May 11, 1948. A. B. ASH ET AL 2,441,540

PRODUCTION OF ALLYL ALCOHOL

Filed June 19, 1943 2 Sheets-Sheet 1

FIGURE I

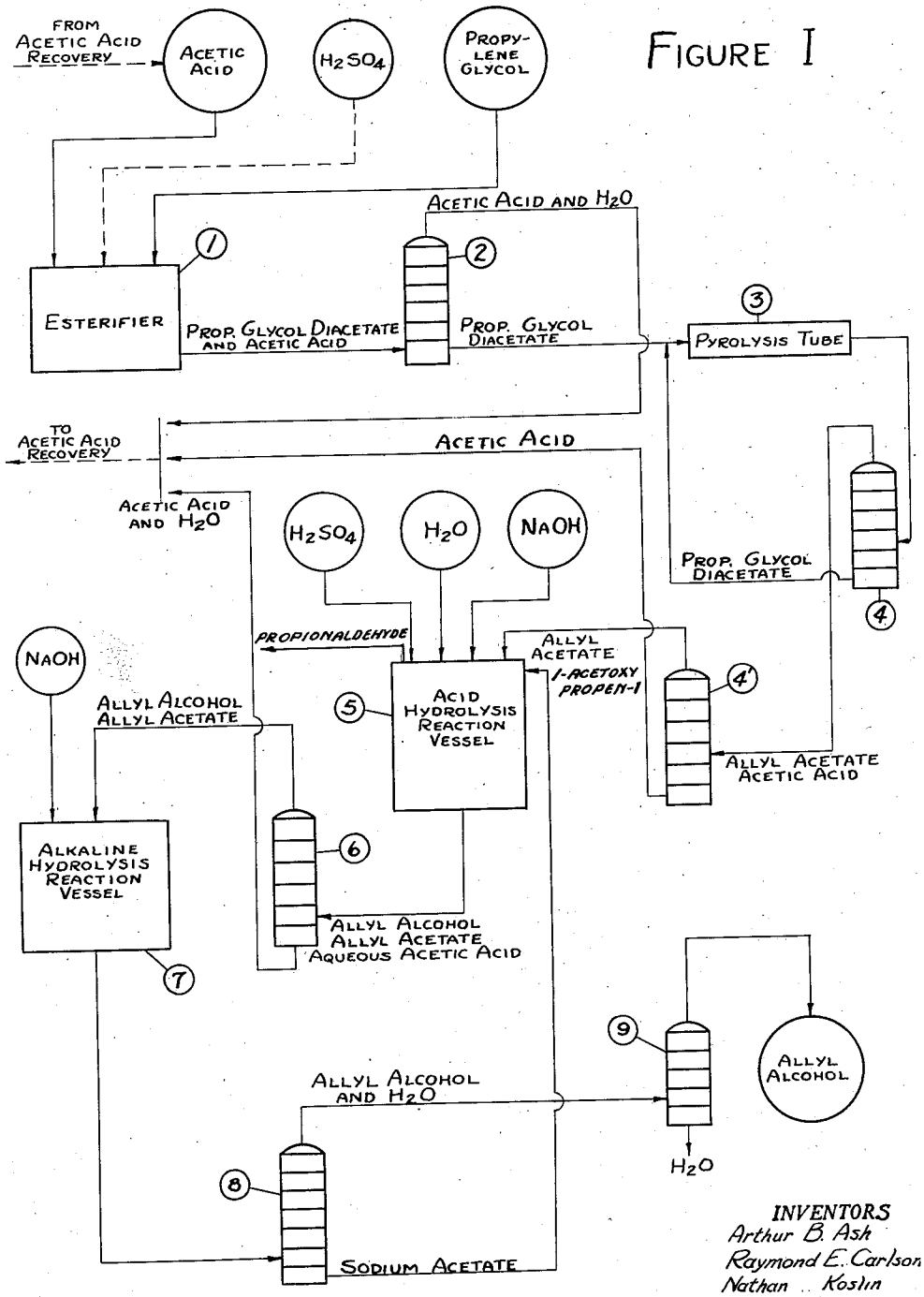

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FIGURE II

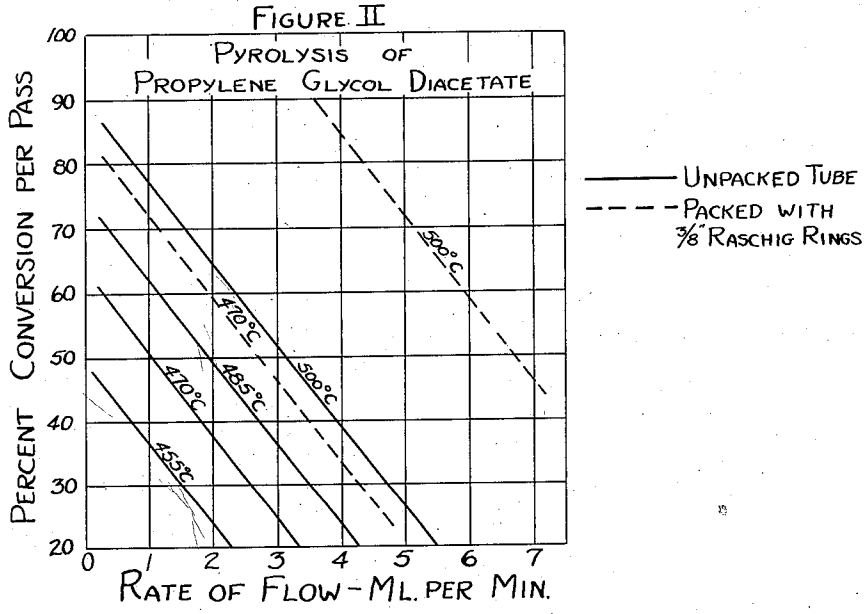
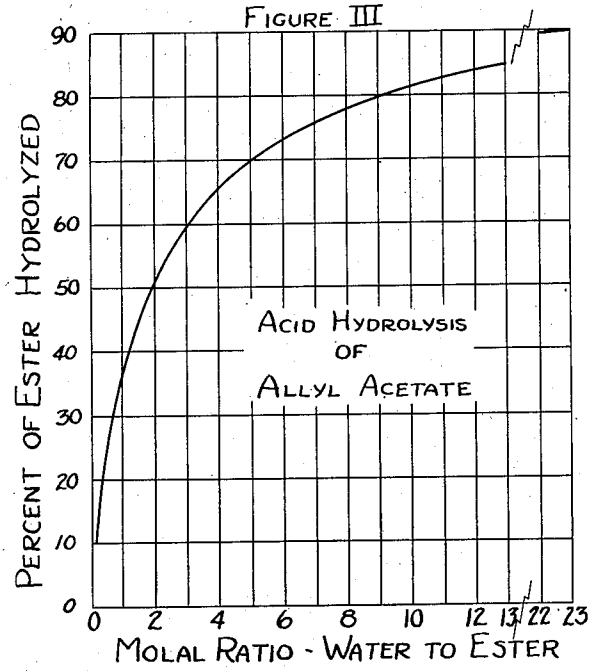


FIGURE III



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2,441,540

PRODUCTION OF ALLYL ALCOHOL

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Application June 19, 1943, Serial No. 491,488

2 Claims. (Cl. 260—638)

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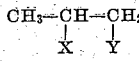
The present invention relates to the manufacture of allyl alcohol. The broad principle of this invention is essentially based upon the pyrolysis of aliphatic, acylated hydrocarbon compounds in which the radical

is split off from the hydrocarbon chain together with one hydrogen atom from an adjacent carbon atom, yielding an allyl ester, then hydrolyzing this unsaturated ester. When a poly-ester of a saturated aliphatic compound of the structural formula



wherein X and Y represent respectively either an inorganic acid residue or an acyl group, but wherein either X or Y must designate an acyl group, is so pyrolyzed, the acyl radical which is split off leaves a double bond carbon to carbon linkage at its point of departure; this results in the production of an unsaturated or alkylenic hydrocarbon chain. When the allyl ester is hydrolyzed allyl alcohol is secured. There is a by-product formation of 1-acetoxy propene-1 in many of the operating conditions in the pyrolysis step where propylene glycol diacetate is treated; and when this is in turn hydrolyzed propionaldehyde results.

