



PROCESS FOR THE PRODUCTION OF ALPHA -GAMMA DICHLOROHYDRINE IN A FLUIDIZED BED REACTOR WITH A SOLID STATE CATALYST

STATUS OF THE ART

The 1, 3 dichloro-2-propanol is an important chemical building block for the production of epichlorohydrine that is, in turn, one of the monomer used for the production of epoxy resins. [1-2].

The synthesis of 1,3 dichloro-2-propanol from hydrochloric acid and glycerol was studied since a long time and there are many processes that run the reaction between hydrochloric acid and glycerol at the presence of an organic acid (acetic acid or a bi-carboxylic acids) as a catalyst.

The reaction between the hydrochloric acid and the glycerol is a two stages reaction. Firstly the hydrochloric acid reacts with the glycerol to form the mono-chlorohydrine and after the mono-chlorohydrins reacts with a second mole of hydrochloric acid to form the 1,3 dichloro-2-propanol. In the same time some secondary reactions can happen leading to the formation of beta-gamma dichlorohydrine.

The historical process is carried on with acetic acid as catalyst and the reaction is run at 80-100⁰C [3,4].

Other processes use inert solvents, not water soluble, but able to dissolve the 1,3 dichloro-2-propanol. [5].

Other patents have complex neutralization and separation steps in order to recovery the 1, 3 dichloro-2-propanol chemical from their reaction processes. [6, 7].

The traditional processes which use acetic acid as catalyst have the following main disadvantages:



-Fast consumption of the catalyst due to its evaporation from the reaction mixture because its boiling point is low (the boiling point of the acetic acid is 117°C).

-The kinetic of the reaction is slow-downed due to the presence of the aqueous solution of the hydrochloric acid and to the formation of water by the reaction itself.

-Difficulties in the separation of 1, 3 dichloro-2-propanol from the reaction mixture.

The processes that use inert solvents have the disadvantage that the solvent has to be recovered at the end and then recycled back. This causes excessive energy consumption and a greater number of equipment is needed.

The above disadvantages and the high cost of the glycerol in the past have hindered the industrial implementation of the above processes.

Today the production of biodiesel has increased many times the availability of glycerol at a low cost and this situation makes it competitive to produce the epichlorohydrine via 1,3 dichloro-2-propanol rather than through propylene, whose cost is directly correlated to the cost of fossil oil.

DESCRIPTION OF THE INVENTION

Purpose of the present invention is to eliminate the disadvantages of the traditional processes for the synthesis of the 1, 3 dichloro-2-propanol having found a process that allows to run the reaction between the hydrochloric acid (either gaseous or in solution) and the glycerol with an heterogeneous catalyst. The solid state catalyst is stable at the reaction temperature and it is not depleted during the time because the catalyst is a solid and it remains confined inside the reactor.

The reactor, according to the present invention, is preferably a fluidized bed type reactor, where the catalyst is kept in suspension in the reaction medium by the same gas phase of the reactor that is recycled through a blower in the bottom of the reactor which fluidize the catalyst particles in the reaction medium.

The solid catalyst, being so finely dispersed and suspended in the reaction medium, has a wide contact surface with the reactants and the reaction can run fast and with a very high conversion.

Another purpose of the present invention is to eliminate the problems related to the quantitative separation of the 1,3 dichloro-2-propanol from the reaction products because, with the present process, the gas phase coming from the reactor is not contaminated with the catalyst. In the present invention the catalyst is in fact a non volatile solid and hence is not entrained in the gas phase of the reactor. The only components of the gas phase of the reactor are water, 1,3 dichloro-2-propanol, the excess hydrochloric acid and small quantities of organic by-products that can be easily separated by condensation and distillation.

For the purpose of the present invention, we can use either gaseous or in solution hydrochloric acid. The gaseous hydrochloric acid is preferred and it can be more efficiently used than the hydrochloric acid in water or non water solution. By using gaseous hydrochloric acid the water content in the reaction medium is sharply reduced and the kinetics of the reaction is increased, but the solid state catalyst used according to present invention, is active even in presence of high percentage of water in the reaction medium.

The new process, object of the present invention, can be carried on in a continuous way by feeding the two reactants hydrochloric acid and glycerol as illustrated below and by withdrawing in continuous the 1,3 dichloro-2-propanol, the water and the volatile byproducts in the gas phase and draining the heavy components from the liquid phase.

The reaction products can be recovered in continuous by evaporation of the water and of 1,3 dichloro-2-propanol from the reaction medium. The evaporation can happen by running the reaction at the boiling point of the reaction mixture or by boosting the evaporation at a lower temperature by injecting an inert gas or (in case of use of gaseous hydrochloric acid by its own molar excess).

The 1, 3 dichloro-2-propanol and water can be easily separated by distillation and the excess of hydrochloric acid, that is at its isotropic composition, can be recycled to the reaction.

