

Description

The present invention relates to a process and an apparatus for cracking hydrocarbons in the presence of steam, intended for the manufacture of olefins and diolefins, particularly ethylene and propylene. It consists particularly in using an infrared spectrophotometer making it possible to analyse the hydrocarbons feeding a cracking furnace, and in controlling, in particular, the yields of olefins and diolefins as a function of this analysis.

It is known to perform hydrocarbon cracking or pyrolysis in the presence of steam, also known as steam-cracking, by passing a mixture of hydrocarbons and steam through a cracking tube arranged in a furnace heated to a high temperature. The hydrocarbons are subjected to a cracking reaction which converts them particularly (i) into a gaseous hydrocarbon fraction comprising particularly olefins containing from 2 to 6 carbon atoms, such as ethylene, propylene and isobutene, and diolefins, such as butadiene and isoprene, (ii) into a liquid hydrocarbon fraction, also called "steam-cracking gasoline", comprising particularly hydrocarbons containing from 5 to 12 carbon atoms, (iii) and into undesirable byproducts, such as methane.

In general, for each type of hydrocarbons to be cracked, the conditions of the cracking reaction are chosen such as to make it possible to manufacture at least one product or a group of products, such as an olefin, a diolefin or a steam-cracking gasoline, in a desired yield which has been preset. A yield of a cracking reaction product means the weight ratio of the manufactured quantity of this product to the quantity of hydrocarbons employed. However, it is commonly observed that a cracking furnace is fed with a mixture of hydrocarbons whose nature and composition can frequently vary with time, according to the source of these hydrocarbons. It therefore appears necessary to modify the conditions of the cracking reaction as often as the

nature and the composition of the hydrocarbon mixture change, if it is intended to manufacture at least one product or a group of products according to a desired yield. From this it follows that, during the cracking reaction, it is important to know and to determine as frequently as possible the characteristics of the mixtures of hydrocarbons to be cracked. However, these characteristics are generally determined by separate and specific measurements, each of which requires the use of a specific apparatus and analytical method, and which require a relatively long time. Thus, when the nature and the composition of the hydrocarbon mixture vary with time, the conditions of the cracking reaction are consequently modified with a relatively long delay, and it is no longer possible to maintain the desired yields at the preset values. The importance of such disadvantages is easily understood when, moreover, the generally considerable size of an industrial hydrocarbon cracking plant is known.

A process and an apparatus for steam-cracking hydrocarbons have now been found, which make it possible to avoid the abovementioned disadvantages and to manufacture olefins and diolefins in the yields which can be preset at desired values. One of the objectives of the present invention is to control the space time yield of one or more products of a hydrocarbon steam-cracking reaction directly with the aid of measurements of absorbance in the near infrared of the hydrocarbon mixture feeding a cracking tube. One of the advantages of the present process is the ability to control the steam-cracking reaction while avoiding trying to find out and to establish the physical and/or chemical characteristics of the mixture of hydrocarbons to be cracked. More precisely, all the numerical data obtained by the measurements of absorbance by the hydrocarbon mixture at wavelengths chosen in the near infrared can be employed as data for controlling the steam-cracking reaction, with a view to obtaining a desired space time yield P of one or

more products of this reaction. In particular, the present invention uses an infrared spectrophotometer which, during the cracking reaction, makes it possible to perform, in an extremely short time, a series of measurements whose results make it possible to determine directly the reaction conditions necessary for the manufacture of olefins, of diolefins and of other reaction products in desired yields.

The subject of the present invention is, therefore, a process for steam-cracking a mixture of hydrocarbons, consisting in passing steam and the mixture of hydrocarbons through at least one heated cracking tube, the process being characterised in that the process is controlled (a) by analysing the mixture of hydrocarbons feeding the cracking tube with the aid of an infrared spectrophotometer to determine n absorbances at n wavelengths ranging from 0.8 to 2.6×10^{-6} m, (b) by using the results of n absorbances to determine at least one value V of one of the conditions of the steam-cracking reaction, and (c) by performing the steam cracking at the value or at the values V thus determined, so as to obtain a desired preset value P of the space time yield of one or more products of the steam-cracking reaction.

One of the essential features of the present invention is carrying out, during the steam-cracking reaction, absorbance measurements of the mixture of hydrocarbons feeding the cracking tube, with the aid of an infrared spectrophotometer operating according to the reflection method, or the transmission method, or else a combination of both these methods. According to the Beer-Lambert law, the absorbance is generally defined as being the decimal logarithm of the relationship between the intensity I_0 of the radiation emitted by the infrared spectrophotometer and the intensity I of the radiation transmitted and/or reflected by the mixture of hydrocarbons.

