Jan. 8, 1963 S. BENICHOU ET AL 3,072,465

APPARATUS FOR THE CATALYTIC OXIDATION OF HYDROCARBONS

Filed May 21, 1959 3 Sheets-Sheet 1

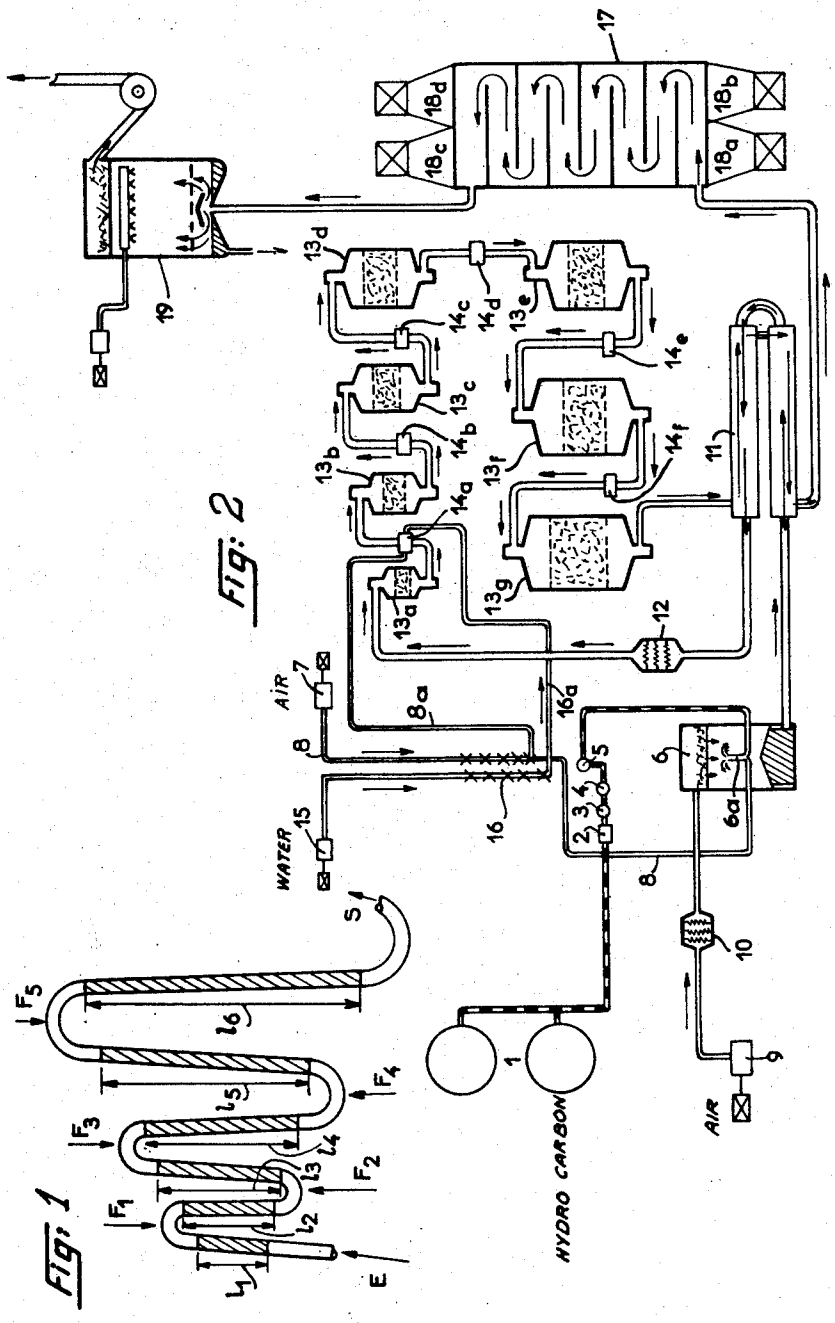


FIG. 2

FIG. 1

Jan. 8, 1963 S. BENICHOU ET AL 3,072,465

APPARATUS FOR THE CATALYTIC OXIDATION OF HYDROCARBONS

Filed May 21, 1959 3 Sheets-Sheet 2

Fig:3

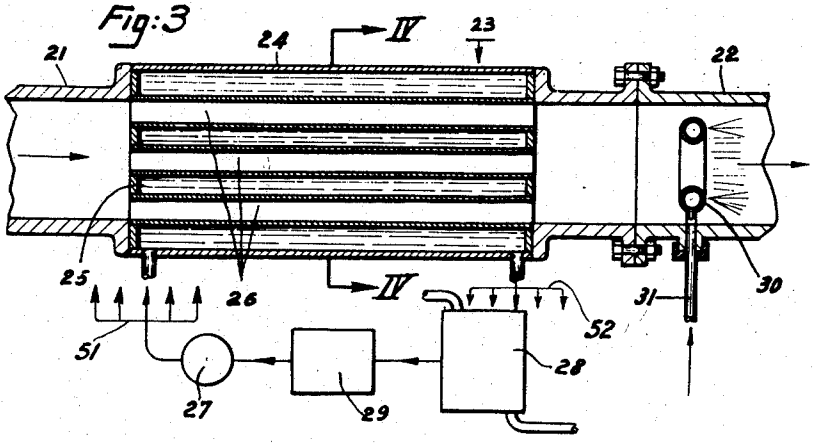


Fig:4

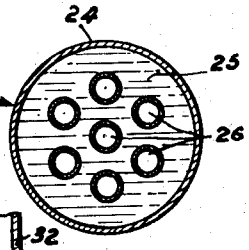


Fig:5

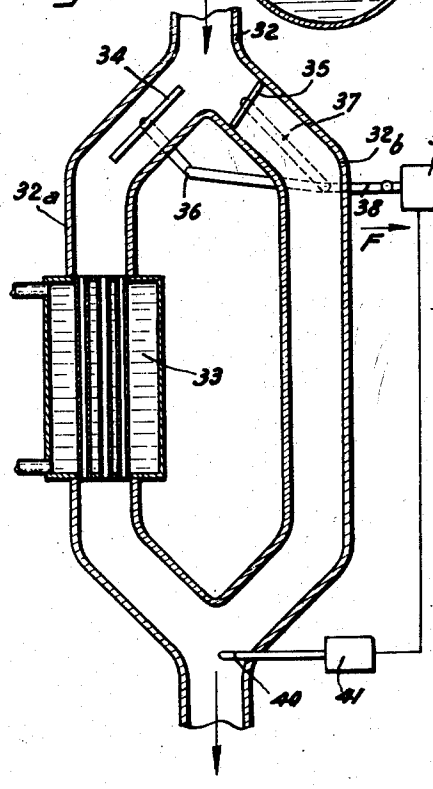
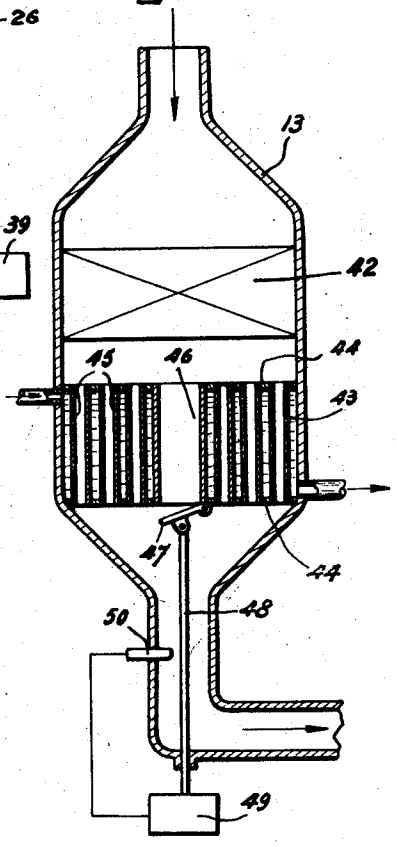


Fig:6

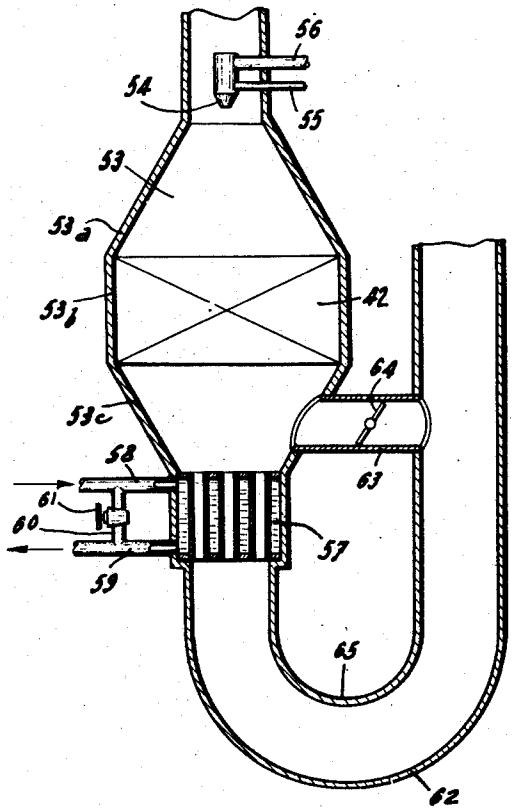


Jan. 8, 1963 S. BENICHOU ET AL 3,072,465

APPARATUS FOR THE CATALYTIC OXIDATION OF HYDROCARBONS

Filed May 21, 1959 3 Sheets-Sheet 3

Fig: 7



United States Patent Office 3,072,465 Patented Jan. 8, 1963

3,072,465
APPARATUS FOR THE CATALYTIC OXIDATION OF HYDROCARBONS

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1 Claim. (Cl. 23—288)

This invention relates to the catalytic oxidation of hydrocarbons.

It is known that many complex chemical products can be obtained by partially oxidizing aliphatic or aromatic hydrocarbons in the presence of a catalyst. The oxidizing agent is generally atmospheric air and the oxidation is effected in one or more successive catalyzing chambers, into which a mixture of hydrocarbon and air is admitted. However, since such mixtures have an explosive character, it is necessary for the initial dilution of the hydrocarbon in air to be relatively low and below a critical value known as the "explosion threshold," above which the danger of spontaneous ignition or explosion of the mixture becomes too great to be acceptable.

