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(12) Patent:

(54) PROCESS FOR GASIFICATION OF HYDROCARBONS TO HYDROGEN AND CARBON MONOXIDE

(54)

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1           The present invention relates to an improved  
2 process for reacting hydrocarbons in a fluidized bed of  
3 hot carbonaceous solids to make a reducing gas  
4 consisting predominantly of carbon monoxide and  
5 hydrogen. More specifically, the present invention  
6 relates to an improved process for converting  
7 hydrocarbonaceous gaseous and liquid fluids into  
8 reducing gases having high CO/CO<sub>2</sub> and high H<sub>2</sub>/H<sub>2</sub>O  
9 ratios in the presence of an oxidizing gas, such as  
10 air, and in the further presence of a fluidized bed  
11 of hot carbonaceous solids. Still more specifically,  
12 the present invention relates to an improved process  
13 for converting heavy oils and residua into a gaseous  
14 product richer in H<sub>2</sub> and CO than processes presently  
15 available.

16           Coking hydrocarbons and gasifying the  
17 product with an oxygen-containing gas, such as air,  
18 oxygen or steam, is well known by this time. The  
19 processes generally involve subjecting a heavy oil  
20 in the presence of a fluidized particulate mass,  
21 such as adsorbents, coke, activated carbon, and the  
22 like, in a gasification zone to contact with an oxidizing  
23 gas. The hydrocarbonaceous material is cracked, and  
24 the cracked products are oxidized. Though the mechanism  
25 is not too clear, probably the initial reaction products  
26 are CO<sub>2</sub> and H<sub>2</sub>O. These interact at least in part with  
27 carbon either present in the bed or formed during the

\*

1 cracking step to produce H<sub>2</sub> and CO. Reaction  
2 temperatures are about 1800-2000°F. and heat for this  
3 is furnished by the combustion process.

4           An important problem connected with this  
5 process is the control of the reaction products' ratios.  
6 In particular when the gases are to be used for reducing  
7 purposes, as in metallurgical operations, it is  
8 important to recover a gas having the highest possible  
9 CO/CO<sub>2</sub> ratio. Ideally, this should be accomplished  
10 by injecting air and hydrocarbons at such stoichiometric  
11 ratios that essentially all of the carbon in the feed  
12 is converted to CO, in accordance with the equation  
13  $CH_x + \frac{1}{x}O_2 \rightarrow CO + \frac{x}{2}H_2$ . However, experience has shown  
14 that substantial portions of the oxygen in the product  
15 gas are in the form of CO<sub>2</sub> and H<sub>2</sub>O rather than CO and H<sub>2</sub>.  
16 The former gases are oxidizing constituents and are  
17 undesirable as constituents of reducing gases.

18           The present invention in its principal  
19 feature is based on the discovery that gas quality,  
20 i.e. the carbon recovery, is markedly improved when the  
21 gasification reactor is operated under "coke consumption  
22 conditions." "Coke consumption" means that part of the  
23 coke bed in the reactor is consumed continuously, and  
24 this is accomplished by lowering the carbon to oxygen  
25 ratio in the feed inlet stream. Thus, for example,  
26 if it is desired theoretically to convert all of the  
27 carbon in the hydrocarbon feed stream to carbon monoxide,

1 it would be necessary, theoretically, to introduce into  
2 the reactor two moles of carbon for every mole of  
3 oxygen. Again, theoretically, the exit gas ratio of  
4  $C/O_2$  will then be 2. This exit gas ratio is termed  
5 the "carbon recovery" and is a convenient measure of  
6 reducing gas quality. If the  $C/O_2$  ratio of the  
7 feed stream is greater than the  $C/O_2$  ratio of the exit  
8 stream, i.e. carbon recovery, coke builds up in the  
9 reactor in accordance with the generalized reaction  
10  $CH_x + O_2 \rightarrow CO_2 + CO + H_2O + H_2 + C$ . The conditions  
11 promoting this reaction are referred to as "coke  
12 deposition" conditions. On the other hand, if the  
13  $C/O_2$  ratio of the feed is less than the  $C/O_2$  ratio of  
14 the product, coke is consumed from the reactor in  
15 accordance with the reaction  $CH_x + O_2 \rightarrow CO_2 + CO + H_2O +$   
16  $H_2 - C$ . This is referred to as "coke consumption"  
17 conditions, and coke is depleted from the reactor, i.e.  
18 it is consumed from the fluidized coke bed.

