

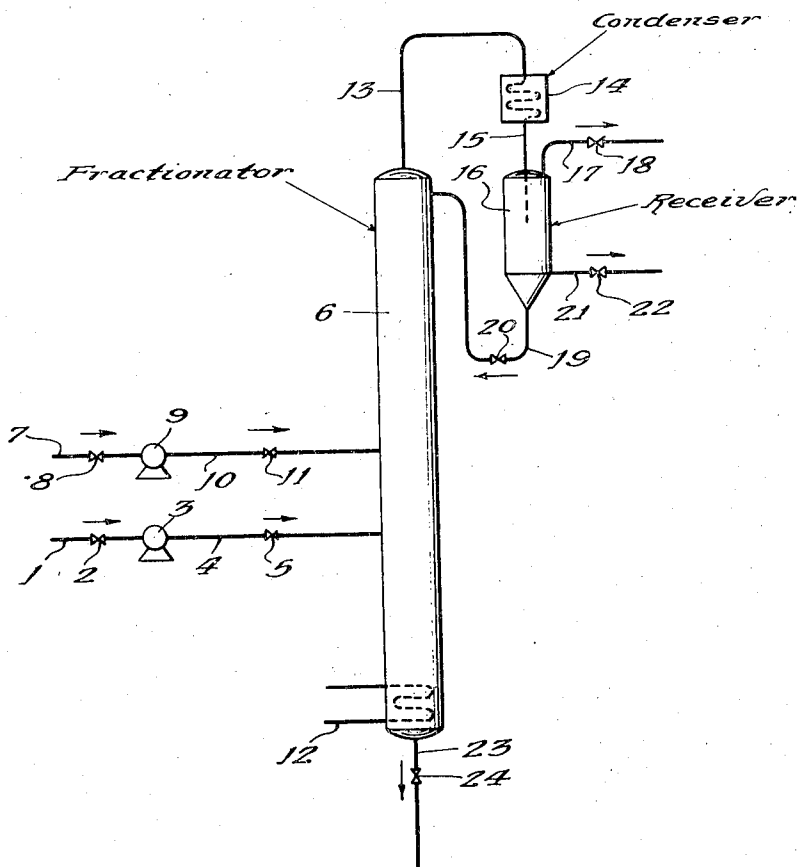
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R. M. DEANESLY

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PROCESS FOR OXIDIZING ALCOHOLS

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Inventor:
Richard M. Deanesly
By: Maynard P. Pennington
Attorney

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PROCESS FOR OXIDIZING ALCOHOLS

Richard M. Deanesly, Hinsdale, Ill., assignor to
Universal Oil Products Company, Chicago, Ill.,
a corporation of Delaware

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This process relates to a process for producing liquid oxidation derivatives of volatile organic compounds by the use of molecular oxygen.

An object of this invention is to produce carbonyl compounds including aldehydes and ketones.

Another object of this invention is to produce an alkyl ketone by oxidation of a secondary alcohol with an oxygen-containing gas.

A further object of this invention is to produce acetone by reacting isopropyl alcohol with air in the absence of catalysts.

One specific embodiment of the present invention relates to a process for producing a carbonyl compound which comprises reacting an alcohol having a hydrogen atom chemically combined with the carbon atom of the carbinol group and oxygen in a fractionating zone at an oxidizing temperature below the critical temperature of said alcohol and at a pressure sufficient to maintain in liquid state a substantial proportion of the alcohol.

Another embodiment of this invention relates to a process for producing a ketone which comprises reacting a secondary alcohol and oxygen in a fractionating zone at an oxidizing temperature below the critical temperature of said alcohol and at a pressure sufficient to maintain in liquid state a substantial proportion of the alcohol.

A further embodiment of this invention relates to a process for producing acetone which comprises reacting isopropyl alcohol and oxygen in a fractionating zone at an oxidizing temperature below the critical temperature of said alcohol and at a pressure sufficient to maintain in liquid state a substantial proportion of said alcohol and continuously discharging acetone from the top of said fractionating zone and withdrawing water from the bottom of said fractionating zone. In another embodiment of the invention, secondary butyl alcohol is reacted with oxygen to produce methyl ethyl ketone.

