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# Towards Demand-side Management of the Chlor-alkali Electrolysis: Dynamic, Pressure-driven Modeling and Model Validation of the 1,2-Dichloroethane Synthesis

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## Abstract

A promising application of demand-side management is the chlor-alkali electrolysis. However, storing the produced chlorine for flexibility should be avoided whenever possible. If PVC is produced from chlorine, storing the intermediate 1,2-dichloroethane resulting from direct chlorination of ethene is a better alternative as it is less toxic than chlorine and can be easily stored. Currently, no dynamic process models to study the process behavior or to develop optimal trajectories for the 1,2-dichloroethane production under different demand response scenarios are available. Hence, we formulate and solve a dynamic, pressure-driven model of the synthesis of 1,2-dichloroethane and validate it with real process data in this contribution. As part of this dynamic model, differentiable formulations for weeping and the flow over a weir of a distillation tray are presented, which are also valid whenever certain trays run dry.

*Keywords:* Dynamic pressure-driven modeling, Chloralkali electrolysis, Ethylene dichloride, Plant flexibilization

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## 1. Introduction

2 The share of renewable energy in the electricity market is increasing in coun-  
3 tries all over the world [1]. This is desirable for many reasons, such as reduced

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4 CO<sub>2</sub> emissions, less dependence on crude oil and natural gas, long-term sustain-  
5 ability, or decentralized energy solutions. On the other hand, it raises new tech-  
6 nical challenges, e.g. net stability for fluctuating energy input and availability.  
7 Finding solutions to these challenges is an important task for the process industry  
8 and demand-side management (DSM) with flexible plant operation is expected  
9 to be an important aspect [2, 3]. In particular, companies with energy-intensive  
10 processes have a large potential for such approaches [4]. According to Ausfelder  
11 et al. [4], the chlor-alkali electrolysis (CAE) has the highest flexibility potential  
12 in the chemical industry due to the large installed capacity of more than 1 GW in  
13 Germany [5, 6, 4].

14 The main product of the CAE is chlorine gas (Cl<sub>2</sub>), which is obtained at the  
15 anode of the electrolyzer. The CAE has been modeled dynamically in the past [7]  
16 and also recently for demand response purposes [8, 9]. Otashu and Baldea [8] used  
17 a dynamic model of the CAE for demand-side management. They showed that  
18 CAE can be used for DSM, but several variables including the cell temperature  
19 must be carefully controlled during load transitions. Brée et al. [9] compared a  
20 standard cathode with an oxygen depolarized cathode by solving a mixed-integer  
21 linear programming problem and showed that the standard cathode is currently  
22 economically superior to the oxygen depolarized one, but this may change in the  
23 future. They also pointed out that storing chlorine for flexibility purposes should  
24 be avoided whenever possible [9].

25 Approximately 30 % of the chlorine produced around the world are processed  
26 to 1,2-dichloroethane (typically known as ethylene dichloride or EDC) and fur-  
27 ther to polyvinyl chloride (PVC) [10]<sup>1</sup>, a thermoplastic polymer mainly used for  
28 construction, domestic use, packaging, and transport [11]. EDC has several ad-  
29 vantageous properties regarding the flexibilization of the process. It can be easily  
30 stored in the liquid state, is less toxic than chlorine and chemically stable. Hence,  
31 using an EDC storage tank is a valid alternative to chlorine storage for a relatively  
32 large amount of the processed chlorine and has been assigned a technical flexibil-  
33 ity potential for load reduction of 10 % [4]. There is no positive potential as the  
34 storage must be refilled and CAE plants operate close to maximum capacity [6].

35 Up to now, no dynamic models of the EDC production have been published. A  
36 dynamic process model is preferred as Sass and Mitsos [12] recently showed that  
37 the inherent dynamics of the system may play a significant role and that quasi-  
38 steady models do only perform well with adequate ramp constraints. For this

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<sup>1</sup>if one considers that part of the chlorine is recycled for the oxychlorination, see Section 2

39 reason, we present a dynamic model to assess the transient behavior of the EDC  
40 synthesis. This model will be used to assess the challenges and limitations during  
41 operation and for different loads, to predict the process behavior, and to obtain  
42 optimal trajectories from one setpoint to another. Due to the limited number of  
43 publications in the literature, e.g. [13], this model development includes the selec-  
44 tion of a thermodynamic model and a review of the available reaction kinetics.

45 In the following, we assume inlet flows of chlorine from the CAE and ethene  
46 as given and focus on the model development for the EDC production. The next  
47 section introduces the fundamentals of the VCM production and shows the parts  
48 of the process subject to flexibilization. Section 3 discusses the process model  
49 for these parts, whereas section 4 presents a case study to illustrate the modeling  
50 approach and presents steady-state and dynamic simulation results. These results  
51 are compared to real process data for model validation.

## 52 **2. Process Description and Modeling Approach**

53 VCM is typically produced in an integrated plant where ethene ( $C_2H_4$ ) is partly  
54 directly chlorinated and partly oxychlorinated [14, p. 10], as shown in Figure 1.  
55 The chlorine for direct chlorination stems from the CAE. In both reaction steps,  
56 EDC is produced and then purified to remove byproducts. Afterwards, EDC is  
57 cracked to produce VCM. During the purification of VCM, hydrogen chloride  
58 (HCl) is removed and recycled back to the oxychlorination. A scheme of the  
59 process is given in Figure 1.

60 As EDC can be stored easily, the process could be made flexible by adding a  
61 storage tank to the flowsheet. In case of electricity shortages or high electricity  
62 costs, this tank is used to ensure the continuous operation of the following units.  
63 In the opposite case, the tank is filled. This way, oxychlorination, EDC cracking,  
64 and VCM purification always operate at nominal operating conditions while di-  
65 rect chlorination and EDC purification must dynamically follow the chlorine feed.  
66 The boundary between flexibly operated units and units at nominal operating con-  
67 ditions is highlighted with a dashed line in Figure 1. As direct chlorination and  
68 EDC purification shall be operated flexibly, these two units are discussed in more  
69 detail to convey a better understanding of the process model in section 3.

In the direct chlorination process, ethene and chlorine are usually reacted in  
the liquid phase consisting mainly of the product EDC in the presence of a Lewis  
acid catalyst, such as  $FeCl_3$  [14, p. 10]. Equation (1) is the main reaction in which  
ethene and chlorine react to EDC. Equation (2) is the side reaction of EDC and  
chlorine to the byproducts 1,1,2-trichloroethane (ETC,  $C_2H_3Cl_3$ ) and hydrogen

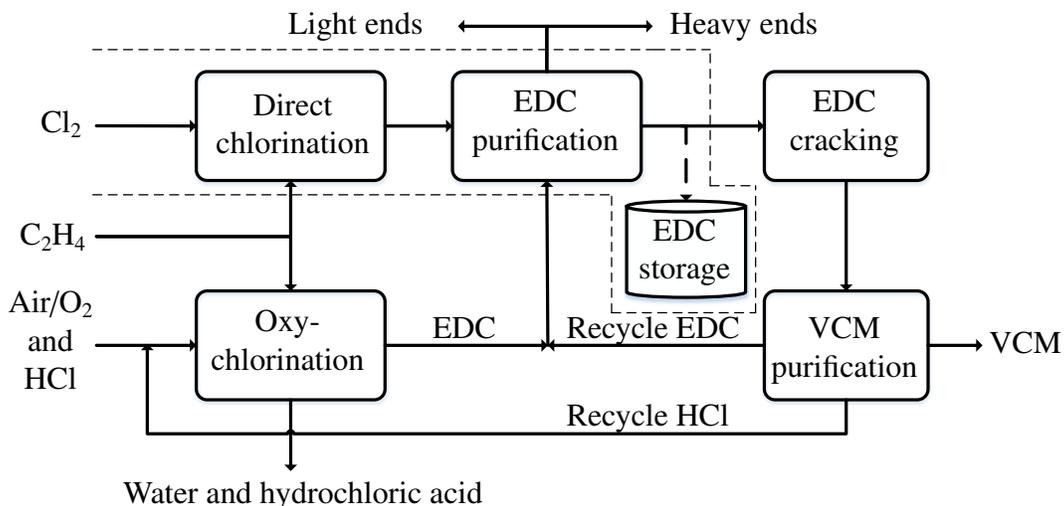
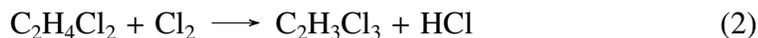


Figure 1: Process scheme of an integrated VCM production plant, based on [14, p. 36]. The dashed line represents the boundary between flexibly operated units and units operating at nominal conditions.

chloride (HCl):



70 In principal, there are two options for direct chlorination: low-temperature chlo-  
 71 rination (LTC) and high-temperature chlorination (HTC) [14, p. 11], which are  
 72 operated at ambient pressure and high conversion rates. In the first case, low tem-  
 73 peratures (20 to 70 °C) lead to higher selectivities ( $\geq 99\%$ ) but increased energy  
 74 demand. In the second case, the heat of reaction is used for EDC purification in a  
 75 distillation process as the heat of reaction is about seven times larger than EDC's  
 76 heat of vaporization [14, p. 11]. While the increased temperatures of 85 to 200 °C  
 77 conventionally led to lower selectivity, current patents claim this not longer to be  
 78 true if highly selective catalysts are applied. For this reason, LTC is hardly built  
 79 anymore [15].

80 In this contribution, the latter case is modeled and the reactor is thus placed  
 81 directly below the distillation tower, as shown in [14, p. 11]. The distillation  
 82 tower is assumed to be a tray column. In addition, we consider a heat exchanger  
 83 located below the reactor to remove additional heat as described in Kahsnitz and  
 84 Polte [15]. This assumed process design is shown in Figure 2, where the control  
 85 volumes of the process model are also indicated (see section 3).