19 In actual practice the carbon recovery of the  
20 product is a long way from 2 and is governed by the  
21 kinetics of the gasification reaction. At low temperatures  
22 and short holding times over a relatively inert solid  
23 such as fluidized coke it may be as low as 1 or even  
24 less. At high temperatures, long holding times and  
25 very active carbonaceous solids, such as activated  
26 carbons, it may be as high as 1.9. Thus under coke  
27 deposition conditions, the following have been observed.

1

TABLE I

2

## Carbon Recoveries

3

Coke:

Fluid CokeActivated Carbon

4

Holding Time, Secs.

155515

5

1800°F.

1.05 1.36

1.45

6

1900°F.

1.22 1.55

1.65

7

2000°F.

1.39 1.74

1.85

8

From these data it is apparent that it is

9

necessary to go to very high holding times and/or to

10

use very high temperatures and/or highly activated

11

carbons in order to obtain good carbon recoveries.

12

The gasification of hydrocarbons may be done

13

for a variety of desired end products, i.e. town gas,

14

synthesis gas, hydro gas, reducing gas, etc. It is

15

clear that the end use of the gaseous product will

16

determine its desired composition. In many applications,

17

specifically in direct iron ore reduction (therefore

18

"reducing gas") the gas must have very high ratios of

19

CO/CO<sub>2</sub> and H<sub>2</sub>/H<sub>2</sub>O to maintain an equilibrium over the

20

iron oxide favorable for iron formation. Ideally, the

21

gas consists of pure hydrogen and CO. Carbon recovery

22

is a convenient measure of the reducing efficiency of

23

a gas. This is illustrated in the following table.

24

TABLE II

25

Iron Ore Reduction at 1800°F.

26

Carbon RecoveryMoles Fe Reduced/Mole C in Gas

27

1.29

0

28

1.6

0.3

29

2.0

0.53

30

Based on C/H ratio of gas = 1.6

1 These numbers are determined solely by the Fe - O -  
2 C - H equilibrium and show that for iron ore reduction  
3 at 1800°F. to proceed at all, the gas must have a  
4 carbon recovery of better than 1.3. For economical  
5 reasons it should be better than 1.6. It is  
6 important to realize that the gasification of  
7 hydrocarbons with air is not thermodynamically  
8 limited above 1800°F. At 1800°F. and above the  
9 thermodynamic equilibrium, carbon recovery is  
10 essentially equal to 2, i.e. greatly favors formation  
11 of CO and H<sub>2</sub>. Despite this favorable thermodynamic  
12 equilibrium Table I points out that high gas qualities  
13 acceptable for iron ore reduction are obtained only  
14 with great difficulty over fluid coke and with  
15 decreased difficulty over activated carbon. In  
16 other words, this is a rate limited process affected  
17 by properties of the solid, over which gasification  
18 is conducted. This invention teaches the unexpected  
19 result that coke consumption conditions in the reactor  
20 greatly enhance the rate of conversion of hydrocarbons  
21 to CO and H<sub>2</sub>. This means that a smaller reactor and  
22 lower temperatures can be utilized.

23 It is therefore an important object of the  
24 present invention to set forth a novel and improved  
25 process for making reducing gases from hydrocarbons  
26 and in particular from heavy hydrocarbon oils, and  
27 obtain high yields of CO and H<sub>2</sub>.

1           It is a further object of the present invention  
2 to set forth a two-stage process for effectively  
3 converting hydrocarbons into reducing gases.

4           Other and further objects and advantages of  
5 the present invention will be more clear hereinafter.

6           It has now been found that gas quality, in  
7 terms of carbon recovery, is markedly improved when  
8 the gasification reactor is operated under coke  
9 consumption conditions. In fact, improvement of conversion  
10 of over 45% has been realized when, under the same  
11 conditions of temperature and residence time, the  
12 gasification reactor has been operated in coke consumption  
13 rather than coke deposition conditions, i.e. with coke  
14 being consumed from the fluidized bed rather than  
15 being deposited therein. These results are unexpected  
16 for the following obvious reasons. The rate of solid-  
17 gaseous reactions is proportional to the time of  
18 exposure over the active surface. That this is so for  
19 the gasification system is shown in Table I. At the  
20 same temperature, longer holding times over fluid coke  
21 gave better gas qualities. And accordingly, when the  
22 holding time is decreased, poorer gas qualities are  
23 obtained.

