Absorption of formaldehyde in water
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Chapter 6

Simulation of industrial formaldehyde absorbers: the behaviour of methanol and non-equilibrium stage modelling.

Abstract

A model is presented for the commercially important formaldehyde absorption in the presence of methanol. Incorporated in the model are a large number of liquid phase reactions, gas liquid heat transfer, and mass transfer with reaction of water, formaldehyde, methylene glycol, methanol and hemiformal. The evaporation of water, methylene glycol and hemiformal in the lower part of the column creates an internal circulation of these components. In this part of the column negative enhancement factors are obtained for mass transfer with reaction of methylene glycol and hemiformal. This indicates that approximate methods for calculating mass transfer enhancement factors due to reaction might fail for absorption with chemical reaction and simultaneous product desorption. The performance of an industrially applied packed column with liquid recirculations is simulated using a non-equilibrium stage model. A solution algorithm is developed and carefully described. The influence of a number of process parameters on the behaviour of methanolic species in the absorber is investigated.

Introduction

Formaldehyde is industrially produced by partial oxidation and dehydrogenation of vapourised methanol in air over a solid catalyst at approximately atmospheric pressure. The reactor product gas stream consists of water vapour, formaldehyde and some unreacted methanol in an inert matrix of nitrogen, hydrogen and carbon dioxide (minor amounts of by-products are neglected in this study). This gas mixture is passed through a partial condenser, where the temperature is reduced to 328 K and part of the water vapour and formaldehyde are condensed. The resulting stream is subsequently fed to the absorber to extract the formaldehyde from the gas, and to obtain the commercial product: a concentrated aqueous formaldehyde solution containing some not-converted methanol.

A scheme of the absorber studied is shown in Fig. 1. The gas stream entering at the bottom of the column passes upwards through two packed beds, randomly filled with a modern high performance Pall-ring like packing. Make-up water enters the top of the column and flows downward, meanwhile exchanging heat and mass with the gas stream. Each of the absorption beds is equipped with an external liquid recirculation with heat exchangers. Just below each bed an amount of liquid is kept to provide buffers for the liquid recirculation pumps.

In a previous paper (Winkelman et al., 1992) a model for the formaldehyde absorber was developed, based on differential equations for the mass and energy balances in each phase. The resulting set of coupled boundary value problems was solved by a semi-transient method. The presence of methanol in the absorber was neglected, and only formaldehyde and water were assumed to be absorbed or desorbed. In this contribution the behaviour of methanol in the absorption process is fully incorporated in the model. Also included in the model are vapourisation and re-absorption of methylene glycol and hemiformal, which are the primary reaction products.
of formaldehyde with water and methanol, and which are formed in the liquid. The absorber is modelled using a non-equilibrium stage model.

**Reactions in aqueous methanolic formaldehyde solutions**

Besides heat and mass transfer between gas and liquid, a number of reactions have to be considered in modelling the performance of formaldehyde absorbers because formaldehyde reacts with both water and methanol. In aqueous solutions the dissolved formaldehyde (F) reacts fast with water (W) to form methylene glycol, CH$_1$(OH)$_1$, denoted by WF$_1$

$$\text{CH}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2(\text{OH})_2.$$  \hspace{1cm} (1)

The reaction rate is given by

$$r_1 = k_h (C_F C_W - C_{WF_1} / K_h),$$  \hspace{1cm} (2)

where $K_h$ is the chemical equilibrium constant for this hydration, defined as
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\[ K_h = \left( \frac{C_{WF_1}}{C_F C_W} \right)_{eq}. \]  

The equilibrium of reaction (1) is far to the right, which means that in an aqueous solution the concentration of free formaldehyde is very low.

Methylene glycol, formed by reaction (1), slowly polymerises to form a series of low molecular weight poly(oxymethylene) glycols, \( \text{HO(CHO)}_n\text{H} \), denoted here by \( \text{WF}_n \)

\[ \text{HO(CHO)}_{n-1}\text{H} + \text{CH}_2(\text{OH})_2 \rightleftharpoons \text{HO(CHO)}_n\text{H} + \text{H}_2\text{O} \quad (n = 2..n_{\text{max}}), \]  

with reaction rates

\[ r_n = k_n (C_{WF_{n-1}} C_{WF_1} - C_{WF_n} C_W / K_n) \quad (n = 2..n_{\text{max}}), \]  

and the equilibrium constants

\[ K_n = \left( \frac{C_{WF_n} C_W}{C_{WF_{n-1}} C_{WF_1}} \right)_{eq} \quad (n = 2..n_{\text{max}}). \]

If methanol (M) is present in the solution, formaldehyde reacts with it in a similar manner as with water, producing hemiformal, \( \text{CH}_3\text{OCH}_2\text{OH} \) \((\text{MF}_1)\)

\[ \text{CH}_2\text{O} + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_2\text{OH}, \]

with the reaction rate

\[ r_{\text{MF}_1} = k_{\text{MF}_1} (C_F C_M - C_{\text{MF}_1} / K_{\text{MF}_1}), \]  

where the equilibrium constant is defined as

\[ K_{\text{MF}_1} = \left( \frac{C_{\text{MF}_1}}{C_F C_M} \right)_{eq}. \]

