

# The production of epichlorohydrin from glycerol.

A Bachelor Integration Project for Delfzijl's Chempark



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IE&M Bachelor Thesis

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## Problem context

The city of Delfzijl (Netherlands) has a chemical park with multiple factories present. The companies at the chemical park have interrelationships with each other which results that if a few of them stop producing products, the other companies will find problems in their own existence. The committee Willems started an investigation how the chemical park should optimize its competitiveness among the business environment nowadays. Willems used to be a high ranked employee of Shell before leaving the company. The committee stated that if the companies on the park want to stay in business, changes within production methods have to be made. A more sustainable production method where green raw materials like biomass are converted into valuable products is the solution to stay competitive. Prof. Dr. Ir. HJ (Erik) Heeres and Dr. Ir. Andre Heeres have conducted research about the possible production opportunities this site has to offer. Seven to nine production opportunities were identified. The production of epichlorohydrin out of glycerol is one possible opportunity companies could invest in. This research goes deeper into the possible options with what methods, catalysts and production conditions the optimal production method of epichlorohydrin from glycerol can be conducted and whether it can compete with traditional production methods of epichlorohydrin. There is a glycerol purification system present at the chemical park Delfzijl from which purified glycerol can be obtained. The result of this research could advise the companies on the chemical park Delfzijl to further invest in this green production method in the near future.

## Stakeholder analysis

-Chemical park Delfzijl is seen as the **problem holder** since these companies have to innovate into more sustainable production methods in order to stay competitive on the current market. Hence, searching for a possible sustainable method to produce epichlorohydrin from glycerol on industrial scale becomes interesting. The park as a whole is in need for solutions.

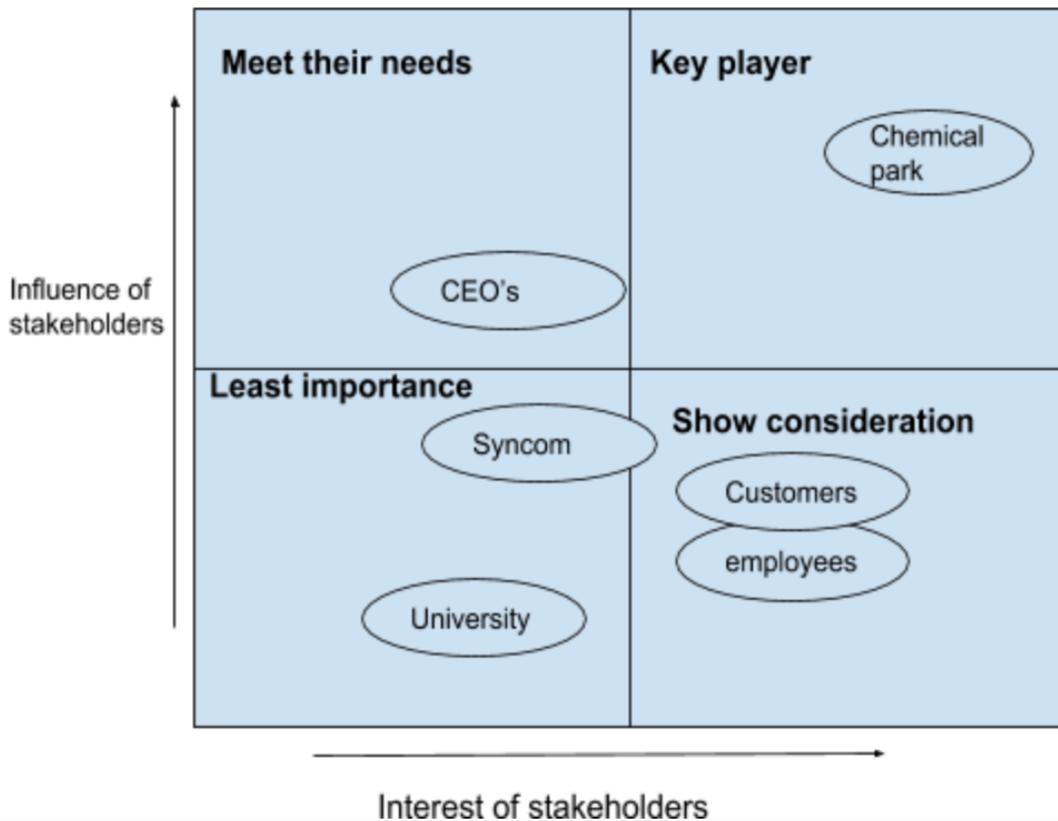
-CEO's of Chemical park's companies: The Chief Executive Officer of the company and is the end-responsible for the successes and failures the company makes. He/she takes the important end decisions that have big impacts on the company as a whole. In order to keep the companies profitable, innovation into green sustainable energy must be made.

-Employees: Employees operating in the company can vary from sales to operations. Opening a new market for the company (epichlorohydrin) would mean closing other divisions or increasing the amount of employees. Their influence is low since directors will make the decisions.

-Customers: epichlorohydrin is a well-known industrial chemical so big companies who will use the epichlorohydrin as their raw material for downstream purposes will be interested in the research and follow activities in production of epichlorohydrin.

-Syncom: the company from who Dr. Ir. Andre Heeres is conducting research together with prof. Dr. Ir. HJ (Erik) Heeres from the RUG into the possible production processes to be used in Delfzijl. Their research can influence the chemical park by advising whether production methods might be profitable or not.

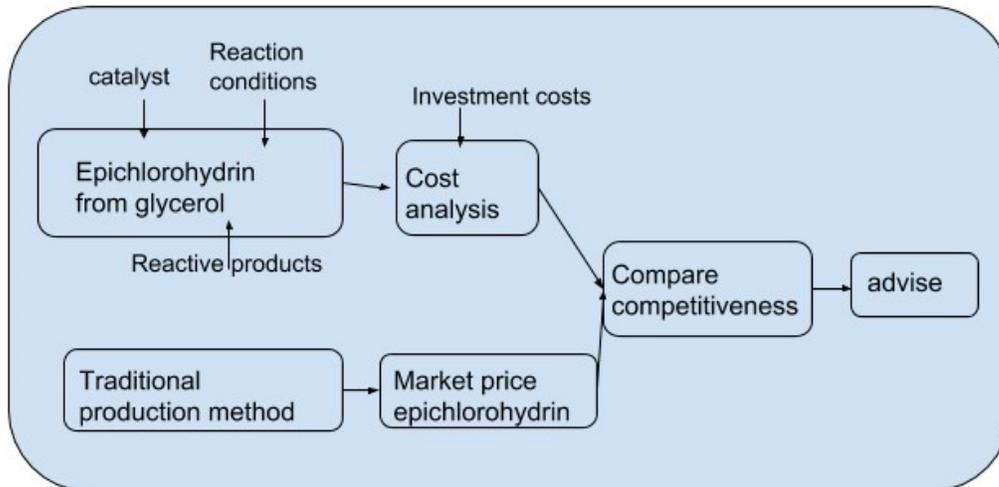
The matrix with all the stakeholders:



## System description

The system as defined in this research are the possible reaction processes methods of epichlorohydrin from glycerol and at the end a cost analysis of the optimal production method found. Conditions as temperature and pressure are taken into account as well as catalyst choices. With the cost analysis, the profit margin can be calculated against the market price of epichlorohydrin at this moment.

System of this research:



Restraints to a competitive production process of epichlorohydrin from glycerol are:

- Availability of glycerol and the price per unit.
- Availability of reactive products at Delfzijl's chemical park and price per unit.
- What catalysts to speed up the process.
- Process conditions of the reactions.

## Goal statement

Find a techno-economically feasible production method applicable, on industrial scale, for the reaction glycerol to epichlorohydrin, in Delfzijl competitive with epichlorohydrin market price.

## Design goal

The goal of this research is to find techno-economically viable production method for epichlorohydrin from glycerol. The outcome will be multiple reaction possibilities compared in a matrix. Once the optimal catalyst and production method is found, an elaboration on it will be made. With this production method and a cost analysis of it, an advice can be made to invest in the production of epichlorohydrin from glycerol or not.

## Scope

The scope remains within the reaction of glycerol to epichlorohydrin with the possible raw materials available in the chemical park's area. In what way the glycerol is made is not of importance and further implementation of epichlorohydrin neither, except for an overview of possible companies at the chemical park present who might be interested in the epichlorohydrin.

## Research questions

### **Main Question:**

Is the production method of epichlorohydrin from glycerol techno-economically viable with the traditional production method of epichlorohydrin? By investigating the production method with glycerol against traditional methods an advice can be made.

### **Sub questions:**

1. Intro to glycerol and epichlorohydrin markets.
2. What is the traditional fissile-based production method of epichlorohydrin?
3. What kind of reaction(s) is/are reported for production of epichlorohydrin from glycerol?
4. What is the influence of temperature, pressure and a catalyst on the process? (Compare results)
5. Can the epichlorohydrin from glycerol route be competitive with the current epichlorohydrin market price?

## Cycle choice

For this research the Rigor Cycle described, by Hevner, is applied most of the time. This research is a market analysis conducted by literature research. This means that most of the time, papers and articles are read from behind the desk in order to answer the research question. The ultimate solution will not be tested (at least not in this research) so the Rigor cycle will be stopped at the moment when the solution is found.

The design cycle will not be of relevance since the production of a design as artifact is not within the scope of this research. This however, is a possibility for further research if the solution is found to be promising on industrial scale.

The relevance cycle will be taken into account partly and briefly since the costs are to be analyzed and whether the product will be competitive on the market. This is interesting for the project since once an optimal production method is established, cost analysis give an indication if it might be a usable technique for a company on the chemical park.