24           Under coke consumption conditions, however,  
25 the reverse is found to be true. Due to the fact that  
26 coke is consumed from the reactor, the fluid bed level  
27 decreases. Thus, the holding time of the reactants over

1 the coke is decreased. It would have been expected  
 2 therefore that under coke consumption conditions  
 3 the gas quality deteriorates rather than improves.  
 4 That the reverse is true is shown by the following run  
 5 record obtained under coke consumption conditions.

6 TABLE III

7	Run	Feed Rate	Air Rate	Coke	Carbon
8	Hour	g/hr.	SCFH	Holdup, Hr.	Recovery
9	3	244	70	29.8	1.49
10	5	"	"	28.4	1.50
11	7	"	"	27.1	1.49
12	9	"	"	25.8	1.53
13	11	"	"	24.6	1.55
14	13	"	"	23.5	1.58
15	15	"	"	22.3	1.66

16 The reasons why operating a gasification zone  
 17 under coke consumption conditions should so markedly  
 18 affect the product gas quality are not exactly known.  
 19 One explanation may lie in the observation that,  
 20 under coke consumption conditions, the surface area  
 21 of the coke comprising the fluidized bed is markedly  
 22 increased, and this more active coke may be more  
 23 efficiently utilized by the reacting gases. Similarly,  
 24 under coke deposition conditions it has been found  
 25 that the coke surface area is destroyed.

26 In accordance with the present invention,  
 27 therefore, a gasification zone wherein an oxidizing



1 gas, such as air, and a hydrocarbonaceous fluid such  
2 as heavy oils, Bunker C, tars and the like, are  
3 contacted at very high temperatures in the presence  
4 of a fluidized bed of coke is operated under coke  
5 consumption conditions.

6           Since coke is depleted from the fluidized  
7 bed, it must be replenished for a continuous operation.  
8 This can readily be effected by adding fresh coke to  
9 the reactor concomitantly with the addition of the  
10 hydrocarbon and the oxidizing gas. In one modification,  
11 a low temperature coking process furnishes the coke  
12 necessary to maintain the coke inventory in the  
13 gasification zone.

14           In operation of the gasification zone, the  
15 fluidizable coke particles have a size of about 40 to  
16 300 microns and form a turbulent dense bed when the  
17 fluidizing gas has a linear velocity in the range of  
18 0.5 to 4 feet per second through the bed.

19           For the gasification reaction in which the  
20 hydrocarbon feed material, liquid or gaseous,  
21 dispersed in the fluidized solids bed, the bed  
22 temperatures are in the range of 1750° to 2400°F.,  
23 preferably 1750° to 2100°F., with a small temperature  
24 gradient preferably less than 100°F. throughout the  
25 bed.

1           Pressures in the gasification reaction zone  
2 are generally slightly above atmospheric, e.g. 0 to 40  
3 psig., but the pressure can be increased.

4           The hydrocarbon feed should be admitted into  
5 the fluidized solids sufficiently above the bottom of  
6 the bed, i.e. where the air enters the bed, to avoid  
7 direct oxidation of the hydrocarbons by oxygen which  
8 causes formation of hot spots that in turn may cause  
9 deactivation and results in a fine carbon black  
10 formation. Such fine carbon black is less than 1 micron  
11 in size generally. Also, the hydrocarbon entrance into  
12 the bed should not be too far up toward the top of the  
13 bed, but where sufficient time of contact is allowed  
14 for the gaseous hydrocarbons from the feed to decompose  
15 in the presence of the coke-bearing fluid solids, at a  
16 temperature above 1750°F. For example, the hydrocarbons  
17 could be made to enter the bed about 1 foot above a  
18 grid, supporting the bed and through which air is  
19 distributed into the bed while a remaining 3 to 10 or  
20 more feed of the bed is above the level where the  
21 hydrocarbon feed enters. Thus, the turbulently  
22 agitated solids receiving carbon and coke deposits  
23 undergo sufficient rapid backmixing into contact with  
24 the air entering the bottom of the bed to obtain  
25 oxidation of such deposits, thus maintaining practically  
26 a uniform temperature throughout the bed.

1           The process of the present invention can be  
2 more clearly understood in connection with the drawing,  
3 wherein Figure 1 shows an apparatus suitable for  
4 carrying out the process of the present invention, and  
5 Figure 2 shows an embodiment employing a two vessel  
6 system including a coker and a gasifier.

