Dec. 25, 1956 J. H. GARDNER ET AL 2,775,510

PRODUCTION OF CHEMICALS

Filed July 24, 1953 2 Sheets-Sheet 1

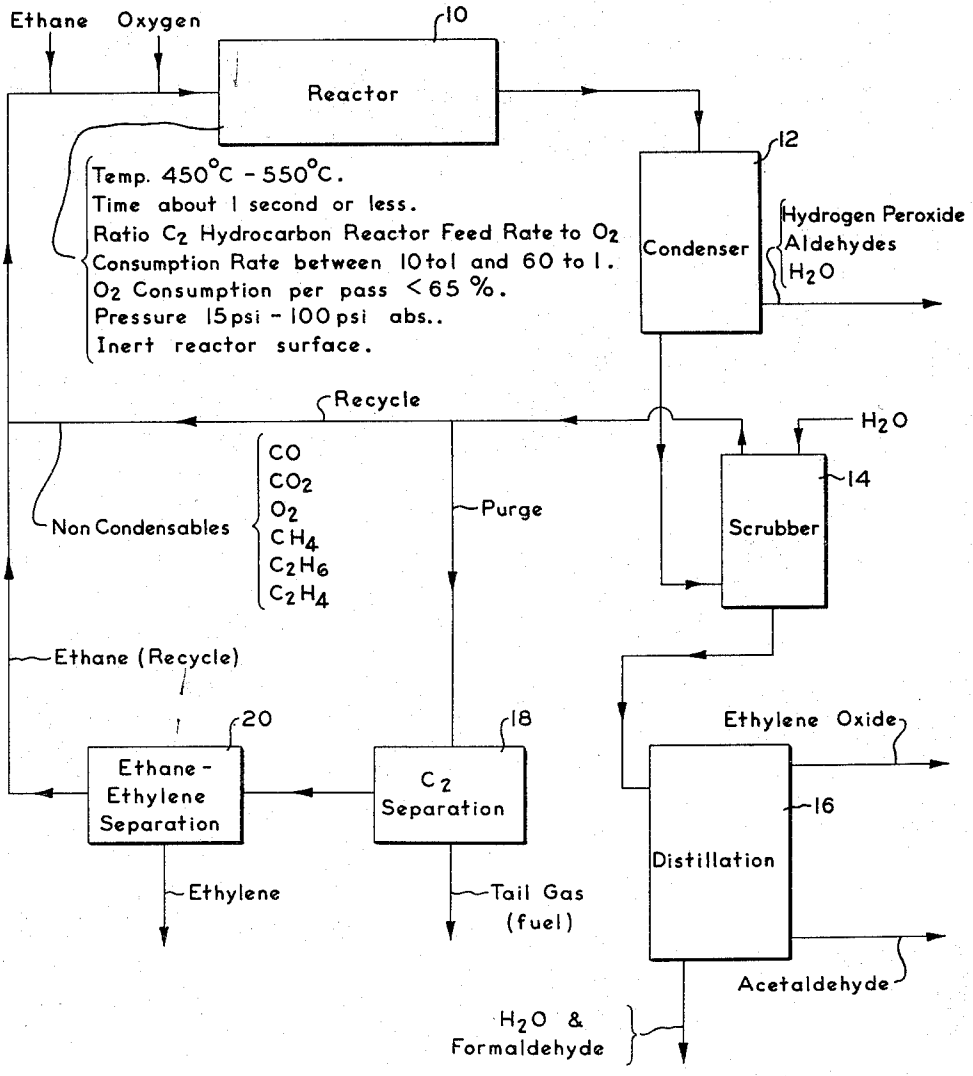


FIG. 1

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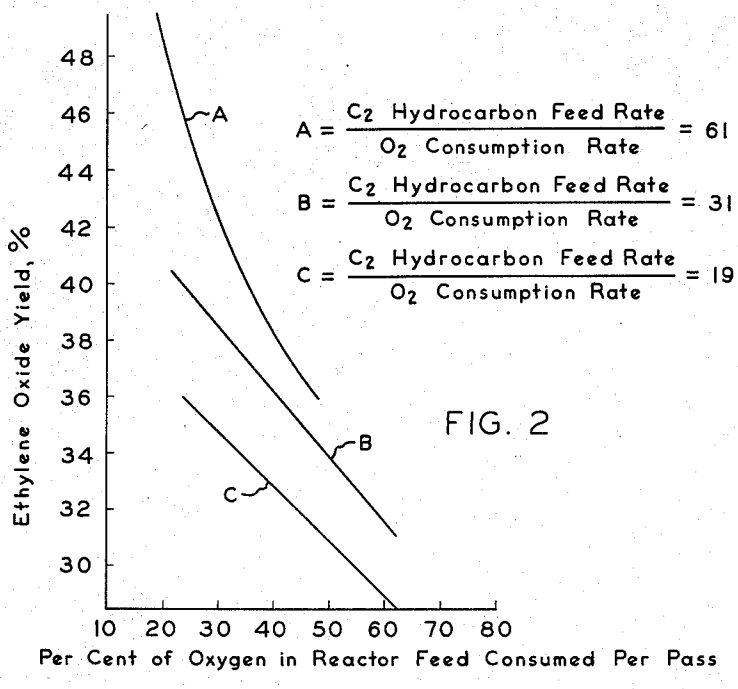


FIG. 2

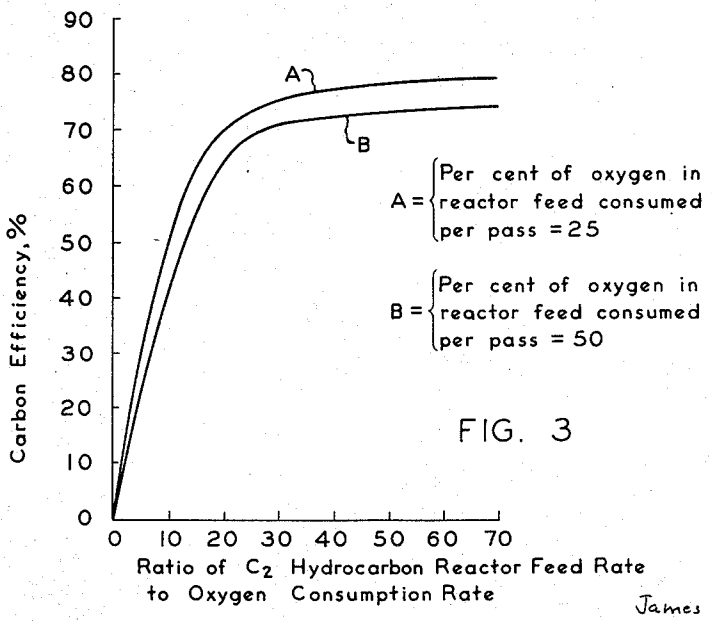


FIG. 3

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PRODUCTION OF CHEMICALS

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Application July 24, 1953, Serial No. 370,065

6 Claims. (Cl. 23—207)

The present invention relates to the production of chemicals and more particularly to the production of ethylene oxide, hydrogen peroxide, and other valuable oxygenated chemicals by the oxidation of ethane.

In recent years the commercial importance of ethylene oxide as a chemical intermediate in the production of numerous end products, such as plastics, anti-freeze, and the like, has lead to many attempts by the workers in the art to arrive at cheaper, more efficient methods of manufacturing ethylene oxide.

As far as is known, the present commercially practiced processes are relatively expensive. One of the most popular processes is the ethylene chlorohydrin process which requires a source of relatively pure ethylene and also involves the consumption of considerable quantities of chlorine.

Another process involves the catalytic oxidation of high purity ethylene with the use of an expensive silver catalyst.