## Abstract

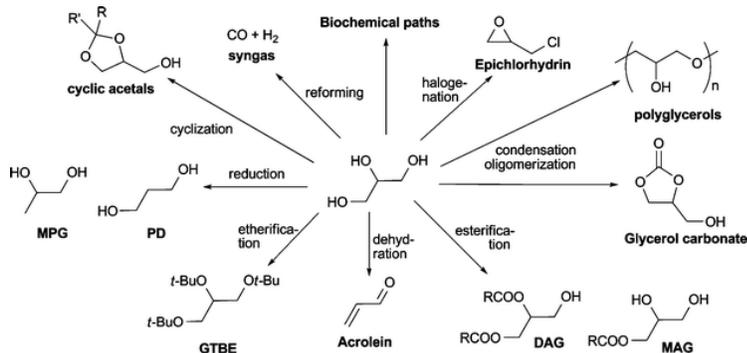
To optimize the competitiveness of bio-diesel with traditional diesel, by-products in the production process like glycerol can be sold or have to find a value adding purpose. This research investigates whether it is techno-economically feasible to make green epichlorohydrin (ECH) from glycerol. The conditions temperature, pressure and yield of catalyst are taken into account to find the optimal production process of epichlorohydrin from glycerol. The most investigated synthetic methodology involves a two-step process, using hydrochloric acid to make a dichlorohydrin intermediate followed by a base catalyzed ring closure to ECH. Hexanoic acid is chosen as optimal catalyst for the hydrochlorination process over acetic acid since yields are similar but separation of the hexanoic acid catalyst is less complicated. This research discusses pressure as well as temperature in the hydrochlorination process; conclusions were that 383K and 670kPa were optimal for hydrochlorination using hexanoic acid as catalyst. The dehydrochlorination of the dichlorohydrin is traditionally done by adding sodium hydroxide operated at 363 K and 30kPa, this research includes this method as well as a solid Mg-Al oxide. Eventually, a cost estimation is made using literature research resulting in a profitable plant for the location Delfzijl.

## Backgrounds

In the sense of renewable products, biodiesel is an interesting alternative for the over-used diesel, an oil derived transport fuel having comparable properties to the green solutions-derived biodiesel (Lari et al., 2018). Biodiesel has been commercially developed, but the production methods of biodiesel still have a lot of possibilities for improvements. In order to make biodiesel more attractive compared to diesel, by-products from producing biodiesel must find a value adding purpose as well. The production of biodiesel generates around 10 to 100kg of glycerol per ton biodiesel; turning this glycerol into a valuable product, would favor the competitiveness of biodiesel (Lari et al., 2018).

### Glycerol

Glycerol, a by-product of reactions in oleochemical- and biodiesel-plants with the chemical formula  $C_2H_8O_3$ , can be used for further value added products (Tan, Abdul Aziz, & Aroua, 2013).



**Figure 1.** The possibilities glycerol has to offer to react into valueable products. (Katryniok et al., 2011)

The possibilities of adding value to glycerol obtained vary from glycerol ethers, ethanol as well as methanol and more (see figure 1) (Almena & Martin, 2016). Market value of glycerol has grown from 100kt in 1995 to 3.5Mt in 2015, a considerable amount that is still growing (Lari et al., 2018). The molecule is very reactive since it contains alcoholic groups on the primary and secondary carbon atoms, hence, it can react to derivatives like aldehyde, amine, ester and ether (Tan et al., 2013). The glycerol obtained from oleochemical and biodiesel plants contain oily, alkali and soap components, this form of glycerol containing impurities is crude glycerol which can be purified (Tan et al., 2013). Crude glycerol has a low value since it is not applicable yet for many chemical usages as feedstock because of the low purity (Tan et al., 2013). Multiple techniques are available for purification of the glycerol such as, distillation, filtration, ion-exchange techniques and adsorption (Tan et al., 2013). The scope of this research does not extend towards the purification of glycerol and considers the glycerol as purified when entering the system's boundaries.

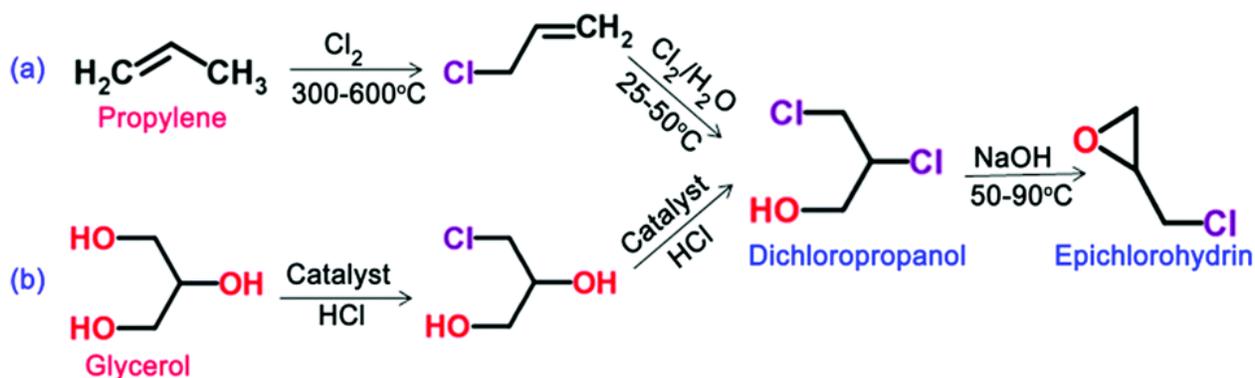
### *Epichlorohydrin*

Epichlorohydrin, a traditional fossil based bulk chemical for industrial purposes, is an epoxide made from synthesizing allyl alcohol, allyl chloride, dichlorohydrin or propylene (Giri, 1997). Epichlorohydrin is largely used in production processes including epoxy resins and manufacturing polymers, giving it a worldwide scale of around 2Mt per year (Lari, Pastore, Mondelli, & Pérez-Ramírez, 2018). One of the applications is to strengthen paper as a strength additive. Using epichlorohydrin enables a paper producer to use less pulp and more fillers while maintaining strength and stiffness (Bower, 2000). Epichlorohydrin usage also can be found in adhesives, elastomers, plastics and rubbers as well. (Pembere AM, Yang M, & Luo Z, 2017).

## Benchmark

### Propylene into epichlorohydrin, via allyl chloride

Traditionally, epichlorohydrin is produced from propylene which would undergo an allylic chlorination and hypochlorination to obtain a 1,3-dichloropropanol and 2,3- dichloropropanol mixture (Pembere AM et al., 2017). Although this method was seen as the ideal production route initially, drawbacks were found at the practical situation where the efficiency of chlorine atoms resulted low as well as a large number of by products for disposal (Bell et al., 2008; Pembere AM et al., 2017). The yield of chlorine atoms attached in the chlorination is only 25% of total chlorine atoms used with 75% of the chlorines as byproduct or waste (Almena & Martin, 2016). Secondly, the hazardous  $\text{Cl}_2$  has to be used as a reagent. Due to the drawback mentioned as well as escalating costs of petrochemical materials, give an opportunity for a more efficient and sustainable production method (Pembere AM et al., 2017).



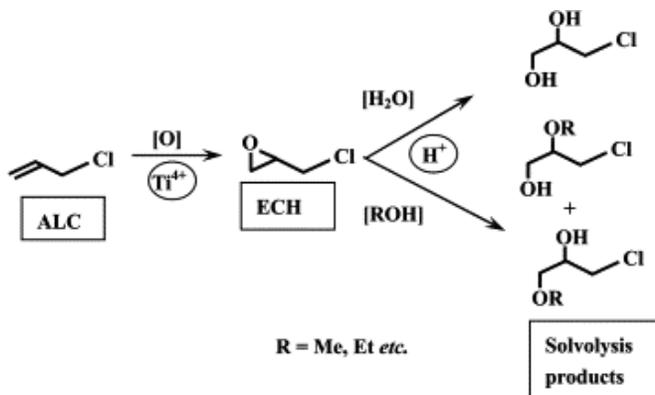
**Figure 2.** (a) The traditional multi-step reaction from propylene to epichlorohydrin. (b) A GTE process possibility to synthesize glycerol to epichlorohydrin (Pembere AM et al., 2017).

### Allyl chloride to epichlorohydrin

After the propylene has undergone a chlorination there remains allyl chloride (ALC). The allyl chloride can be further processed into dichlorohydrin (DCH). This DCH follows a ring closure using NaOH. Another option from the first chlorination step is to use the ALC molecules directly towards epichlorohydrin (ECH) by using an oxidizing agent as well as a catalyst. The following paragraphs cover research conducted using different catalysts and their conversion of ALC and yield of the ECH obtained.

#### TS-1 as catalyst

The product that remains after the chlorination of propylene under high temperatures is allyl chloride (ALC). The ALC can undergo an epoxidation reaction to form epichlorohydrin directly using a catalyst and  $H_2O_2$ . Choosing the catalyst is important for the yield and conversion as well as which by-products are produced. Applying, for example, titanium silicalate-1 (TS-1) as the catalyst in the process, results in three by products: hydrolysis-, re-oxidation- of epichlorohydrin and a reaction of the epichlorohydrin with methanol present (see figure 3) (M. Wang, Zhou, Mao, & Zheng, 2012). TS-1 is a catalyst synthesized by EniChem applicable for green oxidations combined with  $H_2O_2$  as oxidant (M. Wang et al., 2012). The presence of methanol is required in order to form epichlorohydrin (ECH) most efficiently with TS-1 and  $H_2O_2$ . This combination results in the three byproducts mentioned before (L. Wang et al., 2007).



