

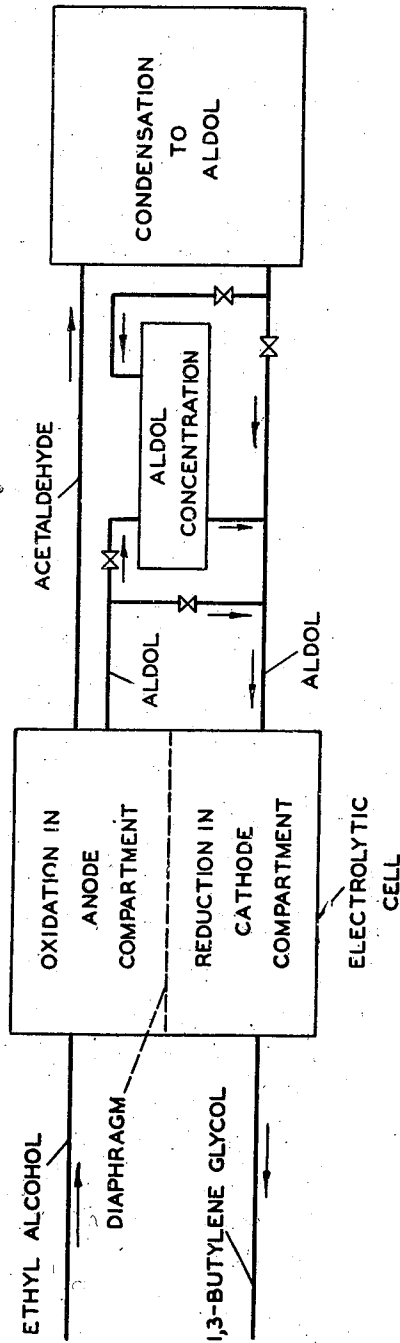
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PREPARATION OF 1,3-BUTYLENE GLYCOL

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## PREPARATION OF 1,3-BUTYLENE GLYCOL

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This invention relates to an improved process for the preparation of 1,3-butylene glycol from ethyl alcohol as a starting material. As is now well-known, butylene glycol may be readily dehydrated to form butadiene which is employed as a monomeric raw material in the preparation of synthetic rubber. Accordingly, 1,3-butylene glycol is a very important chemical compound and its ready and economical preparation from a material as cheap and readily obtainable as ethyl alcohol assumes great importance.

The principal object of the present invention is to provide an improved process for the production of 1,3-butylene glycol from ethyl alcohol. Another object is to devise such a method involving electrochemical steps in an integrated relationship. Another object is to provide such a process involving electrochemical steps wherein substantial savings in power are effected along with other improvements, since one of the principal objections to ordinary electrolytic organic reactions is the relatively large cost of power consumed in carrying out the electrolytic reaction. Another object is to simultaneously carry out one step of the integrated process in the anode compartment of a divided electrolytic cell and another step in the cathode compartment of the same cell. Numerous other objects and advantages of the present invention will be at once apparent to those skilled in the art in the light of this disclosure.

The accompanying drawing, which is self-explanatory, portrays diagrammatically one embodiment of the present invention.

In accordance with my invention, ethyl alcohol is oxidized to acetaldehyde in the anode compartment of an electrolytic cell, the acetaldehyde so formed is condensed to aldol, and the aldol is reduced to 1,3-butylene glycol in the cathode compartment of an electrolytic cell, preferably of the same cell as that in which the acetaldehyde is formed. By simultaneously carrying out the oxidation of the starting ethyl alcohol to acetaldehyde and the reduction of the aldol to 1,3-butylene glycol in the anode and cathode compartments respectively, of one and the same electrochemical cell, great economies and convenience of operation are effected and the same electric current is used for both the electrolytic oxidation and reduction whereby very great savings in power cost are attained.

The condensation of the acetaldehyde to aldol may conveniently be carried out in a separate step. Methods of effecting this condensation are well-known to the art, as illustrated by U. S.

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Patents to Earle et al., 1,094,314; Grunstein, 1,437,139; Matheson, 1,450,984; and Mueller-Cunradi et al., 1,881,853. However, since the condensation of acetaldehyde to aldol may take place in an alkaline alcoholic aqueous solution, this condensation may be effected in the compartment of the cell wherein the acetaldehyde is formed from the ethyl alcohol, by utilizing an alkaline electrolyte for the oxidation of the ethyl alcohol, unreacted alcohol serving to render the anolyte alcoholic. If desired or necessary, the effluent from the anode compartment may be introduced into a receptacle and maintained at condensation temperature for the required period of time to complete condensation of the acetaldehyde to aldol. The aldol solution containing alkali, unreacted alcohol and possibly some uncondensed acetaldehyde may then be introduced into the cathode compartment of the same electrolytic cell where the aldol is reduced to 1,3-butylene glycol. If desired, the aldol-containing solution may be treated in any known manner to concentrate the aldol content thereof prior to introduction of the aldol to the cathode compartment wherein it is reduced to butylene glycol.

