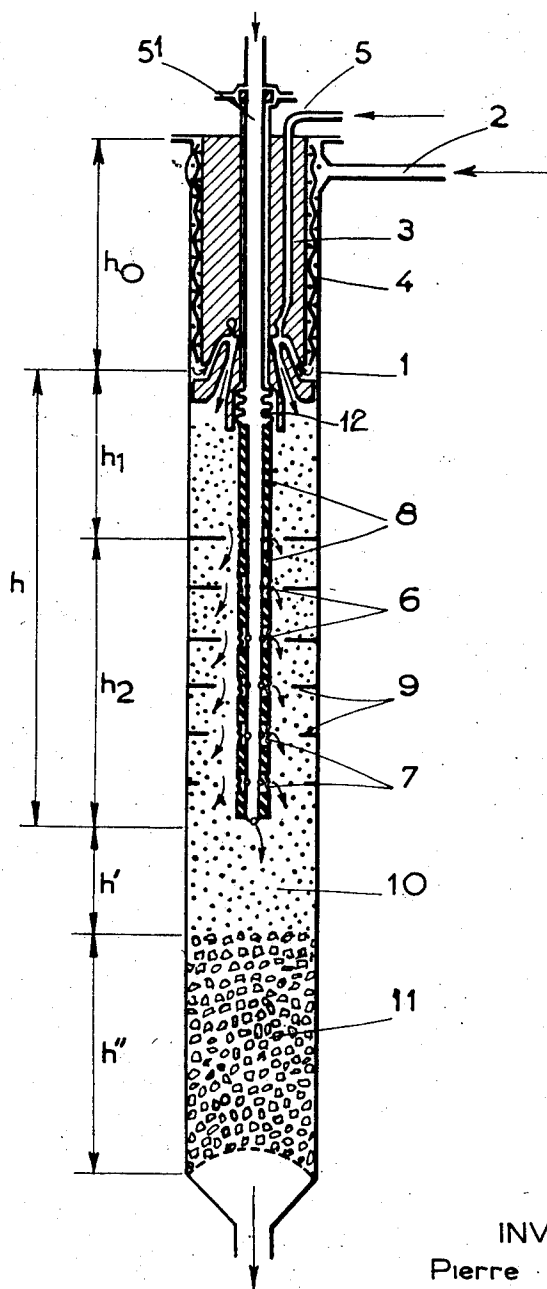


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METHOD FOR THE CATALYTIC DECOMPOSITION OF
HYDROCARBONS BY STEAM
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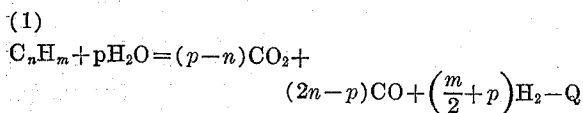
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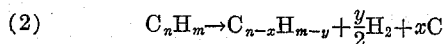
Claims priority, application France May 4, 1951

2 Claims. (Cl. 48—214)

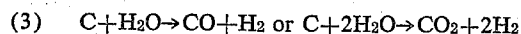
When hydrocarbons are oxidized by means of steam in accordance with an endothermic catalytic reaction of the following type:



calories, it has been ascertained that there exists a critical range of temperatures between the temperatures t_1 and t_2 , of which t_1 designates the threshold of pyrolysis of the hydrocarbons, associated with a deposit of free carbon in accordance with a reaction such as:



while the higher temperature t_2 is that for which the speed of oxidation of the carbon in accordance with the reaction



is higher than the speed of formation of free carbon according to the Reaction 2, referred to above.

Inside this critical range, the carbon may form at a higher rate than that of its oxidation and the deposit of carbon thus produced leads to a number of drawbacks such as the clogging of the flow of gases, an embedding and a poisoning of the catalyst, a disaggregation of the catalyst carrier, etc.

It has already been proposed to cut out these drawbacks by preheating the hydrocarbon or the mixture containing it, to a temperature approximating the temperature t_1 while remaining lower than the latter and then introducing rapidly this primary stream into an oxidizing stream of steam forming a secondary stream that has been previously heated to a sufficiently high temperature, in a manner such that, immediately after the mixture of the two streams, the temperature of the system may be at least equal to t_2 .

