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Abstract: A method of synthesis of allyl alcohol from glycerol, whereby allyl alcohol is produced at a yield of about 80% or greater. The method comprising the heating of a reaction mixture of glycerol and a carboxylic acid under an inert atmosphere and distilling allyl alcohol from the reaction mixture.
CONVERSION OF GLYCEROL FROM BIODIESEL PRODUCTION TO ALLYL ALCOHOL

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CROSS-REFERENCE TO RELATED APPLICATIONS

[001] This application claims priority from U.S. Provisional Patent Application, 60/886,661, filed on January 26, 2007, which is incorporated by reference in its entirety.

STATEMENT OF GOVERNMENTAL SUPPORT

[002] This invention was made during work supported by U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The government has certain rights in this invention.

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

[003] The present invention relates to uses of biodiesel production byproducts, specifically, the conversion of glycerol from biodiesel production to allyl alcohol, for use as in the synthesis of polymers and carbon-based products.

RELATED ART

[004] Biodiesel produced from soybean oil generates large amounts of glycerol as a byproduct which is currently in oversupply. There is currently strong interest in developing ways to produce industrially important chemicals from renewable biological sources rather than petroleum, such as allyl alcohol. Allyl alcohol is currently made from propylene, which is a petroleum feedstock. Allyl alcohol is often used as a starting material in making various polymers, pharmaceuticals, pesticides and other allyl-substituted compounds.

[005] Currently there is no industrial process for the large-scale preparation of allyl alcohol from glycerol. As described below, the most effective synthesis in the open literature, which was published many years ago, is not very adequate. This procedure, described in
Organic Syntheses, Coll. Vol. 1, p.42 (1941); Vol. 1, p.15 (1921), requires heating of glycerol and acid to produce allyl alcohol. However, as it notes, "slow heating causes charring and formation of much acrolein, and thus gives a very low yield of allyl alcohol." Furthermore, more rapid heating is somewhat irreproducible and does not give yields above 50%. Thus, it would be beneficial to provide a method for carrying out this synthesis that is more reliable and that provides a pure product of allyl alcohol in sufficient yield quantities.

BRIEF SUMMARY OF THE INVENTION

[006] The present invention provides a method of synthesis of allyl alcohol from glycerol, whereby allyl alcohol is produced at a yield of 80% or greater, comprising the steps of: providing glycerol and a carboxylic acid, to a reaction mixture, heating the reaction mixture under an inert atmosphere, distilling allyl alcohol from the reaction mixture.

[007] In a preferred embodiment, the carboxylic acid is preferably formic acid. The inert atmosphere is preferably an inert gas such as argon or nitrogen.

[008] Thus the present invention also provides a process for synthesis of allyl alcohol from glycerol, comprising the steps of: (a) providing glycerol and formic acid to a reaction mixture, (b) heating the reaction mixture under an inert atmosphere to between about 230 °C to about 240 °C, and (c) distilling allyl alcohol from the reaction mixture, whereby allyl alcohol is produced at a yield of about 80% or greater.

[009] In one embodiment, the inert atmosphere is an inert gas, such as nitrogen and argon. In another embodiment, in the heating step (b), the reaction mixture is heated to about 235 °C. In another embodiment, during the distillation step (c), the reaction mixture is heated to between about 230 °C and about 240 °C.
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

INTRODUCTION

[010] Allyl alcohol is currently made from propylene, which is a petroleum feedstock. There is currently strong interest in developing ways to produce industrially important chemicals from renewable biological sources rather than petroleum. Thus, the present invention provides such a method for synthesis of allyl alcohol, an often used starting material for polymer materials, pharmaceuticals, pesticides and other allyl-substituted compounds.

DEFINITIONS

[012] As used herein, by the term, "glycerol," it is meant the chemical product, HOCH$_2$(CHOH)CH$_2$OH, which is also commonly referred to as trihydroxypropane or glycerin.

[013] As used herein, by the term, "about," it is meant to include ± 5 of the value(s) indicated.

DESCRIPTIONS OF THE EMBODIMENTS

[014] The present invention provides a method to carry out the synthesis of allyl alcohol from glycerol, producing a clean product in good yield. Glycerol is transformed to allyl alcohol by heating glycerol in a carboxylic acid, the reaction being:

\[
\begin{align*}
\text{HOCH}_2\text{(CHOH)}\text{CH}_2\text{OH} \xrightarrow{\Delta \text{HCO}_2\text{H}} \text{HOCH}_2\text{(CHOH)}\text{CHO} \xrightarrow{} \text{HOCH} = \text{CHO}
\end{align*}
\]

(1.1)

In a preferred embodiment, the carboxylic acid used is formic acid, which generates CO$_2$ as a byproduct of allyl alcohol formation.

[014] It was considered that the charring and inadequate yield may be due to the presence of oxygen during the synthesis, resulting in oxidative decomposition of glycerol.
Therefore a method was developed to carry out the reaction under an inert atmosphere, in the absence of oxygen. In a preferred embodiment, the method is carried out in the presence of an inert gas such as argon or nitrogen. In one embodiment, the synthesis was carried out under nitrogen which eliminated the need for rapid heating, eliminated charring and provided a high yield, 80%, of very pure product. The reaction carried out was:

\[
\text{HO-CH}_2\text{CH-CH}_2\text{OH} \xrightarrow{230^\circ C, N_2} \text{H}_2\text{C=CH-CH}_2\text{OH} \quad (1.2)
\]

The temperature is raised gradually, until a temperature of between about 230°C to about 260 °C is reached, preferably between about 230 °C to about 240 °C, more preferably about 230°C to about 235 °C. One skilled in the art can determine suitable rates of heating to carry out the reaction. In one embodiment, the temperature of the reaction mixture is raised gradually at rates similar to those used in Example 1. Allyl alcohol is distilled directly from the reaction mixture which results in allyl alcohol with some formic acid and traces of allyl formate and glycerol. Heating is continued during distillation to maintain the temperature between about 230 °C to about 260 °C, more preferably between about 230°C to about 240 °C, and then the mixture is allowed to cool to room temperature.