The primary object of the present invention is to efficiently and economically produce allyl alcohol by the hydrolysis of an acyl ester of allyl alcohol. This process is particularly adapted to the production of allyl alcohol from allyl acetate which in turn is secured by pyrolysis of propylene glycol diacetate.

A further object of this invention is the provision of a method of hydrolysis of the allyl ester wherein a high percentage yield of allyl alcohol is secured. More particularly this invention has an object the hydrolysis of the allyl ester by an acid catalyst followed by an alkaline hydrolysis. We have found that the alkaline hydrolysis in tandem relation with the acidic hydrolysis obviates a difficult step of recovery of unreacted allyl acetate. An acid hydrolysis alone can be employed; but there is considerable unreacted allyl acetate left by this mode which must be separated from the allyl alcohol and reintroduced into a subsequent hydrolyzing step to secure a high conversion. Furthermore, from a commercial standpoint, it is necessary to free the

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unreacted allyl ester and propionaldehyde from the allyl alcohol to secure a marketable product. Whereas with a straight aqueous alkaline hydrolysis, the hydrolysis reaction goes to completion, and while this obviates the step of recovery of the unreacted ester, the acetic acid present is converted to sodium acetate; it must be reconverted subsequently to acetic acid by a mineral acid. This greatly adds to the cost. The propionaldehyde can be removed most satisfactorily in the acid hydrolysis, as it tends to polymerize readily in alkaline media.

Our manufacturing process, which is economically and commercially feasible, involves the three essential process steps of (1) esterification, (2) pyrolysis, and (3) hydrolysis.

To the accomplishment of the foregoing and related end, said invention then comprises the features hereinafter fully described and particularly pointed out in the claims, the following description and annexed drawing setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various ways in which the principle of the invention may be employed. It will be understood that other esters of propylene glycol other than propylene glycol diacetate such, for example, as propylene chloroacetate, propylene glycol dipropionate and propylene glycol dibutyrate may be formed initially, pyrolyzed and hydrolyzed. When propylene chloroacetate is pyrolyzed, there is formed allyl chloride and 1 - chloro-propene - 1. Upon hydrolysis, allyl chloride is converted to allyl alcohol, for the 1-chloro-propene-1 is stable to hydrolysis and is recovered unchanged. It will be appreciated that suitable adjustment of operative conditions in accordance with the known differences in character of these esters must be made.

In the annexed drawing:

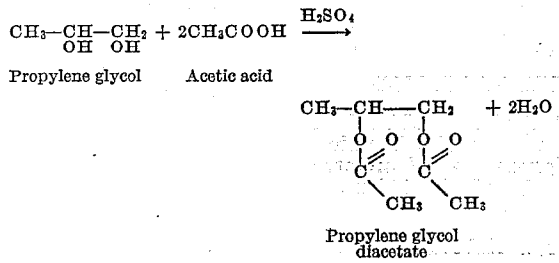
Figure I is a flow sheet illustrating a process for manufacturing allyl alcohol from propylene glycol and acetic acid.

Figure II is a curve showing the relationship of contact times and yields in the pyrolysis step of such process for different temperatures and different agents of increased surface area; these said agents or materials may be of catalytic nature or may be simply inert.

Figure III is a curve showing the relationship of the per cent of allyl acetate hydrolyzed to the water-ester molal ratio in the acid hydrolysis step of the process.

