

## ANALYSIS OF SEPARATION OF A WATER-METHANOL-FORMALDEHYDE MIXTURE

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### Abstract

Vacuum distillation of methanol from aqueous formaldehyde solution is an important step in the production of formaldehyde by the silver process. In this work the separation of this reactive ternary mixture is discussed. The physico-chemical phase equilibrium model proposed by Maurer was used in order to investigate the influence of some operating parameters on the performance of the column. The overall column efficiency was determined and compared with the efficiencies obtained from hydrodynamic conditions. The residence times of the liquid on actual trays were compared with reaction times of the most important chemical reactions in aqueous and methanolic formaldehyde solutions.

### Introduction

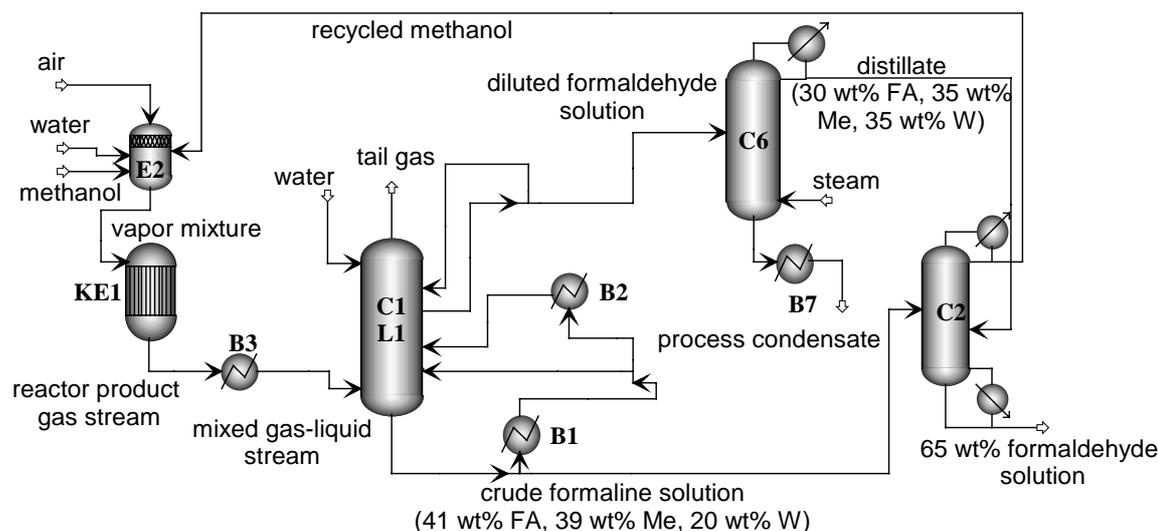
Formaldehyde is an important raw material in the production of a variety of end products like resins, plastics and adhesives, produced by the condensation of formaldehyde with phenol, urea, melamine and some alcohols. The annual production of formaldehyde in Europe is around 3,100 kt (based on pure formaldehyde) distributed among 72 production plants. The annual production growth in the past decade was 3%, while a 2% production growth is expected for the next few years.<sup>1</sup>

Formaldehyde is commercially available in the form of 37 wt% water solution because of its high reactivity. Sometimes small amounts of methanol are added to enhance the solubility of formaldehyde. The manufacturing process starts with the catalytic oxidation of methanol using different types of catalysts. In general two types of processes are used today.<sup>1</sup> The first one, based on partial oxidation and reduction process at 600 °C on silver grains, works with the excess of methanol above the upper explosion limit of the mixture methanol-air. The second metal-oxide process with the excess of air works under the lower explosion limit of the mixture. In Europe the whole production

capacity is equally distributed between both processes, although metal-oxide process plants were mainly built in the last decade.

The conversion of methanol to formaldehyde in the silver process is normally between 77% and 87%, while in some older production plants it can be only 55%. The reactor product gas stream consists of  $N_2$ ,  $H_2$ , water vapor, formaldehyde, unreacted methanol and some by-products. The main difference between the two processes is the composition of the solution leaving the absorber. Namely, the solution in the silver process contains a high fraction of unconverted methanol. This has to be removed by means of vacuum distillation and returned to the reaction stage.

The production of formaldehyde according to the silver process consists of five main steps:<sup>2</sup> preparation of the methanol-air vapor mixture, partial oxidation and reduction, absorption of formaldehyde, vacuum distillation and stripping. The process scheme of formaldehyde production by the silver process is shown in Figure 1.



