Absorption of formaldehyde in water
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Chapter 5: Modeling and simulation of industrial formaldehyde absorbers

Abstract

The industrially important process of formaldehyde absorption in water constitutes a case of multicomponent mass transfer with multiple reactions and considerable heat effects. A stable solution algorithm is developed to simulate the performance of industrial absorbers for this process using a differential model. Good agreement with practice was achieved. Using the model, the conditions of one of the absorbers of Dynea B.V. were optimized, leading to considerable methanol savings.

Introduction

Formaldehyde, CH$_2$O, is produced on a large scale as a raw material for a great variety of end products. Its industrial production starts from methanol. Air and vaporized methanol, combined with steam and recycled gas, are passed over hot silver grains, at ambient pressure. Here the methanol is converted to formaldehyde by partial oxidation and by reduction at about 870 K. To prevent thermal decomposition of formaldehyde, the gases are cooled immediately after the catalyst bed.

The reactor product gas stream has a temperature of 420 K and consists typically of N$_2$ (50%), H$_2$ (15%), water vapor (20%) and formaldehyde (15%). Minor amounts of by-products and unreacted methanol are neglected in this study. This stream is passed through a partial condenser, where the temperature is reduced to 328 K and part of the water vapor and formaldehyde are condensed. The resulting mixed gas-liquid stream is subsequently fed to the absorber.

Because it is impossible to handle in its pure, gaseous form, formaldehyde is almost exclusively produced and processed as an aqueous solution: formalin. The latter is obtained commercially by absorbing the gases leaving the reactor in water.

The goals in optimizing the absorber performance seem conflicting. On the one hand the formaldehyde content of the tail gas should be minimized. On the other hand however, the formaldehyde concentration in the product liquid leaving the absorber should be as high as possible, thereby reducing the absorbing ability of the liquid in the column.

A scheme of the absorber studied is shown in Fig. 1. The gaseous part of the two-phase stream entering at the bottom of the column passes upwards through two beds, randomly filled with modern high performance Pall-ring like packing. The tail gas is partly recirculated to the reactor. Make up water enters at the top of the column and flows downward, meanwhile taking up heat and absorbing formaldehyde and water from the gas stream. Each of the absorption beds has an external liquid recirculation with heat exchangers. Just below the top bed, the absorber is equipped with a partial draw off tray to provide a buffer for the upper liquid recirculation pump. At the bottom of the column a liquid layer is kept as a buffer for the lower liquid recirculation pump.
Reactions in aqueous formaldehyde solutions

Besides direct heat transfer between gas and liquid, and the mass transfer of water and formaldehyde, a number of reactions have to be considered in modeling the performance of formaldehyde absorbers. In formalin the dissolved formaldehyde is present principally in the form of methylene glycol, CH$_2$(OH)$_2$, and a series of low molecular weight polyoxymethylene glycols, HO(CH$_2$O)$_n$H (e.g. Walker, 1964). As an example the equilibrium composition of an aqueous 50 wt.% formaldehyde solution is shown in Fig. 2.

Although the concentration of the unhydrated monomeric formaldehyde is well under 0.1% even in concentrated solutions, all dissolved aldehyde remains available for chemical reaction in downstream processing because of the reversibility of the reactions.

The following reactions take place in the absorber:

\[
\text{hydration} \quad \text{CH}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2(\text{OH})_2
\]  

with kinetics
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\[ r_1 = k_h \left( C_F C_W - C_{WF_1} / K_h \right) \]  \hspace{1cm} (2)

were

\[ K_h = \left( \frac{C_{WF_1}}{C_F C_W} \right)_{eq} \]  \hspace{1cm} (3)

polymerization reactions

\[ \text{CH}_2(\text{OH})_2 + \text{HO(CHO}_2\text{O)}_{n-1}\text{H} \rightleftharpoons \text{HO(CHO}_2\text{O)}_n\text{H} + \text{H}_2\text{O} \quad (2 \leq n \leq n_{\text{max}}) \]  \hspace{1cm} (4)

with kinetics

\[ r_n = k_n \left( C_{WF_n} C_{WF_{n-1}} - C_{WF_n} C_W / K_n \right) \]  \hspace{1cm} (5)

were

\[ K_n = \left( \frac{C_{WF_n} C_W}{C_{WF_n} C_{WF_{n-1}}} \right)_{eq} \]  \hspace{1cm} (6)

