Feb. 5, 1957 N. C. ROBERTSON ET AL 2,780,654

AIR OXIDATION OF ISOBUTYLENE

Filed Oct. 22, 1952 2 Sheets-Sheet 1

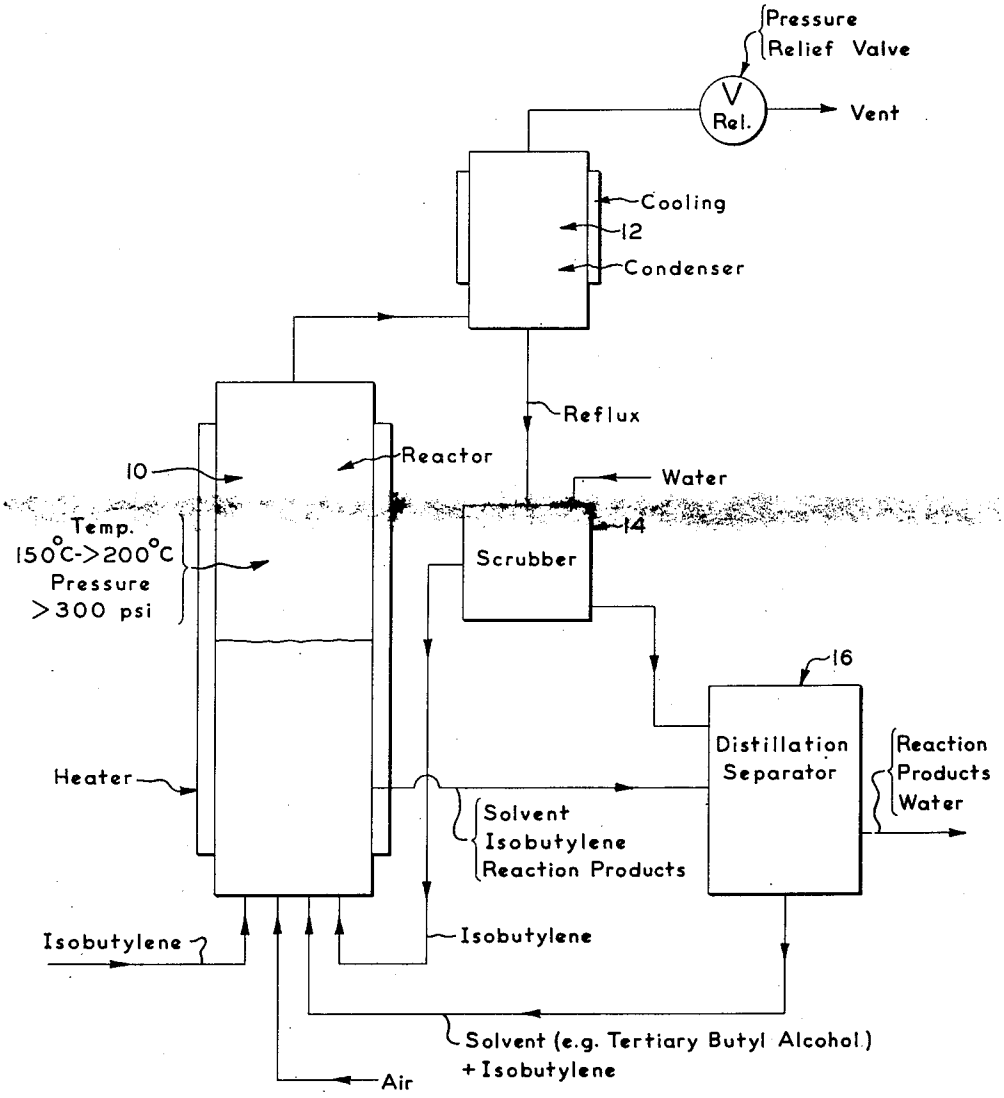


FIG. 1

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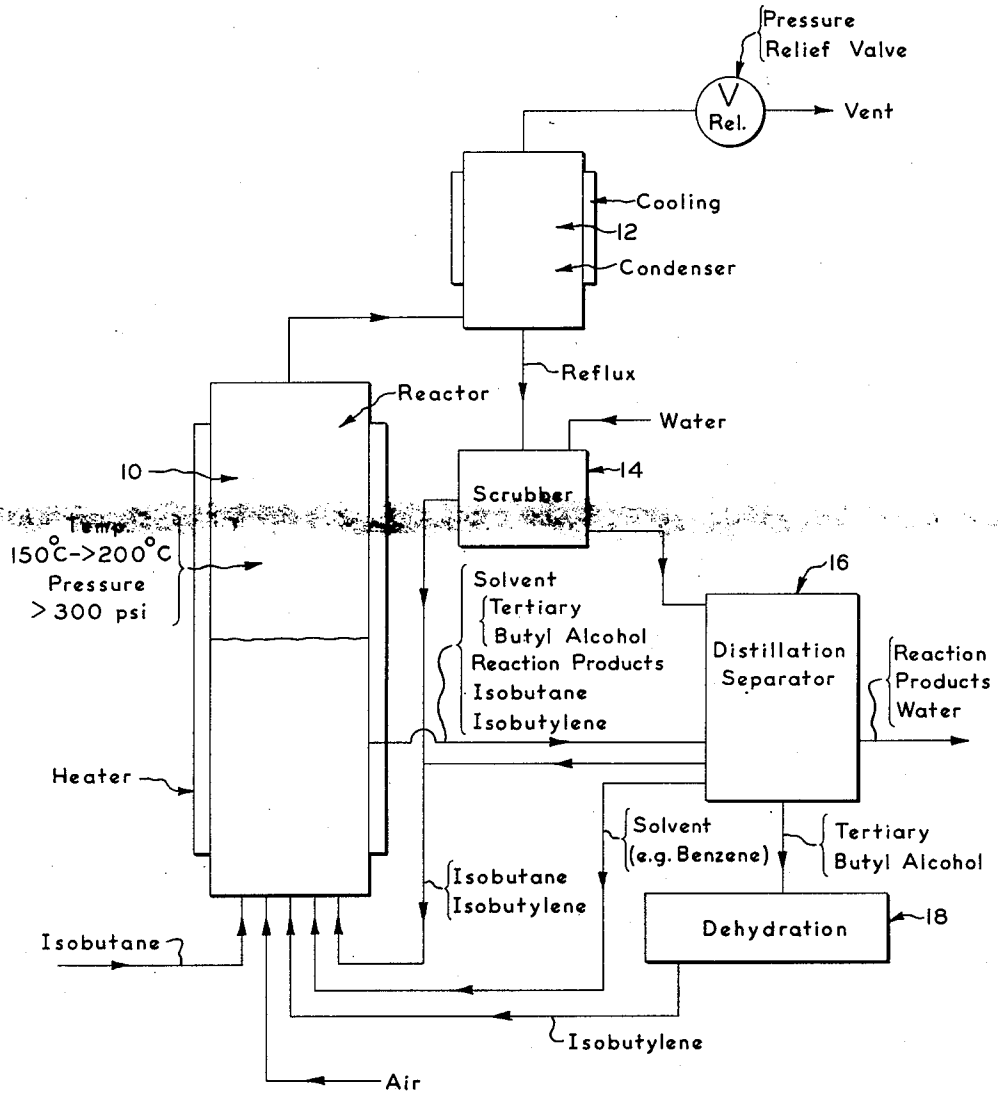


FIG. 2

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AIR OXIDATION OF ISOBUTYLENE

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1 Claim. (Cl. 260—635)

This invention relates to the production of chemicals and more particularly to the production of glycols.

A principal object of the present invention is to produce glycols in good yields by the liquid phase oxidation of normally gaseous hydrocarbons in an organic solvent with an elemental-oxygen-containing gas.

Another object of the invention is to provide a process of the above type which is particularly adapted to the production of isobutylene glycol by the oxidation of isobutylene.

Still another object of the invention is to provide an integrated process which produces high yields of isobutylene glycol when utilizing isobutane as a starting material and air as the oxidizing agent.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and the order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

Fig. 1 is a diagrammatic flow sheet illustrating one embodiment of the invention; and

Fig. 2 is a diagrammatic flow sheet illustrating another embodiment of the invention.