Now referring more particularly to Figure I of the drawing, it will be seen that propylene glycol

and acetic acid are first introduced to the reaction vessel 1, where, in the presence of sulphuric acid, they react to form the ester of such polyhydric, saturated alcohol and said acid, i. e., propylene glycol diacetate, in accordance with the following equation:

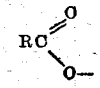


Propylene glycol Acetic acid Propylene glycol diacetate

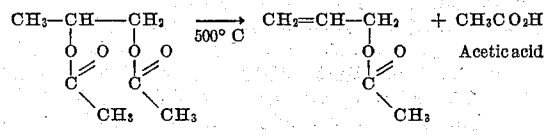
An excess of acetic acid, over and above the stoichiometric amount theoretically required for reaction with the propylene glycol, is present in the esterification reaction. The yield of propylene glycol diacetic in this first esterification step has been found to be 95% or better of the theoretically obtainable yield.

The reaction mixture from the reaction vessel 1 is then conducted to the still 2 where the acetic acid and water are stripped off and returned to the acetic acid recovery system (the latter being not shown in Figure I).

The propylene glycol diacetate from the still 2 is then conducted to the pyrolysis tube 3 where it is subjected to a heat sufficient to split off one of the



radicals, together with one of the carbon-linked hydrogen atoms of the poly-ester, leaving the mono-ester, allyl acetate, and acetic acid, as represented by the following equation:



Propylene glycol diacetate Allyl acetate Acetic acid

There is some formation of 1-acetoxy propene-1 which is isomeric with the allyl acetate.

The pyrolytic conversion of the propylene glycol diacetate occurs in a temperature range of 250–600° C. The amount of yield of the mono-ester, allyl acetate, is dependent upon the rate of feed of the vaporized propylene glycol diacetate through the pyrolysis tube, the temperature and the nature of the increased surface area present in the tube. The pyrolysis will proceed satisfactorily in an unpacked tube, but packed tubes containing glass Raschig rings, glass wool, glass chips, porous plate, calcium chloride, granular charcoal, and the like, have the effect of increasing the per cent of conversion for any given rate of flow or contact time. The following tables show per cent of conversion per pass to allyl acetate and 1-acetoxy propene-1 for varying rates of flow and temperatures through an unpacked tube and a tube packed with glass Raschig rings respectively. The tube employed was "Pyrex" glass 17" length by 1" internal diameter. A conditioning furnace was used as a preheater to vaporize the propylene glycol diacetate and to bring said vapors to within approximately 100° C. of the specified reaction temperatures.

Pyrolysis of propylene glycol diacetate through an unpacked tube as per cent conversion per pass

Temp.	Rate of flow, ml. per min.				
	1 ml.	2 ml.	3 ml.	4 ml.	5 ml.
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*
500° C.	77	67	53	39	26
485° C.	67	54	39	24	11
470° C.	55	39	26	12	
455° C.	35	23	12		

Pyrolysis of propylene glycol diacetate through a tube packed with 3/8" Raschig rings as per cent conversion per pass

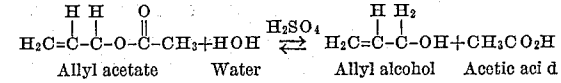
Temp.	Rate of flow, ml. per min.				
	2 ml.	3 ml.	4 ml.	5 ml.	6 ml.
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*
500° C.			85	72	19
470° C.	48	25	13		

The propylene glycol diacetate may be conducted in the vapor phase direct from the still 2 to the pyrolysis tube, or if condensed after emission from the still 2, it is preliminarily vaporized (viz. heated to above its boiling point of 186–190° C.) before introduction into the pyrolysis heating zone.

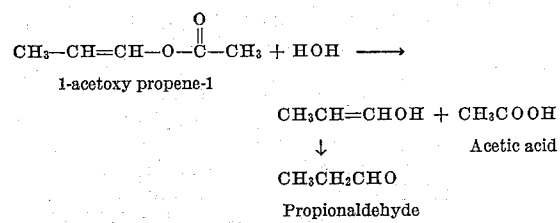
Figure 2 shows various curves derived from the figures given in the above table. Thus, it will be seen that the maximum conversion per pass is obtained at 500° C. in a packed pyrolysis tube. By stripping off the pyrolytic products and recycling the unconverted propylene glycol diacetate through the pyrolysis tube 3, the yield of allyl acetate from this step of the process is 70% or better of the theoretical.