More particularly, what is involved is performing, a number of times during the steam-cracking

reaction, a series of n measurements of absorbance of the mixture of hydrocarbons at n wavelengths chosen in the near infrared region, ranging from 0.8 to 2.6×10^{-6} m, preferably from 1.0 to 2.5 , and more particularly from 1.4 to 2.5×10^{-6} m. The number n of the absorbance measurements is generally from 2 to approximately 20 , preferably from 2 to 10 . The choice of the number n of the absorbance measurements is partly related to the accuracy with which it is subsequently desired to determine the value V of at least one of the conditions of the steam-cracking reaction. It is possible, for example, to choose to perform the absorbance measurements at wavelengths chosen from the following, expressed in 10^{-6} m, or at substantially closely related wavelengths:

2.141, 2.166, 2.181, 2.278, 2.308, 2.347, 2.375, 2.398, 2.439, 2.457 and 2.475.

More particularly, the absorbance measurements may be carried out at the following 5 wavelengths, expressed in 10^{-6} m, or at substantially closely related wavelengths: 2.278, 2.308, 2.398, 2.439 and 2.475.

The wavelengths to be employed in the process with a view to obtaining a desired space time yield P of one or more products of a steam-cracking reaction can be chosen by statistical methods using factorial analyses and multilinear regressions during a standardising procedure. The latter may consist especially in varying the nature of the mixture of hydrocarbons to be cracked and the reaction conditions, according to an orthogonal experiment design carried out in a cracking tube of an industrial production unit or in a laboratory cracking tube, in particular a micropyrolyser, and in choosing the wavelengths in the near infrared so that it is possible to determine, with an optimum accuracy which is sufficient for running the process, a correlation relationship relating the space time yield P to the n results R_i of the n absorbance measurements and to the values V of the reaction conditions. The wavelengths which are generally chosen are those at which the absorbance value varies

greatly during the standardisation procedure.

Another essential characteristic of the present invention is that it sets in an extremely short time, as a function of the absorbance measurements, at least one of the conditions of the cracking reaction so that the space time yield of one or more reaction products is equal to a desired value P. The conditions of the steam-cracking reaction are those usually known in the case of a reaction of this type and may be chosen particularly from the flow rates of steam and of the mixture of hydrocarbons feeding the cracking tube, the cracking temperature at any point in this tube, especially at the entry or the exit of the furnace radiation zone, the cracking pressure at any point in this tube, especially at the exit of the furnace radiation zone, and the weight ratio of the quantity of the hydrocarbon mixture employed to that of steam.

Furthermore, one of the aims of the present invention is to control the steam-cracking process by presetting the space time yield of one or more products originating from the cracking reaction at a desired value P. In particular, it is possible to set the space time yield of an olefin such as ethylene, propylene or 1-butene, the space time yield of a diolefin such as butadiene, or else the space time yield of a number of reaction products such as "steam-cracking gasoline". The space time yield of one or more products of the reaction may be defined by the production rate corresponding to the quantity of the product(s) manufactured per unit time. The space time yield may also be defined as being the yield of the cracking reaction in terms of one or more products. It may also be defined as a ratio of two quantities of manufactured products, such as, for example, the ratio of the manufactured quantities of ethylene to propylene or the ratio of the manufactured quantities of hydrocarbons containing 3 carbon atoms to hydrocarbons containing 4 carbon atoms. In this case this ratio is an indication of the selectivity of the cracking

reaction between two products or two groups of products.

The process of the present invention consists, in particular, in determining the value V of at least one of the conditions of the steam-cracking reaction directly as a function of the n results R_i originating from each series of the n absorbance measurements, as well as as a function of at least one desired value P of a space time yield. Thus, each time a series of n absorbance measurements is performed, at least one of the conditions of the cracking reaction is set at the value V which makes it possible to obtain the desired space time yield. In practice, a number of series of n absorbance measurements are performed and, as a result, the value V is determined a number of times during the steam-cracking reaction, preferably at regular intervals of time, for example once per day or per hour, or once every 5 or 15 minutes.