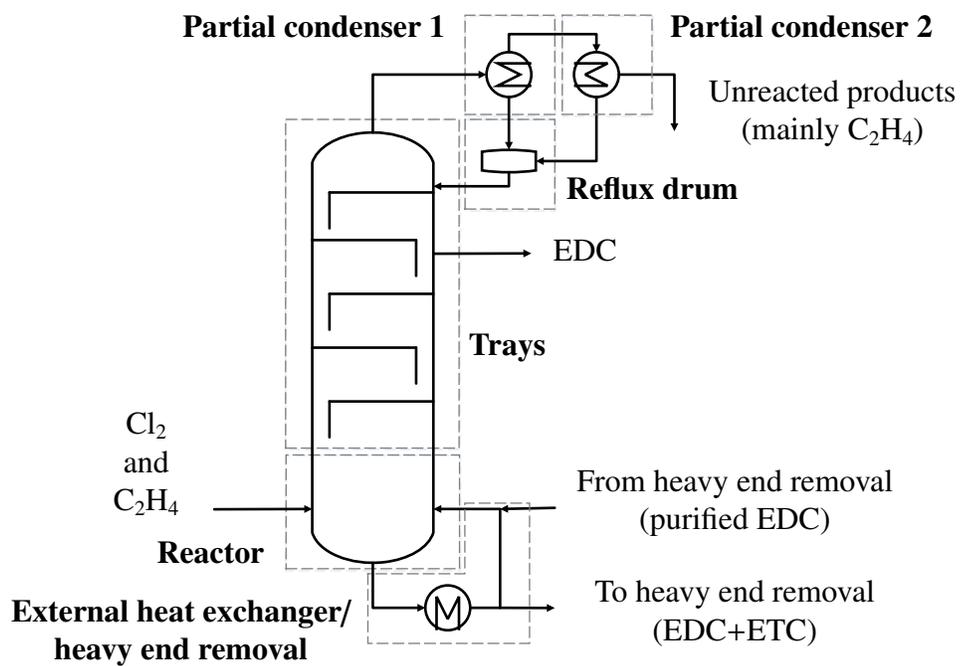


Figure 2: Assumed process design for direct chlorination and EDC purification, based on [14, p. 11]. Also shown are the parts of the process model, see section 3.

### 86 3. Process Modeling

87 In this section, the process model is developed. The first step is the determi-  
88 nation of an appropriate thermodynamic model. Afterwards, the kinetics of the  
89 process are discussed. Finally, the model equations of each unit are introduced.

#### 90 3.1. Thermodynamics

91 This section discusses the thermodynamic models used to describe pure com-  
92 ponent data as well as the mixtures thereof. Both the Soave-Redlich-Kwong  
93 (SRK) equation of state (EoS) and the Peng-Robinson (PR) equation of state were  
94 tested for this system [16, 17]. Better results were obtained with the latter. Hence,  
95 only the PR EoS will be discussed in the following.

##### 96 3.1.1. Pure Components

To test the applicability of the PR EoS, its ability to describe the pure compo-  
nents was checked first by comparing its predictions with fitted empirical equa-  
tions for vapor pressure, saturated liquid density, and the enthalpy of vaporization.  
These empirical equations are assumed to be the ground truth and the quality of  
the PR EoS is evaluated against them. As the temperature range of the plant oper-  
ation is 298 to 423 K, all graphs are limited to this interval.

The PR EoS employed here consists of the following equations

$$P = \frac{RT}{v - b} - \frac{a}{v^2 + 2bv - b^2}, \quad (3)$$

$$a = 0.457235 \frac{(RT_C)^2}{P_C} \alpha(T), \quad (4)$$

$$b = 0.077796 \frac{RT_C}{P_C}, \quad (5)$$

$$\alpha = \left( 1 + m \left( 1 - \sqrt{\frac{T}{T_C}} \right) \right)^2, \quad (6)$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2, \quad (7)$$

97 where  $T_C$  and  $P_C$  are the critical temperature and pressure, and  $\omega$  is the acentric  
98 factor. These three parameters for each component are taken from [18].

99 As shown in the parity plots in Figure 3a to 3e, all three properties can be well de-  
100 scribed for EDC in the temperature range from 298 to 423 K. The error between  
101 experiment and equation of state is typically below 5 % indicated by the black,  
102 continuous lines. Only for lower temperatures, the error in the vapor pressure is

103 up to 10 % at low temperatures. Figure 3b, 3d, and 3f show the parity plots for  
 104 ETC. Both vapor pressure and enthalpy of vaporization always show a deviation  
 105 smaller than 5 %. The error in the liquid density is less than 7 %.

106 The other three components were also carefully checked and demonstrate a rea-  
 107 sonable accuracy. Vapor pressure accuracy is always within  $\pm 5\%$  while larger  
 108 deviations of more than 15 % for liquid density and enthalpy of vaporization are  
 109 observed. However, their pure component vapor-liquid equilibria are not within  
 110 the temperature range at which the plant operates.

### 111 3.1.2. Binary Mixtures

The PR EoS mixture formulation employed here reads:

$$P = \frac{RT}{v_{mix} - b_{mix}} - \frac{a_{mix}}{v_{mix}^2 + 2b_{mix}v_{mix} - b_{mix}^2} \quad (8)$$

$$a_{mix} = \sum_c \sum_{caux} x_c x_j a_{c,caux}, \quad a_{c,caux} = \sqrt{a_c a_{caux}} (1 - k_{c,caux}) \quad (9)$$

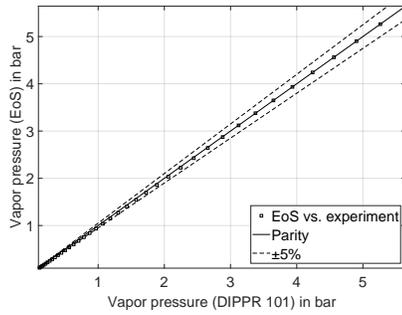
$$b_{mix} = \sum_c x_c b_c, \quad (10)$$

112 where we apply conventional mixing rules and  $k_{c,caux}$  is the binary interaction  
 113 parameter. Unfortunately, experimental data of the most important binary subsys-  
 114 tems ethene/EDC and chlorine/EDC is scarce. This is the most important reason  
 115 why we use an equation of state as they are more reliable when extrapolating  
 116 from the available data. The binary interaction parameter is fitted to the available  
 117 experimental data and is assumed to be temperature-independent. The binary in-  
 118 teraction parameter for the remaining subsystems is set to zero.

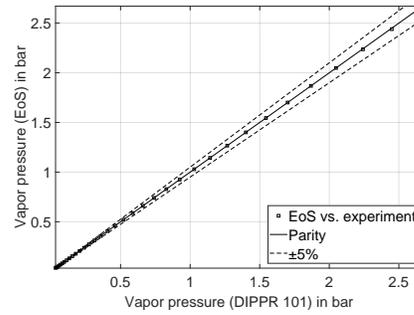
119 The results for the binary systems ethene/EDC and chlorine/EDC are shown in  
 120 Figure 4. Both binary systems can be accurately described with the PR EoS and  
 121 standard mixing rules. The small deviation of the binary interaction parameter  
 122 also indicates that the applied mixing rules are appropriate for the systems at  
 123 hand. The other binary systems are modeled with a binary interaction parame-  
 124 ter of zero due to the following reasoning: ETC and HCl are expected to only  
 125 appear in small concentrations, hence the influence on the mixture should be neg-  
 126 ligible. In addition, experimental results showed that EDC and ETC form an ideal  
 127 solution [19, 20], which is also predicted by the PR EoS.

### 128 3.2. Kinetics

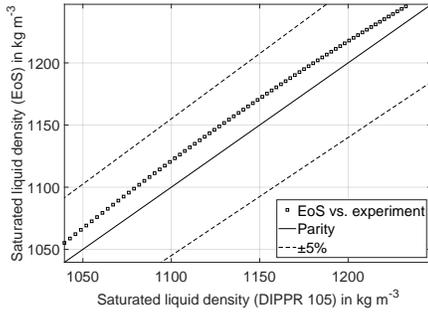
There are three different kinetic models for the reactions in Eq. (1) and (2)  
 available in the literature. Szépvölgyi and Ujhidy [22] and Orejas [13] consider



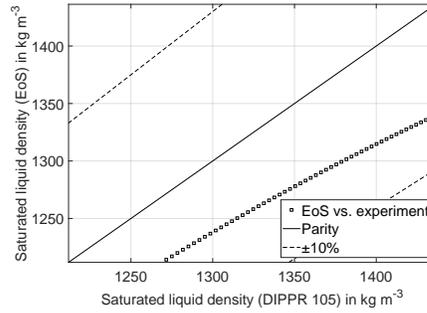
(a) Comparison of PR and DIPPR 101, parameters from [18, p. 2-56].



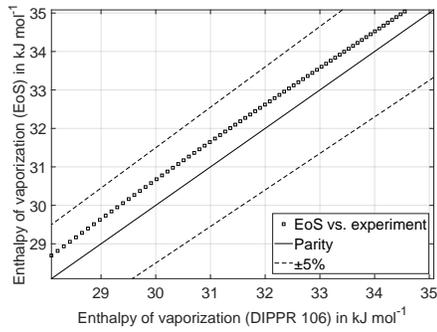
(b) Comparison of PR and DIPPR 101, parameters from [18, p. 2-60].



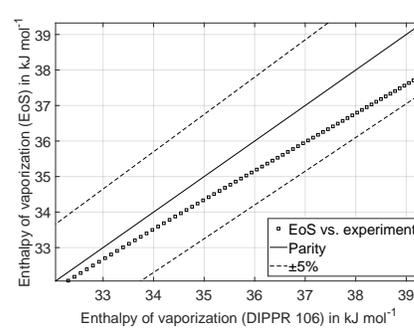
(c) Comparison of PR and DIPPR 105, parameters from [18, p. 2-99].



(d) Comparison of PR and DIPPR 105, parameters from [18, p. 2-103].