Likewise, the acetaldehyde-containing anolyte removed from the anode compartment in which the acetaldehyde is formed may be treated in any suitable manner, if desired, to concentrate the acetaldehyde prior to its introduction to the unit or zone in which it is condensed to aldol.

The electrochemical oxidation of ethyl alcohol to acetaldehyde in the anode compartment is a matter well within the skill of the art and the selection of anolyte composition, temperature, anode, current density and other conditions of this operation will be obvious to those skilled in the art in the light of this disclosure taken in conjunction with the prior art. Accordingly, specific conditions need not be given here in detail.

Ordinarily a current of 3-6 amperes/square decimeter and 3-15 volts will provide suitable current conditions for both the anodic and cathodic reactions described herein.

In many cases it will be desirable to carry out the oxidation of the ethyl alcohol to acetaldehyde in an acid anolyte since under many circumstances use of an acid electrolyte, for example, dilute sulfuric acid, favors the production of acetaldehyde as the principal or main product, as is well known to the art. However, the use of an alkaline electrolyte in the anolyte is not precluded and may be desirable especially where the same divided cell is used for the pro-

duction of the acetaldehyde and for the reduction of the aldol and where an alkaline electrolyte in the catholyte is used. As pointed out above, such use of an alkaline anolyte may be especially desirable where partial or complete condensation of the acetaldehyde to aldol in the anode compartment is sought.

The reduction of the aldol to 1,3-butylene glycol is carried out in the cathode compartment of an electrolytic cell. Here again the selection of conditions and materials is well within the skill of those versed in the art, this reduction per se being well disclosed in the literature as typified by the U. S. Patents to Earle et al., 1,094,315 and 1,094,316; and Delbruck et al., 1,094,539. This reduction may be conducted with either an alkaline or an acid catholyte. Where the catholyte contains alkali metal ions, such as sodium, it is especially desirable to use a mercury or an amalgamated metal cathode on the surface of which sodium amalgam forms. Alternatively, I may use a cathode of platinum, palladium, nickel, iron, copper, zinc, tin, lead, or other metal having catalytic properties for the reaction. Non-catalytic cathodes may also be used since nascent hydrogen is an active reducing agent.

Following reduction in the cathode compartment the catholyte is treated in any suitable manner to recover the 1,3-butylene glycol content thereof. Any uncondensed acetaldehyde present in the catholyte is reconverted to ethyl alcohol, and the ethyl alcohol so formed may be separated from the butylene glycol by distillation and recycled. It is preferred to recover essentially pure butylene glycol where, as ordinarily, it is to be used as a chemical intermediate, for example, as a starting material for the preparation of butadiene.

A batch process may be used. At least the electro-organic oxidation and reduction steps may be conducted batchwise since they may not lend themselves too readily to truly continuous operation. However, continuous operation may be employed throughout if desired. In such case a series of cells may be utilized in order to provide a longer residence time.

It will be understood that while operation with simultaneous oxidation to acetaldehyde and reduction to butylene glycol in anode and cathode compartments, respectively, of the same cell, is highly preferred, I am not limited thereto but may carry out these steps in different cells, as for example, where it is desired to use conditions for one of the reduction and oxidation steps which would be incompatible with the conditions desired for the other of said steps. Such conditions might involve temperature, electrolyte composition, voltage, current, time, etc.

Almost invariably it is preferred that divided cells be used for both the oxidation and the reduction in order to prevent the oxidation products from being reduced at the cathode and the reduction products from being oxidized at the cathode, to preclude other undesirable effects, and to keep the anolyte and catholyte separate. The selection of a suitable diaphragm for this purpose is well within the skill of the art.

As will be obvious, I may periodically or continuously during the electrolysis adjust the composition of anolyte or catholyte or both in any desired manner, for example, by addition of a neutralizing acidic or acid-forming or a basic or base-forming material in suitable amount to prevent the building up of an excessive acidity or alkalinity.

