July 23, 1963 O. HEUSE ET AL 3,098,883

PROCESS AND APPARATUS FOR CARRYING OUT CHEMICAL REACTIONS AT HIGH TEMPERATURES

Filed Feb. 24, 1959 2 Sheets-Sheet 1

FIG. 1

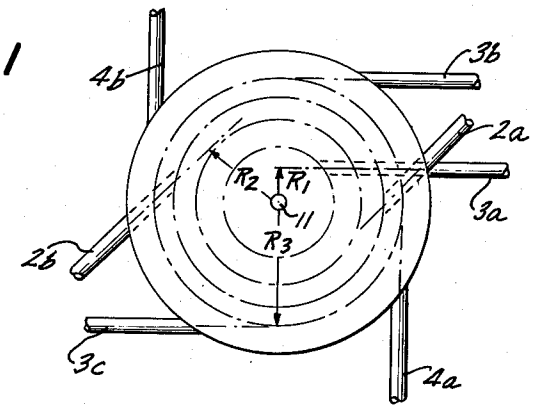
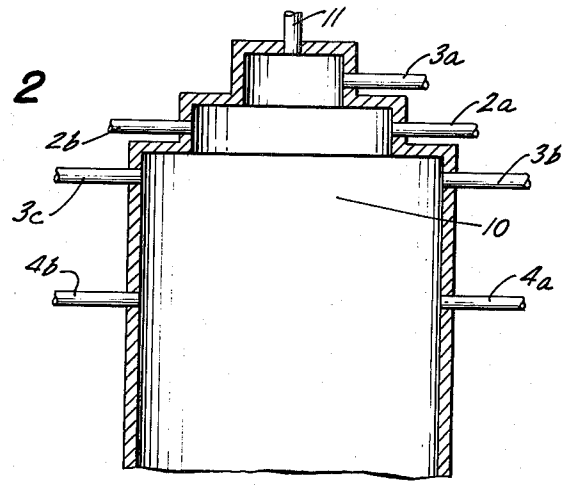


FIG. 2



INVENTORS.
OTTO HEUSE
WERNER FISCHER
FRIEDRICH HORN
RUDOLF WIMMER

BY

Curtis, Morris & Safford

ATTORNEYS.

July 23, 1963 O. HEUSE ET AL 3,098,883

PROCESS AND APPARATUS FOR CARRYING OUT CHEMICAL REACTIONS AT HIGH TEMPERATURES

Filed Feb. 24, 1959 2 Sheets-Sheet 2

FIG. 3

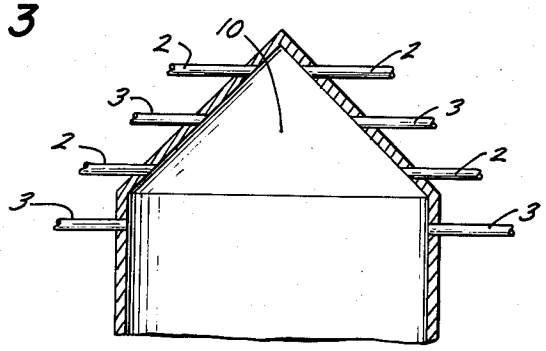


FIG. 4

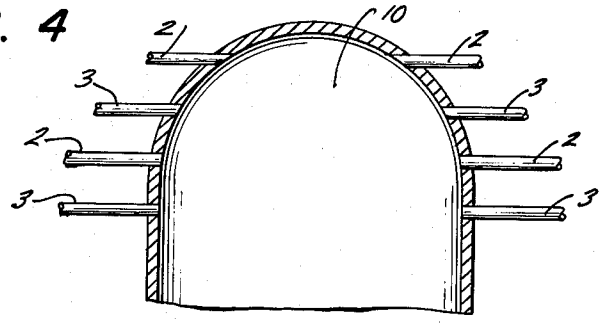
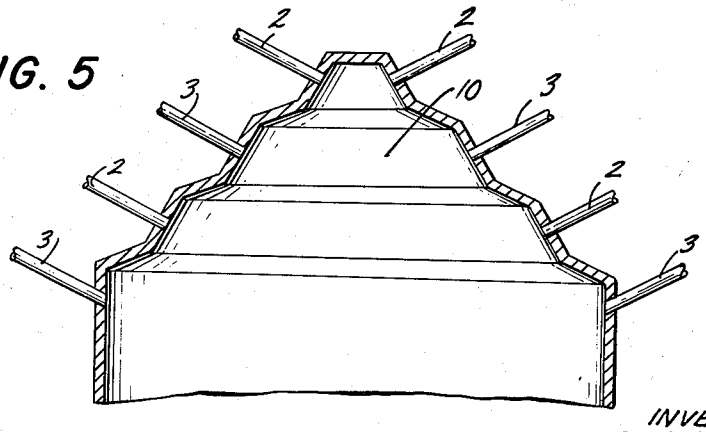


