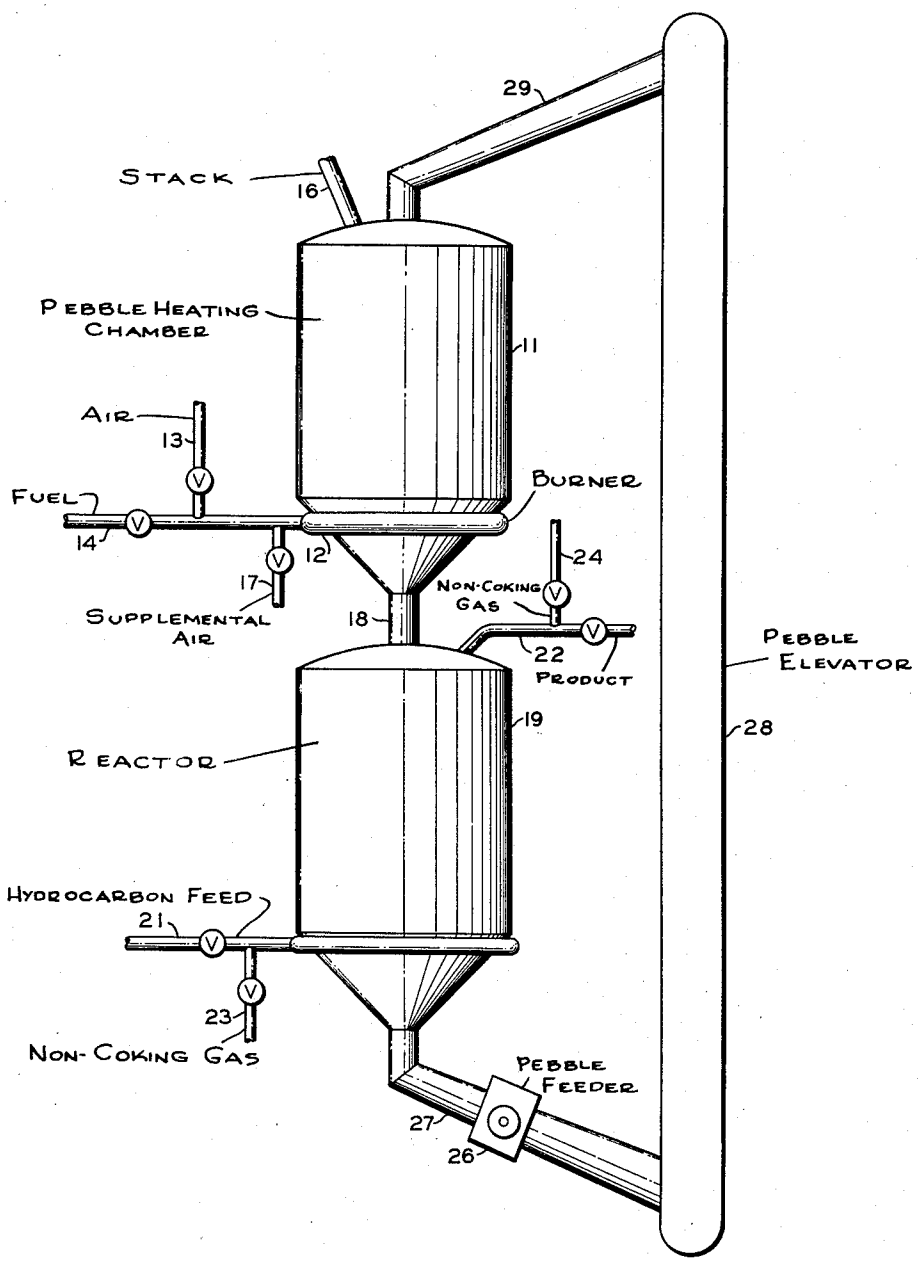
Dec. 22, 1953

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2,663,678

DECOKING OF PEBBLES IN PEBBLE HEATER
CRACKING OF HYDROCARBONS
Filed July 10, 1950



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Patented Dec. 22, 1953

2,663,678

UNITED STATES PATENT OFFICE

2,663,678

DECOKING OF PEBBLES IN PEBBLE HEATER CRACKING OF HYDROCARBONS

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Application July 10, 1950, Serial No. 172,986

13 Claims. (Cl. 196—55)

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This invention relates to hydrocarbon conversion involving cracking and coke deposition in pebble heater type apparatus and to methods of removing coke from the system, particularly from the pebbles.

