

[54] **FLUID COKING PROCESS
INCORPORATING GASIFICATION OF
PRODUCT ORE**

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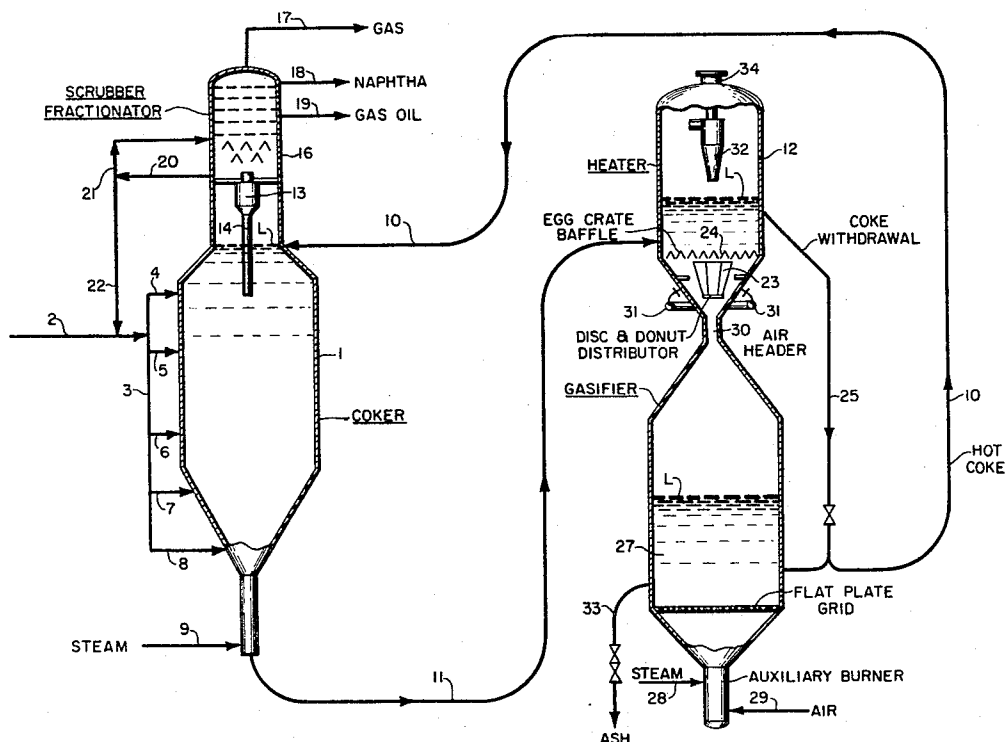
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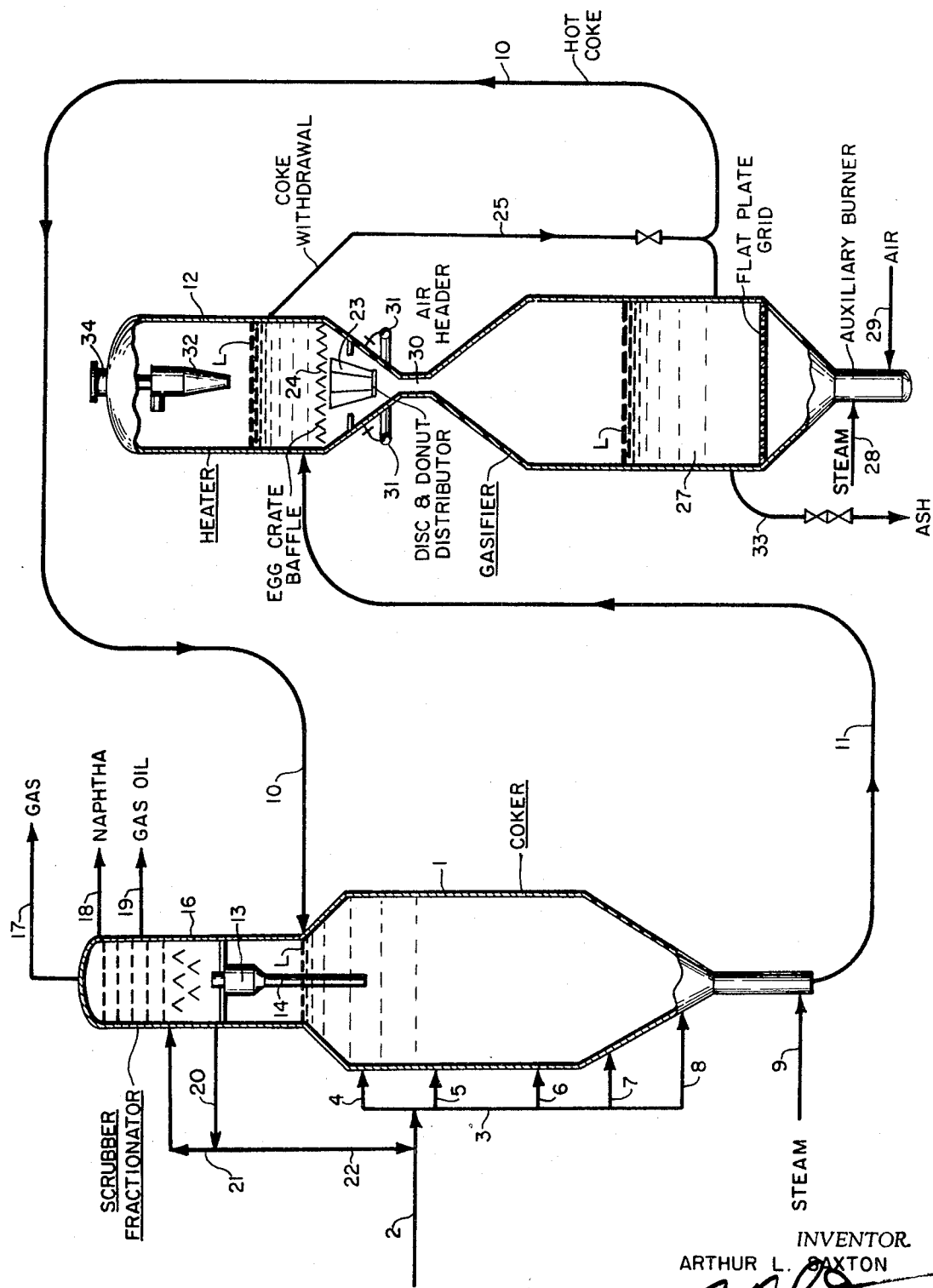
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[57] **ABSTRACT**