The pyrolytic products comprising allyl acetate and acetic acid and some 1-acetoxy propene-1 are fractionated to remove the aforesaid esters from acetic acid. This requires an efficient fractionating column.

The allyl acetate and 1-acetoxy propene-1 recovered from the fractionation column 4 are then introduced to the acid hydrolysis reaction vessel 5, where in the presence of a mineral acid catalyst, such as aqueous sulfuric acid, they are hydrolyzed to allyl alcohol, propionaldehyde respectively and acetic acid according to the following reactions:



Allyl acetate Water Allyl alcohol Acetic acid



1-acetoxy propene-1 Acetic acid Propionaldehyde

The low boiling propionaldehyde (B. P. 47° C.) is distilled off from the mixture undergoing hydrolysis as rapidly as it is formed. The aqueous distilland contains allyl alcohol, acetic acid, water and some unhydrolyzed allyl acetate as indicated in the equilibrium reaction equation supra.

The per cent of conversion of the allyl acetate

ester to produce allyl alcohol and acetic acid is illustrated by the curve in Figure 3. It will thus be seen that as the ratio of water to ester is increased, that the hydrolytic conversion is correspondingly increased. At a molal ratio of water to ester of 23 to 1, approximately 90% conversion is obtained.

The rate of attainment of equilibrium in the hydrolysis reaction is also a function of the amount of mineral acid catalyst present. However, such amount is preferably held to a relatively low value of 5% or less by weight H_2SO_4 or other acid equivalent on the basis of total water present.

In the initial operation of the process system, sufficient amount of an alkali or inorganic base, such as sodium hydroxide, is added to the acid hydrolysis reaction vessel to neutralize the mineral acid catalyst after termination of the aforesaid acid hydrolysis reaction. While not essential, nevertheless neutralization minimizes the reverse reaction of esterification. In subsequent operations of the process, this neutralization is accomplished by a recycling procedure, and will be subsequently described.

The aforesaid reaction mixture from the acid hydrolysis reaction vessel 5, is then introduced to the fractionating column 6 where the allyl alcohol and allyl acetate are separated off from the bulk of the acetic acid. The allyl acetate and alcohol come off as constant boiling mixtures with water at 83° C. and 88° C. respectively. The aqueous acetic is left in the still and is educted to the acetic acid recovery system. Due to the relatively small temperature differential of 5° C. between the two constant boiling mixtures described above, it would be a relatively difficult and expensive process, on a commercial scale, to separate them by fractional distillation. We have discovered, however, that such a separation can be obviated by subjecting the allyl alcohol and allyl acetate mixture (having a slight amount of acetic acid present) to a second hydrolyzing treatment in the alkaline hydrolysis reaction vessel 7, and in which an inorganic base, such as sodium hydroxide, is employed as the hydrolyzing agent.

In the alkaline hydrolysis reaction vessel 7, the allyl acetate, which is present is hydrolyzed to allyl alcohol and sodium acetate. The slight amount of acetic acid present is also neutralized by the sodium hydroxide to form sodium acetate. The allyl alcohol formed in this step supplements the quantity formed in the first hydrolysis stage.

The reaction mixture from the hydrolysis vessel 7 is then introduced to the fractionating column 8 where the constant boiling mixture of allyl alcohol and water can then be conveniently separated from the aqueous sodium acetate. The sodium acetate is then returned to the acid hydrolysis reaction vessel 5 where it is used in place of the original sodium hydroxide, to neutralize the mineral acid catalyst in the acid hydrolysis step.