**figure 3.** Reaction path of allyl chloride to epichlorohydrin and other side reactions (L. Wang et al., 2007).

### *Ti-MWW as catalyst*

Using a stable catalyst with a yield as high as possible results in multiple options to consider for the epoxidation of ALC to ECH. Ti-MWW is taken into account in Wang's investigation to find the catalyst that has the most preferred catalytic properties for the benchmark reaction. L. Wang et al., 2007 provides a comparison in catalysts and their conversions as well as yields to produce ECH from ALC using Ti-MWW as a catalyst. The research makes a distinction between four different types of catalysts: two times a synthesized Ti-MWW: hydrothermally (HTS) and post-synthesized (PS) and two other catalysts: Ti-Beta and Ti-MOR (L. Wang et al., 2007). The research tackled different solvents as well which resulted in an optimal conversion of ALC and ECH yield by applying MeCN or Acetone. Table 1 show a few of their findings considering multiple catalysts. A yield up to 83% can be reached using a Ti-MWW catalyst.

| <b>epichlorohydrin from allyl chloride (with H<sub>2</sub>O<sub>2</sub>)</b> | <b>ALC conversion rate (mol%)</b> | <b>Epichlorohydrin selectivity (mol%)</b> | <b>Yield (%)</b> |
|--|-----------------------------------|---|------------------|
| <b>Ti-MWW-PS-2 (1)</b>   | 83.4                              | 99.9                                      | 83.3             |
| <b>Ti-MWW-HTS (1)</b>  | 68.0                              | 99.9                                      | 67.9             |
| <b>TS-1 (1)</b>  | 75.1                              | 97.2                                      | 73.0             |
| <b>Ti-Beta (1)</b>   | 2.5                               | 98.6                                      | 2.5              |
| <b>Ti-MOR (1)</b>  | 1.6                               | 98.9                                      | 1.6              |

*Table 1. Research by Wang showing conversion of ALC and the selectivity and yield towards ECH (L. Wang et al., 2007).*

### *TRL (readiness level)*

The readiness level of producing ECH from allylic chlorination of propylene is very high since producing is applied on a very large scale already (Bell et al., 2008). Hence innovation in this process is low and know-how is very high developed. The total yield of the production process from propylene to epichlorohydrin is around 73% (Kubicek, Sladek, & Buricova, 2009). At the moment of this research, the price of propylene is 1,000 EUR/ton (Straathof, 2017). The price of propylene fluctuates with the oil price which can bring any production process, even with a high TRL, in financial danger when oil prices further rise.

## **Innovation**

### *Glycerol into epichlorohydrin*

A sustainable alternative production method to produce epichlorohydrin is known as glycerol-to-epichlorohydrin (GTE) (Pembere AM et al., 2017). Since the glycerol is a by-product from bio-based production, using glycerol would make epichlorohydrin a more sustainable, bio-based product. Epichlorohydrin can be obtained using the GTE process in two steps producing dichlorohydrin as an intermediate shown in figure 2b (Almena & Martin, 2016). The simple procedure is difficult to use on industrial levels since the raw material costs of glycerol are higher than propylene costs according to

Pembere. This would result in a more expensive epichlorohydrin, which is difficult to sell commercially (Pembere AM et al., 2017). On top of that, studies have shown that the GTE process, which uses a homogeneous carboxylic acid catalyst, has difficulties separating and recovering the catalyst due to the low boiling point (Pembere AM et al., 2017). However, raw material costs have become more in favor of developing epichlorohydrin from glycerol since developments in the biodiesel industry provide a surplus of glycerol. This abundance in glycerol availability has put downward pressure on the prices of glycerol. Hence, its costs as starting material have reduced and finding an optimal catalyst has shown high interest.

We can conclude there are two different reactions to be looked into; the hydrochlorination process and the ring closure. At the hydrochlorination process, the most important factor for an effective and high yield is the catalyst chosen. The next paragraphs will look into the parameters of temperature, pressure and catalyst to be chosen for the optimization of the hydrochlorination process. Conversion of hydrogen chloride, yield of the preferred product, TRL and ability to recycle are taken into account. The second and last reaction step of the GTE process is the dehydrochlorination of dichlorohydrin (DCH). At a first glimpse this looked to be less complex since sodium hydroxide can be used for this step, but new innovative reaction methods are taken into account as well.

### *Hydrochlorination*

As mentioned in the previous paragraph, a catalyst is used to speed up the reaction rate and conversion of hydrogen chloride with glycerol. The hydrochlorination of glycerol to monochlorohydrin (MCH) and consequently into dichlorohydrin (DCH) (see figure 2b) does not happen straight away. This intermediate process step to MCH has to be taken into account since the MCH molecules will not be ready for ring closure yet and should be recycled to the reactor to become DCH molecules. An advantage of using carboxylic acids (derivatives) as catalyst is that they stop the reaction when DCH is formed instead of reacting to a trichloropropane (TCP) (Bell et al., 2008). Formation of TCP would result in a less efficient process with less DCH obtained from glycerol and an extra separation step to purify the DCH. Table 2 show different catalysts and their conversions, selectivity as well as process conditions and TRL. The TRL score is based on a research of Iowa State University and explanation is given at the Appendix A. In order to find the one or two best production methods applicable for Delfzijl, the research values selectivity, conversion and TRL as the most important factors. Following this paragraph, the catalysts will be discussed to decrease the amount of possible catalysts.

| Catalyst          | 1,3-DCH<br>(S %) | 2,3-DCH<br>(S %) | 1-MCH<br>(S %) | 2-MCH<br>(S %) | Sum<br>(S %) | C <sub>reactant</sub> | Temperature<br>(°C) | Pressure<br>(bar) | TRL<br>(0-10) |
|-------------------|------------------|------------------|----------------|----------------|--------------|-----------------------|---------------------|-------------------|---------------|
| hexanoic acid (1) | 90.67            | 1.91             | 0.79           | -              | 93.36        | -                     | 110                 | 7.85              | 4             |
| hexanoic acid (4) | -                | -                | -              | -              | 98           | 99                    | 110                 | 7.6               | 6             |
| Glycine (1)       | 28.74            | 0.79             | 66.71          | -              | 96.24        | -                     | 110                 | 7.85              | 4             |
| Acetic acid (1)   | 90.55            | 1.93             | 1.83           | -              | 94.31        | -                     | 110                 | 7.85              | 4             |
| Acetic acid (2)   | 29.82            | 0.33             | 63.01          | 5,98           | 99.14        | 99                    | 100                 | 1                 | 3             |
| Acetic acid (5)   | -                | -                | -              | -              | 99           | 99                    | 120                 | 4                 | 5             |
| Adipic acid (2)   | 72.23            | 0.89             | 21.93          | 4,94           | 100          | 100                   | 100                 | 1                 | 3             |
| Malonic acid (2)  | 35.87            | 0.46             | 55.85          | 7,24           | 99.43        | 99                    | 100                 | 1                 | 3             |
| Gold clusters (3) | -                | -                | -              | -              | 100.0        | -                     | -                   | -                 | 1             |

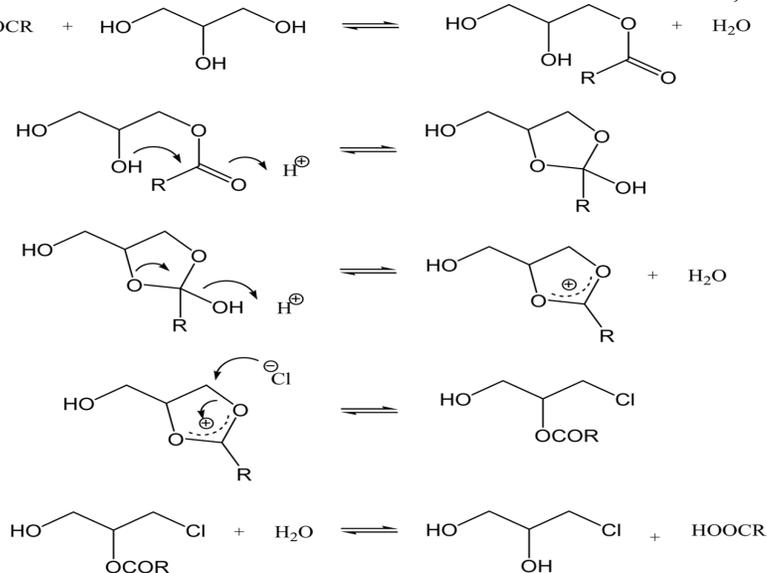
*Table 2. Different catalysts selectivity's and conversions as well as conditions and TRL for the Hydrochlorination of glycerol from different researches. references: (1)WO2006020234A1, (2) (Santacesaria, Tesser, Di Serio, Casale, & Verde, 2009), (3) (Pembere AM et al., 2017), (4) (Almena & Martin, 2016; Lari et al., 2018), (5) (S. Wang, Wong, Jang, & Huang, 2017)*

The catalysts Adipic acid and Malonic acid in table 2 are taken into account as well. Although both acids have been analyzed as catalyst in the GTE process, industrial scale might not give the results preferred. Both molecules have an acidic compound on both sides of the ends. These compounds can further react with the glycerol to an undesired polymer instead of chlorinating the glycerol. Hence, both catalysts will not be taken into account for further research.

The acetic acid in table 2 can be concluded to be the fastest catalyst with a single acidic compound on the molecule although the n-hexanoic acid consumes a similar amount of hydrogen chloride after 4 hours. Glycine converts most of the glycerol but mostly into MCH, which needs a second reactor to react into DCH. Hence, acetic acid and hexanoic acid are preferred for the GTE hydrochlorination process. Both the TRL's of hexanoic acid and acetic acid are higher than the other possibilities, this favors them above the other catalysts as well.

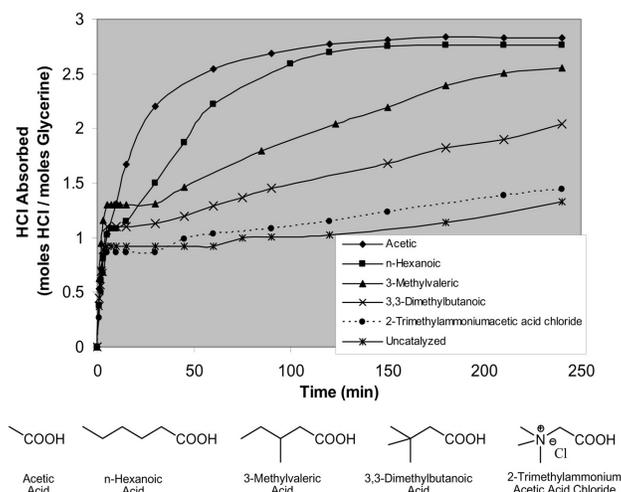
All catalysts mentioned so far are homogeneous, recent research by Anthony M. Pembere resulted in a heterogeneous catalyst for the GTE reaction with a high selectivity towards DCH, the desired product. Gold clusters are used as catalyst in multiple reactions like oxidation of glycerol or propene epoxidation (Pembere AM et al., 2017). Pembere discusses the theoretical possibility of using gold clusters in the GTE process but doesn't translate the theory into practice. Hence, gold clusters cannot be taken into the possibilities of catalyst used for the GTE process.