**Figure 1.** Process scheme of formaldehyde production by the silver process. E2-vaporizer, KE1-reactor, C1L1- absorber, C2- vacuum distillation column, C6- stripping column, B1, B2, B3, B7- heat exchanger, FA- formaldehyde, Me- methanol, W- water

Air saturated with methanol and water vapors is passed over hot silver grains, where methanol is converted to formaldehyde by partial oxidation and reduction at ambient pressure and temperature between 590 °C and 650 °C. The reactor product gas

stream is partially condensed and the gas-liquid stream is fed to the bottom of the absorber with temperature around 115 °C. The absorber is divided into two parts. At the top of the upper part water enters that serves for cooling and absorbing formaldehyde and water from the gas stream. Indirect cooling is additionally provided on some plates by using methanol. The liquid that is partially drawn off the last plate of the upper part is mainly recycled, and a smaller stream is fed to the stripping column. The lower part of the absorber has two recycles. The bottom product (crude formalin), which consists of formaldehyde, methanol and water, represents the main feed stream to the vacuum distillation column, where methanol is separated from the formaldehyde-water mixture.

The modeling and simulation of an industrial formaldehyde absorber was discussed by Winkelman et al.,<sup>3</sup> where the system was simplified by neglecting the presence of methanol in the process. A differential model was used to simulate the performance of the industrial absorber, taking into account chemical reactions in the liquid phase besides the diffusional transport.

Different research groups have been working on modeling of thermodynamic properties of formaldehyde mixtures, which are very complex since formaldehyde reacts with water and methanol and forms different adducts. A successfully applied physico-chemical model has been developed by Maurer.<sup>4</sup> The model has been continuously improved and extended by including new experimental VLE data.<sup>5-9</sup> An enthalpy model has been developed<sup>10</sup> and further improved.<sup>11,7</sup> The reversible hydration of formaldehyde has been studied by Zavitsas et al.,<sup>12</sup> and oligomer distribution of poly(oxymethylene) glycols, appearing in formalin solution has been presented for the first time by Dankelman and Daemen<sup>13</sup> by using GC and NMR analysis. Kinetics of the desolvation of formaldehyde in aqueous and methanolic solutions has been discussed by Rudnev et al.<sup>14</sup> Rate constants for the formation of poly(oxymethylene) glycols in aqueous formaldehyde solutions have been determined by Hasse and Maurer,<sup>15</sup> who measured the density changes of the solution after dilution with water. Chemical equilibria of the poly(oxymethylene) glycol formation in aqueous formaldehyde solutions and of poly(oxymethylene) hemiformal formation in methanolic formaldehyde solutions have been studied by Hahnenstein et al.<sup>16</sup> using <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The rate constants of formaldehyde polymer formation in water, deuterium oxide and methanol, obtained from NMR and high-resolution density data depend on temperature and pH.<sup>17</sup>

Some authors<sup>9,18</sup> have suggested that reaction and transport kinetics become important in the design of separation equipment at lower temperatures. Hahnenstein et al.<sup>18</sup> suppose that at higher temperatures successful design of separation equipment is possible with the presented equilibrium model and that tray efficiencies can be predicted reliably.

In the present work, separation of the ternary mixture water-formaldehyde-methanol in the vacuum distillation column was studied in order to investigate the influence of some operating parameters on the performance of the column. Two streams enter the simulated column. The first one represents the bottom product from the absorber with the approximate temperature 64 °C, and the second one with the temperature 130 °C is a part of the condensed vapors leaving the stripping column. The operating pressure of the column is 0.50 bar. The column should effectively separate methanol from the formaldehyde- water mixture. The allowed maximum concentration of methanol at the bottom of the distillation column is 1.5%. The column has valve trays.

### Methods

An equilibrium stage model was used to describe tray column. The physico-chemical phase equilibrium model for multicomponent formaldehyde-containing mixtures of Maurer<sup>4</sup> was used with further extension and revision.<sup>5-7,10</sup> The enthalpies model was that presented by Hasse and Maurer,<sup>10</sup> improved by Liu et al.<sup>11</sup> and Albert et al.<sup>7</sup>

The following reactions were considered in this work:

- the methylene glycol (HOCH<sub>2</sub>OH) formation



- the formation of di(oxymethylene) glycol and tri(oxymethylene) glycol



- the hemiformal (HOCH<sub>2</sub>OCH<sub>3</sub>) formation



- the formation of di(oxymethylene) hemiformal (HO(CH<sub>2</sub>O)<sub>2</sub>CH<sub>3</sub>)



Empirical rules for valve trays summarized in a book by Lockett<sup>19</sup> and in the manual by Zuiderweg<sup>20</sup> were used to check the process conditions and the type of flow regime on each tray.

