Feb. 27, 1973 TOKUJI OZAWA ET AL 3,718,708

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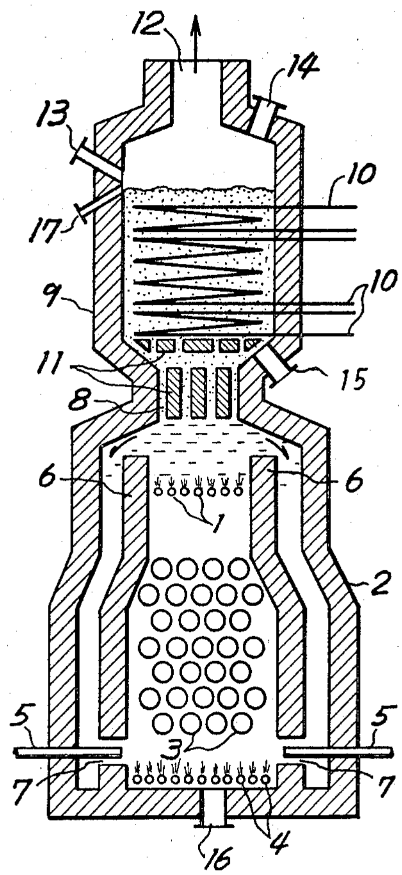
Filed July 16, 1970



3,718,708
Patented Feb. 27, 1973

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METHOD AND APPARATUS FOR THERMAL CRACKING AND QUENCHING

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Filed July 16, 1970, Ser. No. 55,403
Claims priority, application Japan, July 18, 1969, 44/56,987
Int. Cl. C07c 3/00
U.S. Cl. 260—683 R 9 Claims

ABSTRACT OF THE DISCLOSURE

Thermal cracking apparatus having a lower portion comprising a heating and reaction tower and an upper portion comprising a quenching tower. The lower portion includes spouting nozzles for dilution agents which cause circulation of the molten material in the tower, heating tubes, and raw material inlet nozzles, all arranged to be submerged in molten metal. The upper portion is provided with quenching tube bundles which are covered by fluidized solid grains or oils of high boiling point, the material being fluidized by the reaction products and diluents which are discharged from the lower portion.

This invention relates to a method and apparatus for thermal cracking of hydrocarbons into gaseous olefins, particularly, ethylene, propylene and other olefines.

It has been well known in an apparatus for producing olefines by thermal cracking of hydrocarbons to use heat carrier recycle systems, and it has been also well known to employ tubular quenchers for quenching reaction products. An apparatus of heat carrier recycle systems employs in most cases fine grains as the heat carrier and a fluidized bed reactor. However, this system must be provided a regenerator and a recycle system in order to remove cracked cokes deposited on the surfaces of fine grains during the reaction. Accordingly, the system has the disadvantages of providing a complicated regenerator and the recycle system and the apparatus being eroded. In a process comprising tubular quenchers as quencher, cracked coke deposits on the tube surface greatly which results not only in reduction of the heat transfer coefficiency but also in inhibition of the operation in some cases; particularly, when using oils of heavier fraction as raw material, this process can not be applied. Moreover, the problem of conventional processes as to deposition of coke in the transfer line between the reaction zone and the quenching zone has not been well resolved.

The object of this invention is to provide a novel apparatus which may be simplified by means of molten metals used as heat carrier and which can exhaust all the cracked coke formed during the reaction out of the reaction zone with the stream of gaseous and vaporous reaction products. Another object of this invention is to prevent deposition of cracked coke in the transfer line between the reaction zone and the quenching zone and deposition of cracked coke on the tube walls of quenching tube bundles by filling up and fluidizing solid grains or oils of high boiling point in the area from the surface of molten metals to the upper part of quenching tube bundles, as well as to prevent deposition by wetting the said tube walls with entraining molten metals.

According to the present invention, a heating and reaction tower is filled with molten metals, in which dilution agent spouting nozzles for force circulating the molten metals, heating tube bundles and raw material spouting nozzles are submerged. Just above the heating and reaction tower, there is connected a quenching tower which is provided with quenching tube bundles and filled up with fluidized solid grains or oils of high boiling point from the surface of the molten metals to the upper part of the quenching tube bundles. Spouting of dilution agents or raw oils forces the molten metals to circulate and agitate, and the molten metals are heated by the heating tube bundles up to a predetermined temperature, come in contact with the raw oils spouted into the upper or lower portion of the heating tube bundles, and contribute to the thermal cracking reaction. The floating solid grains or oils of high boiling point on the surface of the molten metals are kept in fluidization by means of reaction products and diluent coming out of the heating and reaction tower to prevent deposition of cracked coke in a transfer line and quenching tube bundles in a quenching tower.

