

April 26, 1966

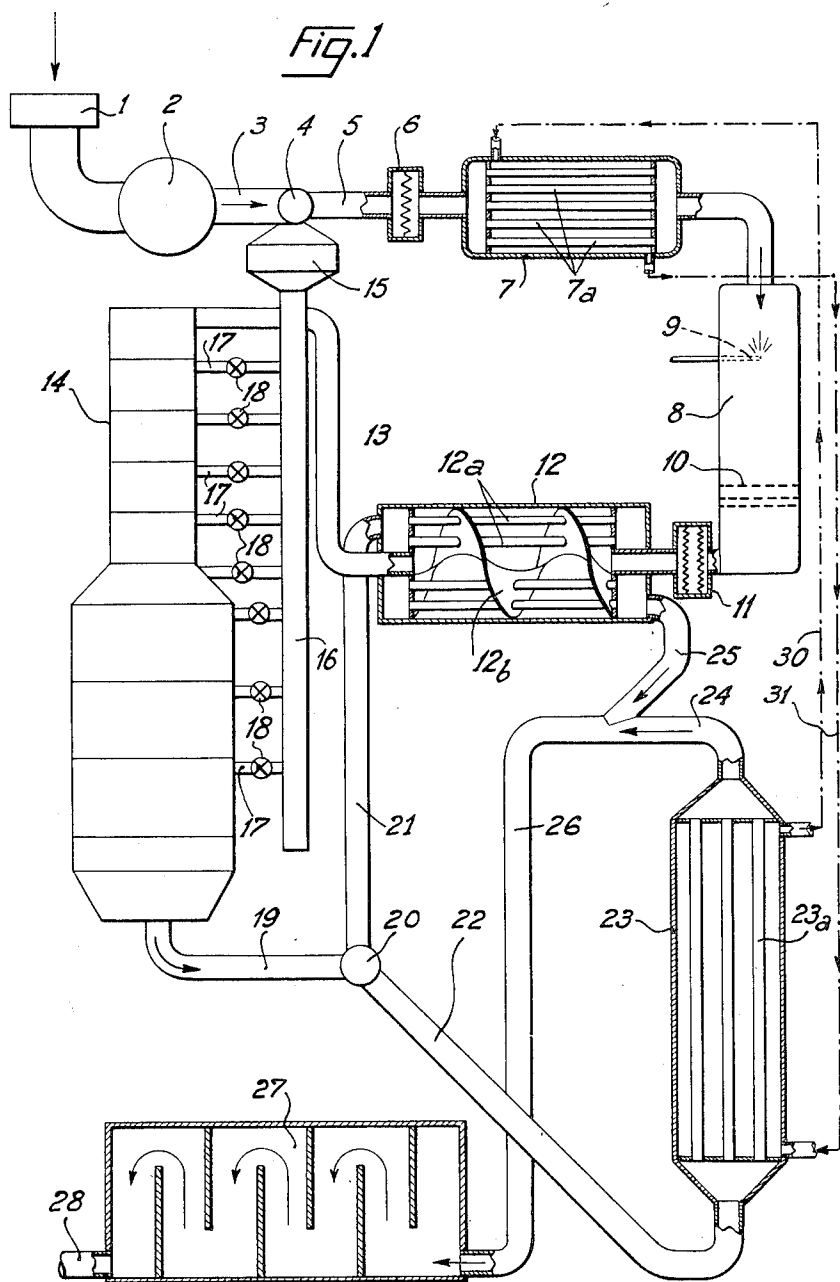
N. R. BEYRARD

3,248,453

PROCESS AND APPARATUS FOR OXIDIZING HYDROCARBONS

Filed May 12, 1961

4 Sheets-Sheet 1



Norbert R. Byrard,
by Mauro & Lewis,
attys.

April 26, 1966

N. R. BEYRARD

3,248,453

PROCESS AND APPARATUS FOR OXIDIZING HYDROCARBONS

Filed May 12, 1961

4 Sheets-Sheet 2

Fig. 2

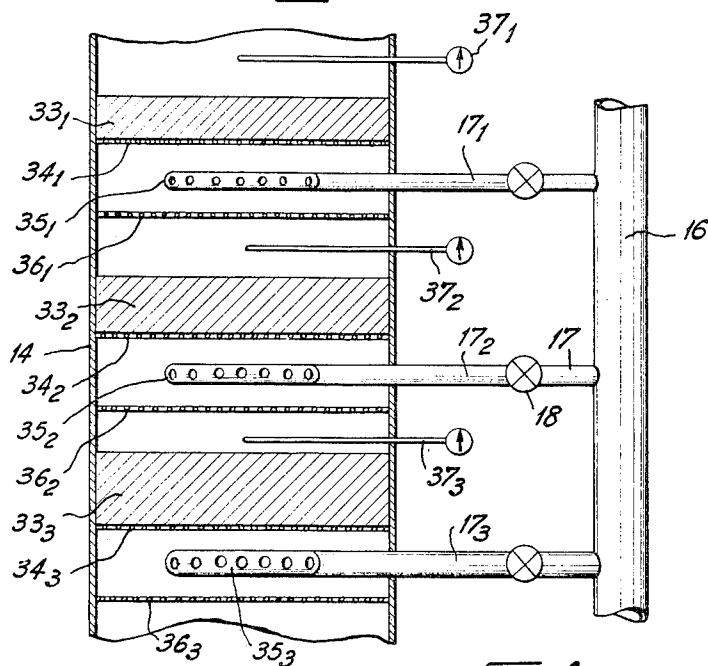
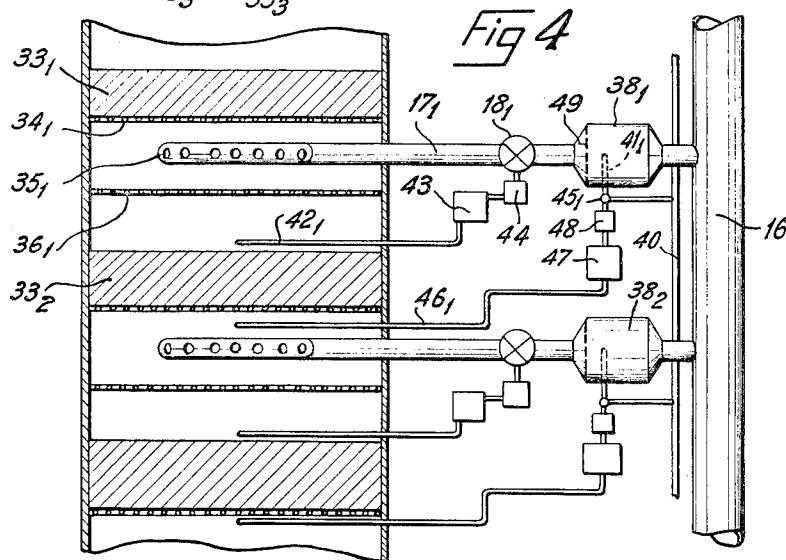


Fig. 4



Norbert R. Beyrard
by Mauro E. Lewis, Attys.