### Results and discussion

The simulation was carried out by using the process simulator ASPEN PLUS<sup>®</sup>. The model accounted for the presence of eight components in the liquid phase, namely monomeric formaldehyde, water, methylene glycol, di- and tri(oxyethylene) glycol, methanol, hemiformal, and di(oxyethylene) hemiformal. Physical interactions between those species as well as chemical reactions via “pseudo”-chemical-reaction equilibrium constants were taken into account. By using this model we tried to reproduce the conditions on the actual column, having 66 single-pass valve trays. The simulation has shown that the required separation in the vacuum distillation column can be achieved by using the reflux ratio 2, which was found as the lowest ratio giving a 99.9% distillate. In order to find the cause of using a high reflux ratio (5.5) on the actual column, hydrodynamic limits of trays were checked along the column.

Design graphs constructed by Zuiderweg,<sup>20</sup> which cover both the entrainment and the bed expansion limits, and operating diagrams by Fair,<sup>21</sup> in terms of flow parameter, were used. Since the trays are of valve type, weeping of the tray was neglected. The trays were checked for entrainment flooding and downflow flooding taking into account the geometrical and physical factors. Considering liquid and gas velocities on the tray, the froth flow regime on the tray was found to be present.

The hydraulic conditions on two check-trays along the column for three different reflux ratios 2, 5 and 5.5 at a constant distillate flow rate are given in Table 1.

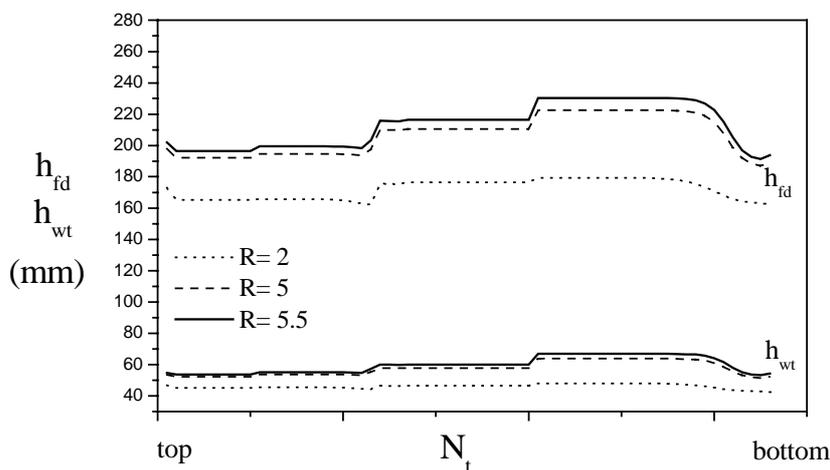
The linear gas velocity, based on the net area, is well below the flooding gas velocity. At reflux ratio 2, it represents around 40% of the flooding gas velocity and at the highest reflux ratio around 88%. In all cases, the flow parameter is small, corresponding to the mixed-froth regime. The estimated entrainment fraction of the liquid due to Fair<sup>19</sup> is small for the first reflux ratio, while at higher reflux ratios the fraction of entrainment can be considerable and can reduce the efficiency.

The downcomer backup was checked not to exceed the tray spacing. It is shown in Figure 2 together with the total pressure drop on the wet tray.

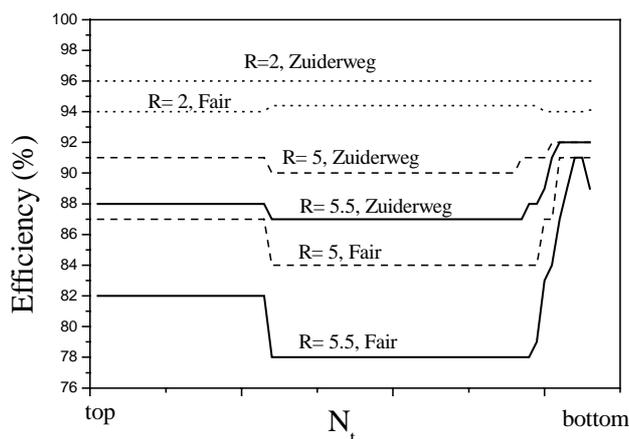
**Table 1.** Hydraulic conditions along the column.

