



## Modelling of combined direct-contact condensation and reactive absorption in packed columns

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### ABSTRACT

Recovery of ammonia from waste or process water is significantly influenced by the presence of carbon dioxide. In order to achieve high recovery efficiency, a selective separation of carbon dioxide from the liquid prior to the ammonia removal is often desired. In this article, a rigorous model is presented that is based on earlier works [E.Y. Kenig, R. Schneider, A. Górak, Reactive absorption: optimal process design via optimal modelling, *Chem. Eng. Sci.* 56 (2001) 343–350; L. Kucka, I. Mueller, E.Y. Kenig, A. Górak, On the modelling and simulation of sour gas absorption by aqueous amine solutions, *Chem. Eng. Sci.* 58 (2003) 3571–3578; B. Huepen, E.Y. Kenig, Rigorous modelling on NO<sub>x</sub> absorption in tray and packed columns, *Chem. Eng. Sci.* 60 (2005) 6462–6471.]. This model describes an integrated process for the selective removal of carbon dioxide comprising steam stripping, subsequent direct-contact condensation (DCC) of the stripping steam and absorption of undesired stripped ammonia in packed columns. Based on the film theory, the model directly considers heat and multicomponent mass transfer rates as well as chemical reaction kinetics. Diffusional interactions typical for multicomponent mass transfer can usually be neglected in absorption and stripping processes, but not necessarily in DCC of multicomponent vapour mixtures consisting of condensable and noncondensable components. Therefore, the rigorous model taking account of diffusional interactions via the Maxwell–Stefan equations is compared with the effective diffusivity method. It is shown that neglecting of molecular interactions may lead to poorly designed direct-contact condensers. The influence of the interactions in the tested system depends on the mixture composition and it increases significantly when an additional component is added to the ternary mixture.

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### 1. Introduction

Waste water containing ammonia (NH<sub>3</sub>) and carbon dioxide (CO<sub>2</sub>) is an inherent part of numerous processes in petrochemical, chemical, food and environmental industry. Usually, air or steam stripping is applied for the ammonia removal complemented by biological denitrification. The stripping requires a pH-value higher than 10 in order to shift the ammonia dissociation equilibrium to molecular species. To keep the pH on the right level, alkaline solution, e.g. caustic soda, is often added to the waste water, although it is undesirable from the economic and environmental point of view. If carbon dioxide is removed from solutions containing ammonia, the pH-value is raised due to the deacidification effect without adding chemicals. Selective carbon dioxide removal prior to the actual ammonia stripping is therefore beneficial. In the decarbonisation stage, carbon dioxide is stripped out from the solution simultaneously with ammonia at ambient pressure. Recovery of

the stripped ammonia can be reached by combining absorption of ammonia and condensation of stripping steam (see Fig. 1). The interaction of the different unit operations of stripping, absorption and direct-contact condensation (DCC) can be arranged in one single packed column (DecaStripp<sup>®</sup>-process, [4]).

The decarbonisation column consists of two sections which are directly interconnected. In the lower part, the preheated solution is fed in on top and steam flows counter-currently from the bottom, carrying the stripped components toward the upper part. In the upper section, the steam is condensed directly into the condensing agent, which also flows counter-currently from the top of the section. Simultaneously, ammonia is absorbed by the liquid, while the low soluble carbon dioxide remains in the vapour phase and leaves the column at the top. The decarbonised solution leaves the column at the bottom and is further treated in order to recover ammonia as a product, i.e. as a 25% ammonia solution. The efficiency of the entire process is significantly affected by the design of the decarbonisation stage.

The modelling of this complex operation requires an adequate modelling framework. In previous studies, the application of the rate-based approach for the modelling of multicomponent reactive

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**Nomenclature**

$a$	constant
$a_{\text{int}}$	interfacial area ( $\text{m}^2 \text{m}^{-3}$ )
$A_{\text{col}}$	column cross section ( $\text{m}^2$ )
$c$	molar concentration ( $\text{mol m}^{-3}$ )
$D$	diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ )
$E$	heat flux ( $\text{J m}^{-2} \text{s}^{-1}$ )
$F$	Faraday's constant
$h$	molar enthalpy ( $\text{kJ mol}^{-1}$ )
$h_{\text{L},0}$	liquid hold-up ( $\text{m}^3 \text{m}^{-3}$ )
$[I]$	unity matrix
$J$	diffusive flux ( $\text{mol m}^{-2} \text{s}^{-1}$ )
$K$	$K$ -value, equilibrium constant
$L$	molar liquid flow ( $\text{mol s}^{-1}$ )
$n$	number of components, stages
$N$	molar flux ( $\text{mol m}^{-2} \text{s}^{-1}$ )
$q$	energy flux due to conduction ( $\text{J m}^{-2} \text{s}^{-1}$ )
$R$	reaction rate ( $\text{mol m}^{-3} \text{s}^{-1}$ ), gas constant
$T$	temperature (K)
$V$	molar vapour flow ( $\text{mol s}^{-1}$ )
$x$	liquid phase molar fraction ( $\text{mol mol}^{-1}$ )
$y$	vapour phase molar fraction ( $\text{mol mol}^{-1}$ )
$Y$	relative concentration, Eq. (21) (%)
$z$	charge number
$\Delta z$	height of a stage (m)

