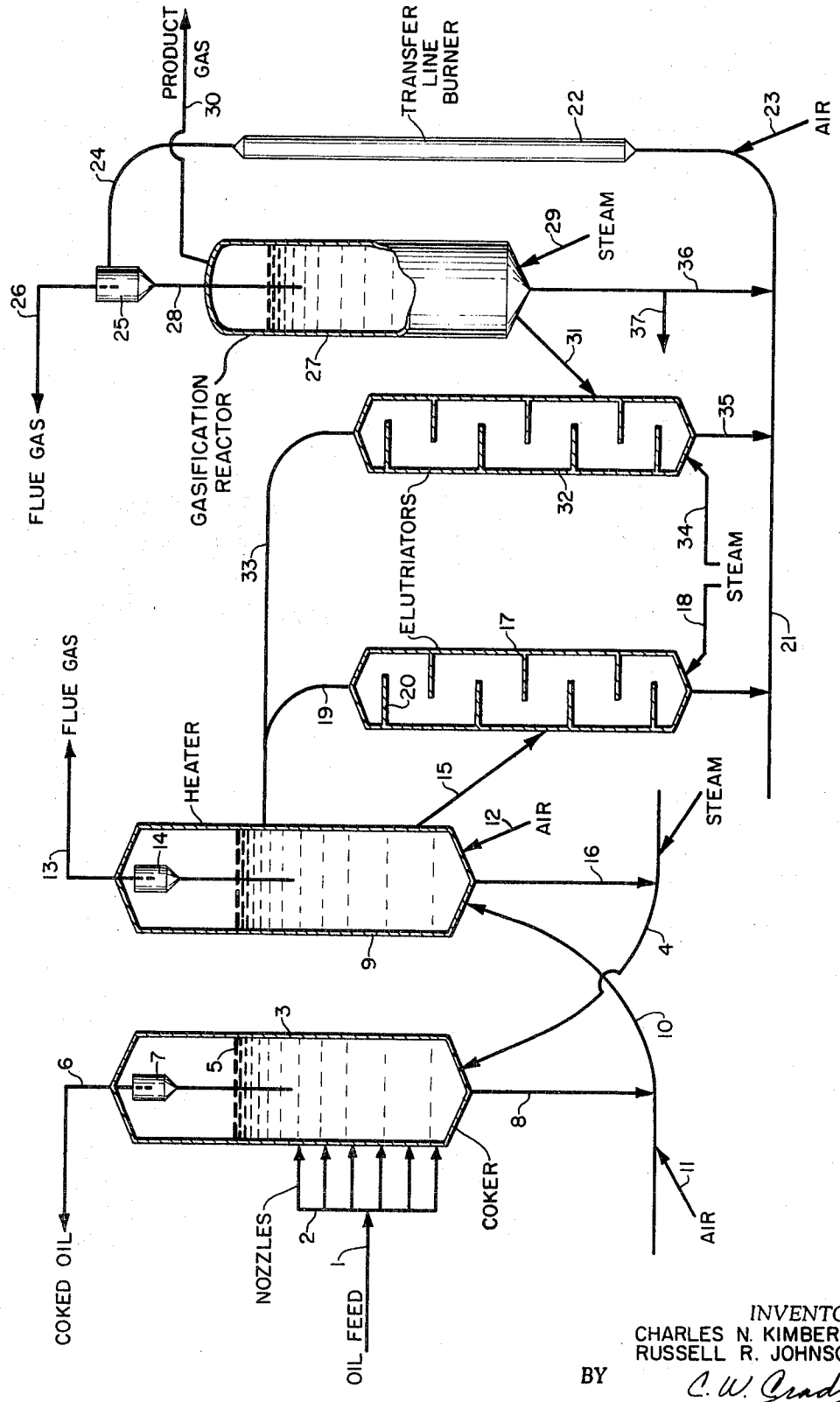
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PROCESS FOR THE PRODUCTION OF HYDROGEN FROM PETROLEUM COKE

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PROCESS FOR THE PRODUCTION OF HYDROGEN FROM PETROLEUM COKE

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5 Claims

ABSTRACT OF THE DISCLOSURE

In an integrated fluid petroleum coking process, hydrogen is produced from petroleum coke by contacting coke of a particular size with steam in a moving bed gasification reactor.