Since acetic acid and hexanoic acid, the two best options as catalyst, are both carboxylic acids derivatives, mechanisms are researched. The reason why no TCP is formed can be understood once the reaction mechanisms using a carboxylic acid catalyst are looked into. Figure 4 shows the reaction mechanism according to (Bell et al., 2008). In the presence of the carboxylic acid, one hydroxyl is esterified, preferably the first hydroxyl. The ester undergoes a cyclization with a second hydroxyl group preferably present at the second position of the glycerol molecule. Water is lost and an acetoxonium cation remains having a positive loading on the molecule. A negative loaded chloride ion can either attack the first or second oxide atom, which share a positive load. An attack at the first oxide atom more likely due to regioselectivity and more preferred (Bell et al., 2008). From describing the first conversion from glycerol to MCH can be concluded that two hydroxyl groups are needed to start the reaction. This requirement explains why TCP cannot be formed in the presence of carboxylic acid since two of the three hydroxyl groups are chlorinated (Bell et al., 2008).



**Figure 4.** Mechanisms of a carboxylic acid in the GTE process (Bell et al., 2008)

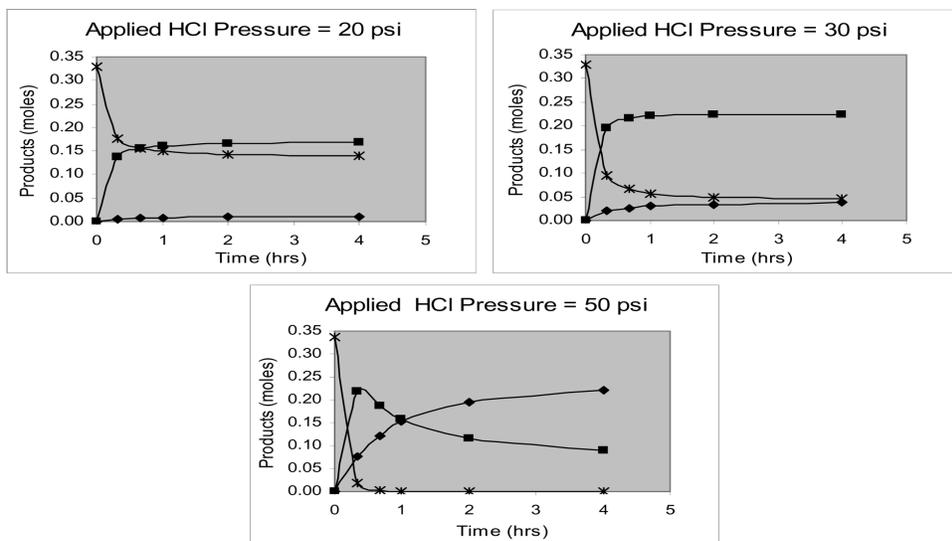
A majority of research concluded that carboxylic acids are effective catalysts for the GTE process; multiple studies analyze acetic acid with a high conversion and yield on batch wise laboratory scale productions (Bell et al., 2008). Although acetic acid seems like an efficient catalyst for industrial scale, there is a drawback to it. When trying to recycle the acetic acid on industrial scale, the acid might vaporize due to its high volatility (Bell et al., 2008). The DCH formed has the highest volatility when not taking acetic acid into account, which makes it easier to separate DCH from the products obtained from the hydrochlorination of glycerol (Bell et al., 2008). The MCH, glycerol, hydrogen chloride and catalyst can be recycled once the DCH molecules are separated, making the production process more efficient. The requirement for the catalyst is that it should be less volatile than the DCH. Any carboxylic catalyst with at least six carbon atoms has a higher boiling point than DCH, hence being less volatile (Bell et al., 2008).



**Figure 5.** Different catalysts used to observe the amount of HCl absorbed by glycerol. (Bell et al., 2008)

Figure 5 shows the absorption of hydrogen chloride with glycerol using different carboxylic acid catalysts against time. Difference in effectivity of catalysts can be because of sterically hindrance; this happens if substituents are close to a carboxylic acid group (Kraft, Gilbeau, Gosselin, & Claessens, 2005). This picture confirms the choice of acetic acid and hexanoic acid for further research.

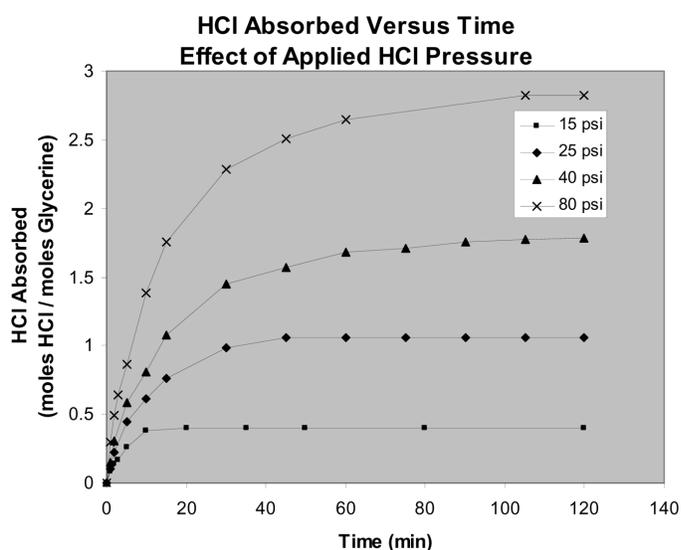
Two other process conditions to determine is whether pressure and temperature can influence the reaction of hydrochlorination of glycerol. Figure 6 a, b and c show experiments conducted with different HCL pressures resulting in different conversions of HCL as well as different composition ratios of MCH and DCH. Concluding, applying a higher pressure than atmospheric pressure results in a higher conversion of glycerol to DCH (Bell et al., 2008) and a higher conversion towards DCH. Although the resemblance of a higher pressure leading to a higher conversion of glycerol is acknowledged following the results, conversion in these experiments are still not as high as what it is preferred to be on industrial scale.



**Figure 6 a, b and c.**  
 Amount of moles of  
 ★ glycerol, ■ 1-  
 MCH and ◆ 1,3-  
 DCH at  
 hydrochloric acid  
 pressures of 20, 30  
 and 50 psi, 120°C  
 and 2 wt% acetic  
 acid (Bell et al.,  
 2008).

Since is concluded that pressure has a direct impact on the hydrochlorination process. Efforts of obtaining DCH at atmospheric pressures with a low amount of catalyst resulted in a low effectiveness. Among the improvements at atmospheric pressures are sparging large volumes of hydrogen chloride gas with the glycerol. The result was that recovered hydrogen chloride contained water as well which needed to be separated before being recyclable (Bell et al., 2008). Using multiple reactive tanks would increase the DCH amount but increases costs as well as system complexity.

Striking is figure 7, and two conclusions can be made analyzing the results. First of all, applying a higher pressure speeds up the conversion of hydrogen chloride according to an equilibrium limited reaction (Bell et al., 2008). Secondly, the hydrogen chloride conversion happens rapidly in the beginning and the rate of consumption increases when increasing pressure. After the quick and high consumption rate, the reaction slows down until it almost ceases to react anymore (Bell et al., 2008). This is an important factor to take into account since applying pressure for a longer period of time than 4 hours will barely increase the conversion of hydrogen chloride. Consequently, process times can be shortened applying this knowledge.



**Figure 7.** Different pressures of HCl applied with glycerol to observe the conversion of HCl. (Bell et al., 2008)

This research takes temperature differences into account as well. As shown in figure 8, different experiments are conducted by Kraft. Looking at experiment 8, 9 and 10, different conversions of glycerol and different DCH ratios are shown at different process temperatures used. The assumption that temperature plays a role in the conversion of glycerol and hydrogen chloride is correct. Different catalysts have their own optimal temperature for their conversion (Kraft et al., 2005).

| Continuous trial No.                         |         | 3      | 4        | 5        | 6        | 7        | 8        | 9        | 10       | 11      |
|--|---------|--------|----------|----------|----------|----------|----------|----------|----------|---------|
| Boiler temperature                           | °C      | 123    | 121      | 123.1    | 130      | 117.6    | 146.4    | 130      | 119.4    | 131.6   |
| Concentrated aq. HCl                         | mol/kg  | 9.59   | 9.59     | 5.29     | 5.29     | 5.29     | 3.95     | 3.95     | 3.95     | 3.94    |
| Nature of the organic acid                   |         | acetic | caprylic | adipic  |
| <b>Feed flow rates</b>                       |         |        |          |          |          |          |          |          |          |         |
| Glycerol                                     | g/h     | 30     | 30       | 30       | 30       | 30       | 22       | 22       | 22       | 25.6    |
| 1,3-dichloropropane-2-ol                     | g/h     | 42     | 42       | 42       | 42       | 42       | 0        | 0        | 0        | 0       |
| Organic acid                                 | g/h     | 3.9    | 9.41     | 9.41     | 9.41     | 9.41     | 6.21     | 6.21     | 6.21     | 3.6     |
| Aq. HCl                                      | g/h     | 79     | 79.5     | 149      | 163      | 148      | 98.7     | 98.7     | 98.7     | 153.5   |
| <b>Overall conversions and selectivities</b> |         |        |          |          |          |          |          |          |          |         |
| HCl conversion rate                          | (%)     | 57.3   | 60.7     | 51.2     | 45.9     | 36.3     | 80.0     | 91.6     | 87.4     | 87.6    |
| Glycerol conversion rate                     | (%)     | 87.8   | 91.8     | 93.0     | 95.2     | 86.4     | 97.7     | 96.7     | 95.0     | 99.4    |
| Org. Ac. in distillate /Org. Ac. used        | mol/mol | 0.55   | 0.02     | 0.11     | 0.13     | 0.16     | 0.11     | 0.14     | 0.20     | <0.0005 |
| Monochloropropanediol selectivity            | (%)     | 61.9   | 56.0     | 51.0     | 57.2     | 47.0     | 27.8     | 29.6     | 25.1     | 7.4     |
| Dichloropropanol selectivity                 | (%)     | 29.7   | 27.1     | 29.5     | 39.7     | 20.4     | 42.8     | 60.3     | 55.2     | 82.3    |
| Oligomer selectivity                         | (%)     | 0.9    | 0.4      | 0.6      | 0.8      | 0.6      | 1.2      | 1.6      | 1.1      |         |