Furthermore, the value V of one of the conditions of the steam-cracking reaction may be advantageously determined by means of a correlation relationship relating the reaction condition to a number of variables. These variables consist, in particular, of the n results R_i of the n absorbance measurements, of at least one desired value P of the space time yield and, if desired, of one or more other reaction conditions. The correlation relationship may be established beforehand by means of a multivariant regression performed by starting with the values of space time yield of products obtained in different cracking conditions for various hydrocarbon mixtures. In particular, it may be a linear function of the n results R_i of the n absorbance measurements, of a value P of at least one space time yield and, if desired, of a value V of at least one of the reaction conditions. The correlation relationship may be, for example, of the general form:

$$P = a + \sum_i b_i \cdot R_i + \sum_m c_m \cdot V_m$$

in which form P denotes a value of the space time yield of one of the products of the reaction, R_i denotes one of

the values of the n absorbance measurements with i varying from 1 to n , V_m denotes one of the values of the reaction conditions, m denotes the number of the controlled reaction conditions and a, b_i and c_m denote whole or decimal, negative or positive numerical coefficients.

The correlation relationship may also be an algebraic function of these same variables and may contain products or quotients of these variables, for example in one of the following general forms:

$$P = a + \sum_{ij} (b_i + k_{ij} \cdot R_j) R_i + \sum_m c_m \cdot V_m$$

or

$$P = a + \sum_{ij} (b_i + k_{ij}/R_j) R_i + \sum_m c_m \cdot V_m$$

or

$$P/V_1 = a + \sum_{ij} (b_i + k_{ij} \cdot R_j) R_i + \sum_m c_m \cdot V_m$$

or

$$P/V_1 = a + \sum_{ij} (b_i + k_{ij}/R_j) R_i + \sum_m c_m \cdot V_m$$

or

$$P/P' = a + \sum_{ij} (b_i + k_{ij} \cdot R_i) R_i + \sum_m c_m \cdot V_m$$

or

$$P/P' = a + \sum_{ij} (b_i + k_{ij}/R_j) R_i + \sum_m c_m \cdot V_m$$

in which forms the variables and the parameters have the same definitions as above, V_1 denotes one of the values V_m of the reaction conditions, k_{ij} denotes a whole or decimal, negative or positive numerical coefficient, R_j denotes one of the values of the n absorbance measurements with j being other than i and varying from 1 to n , and P and P' denote values of the space time yield of two reaction products. This correlation relationship depends on the type of infrared spectrophotometer employed, on the conditions in which it is employed, on the n of the wavelengths chosen, and on the product(s) of the cracking reaction whose space time yield it is desired to preset.

When the process consists, in particular, in

controlling the process by setting two or more conditions of the cracking reaction, it is advisable to determine an appropriate value V for each of these conditions, in particular with the aid of correlation relationships such as previously defined.

The determination of the value V may be advantageously carried out by means of a calculator. The function of the latter is to calculate the value V from the variables on which it depends, in particular of the n results R_i of the n absorbance measurements and of at least one desired value P . When the calculator is connected directly to the infrared spectrophotometer, the acquisition of the n results R_i by the calculator is virtually instantaneous, and the complete determination of the value V can take a few minutes, generally less than 2 minutes.

When the value V of a condition of the cracking reaction has thus been determined, the process is controlled by operating and conducting the reaction at this value by means which are known per se, in particular with the aid of a process computer preferably connected to means of control capable of maintaining the condition at the determined value V , until the time when a new series of n absorbance measurements is carried out. If the nature and/or the composition of the mixture of hydrocarbons to be cracked have changed during the interval between two successive series of n absorbance measurements, a new value V will then be determined from the latest series of measurements carried out and the condition of the cracking reaction will be immediately corrected and set at this new value, in order to maintain the space time yield in respect of one or more reaction products at the preset desired value P .

One of the main advantages of the process of the present invention is the ability to maintain the space time yield in respect of one or more products of the cracking reaction at a constant value, whatever the fluctuations in the nature or in the composition of the

mixture of hydrocarbons feeding the cracking tube. In particular, it is quite remarkable to find that, by virtue of this process, the corrections to the conditions of the cracking reaction are made in an extremely short time, which makes it possible to avoid any, even momentary, drift of the reaction towards the manufacture of undesirable products or of products obtained in unsatisfactory space time yields. This result is obtained in particular by virtue of the fact that the process does not comprise any stage consisting in investigating or determining the physical and/or chemical characteristics of the mixture of hydrocarbons to be cracked. The results of the absorbance measurements can be employed directly in the form of numerical data in the correlation relationships linking the latter with the desired space time yield P and with the values V of the conditions of the steam-cracking reaction. It is especially surprising to find that it is now possible to control a steam-cracking process at a given space time yield level and that it can tolerate large variations in the quality of the hydrocarbons feeding the cracking tube, for example both of the liquid hydrocarbons containing approximately from 5 to 15 carbon atoms, such as naphtha, light gasolines and gas oil, and of the gaseous hydrocarbons such as alkanes containing from 2 to 4 carbon atoms, mixed, if appropriate, with alkenes containing from 2 to 6 carbon atoms or with methane and alkanes containing from 5 to 6 carbon atoms, in particular natural gas, liquified petroleum gas, also known as LPG, ethane, propane, butane or secondary light products originating from the steam cracking of liquid hydrocarbons.

