

## Eco-efficiency improvements in the propylene-to-epichlorohydrin process

Madej, Łukasz; Kiss, Anton A.

**DOI**

[10.1002/jctb.7453](https://doi.org/10.1002/jctb.7453)

**Publication date**

2023

**Document Version**

Final published version

**Published in**

Journal of Chemical Technology and Biotechnology

**Citation (APA)**

Madej, Ł., & Kiss, A. A. (2023). Eco-efficiency improvements in the propylene-to-epichlorohydrin process. *Journal of Chemical Technology and Biotechnology*, 98(9), 2110-2121. <https://doi.org/10.1002/jctb.7453>

**Important note**

To cite this publication, please use the final published version (if applicable). Please check the document version above.

**Copyright**

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

**Takedown policy**

Please contact us and provide details if you believe this document breaches copyrights. We will remove access to the work immediately and investigate your claim.

# Eco-efficiency improvements in the propylene-to-epichlorohydrin process

Łukasz Madej and Anton A Kiss\* 



## Abstract

**BACKGROUND:** Epichlorohydrin (ECH) production is an important industrial process, owing to its importance in windmill blade manufacture, but it suffers from several drawbacks such as high energy use, large wastewater production and low atom efficiency. This original study investigates a novel chlorohydrin-free technology with an enhanced separation system for ECH production. Rigorous process simulations were performed in Aspen Plus for the classic and novel processes, and a fair techno-economic and sustainability comparison was made between the new catalytic oxidation route and the classic chlorohydrin process.

**RESULTS:** For the hydrogen peroxide (HP) process route, a novel separation system was developed using methanol as solvent, which enables high purity of ECH. Moreover, allyl chloride (ACH) purification was optimized using thermally coupled distillation to improve the energy efficiency of ACH production. The novel HP process provides 88% higher atom efficiency, about 10% higher yield and a smaller amount of by-products, as well as a 13% increase in production capacity and major savings of 98% in wastewater production, while also achieving lower energy use ( $<40 \text{ MJ kg}^{-1} \text{ ECH}$ ) and reduced carbon dioxide emission ( $1.13 \text{ kg kg}^{-1} \text{ ECH}$ ).

**CONCLUSION:** The developed HP process route is feasible and economically viable. Also, it can be partly retrofitted to existing ECH plants based on the chlorohydrin route. As both processes use the same intermediate product, only the ECH part of a classic process would be replaced by the novel route, while keeping the common ACH part. This approach is the most profitable, as only 55% of capital expenditure is required for this modification, while the plant would benefit from all the improvements provided by the novel process.

© 2023 The Authors. *Journal of Chemical Technology and Biotechnology* published by John Wiley & Sons Ltd on behalf of Society of Chemical Industry (SCI).

Supporting information may be found in the online version of this article.

**Keywords:** fluid separation; process intensification; dividing-wall column; energy efficiency

## ABBREVIATIONS

1,2-DCPOL	1,2-dichloropropanol
1,3-DCPOL	1,3-dichloropropanol
ACH	allyl chloride
CAPEX	capital expenditure
CDP	1-chloropropane-2,3-diol
CMP	1-chloro-3-methoxypropan-2-ol
DCPA	dichloropropane
DCPE	dichloropropene
ECH	epichlorohydrin
HP	hydrogen peroxide
HPPO	hydrogen peroxide to propylene oxide
LLE	liquid–liquid equilibrium
MP	medium pressure
MCPA	monochloropropane
MCPE	monochloropropene
OPEX	operational expenditure
TCP	trichloropropane
VLE	vapor–liquid equilibrium

## INTRODUCTION

Epichlorohydrin (ECH) is an important commodity used to create a variety of products. The most crucial use of ECH is the production of epoxy resins, which are key components in wind blade manufacture because of their light weight and durability.<sup>1</sup> Thus, sustainable and efficient production of these chemicals is essential for wind energy. However, manufacture of ECH is plagued by high energy usage and the generation of large amounts of wastewater, which increase the cost of the epoxy resins. Introducing a new, more sustainable route for ECH production could contribute to speeding up the transition towards renewable energy sources at lower cost. This poses a significant challenge for ECH

\* Correspondence to: AA Kiss, Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, 2629 HZ, Delft, The Netherlands. E-mail: [tonykiss@gmail.com](mailto:tonykiss@gmail.com)

Department of Chemical Engineering, Delft University of Technology, Delft, The Netherlands

manufacturers as the technologies used currently to produce it are mature and the room for improvement is seriously limited.

### Chlorohydrin process

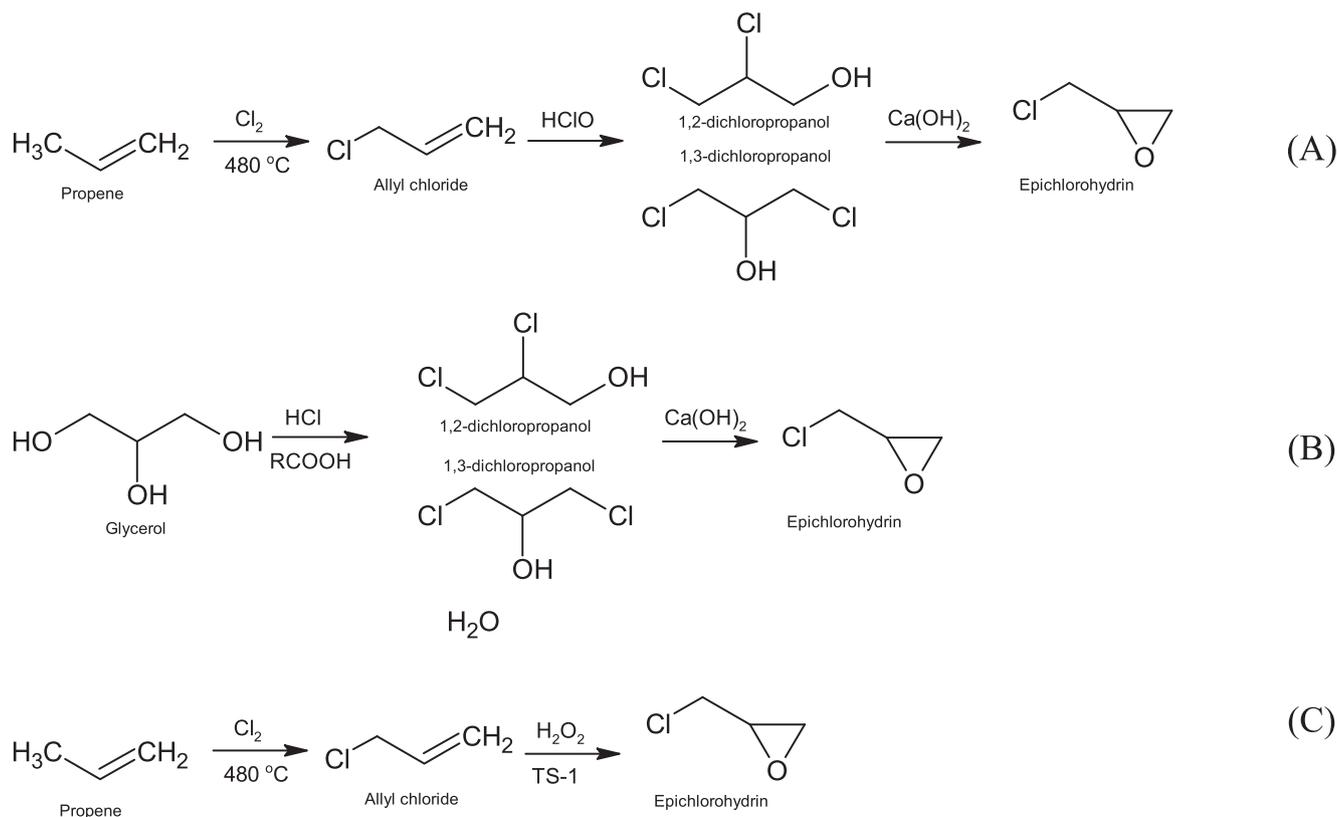
The chlorohydrin-based process was developed in 1947 by Shell,<sup>1</sup> and is the oldest but most used method of producing ECH to this day. It uses propylene, chlorine, milk of lime and water as raw materials. The scheme of chemical reactions taking place in this process is shown in Fig. 1(a). The first step consists of the high-temperature chlorination of propylene to obtain the intermediate allyl chloride (ACH).<sup>2</sup> Then, the reaction mixture is cooled and purified in four distillation columns.<sup>3</sup> Pure ACH is obtained as a distillate in the last column. The next step consists of the hydrochlorination reaction, where ACH reacts with chlorine and water to form a mixture of dichloropropanols (DCPs) and trichloropropane (TCP). This reaction has to be performed at very low ACH concentrations, due to the low solubility of ACH in water.<sup>4</sup> The aqueous solution of DCPs and TCP is sent to the saponification reaction, where it is mixed with milk of lime and purified in a reactive stripping column using steam. The bottom product of this column consists mainly of water, calcium chloride and chlorinated organic compounds.<sup>5</sup> This wastewater stream is challenging to treat due to the low concentration of those compounds, yet it poses a significant threat to aquatic life because of their high toxicity.<sup>6</sup> Owing to operation in highly diluted solutions, this process uses huge amounts of water and generates 30–40 tonnes of wastewater per 1 tonne of ECH,<sup>6</sup> which makes it one of the most water-demanding industrial processes. Other processes have been proposed to make ECH production more sustainable, as follows.