In the present invention a normally gaseous hydrocarbon is converted to the corresponding glycol by oxidation in the liquid phase at a relatively high pressure. In one preferred embodiment of the invention the gaseous hydrocarbon is an unsaturated aliphatic compound, a particular preferred embodiment including isobutylene as the hydrocarbon to be converted to the glycol. In order to obtain a high yield of the glycol, it is desired that the pH of the solution be maintained on the order of at least 5 or above. This has the advantage that, during oxidation, few acids are formed, it being believed that the formation of acids leads to degradation of the products. This pH is preferably maintained at 5 or above by the use of a buffer solution which is maintained in sufficient concentration to neutralize any acids formed. It is also preferable that the oxygen fed to the reactor be controlled so that no excess oxygen exists above the reaction mixture. This has the advantage of both diminishing the possibility of obtaining hazardous concentrations of explosive gases and also of preventing excessive oxidation of the isobutylene glycol which is the desired product of the reaction.

In a preferred embodiment of the invention the conditions of reaction are so adjusted that polymerization of the feed and/or the various intermediate by-products of the reaction is minimized. In one aspect of the invention polymerization is substantially eliminated by the

use of a low concentration of the olefin in the solvent. For example, it has been found that, when the mole percent of the olefin is less than about 30% of the solvent during the oxidation, the creation of undesirable polymeric by-products is minimized. In another embodiment of the invention, the elimination of polymeric materials may be achieved by the use of inhibitors, one preferred type of inhibitor being nitrobenzene.

In another embodiment of the invention, the gaseous hydrocarbon used as a starting material is a saturated aliphatic hydrocarbon, in particular isobutane, the isobutane being converted to isobutylene which is subsequently oxidized to isobutylene glycol.

The invention will be first described in connection with the oxidation of isobutylene to isobutylene glycol, it being understood that the invention is by no means limited by this specific illustration. This preferred embodiment of the invention is set forth in the following nonlimiting example.

Example I

972 grams of a mixture of tertiary butyl alcohol and 810 grams H_2O (as a solvent) together with 1.7 grams of a manganese propionate catalyst and 40 cc. of a pH 5 phosphate buffer solution are charged to a high pressure reactor **10**. 180 grams of isobutylene are now passed into the reactor **10** and the temperature thereof is raised to about 125° C. Air is fed into the reactor until the pressure reaches 690–710 p. s. i., the temperature being raised to 175°–180° C. during this addition. A steady rate of air feed of about four standard cubic feet per hour is commenced. An automatic pressure relief valve vents nitrogen, oxides of carbon, and a small amount of uncondensed reactant downstream of a condenser **12** to maintain 700 p. s. i. in the reactor. Isobutylene is fed at varying rates to roughly replenish the consumption. 60 grams of isobutylene are fed in this manner during a six hour run.

After termination of the run, the reaction mixture is neutralized and fractionated to obtain the following materials indicated as grams of product per 100 grams of isobutylene consumed:

Acetone 27.6 grams; methalyl alcohol 4.96 grams; isobutylene glycol 56.1 grams; formic acid 17.4 grams; acetic acid 4.34 grams; isobutyric acid 10.60 grams; methanol 0.83 gram; 2-butanone 17.7 grams; methyl acetate 1.47 grams; isobutyl acetate 0.51 gram; carbon monoxide 4.21 grams; carbon dioxide 7.35 grams; and polymeric material 13.5 grams. In this specific example 222 grams of product were obtained and 158 grams of isobutylene were consumed.

In the above specific example the concentration of the olefin is rather lean during the oxidation. While not essential to the operation of the process, this aspect of the invention has been found to greatly decrease the amount of polymeric material produced per hundred grams of olefin consumed. In this connection it has been found that best results are achieved when the mole percent of the olefin in the reaction zone is maintained less than about 30% of the reaction mass. This concentration is preferably less than about 20% and in the above example was actually maintained below 15%.

In the above example the solvent was illustrated as a mixture of water and tertiary butyl alcohol. Equally good results are obtained if tertiary butyl alcohol is used alone as the solvent. Benzene and other organic solvents can be utilized in place of the tertiary butyl alcohol.

One example of the use of benzene as an alternate solvent is given in the following nonlimiting example.

Example II

A similar oxidation run of isobutylene was made using

benzene as the solvent in place of the tertiary butyl alcohol used in Example I. The same conditions (of temperature, pressure catalyst, etc.) existed here as above. However, the concentration of isobutylene was about 42 mole percent of the amount of solvent. The products obtained from this reaction were isolated and determined to exist in the following concentrations (indicated as grams of product per hundred grams of isobutylene consumed):

Acetone 17.0 grams; tertiary butyl alcohol 2.6 grams; methallyl alcohol 1.4 grams; isobutylene glycol 29.4 grams; formic acid 8.3 grams; acetic acid 1.6 grams; isobutyric acid 1.2 grams; methanol 1.9 grams; 2-butanone 4.3 grams; mesityl oxide 2.4 grams; isobutyl acetate 4.2 grams; carbon monoxide 3.7 grams; carbon dioxide 2.7 grams; and polymeric material 49.8 grams.