The hydrochloric acid, gaseous or in solution, is fed into the reactor together with the glycerol in a molar ratio range of 2.1 and 3.3 (preferably 2.25) leaving hence a slight excess of hydrochloric acid.

The reaction temperature is in the range between 80 and 110°C, at the boiling point of the reaction mixture which is function of the pressure set in the dome of the reactor. The pressure is kept in the range of 0, 2- 1, 2 bar abs. The control of the reaction temperature is done by means of a proper heating mode of the reactor.

It was found that, when operating the reaction either with hydrochloric acid in solution or gaseous hydrochloric acid, the residence time in the reactor (referred to the volumetric flow rate of glycerol expressed as 100%) has to be in the range between 0.5 and 4 hours.

It was surprisingly found that a strong cationic acid resin is a good solid state catalyst and that its optimal concentration in the reaction mass of the fluidized bed reactor must be in the range from 5 to 20% of the liquid contained inside the reactor and that the reaction temperature cannot exceed 120°C because the catalyst cannot withstand temperatures higher than 130°C.

The fluidized bed reactor operates under constant pressure control in the sense that the release of the gas phase of the reactor, which contains the product 1,3 dichloro-2-propanol, is regulated by a pressure control valve operating in the range from 0,2- 1,2 bar abs.

Part of the vapors, taken from the dome of the fluidized bed reactor, is recycled in the bottom of the reactor itself to become the motive fluid to fluidize the catalyst inside the liquid phase of the reactor. The recycle is done by means of an ejector that compresses the vapors coming from the reactor dome. In the preferred case of the ejector, the motive fluid is the same liquid phase of the reactor circulated by a pump. In this way the recycled vapors are there intimately mixed with the liquid phase of the reactor. It was in fact found that a good inter-phase contact and turbulence are very important to get a good conversion of glycerol into 1, 3 dichloro-2-propanol.

It is possible to use the process object of the present invention to for producing 1, 3 dichloro-2-propanol from the raw glycerol by produced from the biodiesel plants.

The high boiling impurities of glycerol and the salts, coming from the neutralization of the catalyst used in the production of biodiesel, accumulates in the bottom of the reactor and can be drained off.

In the figure 1 an illustrative example is given of the process object of the present invention.

Glycerol and hydrochloric acid fed into the bottom of the reactor (4). Their flow rate is regulated by the control valves (1) and (2): The reactor is kept at the reaction temperature of 110°C by a suitable heating system (for instance a steam jacket). The vapors coming from the reactor reach the condenser (5) are cooled by the refrigerant (11), water and organics are condensed and collected in the vessel (6). The uncondensed hydrochloric acid is recycled in the bottom of the reactor by the ejector (3), while the organics containing the 1, 3 dichloro-2-

propanol are drained through the line (7). The motive fluid of the ejector is the liquid phase of the reactor that is pumped into the ejector by the pump (12). The mixed flow of hydrochloric vapors and liquid phase from the reactor allows the catalyst to be held dispersed in a fluidized state inside the liquid phase of the reactor. The catalyst is confined in the reactor by means of the holding grids (13). The organics collected in the vessel (6) and drained through the line (7) are sent to a distillation unit for the purifying of 1, 3 dichloro-2-propanol. The excess hydrochloric acid reaches, through the line (8), the neutralizing vessel 9. Any pressure excess and inert is released through the line (10).

EXAMPLES

Example 1

A semi-batch reaction is carried on by feeding in a continuous way gaseous hydrochloric acid into a stirred reactor that was previously filled with glycerol and the heterogeneous catalyst.

Equipment;

- Glass flask with four necks 2000 ml capacity fitted with:
- Reflux glass condenser, said condenser is cooled with a mixture of water and glycol at 0°C and the vents from the condenser are bubbled into a flask filled with a 20% solution of sodium hydroxide to neutralize the uncondensed hydrochloric acid.
- thermometer
- stirrer
- electrical heating basket

Procedure

500 grams of 99% anhydrous glycerol and 50 grams of solid state catalyst Amberlist 15, produced by the company Rohm and Haas are poured into the flask. The flask is agitated and heated up to 100°C .

The gaseous hydrochloric is fed into the bottom of the flask by means of a teflon dip pipe, the flow is measured with a rotameter and kept at 50 NL/h equivalent to 126,84 grams/hour. The operating pressure of the reaction system was 1050 mbar absolute.

All the reaction products (water, alpha-monochlorohydrine, beta-monochlorohydrine, 1,3 dichloro-2-propanol, beta-gamma dichlorohydrine) are condensed in the flask on top condenser and refluxed back into the flask. The excess hydrochloric acid is neutralized by a solution of sodium hydroxide through which it is bubbling.

At the beginning the hydrochloric acid reacts with glycerol to form alfa-mono chlorohydrine and no bubbling is noticed in the caustic soda bubbler.

