**United States Patent** [19]
**Moser, Jr. et al.**

[11] **3,816,084**
[45] **June 11, 1974**

# [54] COKELESS COKER WITH RECYCLE OF COKE FROM GASIFIER TO HEATER

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[22] Filed: **May 4, 1972**

[21] Appl. No.: **250,321**

**Related U.S. Application Data**

[63] Continuation-in-part of Ser. No. 28,998, April 16, 1970, abandoned.

[52] **U.S. Cl.** .......................... **48/206,** 48/63, 201/25, 201/31, 201/44, 208/127

[51] **Int. Cl.** .......................... **C10j 3/00,** C10b 49/10

[58] **Field of Search** ............. 201/15, 16, 14, 13, 17, 201/31, 44, 21-24, 25; 208/127; 48/206, 63, 197, 203, 202

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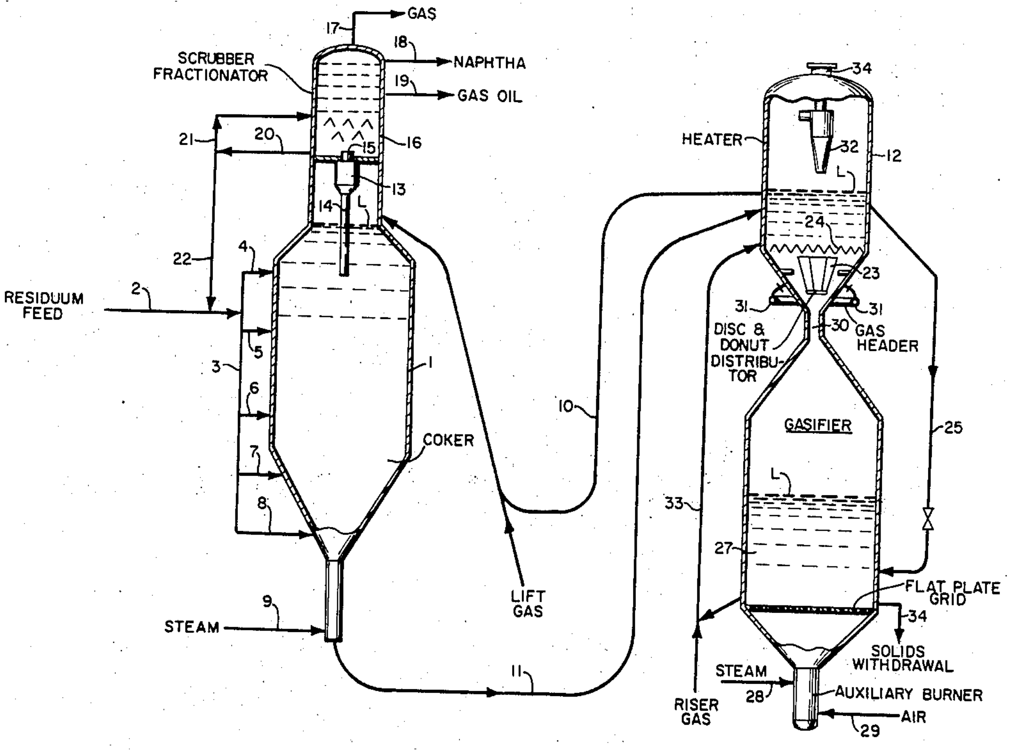
## [57] ABSTRACT

In a fluid coking process in which coke from the coker is passed to a heater and then to a gasifier and in which part of the heat for the heater is supplied by the gases from the gasifier, ungasified coke from the bottom of the gasifier is conveyed through a riser to the heater to supply additional heat and thence back to the coker whereby strength of the coke is increased by fresh coke deposition and in which all the oxygen is injected into the lower gasifier bed thereby eliminating possibility of oxygen breakthrough. The same results can be accomplished by passing the coke from the gasifier directly back to the coke reactor and eliminating the coke stream from the upper heater bed to the reactor.