Alcohols which are oxydized by my process to form aldehydes and ketones include primary and secondary alkanols.

My process is carried out in a fractionator at whatever pressure is necessary to obtain in the upper zone of said fractionator above the point of air or oxygen inlet a temperature of from about 100° to about 300° C., but not in excess of the critical temperature of the alcohol being subjected to oxidation.

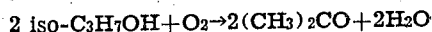
For a given operating pressure, the temperatures prevailing from plate to plate of the combined fractionating and reaction zone will be dependent upon the rates of charge of the alcohol and of the oxygen or air, and on the composition of the reaction mixture prevailing therein as the result of the reflux liquid returned to the fractionator. The condensate taken overhead will, in general, be a three-component mixture of

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water, unconverted alcohol and carbonyl compound with the latter predominating.

One type of apparatus in which my process may be carried out is illustrated by the attached diagrammatic drawing which represents a fractionating column of suitable design to which isopropyl alcohol and oxygen are charged and from which acetone and water are withdrawn. Isopropyl alcohol or an azeotropic mixture of isopropyl alcohol and water is admitted through line 1 and valve 2 to pump 3 which discharges through line 4 and valve 5 into fractionator 6. Air, oxygen, or other oxygen-containing gas is admitted through line 7 and valve 8 to compressor 9 which discharges through line 10 and valve 11 into fractionator 6. Heat is supplied to the lower portion of fractionator 6 by means of heat exchange coil 12 or by other suitable means not illustrated in the diagrammatic drawing. Sufficient heat is supplied by coil 12 to maintain a zone of the fractionator 6 at a temperature above about 100° C. but not in excess of the critical temperature of the alcohol charged thereto. When the alcohol charged to fractionator 6 is isopropyl alcohol, a suitable temperature within this reaction zone of the fractionator is about 150° C. and the maximum temperature is about 235° C., that is, the critical temperature of isopropyl alcohol. Fractionator 6 is also operated at a pressure sufficient to maintain a liquid reflux generated by condenser 14.

The heated mixture of isopropyl alcohol and air interact in the fractionating zone to form acetone and water in about equal molecular proportions. The oxidation reaction corresponds approximately to the following equation:



From near the top of fractionator 6 a mixture of vapors of acetone, water, isopropyl alcohol, nitrogen and unconverted oxygen is discharged through line 13 to condenser 14 from which the liquid and gaseous products are conducted through rundown line 15 to receiver 16 which also serves as a separator for the gases and liquids contained therein. From the top of receiver 16 nitrogen or other inert gases, if present, and unreacted oxygen are discharged through line 17 and valve 18. A portion of the liquid mixture of acetone, water and unconverted isopropyl alcohol is withdrawn from the bottom of receiver 16 and directed by way of line 19 through valve 20 to near the top of fractionator 6 to be returned to the reaction zone and also to serve as reflux liquid and assist in controlling the temperature therein. The liquid mixture of acetone, water and unconverted isopropyl alcohol is also withdrawn from receiver 16 through line 21 and valve 22 to further fractionation and separation treatment not illustrated in the diagrammatic drawing. The liquid mixture so discharged from line

21 is rectified to yield substantially pure acetone by fractionation at lower pressure. Anhydrous acetone is thus separated as a primary fraction from a constant boiling mixture of isopropyl alcohol and water which is returned to fractionator 6 in which the oxidation reaction is carried out.

When the oxidation which occurs in fractionator 6 is slower than desired at particular conditions of temperature and pressure, the reaction rate may be increased by either using deeper fractionator trays with a larger liquid volume holdup or a catalyst such as manganese acetate may be introduced into the reflux liquid returned to the top of the fractionator column. A catalyst may also be carried in suspension in the recycled reflux liquid and it may then be removed from the bottom of the column together with water. Alternatively the packing of at least a part of the fractionating column may be selected to have catalytic effect on the reaction. Water resulting from the oxidation process is discharged from fractionator 6 through line 23 and valve 24.