FIG. 5



INVENTORS.
OTTO HEUSE
WERNER FISCHER
FRIEDRICH HORN
RUDOLF WIMMER

BY
Curtis, Morris & Safford
ATTORNEYS.

United States Patent Office 3,098,883 Patented July 23, 1963

3,098,883

PROCESS AND APPARATUS FOR CARRYING OUT CHEMICAL REACTIONS AT HIGH TEMPERATURES

Otto Heuse, Kronberg, Taunus, Werner Fischer, Bad Soden, Taunus, and Friedrich Horn and Rudolf Wimmer, Frankfurt am Main, Germany, assignors to Farbwerke Hoechst Aktiengesellschaft vormals Meister Lucius & Brüning, Frankfurt am Main, Germany, a corporation of Germany

Filed Feb. 24, 1959, Ser. No. 795,077
Claims priority, application Germany Feb. 28, 1958
13 Claims. (Cl. 260—683)

The present invention relates to a process and to an apparatus for carrying out chemical reactions at high temperatures.

It is known that the production of acetylene, ethylene and higher olefines from methane, ethane or higher hydrocarbons requires the supply within the shortest possible time to the hydrocarbons to be reacted of large amounts of energy.

Thus, for example, the energy may be supplied indirectly by passing the gases to be cracked through externally heated pipes or heat exchangers. This method involves the disadvantage that the walls of the pipes become superheated and thus give rise to pronounced formation of coke and soot. Furthermore, the method referred to is restricted to the use of small diameter pipes, since a pipe of greater diameter entails too slow and incomplete a heat transfer from the walls to the gas. The gases in the border zones become too hot while the gases in the middle zones do not become hot enough and, therefore, do not participate in the reaction.

For the indirect supply of heat there are also used so-called regenerative furnaces heated with a gas mixture obtained by combustion of fuel with air. When the furnace is hot, heating is interrupted and the furnace is rinsed out with an inert gas and then charged with the hydrocarbons to be cracked in contact with the hot filling material of the furnaces. After a minimum temperature has been reached, the furnace is again heated with heating gas. This operation is continually repeated by automatic commutation at intervals of a few minutes. In addition to the necessary complicated automatic reversing device, this process entails the further disadvantages of the inevitable deposition of tarry substances in the regenerative furnace and the constantly changing temperature of the furnace which jeopardize the economy of the process and the yields obtained.

According to another process the energy required for cracking is supplied directly by subjecting part of the hydrocarbon to be cracked to a combustion process in a special combustion device with oxygen, whereby the hydrocarbon itself furnishes the energy for pyrolysis of the hydrocarbon in excess. This process is, however, not applicable when it is desired to prevent the hydrocarbon to be cracked from partial combustion.