Each hydrocarbon thus possesses, in air, at a given temperature, a critical concentration herein referred to as the "explosion threshold" which it is desirable not to exceed.

Since the catalytic oxidation of hydrocarbons is highly exothermic, the temperature of the mixture of air and hydrocarbon in contact with the catalyst tends to rise rapidly. Now, the temperature at which a given compound is formed is fairly critical. Generally speaking, below this temperature, the degree of oxidation is insufficient, while above it the reaction proceeds with excessive rapidity and may result in a complete oxidation of the hydrocarbon to give water and carbon dioxide or carbon monoxide.

In order to maintain the temperature of the reaction close to the optimum value, it has been proposed to cool the reacting mixture in the catalyzing chamber itself. It has also been proposed to operate in a number of successive catalyzing chambers and to cool the mixture as it leaves one chamber and before it enters the succeeding chamber. The said cooling may be effected by an injection of liquid water into the duct connecting two successive chambers, water being used because of its intense heat of evaporation and of its substantial neutrality to the reaction in progress.

In known constructions of this type, the number and the dimensions of the successive chambers are chosen so that the hydrocarbon introduced into the first chamber has become substantially completely exhausted at the delivery end of the last chamber.

The known installations have a relatively poor total output and the utilization of the catalyst (which is the most troublesome element in these installations by reason of the necessity for regeneration and periodical replacement) is far from satisfactory.

It is an object of the present invention to provide an improved apparatus of this type by means of which the total output of the installation can be brought to its optimum value while the catalyst is utilized to the best advantage.

The invention is based upon the observation that if, in the course of catalytic oxidation of a hydrocarbon, the temperature at which the required compound is formed has a fairly precise value, the yield of the oxidation product at temperatures on either side of this value generally remains adequate, a more or less wide temperature range

for the reaction being practical. In other words, if the temperatures are plotted along the abscissae of a graph, and the percentage yields of the conversion into the desired product are plotted along the ordinates, the curve representing this yield has, in the neighbourhood of the temperature corresponding to the formation of the desired compound, a more or less flattened maximum, i.e. there is a range of temperature over which it is possible to choose temperature values giving a satisfactory yield.

It is accordingly an object of the invention constantly to maintain the reaction in this temperature zone in installations comprising a succession of catalyzing chambers with intermediate cooling.

According to the present invention there is provided an apparatus for the catalytic oxidation of hydrocarbons by means of an oxygen-containing gas to produce an oxidation product of which the maximum yield is obtained between two predetermined temperatures which comprises passing the mixture of hydrocarbon and oxygen-containing gas through a series of catalyzing chambers which are interconnected by conduits including cooling means, the quantity of hydrocarbon per unit volume of the mixture being initially chosen to be below the explosion threshold, the number of successive chambers being at most equal to the denominator of that fraction of unity of the said quantity of hydrocarbon, which, when oxidized in each chamber, raises the temperature per unit volume of the mixture from a level substantially equal to the lower temperature existing at the inlet to the said chamber to a level substantially equal to the predetermined upper temperature limit, said chambers being of increasing dimensions and the volume of catalyst in each chamber, at least in respect of the earlier chambers in the series being related to the volume in the preceding chamber by a multiplication factor which more and more rapidly increases from 1.05 to 2.2, for the second chamber with respect to the first and so on, to one of the last chambers with respect to the preceding one.

When the catalyst completely fills the chambers, it is the volumes of the latter which follow the aforesaid law of progression.

The following theoretical considerations serve to explain the features of the process according to the invention, and while the applicants do not wish to be regarded as restricted to any particular theory, these features have in fact essentially been confirmed in their value by the experimental results obtained by the applicants in the course of their research.

In the following explanation, reference will be made particularly to the case of the preparation of phthalic anhydride from naphthalene in the presence of a catalyst such as vanadium oxide or molybdenum oxide, it being understood that this example is intended only to aid the explanation of the invention from the theoretical standpoint and is in no way to be regarded as a limitation of the scope of the invention.

The description which follows refers to the accompanying drawings in which:

FIG. 1 is a diagrammatic illustration of an installation for the oxidation of hydrocarbon according to the invention.

FIG. 2 is a diagram of a complete installation.

FIG. 3 is a longitudinal sectional view of a modified form of a connecting duct between two successive catalyzing chambers.

FIG. 4 is a section along the line IV—IV of FIG. 3.

FIGS. 5, 6 and 7 illustrate in section the connection between one chamber and the succeeding chamber in other modified constructions comprising a coolant and a by-pass in the said connection.

By reason of the aforesaid necessity to maintain the

initial concentration of the hydrocarbon below the explosion threshold, the reaction generally takes place in the presence of a very large excess of air.

Thus, in the aforesaid case of naphthalene, the initial concentration should not exceed 35 g. (0.28 mol) per cubic meter. It will be noted that the conversion into phthalic anhydride of 0.28 mol. of naphthalene requires 1.25 mols of oxygen; 1 cubic meter of air contains 9.5 mols thereof, so that an approximate 8-fold excess of oxygen is present.

