

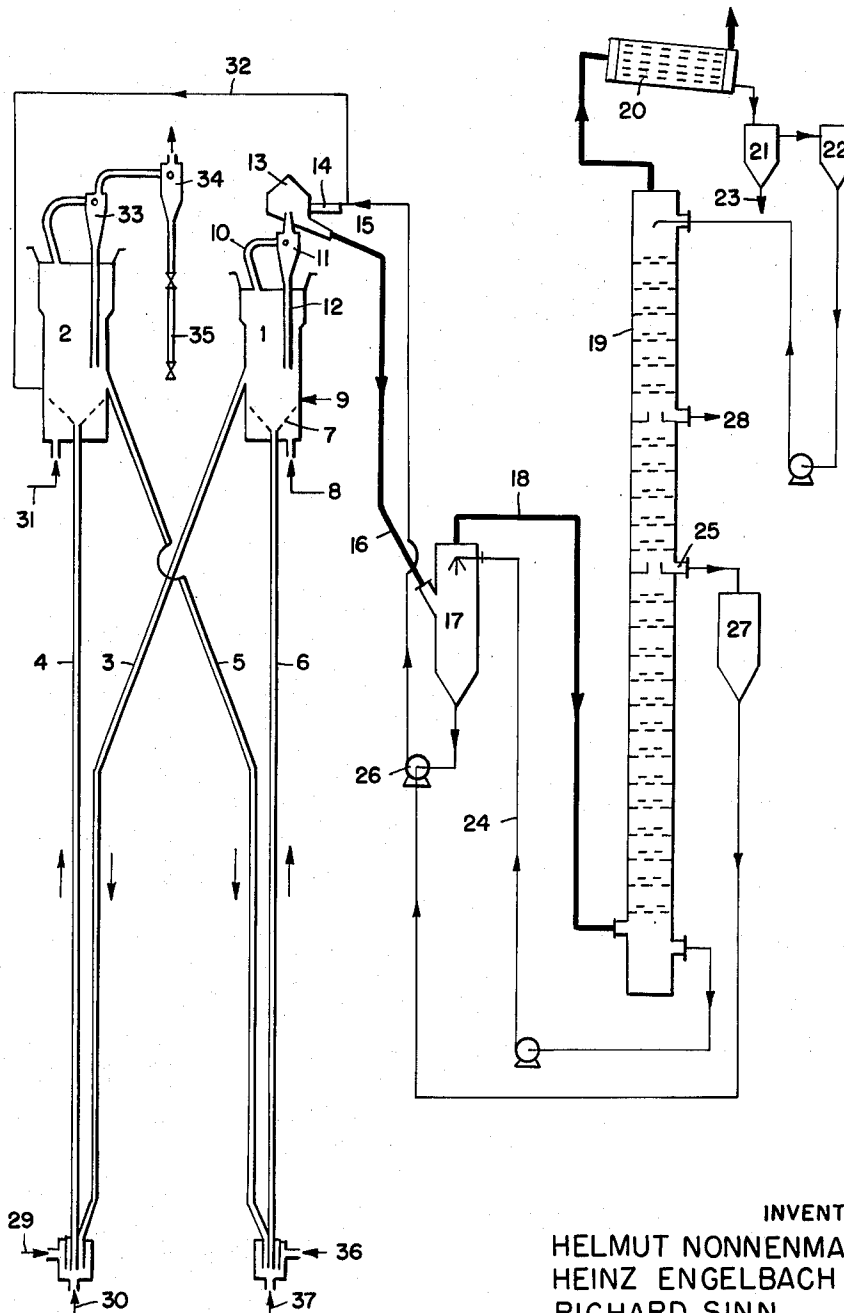
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CRACKING OF HYDROCARBONS TO GASEOUS OLEFINES

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CRACKING OF HYDROCARBONS TO GASEOUS
OLEFINES

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This invention relates to a process for the cracking of hydrocarbons to gaseous olefines. More particularly, the invention relates to a cracking process in which crude oils and similar products are cracked in a fluidized bed to form gaseous olefines.