### GTE process

This process was created by Solvay in 2011,<sup>7</sup> as a reverse to the traditional process of producing glycerol. When inexpensive glycerol became available from large-scale biodiesel production, it became profitable to produce ECH from it.<sup>8</sup> A simplified reaction scheme is shown in Fig. 1(b). The first step consists of glycerol chlorination with gaseous HCl, using a high-boiling-point organic acid as a catalyst.<sup>9</sup> The separation of DCPs from other products and glycerol is challenging due to the high boiling points of the components, so these separations have to be performed under vacuum.<sup>10</sup> The following steps are similar to the traditional ECH process, where DCPs are saponified using NaOH or milk of lime. Overall, this technology exhibits several disadvantages identical to traditional ECH technology, such as high energy use and a large amount of wastewater.<sup>1</sup> However, the main improvement is the replacement of propylene raw material with a possibly more cost-effective and more renewable one (glycerol), although with a rather limited availability (as by-product from biodiesel plants).

### Oxidation route

As a breakthrough in olefin processing, catalytic oxidation of the double carbon–carbon bond was first applied to the production of propylene oxide in the HPPO (hydrogen peroxide to propylene oxide) process.<sup>11</sup> This approach has some advantages over the traditional chlorohydrin route, such as higher atom efficiency and lower wastewater production.<sup>12</sup> Application of catalytic oxidation to the ECH process can significantly improve the atom efficiency and reduce wastewater production, as it replaces the hydrochlorination reaction with a more selective process that does not require operation in diluted solutions. The oxidation



**Figure 1.** Chemistry of various chemical routes for ECH production: (a) chlorohydrin process; (b) GTE process; and (c) oxidation route (using hydrogen peroxide).

path has been described in the literature,<sup>1,13,14</sup> and its kinetics for different solvents has been established. The main reactions occurring are shown Fig. 1(c). Several compounds have been proposed as solvents for this process, such as methanol, acetone, isopropanol and higher alcohols. From the kinetic perspective, methanol is the most suitable solvent, as it does not react with hydrogen peroxide (HP) and provides the highest yields of reaction. However, it is unclear what the best solvent entails, as some papers suggested that methanol should not be used as solvent due to difficulties in the separation section for this case.<sup>15</sup> The choice of solvent for this process is important, because it has a major influence both on the reaction and separation section of the process. Danov *et al.*<sup>13</sup> identified alcohols and ketones as potential solvents for homogenizing the HP/ACH mixture, yet the reactivity of ketones with HP, forming hazardous organic peroxides, excludes them as safe choices. Long-chain alcohols can react with HP to produce ketones or aldehydes, impacting profitability due to HP consumption, and posing safety risks as well. For instance, isopropanol can yield acetone, which can also cause formation of organic peroxides. However, methanol remains unreactive with HP under catalysis, rendering it a cost-effective and abundantly available solvent option.

This original study focuses on improving the novel oxidation process, using methanol as a solvent, and enhancing the common downstream processing part (as in the chlorohydrin route), and is the first to provide simulation results for the full process, quantify the performance provided by the novel route and making a fair comparison. Also, a novel separation sequence for the aforementioned HP process with methanol as solvent is proposed and investigated. Despite literature claims regarding the unfeasibility of using methanol,<sup>15</sup> this study shows that the separation system is actually feasible on an industrial scale, when proper separation constraints and heuristics are applied. It is also beneficial to enhance the production of the ACH compound, as both the traditional and HP route of ECH production use the same intermediate compound. As distillation is one of the most energy-demanding unit operations in the process,<sup>16</sup> the focus is on the separation of ACH. To evaluate the influence of improvements to different propylene-to-epichlorohydrin plants, rigorous Aspen Plus models of the traditional and the HP plant were developed. The results were used to calculate key process parameters such as operating expenditure (OPEX), capital expenditure (CAPEX), CO<sub>2</sub> emissions and other sustainability metrics.

A production capacity of 35 kt a<sup>-1</sup> ECH (operated 7200 h per year) was considered. The plant, operated by Zakłady Chemiczne ZACHEM SA in Bydgoszcz, Poland (during 1976–2005), was chosen as base case because of the many patents and data available in the open literature.<sup>2-4,17-21</sup> ZACHEM's plant, commissioned in the 1970s, has been consistently updated with innovative technologies boosting its production capacity. Many plants built in the same era remain top tier, making the comparisons with today's designs fair and relevant. By basing this process on ZACHEM's

plant, we provide a valid benchmark to evaluate novel technologies and designs.

## PROBLEM STATEMENT

The currently used ECH production processes suffer from significant drawbacks, particularly high energy use and large wastewater production. Novel ways of manufacturing ECH have been proposed, but no clear data are available regarding possible improvements of a new process. Moreover, for the ECH process based on the oxidation route, it is known that using methanol as solvent provides the best yield, but the separation sequence for this path has been considered unviable due to the many separation steps involved and significant energy use.<sup>15</sup> Despite some research on the control and safety aspects of the process,<sup>22</sup> a direct comparison between the full novel oxidation route and chlorohydrin process has not yet been made. To solve these problems, this paper proposes an enhanced downstream processing part (as in the chlorohydrin and oxidation route), and an improved HP process using methanol as solvent to provide the best yield and selectivity. A novel separation sequence was developed to allow us to obtain high-purity ECH at viable costs. These efforts also allow making an accurate comparison between the new and old technology and determining the industrial applicability of the novel process.

## BASIC DATA

### Property model

A suitable property model (fluid package) must be chosen to simulate a chemical system. It is essential to include all the binary interaction parameters, and account for possible formation of azeotropes (see Table 1) and the presence of electrolytes. Based on the property method selection scheme from the literature,<sup>23</sup> ELECNRTL was chosen as the most suitable property model, based on the NRTL (Non-Random Two Liquids) model, extended with electrolyte properties, since some components present in the system are electrolytes (hypochlorous acid, HCl and calcium hydroxide). Furthermore, the NRTL model proved successful in modeling the vapor–liquid equilibrium (VLE) and liquid–liquid equilibrium (LLE) of all components and azeotropes present in the ECH production process. It has been also reported that NRTL provides better accuracy than UNIQUAC.<sup>24,25</sup> The validation of other potentially suitable property models was not reported in the literature and therefore they were not considered. All the binary interaction parameters used in this work are provided in the *Supplementary Information* file.

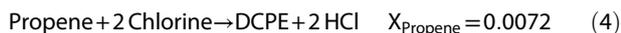
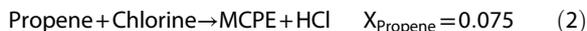
### Reaction conversion and kinetics data

The high-temperature chlorination and the hydrochlorination reactions are rather complex and there are no kinetic data available in the literature. Thus, these reactions were modeled based on the conversion available in patents.<sup>16-20</sup> The values of the

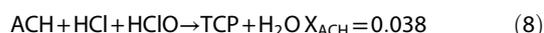
**Table 1.** Azeotropes present in post reaction mixture

Azeotrope	Composition (wt%)	Boiling point (°C)	Azeotrope type
ACH/MeOH	87.7/12.3	39.7	Homogeneous
ACH/water	97.9/2.1	43.4	Heterogeneous
ECH/water	72.0/28.0	89.7	Heterogeneous

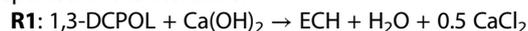
conversions for these reactions are as follows (all conversions were calculated based on propylene):



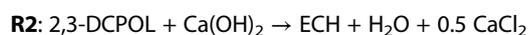
The reactions for the main reactions occurring during the hydrochlorination step are as follows (values of conversion are based on ACH):



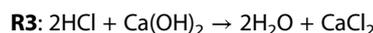
The saponification reactions (R1–R3) and the catalytic oxidation reactions (R4–R7) were modeled according to the kinetics reported in the literature:<sup>26</sup>



$$r_1 = 1.50 \times 10^7 e^{-57.5 \times 10^3 / RT} C_{\text{OH}^-} C_{1,3\text{-DCPOL}} \quad [\text{kmol m}^{-3} \text{ s}^{-1}] \quad (9)$$

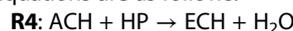


$$r_2 = 4.8 \times 10^6 e^{-58.1 \times 10^3 / RT} C_{\text{OH}^-} C_{2,3\text{-DCPOL}} \quad [\text{kmol m}^{-3} \text{ s}^{-1}] \quad (10)$$



$$r_3 = 4.8 \times 10^6 e^{-58.1 \times 10^3 / RT} C_{\text{OH}^-} \quad [\text{kmol m}^{-3} \text{ s}^{-1}] \quad (11)$$

