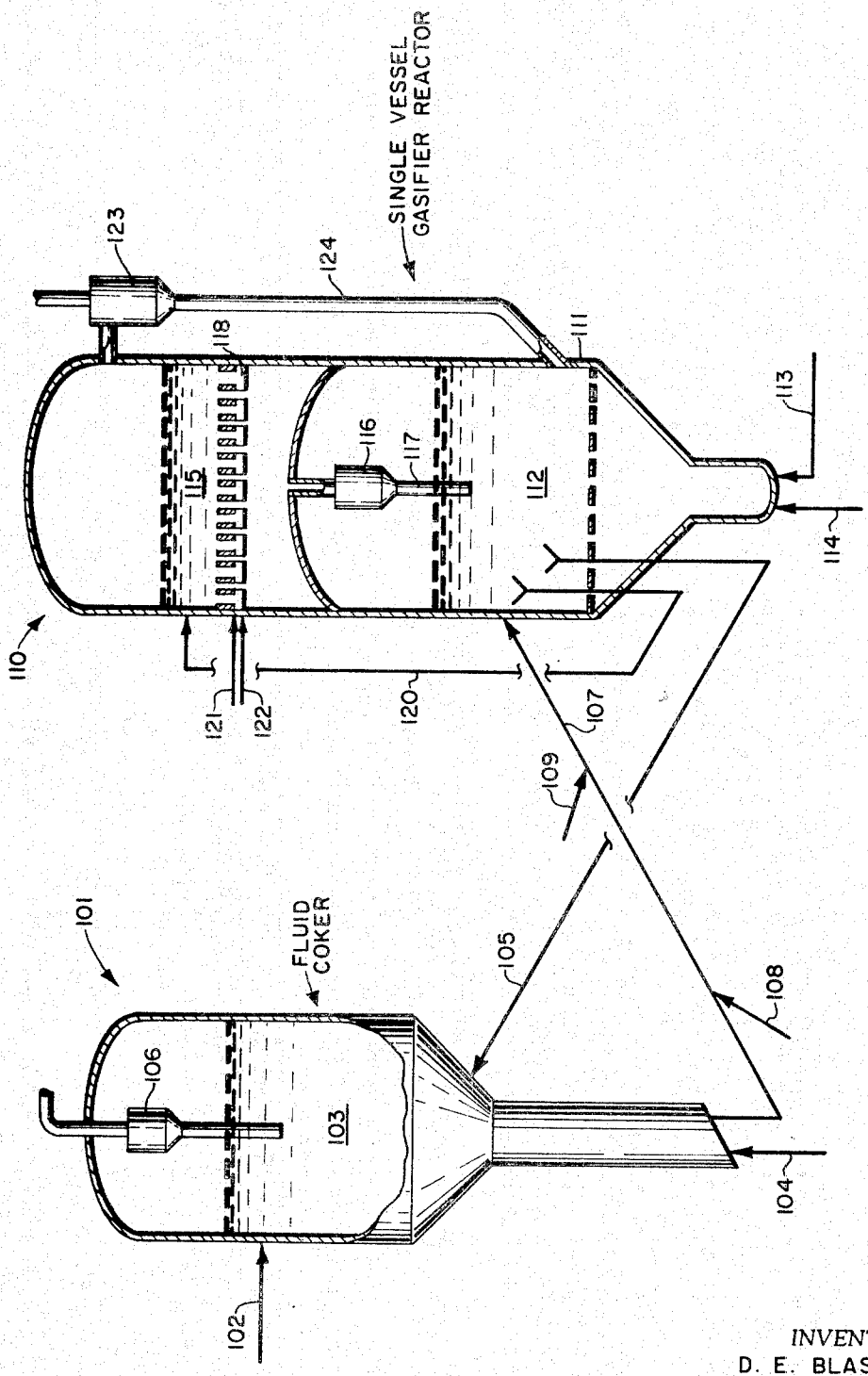
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INTEGRATED FLUID COKING-GASIFICATION PROCESS

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INTEGRATED FLUID COKING-GASIFICATION PROCESS

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ABSTRACT OF THE DISCLOSURE

A process for producing fuel gas whereby coke from a conventional fluid coker is reacted with an oxygen-containing gas in a low temperature zone located in the lower portion of a single vessel reactor to produce flue gas, and then reacting the flue gas along with steam and air or oxygen with coke which has been transferred from the low temperature zone to a high temperature zone located in the upper portion of the single vessel reactor to produce fuel gas.

BACKGROUND OF THE INVENTION

This invention relates to producing fuel gas from coke by a novel gasifying process. More particularly, the gasifying process consists of a two stage process wherein coke is injected into a low temperature zone where it reacts with air or oxygen to produce flue gas, and said flue gas along with additional air or oxygen and steam is contacted in a high temperature zone with hot coke transferred from the low temperature zone to the high temperature zone to produce fuel gas; i.e., hydrogen and carbon monoxide.