It is therefore convenient to assume that, in the course of the reaction, the oxygen concentration does not vary and that, consequently, in a particular temperature zone, the speed of reaction depends only upon the concentration of the hydrocarbon alone.

Such a reaction is called a first order reaction, and it is known that its speed is governed by the differential equation:

$$\frac{dx}{dt}=K(a-x)$$

in which x is the number of hydrocarbon molecules converted by oxidation after time t, a is the initial number of hydrocarbon molecules, and K a coefficient depending upon the reaction envisaged, upon the nature of the catalyst and upon the temperature.

If this differential equation is integrated, taking into account the initial conditions ($t=0$, $x=0$), there is found:

$$Kt=\ln\frac{a}{a-x}$$

which gives the quantity of hydrocarbon converted at the end of a time t and which shows that, under given catalyst and temperature conditions, the quantity of oxidized hydrocarbon depends only upon the time t, i.e. for a continuous operation in which the mixture circulates substantially at constant speed and pressure, it depends upon the number of catalyzing chambers and upon the useful volume of these chambers, that is to say, upon the volume which contains the catalyst in these chambers.

Now, each unit volume of the circulating mixture, for example each cubic meter of air, has substantially a constant specific heat in the course of the reaction, which it is possible to consider as equal to the specific heat of the air, namely about 0.24, having regard to the large excess of air.

In addition, the heat of formation of the desired compound from the chosen hydrocarbon and from oxygen is also known. Thus, in the present example this heat is 3300 large calories per kilogram of oxidized naphthalene.

Assuming that the reaction for the formation of a given compound is possible at any temperature, it is therefore possible to ascertain what would be the total temperature rise of the unit volume of the mixture due to the oxidation of all the hydrocarbon contained in this unit volume. This temperature rise is equal to the quotient of the total calorific power of the unit volume of the mixture by its specific heat.

Thus, in the chosen example, since it is known that one cubic meter of air weighs 1.300 kg., this temperature rise would be:

$$\frac{3300\times 0.035}{1.300\times 0.24}=370 \text{ degrees centigrade}$$

However, it having been assumed that the reaction must take place between two given temperature limits, one above Ts and the other below Ti, it is desirable that, each time the temperature of the mixture reaches the value Ts, this temperature should be reduced to the value Ti before the reaction continues.

In other words, the number n of chambers in each of which a part of the reaction and the heating of the mixture take place, and between which the temperature must be reduced from Ts to Ti by external cooling means,

must be equal to the quotient of the total temperature rise which is possible by the admissible temperature difference:

$$\Delta T=Ts-Ti$$

Thus, in the chosen example of the conversion of naphthalene into phthalic anhydride, the yield is optimum between 350° and 370° C., that is to say, with a temperature difference $\Delta T=Ts-Ti=20°$ C.

It is deducible therefrom that the optimum number of successive chambers to be employed is

$$\frac{370}{20}=18 \text{ chambers}$$

This obviously supposes that the natural dissipation of heat in the chambers is zero, which is substantially true for installations of large capacity mounted in closed factories. This number must obviously be reduced in the case of small, highly ventilated installations, in which the cooling means (for example fins, which are substantially inapplicable to chambers of large volume) can be provided on the walls of the chambers.

Thus, when the heat dissipation of the chambers reaches half the heat evolved therein, the number of chambers must be divided by two.

As previously indicated, a being the quantity of hydrocarbon initially introduced into each cubic meter of air in order that the temperature rise in each chamber may correspond to the difference $Ts-Ti$, it is desirable that the quantity

$$\frac{a}{n}$$

of hydrocarbon should be oxidized in each chamber and, for this purpose, that the dimension of each of the chambers should be accordingly determined.

In the successive chambers starting from the first, the quantity

$$\frac{a}{n},\frac{2a}{n},\frac{3a}{n}\ldots\frac{pa}{n}$$

will be converted in accordance with the aforesaid relation:

$$\ln\neq\frac{a}{a-x}=Kt$$

The times t_1, t_2, t_3 . . . t_p corresponding to these successive oxidations must therefore correspond to:

$$Kt_1=\ln\frac{a}{a-\frac{a}{n}}=\ln\frac{n}{n-1}$$

$$Kt_2=\ln\frac{a}{a-\frac{2a}{n}}=\ln\frac{n}{n-2}$$

. . . . . .

$$Kt_p=\ln\frac{a}{a-\frac{pa}{n}}=\ln\frac{n}{n-p}$$

Assuming, as already indicated, that the mixture circulates at constant pressure and speed, the useful volume of the successive chambers must therefore be proportional to:

$$t_1;\ t_2-t_1;\ \ldots\ t_p-t_{p-1}\ \ldots$$

If c is a constant dependent upon the pressure and the speed of circulation, the successive volumes V_1, V_2 . . . V_p . . . are therefore given by the formulae:

$$V_1=ct_1=\frac{c}{K}\ln\frac{n}{n-1}$$

$$V_2=c(t_2-t_1)=\frac{c}{K}\left(\ln\frac{n}{n-2}-\ln\frac{n}{n-1}\right)=\frac{c}{K}\ln\frac{n-1}{n-2}$$

. . . . . .

$$V_p=\frac{c}{K}\left(\ln\frac{n}{n-p}-\ln\frac{n}{n-p+1}\right)=\frac{c}{K}\ln\frac{n-p+1}{n-p}$$

These formulae show that the volume of the last chamber of order n should be indefinite. In practice, this volume will be experimentally chosen having due regard to the fact that, even if this last chamber were entirely omitted, the loss of initial hydrocarbon would not exceed the fraction

$$\frac{a}{n}$$

which is smaller as n is larger.