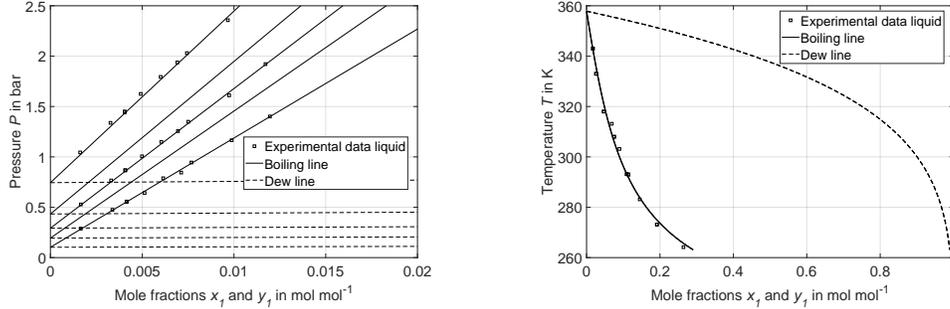


(e) Comparison of PR and DIPPR 106, parameters from [18, p. 2-151].



(f) Comparison of PR and DIPPR 106, parameters from [18, p. 2-155].

Figure 3: Parity plots for EDC (left) and ETC (right) in the temperature range from 298 to 423 K. The DIPPR equation is assumed to represent the true data.



(a) P-x-y diagrams of ethene (1) and EDC (2) at 299.2, 313.15, 323, 333.15, and 348.4 K,  $k_{12} = 0.0347$ . (b) T-x-y diagrams of chlorine (1) and EDC (2) at 1.013 25 bar,  $k_{12} = 0.0336$ .

Figure 4: Binary VLEs of ethene/EDC and chlorine/EDC. Experimental data from the Detherm database [21].

both reactions and use the following reaction rates with differing parameterization:

$$r_1 = k_1 \exp\left(-\frac{E_1}{RT}\right) c_{C_2H_4} c_{Cl_2} \quad (11)$$

$$r_2 = k_2 \exp\left(-\frac{E_2}{RT}\right) c_{C_2H_4} c_{Cl_2}^2. \quad (12)$$

129 Wachi and Morikawa [23] only consider the main reaction. However, as ETC is  
 130 found in real industrial plants, the second reaction cannot be neglected. Conse-  
 131 quently, the kinetics by Wachi and Morikawa [23] were discarded in this work.  
 132 Since there are no further independent experimental studies in the literature to the  
 133 best of our knowledge, both remaining parameter sets were implemented. In gen-  
 134 eral, the parameters from Szépvölgyi and Ujhidy [22] yield higher reaction rates  
 135 than those by Orejas [13]. Both parameter set show an offset to the real plant (see  
 136 section 4.2.1). Therefore, only the newer parameter set by Orejas [13] is used in  
 137 the remainder of this work.

### 138 3.3. Model Equations

139 In the following paragraphs, the essential model equations describing the con-  
 140 densers, the reflux drum, the trays, the reactor, and the external heat exchanger  
 141 are discussed. The whole model is available as supplementary material. The com-  
 142 ponent indices throughout this work are given in Table 1. In addition, we start  
 143 counting the trays at the top (condenser:  $tr = 0$ ). Note that the model is for-  
 144 mulated in terms of component flows. Mole fractions of components are only

145 calculated in post processing. This explains the unusual expressions, see e.g. the  
 146 phase equilibrium.

Table 1: Component indices.

Index c	Component
1	C <sub>2</sub> H <sub>4</sub>
2	Cl <sub>2</sub>
3	EDC
4	ETC
5	HCl

146

### 147 3.3.1. Condenser 1 and 2

148 The first condenser is assumed to be at steady-state due to the smaller hold ups  
 149 and expected temperature changes compared to the rest of the plant:

*Component and energy balances:*

$$0 = F_{tr=1,c}^V - F_{CON,c}^L - F_{CON,c}^V \quad (13)$$

150

$$0 = Q_{CON} + F_{tr=1}^V \cdot h_{tr=1}^V - F_{CON}^L \cdot h_{CON}^L - F_{CON}^V \cdot h_{CON}^V \quad (14)$$

151 The calculation of the vapor enthalpies and the enthalpy of vaporization is ex-  
 152 plained for all control volumes in section 3.3.6. The second condenser is modeled  
 153 in analogy to the first, only the indices are changed.

### 154 3.3.2. Reflux drum

155 The model of the reflux drum contains dynamic mole balances. An energy  
 156 balance is neglected, because the liquid is subcooled and small changes in the  
 157 liquid holdup have only a small temperature influence.

*Component balance:*

$$\frac{dHU_{RD,c}}{dt} = F_{CON,c}^L + F_{CON2,c}^L - F_{tr=0,c}^L \quad (15)$$

*Ideal mixing:*

$$HU_{RD,c} \cdot F_{tr=0}^L = \sum_{c=1}^{NC} HU_{RD,c} \cdot F_{tr=0,c}^L \quad (16)$$

Volume:

$$\sum_{c=1}^{NC} HU_{RD,c} \cdot M_c = V_{RD}^L \cdot \rho_{CON}^L. \quad (17)$$

158 *Volume correlation:* The relation between volume and level of a horizontal cylinder is quite nonlinear; it contains an arccos function and a root. A more robust  
 159 form of this equation is the approximation of this function with a cubic polynomial, in which the coefficients  $p_i$  must be fitted to the actual geometry.  
 160  
 161

$$V_{RD}^L = p_1 \cdot (L_{RD})^3 + p_2 \cdot (L_{RD})^2 + p_3 \cdot L_{RD}. \quad (18)$$

### 162 3.3.3. Trays

163 On every tray, thermodynamic equilibrium and ideal mixing is assumed. Both  
 164 mole and energy balance are formulated dynamically:

$$\frac{dHU_{tr,c}}{dt} = F_{tr-1,c}^L - F_{tr,c}^L + F_{tr+1,c}^V - F_{tr,c}^V - y_{tr}^{\text{side stream,L}} \cdot F_{tr,c}^{\text{side stream,L}}, \quad (19)$$

165

$$\frac{dU_{tr}}{dt} = Q_{tr} + F_{tr-1}^L \cdot h_{tr-1}^L - F_{tr}^L \cdot h_{tr}^L + F_{tr+1}^V \cdot h_{tr+1}^V - F_{tr}^V \cdot h_{tr}^V - y_{tr}^{\text{side stream,L}} \cdot F_{tr}^{\text{side stream,L}} \cdot h_{tr}^L. \quad (20)$$

166 Therein,  $y_{tr}$  is a binary variable that can be set to 1 if a side stream exists on this  
 167 tray. The side stream may be controlled with a controller (see Section 3.3.7).

168 *Pressure drop:* The pressure drop between two stages,

$$\Delta P_{tr} = P_{tr} - P_{tr-1}, \quad (21)$$

169 depends on the superficial vapor velocity and the hydrostatic pressure of the tray  
 170 above [24, p. 463]:

$$\Delta P_{tr} = (\rho_{tr-1}^L \cdot g \cdot h_{cl,tr-1} + \frac{\xi}{2} \cdot (F_{tr}^V)^2) \cdot y_{CON,tr} + 5 \cdot 10^2 \cdot (1 - y_{CON,tr}). \quad (22)$$

171 Again,  $y_{CON,tr}$  is a binary variable that is one for all stages except for the first tray,  
 172 where there is no tray above. Instead, the pressure drop is set to an arbitrary value  
 173 of 500 Pa. The clear liquid height  $h_{cl,tr}$  is correlated to the liquid holdup on this  
 174 tray:

$$A_{\text{active}} \cdot h_{cl,tr} = HU_{tr}^L \cdot v_{tr}^L. \quad (23)$$

175 At the same time,  $h_{cl,tr}$  is a function of froth density  $\rho_{froth,tr}$ , weir height  $h_{weir}$ , and  
 176 height above the weir  $h_{ow,tr}$  [25]:

$$h_{cl,tr} = \rho_{froth,tr} \cdot (h_{weir} + h_{ow,tr}). \quad (24)$$

177 The froth density depends on the gas load, which is expressed by the superficial  
 178 velocity factor [25]:

$$\rho_{froth,tr} = \exp(\pi_1 \cdot (K_{tr})^{\pi_2}). \quad (25)$$

179 The superficial velocity factor is correlated to the F-factor by

$$K_{tr} \cdot \sqrt{\rho_{tr}^L - \rho_{tr}^V} = F_{tr}. \quad (26)$$

180 The F-factor depends on the superficial velocity and the vapor density:

$$F_{tr} = w_{tr}^V \cdot \sqrt{\rho_{tr}^V}, \quad (27)$$

181 which connects the vapor flow and the vapor velocity:

$$A_{column} \cdot w_{tr}^V = F_{tr}^V \cdot v_{tr}^V. \quad (28)$$

182 *Liquid flow over weir:* The liquid height above the weir is calculated with the  
 183 Francis-Weir formula. Due to the coupling of the clear liquid height, the holdup,  
 184 the froth density and the Francis-Weir formula, fulfilling all equations may only  
 185 be possible if  $h_{ow,tr}$  is smaller than zero. Using a negative height above the weir  
 186 leads to numerical errors in Equation (30). Hence, we use a smooth version of a  
 187 max operator to limit the actual height above the weir and use this variable in the  
 188 Francis-Weir formula for a segmental weir:

$$h_{ow,tr}^{actual} = \max(h_{ow,tr}, 0) \approx \frac{h_{ow,tr}}{2} \cdot \left( \frac{h_{ow,tr}}{\sqrt{(h_{ow,tr})^2 + (10)^{-9}}} + 1 \right) + (10)^{-3}, \quad (29)$$

189

$$\left( \frac{h_{ow,tr}^{actual}}{0.664} \right)^{3/2} \cdot \rho_{froth,tr} \cdot L_{weir} = V_{weir,tr}^{L,flow}. \quad (30)$$

190 The last term in Eq. (29) is a small positive value of 1 mm for numerical stability.  
 191 In this way,  $h_{ow,tr}^{actual}$  remains larger than 0. More on smooth approximations of non-  
 192 smooth functions can, for example, be found in [26, p. 771]

193 *Liquid flow through tray holes (weeping)*: Liquid may not only leave a tray over  
 194 the weir, it may also flow through the holes of a tray. This is called weeping. Wijn  
 195 [27] introduced a weeping factor  $\Omega$  to describe the flow through the holes of a  
 196 tray:

$$V_{tr}^{L,flow,weep} = \Omega_{tr}^{actual} \cdot A_{active} \cdot \varphi \cdot \sqrt{2 \cdot g \cdot h_{cl,tr}}. \quad (31)$$