In another embodiment this invention relates to an integrated fluid coking-gasification process. More particularly it relates to a process wherein a heavy hydrocarbon material is coked in a conventional fluid coker and the coke produced is injected into a two stage gasification reactor to produce fuel gas.

In a conventional fluid coking process a heavy hydrocarbon fraction such as vacuum residuum is fed into a fluid coking reactor to produce both a liquid and gas petroleum distillate product and coke. The coke is then fed to a separate heater reactor to heat the coke to a temperature high enough to transfer back to the coking reactor to supply the heat requirements needed.

A fluid coking process such as above has encountered several problems. First, there is generally more coke produced in a coking reactor than is needed in the heater reactor. Since this coke has very little value as a by-product, disposal of excess coke has become a problem. Another problem arises in the burning of the coke in the heater reactor. By-products of this reaction are SO_2 and COS, along with partially combusted hydrocarbon and ammonia, which are released in the air as pollutants. In light of the new federal and state air pollution laws this sulfur and hydrocarbon emission is not acceptable.

In order to alleviate these and other problems created by a conventional fluid coking process, the petroleum industry has proposed addition of a third reactor to the other two fluid coking process reactors to convert the excess coke into fuel gas by reaction with steam. While this eased the coke disposal problem it did little to correct the unacceptable sulfur and hydrocarbon emission in the air from the heater reactor. The addition of an additional gasifier reactor also has the disadvantage that it, along with the necessary transfer lines, adds enormously to the cost of a coking process.

In a desire to overcome the disadvantages of adding a separate gasification reactor, a novel two stage, single vessel, heater-gasifier reactor was designed as described

in pending application Ser. No. 880,219 entitled "Improved Fluid Coking Process Incorporating Gasification of Product Coke," filed on Nov. 26, 1969, now U.S. Pat. 3,661,543, issued May 9, 1972. In this process design the coke produced in a conventional fluid coking reactor was injected into a high temperature gasifying zone (1800° F.) located in the lower portion of a second heater-gasifier reactor. Here the coke was contacted with steam to produce fuel gas. This hot fuel gas (~1800° F.) passed through a gas distributor apparatus and into a low temperature heating zone (~1100° F.) located in the upper portion of the second reactor. Here the hot gases were to both fluidize the heating zone coke bed and to heat this bed to the desired temperature. This design has however created new problems which this invention now overcomes. In the design of the above pending application there exists the possibility that the heating zone bed which is located above the gasifying zone bed in the heater-gasifier reactor would dump into the gasifying zone bed if any of the slide valves stuck or the gas distributor grate separating the two beds was burned through. In such a situation the two stage reactor would have to shut down, and there would be the possibility of oxygen breaking through the beds and causing an explosion. A second disadvantage was the unreliability of the gas distributor to evenly distribute such hot gases in the upper heating zone bed. This results in poor fluidization of the upper bed which in turn creates hot spots within the bed, particularly around the gas distributor leading to the dumping problem described above. A further problem is the fouling of the heater overhead system by hydrocarbons distilled off the coke in the heating zone bed. It is also possible that the gasifier products may revert to equilibrium in the heating zone resulting in the formation of soot and other undesirable sulfur compounds. A still further disadvantage is that the design of Ser. No. 880,219 cannot be attached to existing fluid coker reactors.

It is therefore an object of this invention to provide a process that economically utilizes the excess coke produced in a conventional fluid coking process, while at the same time eliminates the sulfur and hydrocarbon emission into the air which is associated with the conventional fluid coking process.

Another object of this invention is to provide a novel single vessel coke gasification process for producing fuel gas wherein the heating zone bed cannot dump into the gasifying zone bed.

A still further object of this invention is to provide a single vessel coke gasification process for producing fuel gas wherein hydrocarbons distilled off the coke in the heater bed cannot foul the gas removal system located at the top of the vessel.

It is also an object of this invention to provide a single vessel coke gasification process that can be readily adapted to existing fluid coker vessels.

In an alternate form it is an object of this invention to provide a novel integrated fluid coking-gasification process for converting heavy carbonaceous solids into liquid and gaseous petroleum distillate products and fuel gas.

Other objects and advantages of this invention will be obvious from the ensuing description of the invention.

SUMMARY OF THE INVENTION

In one embodiment of this invention a carbonaceous material such as coke is gasified in a two zone single vessel reactor to produce fuel gas. More specifically coke from a conventional fluid coker is introduced into a low temperature zone situated in the lower portion of a single vessel gasifier reactor to produce flue gas and other hot gases by contact with air or oxygen, then contacting these gases

along with steam and air or oxygen with coke in a high temperature zone to produce fuel gas.