The conditions of the cracking reaction can be corrected instantaneously as a function of the nature and composition of the mixture of hydrocarbons to be cracked, and can be set at the values of V included within known limits. In particular, the temperature of the reaction mixture at the entry of the radiation zone of the furnace may be from approximately 400°C to 700°C, the temperature

of the reaction mixture at the exit of this zone may be from approximately 720°C to 800°C, the pressure in the cracking tube at the exit of this zone may be from 120 kPa to 240 kPa, and the weight ratio of the quantity of the hydrocarbon mixture employed to that of steam may be from approximately 1 to 6.

Furthermore, the temperature of the reaction mixture travelling in the cracking tube may increase from the entry to the exit of the radiation zone of the furnace according to a profile such as that described in European Patent Applications No. 252,355 and No. 252,356.

Another subject of the present invention is an apparatus specially designed to make it possible to implement the process described above. The apparatus comprises, on the one hand, a hydrocarbon steam-cracking furnace essentially comprising a heating chamber equipped with means of heating and traversed by at least one cracking tube and, on the other hand, an infrared spectrophotometer capable of operating in at least one range of the near infrared region extending approximately from 0.8 to 2.6×10^{-6} m and intended to perform measurements of absorbance of the mixture of hydrocarbons feeding the cracking tube. The means for heating the heating chamber of the cracking furnace generally consist of burners whose arrangement in the chamber, size and control may be chosen or adapted at will, so that the heating power applied along the cracking tube is distributed in a more or less homogeneous manner, in particular such as described in European Patent Applications No. 252,355 and No. 252,356. The cracking tube may be arranged horizontally or vertically across the heating chamber, particularly in the radiation zone of the furnace. It may include a reaction volume which is constant or which varies between the first and second halves of the length of the cracking tube, from the entry to the exit of the radiation zone of the furnace, as described in European Patent Applications No. 252,355 and No. 252,356.

The measurements of absorbance of the mixture of hydrocarbons feeding the cracking tube are performed with the aid of the infrared spectrophotometer previously described. The latter may be of the Fourier transform infrared spectrophotometer type. Furthermore, it may be advantageously combined with a calculator intended to determine the value V of at least one of the conditions of the cracking reaction, by virtue of a calculation programme containing at least one of the correlation relationships linking this condition to the variables on which it depends.

Furthermore, the steam-cracking furnace may be combined with a process computer and with control systems which make it possible to set and regulate these conditions automatically at the determined values V. The process computer may advantageously also comprise the calculator program enabling the value V to be calculated.

The infrared spectrophotometer may be arranged close to the duct feeding the furnace with the hydrocarbon mixture or to the storage vessel for this mixture, or at a greater or lesser distance from these. It may be equipped with means for transmitting data, such as optical fibres adapted to this particular type of analysis. In this case, these measurements are advantageously performed directly in real time, that is in line in the duct feeding the furnace with the hydrocarbon mixture, or in the storage vessel for this mixture. It is also possible to install a system for sampling the mixture of hydrocarbon to be cracked, comprising either a manual device essentially consisting of a lock equipped with valves, or an automatic device controlled by a programmable robot. In this case, this system may be arranged in the duct for feeding the furnace with a mixture of hydrocarbons, or in the storage vessel for this mixture. The absorbance measurements may also be carried out in nonreal time, that is to say in delayed time.

The present invention is found to be particularly useful in industrial steam-cracking plants of

considerable size and production capacity. In fact, by virtue of this process, any error in space time yield due to fluctuations in the nature and the composition of the mixture of hydrocarbons to be cracked is markedly reduced, or even suppressed, thus avoiding the manufacture either of undesirable products or of products obtained at an unsatisfactory space time yield.

The following examples, which do not imply any limitation, illustrate the present invention.

Example 1

Manufacture of ethylene by a steam-cracking reaction of a naphtha of variable composition with an ethylene yield set at 22%.

A naphtha steam-cracking reaction is carried out in a furnace essentially comprising a brickwork radiation heating chamber consisting of a rectangular parallelepiped having an internal length of 9.75 m, an internal width of 1.70 m and an internal height of 4.85 m. In this heating chamber there is arranged a cracking tube made of refractory steel based on nickel and chromium having a total length of 80 m, an internal diameter of 108 mm and a thickness of 8 mm. The cracking tube is in the shape of a zigzag comprising 8 horizontal straight sections, each of equal length connected to each other by elbows.