Pebble heater apparatus is finding increasing favor in the conversion of hydrocarbons at elevated temperatures in the range of 1500 to about 2500° F. because of the fast heating rate-continuous operation, and other process advantages provided by the pebble heater. A conventional pebble heater utilizes a pebble heating chamber having means for passing hot combustion gas upwardly through a gravitating mass of refractory pebbles which are heated therein before descending through an axially positioned throat to a reaction chamber of similar shape and construction to the pebble heating chamber. The pebbles are contacted in the conversion zone or chamber with a countercurrent stream of the hydrocarbon to be reacted, or converted, so as to heat the same to reaction temperature and supply the heat of reaction required to effect the conversion. The pebbles then gravitate from the lower end of the reactor to the bottom of an elevator which lifts them to a point above the top of the pebble heater chamber from whence they gravitate to that chamber for reheating and gravitation to the reaction chamber. The system from the pebble inlet in the heating chamber to a pebble feeder device in the conduit between the bottom of the reaction chamber and the lower end of the elevator is maintained full of a compact gravitating mass of pebbles at all times during operation of the unit.

When effecting hydrocarbon conversion involving cracking in a pebble heater, it has been found that the pebbles and certain areas in the reactor acquire coke deposits which eventually interfere with pebble circulation and cause shutdowns. Even when operating with a substantial excess of oxygen in the combustion chamber of the pebble heating chamber, pebble and carbon agglomerates are gradually built up which interfere with uniform gravitation of pebbles through the system and particularly through the pebble feeder and the ducts leading from the bottom of the reactor to the feeder.

It is with the prevention of shutdowns due to coking of pebbles in the conversion of hydrocarbons in a pebble heater apparatus that this invention is primarily concerned. One of the principal objects of the invention is to remove coke deposited on the pebbles during hydrocarbon conversion before pebble flow is appreciably impeded

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or stopped. Another object of the invention is to remove coke deposited in the reactor of a pebble heater. It is also an object of the invention to increase the onstream time in the pebble heater cracking of hydrocarbons. Other objects of the invention will become apparent from a consideration of the accompanying disclosure.

The invention provides for the removal of coke from the pebbles in the pebble heater conversion of hydrocarbons by combustion of the coke in the pebble heating chamber while diminishing the coke deposition in the reactor by decreasing the flow of hydrocarbon therethrough and supplementing the hydrocarbon feed with a non-deleterious, non-coking gas such as steam, regeneration gas, flue gas, CO_2, nitrogen, or methane. In normal pebble heater conversion of hydrocarbons which involves deposition of coke on the pebbles, a portion of the coke is burned off due to the presence of an excess of oxygen in the combustion gas passing through the pebble heating chamber. However, after continuous operation for a period of a week or more it is often times found that the rate of formation of coke in the reactor and on the pebbles is such that an accumulation of carbon takes place to such an extent that coke and pebble clusters or agglomerates form in the reactor and interfere with the free flow or gravitation of pebbles from the bottom of the reactor to the bottom of the elevator and particularly through the pebble feeder.

The invention provides for a catching-up period on the removal of coke from the pebbles in the system and from the reactor. In accordance with the invention, the flow of hydrocarbon through the reactor is diminished appreciably or cut off entirely and supplemented or replaced with one of the non-coking gases enumerated hereinbefore, and the coke burning process in the pebble heating chamber is continued until the pebbles are relatively free of coke deposit. The non-coking gas passing through the reactor during this operation functions to control the temperature of the pebbles so that they are not too hot for the elevator apparatus and ducts between the reactor and the pebble preheater. When utilizing steam and when the temperature is sufficiently high in the reactor, this non-coking gas serves a dual purpose including the removing of coke deposit from the reactor dome and other surfaces in the reactor by the well known water gas reaction and possibly by some vaporization of heavy tarry polymers. When the temperature of the pebbles coming into the reactor is upwards of about 2100° F. the temperature in the upper section of the re-

actor can be maintained above about 2000° F. which will support the water gas reaction.

In cases where the coke deposit is sufficiently heavy that the burning thereof in the pebble heating chamber in conjunction with the heating effected by the combustion of fuel and oxygen therein raises the temperature of the pebbles considerably above the operating temperature thereof during the onstream conversion of hydrocarbon, the amount of combustion can be reduced by decreasing the fuel supply to the combustion chamber in the lower portion of the pebble heating chamber so as to effectively reduce the amount of heat imparted to the pebbles in this chamber.

