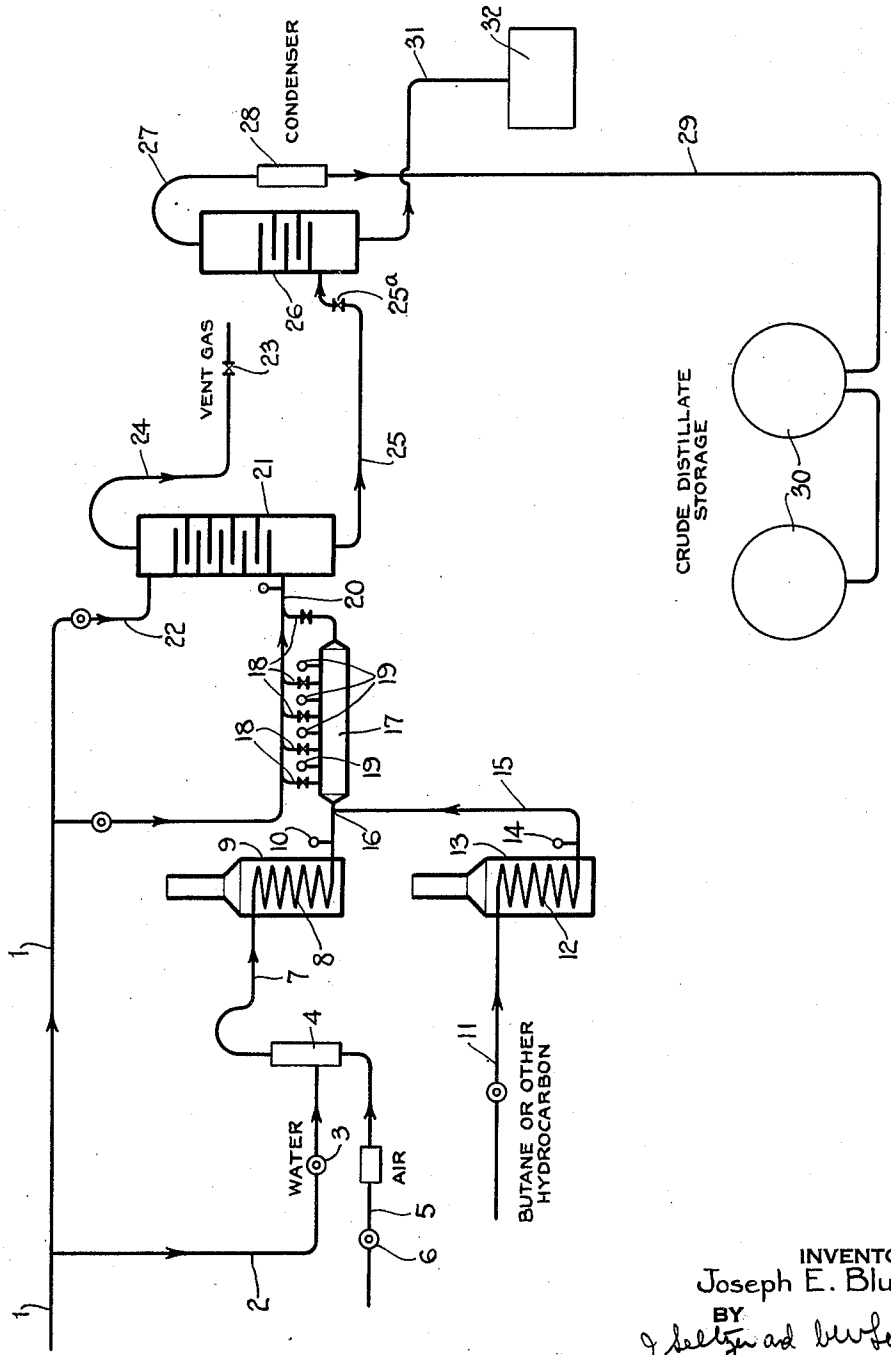
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PREPARATION OF OXYGENATED COMPOUNDS

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PREPARATION OF OXYGENATED COMPOUNDS

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This invention relates to the preparation of oxygenated compounds by processes involving the oxidation of hydrocarbons and relates more particularly to the formation of lower aliphatic oxygenated compounds in relatively large yields.

An object of my invention is to prepare oxygenated compounds by the oxidation of hydrocarbons in such a manner that the nature of the products formed may be controlled. A further object of my invention is to provide a process for the oxidation of hydrocarbons wherein the number of oxygenated compounds formed is relatively small and whereby such compounds may be separated in relatively pure form from the products of reaction. Other objects of this invention will appear from the following detailed description.