It is known that various hydrocarbon oils such as crude oils, crude oil fractions or distillation residues, can be cracked in a zone containing fluidized solid particles heated to high temperatures. Ethylene, propylene, and other gaseous olefines can be produced by this process. An inert solid is used as the heat carrier which usually is the petroleum coke formed in the process. The petroleum coke is often used in a grain size of 50 to 400 microns, i.e., so fine that even in the down pipes it can be kept in pseudo-liquid condition by blowing in a ventilating gas. It is furthermore known to satisfy the heat requirement of the plant by burning part of the petroleum coke formed in the process or part of the charge in a separate regenerator, the heat carrier being circulated by a fluidized flow method between the reactor and the regenerator through a system of down pipes and rising pipes.

These known methods are attended by disadvantages. Thus, the usual grain sizes of the inert heat carrier permits only relatively low throughputs. Furthermore, the petroleum coke constantly required must largely be produced by returning part of the cracked oil obtained to the reactor. It is therefore necessary to combine the cracking reaction, which requires a short residence period, with the coking reaction, which requires 10 to 100 times as long. In order to equalize this difference, the amount of cracked oil present must be circulated at such a rate that the amount of oil passing through the reactor is a multiple of the amount present, only a fraction of the cracked oil injected into the reactor being coked. Moreover, carbon black is formed during the coking and this has to be washed out from the cracked gas.

Another known cracking method uses sand rather than coke as the heat carrier. The sand is heated in an up-current pipe by burning the carbon deposits and residual oil adhering thereto. It is a disadvantage of this process, however, that mechanical control of the circulation of solid by means of throttle valves is necessary. Moreover, when using naturally occurring sand it is necessary, by reason of the low resistance to fracture and attrition of sand at high temperatures, continuously to discharge relatively large amounts of fine dust and to replace it by fresh material.

It is an object of the present invention to provide a cracking process which avoids the disadvantages of the prior art methods.

Another object of the invention is to provide a process for cracking hydrocarbons by which it is possible to obtain a high throughput.

Another object of the invention is to provide a cracking process which can be carried out in a simple manner and which requires less complicated equipment than the known processes.

Other objects will become apparent to those skilled in the art from the following detailed description of the invention.

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In general, the invention comprises the discovery that hydrocarbons containing high boiling constituents can be cracked more efficiently in a fluidized reactor where the fluidized particles have a grain size of between about 0.05 mm. and about 4.0 mm. and wherein at least 10% by weight of the particles have a grain diameter greater than 1 mm. In a preferred embodiment of the invention the diameter of the grain particles ranges between about 0.10 mm. and 3.0 mm. and at least 20% by weight of the particles have a grain diameter greater than 1 mm.

The hydrocarbons are cracked at temperatures from about 680° to about 850° C. to produce gaseous olefines such as ethylene and propylene. The cracked gases and vapors leaving the fluidized reactor are freed in a cyclone from the bulk of the entrained solid particles and are then quenched to a temperature of less than 400° C. by oil residues formed in the process which boil above 200° C. The cracked gases are then freed from residual solid particles and are separated in a fractionating column into vaporizable liquid, cracked oil, and cracked gas.

In the process, solid particles having high resistance to attrition and heat, and having a grain size of between about 0.05 mm. and about 4.0 mm. are circulated between the reactor and a regenerator. Particles are withdrawn from the reactor in the regenerator through down pipes and are returned to both vessels through rising pipes. The particles flow downwardly in the pipe as a compact mass. The particles are then returned to the reactor and regenerator as a dilute suspension by means of proportioning or metering gases. The heat necessary for the cracking reaction is produced by the combustion of carbon deposits formed on the inert particles and by combustion of part of the quenching oil in the regenerator.