**Figure 8.** The table Kraft created shows with experiment 8, 9 and 10 that a different temperature changes conversion of glycerol by using caprylic acid as catalyst. (Kraft et al., 2005)

To sum up the condition results. Figure 6a, b and c have shown the composition of hydrogen chloride, MCH and DCH over time at different pressures. It is concluded that the conversion of hydrogen chloride happens rapidly and at low pressures it is converted into MCH mostly. At a pressure of 50 psi, the ratio composition between MCH and DCH changes since after 1 hour the amount of DCH becomes greater than MCH. Pressures of hydrogen chloride are preferably between 55 and 150 psi (Kraft et al., 2005). Concluding that applying a higher pressure results in a greater amount of DCH formed than MCH. At a pressure of 110 psi and 110 degrees Celsius, the DCH concentration is 93mol% of the total (Bell et al., 2008). Acetic acid was used as a catalyst with an amount of 5 mol% and the reaction was conducted in a closed vessel for 4 hours (Bell et al., 2008). The ratio of 1,3-DCH to 2,3-DCH was established at 46:1 respectively giving the composition an advantage over the regular ECH process methods with propylene (Bell et al., 2008). Hexanoic acid has similar conversion and selectivity as acetic acid, but is less volatile.

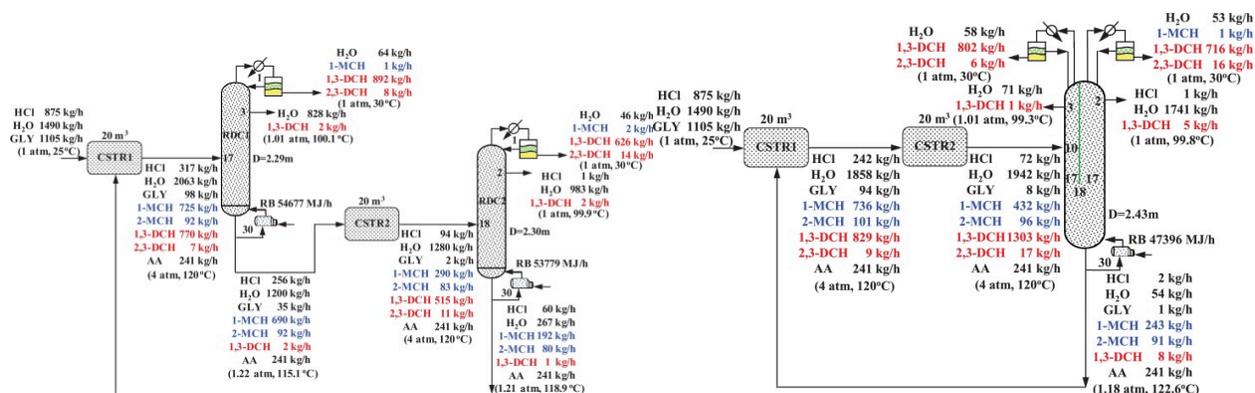
Besides the advantage that GTE processes a more favorable DCH ratio, there is a second advantage compared to the propylene production method. When applying the high pressure GTE, water is formed due to hydrochlorination. The water reduces possibilities of forming by-products like chlorinated ethers and chloroacetone (Bell et al., 2008). This saves costs in materials and disposal costs of by-products formed. Further research will now be done in the catalysts hexanoic acid and acetic acid about their production process in literature.

### *Hexanoic acid*

Almena & Martin describe a process method of epichlorohydrin from glycerol in a research using hexanoic acid as a catalyst. The first step in their research is the purification of glycerol. This research uses an already purified glycerol as input of the system so does not take the purification into account. The process of GTE starts with purified glycerol and hydrogen chlorides as the hydro chlorinating agent. Using a semi-batch reactor prevents the reaction of glycerol to trichloropropane since hydrogen chloride concentrations are remained low. If high concentrations of hydrogen chloride are used, the three-hydroxyl groups could be replaced with three chloride atoms where the last chloride atom attacks the DCH without help of the carboxylic acid. The optimal conditions for the reaction to perform are at 383K and 760kPa while using a catalyst (Almena & Martin, 2016). The catalyst taken is hexanoic acid with an amount of 0.08 mol per mol of glycerol inserted to the reactor. Using a high pressure gas inflow results in a higher absorption of gas in the liquid phase to increase in dichlorohydrin (DCH) formation. The chlorinating agent in gas state, which is not dissolved in the mixture, is exported out of the reactor together with the water stream evaporated by the reaction. The two different dichlorohydrin molecules formed are 1,3-DCH and 2,3-DCH with a respectively mole ratio of 30-50:1 mixture. The GTE production process of obtaining DCH is more favorable than the propyl based hydrochlorination since a 1,3-DCH is more desired than the 2,3-DCH molecule. The reason for this lays in the next process step where a 1,3-DCH undergoes a cyclization up to 300 times faster than a 2,3-DCH molecule would react (Almena & Martin, 2016). The reaction process can be smaller, shorter and more efficient obtaining a surplus of 1,3-DCH over 2,3-DCH. Besides the DCH formed, there are monochlorohydrin (MCH), water and the catalyst in a by-stream as well.

The lighter weighing components; dichlorohydrin, water and hydrochloric acid, can be separated from the monochlorohydrin, catalyst and glycerol molecules which have not reacted to DCH yet. This heavier stream can be used as feedstock to be recycled into the reactor again. The organic DCH is separated from the aqueous hydrochloric acid using a liquid-liquid separator and send to the next reactor. The aqueous phase is treated with sodium hydroxide and diluted to a concentration that can be used in the next reactor together with the organic DCH. There is an excess of sodium hydroxide for the DCH molecules as well as a surplus to neutralize the hydrochloric acid from the first reaction. Both streams come together in the reactor to dehydrochlorize the DCH molecules using the sodium hydroxide at 363K. Using a reactive distillation column shortens the contact time of epichlorohydrin with water; this minimizes the chances of hydrolyzing de formed epichlorohydrin and enlarging the yield of the process (Almena & Martin, 2016). The last step where sodium hydroxide is used for ring closure is a well-known process but has the disadvantage of forming salt by-products. Further on in the investigation will be looked at alternative solutions to deal with this.





**Figure 10 a and b.** (a) The first simulation of DCH from glycerol where a CISTR is attached to a separator which's waste stream is attached to another CISTR and separator. (b) The optimized DCH production system with two CISTR's in series. (S. Wang et al., 2017)

Considering hexanoic acid and acetic acid have similar conversions and selectivity's, hexanoic acid is taken as most optimal as in the literature of (Almena & Martin, 2016).

### Dehydrochlorination

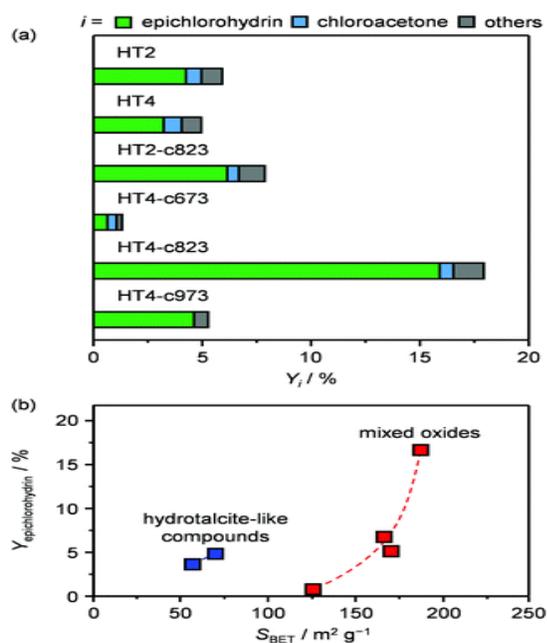
The traditional way to enhance the ring closer of dichlorohydrin, is to use a liquid base like sodium hydroxide. By-products of this reaction are salts like sodium chloride. The dichlorohydrin mixed inside a reactor with the sodium hydroxide is operated at 363 K and 30kPa (Almena & Martin, 2016). In order to process the ECH greener, waste reduction should be optimized as much as possible. Re-usable products would be more in favor for the ring close process, hence, the search for a heterogeneous catalyst starts.

Homogeneous compounds are used in the traditional ring closure reaction; the expectation is that solid alkali oxides or zeolites can offer the same ring closer while hydrochloric acid is formed (Lari et al., 2018). Due to the hydrochloric acid, activity loss of the base becomes an issue, adding reusability to the parameters to take into account.