A heavy carbonaceous material such as petroleum residuum (1,050° F.+) is converted completely to distillate and gaseous products by an integrated process consisting of a conventional fluid coking reactor, a circulating coke heater, and a gasifier in which the coke formed in the reactor is converted to an H₂ and CO rich gas by reaction with steam and an oxygen-containing gas. The process can also be operated by yield a net product of good quality coke.

10 Claims, 1 Drawing Figure





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FLUID COKING PROCESS INCORPORATING GASIFICATION OF PRODUCT ORE

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 Net coke above that consumed in the burner is withdrawn as product coke.

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 two above 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.

SUMMARY OF THE INVENTION

In accordance with the present invention, the above difficulties can be overcome and the attractiveness of the basic fluid coking process greatly enhanced by replacing the coke burner used in the normal fluid coking process with an integrated coke heater and gasifier system comprising two fluidized beds of coke separated by a grid or other means, wherein coke is gasified in the lower zone in the presence of steam and air or commercially pure oxygen forming hot gases which pass into the upper bed, releasing heat which is transferred to the reactor via a circulating coke stream. Alternatively, the gases from the gasification zone could be combined with the circulating coke from the reactor and conducted through a transfer line into a separator vessel from which the hot coke circulates back to the reactor to supply its heat requirements. In either case, entrained coke will also pass to the heater to provide additional heat for the coker-reactor. Air, O_2 , or other oxygen-containing gas may be added to the heating zone to burn a portion of the CO and hydrogen and thus provide any additional heat which is required to satisfy the coking reactor heat requirement.

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.

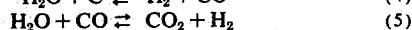
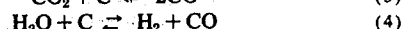
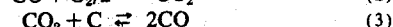
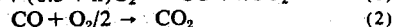
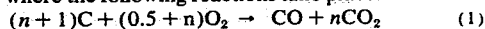
BRIEF REFERENCE TO THE DRAWING

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.