However, when it is desired to oxidize through such a method heavy hydrocarbons such as gas oil or fuel oil, it is generally necessary to vaporize them and to carry them along by means of a large amount of steam so as to form a primary stream having a high thermal capacity and the temperature of which should be held below the threshold temperature t_1 ; similarly, when hydrocarbons are treated that are readily decomposed by a rise in temperature, it is also necessary to dilute them in a mass of steam. The increase in the thermal capacity of the primary stream of hydrocarbon thus diluted in steam, has for its result to require a considerable corresponding increase in the thermal capacity of the secondary stream of steam and/or a large rise in the temperature of the latter; the very high temperature which should thus be reached cannot generally be obtained through simple or conventional means; the increase in the volume of said secondary stream constituted by steam possibly laden with air, with oxygen or with CO_2 , corresponds to a further

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expenditure of steam which it is difficult to recover, to a large increase of the heat-exchanging surfaces operating at a high temperature and also to various other drawbacks, such as a shifting of the chemical equilibrium, an increase in the contents of CO_2 in the gas that is finally obtained, an increase in the circulating mass of gases, a drop in pressure as the stream passes through the catalyst, etc.

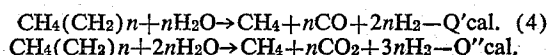
Now, our invention has for its object to remove the drawbacks of the above method while retaining its advantages and reducing the amount of the secondary stream of steam, whether admixed with other gases or otherwise, to be incorporated to the primary streams of hydrocarbons generally admixed with steam.

To this end, our invention consists chiefly in subdividing the primary stream containing heavy hydrocarbons into a number of elementary stream fractions that are introduced separately at corresponding points of the reaction stream constituted by the secondary stream to which the successive fractions of the primary stream are being introduced in succession for cracking in the presence of a catalyst submitted to the action of external heating means. At each point of introduction of an elementary fraction of the primary stream, said fraction mixes speedily and completely with the totality of the circulating mixture undergoing reaction.

The outward heating of the catalyst should be sufficient for the heat transferred to the gasiform mixture undergoing reaction in the path separating two successive points of introduction of the primary mixture to produce the following results: raising suddenly the temperature of the fraction of the primary mixture that has just been introduced from a value below t_1 to a value above t_2 —making up for the endothermic character of the reaction—keeping the mixture undergoing reaction between the successive points of introduction of the elementary fractions at a temperature above t_2 in a manner such that in spite of the addition of the following elementary fractions of the primary stream that remain at a temperature below t_1 the temperature of the compound mixture may lie in all cases above t_2 .

Furthermore, the secondary stream introduced at the beginning of the reaction should remain at a temperature higher than t_2 and its amount should be sufficient for the first fraction of the primary fluid introduced at a temperature below t_1 to be suddenly brought through this incorporation to the secondary stream to which it is admixed and with which it is stirred, to a temperature above t_2 . As this addition of a primary fluid may be comparatively small, the amount of secondary fluid used may in its turn be comparatively small and this is all the more true when its temperature is higher. Thereafter, as the reaction continues with the further addition of fractions of the primary fluid, the temperature of the fluid stream undergoing reaction will always remain, as stated, above t_2 .

From the following disclosure it appears that it is of interest to fill the reaction chamber over a height at least equal to h inside the area intended for the introduction of the primary stream with a catalyst the threshold of activity of which is not substantially below the temperature t_2 , in a manner such that the endothermic character of the reaction may not lower the temperature of the gases to a value underneath the critical temperature. Furthermore, we use preferably catalysts that do not lead, at temperatures approximating t_2 , to a dehydrogenization producing a deposit of free carbon, but lead only to a splitting of the heavy molecules into groups CH or CH_2 , which are readily attacked by steam, and into CH_4 in accordance with the reactions performed on hydrocarbons, such as



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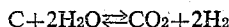
It has been found, according to our invention, that such catalysts may advantageously be constituted by zircon associated with magnesia and carried by refractory carriers having e. g. a basis of zircon or alumina.

These catalysts do not contain substantial amounts of metals and in particular no metals of the nickel type and they have consequently no dehydrogenizing capacity. They allow a large fraction of CH_4 to remain in the gaseous mixture at a temperature t_2 , whereby the system of Reactions 4 is much less endothermic than the Reaction 1 and this allows reducing the amount of heat to be transmitted to the fluid during its movement over the height h and consequently, this height may, in fact, be reduced.