The formed hemiformal also polymerises slowly to a series of polymers, higher hemiformals in this case, \( \text{CH}_3\text{O(CHO)}_n\text{H} \), denoted by \( \text{MF}_n \)

\[ \text{CH}_3\text{O(CHO)}_{n-1}\text{H} + \text{CH}_3\text{OCH}_2\text{OH} \rightleftharpoons \text{CH}_3\text{O(CHO)}_n\text{H} + \text{CH}_3\text{OH} \quad (n = 2..n_{\text{max}}) \]  

with reaction rates
\[ rm_n = k m_n \left( C_{MF_i} C_{MF_{n+1}} - C_M C_{MF_n} / K M_n \right) \quad (n = 2..n_{max}) , \]  

and equilibrium constants

\[ K M_n = \left( \frac{C_{MF_n} C_M}{C_{MF_{n+1}} C_{MF_i}} \right)_{eq} \quad (n = 2..n_{max}) . \]

Here, \( n_{max} \) denotes the largest polymer. In Fig. 2 the equilibrium molar fractions are shown of an aqueous solution containing 55 wt % formaldehyde and 1 wt % methanol. The concentrations of the higher poly(oxymethylene) glycols and hemiformals decrease rapidly with increasing molecular weight. Therefore the largest polymers considered here are WF_{10} and MF_{10}, with \( n_{max} = 10 \) for both types of polymers. This way, there are 20 chemical reactions in the liquid phase, and the total number of liquid phase components amounts to 23. The production rates of the individual species are found from

\[ R_i = \sum_{k=1}^{n_{max}} (v_{i,k} r_k + v m_{i,k} r_m k) , \]

where \( v_{i,k} \) denotes the stoichiometric coefficient of component \( i \) in the reaction forming the \( k \)-th poly(oxymethylene) glycol (negative for reactants and positive for reaction products). Likewise, \( v m_{i,k} \) denotes the stoichiometric coefficient in the formation of the \( k \)-th hemiformal. From eq (13) and the stoichiometry of the reactions (1), (4), (7) and (10) it follows

![Fig. 2. Equilibrium molar fractions in an aqueous solution containing 50% by weight formaldehyde and 1% by weight methanol, at 333 K.](image-url)
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\[ R_F = -\eta_1 - r_{m_1}, \]  \( (14) \)
\[ R_W = -\eta_1 + r_2 + \ldots + r_{n_{max}}, \]  \( (15) \)
\[ R_{WF_1} = \eta_1 - 2r_2 - r_3 - \ldots - r_{n_{max}}, \]  \( (16) \)
\[ R_{WF_2} = r_n - r_{n+1} \quad (2 \leq n < n_{max}), \]  \( (17) \)
\[ R_{WF_3} = r_n \quad (n = n_{max}), \]  \( (18) \)
\[ R_M = -r_{m_1} + r_{m_2} + \ldots + r_{m_{n_{max}}}, \]  \( (19) \)
\[ R_{MF_1} = r_{m_1} - 2r_{m_2} - r_{m_3} - \ldots - r_{m_{n_{max}}}, \]  \( (20) \)
\[ R_{MF_2} = r_{m_n} - r_{m_{n+1}} \quad (2 \leq n < n_{max}), \]  \( (21) \)
\[ R_{MF_3} = r_{m_n} \quad (n = n_{max}). \]  \( (22) \)

The concentration of the unhydrated monomeric formaldehyde is very low due to the reactions mentioned above: well under 1%, even in concentrated solutions. However, the total amount of dissolved aldehyde remains available for chemical reactions in downstream processing because of the reversibility of the reactions.

Vapour-liquid equilibria in formaldehyde-water-methanol mixtures

Several models have been put forward to describe the vapour-liquid equilibria in pseudo binary formaldehyde-water systems (e.g.: Kogan et al., 1977; Brandani et al., 1980). A method to model the vapour-liquid equilibria in pseudo ternary formaldehyde-water-methanol mixtures has been presented by the group of Maurer (Maurer 1986; Albert et al., 2000). This method is used here to calculate the vapour-liquid equilibria at the gas-liquid interface in the absorber.

Several substances in a formaldehyde-water-methanol mixture can vaporise. These are not only the monomeric formaldehyde, water and methanol, but also the first reaction products of formaldehyde with water and methanol which are methylene glycol and hemiformal, respectively. The higher polymers always remain in the liquid phase because of their high boiling points and negligible vapour pressure (Maurer, 1986). With the method of Maurer, the thermodynamic equilibrium of the vapour-liquid system is calculated from the overall composition of the liquid (e.g. weight percentages formaldehyde and methanol) using chemical equilibrium conditions and overall composition balances in the liquid phase, combined with the physical equilibria for the components that can vaporise,

\[ y_i P_{tot} = x_i P_i^g \quad (i = F, W, WF_1, M, MF_1), \]  \( (23) \)

where the activity coefficients, \( \gamma_i \), are calculated with the UNIFAC method (Gmehling et al., 1982). In the column simulations, however, the liquid phase in a stage is not at chemical equilibrium. To calculate the gas phase concentrations at the interface, in equilibrium with the liquid phase concentrations at the interface, we proceed in the following way. The equilibrium molar fractions are calculated from the overall composition of the liquid according to the method of Maurer. Once the equilibrium molar fractions are known, the activity coefficients and partial pressures can be calculated. These partial pressures are then corrected for the deviations of the
actual liquid phase molar fractions at the interface from those calculated from the chemical equilibrium conditions. Here it is assumed that the activity coefficients do not vary substantially with the change in composition from chemical equilibrium to the actual composition at the interface.

