

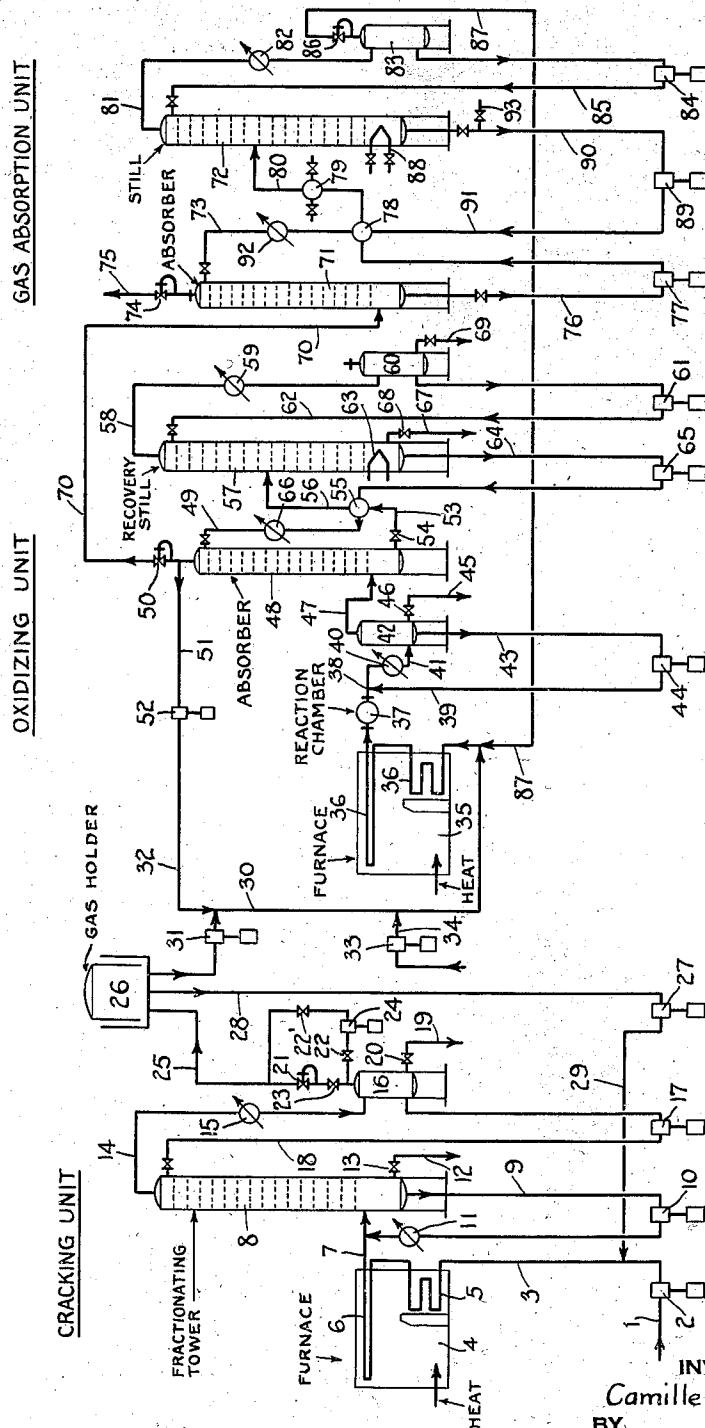
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OXIDATION PROCESS

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OXIDATION PROCESS

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1 Claim. (Cl. 260—533)

This invention relates to the oxidation of hydrocarbons and relates more particularly to the oxidation of unsaturated hydrocarbons.

An object of my invention is to oxidize unsaturated hydrocarbons to produce valuable oxygenated products.

Another object of my invention is to oxidize said unsaturated hydrocarbons to obtain oxygenated products in relatively high yields.

Other objects of my invention will appear from the following detailed description.

In the accompanying drawing there is shown diagrammatically a form of apparatus that may be used in carrying out my invention.