The calculation just made, while having the merit of strict accuracy, has the disadvantage that it does not show the law of progression of the volume of the chambers in a readily understandable manner. This law can be more appropriately shown in the following manner:

A catalytic oxidation apparatus will be considered (FIG. 1) which consists of a tube of constant cross-section in which successive lengths l_1, l_2 . . . l_6 are filled with catalyst with uniform density. Each of these lengths of tube can be regarded as a catalysing chamber of volume proportional to l_1, l_2 . . . l_6. The mixture enters at E and leaves at S and, between the catalysing chambers, there is effected, as diagrammatically indicated by the arrows F_1 . . . F_5, a cooling of the mixture (for example by injection of water) or by other means such as those hereinafter described, so as to lower towards the temperature T*i* the temperature of the mixture leaving each of the chambers at a temperature in the neighborhood of T*s*.

The $(n-1)$ first chambers will be considered, in each of which the fraction

$$\frac{a}{n}$$

of hydrocarbon is oxidized.

The mean speed V_1 of the reaction in the first chamber l_1 that is to say, the speed of the reaction corresponding, in this chamber, to the conversion of the fraction

$$\frac{a}{2n}$$

(one half of the total fraction

$$\frac{a}{n}$$

oxidized in this chamber) will therefore be

$$V_1=K\left(a-\frac{a}{2n}\right)=Ka\left(\frac{2n-1}{2n}\right)$$

There enters the second chamber a mixture in which, in each unit volume of air, the fraction

$$\frac{a}{n}$$

has already been converted; the mean speed V_2 of the reaction in this second chamber will therefore be

$$V_2=K\left[a-\left(\frac{a}{n}+\frac{a}{2n}\right)\right]=Ka\left(\frac{2n-3}{2n}\right)$$

Similarly, there would be obtained in the third chamber:

$$V_3=K\left[a-\left(\frac{2a}{n}+\frac{a}{2n}\right)\right]=Ka\left(\frac{2n-5}{2n}\right)$$

and so on until the antepenultimate

$$V_{b-2}=K\left[a-\frac{(n-3)a}{n}-\frac{a}{2n}\right]=Ka\frac{5}{2n}$$

and the penultimate

$$V_{n-1}=K\left[a-\frac{(n-2)a}{n}-\frac{a}{2n}\right]=Ka\frac{3}{2n}$$

If W is the speed of circulation of the mixture in the tube T, the tube lengths l_1, l_2 . . . l_{n-1} are such that the

period of contact of the mixture with the catalyst in the chamber of order p, i.e.

$$\frac{lp}{W}$$

produces the conversion of the quantity

$$\frac{a}{n}$$

of the hydrocarbon at the speed of conversion V_p which has just been established for the corresponding chamber. Therefore, referring to the successive chambers, we have:

$$V_1\frac{l_1}{W}=V_2\frac{l_2}{W}=V_3\frac{l_3}{W}\cdots=V_{n-1}\frac{l_{n-1}}{W}$$

$$\frac{l_1}{W}Ka\frac{2n-1}{2n}=\frac{l_2}{W}Ka\frac{2n-3}{2n}\cdots=\frac{l_{n-1}}{W}Ka\frac{3}{2n}$$

The lengths l_1, l_2 . . . l_{p-1}, that is to say the volumes of these chambers which are occupied by the catalyst, must therefore conform to the following law of progression:

$$\frac{l_2}{l_1}=\frac{2n-1}{2n-3}$$

$$\frac{l_3}{l_2}=\frac{2n-3}{2n-5}$$

. . . . . .

$$\frac{l_{n-1}}{l_{n-2}}=\frac{5}{3}=1.67$$

Thus, for a number of chambers at least equal to 5, the ratio of the volume of one chamber to that of the preceding chamber is at least 1.05 and increases so as always to rise to 1.67 between the penultimate chamber $(n-1)$ and that which precedes it.

This result in also very substantially obtained by drawing the ratio of the directly calculated volumes of the chambers $(n-2)$ and $(n-1)$. Thus:

$$\frac{\ln\frac{3}{2}}{\ln 2}\neq\neq 1.70$$

Although strict calculation shows that the nth chamber should have an indefinite volume for the complete exhaustion of the hydrocarbon, the present approximate calculation (which is equivalent to replacing a logarithmic curve by a succession of tangents) permits a choosing also the volume of nth chamber.

There is thus found by applying the same law:

$$\frac{l_n}{l_{n-1}}=3$$

In other words, if it is desired to obtain a substantially complete exhaustion of the hydrocarbon, it is desirable to give the last chamber three times the volume of the penultimate chamber when the exhaustion of the last fraction

$$\frac{a}{n}$$

is of economic interest, taking into account the necessary volume of catalyst.