For the catalytic oxidation reaction, the paper by Danov describing the kinetics was used, in which all the kinetic parameters were measured for the reactor conditions ( $T = 60 \text{ }^\circ\text{C}$ ,  $P = 2.5\text{--}3.5 \text{ bar}$ ).<sup>14</sup> The chemical reactions (R4–R7) and their rate equations are as follows:



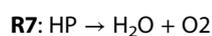
$$r_4 = \frac{A_4 e^{-E_{a,4}/RT} \times b_{\text{HP},4}^0 e^{Q_{\text{HP},4}/RT} C_{\text{HP}} C_{\text{ACH}}}{1 + b_{\text{HP},4}^0 e^{Q_{\text{HP},4}/RT} C_{\text{HP}} + b_{\text{ECH},4}^0 e^{Q_{\text{ECH},4}/RT} C_{\text{ECH}}} \quad [\text{kmol m}^{-3} \text{ s}^{-1}] \quad (12)$$



$$r_5 = \frac{A_5 e^{-E_{a,5}/RT} \times b_{\text{ECH},5}^0 e^{Q_{\text{ECH},5}/RT} C_{\text{ECH}} C_{\text{W}}}{1 + b_{\text{HP},5}^0 e^{Q_{\text{HP},5}/RT} C_{\text{HP}} + b_{\text{ECH},5}^0 e^{Q_{\text{ECH},5}/RT} C_{\text{ECH}}} \quad [\text{kmol m}^{-3} \text{ s}^{-1}] \quad (13)$$



$$r_6 = \frac{A_6 e^{-E_{a,6}/RT} \times b_{\text{ECH},6}^0 e^{Q_{\text{ECH},6}/RT} C_{\text{ECH}} C_{\text{MeOH}}}{1 + b_{\text{HP},6}^0 e^{Q_{\text{HP},6}/RT} C_{\text{HP}} + b_{\text{ECH},6}^0 e^{Q_{\text{ECH},6}/RT} C_{\text{ECH}}} \quad [\text{kmol m}^{-3} \text{ s}^{-1}] \quad (14)$$



$$r_7 = \frac{A_7 e^{-E_{a,7}/RT} \times b_{\text{HP},7}^0 e^{Q_{\text{HP},7}/RT} C_{\text{HP}}}{1 + b_{\text{HP},7}^0 e^{Q_{\text{HP},7}/RT} C_{\text{HP}} + b_{\text{ECH},7}^0 e^{Q_{\text{ECH},7}/RT} C_{\text{ECH}}} \quad [\text{kmol m}^{-3} \text{ s}^{-1}] \quad (15)$$

Table 3 provides the values of all kinetic parameters used in reaction rates for R4–R7.

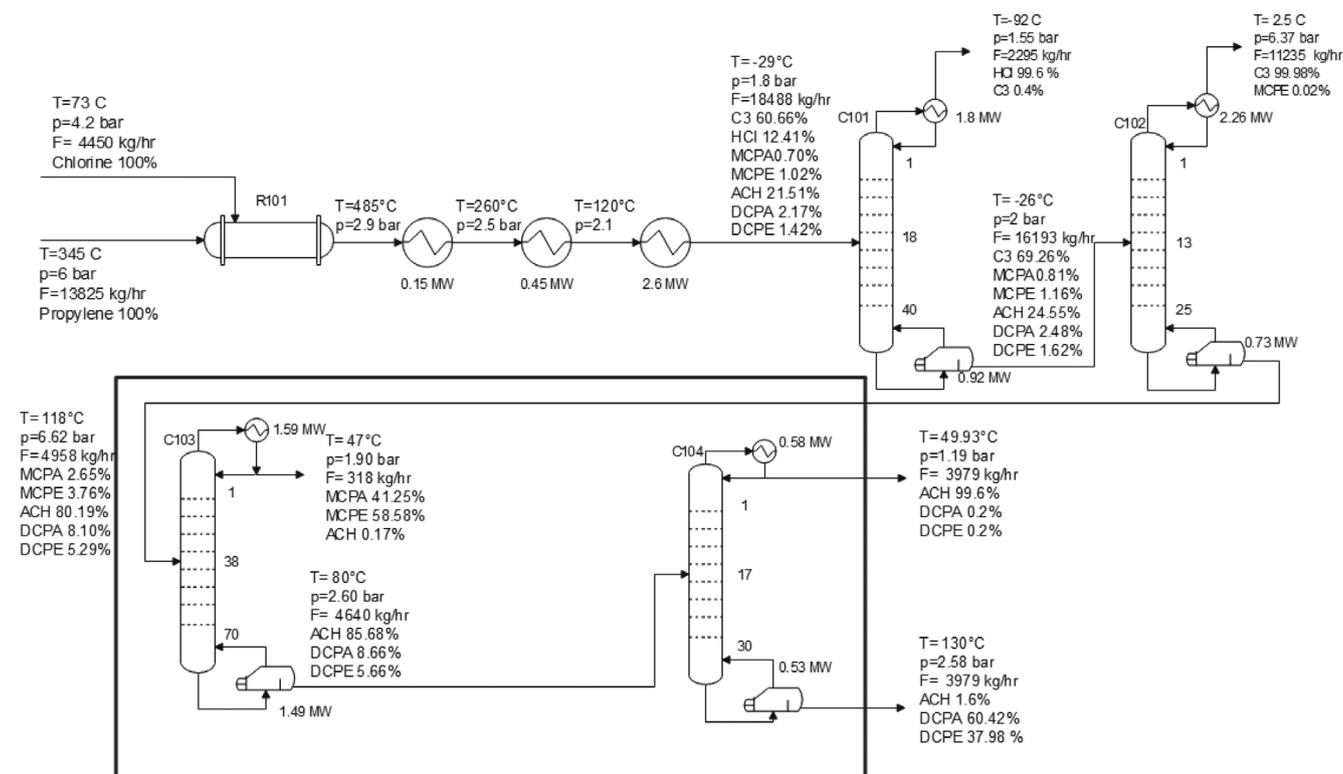
## RESULTS AND DISCUSSION

This section presents the main results of improving the ACH separation (Fig. 2), the base case scenario using the chlorohydrin process (Fig. 3), and the enhanced process based on the oxidation route (Fig. 4), using methanol as solvent recovered in a novel separation sequence. The processes are described below, and then compared in terms of technical and economic performance, and sustainability metrics. The complete mass and energy balances are provided in the *Supplementary Information*.

### ACH separation improvement

The flowsheet related to the ACH manufacturing process is shown in Fig. 2. The energy requirements of this part process are mainly determined by the separation section, because the conditions of the reactor and coolers are limited by the chlorination kinetics. Additionally, the duties of the reboilers and condensers used in the separation section of the plant significantly exceed the duties of the post-reaction coolers (with limited heat integration options), which indicates that optimization of this section of the ACH process can be more beneficial. Columns C103 and C104 have a high number of stages and operate with relatively high reboiler duty; therefore, those columns were chosen as primary targets for improvement. Various distillation techniques were qualitatively investigated to improve these columns, such as cyclic distillation, heat-pump-assisted distillation, heat-integrated distillation column and dividing wall column (DWC). The results of the initial investigation of potential improvements of each technology are listed in Table 2.<sup>27–29</sup> Among them, DWC can provide the best improvement by simultaneously reducing the energy use, column size and number of units required to perform the separation. Moreover, the difference between boiling points of the key components (light: MCPE; heavy: DCPA; medium: ACH) is within the range recommended for DWC. Notably, the DWC distillation option can be applied to both traditional and novel processes for ECH production.

The design of the DWC was performed according to the algorithm proposed in the literature,<sup>30</sup> which covers the design of a four-product DWC, but the design steps can be easily adapted to design a three-product DWC by suitably modifying the process configuration to eliminate one of the side streams. This approach is consistent with the methodology proposed earlier by the same group for the design of three-product DWC units. The first step is creating the  $V_{\text{min}}$  diagram – a graph which plots the vapor flow above the feed divided by feed flow rate ( $V/F$ ) versus the product flow rate divided by feed flow rate ( $D/F$ ).<sup>31</sup> The values needed to create this graph can be obtained either by solving the Underwood equation or by simulating each binary split in Aspen Plus and retrieving the values of the flows directly from the process simulator. As the analytical method uses the assumption of constant relative volatilities, it was decided to use the more accurate, rigorous simulation-based approach. The values obtained from the  $V_{\text{min}}$  diagram were used to initialize the four-column model of the DWC. This simulation approach is difficult to initialize but it provides the best accuracy.<sup>23</sup> The diameter of the DWC was



**Figure 2.** Process flow diagram of the ACH section of the ECH plant, with marked columns combined into DWC.

determined using the correlation for the flooding condition proposed by Premkumar and Rangaiah.<sup>32</sup> The final values of internal flows along with stage requirements are shown in Fig. 5. The feed is introduced at the 8th stage of the prefractionator, which consists of 15 stages in total. The small number of stages in this part of the column is caused by the big difference in boiling points of DCPA and MCPE. The ACH stream is obtained from stage 47 of the main column, which shows that separation of ACH and MCPE is more difficult than ACH and DCPA (consistent with the boiling points of those components). The values of reflux and boil-up ratio for the DWC column have relatively high values (47.21 and 25.8) due to much lower flow rates of both top and bottom product in comparison to the side product. Table 4 provides a comparison between the direct sequence and DWC. In the given case, DWC can provide over 30% energy savings compared to direct sequence. Furthermore, the number of stages required to obtain the same purity is 20% lower for this advance distillation technique, which results in lower equipment cost. Note that the energy use in DWC is lower than the energy required in the first ACH column, which indicates that an indirect sequence may be more energy efficient. Despite higher energy usage compared to an indirect sequence, using a direct sequence as base case facilitates accurate comparison with actual Zchem plant data. Following patent specifications ensured an accurate representation of the plant operation, enabling a reliable evaluation of process performance and potential improvements.