April 26, 1966

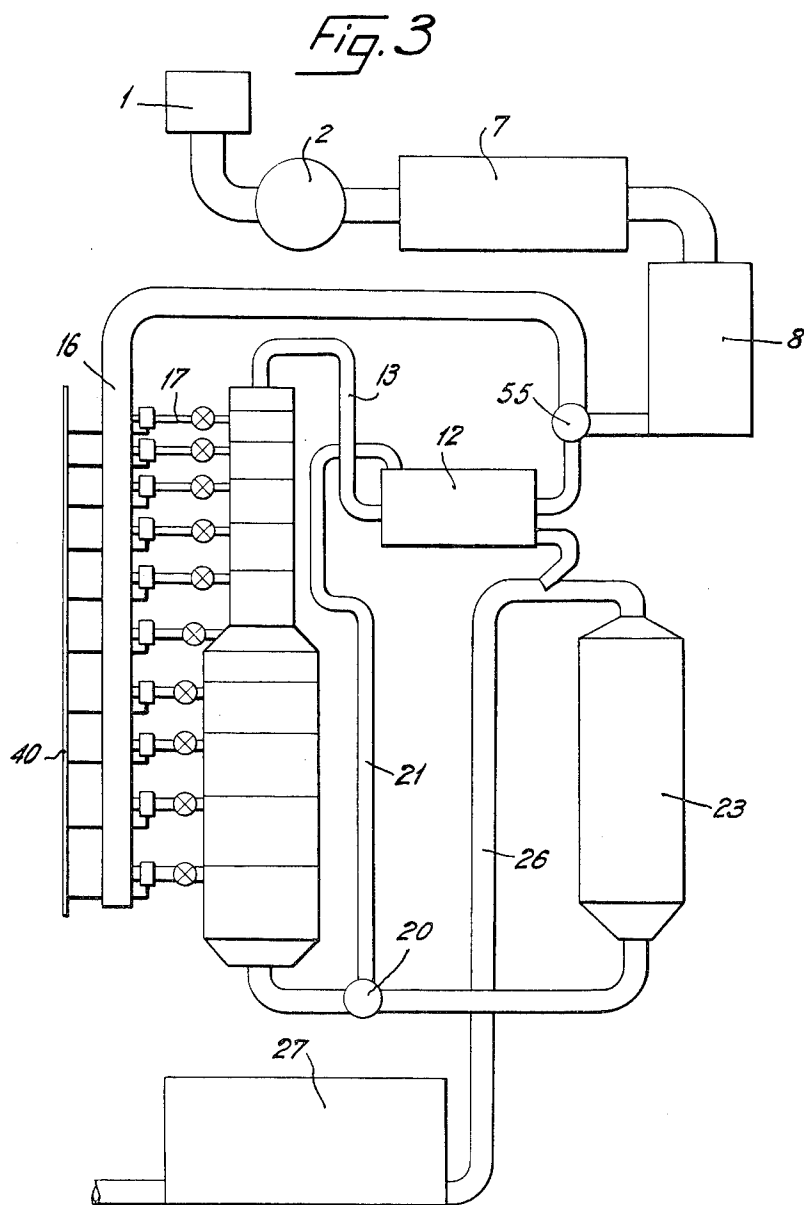
N. R. BEYRARD

3,248,453

PROCESS AND APPARATUS FOR OXIDIZING HYDROCARBONS

Filed May 12, 1961

4 Sheets-Sheet 3



Norbert R. Beyrard
by Mauro & Lewis, Attys.

April 26, 1966

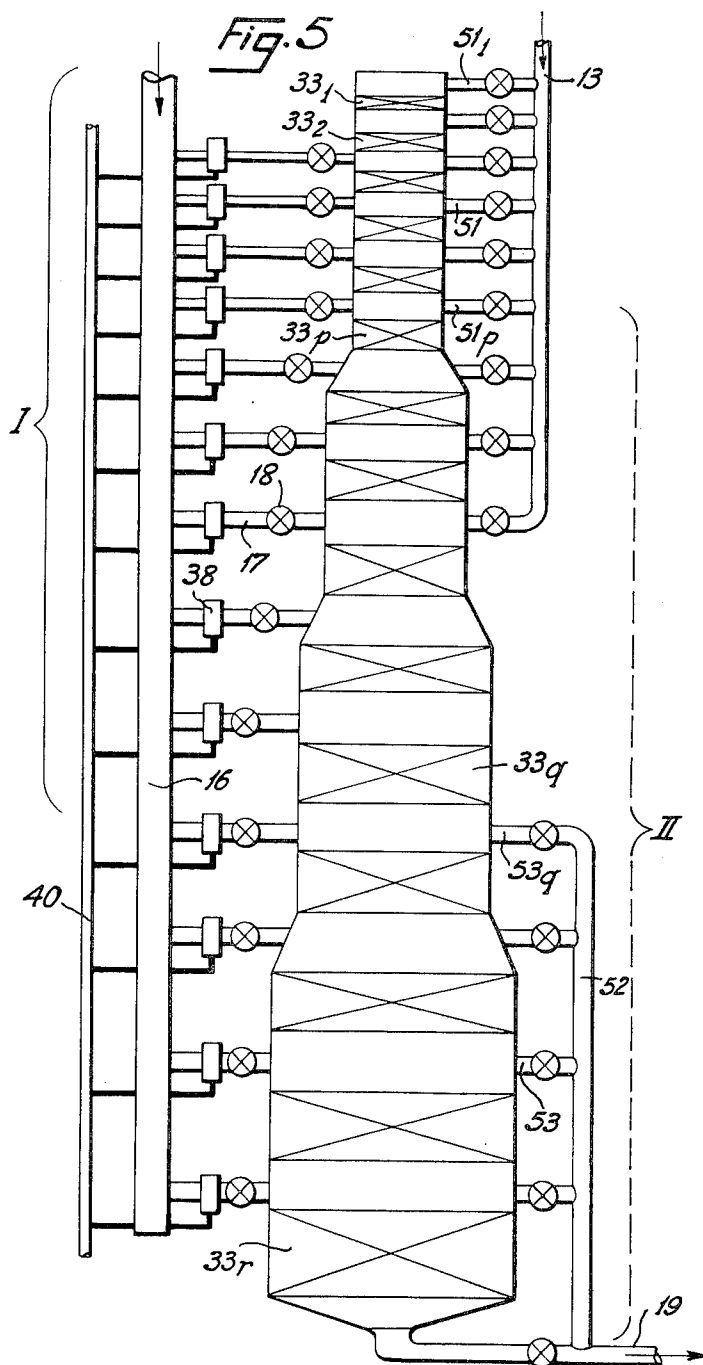
N. R. BEYARD

3,248,453

PROCESS AND APPARATUS FOR OXIDIZING HYDROCARBONS

Filed May 12, 1961

4 Sheets-Sheet 4



Norbert R. Beyard
by Mauro & Lewis, Attys.