The present invention will be explained by the accompanying drawing which illustrates an apparatus wherein a quenching tower filled with solid grains is directly connected with a heating and reaction tower of a type of forced circulating action of convection current. A heating and reaction tower **2** is filled with single metallic elements of low melting point such as lead, tin, zinc, bismuth, and cadmium or alloys mainly consisting of these elements in a molten state. Liquid or vaporous hydrocarbons are, preferably after pre-heating, charged to a middle part of the heating and reaction tower **2**, that is an upper part of heating tube bundles **3** positioned in the heating and reaction tower, through a feedstock supplying nozzle **1** alone or together with diluents such as water vapour. The hydrocarbons supplied through the feedstock supplying nozzle **1** come in contact with molten metals heated at 700–1100° C. in the heating tube bundles **3** to contribute to thermal cracking reaction for the residence time of shorter than 0.5 second, and then convert to reaction products mainly consisting of gaseous olefines, particularly ethylene, propylene or other olefines and aromatics. Metallic elements of low melting point or alloys mainly consisting of these elements in a molten phase, that is molten metals are accelerated and forced to ascend by the action of spouting hydrocarbons from the feedstock supplying nozzle **1**, by the spontaneous circulating action of convection current due to heating in the heating tube bundles **3**, by the action of ejecting and spouting diluents, from a high velocity spouting nozzle **4** for dilution agents such as water vapour positioned in the lower part of the heating tube bundles **3**, or by the action of ejecting and spouting diluents from a diluents spouting nozzle **5** for regulating the molten metals. After contributing to the reaction, the molten metals overflow over an overflowing weir **6** and flow downward along the inner wall of the heating and reaction tower **2**. Molten metals, thus, are convectively circulated, and depending of this action the heat of reaction necessary for endothermic cracking reaction can be transferred. In other words, the molten metals serve as heat carrier. The molten metals, whose temperature falls to 600–1000° C. due to the reaction, through an opening **7** provided at the lower part of the overflow weir **6**, and heated up to 700–110° C. in contact with the heating tube bundles **3**. The heating tube bundles **3** are heated by flowing high-temperature fluids such as high-temperature flue gas in the tubes or directly by burning fuels by burners, for instance, a tunnel burner system. The diluent high velocity spouting nozzle **4** is positioned in the lower part of the heating tube bundles **3** for accelerating the molten metals to flow upward and make a uniform ascending current. The circulating rate of the molten metals can be controlled by adjusting the spouting rate of the diluents from the said nozzle. To the said nozzle, not only diluents, but also raw materials can be supplied. The diluent spouting nozzle **5** for flow regulation is positioned at the opening **7** in the lower part of the overflow weir **6** for more severely flow adjustment, and the circulating rate can be varied by adjusting the spouting rate from the said nozzle.

The cracked coke formed during the thermal cracking reaction has the specific gravity smaller than that of molten metals, so that it is readily separated from the molten metals and exhausted together with reaction products from the heating and reaction tower **2**, without circulating together with the molten metals. The reaction products accompanied with diluents, cracked coke and entrained molten metals enter a quenching tower **9** through a transfer line **8** directly joined with the upper part of the heating and reaction tower **2**. Inside the quenching tower **9** quenching tube bundles **10** are provided for quenching the reaction products. Solid grains such as sand are contained in an area from the surface of the molten metals to the upper part of the quenching tube bundles **10** and are kept in a fluidization state by reaction products and diluents.

The transfer line **8** is formed in a smaller way in cross section and separates the heating and reaction tower **2** from the quenching tower **9**. In the transfer line **8** there is provided a uniformly distributing structure **11** built up with fireproof materials to reduce the cross section at area, and by the structure the reaction products and diluents coming from the heating and reaction tower **2** are uniformly distributed to keep the solid grains in a uniform fluidization state in the quenching tower **9**. The cross section of the transfer line **8** is reduced in order to raise the flow rate of the reaction products and diluents not to allow the solid grains to fall down frequently from the upper part and absorb heat of the molten metals. The solid grains kept in the fluidization state in the transfer line **8** collide against the wall of the transfer line and remove cracked coke which is going to deposit on it. Moreover, since the molten metals accompanied with the reaction products and entraining to the quenching tower **9** flow down along the inner wall of the transfer line **8** to the heating and reaction tower **2** wetting the said wall, cracked coke can never deposit on the wall.

The average temperature of the solid grain layer which is kept in fluidized motion in the quenching tower **9** provided with the quenching tube bundles **10** is kept at 200–600° C. The temperature of the reaction products and diluents such as water vapour ascending from the heating and reaction tower **2** is 600–1000° C., and they are quenched to 200–600° C. in contact with the solid grain layer and the quenching tube bundles **10**. The coke formed in quenching is apt to deposit on the walls of the quenching tube bundles **10**, but it is immediately stripped off and removed by frictional collision of the solid grains. The entrained molten metals coming from the heating and reaction owner **2** also promote the action of the stripping off and removing of deposits on the tube walls. More particularly, the molten metals collide against the tube walls of the quenching tube bundles **10** and wet them to prevent the coke from depositing directly on the tube walls.