The total number of stages was reduced to minimize the  $N \cdot (R + 1)$  value, which is directly proportional to the annual costs of a distillation column. The feed stage was determined by performing an analysis of feed stage influence on ACH purity, with the highest ACH purity possible when the 47th tray is used as feed stage. The

liquid and vapor splits that offer the best quality of the intermediate product (ACH) are equal 0.1282 and 0.3054, respectively.

Figure 6 shows the temperature and liquid composition profiles along the DWC. The temperature difference between the main column and prefractionator side increases with the difference in concentration, reaching up to 50 °C. This means that the inner dividing wall should be insulated in order to reduce undesired heat transfer between the two sides of the dividing wall, which can reduce the energy savings potential.<sup>33</sup> Thanks to the DWC technology and use of structured packing, two large columns can be replaced by one compact unit, with a smaller size and requiring less area (as well reduced equipment cost).

### Base case traditional process

The flowsheet of the chlorohydrin process was developed based on the available patents.<sup>6-20</sup> Figure 3 shows the flowsheet of this process for ECH manufacturing. Note that the industrial plant used the dry method of ACH production, relying on distillation to separate HCl and propylene; this is contrary to the wet process, where absorption of HCl in water is used instead. As no data were available in the literature on the kinetics of propylene chlorination, the conversion values were specified as described earlier. To do so, a stoichiometric reactor was used in Aspen Plus, and the temperature and pressure data were specified ( $T = 485$  °C;  $P = 2$  bar) based on literature data.<sup>2</sup> The design parameters of the column, such as the number of trays, was obtained from patents and the rest of the parameters were obtained using the Aspen DSTWU model, with specified recoveries of components; for HCl and propylene the recoveries were specified equal to 0.999 to prevent by-product formation and substrate losses. In the case of final ACH purification, MCPE recovery was also set to 0.999, while for the pure ACH the amount of heavy components

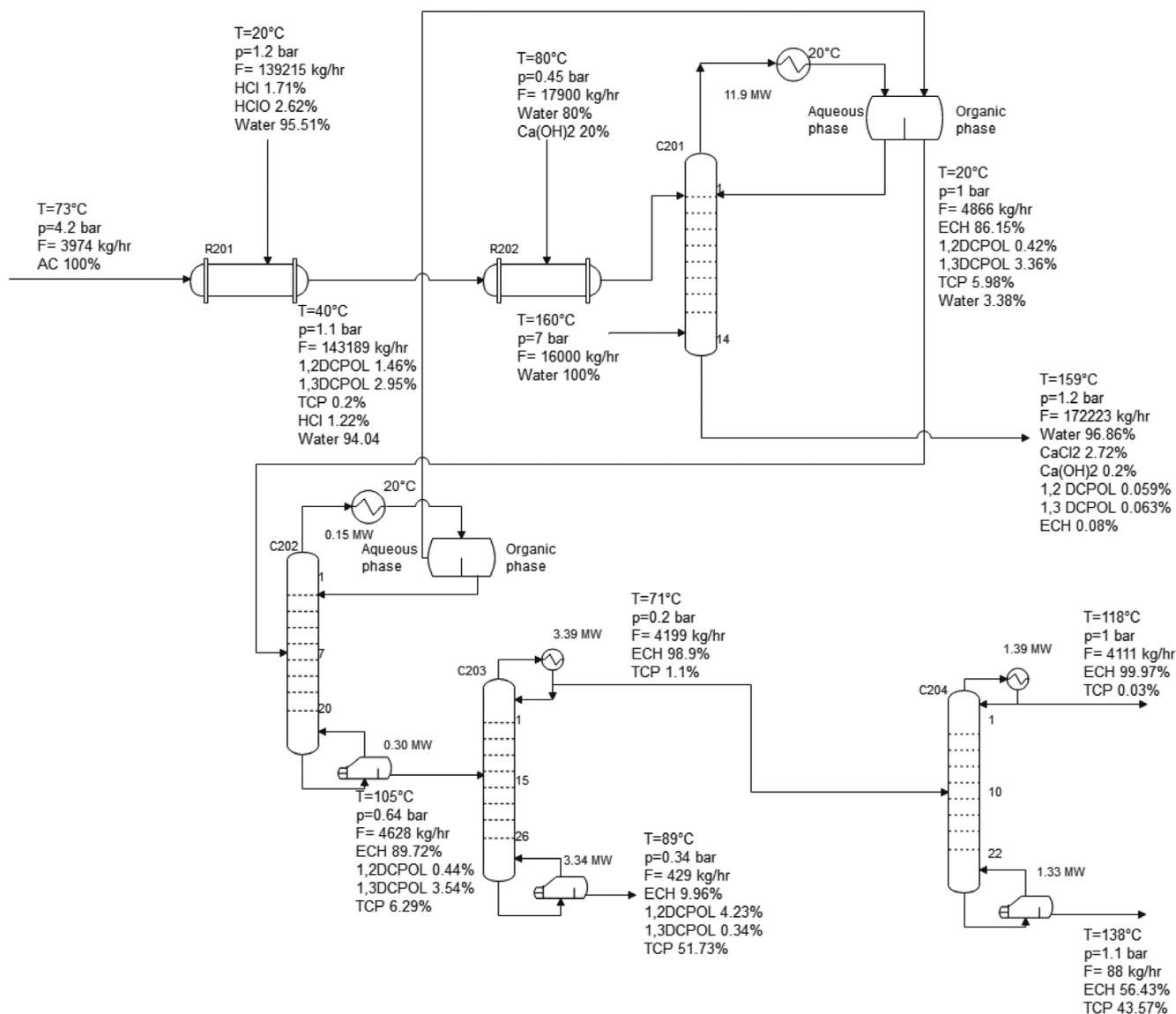
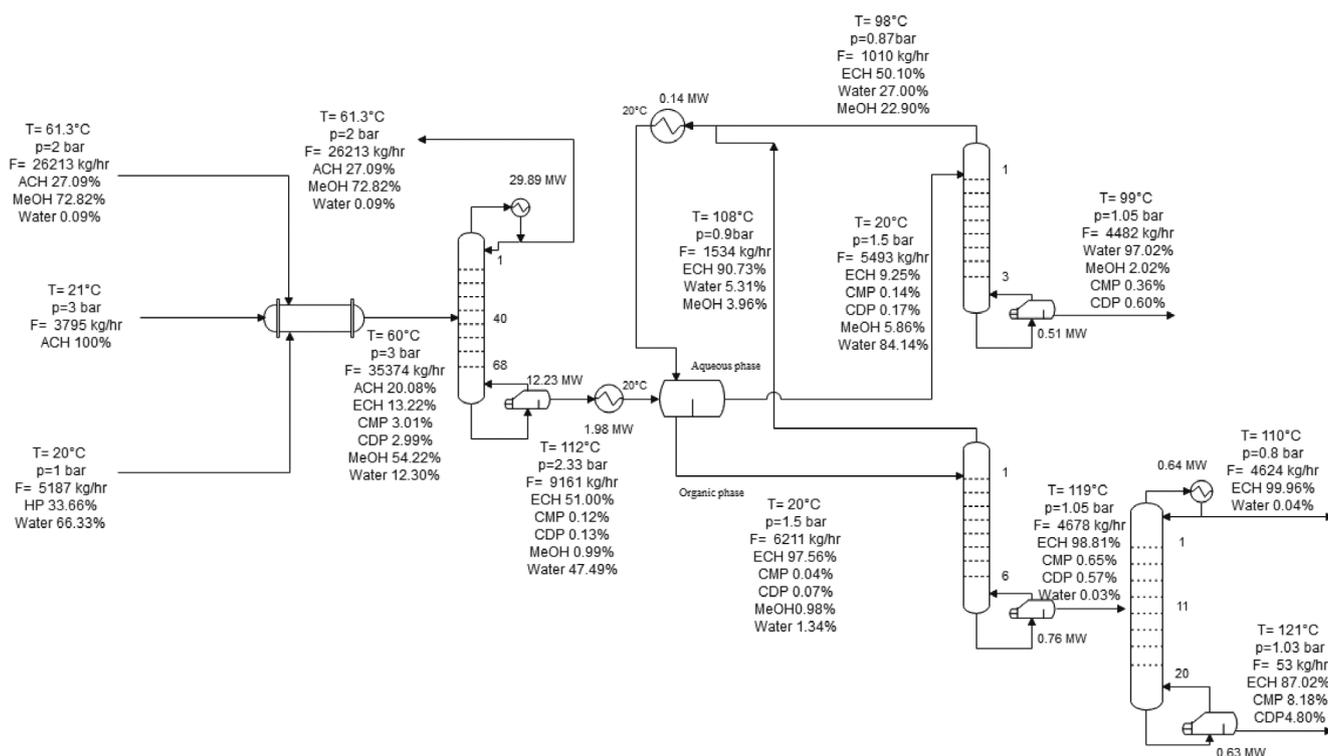