The constant boiling mixture of allyl alcohol and water from the fractionating column 8 is then subjected to azeotropic distillation in the still 9 where the allyl alcohol is separated from the water, thus producing the final product. Entraining agents, such as benzene or methylene chloride may be suitably employed in the azeotropic distillation of the allyl alcohol-water constant boiling mixture.

The acetic acid from the acetic acid recovery system is recycled back to the esterification reaction vessel 1. Through the recovery of acetic acid, it is therefore necessary to add only a limited amount of virgin acetic acid to make up for acetic acid unavoidably lost in mechanical operations.

The pyrolysis may be applied to esters of propylene glycol wherein the carboxyl group or groups are attached to either aromatic or the aliphatic residues. We have found that saturated esters of the various lower membered aliphatic carboxylic acids are suitable. While the ester of acetic acid is preferred, other of the series such as propionic, n-butyric and hexoic can be used. Various of the monobasic aromatic acids can be used, such as benzoic acid. In these cases these respective carboxylic acids would be split off instead of acetic acid. Suitable acylating agents for the polyhydric saturated alcohols, chlorohydrins or alkylenic oxides are the carboxylic acids, their anhydrides or acid halides, such as the chlorides.

The following examples serve to explain the principle of our invention to those skilled in the art and more readily to enable them to understand and practice the same:

Example 1

76 gms. propylene glycol were fed into a reaction chamber connected to a column and condenser containing 210 gms. of boiling acetic acid. 0.3 gm. of concentrated sulphuric acid were dissolved in the acetic acid. The amount of acetic acid present represented 3½ mols to 1 mol of propylene glycol, or a 75% excess of the stoichiometric theoretical amount. The propylene glycol was added over a period of 45 to 60 minutes and the reflux continued for an additional one-half hour. The water formed in the reaction was removed along with some acetic acid by partial take-off of the reflux condenser.

The reaction mixture was then distilled, to separate the propylene glycol diacetate from the acetic acid-water mixture, giving 157 gms. of propylene glycol diacetate. This represented 98% of the theoretical yield.

The propylene glycol diacetate was then passed through a preheating tube heated in the range of 350–400° C., and thence passed through an unpacked Pyrex tube (1" by 17") heated to a temperature of 500 C., and at the rate of 23–4 cc. per minute. The conversion rate per pass under these conditions was about 45%. Under repeat passes, the 157 gms. of propylene glycol diacetate yielded 73.5 gms. of allyl acetate, or 75% of the theoretically obtainable yield and 2.45 gms. of 1-acetoxy propene-1. The other components are unconverted propylene glycol diacetate and acetic acid.

100 gms. of the isomeric propenyl acetates, fractionally distilled from the product of the foregoing pyrolysis treatment was then added, together with 180 gms. of water (representing 10 to 1 H_2O : esters molal ratio) and 9 gms. concentrated sulphuric acid, to a reaction vessel connected to a fractionating column and refluxed. Propionaldehyde which is formed by hydrolysis of the 1-acetoxy propene-1 was continuously removed during the hydrolysis. It weighed 14 gms. The amount of sulphuric acid present represented 5% by weight on the basis of the water present. 14.7 gms. of 50% sodium hydroxide were then added to the distilland to neutralize the sulphuric acid. The mixture was distilled under reflux conditions; no attempt was made to keep the fractions separated. The allyl acetate-water

azeotrope mixture boiling at 83° C. distilled off rapidly, followed by the allyl alcohol-water constant boiling mixture which boils at 88° C. The reflux ratio was then progressively increased until the temperature of 100° C. was attained, leaving a residue of acetic acid and water. This combined distillate after the said neutralization had a composition of 15 gms. of allyl acetate, 35 gms. of allyl alcohol and 20 gms. of water and about 1.5 gms. of acetic acid.