The cracked coke adhering on the surface of solid grains, the cracked coke stripped off from tube walls and other places, and the cracked coke formed in reaction in the heating and reaction tower **2** are pulverized by friction and collision in the solid grain layer, exhausted through an exhaust tube **12**, together with the reaction products and diluents, and treated by a well-known method. As modification of the present invention, a transfer line **8** and a quenching tower **9** can be directly connected to a reaction tower **2** which is not provided with a diluent spouting nozzle for flow regulation **5**, an overflow weir **6** and an opening **7**, a so-called reaction tower of a forced agitating type. In such a process, raw materials of hydrocarbons are preferably supplied from a diluent high velocity spouting nozzle **4**.

According to the present invention, furthermore, the quenching tower **9** can be filled with oils having high

boiling point, instead of solid grains. When using the oils having high boiling point, cracked coke is not exhausted through an exhaust tube **12** but contained in the oils having high boiling point. Accordingly, it should be noted that Conradson carbon in the oils must not exceed 40% by weight.

Solid grains or oils of high boiling point and molten metals are made up intermittently from a make-up nozzle **13**. On starting up the operation solid grains or oils of high boiling point and solid metals are supplied from a supply nozzle **14**. In shutting down the operation, solid grains or oils of high boiling point are discharged from a discharge nozzle **15** and molten metals are exhausted from an exhaust nozzle **16**. The entrained molten metals gather together in the lower part of a quenching tower **9** during the operation and flow down along the inner wall of a transfer line **8**. When the surface of a solid grain layer or a layer of oils having high boiling point raises during the operation, the solid grains or oils of high boiling point are discharged from a discharge nozzle **17** by a well-known method to keep the surface of the layer in the quenching tower **9** at predetermined level.

As clearly seen from the above description, fluid molten metals are used as heat carrier in this invention, there is no need to employ such a regenerator for heat carrier grains as used in a conventional heat carrier grain circulation system. Heating of the molten metal heat carrier and thermal cracking of the hydrocarbons can be performed successively by circulating molten metal heat carrier or agitating it in a tower. As the result, the apparatus is very simplified, the investment cost is low, the site area is reduced and the operation becomes very easy. As cracked coke formed in thermal cracking reaction accompanies reaction products to be exhausted from the heating and reaction tower, the reaction system is never inhibited by coke. Since the quenching tower filled with fluid solid grains or oils of high boiling point from the surface of molten metals to the upper part of the quenching tube bundles is installed just above the heating and reaction tower, the problem of coke deposition in the transfer line between the heating and reaction tower and the quenching tower is resolved by continuous removal of cracked coke due to collision of solid grains or flow of oils of high boiling point, and also the deposition of coke is prevented by molten metals wetting the inner wall of the transfer line. Cracked coke which is going to deposit on the walls of quenching tube bundles in quenching is similarly continuously removed by collision of solid grains or flow of oils of high boiling point, and cracked coke hardly deposits on the walls as entraining solid metals also collide against the walls and wet them. Thus, there can be treated hydrocarbons having high boiling point and those containing much Conradson carbon.

We claim:

1. In a method for the thermal cracking of hydrocarbons in which a hydrocarbon feed stock is introduced into a bath of molten metal in a reaction zone and in which gaseous hydrocarbon reaction products and coke are separated from the molten metal which is recycled to the reaction zone, the improvement which comprises: heating said feed stock and molten metal simultaneously with violent agitation and cracking of the feed stock in the reaction zone by direct contact with heating elements to a temperature in the range from about 700° C. to about 1100° C., separating the resulting reaction products and coke from the metal bath by gravity separation and immediately quenching said reaction products to a temperature in the range from about 200° C. to about 600° C. in a quenching zone by admixture with a violently agitated quenching material in direct contact with cooling elements; the deposition of coke on the walls of said reaction zone, heating elements, quenching zone and cooling elements being prevented by the wetting of the said walls with said molten metal and by the scouring action of the violent agitation of said molten metal and quenching materials in said reaction and quenching zones.

2. A method according to claim 1 wherein the quenching material is a solid granular material.

3. A method according to claim 2 wherein said feed stock, which is introduced above the heating elements in said reaction zone, causes circulation and agitation of the bath in said reaction zone.

4. A method according to claim 3 wherein a fluid diluent, which is introduced to said reaction zone below said heating elements, aids in the agitation and circulation of the bath in said reaction zone.

5. A method according to claim 1 wherein the flow of reaction products through said quenching zone causes said violent agitation of said quenching material.

6. A method according to claim 1 wherein the quenching material is a high boiling oil.

7. A method according to claim 6, wherein said feed stock, which is introduced above the heating elements in said reaction zone, causes circulation and agitation of the bath in said reaction zone.

8. A method according to claim 6 wherein a fluid diluent, which is introduced to said reaction zone below said heating elements, aids in the agitation and circulation of the bath in said reaction zone.

9. A method according to claim 6 wherein the flow of

reaction products through said quenching zone causes said violent agitation of said quenching material.

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U.S. Cl. X.R.

48—92; 23—277; 208—48