However, the influence of the heat dissipation by the chambers varies not only their number, but also their progression.

The cooling of the chambers is roughly proportional to their external surface, that is to say, in this instance proportional to l_1, l_2.

Assuming that, in the chamber l_1 the fraction D of the heat Q which is produced escapes through the walls and that nevertheless the temperature difference Δt between

the inlet and the outlet is equal to $Ts-Ti$, the chamber l_2 will under these conditions dissipate the fraction

$$\frac{2n-1}{2n-3}D$$

of the quantity of heat produced therein, and the fraction remaining in the chamber will therefore be

$$Q\left(1-\frac{2n-1}{2n-3}D\right)$$

so that the additional quantity of heat ΔQ dissipated in relation to the first chamber is

$$\Delta Q=\left(\frac{2n-1}{2n-3}-1\right)DQ$$

The length l_2 of the second chamber can therefore be increased by a proportional quantity to maintain the difference Δt. We therefore have:

$$l_2=l_1\frac{2n-1}{2n-3}\left[1+D\left(\frac{2n-1}{2n-3}-1\right)\right]$$

and so on for the other chambers.

In this expression, D is an experimental datum which varies considerably with the shape of the chambers and their absolute volume (D is smaller as the chambers are larger).

If, however, as previously mentioned, the heat dissipation reaches half the heat evolved: $D=½$ and the corrective factor

$$1+D\left(\frac{2n-1}{2n-3}-1\right)$$

is negligible for the chambers immediately succeeding the first chamber, this factor rises to

$$1+⅔\times½=1.33$$

for the chamber $(n-1)$ in relation to the chamber $(n-2)$. The volume of the latter therefore becomes:

$$l_{n-1}=l_{n-2}\times 1.67\times 1.33$$
$$=1_{n-2}\times 2.2$$

It will finally be seen that the number of chambers n having been so determined that the quantity

$$\frac{a}{n}$$

of initial hydrocarbon is oxidized in each of them, the useful volume of each chamber is derived from that of the preceding chamber by multiplication by a regularly increasing coefficient staggered between 1.05 and 2.2, this coefficient increasing from the second chamber to the last, while an additional chamber of arbitrary volume may be added for the completion of the reaction.

The nature of the hydrocarbon employed and the desired product of oxidation determine the number n, but regardless of the reaction employed, the progression of the chambers remains the same as hereinbefore indicated.

There will now be described an example of the application of the invention to the case of the oxidation of naphthalene employing an installation as illustrated in FIG. 2 of the accompanying drawings.

The naphthalene arrives alternately from the two chambers 1 heated by low-pressure steam. It is taken up by a pump **2**, passes successively through a regulating valve **3**, a pressure balancing receptacle **4** and a rotary flow meter for measuring the quantity of naphthalene injected. It then enters the mixer **6**, in which it is mixed with air in the proportion of 30 grams per cubic meter. A small quantity of air coming from the compressor **7** under a pressure of 3 kg. through the duct **8**, first sprays the hot naphethalene through a nozzle **6***a*. On the other hand, a rotary compressor **9** having a much higher delivery than the preceding one, feeds the greater part of the air under a superatmospheric pressure of 0.75 kg., through an electric heater **10**, which raises its temperature to 140° C. This temperature is necessary for a good atomization of the naphthalene.

About 60 kg. of naphthalene per hour are thus injected into 2000 m.³ of air. The mixture of air and naphthalene thereafter passes through a heat exchanger **11** of conventional type comprising a cluster of tubes, in which the hot gases arriving from the catalyzing chambers and circulating in opposite directions give up some of their calories thereto.

Situated between the said exchanger and the first catalytic converter **13***a* is an electric heater **12**, which is principle is used only for starting the installation and which is placed out of circuit when the reaction has commenced. The heat exchanger is then able to bring the mixture to the required temperature of 350° C.

The mixture of air and naphthalene at 350° C. enters a first catalyzing chamber **13***a* comprising in its upper part, a dust-retaining grid, and then a bed of catalyst in the form of pellets several millimeters in diameter. In passing through the catalyst, a part of the naphthalene is converted into phthalic anhydride and the reaction heat raises the gaseous mixture to about 410°. Before entering the second converter **13***b*, the said mixture is cooled to 350° C. by an injection of liquid water atomized at **14***a* by means of compressed air coming from the compressor **7** by way of the duct **8***a*. The water is injected by the pump **15** and the duct **16**–**16***a*.

The reaction mixture thereafter successively passes through theo ther six converters **13***b*–**13***g*, its temperature being brought in each instance to 350° C. by similar water injections effected at **14**–*b*–*c*–*d*–*e* and –*f*. The corresponding valves are shown in the duct **16**, as also the air valves in the duct **8** of the compressor **7**. The various air and water ducts analogous to **6***a* and **8***a* have been omitted from the drawing for the sake of clarity.

In this construction, the number of chambers has been made equal to 7 and in this case, as previously indicated, the temperature difference is

$$\frac{370}{7}=50°$$

In addition, by applying the corresponding progression, there are found for the first six chamber volumes proportional to 7/6, 6%5, 5/4, 4/3, 3/2 and 2, the seventh chamber having a volume which may be three times as great as that of the penultimate chamber, namely **6**.