Here, \( n_{\text{max}} \) denotes the largest polymer considered. The concentration of the polyoxymethylene glycols decreases rapidly with increasing molecular weight, even for concentrated solutions (Fig. 2). Therefore, the largest polymer considered here is \( WF_{10} \) (\( n_{\text{max}} = 10 \)). This way, there are ten reactions in the liquid between twelve components.

The reaction rate of a species can be represented as

\[ R_i = \sum_{j=1}^{n_{\text{max}}} v_{i,j} r_j . \]  \hspace{1cm} (7)

From eq (7) and the stoichiometry of reactions (1) and (4) it follows

\[ R_F = -r_1 \]  \hspace{1cm} (8)

\[ R_W = -r_1 + r_2 + r_3 + \ldots + r_{n_{\text{max}}} \]  \hspace{1cm} (9)

\[ R_{WF_1} = r_1 - 2r_2 - r_3 - r_4 - \ldots - r_{n_{\text{max}}} \]  \hspace{1cm} (10)

\[ R_{WF_n} = r_n - r_{n+1} \quad (2 \leq n < n_{\text{max}}) \]  \hspace{1cm} (11)

\[ R_{WF_{n}} = r_n \quad (n = n_{\text{max}}) . \]  \hspace{1cm} (12)
Development of absorber model

The methods found in the literature for the modeling of packed columns generally belong to either of two types. In the first type the packed height is divided into a number of segments. Within each segment the conditions are supposed to be uniform in both phases. This type of models can be subdivided into equilibrium stage models (p.e. King, 1980), where the streams leaving each stage are assumed to be in equilibrium with each other and departures from this assumption are accounted for by one of several types of stage efficiencies, and nonequilibrium stage models (p.e. Krishnamurty & Taylor, 1985), where material and energy balance relations for each phase are solved simultaneously with mass and energy transfer rate equations.

In the second type of models, differential mass and energy balances for each phase are written for a small section of packing, and the differential equations are numerically integrated over the total packed height (p.e. Hitch et al., 1986).

Our model for the formaldehyde absorber belongs to the second type. In a subsequent paper a stage model will be introduced for this type of column.

Since our first goal is the simulation of existing industrial formaldehyde absorbers, the height of the packing in the absorption beds is fixed. Major assumptions of the model are: (1) the absorption beds operate adiabatic; (2) the packing is fully wetted, therefore the interfacial area is the same for heat and mass transfer; (3) heat and mass transfer relations are based on the resistances in series model; (4) the counter current gas and liquid streams in the absorption beds are in plug flow; (5) gas to liquid mass transfer of N\textsubscript{2} and H\textsubscript{2} is negligible because of their low solubility in formalin; (6) the liquid in the partial draw off tray and at the bottom of the column (the buffers for the recirculation pumps) is ideally mixed and heat and mass transfer to this liquid is negligible.

With these assumptions, the component balances for the gas and liquid phases read...
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\[ \frac{dv_i}{dz} = -J_{i,g}aS \quad (i = F, W) \]  
(13)

\[ \frac{dl_i}{dz} = -J_{i,l}aS - R_i \varepsilon_i S \quad (i = F, W, WF_n; n = 1, n_{max}) \]  
(14)

The energy balances for the gas and liquid phases are

\[ \sum_i \left( v_i C_{p,i,g} \right) \frac{dT_g}{dz} = -q_g aS \]  
(15)

\[ \sum_i \left( l_i C_{p,i,l} \right) \frac{dT_l}{dz} = -q_l aS - \varepsilon_i S \sum_j r_j (-\Delta H_R)_j \]  
(16)