Therefore, it has repeatedly been proposed to supply the energy by means of a carrier gas, for example hydrogen or a combustion gas such as steam heated to a high temperature, which is then mixed in a suitable manner with the hydrocarbons to be cracked. In this case, it is especially advantageous to use as fuel hydrogen and to subject this substance together with oxygen to a combustion process since, after the reaction, the steam formed can be easily separated from the resulting gas by condensation and since the subsequent separation of the gas is thereby rendered less difficult. As heating gas there may also be used all products obtained by combustion of any combustible substance. Furthermore, it is particularly advantageous to perform the combustion of the fuel within a fairly small space and to provide for as short a distance as possible between the end of the combustion zone and the hydrocarbon to be cracked, so that the inevitable heat losses caused by dissipation are kept as small as possible. Accordingly a fairly short flame is required which furnishes large amounts of energy but burns only for a short distance. To this end, the combustion gas and the oxidizing agent are often pre-mixed in a separate mixing chamber before they are introduced into the combustion chamber proper. The use of combustion devices supplied with pre-mixed gases involves the risk, however, that the flame may flash back into the mixing chamber and destroy the whole apparatus unless the gas supply lines are provided with very sensitive and in most cases technically complicated control devices to maintain constant pressure and velocity of flow of the mixture of oxygen and vaporized or gaseous fuel, such as hydrogen, as is the case with combustion devices used for the incomplete combustion of methane or natural gas with oxygen.

All these disadvantages are overcome by the present invention which provides a combustion chamber for performing any pyrolytic reaction. More particularly, the present invention provides a process for the production of acetylene and/or ethylene and/or higher olefinic hydrocarbons having 2–4 carbon atoms by pyrolysis of a hydrocarbon in contact with very hot combustion gases produced in a combustion chamber by the continuous combustion of fuel and gaseous oxidizing agents. The hydrocarbon can be introduced in the form of a gas or vapor either radially or tangentially with the same or opposite direction of rotation of the combustion gases. After a short time of reaction the hot gas mixture is chilled. The combustion gases are produced by introducing the fuel and a deficiency of oxidizing gas separately into the combustion chamber, for example at a velocity corresponding to a Mach-number of at least 0.8, for instance at sonic speed, where they are subjected to a combustion process.

It may likewise be possible to introduce the gases at a lower velocity than corresponds to a Mach-number of 0.8.

In some cases it is suitable to carry out said reaction with a small angular momentum or even in a manner such that the reactants do not possess any angular momentum at all. This fact sometimes involves the advantage that the low degree of formation of soot or carbon particles on the wall of the reaction chamber, which may occur when especially high boiling oils are used as starting materials, can be still further reduced. The combustion process can be also carried out in a manner such that the wall of the combustion chamber is largely separated from the combustion gas by a layer of the fuel or the oxidizing agent.

These results can be achieved by introducing the fuel and the oxidizing agent in several planes through several bore holes into the upper part of the burner which is opposite to the mouth of the burner, the walls of the said upper part being formed in a manner such that the bore

holes are at different distances from the center of the burner as shown, for example, in FIGURE 1 of the accompanying drawings. Thus the fuel and the oxidizing agent form in the burner contrarotating atmospheres of coaxial hollow spaces of different diameters.

The fuel and the oxidizing agents are mixed so completely that a very short flame is produced. By mixing and swirling as described above fuel and oxidizing agents undergo so rapid a combustion that the resulting flame ceases to burn after a very short distance.

It is, therefore, possible to operate the combustion chamber with very high loads. Industrially, it is especially advantageous to operate the combustion chamber with evolution of heat at the rate of 1 billion or more Kcal./m.^{3}h. (10^9 Kcal.). The combustion chamber as used in the process of this invention involves the particular advantage that the whole combustion process is performed within the smallest space—as is the case with flames produced with pre-mixed gases—so that the heat losses caused by dissipation are small in relation to the energy produced. Contrary to the known devices, a combustion chamber as used herein prevents the flame from flashing back into the mixing chamber and requires no complicated control mechanism.

The term "Mach-number" is used herein to indicate the ratio between the gas velocity applied and the sonic speed at the corresponding temperature.

The operating procedure according to this invention involves the further advantage that the combustion gases leaving the combustion chamber at flame temperature possess such a high turbulence—due to their having been swirled in said chamber—that they are practically instantaneously mixed with the reactant that is to undergo pyrolysis. Thus, the heat is particularly well transferred from the combustion gas to the reactants (hydrocarbons), whereby it is possible to perform a practically complete reaction.