**17 Claims, 2 Drawing Figures**



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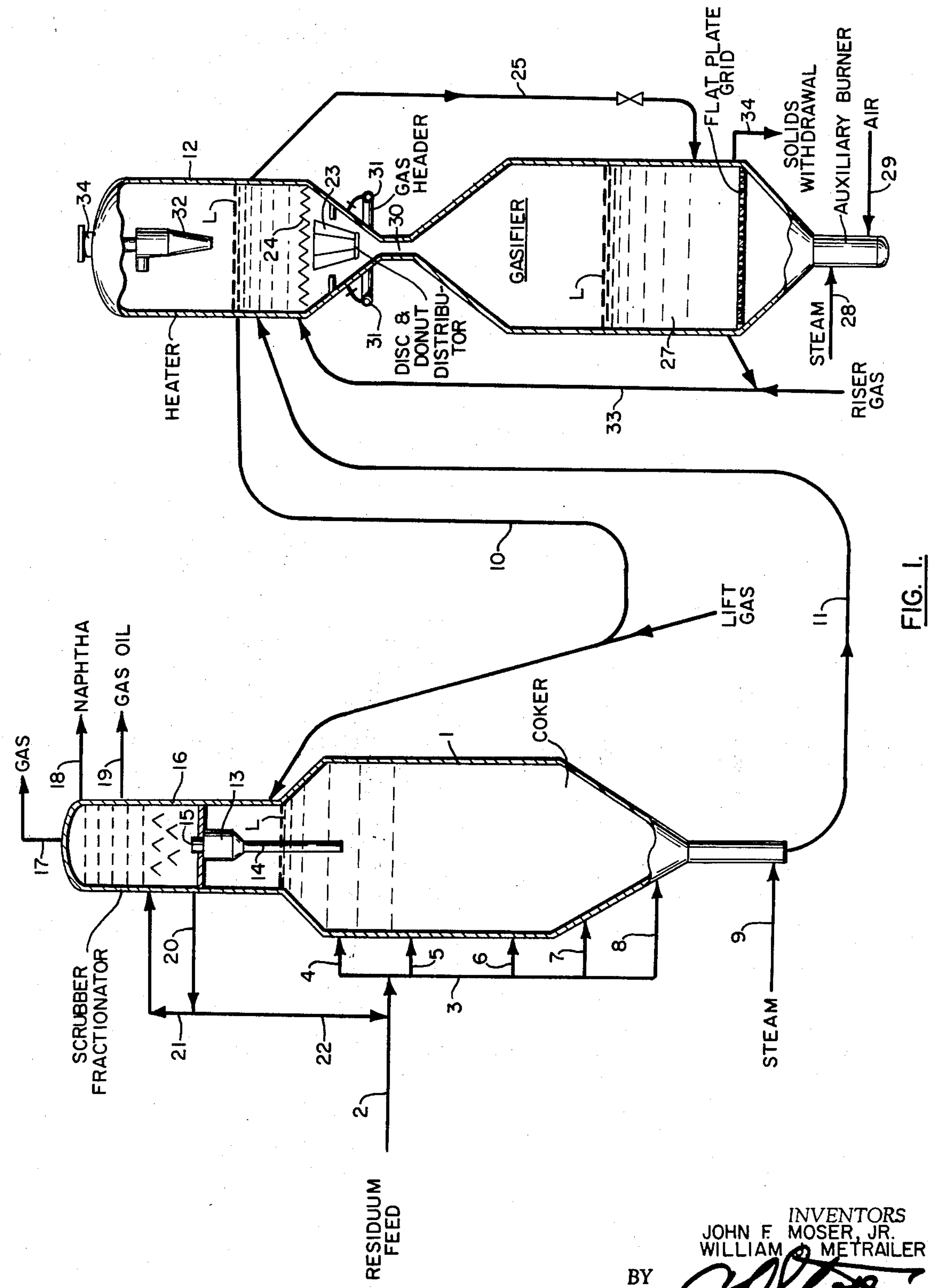

FIG. 1.