**Greek letters**

$\alpha$	heat-transfer coefficient ( $\text{W m}^{-2} \text{s}^{-1}$ )
$\beta$	mass transfer coefficient ( $\text{m s}^{-1}$ )
$\delta$	film thickness (m)
$\delta_N$	relative error of transferred flux
$\eta$	film coordinate (m)
$\lambda$	thermal conductivity ( $\text{W m}^{-1} \text{s}^{-1}$ )
$\Xi$	high-flux correction factor
$[\Xi]$	high-flux correction matrix
$\Phi$	rate factor (scalar)
$\varphi$	electrical potential (V)
$[\Psi]$	matrix of rate factor

**Subscripts**

av	average
B	bulk phase
eff	effective diffusivity method
H	heat transfer
$i$	component $i$
I	interface
in	entering stage
$j$	component $j$
L	liquid phase
$n$	stage number
out	leaving stage
t	total
V	vapour phase

**Superscripts**

$\Xi$	no consideration of correction factors
Eff	effective diffusivity method
GB	gas (vapour) bulk
GF	gas (vapour) film
I	interface
L	liquid phase

LB	liquid bulk
LF	liquid film
MS	Maxwell–Stefan

separation processes has proved to be superior to other concepts like the equilibrium stage model. The rate-based approach is physically more consistent and overcomes, amongst others, the drawbacks of multicomponent efficiencies and HETP values [5–9]. By the rate-based approach, reaction kinetics and the heat and mass transfer rates are accounted for directly, the vapour and liquid phases are balanced separately and the heat and mass fluxes across the interface are considered, assuming thermodynamic equilibrium at the interface [10]. The influence of chemical reactions on the mass fluxes is taken into account using reaction rates as source terms in the balance equations [8]. In multicomponent mixtures, reverse mass transfer (transport of the component in the opposite direction of its driving force), osmotic mass transfer (transport of the component when its driving force equals zero) and mass transfer barrier (no transport despite an existing driving force) may be observed [10]. In this case, the component fluxes across the interface are usually calculated using the Maxwell–Stefan equations, which consider these effects.

Previous works have shown that simplified models like the effective diffusivity method are sufficient in order to describe most of reactive absorption and stripping processes [2,3]. Since the mixtures in these processes are mostly diluted, the diffusional interactions can usually be neglected. The complexity of the set of equations and calculation time can therefore be reduced.

This does not hold for DCC, which is used in the decarbonisation process (Fig. 1). Here, the ternary (or quaternary) vapour phase is not diluted; thus, diffusional interactions may not be neglected without prior investigations. Taylor et al. [11] and Webb et al. [12] presented non-equilibrium models for the description of physical condensation processes in tubular condensers. They investigated different mixtures of hydrocarbons in non-reactive systems and showed the limited applicability of simplified methods neglecting diffusional effects for the design of tubular condensers for the

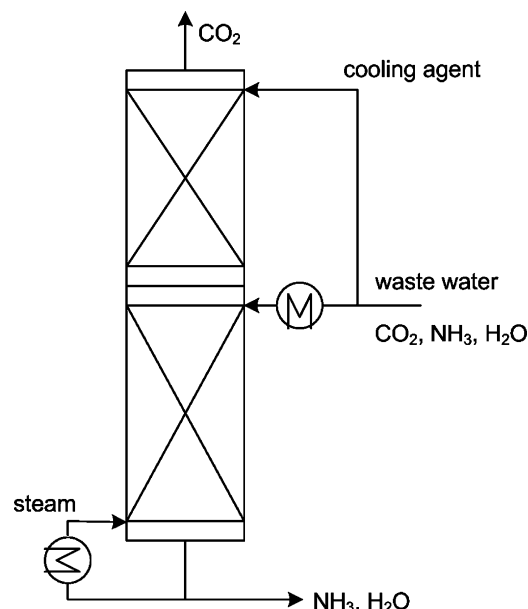


Fig. 1. Scheme of the two-stage decarbonisation column.

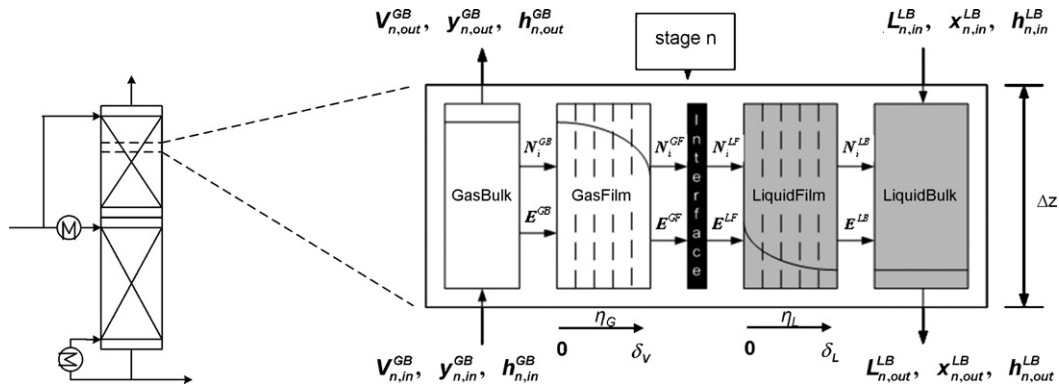


Fig. 2. Structure of an axial segment of the column according to the film theory.

studied mixtures. In our work, modelling of a process for a reactive system is presented, considering simultaneous absorption, direct condensation and stripping. This combination has not been investigated up to now. The model developed earlier [1–3,8,9] is extended and adjusted in order to properly consider the interaction of all these separation steps.