1

3,248,453

PROCESS AND APPARATUS FOR OXIDIZING HYDROCARBONS

Norbert R. Beyrard, Paris, France, assignor to Societe de Synthese et d'Oxydation Synoxy, Paris, France, a company of France

Filed May 12, 1961, Ser. No. 109,633

Claims priority, application France, May 18, 1960, 827,598

9 Claims. (Cl. 260—687)

This invention relates to processes and apparatus for oxidising hydrocarbons.

It is known that it is possible to obtain valuable synthetic products by controlled oxidation of hydrocarbons in the presence of catalysts. For example, phthalic anhydride can be obtained by oxidation of naphthalene or o-xylene by means of catalysts such as vanadium oxides. Generally speaking, the oxidising substance is simply atmospheric air in which the hydrocarbon to be oxidised is incorporated in the form of vapour in a quantity below the explosion threshold.

It is also known that the temperature at which a particular product is obtained is somewhat critical. If this temperature is not reached, the oxidation is not obtained, while if it is exceeded the oxidising reaction is accelerated and the hydrocarbon tends to be completely destroyed.

Since the oxidising reaction is exothermic, it has already been proposed, in order to maintain the reaction temperature at the desired value, to incorporate in the catalysing chamber heat exchangers whose operating temperature is stabilised by a thermostat.

It has also been proposed to divide the reaction into a succession of stages each effected in a different catalysing chamber and, while circulating the reaction mixture from one chamber to the other, to cool this mixture as it leaves one chamber and before it enters the succeeding chamber.

This cooling can be effected by means of a heat exchanger, or by injection of a cold fluid diluent into the mixture. In particular, it has been proposed to inject a predetermined quantity of liquid water between two successive chambers, the vaporisation of this water effecting the desired cooling.

Although the dilution of the reaction mixture by means of water scarcely has any disadvantages effect on the reaction itself, the thermal energy dissipated by the evaporation of this water is difficult to recover since, finally, the extraction of the product obtained is effected by condensation at low temperature. The water injected into the mixture then condenses at this low temperature and interferes with the said condensation without having any useful effect.

The use of intermediate coolants between two successive reaction chambers complicates the construction of the installations and increases their cost when it is desired to recover the heat absorbed by these coolants.

It is an object of the present invention to provide an oxidising process which obviates these disadvantages, and apparatus for carrying out such process.

According to the present invention there is provided a process for the multistage exothermic oxidation of hydrocarbons by means of atmospheric air, which comprises bringing the reaction mixture of hydrocarbon vapour and oxidising gas in successive adiabatic stages into contact with successive quantities of catalyst at a temperature below the optimum reaction temperature, and cooling the mixture, after the said contact, from the temperature, above the said optimum temperature, which it reaches, to the said lower temperature, the said cooling being effected by the addition of an appropriate quantity of air and the final mixture, obtained after the last stage, being di-

2

rected to at least one heat exchanger for recovering the heat content of the said mixture.

Thus, a single heat exchanger may be sufficient to recover, at the temperature level at which the mixture is discharged, all the utilisable calories contained therein.

Since the quantity of heat thus recovered is largely in excess of that required for the heating of the mixture entering the installation, in an advantageous embodiment of the invention the flow leaving the last stage is divided into two portions entering two separate heat exchangers, one of which is intended for heating the initial mixture of air and hydrocarbons entering the installation, while the other supplies useful heat for the accessory services of this installation, for example for purifying by distillation the product obtained.

As will hereinafter be shown, it is particularly advantageous for the quantities of air injected between two successive stages of the reaction to increase with a geometrical progression, the ratio of which is low when the fraction of hydrocarbon converted at each of the stages is small.

The apparatus for carrying out the process of the invention may be very simple, since it is essentially sufficient, between two successive stages, to ensure an admission of air into the mixture and to effect homogenisation of this air and the mixture before it comes into contact with the catalyst of the succeeding stage.

Consequently, in its preferred and simplest constructional form, this apparatus comprises a vertical tower in which the reacting mixture circulates from the top downwards, which tower comprises a succession of permeable stages supporting beds of catalyst and, between two successive stages a lateral air admission duct opening immediately below one stage, and below this duct a diffusion grid which ensures homogenisation of the cooling air and of the mixture before they come into contact with the stage situated immediately below.

Instead of introducing pure air for cooling the reaction, at each of the stages, it may be more advantageous to introduce air containing an addition of fresh hydrocarbon already homogenised in the said additional air.

It is also possible to increase the yield of the successive catalyst beds and the final quantity of product obtained.

The injection of fresh hydrocarbon between two stages of the reaction is known per se. However, the direct injection of fresh hydrocarbon into the reaction mixture at high temperature, as already proposed, has serious disadvantages, because owing to the temperature of the mixture, it is difficult with such an injection to avoid a local excessive concentration of hydrocarbon exceeding the ignition threshold of the latter. The risks of ignition and even explosion of the mixture are therefore very serious.

On the other hand, if this fresh hydrocarbon is already diluted and homogenised with the additional cooling air when supplied, these dangers disappear and the operation can be carried out safely and with full advantage.

The quantities of cooling air and of fresh hydrocarbon may be pre-adjusted. However, experience shows that the catalytic actions are not absolutely constant in time and that an additional adjustment may prove necessary. This adjustment has essentially the object of maintaining on entry into contact with a bed of catalyst and on leaving the latter, two clearly defined temperature levels on either side of the most favourable temperature level for the desired reaction.

In accordance with one feature of the invention, the adjustment of the quantity of cooling air is rendered dependent upon the temperature of the mixture before it comes into contact with a catalysing bed, while the adjustment of the quantity of fresh hydrocarbon added to this air is rendered dependent upon the temperature at which it leaves the said catalysing bed.

Thus, for example, when the entry temperature rises, the quantity of cooling air is increased, while it, for example, the entry temperature is correct and the outlet temperature decreases, a further supply of fresh hydrocarbon is sent into the mixture, which tends to raise the said outlet temperature.