Furthermore, by reason of their affinity with reference to H_2O and CO_2 , these catalysts further energetically the reactions



and



In contradistinction, they exert no marked action on the transformation



When it is desired to obtain a gas the contents of CH_4 in which are very low, we provide beyond this first layer of a catalyst producing a reduction in molecular weight, and starting from a point on the downstream side of the last point of introduction of a fraction of the primary mixture, a layer of a highly reacting catalyst having a low thermal threshold; said catalyst incorporating possibly a large amount of nickel is associated with a refractory carrier having a zircon, alumina and/or magnesia basis; as a matter of fact, as soon as the heavy hydrocarbons have been replaced by simpler and more resistant molecules, the possibility of formation of free carbon is very reduced and it is, therefore, possible to use active dehydrogenation catalysts capable of operation at a lower temperature.

Further objects and features of our invention will appear in the reading of the following description, referring to accompanying drawing the single figure of which illustrates diagrammatically and in a non-limiting manner, a preferred embodiment of our invention.

Said single figure is a vertical cross-section of a catalyzing column according to our invention.

In said figure, the column 1 is made of refractory steel having a diameter of the magnitude of 20 to 25 cm. It is heated by external means and brought to a temperature of about 800 to 1000° C. or above.

It receives steadily through the pipe 2 an amount of steam at the rate of say 30 to 33 kg. per hour; said steam previously heated to about 500° C., flows inside the annular chamber comprised between the inner wall of the column 1 and the core 3 that is held centrally of said column through the agency of a metal gauze.

This arrangement provides over the height h_0 means for superheating speedily the steam to a temperature of about 800–850° C., but any other manner of superheating steam may be used, provided it allows reaching said temperature.

On the other hand, the arrangement includes a first pipe 5 and a second pipe 5¹ feeding vapors of the hydrocarbons to be transformed.

The pipe 5 allows introducing steadily a portion of the primary preheated stream of a mixture, say, of hydrocarbons and steam brought to about 400–450° C. and including 10 kg. per hour of hydrocarbons and 5 to 10 kg. per hour of steam. This fluid is projected at a considerable speed by means of an injector system that provides simultaneously a perfect admixture of this primary mixture with the steam that has been superheated during its travel over the height h_0 along the wall of the column 1, while this injector also urges the mixture speedily into the catalyzing area. It has been ascertained, as a matter of fact and in accordance with our invention, that the thermic dissociation of the superheated mixture accom-

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panied by the formation of carbon black may be avoided, provided the contacting with the catalyst is performed after a very short lapse of time that is less than one third or even than one tenth of a second; this dissociation is performed in practice in accordance with a procedure the speed of which depends on the temperature and on the nature of the reacting hydrocarbons. The catalyst furthers the oxidizing action of the steam and consequently prevents efficiently the formation of free carbon. When in contact with the mass of the catalyst that is outwardly heated over a height h_1 of a magnitude of 0.50 to 1 m., the mixture is transformed into CO , CO_2 , H_2 with the accompaniment of a certain amount of light hydrocarbons such as C_2H_6 , C_2H_4 , CH_4 .

Through the pipe 5¹ that is possibly also provided with expansion chambers we introduce at a temperature of about 400 to 450° C. about 25 kgs. per hour of vaporized hydrocarbons preferably diluted in 16 to 20 kgs. of steam. This mixture passes out of the pipe 5¹ into a sleeve-shaped space and thence inwardly through gauged perforations 6 that ensure its rapid projection, and that are distributed over a height h_2 at different superposed levels spaced by 20 to 30 cm.; screens 7 made of stainless steel located in front of the perforations 6 distribute radially the fluid thus introduced into the surrounding nickel-free catalyst 10. Between the perforations 6, the sections of the pipe 8 protect the mixture inside the latter against external superheating.

At the same level as the fluid-distributing gauged perforations 6, we provide inside the mass of nickel-free catalyst, baffle plates 9 that shift the downwardly moving gasiform flow towards the axis of the pipe in the vicinity of the distributing ports or perforations 6. The mass of nickel-free catalyst 10 extends downwardly by 50 to 75 cm. over a height h' beyond the lowermost row of distributing ports or perforations; the tube is filled in its remaining lower portion i. e. over the height h'' with a nickel-containing catalyst 11.