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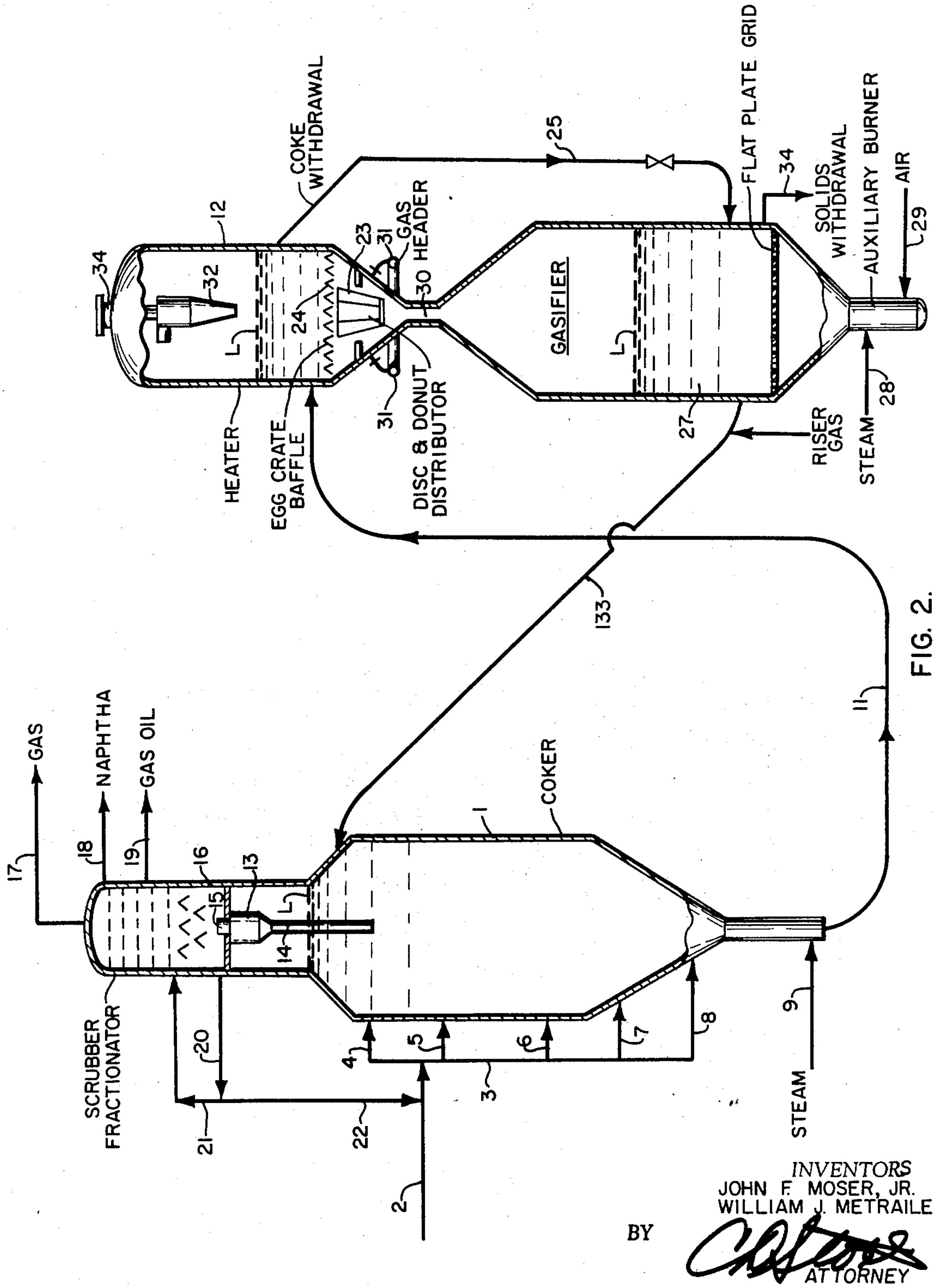

FIG. 2.

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# COKELESS COKER WITH RECYCLE OF COKE FROM GASIFIER TO HEATER

## RELATED APPLICATIONS

This application is a continuation-in-part of Ser. No. 28,998 filed Apr. 16, 1970, now abandoned.

## BACKGROUND OF THE INVENTION

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.

Carbonaceous feeds suitable for the coking process include heavy hydrocarbon oil crudes, atmospheric and vacuum bottoms, pitch, asphalt, bitumen from coal, tar sands or shale, other heavy hydrocarbon residua and mixtures thereof. Typically such feeds have an A.P.I. gravity of about 0° to 20° and a Conradson carbon content of about 5 to 40 weight percent (as to Conradson carbon residue, Sec. A.S.T.M. Test-D-189-65).

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 an 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.

These two problems have been overcome by providing an integrated gasifier-heater assembly in which the heater is placed on top of the gasifier and is operated at a lower temperature with part of the oxygen for burning the coke being introduced into the bottom of the gasifier and all of the gas from the gasifier being passed through the heater. This process is described in Ser. No. 880,219 filed Nov. 26, 1969, now U.S. Pat. No. 3,661,543.