According to a further feature of this invention there is provided apparatus suitable for carrying out the aforesaid processes which comprises a vertical tower and means for feeding a reaction mixture through the tower from the top downwards, the said tower comprising a plurality of superimposed units each comprising a stage to carry catalyst, a gas-diffusion grid located above the stage and spaced therefrom, and a lateral duct for the supply of air opening immediately below the stage of one unit and above the gas-diffusion grid of the next lower unit.

A form of apparatus according to the present invention is illustrated in the accompanying drawings in which:

FIGURE 1 is an overall diagrammatic view of an installation according to the invention.

FIGURE 2 is a fragmentary section of the reaction tower in the simplest constructional form.

FIGURE 3 illustrates a variant of the overall layout of the installation.

FIGURE 4 is a fragmentary section of the tower illustrated in FIGURE 3.

FIGURE 5 is a diagrammatic illustration of a reaction tower with which various rates of operation are possible.

In the installation illustrated in FIGURE 1, the atmospheric air entering through the filter 1 is sent by the compressor 2 into the duct 3, which divides it into two flows by means of the diffuser-distributor 4.

The flow passing through the duct 5 is sent into a heater 6 having auxiliary heating, for example of electrical form, and then into a heating heat exchanger 7. It then enters the chamber 8 in which hydrocarbon under pressure, supplied at evaporation temperature, is diffused through the nozzle 9. The diffusion grids 10 effect homogenisation of the mixture of air and hydrocarbon.

On leaving the chamber 8, the mixture passes through a heater 11 and then through the heating heat exchanger 12.

From there, the mixture passes through the duct 13 to the top of the reaction tower 14 which is divided into stages.

The second flow issuing from the diffuser-distributor 4 first passes through a heat exchanger 15 and is then fed through a duct 16 which is vertical and parallel to the tower 14. There extends from this duct the pipes 17 provided with adjustment valves 18, which thus feed air to each of the stages of the tower, except the top stage.

At the bottom of the tower, the gas flow which has passed therethrough and has undergone the action of the successive stages of catalyst, leaves by way of the pipe 19. The diffuser-distributor 20 divides this flow into two, one of which is sent through the pipe 21 into the heat exchanger 12 and the other through the pipe 22 into the heat recovery exchanger 23.

The outlets 24 and 25 respectively of the heat exchangers 23 and 12 are connected to form a common duct 26 which directs the cooled gas flow towards the condensation chambers 27 in which the product obtained condenses. The outlet 28 from these condensation chambers is directed towards the atmosphere after passing through a purifying device of any form (e.g. scrubbing tower or cyclone).

The air leaving the compressor 2 is at a temperature of about 80° C. The exchanger 15 can restore it substantially to atmospheric temperature. In some cases, as will hereinafter be seen, this exchanger may be a heater.

In the case of the conversion of naphthalene into phthalic anhydride, the heater 7 raises the temperature of the air from 80° to 140° C. This heater is formed

of parallel tubes 7a immersed in a hot liquid emanating from the heat recovery exchanger 23 and returning thereto after cooling, as indicated by the circuits 30 and 31.

The naphthalene is injected at this temperature of 140° C. into the chamber 8 through the nozzle 9.

The heat exchanger 12 contains a cluster of parallel tubes 12a through which there flow the gases arriving through the pipe 21, while the air charged with naphthalene is constrained to circulate helically around the said tubes by way of the sheet-metal screw 12b.

This arrangement has the following advantage: The rectilinear tubes 12a, through which the hot gases containing the condensable products pass, can readily be periodically cleaned, while the danger of condensation of the impurities of the naphthalene around these hot tubes is negligible.

In the exchanger 12, the mixture of air and naphthalene flowing therethrough from right to left is brought from 140° C. to about 350° C., while the gases coming from the pipe 21 and passing through the exchanger 12 from left to right enter the latter at about 380° C. and leave it at about 175° C.

The heat recovery exchanger 23 operates with a liquid flowing over the cluster of rising tubes 23a. The gases entering by way of the pipe 22 are also cooled therein from 380° to about 175° C. If it is necessary for the requirements of the installation, the heat recovery exchanger 23 may consist of a number of such exchangers through which the same flow of gas passes in series. The temperatures of the liquids employed in these successive exchangers is thus graded and adapted to each particular application.

At the temperature of 175° C., the gases carrying the products of the reaction are introduced into the condensing device 27, which may be of any type and more especially of the alternating type known as a "Von Heyden" condenser.

The stages of the tower 14 (FIGURES 2 and 4) consist of beds of catalysts in tablet form, for example, in the case of the preparation of phthalic anhydride, of tablets of silica gels impregnated with vanadium pentoxide.

The said beds 33₁, 33₂, etc., are supported by fine-meshed grids 34₁, 34₂ Since the reaction mixture flows from the top downwards in the tower 14, the corresponding pipe 17 (17₁, 17₂ . . .) introduces air through a diffusion nozzle 35₁, 35₂ below each bed of catalyst. As illustrated, these nozzles may be hollow rings formed with peripheral orifices. Disposed below each nozzle 35 is a grid 36₁, 36₂ . . . which homogenises the mixture of gas and air in its downward path.

It will be noted that the beds of catalyst are of increasing thickness and that the pipes 17₁ to 17₃ and the nozzles also have increasing dimensions.

Finally, thermometric measuring instruments 37₁, 37₂ give the temperature of the gas flow as it enters each stage for the control of the installation.

The arrangement illustrated in FIGURES 1 and 2 is suitable in cases where pure air is sent into the reaction mixture at each stage succeeding the first.

On the other hand, when not only air, but also hydrocarbon is sent to each stage, the installation is advantageously modified as illustrated in FIGURE 3.

All the air supplied by the compressor is sent into the chamber 8, in which this air is charged with hydrocarbon in a quantity below the explosion threshold. At the outlet of the chamber 8, the diffuser-distributor 55 directs the mixture thus obtained on the one hand into the pipe 16 and on the other hand into the exchanger 12. As will hereinafter be seen, the quantity of air sent into the pipe 16 is then much greater than that sent into the exchanger 12. Moreover, the concentration of the mixture entering the tower, on the one hand, through the pipe 13 and on the other hand through the branches 17 of the pipe 16,

is the same and in addition this concentration is the highest possible which is compatible with the danger of spontaneous ignition, which affords a number of advantages, as will hereinafter be seen.

Each of the stages of the tower is then preferably arranged as illustrated in FIGURE 4.

Each pipe 17, 17₁, for example, widens into a chamber 38₁ in which a small additional quantity of fresh hydrocarbon emanating from the general duct 40 can be evaporated by way of the nozzle 41₁ and homogenised by the grid 49.