The process is especially suitable for the pyrolytic cracking of hydrocarbons which contain high boiling constituents. By the use of particular solid particles as the fluidized material and the heat carrier, high throughputs can be obtained with small reaction chambers. The inert incombustible solids used may be granular or globular solids having high resistance to attrition and heat and high stability to changes in temperature. It is advantageous to use inert solids which have a small inner surface and are not porous, for example aluminum silicates which contain 50% by weight or more of aluminum oxide. Other inert solids can be used in place of aluminum silicates provided they have the above-specified properties at temperatures of 700° to 1,000° C. Examples are corundum, sillimanite and mullite.

As indicated above, at least 10%, preferably at least 20%, by weight of the particles, for example, should have a diameter greater than 1 mm. Below are two grain size distributions which are suitable for the heat-carrying particles.

Above 1.5 mm. -----	1 to 10%, 1 to 10%
1.0 to 1.5 mm. -----	20 to 50%, 40 to 80%
0.75 to 1.0 mm. -----	5 to 20%, 10 to 30%

or

0.5 to 0.75 mm. -----	20 to 40%, 1 to 5%
Below 0.5 mm. -----	10 to 20%, 0 to 10%

The above grain size distribution does not insure an ideal pseudo-liquid layer such as can be produced with finely particled materials. However, a uniform temperature prevails in the fluidized layer even at these grain size distributions. The particles can be conveniently led downward through a non-vented down pipe. No mechanical devices are needed to control the circulation of solid particles because the stream of solid particles moving in a compact mass can readily be suspended in a current of conveyor gas in proportionable amounts. In contrast to

the known vented down pipes in which the solid particles in fluidized condition always include entrapped gas, relatively small amounts of sealing gas are needed in order to separate the oxidizing from the reducing medium at the points where the down pipe meets the rising pipe.

The special grain size distribution of the solid incombustible solids makes it possible to apply high gas velocities. Therefore, only a small reaction space is necessary in the reactor and regenerator. The coarse grains can be removed in the down pipe without the necessity of using special devices for controlling circulation. Circulation is controlled only by a gas proportioning means provided at the lower end of the down pipe. This is a special advantage because mechanical devices for controlling circulation as required in the conventional processes, which are difficult to operate at high temperatures and which are subject to considerable corrosion at high temperatures are not necessary in the instant process.

Starting materials for the instant process are crude oil and crude oil distillates, especially those having a final boiling point between 200° and 400° C. By "final boiling point" we understand the temperature at which a substance has passed over substantially without a residue. The distillates may also contain volatile components with boiling points below 200° C. Other starting materials are crude oil distillate residues and top crude oil. Besides ethylene and propylene, the main products formed in the cracking process, butylene and butadiene are obtained. Valuable by-products of the process include gases of high calorific value which can be processed into synthesis gas, low boiling aromatic compounds such as benzene and toluene.

The high boiling point constituents of the cracked product and the non-vaporizable portions are burned in the regenerator together with the carbon deposit to cover the heat requirement of the process. In the fractionation of the cracked products obtained it is advantageous to withdraw from the separating column only so much of the liquid vaporizable cracked products that the remainder of higher boiling point and the coke deposited on the solid particles are sufficient to cover the heat requirements. For the combustion of the non-vaporizable fraction of the cracked product, which contains asphalts and the solid washed out from the cracked gas, it is convenient to set up a small excess of oxygen of 0.3 to 3% by volume in the smoke gas. In this way and by a preliminary cracking on the hot heat carrier, the combustion in the regenerator can be carried out with optimum utilization of the heating power, i.e., without the formation of carbon monoxide.

During operation, the cyclone in the reactor is preferably adjusted so that not all the solid particles are separated and a certain concentration of solids is present in the gas outlet pipe. As a result of internal abrasion on the walls of the gas outlet pipe formation of carbon deposits is then prevented. After leaving the cyclone, the vapors should advantageously contain 5 to 50 grams per cubic meter (S.T.P.) of solid particles originating from the fluidized mass. This amount of solid particles is absorbed during quenching by the oil used for quenching which is partly injected into the regenerator to assist in covering the heat requirement. The solid particles withdrawn from the reactor thus return to the regenerator by way of the quenching oil. At the same time, excessive enrichment of solid particles in the quenching oil is avoided. It is preferable to maintain a content of solid of less than 10% by weight.