The component and energy balances for the liquid on the partial draw off tray and at the bottom of the column read

\[ l_i^{out} = l_i^{in} + V_B R_i \]  
(17)

\[ (T^{out} - T^{in}) \sum_i l_i^{in} C_{p,i,l} = V_B \sum_j r_j (-\Delta H_R)_j \]  
(18)

**Mass transfer rates**

The gas phase mass fluxes are calculated from

\[ J_{i,g} = k_{g,i} (C_{i,g} - C_{i,g}^I) \quad (i = F, W) \]  
(19)

were the interfacial concentrations are coupled by

\[ C_{i,l}^I = m_i C_{i,g}^I \quad (i = F, W) \]  
(20)

The fluxes on both sides of the interface are equal:

\[ J_{i,g} = J_{i,l}^I \]  
(21)

In the liquid, the diffusional transport is accompanied by chemical reactions, which causes mass transfer enhancement. Therefore the enhancement factor, \( E_i \), is incorporated in the fluxes at the liquid side of the interface

\[ J_{i,l}^I = k_{I,i} E_i (C_{i,l}^I - C_{i,l}) \]  
(22)
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Also, the fluxes into the liquid bulk, \( J_{i,\ell} \), become different from the fluxes at the interface, \( J_{i,\ell}^l \). In a preliminary study this situation was assessed by solving the differential equations for mass transfer with reactions in the film

\[
D_{i,\ell} \frac{d^2 C_i}{dx^2} = -R_i \quad (i = F, W, WF_n; n = 1..n_{max}).
\]

Assuming the polyoxymethylene glycols are nonvolatile, the boundary conditions of eq (23) are

\[
x = 0 : \frac{dC_F}{dx} = \frac{J_{F,\ell}^l}{D_{F,\ell}}, \quad \frac{dC_W}{dx} = \frac{J_{W,\ell}^l}{D_{W,\ell}}, \quad \frac{dC_{WF_n}}{dx} = 0
\]

\[
x = \delta_\ell : C_i = C_{i,\ell}.
\]

The eqs (19)-(25) were solved numerically for a variety of conditions expected to prevail in formaldehyde absorbers, using a fourth order Runge-Kutta method in combination with a shooting method. The results showed that the polymerization reactions (4) are by far too slow to have any influence on the diffusion fluxes, and the gradients of the concentrations of the higher polyoxymethylene glycols in the film are negligible,

\[
C_{WF_n}(0 \leq x \leq \delta_\ell) = C_{WF_n,\ell} \quad (n = 2..n_{max}).
\]

On the other hand, the hydration reaction (1) causes significant mass transfer enhancement.

In column simulations it is not convenient to calculate the fluxes from the numerical integration procedure described above. Therefore, an approximate method was developed, similar to the method of Onda et al. (1970). The differential equations (23) for the formaldehyde and methylene glycol concentrations in the film are linearized by taking the water concentration in the film equal to that in the bulk. The resulting set of equations can be solved analytically to give expressions for \( E_F \) and \( J_{F,\ell}^l \)

\[
E_F = \frac{1 + \frac{D_{WF_1,\ell}}{D_{F,\ell}} K_1 C_{WF_1,\ell}}{1 + \frac{D_{WF_1,\ell}}{D_{F,\ell}} K_1 C_{WF_1,\ell} - \frac{1}{\phi_R} (1 - \frac{1}{\cosh[\phi_R]})}
\]

\[
J_{F,\ell}^l = J_{F,\ell}^l - \frac{1}{\cosh[\phi_R]} \left[ k_{WF_1} (K_1 C_{WF_1,\ell} - C_{WF_1,\ell}) + k_{WF_1} (C_{F,\ell} - C_{F,\ell} - J_{F,\ell}^l) \right]
\]
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with

$$\phi_R = \delta_t \sqrt{\frac{k_h}{D_{F,\ell}} \left( C_{W,\ell} + \frac{D_{F,\ell}}{D_{WF,\ell}} K_h \right)}.$$  \hspace{1cm} (29)

Given the bulk concentrations in both phases, all the fluxes can now be calculated iteratively from eqs (19)-(22), (27)-(29) and the balances

$$J_{W,\ell} = J_{W,\ell}^f - (J_{F,\ell}^f - J_{F,\ell})$$  \hspace{1cm} (30)

$$J_{WF,\ell} = (J_{F,\ell}^f - J_{F,\ell}).$$  \hspace{1cm} (31)

The mass transfer rates calculated this way proved almost identical to the ones obtained by numerically solving eqs (19)-(25).