The control of the valve 18₁ is dependent upon the thermometric detector, for example a thermoelectric couple or a resistance 42₁ varying with the temperature and sensitive to the temperature at the entrance to the succeeding bed of catalyst 33₂ through the electronic amplifier 43 and the servomotor 44.

The valve 45₁ for supplying the additional hydrocarbon injected into the chamber 38₁ is controlled in dependence upon the thermometric detector 46₁ sensitive to the temperature beyond the succeeding bed 33₂ by way of the electronic amplifier 47 and the servomotor 48.

The servomechanism 42₁, 43, 44 is adjusted to increase the opening of the valve 18₁ in the event of an increase in the temperature of the thermometric device 42₁. Consequently, if the mixture tends to arrive too hot at the catalysing stage 33₂ an increase in the quantity of air admitted through the nozzle 35₁ cools this mixture, and vice versa if the mixture arrives too cold at the level of the bed 33₂.

On the other hand, the valve 45₁ is normally closed, since the air coming from the pipe 16 is already charged with the desired quantity of hydrocarbon.

The servomechanism 46₁, 47, 48 is adjusted to permit the opening of the valve 45₁ in the event of a reduction in the temperature of the thermometric device 46₁. Thus, a small addition of oxidisable hydrocarbon enters the mixture, whereby the temperature of the reaction is increased as it passes through the bed 33₂, and the temperature at the outlet of this catalyst bed is increased.

The formation of a predetermined reaction product from a given hydrocarbon in the presence of a particular catalyst takes place with its maximum yield at a well defined temperature. Below and above this temperature, the yield of the reaction rapidly decreases.

Since the passage of the mixture through each catalyst bed is adiabatic, it is therefore desirable that the temperature of this mixture at the entrance to the bed should be lower than the optimum temperature and that it should leave the bed at a higher temperature.

The optimum temperature difference ΔT is made the same for all the catalysing beds, so that the temperature conditions for all of them are the most favourable. The mixture thus enters the successive beds at the temperature θ and leaves them at the temperature $\theta + \Delta T$.

Since the mixture has constant specific heat (substantially equal to that of the atmospheric air) and the pressure is substantially constant, this temperature difference ΔT therefore corresponds to a like quantity of oxidised hydrocarbon per unit of volume of this mixture at each of the reaction levels.

The gas flows before the stages 33₁, 33₂ . . . will be called D_1 , D_2 . . . D_n and it will be assumed that the pipe 17 supplies to any stage a fraction α of the flow at the entrance to this stage.

Under these conditions, in relation to the preceding flow D_{n-1} , the flow D_n is given by $D_n = D_{n-1}(1 + \alpha)$.

The temperature of the air contained in the pipe 16 and fed through the pipes 17 will be called T_0 .

In order to restore the temperature of the mixture from the temperature $\theta + \Delta T$ to the temperature θ , it is necessary to have $\alpha D_{n-1}(\theta - T_0) = D_{n-1} \Delta T$ that is to say, the quantity of heat absorbed by the additional air is equal to the quantity of heat by which the mixture has become

enriched in passing through the corresponding stage.

There is deduced therefrom:

$$\alpha = \frac{\Delta T}{\theta - T_0} \quad (1)$$

Since ΔT , θ and T_0 are constant values, α itself is constant.

In other words, the proportion of air added after each stage is constant, that is to say, that:

$$D_2 = D_1(1 + \alpha); D_3 = D_1(1 + \alpha)^2 \dots D_n = D_1(1 + \alpha)^{n-1} \quad (2)$$

The supplies of mixture must therefore increase with the successive stages with a geometrical progression of ratio $1 + \alpha$.

In the successive gas flows D_1 , D_2 . . . , the concentration of the hydrocarbon, that is to say, the quantity of hydrocarbon contained per unit of volume, decreases but, for the reasons already indicated, the reduction γ of concentration at each of the stages is constant in order to ensure a constant value of ΔT .

If the hydrocarbon concentration before the stage n in the gas flow is denoted by C_n , the concentration C'_n at the outlet from this stage will therefore be $C'_n = C_n - \gamma$.

In addition, the air fed through the pipe 17 before the stage n may contain a certain concentration c_n of fresh hydrocarbon (c_2 at the second stage, c_3 at the third stage, etc.).

By writing that the total quantity of hydrocarbon contained in the mixture before the stage n is equal to the quantity emanating from the preceding stage, plus the quantity introduced by means of the additional air, there is obtained

$$C_n D_n = C_n D_{n-1}(1 + \alpha) = D_{n-1}(C_{n-1} - \gamma) + \alpha D_{n-1} c_n$$

whence

$$C_n = \frac{C_{n-1} + \alpha c_n - \gamma}{1 + \alpha}$$

By recurrently calculating C_n from the concentration C_1 of the mixture introduced at the inlet to the first stage, there is obtained:

$$C_n = \frac{C_1}{(1 + \alpha)^{n-1}} + \alpha \left[\frac{c_2}{(1 + \alpha)^{n-1}} + \dots + \frac{c_n}{1 + \alpha} \right] - \gamma \left[\frac{1}{1 + \alpha} + \dots + \frac{1}{(1 + \alpha)^{n-1}} \right]$$

However, there is no reason a priori to introduce at each stage different concentrations of fresh hydrocarbon into the additional air and, as is shown by FIGURE 3, with the simplest arrangement the same hydrocarbon concentration is given to the air sent to all the stages.

We therefore have $c_2 = \dots c_n = c_0$ and by summing the geometrical progressions developed between the square brackets, we obtain

$$C_n = \frac{C_1}{(1 + \alpha)^{n-1}} + \frac{\alpha c_0 - \gamma}{\alpha} \left[1 - \frac{1}{(1 + \alpha)^{n-1}} \right] \quad (3)$$

The Equations 1, 2 and 3 make it possible to choose the dimensions of the apparatus in the various operating conditions. Of all the possible operating conditions, two afford a particular interest, namely:

(1) The case where all the hydrocarbon entering into reaction is introduced all at once into the mixture at the level of the first stage, and

(2) The case where, on the contrary, there is introduced before each stage a quantity of hydrocarbon which will be completely consumed in the course of the passage to the following stage.

In the following, it will be shown that the first case gives the simplest constructional form, but necessitates the highest consumption of energy, while the second case, although involving more complex apparatus, makes it possible to use an installation having very great flexibility which in particular can be adapted to various hydrocar-

bons as starting materials for supplying the same final product.

When the hydrocarbon is introduced all at once, the apparatus is that illustrated in FIGURES 1 and 2, and the term θ in Equation 3 is zero.