Model development

Simulation of continuous absorption processes is often based on stage models. The column is assumed to consist of a sequence of stages, each representing a section of the packing. Within each stage the temperature and composition of the gas and liquid phases are assumed to be constant. In this context, equilibrium stage models are widely used: the streams leaving a stage are assumed to be in equilibrium with each other and departures from this assumption are accounted for by a stage efficiency.

Krishnamurthy and Taylor (1985a,b) pointed out several drawbacks of the equilibrium stage approach for separation processes. They developed a non-equilibrium stage model, where material and energy balances for each phase are solved simultaneously with the mass and energy transfer rate equations. In modelling the formaldehyde absorber, we followed the same approach.

A schematic representation of a non-equilibrium stage is shown in Fig. 3. The packed beds shown in Fig. 1 consist each of a number of such stages, see Fig. 4. Vapour and liquid streams from adjacent stages are brought into contact on the stage and are allowed to exchange mass and energy across their common interface. The model of a stage consists of material and energy balances for each phase and rate equations for inter-phase mass and energy transfer.
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The balance equations are denoted by $\Psi$. The component balance for component $i$ on stage $j$ reads for the gas phase

$$\Psi_{i,g}^{j} = v_{i}^{j} - v_{i}^{j+1} + j_{i,g}^{j} A^{j} = 0 , \tag{24}$$

and for the liquid phase

$$\Psi_{i,l}^{j} = t_{i}^{j} - t_{i}^{j-1} - J_{i,l}^{j} A^{j} - \epsilon_{i}^{j} S R_{i} A Z - t_{i}^{f,j-1} + t_{i}^{D,j} = 0 . \tag{25}$$

The energy balance on stage $j$ for the gas phase is given by

$$\Psi_{E,g}^{j} = \sum_{i} v_{i}^{j} H_{i,g}^{j} - \sum_{i} v_{i}^{j+1} H_{i,g}^{j+1} + A^{j} q_{g}^{j} + A^{j} \sum_{i} J_{i,g}^{j} H_{i,g}^{j} = 0 , \tag{26}$$

and for the liquid phase

$$\Psi_{E,l}^{j} = \ldots$$
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\[
\Psi^j_{E,\ell} = \sum_i [H^j_{i,\ell} - \sum_i l_{i,j} H^{j-1}_{i,\ell} - q^j_{i,\ell} A^j - A^j \sum_i J^j_{i,\ell} H^j_{i,\ell} - \sum_i J^F_{i,\ell} H^{F,j}_{i,\ell} + \sum_i J^{D,j}_{i,\ell} D^j_{i,\ell} = 0. 
\] (27)

With the assumption of constant heat capacities of the components over the temperature range of adjacent stages, the energy balance eqs (26) and (27) are rewritten in terms of temperatures and molar flows. For the gas phase this gives

\[
\Psi^j_{E,g} = (T^j_g - T^{j+1}_g) \sum_i v^j i \Delta T_{pi,g} + A^j q^j_g = 0. 
\] (28)

Similarly, for the liquid phase it follows

\[
\Psi^j_{E,l} = (T^j_l - T^{j+1}_l) \sum_i v^j i \Delta T_{pi,l} - q^j_l A^j + (T^j_l - T^{j+1}_l) \sum_i J^F_{i,\ell} C_{pi,l} - \Delta Z \sum_k (\Delta H_R)_k + \Delta m (\Delta H_m)_k = 0. 
\] (29)

The lowest stage in each of the packed sections represents the buffer for the liquid recirculation pumps (see Figs 1 and 4). The interfacial area is very small here, and in the model it is assumed to be zero.

**Mass transfer rates**

For clarity, the subscript \( j \), indicating the stage number, has been dropped from all symbols throughout this section. The calculation of the fluxes is based on the two film concept, with the positive direction defined from the gas to the liquid phase. The gas phase mass transfer rates are given by

\[
J^j_{l,g} = k_{g,l}(C^j_{l,g} - C^j_{i,g}) \quad (i = F, W, WF_1, M, MF_1), 
\] (30)

where the gas phase concentrations at the interface, \( C^j_{i,g} \), are coupled to those in the liquid phase by

\[
C^j_{i,l} = m_i C^j_{i,g} \quad (i = F, W, WF_1, M, MF_1). 
\] (31)

For the calculation of the equilibrium ratios, \( m_i \), see the section on vapour-liquid equilibria. The fluxes on either side of the interface are equal:

\[
J^j_{l,g} = J^j_{i,l} \quad (i = F, W, WF_1, M, MF_1). 
\] (32)
At the liquid side of the interface, the diffusional transport of the transferred components is accompanied by chemical reactions. This causes enhancement of the mass transfer rates. Also, the fluxes into the liquid bulk, $J_{l, i}$, differ from those at the interface, $J_{i, l}^I$. In a previous paper, we showed the polymerisation reactions to be too slow to have any influence on the diffusion fluxes in the film, and the gradients of the concentrations of the higher polymers in the liquid film to be negligible (Winkelman et al., 1992). So, the hydration of formaldehyde, eq. (1), and the hemiformal formation, eq. (7), are the only reactions affecting the fluxes of the transferred components.