This invention relates to a process for the production of hydrogen. More particularly the invention relates to a process for the production of a gas rich in hydrogen from petroleum coke. In the process the coke is used as the sole source of heat and it is preferably recycled to extinction.

The use of hydrogen in the refining of petroleum fractions is increasing with every passing year. Many refineries are adding hydrogen plants for use in hydrodesulfurization, hydrodenitrogenation, saturating olefins and aromatics, hydrodealkylation, hydroisomerization, hydrocracking, etc. because the supply of by-product hydrogen from reformers in insufficient.

Manufactured hydrogen is produced in two major steps comprising conversion of the hydrocarbon raw material into raw hydrogen-rich gas and purification of the raw gas to provide hydrogen having a purity of at least 90%.

The most economical process developed up to this time involves steam reforming of light hydrocarbons such as natural gas over a nickel catalyst. There is also considerable interest in partial oxidation of heavy oils with high purity oxygen.

Another field of interest for manufacturing hydrogen is petroleum coke. Many refiners employ coking to dispose of residual fractions and this gives rise to the problem of disposing of the coke. Much of the coke is used as fuel. A substantial portion is calcined and otherwise treated to make electrodes, foundry coke, carbon and graphite.

The major commercial coking process is delayed coking, however, fluid coking is an increasingly important source of petroleum coke. Coker feeds include bottoms from crude distillation units, tar from thermal crackers and clarified oil from catalytic crackers.

Inspections of three typical fluid petroleum cokes are set forth below. Sample No. 1 is a high sulfur, low metals material. Sample No. 2 is a low sulfur, high metals material and Sample No. 3 is a high sulfur, high metals material. In preparing this coke, the pressure drop across the feed nozzles supplying oil to the coker was 40–60 p.s.i.

TABLE I.—GREEN FLUID COKE ANALYSES

	Sample Number		
	1	2	3
Sulfur (dietert), wt. percent	5.75	1.38	6.55
Moisture, wt. percent	1.58	3.42	0.26
Ash (dry), wt. percent	0.10	0.43	0.19
Real density, g./cc.	1.53	1.5	1.46
Bulk density, g./cc.	1.060	0.975	0.995
Volatiles, wt. percent at 950° C.	7.40	11.0	5.94
Grindability, hardgrove index	20	16	20
Metals, p.p.m.:			
V	310	259	1,150
Ti	<50	<50	<50
Ni	155	867	325
Fe	<50	708	195
Si		770	100
Ca	90	219	<50
Na	<50	808	<50
Cu	<50	<50	<50
Al	<50	155	<50
Cr	<50	<50	<50
Zn	<50	125	125
Screen size, wt. percent (cumulative):			
4 mesh	1.3		2.0
8 mesh	3.5		4.1
14 mesh	6.3		4.8
20 mesh	7.1		5.0
28 mesh	7.9	[1]	5.2
35 mesh	10.2	1.0	5.8
48 mesh	25.0	6.0	10.4
65 mesh	55.0	20.4	25.4
100 mesh	83.6	49.0	62.4
150 mesh	95.4	76.7	84.9
200 mesh	98.8	89.9	95.1
325 mesh	99.1	98.6	99.1
Pan	100.0	100.0	100.0

[1] Trace.

The basic fluid coking process involves injection of a heavy petroleum oil into a fluidized bed of hot coke particles. A portion of the coke is withdrawn from the coking reactor and is passed to a heater where some of the coke is burned to heat the remaining coke and the latter is recycled to the coking reactor. As a result of this cyclic treatment, the coke particles become spherical with a number of onion-skin layers. Fluid coke is well suited to the process of the invention because it is so much more attrition-resistant than delayed coke.

The gasification reaction is endothermic and in the process of the invention heat is supplied by combustion of a part of the coke rather than by using an external source of heat such as gas or oil. It is a feature of the invention that the combustion step is carried out in a unit external to the gasification reaction. By this means flue gas is separated prior to the entry of the hot coke into the gasification reactor and thus the product gas is not contaminated with large amounts of flue gas which would require separation in the hydrogen purification steps.