The original concentration C_1 having been determined, the number of stages of the reaction tower is defined by the condition $C_n \leq \gamma$.

In fact, the reaction is substantially complete when the concentration obtained at a stage falls below the difference of concentration γ obtained by the oxidation of the hydrocarbon in the passage to each of the stages.

In accordance with Equation 3, it is then necessary to have:

$$\frac{C_1}{(1+\alpha)^{n-1}} - \frac{\gamma}{\alpha} \left[1 - \frac{1}{(1+\alpha)^{n-1}} \right] \leq \gamma$$

which may be written

$$(1+\alpha)^{n-1} \geq \frac{C_1\alpha + \gamma}{\gamma(1+\alpha)}$$

or

$$n-1 \geq \frac{\log \frac{C_1\alpha + \gamma}{\gamma(1+\alpha)}}{\log (1+\alpha)}$$

The following specific examples will serve to illustrate the invention:

Example 1

In the case of naphthalene oxidised by air in the presence of vanadium oxide, the concentration C_1 , at the limit of the explosion threshold, is about 30 g. per cubic metre of air at the temperature $\theta = 350^\circ \text{C}$.

With the knowledge of the heat evolved by the oxidation of one molecule of naphthalene into phthalic anhydride, it is possible to choose either the variation of concentration γ , which gives the values of ΔT and consequently, in accordance with Equation 1, that of α by choosing the temperature T_0 of the additional air, or to choose a priori ΔT in order to maintain a favourable temperature difference, whereby α and γ are determined, the choice of T_0 remaining arbitrary.

For example, by choosing $\gamma = 3$ g. per cubic metre, we find $\Delta T = 33^\circ \text{C}$. (this reaction taking place between 350° and 383°C).

If the additional air is injected at 20°C ., we then find:

$$a = \frac{\Delta T}{\theta - T_0} = \frac{33}{350 - 20} = 0.1$$

The following is then deduced therefrom:

$$n-1 \geq \log \left[\frac{3+3}{3 \cdot 1.1} \right] \times \frac{1}{\log 1.1}$$

$$n-1 \geq \frac{\log 1.8}{\log 1.1} \approx 6$$

Seven stages are sufficient substantially to exhaust the naphthalene originally introduced.

This result, which is surprising because it seems that ten stages at least would be necessary owing to the fact that the mixture originally contains 30 g. of naphthalene per cubic metre and the reduction of concentration is only 3 g. per cubic metre and per stage, is explained as follows:

Since additional air is supplied to each stage, the concentration of the hydrocarbon in the mixture decreases more rapidly than if this reduction of concentration were due only to the oxidation of the hydrocarbon. In the catalysing beds succeeding the first one, the same reduction of concentration therefore corresponds to the oxidation of a substantially larger quantity of hydrocarbon than would be the case if the mixture were not diluted. On the other hand, the thicknesses of the catalysing beds must follow a law of rapid increase. Moreover, the quantity of air employed is important, since the rate of

flow D_7 at the outlet from the last bed is in this example given (Formula 2) by $D_7 = D_1 \times (1.1)^6 = 1.8D_1$.

Therefore, an 80% excess of air is utilised and the rate of flow in the duct 16 (FIGURE 1) is almost equal to the flow sent into the duct 5.

The consumption of the compressor set is correspondingly increased. However, since the number of stages is reduced, the grids 34, 36, which are one of the main causes of pressure drops, are small in number and the increase in the volume of the circulating gas is compensated for by the lower pressure necessary for circulating this volume.

Finally, the total balance is favourable because, in addition, almost all the heat generated is recovered in the exchangers 12 and 13.

When additional hydrocarbon is supplied between two successive stages, the equation of the mixture of the flows leaving the stage n can also be written:

$$C_n D_n = (C_{n-1} - \gamma) D_{n-1} + \alpha D_{n-1} C_0$$

$$C_n D_n = C_{n-1} D_{n-1} + (\alpha C_0 - \gamma) D_{n-1}$$

In this equation, $C_n D_n$ and $C_{n-1} D_{n-1}$ represent respectively the quantities of hydrocarbon contained in the mixture after and before it leaves the stage n , while $(\alpha C_0 - \gamma) D_{n-1}$ corresponds to the difference between the quantities of hydrocarbon added after this stage and consumed during the passage through the latter, respectively. Obviously, the mixture must not contain more hydrocarbon at the outlet than at the inlet. Therefore, the quantity $\alpha C_0 - \gamma$ must be negative or at most zero if it is assumed that the mixture may contain at the start a certain quantity of hydrocarbon (and consequently of air), which quantity may be expected to be found in the mixture at the outlet or may be extracted in a final stage without injection of fresh hydrocarbon.

Thus, it may be desirable, by making $\alpha C_0 - \gamma = 0$, to supply air and hydrocarbon as the reaction progresses, in quantities such that this air and this hydrocarbon are consumed at each of the stages to which they are supplied. In this case, the initial supply of hydrocarbon is useful only for maintaining the hydrocarbon concentration at a sufficient level for the speed of reaction to remain high, whereby it is possible to reduce the quantity of catalyst employed and to increase the yield of the latter.

In this case, Equations 1 and 2 remain unchanged, Equation 3 being considerably simplified and becoming:

$$C_n = \frac{C_1}{(1+\alpha)^{n-1}} \quad (31)$$

The successive volumes of catalyst may be deduced therefrom.

In that, the volume of catalyst V_n necessary at each stage is proportional to the rate of flow and inversely proportional to the hydrocarbon concentration in the mixture.

At stage n , the mean concentration C_n^1 is equal to the concentration before this stage less $\gamma/2$, since the total reduction of concentration in the passage through this stage is γ .

We therefore have:

$$C_n^1 = \frac{C_1}{(1+\alpha)^{n-1}} - \frac{\gamma}{2}$$

In addition, the quantity of catalyst is inversely proportional to the coefficient K of the reaction.

It will be recalled that a reaction for the oxidation of hydrocarbon in the presence of an excess of air is essentially a primary reaction for which the speed S of the reaction is governed by the differential equation:

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

In this equation x is the number of molecules oxidised after the time t , and a is the number of hydrocarbon molecules initially present.