The radiation heating chamber of the furnace is provided with burners arranged on the walls of the chamber, in 5 horizontal rows, situated at an equal distance from each other. The heating power of all these burners is distributed homogeneously among these 5 rows.

The cracking tube is fed, on the one hand, with steam at a constant rate of 900 kg/h and, on the other hand, with a naphtha of a composition which can vary with time, at a constant rate of 2800 kg/h. Over a period of 24 h, the composition of the naphtha employed varies so that its weight content of paraffins changes from 72% to 68%, its weight content of naphthenic compounds from 20% to 23%, its weight content of aromatic compounds from 8% to 9%, and its relative density from 0.713 to 0.719.

The pressure of the reaction mixture at the exit of the radiation zone of the furnace is approximately 165 kPa. The cracking temperature T at the exit of this zone can vary in the course of this manufacture and is determined so that the yield of ethylene is constantly equal to 22%. The cracking temperature at the entry of the radiation zone of the furnace, initially close to 550°C, is subject to slight variations in the course of time, due to those of the exit temperature T.

Once every 15 minutes, a sample of naphtha feeding the cracking tube is analysed by means of an "Infraalyzer 500"® infrared spectrophotometer, sold by Bran-Luebbe (United States of America). At each analysis, a series of 5 absorbance measurements is performed according to a method combining transmission and reflection and corresponding to the Beer-Lambert absorption law, at the following 5 wavelengths, expressed in 10^{-6} m: 2.278, 2.308, 2.398, 2.439 and 2.475. The results of these 5 measurements are denoted R_1 , R_2 , R_3 , R_4 and R_5 respectively.

These results are transmitted to a "Solar 16/65"® process computer sold by Bull (France), linked directly to the infrared spectrophotometer. The process computer is, in particular, equipped with a program making it possible to calculate the value of the cracking temperature T at the exit of the radiation zone of the furnace as a function of the results R_1 , R_2 , R_3 , R_4 and R_5 of the 5 absorbance measurements, of the desired yield of ethylene, EY, preset at 22%, by the application of the following correlation relationship:

$$T = 509 + 11.63 \text{ EY} + 326 R_1 - 448 R_2 + 688 R_3 - 692 R_4 + 611 R_5$$

with T expressed in degrees Celsius. When the value of the cracking temperature T has thus been determined, the process computer immediately sets the cracking temperature at the exit of the radiation zone of the furnace at this value.

During the 24 h period when the composition of the naphtha has varied as shown above, it is observed that the cracking temperature T has itself varied within a range from 788°C to 806°C. During this same period it is found that the ethylene output has remained constant at 616 kg/h and that, consequently, the yield of ethylene has been maintained at 22%, despite the variations in the composition of the naphtha.

Example 2

Manufacture of ethylene and of propylene by a steam-cracking reaction of a naphtha of variable composition, with a ratio of the yield of propylene to that of ethylene set at 0.6.

The cracking reaction is carried out in a furnace identical with that described in Example 1.

The cracking tube is fed, on the one hand, with steam at a constant rate of 964 kg/h and, on the other hand, with a naphtha of a composition which can vary with time, at a constant rate of 3000 kg/h. Over a 24 h period, the composition of the naphtha employed varies so that its weight content of paraffins changes from 68% to 76%, its weight content of naphthenic compounds changes from 23% to 19%, its weight content of aromatic compounds changes from 9% to 5% and its relative density from 0.719 to 0.697.

The pressure of the reaction mixture at the exit of the radiation zone of the furnace is approximately 165 kPa. The cracking temperature T at the exit of this zone can vary in the course of this manufacture and is determined so that the ratio of the yield of propylene to that of ethylene is constantly equal to 0.6. The cracking temperature at the entry of the radiation zone of the furnace, initially close to 550°C, is subjected to slight variations in the course of time, due to those of the exit temperature T.

Once every 15 minutes, a sample of the naphtha feeding the cracking tube is analysed by means of an "Infraalyzer 500"^R infrared spectrophotometer, sold by

Bran-Luebbe (United States of America). At each analysis, a series of 5 absorbance measurements is performed according to a method combining transmission and reflection and corresponding to the Beer-Lambert absorption law, at the following 5 wavelengths, expressed in 10^{-6} m:

2.278, 2.308, 2.398, 2.439 and 2.475. The results of these 5 measurements are denoted M_1 , M_2 , M_3 , M_4 and M_5 respectively.

