen from coal, tar sands or shale which may contain 15–20 percent inert solids. The solids, such as fine sand, metal oxides, or the like, contained in the bitumen are released in the captive bed in the gasifier and being smaller than coke are more easily entrained out and carried upwardly through the heat exchange bed. Entrainment will also be high if the residuum fed to the unit has an unusually high Conradson carbon content, resulting in high coke yield.

If there is considerable entrainment from cyclone **23** into line **9** feeding the coking zone, then the particle size of the solids in the unit will depend upon the number of small particles that are entrained in line **9**. If the number is greater than the number normally provided by attrition in the unit, the average particle size in the unit will decrease and stabilize at a lower than normal average particle size which is generally 160 microns. If entrainment rates are excessive, the particle size in the coking zone **4** will become so small that there will be a very high solids loss from the coker and separator-heater **11**. In this situation, inert solids are added to stabilize the particle size in the unit. This may be done through line **30**. Thus, particle size control can be maintained by the ratio of particles added through line **30** and withdrawn through line **22**.

In any case, the particle size should be adjusted to balance surface area required for good coking with high vessel velocities. A particularly desirable distribution of particle size is one in which the mix contains relatively dense small diameter particles and less dense large particles as described in Ser. No. 782,377 filed Dec. 9, 1968 for E. C. Luckenbach. In any case, the average particle size is maintained between 60 and 190μ.

The nature and advantages of the present invention having thus been fully set forth and specific illustration of the same given, what is claimed as new, useful, and unobvious and desired to be secured by Letters Patent is:

1. A continuous dependent fluid coking-gasification process for the production of coke and gases having a high concentration of H_2 and CO comprising:

a. circulating fluidized solid particles through a system comprising a coking zone, a gasifier and a gas-solids separating zone each of said zones having operating conditions dependent on each of said other zones;

b. coking carbonaceous material in the presence of said fluidized solid particles in said coking zone whereby said coke is deposited on said particles;

c. conveying said coke-covered particles from the bottom of said coking vessel to said separating zone by means of a hot lifting gas which departs a substantial portion of its heat to said coke-covered particles;

d. separating said lifting gas from said coke-coated solids in said separating zone;

e. passing a portion of said coke-coated solids from said separating zone to said gasifier and passing another portion of said solids to said coking zone;

f. contacting said coke-coated particles in said gasifier with oxygen-containing gas and steam at a temperature between 1,400°–2,800°F. to convert said coke to a mixture of H_2, CO and CO_2;

g. and withdrawing said mixture of gases from said gasifier and using it as said lifting gas to convey solid particles from said coking zone to said separating zone.

2. The process of claim 1 in which the solid particles consist of coke formed in the process and in which the average particle size of the circulating coke is maintained within the range of 60 and 190μ by controlling attrition and solids entrainment losses in various parts of the unit.

3. The process of claim 1 in which the solid particles consist of a captive bed of inert particles.

4. The process of claim 1 in which hot solid particles are withdrawn from said gasifier and introduced into said lift gas stream to increase the temperature therein.

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