It will be understood that where a single cell is used, the oxidation being conducted in the anode compartment and the reduction being carried out in the cathode compartment, the conditions for each will have to be so selected as to be compatible with one another. This is especially true of the electrolyte. Thus both the anolyte and catholyte may be either acid or alkaline in reaction, or one may be acid and the other alkaline, provided other conditions are adjusted accordingly. If desired I may use an electrolyte containing a salt such as an alkali sulfate, for example, sodium sulfate, whereby sulfuric acid is continuously formed in the anolyte and maintains it acid while alkali hydroxide is formed in the catholyte. In this way, especially in the preferred embodiment involving simultaneous oxidation in the anode compartment and reduction in the cathode compartment of the same cell, the oxidation of the ethyl alcohol to acetaldehyde is conducted in an acid anolyte which may be especially desirable where it is sought to produce acetaldehyde in maximum yield and to minimize side reactions such as polymerization, etc., while the reduction of aldol to butylene glycol is carried out in an alkaline catholyte which is frequently very desirable. Of course free sulfuric acid may be used as an initial component of the anolyte when such a salt is used, if desired.

In some cases it may be desirable to use an alkali carbonate as an electrical conducting salt in the anolyte and catholyte. In such case the acetaldehyde formed in the anolyte may be largely or completely condensed to aldol as it is formed, since alkali carbonate is a well-known catalyst for aldol condensation. The withdrawn anolyte with or without additional treatment steps such as adjustment of composition, partial neutralization, concentration of aldol, a separate condensation step to complete condensation of the acetaldehyde to aldol, may then be passed to the cathode compartment where reduction to butylene glycol takes place especially well in the presence of alkali carbonate. Instead of alkali carbonate, the bicarbonate may be used. Likewise, if desired, carbon dioxide may be intermittently or continuously passed into the catholyte to keep the alkalinity therein from becoming excessive.

In many cases it will be desirable to carry out the electrolytic reduction of the aldol to the 1:3 butylene glycol in the presence of dilute sulfuric acid. An especially desirable mode of operation is to use a common divided cell and a common electrolyte, namely, dilute sulfuric acid in both anode and cathode compartments, whereby the oxidation of the ethyl alcohol is done in a sulfuric acid anolyte which frequently gives maximum yields of acetaldehyde and eliminates condensation thereof to aldol or other reactions which would occur in an alkaline anolyte, and whereby the reduction of the aldol (which is produced by condensation of the acetaldehyde in a separate unit apart from the cell) to butylene glycol takes place in a sulfuric acid catholyte.

The electrolytic oxidation and reduction steps of the process of the present invention, and especially the reduction, are ordinarily and preferably carried out at low temperature, i. e., at below room temperature (commonly taken as 20° C.). Generally temperatures not above 10° C. and varying downwardly therefrom to the freezing point of the electrolyte are employed. Use of such low temperatures promotes the desired reactions to a maximum and minimizes objectionable side reactions, polymerization, formation of resins,

etc. In many cases, where a separate aldol condensation step is interposed, it will also be desirable to conduct this step at the same relatively low temperatures.

*Example*

An alcoholic aqueous solution containing 10% water and 90% ethyl alcohol to which solution has been added about 4% NaOH, is introduced into the anode compartment of an electrolytic cell separated from the cathode compartment by a porous clay diaphragm. Initially, the same electrolyte may be placed in the cathode compartment. The electrolyte is subjected to electrolysis using a carbon anode and a current density of 5 amperes/square decimeter at a voltage of 6 volts. The electrolysis is conducted at a temperature of about 10° C. with stirring for a sufficient length of time to effect substantial conversion of ethyl alcohol to acetaldehyde, along with at least partial condensation of acetaldehyde to aldol, say 2-10 hours. The resulting electrolyte containing ethyl alcohol, water, NaOH, aldol and acetaldehyde, is then introduced into the cathode compartment of the cell using an amalgamated lead cathode and the same current conditions as in the anode compartment. The aldol is reduced to 1,3-butylene glycol, while residual acetaldehyde is re-converted to ethyl alcohol. Simultaneously, a fresh quantity of alkaline aqueous ethyl alcohol is being oxidized in the anode compartment. The catholyte is distilled after reduction to separate the glycol from the ethyl alcohol and water; which may be recycled to the anode compartment, after washing to remove alkali, substantially pure 1,3-butylene glycol is obtained.

The above example describes a batch operation. If it is desired to operate in a continuous manner, the anolyte flows continuously through the anode compartment while being oxidized and may then flow either through a storage zone where the acetaldehyde will have a sufficient residence time to complete condensation to aldol, or where the aldol formation has taken place in the anode compartment, may flow directly into and through the cathode compartment. In order to increase reaction time the major portion of the electrolyte in each cell may be continuously recycled, or a series of cells in parallel may be used.