7           The reactor shown in Figure 1 comprises  
8 vessel 1 containing fluidized solids and having  
9 communicating parts. Vessel 1 may be a heat-resistant  
10 steel shell lined with heat-resistant refractory material.

11           A central draft tube 2 constructed of suitable  
12 refractory material; e.g., silicon carbide, ceramics,  
13 metal alloy, or metal with refractory lining, is  
14 disposed in vessel 1 to partition off an interior  
15 reaction zone 3 where oxidation of coke or carbon  
16 deposits on the circulated solids takes place.

17           Carbon containing solids are passed from  
18 fluidized bed 4 of the hydrocarbon decomposition zone  
19 by way of pipe 5 and inlet pipe 6 into zone 3.

20           A free oxygen containing gas; e.g., air or  
21 enriched air, for oxidation of the coke deposits on  
22 the solids circulated to zone 3 is supplied from line 7.  
23 This air may be preheated; e.g., to a temperature of  
24 400° to 1000°F.

25           The fluid hydrocarbon feed, such as methane,  
26 liquid hydrocarbon, or both gaseous and liquid  
27 hydrocarbons, is introduced through feed line 8 into

1 solids bed 4 where the hydrocarbon material is  
2 decomposed to form hydrogen and coke deposits at a  
3 temperature in the range of 1750° to 2000°F. A  
4 hydrocarbon feed introduced as liquid may have a  
5 preheat temperature of 200° to 650°F. Gaseous  
6 hydrocarbon feeds may have a higher preheat  
7 temperature; e.g. up to 1200°F.

8           The heat carrying solids are maintained in a  
9 fluidized state in both the cracking and oxidation  
10 zone. By fluidized is meant the maintaining of solid  
11 particles having a size in the range of 25 to 1000  
12 microns in the form of a dense bed having a fairly  
13 distinct upper level using a fluidizing gas with a  
14 superficial gas velocity in the range of 0.2 to 10  
15 ft./sec., preferably 0.5 to 3 ft./sec., and the  
16 maintaining of such sized particles in a more dilute  
17 entrained state at such gas velocities, with the  
18 solids in both instances occupying at least 20 vol. %  
19 of the gas solids mixture. The fluidized solids  
20 provide turbulent mixing and excellent heat transfer  
21 between the zones. By the turbulent mixing of the  
22 solids, the temperature variation ( $\Delta T$ ) throughout  
23 the bed 4 is kept sufficiently small to prevent hot  
24 spot formation. Heat is added to the solids in bed 4  
25 by conduction and radiation from tube 2, from walls of  
26 vessel 1, and from solids overflowing from tube 2 at  
27 its upper end. A deflecting baffle 12 may be located

1 above the upper outlet of tube 2.

2           Gaseous product is withdrawn from vessel 1  
3 through gas exit line 10. It consists principally of  
4 carbon monoxide formed inside tube 2 and free hydrogen  
5 rising from bed 4, which become admixed in the solids  
6 disengaging space above the zones. This gaseous  
7 product passes through one or more cyclone separators  
8 11 having inlet ports 13, dip legs 15 for return of  
9 solids separated from the gases back to bed 4, and gas  
10 outlet lines 17 to main gas line 10 which conducts the  
11 gases to any unit or plant where they are used; e.g.  
12 for reducing an iron oxide. The product gases may  
13 be given other treatment if desired; e.g. by hot  
14 carbon to increase the concentration of carbon monoxide  
15 or a catalytic water gas shift treatment that increases  
16 the yield of hydrogen by the reaction of the carbon  
17 monoxide component with water.

18           Adequate turbulence of the solids in bed 4 to  
19 keep the  $\Delta T$  low; i.e. below 100°F., throughout the bed  
20 is obtained by regulated flow rate of the hydrocarbon  
21 feed into the bed. Even when injecting a liquid  
22 hydrocarbon feed sufficient quantities of gaseous  
23 decomposition products, vapors and hydrogen are  
24 formed instantaneously and maintain fluidization of  
25 the solid particles. Thus, the dense bed of solid  
26 particles 4 can be kept free of undesired gases,  
27 especially oxygen or oxidizing gases.

1           Solid coke particles of suitable size for  
2 fluidization, e.g. petroleum coke or activated coke,  
3 are added through inlet 19 when the solids require  
4 replenishment. Used solids can be withdrawn through  
5 line 20.