The hydrocarbons to undergo pyrolysis can be introduced into the combustion chamber radially or tangentially either in one or both directions of rotation. Furthermore, it may be advantageous to force the combustion gases, prior to their being mixed with the reactant, through a constricted opening, for example a nozzle, in order to increase their axial velocity.

In the following a ring or circle of bore holes means a group of inlets which are arranged in a plane, for example, in a position perpendicular to the axis of the burner. In the extreme case a ring of bore holes only contains one inlet. All bore holes mentioned in the present specification serve to supply the burner either with the oxidizing agent or with the fuel, which may be a gas mixture. One ring of bore holes may likewise be provided with inlets for the different reactants.

For carrying out the process according to the present invention a device may be used as shown diagrammatically in the accompanying drawings.

It is of advantage to introduce into the upper part of a burner 10 through one ring or circle of bore holes 2 (cf. FIGURES 1 and 2) the fuel in one direction of angular momentum and through the following ring of inlets 3 the oxidizing agent in opposite direction of angular momentum. By this means the fuel and the oxidizing agent form in the burner atmospheres having approximately the shape of concentric hollow cylinders (annuli) which contrarotate in one another and which mix thoroughly at the border surfaces due to the high relative velocity formed.

The desired effect can be further improved by additionally providing the upper part of the burner with one or more bore holes, for example in the direction of the axis of the burner, as shown in FIGURE 2. Inlet 11 is in the center of the upper part of the burner. It is of advantage to introduce fuel through that inlet when oxidizing agent is supplied through the upper circle of bore holes and vice versa.

By suitably selecting the amounts of fuel and oxidizing agent supplied through the individual inlets, the inlet velocity into the burner, the direction of the bore holes and finally the diameter of the circle of nozzles the complete angular momentum of the combustion gases produced can be largely varied or even wholly suppressed. Furthermore it is not necessary that the bore holes have a tangential direction; it is preferred, however, to arrange the bore holes in a manner such that the projection of the axis of the bore holes of one circle, preferably the inlets for the fuel, forms clockwise an angle of less than 90° with the projection of the appertaining tangent to the inner wall of the burner. Contiguous to said circle of bore holes there is suitably arranged a ring of bore holes in which the projection of the axis of the bore holes forms clockwise an angle of more than 90° with the projection of the appertaining tangent to the inner wall of the burner. The projections are referred to a plane in vertical position to the axis of the burner. Tangential inlets are especially preferred.

In case further gases, such as secondary gases, are supplied in addition to the fuel and the oxidizing agent, for example through inlets 4*a* and 4*b*, the amount and nature of the secondary gases used, the position and direction of their inlets may further regulate the angular momentum of the gases in the burner. It has proved advantageous to provide the burner with inlets for the secondary gas where the gases streaming on the wall and supplied through the circle of inlets being next to the burner outlet have just burned. Thus the wall of the burner is effectively cooled and the secondary gases do not impair the combustion. It is furthermore advisable to arrange the inlets for the secondary gas in a direction such that an angular momentum is imparted to the secondary gas, the direction of which corresponds to that of the medium streaming off the next higher ring of nozzles.

In general burners of the type described above are shaped in axially symmetric manner round the axis which is vertical according to the drawings. It is likewise possible, however, to use other variants which are elliptic or polygonal. In this case the terms used in the present specification which are taken from the nomenclature of the rotation symmetry, such as circle or cylinder, are to be replaced by analogous terms.

Although it is possible to arrange inlet rings of different diameters on various bodies, for example on a top of a burner having the form of a cone-shaped shell (FIGURE 3) or a dome-shaped shell (FIGURE 4) it proved to be particularly advantageous to use a burner the upper part of which is composed of concentric cylinder jackets provided with bore holes and of interconnecting circular ring disks (FIGURES 1 and 2). This arrangement presents the additional advantage that the inlets can be disposed in the combustion chamber at positions where the mixing ratio of the two participants in the combustion process is still below the ignition limit. Thus the combustion and the thermal stress of the wall near the inlets is avoided. The last mentioned arrangement furthermore serves best to the second purpose of the invention, namely to separate the wall of the burner by fresh gas from the hot combustion gases.