In these chambers, the volumes of catalyst (or the weights of catalyst, which is assumed to be homogeneous) are proportional to these numbers.

In the described installation, the total mass of catalyst employed was of the order of 1.5 metric tons.

In the illustrated construction, the various converters are substantially similar to one another but, by analogy with FIG. 1, these converters could have a base of constant cross-section and heights varying in accordance with the law indicated. Also, when the external cooling is negligible and the number of chambers is large (it has hereinbefore been stated that in the case of phthalic anhydride this number would have to be equal to 18), groups of chambers of like volume could be provided and there could be disposed within the latter only that quantity of catalyst which corresponds to the aforesaid law of progression.

The catalysing operation thus effected permits a substantially complete exhaustion of the naphthalene, which is converted into phthalic anhydride in a yield in the neighbourhood of 95%.

This part of the installation comprises in addition (not shown in the figure) a water filter and a control and measuring panel with the various temperature regulating members, a flow meter for measuring the quantity of water injected and the aforesaid regulating valves.

On leaving the last converter, the hot gases pass through the exchanger **11**, in which they heat the initial mixture, whereafter they enter an assembly of condensing cham-

bers 17, in which they travel along a sinuous path through twenty successive baffle elements. The chambers consist of ordinary double walled sheet metal cooled by a forced air circulation with the aid of four axial-flow fans 18–*a*, –*b*, –*c* and –*d*. The gases enter the chambers at a temperature of 155° C. and leaves them at 65° C., after having deposited therein the phthalic anhydride produced, as also the impurities formed by the reaction, such as naphthoquinone and maleic acid. The phthalic anhydride collected is thereafter distilled for purification.

On leaving the condensing chambers the air, still containing a small quantity of phthalic anhydride and naphthoquinone, is washed in an ordinary water sprinkler tower 19, in which it is completely freed from the entrained compounds. It is thereafter discharged into the atmosphere. The washing tower is a receptacle about 4 m. high and the sprinkler device comprises 64 water injection nozzles effecting a good atomization.

The washing water is discharged because the good catalysis yield obtained in the installation according to the invention, in combination with the effectiveness of the condensing chambers, makes it scarcely worthwhile to recover the products contained in the washing water leaving the production cycle.

In the apparatus hereinbefore described, the cooling between two successive chambers is effected solely by means of injected water. The latter, which changes to the form of steam, has the advantage of diluting the mixture and consequently of reducing the danger of explosion. However, this cooling means has, on the other hand, the following disadvantages:

Although the reaction is extremely exothermic, no heat can be recovered therefrom. Moreover, when the product of oxidation must be recovered by condensation on leaving the last chamber, the presence of a considerable quantity of water in the mixture may be troublesome, because if the quantity of steam contained in the mixture is too high it is impossible to cool this mixture sufficiently without the water itself condensing instead of remaining in the form of dry steam permitting direct separation of the oxidation product.

Thus, for example, in the particular case hereinbefore considered, the quantity of water produced by the reaction would make it possible, at the end of the reaction, to lower the mixture to about 35° C., in order to recover the phthalic anhydride without this water condensing, while if water alone is employed to cool the mixture in the course of the reaction the quantity of water contained in the final mixture is such that it is not possible to reduce the temperature below 60° C. without this water condensing. Now, at 60° C., the vapour pressure of phthalic anhydride is appreciable, so that some of the product of the reaction is lost.

Finally steam acts as a diluent which increases the volume of the treated mixture.

Preferably, therefore, at least a part of the cooling, between two successive catalyzing chambers, is effected by passing this reacting mixture through a cooling heat exchanger.

The dimensions of this heat exchanger may be such that the cooling effected is always slightly insufficient, so that only a small, appropriately adjusted addition of water is required to bring the mixture to the desired temperature.

The heat exchanger is amply dimensioned and is arranged in parallel with a by-pass, so that, in order to bring the mixture leaving one chamber to an appropriate temperature before its entry into another chamber, it is sufficient to adjust the respective proportions of this mixture which pass, on the other hand, through the cooler and, on the other hand, through the by-pass.

The tubular passage shown in FIGURE 3 comprises a portion 21 which is connected to the outlet of one catalyzing chamber and a portion 22 which is connected to the inlet of the succeeding chamber. Between these two portions is disposed a cooling heat exchanger 23 which consists, similarly to a smoke tube boiler, of an external jacket 24, provided with perforated end plates 25, in which are expanded the tubes 26 through which the treated mixture passes.

The jacket 24 contains a liquid, for example a mineral oil, which is conveyed by a pump 27. The liquid leaving the jacket 24 is passed into a heat exchanger 28, for example for heating the air intended to be introduced in mixture with the hydrocarbon to be oxidized. On leaving the exchanger 28, the liquid is passed into a reservoir 29, from which it is extracted by the pump 27.

Since the progression of the useful volmes of the chambers has in practice the effect of producing the same quantity of heat in all these chambers, all the exchangers disposed between two consecutive chambers may have equal dimensions and may be connected in parallel with a header 51 connected to the pump 27. Similarly, their outlets may be connected in parallel by a header 52 for admission into the exchanger 28.