6           The air used for reaction with carbon deposits  
7 on the solids is preferably introduced in a zone  
8 sufficiently separate from the hydrocarbon cracking  
9 zone to prevent partial oxidation of the hydrocarbon  
10 feed. In the operation of the reactor shown in  
11 Figure 1, air is introduced into the lower end of  
12 draft tube 2 and converts the carbon on the solids  
13 circulated from bed 4 by line 5 to carbon oxides. The  
14 oxidizing reaction in zone 3 is highly exothermic and  
15 permits a temperature above 2000°F. to be maintained  
16 in zone 3. Over 75% of the heat requirements of the  
17 gasification process of this invention are supplied by  
18 this oxidation of the carbon deposits.

19           The high temperatures in zone 3 favor  
20 formation of a high proportion of carbon monoxide  
21 relative to carbon dioxide. The reaction in the  
22 oxidizing zone 3 between carbon and oxygen from the  
23 air is a stepwise process in which first the carbon is  
24 believed to be oxidized to carbon dioxide. This  
25 reaction is very fast and highly exothermic. As carbon  
26 dioxide is formed, a second reaction takes place  
27 between carbon dioxide and carbon to form carbon

1 monoxide. The second reaction is endothermic and  
2 relatively slower than the first reaction and is  
3 favored by high temperatures, preferably temperatures  
4 above 2000°F. to go to completion. Thus, the conversion  
5 to carbon monoxide and the temperature in the oxidizing  
6 zone inside the draft tube are interrelated. The  
7 operation of the oxidation zone 3 and preheating  
8 requirements depend on the carbon monoxide concentration  
9 desired in the gas formed. For approximately complete  
10 conversion of the oxygen from the air to carbon  
11 monoxide, temperatures of 2200°F. and above are usually  
12 required for a convenient short holding time in the  
13 oxidation zone. In order to reach such elevated  
14 temperature, the air should be preheated to above  
15 500°F.

16           While gas containing mainly nitrogen and  
17 carbon monoxide flows out at the upward open end of  
18 tube 2 when air is used as the source of oxygen, nearly  
19 pure hydrogen is produced in the bed 4 by the cracking  
20 of the hydrocarbon feed in this bed. A relatively  
21 small amount of water is formed inside the oxidation  
22 zone 3 by oxidation of hydrogen in and absorbed by the  
23 coke on the solid particles. In the upper part of the  
24 reactor a small amount of water may be formed by the  
25 reversible reaction of carbon dioxide with hydrogen.

26           The location of the oxidation zone is inside  
27 the vertical draft tube 2 of Figure 1 so that it is

1 separated from, but in good heat transfer relationship  
2 to, the hydrocarbon cracking zone. Much of the heat  
3 formed in the oxidation of the coke deposits can be  
4 conducted through the tube wall and then be radiated  
5 into the surrounding bed 4 on all sides. Thus in the  
6 hydrocarbon cracking zone 3, a temperature in the range  
7 of 1750° to 2000°F. can be maintained with low  
8 variation in temperature throughout the bed.

9           The height and diameter of the draft tube 2  
10 is designed for maximum efficiency in oxidizing carbon  
11 and coke deposits on the solids to carbon monoxide with  
12 a linear gas flow rate up through the tube in the range  
13 of 3 to 10 feet per second. With this rate of flow,  
14 the gas products, mainly carbon monoxide with a small  
15 amount of carbon dioxide, carry solids in suspension up  
16 to the top of the tube where the solids spill over into  
17 the surrounding cracking zone bed where the hot solids  
18 add heat, serve to promote the cracking reaction and  
19 accumulate fresh coke deposits from the cracking of  
20 the hydrocarbon feed.

21           Vessel 1 is operated, in accordance with the  
22 present invention, to maintain carbon consumption  
23 conditions. Table I lists pertinent operating  
24 conditions and provides a specific example thereof,  
25 drawn with reference to Figure 1.



TABLE IV

Operating Conditions for Coke Consumption

	<u>Broad</u>	<u>Preferred</u>
4 Temperature, °F.	1700-2200	1800-2000
5 Pressure, psig	0-100	20-50
6 Feed, C/O <sub>2</sub> mole ratio	0.5-1.5	1.0-1.5
7 Superficial velocity, Ft./Sec.	0.5-4.0	1.0-2.5
8 Lbs. solids holdup/mole O <sub>2</sub>		
9 in air/hr.	100-2000	300-1000
10 Solids may be any form of coke or carbonaceous solids.		