197 This weeping factor may vary between 0 and 1, depending on the fluiddynamic  
 198 state of the column. For small gas loads, the weeping factor is 1 up to a certain  
 199 gas load. At this point, the weeping factor starts to drop and goes to zero for high  
 200 gas loads. This behavior can be described with a min operator:

$$\Omega_{tr} = \min(1, f_{tr}(F_{tr})). \quad (32)$$

201 Staak [28] conducted experiments to fit the parameters  $A_{weep}$ ,  $B_{weep}$ , and  $C_{weep}$  in  
 202 the function  $f_{tr}$ , which depends on F-factor and free area ratio  $\varphi$ :

$$f_{tr} = C_{weep} \cdot \exp\left(-B_{weep} \cdot \frac{F_{tr+1}}{\varphi} + A_{weep}\right). \quad (33)$$

203 The min operator in Eq. (32) is again reformulated to a smooth form:

$$\Omega_{tr}^{actual} = \frac{f_{tr} - 1}{2} \cdot \left( \frac{-(f_{tr} - 1)}{\sqrt{(f_{tr} - 1)^2 + (10)^{-9}}} + 1 \right) + 1. \quad (34)$$

204 The behavior of this smooth version is demonstrated in Figure 5 for three differ-  
 205 ent values of  $\varphi$ . The discrete min operator is compared to the behavior of the  
 206 smoothed form. It is visible that the non-smooth behavior is well described by  
 207 our approximation.

### 208 3.3.4. Reactor

209 As Orejas [13] pointed out, there are only a few articles studying and modeling  
 210 direct chlorination reactors for EDC production, namely the work of Balasubra-  
 211 manian et al. [29], the kinetic investigations of Szépvölgyi and Ujhidy [22] and  
 212 Wachi and Morikawa [23], and two articles by Orejas [30, 13]. Balasubramanian  
 213 et al. [29] studied a stirred reactor while the other authors focussed on a bubble  
 214 column, which seems to be the dominating reactor type in industry nowadays [31,  
 215 p. 221].

216 Nevertheless, this work applies a simplified dynamic, two-phase CSTR model to  
 217 describe the reactor to avoid a partial differential equation system at this point.  
 218 This assumption will be revisited in section 4.

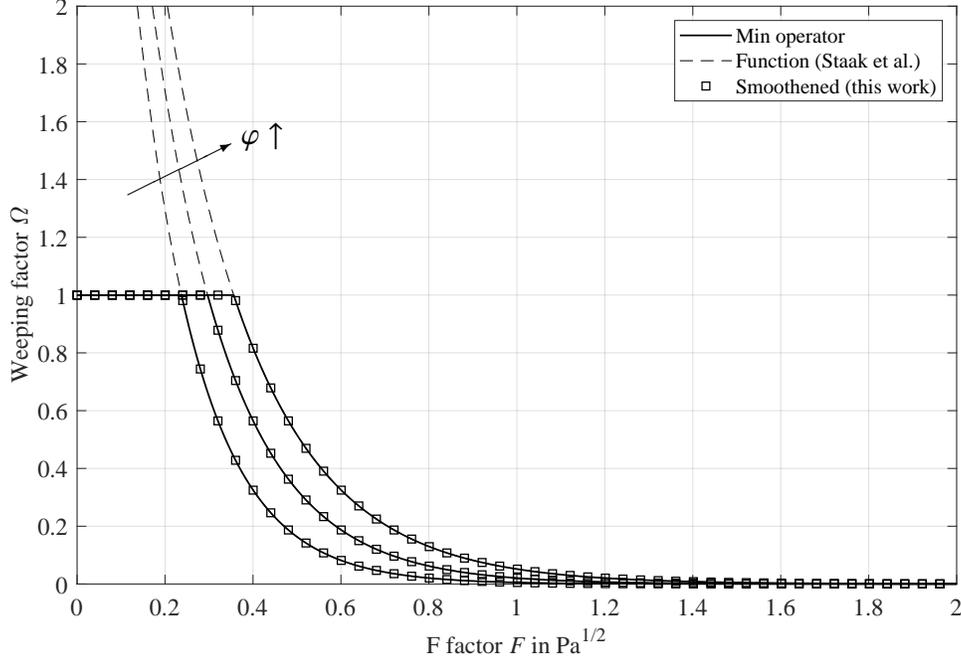


Figure 5: Weeping factor as a function of the F-factor for a free area ratio of  $\varphi = \{0.1, 0.125, 0.15\}$ .

*Component and energy balances:* The component balance includes the reactor feed, the liquid flow from the tray above  $F_{tr=NTR,c}^L$ , the liquid outlet to the heat exchanger  $F_{tr=NTR+1,c}^L$ , the vapor flow to the tray section  $F_{tr=NTR+1,c}^V$ , the reaction rates, the incoming flow from the heat exchanger  $F_{HE,c}$ , a possible additional flow from a secondary reactor  $F_{secR,c}$  in which unreacted chlorine from the first reactor is processed, and the inlet from the heavy end removal  $F_{rec,c}^{in}$ :

$$\begin{aligned}
 \frac{dHU_{c,tr=NTR+1}}{dt} &= \frac{P_N \cdot V_{N,c}^{\text{feed, flow}}}{R \cdot T_N \cdot 3600} + F_{tr=NTR,c}^L - F_{tr=NTR+1,c}^L - F_{tr=NTR+1,c}^V \\
 &\quad + V_{tr=NTR+1}^L \cdot \sum_{r=1}^{NR} \nu_{c,r} \cdot r_{tr=NTR+1,r} + F_{HE,c} + F_{SecR,c} \\
 &\quad + F_{rec,c}^{in} \cdot \psi_c.
 \end{aligned} \tag{35}$$

Therein,  $\psi_c$  indicates a simple removal factor, which is zero if a component is removed (this is true for ETC) and 1 otherwise. The expressions for the reaction rates are taken from Equations (11) and (12). The energy balance contains the

same terms as the mole balance, only the reaction does not directly appear as the heats of formation are used as reference points (see section 3.3.6). It is assumed that the flows from the secondary reactor and from the heavy end removal have the same molar enthalpy:

$$\begin{aligned} \frac{dU_{tr=NTR+1}}{dt} &= Q_{tr=NTR+1} + F^{\text{feed}} \cdot h^{\text{feed}} + F_{tr=NTR}^L \cdot h_{tr=NTR}^L \\ &\quad - F_{tr=NTR+1}^L \cdot h_{tr=NTR+1}^L - F_{tr=NTR+1}^V \cdot h_{tr=NTR+1}^V + F_{\text{HE}} \cdot h_{\text{HE}} \\ &\quad + \left( \sum_{c=1}^{NC} F_{\text{SecR},c} + F_{\text{rec},c}^{\text{in}} \cdot \psi_c \right) \cdot h_{\text{SecR}} \end{aligned} \quad (36)$$

219 *Pressure drop equations:* Again, the same approach for the pressure drop as in  
 220 the tray section is taken. However, the hydrostatic pressure of the reactor is also  
 221 added.

### 222 3.3.5. External heat exchanger and heavy end removal

223 The heat removed in the external heat exchanger is determined by an energy  
 224 balance at steady-state:

$$0 = -Q_{\text{HE}} + F_{tr=NTR+1}^L \cdot (h_{tr=NTR+1}^L - h_{\text{HE}}). \quad (37)$$

225 The heat flow is calculated with an overall heat transfer coefficient (OHTC, as-  
 226 sumed value:  $0.45 \text{ kW m}^{-2} \text{ K}^{-1}$  [32, p. 85]). The typical logarithmic temperature  
 227 difference is replaced by the arithmetic mean temperature difference for numerical  
 228 stability:

$$Q_{\text{HE}} = \text{OHTC}_{\text{HE}} \cdot A_{\text{HE}} \cdot \frac{(T_{tr=NTR+1} - T_{\text{hw}}^{\text{out}}) + (T_{\text{HE}} - T_{\text{hw}}^{\text{in}})}{2}$$

229 The cold side of the heat exchanger is also balanced to determine the mass flow  
 230 of generated hot water:

$$0 = Q_{\text{HE}} + m_{\text{hw}} \cdot c_{\text{hw}} \cdot (T_{\text{hw}}^{\text{in}} - T_{\text{hw}}^{\text{out}}). \quad (38)$$

231 After the heat exchanger, the outlet is split into two streams. One stream is directly  
 232 recycled to the reactor ( $F_{\text{HE}}$ ), the second one enters the heavy end removal ( $F_{\text{rec}}^{\text{in}}$ ).

### 233 3.3.6. Thermodynamic Properties and Simplifications

234 *Fugacity coefficients:* Fugacity coefficients are necessary to calculate thermody-  
 235 namic phase equilibria in the partial condensers, on all stages, and inside the reac-  
 236 tor. They are calculated with the PR EoS using the binary interaction parameters  
 237 estimated in Section 3.1.2.

238 *Vapor enthalpies:* Vapor enthalpies are calculated by taking the enthalpy of for-  
 239 mation at 25 °C for the ideal gas as reference point. The temperature dependence  
 240 of the ideal gas heat capacities is described by linearized forms of the hyperbolic  
 241 expressions in [18, p. 2-176]:

$$h^V = \Delta_f h_c + \frac{CPA_c}{2} \cdot (T^2 - T_{\text{ref}}^2) + CPB_c \cdot (T - T_{\text{ref}}) \quad (39)$$

242 *Enthalpy of vaporization:* The enthalpy of vaporization is computed with the PR  
 243 EoS: The actual expression can be found in the literature, e.g. [33, p. 339], and  
 244 has been implemented for every control volume:

### 245 3.3.7. Controllers

246 In addition to balances and phase equilibria, the process model additionally  
 247 contains controller equations. In our approach, the level in the reflux drum is  
 248 controlled by the reflux. We use a PI controller for this task. The first summand  
 249 is the feed-forward control to maintain the set-point, the second summand is the  
 250 proportional term, and the third term contains the integral of the control deviation:

$$F_{tr=0}^L = F_{tr=0}^{L,SP} + K_{RD} \cdot (L_{RD} - L_{RD}^{SP}) + \frac{K_{RD}}{T_{RD}} \cdot L_{RD}^{int}. \quad (40)$$

252 This integral is calculated with an additional differential equation:

$$\frac{dL_{RD}^{int}}{dt} = L_{RD} - L_{RD}^{SP}. \quad (41)$$

The side stream on tray  $tr$  is coupled to the liquid volume fraction in the reactor:

$$F_{tr}^{L, \text{side stream}} = F_{tr}^{L, SP, \text{side stream}} + K_{tr}^{\text{side stream}} \cdot (\varepsilon_{tr=NTR+1}^L - \varepsilon_{tr=NTR+1}^{L, SP}) + \frac{K_{tr}^{\text{side stream}}}{T_{\text{side stream}}} \cdot \varepsilon_{tr=NTR+1}^{L, int}, \quad (42)$$

$$\frac{d\varepsilon_{tr=NTR+1}^{L, int}}{dt} = \varepsilon_{tr=NTR+1}^L - \varepsilon_{tr=NTR+1}^{L, SP}. \quad (43)$$

254 The coupling of the side stream to the volume fraction of the liquid phase in the  
 255 reactor turned out to be the most reliable solution. However, a more realistic con-  
 256 trol setup would be using the liquid level or the hydrostatic pressure of the reactor.  
 257 Finally, a P controller is used to controller the outlet temperature of the heat ex-  
 258 changer on the process side via the the mass flow of the hot water. Originally, all

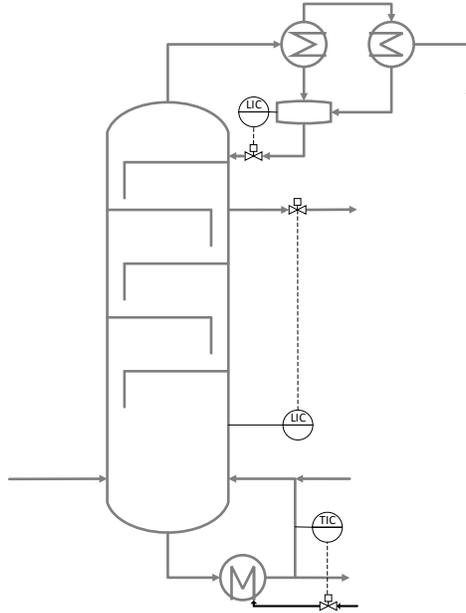


Figure 6: Process control scheme.

259 controllers were intended to be P controllers to keep the control structure as sim-  
 260 ple as possible. However, it was necessary to use PI controllers for both product  
 261 stream and level control in the reflux drum to mimic the oscillating behavior of  
 262 the obtained real plant data. In the future, these controllers will be replaced by  
 263 control actions determined by optimization.

$$m_{hw} = m_{hw}^{SP} + K_{hw} \cdot (T_{HE} - T_{HE}^{SP}). \quad (44)$$

264 The assumed process control scheme is shown in Figure 6.

### 265 3.4. Implementation

266 In addition to the described dynamic model, a steady-state model was also  
 267 formulated. As its main difference compared to the dynamic one are the absence  
 268 of time derivatives and its lack of controller equations, the model is not presented  
 269 here, but it can be deduced from the dynamic model. As part of this work, both  
 270 steady-state and dynamic model have been implemented in MOSAICmodeling,  
 271 a web-based modeling, simulation, and optimization environment [34, 35]. Us-  
 272 ing its code generator for various programming languages and modeling environ-

273 ments, the steady-state system is exported to AMPL [36] and solved with IPOPT  
274 [37], while the dynamic system is exported to the gPROMS model builder [38].

## 275 **4. Simulation Results**

276 In the following section, the results of steady-state and dynamic simulations  
277 are presented and they are compared to real plant data.

### 278 *4.1. Case Study: Dynamic Tray Model*

279 To demonstrate the performance of the dynamic tray model and the applied re-  
280 laxations presented in section 3.3.3, we begin this section with a small case study,  
281 in which we demonstrate the system's response to a decrease and a subsequent  
282 increase of the vapor flow from the reactor section. This is added to (i) demon-  
283 strate the advantages of the presented modeling approach and (ii) present a small  
284 study with actual physical units as the model validation in the following section is  
285 carried out with normalized variables.

286 The design specifications of the case study are shown in Table 2 while the  
287 feed specifications are given in Table 3. The system is initialized at steady-state,  
288 which yields consistent initial conditions. For this case study, the reflux from  
289 the condenser is assumed to be pure EDC while the vapor flow from the reactor  
290 contains unreacted chlorine and ethene, as well as some ETC and HCl. This  
291 vapor flow rate is now continuously reduced and then increased again while the  
292 feed composition is kept constant (Figure 7). A possible explanation for such a  
293 scenario is, for example, a failing reboiler. For this simple example, we consider  
294 a column with 5 trays. The resulting pressure profile is shown in Figure 8. As the  
295 vapor flow rate from the bottom decreases, the pressure on the lower trays drops  
296 towards the fixed column pressure of 1.5 bar. This is an important difference to  
297 conventional dynamic simulations in which the pressure profile is always assumed  
298 to be given or fixed. There are two phases in the profiles: First, the pressure  
299 decreases slowly (time between 0 and 0.5 h). After 0.5 h, the pressure drops to the  
300 top pressure within a few minutes, as the single trays run dry in this time period  
301 (not shown here). In addition, the liquid height above the weir goes to zero due to  
302 the low gas load (Figure 9). At this point, conventional formulations of the Francis  
303 weir formula would not converge anymore, as the variable becomes negative. Our  
304 formulation avoids this issue by using the bounded liquid height in the Francis  
305 weir formula. In this way, our model can be solved dynamically for decreasing  
306 loads as well. The decrease in the liquid height above the weir results in a drop  
307 of the liquid volume flow above the weir, which disappears completely after 0.5 h

Table 2: Design specifications (case study).

Variable	Value	Unit
$\kappa$	0.1	–
$\rho_{tr=0}^L$	1175	$\text{kg m}^{-3}$
$\xi$	300	–
$A_{\text{active}}$	1	$\text{m}^2$
$A_{\text{column}}$	1.2	$\text{m}^2$
$L_{\text{weir}}$	1	m
$P_{tr=0}$	1.5	bar
$V_{tr}$	2.5	$\text{m}^3$
$h_{\text{weir}}$	0.04	m

Table 3: Feed specifications (case study).

Variable	Value	Unit
$F_{tr=0}^L$	50	$\text{mol s}^{-1}$
$F_{tr=0,c=3}^L$	50	$\text{mol s}^{-1}$
$F_{tr=6}^V$	51.100 02	$\text{mol s}^{-1}$
$F_{tr=6,c=1}^V$	1	$\text{mol s}^{-1}$
$F_{tr=6,c=2}^V$	0.1	$\text{mol s}^{-1}$
$F_{tr=6,c=3}^V$	50	$\text{mol s}^{-1}$
$F_{tr=6,c=4}^V$	$10^{-5}$	$\text{mol s}^{-1}$
$F_{tr=6,c=5}^V$	$10^{-5}$	$\text{mol s}^{-1}$
$F_{tr=6}$	1.85	$\text{Pa}^{0.5}$

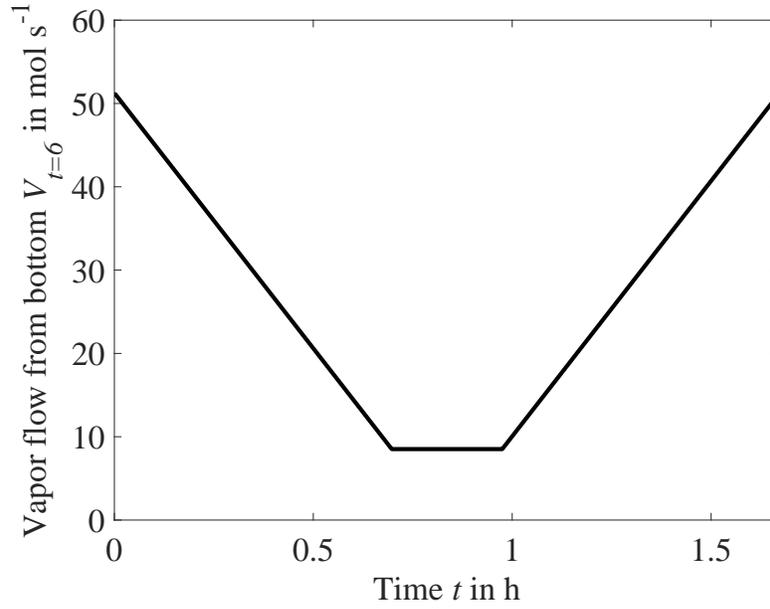


Figure 7: Profile of the feed vapor flow entering the column at the bottom.

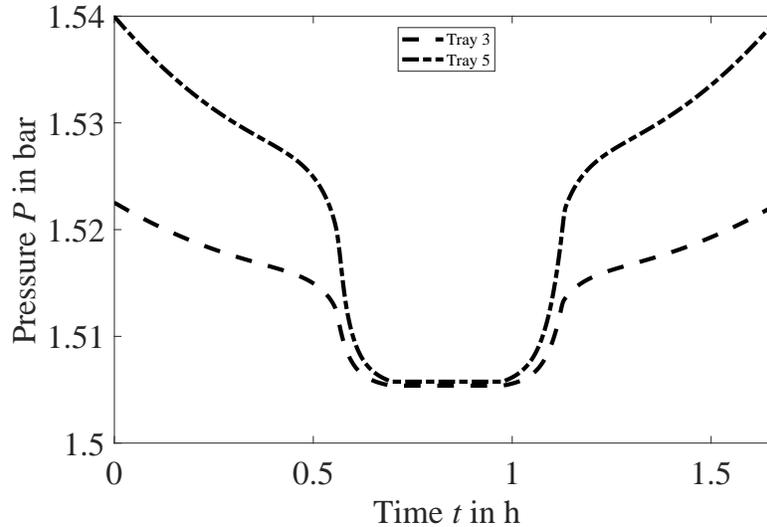


Figure 8: Profile of the pressure on tray 3 and tray 5.

308 and rises again as soon as the vapor flow is increased again. At the same time,  
 309 the liquid volume flow by weeping increases notably with decreasing gas load  
 310 (Figure 10). Note that there is always a maximum in the profiles on all trays, but  
 311 with varying amplitude. This maximum can be explained by two influences on  
 312 the weeping: On the one hand, weeping is increased by the weeping factor, which  
 313 increases with decreasing gas load; on the other hand, weeping depends on the  
 314 height of clear liquid on the tray. The weeping increases while the weeping factor  
 315 still grows exponentially. As soon as it reaches its steady value of 1, weeping  
 316 cannot increase anymore and reaches an equilibrium between liquid entering the  
 317 tray from above and the liquid weeping through the holes.

#### 318 4.2. Steady-State Results

319 The previous case study demonstrated the successful implementation of a  
 320 pressure-driven dynamic model for a tray column. The complete model of section  
 321 3 is now solved at steady-state and in the dynamic case and its results are  
 322 compared to real plant data. As stated above, all profiles are normalized as they  
 323 are compared to real process data.

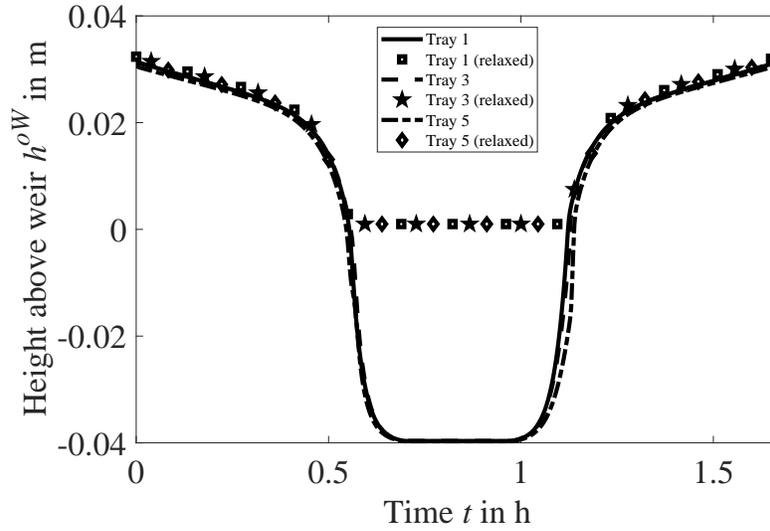


Figure 9: Profile of the liquid height above the weir on tray 1, 3, and 5. The relaxed variable is printed without a line for visual clarity.

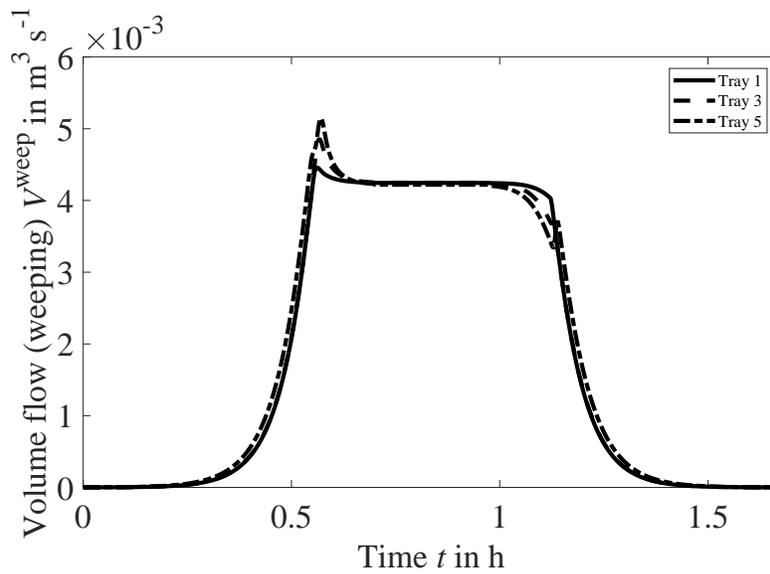


Figure 10: Profile of the liquid volume flow (weeping) on tray 1, 3, and 5.

#### 324 4.2.1. *Enhancement of Reaction*

325 Early in the model development, it was evident that temperature and pressure  
326 profiles on the trays can be well described. However, when comparing the model  
327 results to real plant data, the hot water stream in the bottom heat exchanger and the  
328 liquid reflux at the top could not be matched as can be seen in Table 4. The reflux  
329 from the condenser was about 13 % smaller than in the real plant while a lot of heat  
330 had to be removed in the bottom heat exchanger. The increased heat removal is  
331 attributed to the larger pressure – and, consequently, temperature – in the reactor.  
332 It was deduced that the reaction rate in the model was smaller than in the real plant  
333 due to the assumptions of a CSTR and thermodynamic equilibrium at the bottom  
334 of the reactor. If the reaction is not fast enough, the released heat of reaction is  
335 too small to evaporate enough liquid and the conversion is too small. Hence, the  
336 hydrostatic pressure in the reactor increases and thus its temperature. This leads  
337 to an increase of  $Q_{HE}$ , which is governed by the temperature difference of process  
338 medium and water. This effect was studied by multiplying the main reaction rate  
339 with an enhancement factor  $\beta$ . Varying this value between 1 and 30 leads to the  
340 results given in Table 4 to Table 7. It is obvious that simply increasing the reaction  
341 rate improves the calculated reflux, but the deviation in the hot water flow, which  
342 cools the process stream in the external heat exchanger, increases again for larger  
343 values of  $\beta$ . Due to these observations, a value of  $\beta = 10$  is used in the remainder  
344 of this work. This is the only model parameter, which was adapted to the plant  
345 data.

346 Additionally, it must be pointed out that increasing  $\beta$  to 10 does not influence  
347 the temperature (Figure 11) or pressure profile (Figure 12) over the normalized  
348 tray number (0 = condenser), because the pressure drop on the trays is virtually  
349 identical and the vaporized EDC is fairly pure (vapor mole fraction > 97 %) in  
350 all cases. Comparing the results in Figure 11 and Figure 12 with the temperature  
351 and pressure profile of the plant at nominal operating point, it becomes obvious  
352 that it is currently not possible to match both temperature and pressure profiles  
353 perfectly, but model and plant are generally in good agreement. This is an aspect,  
354 which can certainly be improved in the future, e.g. by dropping the assumption of  
355 a CSTR or by modeling the reactor as plug flow or bubble column reactor with  
356 spatial discretization. This effect is possibly enlarged by an incorrect temperature  
357 dependence of the reaction rates. The parameters taken from Orejas [13] were  
358 only reported for temperatures up to 340 K and showed a large variation. In addi-  
359 tion, they differ significantly from the values reported by Szépvölgyi and Ujhidy  
360 [22].

Table 4: Relative deviation between real plant and model with  $\beta = 1$ .

Variable	Deviation
$T_{\text{HE}}$	-0.4 %
$F_{t=0}^L$	-13.2 %
$m_{\text{hw}}$	62.1 %
$Q_{\text{HE}}$	65.0 %

Table 5: Relative deviation between real plant and model with  $\beta = 10$ .

Variable	Deviation
$T_{\text{HE}}$	-0.9 %
$F_{t=0}^L$	-3.9 %
$m_{\text{hw}}$	-0.7 %
$Q_{\text{HE}}$	1.1 %

Table 6: Relative deviation between real plant and model with  $\beta = 20$ .

Variable	Deviation
$T_{\text{HE}}$	-1.0 %
$F_{t=0}^L$	-2.7 %
$m_{\text{hw}}$	-7.6 %
$Q_{\text{HE}}$	-6.0 %

Table 7: Relative deviation between real plant and model with  $\beta = 30$ .

Variable	Deviation
$T_{\text{HE}}$	-1.0 %
$F_{t=0}^L$	-2.0 %
$m_{\text{hw}}$	-12.3 %
$Q_{\text{HE}}$	-10.7 %

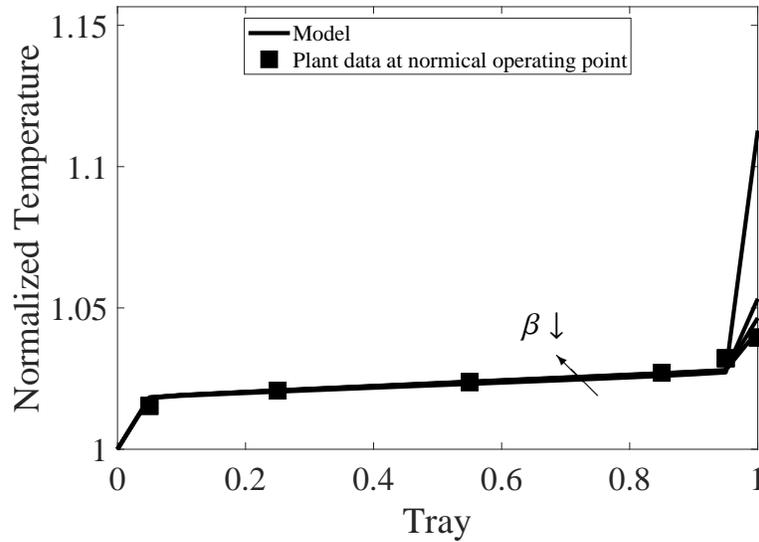


Figure 11: Normalized temperature for varying kinetic enhancement factor  $\beta = 1, 10, 20,$  and  $30$ . The temperature is normalized with the condenser temperature. The feed gas load is at 100 % of the nominal gas load.

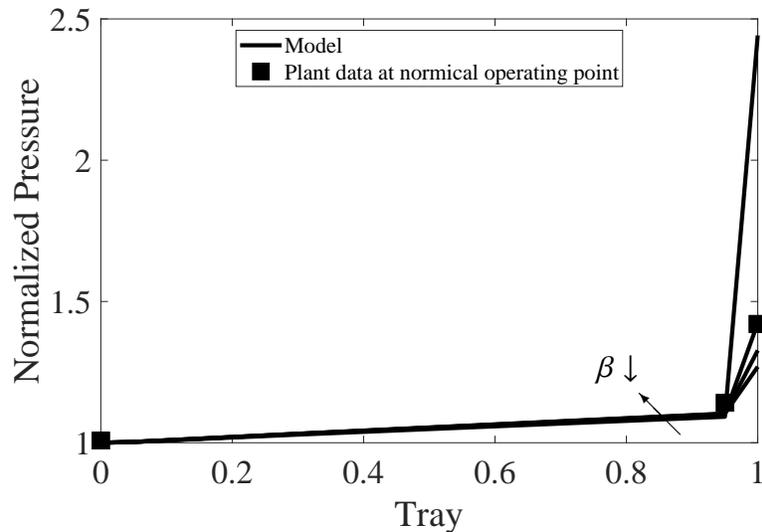


Figure 12: Normalized pressure for varying kinetic enhancement factor  $\beta = 1, 10, 20,$  and  $30$ . The pressure is normalized with the condenser pressure. The feed gas load is at  $100\%$  of the nominal gas load.

#### 361 4.2.2. Steady-State Profiles

362 In the following, the steady-state profiles of the EDC production unit are  
 363 looked at more closely for varying feed flows. As the data are compared to real  
 364 plant data, all results are normalized.

365 The liquid height above the weir is shown in Figure 13 over the normalized  
 366 tray number ( $0 =$  condenser). As expected, it decreases for decreasing feed gas  
 367 load. The drop at approximately one third of the column is due to the side stream,  
 368 in which liquid EDC is removed. At loads below  $70\%$ , there is a superlinear  
 369 drop; and for  $50\%$ , all trays are essentially dry. This result is of high importance  
 370 regarding flexibilization as this region should be avoided whenever possible. At  
 371 such low loads, weeping increases by a factor of  $100$  compared to the nominal  
 372 load.

373 In Figure 14, the normalized pressure profile is presented and compared to  
 374 the steady-state profile of the plant at nominal conditions. The pressure profile  
 375 shows good agreement between model and plant data, only the pressure drop on  
 376 the trays is underestimated by  $3.5\%$ . In addition, the change of the pressure drop  
 377 with decreasing gas load is shown. In this case, the gas load on the trays is reduced  
 378 and the pressure profile flattens out.

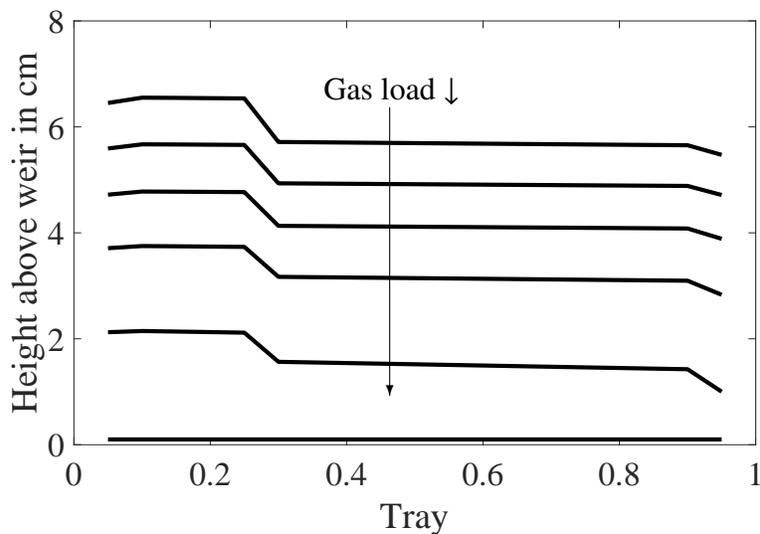


Figure 13: Liquid height above the weir for 100, 90, 80, 70, 60, and 50 % of the nominal feed load.

379 The normalized temperature profile is shown in Figure 15. For 100 % of feed  
 380 gas load, the real plant data are also shown. Model and real data show an excellent  
 381 correspondence. The largest deviations appear in the reactor section. Again, this  
 382 is attributed to the simplified model of the reactor, which leads to deviations of  
 383 about 5 %.

#### 384 4.3. Dynamic Results

385 In the last section, the obtained dynamic results are analyzed and compared to  
 386 real plant data. For this purpose, 24 h of a plant operation in November 2017 were  
 387 simulated. Typically, the plant operates at steady-state throughout the year. How-  
 388 ever, during this period, some changes in the chlorine feed occurred as is shown  
 389 in Figure 16. The chlorine feed drops to about 87 % and is then increased to  
 390 92 %. We mimicked this case in our dynamic simulation. All dynamic measure-  
 391 ment data was filtered and approximated linearly between single setpoints, which  
 392 yields a reasonably accurate feed profile.

393 The resulting temperature profile is shown in Figure 17. In agreement with  
 394 the steady-state results, deviations in the middle of the column are very small.  
 395 Slightly larger deviations are observed closer to the top and the bottom. The  
 396 maximum error is 3.5 %. The pressure profile is shown in Figure 18. In the reactor,

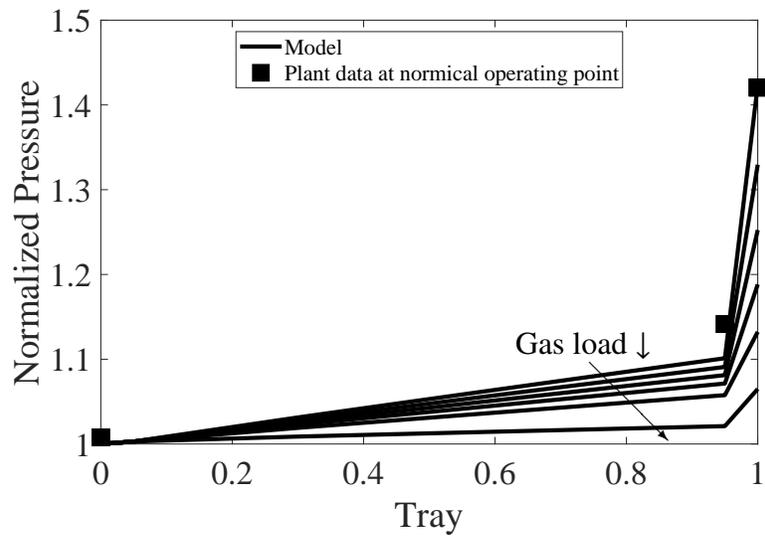


Figure 14: Normalized pressure for 100, 90, 80, 70, 60, and 50 % of the nominal feed load. The pressure is normalized with the condenser pressure.

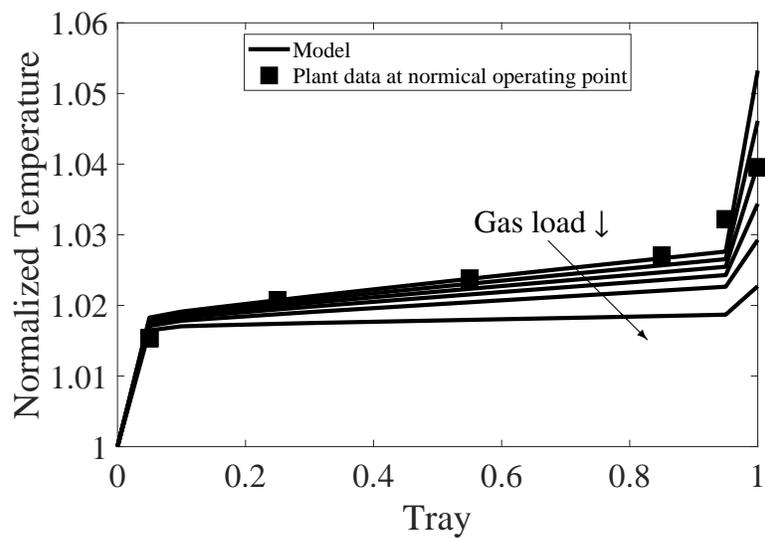


Figure 15: Normalized temperature for 100, 90, 80, 70, 60, and 50 % of the nominal feed load. The temperature is normalized with the condenser temperature.

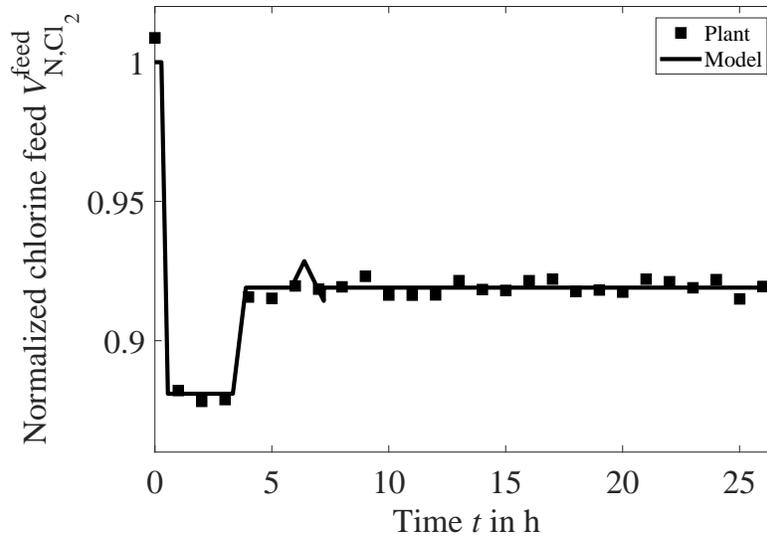


Figure 16: Normalized chlorine feed over time. The chlorine feed is normalized with its nominal setpoint.

397 fluctuations of the hydrostatic pressure can be observed, which will be correlated  
 398 to the side stream in the next figure. Similarly to the steady-state results, the  
 399 pressure profile is well described with small deviations for the pressure above the  
 400 reactor. The maximum error is 3.5%. Both temperature and pressure profile are  
 401 almost independent from the feed gas load, which is confirmed by the plant data  
 402 and has already been pointed out in section 4.2.1.

403 Figure 19 presents the resulting product flow, i.e. the side stream of liquid  
 404 EDC. Using the PI controller introduced in section 3.3.7, the fluctuations in the  
 405 product outlet can be well described, although the frequency in the model is higher  
 406 than in the real plant. This is attributed to effects, such as sample time for an  
 407 industrial process control system. This will always lead to lower frequencies than  
 408 in the numerical model, in which the current value of the controlled variable is  
 409 directly fed back to the controller without noise. Moreover, a perfect match in  
 410 the controller behavior is not necessary as the controllers will be removed from  
 411 the model in the future. Instead, optimized trajectories between setpoints will  
 412 be obtained using an optimization approach and the presented process model, in  
 413 which the controls are degrees of freedom in the optimization problem.

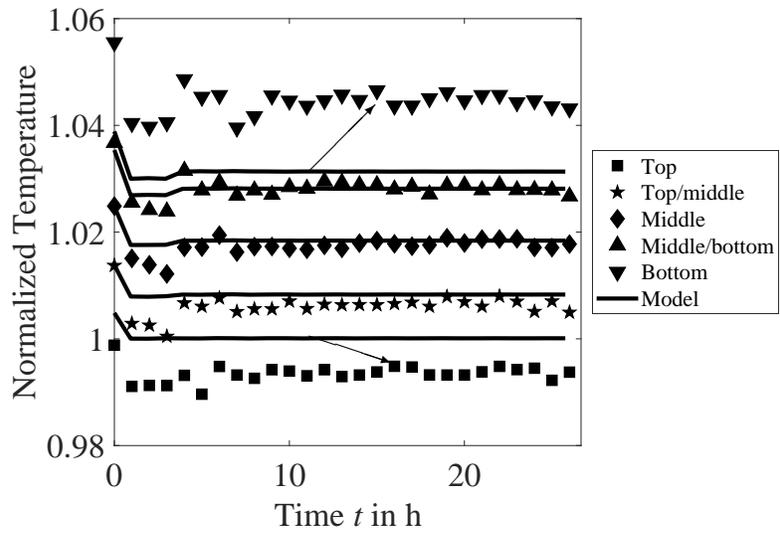


Figure 17: Normalized temperature over time. The temperature is normalized with the condenser temperature.

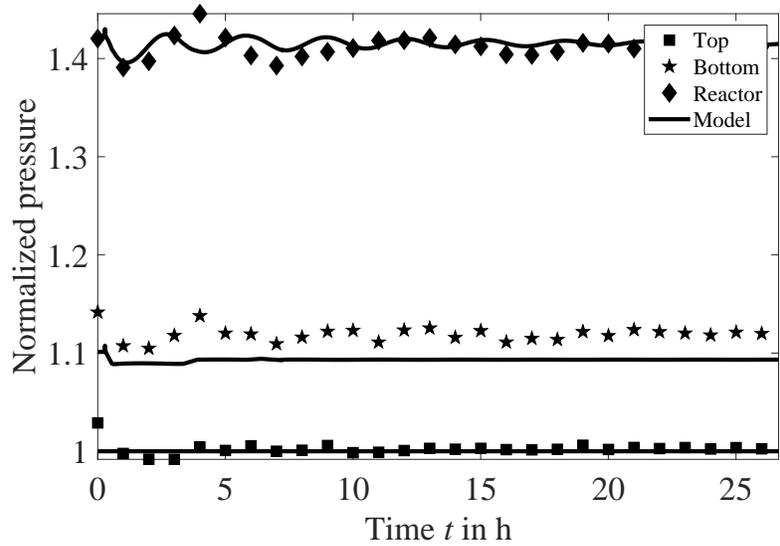


Figure 18: Normalized pressure over time. The pressure is normalized with the condenser pressure.

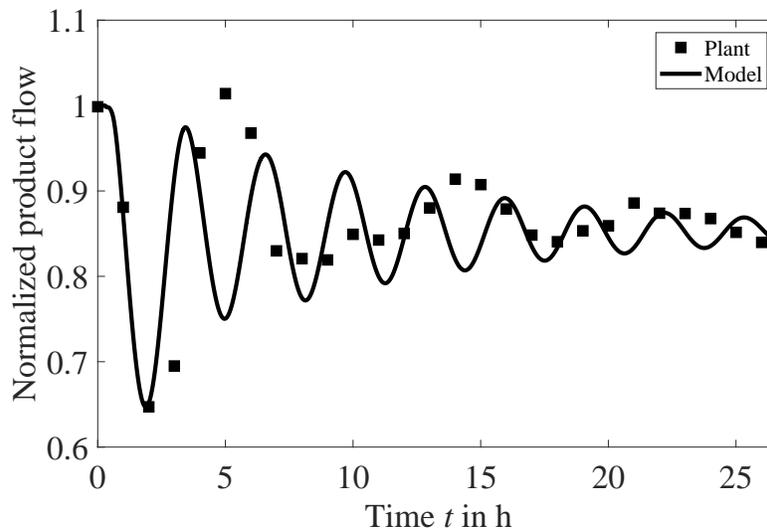


Figure 19: Normalized product flow over time. The product flow is normalized with its nominal setpoint.

## 414 5. Conclusion and Outlook

415 In this contribution, demand-side management was introduced as a counter-  
 416 measure regarding electricity grid instabilities. In order to assess the real poten-  
 417 tial of demand-side management, the ChemEFlex project investigates technical  
 418 and economical limitations for the chlor-alkali electrolysis and its downstream  
 419 processes. For this purpose, a dynamic, pressure-driven model of the direct chlo-  
 420 rination of ethene was formulated. This model consists of the reactor section, the  
 421 tray section, two condensers, the reflux drum, and the peripheral units at the bot-  
 422 tom. The model considers weeping and the flow over the weir for the liquid outlet  
 423 of a tray, whereas the vapor flow is pressure-driven. To avoid convergence issues  
 424 in case of low gas load and dry trays, the model equations for the liquid flow were  
 425 relaxed using smooth min/max operators. The effect of these reformulations was  
 426 demonstrated in a small case study. Afterwards, the model was successfully val-  
 427 idated with real plant data of an EDC production for steady-state and dynamic  
 428 conditions. All accessible measurements from the real plant can be reproduced  
 429 with a maximum deviation of 5 %; in addition, we can show that stages start run-  
 430 ning dry at gas loads below 70 % of the nominal operating conditions.

431 Although the assumption of a CSTR for the reactor section should satisfying

432 results for both steady-state and dynamic simulations using a kinetic enhancement  
433 factor, modeling the reactor as plug flow or bubble column reactor will be consid-  
434 ered. All disregarded effects of such spatially distributed units are lumped into this  
435 enhancement factor and are subject to future research. In addition, the dynamic  
436 tray model will be further expanded as there are still many aspects uncovered in  
437 this approach, e. g. the downcomer holdup, entrainment, heat and mass transfer,  
438 etc.

439 In the future, we will use the presented process model to determine optimal  
440 trajectories for the plant from one operating point to the other under demand re-  
441 sponse scenarios. Therein, we we will focus on day-ahead and balancing markets.  
442 These trajectories will be used to investigate any undesired concentration, temper-  
443 ature, or pressure profiles during the transition. Secondly, the obtained trajectories  
444 may serve as ramp constraints in a simplified linear model.

#### 445 **Acknowledgements**

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449

#### **Abbreviations**

CAE	Chlor-alkali electrolysis
CSTR	Continuously stirred tank reactor
EDC	Ethylene dichloride
EoS	Equation of state
ETC	Ethylene trichloride
HCl	Hydrogen chloride
HTC	High-temperature chlorination
LTC	Low-temperature chlorination
PR	Peng-Robinson
PVC	Polyvinyl chloride
SRK	Soave-Redlich-Kwong
VCM	Vinyl chloride monomer

#### **Greek Symbols**

$\alpha$	Parameter in Peng-Robinson EoS
$\beta$	Kinetic enhancement factor

$\delta$	Binary interaction parameter
$\phi$	Fugacity coefficient
$\varphi$	Free area ratio
$\Delta$	Difference
$\rho$	Mass density
$\Omega$	Weeping factor
$\omega$	Acentric factor
$\xi$	Drag coefficient
$\varepsilon$	Volume fraction

### Latin Symbols

$A$	Area
$a$	Cohesion parameter in PR-EoS
$b$	Covolume parameter in PR-EoS
$c$	Molar concentration
$E$	Activation energy
$F$	Mole flow
$F$	F factor
$g$	Gravitational acceleration
$h$	Molar enthalpy
$h$	Height
$HU$	Holdup
$K$	Gas velocity factor
$K$	Proportional constant of P controller
$k$	Pre-exponential factor in reaction kinetics
$L$	Length
$M$	Molecular weight
$m$	Mass flow
$OHTC$	Overall heat transfer coefficient
$P$	Pressure
$p$	Parameter for volume correlation
$Q$	Heat flow
$R$	Universal gas constant
$r$	Reaction rate
$T$	Temperature
$T$	Integration time of PI controller
$U$	Internal energy
$V$	Volume or volume flow (with superscript flow)
$v$	Molar volume

<i>w</i>	Superficial velocity
<i>y</i>	Binary variable
<b>Indices</b>	
<i>c</i>	Component index $\in [1 \dots NC]$
<i>caux</i>	Auxiliary component index $\in [1 \dots NC]$
<i>tr</i>	Tray index $\in [1 \dots NTR]$
<b>Subscripts</b>	
active	Active area
C	Critical
cl	Clear liquid
column	For the column
CON	Condenser
f	Formation
froth	Of the froth
HE	Heat exchanger
hw	Hot water
mix	Mixture
N	Norm
ow	over weir
RD	Reflux drum
rec	Recover
ref	Reference
weir	Of the weir
<b>Superscripts</b>	
actual	Relaxed variable
feed	Of the feed
flow	Of the flow
in	Inlet
int	Integral part of a controller
<i>L</i>	Liquid
side stream	Side stream
out	Outlet
Ph	Phase <i>V</i> or <i>L</i>
reactor	Of the reactor
SP	Setpoint
<i>V</i>	Vapor
<i>VL</i>	Vapor-liquid, e.g. enthalpy difference between <i>V</i> and <i>L</i>
weep	Weeping

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