Finally, the volume V_n of catalyst necessary at stage n may be written:

$$V_n = \frac{1}{K} \times D_n \times \frac{1}{C_n}$$

$$V_n = \frac{1}{K} D_1 (1+\alpha)^{n-1} \times \frac{1}{\frac{C_1}{(1+\alpha)^{n-1}} - \frac{\gamma}{2}}$$

$$V_n = \frac{1}{K} D_1 (1+\alpha)^{2n-2} \times \frac{2}{2C_1 - \gamma(1+\alpha)^{n-1}}$$

However, γ is only a small fraction of C_1 and α is also a small fraction in relation to unity. Consequently, if n remains relatively small, it is possible to neglect the quantity $\gamma(1+\alpha)^{n-1}$, and to write

$$V_n = \frac{1}{K} \frac{D_1}{C_1} (1+\alpha)^{2n-2} \quad (4)$$

It will thus be seen that the quantity of catalyst employed in the successive beds are a geometrical progression whose ratio is $(1+\alpha)^2$.

As previously, the number of stages to be used is obtained by assuming that the concentration after the n th stage becomes lower than γ , that is to say, in accordance with Equation 3;

$$C_n = \frac{C_1}{(1+\alpha)^{n-1}} \leq \gamma$$

$$n-1 \geq \frac{\log \frac{C_1}{\gamma}}{\log (1+\alpha)}$$

Example II

In the case where, for the production of phthalic anhydride, o-xylene is employed, which is oxidised at a temperature $\theta=350^\circ$ C. using vanadium oxide catalyst, the concentration of the hydrocarbon in the mixture is always advantageously made as high as possible, provided that it remains below the explosion threshold. In fact, the higher the concentration the higher the speed of reaction and the larger the quantity of catalyst reduced.

Thus, as in Example I, there may be chosen

$$C_1 = c_0 = 30 \text{ g./m.}^3$$

As in Example I, with the knowledge of the heat evolved by the oxidation of one molecule of o-xylene into phthalic anhydride, it is possible to choose γ or ΔT and to calculate the other from the chosen quantity.

Thus, if $\gamma=3$ g. per m.³ is chosen, then $\Delta T=23^\circ$ C. In this case, α is determined by the relation $\alpha c_0 - \gamma = 0$ or $30\alpha - 3 = 0$.

Therefore, α must be equal to one-tenth (0.1).

Equation 1 then gives the value of T_0 :

$$\alpha = \frac{\Delta T}{\theta - T_0} = 0.1 = \frac{23}{350 - T_0}$$

and hence $T_0=120^\circ$ C.

The injection of air charged with o-xylene must therefore be carried out at 120° C. in this case. In addition, it is necessary that the choice of α , γ and ΔT be such that the temperature T_0 is high, because the hydrocarbon added at the same time as the air must be in the form of vapour therein. However, in the case of o-xylene, the temperature may without disadvantage be very much lower than 120° C.

Calculation of the number of stages then gives:

$$n-1 = \frac{\log \frac{30}{3}}{\log 1.1} = \frac{\log 10}{\log 1.1} \approx 26$$

The number of stages required is therefore 27.

This result can also be reached intuitively.

A certain quantity of hydrocarbon mixed with air is introduced in the first stage of the apparatus. In the

succeeding stages, air and hydrocarbon are simultaneously added in quantities such that the air added is heated to the lower temperature level of the reaction, while the mixture is brought from the upper temperature of the reaction to the said lower temperature. In addition, the quantity of hydrocarbon added corresponds to that which is consumed at each stage. The initial quantity of hydrocarbon introduced is therefore maintained and is progressively diluted in an increasing quantity of air.

The reaction is therefore completed when the concentration of the initial quantity of hydrocarbon falls below the drop in concentration γ at each stage.

In the numerical example just considered, the initial concentration is 30 g. per cubic metre of air and the variation of concentration at each stage is 3 g. per cubic metre. The concentration of hydrocarbon will therefore fall below 3 g. per cubic metre when the volume of mixture, i.e. substantially the volume of air, has been multiplied by ten. Now, this volume of air increases in accordance with the law of flow given by the Equation 2:

$$D_n = (1+\alpha)^{n-1} D_1$$

The reaction will be complete when

$$10D = (1+\alpha)^{n-1}$$

i.e. as before

$$n-1 = \frac{\log 10}{\log (1+\alpha)} = \frac{\log 10}{\log 1.1}$$

This calculation also shows that the rate of flow D_1 is only one-tenth of the final rate of flow.

Moreover, both before the first stage and in the course of the succeeding stages, the air employed contains a constant concentration ($C_1=c_0$) of hydrocarbon.

This has two important consequences:

(1) No excess of air over that necessary for maintaining the hydrocarbon concentration below the explosion threshold is ever introduced into the mixture, and

(2) In the first stages of the reaction apparatus, the quantity of gas circulating is very small and the gas flow reaches its complete magnitude only towards the last stages, notably at the last stage.

Consequently, the work which must be done by the compressor is a minimum since, on the one hand, the quantity of circulating air is reduced to what is essential and, on the other hand, the pressure drops due to the passage through the successive catalysing beds are also reduced to those which are absolutely necessary for causing the reaction mixture usefully to pass through the said catalysing beds.

Such an arrangement affords a further advantage.

It is known that, starting with different hydrocarbons, a particular catalyst is substantially specific to the preparation of a given oxidised substance. Thus, the higher oxides of vanadium makes it possible to prepare phthalic anhydride both from naphthalene and from xylenes, and notably from o-xylene. Only the speed of reaction K is different.

In accordance with Equation 4, the volumes of catalysts increase in a geometrical progression whose ratio is $(1+\alpha)^2$, and in addition proportionally to the rate of flow D_1 and, finally, inversely proportionally to K and to C_1 .

Assuming that the concentration (C_1), the rate of flow before the first bed of catalyst (D_1) and the quantity (α) are constant, the volume of catalyst depends only upon K .

For example, in the case of o-xylene, the speed of reaction K is three times higher than in the case of naphthalene.

Therefore, a quantity of catalyst one-third as large will be sufficient to ensure the reaction in the first stage. Thereafter, in both cases, the laws of increase of the quantities of catalysts are the same.

It is thus possible, as shown in FIGURE 5, to con-

struct the reaction tower with a succession of numerous catalysing beds 33_1 to 33_r for which the quantity of catalyst increases in accordance with the indicated geometrical progression from the first (at the top) to the last (at the bottom).

The pipe 16 with its branches 17, and the pipes 40 for the additional supply of hydrocarbon extend over the entire height of the tower. In addition, in the top portion of the latter, the pipe 13 (FIGURE 1) is extended by an admission collector comprising the branches 51 provided with valves opening between two beds of the upper stages. Similarly, a discharge pipe 52 provided with branches comprising valves 53 leads to the discharge pipe 19.

Under otherwise equal conditions, for the treatment of o-xylene the reaction may commence at the bed 33_1 and end at the bed 33_a (portion I of the tower), the gases entering through the branch 51₁ being discharged after reaction through the branch 53_a.