My method of carrying out the oxidation of a secondary alcohol to a ketone in a fractionator may be applied to the oxidation of other organic liquids with air or oxygen and particularly to reactions in which the hydroxyl group of a volatile compound is oxidized to a carbonyl group. This type of operation has the merit of providing inherent exact temperature control by vaporization from the point of reaction and so controlling the large exothermic heat of such reactions.

The following example is given of results obtainable by my process but these should not be misconstrued to impose undue limitations upon the broad scope of the invention.

A steel fractionator column of the type illustrated in the diagrammatic drawing is operated at a temperature of 150° C. and at a pressure of 28 atmospheres on a reaction mixture having a partial pressure of isopropyl alcohol of 8 atmospheres, an initial partial pressure of oxygen of 4 atmospheres, and a partial pressure of nitrogen of 16 atmospheres. As portions of the isopropyl alcohol and oxygen react forming acetone and water, additional quantities of isopropyl alcohol and air are charged thereto. As the oxidation reaction proceeds, approximately 2 molecular proportions of isopropyl alcohol react with 1 molecular proportion of oxygen to form 2 molecular proportions each of acetone and water as illustrated by the equation aforementioned. The acetone is distilled overhead together with some isopropyl alcohol while some of the water formed in the process is withdrawn from the bottom of the fractionator. Isopropyl alcohol is charged to the fractionator at a sufficient rate to replace that oxidized to acetone and removed from the reaction zone.

I claim as my invention:

1. A process for oxidizing an alcohol having a hydrogen atom attached to the carbon atom of the carbinol group which comprises introducing said alcohol into a fractionating column, introducing an oxygen-containing gas into said column, supplying heat to said column to maintain a reaction zone therein at an oxidizing temperature below the critical temperature of said alcohol, maintaining said column at a pressure sufficient to retain a substantial portion of said alcohol in liquid phase therein, reacting said alcohol and said oxygen in said reaction zone to form a carbonyl compound from said alcohol, simulta-

neously fractionating the reaction products in said column, withdrawing said carbonyl compound from the upper portion of said column, and withdrawing water produced in the oxidation reaction from the lower portion of said column.

2. The process of claim 1 further characterized in that said oxygen-containing gas comprises air.

3. A process for oxidizing a secondary alcohol to a ketone which comprises introducing said alcohol into a fractionating column, introducing an oxygen-containing gas into said column, supplying heat to said column to maintain a reaction zone therein at an oxidizing temperature below the critical temperature of said alcohol, maintaining said column at a pressure sufficient to retain a substantial portion of said alcohol in liquid phase therein, reacting said alcohol and said oxygen in said reaction zone to form a ketone from said alcohol, simultaneously fractionating the reaction products in said column, withdrawing said ketone from the upper portion of said column, and withdrawing water produced in the oxidation reaction from the lower portion of said column.

4. A process for oxidizing isopropyl alcohol to acetone which comprises introducing said alcohol into a fractionating column, introducing air into said column, supplying heat to said column to maintain a reaction zone therein at an oxidizing temperature below the critical temperature of said alcohol, maintaining said column at a pressure sufficient to retain a substantial portion of said alcohol in liquid phase therein, reacting said alcohol and the oxygen in said air in said reaction zone to form acetone from said alcohol, simultaneously fractionating the reaction products in said column, withdrawing said acetone from the upper portion of said column, and withdrawing water produced in the oxidation reaction from the lower portion of said column.

5. A process for oxidizing secondary butyl alcohol to methyl ethyl ketone which comprises introducing said alcohol into a fractionating column, introducing air into said column, supplying heat to said column to maintain a reaction zone therein at an oxidizing temperature below the critical temperature of said alcohol, maintaining said column at a pressure sufficient to retain a substantial portion of said alcohol in liquid phase therein, reacting said alcohol and the oxygen in said air in said reaction zone to form methyl ethyl ketone from said alcohol, simultaneously fractionating the reaction products in said column, withdrawing said methyl ethyl ketone from the upper portion of said column, and withdrawing water produced in the oxidation reaction from the lower portion of said column.

6. The process of claim 1 further characterized in that said oxidizing temperature is from about 100° C. to about 300° C.

RICHARD M. DEANESLY.

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