The gasification reaction is carried out in a moving bed of petroleum coke particles. For this reason it is necessary that the coke particles be sized in such a manner that they will circulate freely in the moving bed but will not be carried out of the reactor. There are additional reasons for the proper sizing of the coke. Coke particles that are partially burned in the transfer line burner prior

to gasification shrink in size. Furthermore the particles are continuously attrited by circulation in the piping connecting the process units and by circulation within the moving bed.

It is an object of this invention to provide a process for the production of a gas comprising hydrogen which is essentially free of combustion gases and coke particles.

Broadly summarizing the process of the invention, petroleum coke having a particular size range is recovered from a coker, a portion of the coke is burned in a transfer line reactor, flue gas is separated from the hot coke and the latter is gasified with steam in a moving bed to produce a product gas comprising hydrogen. The product of the process is a raw hydrogen and CO containing gas which serves as feed to a purification complex comprising a shift converter, one or more CO_2 removal steps and possibly a methanator. The purification steps are conventional and they do not constitute a part of the invention.

Further details and advantages of the process are described below with reference to the drawing which is a flow sheet illustrating a preferred embodiment of the invention.

Referring to the drawing a petroleum residuum feed is passed by line **1** to plurality of feed nozzles **2** spaced along the side of a coking reactor **3**. Suitable coker feeds include atmospheric residuums, vacuum residuums, thermal tars, cat cracked fractions and other heavy petroleum oils. In a preferred embodiment of the invention at least one of the nozzles has a smaller pressure drop than the pressure drop across the conventional nozzles. The lower pressure would be in the range of 1–15, preferably 1–4 pounds. The lower pressure drop tends to cause agglomeration of the particles resulting in coke having a particle diameter of ⅛–½ inch and predominantly in the range of ¼ to ⅜ inch. From 1–15 preferably 5–10 vol. percent of the coke particles are formed into the ⅛ to ½ inch size range. These particles are especially desirable for use in a moving bed gasification unit.

The coking reaction is carried out in a conventional fluidized bed. Coking temperatures in the range of 850° F. to 1050° F. and pressures in the range of 10 to 50 p.s.i.g. are suitable. Steam from line **4** is used to fluidize the bed and the upper level of the bed is designated by reference numeral **5**. Coked oil is removed from the reactor by line **6**. Solids are removed from the oil in separator **7**.

Relatively cool coke including large particle coke is removed from the coker by line **8** and passed to the coker heater **9** by transfer line **10**. Air from line **11** is the transfer medium for the coke. A portion of the coke in heater **9** is burned to heat coke for the coking reactor. Air is supplied by line **12** and continuous combustion takes place in the heater. Flue gas is removed by line **13**. Solids are removed from the flue gas in separator **14**. Hot coke is returned to the coking vessel via lines **16** and **4**.

A portion of the coke in heater **9**, i.e. 5 to 20 vol. percent is passed by line **15** to a first elutriator **17**. Steam is passed by line **18** into the elutriator. The velocity of steam in the elutriator is 5 to 10 ft. per second to lift the majority of the coke particles having a diameter of less than about ⅛ inch up and out of the elutriator and back to the coke heater by line **19**. Elutriator **17** is a conventional unit and in one embodiment comprises an elongated shell-type vessel having spaced internal trays designated generally by reference numeral **20**. The trays are attached to the vertical wall of the vessel and extend inwardly a suitable distance defining a curved path for the upwardly flowing mixture of steam and entrained relatively small and light weight coke particles which are being returned to the coke heater.

Coke having an average diameter of ⅛ to ½ inch is passed by line **21** to transfer line burner **22**. Combustion air is supplied by line **23**. The heat required to conduct the endothermic gasification reaction is supplied by coke particles heated to a temperature well above that of the reactor.