**Energy transfer rates**

The energy transfer rates contain a conductive and a convective part

$$E_j = q_j + \sum_i J_{i,j} H_{i,j}(T_j) \quad (j = g \text{ or } \ell).$$  \hspace{1cm} (32)

The film model of simultaneous mass and energy transfer leads to (p.e. Krishna and Taylor, 1986)

$$q_j = h_j A_f (T_j - T^f) \quad (j = g \text{ or } \ell)$$  \hspace{1cm} (33)

where $A_f$ is the Ackermann heat transfer correction factor for non-zero mass transfer fluxes in phase $j$

$$A_f = \frac{C_f}{e^{C_f} - 1}$$  \hspace{1cm} (34)

$$C_f = \frac{\sum_i J_{i,j} C_{p,i,j}}{h_j} \quad (j = g \text{ or } \ell).$$  \hspace{1cm} (35)

The interfacial temperature, $T^f$, follows from a balance around the interfacial region, $E_g = E_{\ell}$:

$$q_g + \sum_i J_{i,g} H_{i,g}(T_g) = q_{\ell} + \sum_i J_{i,\ell} H_{i,\ell}(T_{\ell}).$$  \hspace{1cm} (36)
This balance can be rewritten as

\[ q_i = q_g + \sum_i J_{i,g} \left[ C_{i,g} \left(T_g - T_i\right) + \Delta H_{vap,i}\right] + \sum_i J_{i,i} C_{i,i} \left(T_i^f - T_i\right) + (J_{F,i}^f - J_{F,i})(-\Delta H_R)_h \]  \hspace{1cm} (37)

### Physical and chemical parameters

The mass transfer coefficients, \( k_{i,g} \) and \( k_{i,i} \), and the specific area, \( a \), were calculated from Onda et al. (1968). The partial liquid hold up, \( \varepsilon_i \), was taken from Otake and Kunigita (1958). The heat transfer coefficients, \( h_g \) and \( h_i \), were evaluated from the mass transfer coefficients using the Chilton-Colburn analogy.

To predict the heat and mass transfer coefficients, pure component and mixture physical properties are needed. The pure component properties were taken from Daubert and Danner (1985), or if not available, calculated using the predictive methods recommended by Reid et al. (1988). Densities and viscosities of the liquid were taken from Appendix A. Other mixture properties were calculated from the mixing rules recommended by Reid et al. (1988).

The reaction rate and equilibrium constant of the hydration reaction, \( h_k \) and \( h_K \), were taken from the results reported in Chapters 2 and 4 of this thesis. The reaction rate and the equilibrium constants of the polymerization reactions, \( k_j \) and \( K_j \) \((j=2..n_{max})\), were measured by Dankelman et al. (1988) over the temperature range of 293-353 K.

### Vapor liquid equilibria

Generally, at low pressure, vapor phase non-ideality can be neglected, and vapor-liquid equilibria can be described with

\[ y_i P = \gamma_i x_i P_i^F \]  \hspace{1cm} (38)

where the liquid phase non-ideality is accounted for by the activity coefficient, \( \gamma_i \), which usually is temperature and composition dependent.

The interpretation of published vapor-liquid equilibrium data for the formaldehyde-water system is complicated by the fact that the analytical methods, used by various authors, do not distinguish between different forms of formaldehyde present in the system, and the experimental results are presented in terms of overall compositions.