The process may be carried out, for example, in the following way: granular or globular inert solid particles, whose size lies between 0.05 and 4.0 mm. and which have been heated to a high temperature circulate in a system comprising a reactor fluidized layer, a regenerator fluidized layer and the two down pipes and rising pipes connecting them. The dilute phases above the fluidized layers in the reactor and regenerator are preferably kept at the same pressure. The liquid or partly vaporized initial oil may be injected into the fluidized layer of the reactor by means

of an atomizing agent, for example, steam, and cracked therein at temperatures between about 680° and 850° C. The preferred temperature range is between 720° and 780° C. Superheated steam is preferred as the fluidizing gas. The cracked gas and vapor leaving the reactor are first separated from the bulk of the entrained solids in a cyclone which leads back into the fluidized layer of the reactor. The cyclone outlet is kept free from coke deposits by means of a small amount of solids not separated from the gas in the cyclone. Immediately after leaving the cyclone, the cracked gas obtained is quenched to a temperature below 400° C. with the cracked oil residue boiling above 200° C. formed in the cracking, and at the same time the residual solid particles contained in the gas and any carbon black are washed out. In an attached fractionation column, the cracked products are separated into condensable cracked oil and cracked gas. The condensed fraction is returned from the bottoms of the column into the circulating quenching oil.

The cooled solid particles are withdrawn from the reactor fluidized layer through a down pipe and move as a compact mass downwardly through a substantially vertical tube. It is advantageous to arrange for a deviation from the vertical of not more than 20°. In order that at such an inclination the same amount of solid should be conveyed, inclined pipes may be dimensioned about one and a half times the cross-section of a vertical pipe. At the lower end of the down pipe, the solid particles are supplied in a regulatable amount by a proportioning gas current to the actual conveyor gas stream and suspended therein. Depending on pressure conditions, part of this proportioning gas stream flows in countercurrent to the particles descending in the down pipe, the reducing medium in the reactor thus being separated from the oxidizing medium in the regenerator and the small amount of cracked gas entrained by the solid being stripped and returned to the reactor. It is advantageous to use steam as the proportioning gas, but other gases, as for example nitrogen, smoke gas, hydrocarbons or even air, may also be used. The overflow into the down pipe may be constructed as a stripper.

The conveyor gas, for example, air, smoke gas, or nitrogen, carries the solid particles into the regenerator in which fluidization is effected with air or oxygen-containing gases, where it is heated to 700° to 1,000° C. The deposited coke adhering to the particles may be partly burnt off in the rising pipe. At the same time, part of the quenching oil together with the solids contained therein and originating from the fluidized material, and also the carbon black washed out are injected into the regenerator fluidized layer; air, steam or nitrogen, for example, may be used as the injection medium. The smoke gas leaving the regenerator is substantially freed from solid particles in a cyclone. The dust formed (grain size below about 0.05 mm.) may be discharged and separated in an external cyclone. To maintain the desired grain spectrum, the fluidized material is replenished by adding appropriate amounts of coarser material. The solid particles which have been heated up return to the reactor through an analogous arrangement of a down pipe and a rising pipe. It is preferred to use steam as the proportioning and conveying gas in order to obtain a concentrated cracked gas. In this case also, the proportioning gas provides a separation of the various media on the reactor and regenerator sides.

The excess of cracked oil is withdrawn at a tray in the column; it is a standard fuel oil.

An apparatus suitable for carrying out the process according to this invention will now be described with reference to the accompanying diagrammatic drawing.