In another embodiment of this invention a heavy hydrocarbon material such as vacuum residuum is converted into liquid and gaseous petroleum ditsillate products and fuel gas by an integrated fluid coking-gasification process. More specifically the vacuum residuum is fed into a conventional fluid coking reactor to produce a liquid or gaseous petroleum distillate product which is recovered from the reactor and coke which is transferred to a low temperature zone situated in the lower portion of a single vessel gasifier reactor to produce flue gas and other hot gases by contact with air or oxygen, then contacting these gases along the steam and air or oxygen with coke in a high temperature zone to produce fuel gas.

BRIEF DESCRIPTION OF THE DRAWING

The figure schematically illustrates the preferred embodiments of the process of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

As seen in the figure a heavy hydrocarbon feed is introduced into a conventional fluid coking reactor **101** by means **102**. This feed could include any carbon-containing material, but for economic and availability reasons vacuum or atmospheric distillation residuum (boiling point greater than about 1050° F.) is preferred. This residuum forms bed **103** which is maintained in a fluidized state by a fluidizing gas such as steam injected into bed **103** by means **104** and by the cracked hydrocarbon vapors produced in bed **103**. This fluidized bed **103** is maintained at a temperature between 900° and 1100° F. in part by coke from the heating zone **111** of the single vessel gasifier reactor **110** introduced to the fluidized bed **103** by transfer line **105**. If it is desired the feed could be preheated in a furnace or heat exchanger, not shown, before being injected into the fluid coking reactor **101**.

Inside fluid coking reactor **101** the residuum is cracked to produce light liquid and gas distillate products which are removed from the reactor by cyclone means **106**. A coke by-product is also produced by the reactors in bed **103** and is removed by transfer line **107** and transferred to the single vessel gasifier reactor **110** by a fluidizing gas such as steam introduced into transfer line **107** by line **108** and if needed by supplementary air or oxygen injected in transfer line **107** by line **109**.

The coke is then injected into the heating zone **111** to form bed **112** in the lower portion of reactor **110**. Bed **112** is maintained in a fluidized condition by air or oxygen from line **113**. If desired small quantities of steam could also be added by line **114** to aid in maintaining the temperature of bed **112** between 1100° and 1500° F.

The temperature of bed **112** is increased principally by the exothermic reaction of carbon with oxygen:

$$C+O_2 \rightleftharpoons CO_2+169{,}300 \text{ B.t.u.}$$

and secondarily by the reaction

$$C+\tfrac{1}{2}O_2 \rightleftharpoons CO+47{,}500 \text{ B.t.u.}$$

Under the time and temperature conditions proposed, the CO/CO_2 ratio will be from 0.25 to 1 as set by kinetic and equilibrium considerations. Therefore the more oxygen introduced in bed **112** the more heat that will be given off and absorbed in the bed, thus raising the bed temperature. Since it is not desirable to operate bed **112** above about 1500° F. the amount of oxygen that can be injected into the bed is limited.

For a typical residuum feedstock, the air to the lower bed **112** will be from 0.4 to 1.5 moles air/moles C/hour and, preferably 0.71 mole per mole of coke produced. If oxygen is fed to the lower bed **112** then a gas rate between 0.1 and 0.3 mole O_2/moles C/hour will be needed. Total coke produced will be about 36% on residuum feed of which about 20% (7% on residuum feed) is consumed in bed **112**.

The hot flue gas and other gases, such as H_2S, SO_2, COS and other light hydrocarbons produced by reactions in bed **112** are passed through cyclone **116** to remove any fines or ash that may have risen with these gases. These fines and ashes are then returned to bed **112** by dipleg **117**. The hot gases then pass through a gas distributor **118** into gasifier bed **115**.

A portion of the hot coke in bed **112** is recycled to fluid coker reactor **101** by transfer line **105** to maintain bed **103** at the proper temperatures. Another portion of the coke in bed **112** is transferred to gasifier bed **115** by transfer line **120** to supply the necessary carbon needed in the gasifier bed reactions to produce hydrogen and carbon monoxide.

As stated above the hot flue gases (at temperatures between 1100° and 1500° F., preferably between 1100° and 1200° F.) along with other gases produced in heater bed **112** are distributed evenly throughout gasifier bed **115** by the gas distributor **118**. Because these gases are at temperatures below 1500° F. gas distributors known in the art may be used satisfactorily to achieve excellent gas distribution. This means that the much hotter bed **115** can be maintained in a fluidized state without forming any hot spots which could have led to the destruction of the gas distributor **118**. Thus under the process of this invention there is virtually no danger of the gasifier bed **115** dumping into the heater bed **112**. Also contacted with the coke in gasifier bed **115** is additional steam and air or oxygen introduced by lines **121** and **122** respectfully, in order to aid in maintaining bed **115** in a fluidized state and to raise its temperature to between 1500° and 2200° F. If hydrogen and carbon monoxide are the desired products then the bed is preferably between 1700° and 1900° F., and most preferably about 1800° F.