The flow of gas through the reactor during the coke removal phase of the operation is preferably regulated so that the temperature of the outgoing pebbles is about the same as the temperature during hydrocarbon conversion, i. e., in the range of about 500 to 950° F. It is also desirable during this period to regulate the heating in the pebble heating chamber and the flow of gas through the reactor so that the pebbles coming into the reactor at the end of the coke removal phase is suitable for the hydrocarbon conversion being effected.

It is not necessary in most instances to entirely cut off the supply of hydrocarbon feed to the reactor during the coke removal step, but it is usually essential to reduce the hydrocarbon feed to below 60 weight per cent of the feed on normal onstream operation. For the most rapid removal of the coke from the pebbles by combustion in the pebble heating chamber it is essential to completely supplement the hydrocarbon feed with non-deleterious, non-coking gas.

In some types of operation it has been found expedient to flow considerable superheated steam into the dome of the reactor during the hydrocarbon conversion phase of operation. Even when using this technique it is found necessary to remove coke from the pebbles in some manner and the process of the invention has been found most effective.

For the purpose of the invention, methane is regarded as a non-coking gas since it can readily be passed through the reactor at a rate which avoids appreciable coke deposition. Combustion gas for the feed to the reactor during the coke removal step is readily obtained from the pebble heating chamber effluent. Nitrogen or CO_2 from this source can also be used to advantage when desired.

For a more complete comprehension of the invention, reference may be had to the drawing which shows diagrammatically an arrangement of pebble heater apparatus and flow therethrough in accordance with the invention.

Referring to the drawing, pebbles in pebble heating chamber 11 are heated by contact with hot combustion gas formed in the bottom of the chamber by means of burner 12 to which is fed a combustible mixture of air and fuel through lines 13 and 14, respectively. The hot combustion gas passes upwardly through the gravitating bed of pebbles in chamber 11 and passes out stack 16. Line 17 serves to introduce supplemental air or other oxygen-containing gas during the coke burning phase of operation or this additional supply of oxygen can be supplied through line 13, if desired. By proper operation of the valves shown in lines 13, 14, and 17, the proportions of oxygen and fuel can be regulated in any desirable manner.

After the pebbles are heated in chamber 11, they descend through an interconnecting throat 18 to reactor 19 where they are contacted with a suitable hydrocarbon feed introduced through a distributing member (not shown) in the bottom of the chamber through line 21. The hydrocarbon effluent from reactor 19 is taken off through line 22. Line 23 serves to introduce the non-deleterious, non-coking gas to be supplied to the reactor either alone or in admixture with hydrocarbon fed through line 21. The effluent non-coking gas may be taken off through line 24 by proper manipulation of the valves in lines 22 and 24 when it is desired to avoid passing the non-coking gas into the same separation or treating system as is used for the effluent hydrocarbon.

The hot pebbles entering reactor 19 pass downwardly therethrough and are cooled by transmission of sensible heat to the incoming hydrocarbon feed and/or non-coking gas so that the temperature is below about 950° F. to permit their transfer through the duct and elevator system to the top of preheater 11. In normal operation, pebble feeder 26 in duct 27 is operated in conjunction with elevator 28 to maintain a level of pebbles in the top of pebble heating chamber 11, thereby maintaining this chamber together with throat 18 and reactor 19 filled with a compact stream of pebbles. Pebble duct 29 serves to deliver pebbles from the top of the elevator to the pebble inlet to preheater 11. Elevator 28 may be of the screw, bucket, or gas-lift type.

Example

In a commercial pebble heater process in which an average of approximately 70,000 s. c. f. h. of a fractionator overhead having an average composition of 20% methane, 58% ethane, and 22% propane (by weight) was fed into the bottom of the reactor, the cracking temperature was maintained at an average of about 1500° F. by feeding pebbles into the reactor at an average temperature of about 1900° F. at an average flow rate of about 41,000 pounds per hour.

During the seventh day of continuous operation, the ammeter on the elevator motor indicated an irregular and subnormal pebble flow to the elevator and it was found that clusters of pebbles and coke were interfering with regular pebble flow. The flow of hydrocarbon was gradually replaced with steam, the fuel supply to the pebble heater burner was reduced after a short period so as to control the temperature, and the air supply to the burner was increased so as to burn off coke from the pebbles in the pebble heating chamber. After about 8 hours of this coke burning operation the pebbles were found to be substantially free of coke and onstream cracking of hydrocarbons was resumed. During the coke burning phase of the cycle and particularly in the latter stages, the temperature of the pebbles passing into the reactor was adjusted to that required in the onstream conversion of hydrocarbon.