## SUMMARY OF THE INVENTION

The present invention is an improvement on the process described in Ser. No. 880,219 now U.S. Pat. No. 3,661,543. In that case all the gases from the gasifier pass through the heater, but it has been found that these are not normally sufficient to provide all the necessary heat. Therefore supplementary air must be supplied to the heater. The present invention overcomes this deficiency of Ser. No. 880,219 now U.S. Pat. No. 3,661,543, by passing coke from the bottom of the gasifier to the heater. This coke together with the gases from the gasifier supply all the necessary heat needed in the heater and no additional air or oxygen needs to be added to the heater.

In an alternate embodiment the coke from the bottom of the gasifier goes directly to the coke reactor and the coke stream from the upper bed to the reactor is eliminated. This embodiment has the same advantage as the first embodiment in strengthening the coke to prevent its attrition.

Both of these embodiments permit the eventual return of partially gasified coke particles to the reactor where fresh coke is deposited on the coke and gives added strength thereto preventing its attrition and loss as fines. This also permits the injection of all the oxygen into the higher temperature gasification bed and thereby eliminates the possibility of oxygen breakthrough into the fuel gas which could create a dangerous situation.

The gas product from the heater is rich in $H_2$ and CO and is an attractive feed gas for manufacturing a concentrated $H_2$ stream via the well-known water-gas-shift reaction, or for other chemical processes. It is also a good quality fuel. For most purposes the gases will require further treatment — to remove sulfur which is primarily in the form of $H_2S$ and readily removable by available processes such as the Stretford process, and to remove the ash which has been released from the gasified coke. Valuable by-products, sulfur and metals-rich ash, are recoverable from the gas treating facilities.

This improved fluid coking process can be operated to gasify all the coke produced in the coking reactor, or any desired portion of the coke product can be withdrawn.

## BRIEF REFERENCE TO THE DRAWINGS

The invention will be better understood by reference to the accompanying drawing in which

FIG. 1 represents in diagrammatic form one embodiment of the invention in which coke from the gasifier is passed to the heater and in which

FIG. 2 represents another embodiment in which the coke from the gasifier is passed directly to the reactor and the coke stream from the heater to the reactor is eliminated.

## PREFERRED EMBODIMENTS

Referring now to FIG. **1**, a carbonaceous material having a Conradson carbon of about 15 percent, such as heavy residuum boiling 1050°F.+, is passed into coking zone **1** by line **2**, manifold **3** and multiple feed nozzles represented by lines **4, 5, 6, 7** and **8** onto a fluidized bed of solids, e.g., coke of 40 to 1000 microns in size, having an upper level L. Carbonaceous feeds suitable for the present invention are heavy or reduced crudes, atmospheric bottoms, vacuum bottoms, pitch, asphalt, bitumen, other heavy hydrocarbon residua and mixtures thereof. Typically, such feeds may have an A.P.I. gravity of about 0° to 20° and have a Conradson carbon residue of at least about 5 weight percent to about 40 weight percent, preferably above about 7 weight percent. A fluidizing gas, e.g., steam, is admitted to the base of the vessel through line **9** in amounts sufficient to obtain superficial fluidizing gas velocities in the range of 0.5 to 4 ft./sec. Coke at a temperature 100° to 300° F. above the coking temperature is admitted to the coker by line **10** in amounts sufficient to maintain a coking temperature in the range of 900° to 1200°F. The pressure in the coker is maintained in the range of about 10 to 150 lbs. per square inch gauge (psig), preferably in the range of about 10 to 100 psig, more preferably at a pressure not greater than 45 psig, most preferably at a pressure in the range of about 10 to 25 psig. The lower portion of the coker serves as a stripping zone to remove occluded hydrocarbons from the coke. Coke is withdrawn from this stripping zone by line **11** and is circulated to heater **12.** Conversion products are passed through cyclone **13** to remove entrained solids which are returned to the coker through dipleg **14.** The vapors leave the cyclone through line **15** and pass into scrubber-fractionator **16** where they are fractionated to gas leaving by line **17,** naphtha by line **18** and gas oil by line **19.** A heavy stream is removed through line **20,** a portion of which is circulated through conventional heat removal exchangers and returned to scrubber as pumparound by line **21**; another portion is recycled to the coker by line **22.** A small amount of fine solid particles which pass through the reactor cyclone is returned to the coker reactor with this recycle stream.