When air is introduced by line **122** these temperatures can be achieved and bed **115** maintained in a fluidized state if the steam rate from line **121** together with any steam from bed **112** is between 0.1 and 0.4 moles H_2O/moles C/hour and the air rate is introduced at a rate between 1.5 and 2.0 moles air/moles C/hour. At the preferred temperature range of 1700° to 1900° F., a steam rate between 0.25 and 0.35 H_2O/moles C/hour, along with an air rate between 1.7 and 1.9 moles air/moles C/hour is preferred. For the most preferred temperature of 1800° F. a steam rate of about 0.3 moles H_2O/moles C/hour and air rate of about 1.8 moles air/moles C/hour is preferred.

On the other hand if oxygen is introduced by line **122** a temperature between 1500° and 2200° F. can be maintained in bed **115** with a steam rate between 0.3 and 0.5 moles H_2O/moles C/hour and an oxygen rate between 0.2 and 0.4 moles O_2/moles C/hour, whereas the preferred temperature range is maintained with gas rates of between 0.35 and 0.41 moles H_2O/moles C/hour and 0.28 and 0.31 moles O_2/moles C/hour. At the most preferred temperature of 1800° F. gas rates of about 0.39 moles H_2O/moles C/hour and 0.3 moles O_2/moles C/hour are preferred.

At these conditions the following reactions are predominant:

$$H_2O+C \rightleftharpoons H_2+CO\text{—}56{,}572 \text{ B.t.u.}$$
$$CO_2+C \rightleftharpoons 2CO\text{—}74{,}260 \text{ B.t.u.}$$
$$C+\tfrac{1}{2}O_2 \rightleftharpoons CO\text{—}47{,}520 \text{ B.t.u.}$$

which results in a major portion of the gases exiting reactor **110** by cyclone means **123** being hydrogen and carbon monoxide.

The fines and ashes that may be swept up with the exiting gas are returned to heater bed **112** by dipleg **124**. There will also be some H_2S, SO_2, and COS in the exiting gas, but about 90% of these pollutants will now be in the form of H_2S rather than only about 70% which

normally exit from a heating zone such as zone **112**. This conversion to H_2S is highly desirable since H_2S is much easier, and thus cheaper, to separate and recover from the other exiting gases such as hydrogen and carbon monoxide.

Having described and illustrated the invention, what I claim as novel, useful and unobvious, and desire Letters Patent is:

1. A process for producing hydrogen and carbon monoxide from coke in a two-zone, single vessel reactor which comprises:

(a) introducing coke into a fluid heater bed operated at temperatures between 1100° and 1500° F. and positioned in the lower zone of said reactor;

(b) introducing an oxygen-containing gas into said fluid heater bed to maintain said fluid heater bed in a fluidized state and to react with said coke to produce hot carbon-containing gases;

(c) passing a portion of said coke from said fluid heater bed to a fluid gasifying bed operated at temperatures between 1500° and 2200° F. and positioned in the upper zone of said reactor;

(d) contacting said hot carbon-containing gas with the coke in said gasifying bed along with steam and an oxygen-containing gas which have been introduced into said gasifying bed to maintain said gasifying bed in a fluidized state and to produce hydrogen and carbon monoxide; and

(e) recovering said hydrogen and carbon monoxide from said reactor.

2. The process of claim **1**, wherein the oxygen-containing gas introduced into said fluid heater bed is oxygen fed at a rate between 0.1 and 0.3 mole O_2/mole C/hour.

3. The process of claim **1**, wherein said oxygen-containing gas introduced into said fluid heater bed is air fed at a rate between 0.4 and 1.5 moles air/mole C/hour.

4. The process of claim **1**, wherein the oxygen-containing gas introduced into said gasifying bed is oxygen and wherein said oxygen is introduced at a rate between 0.2 and 0.4 mole O_2/mole C/hour and said steam is introduced at a rate between 0.3 and 0.5 mole H_2O/mole C/hour.

5. The process of claim **1** wherein the oxygen-containing gas introduced into said gasifying bed is air and wherein said air is introduced at a rate between 1.5 and 2.0 moles air/mol C/hour and said steam is introduced at a rate between 0.1 and 0.4 mole H_2O/mole C/hour.

6. The process of claim **1** wherein the gasifying bed is operated at a temperature between 1700 and 1900° F.

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