The same advantage present, for example, an upper part of the burner as shown in FIGURE 5, which is composed of cone-shaped shells having different inclinations in which a cone-shaped shell of greater inclination carrying a circle of bore holes is followed by a cone-shaped shell of inferior inclination which is free from bore holes and other variants thereof. Although the purpose of the present invention can be achieved by very different combinations of the above features the best results are obtained when the axes of the bore holes of one ring are arranged in general in one plane. For reasons of production an inclination of the axes of the bore holes may likewise be advisable (cf. FIGURE 5). In order to produce

optimum conditions of flow it is particularly desirable to arrange the axes of the major part of the inlets or of all inlets of a circle so that their projection on a plane in vertical position to the axis of the burner does not cut the projection of the next higher circle of bore holes and to install between the combustion chamber and the point of introduction of the reactant a constriction, for example in the form of a nozzle.

When it is desired to manufacture acetylene and/or ethylene and/or higher olefin-containing gases, i.e. gases which in addition to acetylene and/or ethylene contain propylene, n-butylene, iso-butylene, etc., that is chiefly olefins with 3 or 4 carbon atoms, it is especially suitable to admix, between the flame end and the place where the reactant is introduced, a secondary gas, preferably steam and/or hydrogen.

The secondary gas shall suitably have a temperature of at least 150° C. and below the temperature of the combustion gas. The addition of said secondary gas reduces the proportion of oxygen-containing radicals, oxygen atoms and oxygen molecules in the combustion gas. By this means it is furthermore possible to influence the angular momentum of the combustion gases or to compensate completely the residual angular momentum thereof.

This operating procedure is especially suitable if fuels are used that produce flames and combustion gases, such as have very high temperatures, for example hydrogen. In this case, the secondary gas can be introduced into the combustion gas radially or tangentially and in one or both directions of rotation.

The secondary gas may likewise be introduced axially, that is to say through the cover of the burner or the outer circular ring disk, for example via bore holes or a ring slot. By this latter step a layer of secondary gas, for example steam, is formed between the wall of the burner and the center of the flame so that a separation of carbon is impossible and the dissipation of heat is considerably reduced. It is especially advantageous to use as secondary gas hydrogen and/or steam in an amount of 1–80 parts by weight, preferably 30–70 parts by weight, calculated on the total amount of the combustion gases.

In the pyrolysis the hydrocarbon shall be introduced in amounts such that with a reaction time of 10^{-1}–10^{-4} seconds a temperature of 700° C. is attained at the end of the reaction. When olefins, especially ethylene, are to be produced, it is advantageous to operate with a reaction time of 10^{-1}–10^{-3} seconds and when acetylene is to be produced it is advisable to add an amount of hydrocarbons such that the temperature of the reaction mixture at the end of the reaction amounts to 1000° C. In this case it is expedient to operate with a reaction time of 10^{-2}–10^{-4}.

For the production of acetylene and/or ethylene and/or other olefines containing 2 to 4 carbon atoms, for example propylene or butylene using a combustion device according to this invention, aliphatic hydrocarbons which may have been pre-heated are introduced in liquid or gaseous form—which term is intended to include the vapourized state—either radially or tangentially or in any other known manner into the current of combustion gases so that they are mixed with the latter gases rapidly and completely, and the reacted mixture is chilled in known manner after a short time of reaction, for example by injection of water. In this case it is especially advantageous to line the reaction chamber, for example the reaction tube, with ceramic material to suppress undesirable soot formation which is favoured by metal surfaces.

For the construction of the combustion chamber it is expedient to use a metal which is cooled by means of a cooling agent, for example water; however, there may also be used ceramic material or metal lined with ceramic material. In the case of a cooled metal combustion chamber, the heat taken up by the cooling agent can be recovered and used for other purposes.