To this mixture 16 gms. of 50% sodium hydroxide was added. This mixture was then refluxed until the allyl acetate was approximately completely cleaved, which was within a half-hour. The solution was distilled, and the constant boiling mixture of allyl alcohol-water came off at about 88–90° C. The amount of allyl alcohol in this distillate was 42.6 gms. which represents a 98% theoretical yield. The allyl alcohol-water constant boiling mixture was then dehydrated by azeotropic distillation, yielding 42 gms. of anhydrous allyl alcohol, representing 97% allyl alcohol yield of that theoretically obtainable from the 75 gms. of allyl acetate.

Example 2

The vapors of 174 gms. of propylene oxide were passed into 540 gms. of boiling glacial acetic acid containing 0.92 gm. of concentrated sulphuric acid. The reaction mixture was then distilled to remove the unreacted acetic acid and water, yielding 458 gms. of propylene glycol diacetate. The so-formed propylene glycol diacetate was then pyrolyzed, as set out in Example 1 above.

100 gms. of the isomeric propenyl acetates, fractionally distilled from the product of the foregoing pyrolysis treatment was then added, together with 414 gms. of water (representing 23 to 1 H_2O-allyl acetate molal ratio) and 20.7 gms. concentrated sulphuric acid, to a reaction vessel connected to a fractionating column set at total reflux and refluxed for one hour until equilibrium was obtained. Propionaldehyde is distilled off from the reaction mixture thru the fractionating column at 47–50° C. 50.7 gms. of 50% sodium hydroxide were then added to the distilland to neutralize the sulphuric acid.

The mixture was fractionated under a 2:1 reflux ratio. The fraction coming over between 83° C. and 88° C. contained practically all of the unconverted allyl acetate, a small amount of allyl alcohol and some water. When the temperature reached 88° C., a constant boiling mixture of allyl alcohol and water came over. This amounted to 62 gms. and contained 70% allyl alcohol by weight. This was subjected to dehydration by the same mode indicated in Example 1. The fraction which contained the unconverted allyl acetate was returned to the succeeding charge of allyl acetate to be subjected to the acid hydrolysis.

Example 3

100 grams of the isomeric propenyl acetates secured as indicated above and 42 gms. of sodium hydroxide in a 20% water solution were refluxed

from 1–2 hours to hydrolyze the esters. The propionaldehyde formed is condensed or polymerized in this step by the action of caustic. The allyl alcohol-water constant boiling mixture was distilled off, leaving aqueous sodium acetate and the polymer in the still pot. Approximately 59 gms. of allyl alcohol-water distillate were obtained, which analyzed 71% allyl alcohol. The allyl alcohol was dehydrated as in Example 1.

Other modes of applying the principle of the invention may be employed, changes being made as regards the details described, provided the features stated in any of the following claims or the equivalent of such be employed.

We therefore particularly point out and distinctly claim as our invention:

1. In the method of simultaneously making allyl alcohol and propionaldehyde, the steps of pyrolyzing the diacylated ester of propylene glycol to split off a carboxylic acid, removing said acid from the pyrolysis reaction products, subjecting the resultant allyl ester and isomeric acyl ester in the presence of each other to an acid hydrolysis to form allyl alcohol, more carboxylic acid and propionaldehyde, respectively, distilling off the propionaldehyde during such hydrolysis, distilling off the last-formed carboxylic acid, and then subjecting the resultant allyl alcohol and remaining allyl ester to an alkaline hydrolysis, the several quantities of carboxylic acid produced in the foregoing steps being recovered and recycled to the process as a starting material to form more of the propylene glycol ester.

2. In the method of simultaneously making allyl alcohol and propionaldehyde, the steps of pyrolyzing propylene glycol diacetate to form allyl acetate, 1-acetoxy propene-1, and acetic acid, removing said acetic acid and thereafter hydrolyzing allyl acetate and 1-acetoxy propene-1 in the presence of an acid catalyst to form allyl alcohol and propionaldehyde respectively, additional acetic acid also being formed in such hydrolysis, distilling off the propionaldehyde during such hydrolysis, distilling off the last-formed acetic acid and then subjecting the allyl alcohol and remaining allyl acetate to an alkaline hydrolysis.

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