PREFERRED EMBODIMENT OF THE INVENTION

Referring now to the drawing, a carbonaceous material having a Conradson carbon of about 15 percent, such as heavy residuum boiling $1,050^\circ F.$ +, or a coal char slurry, 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 1,000 microns in size, having an upper level L. 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 $300^\circ F.$ 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 $1,200^\circ F.$ 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. The 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 heated by fuel gas passing upward through disc and donut distributor 23 and egg crate baffle 24. Hot coke is removed from the fluidized bed in heater 12 by line 25 and a portion is passed by line 26 to a bed of fluidized coke having a level L in gasifier 27. Another portion is recycled to the coker by line 10 to supply heat thereto. 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 where the following reactions take place:



When coke is oxidized, the initial product is a mixture of CO and CO_2 as shown in equation 1. At temperatures of $1,600^\circ F.$ 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 $1,700^\circ$ – $1,750^\circ F.$ and pressures of 2.7 atmospheres pressure or lower 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. 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 into the heater by way of the narrow neck portion 30. Additional air or oxygen may be admitted to the heater by lines 31 to burn a small portion of these gases and supply additional heat to the coke in the heater. The gases leave heater 12 through cyclone 32 where any entrained coke particles are returned to the gasifier. The gases then leave by exit 34 and have the following typical composition when air is used for gasification:

	Mol.% Including	Mol.% Excluding
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	H ₂ O + H ₂	H ₂ O + H ₂ S
H ₂	6.5	6.8
H ₂ O	2.9	-
CO	19.9	20.6
CO ₂	7.9	8.2
N ₂	61.9	64.4
H ₂ S	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 ₂ S + H ₂ O	Mol.% Excluding H ₂ S + H ₂ O
H ₂	24.2	30.9
H ₂ O	20.0	-
CO	34.2	43.6
CO ₂	19.8	25.3
N ₂	0.1	0.2
H ₂ S	1.7	-
Total	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 composition will vary somewhat depending on the coker reactor feed and on reaction and stripping conditions.

Some net product coke may be withdrawn if desired through line 33. Agglomerates of foreign solids, which may form in some cases, can also be purged via this line through an elutriator from which any included coke can be blown back into the gasifier.

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 μ) 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. 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. 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 residuum, 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 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.

EXAMPLE

A Kuwait vacuum residuum containing 5.5 wt. percent sulfur, boiling 1,050° F. + and having a Conradson carbon of 21.8 is introduced into the fluidized bed of coker 1, operating at 975° F. The coke produced is passed to heater 12 at 950°-975° F. and heated with gases from gasifier 27 at 1,800° F. This gas is formed from coke gasified in gasifier 27 by air or oxygen and steam introduced thereto. The gas leaves the heater at 1,150° F. After transferring heat to the circulating coke. Virtually all solid material is removed from the gas by cyclone 32.

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Steam/air rates are controlled to maintain the gasifier bed at a temperature of about 1,800° F. The heater operates at a pressure of 20 psig and the gasifier at 25 psig.

The following data are obtained:

TABLE I

Operating Conditions and Feed and Product Compositions

Coker Feed and Operating Conditions

Coker feed	12,000 B/SD
Rate	Kuwait 1050°F.+Residuum
Source	
Con. carbon, wt. %	21.8
Sulfur, wt. %	5.5
Gravity, °API	5.7
Va, ppm	113
Ni, ppm	25
Total ash, ppm	252

Operating conditions

Reactor temperature, °F.	975
Reactor product final cut point, °F.	950
Coke circulation rate, tons/min.	15.5
Heater zone temperature, °F.	1150
pressure, psig	20
Gasifier zone temperature, °F.	1800
pressure, psig	25