To find vapor liquid equilibrium relationships for formaldehyde and water, experimental data were used of Kogan et al. (1977), Maurer (1986) and Hasse (1990). First the true molar fractions were calculated from the reported overall composition and the equilibrium relations (3) and (6). After this, for each experimental point, the quantity \( \gamma_i P_i^F \) was calculated.

Finally, $\gamma FP_F^S$ and $\gamma WP_W^S$ were smoothed as a function of T and liquid phase composition

$$\gamma FP_F^S = \exp[25.4822 - \frac{3146.86}{T} - 7.3681 \times 10^{-5} W_F T + 3.0723 \times 10^{-2} W_F^2 - 7.9198 \times 10^{-5} W_F^2] \quad (39)$$

$$\gamma WP_W^S = \exp[22.0428 - \frac{3140.75}{T - 74.65}]. \quad (40)$$
Equations (39) and (40) are illustrated in Figs 3 and 4. The deviation of the calculated lines from the experimental points is generally within the experimental accuracy limits, the mean deviations are 3.4% for formaldehyde and 1.5% for water. The equilibrium ratio \( m_i \) (eq 20) can now easily be calculated from

\[
m_i = \frac{C_{\text{tot},i}RT}{\gamma_i P_i^s}.
\]  

(41)
Computational method

The eqs (13)-(16) form a set of 16 coupled non-linear differential equations which describe an absorption bed. If the entering gas and liquid streams are specified, a two point boundary value problem results. Several strategies for solving this type of problems for absorbers have been put forward.

Treybal (1969) used a shooting method to model single solute systems. This method starts by assigning trial values to the outlet gas stream conditions, and calculating the outlet liquid conditions from overall balances. The numerical integration from bottom to top has to be repeated until convergency is achieved on the trial values. Feintuch and Treybal (1978) extended this model to multicomponent systems, but reported convergence problems due to equations becoming mathematical indeterminate in one of several nested iteration loops. Kelly et al. (1984) used the shooting method to model the physical absorption of acid gases in methanol.

Another way to solve the set of equations is by dynamic simulation. Von Stockar and Wilke (1977), using a relaxation technique developed by Stilchmair (1972) and Bourne et al. (1974) for plate columns, could avoid convergence problems by simulating the packed column start-up and integrating the model equations with respect to time up to steady state. Hitch et al. (1987) also developed an unsteady-state solution algorithm. Besides the advantage of providing information on transient behaviour, they state that the relaxation method can handle complex systems without the convergence problems encountered with other methods. This type of method is highly stable because it follows the actual behaviour of start-up procedures.

Srivastava and Joseph (1984) solved the two-point boundary value problem associated with packed separation columns by using orthogonal collocation for the spatial discretisation. Though the method worked well for the steady state calculation of a binary system, with multicomponent systems no steady state solution could be obtained directly. A dynamic simulation had to be carried out to find the steady state as the asymptote of the transient response.

All methods mentioned above have been applied for single absorption beds, with specified entering gas and liquid streams. The formaldehyde absorber considered here, however, consists of two packed beds (Fig. 1). A further complicating factor, from the problem solving point of view, is the presence of the liquid recirculations around each packed bed. Figure 5 shows the streams that have to be considered in modeling the formaldehyde absorber. Specified are the input streams 1A, 7 and 10, and the temperature and total mass flow of the liquid recycle streams 5A and 5B. The actual entering streams of the packed beds are a priori unknown.