11 In Figure 2 there is shown diagrammatically  
 12 a simplified scheme for providing coke to replenish  
 13 that consumed in the operation of the gasification  
 14 step. Hydrocarbon feed, such as Bunker C oil, is  
 15 precoked in vessel 50 at normal coking temperatures,  
 16 in the range of 900° to 1300°F., and in a conventional  
 17 manner well known per se, enough air is admitted to  
 18 coker 50 solely to maintain a heat balance. There-  
 19 after, both coke and product gases, mostly hydrocarbons  
 20 with some oxides of carbon, water, nitrogen, etc., are  
 21 passed via lines 52 and 53 respectively to gasification  
 22 vessel 60. Here the temperature is raised to the  
 23 desired gasification temperature by further air  
 24 addition through line 58. In this manner the  
 25 gasification stage is always operated under coke  
 26 consumption conditions. A further advantage of this  
 27 two stage system is that the H<sub>2</sub>/CO ratio of the

1 product gases may be varied at will by withdrawing  
 2 portions of the gaseous product from vessel 50 through  
 3 line 55 or by admitting further hydrocarbon feed to  
 4 vessel 60 through line 62. No heat losses are  
 5 incurred because the over-all balance remains the  
 6 same.

7 The process of the present invention may be  
 8 further illustrated by the following specific examples.

9 Example 1

10 In a gasification process wherein a high  
 11 Conradson carbon petroleum fraction was gasified by  
 12 injection into a bed of fluidized coke, a 45% increase  
 13 in conversion was obtained when, under the same  
 14 conditions of temperature and holding time, the  
 15 gasification was carried out under coke consumption  
 16 conditions rather than coke deposition conditions.

17 Carbon Recovery over Fluid Coke at 1915°F.

18 <u>Coke Consumption</u>		19 <u>Coke Deposition</u>
19 10 secs.	20 Holding Time	10 secs.
20 1.57	21 Carbon Recovery	1.13

21 At 2000°F., the following results were  
 22 obtained:

23 <u>Coke Consumption</u>		24 <u>Coke Deposition</u>
24 0.017	25 Feed Rate, W/H/W	0.017
25 1.85	Carbon Recovery	1.74

26 These data were obtained with 35% coke  
 27 consumption, based on feed. Depending on the C/O<sub>2</sub>

1 ratio of the feed, the coke in the reactor may be  
2 consumed rapidly or slowly.

3 Example 2

4           The coke holdup in the reactor is 30.9 lbs.  
5 The feed is a Bunker C fuel oil with a gravity of  
6 12.6°A.P.I., a C/H of 8.36 and a Conradson carbon of  
7 16.0 wt.%. It is atomized into the reactor, one foot  
8 above the grid, with an inert N<sub>2</sub> stream at a rate of  
9 445 g/hr. Air is admitted to the reactor below the  
10 grid at a rate of 70 SCFH. This corresponds to a  
11 C/O<sub>2</sub> molar feed ratio of 1.5 and an inverse space  
12 velocity (lbs. C/mole O<sub>2</sub>/hr) of 800. Reactor  
13 temperature is 1900°F. Superficial velocity through  
14 the reactor, based on outlet gas rate, is 0.67 ft/sec.  
15 The average product dry gas analysis is:

16	H <sub>2</sub>	-	8.8
17	N <sub>2</sub>	-	72.6
18	CH <sub>4</sub>	-	1.0
19	CO	-	12.5
20	CO <sub>2</sub>	-	5.1
21	H <sub>2</sub> O*	-	3.2

22           \*Based on wet gas

23           This corresponds to a carbon recovery of 1.35.

24           The carbon/O<sub>2</sub> ratio of the feed, therefore,  
25 is somewhat higher than the C/O<sub>2</sub> ratio of the product.  
26 Due to losses of carbon black and entrainment, however,  
27 the coke level in the reactor remained constant at

1 about 30 to 31 lbs.

2           The feed rate is now lowered to 250  
3 grams/hour, with the air rate remaining constant.  
4 Over the first four to five hours no change in product  
5 gas quality is noted, in agreement with previous  
6 experience which indicated that product gas quality  
7 is dependent on the inverse oxygen space velocity  
8 (lbs. C/mole O<sub>2</sub>/hr.) only, and independent of  
9 hydrocarbon feed rate.