As starting materials suitable for use in the process of this invention there can be used the known hydrocarbons,

for example saturated or unsaturated hydrocarbons containing up to 30 or more carbon atoms. It is particularly advantageous to employ saturated hydrocarbons, such as methane, ethane, propane, butane, pentane, heptane, octane, decane, dodecane, especially in the form of liquid commercial mixtures, such as petroleum distillates or hydrocarbon oils, for example topped Kuwait oil, or also in the form of technical gases such as natural gas. Instead of aliphatic saturated hydrocarbons containing from 1 to about 30 or more carbon atoms there may also be used unsaturated hydrocarbons and hydrocarbons having a branched chain. As branched hydrocarbons there are concerned, for example isobutane, isooctane, isoheptane, isohexane, etc. It is not advisable to use unsaturated hydrocarbons unless it is desired to produce acetylene or unless they are contained in small amounts in other hydrocarbons. Thus, for example, ethylene, propylene, n- or iso-butylene may be used for the production of acetylene.

As fuels suitable for use in the production of acetylene and/or ethylene and/or higher hydrocarbons there may be used any gaseous or other hydrocarbons that are liquid or can be liquefied by heating. Such fuels are used in a finely divided form for operating the combustion chamber according to this invention and for the production of the aforesaid unsaturated hydrocarbons. The term "finely divided form" as used herein is intended to comprise fine atomization of liquid hydrocarbons and also the gaseous and vapour states. As fuels there may also be used hydrogen, carbon monoxide or water gas which contains an excess of hydrogen and/or carbon monoxide.

As oxidizing agent there may advantageously be used commercial pure oxygen, if desired in admixture with air, the oxidizing agent being always employed in a theoretically insufficient quantity.

The following examples illustrate the invention, but they are not intended to limit it thereto.

EXAMPLE 1

The table illustrates an example to be understood with the aid of FIGURES 1 and 2. Only relative values are given and the production of angular momenta in the burner is chosen so that their sum disappears. The active radius (R_i) in column E represents the radius of the circle round the axis of the burner to which the projection of the appertaining axis of the bore holes forms the tangent.

R_i is in relation with the radius R of the ring of bore holes and the angle φ formed by the projection of the axis of the inlets with the projection of the appertaining tangent to the circle of nozzles: $R_i = R \cdot \cos \varphi$.

In the following table m stands for mass, l for length and t for time.

Table

A	B	C	D	E	F	G
Inlet	Medium	Direction of angular momentum	Flow	Active radius (R_i)	Inlet velocity	Production of angular momentum G=DEF
			$m \cdot t^{-1}$	l	$l \cdot t^{-1}$	$m \cdot l^2 \cdot t^{-2}$
1	O_2		7	0	300	0
3a	Fuel	Left	2	15	250	−7500
2a	O_2	Right	7	30	300	+63000
2b	O_2	Right	7	30	300	+63000
3b	Fuel	Left	2	45	250	−22500
3c	Fuel	Left	2	45	250	−22500
4a	Sec.-gas	Left	5	45	163	−36750
4b	Sec.-gas	Left	5	45	163	−36750
						± 0

EXAMPLE 2

6 kilograms of light gasoline, 2 m.³ of hydrogen (measured at N.T.P.) and 15.8 m.³ of oxygen (at N.T.P.) are burned per hour in a combustion chamber into which

fuel and oxidizing agent are introduced with opposite angular momentum so that they form in the burner atmospheres of co-axial hollow spaces of different diameters. The combustion gases are mixed per hour with 13 kilograms of secondary gas (steam) and the gas mixture thus obtained is supplied per hour with 24.4 kilograms of light gasoline. After having chilled with water and condensed the components which are liquid at room temperature there are obtained per hour 40.6 m.^{3} (at N.T.P.) of a gas mixture composed (in percent by volume) of

N_2+O_2	1.3
CO_2	14.5
CO	14.8
H_2	25.6
CH_4	11.6
C_2H_2	8.0
C_2H_4	18.7
C_2H_6	1.3

The residue contains various higher hydrocarbons.

We claim:

1. In a process for the pyrolysis of aliphatic hydrocarbons by continuously forming a stream of hot combustion gas in a combustion zone, contacting said combustion gas for a short time with an atomized aliphatic hydrocarbon for pyrolysis thereof to yield C_2- to C_4-unsaturated hydrocarbons having less hydrogen in the molecule than the starting material, and chilling the effluent mixture of pyrolyzed hydrocarbon and combustion gas, the improvement which comprises introducing into the combustion zone an excess of atomized fuel and an oxidizing gas therefor separately and with an oppositely directed angular momentum at a different distance from the axis of said combustion zone to form rotating coaxially arranged hollow atmospheres of different diameter which contrarotate in one another.

