

[54] **METHOD OF THERMAL CRACKING OF HYDROCARBONS**

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[51] Int. Cl.....**C07c 3/00**

[58] Field of Search208/48, 122; 260/679, 683; 23/209.4

[56]

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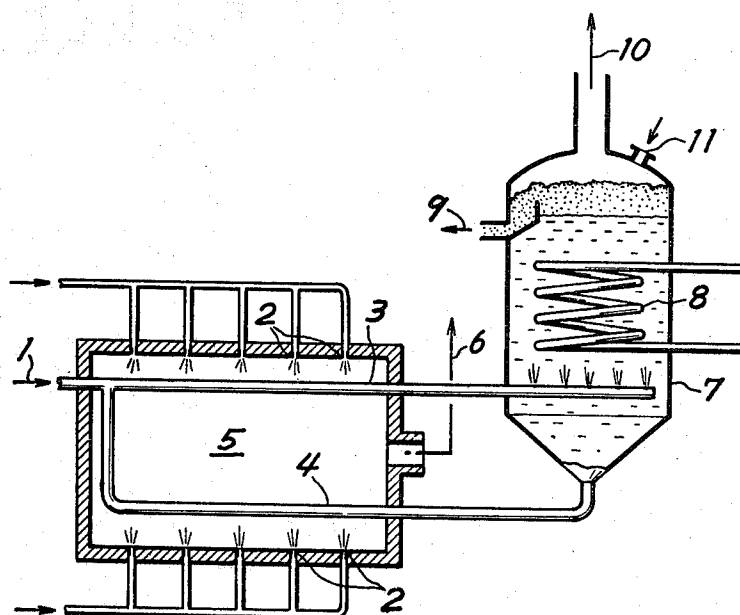
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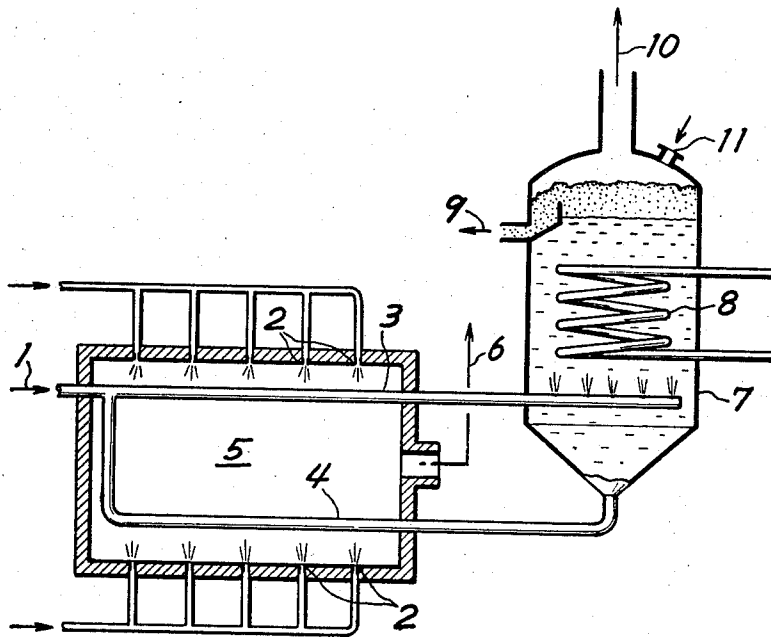
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ABSTRACT

Thermal cracking apparatus in which the reaction transfer, quenching and separation are carried out in circulating molten metals which are maintained molten by circulation through a preheater tube prior to circulation through the reaction tube. The preheater tube and the reaction tube are heated by burners. Feed stock or a diluent such as steam is sprayed into the quenching tower through the reaction tube to assist the circulation.

6 Claims, 1 Drawing Figure





METHOD OF THERMAL CRACKING OF HYDROCARBONS

The present invention relates to a method of producing olefins such as ethylene by thermal cracking of hydrocarbons in the presence of molten metals as circulating fluid.

For production of unsaturated hydrocarbons by thermal cracking of hydrocarbons, there have been publicly known tubular cracking furnace of external heating system, heat carrier recycle process and partial combustion process. However, in the known apparatuses, it is almost impossible to use hydrocarbons extending over a wide range from naphtha fractions of low boiling points to crude oil in which are included kerosene, light oil, heavy oil and crude oil. If such hydrocarbons are used, long run continuous operation is interrupted by cracked coke deposited and accumulated in reactor, transfer line or on the surface of quencher tubes. Further, conventional apparatuses have not sufficient functions in all of points of the reaction system, quenching system, heat recovery system and system of cracked coke removal. For fulfil functions of those systems, a considerably complicated apparatus have been required and not practical.

The present invention is to provide very simple thermal cracking method and apparatus in which hydrocarbons extending over a wide range from oils of lighter fraction to oils of heavier fraction such as heavy oil and crude oil can be used, which is fit for long run continuous operation and which is provided with all of thermal cracking, quenching, heat recovery and cracked coke removal systems.

The apparatus according to the present invention is characterized by being composed of a tubular cracking furnace containing a preheater tube for preheating molten metals and a reaction tube for thermal cracking of hydrocarbons and a quenching tower for quenching reaction products and molten metals and also for separating and removing cracked coke, the molten metals being circulated in the apparatus, whereby hydrocarbons are thermally cracked effectively and long run continuous operation can be effected.

