

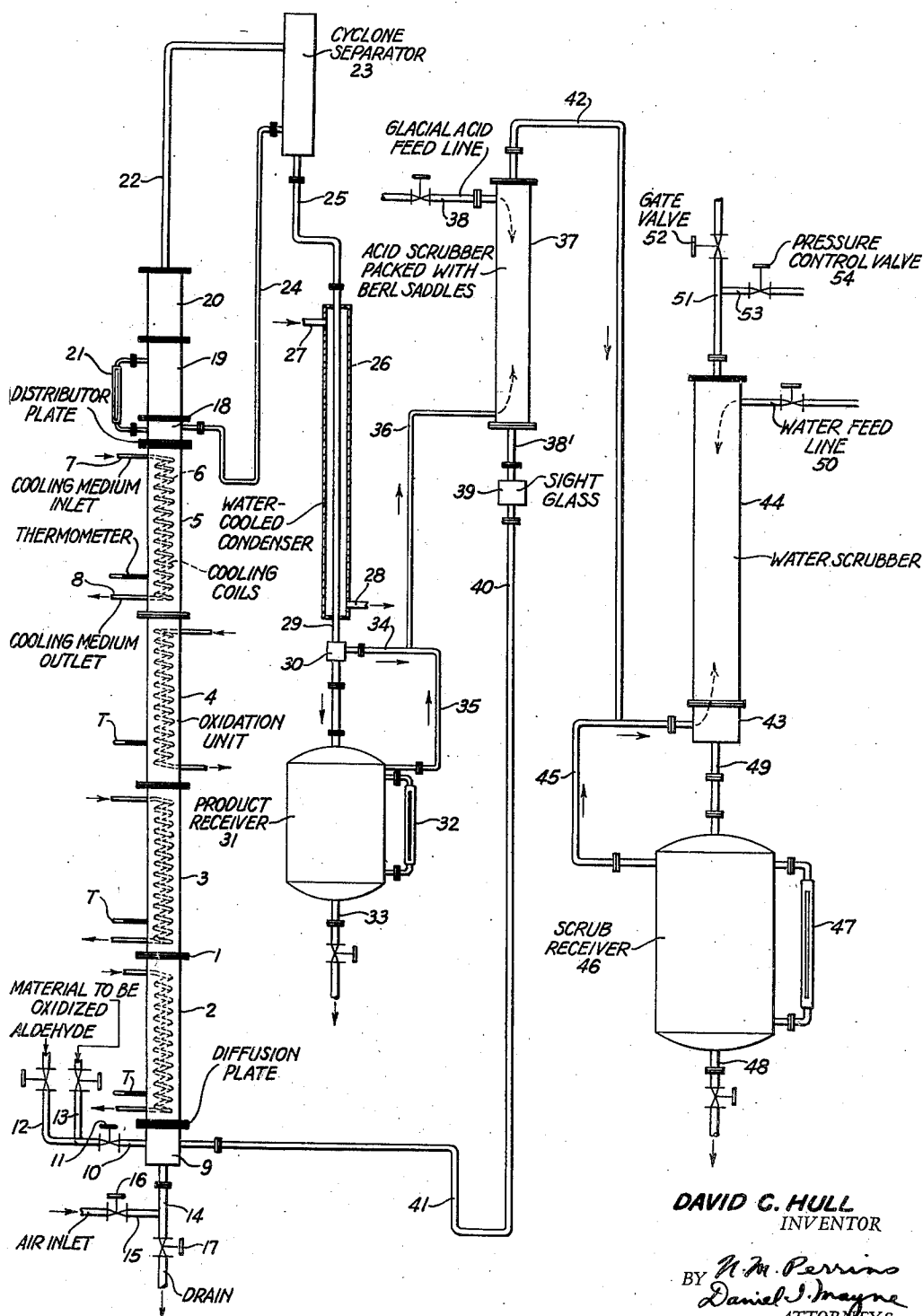
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OXIDATION OF ETHERS USING ALDEHYDE-ACTIVATED CATALYSTS

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OXIDATION OF ETHERS USING ALDEHYDE-ACTIVATED CATALYSTS

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This invention relates to the liquid phase catalytic oxidation of aliphatic and aromatic compounds containing ether linkages and more particularly to the oxidation, by means of aldehyde-activated metal catalysts, of ethers and acetals typified by such compounds as diethyl ether, diethyl acetal, dibenzyl ether and the like to acids such as acetic, benzoic and others.

For many years in the carrying out of oxidations such as the conversion of various aliphatic alcohols to the corresponding acids it was necessary to employ a roundabout and indirect procedure involving a multiplicity of steps and complicated apparatus. For example, in the conversion of ethyl alcohol to acetic acid it was the practice first to oxidize the alcohol to acetaldehyde in one step and then, by a separate step, to oxidize the aldehyde to the acid. In later years a greatly improved and far more economical technique has been developed, whereby the alcohol may be converted directly, at relatively low temperature and pressure, into the corresponding acid without the necessity of a separate procedure for first obtaining the aldehyde. For example, in my United States Patents Nos. 2,287,803; 2,353,157; 2,353,158; 2,353,159; 2,353,160; 2,425,878; 2,425,879; 2,425,880; 2,425,881; 2,425,882, I have an improved process wherein an alcohol, such as ethyl alcohol, may be converted directly to acetic acid by oxidizing the alcohol in the liquid phase by means of oxygen or an oxygen-containing gas in the presence of certain metal catalysts dissolved in an aliphatic acid and maintained in an active state through the agency of a continuous supply of aldehyde. This process has proved to be extremely effective and economical for the production of aliphatic acids.

The catalytic oxidation of other organic compounds employing a somewhat similar technique, although operated, in general, under conditions which differ substantially from the low temperature processes described in my above-mentioned patents, has been applied to various aliphatic, alicyclic and aromatic ketones, including acetone, methyl ethyl ketone, cyclohexanone, methyl cyclohexanone and acetophenone to convert them to monobasic and dibasic acids such as acetic, propionic, adipic, methyl adipic and benzoic acids. Such a process is described in Flemming et al. 2,005,183.

In Patent 2,223,493 Loder has described the liquid phase catalytic oxidation of cyclic saturated hydrocarbons such as cyclohexane, cyclopentane, cyclobutane and their substituted derivatives to obtain the corresponding aliphatic dibasic acids, 55

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such as adipic, glutaric and succinic. In Patent 2,223,494 Loder describes a similar process for converting cyclic saturated hydrocarbons to cyclic alcohols and ketones, while in Patent 2,265,948 he describes a process involving conversion of open chain aliphatic hydrocarbons to acids, ketones, esters and alcohols.

A further extension of the broad concept of oxidizing organic compounds in the liquid phase is described by Loder in Patent 2,245,528 in which reference is made to the oxidation of alkyl-substituted aromatic compounds such as ethyl benzene, toluene and the xylenes to the corresponding aromatic acids such as benzoic, toluic, phthalic and the like. A similar but more specific process is disclosed in the patent to Henke 2,276,774.

To the best of my knowledge and belief, none of the workers in the field to which the present invention relates has recognized the fact that compounds with ether linkages such as the simple and mixed aliphatic ethers and acetals or the aromatic ethers may be converted to aliphatic and aromatic acids by applying the principle of aldehyde activation to such oxidations. Furthermore, not only have none of these researchers recognized or applied the principle of aldehyde activation to such oxidations, but they also have operated under relatively high temperature conditions and obtained relatively low yields of their respective products.

The present invention has for its principal object to provide a process for the economical, efficient conversion of aliphatic and aromatic compounds containing ether linkages to acids. A further object is to provide a process whereby compounds such as diethyl ether, di-normal propyl ether, di-normal butyl ether, the diethyl acetal of acetaldehyde, the diethyl acetal of benzaldehyde and various other compounds containing ether linkages may be converted to the corresponding carboxylic acids. A still further object is to provide a process whereby such compounds may be directly oxidized to the desired products in a single step. Another object is to provide a process for oxidizing such ether-type compounds to valuable acid products in a manner which is both efficient and economical and may be carried out with a minimum of procedural steps. Other objects will appear hereinafter.

These objects are accomplished by the following invention which, in its broader aspects, comprises first preparing an active catalyst solution by dissolving an appropriate metal, metal oxide or other suitable metal compound in an aliphatic acid, such as acetic acid, treating the solution

with an oxygen-containing gas and simultaneously adding an aldehyde such as acetaldehyde, thereby to bring the metal catalyst into a highly active state, and thereafter feeding the ether or compound containing an ether linkage, together with an excess of oxygen, into the catalyst solution while maintaining the catalyst in the solution in an active state by continuously adding aldehyde. In accordance with the invention, the solution is maintained under such conditions of temperature and pressure that the solution is maintained in the liquid phase and the ether or compound containing an ether linkage in the solution is directly converted to the desired acid. For example, by maintaining a body of active catalyst solution in an appropriate vessel at a temperature within the range of -5°C. and 90°C. and approximately atmospheric pressure and continuously adding diethyl ether, acetaldehyde and oxygen or air to the solution, I obtain substantial yields of acetic acid. Likewise, other ethers as well as various acetals and other compounds containing ether linkages may be converted to acetic acid and various other corresponding acids.

In the following examples and description, I have set forth several of the preferred embodiments of my invention, but they are included merely for purposes of illustration and not as a limitation thereof.

The single figure of the drawing represents one form of apparatus which may be employed for the practice of my invention. Other suitable forms of apparatus which may be employed for the carrying out of such a process are illustrated in my above-mentioned patents for example, Patents 2,287,803 and 2,353,157.

My invention will be more fully understood by a preliminary discussion of the preparation and the composition of my improved catalyst solutions and the general conditions under which my process is operated.

As indicated, I employ what I have described as an aldehyde-activated metal catalyst solution. Such a solution can appropriately be prepared, by dissolving a suitable catalyst metal or one of its aliphatic acid-soluble oxides, salts or other compound in an aliphatic acid such as acetic, propionic or butyric acid. While in accordance with my invention, I may employ almost any metal which will produce metallic ions in solution, I have found cobalt to be an especially valuable catalyst. In the same class with cobalt may be mentioned manganese, iron, nickel and copper. Other metals which may be employed as catalyst with substantially equal facility are lithium, beryllium sodium, potassium, rubidium, caesium, calcium, strontium, barium, magnesium, zinc, aluminum, scandium, yttrium, lanthanum, neoytterbium, gallium, indium, thallium, cerium, ruthenium, rhodium, palladium, osmium, iridium, platinum, gold, tin, antimony, mercury, lead, chromium, molybdenum, tungsten, uranium, tantalum, vanadium, columbium (niobium), titanium, thorium, neodymium, praseodymium, illinium, samarium, holmium, europium, erbium, gadolinium, thulium, terbium, dysprosium, and lutecium.

While in general I prefer to employ a single metal as the catalyst and in the form of one of its oxides, salts or other compound which is easily soluble in the aliphatic acid selected as the solvent medium, I may, if desired, employ a plurality of such metals. For example, while I prefer to employ a solution of cobaltous acetate



in glacial acetic acid, I may employ a plurality of metals in the form of their acetates, propionates or butyrates, or in the form of oxides which form the corresponding aliphatic acid salts in the acid solution. Likewise, while I prefer to use acetic acid alone as the solvent, I may employ aliphatic acids such as acetic, propionic, butyric, and the like, either singly or in various combinations one with another.

As to the matter of concentration, I may dissolve the catalyst metal in the acid to produce solutions containing anywhere from 0.10% to 8% of the metal salt, although, in general, I prefer to keep within the range of 5% to 6%. Likewise, although I prefer to dissolve the catalyst in anhydrous acid, a more dilute acid may be employed. In general, I have found that, in use, more satisfactory yields of product are obtained if the acid concentration of the catalyst solution is at all times maintained at approximately 85% or above.

Once the catalyst solution has been prepared as above described and charged into a suitable reaction vessel, it is brought into a highly active or "activated" condition by simultaneously feeding in an aliphatic aldehyde, such as acetaldehyde, and oxygen or an oxygen-containing gas at such a rate and at such a temperature as to cause the catalyst to become and remain active, a condition usually initially indicated by a change in color of the original solution. The oxygen feed is regulated to provide a slight excess of oxygen over and above that required for the oxidation reaction, such excess being indicated by the presence of a few per cent of oxygen in the gaseous effluents from the process. It will, of course, be understood that such matters as feed rates of aldehyde and oxygen, temperature and the like, in general, have to be determined for each particular catalyst and with reference to the compound to be oxidized. In the case of a cobalt catalyst in acetic acid, the original solution, which is pink, changes to green upon activation, indicating that the cobalt ions have changed from a lower to a higher state of valence, that is, from the cobaltous to the cobaltic state and that the solution is in the desired catalytically active condition.

While air is the most economical source of oxygen, I may employ any suitable oxygen-containing gas such as pure oxygen, ozone, or mixtures of such gases with inert gaseous diluents. Likewise, although I prefer to use acetaldehyde, I may employ other aliphatic aldehydes such as propionaldehyde, butyraldehyde and the like, all of which aldehydes may be employed singly or in various combinations one with another. In general, the aldehyde feed will be so regulated as to maintain .1% to 5% of the aldehyde in the reaction liquid.

While in some cases the catalyst solution will become active merely upon introduction of the aldehyde and blowing with air or oxygen at ordinary atmospheric temperatures, it may be necessary to heat the solution moderately, say, to a temperature in the vicinity of $50-60^{\circ}\text{C.}$ in order to initiate catalyst activity.

As to the matter of temperature, I may oxidize ethers and ether type compounds in accordance with my invention at a temperature within the range of 5°C. to 150°C. , although I prefer to operate in the vicinity of 80°C. to 110°C. In general, high temperatures, that is, temperatures in excess of the boiling point of the solvent or product, are to be avoided in the interest of pre-

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cluding degradation of reactants or products, or losses by evaporation, polymerization or like phenomena. In view of the fact that the oxidation reactions here involved are exothermic in character, it is usually necessary continuously to cool the reaction medium in order to keep the temperature within the desired limits, to prevent excessive loss of reactants by evaporation and to preclude the possibility of the reaction becoming too greatly accelerated. On the other hand, under certain circumstances, it may be necessary actually to supply heat, as, for example, in the case of first starting the process, in order to initiate catalyst activity.

As to pressure, while I prefer to operate at atmospheric pressure, or even below, I may operate at pressures as high as 3-4 atmospheres or more. Use of pressures above atmospheric in general permits operation at higher temperatures. It will of course be understood that the temperature and pressure will vary according to the requirements of the particular material undergoing oxidation, the rate of feed of the several reactants and with other variables, the control of which is within the skill of the trained chemist or chemical engineer.

It will, of course, be understood that in oxidizing ethers or ether type compounds in accordance with my invention the oxygen supplied by continuous introduction of air or other oxygen-containing gas, as explained above, is the fundamental source of oxygen for the oxidation reaction. The chief reaction product will be an aliphatic acid such as acetic, propionic, butyric, benzoic, etc., the particular acid of course depending on the particular compound oxidized. For example, diethyl ether may thus be oxidized to acetic acid, di-normal propyl ether to propionic acid, di-normal butyl ether to acetic, propionic and butyric acids, dibenzyl ether to benzoic acid, and so on. In a similar manner, various acetals may likewise be converted to acids. For example, acetal (the di-ethyl acetal or acetaldehyde) may be converted to acetic acid, the di-ethyl acetal of benzaldehyde to benzoic acid and acetic acid.

My invention will now be more clearly understood by reference to a practical operation which may be conveniently carried out in an apparatus such as that illustrated in the single figure of the drawing.

The numeral 1 designates an oxidation unit which may consist of a plurality of flanged stainless steel tubes of six-inch inside diameter and approximately ten feet long, or any other convenient size or proportions, superimposed one on top of the other and bolted together, the main sections being represented by numerals 2, 3, 4 and 5. Each section is provided with a suitable cooling means which may take the form of an internal centrally disposed stainless steel coil such as coil 6 of section 5, of one-half inch or other appropriate inside diameter, each coil being supplied with cooling medium, such as water through inlet 7 and emerging therefrom through outlet 8. Each section is also supplied with a thermometer, as shown, inserted through the wall of each section by means of a thermometer well (not shown).

The lowermost section of the oxidation unit consists of a tubular stainless steel member 9 of the same inside diameter as the upper sections of the unit, flanged at the top and closed at the bottom. To section 9 is connected inlet conduit 10, flow of liquid through which is controlled by valve 11. Connected into conduit 10 is valved aldehyde feed conduit 12 and another valved con-

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duit 13 for supplying the material to be oxidized to the oxidation unit. While the valves in these feed lines may be so operated as to provide a regulated or metered flow of materials to the unit, a somewhat more convenient method is to provide rotameters or other metering devices for this purpose.

Section 9 has tapped into its lower closed end another inlet conduit 14 into which is connected air inlet conduit 15, flow of air or other oxygen-containing gas through which is controlled by valve 16. Conduit 14 is extended beyond its junction with conduit 15 as shown, the extension being equipped with a valve 17 to provide a means for draining the unit when not in use or between successive runs.

A perforated diffusion plate is inserted and bolted in place between the lower flange of section 2 and the flanged top of bottom section 9 to provide a means of evenly distributing the liquid-gaseous mixture which enters the bottom of the unit.

The topmost portion of the oxidation unit may conveniently comprise three sections 18, 19 and 20, each of which is flanged and bolted together as previously described. A distributor plate, which may include a bubble cup and downcomer, is positioned between the upper flange of section 5 and the lower flange of section 18. To sections 18 and 19 there is connected a high-pressure sight glass 21 for indicating the level of liquid in the upper part of the unit.

The upper closed end of section 20 is provided with an outlet conduit 22 adapted to conduct vapors and gas evolved from the top of the unit to cyclone separator 23 where any entrained liquid is separated from the mixture and conveyed back into the upper part of the oxidation unit at section 18 through conduit 24, the latter being so formed at its end as to provide a liquid seal in proximity to its junction with section 18.

Cyclone separator 23 is also provided with an outlet conduit 25 which conveys gaseous and vaporous materials to water-cooled condenser 26 of appropriate size and design, cooling medium for which is supplied through inlet 27 and emerges through outlet 28. Condenser 26 is also connected through conduit 29 and sight glass 30 to product receiver 31, the latter also being provided with a sight glass 32 for indicating the level therein. The product receiver is also equipped with valved conduit 33 for withdrawing product therefrom as desired.

Vapors not condensed in condenser 26 may find their way in the direction indicated by the arrows, through conduits 34, 35 and 36, into the bottom of scrubber 37 which may take the form of a stainless steel tube of appropriate diameter packed with a liquid distributing material such as berl saddles or Raschig rings. Scrubber 37 is provided near its upper closed end with conduit 38 through which glacial acetic acid is supplied in metered amounts passing in countercurrent to the vapor-gas stream ascending in 37 and thereby dissolving out any portions of products or reactants which may have escaped entrapment in separator 23 or condenser 26.

The lower end of scrubber 37 is connected, through conduit 38', sight glass 39 and conduit 40 with bottom section 9 of the oxidation unit. Conduit 40 may be provided with liquid seal 41 through which the glacial acetic acid from scrubber 37 may be fed to the oxidation unit to maintain the acid content of the reaction mixture at the desired value.

Scrubber 37 is also provided at its upper end with a vapor or gas outlet conduit 42 connected as shown to the lower portion 43 of water scrubber 44 through junction with conduit 45, which also connects the upper part of scrub receiver 46 with the water scrubber. Means is thus provided through conduit 45 for permitting any entrapped gases or vapors to escape from the scrub receiver into the water scrubber. The scrub receiver is equipped with sight glass 47 and a valved outlet conduit 48 for withdrawing material therefrom as desired. The scrub receiver is also directly connected to water scrubber by means of conduit 49.

The water scrubber has connected to its upper end a valved water feed line 50 and is also provided with outlet conduit 51 which provides means for escape of non-condensables from the system. This conduit 51 is provided with jet valve 52 and is also provided with auxiliary pressure control means through the agency of conduit 53 provided with pressure control valve 54.

The operation of the apparatus when used to carry out the process of my invention will be apparent on inspection. In starting oxidation unit 4 is filled somewhat less than full with catalyst solution, which may conveniently take the form of a 3% solution of cobaltous acetate in glacial acetic acid. Air valve 16 is opened slightly and aldehyde feed is put on the unit by opening the valve in feed line 12. It will, of course, be understood that a suitable cooling medium such as water is supplied to the several coils of the unit and that the thermometers are in place in the respective thermometer wells for taking readings of the temperature of the solution.

If the catalyst solution does not become active, as indicated by change in color from pink to green, after the elapse of several hours, it may be necessary to supply steam to the coils instead of cooling medium thus to raise the temperature to approximately 60° C. When the catalyst has become active, it is generally desirable to add more cobalt acetate to bring the concentration up to approximately 6%. The amount of catalyst dissolved in the original solution will vary, not only with the particular catalyst selected, but also with the temperature and various other conditions. Suffice it to say that a few per cent of the material is generally sufficient for effective operation.

Once the catalyst has been activated, the material to be oxidized is introduced into the oxidation unit through conduit 13 and the aldehyde and air feeds are adjusted so as to provide the proper proportion of each material to perform their respective functions. In general, the rate of aldehyde introduction will be controlled so as to maintain the catalyst at all times in an active condition, while the rate of oxygen feed will be so regulated as to provide a slight excess of oxygen over and above that actually required for oxidation of the material being converted, as indicated by a few per cent of free oxygen in the effluents from the process.

Assuming the material to be oxidized, and aldehyde and air or oxygen, are being continuously fed, oxidation product will be vaporized and continuously conveyed out of the unit through conduit 22. A certain amount of gaseous and liquid material also passes out of the device along with the product, the liquid portions being separated from the gaseous or vaporous portions in cyclone separator 23 and eventually returned to the zone of oxidation through conduit 24.

The major portion of the condensable vapors, consisting mainly of the products of oxidation, are condensed in condenser 26 and find their way into product receiver 31 from which they are continuously removed at such a volume rate as to maintain the proper liquid level in the oxidation unit. The uncondensable gases and vapors are conveyed through conduits 34, 35 and 36 into acid scrubber 37, passing upwardly in countercurrent to a stream of glacial acetic acid. Any vaporized materials which have escaped condensation in condenser 26 are thus dissolved in the acetic acid and returned to the oxidation unit via conduit 40. The amount of acid thus introduced into the unit is so regulated as to maintain the acid concentration in the reaction liquid at approximately 85% or above, it having been found that this is an acid concentration, which, in general, gives the most satisfactory operation.

Non-condensable gases such as carbon dioxide and nitrogen (from air, if air is used as the source of oxygen) emerges from the top of scrubber 37 through conduit 42 and eventually into water scrubber 44, where they meet a down-coming stream of water, introduced through conduit 50, which dissolves out any water-soluble values which may have escaped previous separation steps. Non-condensables pass out of the system through valve 52.

The product of the process, which may be in the form of a more or less dilute acid or other oxidation product, may be removed from product receiver 31 and conveyed to any desired concentrating or purifying steps for conversion into the desired concentrated acid or other product. Likewise, the acid or other materials which have been scrubbed out of the vapor-gas stream passing through scrubber 44 may be removed from scrub receiver 46 through valved conduit 48 and treated in any appropriate manner for recovery of the dissolved materials.

As to the matter of temperature, I may conveniently carry out oxidations in accordance with my process, when operated at atmospheric pressure, within the range of -5° C. to 90° C. Since the reactions involved are exothermic, it is generally necessary continuously to supply a cooling medium to the coils of the oxidation unit in order to maintain the temperature within the indicated limits. However, in some cases, as for example, in oxidizing materials of high boiling points, or in accelerating the oxidation reaction, it may be desired to employ higher temperatures than those indicated. When such higher temperatures are employed, pressures in excess of atmospheric will be desirable in order to prevent boiling away, either of the acetic or other aliphatic acid catalyst solvent or of the product of the reaction itself. When employing apparatus such as described herein for the carrying out of oxidation reactions at higher temperatures, say in the range of 100° C. to 150° C., it will be understood that valves 52 and 54 will be closed and provision made for maintaining the desired pressure in the system. Pressure operation will of course require that reactants and scrubbing media be introduced under a pressure sufficient to compensate or balance the pressure existing in the system. While the pressure may under such circumstances vary over a wide range, depending on the temperature it is desired to maintain in the oxidation zone and on various other factors, in general pressures ranging from atmospheric to 3 to 4 atmospheres are satisfactory.

My invention will be more fully understood by

reference to a number of specific examples illustrating typical conversions carried out in accordance therewith.

Example I.—Oxidation of diethyl ether to acetic acid

A catalyst solution was prepared by dissolving cobalt acetate in acetic acid in such an amount as to obtain a 3% concentration of the cobalt salt in the acid. This solution was fed into an oxidation unit such as that illustrated in the single figure of the drawing until the unit was approximately two-thirds full. A small amount of acetaldehyde was then introduced and air was also permitted to flow into the bottom of the unit along with the aldehyde. Since at ordinary temperature the catalyst did not become active, steam was put on the coils of the unit to bring the solution temperature up to approximately 60° C., whereupon the catalyst became active as indicated by a change in the color of the solution from pink to green. At this time, diethyl ether was fed into the unit at the rate of 21 pounds per hour and the aldehyde feed was so regulated as to supply 29 pounds of acetaldehyde per hour. Once the process was in full operation glacial acetic acid was introduced into the bottom section of the unit at the rate of approximately 130 pounds per hour, this rate of acid feed being sufficient to maintain the concentration of acid in the reaction mixture at 80 to 85% or higher. By operating under the above conditions it was found that 32.2% of the diethyl ether introduced was converted to acetic acid.

Example II.—Oxidation of di-normal propyl ether to propionic acid

A catalyst solution was prepared and activated in a manner to that described in Example I. When activation was complete, di-normal propyl ether was fed into the unit at the rate of 29 pounds per hour and the aldehyde feed was so regulated as to supply 29 pounds of acetaldehyde per hour. Glacial acetic acid was introduced into the bottom section of the unit at a rate of approximately 135 pounds per hour, this being sufficient to maintain the concentration of acid in the reaction mixture at 85% or better. By operating under these conditions, 30.1% of the di-normal propyl ether introduced was converted to propionic acid.

Example III.—Oxidation of di-normal butyl ether to acetic, propionic and butyric acids

A catalyst solution was prepared by dissolving cobalt acetate in acetic acid in such an amount as to obtain approximately a 3% concentration of the cobalt salt. This solution was fed into an oxidation unit, such as that illustrated in the drawing, until the unit was approximately $\frac{2}{3}$ full. Acetaldehyde feed was then introduced and air was permitted to flow in at the bottom of the unit. After an hour a temperature rise was noticed and water was used on the coils to maintain the temperature at 60–70° C. After another hour, 3% more cobalt acetate was added, so as to obtain approximately a 6% concentration of the cobalt salt. After this addition, operation was continued for two hours more with acetaldehyde feed alone and with air flowing through the unit, and maintaining the temperature at 60–70° C. At this time di-normal butyl ether was fed into the unit at a rate of 30 pounds per hour and acetaldehyde at the rate of 39 pounds per hour. Glacial acid feed was also

introduced into the bottom of the unit at the rate of approximately 130 pounds per hour so as to maintain the concentration of acid in the reaction mixture at 85–90%. By operating under the above conditions it was found that 28% of the di-normal butyl ether was converted to butyric acid, 0.5% to propionic acid and 0.5% to acetic acid.

Example IV.—Oxidation of diethyl acetal of acetaldehyde to acetic acid

A catalyst solution was prepared and activated in a manner similar to that described in Example III. After an active catalyst was obtained, the diethyl acetal of acetaldehyde was fed into the unit at the rate of 27 pounds per hour and acetaldehyde at a rate of 21 pounds per hour. Glacial acetic acid was also fed into the unit at the rate of 135 pounds per hour so as to maintain the concentration of acid in the reaction mixture at 85–90%. By analysis of the products from this continuous oxidation it was found that 25% of the diethyl acetal was converted to acetic acid.

Example V.—Oxidation of dibenzyl ether to benzoic acid

A catalyst solution was prepared and activated in a manner similar to that described in Example III. When the catalyst was in a very active state, dibenzyl ether was fed into the unit at the rate of 39 pounds per hour and acetaldehyde at a rate of 44 pounds per hour. Glacial acetic acid was also fed into the unit at the rate of approximately 125 pounds per hour so as to maintain the concentration of acid in the catalyst solution at 85% or above. Operation was carried out at 75–80° C., and due to the fact that benzoic acid will not distill at this temperature, it was necessary to overflow the catalyst solution from the top of the unit (by an appropriate outlet not shown on the drawing), cool it down to crystallize out the benzoic acid, filter and return the catalyst solution to the unit. The benzoic acid thus obtained was recrystallized for further purification and then sublimed for final purification. By continuous oxidation in this manner, it was found that 22.5% of the dibenzyl ether was converted to benzoic acid.

What I claim is:

1. A process for the direct oxidation of an organic compound containing an ether linkage having the graphic formula $R-O-R'$ wherein R and R' each is a radical selected from the group consisting of the alkyl and aralkyl groups to the corresponding carboxylic acid which comprises treating a solution of a metal ion in a lower aliphatic acid with an aldehyde and a gaseous oxidizing medium to form a catalyst solution, simultaneously introducing material amounts of the ether-type compound and additional aldehyde into the solution, oxidizing the content of ether-type compound of the resulting solution of catalyst compound and aldehyde by treating the solution with gaseous oxidizing medium, maintaining the solution under temperature and pressure conditions during introduction of the oxidizing medium such that the solution is maintained in the liquid phase, and thereafter recovering the acid produced.

2. A process for the direct oxidation of an organic compound containing an ether linkage having the graphic formula $R-O-R'$ wherein R and R' each is a radical selected from the

group consisting of the alkyl and aralkyl groups to the corresponding carboxylic acid which comprises treating a solution of a metal ion in a lower aliphatic acid with an aldehyde and a gaseous oxidizing medium to form a catalyst solution, simultaneously introducing material amounts of the ether-type compound and additional aldehyde into the solution, oxidizing the content of ether-type compound of the resulting solution of catalyst compound and aldehyde by treating the solution with a gaseous oxidizing medium, maintaining the solution, during introduction of the oxidizing medium, at a temperature within the range of 10° C. to 150° C. and at a pressure such that the solution remains in the liquid phase, and thereafter recovering the acid produced.

3. A process for the direct oxidation of diethyl ether to acetic acid which comprises treating a solution of a metal ion in a lower aliphatic acid with an aldehyde and a gaseous oxidizing medium to form a catalyst solution, simultaneously introducing material amounts of the ether and additional aldehyde into the solution, oxidizing the content of ether of the resulting solution of catalyst compound and aldehyde by treating the solution with a gaseous oxidizing medium, maintaining the solution under temperature and pressure conditions during introduction of the oxidizing medium such that the solution is maintained in the liquid phase, and thereafter recovering the acid produced.

4. A process for the direct oxidation of an acetal which comprises treating a solution of a metal ion in a lower aliphatic acid with an aldehyde and a gaseous oxidizing medium to form a catalyst solution, simultaneously introducing material amounts of the acetal and additional aldehyde into the solution, oxidizing the content of acetal of the resulting solution of catalyst compound and aldehyde by treating the solution with a gaseous oxidizing medium, maintaining the solution under temperature and pressure conditions during introduction of the oxidizing medium such that the solution is maintained in the liquid phase, and thereafter recovering the acid produced.

5. A process for the direct oxidation of diethyl ether to acetic acid which comprises dissolving cobalt acetate in acetic acid to obtain an approximately 3 per cent solution of the cobalt salt in the acid, treating the solution with acetalde-

hyde and a gaseous oxidizing medium to form an active catalyst solution, simultaneously introducing material amounts of diethyl ether and additional acetaldehyde into the solution, oxidizing the content of diethyl ether of the resulting solution by continuing to treat the solution with the gaseous oxidizing medium while maintaining the solution under a temperature of approximately 60° C. and a pressure such that the solution is maintained in the liquid phase and thereafter recovering the acetic acid formed in the oxidation reaction.

6. A process for the direct oxidation of di-normal propyl ether to propionic acid which comprises dissolving cobalt acetate in acetic acid to obtain an approximately 3 per cent solution of the cobalt salt in the acid, treating the solution with acetaldehyde and a gaseous oxidizing medium to form an active catalyst solution, simultaneously introducing material amounts of di-normal propyl ether and additional acetaldehyde into the solution, oxidizing the content of di-normal propyl ether of the resulting solution by continuing to treat the solution with the gaseous oxidizing medium while maintaining the solution under a temperature of approximately 60° C. and such a pressure that the solution is maintained in the liquid phase and thereafter recovering the propionic acid formed in the oxidation reaction.

DAVID C. HULL.

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