In heater **12,** stripped coke from the reactor (commonly called cold coke) is introduced by line **11** to a fluid bed of hot coke having a level L. The bed is partially heated by fuel gas passing upward through disc and donut distributor **23** and egg crate baffle **24.** Supplementary heat is supplied by coke circulating in line **33.** Hot coke is removed from the fluidized bed in heater **12** and recycled to the coker by line **10** to supply heat thereto. Another portion is removed from heater **12** by line **25** and passed to a bed of fluidized coke having a level L in gasifier **27.** The coke introduced to the fluidized bed in the gasifier **27** is contacted with steam introduced by line **28** and air or oxygen by line **29.** The pressure in the gasifier is maintained at a level not greater than 150 lbs. per square inch gauge (psig), preferably not greater than about 60 psig, more preferably not greater than about 45 psig. The temperature of the bed in the gasifier is maintained at a level in the range of about 1400°–2800°F., preferably at a temperature greater than about 1600°F., more preferably at a temperature in the range of about 1700° to 1900°F., most preferably at a temperature in the range of about 1800° to 1850°F., by preheating the inlet air, steam, oxygen stream, and/or varying the steam and air or oxygen ratio according to the well known equilibrium relationships in the gasifier **27,** where the following reactions take place:

$$(N+1)C+(0.5+n)O_2 \rightarrow CO+nCO_2 \tag{1}$$

$$CO+O_2/2 \rightarrow CO_2 \tag{2}$$

$$CO_2+C \rightarrow 2CO \tag{3}$$

$$H_2O+C \rightarrow H_2+CO \tag{4}$$

$$H_2O+CO \rightleftarrows CO_2+H_2 \tag{5}$$

When coke is oxidized, the initial product is a mixture of CO and $CO_2$ as shown in equation (1). At temperatures of 1600°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. Thus, equilibrium would favor very high $CO/CO_2$ ratios at temperatures greater than about 1600°F. and low pressures in the gasifier. Steam will also gasify coke as represented by equation (4). This 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. This fact is used to control the temperature of the gasifier. 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 small amount of COS being formed, in accordance with the equations:

$$S+O_2 \rightarrow SO_2$$

$$SO_2+3H_2 \rightarrow H_2S+2H_2O$$

The gases formed by the above reactions pass upwardly through the gasifier and into the heater by way of the narrow neck portion **30.** The gases leave heater **12** through cyclone **32** where any entrained coke particles are returned to the gasifier. Additional inert fluidizing gas may be admitted to the heater by header **31.** The gases then leave by exit **34** and have the following typical composition 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 | — |
| | 100 | 100 |

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 $H_2S + H_2O$ | Mol.% Excluding $H_2S + H_2O$ |
|---|---|---|
| $H_2$ | 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 | — |
| | 100 | 100 |

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

Small quantities of cracked hydrocarbon materials will also be present in the product gases and will increase the heating value of the product gases. The quantity and compositions will vary somewhat depending on the coker reactor feed and on reaction and stripping conditions.

Coke from the bottom of gasifier **27** is passed by line **33** to the heater at a point just above grid **24.**

Riser **33** permits the return of partially gasified coke to the upper bed in heater **12** and aids in controlling the temperature in the heater **12.** The coke is passed subsequently to reactor **1** where fresh coke is deposited in the pores generated in the gasifier. This gives added strength to the particle and prevents its attrition and loss of fines into the fuel gas or product recovery system. Line **34** is provided for withdrawing solids from the gasifier whenever desired.

Referring now to FIG. **2,** this drawing is identical with FIG. **1** except that line **133** takes the coke directly from the bottom of the gasifier to the top of the bed in coker **1** and line **10** of FIG. **1** is eliminated. The same advantages are obtained by this embodiment as are obtained by the embodiment of FIG. **1.**

While the process has been described with respect to the circulation of coke as the fluidized medium used in the process, it is to be understood that a captive bed of fluidized inert particles, such as alundum or mullite, may be used in the gasifier **27.** This can be advantageous for systems in which substantial quantities of very fine (<about 10$\mu$) particles of foreigh 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. Such a captive bed 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 heater **12.** This type of process would be preferable when processing feeds containing much higher solids than are normally present in petroleum residuum, e.g., bitumen from coal, tar sands or shale which may contain 15–20 percent inert solids. The solids, such as fine and, metal oxides, or the like, contained in the bitumen are released in the captive bed in the gasifier and being smaller than the coke are more easily entrained out and carried upwardly through the heat exchange bed. These fine particles will also pass through the conventional cyclones in the heater vessel but can be recovered by a downstream electrical precipitator.