To account for these parallel reactions in the liquid phase, the film model is applied

$$D_l \frac{d^2 C_i}{dx^2} = - \nu_{i, l} r_1 - \nu_{m, l} r_m$$

with the boundary conditions

$$x = 0: \quad -D_l \frac{dC_i}{dx} = J_{i, l}^I,$$

$$x = \delta: \quad C_i = C_{i, l}.$$

The set of eqs (30)-(35) can not be solved analytically because of the non-linearity of the reaction rates in eqs (33). Therefore, an iterative shooting method was used to calculate the interfacial concentrations and the mass fluxes, given the bulk phase concentrations. From an initial guess of the interfacial concentrations, the gradients at the interface were calculated with eqs (30)-(32) and (34), and the differential eqs (33) were numerically integrated from $x = 0$ to $x = \delta$ using a fourth order Runge-Kutta method. The interfacial concentrations were repeatedly updated, using a multi-dimensional Newton-Raphson method, until the obtained concentrations at $x = \delta$ match the liquid phase bulk concentrations. From the numerically calculated gradients at $x = \delta$, the flux into the liquid bulk is obtained

$$J_{i, l} = -D_l \left( \frac{dC_i}{dx} \right)_{x=\delta}.$$

The numerical effort of the above procedure is greatly reduced by noting the mutual dependency of several interfacial concentrations and fluxes. This can be understood from considering methanol and hemiformal as an example. Addition of eqs (33) for these two components results in

$$D_M \frac{d^2 C_M}{dx^2} + D_{MF} \frac{d^2 C_{MF}}{dx^2} = 0.$$

Integrating twice while applying boundary conditions (34) and (35) gives an explicit relation for the interfacial concentration of methanol as a function of the interfacial concentration of hemiformal:
$$C_{M,\ell} = [k_{g,M}C_{M,G} + k_{\ell,M}C_{M,\ell} + k_{g,\ell,M}C_{MF_1,G} - C_{MF_1,\ell} / m_{MF_1}]$$
$$- k_{\ell,\ell,M} (C_{MF_1,\ell} - C_{MF_1,\ell})] / (k_{\ell,M} + k_{g,M} / m_M). \hspace{1cm} (38)$$

Similar equations are obtained for $C_{W,\ell}$ as a function of $C_{W,F_1,\ell}$, and for $C_{F,\ell}$ as a function of $C_{MF_1,\ell}$ and $C_{WF_1,\ell}$. Thus, if the values for $C_{WF_1,\ell}$ and $C_{MF_1,\ell}$ are chosen or updated, the values of $C_{F,\ell}$, $C_{W,\ell}$, and $C_{MF_1,\ell}$ can be calculated from eq (38) and its analogs. This way, the problem of mass transfer of five components, with two parallel reactions can be solved by iteration on two interfacial concentrations only.

**Energy transfer rates**

The film model gives the following expressions for the conductive heat fluxes from the gas phase, $q_g$, and into the liquid phase, $q_\ell$, (Krishna and Taylor, 1986)

$$q_g = h_g A_f (T_g - T^I), \hspace{1cm} (39)$$
$$q_\ell = h_\ell (T^I - T_\ell). \hspace{1cm} (40)$$

The Ackermann factor, $A_f$, corrects the conductive energy transfer rate in the gas phase for non-zero mass transfer rates.

$$A_f = \frac{C_f}{e^{C_f} - 1}, \hspace{1cm} \text{where} \hspace{1cm} C_f = \frac{1}{h_g} \sum_i J_{i,g} C_{pi,g}. \hspace{1cm} (41)$$

For the liquid phase, this correction is negligible.

If heat and mass transfer occur simultaneously, the total energy transfer rate contains a conductive and a convective contribution on either side of the interface. From a balance around the interface it follows that the total energy fluxes out of the gas phase and into the liquid phase must be equal

$$q_g + \sum_i J_{i,g} H_{i,g} = q_\ell + \sum_i J_{i,\ell} H_{i,\ell}, \hspace{1cm} (42)$$

where the summations are over all transferred species. Expressing the enthalpies in terms of heat capacities and temperature differences, and introducing heats of vaporisation and reaction gives

$$q_\ell = q_g + (T_g - T^I) \sum_i J_{i,g} C_{pi,g} + \sum_i J_{i,g} \Delta H_{vap,i} + (T^I - T_\ell) \sum_i J_{i,\ell} C_{pi,\ell} + (J_{WF_1,\ell} - J_{WF_1,G})(-\Delta H_{R,1}) + (J_{MF_1,\ell} - J_{MF_1,G})(-\Delta H_{m,1}) \hspace{1cm} (43)$$
In deriving eq (43), it is assumed that the variation of the heat capacities is negligible if the temperature changes from $T_g$ to $T'$ and from $T'$ to $T_f$ and that the heats of reaction of both the hydration of formaldehyde and the hemiformal formation in the film are liberated at the interface. Further, the reaction products of these two reactions are taken as key components, thus allowing the reaction rates in the film to be expressed as flux differences of these key components. From eqs (39)-(43), both the interfacial temperature and the values of the heat transfer rates, $q_g$ and $q_f$, were calculated.

Method of solution.