It is known that the most efficient utilization of both the carbon in the coke and the oxygen in the combustion air is achieved by controlling the combustion of the coke to favor the production of CO_2 over the production of CO. In terms of units of heat generated in the exothermic reactions, the formation of CO requires a much greater quantity of carbon and oxygen to produce the same amount of heat. The transfer line burner is a unit capable of operation at the partial combustions which provide maximum calorific efficiency even though an excess of carbon is present in the burner. The formation of CO is minimized by controlling velocity, residence time and the density of the solids per unit of volume of the burner. The burner has a length to diameter ratio of 2/1 to 20/1. Velocities of 20 ft./sec. to 60 ft./sec., residence times of .2 second to 3.0 seconds and solids densities of 1 to 5 #/ft.^{3} are suitable. At these conditions the partial combustion of the coke is accomplished within a relatively short combustion period favoring CO_2 production. In addition to the combustion reaction, sulfur in the coke is converted to SO_2 in the transfer line burner. It is very desirable that sulfur conversion take place at this stage of the process since the sulfur is eliminated from the feed in the form of SO_2 and does not contaminate the feed to the gasification reactor or the raw product gas. The temperature in the transfer line burner will range from 1800 to 2400° F.

Hot coke is passed by line **24** to gas-solids separator **25** and flue gas containing sulfur as SO_2 is removed by line **26**. Hot coke is passed into gasification reactor **27** by line **28**. Steam is supplied by line **29**. In the embodiment shown in the drawing a moving bed gasification reactor is disclosed, however any suitable type of reactor can be used. The hot coke passes downwardly through the reactor in intimate counter current contact with the upwardly moving steam. Steam is preferably supplied at a temperature of 1200 to 1800° F. Reactor temperature ranges from 1200 to 2400° F. Contact times for the downwardly moving coke ranging from about 8 to about 20 minutes are suitable. Reactor pressure is maintained in the range of 10 to 50 p.s.i.g. Raw product gas containing 80 to 95 vol. percent H_2 and CO of which 40–50% is hydrogen and lesser amounts of CO_2, CH_4, H_2S, N_2 and H_2O is removed from the reactor by line **30**. It is a feature of the process that product gas is isolated from flue gas and from any other diluent or contaminating gases. No air is fed to the gasification reactor and therefore the product gas is not contaminated with large amounts of nitrogen.

A part of the coke in the bottom portion of reactor **27** is continuously removed by line **31** and passed into a second elutriator **32**. This unit is operated in a manner similar to unit **17**, described previously. Small diameter coke which is unsuitable for further use in gasification is passed by line **33** to burner **9** by means of a steam elutriation and transport gas supplied by line **34**. Coke which is still suitable for use in the burning and gasification steps is recycled by lines **35** and **21**. In addition coke leaving the bottom of unit **27** is recycled by lines **36** and **21**. When it is desirable small quantities of coke can be withdrawn from the system by line **37**.

The process of the invention provides an optimized means of producing hydrogen from petroleum coke using air and steam. Such a process requires the movement of large quantities of solids and gases in a continuous cyclic manner. The described process produces the heat economies by employing heat exchange and other low costs required for producing hydrogen from fluid petroleum coke. The moving bed permits countercurrent contact of steam and coke thus conserving heat.

We claim:

1. A process for the preparation of a hydrogen-containing gas comprising the steps of:

(a) passing coke from a fluid coker to a solids elutriator and therein separating gasification coke having a

minimum particle size in the range of from about ⅛ to about ¼ inch in diameter.

(b) burning a portion of said gasification coke in a transfer line burner to produce hot gasification coke heated to a temperature in the range of 1800 to 2400° F.

(c) separating flue gas from the coke.

(d) passing the hot gasification coke to the top of a moving bed reactor and introducing steam into the coke at the bottom of said moving bed and passing it countercurrent to said moving bed of coke at a temperature in the range of 1200 to 2400° F. to produce a hydrogen-containing gas and

(e) recovering said gas.

2. Process according to claim 1 in which said hydrogen-containing gas contains 40 to 50 mole percent hydrogen.

3. Process according to claim 1 in which the coke passed to the elutriator is obtained from the heater section of the said fluid coker.

4. Process according to claim 1 in which a portion of the coke in the bottom portion of the gasification reactor

is passed to an elutriator and coke having a particle size of less than about ⅛ inch in diameter is recovered and recycled to said fluid coker.

5. Process according to claim 1 in which the velocity of the air-coke mixture in the transfer line burner is in the range of 20 to 60 ft./sec.

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