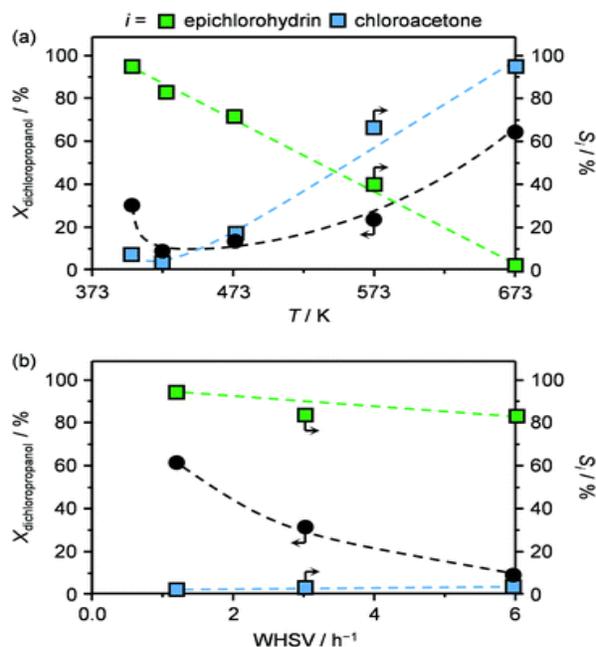
| Oxide:           | Xconv (%) | S (%) | T (K) | P (bar) | T (h) |
|------------------|-----------|-------|-------|---------|-------|
| MgO              | 5         | 30    | 473   | 1       | 0.5   |
| HTlc             | 6         | 70    | 473   | 1       | 0.5   |
| Mg-Al            | 8         | 80    | 473   | 1       | 0.5   |
| Mg-Al (HT4-c823) | 10        | 95    | 423   | 1       | 0.5   |

**Table 3.** Conversions of DCH to ECH, selectivity's and reaction conditions. (Lari et al., 2018)

Lari did research about different solid bases with results shown in table 3 using a TRL 3 lab scale batch process. The performance of Mg-Al oxide stands out with a relative high selectivity of 80%. Since the Mg-Al oxide was performing best, further investigation was started using different compositions of Mg-Al (Lari et al., 2018). HT4-c823, one of the compositions with an Mg/Al ratio of 4, showed the best results in terms of conversion as well as selectivity (see table3). The 823 in the name stands for the calcination of the material conducted at 823 degrees Kelvin but these mechanisms are not taken into account in this research. Figure 11 shows HT2 (Mg/Al ratio of 2) as well as HT4 under different calcination temperatures and their yields of epichlorohydrin. Since from this experiment was concluded that HT4-c823 is the best oxide performer, optimization of conditions were tested further as results are shown in figure 12. From these two figures can be concluded that the optimal conditions are at a T of 423K and WHSV of 1,2h<sup>-1</sup> (Lari et al., 2018). The last element looked at is the reusability of the oxide structure. The chloride atoms will attach on the solid releasing hydrogen oxide instead.



**Figure 11 a and b.** The epichlorohydrin yield of different solid oxides to enforce the ring closure of DCH into epichlorohydrin. (Lari et al., 2018)



**Figure 12 a and b.** (a) Different temperatures applied to determine the optimal temperature of the dechlorination process of DCH. (b) Different WHSV values applied to determine optimal WHSV (Lari et al., 2018)

|                      | Molar Mg/Al | Surface area | C <sub>basic sides</sub> | Cl (wt%) |
|----------------------|-------------|--------------|--------------------------|----------|
| <b>Fresh</b>         | 3.50        | 233          | 483                      | -        |
| <b>Trial 1</b>       | 3.25        | 125          | 6                        | 10.7     |
| <b>Calcination 1</b> | 3.41        | 205          | 425                      | 0.9      |
| <b>Trial 2</b>       | 3.38        | 110          | 8                        | 10.0     |
| <b>Calcination 2</b> | 3.45        | 199          | 409                      | 1.1      |
| <b>Trial 3</b>       | 3.32        | 112          | 5                        | 11.3     |
| <b>Calcination 3</b> | 3.38        | 195          | 397                      | 0.8      |

**Table 4.** The Mg/Al catalyst used and cleaned for multiple times and the results from analysis before and after cleaning every time (Lari et al., 2018).

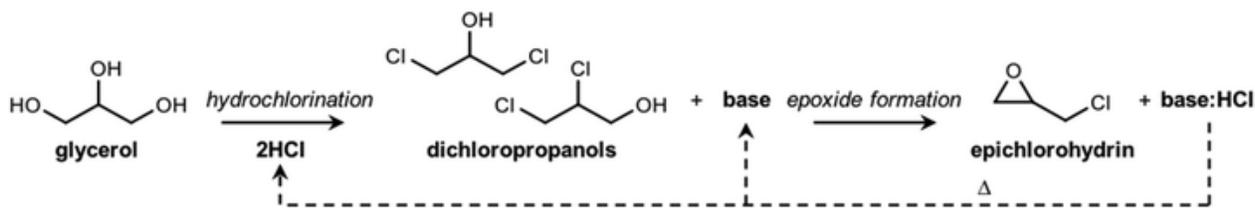
Table 4 show results from analysis of the solid oxide where the number of basic sides per surface area is relatively as high after calcination as from the fresh starting material (Lari et al., 2018). Lari stated:

*‘In addition, the mass and Mg/Al ratio of the calcined sample were equivalent to the data measured for the fresh solid, considering the amount of chlorine that remained in the material, indicating that metals leaching was negligible’* (Lari et al., 2018).

The recovering of the basic oxide structure can be obtained using water, a by-product of the reaction is hydrogen chloride (Lari et al., 2018). Fortunately, hydrogen chloride is used in the hydrochlorination process of glycerol giving the waste stream an additional value to the entire process. The mechanism of recovering is as follows:



The production method following this research would improve the total GTE process with less waste and a greener production method. Three aspects would improve the transformation to a greener process. First, by-products in the process will be limited since the salt product will not be generated any more. Secondly, the by-product that is formed is hydrogen chloride which can be recycled into the hydrochlorination reactor. Thirdly, the non-toxic solid reactant can be regenerated and used multiple times reducing materials needed.



**Figure 13.** The total GTE process if a solid base is used for the epoxide formation and the waste stream reused in the hydrochlorination process. (Lari et al., 2018)

Although costs in materials will decrease following the new ring closing method, costs in terms of energy will increase substantially (Lari et al., 2018). First of all, the processing temperature of the new method is 80 degrees higher than the conventional method. Secondly, the regeneration of the oxide requires energy. Thirdly, water is used as a solvent which has to be evaporated before entering the reactor and again when distillation from the epichlorohydrin. The competitiveness of the greener method would be improved if a lower energy price from a renewable source was available what might happen in near future (Lari et al., 2018). A strategic advantage of the position Delfzijl is the possibility to buy renewable energy from the Germans close to the border. There are many windmill's producing green energy close to the area providing a possibility for an even greener process.

#### *TRL (readiness level)*

TRL indicates how far a certain process is in industrial applicability. The more a process is used on industrial scale, the more advanced is the innovation. The readiness of glycerol-to-epichlorohydrin is a process still in development although multiple factories are producing following the reaction mechanism already. Looking at the experiment of (Bell et al., 2008) gives an insight at the smallest level where a 100mL Hastalloy clave was used (Bell et al., 2008). The distinctions made in readiness are resembled in the figure at Appendix A. From table 2 can be read that hexanoic acid has the highest TRL of 6.

#### **Cost analysis**

The traditional method of producing ECH is dependent on oil prices (since propylene depends on it). At the moment of the research, propylene price is around 1,000 EUR/ton (Straathof, 2017) making it hard to provide a cost estimation where epichlorohydrin is profitably produced following this propylene based method. When looking at prices from 2016 propylene was sold around 600 EUR/ton (ICIS), providing a profitable production method. The increase in price of propylene over the two years can be deducted from the increase of oil price over the same time. Although at the moment of this research propylene prices are high, a cost estimation was made. Appendix E shows the calculations conducted using a process yield of 73% from literature and feedstock prices from Almena and Straathof. Besides material costs, other production costs like utility and administration are estimated around 20% resulting in a production price of 1,987€/t. With the selling price of epichlorohydrin at 1,800€/t, no profit can be made following the traditional production method.

It is disputable whether production is truly done at this cost estimation price since companies are actually still producing following this method and if the estimation is right, no profit is made. The estimation from this research does not give a profitable production from propylene. Hence, this research focusses on the production of ECH from glycerol to see if profit can be made following an ECH market price of 1,800€/t.

### *Hexanoic acid process costs*

Since hexanoic acid has been described by Bell as well as Almena to be separated more easily from the hydro chlorinated stream while giving similar yields as acetic acid, this method will be described in the cost analysis. Within the costs analysis, the distinction is made between the investment costs and the production costs. The production amount for a plant by Almena is 26,000 t/yr, this research assumes a doubled epichlorohydrin production capacity of 53,000 t/yr based on the research of Almena.