It has been proposed to form oxygenated compounds by the oxidation of hydrocarbons. However in such prior processes, the number of oxygenated compounds formed in the reaction is very large with the result that it is practically impossible to separate them into commercially pure components. Moreover the yields of desired lower aliphatic compounds, such as acetaldehyde, acetone, methyl alcohol, etc., have been relatively small. I have found that if the oxidation of the hydrocarbons is permitted to proceed over a relatively large range of temperatures and for a relatively extended period of time, secondary reactions causing the formation of the large number of oxygenated compounds take place.

On the other hand, I have found that if the oxygenation process is allowed to proceed for a relatively short time under conditions whereby the hydrocarbon is raised to the desired reaction temperature substantially immediately upon its contacting with the oxygen-containing gas, large yields of lower aliphatic oxygenated compounds are produced, the number of which compounds is relatively small whereby the compounds may be separated into relatively pure state quite readily.

Moreover I have found that if a large amount of diluent, such as steam, nitrogen or other inert gas or vapor is present during the oxidation process, such diluent prevents or diminishes undesirable reactions and formation of undesired products by absorbing the heat generated during the oxidation process and thus preventing the rise of temperature to the point where such undesired reactions take place.

Conveniently the process may be carried out by separately heating a relatively large amount of steam or other diluent in admixture with the required amount of air or other oxygen-containing gas to the high temperature required for the reaction and then mixing therewith the hydrocarbon to be oxygenated under conditions whereby rapid and thorough mixing is attained. Prior to admixture with the heated mixture of air and steam, the hydrocarbon may or may not be preheated, but if it is preheated it should be at a temperature below the decomposition point thereof. Upon this mixing of the hydrocarbon with the heated steam and oxygen-containing gas, the entire mass is brought to reaction temperature and oxygenation of the hydrocarbon takes place. After the oxygenation reaction is initiated, the steam serves the purpose of maintaining dilution and by absorbing heat acts as a heat dampener to prevent rise of temperature to an undesired extent.

The time during which the oxidation reaction is permitted to occur should be sufficiently short so as to inhibit the setting in of decomposition reactions that tend to form undesirable products. Ordinarily the reaction is permitted to proceed for a period of 0.2 to 3 seconds, preferably 1 to 1.5 seconds. The time at which the mass is permitted to remain at the temperature of reaction is conveniently controlled by spraying or otherwise injecting water or other cooling liquid into the reaction mass in sufficient quantities to quench the gases and vapors so as to reduce the temperature thereof to below the decomposition temperature and preferably below 350° F. The resulting vapors and gases are then conducted to a suitable system for the recovery and separation of the oxygenated products formed.

While I prefer to employ butane as the hydrocarbon to be oxygenated, other hydrocarbons such as propane, pentane, light petroleum distillates, gas oil, etc., either alone or in admixture with each other, may be oxygenated by this process.

The amount of steam, nitrogen or other gas used as heat transfer agent, diluent and heat dampener is large in order to control the reaction properly, and is from 90 to 200 or more, preferably 100 to 120, parts by volume per one part by volume of the hydrocarbon gas or vapor to be oxygenated.

The amount of oxygen employed in the reaction is also of importance in determining the nature and yields of the oxygenated product formed. For the best results, the amount of oxygen employed is that equivalent to that pres-

ent in 7 to 14, preferably 9 to 11, parts by volume of air per one part by volume of the hydrocarbon gas or vapor to be oxygenated.

The mixture of air and steam or other diluent should be raised to suitable temperatures immediately prior to admixture with the hydrocarbon, which temperatures are from 550 to 850° F., preferably 750 to 800° F.

The hydrocarbon may be preheated prior to admixture with the air and steam, but should be preheated to a temperature below that at which decomposition tends to take place which is about 450° F. Preferably the preheating is at a temperature below 350° F.

In order to obtain rapid heating of the hydrocarbon and consequently rapid reaction, the air and steam and the hydrocarbon are caused to approach at a high velocity to a suitable mixing device that causes mixing at high turbulence.

The reaction is preferably conducted under superatmospheric pressures, say on the order of 200 to 1,000 pounds per square inch. Generally 300 to 400 pounds per square inch pressure are sufficient to produce the desired results.

By my process, there are formed products of great commercial value and which can be separated into pure or substantially pure chemical compounds, such as acetaldehyde, formaldehyde, acetone, methyl alcohol, acetic and other organic acids, as well as small proportions of propyl and butyl alcohol.

The accompanying drawing shows diagrammatically a form of apparatus that may be used in carrying out the invention.

The pipe 1 is a water supply line, from which the branch 2 leads through the measuring, pumping and control device 3 to a mixer 4 where it is mixed with air that is passed through the pipe 5 and measuring, pumping and control device 6. The mixture from the mixer 4 is conducted by the line 7 to the heating coil 8 in the furnace or other heating device 9 where it is heated to the desired temperature as indicated by the pyrometer 10.