Reactor 1 and regenerator 2 form with down pipes 3 and 5 and rising pipes 4 and 6 a flow system in which granular or globular solid with a grain size of 0.05 to 4.0 mm., preferably 0.1 to 3 mm., circulates as a heat carrier. It is fluidized in the reactor 1 by superheated

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steam which is supplied to a distributor grate 7 through a pipe 8. Instead of a conical grate as shown, other grate constructions may be used. It is also possible to introduce the fluidizing medium through jets without a grate. The oil to be cracked, atomized with steam, is introduced through a pipe 9 into the reactor fluidized layer which is at a temperature of 650° to 850° C. The cracked gas and vapor pass through a pipe 10 into a cyclone 11 whose drain 12 returns to the fluidized layer. In order that the gas outlet pipe of the cyclone may be kept free from coke deposits, a small amount of solid from the fluidized layer is allowed to remain in the gas. This solid is washed out in a quenching vessel 13 together with the carbon black formed in the process by the cracked oil residues introduced through pipes 14 and 15. At the same time, the cracked gas and vapor are cooled to a temperature below 400° C. Gas and washing liquid flow through a pipe 16 to a receiver 17. The residual gaseous fraction is supplied through a pipe 18 to a fractionating column 19. The top product thereof is partly condensed in a condenser 20; water and a gasoline fraction are separated in a separating vessel 21. The water is drained off through a drain valve 23 while the gasoline fraction is in part returned through a reservoir 22 to the column 19, a temperature between 100° and 130° C. being maintained at the top of the column. The level of the separating layer in the vessel 21 can, for example, be maintained by a regulator which actuates drain valve 23.

The bottoms of the column return through a pipe 24 and the receiver 17 into the circulating quenching oil. At about the middle of the column 19 there is withdrawn from a tray 25 a middle oil which serves as rinsing oil for the quenching oil circulatory pump 26. The excess of cracked oil less the amount required in the regenerator is withdrawn as a standard fuel oil from column 19 through a pipe 28 which usually lies above pipe 25 where the rinsing oil is withdrawn. The cooled solid particles are withdrawn from the reactor 1 through the down pipe 3 in a compact mass. They are proportioned at the lower end of down pipe 3 by means of a gas stream 29 into the rising pipe 4 and conveyed from a pipe 30 by means of air, preferably preheated air, or an inert gas into the regenerator 2.

The fluidized material in the generator is preferably fluidized with preheated air through pipe 31. On the pressure side of the quenching oil circulatory pump 26, a partial stream is introduced through pipe 32 into the regenerator. It may be atomized, for example, with air, inert gas or steam. Introduction is preferably combined with the proportioning step. A temperature of 700° to 1,000° C. is maintained. To insure combustion without carbon black formation it is advantageous to use an excess of oxygen of 0.3 to 3% by volume in the smoke gas. The latter leaves the regenerator through an inner cyclone 33 and an outer cyclone 34. By this arrangement, the dust formed in the system (grain sizes below about 0.05 to 0.1 mm. in diameter) can be removed and separated in a discharge 35. The heat of the CO-free gas may be utilized in a heat exchanger (not shown) in conventional manner.

The solid particles which have been heated up are withdrawn from the regenerator through pipe 5, supplied to the rising pipe 6, preferably with steam from a pipe 36, and are conveyed into the reactor with steam from a pipe 37.

The invention is illustrated but not limited by the following example.

Example

About 2.5 metric tons of sillimanite with a grain size between 0.2 and 2 mm. circulate per hour in a plant according to the drawing. At the same time, 98 kilograms of a preheated crude oil with a paraffinic base are injected together with 15 kilograms of superheated steam into reactor 1, a temperature of 740° C. being set up. The layer in the reactor is fluidized with about 70 kilograms

per hour of superheated steam which is introduced partly below the grate through pipe 8 and partly as conveyer steam through pipe 37. The vapors leaving the reactor are quenched to below 300° C. in vessel 13 and freed in column 19 from the residual high boiling fraction.

The cooled heat carrier particles are heated up to about 900° C. in regenerator 2 by burning the cracked coke deposited thereon and also by injecting about 16 kilograms per hour of the high boiling oil occurring in vessel 13. The layer in the regenerator is fluidized with such an amount of preheated air that the smoke gas contains about 2% by volume of oxygen.