10           After several hours, however, the coke level  
11 in the reactor begins to drop significantly because  
12 of the excess O<sub>2</sub>, thereby decreasing the inverse space  
13 velocity. The expected decrease in gas quality does  
14 not take place, but on the contrary steadily improves.  
15 After 15 hours of running time the coke holdup in the  
16 reactor has dropped to 22.3 lbs., with an inverse  
17 space velocity of 574 lbs. C/mole O<sub>2</sub>/hr. The dry  
18 product gas now analyzes as follows:

19	H <sub>2</sub>	-	7.6
20	N <sub>2</sub>	-	70.6
21	CH <sub>4</sub>	-	0.3
22	CO	-	18.8
23	CO <sub>2</sub>	-	2.7
24	H <sub>2</sub> O*	-	1.7

25           \*On wet basis

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1           This is a radical improvement over the  
2 initial gas product, corresponding to a carbon  
3 recovery of 1.66. Notice that the CO concentration  
4 has risen from 12.5 to 18.8 vol. %, while CO<sub>2</sub> and  
5 water fell from 5.1 and 3.2 to 2.7 and 1.7  
6 respectively. This corresponds to an increase of  
7 CO/CO<sub>2</sub> ratio from 2.5 to 7.0. This has taken place  
8 despite the fact that the total residence time of the  
9 vapors over the coke has decreased by 30%.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1                   1. In a process wherein a fluidized bed of  
2 coke formed by coking a hydrocarbonaceous liquid is  
3 gasified in a coking zone in the presence of air at a  
4 temperature of 1700° to 2200°F. and in the further  
5 presence of components formed in said coking stage  
6 to produce a reducing gas containing H<sub>2</sub> and CO, the  
7 improvement which comprises maintaining the  
8 gasification zone under conditions such that the  
9 carbon/oxygen ratio of the feed components to said  
10 gasification zone is less than the carbon/oxygen  
11 ratio of the gasification product and coke carbon is  
12 consumed from said bed at a higher rate than it is  
13 deposited.

1                   2. An improved process for producing a gas  
2 stream of high reducing capacity rich in H<sub>2</sub> and CO  
3 which comprises maintaining a dense turbulent bed of  
4 fluidized solids in a reaction zone, introducing a  
5 hydrocarbonaceous feed into said bed, cracking said  
6 feed to form hydrogen and coke deposits on said  
7 fluidized solids, introducing air into said bed to  
8 supply oxygen for converting said coke to oxides of  
9 carbon, maintaining said bed at a temperature of from  
10 about 1700° to 2200°F. and 0 to 100 psig. pressure and  
11 operating said gasification under conditions such that  
12 the carbon/oxygen ratio of the feed components is less  
13 than the carbon/oxygen ratio of the product gases and  
14 coke carbon is consumed from the bed at a higher rate  
15 than it is deposited.

1           3. A process for producing a hot gas stream  
2 containing principally  $N_2$ , CO, and  $H_2$ , which comprises  
3 supplying carbonaceous solids to form a turbulent  
4 dense fluidized solids bed, introducing a hydrocarbon  
5 feed into a cracking zone of said bed where the  
6 hydrocarbon feed is cracked to form  $H_2$  and coke  
7 deposits on said particles maintained at a temperature  
8 in the range of  $1700^\circ$  to  $2200^\circ F.$  by heat radiated and  
9 conducted from an adjacent combustion zone, fluidizing  
10 said particles carrying coke deposits in said  
11 combustion zone by air of which oxygen reacts with  
12 said coke deposits to form carbon oxide gases and heat  
13 the particles to a temperature in the range of  $1700^\circ$   
14 to  $2200^\circ F.$ , turbulently admixing heated particles  
15 fluidized from the combustion zone into said cracking  
16 zone, contacting gaseous hydrocarbon and hydrogen from  
17 the cracking zone and gases containing CO,  $CO_2$ , with  
18  $N_2$  from the combustion zone at a temperature in the  
19 range of  $1700^\circ$  to  $2200^\circ F.$  with coke deposits of  
20 upwardly fluidized activated particles from the  
21 cracking zone, making said gases richer in CO and  $H_2$ ,  
22 and separating a resulting hot gas stream containing  
23 mainly  $N_2$ , CO and  $H_2$  with relatively small amounts of  
24  $CO_2$ ,  $H_2O$  and gaseous hydrocarbon, said gasification  
25 being carried out such that the rate of coke deposition  
26 on said bed is less than the coke consumed from said  
27 bed.