## 2. Modelling

The key element of the rate-based model is an axial segment of a packed column in which simultaneous mass transfer and chemical reaction are described according to the extended film model (see Fig. 2). The model is based on mass and heat balances formulated separately for the vapour and liquid phases. These balances are linked by the interfacial heat and mass fluxes,  $E$  and  $N_i$ , which are equal for both phases. Thermodynamic equilibrium between the phases is assumed at the interface. The resistance to mass and heat transfer is concentrated in thin films adjacent to the phase boundary. The axial arrangement of the segments allows for the modelling of gas/vapour–liquid separators, e.g. for packed columns. Packing specific fluid dynamics, relevant mass transfer correlations, physical properties and the component specific reaction rates are accounted for by adequate sub models. The description of external elements like reboilers and heat exchangers complement the model.

### 2.1. Balance equations

According to the film theory, neither temperature nor composition gradients exist in the bulk phases due to perfect mixing. The mass and heat balances for the vapour phase for any arbitrary stage are as follows:

$$V_{in}^{GB} y_{i,in}^{GB} - V_{out}^{GB} y_{i,out}^{GB} - N_i^{GB} a_{int} A_{col} \Delta z = 0 \quad (1)$$

$$V_{in}^{GB} h_{in}^{GB} - V_{out}^{GB} h_{out}^{GB} - E_{GB} a_{int} A_{col} \Delta z = 0 \quad (2)$$

The effective segment height  $\Delta z$  is determined by the ratio of the packing height and the number of stages.

As chemical reactions take place in the liquid phase, the balance equation for the liquid bulk is extended by a reaction term:

$$L_{in}^{LB} x_{i,in}^{LB} - L_{out}^{LB} x_{i,out}^{LB} + N_i^{LB} a_{int} A_{col} \Delta z + R_i A_{col} \Delta z h_{L,0} = 0 \quad (3)$$

The energy balance for the liquid bulk is similar to that given by Eq. (2).

Chemical reactions in the liquid phase may not only occur in the bulk phase, but, due to the high rate of reaction, also in the film region. Therefore, the liquid–film balance equation should also

contain a source term:

$$\frac{\partial N_i^{LF}}{\partial \eta_L} - R_i = 0 \quad (4)$$

This equation is non-linear and usually requires a numerical solution [2,3].

In the vapour phase no chemical reactions occur and the vapour–film balance reads:

$$\frac{\partial N_i^{GF}}{\partial \eta_G} = 0 \quad (5)$$

Whereas the energy balance can be written as follows:

$$\frac{\partial E^{GF}}{\partial \eta_G} = 0 \quad (6)$$

In a similar way, the energy balance for the liquid phase is expressed:

$$\frac{\partial E^{LF}}{\partial \eta_L} = 0 \quad (7)$$

The heat of reaction in the liquid phase is taken into account via the enthalpies.

For the phase interface, we adopt the conventional assumption that there is no resistance to mass transfer. Thus it is described by the equilibrium relation:

$$y_i^I = K_i x_i^I \quad i = 1, \dots, n \quad (8)$$

The equilibrium coefficients  $K_i$  are evaluated as functions of interfacial temperature, pressure and composition [10].

### 2.2. Mass transfer in the film region

The component molar fluxes  $N_i$  comprise diffusive and convective parts [10,13].

$$(N) = (J) + (y)N_t \quad (9)$$

If condensation is intensive, the convective terms in Eq. (9) are usually not negligible relative to the first term. In this case, the concentration and temperature profiles in the film deviate from straight lines. This is usually referred to as rapid or high-flux mass transfer [10,13]. For high transfer rates, Bird et al. [13] introduced a modified concept applying the high-flux mass transfer coefficient  $\beta_i^*$  which accounts for the distortions of the concentration and temperature profiles:

$$\beta_i^* = \frac{J_i}{c_t \Delta y_i}, \quad i = 1, \dots, n \quad (10)$$

Usually the Maxwell–Stefan equations are used to determine the fluxes in multicomponent systems. In this work, the linearized theory presented by Toor [14] and Stewart and Prober [15] has been applied to handle the Maxwell–Stefan equations. Its main assumption, which has proven to be of excellent accuracy for the majority of mass transfer processes, is that diffusion coefficients remain constant in the film region. Using the definition of mass transfer coefficients by Eq. (10), the mass fluxes in multicomponent mixtures are determined as:

$$(N) = (J_B) + (y_B)N_t = c_t[\beta_{av}^*](y_B^{GF} - y_1^{GF}) + (y_B)N_t \quad (11)$$

The subscript B denotes that bulk phase diffusion fluxes are used and thus bulk phase concentrations are applied for the convective term. The subscript av indicates that diffusion coefficients used for the estimation of mass transfer coefficients are calculated based on the average molar composition in the film.

The low-flux mass transfer coefficients  $\beta_{ij}$  are the coefficients usually available from correlations of mass transfer data. In ref. [13], they are related to vanishingly small mass transfer rates and thus negligible convective transport. Written in matrix form, the high-flux coefficients in Eq. (11) are expressed via the low-flux coefficients by [10]:

$$[\beta_{av}^*] = [\beta_{av}][\mathcal{E}_B] \quad (12)$$

The matrix of low-flux coefficients is calculated based on binary mass transfer coefficients  $\beta_{ij}$  according to the approach suggested by Krishna and Standart [16]. The matrix of high-flux correction factors  $[\mathcal{E}_B]$  is defined according to the following equation [10,17]:

$$[\mathcal{E}_B] = \frac{[\Psi]}{\exp([\Psi]) - [I]} \quad \text{with} \quad [\Psi] = \frac{N_t}{c_t}[\beta_{av}]^{-1} \quad (13)$$

There are several methods to calculate the exponential of the matrix of rate factors  $[\Psi]$ , see for e.g. [18]. In this work, an approximate method presented by Alopaus et al. [19] is used. Exponential function series expansion of Eq. (13) leads to a form which can be linearized for negligible flux ( $[\Psi]=0$ ) and a simple expression is obtained, which provides an excellent stability and a short calculation time compared to other methods [19]:

$$[\mathcal{E}_B] = [I] - a[\Psi] \quad (14)$$

where  $a=0,46-0,50$  for the film model [19].