As will be noted, the amount of polymeric material produced in this Example II is considerably in excess of the amount obtained in Example I. The formation of this polymeric material can be substantially inhibited by maintaining the olefin concentration low in the reaction mass in the same manner as discussed in connection with Example I. Naturally, inhibition of the polymer formations is desirable but is not necessarily essential to the commercial utility of the process.

When the process is operated on a continuous basis, the condenser **12** continuously refluxes isobutylene, isobutylene glycol and other oxygenated products to a water scrubber **14**. The refluxed isobutylene is separated from the remainder of the reflux in the scrubber **14** and is recycled to the bottom of the reactor **10**. From the scrubber **14** the reflux and the scrub water are directed into a distillation separation apparatus **16** (which may include several conventional styles) where the contained water and various reaction products are removed from the solvent (e. g., benzene or tertiary butyl alcohol) contained in the reflux stream. The solvent is recycled to the reactor **10**. As can be seen from Fig. 1 some of the liquid in the reactor **10** is also fed to the distillation apparatus **16** so as to provide for continuous removal of the various oxygenated products which are not carried off as vapors and condensed in the reflux condenser **12**.

While one specific example of the present invention has been given above, it is subject to wide variation without departing from the scope thereof. For example, the manganese propionate (of about 0.1% concentration) is a well-known oxidation catalyst. Other manganous salts or salts of oxides of metals of variable valence are equally effective. An important purpose of utilizing an oxidation catalyst is to prevent the creation of large concentrations of dangerously explosive hydroperoxides. It is believed that the metal walls of the reaction chamber may have sufficient catalytic effect to prevent the formation of such hydroperoxides. Similarly, while the use of a phosphate buffer solution (which is obtained by titrating a solution of trisodium phosphate with phosphoric acid) is quite effective, numerous other well-known buffer solutions may be employed. Equally, the pH of the solution may be kept above about 5 by use of an alkali such as sodium hydroxide which can be added as required during the reaction. The range of operating pressures and operating temperatures is quite broad and can be varied within considerable limits.

With regard to pressure it should be pointed out that it is preferably maintained above 300 lbs. per square inch, but that considerably higher pressures may be utilized where design considerations indicate the desirability of such higher pressures. The temperature within the reactor **10** may be varied between about 150° C. and above 200° C. or higher.

The specific procedure described for the oxidation of isobutylene to isobutylene glycol can be applied to olefins in general. Other olefins which may be oxidized to their respective glycols are ethylene, propylene and amylenes.

While the invention has been described with particular reference to preferred embodiments thereof wherein controlled concentrations of the olefin feed have been employed to prevent substantial polymer formation, other techniques may be equally employed. For example, polymerization inhibitors can be incorporated in the reaction mass so as to substantially reduce the amount of polymeric material formed. One such inhibitor, which has been found to be very effective, is nitrobenzene. One method of using such an inhibitor is set forth in the following nonlimiting example:

Example III

Fifteen hundred cubic centimeters of tertiary butyl alcohol (as a solvent) together with 1.4 grams of a manganese propionate catalyst, 40 cc. of a pH 5 phosphate buffer solution and 58.5 grams of nitrobenzene are charged to high pressure reactor 10. Eight hundred and fifty grams of isobutylene are now passed into the reactor and the temperature is raised to about 125° C.; air is fed until the pressure reaches 720 p. s. i., the temperature being raised to 177° C. during this addition. A steady rate of air feed of about 4 standard cubic feet per hour is maintained and isobutylene is fed in at varying rates to replenish the consumption. 160 grams of isobutylene are fed in this manner.

At the end of the reaction (about 6 hours) the reaction mixture is neutralized with a sodium hydroxide solution to a pH of 7 and then fractionated to yield the following products (indicated as grams of product per hundred grams of isobutylene consumed):

Acetone 26.0 grams; methallyl alcohol 13.02 grams; isobutylene glycol 58.2 grams; formic acid 3.11 grams; acetic acid 7.29 grams; isobutyric acid 2.8 grams; methanol 1.74 grams; 2-butanone 8.94 grams; methyl acetate 0.77 gram; isobutyl acetate 5.75 grams; carbon monoxide 7.07 grams; carbon dioxide 8.18 grams; and polymeric material 11.7 grams.