Similar operating conditions are used with other electrolytes, such as sulfuric acid or sodium sulfate, except that where the oxidation of the alcohol takes place in an acid medium, the electrolyte must be neutralized after oxidation and made alkaline in order that the aldol condensation may take place in an alkaline medium.

The alcohol concentration in the anolyte may vary over a wide range; ordinarily 50-95% alcohol is suitable. When an alkaline solution is desired, alkali concentrations corresponding to 1-10% or more of NaOH may be used. Where electrolytes acidified with acids, such as sulfuric acid, are used, the acid concentration may desirably be from 5-15%.

A great many advantageous features of the process of the present invention will be apparent to those skilled in the art. Among these, the following may be enumerated. The most important advantage is that the invention accomplishes production of very valuable 1,3-butylene glycol in a simple and economical manner from ethyl alcohol. Yields in each step, and consequently, the overall yield, are very good. The invention permits utilization of the same electric

power for both the oxidation and the reduction step. It conducts both oxidation and reduction in the same electrolyte. It permits at least partial condensation of the acetaldehyde in the oxidation zone. It eliminates the necessity for separation of the aldol prior to the reduction step. It effects reconversion in the cathode compartment of unreacted acetaldehyde to alcohol which may then be recycled. It makes possible a semi-continuous or even a continuous method. Recycle of unreacted materials is readily accomplished and to a maximum extent whereby yields are improved.

I claim:

1. The process of making 1,3-butylene glycol from ethyl alcohol which comprises introducing an alcoholic aqueous solution containing 10% water and 90% ethyl alcohol to which about 4% NaOH has been added into the anode compartment of an electrolytic cell having its cathode compartment separated from its anode compartment by a porous diaphragm, subjecting said solution to electrolytic oxidation at a carbon anode in said anode compartment with a current density of 5 amperes per square decimeter at 6 volts and at a temperature of about 10° C. with stirring for a length of time of from 2-10 hours sufficient to effect substantial conversion of ethyl alcohol to acetaldehyde by electrolytic oxidation and simultaneous condensation of said acetaldehyde to aldol in said anode compartment, introducing the resulting electrolyte containing ethyl alcohol, water, NaOH, aldol and acetaldehyde into the cathode compartment of the same cell, and subjecting said electrolyte to electrolytic reduction therein at an amalgamated lead cathode under the same current conditions as in the anode compartment and thereby reducing said aldol to 1,3-butylene glycol at said cathode and re-converting said acetaldehyde to ethyl alcohol, simultaneously oxidizing a fresh quantity of said aqueous alkaline ethyl alcohol solution in said anode compartment, maintaining the anolyte and catholyte separate during the process by means of said diaphragm, withdrawing the catholyte from said cathode compartment after reduction of said aldol to 1,3-butylene glycol therein, separately recovering the 1,3-butylene glycol in substantially pure form and the ethyl alcohol from the catholyte, and recycling said ethyl alcohol to the anode compartment.

2. The process of making 1,3-butylene glycol from ethyl alcohol which comprises introducing an alcoholic aqueous solution containing from 50 to 95 per cent ethyl alcohol to which solution has been added about 4% NaOH into the anode compartment of an electrolytic cell having its cathode compartment separated from its anode compartment by a porous diaphragm, subjecting said solution to electrolytic oxidation at a carbon anode in said anode compartment with a current density of 3 to 6 amperes per square decimeter at 3 to 15 volts and at a temperature of about 10° C. with stirring for a length of time of from 2-10 hours sufficient to effect substantial conversion of ethyl alcohol to acetaldehyde by electrolytic oxidation and concomitant condensation of said acetaldehyde to aldol in said anode compartment, introducing the resulting electrolyte containing ethyl alcohol, water, NaOH, aldol and acetaldehyde into the cathode compartment of the same electrolytic cell, subjecting said electrolyte to electrolytic reduction therein at an amalgamated lead cathode under the same range of current conditions as in the anode

compartment and thereby reducing said aldol to 1,3-butylene glycol at said cathode and reconverting said acetaldehyde to ethyl alcohol, simultaneously oxidizing electrolytically a fresh quantity of said aqueous alkaline ethyl alcohol solution in said anode compartment at the foregoing conditions, maintaining the anolyte and catholyte separate during the process by means of said diaphragm, withdrawing the catholyte from said cathode compartment after reduction of said aldol to 1,3-butylene glycol therein, separately recovering the 1,3-butylene glycol in substantially pure form and the ethyl alcohol from the catholyte, and recycling said ethyl alcohol to the anode compartment.

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