Figure 3. ECH production section of the base case classic process.

was set to be below 0.5% in the final ACH.<sup>2</sup> For the DSTWU column a reflux ratio of 1.2  $R_{\min}$  was used and then optimized using the RADFRAC model. The DSTWU shortcut model served only as a preliminary step, providing initial estimates for column parameters like stages and reflux ratios, despite its limitations. These estimates initiated the more detailed RADFRAC model analysis. Using the DSTWU-derived initial design, the RADFRAC model was refined by incorporating actual vapor–liquid equilibrium behavior. Design specifications added to the RADFRAC model ensured product purity compliance and facilitated fine-tuning of column parameters such as reflux ratios, feed stage locations and reboiler/condenser duties. The procedure was performed for all four columns present in the ACH purification sequence. The hydrochlorination reaction was also simulated using a stoichiometric reactor (R201) in Aspen Plus with conversion values mentioned earlier, and specific parameters ( $T = 40^{\circ}\text{C}$ ,  $P = 1.1\text{ bar}$ ), as no kinetic data are available in the literature. Note that the DCPA/DCPE impurities can be neglected in the feed to the reactor, as those components do not undergo any reactions in this system

and thus act as inerts. Furthermore, their low concentrations do not change the properties of the mixture significantly, and the small flow rates do not influence the conditions in the reactor. The water stream used to dissolve the ACH for the reaction was specified in such a way to ensure full dissolution of ACH in water ( $33\text{ kg water kg}^{-1}\text{ ACH}$ ), based on solubility described by Spadło *et al.*<sup>21</sup> Chlorine flow was calculated based on the patent specifying the ACH/chlorine ratio (1 mol/1.03 mol).<sup>34</sup> The chlorine stream was input as an equimolar aqueous mixture of HCl and HClO, since chlorine forms those two compounds when dissolved in water. The subsequent step – saponification reaction – was specified based on the kinetics described in the literature.<sup>26</sup> As the industrial plant was using milk of lime (not sodium hydroxide), the appropriate kinetics were used. Notably, the industrial setup used a similar combination of a plug-flow reactor (PFR) (R202) and a reactive stripping column (C201), as described by Sun *et al.*<sup>4,26</sup> The PFR size was determined ( $D = 4\text{ m}$ ,  $H = 8\text{ m}$ ) to ensure 30% DCP conversion, according to the literature.<sup>4,26</sup>



**Figure 4.** New separation scheme proposed for the AC oxidation route.

**Table 2.** Comparison between different advanced distillation techniques

	Energy savings	Column size reduction	Reduction in number of columns
Heat-pump-assisted distillation	Yes	No	No
Heat-integrated distillation column	Yes	No	No
Cyclic distillation	Yes	Yes	No
Dividing wall column	Yes	Yes	Yes

**Table 3.** Kinetic parameters for the catalytic epoxidation reactions

Reaction	A ( $\text{kmol m}^{-3} \text{s}^{-1}$ )	$E_a$ ( $\text{J mol}^{-1}$ )	$b_{\text{HP}}^0$ ( $\text{m}^3 \text{kmol}^{-1}$ )	$b_{\text{ECH}}^0$ ( $\text{m}^3 \text{kmol}^{-1}$ )	$Q_{\text{HP}}$ ( $\text{J mol}^{-1}$ )	$Q_{\text{ECH}}$ ( $\text{J mol}^{-1}$ )
R4	$11.05 \times 10^3$	$56.75 \times 10^3$	$3.03 \times 10^{-4}$	$5.71 \times 10^{-4}$	$19.36 \times 10^3$	$18.69 \times 10^3$
R5	$5.94 \times 10^3$	$70.09 \times 10^3$	$3.08 \times 10^{-4}$	$4.57 \times 10^{-4}$	$19.56 \times 10^3$	$17.53 \times 10^3$
R6	$1.10 \times 10^3$	$65.20 \times 10^3$	$3.05 \times 10^{-4}$	$4.79 \times 10^{-4}$	$19.75 \times 10^3$	$18.58 \times 10^3$
R7	5.11	$50.19 \times 10^3$	$5.70 \times 10^{-4}$	$4.27 \times 10^{-4}$	$19.45 \times 10^3$	$18.55 \times 10^3$

The stripping column was simulated using the rigorous RADFRAC model. Energy is supplied to this column by medium-pressure steam, fed directly to the bottom of the column. Additionally, reflux to this column is provided by the aqueous phase from the decanter. The top stream from this column is condensed and then sent to the decanter, where phase splitting occurs. The aqueous phase is fed back to the column as reflux, while the organic phase (consisting mostly of the ECH, organic byproducts and some water) is sent for purification. ECH purification is not as straightforward as that for ACH, due to the ECH/water azeotrope and the low solubility of ECH in water.<sup>24</sup> In the industrial

plant, separation was performed in columns C202, C203 and C204.<sup>21</sup> C202 separates the remaining water content from the organic phase. The column was simulated as RADFRAC equipped only with reboiler as the top stream is again condensed and sent to the decanter. The anhydrous organic mixture is then sent to the direct distillation sequence, which was simulated in the same way as described for the other distillation units. Column C203 separates the light ECH fractions from the ECH and heavy fractions. ECH is obtained at high purity as the top stream from column C204. This PFD was used to calculate the total energy use and sustainability metrics of the plant. The bottom stream of the reactive

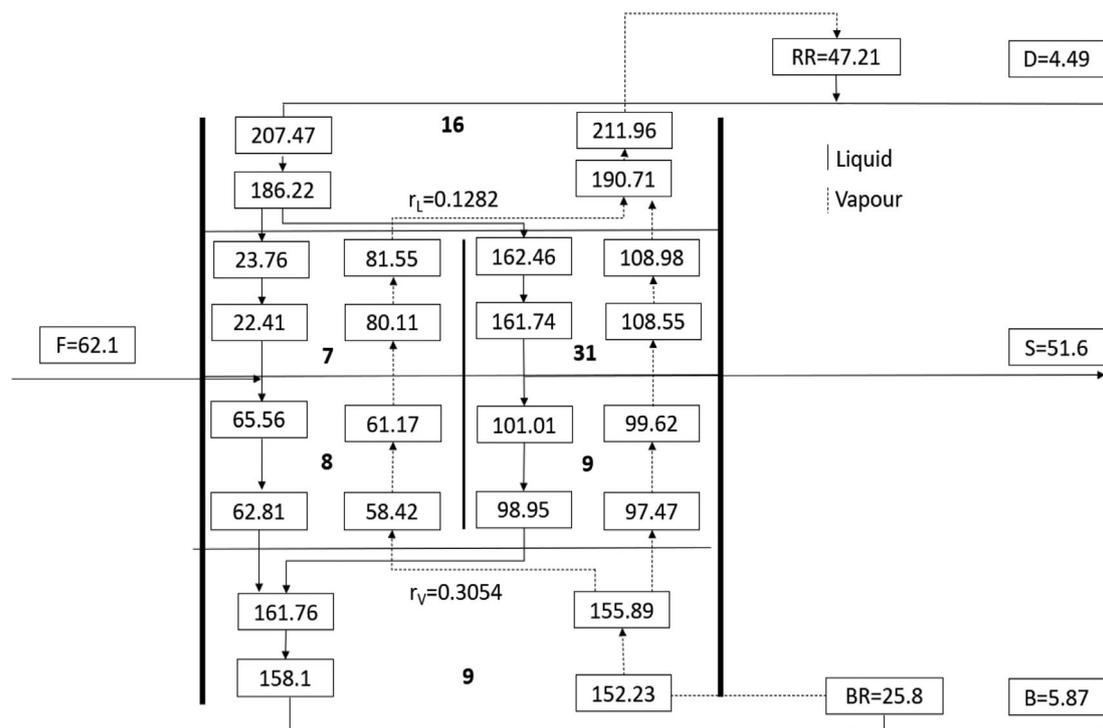


Figure 5. Stage requirements and internal vapor and liquid flow rates for the DWC.

Table 4. Comparison between the direct sequence and the DWC alternative

	Column 1	Column 2	DWC	Difference (%)
Top pressure (bar)	1.9	1.19	1.9	
Number of stages	70	30	80	-20%
Feed stage	42	15	43	
Reflux ratio (mol/mol)	56.60	0.3927	46.19	
Condenser duty (MW)	-1.597	-0.576	-1.471	
Total cooling required (MW)		-2.173	-1.471	-32%
Reboiler duty (MW)	1.486	0.529	1.342	
Total heating required (MW)		2.105	1.342	-36%

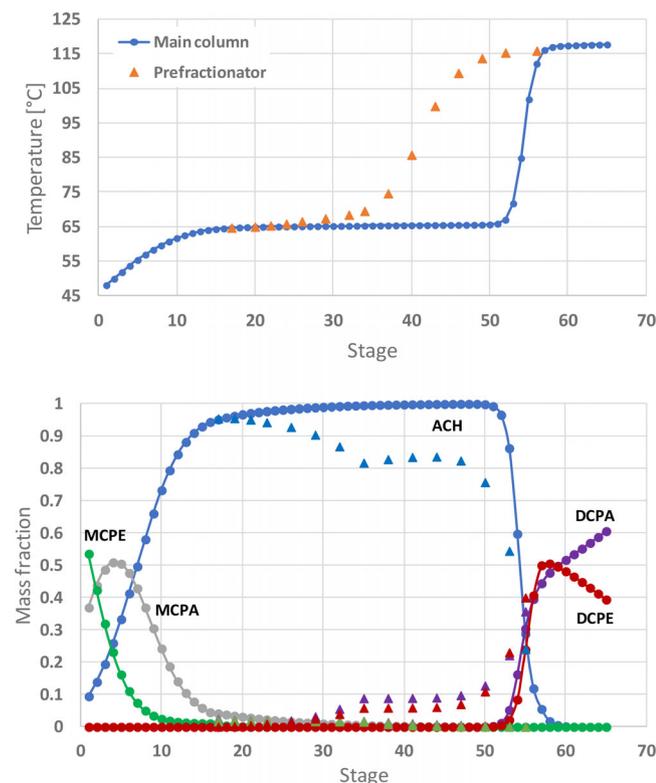
stripping column can be considered as the only wastewater stream in the plant, because it is the only aqueous waste stream obtained, at a very high flow rate (over  $170 \text{ t h}^{-1}$ ).

### Enhanced oxidation process

For the enhanced process, the ACH separation section remains the same, as it is using the same intermediate (ACH) as in the chlorhydrin process. The main advantage of this process is the replacement of the hydrochlorination and saponification reactions with a more selective, single oxidation reaction. A mild oxidation agent such as hydrogen peroxide (HP) can be used, with titanium silicate (TS-1) as catalyst. Using this reaction prevents operation in diluted solutions and thus drastically reduces wastewater production. Another advantage of the oxidation process is that using a single reaction (instead of two) increases the overall yield of the process. The flowsheet of this process is shown in Fig. 4.

The reactor (R301) was modeled using the PFR model in Aspen Plus, using the kinetics described earlier. The reactor size was

determined ( $L = 5 \text{ m}$ ,  $D = 0.75 \text{ m}$ ) to obtain full conversion of HP. The kinetics of the ACH epoxidation (using methanol as solvent) are known, along with the concentrations of the solvents and reactants. Other proposed solvents are ethanol, isopropanol and butanol, acetone and methyl ethyl ketone. Based on research on influence of solvent on reactor yield, methanol provides the best results, as yield decreases with longer carbon chain in the alcohol. However, ketones should not be used as they tend to form unstable peroxides when exposed to HP, which significantly impacts the safety of the plant.<sup>13</sup> Some papers<sup>15</sup> state that other solvents should be used due to the toxicity of methanol, but those claims are questionable. Notably, ECH is the most toxic compound present in the reaction mixture, and thus using a solvent with lower toxicity than methanol would not provide any significant improvements to the safety of the plant. It was also suggested that isopropanol could be used instead since the separation sequence for methanol is unfeasible (as the reactor effluent contains components that form azeotropes, such as ACH/MeOH, ECH/water and ACH/water).<sup>15</sup> This claim is incorrect in the process



**Figure 6.** Temperature and composition profiles along the DWC (lines with markers: main column; markers only: prefractionator side).

context, and this study clearly proves that with proper constraints the separation sequence (using methanol as solvent) is actually possible, and this is further compared to the work by Wang *et al.*<sup>22</sup> The previously proposed separation schemes<sup>35</sup> focused on the separation of every component in the mixture, which poses difficulties due to the fact that multiple azeotropes need to be broken by using a solvent, and this makes the separation sequence difficult and very energy demanding. However, these difficulties can be overcome by developing the separation system in such a way that only the necessary splits are performed. For example, the ACH and methanol should not be separated into pure components, as unreacted ACH will be recycled back to the reactor and mixed again with methanol. This separation is not required for the process and therefore unnecessary. In the case of ECH/water azeotrope, the limited solubility of ECH in water can be used to perform the separation. The azeotropic mixture of ECH and water separates into two liquid phases. This property has already been effectively exploited in the ECH purification (in the chlorohydrin process); therefore applying this method in the novel HP process should be certainly considered.

Based on the kinetics of the reaction mentioned earlier, it was found that formation of CMP is highly dependent on the methanol concentration in the mixture, and the reaction rate constant for this component is higher than for other byproducts. To avoid the formation of excess amount of this byproduct, it is advisable to separate methanol first. This decision aligns with heuristics from the literature,<sup>36</sup> to first remove the component with the highest concentration. The ACH column (C301) was designed to remove methanol and ACH from the reaction mixture as those components form an azeotrope, and the ACH/methanol recovery rate was specified as a minimum of 99% to prevent substrate and

solvent losses. The top stream of this column can be mixed with fresh ACH and make-up solvent and then fed back to the epoxidation reactor (R301). Note that the recycle loop is not closed in the process simulation, but a separate recycle stream is introduced into the epoxidation reactor in order to improve the convergence of the flowsheet. The bottom stream from this column consists of ECH, water and organic byproducts. This stream needs to be cooled to 20 °C for the phase splitting to occur effectively. The aqueous phase is then sent to the stripper (C303). This column is used to recycle ECH, which remains in the aqueous phase and to purify the water stream, which will then be sent for treatment. This separation requires only a few stages, as it is only possible to obtain the azeotrope in the top vapor stream. As this column operates as a stripper the feed needs to be introduced on the first tray. The total number of stages required for this separation is three, and a further increase in the number of stages does not provide any improvement in the top stream concentration. The top stream is condensed and sent back to the decanter. The organic phase from the decanter is also sent to the stripper (C302) to remove the remaining water content. The goal is to reduce the water content in this stream below 300 ppm to prevent formation of CDP and therefore losses in ready ECH. This stripper requires only six stages to obtain the desired separation. The top steam needs to be cooled and sent back to the decanter. The bottom stream from this stripper consists of ECH and organic byproducts such as CDP and CMP. The last column (C304) has 20 stages and it purifies the ECH top stream to over >99.9 wt%. The final separation scheme has some similarities to the one described by Wang *et al.*,<sup>22</sup> but the sequence proposed in this work allows us to obtain higher purities of the ECH product in an effective way. Note that the presence of HP requires careful safety considerations associated with thermal decomposition of HP to water and oxygen. The gaseous oxygen can build up at the top of the distillation column C301 and can cause formation of AC/MeOH/oxygen, which can lead to violent decomposition and put plant operation at risk. However, those risks can be mitigated, as described by Wang *et al.*,<sup>22</sup> who recommended mitigating explosion risks nitrogen vapor introduction, thus decreasing oxygen levels below the lower explosion limit (LEL). This requires a post-condenser flash to circumvent nitrogen accumulation. Notably, a parallel approach has been successful in the HPPO process, using a post-reactor flash step to avert hazards. Adapting this tactic, introducing a flash step between the ECH plant reactor and C301 could minimize oxygen-related risks. In essence, process safety could be improved by implementing a nitrogen purge at the top of the distillation column, incorporating a flash drum between the reactor and column, or combining these techniques.

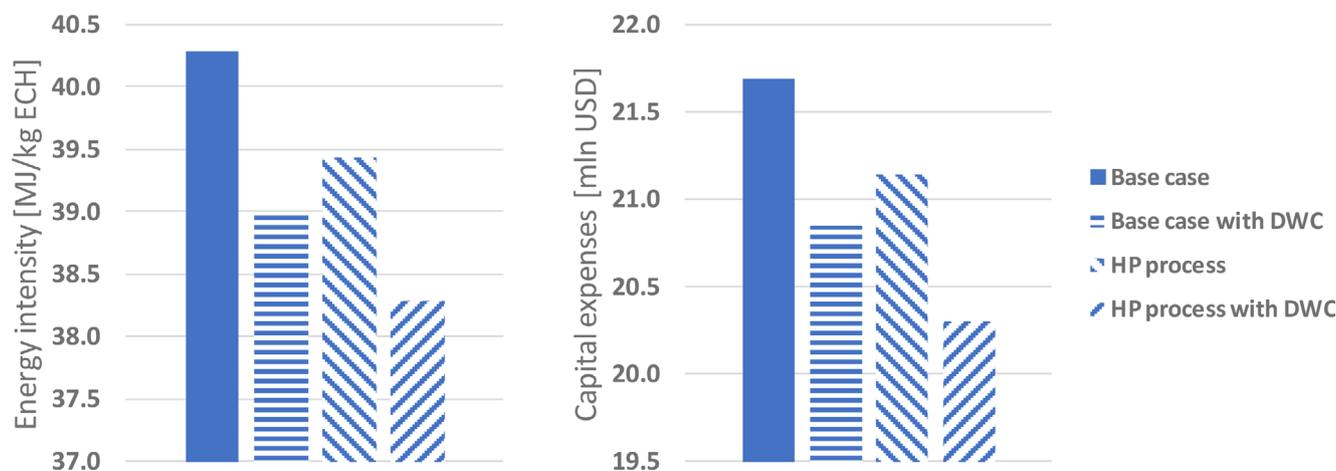
### Economic evaluation

The economic parameters of the processes were calculated based on the mass and energy balance, as well as the appropriate equipment sizing. CAPEX was estimated using cost correlations, based on the equipment size, according to the method described by Seider *et al.*<sup>37</sup> The following components were specified as raw material for the base case process: propylene, chlorine, milk of lime and water. Prices of the chemicals were based on their recent market value (USD per tonne): propylene, 1148;<sup>38,39</sup> chlorine, 175;<sup>40</sup> HP, 483;<sup>41</sup> and milk of lime, 87.<sup>42</sup>

The key economic parameters for both processes are listed in Table 5. The novel route offers a slightly lower investment cost, as this route requires fewer decanters and reactors, which reduces the CAPEX of the new HP process. The most significant improvement is in terms of wastewater generated, as the HP process can reduce the total amount of wastewater by almost 98%. This is also

**Table 5.** Comparison of key economic parameters for the base case and the HP process

Parameter	Base case	HP process	Difference (%)
Investment cost (million USD)	21.687	21.139	-2.5
Raw material cost (million USD)	39.80	51.80	+30
Annual production capacity (tonnes)	34 524	39 160	+12
Annual sales (million USD)	82.65	93.95	+14
Annual operating costs (million USD)	52.04	61.09	+17
Annual profit (million USD)	30.61	32.86	+7



**Figure 7.** Comparison between the classic technology and the new HP process.

important economically, as it can provide annual savings of nearly USD 2000k while also reducing the investment costs for a wastewater treatment unit. Moreover, the novel route provides higher ECH yield in terms of propylene, which means that fewer by-products are formed during processing. This is essential nowadays, as propylene prices are increasing steadily and this compound is one of the most expensive raw materials used.<sup>41</sup>

On the downside, the prices of raw materials for the novel process are higher than for the base case due to the higher price of HP compared to lime (USD 483 per tonne vs. USD 87 per tonne).<sup>41,42</sup>

Despite this fact, the novel HP route can still provide a higher annual profit, due to the higher yield and production capacity, which is the result of a more efficient process. It is worth noting that chlorine prices are strongly dependent on electricity prices and on sodium hydroxide prices, as these compounds are both products of brine electrolysis. The new HP process is more independent of chlorine prices, which may actually be more beneficial.

For the ACH separation part, Fig. 7 illustrates the positive effect of using a DWC on the energy requirements and CAPEX for the process. Relative to the full process, the savings are about 5% of the total energy use (savings of USD 390k per year). The application of DWC leads also to about a 4% decrease in the overall CAPEX, due to the reduced number of columns and supporting equipment in the ACH section of the plant.

### Sustainability metrics

One of the most important benchmarks used in industry nowadays are sustainability metrics, which allow a fair comparison between processes using different technologies and production capacities. The following sustainability metrics were used to

compare the ECH production processes: material and energy intensity, water consumption, toxic and pollutant emissions, greenhouse gas (GHG) emissions – with lower values meaning better performance.<sup>43</sup>

Table 6 provides an overview of the of sustainability metrics. There are several improvements in the novel HP process. The largest decrease of 98% is observed for wastewater generation, which is possible due to the fact that the original operation in diluted aqueous solution has been replaced by a more efficient catalytic oxidation. This is crucial for plant operation as handling wastewater is one of the most important factors for the ECH plant. Furthermore, due to replacement of the hydrochlorination reaction, the use of process water has been decreased to zero. This means that the plant can operate without using water as solvent or reagent and thus its impact on local water resources will be drastically decreased. Cooling water still has to be used in the process, as well as steam, but these utilities can be circulated in closed loops.

The second major improvement is in terms of chlorine atom efficiency, which relates the amount of chlorine atoms used to produce one molecule of ECH with how many of those atoms are present in the final product. The chlorine efficiency for the traditional process is equal to 0.476, which means that most of the chlorine used in the synthesis will not end up in the final product but in other by-products. Those chlorine molecules would form chlorine ions and end up in the wastewater streams. For the oxidative process, the chlorine efficiency is significantly increased to 0.895, which translates into a substantial waste reduction. Notably, chlorine manufacturing requires significant amounts of electric power; thus effective utilization of this material is beneficial for the whole industrial chain.

**Table 6.** Key sustainability metrics for the base case and the HP process

Sustainability metrics	Base case	HP process	Difference (%)
Wastewater produced (kg kg <sup>-1</sup> ECH)	48.29	1.04	-98
Yield [%]	71	78	+10
Process water usage (kg kg <sup>-1</sup> ECH)	23.82	0	-100
Atom efficiency (in terms of chlorine)	0.476	0.895	+88
Energy intensity (MJ kg <sup>-1</sup> ECH)	40.28	39.43	-2
CO <sub>2</sub> emissions (kg kg <sup>-1</sup> ECH)	1.17	1.13	-3

Note: The term 'process water' used here refers to the water used as solvent and/or reactant, and does not include cooling water.

Additionally, the overall yield of the process has increased relatively by about 10% (from 71% to 78%), which leads to a lower material intensity (since less raw material is required to make the same amount of product). Finally, the energy intensity and GHG emissions have also slightly decreased, by 2% and 3%, respectively. This change may not appear significant, but for a plant capacity of 35 kilotonnes per year this translates to a reduction of 1400 kilotonnes of CO<sub>2</sub> emissions per year.

## CONCLUSIONS

This work proved that for the HP process route, using methanol as a solvent, a novel separation system is possible, which enables high purity of ECH product. Also, the ACH purification sequence can be optimized by thermally coupled distillation to improve the energy efficiency of the ACH production, in both classic and new HP processes.

The comparison between ECH production processes strongly indicates that the HP process can provide significant reductions of 98% in wastewater (thus removing the dependency on wastewater treatment units in proximity), while also achieving lower energy intensity and CO<sub>2</sub> emissions. Furthermore, the atom efficiency in the new HP process increased by 88% to 0.895 (in terms of chlorine), while the production capacity increased by 13%. Also, the ECH yield with respect to propylene is increased (from 71% to 78%), this being crucial for the plant profitability, as the propylene market is expected to experience fluctuations caused by the global macroeconomic situation. Yield improvement results from replacing the hydrochlorination–saponification process with a single oxidation step. Hydrochlorination is susceptible to TCP formation when the organic phase remains undissolved, causing ACH losses and reduced yield. Moreover, the reactive stripping column's saponification reaction contributes to DCP losses. Despite low concentrations, significant flow rates indicate notable component losses. However, oxidation utilizes a catalyst-enhanced selective reaction, improving overall yield. For the common downstream processing of the ACH intermediate in both processes, the use of DWC technology allows 34% savings (about USD 390k) in utilities and carbon emissions, as compared to the classic sequence of columns.

Furthermore, the new HP route can be partly retrofitted to existing ECH plants based on the chlorohydrin route. As both processes use the same intermediate (ACH), only the ECH part of the traditional plant would be replaced by the novel route, while keeping the ACH part from the classic process. In this case, only 55% of investment costs is needed (USD ~11 million) for this modification, while the plant would benefit from all improvements of the new process.

Besides the academic research and industrial development interest in this topic, the new ECH production process is also very suitable for teaching activities, such as the Design Project.<sup>44</sup>

## SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

## REFERENCES

- Okhlopova EA, Serafimov LA and Frolkova AV, Methods of preparing Epichlorohydrin. *Theor Found Chem Eng* **53**:864–870 (2019).
- Madej W, Stajszyk M, Spadło M, Lewandowski G and Lauer A, Sposób wytwarzania chlorku allilu. Urząd Patentowy Polskiej Rzeczypospolitej Ludowej PL139088B1 (1988).
- Stajszyk M, Wasilewski J, Spadło M, Pokorska Z, Pers B, Klimaszewski R *et al.*, Sposób rozdzielania mieszaniny poreaakcyjnej z wysokotemperaturowego chlorowania propylenu. Urząd Patentowy Polskiej Rzeczypospolitej Ludowej PL132696B1 (1986).
- Brzeżicki A, Pokorska Z, Madej W, Zawiski Z, Cierielewski L, Rosiński M *et al.*, Sposób wytwarzania epichlorohydriny. Urząd Patentowy RP PL154680B1 (1992).
- Milchert E, Goc W and Myszkowski J, Recovery of epichlorohydrin and dichloropropanols from waste. *J Chem Technol Biotechnol* **56**:109–111 (1993).
- Bijsterbosch JW, Das A and Kerkhof FPJM, Clean technology in the production of epichlorohydrin. *J Clean Prod* **2**:181–184 (1994).
- Cespi D, Cucciniello R, Ricciardi M, Capacchione C, Vassura I, Passarini F *et al.*, A simplified early stage assessment of process intensification: glycidol as a value-added product from epichlorohydrin industry wastes. *Green Chem* **18**:4559–4570 (2016).
- Pagliari M, Ciriminna R, Kimura H, Rossi M and Della Pina C, From glycerol to value-added products. *Angew Chem Int Ed* **46**:4434–4440 (2007).
- Santacesaria E *et al.*, New process for producing epichlorohydrin via glycerol chlorination. *Ind Eng Chem Res* **49**:964–970 (2010).
- Almena A and Martín M, Technoeconomic analysis of the production of Epichlorohydrin from glycerol. *Ind Eng Chem Res* **55**:3226–3238 (2016).
- Russo V, Tesser R, Santacesaria E and Di Serio M, Chemical and technical aspects of propene oxide production via hydrogen peroxide (HPPO process). *Ind Eng Chem Res* **52**:1168–1178 (2013).
- Schmidt F, Bernhard M, Morell H and Pascaly M, HPPO process technology a novel route to propylene oxide without coproducts. *Chim Oggi* **32**:31–35 (2014).
- Danov SM, Sulimov AV and Sulimova AV, Solvent effect on epoxidation of allyl chloride with hydrogen peroxide on titanium-containing silicalite. *Russ J Appl Chem* **81**:1963–1966 (2008).
- Sulimov AV, Danov SM, Ovcharova AV, Ovcharova AA and Flid VR, Kinetics of allyl chloride epoxidation with hydrogen peroxide catalyzed by extruded titanium silicalite. *Kinet Catal* **55**:712–721 (2014).
- Okhlopova EA and Frolkova AV, Comparative analysis of separation schemes of reaction mixtures of epichlorohydrin production in the presence of various solvents. *Theor Found Chem Eng* **53**:1028–1034 (2019).

- 16 Engelen HK and Skogestad S, Selecting appropriate control variables for a heat-integrated distillation system with prefractionator. *Comput Chem Eng* **28**:683–691 (2004).
- 17 Pokorska Z, Spadlo M, Wasilewski J, Stajszczyk M, Zobel J, Klimaszewski R *et al.*, Sposób wytwarzania chlorku allilu. Urząd Patentowy Polskiej Rzeczypospolitej Ludowej PL126304B1 (1980).
- 18 Wasilewski J, Stajszczyk M, Lewandowski G, Madej W, Spadlo M, Pokorska Z *et al.*, Continuous method for the manufacture of allyl chloride. Urząd Patentowy Polskiej Rzeczypospolitej Ludowej PL138938B1 (1984).
- 19 Madej W, Wilusz T, Gorzka A, Pokorska Z, Spadlo M, Wasilewski J *et al.*, Sposób wytwarzania chlorku allilu na drodze wysokotemperaturowego chlorowania propylenu. Urząd Patentowy RP PL183285B1 (1998).
- 20 Madej W, Spadlo M, Pokorska Z, Wasilewski J, Spadlo M, Lewandowski G *et al.*, Sposób wydzielenia chlorowodoru z mieszaniny poreakcyjnej pochodzącej z wysokotemperaturowego chlorowania propylenu. Urząd Patentowy Polskiej Rzeczypospolitej Ludowej PL154680B1 (1984).
- 21 Spadlo M, Brzezicki A, Dula J, Madej W, Gorzka A, Koziel T *et al.*, Sposób wydzielenia epichlorohydrynu o wysokiej czystości. Urząd Patentowy RP PL174464B1 (1994).
- 22 Wang SJ, Wong DSH, Lim IJQ, Chen YT and Huang CC, Design and control of a novel plant-wide process for epichlorohydrin synthesis by reacting allyl chloride with hydrogen peroxide. *Ind Eng Chem Res* **57**:6926–6936 (2018).
- 23 Kiss AA, Advanced Distillation Technologies Advanced Distillation Technologies (2013). <https://doi.org/10.1002/9781118543702>.
- 24 Danov SM, Sulimov AV and Ovcharova AV, Modeling of the vapor-liquid equilibrium in the system formed by the epichlorohydrin synthesis products. *Theor Found Chem Eng* **46**:31–43 (2012).
- 25 Yue Q, Zhu JW, Wu YY, Yuan XQ and Ma L, Liquid-liquid equilibria and vapor-liquid equilibria for the binary system of epichlorohydrin and water. *Fluid Phase Equilib* **283**:12–16 (2009).
- 26 Sun X, Xia L and Xiang S, The simulation of epichlorohydrin production process by using NaOH instead of Ca(OH)<sub>2</sub> based on the reaction kinetics. *Chem Eng Trans* **61**:1801–1806 (2017).
- 27 Kiss AA, Distillation technology – still young and full of breakthrough opportunities. *J Chem Technol Biotechnol* **89**:479–498 (2014).
- 28 Bildea CS, Pătruț C, Jørgensen SB, Abildskov J and Kiss AA, Cyclic distillation technology – a mini-review. *J Chem Technol Biotechnol* **91**:1215–1223 (2016).
- 29 Kiss AA, Novel applications of dividing-wall column technology to biofuel production processes. *J Chem Technol Biotechnol* **88**:1387–1404 (2013).
- 30 Dejanović I, Matijašević L, Halvorsen IJ, Skogestad S, Jansen H, Kaibel B *et al.*, Designing four-product dividing wall columns for separation of a multicomponent aromatics mixture. *Chem Eng Res Des* **89**:1155–1167 (2011).
- 31 Ränger LM, Preißinger U and Grütznert T, Robust initialization of rigorous process simulations of multiple dividing wall columns via Vmin diagrams. *ChemEngineering* **2**:1–19 (2018).
- 32 Premkumar R and Rangaiah GP, Retrofitting conventional column systems to dividing-wall columns. *Chem Eng Res Des* **87**:47–60 (2009).
- 33 Ehlers C, Schoder M and Fieg G, Influence of heat transfer across the wall of dividing wall columns on energy demand. *AIChE J* **61**:1649–1662 (2015).
- 34 Myszkowski J, Sposób wytwarzania dichloropropanoli. 1–4 (1987).
- 35 Okhlopova EA, Serafimov LA, Frolkova AV and Tsekin PP, Separation of multicomponent system formed in the production of epichlorohydrin. *Theor Bases Chem Technol* **11**:36–42 (2016).
- 36 de Haan AB, Burak E and Boelo S, *Industrial Separation Processes*. De Gruyter, Berlin, Germany (2020).
- 37 Seider WD, *Product and Process Design Principles: Synthesis, Analysis and Evaluation*. John Wiley & Sons, Hoboken, NJ/USA (2016).
- 38 Price of propylene worldwide from 2017 to 2021 Available <https://www.statista-com.tudelft.idm.oclc.org/statistics/1170576/price-propylene-forecast-globally> [07 March 2022].
- 39 Epichlorohydrin price. Available: [https://www.alibaba.com/product-detail/CAS-106-89-8-rubber-intermediates\\_1600427725325.html?spm=a2700.7724857.normal\\_offer.d\\_title.445675f9FDIB84](https://www.alibaba.com/product-detail/CAS-106-89-8-rubber-intermediates_1600427725325.html?spm=a2700.7724857.normal_offer.d_title.445675f9FDIB84). [01 April 2022].
- 40 Chlorine price. Available: <https://www.westlake.com/industry-product-pricing>. [01 April 2022].
- 41 Hydrogen peroxide price. Available: <https://www.globaltrademag.com/global-hydrogen-peroxide-market-india-55m-germany-54m-and-the-u-s-48m-are-the-most-promising-overseas-markets/>. [01 April 2022].
- 42 Milk of lime price. Available: <https://arjco.com/quick-lime-price/>. [02 April 2022].
- 43 Sheldon RA, Metrics of green chemistry and sustainability: past, present, and future. *ACS Sustain Chem Eng* **6**:32–48 (2018).
- 44 Kiss AA and Webb C, The Manchester perspective on using the design project to enhance the education of chemical engineering students. *J Chem Technol Biotechnol* **96**:1453–1464 (2021).