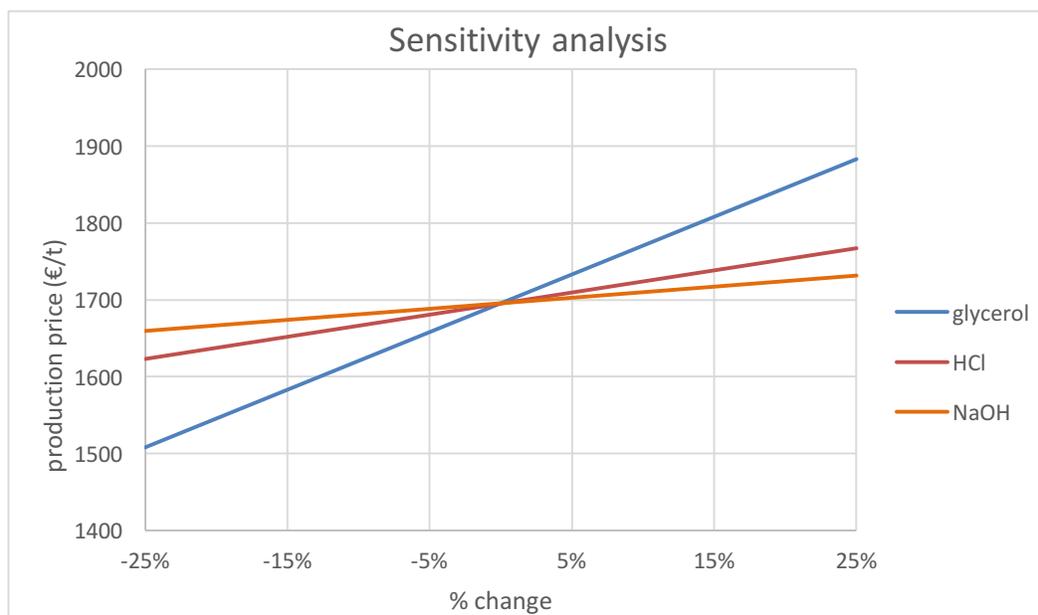
#### Assumptions:

- All information taken from Almena's research will be doubled in streams going in and out of the system.
- The glycerol entering the system in Almena's research has a purity of 80%, this glycerol is purified in their own system by a purification system. This research uses an already purified glycerol since a purification system is present in Delfzijl according to information from Dr. Ir. Andre Heeres. Due to this fact, the amount of glycerol needed is only 80% of what is used in Almena's research.
- The market price of 99 w% hydrogen chloride is 261.34€/t and 99 w% sodium hydroxide 252.74€/t (Almena & Martin, 2016). The water stream in t/yr is obtained from Wang's research with a price of 1€/t using the same ratio of water against glycerol entering the system.
- Another adaption is the cost per ton of the glycerol bought. It is known that crude glycerol is cheaper than purified glycerol so a higher price per ton will be set on 600€/t following a report of Oleonline (see Appendix B). Since the process of purifying glycerol does not have to be taken into account in this research, due to starting with purified glycerol in the system, costs of equipment and energy are lower than Almena had estimated in his research.
- Following the production process yield of 80% from Almena give that the production of epichlorohydrin with a purity of 99,9% is 26,540 t/yr (Almena & Martin, 2016). The production costs cover labor, utilities, maintenance, insurance, taxes and supplies besides the raw materials and management, which are the two biggest costs (Almena & Martin, 2016). The administration, utilities, labor and other production costs besides raw materials are multiplied by 1.5 based on this doubling of capacity to 53,000 t/yr.

This research estimates the total production costs around 90 M€/yr which means a total unit cost of 1,697€/t (Appendix C). The investment costs needed to build the plant as well as all of the startup costs are estimated at 51M Euro. This investment is lower compared to the investment costs in Almena's research (63,7M Euro) since the purification process of glycerol had to be built in their research as well. This research does not need the purification system to be built since purified glycerol is directly bought from a supplier at high

percentage in Delfzijl. Appendix C show the excel calculations with references to Almena and Oleonline. The profit will be around 5.56M Euro foreseeing a payback time of the full investment with around 9 years' time. Considering the plant to producing for at least 20 years, the plant will be profitable before being at half of its life.

Since the raw material prices may vary a lot over time, especially the glycerol price, it is interesting to see what happens with the production costs when raw material prices shift. Figure 14 shows the sensitivity analysis conducted in excel covering a range of -25% to 25% change in feedstock price of glycerol, hydrogen chloride and sodium hydroxide. The cost price of epichlorohydrin is very sensitive to the glycerol price and since history has shown large changes in glycerol price (see appendix B), this can be a big influence on profit. Hydrogen chloride and sodium hydroxide have a relatively low impact on the production cost since their cost price per ton is lower and less tons are used.



*figure 14. The sensitivity analysis with % changes in raw material cost set out against the new production cost price.*

### *Solid oxide costs*

Although no research has included a cost analysis using a solid oxide catalyst in the second step of the GTE process, this research will make an estimation of what the innovative method of Lari would do to the production costs. The estimations of the paragraph above remain the same with a few changes. First of all, the hydrogen chloride costs as raw material can be cut in half since half of this raw material will come from the process of dehydrochlorination. The waste stream from reobtaining the solid catalyst contains hydrogen chloride; this is used in the hydrochlorination process again. Secondly, costs of the raw material sodium hydroxide will be replaced by the solid catalyst which needs a production process for the reuse. Since the catalyst can be used multiple times in the ring closure, the catalyst will not be seen as a raw material instream

but as an investment cost. Due to the preparation of the solid before used again, the utilities in electricity and energy will be higher than in the first cost analysis and an increase of 30% is assumed. In order to clear the solid catalyst from chlorides, water is used, this is taken in the calculations as well with a stream of 14,450 t/yr added to the water stream already present in the previous cost analysis. To the investment cost is an additional amount of 5M added for the recovering system of the catalyst. The whole excel calculation is presented in Appendix D. Utilities are estimated to be higher since energy costs of the renewal of the solid oxide are high due to working at high temperatures. Cost estimations for this alternative, innovative process step give a product price of only €1,489/ton.

## Discussion and Conclusions

Finding value adding products from glycerol can enhance the competitiveness of bio-diesel versus the traditional diesel. One option would be to use the glycerol to produce other chemicals like epichlorohydrin and create additional profit. The traditional production method to make epichlorohydrin is to chlorinate propylene under high temperatures to an allyl chloride; the allyl chloride can then be turned into epichlorohydrin. The research concludes that the two-step method of turning glycerol into epichlorohydrin (GTE) can be value adding, as it is competitive with the traditional production route.

A carboxylic acid is used as catalyst preferably hexanoic acid. A production process with acetic acid is available as well, though it requires a more difficult separation process of the catalyst. The second stage of a ring closure of dichlorohydrin can be conducted by using sodium hydroxide. Results from a TRL 6 process from Almena indicate hexanoic acid reaches an 80% yield of the total process.

The optimal conditions for the hydrochlorination reaction to perform are at 383K and 760kPa while using 0,08 mol hexanoic acid per mol of glycerol. The hexanoic acid can be recycled within the process for re-use to cut costs and disposal costs. Once dichlorohydrin is obtained from evaporation, the dehydrochlorination is the final step using the traditional method, sodium hydroxide, or an innovative method using an Mg/Al oxide solid. The dichlorohydrin mixed inside a reactor with the sodium hydroxide is operated at 363 K and 30kPa. The epichlorohydrin is easily purified by evaporation from wastewater.

Following this traditional GTE production method, production costs are estimated to be around €1,697/ton. An innovative second step in the GTE process would be to use an Mg/Al oxide solid for the ring closure. The salt by-product, NaCl would be avoided following this method and the HCl obtained could be re-used in the hydrochlorination process decreasing material costs. Drawbacks with this method lay in cleaning the catalyst to ensure its effectivity. While cleaning the catalyst from chloride, the catalyst cannot be used in the production process. A solution would be to use a second catalyst while the other catalyst is undergoing a cleaning process. Cost estimations for this alternative, innovative process step give a product price of only €1,489/ton. Since market price of epichlorohydrin is around 1800 €/ton, a profit will be possible following either one of the glycerol to epichlorohydrin production methods. The traditional method requires propylene, which relies on the oil price and at the moment of research is €1,000/ton.

The conclusion is that the GTE process using glycerol as base material can be techno-economically viable with the traditional production method of epichlorohydrin which has a higher production cost.

## References

- Almena, A., & Martin, M. (2016). Technoeconomic analysis of the production of epichlorohydrin from glycerol. *Industrial & Engineering Chemistry Research*, 55, 3226-3238.
- Bell, B. M., Briggs, J. R., Campbell, R. M., Chambers, S. M., Gaarenstroom, P. D., Hippler, J. G., et al. (2008). Glycerin as a renewable feedstock for epichlorohydrin production. the GTE process. *CLEAN – Soil, Air, Water*, 36(8), 657-661.
- Bower, B. K. (2000). *Polyamidoamine/epichlorohydrin resins bearing polyol sidechains as dry strength agents*. Washington, DC: U.S.: U.S. Patent No. 6,165,322.
- Giri, A. K. (1997). *Genetic toxicology of epichlorohydrin: A review* doi:[https://doi.org/10.1016/S1383-5742\(96\)00042-7](https://doi.org/10.1016/S1383-5742(96)00042-7)
- Katryniok, B., Kimura, H., Skrzyńska, E., Girardon, J., Fongarland, P., Capron, M., et al. (2011). Selective catalytic oxidation of glycerol: Perspectives for high value chemicals. *Green Chemistry*, 13(8), 1960-1979.
- Kraft, P., Gilbeau, P., Gosselin, B., & Claessens, S. (2005). *Wo2005054167 (a1) - process for producing dichloropropanol from glycerol, the glycerol coming eventually from the conversion of animal fats in the manufacture of biodiesel* WO2004EP53008 20041118.
- Kubicek, P., Sladek, P., & Buricova, I. (2009). (U.S. Patent No. 7,473,809. ed.). Washington, DC: Google Patents.
- Lari, G. M., Pastore, G., Haus, M., Ding, Y., Papadokonstantakis, S., Mondelli, C., et al. (2018). Environmental and economical perspectives of a glycerol biorefinery. *Energy & Environmental Science*,
- Lari, G. M., Pastore, G., Mondelli, C., & Pérez-Ramírez, J. (2018). Towards sustainable manufacture of epichlorohydrin from glycerol using hydrotalcite-derived basic oxides. *Green Chemistry*, 20(1), 148-159.
- Pembere AM, Yang M, & Luo Z. (2017). Small gold clusters catalyzing the conversion of glycerol to epichlorohydrin. *Physical Chemistry Chemical Physics : PCCP*, 19(38), 25840-25845.