The line 11 is for the introduction of the butane or other hydrocarbon to be treated which passes through the measuring, pumping and control device shown through the heating coil 12 in the heating device 13 where it is raised to the desired temperature as indicated by the pyrometer 14. While the heating coils 8 and 12 are shown as being placed in separate heating units, they may be placed in the same furnace, in which case the coil 12 is preferably heated by the cooler combustion gases after they have heated the coil 8.

The line 15 leads the preheated hydrocarbon to the pipe 16 where it meets the heated mixture of air and steam from the coil 8 at which point there may be a mixer to cause turbulent mixing and the mixture is at once conducted to the reaction zone 17 which is preferably lagged or insulated. This reaction zone may be in the form of an enlarged chamber which need contain no baffles or other internal mechanical devices upon which the reaction might depend.

A plurality of spaced valve pipes 18 are provided to conduct the reaction mixture from the reaction chamber 17 to be admixed with cold water from the pipe 20 to reduce the mixture below the reaction or decomposition temperature, and preferably to the point where the vaporized liquids will condense at the prevailing pressures. The reaction mixture is caused to leave the chamber 17 from such exit pipe 18 as will be required to permit the reaction to proceed in the optimum short time already specified as being adapted to produce the best results. Pyrometers 19 are provided in the reaction chamber 17 to indicate the temperatures at the various points.

The cold mixture is then passed by pipe 20 to the absorber and contact cooler 21 where the gases and vapors are separated, cooled and washed with a descending stream of cold water from the pipe 22. The uncondensed gases are vented through the pressure release valve 23 in the line 24, while the liquid portions are passed through the line 25 and pressure release valve 25a to the chamber 26 where the more volatile portions are flashed from the water and are conducted through the pipe 27, the condenser 28 and line 29 to the storage tanks 30. The water and the oxygenated compounds dissolved therein are conducted through pipe 31 to storage tank 32.

In order further to illustrate my invention but without being limited thereto, the following specific example is given.

Example

Butane in liquid condition but in amount equivalent to one part by volume of gas (one part by weight) is passed through the heating coil 12 where it is heated to 300° F. Water equivalent to 110 volumes of steam (34 parts by weight) is introduced through the pipe 2 and is admixed in the mixer 4 with 10 parts by volume of air (5 parts by weight) introduced by the pipe 5. The mixture is passed through the heating coil 8 where its temperature is raised to 750° F. The mixture of air and steam and the butane are caused to travel at high velocity to the point 16 where they are mixed under high turbulence and the butane is immediately raised to the reaction temperature. This mixture is then passed to the reaction chamber 17 and is removed by such valve exit pipe 18 to be quenched by water from the pipe 20 below the temperature of decomposition, e. g. 300° F., and the time of reaction is about 1.15 seconds.

The mixture is then introduced into the absorber and cooler 21 where it is scrubbed and cooled by water introduced by pipe 22, the uncondensed gases passing out through the pressure release valve 23, while the water and condensed oxygenated compounds leave through the line 25 and pressure release valve 25a to the chamber 26.

The pressure release valves 23 and 25a are set so as to cause a pressure of 300 to 400 pounds per square inch in the apparatus where the oxygenating process occurs.

Owing to release of pressure in the chamber 26, upon the addition of sufficient heat if necessary, oxygenated products such as acetaldehyde, methyl alcohol, acetone, propanyl and butyl alcohol pass off as vapors through the line 27 and after condensation in the condenser 28 are collected in storage tanks 30. This mixture can be readily separated into the individual components by fractional distillation, and may then be purified by slight chemical treatment if necessary.

The water carrying formaldehyde and organic acids leaves the chamber 26 by pipe 31 to storage and may be treated to recover and separate its components.

By way of illustration of the nature and yield of the products produced, it may be stated that for each 100 pounds of butane treated by the foregoing process, there are produced 19.6 pounds of acetaldehyde, 7 pounds of acetone, 19 pounds of methyl alcohol, 1 pound of propyl alcohol, 0.5 pound of butyl alcohol, 11.4 pounds of organic acids and 15.2 pounds of formaldehyde. The

acetaldehyde may be oxidized to form acetic acid in a subsequent process.

It is to be understood that the foregoing detailed description is given merely by way of illustration and 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:

1. The method of producing oxygenated compounds comprising admixing a hydrocarbon that is below its decomposition temperature with a heated mixture of air and steam the amount of steam present being from 90 to 200 parts by volume per 1 part by volume of the hydrocarbon gas or vapor and the temperature of the same being sufficient to raise the temperature of the hydrocarbon substantially immediately to the reaction temperature and then suddenly cooling such mixture to below the decomposition temperature.