Coke composition	Gross	Oil	Net to gasification
Hydrogen, wt. %	6.0	14.7	2.5
Carbon, wt. %	86.6	77.9	90.1
Sulfur, wt. %	7.4	7.4	7.4
Va, ppm	410	—	—
Ni, ppm	90	—	—
Total ash, ppm	906	—	—
Product gas composition	Air/Steam Gasification	Oxygen/Steam Gasification	
Composition, mol. %			
CO	20.4	42.0	
CO ₂	6.6	18.0	
H ₂	4.4	18.7	
H ₂ O	1.4	6.7	
(CH) ₄	5.0	11.0	
H ₂ S	1.2	2.6	
N ₂	61.0	1.0	
	100.0	100.0	
Fuel gas heating value (HHV) BTU/SCF (ex. H ₂ S)	150	350	

The material balance on the heater gasifier is as follows:

TABLE II.—HEATER-GASIFIER HEAT AND MATERIAL BALANCE

Material Balance: (Number for oxygen/steam gasification shown in parenthesis where different from air/steam gasification.)

	1	2	3	4	5
	Air or (oxygen)	Steam	Cold coke from reactor	Entrained oil	Hot coke to reactor
Steam					
Temp., ° F	350	353	975	975	1,150
M#/hr.		4(14)	1,895	14.4	1,860
Mol/hr.	6,030(1,070)				
ACF/min.					
	6	7	8	9	10
	Gasifier feed	Gasifier stage product gas	En- trained coke to heater	Supple- mentary air (or oxygen) to upper zone	Product gas
Temp., ° F	1,150	1,800	1,800	350	1,150
M#/hr.	136(132)		100(96)		
Mol/hr.	8,100(3,917)		1,630(460)	9,980(4,446)	
MACF/min.	82.3(39.9)			83.7(37.4)	
Heater section heat balance			Air/steam	Oxygen/steam	
Heat load:					
Heat to circulating coke			130.0		130.0
Entrained oil heat of cracking			5.0		5.0
Heat to transfer line steam			3.4		3.4
Heater heat losses			3.6		3.6
Total			142.0		142.0
Heat supply:					
Gas from gasifier			42.0		20.1
Entrained coke			28.6		28.5
Combustion of CO and H ₂ in heater			71.4		93.4
Total			142.0		142.0

It will be appreciated that operating conditions, product gas composition and the overall heat and material can vary substantially from the above data, depending on such variables as the coker reactor feed and the coker product objectives.

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

1. An integrated fluid coking-gasification process which comprises:
 - treating a carbonaceous material in a low pressure fluid coking zone comprising a fluid bed of particles operating at a temperature between about 900° and about 1,200° F. to produce coke and light hydrocarbon material, some of which may adhere to said coke;
 - heating to a higher temperature said coke in a low pressure heating zone comprising a separate fluid bed of particles;
 - passing a portion of said heated coke to said fluid coking zone and another portion of said heated coke to a low pressure gasification zone;
 - contacting said heated coke in said gasifying zone with steam and an oxygen-containing gas to produce a metal-rich ash and a gaseous stream containing hydrogen and carbon oxide gases;
 - passing said ash and gaseous stream to said heating zone to provide a substantial part of the heat required in said heating zone;
 - recovering said gaseous stream of said heating zone.

2. A process according to claim 1 wherein the pressure in said fluid coking zone, said heating zone and said gasifying zone is less than about 3.0 atmospheres.

3. A process according to claim 1 wherein said gasifying zone comprises a separate bed of fluidized particles.

4. A process according to claim 3 wherein said gaseous stream leaving said gasifying zone passes through a distributing zone before entering said heating zone to provide for more even gas flow in said heating zone, as well as, better fluidizing of said heating zone bed.

5. A process according to claim 4 wherein additional oxygen-containing gases are mixed with said gaseous stream and said mixture passed through said distributing zone and then into said heating zone.

6. A process according to claim 1 wherein said coke produced in said fluid coking zone is passed through a stripping zone and contacted with a stripping gas to remove a major portion of said adhering light hydrocarbon material before said coke is heated in said heating zone.

7. A process according to claim 6 wherein said stripping gas is steam.

8. A process according to claim 1 wherein said metal-rich ash is recovered from said heating zone by cyclone means.

9. A process according to claim 5 wherein a portion of said metal-rich ash is recovered from said gasifying zone.

10. A process according to claim 1 wherein a portion of said steam treated, heated coke in said gasifying zone is removed from said gasifying zone.

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