- Santacesaria, E., Tesser, R., Di Serio, M., Casale, L., & Verde, D. (2009). New process for producing epichlorohydrin via glycerol chlorination. *Industrial & Engineering Chemistry Research*, 49(3), 964-970.
- Straathof, Adrie JJ; Bampouli, Ariana. (2017). Potential of commodity chemicals to become bio-based according to maximum yields and petrochemical prices. *Biofuels, Bioproducts and Biorefining*, 11, 5, 798-810, Wiley Online Library
- Tan, H. W., Abdul Aziz, A. R., & Aroua, M. K. (2013). *Glycerol production and its applications as a raw material: A review* doi:<https://doi.org/10.1016/j.rser.2013.06.035>
- Wang, M., Zhou, J., Mao, G., & Zheng, X. (2012). Synthesis of TS-1 from an inorganic reactant system and its catalytic properties for allyl chloride epoxidation. *Industrial & Engineering Chemistry Research*, 51(39), 12730-12738.
- Wang, L., Liu, Y., Xie, W., Zhang, H., Wu, H., Jiang, Y., et al. (2007). *Highly efficient and selective production of epichlorohydrin through epoxidation of allyl chloride with hydrogen peroxide over Ti-MWW catalysts* doi:<https://doi.org/10.1016/j.jcat.2006.12.003>
- Wang, S., Wong, D. S., Jang, S., & Huang, S. (2017). *Novel plant-wide process design for producing dichlorohydrin by glycerol hydrochlorination* doi:<https://doi.org/10.1016/j.jtice.2016.05.055>

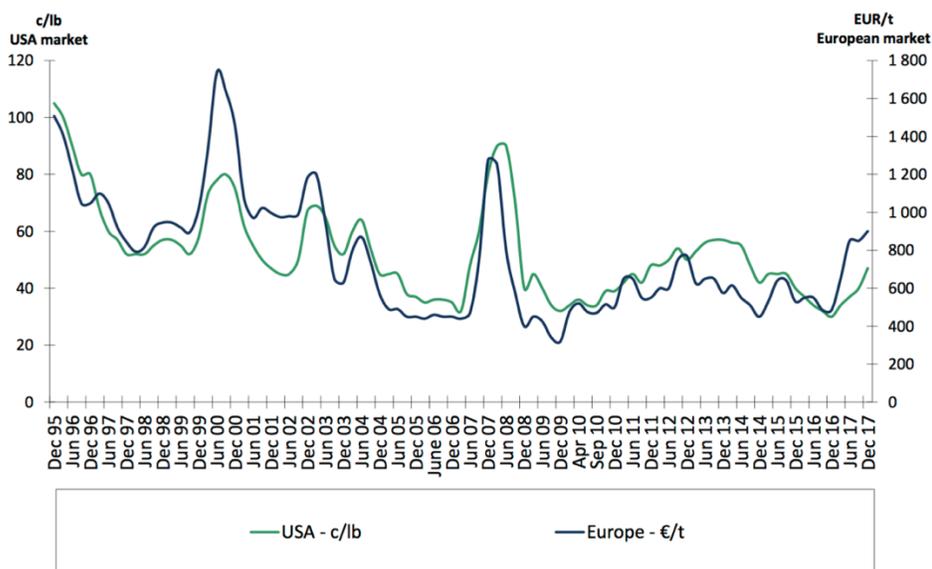
## Appendix



### Technology Readiness Levels

- 1 – Basic Research
- 2-4 – Technology concept / Proof of Concept / Lab validation
- 5 – Validation in relevant environment
- 6 – Demonstration in relevant environment
- 7 – Demonstration in operational environment
- 8 – System complete and qualified
- 9 - Deployment

*Appendix A. Figure for the explanation of TRL chosen for each reaction found. The higher the TRL, the more certain applicableness is on industrial level at Delfzijl. (Horizon 2020 programme, SusChem site)*



Source: HBI

*Appendix B. Figure of the price of purified glycerol in Europe and the USA. (Oleonline, glycerine market report)*

| Yield and conversion from Almena            | %      | Investment costs                              | €        | Feedstock             | €          |
|---|--------|---|----------|-----------------------|------------|
| conversion of glycerol                      | 99     | Total of Almena                               | 63700000 | Raw material          | 62927355   |
| Production process Yield of epichlorohydrin | 80     | Glycerol purification system                  | 12740000 | admin                 | 12960000   |
|   |        | Total investment needed                       | 50960000 | utilities             | 14256000 + |
| Streams                                     | ton/yr |   |          | total                 | 90143355   |
| Glycerol                                    | 66400  | Other production costs from Almena (80%) *1,5 | €        | unit costs (€/t)      | 1697       |
| Hydrogen chloride                           | 58600  | admin   | 12960000 | Revenue               | €          |
| Sodium hydroxide                            | 30400  | Utilities, labor, other                       | 14256000 | epichlorohydrin       | 95616000   |
| water                                       | 89535  |   |          | Profit                | 5472645    |
| Price raw material                          | €/t    | Output  | ton/yr   | profit per unit (€/t) | 103        |
| Glycerol                                    | 600    | epichlorohydrin                               | 53120    |                       |            |
| Hydrogen chloride                           | 261,34 | selling price on market                       | €        |                       |            |
| Sodium hydroxide                            | 252,74 | epichlorohydrin                               | 1800     | ROI                   | 9,31       |
| water                                       | 1      |   |          |                       |            |

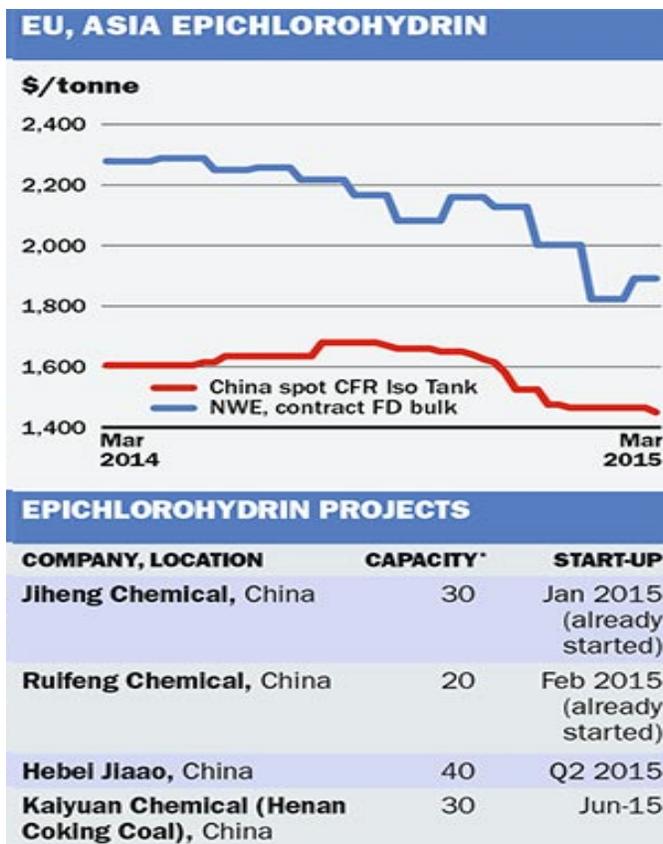
*Appendix C. Calculations in Excel following the research of Almena applied to a system without purification of glycerol and purified glycerol as raw material.*

| Yield and conversion from Almena            | %      | Investment costs                                   | €         | Feedstock       | €          |
|---|--------|--|-----------|-----------------|------------|
| conversion of glycerol                      | 99     | Total of Almena                                    | 63700000  | Raw material    | 47601247   |
| Production process Yield of epichlorohydrin | 80     | Glycerol purification system                       | 12740000  | admin           | 12960000   |
|   |        | Recovering system for catalyst                     | 5000000   | utilities       | 14256000 + |
| Streams                                     | ton/yr | Total investment needed                            | 111920000 | Recovery system | 4276800 +  |
| Glycerol                                    | 66400  |  |           | total           | 79094047   |
| Hydrogen chloride                           | 29300  | Other production costs from Almena (80%)           | €         | unit costs      | 1489       |
| Sodium hydroxide                            | 0      | admin  | 12960000  | Revenue         | €          |
| water                                       | 103985 | Utilities, labor, other                            | 14256000  | epichlorohydrin | 95616000   |
|   |        | Recovery system for catalyst 30% extra of total ut | 4276800   | Profit          | 16521953   |
| Price raw material                          | €/t    | Output   | ton/yr    |                 |            |
| Glycerol                                    | 600    | epichlorohydrin                                    | 53120     | ROI             | 6,77       |
| Hydrogen chloride                           | 261,34 | selling price on market                            | €         |                 |            |
| Sodium hydroxide                            | 252,74 | epichlorohydrin                                    | 1800      |                 |            |
| water                                       | 1      |  |           |                 |            |

*Appendix D. Calculations in Excel following the research of Almena applied to a system without purification of glycerol and purified glycerol as raw material. But without the NaOH and using a solid oxide for the second step in the GTE process.*

| Yield from Kubicek                          | %      | Investment costs             | €        | Feedstock              | €           |
|---|--------|------------------------------|----------|------------------------|-------------|
| Production process Yield of epichlorohydrin | 73     | Total                        | 40000000 | Raw material           | 169200000   |
|   |        | Total investment needed      | 40000000 | total other prod costs | 33840000    |
| Streams                                     | ton/yr |                              |          | total                  | 203040000 + |
| Propylene                                   | 140000 | Other production costs (20%) | €        | per unit costs         | 1987        |
| Cl2   | 140000 | total                        | 33840000 | Revenue                | €           |
| Sodium hydroxide                            | 0      |                              |          | epichlorohydrin        | 183960000   |
| H2O2  | 100000 | Output                       | ton/yr   | Profit                 | -19080000   |
| Price raw material                          | €/t    | epichlorohydrin              | 102200   |                        |             |
| Propylene                                   | 1000   | selling price on market      | €        |                        |             |
| Cl2   | 180    | epichlorohydrin              | 1800     | ROI                    | -2,10       |
| Sodium hydroxide                            | 252,74 |                              |          |                        |             |
| H2O2  | 40     |                              |          |                        |             |

*Appendix E. Calculations in Excel following the traditional production method of ECH from propylene using H2O2 after obtaining allyl chloride. These are strictly assumptions to indicate the ECH price from propylene is not very low since propylene has a cost price of around 1000 EUR per ton.*



*Appendix F. the market price of epichlorohydrin on the Chinese and Europe market. (Syncom)*