Newton's method for simultaneous correction was used to solve the model because it is more effective than tearing algorithms (Krishnamurthy and Taylor, 1985a). The total number of unknown bulk phase variables on a stage $j$ is 30: 5 gas phase molar flow rates, the gas phase temperature, 23 liquid phase molar flow rates and the liquid phase temperature. These are stored in a vector $(X_j)$

$$(X_j)^T = (v_F, v_W, \nu_{WFi}, \nu_M, \nu_{MFi}, T_g, \nu_F, \nu_W, \nu_{WFi}, \nu_M, \nu_{MFi}, T_f). \quad (44)$$

Other quantities, such as the mass and energy transfer rates and the temperature and concentrations at the gas-liquid interface, are functions of the bulk phase variables, and are therefore not considered as independent variables in the solution process. The unknown variables in $(X_j)$ must be found by solving the component balance eqs (24) and (25), and the energy balance eqs (28) and (29). These equations are ordered in a vector $(\Psi_j)$

$$(\Psi_j)^T = (\Psi_{F,g}, \Psi_{W,g}, \Psi_{WFi,g}, \Psi_{M,g}, \Psi_{MFi,g}, \Psi_{E,g}, \Psi_{F,l}, \Psi_{W,l}, \Psi_{WFi,l}, \Psi_{M,l}, \Psi_{MFi,l}, \Psi_{E,l}). \quad (45)$$

Specified quantities are the molar flow rates and the temperature of the feed to the last stage, the make-up water molar flow rate and its temperature, the mass flow rates of the two liquid recirculation streams and the temperatures of the recirculation streams entering the first stage of each of the two packed beds. From initial estimates, the variables are repeatedly updated with Newton's method, using the equation

$$[J][X]_{\text{next}} - (X)_{\text{current}} = -[\Psi]_{\text{current}}, \quad (46)$$

where $(X)_{\text{current}}$ and $(X)_{\text{next}}$ denote the current and next estimate for the vector $(X)$ which contains all bulk phase variables

$$(X)^T = ((X_1), ..., (X_n))^T. \quad (47)$$
$(\Psi)$ denotes the vector of current discrepancies of the set of equations to be solved and whose solution is given by $(\Psi) = 0$

$$(\Psi)^T = ((\Psi_1)^T \ldots (\Psi_n)^T),$$  

(48)

and $[J]$ denotes the Jacobian matrix with elements

$$J_{i,j} = \frac{\partial \Psi_i}{\partial X_j}. \quad (49)$$

The variables and equations are grouped in such a way that the Jacobian matrix has the well known block tridiagonal structure, shown in Fig. 5. The top bed of the absorber contributes to the Jacobian the submatrices $[S]$, $[T]$ and $[U]$, which contain the partial derivatives of the functions pertaining to stage $j$ with respect to the variables of the stages $j-1, j$, and $j+1$, respectively. In a similar way, the submatrices $[A]$, $[B]$ and $[C]$ originate from the bottom bed in the absorber. Formally, the submatrices have dimensions $(30 \times 30)$, but $[S]$ and $[A]$ are very sparse. The solution algorithm is adapted to use this sparseness, in order to save on computer storage requirements and calculation time. Because of the presence of the liquid recirculations, the composition of the liquid on the first stage of each absorption bed depends partly on the composition of the last stage. This is reflected in the presence of the two off-diagonal submatrices $R_T$ and $R_B$ in Fig. 5.

Fig. 5. Structure of the Jacobian matrix for the formaldehyde absorber.
Despite the presence of the two off-diagonal submatrices, the matrix generalisation of the Thomas algorithm can be used to solve eq. (46) for $X_{next}$. With this algorithm, the Jacobian matrix is first converted to the so-called upper diagonal form by a recursive elimination. Most of the sparsity of the Jacobian is preserved during the elimination process. Additional entries appear only in the columns between the submatrices $[R_T]$ and $[T_N]$, and between $[R_B]$ and $[B_N]$. From the upper triangular form, the solution for $X_{next}$ is found by repeated back substitution.

Unfortunately, the solution method described above showed a poor convergence (e.g. large computation time) or did not result in a solution at all. The latter particularly if the initial estimates of the variables were not very close to the final solution. The reason for this unsatisfactory behaviour is not completely clear, but possibly part of the problem is caused by the great difference in the orders of magnitude of the terms in the energy balances compared to those in the mass balances. Therefore, the solution method was changed in such a way that the energy balance equations and the temperatures were skipped from eq. (46). The remaining modified eq. (46) now contains only the component balance equations and the molar flow rates, and is solved in an inner loop

$$
(X_j)^{T}_{\text{inner}} = \begin{pmatrix} v_F, v_W, v_{WF_1}, v_M, \nu_{MF_1}, l_F, l_W, l_{WF_1}, \ldots, l_{WF_{10}}, \nu_{MF_1}, \ldots, \nu_{MF_{10}} \end{pmatrix}_j
$$

$$
(\Psi_j)^{T}_{\text{inner}} = \begin{pmatrix} \Psi_{F,G}, \Psi_{W,G}, \Psi_{WF_1,G}, \Psi_{M,G}, \Psi_{MF_1,G}, \Psi_{F,f}, \Psi_{W,f}, \Psi_{WF_1,f}, \ldots, \Psi_{WF_{10},f}, \Psi_{M,f}, \Psi_{MF_1,f}, \ldots, \Psi_{MF_{10},f} \end{pmatrix}_j
$$