These results are transmitted to a "Solar 16/65" process computer sold by Bull (France), linked directly to the infrared spectrophotometer. The process computer is, in particular, equipped with a program which makes it possible to calculate the value of the cracking temperature T at the exit of the radiation zone of the furnace as a function of the results M_1 , M_2 , M_3 , M_4 and M_5 of the 5 absorbance measurements, of the desired ratio (PY/EY) of the yield of propylene to that of ethylene, preset at 0.6, by application of the following correlation relationship:

$$T = 994 - 357 \text{ PY/EY} + 161 M_1 - 222 M_2 + 341 M_3 - 342 M_4 + 303 M_5$$
with T expressed in degree Celsius.

When the value of the cracking temperature T has thus been determined, the process computer immediately sets the cracking temperature at the exit of the radiation zone of the furnace at this value.

During the 24 h period where the composition of the naphtha has varied as shown above, it is observed that the cracking temperature T has itself varied in a range from 800°C to 785°C. During this same period it is found that the ratio of the yield of propylene to that of ethylene has remained constant at 0.6, despite the variations in the composition of the naphtha.

Example 3

Manufacture of ethylene at a constant rate of 0.640 t/h and of propylene at a constant rate of 0.370 t/h by a steam-cracking reaction of a naphtha of variable composition.

The cracking reaction is performed in a furnace identical with that described in Example 1. The cracking tube is fed with steam and with naphtha of a composition which can vary with time. Over a period of 24 hours the composition of the naphtha employed varies so that its weight content of paraffins changes from 76% to 72%, its weight content of naphthenic compounds from 19% to 20%, its weight content of aromatic compounds from 5% to 8% and its relative density from 0.697 to 0.713.

The pressure of the reaction mixture at the exit of the radiation zone of the furnace is approximately 165 kPa. The cracking temperature T at the exit of the radiation zone of the furnace and the naphtha feed rate Q to the tube can vary during this manufacture and are determined so that the output rates of ethylene and of propylene are constantly equal to 0.640 t/h and 0.370 t/h respectively. The cracking temperature at the entry of the radiation zone of the furnace, initially close to 550°C, is subject to slight variations with time, due to those of the exit temperature T . The steam feed rate varies with time so that the weight ratio of the quantity of hydrocarbon mixture employed to that of steam is constant at 3.

Once every 10 minutes a sample of naphtha feeding the cracking tube is analysed by means of an "Infralyzer 500"® infrared spectrophotometer sold by Bran-Luebbe (United States of America). At each analysis, a series of 5 absorbance measurements is performed according to a method combining transmission and reflection and corresponding to the Beer-Lambert absorption law, at the following 5 wavelengths, expressed in 10^{-6} m = 2.278, 2.308, 2.398, 2.439 and 2.475. The results of these 5 measurements are denoted L_1 , L_2 , L_3 , L_4 and L_5 .

These results are transmitted to a "Solar 16/65"® process computer sold by Bull (France), linked directly to the infrared spectrophotometer. The process computer is, in particular, equipped with a program which makes it possible to calculate the value of the naphtha feed rate Q to the cracking tube, and of the cracking temperature

T at the exit of the radiation zone of the furnace as a function of the results L_1 , L_2 , L_3 , L_4 and L_5 of the output rate of ethylene Q_E set at 0.640 t/h and of the output rate of propylene Q_p set at 0.370 t/h by the application of the following two correlation relationships:

$$100 Q_E = Q(-36.4 + 0.086 T - 2.65 Q - 28 L_1 + 38.5 L_2 - 59.2 L_3 + 59.5 L_4 + 52.56 L_5)$$

$$Q_p = Q_E (2.552 - 0.0028 T + 0.0775 Q + 0.451 L_1 - 0.6206 L_2 + 0.954 L_3 - 0.958 L_4 + 0.847 L_5)$$

with T expressed in degrees Celsius and the flow rates Q, Q_E and Q_p in tonnes/hour.

When the values of the cracking temperature T and the naphtha feed rate Q to the cracking tube have thus been determined, the process computer immediately sets the cracking temperature at the exit of the radiation zone of the furnace and the naphtha feed rate to the cracking tube at these values.

During the 24-hour period during which the composition of the naphtha has varied as shown above, it is observed that the cracking temperature T has itself varied within a range from 789°C to 795°C, while the naphtha feed rate Q to the cracking tube has varied within a range from 2.8 t/h to 2.9 t/h. During this same period, it is found that the output rate of ethylene has remained constant at 0.640 t/h and the output rate of propylene has remained constant at 0.370 t/h, despite the variations in the naphtha composition.