2. The process of producing oxygenated compounds comprising admixing a hydrocarbon that is below its decomposition temperature with a mixture of air and steam heated to 550 to 850° F., the amount of steam present being 90 to 200 parts by volume, and the amount of air present being 9 to 14 parts by volume per 1 part by volume of the hydrocarbon gas or vapor, permitting the reaction to proceed from 0.2 to 3 seconds and then suddenly cooling such mixture by the injection of water.

3. The method of producing oxygenated compounds comprising admixing butane that is below its decomposition temperature with a heated mixture of air and steam, the amount of steam present being from 90 to 200 parts by volume per 1 part by volume of the butane gas and the temperature of the steam being sufficient to raise the temperature of the butane substantially immediately to the reaction temperature and then suddenly cooling such mixture to below the decomposition temperature.

4. The method of producing oxygenated compounds comprising admixing under superatmospheric pressure butane that is below its decomposition temperature with a mixture of air and steam heated to 750 to 800° F., the amount of steam present being from 90 to 200 parts by volume, and the amount of air present being from 9 to 11 parts by volume per 1 part by volume of the butane gas, permitting the reaction to proceed from 1 to 1.5 seconds and then suddenly cooling such mixture by the injection of water.

5. The method of producing oxygenated compounds comprising admixing under superatmospheric pressure a light aliphatic hydrocarbon that is below its decomposition temperature with a heated mixture of air and steam, the amount and temperature of the steam being sufficient to raise the temperature of the hydrocarbon substantially immediately to the reaction temperature, the amount of air present being 9 to 14 parts of volume per 1 part of volume of the hydrocarbon gas or vapor and then suddenly cooling such mixture to below the decomposition temperature.

6. Process in accordance with claim 1 wherein the reaction is conducted under superatmospheric pressure.

7. Process in accordance with claim 2 wherein the reaction is conducted under superatmospheric pressure.

8. Process for the manufacture of acetaldehyde and other oxygenated compounds, which comprises mixing with a light aliphatic hydrocarbon in the vapor phase at a temperature below 450° F. and under superatmospheric pressure, a gas mixture under a similar pressure and at a temperature between 550° and 850° F., containing air and at least 90 times the volume of the hydrocarbon vapors of steam, and after a short time suddenly cooling the mixture.

9. Process for the manufacture of acetaldehyde and other oxygenated compounds, which comprises mixing with gaseous butane at a temperature below 450° F. and under superatmospheric pressure, a gas mixture under a similar pressure and at a temperature between 550° and 850° F., containing air and at least 90 times the volume of the butane of steam, and after a short time suddenly cooling the mixture.

10. Process for the manufacture of acetaldehyde and other oxygenated compounds, which comprises heating a light aliphatic hydrocarbon in the vapor phase under superatmospheric pressure to a temperature of at most 350° F., adding thereto a gas mixture under a similar pressure and at a temperature between 550° and 850° F., containing air and at least 90 times the volume of the hydrocarbon vapors of steam, and after a short time suddenly cooling the mixture by the injection of water.

11. Process for the manufacture of acetaldehyde and other oxygenated compounds, which comprises heating gaseous butane under superatmospheric pressure to a temperature of at most 350° F., adding thereto a gas mixture under a similar pressure and at a temperature between 550° and 850° F., containing air and at least 90 times the volume of the butane of steam and after a short time suddenly cooling the mixture by the injection of water.

12. Process for the manufacture of acetaldehyde and other oxygenated compounds, which comprises heating a light aliphatic hydrocarbon in the vapor phase under superatmospheric pressure to a temperature of at most 350° F., adding thereto a gas mixture at a similar pressure and at a temperature between 550° and 850° F., containing air in amount between 7 and 14 times, and steam in amount between 90 and 200 times, the volume of the hydrocarbon vapor, and after a short time suddenly cooling the mixture by the injection of water.

13. Process for the manufacture of acetaldehyde and other oxygenated compounds, which comprises heating gaseous butane under superatmospheric pressure to a temperature of at most 350° F., adding thereto a gas mixture at a similar pressure and at a temperature between 550° and 850° F., containing air in amount between 7 and 14 times, and steam in amount between 90 and 200 times the volume of the butane, and after a short time suddenly cooling the mixture by the injection of water.

14. Process for the manufacture of acetaldehyde and other oxygenated compounds, which comprises heating gaseous butane under superatmospheric pressure to a temperature of at most 350° F., adding thereto a gas mixture at a similar pressure and at a temperature between 750° and 800° F., containing air in amount between 9 and 11 times, and steam in amount between 100 and 120 times, the volume of the butane, and after a short time suddenly cooling the mixture by the injection of water.

JOSEPH E. BLUDWORTH.