The inner loop iterations continued until the sum of square residuals of the mass balances, $SSR_M$, satisfied the condition

$$
SSR_M = \sum_j \sum_i \left( (\Psi_{i,j,G})^2 + (\Psi_{i,j,f})^2 \right) < 10^{-6} \quad [\text{mol/s}]^2.
$$

Subsequently, the temperatures were found by solving the energy balances in an outer loop using eq. (46) with $(X_j)$ and $(\Psi_j)$ now defined as

$$
(X_j)^{T}_{\text{outer}} = (T_G, T_f)_j,
$$

$$
(\Psi_j)^{T}_{\text{outer}} = (\Psi_{E,G}, \Psi_{E,f})_j.
$$

Convergency of the energy balances was supposed to be obtained once the sum of square residuals of the energy balance equations, $SSR_E$, satisfied the condition

$$
SSR_E = \sum_j \left( (\Psi_{E,G})^2 + (\Psi_{E,f})^2 \right) < 10^3 \quad [\text{J/s}]^2.
$$
The solution algorithm is summarised in Fig. 6. The calculations are initialised by assigning guessed values to the molar flow rates and to the temperatures at the first stage, and by simply taking the conditions at the other stages identical to the first stage. Although the initialisation is not very sophisticated, the algorithm converges readily to a solution defined by eqs (52) and (55).

Once calculated solutions were available for some situations, these were used as starting values, to initialise the calculations for other sets of operating parameters. This leads to a considerable reduction of the calculation time.

The transfer coefficients and other physical and most of the chemical properties needed in the calculations were obtained as described by Winkelman et al. (1992). The chemical equilibrium constants for reactions involving formaldehyde and methanol where taken from Maurer (1986). Because no open literature is available on the rates of reactions involving methanol these rates were taken equal to the rates of the corresponding reactions involving water, i.e.: $k_{m i} = k_i$ (i = 1..n_{max}).
Results

Fig. 7 shows a typical example of the convergence behaviour of the double-loop solution algorithm. In this figure, the values of \( \text{SSR}_M \) calculated with inner loop iterations are plotted against the values of \( \text{SSR}_E \) from the outer loop. The calculations were initialised by using the same guessed molar flow rates and temperatures for all the stages. To cut calculation time, the value of \( \text{SSR}_E \) was not calculated during the inner loop calculations. In constructing Fig. 7, the value of \( \text{SSR}_E \) during the inner loop iterations was therefore assumed to equal the one calculated from the next outer loop iteration. It is seen that the number of inner loop iterations per outer loop iteration reduces steadily from four to just one as the conditions approach the final solution. Fig. 7 also illustrates that the improvement per individual iteration is greater the closer we are to the final solution (up to several decades in terms of \( \text{SSR} \)-values). This is typical for Newton’s method.

The concentrations necessary for the calculations of the mass transfer fluxes from eqs (30)-(38) can be calculated from the molar flow rates in several ways (Krishnamurthy and Taylor, 1985a,b). The simplest option is to assume constant bulk compositions, and to calculate the concentrations from the molar flow rates leaving the stage. If the bulk compositions are assumed to vary linearly, then the concentrations have to be calculated from the average of the molar flow rates entering and leaving the stage. For the simulation of packed columns, Krishnamurthy and Taylor (1985c) obtained the best results using the average composition for the bulk vapour

\[
C_{i,g} = 0.5 \left( \frac{\nu_i + \nu_{i+1}}{\sum_i \nu_i} + \frac{\nu_{i+1}}{\sum_{i+1} \nu_i} \right) C_{i,v}^{f},
\]

(56)

Fig. 7. Typical convergence path. Numbers indicate the largest temperature correction.
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in either phase with an outer loop iteration step. Dashed lines: inner loop iterations. Solid lines: outer loop iterations.

Fig. 8. Relative amount of vapour phase methanol leaving the bottom-bed vs. the total number of stages applied; (●): fluxes based on average vapour composition; (○): fluxes based on exit vapour composition.

and using the exit composition for the bulk liquid

\[ C_{i,\ell}^{j} = \frac{l_{j}^{i}}{\sum l_{j}^{i}} C_{\text{tot},\ell}^{j}. \]  

(57)

We, therefore, applied the same method. The influence of the method of calculating the vapour bulk composition is illustrated in Fig. 8, where, as an example, the relative methanol vapour phase molar flow rate leaving the bottom-bed is shown as function of the total number of stages applied. The bulk liquid phase composition was always calculated from the exit liquid molar flows. Using the stage exit molar flows to calculate the fluxes leads to lower driving forces for mass transfer, and therefore less absorption of methanol. The effect of the total number of stages on the solution was studied by varying this number while always allocating 50% to the top- and the bottom-bed, respectively. The many calculated output variables (molar flow rates and temperatures) all asymptotically approached a constant value with increasing the number of stages. Again, Fig. 8 may serve as a typical example.

Generally, the variation in the results appeared to become negligible above 60 stages. Therefore all remaining calculations were performed with 60 stages (30 in each absorption bed).