Because of its superior convergency and stability characteristics, a transient approach was used to solve the equations that describe the absorber. Initially, the composition of the liquid in both packed beds, and of the liquid streams shown in Fig. 5, are all set equal to that of the make-up stream 1A (pure water). The liquid temperatures in and around each bed are initially set equal to the corresponding liquid recycle stream temperatures, which are input parameters.
After initialization, a two-step cycle procedure is started. The first step starts with the specified conditions of the gas feed stream 7, to integrate the eqs (13) and (15) up the bottom bed. The resulting molar flows and temperature of stream 8 are used as the starting values to integrate eqs (13) and (15) up the top bed. During the integrations, the interphase fluxes are calculated using the stored liquid phase conditions. The calculated values of $g_T$, $v_F$, and $v_W$ in the absorption beds are stored. In the second step, new liquid phase conditions are calculated. Starting with the specified conditions of stream 1A and the old values of stream 5A, the molar flows and temperature of stream 2A are calculated, and used as starting values for the integration of eqs (14) and (16) down the top bed. During this integration, the calculated liquid phase conditions are used in conjunction with the stored gas phase conditions to obtain the mass and heat fluxes. Next, eqs (17) and (18) are used to calculate stream 4A. The molar flows of stream 5A follow from the molar fractions, and the specified total mass flow rate of stream 5A. The temperature of 1B is set equal to that of 4A, and the molar flow rates follow from the differences between 4A and 5A. Now, the same sequence is repeated for the lower section of the formaldehyde absorber, to arrive at stream 6.

The sequential update of gas and liquid phase conditions is repeated until the differences between successively calculated molar flow rates and temperatures have fallen below preset criteria, and steady state is reached, see Fig. 6. In practice 40 to 60 iterations were required, depending somewhat on the operating conditions.

In contrast to the unsteady-state algorithms found in the literature, this algorithm does not need a separate routine for the calculation of time derivatives and advancement in the time direction. Furthermore, our algorithm contains only one level of nested iteration (which is the calculation of the interfacial conditions necessary to obtain the fluxes in the packed beds, and the calculation of the streams 4A and 4B from the non-linear algebraic eqs (17) and (18)).
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Fig. 6. Logic flow diagram for computing the absorber.

Results

A typical set of calculated temperature and vapor phase molar flow profiles is shown in Fig. 7. The presence of two packed absorption beds is clearly revealed in this figure. The occurrence of temperature maxima, found here in the bottom bed, is often encountered in exothermic absorption with solvent evaporation (e.g. experimental observations of Raal and Khurana (1973) and Bourne et al. (1974), and calculations of Stockar and Wilke (1977) and Krishnamurty and Taylor (1986)). The liquid flowing down from the upper part of the bottom bed increases in temperature due to the heats of absorption and reaction. But lower in the bottom bed, the liquid meets an unsaturated gas flow, and the heat effect of solvent evaporation causes a drop in $T_l$. Because $T_{ln} < T_i$ the gas temperature rises while flowing upwards, until a maximum is reached. Above the maximum $T_g$ exceeds $T_i$, with the former decreasing because the energy transfer is now directed towards the liquid.

The features of the temperature profiles are reflected in the profile of the molar flow rate of water in the gas phase, see Fig. 7. The mass transfer of formaldehyde, on the other hand, is always directed towards the liquid and is not influenced much by the changes in temperature. Therefore, the gas phase molar flow rate of formaldehyde is monotonously decreasing. The profiles of the liquid phase molar flows are not very exciting due to the large liquid recycle ratio's used in formaldehyde absorbers.

The influence of several operating parameters on the performance of the absorber was investigated. Important output parameters are the temperature rise of the liquid in each of the packed beds, $\Delta T_l$, the relative amount of formaldehyde that leaves the absorber with
the tail gas, $v_F^{\text{out}} / v_F^{\text{in}}$, and the composition of the liquid streams leaving each of the packed beds, calculated here as the overall weight percentage formaldehyde, $W_F$.

The influence of the recycle ratio's is shown in Figs 8 and 9. $R$ is defined here as the ratio of the liquid mass flow rates of 5A and 1B for the top bed, and 5B and 6 for the bottom bed (see Fig. 5). Increasing the recycle ratio increases the absorber efficiency, i.e. reduces $v_F^{\text{out}} / v_F^{\text{in}}$. This is caused by a combination of more favourable hydrodynamics and lower mean temperatures. For example, increasing $R_b$ has virtually no influence on $\Delta T_{f, b}$, but decreases the internal maximum of the temperature profile.