When utilizing nitrobenzene as a polymerization inhibitor, it has been found that concentrations from about 2% to 10% by weight of the solvent are satisfactory. It is possible that somewhat lower concentrations than 2% may be effective, but it is preferred to operate in the above range. While concentrations of above 10% may be employed, it is not necessary and has only the effect of producing greater amounts of nitrobenzene degradation products. The consumption of nitrobenzene naturally, in this case, would add to the cost of the final products. When the polymerization inhibitor (i. e., nitrobenzene) is not employed, the degree of polymer formation is on the same order of magnitude as occurred in Example II, other conditions, such as olefin concentration, being comparable and benzene used as a solvent in place of the tertiary butyl alcohol of Example II.

The above discussion of the invention has been primarily concerned with the oxidation of olefins to their corresponding glycol. The invention is equally applicable to the use of saturated hydrocarbons containing tertiary hydrocarbons, such as isobutane and the like, as starting materials. Fig. 2 is a flow sheet illustrating this aspect of the invention. As can be seen, like numbers in Fig. 2 correspond to like elements and steps in Fig. 1. In Fig. 2, however, the reactor serves the dual purpose of oxidizing both isobutane and isobutylene. In this embodiment of the invention, the isobutane is oxidized in benzene as a solvent to form tertiary butyl alcohol as the primary reaction product. This tertiary butyl alcohol is then dehydrated (at 18) to isobutylene by the use of a heated dehydrating agent such as aluminum oxide (Al_2O_3). The technique for utilizing such dehydration agents is well known and described in numerous texts such as page 52 of "Chemistry of Organic Compounds" Conant and Blatt, published by MacMillan in November, 1947.

The method of operating the reactor **10** to produce

tertiary butyl alcohol is set forth in the following non-limiting example:

Example IV

Thirteen hundred grams of benzene solvent together with 1.5 grams of manganese propionate catalyst are charged to high pressure reactor **10**. 850 grams of isobutane are now passed in and the reactor temperature is raised to about 125° C. Air is fed until the pressure reaches about 700 p. s. i., the temperature during this addition being raised to about 185° C. A steady rate of air feed of about 4 standard cubic feet per hour is maintained and isobutane is fed at varying rates to replenish the consumption. 372 grams of isobutane are fed in this manner. At the end of the reaction (about 5 hours) the mixture is repeatedly extracted with water and fractionation of the water washings yields the following products (indicated as grams of product per hundred grams of isobutane consumed):

Acetone 25.5 grams; tertiary butyl alcohol 80.1 grams; isobutyl alcohol 11.9 grams; acetic acid 4.9 grams; methanol 2.9 grams; 2-butanone 1.2 grams; carbon monoxide 5.3 grams; and carbon dioxide 6.5 grams.

The tertiary butyl alcohol is separated from the reaction products in the distillation separator **16** and is fed to a dehydration step **18** where the tertiary butyl alcohol is converted to isobutylene, which in turn may be oxidized in accordance with the technique described in Example I. If the process is to be run on a continuous basis, with a single reactor, the isobutylene is fed back to the same reactor in which the isobutane is oxidized to tertiary butyl alcohol. This is the modification of the invention shown in Fig. 2. The recycling of the various solvents and reactants is also shown in Fig. 2. In this connection it should be pointed out that oxygenated products are continuously removed while unreacted isobutane and isobutylene are continuously recycled. Equally, the tertiary butyl alcohol is continuously recycled (after it has been dehydrated to isobutylene).

In other respects the operation of the process of Fig. 2 is similar to that previously described in connection with the discussion of Fig. 1.

Since certain changes may be made in the above process without departing from the scope of the invention herein invloved, it is intended that all matter contained in the above description, or shown in the accompanying drawings, shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

A method of forming isobutylene glycol and tertiary butyl alcohol which comprises dissolving a mixture of isobutane and isobutylene in an inert organic solvent, passing an elemental-oxygen-containing gas into said solution while said solution is held under superatmospheric pressure and maintained at a temperature above about 150° C. to oxidize said isobutane to tertiary butyl alcohol and said isobutylene to isobutylene glycol, and recovering said tertiary butyl alcohol and isobutylene glycol.

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