A typical set of calculated bulk vapour and liquid temperature profiles is shown in Fig. 9. The cooler gas stream entering the bottom-bed is quickly heated up to the liquid temperature because of a large heat transfer capability and a much lower heat capacity of the gas stream relative to the liquid stream. Similarly, the warm gas stream entering the top-bed from the
bottom-bed is rapidly cooled down to the liquid temperature level. As the liquid flows downwards, its temperature rises, predominantly due to the heat effects connected with condensation and reaction. In the lower part of the bottom-bed, solvent evaporation results in a temperature maximum. Interestingly, the temperature profiles obtained here using a non-equilibrium stage model are quantitatively similar to those obtained previously with a differential model (Winkelman et al., 1992).

After inspection of the results, it turned out that the Ackermann correction factor for the vapour phase, \( A_{fg} \), deviates very little from unity. This can be easily understood. For mass transfer to have a significant influence on the vapour phase conductive energy flux, say more than 5% (\( A_{fg} \leq 0.95 \)), it follows from eq. (41) that \( C_f > 0.1 \). With typical values for the vapour phase heat capacity \( C_{p,g} \approx 40 \text{ J/(mol K)} \) and the heat transfer coefficient \( h_g \approx 40 \text{ J/(m}^2 \text{K s)} \) this results in a condition for the fluxes: \( \sum_i J_{i,g} \geq 0.1 \text{ mol/(m}^2 \text{s)} \), which is larger than can be expected in absorption columns for the solubilities typical in formaldehyde absorption. Further, the temperature differences in the liquid film, \( T_{l,i} - T_{l,f} \), are generally well below 0.1 K because of the low resistance against heat transfer in the liquid phase. According to these observations, the following assumptions are justified: \( A_f = 1 \) and \( T_{l,i} = T_{l,f} \). This allows for considerable simplifications in the calculation of the energy transfer rates because apparently there is no need to calculate the interfacial temperature. This way, eqs (39)-(43) reduce to

\[
q_g = h_g (T_g - T_f), \quad (58)
\]

\[
q_i = q_g + (T_g - T_f) \sum_i J_{i,g} C_{p,i,g} + \sum_i J_{i,g} \Delta H_{vap,i} + (J_{WF,f} - J_{WF,g})(-\Delta H_{R,1}) + (J_{WF,\ell} - J_{WF,g})(-\Delta H_{R,1}). \quad (59)
\]

Fig. 10 shows typical profiles of relative vapour phase molar flow rates in the formaldehyde absorption column. Because of the large liquid/gas ratio, the liquid phase composition does not

\[
q_g = h_g (T_g - T_f), \quad (58)
\]

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q_i = q_g + (T_g - T_f) \sum_i J_{i,g} C_{p,i,g} + \sum_i J_{i,g} \Delta H_{vap,i} + (J_{WF,f} - J_{WF,g})(-\Delta H_{R,1}) + (J_{WF,\ell} - J_{WF,g})(-\Delta H_{R,1}). \quad (59)
\]

Fig. 10 shows typical profiles of relative vapour phase molar flow rates in the formaldehyde absorption column. Because of the large liquid/gas ratio, the liquid phase composition does not
change much with the stage number of the packed section and is therefore not shown in Fig. 10.

Fig. 10. Typical profiles of relative vapour phase molar flow rates.

Similar to the temperature profiles, also these profiles clearly reveal the division of the packed height in two absorption beds. The gas feed to the absorber is undersaturated with water. In the lower part of the bottom bed this leads to desorption of water. In the upper part of the bottom-bed, but even more in the top-bed, the water vapour condenses. This way an internal circulation of water is created. The mass transfer of both formaldehyde and methanol is always directed towards the liquid. Again, the profiles obtained here for formaldehyde and water using a non-equilibrium stage model are very similar to those obtained previously using a differential model.

The relative vapour molar flow rates of the reaction products methylene glycol and hemiformal are shown in Fig. 11. These components are not present in the gas feed, and similar to water, they are desorbed in the lower part of the bottom-bed and re-absorbed higher in the column.
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Fig. 11. Typical profiles of relative molar flow rates of the vaporised reaction products.

Fig. 12. Fraction of converted formaldehyde and methanol in the gas phase relative to the uncombined, free components.

Fig. 12 shows that the amount of formaldehyde that is transported in the gas phase in associated form is relatively low compared to the amount of free formaldehyde: it always accounts for less than 10% of the total amount of formaldehyde in the gas phase. On the other hand, the amount of hemiformal is substantial compared to the amount of free methanol in the gas phase (in the bottom-bed it becomes even the larger one of the two). But both the amounts of methanol and hemiformal are small relative to formaldehyde and water.

The numerical evaluation of the fluxes, as described in the section on mass transfer rates, allows for the calculation of the mass transfer enhancement factors, $E_i$

$$E_i = \frac{-D_i \left( \frac{dC_i}{dx} \right)_{x=0}}{k_{f,l}(C_{i,l} - C_{i,l})}$$

(60)

Remarkable results are obtained for the reaction products methylene glycol and hemiformal, see Fig. 13. The enhancement factor of hemiformal is smaller than one in many of the stages. Methylene glycol has even negative enhancement factors in some of the stages. This phenomenon is not some numerical peculiarity, but results from the combined action of mass transfer and reaction. This becomes clear by taking a closer look at the concentration profiles of methylene glycol in the stagnant liquid film adjacent to the gas-liquid interface. These profiles are shown in Fig. 14 for the stages 50 to 54 (the stage numbers are also indicated in Fig. 13). The profiles were obtained from the numerical method described in the section on mass transfer rates. In these stages, the positive gradient of the concentration near $x = 0$ indicates that the flux of methylene glycol at the interface is directed towards the gas phase. Therefore the numerator of eq (60) is always negative here. However, the concentration difference of methylene glycol over the
film in the denominator of eq (60), \( \frac{C_{WF_i,t}}{C_{WF_i,t'}} \), changes sign in going from stage 52 to 53.