1           4. A process for producing a hot gas  
2 stream containing H<sub>2</sub>, CO and N<sub>2</sub> as principal  
3 components, which comprises maintaining a dense  
4 turbulent bed of fluidized carbonaceous solids,  
5 introducing a hydrocarbon feed into an intermediate  
6 part of said bed between an upper major part and a  
7 bottom part of said bed, cracking the hydrocarbon  
8 feed to form hydrogen and coke deposits on said  
9 solids in said intermediate part, introducing air  
10 into said bottom part of the bed to supply oxygen  
11 which converts said coke deposits to gaseous oxides  
12 of carbon with evolution of heat for maintaining the  
13 bed of solids at a temperature in the range of 1700°  
14 to 2200°F., admixing gaseous carbon oxides and N<sub>2</sub>  
15 from the bottom part with hydrogen and hydrocarbon  
16 gases in the intermediate part, passing the  
17 resulting gas mixture up through the upper major  
18 part of the bed for further reaction that enriches  
19 the gas mixture in H<sub>2</sub> and CO, and maintaining  
20 gasification conditions such that the carbon/oxygen  
21 ratio of the feed is less than the carbon/oxygen ratio  
22 of the product gas stream and coke is consumed from  
23 said bed at a higher rate than it is deposited in  
24 the coking step.

1           5. The process defined in claim 4 wherein  
2 the hydrocarbon feed is a liquid hydrocarbon that is  
3 atomized into the cracking zone with a gas  
4 substantially free of oxygen.



6. The process of claim 4 wherein said coke consumption conditions include a temperature in the range of 1800° to 2000°F., a pressure of 20 to 50 psig., a carbon/oxygen ratio in the feed of 1.0 to 1.5, a superficial velocity of 1.0 to 2.5 feet/second, and a solids holdup-mol O<sub>2</sub> in air/hour ratio of 300 to 1000 lbs.

7. The process of claim 4 wherein said solids are fluidized coke.

8. An improved two-stage process for producing a gas stream of high reducing capacity rich in H<sub>2</sub> and CO which comprises passing a hydrocarbon stream into a fluidized coking zone, maintaining a bed of fluidized carbonaceous solids in said zone, maintaining a coking temperature of 900° to 1300°F. in said bed by addition of only enough air sufficient to maintain heat balance, thereafter passing product gases and fluidized coke to a gasification zone, passing air into said zone, maintaining temperatures of 1700° to 2200°F. in said zone, and maintaining said gasification zone under coke consumption conditions.

FIGURE 1

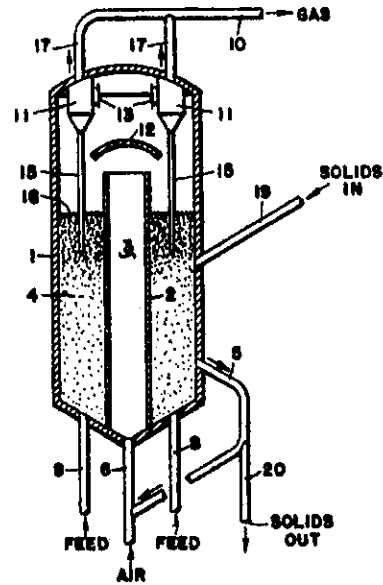
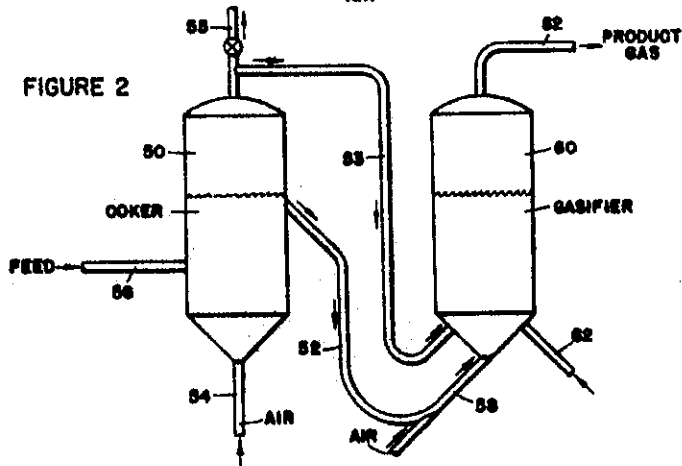


FIGURE 2



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