Mixtures of gases containing varying amounts of unsaturated hydrocarbons are formed as the by-product of a number of industrial processes, such as, for example, petroleum cracking. Such gas mixtures are frequently employed as industrial heating media since the gaseous combustion reaction may be easily and accurately controlled. While the gas mixtures are valuable as heating media, they are even more valuable as a raw material for the manufacture of various oxygenated organic compounds.

I have now discovered that unsaturated aliphatic gaseous hydrocarbons may be oxidized at elevated temperatures and pressures with free oxygen to yield valuable oxygenated organic compounds. The products which may be obtained in accordance with my invention are, for example, ethylene oxide, acetaldehyde, ethyl alcohol, acetic acid, formaldehyde, methyl alcohol, acetone and higher ketones and alcohols.

The gaseous mixtures containing unsaturated aliphatic gaseous hydrocarbons employed in accordance with my novel process may be obtained from any suitable source. Preferably, the gaseous mixtures employed are those obtainable by cracking saturated hydrocarbons and mixtures of said hydrocarbons, either in the liquid or vapor phase, which produces a mixture of gases predominantly unsaturated in character, containing substantial quantities of ethylene and higher unsaturated aliphatic hydrocarbons. The charging stock supplied to the cracking unit may be either liquid or gaseous in character. The conditions of operation in the cracking unit may be varied to handle the different types of charging stock and to crack them to maximum yields of unsaturated aliphatic hydrocarbon gases. The cracking unit may operate at temperatures of from 1000 to 2000° F. and the pressure may range from subatmospheric pressures of from about 1 pound per square inch absolute to super-atmos-

pheric pressures of 15 to 200 pounds per square inch absolute.

In carrying out the oxidation of the gaseous unsaturated aliphatic hydrocarbons, free oxygen may be employed. Preferably, I employ air as the source of oxygen although any mixture comprising oxygen and suitable inert diluents is suitable. The oxidation reaction may be carried out at temperatures of from 400 to 800° F. while the pressure employed may be from slightly above atmospheric pressure to pressures of 500 pounds per square inch gauge.

For the oxidation reaction, the ratio of oxygen employed to the volume of gaseous unsaturated hydrocarbon employed, may vary. Satisfactory results may be obtained if, for each volume of gaseous hydrocarbon added to the system, there are added from 3 to 10 volumes of air while at the same time from 20 to 80 volumes of unreacted hydrocarbon gas are recycled. Optimum results are obtained when there are added to the system about 7 volumes of air for each volume of gaseous hydrocarbon and 50 volumes of gaseous hydrocarbons are recycled.

After the oxidation reaction the oxygenated products, together with the unreacted gases, are passed to an absorption system wherein the oxygenated products are separated. The absorption system also may operate under pressure. The unreacted hydrocarbon gases are removed from the gases which remain and are recycled to the oxidation zone. The nitrogen, carbon monoxide, carbon dioxide and oxygen which remain after removal of the hydrocarbon gases are then vented to the atmosphere.

The process of my invention will now be described with reference to the accompanying drawing.

The charge stock, which is cracked to yield the gaseous mixture of unsaturated aliphatic hydrocarbons, is caused to enter the system through a line 1. The stock is forced in under the desired pressure by a pump 2 which may be either a liquid pump or a gas compressor, depending upon whether or not the charging stock is liquid or gaseous in nature. When the cracking unit is operated under sub-atmospheric pressures, the pump may be eliminated or by-passed. From pump 2, the charging stock is passed through a line 3 to the cracking furnace 4 where it enters coils 5 and 6 and is heated to cracking temperature. The cracking temperature will vary depending upon the nature of the charging stock. From the furnace, the cracked mixture flows through a line 7 to a fractionating tower 8 after

having been quenched by a portion of the residual product from the bottom of the fractionating tower 8. The quenching liquid is drawn through a line 9 and forced by a pump 10 through a cooler 11 and into line 7. This quenching operation serves to arrest the cracking reaction and to reduce the temperature at the base of the fractionating tower. Heavier residual liquid products formed in the cracking operation are removed from the base of the tower through line 12 which is provided with a valve 13. The cracked gaseous mixture passes overhead from the tower through line 14, enters a condenser 15 and is collected in a receiver 16. A portion of this gaseous mixture condenses and accumulates at the base of receiver 16. This liquid is returned to the top of the fractionating tower as a reflux medium through pump 17 and line 18. Any excess liquid condensation product accumulating in the receiver 16 may be removed from the system through line 19 which is provided with a valve 20. This excess liquid may be returned to the charging stock and recycled through the process to yield more cracked gases.