The reaction is carried on for three hours and at the end the results of the analysis of the organic phase were the following: (mass percentages)

residual glycerol 0,5 %

1,3 dichloro-2-propanol 85,05%

alfa-beta dichlorohydrine 1,15%

beta-monochlorohydrine 13,30%

Example 2

Continuous process carried on with gaseous hydrochloric acid. The hydrochloric acid is continuously fed into a fluidized bed reactor containing a suspended solid state catalyst. Glycerol is fed in a continuous way too.

Equipment:

-Glass cylinder having a diameter of 50 mm and 1000 mm long, endowed with an electrical heating ribbon. The top end of the cylinder is connected to a glass condenser. Uncondensed vapors are recycled in the bottom of the cylinder by a blower. The cylinder has a porous sect in the bottom through which the recycled vapors and the fresh hydrochloric acid are fed into the upper part holding the catalyst.

- Metering pump to feed the glycerol into the glass cylinder through a lateral nozzle located at about 20 centimeters from the cylinder bottom.
- Hydrochloric acid gas cylinder with pressure reducer and flow-meter. Hydrochloric acid enters the cylinder bottom.
- Glass condenser, said condenser is cooled with a water glycol mixture at 0°C coming from a cryostat.
- 2000 ml glass flask to collect the condensate coming from the condenser, vent is bubbled into a flask filled with a 20% solution of sodium hydroxide to neutralize the uncondensed hydrochloric acid.

Procedure

About 400 ml of glycerol are filled into the cylinder up to the glycerol inlet nozzle. 40 grams of catalyst Amberlist 15, produced by the company Rohm and Haas is added to the cylinder which is heated up to 110°C and the circulated through an ejector. The catalyst become dispersed in the liquid phase and fed with hydrochloric acid simultaneously. The flow rate is regulated at 27 NL/h or equivalent to 43.6 grams/hour. The molar ration between glycerol and hydrochloric acid is fixed at 2.2. The flow rate of glycerol is 50 grams/hour.

During the first two hours, only hydrochloric acid is fed to react with the initial charge of glycerol then both glycerol and hydrochloric acid are fed simultaneously:

The operating pressure of the reaction system was 1,070 mbar absolute.

All the reaction products (water, alpha monochlorohydrine, beta monochlorohydrine, 1,3 dichloro-2-propanol, beta-gamma dichlorohydrine) are condensed in the glass condenser and are collected in the collecting vessel. The uncondensed hydrochloric acid is neutralized with the solution of sodium

hydroxide that is contained in the bubbler flask that acts as hydraulic seal of the system.

At the beginning the hydrochloric acid reacts with glycerol to form alpha-mono chlorohydrine and no bubbling is noticed in the caustic soda bubbler.

The reaction was carried on for four hours. At the end the results of the analysis of the organic phase, collected downstream the condenser, were the following: (mass percentages)

glycerol	0,0%
1,3 dichloro-2-propanol	97,87%
alpha-beta dichlorohydrine	1,33%
beta-monochlorohydrine	0,8 %

REFERENCES

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[3] Organic Syntheses, CV 1, 294

[4] A.J. Hill and E.J. Fischer, J. Am. Chem. Soc, (1922), Vol. 44, p. 2586- 2594

[5] E.G. Britton, R.X. Heindel, US 2,144,612 (1939)

[6] E.C. Britton, H.R. Slagh, US 2,198,600 (1940) [7] EP 931211 (1963)

CLAIMS

- 1) A continuous process for the production of 1,3 dichloro-2-propanol where the glycerol and the hydrochloric acid (in gas or in solution form) is reacted at the presence of an heterogeneous strong acid catalyst, for example, the cationic resin Amberlist 15 or Amberlist 36 produced by the company Rohm and Haas.
- 2) As per above claim 1) where the temperature of reaction is within the range from 80 to 110°C and the pressure is in the range from 0,5 bars absolute to 2 bars absolute (preferably 1 bar absolute).
- 3) As per above claims 1) and 2 where the vapors coming from the reactor are sent to a condenser cooled with a refrigerant and where the uncondensed vapors thereof are recycled back into the reactor by an ejector where motive fluid (which is the liquid phase of the reactor) are transferred into the ejector by a suitable pump.
- 4) As per above claims 1) and 2) where the reactor is a three-phase fluidized bed and where the catalyst particles are kept in suspension by the vapors taken from the vapor phase and compressed back into the bottom of the reactor.
- 5) As per above claim 3) where the vapors driven to the ejector are taken directly from the gas phase of the said reactor.
- 6) As per above claim 4) where the catalyst is permanently confined in the reactor shell between two proper grids or sieve plates through which the gas and the liquid phases can flow but not the catalyst particles.
- 7) As per above claims where the residence time of glycerol (expressed as 100%) is in the range from 0.5 to 4 hours , preferably 1 hour.