The calorific capacity of this cooler is made such that the quantity of heat which it extracts from the mixture is slightly less than that which would be necessary to bring the mixture to the temperature suitable for its admission into the succeeding chamber. A further cooling is effected by water which is injected into the mixture by the ring of orifices 30 which is fed under pressure through the passage 31. The quantity of water may be adjusted as a function of the temperature at the outlet of the cooling exchanger.

In the construction illustrated in FIGURE 5, the channel 32 connecting two consecutive chambers is divided into two parts 32*a* and 32*b*, of which the first extends through a cooling heat exchanger 33, while the second constitutes a by-pass for this cooler. The butterfly valves 34, 35 control the passage of the mixture through each of the two branches 32*a* and 32*b*. The said valves are connected to crank pins 36 and 37 respectively, which are controlled by the linkage 38 and the servo-motor 39. A movement of this linkage in the direction of the arrow F tends to close the valve 34 and to open the valve 35. The servo-motor is controlled by a temperature-responsive element 40 (of the resistance, thermo-electric couple or other type) through an amplifier 41.

When the temperature at the level of the element 40 tends to become excessive, the linkage 38 is moved in the direction corresponding to the closing of the valve 35 and to the opening of the valve 34, and vice versa.

Since the loss of pressure at the passage through the branch 32*b* is low, while that corresponding to the passage through the exchanger 33 is much higher, a very small variation in the opening of the valve 35 is sufficient to modify considerably the flow through the branch 32*b*, while a much greater variation in the opening of the valve 34 is necessary for obtaining a variation of the flow through the branch 32*a*. Consequently, the control crank pins 36 and 37 are advantageously unequal in order that, in the combined movement of the two valves, the angular movement of the valve 34 may be greater than that of the valve 35.

In the constructional form illustrated in FIGURE 6, a catalyzing chamber 13 contains in its upper portion the catalyst 42, which occupies a volume corresponding to the law of progression set forth above and in its lower portion, a heat exchanger 43. The said heat exchanger is, as before, formed of two circular end plates 34 through which there extends the small tubes 45. In addition, it comprises at its center a wide duct 46 which may be closed by a shut-off member 47. The said shut-off member is controlled through the rod 48 by means of a servo-motor 49 which, as before, is controlled by a temperature-responsive member 50 disposed in the outlet of the chamber.

In this case, by reason of the large pressure loss to which the fluid is subjected in passing through the small tubes 45, it is sufficient to adjust the opening of the shut-

off member 47 in order to modify the proportion of the mixture flowing, on the one hand, through the exchanger and, on the other hand, through the central duct 46.

In the construction illustrated in FIGURE 7, the chamber 53 comprises two opposing frusto-conical portions 53*a* and 53*c* connected by a cylindrical portion 53*b*, which defines the volume 42 for the reception of the catalyst. The inlet of the frusto-conical portion 53*a* and the outlet of the frusto-conical portion 53*c* are of equal dimensions in all the chambers. At the level of the inlet at 53*a*, there is disposed the atomized water injector comprising, in the nozzle 54, the water inlet 55 and the atomising compressed air inlet 56.

Disposed at the outlet of the cone 53*c* is the tube-cluster cooler 57, of which the inlet 58 and the outlet 59 are connected by the by-pass 60 provided with the adjusting valve 61.

The outlet passage 62 is curved in such manner as to rise to the level of the inlet of the succeeding chamber. Disposed between the said passage and the lower portion of the chamber is the by-pass 63 provided with the adjusting valve 64. Finally, the assembly comprising the chamber and the ducts is coated with heat insulation 65 in order to prevent heat losses to the atmosphere and to reduce the disturbing effect of the ambient temperature on the temperature adjustment.

An increase of the outlet temperature may be obtained either by opening the gas by-pass 64 or by opening the by-pass 60 of the liquid cooler, and vice versa.

The heat recovered by the coolers can also be utilized to fuse the condensed oxidation product obtained at the outlet from the chambers, as also for the distillation of this product (for example phthalic anhydride) in vacuo for the purpose of purifying it.

We claim:

Apparatus for the controlled, continuous exothermic oxidation of hydrocarbons, said reaction having a temperature level of explosive potential, comprising: a series of reaction chambers each having an inlet and an outlet; means to deliver to said series of chambers a reactive mixture of hydrocarbon and an oxidizing gas at a constant volume per unit of time; means in each chamber for supporting a predetermined quantity of a catalyst between the inlet and the outlet for passage through such catalyst of said mixture to be oxidized; each of said chambers and its associated catalyst supporting means being of predeterminably greater volumetric capacity than the preceding unit, whereby to provide in each unit progressively longer contact with progressively larger quantities of catalyst; means connecting the outlet of each chamber with the inlet of the next succeeding chamber; temperature sensing means adjacent the inlet of each chamber; means in connection with each such duct for cooling the mixture emerging through the outlet of the preceding chamber, said cooling means including water injecting means, means for controlling said cooling means and means connecting said temperature sensing means and said cooling control means for stabilizing at a predetermined value the inlet temperature of the mixture entering each chamber.

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