Still other workers in the art have proposed the direct noncatalytic oxidation of ethylene to ethylene oxide. One example of such a proposal is the old patent to Lenher, 1,995,991. In the present invention the low yields, high costs, and requirements for a separate ethylene manufacturing step are completely eliminated in the manufacture of ethylene oxide.

Accordingly, a principal object of the present invention is to provide a novel method of producing high yields of ethylene oxide from ethane.

Another object of the present invention is to provide a process of the direct oxidation of ethane with oxygen to provide high yields of ethylene oxide, hydrogen peroxide, and other valuable oxygenated hydrocarbons.

Still another object of the invention is to provide processes of the above type which are operable at relatively low pressures and in the absence of expensive catalysts.

Still another object of the invention is to perform the direct oxidation of ethane using a recycle system which is particularly adaptable to a continuous commercial process providing a high yield of valuable products.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and the order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

Fig. 1 is a flow sheet illustrating one preferred embodiment of the invention;

Fig. 2 is a graph showing the ethylene oxide yield as a function of percent oxygen consumed per pass; and

Fig. 3 is a graph showing the carbon efficiency defined as a function of the ratio of C_2 hydrocarbons reactor feed rate to oxygen consumption rate.

In the present invention ethane is oxidized at low pressures (on the order of about 15 p. s. i. to 100 p. s. i. abs.) without the use of catalysts. The products of this oxidation are primarily ethylene oxide and hydrogen peroxide. This oxidation is preferably achieved by operating the system under recycle conditions so that a mixture of ethane and large quantities of recycle gas, containing substantial quantities of ethane and ethylene, are fed into a catalyst-free reaction zone. In a preferred embodiment of the invention at least 20 percent by volume of the C_2 hydrocarbons in the mixture entering the reaction zone is ethylene. This reaction is preferably maintained at a temperature of about 450° C. and about 550° C., the preferred range being between about 460° C. and 500° C. A small quantity of oxygen is fed into the reaction zone with the mixture of ethane and recycle gas, the quantity of oxygen preferably being such that the mixture contains much less oxygen than C_2 hydrocarbons. This gaseous mixture of oxygen, C_2 hydrocarbons, and other recycle gases is passed through the heated reaction zone in a period of time which is preferably on the order of about one second or less.

In a preferred embodiment of the invention the time of passage of the gases through the reaction zone, and the temperature in the reaction zone, are so adjusted as to provide for consumption of less than about 65 percent of the oxygen entering the reaction zone. Highest yields of ethylene oxide are obtained when the oxygen consumption per pass is less than about 35 percent of the oxygen fed to the reactor. The relative flow rates of the C_2 hydrocarbons and oxygen into the reaction zone are also preferably controlled so that the ratio of the molar rate of C_2 hydrocarbons fed to the reaction zone to the molar rate of oxygen consumed in the reaction zone is between about 10 to 1 and about 60 to 1. In a preferred embodiment, this ratio is maintained between about 20 to 1 and about 35 to 1.

As a general proposition, high yields of ethylene oxide at high production rates will depend upon a number of economic considerations. As pointed out above, it is highly desirable to maintain a high ratio of C_2 hydrocarbon reactor feed rate to oxygen consumption rate in the reactor. This high ratio may be maintained by feeding high rates of fresh ethane to the system so that the recycle stream will contain high quantities of ethane and ethylene. Additionally, this high ratio of C_2 hydrocarbon reactor feed rate to oxygen consumption rate may be maintained, in a given plant size, by purging a large quantity of the inert gases (i. e., CO, CO_2, methane, etc.) which would otherwise be carried back in the recycle stream. This will, in most cases, increase the cost of a separation of the C_2 hydrocarbons from the purge gas.

Still another method of obtaining a high production rate of oxygenated products in a given plant size is to increase the percentage of oxygen in the reactor. Thus, even though the percentage of oxygen consumed per pass remains low, the total quantity of oxygen consumed per pass is high. In this connection it should be pointed out that it is highly undesirable to operate with such a high percentage of oxygen in the reactor that the explosive limits are reached. While it is difficult to calculate what these explosive limits may be, experimental data indicate unsteady operation at oxygen concentrations in the reactor of around 15 percent and above. Accordingly, it is preferred to operate the reactor at oxygen concentrations of less than about 15 percent.