On the other hand, when naphthalene is treated, the reaction will start at the bed 33_p (in which the quantity of catalyst is, by geometrical progression, equal to three times the quantity contained in the bed 33_1), the air containing naphthalene entering at 51_p and will continue to the bed 33_r (portion II of the tower).

In both cases, the same adjustments of the admission of additional air and hydrocarbon are suitable, since the concentrations C_1 and C_0 are advantageously maintained at the value corresponding to the explosion threshold.

The same installation (depending upon the hydrocarbon available as starting material) is suitable in both cases for the same total production.

If the production is modified by varying the rate of flow D_1 , it is also possible to choose the discharge stage and the admission stage in such manner that the quantities of catalysts of the beds employed are also suitable. It is thus possible to change the rate of production of the installation without its even being necessary to stop the latter.

It is likewise possible with a suitable catalyst, for example for obtaining phthalic anhydride, to inject into the flow of air leaving the compressor before the exchanger 7 (temperature about 80° C.), o-xylene and, after this exchanger (temperature 140° C.), naphthalene in order simultaneously to oxidise these two gases.

The tower may be surrounded by a framework by which it can be raised and the various stages may consist of cylindrical rings which are detachable for the periodic renewal of the catalyst or for cooling the latter.

I claim:

1. A method of continuously oxidizing a hydrocarbon comprising forming and advancing a mixture of hydrocarbon with a large excess of atmospheric air; bringing the mixture in successive individually adiabatic stages into contact with successive and increasing quantities of catalyst at a temperature θ just below the optimum reaction temperature; limiting the reaction in each stage to a predetermined temperature rise ΔT ; and cooling the mixture after said contact from the temperature $\theta + \Delta T$ above the optimum reaction temperature to the lower temperature θ , the said cooling being effected by addition of atmospheric air at a constant temperature T_0 in an amount for each stage equal to a fraction

$$a = \frac{\Delta T}{\theta - T_0}$$

of the reaction mixture flow whereby the supplies of mixture to the successive stages increases in a geometrical progression of ratio $1+a$ with successive stages.

2. A method according to claim 1 wherein additional air contains fresh hydrocarbon with a constant concentration chosen so that the quantity of fresh hydrocarbon admixed with air before one stage is equal to that which is oxidized by the contact with the next succeeding quantity of catalyst of the following stage, said successive in-

creasing quantities of catalyst being proportional to a geometrical progression of ratio $(1+a)^2$.

3. A method of continuously oxidizing a hydrocarbon comprising forming and advancing a mixture of hydrocarbon with a large excess of atmospheric air, bringing the mixture in successive individually adiabatic stages into contact with successive and increasing quantities of catalyst at a temperature below the optimum reaction temperature, and cooling the mixture, after the said contact, from the temperature, above the said optimum temperature, which it reaches, to the said lower temperature, the said cooling being effected by the addition of air at a constant definite temperature, the temperature rise of the mixture between the beginning and the end of the contact with each quantity of catalyst being constant for each stage and the amounts of additional air being increased in a manner that the supplies of mixture increases in a geometrical progression with successive stages.

4. A method of continuously oxidizing a hydrocarbon comprising forming and advancing a mixture of hydrocarbon with a large excess of atmospheric air; bringing the mixture in successive individually adiabatic stages into contact with successive and increasing quantities of catalyst at a temperature below the optimum reaction temperature, and cooling the mixture, after the said contact, from the temperature, above the said optimum temperature, which it reaches, to the said lower temperature limiting the reaction in each stage to a predetermined temperature rise, the said cooling being effected by the addition of an appropriate quantity of air at a constant definite temperature admixed with a quantity of fresh hydrocarbon equal to that which is consumed by the contact with the next succeeding quantity of catalyst while the supplies of mixture to the successive stages is increased in a geometrical progression.

5. A method of continuously oxidizing a hydrocarbon comprising forming and advancing a mixture of hydrocarbon with a large excess of atmospheric air; bringing the mixture in successive individually adiabatic stages into contact with successive and increasing quantities of catalyst at a temperature below the optimum reaction temperature, and cooling the mixture, after the said contact, from the temperature, above the said optimum temperature, which it reaches, to the said lower temperature, the said cooling being effected by the addition of increasing quantities of air at a constant definite temperature providing supplies of mixture increasing according to a geometrical progression in the successive stages and the quantities of catalyst being greater in the said successive stages in a geometrical progression in a ratio equal to the square of the progression ratio of the rates of mixture supplies.

6. An apparatus for continuous catalytic partial oxidation of hydrocarbon with air wherein the desired oxidation reaction takes place within a narrow temperature range including a vertical tower having a plurality of horizontally supported catalyst beds, the quantity of catalyst in the beds increasing progressively from top to bottom of the tower, said beds being spaced apart to provide a substantial free space above each bed; means in the free space above the uppermost catalyst bed for evenly diffusing a mixture of air and hydrocarbon into said space; means for maintaining the entering charge of air and hydrocarbon at a predetermined constant temperature below the desired reaction temperature; separate, individual means in the free spaces above each of the catalyst beds below the first, for diffusing air into the respective free spaces; corresponding separate means for separately regulating the amount of air supplied to the diffusing means, individual temperature sensing devices in each of the free spaces except the first; means connecting the respective temperature sensing devices with the respective air regulating means whereby a sufficient amount of air is introduced to cool the reaction mixture, which has been heated by passage through the catalyst bed next above the free space, to substantially the temperature of

13

the charge entering the tower; and means for conducting away the reaction product emerging from the lowermost catalyst bed.

7. The apparatus according to claim 6 including means for adding additional feed hydrocarbon to the air supplied to the free spaces between the catalyst beds. 5

8. The apparatus according to claim 7 wherein there is a common source for all of the air supplied to the free spaces including means for supplying feed hydrocarbon to said source and means for individually supplying additional amounts of hydrocarbon to each of the diffusing means. 10

9. The apparatus according to claim 6 wherein the ratio of increase of catalyst in the beds in the tower is substantially a geometric ratio.

14

References Cited by the Examiner

UNITED STATES PATENTS

2,475,855	7/1949	Peters	23—288
2,512,562	6/1950	Cummings	23—288
2,535,944	12/1950	Mathy	23—288
2,548,966	4/1951	Gilmore	23—288
2,605,238	7/1952	Krantz	260—346.8
2,632,692	3/1953	Korin	23—288
3,072,465	1/1963	Benichou et al.	260—346.4
3,072,682	1/1963	Benichou et al.	260—346.4

HENRY R. JILES, *Acting Primary Examiner.*

15 IRVING MARCUS, *Examiner.*