In diluted systems, the effective diffusivity methods lead to results with satisfactory accuracy, because diffusional interactions between the individual species can be neglected [20]. In this case, mass transfer equations are reduced to a set of  $n-1$  algebraic equations:

$$J_{B,i} = c_t \beta_{i,\text{eff}}^* (y_{i,B}^{GF} - y_{i,l}^{GF}) = c_t \beta_{i,\text{eff}} \mathcal{E}_{B,i} (y_{i,B}^{GF} - y_{i,l}^{GF}), \quad i = 1, \dots, n-1 \quad (15)$$

The correction factors  $\mathcal{E}_{i,\text{eff}}$  used in Eq. (15) can be obtained from the following equation [10,17]:

$$\mathcal{E}_{B,i} = \frac{\Phi_{i,\text{eff}}}{\exp(\Phi_{i,\text{eff}}) - 1} \quad \text{and} \quad \Phi_{i,\text{eff}} = \frac{N_t}{c_t \beta_{i,\text{eff}}}, \quad i = 1, 2, \dots, n-1 \quad (16)$$

In the liquid phase, ionic species are present due to dissociation and chemical reaction in the  $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$  system. The different charges of the ions can result in an additional driving force for mass transfer. This effect is usually allowed for by the Nernst–Planck equations [10,21].

$$J_i = c_t \beta_{i,\text{eff}} \mathcal{E}_{i,\text{eff}} (x_{i,l}^{\text{LF}} - x_{i,B}^{\text{LF}}) + c_{i0} z_i D_{i,\text{eff}}^L \frac{F \nabla \varphi}{RT} \quad (17)$$

According to Schneider [20], the last term of this equation can be neglected for most industrial absorption processes.

For vanishingly small mass fluxes,  $N_t \rightarrow 0$ , and the high-flux correction factor  $\mathcal{E}_B$  approaches unity, resulting in a linear concentration profile across the film.

### 2.3. Heat transfer

The heat transfer in the films occurs simultaneously with mass transfer. The heat fluxes are supposed to be continuous across the phase boundary and, similar to mass fluxes, comprise a conductive and convective term. The energy flux  $E^{GF}$  in the gas/vapour film is determined from the following equation [10]:

$$E^{GF} = q^{GF} + \sum_{i=1}^n N_i^{GF} h_i^{GF} = \alpha \mathcal{E}_H (T_{\text{in}}^{GF} - T_{\text{out}}^{GF}) + \sum_{i=1}^n N_i^{GF} h_i^{GF} \quad (18)$$

The energy flux in the liquid film is determined in an analogous way, using the equivalent liquid phase variables.

The correction factor for heat transfer  $\mathcal{E}_H$  shows a similar behaviour as the corresponding correction factor for mass transfer  $\mathcal{E}_B$ .

According to the film theory and the analogy of heat and mass transfer [22], the heat transfer coefficient  $\alpha$  can be determined using an average film thickness:

$$\alpha = \frac{\lambda}{\delta} \quad (19)$$

For the film model, the film thickness is specified as the ratio of the diffusion coefficient and the mass transfer coefficient. The independent estimation of mass transfer and diffusion coefficients via suitable correlations may, for a  $n$ -component multicomponent system, lead to  $n$  different film thicknesses for each phase. However, for reactive systems, the applicability of the film model requires only *one* film thickness for the liquid and *one* for the vapour phase. In this work, the average film thickness is determined using weighted summation of mass transfer and diffusion coefficients.

$$\bar{\delta} = \frac{\bar{D}}{\bar{\beta}} = \frac{\sum_{i=1}^n \beta_i y_{\text{av},i}}{\sum_{i=1}^n \frac{D_i y_{\text{av},i}}{\delta}} \quad (20)$$

### 2.4. Model implementation and parameters

In this work, a fully numerical algorithm for the solution of the rate-based equations is applied. The liquid and the gas/vapour film are subdivided into a certain number of discrete elements in order to describe the nonlinear concentration and temperature profiles [2,3,10,16]. To solve the system of equations, the model has been implemented into the commercial simulation environment Aspen Custom Modeler<sup>®</sup>. The simulation tool offers a direct link to the software package Aspen Properties<sup>®</sup> for the calculation of the required physical properties. Along with the complete matrix-based model (further denoted as model 1) a simplified approach based on the effective diffusivities (model 2) is tested.

Within these models, the correct determination of the diffusion coefficients is of high importance. The diffusion coefficients significantly influence the mass transfer rates, because the mass transfer coefficients are determined as functions of diffusion coefficients. Besides in terms of the film model, diffusion coefficients are essential to determine the film thicknesses (Eq. (20)).

The low-flux mass transfer coefficients are calculated in this work using correlations taken from the literature [23,24]. For the model 1, they are determined using diffusion coefficients of binary pairs  $D_{ij}$ . The Wilke–Lee method [25] is applied to estimate the vapour phase binary diffusion coefficients. For the

effective diffusivity method (model 2), the effective low-flux mass transfer coefficients  $\beta_{i,\text{eff}}$  are determined using the same empirical correlations as for calculation method 1. Instead of the binary Maxwell–Stefan diffusivities, the effective diffusivities  $D_{i,\text{eff}}$  are applied to determine the mass transfer coefficients. The Chapman–Enskog–Wilke–Lee model is used for the vapour phase coefficients, the liquid phase effective diffusivities are calculated based on the Nernst–Hartley electrolyte model [26].

The pressure drop along the column is considered via packing specific correlations according to [27,28]; a correlation from the same source is used to calculate the liquid hold-up of the packed column.

### 3. Case study

The models described above are tested using the decarbonisation process shown in Fig. 1. The main focus in this study is a comparison of the Maxwell–Stefan and the effective diffusivity approaches in order to evaluate the necessary model complexity. The model equations have been implemented into the commercial simulation environment Aspen Custom Modeler™ which provides a fully numerical solver for the set of model equations. For the determination of model parameters which describe mass transfer and fluid dynamic characteristics in the investigated packed column, empirical correlations are used. The parameters include mass transfer coefficients for vapour and liquid phase, effective interfacial area as well as liquid hold-up and pressure drop. The relevant correlations were taken from literature [23,24,27,28] and have been incorporated into the system of model equations. For the calculation of the component specific reaction rates, which are considered directly in the balance Eqs. (3) and (4), temperature dependent rate and equilibrium constants are taken from literature [29–31].

In order to evaluate the necessary model complexity, both sub-processes of the decarbonisation process, stripping and condensation, are investigated individually. The presented model is used to simulate both, the stripping and the condensing section, which are designed as packed columns. Therefore, a steel column with diameter of 0.3 m and packing height of up to 2.0 m filled with Mc-Pac random packings [23] has been considered. As a condensing agent entering at the top of the condenser, cold waste water is used. The composition of the waste water entering the column can vary, depending on the origin, and the vapour phase is either a ternary mixture of water, ammonia and carbon dioxide or a quaternary mixture with hydrogen sulphide as an additional component. In this study typical compositions for waste water from biogas production plants are used. Within the vapour phase, water and ammonia are specified as condensable components, whereas carbon dioxide and hydrogen sulphide are regarded as non-condensable, due to their low boiling point. The amount of condensable components in the vapour phase can change, due to the varying steam consumption in the stripping section and the varying composition of the waste water feed. Consequently, the concentration of condensable species in the ternary and quaternary vapour mixtures investigated varied from 50 to 90% what can be expected in industrial plants. Typical initial gas/vapour compositions met in industrial applications are given in Tables 1 and 2. The investigation of the vapour mixtures consists of three simulation runs for both ternary (Table 1) and quaternary (Table 2) systems, whereas the initial concentration of the condensable components water and ammonia decreased from 90% over 70% up to 50%.

The vapour flow rate is kept constant during all simulations. The packing height and column diameter also remain unchanged. The constant geometrical surface of the condenser ensures the comparability of results. The composition of the condensing agent is

**Table 1**  
Ternary mixture compositions studied

No.	Condensable		Non-condensable
	$y_{\text{H}_2\text{O}}$ (vol.%)	$y_{\text{NH}_3}$ (vol.%)	$y_{\text{CO}_2}$ (vol.%)
1	88	2	10
2	60	10	30
3	30	20	50

also constant, and, in the case of the quaternary feed mixture, hydrogen sulphide is additionally considered in the liquid phase. With this set-up, simulations are carried out for each composition (Tables 1 and 2) using either the Maxwell–Stefan equations (model 1) or the effective diffusivity method (model 2). A criterion is required to evaluate the importance of diffusional interactions in the studied system. Following the suggestion of Webb et al. [12] we consider diffusional effects as negligible if the relative deviation in the fluxes is below 20%.

$$\delta_{N_t} = \frac{N_t^{\text{MS}} - N_t^{\text{Eff}}}{N_t^{\text{Eff}}} < 0, 2 \quad (21)$$

We use this value in order to ensure comparability with previous works on classical, surface-type condensers. Furthermore, the effect of the deviation in component fluxes on the flow rates has to be considered. In many cases in which concentration of the transferring components is small, even large deviations in the fluxes do not significantly influence the component flow rates and the latter remain nearly constant along the column. However, it is just the component flow rates which are of central importance to the column design, because they determine the specifications of the streams leaving the process. In the studied case, the concentrations are not small, and thus, the effect of the deviation in calculated fluxes on the flow rates along the column cannot be neglected automatically. It varies, depending on the composition of the gas phase and the degree of condensation. All investigations carried out within the scope of this work show that deviations in fluxes by 20% cause a deviation in flow rates along the column of less than 10% which can be regarded as negligible for design purposes. A similar expression to Eq. (21) can be used to quantify the deviation in individual fluxes for the condensable species:

$$\delta_{N_i} = \frac{N_i^{\text{MS}} - N_i^{\text{Eff}}}{N_i^{\text{Eff}}} < 0, 2 \quad i = (\text{NH}_3, \text{H}_2\text{O}) \quad (22)$$

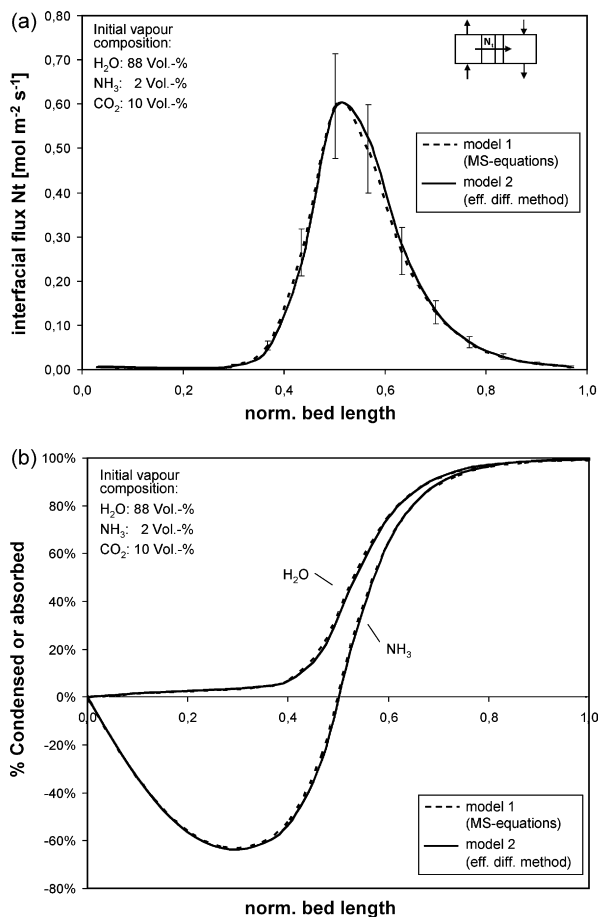
Depending on whether the total flux or the individual fluxes of the condensable species are of interest, either Eq. (21) or Eq. (22) can be used to determine the relative deviation in fluxes caused by diffusional interactions.

### 4. Results

In the stripping part of the decarbonisation column, the liquid phase concentrations of the transferred components are small, the main resistance to mass transfer for the desorption of carbon dioxide is in the (diluted) liquid phase. For the tested conditions, which cover a typical range of concentrations for the decarbonisation of

**Table 2**  
Quaternary mixture compositions studied

No.	Condensable		Non-condensable	
	$y_{\text{H}_2\text{O}}$ (vol.%)	$y_{\text{NH}_3}$ (vol.%)	$y_{\text{CO}_2}$ (vol.%)	$y_{\text{H}_2\text{S}}$ (vol.%)
4	88	2	6	4
5	60	10	20	10
6	30	20	40	10



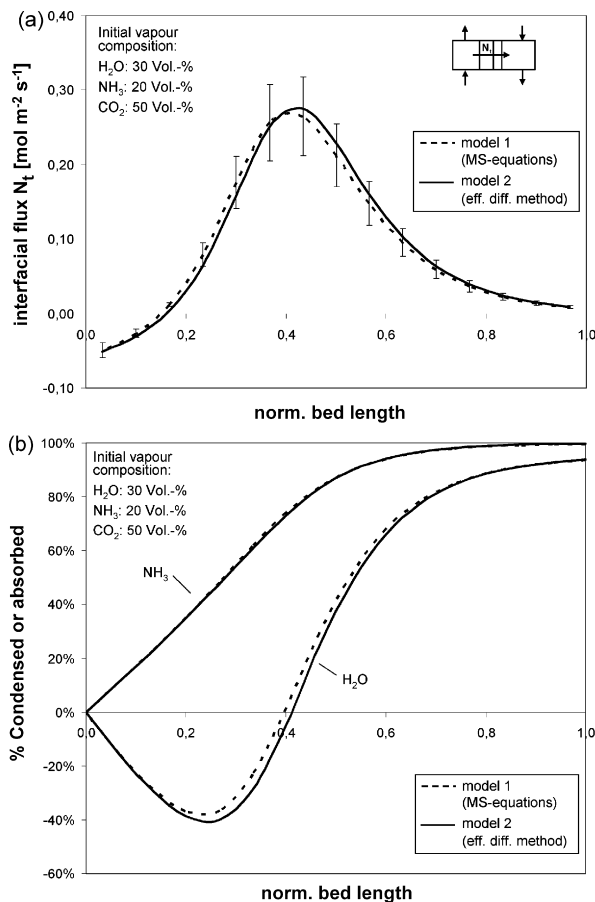
**Fig. 3.** (a) Total flux for the lowest amount of condensable components (ternary mixture – case no. 1). Error bars indicate 20% relative deviation. (b) Relative concentrations  $Y_i$  of ammonia and water, Eq. (23) (ternary mixture – case no. 1).

waste water from biogas production plants, the deviation in mass fluxes between the calculation according to model 1 (linearized theory) and model 2 (effective diffusivity method) does not exceed 1%. Thus, diffusional effects can be neglected in the lower part of the decarbonisation column, in which the volatile components are stripped by means of steam. The comparison between the effective diffusivity method and the Maxwell–Stefan approach are in line with previous works on absorption and stripping processes [2,9,32].

For the upper section of the column in which the condensation takes place, the concentration profiles along the section and the fluxes are examined for each case study. The results are displayed in two diagrams for selected simulation runs according to Tables 1 and 2, (Figs. 3–6). In part a, the total flux according to both studied models is shown as a function of the condenser bed length. In part b, the flow rates of the condensable components ammonia and water, expressed as degree of condensation or absorption  $Y_i$ , are displayed as a function of the bed length.

$$Y_i = \left( 1 - \frac{L_i y_i}{L_{t,in} y_{i,in}} \right) \times 100\% \quad i = (\text{NH}_3, \text{H}_2\text{O}) \quad (23)$$

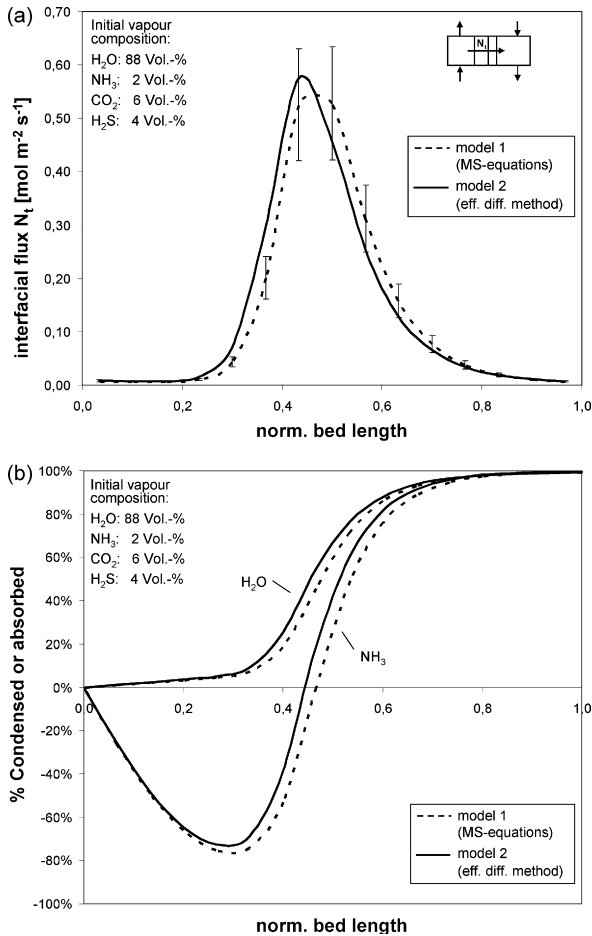
Additionally, the average relative deviation  $\delta_{N_t}$  for the calculated total fluxes according to Eq. (21) is calculated. It increases with increasing amount of inert components in the initial vapour mixture. For the case no. 1, representing the experiment with the lowest amount of inerts, the maximum deviation between the two calculation methods is about 6% (Fig. 3a) whereas it increases



**Fig. 4.** (a) Total flux for the highest amount of condensable components (ternary mixture – case no. 3). Error bars indicate 20% relative deviation. (b) Relative concentrations  $Y_i$  of ammonia and water, Eq. (23) (ternary mixture – case no. 3).

from 8% for the case no. 2 to about 20% for case no. 3 with the highest amount of condensable components. The highest deviations occur in the lower part of the column (Fig. 4a). The influence on total flow rates at the top of the condenser never exceeds 3.5% (see Figs. 3b and 4b). Slightly higher deviations in component flow rates can be expected for the transferred components water and ammonia, which reach values of around 4.5% and 10% respectively in case of the highest amount of inert components (Fig. 4b). In all tested conditions for the ternary mixtures according to Table 1 neither the deviation in total nor in the component fluxes exceeds 20%. The diffusional effects can therefore be neglected and it can be stated, that the simplified method (model 2) provides satisfactory accuracy for design purposes under these conditions. These results for DCC of ternary mixtures with a reactive condensing agent go in line with the findings of Webb et al. [12] on condensation of ternary mixtures of hydrocarbons in tubular condensers.

The criterion according to Eq. (21) can also be extended to quaternary mixtures. In general, interactions between the particular components become more intense with an additional component. The deviation in the fluxes increases and exceeds 20% for all cases given in Table 2, although diffusion coefficients are all within a similar range. This leads to maximum local deviations in total flow rate between the two calculation methods of up to 15% and for the individual flows of water and ammonia of up to 20% and 35% respectively. These larger deviations are located in the left part of the curves shown in Figs. 5a and 6a. On top of the condenser, the highest deviations in individual flow rates of water



**Fig. 5.** (a) Total flux for the lowest amount of condensable components (quaternary mixture – case no. 4). Error bars indicate 20% relative deviation. (b) Relative concentrations  $Y_i$  of ammonia and water, Eq. (23) (quaternary mixture – case no. 4).

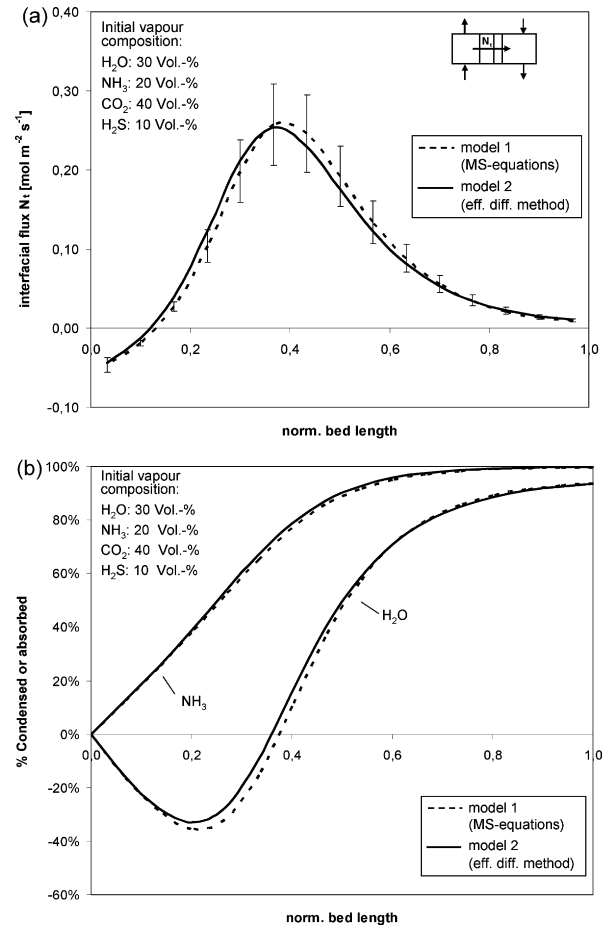
and ammonia are 10% and 20% respectively and 11% in total flow rate.

Compared to DCC of ternary mixtures (Table 1), the deviations in fluxes between the two calculation methods are generally higher for the quaternary mixtures and exceed the criteria given by Eqs. (21) and (22). Diffusional effects can therefore no longer be neglected and the application of Maxwell–Stefan equations (model 1) is recommended for the design of the condensing section in the decarbonisation process. The effective diffusivity method causes deviations that exceed the critical value of 10%, what might lead to over or under design of the condenser.

#### 4.1. High-flux correction

In fluid separation processes, e.g. absorption and distillation, correction factors in flux calculations are usually neglected because of its minimal influence on mass fluxes [10,33]. This assumption has been verified by simulation studies for the stripping section of the decarbonisation process using typical conditions for this part of the column. In this case, total mass fluxes are relatively small because the system is diluted and thus the correction factors rarely exceed unity. The influence of the high-flux correction on mass transfer calculations can thus also be neglected for stripping processes (bottom section) with the ternary and quaternary mixtures studied.

In DCC, especially when a large excess of condensable components is present, the total fluxes are significantly higher than in stripping or absorption processes. Therefore, simulations accord-



**Fig. 6.** (a) Total flux for the highest amount of condensable components (quaternary mixture – case no. 6). Error bars indicate 20% relative deviation. (b) Relative concentrations  $Y_i$  of ammonia and water, Eq. (23) (quaternary mixture – case no. 6).

ing to the conditions given in Tables 1 and 2 have been performed to analyse the influence of correction factors on mass transfer calculations in the condensation section of the decarbonisation process. According to Eqs. (13) and (16), the influence of correction factors and matrices increases with an increasing total flux  $N_t$ . A condition analogous to Eq. (21) is used to quantify the deviation caused by neglecting the high-flux correction factors:

$$\delta \bar{N}_t^{\bar{E}} = \frac{N_t - N_t^{\bar{E}}}{N_t} < 0, 2 \quad (24)$$

The calculation of the mass transfer fluxes ( $N_t^{\bar{E}}$ ) without the use of correction factors is performed by neglecting the appropriate factors in Eqs. (15) and (18) and/or the correction matrix in Eq. (12). In this case, the convective part must be calculated based on the mean concentration in the film in contrast to the formulation according to Eq. (11), in which the concentration in the bulk phase is applied:

$$(N_t^{\bar{E}}) = (J) + (y_{av})N_t \quad (25)$$

The relative deviation between the calculation methods with (Eq. (11)) and without consideration of high-flux correction (Eq. (25)) does not exceed 3% for all test conditions, given in Tables 1 and 2. The effect of the deviation in the mass transfer fluxes on the flow rates along the column is therefore negligible not only for stripping and absorption processes, but also for DCC.

## 5. Conclusions

In the present article, the decarbonisation process is presented, which allows a selective separation of carbon dioxide from liquid mixtures containing ammonia in packed columns. The process consists of two interconnected sections, the lower one, in which the liquid mixture is stripped, and the upper section, in which the stripping steam is condensed and ammonia is absorbed. A model for describing the decarbonisation process is developed and implemented into a commercial simulation environment. It describes the integrated process consisting of stripping, DCC and simultaneous absorption. Two approaches for the calculation of mass transfer fluxes, the Maxwell–Stefan equations (model 1) and the effective diffusivity method (model 2) are used for a comparative study in order to analyse the importance of diffusional effects. The evaluation of the influence of diffusional interactions is performed using the criteria introduced by Eq. (21) for total fluxes and Eq. (22) for individual fluxes. The evaluation of column profiles shows, that diffusional effects can be neglected, if the relative deviation between the fluxes computed with model 1 and model 2 is below 20%. In this case, the influence on the total and individual flow rates in the column is below 10%, what can be regarded as negligible for design purposes.

In the decarbonisation process, diffusional effects can be neglected for the steam stripping in the lower part of the column. For both the ternary system  $\text{NH}_3\text{--CO}_2\text{--H}_2\text{O}$  and the quaternary system  $\text{NH}_3\text{--CO}_2\text{--H}_2\text{S--H}_2\text{O}$ , deviations between the fluxes calculated with the two methods are far below the 20% level due to the low concentration in the process water. In this case, the effective diffusivity method is sufficient for the design of this part of the decarbonisation process.

In the DCC of vapour mixtures, the concentrations of the transferred components are no longer low, so that diffusional interactions should be taken into account, in particular in quaternary systems. For ternary vapour mixtures, the deviation in the calculated mass transfer fluxes did not exceed 20% for the studied conditions. The maximum deviation in total flow rates did not exceed 3.5% and the deviation for the individual flow rates of the condensable components ammonia and water are lower than 10%. The average relative deviation  $\delta_N$  in the fluxes decreases with decreasing amount of inert components in the initial vapour mixture. The effective diffusivity method should, therefore, provide sufficient accuracy for the design of direct-contact condensers for the ternary mixture.

For quaternary mixtures, deviations are significantly larger and exceed the critical value for the deviation of fluxes of 20%, this leads to deviations in flow rates of up to 11% for total and 20% for component specific flow rates. The design of direct-contact condensers for quaternary mixtures, in particular within the decarbonisation process, should thus be carried out using the Maxwell–Stefan equations.

The calculation of the mass fluxes in the presented integrated stripping, absorption and DCC process can be simplified for both the effective diffusivity method and the Maxwell–Stefan equations by neglecting the high-flux correction terms. In this case, average film concentrations are used for the determination of the convective term according to Eq. (25). The errors caused by neglecting the high-flux correction are always below 3% and thereby small enough such that sufficient accuracy for design purposes is ensured.

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