In a preferred embodiment, the total yield is equal to or greater than about 80%. Glycerol, as the starting material, can be put back through the reaction, or may be converted completely to product by further treatment of the product mixture with additional amounts of formic acid. The allyl formate can be hydrolyzed directly to the desired product allyl alcohol with inexpensive sodium hydroxide solution.

**EXAMPLE 1: PREPARATION OF ALLYL ALCOHOL**

In a 100 mL three neck round-bottomed flask are placed 150 mmol (13.8 g) of glycerol and 89 mmol of 85 to 99 percent formic acid. The flask is connected with a
condenser set: fractioning column, reflux condenser and collecting flask. The temperature in
the reaction mixture is monitored by a thermometer. A tube is run from the side arm of the
distilling flask to a bubbler containing sodium hydroxide solution. For example, sodium
hydroxide dissolved in water for a final concentration of 0.1 M, however, other
concentrations of sodium hydroxide can be used.

[018] Nitrogen was bubbled through the mixture, using a perforated tube immersed in
the solution, for 20 minutes at room temperature. The mixture was then heated over a
preheated sand bath, with continuation of the nitrogen bubbling. The temperature was raised
gradually, until a temperature of 235 °C was reached after 30 minutes. Under these
conditions, distillation of the product takes place over about 45 minutes. Heating was
continued until the temperature reached 230 °C to 260 °C and then the mixture is allowed to
cool to room temperature. A second portion of 85 percent formic acid (63.5 mmol) was added
and the distillation was repeated in exactly the same manner as described above. Finally a
third formic acid/distillation cycle was carried out. The three distillates contain allyl alcohol
with some formic acid and traces of allyl formate and glycerol. The total yield was greater
than 80%.

EXAMPLE 2: LARGE-SCALE PROCESS OF ALLYL ALCOHOL SYNTHESIS

[019] The reaction 1.1 can be carried out as a large-scale process. Calculated amounts of
glycerol and a carboxylic acid such as formic acid to form a reaction mixture can be provided
to stainless steel vessels for distillation. It may be preferred to have heating coils surrounding
the vessels to enable distillation of allyl alcohol. The temperature in the reaction mixture is
monitored. The vessel containing the reaction mixture is also connected to a bubbler
containing sodium hydroxide solution. For example, sodium hydroxide dissolved in water
can be used.
Nitrogen is bubbled through the mixture, for example, by using a perforated tube immersed in the solution, for a sufficient time at room temperature. The reaction mixture is then heated with continuation of the nitrogen bubbling. The temperature is raised gradually, until a temperature of between about 230 and about 240 °C, preferably about 235 °C, is reached. Under these conditions, distillation of the product takes place. Heating is continued to maintain the temperature between about 230 °C to about 240 °C and then the mixture is allowed to cool to room temperature. Formic acid can be added multiple times and the distillation process repeated in the same manner as described above. The distillates should contain allyl alcohol with some formic acid and traces of allyl formate and glycerol at a high yield. In one embodiment, the total yield is greater than about 80%.

The above chemical structures, reagents, reactions and examples are provided to illustrate the invention but not to limit its scope. Other variants of the invention will be readily apparent to one of ordinary skill in the art and are encompassed by the appended claims. All publications, databases, and patents cited herein are hereby incorporated by reference for all purposes.
What is claimed is:

1. A method of synthesis of allyl alcohol from glycerol, comprising the steps of: providing glycerol and a carboxylic acid to a reaction mixture, heating the reaction mixture under an inert atmosphere, and distilling allyl alcohol from the reaction mixture, whereby allyl alcohol is produced at a yield of about 80% or greater.

2. The method of claim 1 wherein the carboxylic acid is formic acid.

3. The method of claim 1, wherein the inert atmosphere is an inert gas.

4. The method of claim 3, wherein the inert gas is argon or nitrogen.

5. A process for synthesis of allyl alcohol from glycerol, comprising the steps of: (a) providing glycerol and formic acid to a reaction mixture, (b) heating the reaction mixture under an inert atmosphere to between about 230 °C to about 240 °C, and (c) distilling allyl alcohol from the reaction mixture, whereby allyl alcohol is produced at a yield of about 80% or greater.

6. The process of claim 5 wherein the inert atmosphere is an inert gas.

7. The process of claim 6, wherein the inert gas is argon or nitrogen.

8. The process of claim 5, wherein in the heating step (b), the reaction mixture is heated to about 235 °C.

9. The process of claim 5, wherein during the distillation step (c), the reaction mixture is heated to between about 230 °C and about 240 °C.
A CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

B FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

USPC-568/877

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Google, WEST terms-large scale allyl alcohol synthesis glycerol, oxidative decomposition of glycerol, allyl alcohol, process, glycerol, distillation, inert gas

SciFinder reaction search

C DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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Date of mailing of the international search report 23 MAY 2008

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

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