In a thermal cracking apparatus for hydrocarbons, a trouble is caused by accumulation of cracked coke, etc., in the reactor, transfer line and quencher. Under a certain cracking condition, the coke, etc., are due to the amount of Conradson carbon in the crude oil in general. In heavier hydrocarbons containing a larger amount of Conradson carbon, by-produced coke, etc., are larger and cannot decreased into zero, even if they can be reduced to some extent by selection of operation condition. The apparatus of the present invention is not provided with reactor, transfer line and quencher sections which invite accumulation of cracked coke. In the apparatus of the present invention, the reaction, transfer, quenching and separation of cracked coke, etc., are carried out in molten metals as circulating fluid. Accordingly, troubles caused by cracked coke as in the conventional apparatuses are not observed in the apparatus of the present invention.

The construction and effects of the present invention will be described with reference to the drawing which is an explanatory illustration showing the method of the present invention.

Naptha, kerosene, light oil, heavy oil, residual oil or crude oil each as petroleum fraction in liquid or in vapor form, preferably pre-heated, is supplied alone or together with a diluent such as steam under a high pressure into a vertically or horizontally arranged reaction tube 3 in a cracking furnace 5 through suitably arranged feed stock supplying nozzles 1. By the feed stock injection, molten metal heated to a temperature of 700°–1,000° C in a pre-heater 4 is sucked into the reaction tube. While passing through the reaction tube 3, the hydrocarbons are contacted effectively with the molten metal and thermally cracked. Heat energy required for the cracking is given by burners 2 through an outer wall of the preheater tube 4 or reaction tube 3. A long run continuous operation is possible, because cracked coke produced in the reaction does not deposit on the wall of the reactor 3 but in the circulating molten metal. Flue gas is discharged through 6. The reaction tube 3 is inserted and opened in a quenching tower 7 in which a quencher tube 8 is set. The molten metal of 700°–1,000° C from the cracking furnace containing reaction products, diluent such steam and cracked coke is directly injected into molten metal in the quenching tower 7 and quenched to 300°–500° C in order to avoid secondary reaction of hydrocarbons as much as possible. The quenching tower 7 is filled with molten metal supplied through an inlet 11, in which the quencher tube 8 is placed. The gaseous reaction products are vigorously mixed with the molten metal and thereby quenched. The gaseous reaction products and the diluent ascend and are discharged through an outlet 10. On the other hand, cracked coke, etc., produced in the reaction tube 3 and the quenching tower 7 float on the surface level of the molten metal in the quenching tower 7 owing to difference in specific gravity, whereby they are separated from the molten metal and taken out through a side outlet 9. Thus, in the quenching tower 7, the molten metal as circulating liquid, reaction products and diluent from the reaction tube are quenched and also the gaseous reaction products containing the diluent and cracked coke can be separated from the molten metal and taken out from the system separately. The quenched molten metal is sent from the bottom of the quenching tower into the cracking furnace 5 again, preheated and circulated into the reaction tube for thermal cracking of hydrocarbons. The circulation of the molten metal as circulating liquid is facilitated by keeping the surface of the molten metal in the quenching tower at a level higher than the reaction tube 3 and by spraying liquid or gaseous hydrocarbon feed stock or a diluent such as steam through the feed stock supplying nozzles at a high speed. The molten metal thus circulates in the cracking furnace and the quenching tower, and so conveying equipment as pump is unnecessary and loss of molten metal is quite small.

As described above in detail, according to the present invention, hydrocarbons can be thermally cracked, the reaction products can be quenched and cracked coke can be removed by circulating molten metal as circulating fluid in the system. In other words, the present invention has a merit of carrying out all of quenching, transfer and separation of cracked coke at the same time in a simple quenching tower without necessitating respective devices. In addition, reaction

temperature, residence time or the like can be selected optionally by varying amount of feed stock, length, diameter and number of the reactor tubes, consumption of fuel oil and kind and circulating amount of molten metals.

We claim:

1. A process for the thermal cracking of hydrocarbons which comprises flowing molten metal at a temperature of at least about 700° C. together with a hydrocarbon feed stock through an elongated metal reaction tube whereby said feed stock is vaporized and thermally cracked, discharging the effluent molten metal and vaporized hydrocarbon reaction products directly from said reaction tube into a quenching zone below the surface of a bath of molten metal to cool said reaction products to a temperature in the range from about 300° to about 500° C., and withdrawing the vaporized hydrocarbon reaction products from said quenching zone, whereby any coke formed in the cracking operation and any other carbonaceous

material present in other than vapor form accumulates in the molten metal bath and floats to the surface thereof.

2. A process according to claim 1 wherein steam is introduced with the hydrocarbon feed stock.

3. A process according to claim 1 wherein said reaction tube is externally heated.

4. A process according to claim 1 wherein molten metal is withdrawn from said quenching zone, heated to a temperature of at least 700° C. and recycled to said reaction tube.

5. A process according to claim 1 wherein molten metal is withdrawn from said quenching zone and recycled to said reaction tube through a conduit, and wherein said reaction tube and said conduit containing recycled molten metal are heated externally.

6. A process according to claim 5 wherein steam is introduced with the hydrocarbon feed stock.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,696,166

Dated October 3, 1972

Inventor(s) Tokuji Ozawa et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

On the cover sheet insert -- [73] Assignee: Mitsui Shipbuilding and Engineering Company, Ltd., Tokyo, Japan, a corporation of Japan --. Column 2, line 23, "such steam" should read -- such as steam --.

Signed and sealed this 10th day of April 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents