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[54] PROCESS FOR ISOLATING ACRYLIC ACID FROM THE REACTION GASES OBTAINED BY THE OXIDATION OF PROPYLENE OR A ACROLEIN

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[51] **Int. Cl.** **C07c 57/04**

[58] **Field of Search** ..... 260/533 U, 530 U

[56] **References Cited**

UNITED STATES PATENTS

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FOREIGN PATENTS OR APPLICATIONS

948,687	2/1964	Great Britain	260/533 U
999,836	7/1965	Great Britain	260/530 U
967,485	8/1964	Great Britain	260/533 U

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[57] **ABSTRACT**

Process for isolating acrylic acid from the reaction gases obtained by the oxidation of propylene or acrolein, wherein the hot reaction gases, which have a temperature of 300° to 600°C, are pre-cooled, wherein the resulting aqueous acrylic acid solution is heated to be freed from the acrolein contained therein, and wherein the resulting vapors, together with non-liquefied, acrolein-containing residual gas, are returned to the oxidation zone, the said process comprising the steps of pre-cooling the reaction gas inside a heat exchanger down to a temperature of 100° to 200°C, subjecting thereafter the pre-cooled gases to direct scrubbing with water having a temperature of 10° to 50°C and thereby cooling them further down to a temperature between 30° and 90°C, and heating the resulting aqueous, 10 to 45 percent acrylic acid solution to a temperature of about 100° to 120°C to expel residual acrolein therefrom.

6 Claims, 2 Drawing Figures

FIG. 1

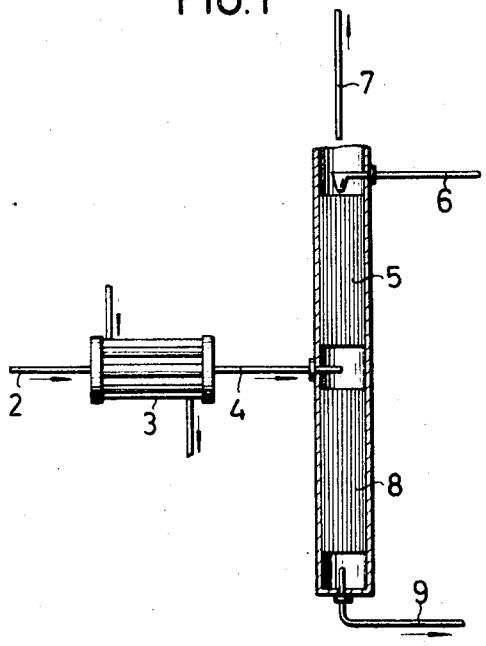
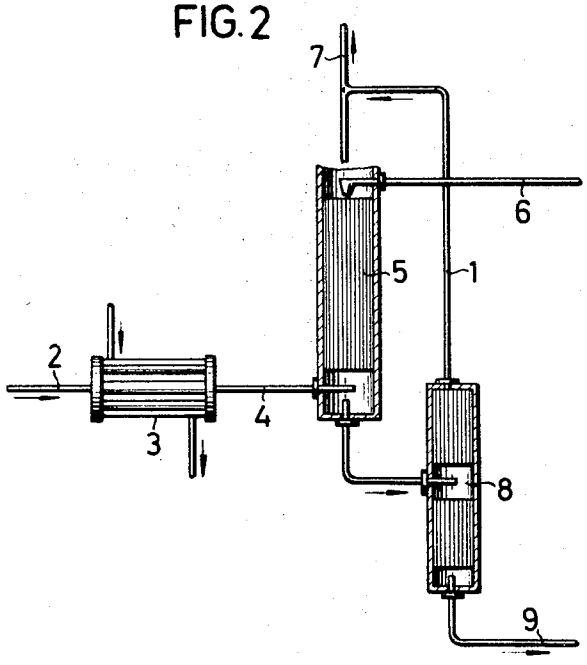


FIG. 2



PROCESS FOR ISOLATING ACRYLIC ACID FROM THE REACTION GASES OBTAINED BY THE OXIDATION OF PROPYLENE OR A ACROLEIN

The catalytic oxidation of propylene or acrolein in the gas phase is known to be an important commercial process for the production of acrylic acid. In this process, propylene and/or acrolein are reacted with oxygen in the presence of oxidation catalysts (for example, oxides of the elements comprising molybdenum, chromium, vanadium, iron, cerium, titanium, nickel, tungsten, bismuth, tin, antimony, cobalt and phosphorus), at temperatures between 300°and 600°C, to give acrylic acid. The reaction which is strongly exothermal, calls for the presence of inert gases as a diluent. These include, for example, the carbon oxides evolved by decomposition during the reaction or—in discontinuous processes—the nitrogen included in the air as the oxidizing agent. To increase the selectivity of this reaction, it is furthermore necessary to provide for the presence of steam, which is added to the starting gas in a proportion of 5 to 60 percent by volume. The carbon monoxide and steam undergo conversion and partially produce hydrogen and carbon dioxide. These latter gases are also inert diluents. The reaction results in the formation of a gas mixture with a content of acrylic acid not higher than 0.2 up to a maximum of 3 percent by volume, depending on the reaction conditions. Unreacted propylene and/or acrolein are isolated from the acrylic acid and returned to the reactor.

The isolation of acrylic acid has been achieved heretofore by low temperature cooling of the reaction gases. For example, reference is made to British Patent 948,687 and its disclosure not only of acrylic acid production by propylene-oxidation, which does not form part of the present invention, but also of acrylic acid-isolation from the reaction gases originating from the oxidation of propylene and acrolein, wherein the reaction gases, that have a temperature of 280°to 450°C and are formed substantially of propylene, acrolein, acrylic acid, oxygen, inert gases and steam, are indirectly cooled down to a temperature of about 10°C, wherein the resulting aqueous acrylic acid solution is heated, for example by injecting steam, to expel the acrolein contained therein, and wherein the resulting vapors, together with non-liquefied acrolein-containing residual gas, are returned, after addition of fresh propylene, oxygen and steam, to the oxidation zone. As taught in British Patent 953,763, the low temperature cooling of the reaction gases can also be achieved by scrubbing them directly with an acrylic acid solution pre-cooled, for example to a temperature of 5°to 10°C, and thereafter cooling them indirectly in low temperature-heat exchangers. In either of these two processes, not only the acrylic acid, but also the total steam, comprised of the steam added as the diluent and the steam evolved during the reaction, as well as the bulk of unreacted acrolein are subject to condensation; the acrolein is required to be distilled off from the aqueous acrylic acid solution and to be added to the starting gas, which in turn is required to be saturated again by means of steam.

Though considerable commercial and technical disadvantages comprising the erection of large refrigerating facilities and considerable loss in energy, originating from the cooling and subsequent evaporation steps, have been found to be associated with the isolation of acrylic acid by low temperature cooling, this type of process is continued to be used in attempt to obviate losses of acrolein and acrylic acid that would accrue when the compounds were allowed to undergo further reaction. The reason is that acrolein in aqueous solution, in the presence of an acid, can be found to react irreversibly, and elevated temperatures favor this, in some type of a simultaneous aldol- and dehydration reaction with the resultant formation of pyrane-derivatives, i.e., so-called acrolein dimers and trimers. At the same time, the homo and copolymerization of acrolein and acrylic acid are found to be catalyzed by the elevated temperatures and the oxygen present in the gas.

The disadvantages reported above are obviated in the process of the present invention, which enables acrylic acid to be recovered almost quantitatively in technically simple manner and under economic conditions, without any loss of acrolein, from the reaction gases obtained by the oxidation of propylene and/or acrolein, by extraction of those gases with water at elevated temperature. The temperature at which the acrylic acid is extracted, is selected to obviate liquefaction of the acrolein and steam needed for the reaction. After the propylene or acrolein and the oxygen consumed in the reaction have been replaced with fresh gases, it is possible to return the reaction mixture to the reactor, without any further addition of steam. The acrylic acid is obtained in the form of an aqueous solution free of acrolein.

The process of the present invention will now be described with reference to FIGS. **1** and **2** of the accompanying drawing.

Hot reaction gas with a temperature of about 300°to 600°C leaving the reactor, is caused to travel through line **2** to heat exchanger **3** to be cooled therein down to a temperature of 100°to 200°C, preferably 110°to 150°C. The heat set free during that operation is used for the generation of steam. The gas then flows through line **4** into column **5**—usually a tray or packed column—in which the gas is cooled down to a temperature lower than 100°C, preferably 30°up to 90°C, by means of fresh water supplied through line **6** near the column head, whereby acrylic acid is extracted from the reaction gas. The gas enters the column at a constant temperature, but the fresh water-temperature, usually 10°to 50°C, preferably 20°to 40°C, is regulated in each particular case, depending on the outlet-temperature desired for the gas, at the head of column **5**. The gas outlet-temperature in turn determines the steam partial pressure desired to prevail in the issuing gas. The quantity of fresh water needed is determined primarily by the concentration desired for the acrylic acid solution, usually 10 to 35 percent. In the case of rather prolonged operation periods, it has been found advantageous to add to the fresh water small proportions of inhibitors for unsaturated compounds, e.g., hydroquinone, methylene Blue, pyrogallol, p-tertiary butyl pyrocatechol, tertiary butyl catechol, thiodiphenyl amine, butyl mercaptane, thiglycolic acid, mercaptobenzthiazol, copper acetate, copper acrylate or copper oleate. The acrylic acid solution leaving column **5**, is freed from traces of dissolved acrolein by heating the said solution to 100°to 120°C in stripping column **8**, that is connected either directly to scrubbing column **5**

(FIG. 1) or connected to be parallel with that column 5 (FIG. 2). As shown in FIG. 1, gaseous acrolein is introduced either directly into the ascending reaction gas stream, or is supplied through line 1 to gas stream 7, as shown in FIG. 2. Acrylic acid solution free from acrolein can be withdrawn from the bottom portion of column 8. Line 7 is the discharge line for gas freed from acrylic acid, the gas containing all of the unreacted acrolein, inert gases and the desired proportion of steam. After the addition of fresh propylene or acrolein and oxygen, the gas is returned to the reactor.

The acrylic acid can be extracted at atmospheric pressure, or under slightly elevated or reduced pressure, preferably under a pressure between 0.5 and 3 atmospheres absolute.

The advantage associated with the isolation of acrylic acid by the process of the present invention is seen to reside in the energetically well-balanced conditions under which the process is carried out. The costly low-temperature cooling and subsequent re-evaporation are replaced by an extraction step which requires no more than the use of commercially inexpensive water of circulation. The short sojourn time of polymerizable substances inside the column obviates their polymerization, even at elevated temperatures and ensures high yields of monomeric acrylic acid.

The present process for isolating acrylic acid from reaction gases obtained by the oxidation of propylene or acrolein, wherein the hot reaction gases, which have a temperature of 300°to 600°C and are formed essentially of acrolein, acrylic acid, oxygen, inert gases, steam and possibly propylene, are cooled, wherein the resulting aqueous acrylic acid solution is heated to expel the acrolein contained therein, and wherein the resulting vapors, together with non-liquefied, acrolein-containing residual gas, are returned to the oxidation zone, comprises more especially pre-cooling the hot reaction gases inside a heat exchanger down to a temperature of 100°to 200°C, preferably 110°to 150°C, subjecting thereafter the said pre-cooled gases to direct scrubbing with water having a temperature of 10°to 50°C, preferably 20°to 40°C and thereby cooling them further down to a temperature between 30°and 90°C, and heating the resulting aqueous, 10 to 45 percent acrylic acid solution to a temperature of about 100°to 120°C to expel residual acrolein therefrom. The acrylic acid solution can be used in admixture with 0.001 to 2 percent by weight of a customary stabilizer. The pre-cooled reaction gases are preferably scrubbed with 50 to 500 cc water per normal cubic meter (measured at N.T.P.) reaction gas.

EXAMPLE 1

1,037 normal liters/hour reaction gas having a temperature of 410°C, formed of propylene, oxygen and inert gases as well as of 1.5 percent by volume acrylic acid, 4.8 percent by volume acrolein and 23.2 percent by volume (=241 normal liters) steam, were pre-cooled inside a heat exchanger, under a pressure of 1.2 atmospheres absolute, down to a temperature of 110°C. The pre-cooled reaction gas was introduced thereafter into a tray column 80 cm wide with 24 trays, which was fed, per hour, with 160 cc water at 20°C, supplied near the column head. A gas temperature of 64°to 65°C was found to prevail in the column. This enabled 973 normal liters, per hour, of a gas mixture containing propylene, oxygen and inert gases as well as 5.1 percent by volume acrolein (=99 percent of the acrolein used), 19.8 percent by volume (=193 normal liters) steam and very minor traces of acrylic acid, to be removed at the column head and returned to the reactor. The 241 normal liters steam contained in the initial reaction gas mixture, were comprised of 193 normal liters cycled steam plus 48 normal liters reaction steam, which was required to be condensed during each passage and appeared in the acrylic acid solution.

The hot acrylic acid solution leaving the tray column, was introduced into a packed column (30 ×800 mm), the bottom portion of which was maintained at a temperature of 103°to 105°C to evaporate last traces of acrolein. The acrylic acid solution was stabilized by the addition of 0.1 percent by weight methylene Blue. In this manner, there were obtained, per hour, 249 grams of an aqueous, 19.7 percent by weight acrylic acid solution, corresponding to a yield of 98 percent, referred to the acrylic acid contained in the reaction gas.

EXAMPLE 2

2,600 normal liters/hour of a reaction gas mixture having a temperature of 450°C, formed of propylene, oxygen and inert gases as well as of 1.76 percent by volume acrylic acid, 6.92 percent by volume acrolein and 21.3 percent by volume (=554 normal liters) steam, were pre-cooled down to a temperature of 140°C, substantially in the manner set forth in Example 1, under a pressure of 1.1 atmospheres absolute, and introduced thereafter into the tray column (extraction column), which was fed, per hour, with 200 cc water at 20°C, supplied near the column head. A gas temperature of 63°to 65°C was found to prevail in the column. This enabled 2,467 normal liters of a gas mixture formed of propylene, oxygen and inert gases as well as of 7.3 percent by volume acrolein, 18.95 percent by volume (=467 normal liters) steam and very minor traces of acrylic acid, to be removed at the column head and returned to the reactor. The 554 normal liters steam contained in the initial reaction gas mixture, were comprised of 467 normal liters cycled steam plus 87 normal liters reaction steam, which was required to be condensed during each passage and appeared in the acrylic acid solution.

The hot acrylic acid solution leaving the tray column, was introduced into the second column, the bottom portion of which was maintained at a temperature of 105°to 106°C to evaporate last traces of acrolein, which is introduced into the cycled gas. The acrylic acid solution was stabilized by the addition of 0.05 percent by weight methylene Blue. In this manner, there were obtained, per hour, 411 grams of an aqueous, 34.4 percent by weight acrylic acid solution, corresponding to a yield of 96.2 percent, referred to the acrylic acid contained in the reaction gas.

The above examples shown that the content of steam in the gas cycled substantially does not depend on the water-content of the aqueous acrylic acid solution.

We claim:

1. In the process for isolating acrylic acid from the reaction gases obtained by the oxidation of at least one member selected from the group consisting of propylene and acrolein, wherein the hot reaction gases,

which have a temperature of 300° to 600°C and are formed essentially of acrolein, acrylic acid, oxygen, inert gases and steam, are cooled, wherein the resulting aqueous acrylic acid solution is heated to expel the acrolein contained therein, and wherein the resulting vapors, together with non-liquefied acrolein-containing residual gas, are returned to the oxidation zone, the improvement which comprises pre-cooling the hot reaction gases inside a heat exchanger down to a temperature of 100° to 200°C, subjecting thereafter the said pre-cooled gases in a tray or packed column to direct scrubbing with water having a temperature of 10° to 50°C and thereby cooling them further down to a temperature between 30° and 90°C so as to provide a residual gas for return to the oxidation zone which includes steam in an amount of at least 5 percent by volume of the gas subjected to oxidation, and heating the resulting aqueous, 10 to 45 percent acrylic acid solution to a temperature of about 100° to 120°C to expel residual acrolein therefrom and returning the resultant vapors together with the non-liquefied residual gas, which contains acrolein and the steam which is needed for the reaction, to the oxidation zone.

2. The process of claim 1, wherein the said reaction gases also contain propylene.

3. The process of claim 1, wherein the said reaction gases are pre-cooled inside the said heat exchanger down to a temperature of 110° to 150°C.

4. The process of claim 1, wherein the scrubbing water has a temperature of 20° to 40°C.

5. The process of claim 1, wherein the said pre-cooled reaction gases are scrubbed with 50 to 500 cc water per normal cubic meter reaction gas.

6. The process of claim 1, wherein the aqueous acrylic acid solution is stabilized by the addition of 0.001 to 2 percent by weight of a customary stabilizer.

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