The cracking unit may operate under sub-atmospheric or super-atmospheric pressures. When operating under super-atmospheric pressure the pressure is controlled by valve 21 with valve 22 closed and valve 23 open. When operating under vacuum, valve 23 is closed, valves 22 and 22' are opened and the desired vacuum is maintained on the system by means of a vacuum pump 24.

The mixture of unsaturated aliphatic gaseous hydrocarbons from receiver 16 is delivered through line 25 to a gas holder 26. Any desired portion of the gas may be returned to the cracking zone for further cracking by means of a compressor 27 through lines 28 and 29 in order to increase the proportion of unsaturated hydrocarbons in the gases.

The gaseous mixture of unsaturated aliphatic hydrocarbons from holder 26 is charged to the oxidizing section through line 30 by means of a compressor 31 which compresses the gas from the gas holder pressure to the higher operating pressure required in the oxidizing section. The charge of gas is joined by recycle gas which enters through a line 32. Air is forced into the mixed gases in line 30 by a compressor 33, the air entering through a line 34. The mixture of charge gas, cycle gas, and air is then passed to the furnace 35 where it enters coils 36 and is brought up to optimum reaction temperature. The oxidizing reaction is continued in the reaction chamber 37 located just beyond the furnace discharge. The reaction chamber 37 is so designed as to provide a variable volume and in this way the reaction time may be controlled. The smaller the volume provided, the shorter will be the reaction period since, with a given volumetric velocity, the reacting gases will pass through the reaction chamber after being subjected to the reaction conditions for only a relatively short period of time. The greater the volume provided, with the same volumetric velocity, the longer will be the reaction time, due to the more extended period during which the reacting gases are subjected to reaction conditions. As the hot gas mixture leaves the reaction chamber, it is quenched by the injection of cold liquid at 38 through line 39 and the whole mixture is cooled in a cooler 40 and flows through a line 41 to a separator 42. A portion of the liquid condensate is returned through a line 43 by a pump 44

to enter at 38 and to quench the hot gases leaving the reaction chamber 37.

The reaction chamber of variable volume may comprise a reactor containing a movable piston which is adjustable so that the volume of the reaction chamber may be increased or decreased. A variable effective volume may also be obtained by employing a reaction chamber which is provided with a plurality of valved discharge ports extending the length of the chamber. By opening any one of the several valved discharge ports and closing the remainder, the effective volume of the reaction chamber may be varied. If, for example, the discharge port furthest from the inlet is opened and the others closed, the reacting gases will traverse the full length of the reaction chamber. The reaction time will, therefore, be long. If, however, the discharge port closest to the inlet is opened and the remainder closed, the reacting gases will be in the reaction chamber for only a relatively limited period and the reaction time will be quite short.

The liquefied portion of the products in separator 42 is withdrawn through a line 45 provided with a valve 46 and directed to a recovery stage (not shown). This product contains formaldehyde and a small amount of recoverable volatile products in water solution. The volatile products are removed from this solution and the formaldehyde may be concentrated to a suitable concentration of commercial utility.

The gaseous portion of the oxidized products leaves separator 42 through line 47 and enters an absorber 48 where the water-soluble components are absorbed in water entering the top of the absorber through line 49. The absorber is operated under a pressure of, for example, 100 pounds per square inch. This pressure is controlled by the pressure control valve 50. This valve likewise controls the pressure on the oxidizing zone. On the upstream side of the pressure control valve 50, a portion of the gas which is unabsorbed is recycled through line 51, booster compressor 52 and line 32 back to the furnace 35.