The reaction zone is preferably defined by surfaces which have no catalytic effect upon the oxidation reaction. These surfaces preferably are formed of inert materials such as Vycor or other similar materials. Equally good results have been obtained with reactors

whose inner surfaces have been coated with fused boric acid. In this connection it is believed to be highly desirable to maintain these reactor surfaces essentially free of metal oxides and metallic elements. Vycor and some similar materials may be kept clean by periodically treating them with hot nitric acid to dissolve contaminants which may deposit thereon from time to time. The boric acid surfaces can be renewed by depositing boric acid from saturated solutions and then heating to about 700° C. to produce a glossy coating.

The gases leaving the reactor are cooled to condense the hydrogen peroxide, and are then preferably passed in countercurrent to a low temperature absorption liquid, such as buffered cold water, so as to scrub out condensable oxygenated products from the exit gases. A portion of the noncondensables is purged and the remaining noncondensables are recycled to the reactor.

Referring now to Fig. 1, there is shown a flow sheet which illustrates one preferred embodiment of the invention. In this preferred form of the process, oxygen, ethane, and recycle gas which contains ethylene are mixed together and fed into a reactor **10** where controlled oxidation of the C_2 hydrocarbons takes place. This oxidation preferably is achieved at temperatures on the order of 450° C. with a reaction time of about one second or less. In general, the higher the temperature the shorter the reaction time. Thus, when the temperature in the reaction zone is on the order of 550° C., the time of residence of gases in the reaction zone should be considerably less than one second. When the temperature is on the order of 450° C., the time of residence in the reaction zone may be somewhat more than one second. In a preferred embodiment, the ratio of the C_2 hydrocarbon reactor feed rate to the oxygen consumption rate is between about 20 to 1 to about 35 to 1. The reaction is also so controlled that the oxygen consumption per pass is less than about 35 percent of the oxygen entering the reactor. The reaction is preferably carried out at a low pressure, this pressure ranging between about 15 lbs. per square inch to about 100 lbs. per square inch absolute.

The oxygenated hydrocarbons and other gases leaving the reactor are passed through a condenser **12** where hydrogen peroxide, water and some aldehydes are stripped from the gas stream. The hydrogen peroxide can be purified by a procedure such as described in U. S. Patent 2,461,988. The condenser **12** is preferably operated at a temperature between about —5° C. and about 40° C., depending upon the pressure of the gases entering the condenser. Thereafter, the gases leaving the condenser **12** are passed to a countercurrent scrubber **14** where ethylene oxide and aldehydes are absorbed from the gas stream. The mixture of ethylene oxide, aldehydes, and water leaving the scrubber **14** passes through a suitable separation step, such as a distillation column **16**, wherein the ethylene oxide, acetaldehyde, formaldehyde, and water are suitably separated. The noncondensable gases passing through the scrubber **14** are preferably recycled to the reactor. These noncondensable recycle gases include carbon monoxide, carbon dioxide, oxygen, methane, ethane, and ethylene.

In order to maintain a steady-state operation, and to prevent the undesired build-up of reaction by-products, a small portion of these noncondensable gases are purged. In one preferred method of opertion, about 5 to 6 percent of the noncondensable gases are purged and passed through a C_2 separation step (indicated at **18**) where ethane and ethylene are stripped from the purge gases. The residual gases are preferably used for fuel.

The C_2 stream from the separation step **18** can be returned directly to the reactor, or can be subjected to another separation step schematically indicated at **20**. The desirability of this additional separation step will naturally depend, to a large extent, upon the uses and market price of ethane and ethylene, respectively, in the plant area.