The cracked gas contains hydrocarbons up to and including C₄, of which 39.0% by volume is ethylene and 12.3% by volume propylene. The yield of the said olefines, with reference to a metric ton of crude oil, is 281 kilograms of ethylene and 133 kilograms of propylene.

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for cracking hydrocarbons which contain high boiling constituents to produce gaseous olefines which comprises: injecting said hydrocarbons into a reactor containing fluidized solid particles, said reactor being maintained at a temperature of from about 680° to about 850° C., said fluidized solid particles being inert heat carriers having a grain size of between about 0.05 and about 4.0 mm., wherein at least 10% by weight of said particles have a grain size greater than about 1 mm., said particles being circulated between said reactor and a fluidized layer regenerator wherein said particles are reheated, the particles being withdrawn from the reactor and regenerator through down pipes in which they move as a compact mass, said particles being returned to said reactor and said regenerator through rising pipes in the form of a dilute suspension which is formed by the introduction of the gas into the compact mass; passing the cracked gas and vapor leaving the fluidized reactor into a cyclone wherein the bulk of the entrained solid particles are separated from said gas and said vapor, from 5 to 50 grams of solid per normal cubic meter of cracked gas being left in the cracked gas leaving said cyclone; passing the gas and vapor to a quenching zone wherein said products are quenched to a temperature below about 400° C. by oil residues boiling above 200° C. which are formed in the cracking process; separating the quenching oil and residual solid particles from said gas and said vapor; recycling said quenching oil and said solids to said quenching zone, a portion of said quenching oil and said solids being passed to said regenerator and separating said gas and vapor products in a fractionating column into a vaporizable liquid, cracked oil and cracked gas; the heat necessary for said cracking reaction being produced by burning carbon deposits which are formed on the inert particles and by burning a portion of the quenching oil in the regenerator.

2. A process as in claim 1 wherein equal pressures are maintained in the space above the dense fluidized layer in the reactor and in the regenerator.

3. A process as in claim 1 wherein said quenching oil has a solids content of less than 10% by weight.

4. A process for cracking hydrocarbon selected from the group consisting of crude oil and crude oil distillates having a final boiling point between 200° C. and 400° C. to produce gaseous olefines which comprises: injecting said hydrocarbons into a reactor containing fluidized solid particles, said reactor being maintained at a temperature of from about 680° C. to about 850° C., said fluidized solid particles being inert heat carriers having a grain size of from about 0.1 and about 3.0 mm., wherein at least 20% by weight of said particles have a grain size greater than about 1 mm., said particles being cir-

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culated between said reactor and a fluidized layer regenerator wherein said particles are heated, said particles being withdrawn from the reactor and regenerator through down pipes in which they move as a compact mass, said particles being returned to said reactor and said regenerator through rising pipes in the form of a dilute suspension which is created by the introduction of a gas into the compact mass; passing the cracked gas and vapor leaving the fluidized reactor into a cyclone wherein the bulk of the entrained solid particles are separated from said gas and said vapor, from 5 to 50 grams of solid per normal cubic meter of cracked gas being left in the cracked gas leaving said cyclone; passing the gas and vapor to a quenching zone wherein said products are quenched to a temperature below about 400° C. by oil residues boiling above 200° C. which are formed in the cracking process; separating the quenching oil and residual solid particles from said gas and said vapor; recycling said quenching oil and said solids to said quenching zone, a portion of said quenching oil and said solids being passed to said regenerator and separating said gas and vapor products in a fractionating column into a vaporizable liquid, a cracked oil, and a cracked gas; said temperature of from

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about 680° C. to about 850° C. being maintained in said reactor by burning carbon deposits which are formed on the inert particles and by burning a portion of the quenching oil in said regenerator.

5 5. A process as in claim 4 wherein equal pressures are maintained in the space above the dense fluidized layer in the reactor and in the regenerator.

6. A process as in claim 4 wherein said quenching oil has a solids content of less than 10% by weight.

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