Claims

1. Process for steam-cracking a mixture of hydrocarbons, consisting in passing steam and the mixture of hydrocarbons through at least one heated cracking tube, the process being characterised in that the process is controlled (a) by analysing the mixture of hydrocarbons feeding the cracking tube with the aid of an infrared spectrophotometer to determine n absorbances at n wavelengths ranging from 0.8 to 2.6×10^{-6} m, (b) by using the n absorbance results to determine at least one value V of one of the conditions of the steam-cracking reaction, and (c) by performing the steam cracking at the value or values thus determined, so as to obtain a desired preset value P of the space time yield of one or more products of the steam-cracking reaction.

2. Process according to Claim 1, characterised in that the condition of the steam-cracking reaction is chosen from the flow rates of steam and of the mixture of hydrocarbons feeding the cracking tube, the cracking temperature or the cracking pressure at any point in this tube, and the weight ratio of the quantity of the hydrocarbon mixture employed to that of steam.

3. Process according to Claim 1, characterised in that the space time yield of one or more products of the reaction is defined by a yield, by a flow rate or by a ratio between two quantities of products or of groups of products manufactured.

4. Process according to Claim 1, characterised in that the number n of absorbances is from 2 to 20.

5. Process according to Claim 1, characterised in that the absorbances are performed at wavelengths expressed in 10^{-6} m, or substantially closely related wavelengths, chosen from 2.141, 2.166, 2.181, 2.278, 2.308, 2.347, 2.375, 2.398, 2.439, 2.457 and 2.475.

6. Process according to Claim 1, characterised in that the value V is determined by means of a linear or algebraic correlation relationship relating the condition of the cracking reaction to the n results R_i of the n



absorbance measurements, to at least one desired value P of a space time yield of one or more products of the reaction and, if appropriate, to one or more other conditions of the reaction.

5 7. Apparatus for implementing the process according to Claim 1, characterised in that it comprises, on the one hand a hydrocarbon steam-cracking furnace essentially containing a heating chamber equipped with means of heating and traversed by at least one cracking tube, and, 10 on the other hand, an infrared spectrophotometer capable of operating in at least one range of the near infrared region extending from 0.8 to 2.6×10^{-6} m and intended to perform measurements of absorbance of the mixture of hydrocarbons feeding the cracking tube.

15 8. Apparatus according to Claim 7, characterised in that the infrared spectrophotometer is combined with a calculator intended to determine the value V of at least one of the conditions of the cracking reaction, by virtue of a calculation program containing a linear or algebraic 20 correlation relationship relating the condition of the reaction to the n results R_i of the n absorbance measurements, to at least one desired value P of a space time yield of one or more products of the reaction and, if appropriate, to one or more other conditions of the 25 reaction.



EP 0 345 182 B1

As printed

Patentansprüche

1. Verfahren zum Dampfcracken einer Mischung von Kohlenwasserstoffen, welches darin besteht, daß Wasserdampf und die Mischung von Kohlenwasserstoffen durch mindestens eine geheizte Crackröhre geleitet werden, dadurch gekennzeichnet, daß das Verfahren kontrolliert wird, indem (a) die die Crackröhre speisende Mischung von Kohlenwasserstoffen mit Hilfe eines Infrarot-Spektrofotometers zur Bestimmung von n Absorptionen bei n Wellenlängen in einem Bereich von $0,8$ bis $2,6 \cdot 10^{-6}$ m analysiert wird, (b) die Resultate der n Absorptionen zur Bestimmung von mindestens einem Wert V einer der Bedingungen der Dampfcrackreaktion verwendet werden, und (c) das Dampfcracken mit dem/den so bestimmten Wert(en) betrieben wird, sodaß ein zuvor festgelegter Sollwert P für die Produktivität an einem oder mehreren Produkten der Dampfcrackreaktion erzielt wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Bedingung der Dampfcrackreaktion ausgewählt ist aus den Durchflußmengen des Wasserdampfs und der Kohlenwasserstoffmischung, die die Crackröhre speisen, der Cracktemperatur oder dem Crackdruck an irgendeiner Stelle dieser Röhre sowie dem Gewichtsverhältnis zwischen der eingesetzten Menge an Kohlenwasserstoffmischung und jener an Wasserdampf.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Produktivität an einem oder mehreren Reaktionsprodukten durch eine Ausbeute, durch eine Durchflußmenge oder durch ein Verhältnis zwischen zwei Mengen von erzeugten Produkten oder Produktgruppen definiert ist.

4. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Zahl n der Absorptionen 2 bis 20 beträgt.

5. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Absorptionen bei Wellenlängen bewirkt werden, die in 10^{-6} m ausgedrückt werden, oder bei im wesentlichen benachbarten Wellenlängen, ausgewählt aus 2,141-2,166-2,181-2,278-2,308-2,347-2,375-2,398-2,439-2,457 und 2,475.

6. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der Wert V mittels einer linearen oder algebraischen Korrelationsgleichung bestimmt wird, in welcher die Bedingung der Crackreaktion mit n Resultaten R_i der n Absorptionsmessungen, mit mindestens einem Sollwert P für eine Produktivität an einem oder mehreren Reaktionsprodukten und gegebenenfalls mit einer oder mehreren anderen Reaktionsbedingungen in Beziehung gebracht wird.

7. Vorrichtung zur Durchführung des Verfahrens nach Anspruch 1, dadurch gekennzeichnet, daß sie einerseits einen Ofen zum Dampfcracker von Kohlenwasserstoffen mit im wesentlichen einer Wärmезelle, die mit Heizeinrichtungen versehen und von mindestens einer Crackröhre durchsetzt ist, und andererseits ein Infrarot-Spektrofotometer, das in mindestens einem Bereich des nahen Infrarotgebiets, der von $0,8$ bis $2,6 \cdot 10^{-6}$ m geht, funktioniert und zur Durchführung von Absorptionsmessungen der die Crackröhre speisenden Kohlenwasserstoffmischung bestimmt ist, umfaßt.

8. Vorrichtung nach Anspruch 7, dadurch gekennzeichnet, daß das Infrarot-Spektrofotometer mit einem Rechner zur Bestimmung des Werts V mindestens einer der Bedingungen der Crackreaktion mit Hilfe eines

Rechenprogramms, das eine lineare oder algebraische Korrelationsgleichung enthält, in der die Bedingung der Crackreaktion mit n Resultaten R_i der n Absorptionsmessungen, mit mindestens einem Sollwert P für eine Produktivität an einem oder mehreren Reaktionsprodukten und gegebenenfalls mit einer oder mehreren anderen Reaktionsbedingungen in Beziehung gebracht wird, kombiniert ist.



As printed

Claims

1. Process for steam cracking a hydrocarbon mixture, consisting in passing steam and the hydrocarbon mixture through at least one heated cracking tube, the process being characterised in that it is controlled by (a) analysing the hydrocarbon mixture feeding the cracking tube using an infrared spectrophotometer to determine n absorbance readings and n wavelengths ranging from 0.8 to 2.6×10^{-6} m, (b) using the n absorbance results to determine at least one value V of one of the conditions of the steam cracking reaction, and (c) performing the steam cracking at the value or values thus determined, so as to obtain a desired preset value P of the productivity with respect to one or more products of the steam cracking reaction.

2. Process according to Claim 1, characterised in that the condition of the steam cracking reaction is chosen from the flow rates of water and of the hydrocarbon mixture feeding the cracking tube, the cracking temperature or the cracking pressure at any point in this tube, and also the weight ratio of the quantity of the hydrocarbon mixture employed to that of steam.

3. Process according to Claim 1, characterised in that the productivity with respect to one or more products of the reaction is defined by a yield, by a flow rate or by a ratio between two quantities of products or of groups of products manufactured.

4. Process according to Claim 1, characterised in that the number n of absorbance readings is from 2 to 20.

5. Process according to Claim 1, characterised in that the absorbance readings are performed at wavelengths, expressed in $\times 10^{-6}$ m, or substantially similar wavelengths, chosen from 2.141, 2.166, 2.181, 2.278, 2.308, 2.347, 2.375, 2.398, 2.439, 2.457 and 2.475.

6. Process according to Claim 1, characterised in that the value V is determined by means of a linear or algebraic correlation relationship relating the condition of the cracking reaction to the n results R_i of the n absorbance measurements, to at least one desired value P of a productivity with respect to one or more products of the reaction and, if appropriate, to one or more other conditions of the reaction.

7. Apparatus for carrying out the process according to Claim 1, characterised in that it comprises, on the one hand a hydrocarbon steam-cracking furnace essentially containing a heating chamber equipped with means of heating and traversed by at least one cracking tube, and on the other hand an infrared spectrophotometer capable of operating in at least one range of the near infrared region extending from 0.8 to 2.6×10^{-6} m and intended for performing absorbance measurements of the hydrocarbon mixture feeding the cracking tube.

8. Apparatus according to Claim 7, characterised in that the infrared spectrophotometer is combined with a computer intended for determining the value V of at least one of the conditions of the cracking reaction, by means of a calculation programme containing a linear or algebraic correlation relationship relating the condition of the reaction to the n results R_i of the n absorbance measurements, to at least one desired value P of a productivity with respect to one or more products of the reaction and, if appropriate, to one or more other conditions of the reaction.