A more detailed description of moderate pressure oxidation of ethane to produce high yields of ethylene oxide and hydrogen peroxide is given in the following nonlimiting examples:

EXAMPLE I

1.94 volumes of ethane and 1.97 volumes of oxygen are mixed with 59.4 volumes of recycle gas. The analysis of the reactor feed (including the recycle gas) is shown in Table I. The gas mixture is passed through a heated, unpacked reactor in the absence of catalysts and at a pressure slightly in excess of atmospheric pressure. The reactor is a cylindrical Vycor tube having a diameter of 1.66 cms. in a length of 83 cms. The walls of the reactor are heated to about 486° C. The total residence time of the gases in the reactor is about one second. Under these conditions the oxygen consumption per pass was approximately 34 percent of the oxygen fed into the reactor, and the ratio of the C_2 hydrocarbon reactor feed rate (in moles) to the oxygen consumption rate (in moles) was 20 to 1. The hot gas mixture leaving the reactor is passed through a condenser cooled by ice water to about 0° C., thereby chilling these gases to within a few degrees of 0° C. The hydrogen peroxide in the gas stream is completely condensed in this condenser along with some acetaldehyde and formaldehyde. The residual gases leaving the condenser are passed through a plate column. A phosphate buffer solution (pH 6) cooled to 0° C. is passed down the column at a rate of 0.002 volume of solution per standard volume of gas. This removes from the gas stream the residual oxygenated hydrocarbons, these being primarily ethylene oxide with some aldehydes. The uncondensable gases which come from the column are divided into two streams. One is used to furnish the 59.4 volumes of recycle uncondensable gases, and the remainder is purged. The product structure is shown in Table II.

EXAMPLE II

This experiment was similar to Example I with the exception that the reactor feed was somewhat different, as shown in Table I, and the reactor wall temperature was 483° C. The percentage of oxygen consumed per pass was 31 percent and the ratio of the C_2 hydrocarbon reactor feed rate to the oxygen consumption rate was 32 to 1. The product structure is shown in Table II.

EXAMPLE III

This experiment was similar to Examples I and II with the exception that the reactor was provided with a boric acid coating. The reactor wall temperature was about 495° C. and the feed to the reactor was as indicated in Table I. The percentage of the oxygen consumed per pass was 47 percent and the ratio of the C_2 hydrocarbon reactor feed rate to the oxygen consumption rate was 19. The product structure is shown in Table II.

EXAMPLE IV

This experiment was similar to Example III with the exception that the reactor wall temperature was 489° C., the feed being as indicated in Table I. In this experiment the percentage of oxygen consumed per pass was 44 percent and the ratio of the C_2 hydrocarbon reactor feed rate to the oxygen consumption rate was 56. The product structure is shown in Table II.

EXAMPLE V

This experiment was like Example IV, the reactor feed being indicated in Table I, and the reactor temperature being 485° C. The percentage of the oxygen consumed per pass was 19 percent and the ratio of the C_2 hydrocarbon reactor feed rate to the oxygen consumption rate was 58. The product structure is shown in Table II.

Set forth below are two tables. Table I shows the percentage of various components of the reactor feed. These percentages are expressed in terms of volume percent. Table II shows the products obtained from the reactor. These products are expressed as percent of the consumed carbon which goes to each product. In this connection it should be pointed out that ethylene is not listed as a product since all of the ethylene can be recycled to the reactor for further oxidation.

Table I

Reactor Feed Composition	Example I	Example II	Example III	Example IV	Example V
C_2H_6	30.8	55.4	42.8	70.5	69.0
C_2H_4	25.0	23.8	25.0	18.7	18.4
CO	21.0	7.8	16.4	3.2	2.6
CO_2	6.2	1.2	3.4	0.4	0.4
CH_4	6.6	2.7	5.7	3.2	1.3
H_2	3.4	1.1	1.5	0.7	0.4
O_2	7.6	8.1	5.2	3.4	8.0

Table II

Products	Example I	Example II	Example III	Example IV	Example V
$(CH_3)_2O$ [1]	35.8	38.5	31.9	37.0	49.2
CH_3CHO [1]	13.3	26.9	26.3	20.4	24.3
HCHO [1]	21.3	10.8	10.5	16.0	10.1
CO [1]	18.6	15.7	20.2	12.3	10.1
CO_2 [1]	5.5	2.5	4.2	1.8	1.6
CH_4 [1]	5.5	5.5	7.0	12.3	4.8
H_2O_2 [2]	0.29	0.61	0.33	0.64	0.84

[1] Expressed as percent of consumed carbon which goes to each product.
[2] Expressed as grams of H_2O_2 per gram of consumed carbon.