There is finally obtained at the output end of the cracking column 1, i. e. at its lower end, a gaseous mixture, at a temperature of 750 to 780° C., formed by a stream feeding approximately 178 cbm. of gas per hour, admixed with about 25 cbm. of steam per hour. The composition of gas obtained is approximately the following:

$\text{CO}_2=11$ cbm./h.; $\text{CO}=44$ cbm./h.
 $\text{H}_2=121$ cbm./h.; $\text{CH}_4=2$ cbm./h.; $\text{H}_2\text{O}=25$ cbm./h.

i. e. a centesimal composition of the gas considered dry, which is as follows:

$\text{CO}_2=6.2$; $\text{CO}=24.7$; $\text{H}_2=68.1$; $\text{CH}_4=1.0$

When it is desired to obtain a gas containing substantial amounts of nitrogen, it is possible to use a secondary fluid constituted by steam diluted in air and it is thus possible to treat inside the precedingly described column, 40 kg./h. of oil vapor and 80 kg./h. of steam or thereabouts, and to dilute gradually said primary mixture inside a secondary mixture constituted by 60 cbm./h. of air admixed with 35 kg./h. of steam, and we obtain finally 230 cbm./h. of a gas containing in percentages:

$\text{CO}_2=6.5$; $\text{CO}=20.4$; $\text{H}_2=51.3$; $\text{CH}_4=0.9$; $\text{N}_2=20.9$

If it is desired to produce a cracked gas containing large amounts of CO , the secondary mixture should be constituted by steam admixed with CO_2 and possibly with air, if required.

During this operation, there is not observed any formation of carbon black. It should, however, be remarked that a partial clogging of one or more pipes feeding the primary mixture by a deposit of carbon would lead to a reduction in the feed of hydrocarbons towards the corresponding area, while the continuous passage of secondary steam, which is then considerably superheated by reason of the reduction in the heat developed by the endothermic reaction, has for its result to oxidize the deposits of carbon and to remove same in the shape of water gas.

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The arrangement shows thus the advantage of a high stability, while it removes automatically the carbon deposits which might have a tendency to form in the catalyst-containing area.

What we claim is:

1. A method for the catalytic decomposition of heavy hydrocarbons by steam consisting in preheating a primary stream of heavy hydrocarbons admixed with steam to a temperature of about 400 to 450° C. and lower than the threshold of pyrolysis leading to the formation of free carbon, subdividing said heated stream into a plurality of successive elementary fractions, the first of which contains less than about one third of the total throughput of the primary stream, heating a secondary gasiform stream containing steam to a temperature substantially above the threshold of thermal hydrolysis at about 800 to 850° C., maintaining said stream permanently above said threshold temperature, introducing the different fractions of the first stream into corresponding successive points of the secondary stream to obtain at each of said points a homogeneous reaction mixture, the temperature of which is still higher than said threshold of thermal hydrolysis and causing said successive portions of the secondary stream admixed with the primary stream fractions to react with a zircon-containing nickel-free catalyst to produce the cracking of the heavy hydrocarbons.

2. A method for the catalytic decomposition of heavy hydrocarbons by steam consisting in preheating a primary stream of heavy hydrocarbons admixed with steam to a temperature of about 400 to 450° C. and lower than the threshold of pyrolysis leading to the formation of free carbon, subdividing said heated stream into a plurality of successive elementary fractions, the first of which contains less than about one third of the total throughput of the primary stream, heating a secondary gasiform

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stream containing steam to a temperature substantially above the threshold of thermal hydrolysis, at about 800 to 850° C., maintaining said stream permanently above said threshold temperature, introducing the different fractions of the first stream into corresponding successive points of the secondary stream to obtain at each of said points a homogeneous reaction mixture, the temperature of which is still higher than said threshold of thermal hydrolysis, causing said successive portions of the secondary stream admixed with the primary stream fractions to react on a zircon-containing nickel-free catalyst to produce the cracking of the heavy hydrocarbons and to split the heavy hydrocarbon molecules into hydrocarbons of a lower molecular weight and subjecting the converted stream to a more energetic nickel-containing catalyst, for reaction in the presence thereof.

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