2. In a process for the pyrolysis of aliphatic hydrocarbons by continuously forming a stream of hot combustion gas in a combustion zone, contacting said combustion gas for a short time with an atomized aliphatic hydrocarbon for pyrolysis thereof to yield C_2- to C_4-unsaturated hydrocarbons having less hydrogen in the molecule than the starting material, and chilling the effluent mixture of pyrolyzed hydrocarbon and combustion gas, the improvement which comprises introducing into the combustion zone an excess of atomized fuel and an oxidizing gas therefor separately through at least two sets of nozzles arranged in annular manner, said annular sets of nozzles being at different distances from the axis of said combustion zone and one set of nozzles for the fuel being adjacent and having an angular direction opposite to a set of nozzles for the oxidizing gas, whereby rotating coaxially arranged hollow atmospheres of different diameter are formed which contrarotate in one another.

3. A process as claimed in claim 1, wherein the fuel and the oxidizing gas are introduced into the combustion zone in a manner such as to yield a total angular momentum of the gases in the combustion zone which is substantially about nil.

4. A process as claimed in claim 1, wherein the fuel and the oxidizing gas are introduced into the combustion zone in such a manner that the projection of the axis of the streaming direction forms an angle of less than 90° with the projection of the appertaining tangent to the outer limitation of the combustion zone, the projection being referred to a plane perpendicular to the axis of the combustion zone.

5. A process as claimed in claim 1, wherein at least one of the reactants of the combustion reaction is tangentially introduced into the combustion zone.

6. A process as claimed in claim 1, wherein a secondary gas is admixed to the combustion gases.

7. A process as claimed in claim 6, wherein the secondary gas is introduced into the combustion zone in such a direction that it is given an angular momentum in the combustion zone in the same direction as has the medium which is introduced through the adjacent nozzles.

8. A process as claimed in claim 1, wherein the velocity of the combustion gases is increased when leaving the combustion zone but before the hydrocarbon to be pyrolyzed is introduced.

9. An apparatus suitable for the manufacture of unsaturated hydrocarbons consisting of a unitary combustion chamber having a wall provided with at least three annular sets of nozzles for fuel and oxidizing gas, the annulus in which the nozzles for the fuel are arranged having a diameter different from that of the annulus in which nozzles for the oxidizing gas are arranged and a set of nozzles for the fuel being adjacent and having an angular direction opposite to a set of nozzles for the oxidizing gas so that rotating axially arranged hollow atmospheres of different diameter are formed which contrarotate in one another and contact each other along their interface.

10. An apparatus as defined in claim 9 wherein the projections of the axes of the nozzles of one set of nozzles do not intersect the projection of the wall which contains the nozzles of an adjacent set, referred to a plane perpendicular to the axis of the combustion chamber.

11. An apparatus as claimed in claim 9, wherein sets of nozzles are adjacent with each other in which the projections of the axes of the nozzles of one set with the projection of the appertaining tangent to the inner wall of the combustion chamber form clockwise a smaller angle than 90° while the projections of the axes of an adjacent set of nozzles with the appertaining tangent to the inner wall of the combustion chamber forms clockwise an angle of more than 90°.

12. An apparatus as claimed in claim 9, wherein the upper part of the combustion chamber is composed of concentric cylindrical jackets provided with bore holes and of interconnecting circular ring disks.

13. A modification of the apparatus claimed in claim 9, wherein the upper part of the combustion chamber is additionally provided with at least one nozzle for at least one of the reactants which is arranged in an axial direction.

References Cited in the file of this patent

UNITED STATES PATENTS

2,162,433	Hillhouse	June 13, 1939
2,353,509	Schultze	July 11, 1944
2,375,795	Krejci	May 15, 1945
2,413,407	Dreyfus	Dec. 31, 1946
2,813,138	MacQueen	Nov. 12, 1957