As can be seen from the above results, the best yield of product was obtained in Example V which had (*a*) the highest ratio of C_2 hydrocarbon reactor feed rate to oxygen consumption rate, and (*b*) the lowest percentage consumption of oxygen per pass. Similarly, the lowest yield of product was obtained in Example III which had (*a*) the lowest ratio of the C_2 hydrocarbon reactor feed rate to the oxygen consumption rate, and (*b*) the highest percent consumption of oxygen per pass.

The importance of the ratio of the C_2 hydrocarbon reactor feed rate to the oxygen consumption rate, and the importance of the percentage of the oxygen consumed per pass are graphically illustrated in Figs. 2 and 3. In Fig. 2 the ethylene oxide yield is plotted against the percentage of oxygen in reactor feed consumed per pass. The ethylene oxide yield is shown as percentage of ethane consumed. In this Fig. 2 three typical curves are shown, these curves being displaced downwardly as the ratio of the C_2 hydrocarbon reactor feed rate to the oxygen consumption rate decreases. All three curves slope downwardly with increasing oxygen consumption per pass. Thus, maximum ethylene oxide yields are shown to be obtained with high ratios of C_2 hydrocarbon reactor feed rate to oxygen consumption rate and low oxygen consumption per pass. While these curves indicate even a higher yield of ethylene oxide as the percentage of oxygen consumption falls below 20 percent, the economics of the system become less attractive with small percent oxygen consumption. This is due to the fact that the reactor must be made considerably larger per ton of product, and the recycle rate becomes unduly large.

The same situation applies with respect to increasing the ratio of the C_2 hydrocarbon reactor feed rate to the oxygen consumption rate. While operation at ratios above 60, for example, will give higher ethylene oxide yields, at a given percent oxygen consumption, the problems of recycling become more complex. Accordingly, it is desirable to operate at ratios of C_2 hydrocarbon reactor feed rate to oxygen consumption rate below 60. As stated previously, range of ratios is preferably between about 35 to 1 and about 20 to 1. As this ratio

gets below about 20 to 1, the ethylene oxide yield decreases very substantially. As the ratio increases above 35 to 1, the recycling costs become unattractive. This ratio is preferably controlled by adjusting the individual flow rates of the feed and recycle streams relative to one another.

Fig. 3 primarily illustrates the rise in carbon efficiency with the increase in the ratio of C_2 hydrocarbon reactor feed rate to oxygen consumption rate, the curve beginning to flatten at a ratio on the order of 35 to 1. The calculated carbon efficiency does not include the ethylene in the recycle stream since this ethylene can be returned to the reactor. The illustrated carbon efficiency is based only on the yield of ethylene oxide, acetaldehyde, and formaldehyde. Methane, carbon monoxide, carbon dioxide, and hydrogen are considered to be degradation products, insofar as carbon efficiency is concerned.

Fig. 3 also illustrates a slight but significant decrease in carbon efficiency with increased percentage of oxygen consumed per pass. As pointed out in the discussion of Fig. 2, the effect of increased oxygen consumption is most pronounced in connection with ethylene oxide yield. The percentage of oxygen consumed per pass is preferably controlled by measuring the percentage of oxygen in the exit gas from the reactor and adjusting (in accordance with the measured percentage) either (*a*) the total flow of gases through the reactor, or (*b*) the temperature of the reaction zone, or both.