Figures 10 and 11 show that increasing the temperature of a liquid recycle has a negative effect on the absorber efficiency. Increase of $T_{f, \text{Rec}}$ causes a decrease of the amount of formaldehyde absorbed in the top bed, but an even larger decrease of the amount of water absorbed in this bed. This results in a reduction of the temperature rise of the liquid in the top bed, and a larger weight percentage formaldehyde in the liquid leaving both beds, see Fig. 10. The overall temperature rise of the liquid in the bottom bed with increasing $T_{b, \text{Rec}}$ becomes even negative, see Fig. 11, due to the increasing water evaporation. This is of course a hypothetical situation, because it would mean that the heat exchanger in the recycle would have to heat up instead of cooling the liquid stream.
Fig. 8. Influence of $R_t$ on $\Delta T_f$, $v_F^{\text{out}} / v_F^{\text{in}}$ and $W_F$.

Fig. 9. Influence of $R_b$ on $\Delta T_f$, $v_F^{\text{out}} / v_F^{\text{in}}$ and $W_F$. 
Fig. 10. Influence of $T_t^{Re}$ on $\Delta T_t$, $v_F^{out}/v_F^{in}$ and $W_F$.

Fig. 11. Influence of $T_b^{Re}$ on $\Delta T_t$, $v_F^{out}/v_F^{in}$ and $W_F$. 
Increasing the amount of make-up water has a positive influence on the absorber efficiency, see Fig. 12. This is caused by a reduction of the formaldehyde content of the liquid, which reduces the backpressure from the liquid phase. However, this reduction in $W_F$ is often undesirable because of extra storage and transport costs.

A higher pressure increases the driving forces for absorption, thus reducing $v_F^{\text{out}} / v_F^{\text{in}}$, see Fig. 13. However, the extra water absorption is even higher, so that $W_F$ still will be reduced. In practice, this can be compensated for by reducing the amount of make-up water.

Finally, the influence of varying the total feed rate (streams 7 and 10 in Fig. 5) is illustrated in Fig. 14 for both a constant and a proportionally increased make-up water supply. With increasing column loads, $\Delta T_t^L$ increases while the absorption efficiency $(1 - v_F^{\text{out}} / v_F^{\text{in}})$ goes down. With a constant make-up, not only a decrease but surprisingly also an increase in the relative feed rates results in a diluted liquid product. The latter effect is caused by a stronger reduction of formaldehyde absorption efficiency relative to water: a maximum of $W_F$ results.

The model was tested by simulating industrial absorbers of two plants of Dynea B.V., The Netherlands: one absorber with a configuration as shown in Fig. 1, and another absorber with three packed beds and a slightly different configuration. In both cases, using the actual operating parameters, the model could very well predict the performance of the columns.
Next, the model was used to optimize the performance of the first absorber, by simultaneously varying the parameters shown in Figs 8-12 and 14. This resulted in a savings of 1% in the costs of methanol (the basic material for making formaldehyde) for this particular formaldehyde plant.

Conclusions

The absorption of formaldehyde is an important step in the industrial formalin production. In the absorber column, the process of formaldehyde and water absorption is accompanied by a number of reactions in the liquid phase and considerable heat effects, necessitating separate liquid recycles with external heat exchangers. For the simulation of this type of column we developed a model based on the appropriate differential equations, without using HETP or HTU concepts. The model is completely predictive. The convergence problems often encountered with this type of complex modeling could be avoided by using a stable, semi-transient solution-algorithm.
Fig. 14. Influence of the relative feed rate on $\Delta T_L$, $v_F^\text{out} / v_F^\text{in}$ and $W_F$.

Our results from simulations with varying process parameters suggest favourable absorber performance with high liquid recycle ratio's (Figs 8 and 9), low temperatures of the recirculated liquid (Figs 10 and 11) and a large amount of make-up water (Fig. 12), although the latter may be limited by a minimum desired formaldehyde content of the product stream.

The suggestions mentioned above have been tested in practice and have led to a more efficient absorption column.