What we claim is:

**1.** In an integrated fluid coking-gasification process for the production of coke and a gaseous stream containing $H_2$ and CO, which comprises:

a. reacting carbonaceous material having a Conradson carbon content of at least 5 wt. percent in a fluid coking zone operating at temperatures between 900°F. and 1200°F. to form coke;

b. introducing at least a portion of said coke into a heating zone operating at a temperature 100° to 300°F. greater than said fluid coking zone temperature to heat said coke;

c. recycling a first portion of the heated coke from said heating zone to said fluid coking zone to provide heat to said fluid coking zone and introducing a second portion of said heated coke to a gasifying zone operating at a temperature greater than the temperature of said heating zone;

d. reacting said second portion of coke in said gasifying zone with steam and an oxygen-containing gas to produce a hot gaseous stream containing $H_2$ and CO;

e. introducing said hot gaseous stream containing $H_2$ and CO and entrained coke into said heating zone, and

f. recovering from said heating zone the resulting cooled gaseous stream containing $H_2$ and CO,

the improvement which comprises: passing a sufficient amount of additional coke from said gasifying zone to said heating zone such that said hot gaseous stream and entrained coke and said additional coke provide all of the heat requirements of said heating zone, coke being the only volatilizable normally solid carbonaceous material introduced into said heating zone.

**2.** A process according to claim **1** wherein said gasifying zone is operated at temperatures greater than about 1600°F.

**3.** A process according to claim **1** wherein said fluid coking zone, said heating zone and said gasifying zone are operated at a pressure not greater than about 150 psig.

**4.** A process according to claim **1** wherein said gasifying zone is operated at a pressure not greater than about 60 psig.

**5.** The process according to claim **1,** wherein said gasifying zone is operated at a pressure not greater than about 45 psig.

**6.** A process according to claim **1** wherein said hot $H_2$ and CO containing gaseous stream is at a temperature greater than about 1600°F.

**7.** A process according to claim **1** wherein an inert fluidizing gas may be introduced to said heating zone in addition to said hot $H_2$ and CO containing gaseous streams.

**8.** A process according to claim **1,** wherein said carbonaceous material is a heavy petroleum oil residuum having a Conradson carbon content of at least about 7 weight percent.

**9.** The process of claim **1,** wherein said heating zone also contains an inert solid.

**10.** In an integrated fluid coking-gasification process for the production of coke and a gaseous stream containing $H_2$ and CO, which comprises:

a. reacting a carbonaceous material having a Conradson carbon content of at least 5 wt. percent in a fluid coking zone operating at a temperature between 900°F. and 1200°F. to form coke;

b. introducing at least a portion of said coke into a heating zone operating at a temperature 100° to 300°F. greater than said fluid coking zone temperature to heat said coke;

c. introducing a portion of the resulting heated coke to a gasifying zone operating at a temperature greater than said temperature of said heating zone;

d. reacting said heated coke portion in said gasifying zone with steam and an oxygen-containing gas to produce a hot gaseous stream containing $H_2$ and CO, whereby the remaining coke is heated to the operating temperature of said gasifying zone,

the improvement which comprises:

e. passing said hot gaseous stream containing $H_2$ and CO and entrained coke to said heating zone to provide all of the heat requirements of said heating zone, coke being the only volatilizable normally solid carbonaceous material introduced into said heating zone,

f. recovering the resulting cooled gaseous stream containing $H_2$ and CO from said heating zone, and

g. passing a portion of the remaining heated coke of step (d) directly from said gasifying zone to said fluid coking zone to provide heat to said fluid coking zone.

**11.** The process of claim **10,** wherein said heating zone additionally contains an inert solid.

**12.** A process according to claim **10,** wherein said gasifying zone is operated at temperatures greater than about 1600°F.

**13.** A process according to claim **10** wherein said fluid coking zone, said heating zone and said gasifying zone are operated at a pressure not greater than about 150 psig.

**14.** The process according to claim **10,** wherein said gasifying zone is operated at a pressure not greater than about 60 psig.

**15.** The process according to claim **10,** wherein said gasifying zone is operated at a pressure not greater than about 45 psig.

**16.** A process according to claim **10** wherein said hot $H_2$ and CO containing gaseous stream is at temperatures greater than about 1600°F.

**17.** A process according to claim **10** wherein an inert fluidizing gas may be introduced to said heating zone in addition to said hot $H_2$ and CO containing gaseous stream.

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