Although specific operating conditions and apparatus are described in the above examples, the invention is not to be limited to those specific elements and steps described. For example, the reactor can be packed with inert material, such as Vycor Raschig rings, without appreciably affecting the product yield. Equally numerous other modifications in the invention may be made within the skill of the art.

Since certain changes may be made in the above process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description, or shown in the accompanying drawings, shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A process for the production of ethylene oxide and hydrogen peroxide which comprises feeding a mixture of gases into a catalyst-free reaction zone having substantially inert surfaces, the mixture comprising ethane and ethylene, at least 20 percent by volume of the C_2 hydrocarbons in the mixture being ethylene, maintaining said reaction zone at a temperature between about 450° C. and about 550° C., feeding with said mixture a quantity of oxygen such that said mixture contains substantially less oxygen than C_2 hydrocarbons, maintaining said gaseous mixture at a pressure between about atmospheric and about 100 p. s. i., said gaseous mixture being passed through said heated reaction zone for a period of time on the order of one second, said time and temperature being adjusted to effect consumption of between about 30 percent and about 65 percent of the oxygen entering the reaction zone, the relative flow rates of C_2 hydrocarbons and oxygen into the reaction zone being controlled to give a ratio of C_2 hydrocarbon reactor feed rate to oxygen consumption rate of between about 10 to 1 and about 40 to 1, and separating oxygenated hydrocarbons and hydrogen peroxide from the exit gases.

2. A process for the production of ethylene oxide and hydrogen peroxide from ethane which comprises the steps of feeding a mixture of ethane and large quantities of recycle gas, high in ethylene content, into a catalyst-free reaction zone having substantially inert surfaces, at least 20 percent by volume of the C_2 hydrocarbons in the mixture being ethylene, maintaining said reaction zone at a temperature between about 450° C. and about 550° C., feeding with said mixture a quantity of oxygen such that said mixture contains less oxygen than C_2 hydrocar-

bons, maintaining said gaseous mixture at a pressure between about atmospheric and about 100 p. s. i., said gaseous mixture being passed through said heated reaction zone in a period of time of less than about one second, said time and temperature being adjusted to effect consumption of between about 30 percent and about 65 percent of the oxygen entering the reaction zone, the relative flow rates of C_2 hydrocarbons and oxygen into the reaction zone being controlled to give a ratio of C_2 hydrocarbon reactor feed rate to oxygen consumption rate of between about 10 to 1 and about 60 to 1, separating oxygenated hydrocarbons and hydrogen peroxide from the exit gases, and recycling at least a portion of the unoxygenated hydrocarbons and unconsumed oxygen to the reaction zone.

3. The process of claim 2 wherein the ratio of C_2 hydrocarbon reactor feed rate to oxygen consumption rate is maintained between about 20 to 1 and about 35 to 1.

4. The process of claim 2 wherein the volume percent of the oxygen entering the reaction zone is maintained below about 15 percent.

5. The process of claim 1 wherein the ratio of C_2 hydrocarbon reactor feed rate to oxygen consumption rate is maintained between about 20 to 1 and about 35 to 1.

6. A process for the production of ethylene oxide and hydrogen peroxide from ethane which comprises the steps of feeding a mixture of gases into a catalyst-free reaction zone having substantially inert surfaces, the mixture comprising ethane and ethylene, at least 20 percent by volume of the C_2 hydrocarbons in the mixture being ethylene maintaining said reaction zone at a temperature between about 450° C. and about 550° C., feeding with said mixture a quantity of oxygen such that said mixture contains less oxygen than ethane, said mixture having a volume percent of oxygen of less than about 15 percent, maintaining said gaseous mixture at a pressure between about atmospheric and about 100 p. s. i., said gaseous mixture being passed through said heated reaction zone for a period of time from about a fraction of a second to two seconds, said time and temperature being controlled to effect consumption of less than about 65 percent of the oxygen entering the reaction zone, separating the oxygenated hydrocarbons and hydrogen peroxide from the exit gases, and recycling at least a portion of the exit gases to the reaction zone.

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