For the stage numbers 53 and 54 the denominator is negative, resulting in positive enhancement factors, whereas for the stage numbers 50-52 the denominator is positive, resulting in negative enhancement factors. Recently, the possible occurrence of negative enhancement factors was shown also by analytically solving the case of mass transfer with a single first-order reversible reaction (Winkelmann and Beenackers, 1993).

In a previous contribution, we already discussed the influence of several operating parameters on the temperature rise of the liquid in the packed beds, on the formaldehyde absorption efficiency and on the overall weight percentage of formaldehyde in the liquid leaving
the packed beds (Winkelman et al., 1992). New aspects here are the role of methanol and hemiformal. Below, we focus on these aspects only.

Fig. 15 illustrates the influence of the temperature of the liquid recycle stream of the top-bed, $T_{\text{Rec}}^t$. Increasing $T_{\text{Rec}}^t$ results in higher partial pressures of methanol and hemiformal, and therefore in increasing relative molar flows of these components in the gas stream leaving the top-bed and thus in less absorbed methanol in the liquid leaving the bottom-bed. With increasing $T_{\text{Rec}}^b$ the vapour pressures of methanol and hemiformal in the bottom-bed increase. This causes increased levels of these components in the top-bed, and higher amounts leaving the absorber with the gas stream, see Fig. 16. Although the higher amounts of absorbed methanolic compounds enter the bottom-bed with the liquid flowing down from the top-bed, this cannot completely compensate for the decreased absorption of methanol and hemiformal in the bottom-bed and the overall amount of methanol leaving the bottom-bed with the liquid stream decreases.

![Fig. 15. Influence of $T_{\text{Rec}}^t$ on the relative amounts of methanolic compounds in the exit gas and in the exit liquid stream.](image_url)
The influence of $R_b$, the amount of liquid recycled around the top-bed, is illustrated in Fig. 17. The amounts of methanol and hemiformal leaving the absorber with the gas stream decrease with increasing $R_b$, while at the same time the weight percentage of methanol in the liquid leaving the absorber at the bottom is almost constant. This might seem conflicting, but is caused mainly by a decrease of the temperature rise of the liquid in the top-bed with increasing $R_b$. The
result is even more formaldehyde and water absorption, and therefore an increase of the total amount of liquid entering the bottom-bed from the top-bed which tends to dilute the methanolic species. Similarly, the temperature rise of the liquid in the bottom-bed decreases with increasing $R_b$, leading to more formaldehyde and water absorption in the bottom-bed, dilution of the methanol and lower weight percentages of methanol in the liquid leaving the absorber, see Fig. 18. On the other hand, the increased absorption of formaldehyde and methanol in the bottom-bed results in lower amounts of these components absorbed in the top-bed. This reduces the liquid flow in the top-bed, resulting in a higher temperature rise, increased vapour pressures of methanol and hemiformal, and higher amounts of these components leaving the top-bed with the gas stream.

Interesting phenomena were observed if the amount of make-up water is varied. In both absorption beds, the amount of methanol in the gas stream increases with increasing amounts of make-up water, whereas the amount of hemiformal decreases. This is caused by a shift in the relative amounts of reaction products in the liquid phase. Due to the lower overall amounts of formaldehyde present in the liquid, less methanol combines with formaldehyde to form hemiformal, and more methanol is present in the uncombined form. This results in a higher partial pressure of methanol and a lower partial pressure of hemiformal. The amounts of these components leaving the absorber with the gas stream react correspondingly to increasing amounts of make-up water, see Fig. 19.

![Graph](image-url)

**Fig. 19.** Influence of the relative amount of make-up water on the relative amounts of methanolic compounds in the exit gas and in the exit liquid stream.
Conclusions.

The industrially important process of formaldehyde absorption in the presence of methanol is simulated using a non-equilibrium stage model. The model takes into account the mass transfer of formaldehyde, water and methanol, and their primary reaction products methylene glycol and hemiformal. In the liquid a large number of reactions take place, giving rise to numerous liquid phase components.

The double loop solution algorithm, solving the component balances in an inner loop and the energy balances in an outer loop, proved to be stable and converged readily despite a simple initialisation and a large number of equations. The non-zero mass flux correction of the conductive energy fluxes proved to be negligible. Similarly, it was found that the resistance against energy transfer in the liquid phase is negligible under practical conditions. In this type of modelling it is useful to check whether these simplifications are possible, because they reduce the calculation effort significantly.

The evaporation of water, methylene glycol and hemiformal in the lower part of the column creates an internal circulation of these components. In this part of the column negative enhancement factors are obtained for mass transfer with reaction of methylene glycol and hemiformal. This indicates that approximate methods for calculating mass transfer enhancement factors due to reaction might fail for absorption with chemical reaction and simultaneous product desorption.