The water used for absorption, together with the water-soluble products dissolved therein, is removed from the base of the absorber through line 53 and valve 54 and is passed through a heat exchanger 55 and then through a line 56 into a recovery still 57 for recovery of the volatile products. Still 57 operates at substantially atmospheric pressure. The volatile, water-soluble products are distilled overhead through a line 58 and a condenser 59 and collected in the receiver 60. A portion of the condensate from the receiver 60 is returned to the top of the tower for reflux medium through pump 61 and line 62. Still 57 may be heated by any conventional means such as by a steam heating coil 63. A portion of the stripped aqueous residue from the base of the still is returned by line 64 and pump 65 through heat exchanger 55 and cooler 66 to the absorber 48 to be used for absorbing more water-soluble products. Excess stripped water is removed from the still through line 67 which is provided with a valve 68. The condensed product collected in receiver 60 is a mixture of ethylene oxide, acetaldehyde, ethyl alcohol, acetic acid, methyl alcohol, acetone and higher alcohols and ketones, and this mixture is directed through a line 69 to a purification stage (not shown), where the mixture may be separated into several individual components in any suitable manner.

The gas exhausted from the absorber 48

through pressure control valve 50 contains unconverted hydrocarbon gases, together with nitrogen, carbon monoxide, carbon dioxide and a small amount of oxygen remaining from the air injected into the system. This gas passes through a line 70 to a gas absorption unit. This unit comprises an absorber 71 and a still 72. The entering gas flows upward and counter-current to the downward flow of absorber oil which enters the top of the absorber through line 73. The desired pressure is maintained on the absorber 71 by a pressure control valve 74 and is held at a point somewhat below the operating pressure in the absorber 48 in order to permit flow of the gas through line 70 to absorber 71. The downward flowing absorber oil absorbs the hydrocarbon gases. The remaining gas, free of hydrocarbon constituents, leaves absorber 71 through a vent pipe 75 and is discharged to the atmosphere.

The absorber oil containing the absorbed hydrocarbon gases is discharged from the base of the absorber 71 through line 76 and is forced by a pump 77 through heat exchanger 78, a preheater 79 and a line 80 into recovery still 72. In this still the dissolved hydrocarbon gases are distilled overhead through line 81 and enter a condenser 82 where they are cooled and partially liquefied. The partially liquefied product enters a receiver 83 for collection and separation. The temperature of condenser 82 is adjusted so that only that amount of liquid required for reflux in still 72 is condensed. This liquefied portion is returned as reflux to the top of still 72 by a pump 84 through line 85. The balance of the recovered hydrocarbons are discharged as a gaseous mixture through pressure controller 86 and are recirculated to the furnace 35 through line 87. The pressure on still 72 is maintained at a point high enough to return the hydrocarbon gas mixture

from receiver 83 back to the oxidizing furnace under its own pressure.

Recovery still 72 may be heated by any convenient means such as a steam coil 88. The stripped absorption oil is then returned to the top of the absorption tower by a pump 89 through lines 90 and 91. The oil passes through heat exchanger 78 and a cooler 92 and enters the top of absorber 71 through line 73. Fresh absorber oil may be supplied to the system through a line 93.

The operation of my novel process is relatively simple and produces excellent yields of oxygenated products without the formation of excessive amounts of tar and other products such as carbon monoxide and carbon dioxide.

It is to be understood that the foregoing detailed description is given merely by way of illustration and that many variations may be made therein without departing from the spirit of my invention.

Having described my invention, what I desire to secure by Letters Patent is:

Process for the production of oxygenated organic compounds, which comprises mixing one volume of a gaseous unsaturated aliphatic hydrocarbon with about 7 volumes of air and adding to said mixture about 50 volumes of anhydrous unreacted gaseous unsaturated aliphatic hydrocarbon recycle, heating the anhydrous mixture to a temperature of 400 to 800° F. while under a superatmospheric pressure of not more than 500 pounds per square inch, passing said reacting mixture to a catalyst-free reaction zone, allowing the reaction to continue therein to form oxygenated organic compounds, condensing the mixture of gases formed and injecting a portion of the condensate into the gaseous mixture leaving the reaction zone to halt further oxygenation.

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