During the process, maximum ethylene and propylene production amounted to 53,000 and 6,000 pounds per day, respectively.

The illustrative details set forth herein are not to be construed as imposing unnecessary limitations upon the invention, the scope of which is set forth in the claims.

I claim:

1. In a process for conversion of hydrocarbons in a pebble heater in which refractory heat carrying pebbles are successively heated to a temperature above conversion temperature in the

range of 1500 to 2500° F. in an upper chamber by contact with hot combustion gas, gravitated to a lower chamber in which they are contacted with a stream of hydrocarbon under cracking conditions so as to deposit coke on said pebbles and gradually cause pebble and coke agglomerates to form, and then said pebbles are transferred to said upper chamber for reheating; the method of removing said coke from said pebbles which comprises discontinuing the flow of hydrocarbon through said lower chamber and passing therethrough a stream of non-deleterious, non-coking gas under the conditions in the reaction zone while simultaneously contacting the pebbles in said upper chamber with an oxygen-containing gas in excess of that present in said upper chamber prior to discontinuing the flow of hydrocarbon to the lower chamber so as to burn coke therefrom; continuing the flow of said last-named gases and said pebbles at least until the major portion of the coke on said pebbles has been removed; and thereafter discontinuing the flow of said gases and resuming said hydrocarbon conversion and heating of said pebbles.

2. The process of claim 1 in which said non-deleterious, non-coking gas is steam.

3. The process of claim 1 in which said non-deleterious, non-coking gas is methane.

4. The process of claim 1 in which said non-deleterious, non-coking gas is combustion gas.

5. The process of claim 1 in which said non-deleterious, non-coking gas is nitrogen.

6. The process of claim 1 in which said non-deleterious, non-coking gas is CO_2.

7. In a process for conversion of hydrocarbons in a pebble heater in which refractory heat carrying pebbles are successively heated to a temperature above a conversion temperature in the range of 1500 to 2500° F. in an upper chamber by contact with hot combustion gas, gravitated to a lower chamber in which they are contacted with a stream of hydrocarbon under cracking conditions so as to deposit coke on said pebbles and gradually cause pebble and coke agglomerates to form, and then said pebbles are transferred to said upper chamber for reheating, the method of removing said coke from said pebbles which comprises reducing the flow of hydrocarbon to less than 60 per cent of the onstream flow and substituting therefor at least an equal amount of a non-deleterious, non-coking gas under the conditions in the reaction zone while continuing pebble flow through the system and contacting of pebbles in said upper chamber with an oxygen-containing gas in excess of that present in said upper chamber prior to reducing the flow of hydrocarbon to the lower chamber so as to burn off the major portion of the coke on said pebbles; and thereafter resuming the full onstream flow

of hydrocarbon in the lower chamber and combustion gas in the upper chamber.

8. The process of claim 7 in which the non-coking gas is steam.

9. The process of claim 7 in which the hydrocarbon is completely replaced with steam.

10. The process of claim 9 in which the temperature of the pebbles entering said lower chamber is maintained above 2000° F. so as to effect the water gas reaction between the coke and steam, thereby aiding in the removal of coke from the system.

11. The process of claim 9 in which the temperature of the pebbles entering said lower chamber is maintained below 2000° F. and substantially all of the coke removed from said pebbles is by oxidation in the upper chamber.

12. In a process for conversion of hydrocarbons in a pebble heater system in which a gravitating stream of refractory heat carrying pebbles are successively heated to a temperature above conversion temperature in the range of 1500 to 2500° F. by contact with combustion gas produced by burning a combustible mixture of fuel and excess oxygen in a combustion zone in the bottom of an upper pebble heating chamber, gravitated to a lower chamber in which they are contacted with a stream of hydrocarbon under cracking conditions so as to deposit coke on said pebbles and gradually cause pebble and coke agglomerates to to form, and said pebbles are transferred from said lower to said upper chamber for reheating, the method of removing said coke from said pebbles which comprises diminishing the flow of said hydrocarbon and supplementing the same with a non-deleterious, non-coking gas under the conditions in the reaction zone while continuing the flow of pebbles through the system and decreasing the proportion of fuel in said combustible mixture so as to provide sufficient excess of oxygen to burn off coke from said pebbles; continuing the preceding operation until the major portion of coke is burned from said pebbles in the entire system; and thereafter resuming the full onstream flow of hydrocarbon and combustion gas.

13. The process of claim 12 in which the heating in the pebble heating chamber and cooling in the reactor are coordinated to effect a pebble entrance temperature to the reactor at the level of their conversion inlet temperature.

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