R	2		5		5.5	
Tray position	top	bottom	top	bottom	top	bottom
L(kg/h)	4939.2	8757.1	12348.0	13166.9	13582.8	13867.3
V(kg/h)	7377.6	4910.6	14786.4	9320.3	16021.2	10020.7
Q <sub>L</sub> (l/min)	106.9	137.1	267.1	218.5	293.8	231.3
Q <sub>V</sub> (l/s)	3384.7	4272.9	6783.8	8158.1	7350.3	8775.0
ρ <sub>L</sub> (kg/m <sup>3</sup> )	770.4	1064.5	770.4	1004.5	770.4	999.3
FP (/)	0.019	0.031	0.023	0.025	0.024	0.025
CF' (ft/s)	0.24	0.23	0.24	0.23	0.24	0.23
U <sub>vn,flood</sub> (m/s)	2.60	3.26	2.60	3.17	2.61	3.16
Q <sub>v,flood</sub> (l/s)	9070.5	11373.1	9070.5	11054.2	9108.3	11025.8
U <sub>vn,actual</sub> (m/s)	1.06	1.34	2.13	2.57	2.31	2.76
(Q <sub>L</sub> /L <sub>w</sub> )*1000 (m <sup>3</sup> m <sup>-1</sup> s <sup>-1</sup> )	1.179	1.513	2.949	2.411	3.243	2.553
σ/ρ <sub>V</sub> (m <sup>3</sup> s <sup>-2</sup> )	0.034	0.185	0.034	0.188	0.034	0.189
ρ <sub>L</sub> -ρ <sub>V</sub> (kg/m <sup>3</sup> )	769.8	1064.2	769.8	1004.2	769.8	999.0
U <sub>s, Hofhuis</sub> (m/s)	0.748	0.738	0.799	0.771	0.807	0.776

U<sub>s, Ramm</sub> = 0.582 m/s; FP = (L/V)(ρ<sub>V</sub>/ρ<sub>L</sub>)<sup>0.5</sup>; CF' = U<sub>vn,flood</sub>(20/σ)<sup>0.2</sup>(ρ<sub>V</sub>/(ρ<sub>L</sub>-ρ<sub>V</sub>))<sup>0.5</sup>; λ<sub>s</sub> = U<sub>vn</sub>(ρ<sub>V</sub>/ρ<sub>L</sub>)<sup>0.5</sup>  
D = 76.1 kmol/h (2430 kg/h).

**Figure 2.** The calculated total pressure drop on the wet tray and downcomer backup along the column.

From hydrodynamic conditions tray efficiencies were determined (Figure 3) using the capacity factor<sup>21</sup> and load factor λ<sub>s</sub> given by Zuiderweg.<sup>20</sup>

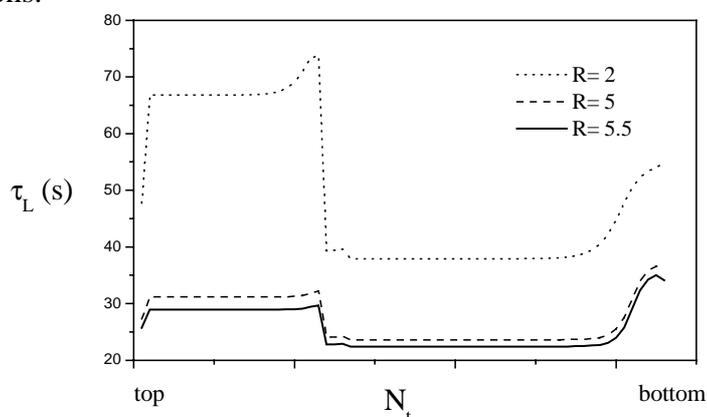


**Figure 3.** Efficiencies obtained from hydrodynamic conditions along the column using two sources.

It can be noticed that tray efficiencies are quite high with both sources. At the highest reflux ratio there is a decrease in efficiency, mainly due to a higher entrainment fraction. Tray efficiencies as well as the downcomer backup (liquid height in the downcomer is well below the tray spacing) imply that the vacuum distillation column works in a stable region even at the highest reflux ratio.

The calculation of the number of theoretical plates needed for separation that obeys the required specification has shown that only 12 equilibrium stages are needed. The overall column efficiency, expected to be above 80% considering the hydrodynamic conditions, does not exceed 20% when the equilibrium model is applied. The discrepancies in efficiencies, as pointed out by several authors, are due to departure from the equilibrium state that can be caused by mass transfer and chemical reaction kinetics.

The residence times of the liquid on actual trays were calculated at different reflux ratios (Figure 4) and compared with the approximate reaction times of the most important reactions.



**Figure 4.** The residence times of the liquid along the column.

The formation of methylene glycol and hemiformal is very fast. The former reaction time along the column is estimated at 20 ms for formation and 6 s for degradation, the latter at 9 ms for formation and 60-90 s for degradation. As can be seen, the residence times of the liquid on trays at a higher reflux ratio are approx. half (25 s) of the average at reflux ratio 2 (70 s in the upper part and 40 s in the lower part of the column). The reactions with the same order of magnitude as the residence times of the liquid are di- and tri(oxymethylene) glycol formation and degradation, while the reaction time to form di(oxymethylene) hemiformal is much longer (expressed in min). The estimated average reaction times for the formation and degradation of some relevant reactions using the temperature profile along the column at a higher reflux ratio and pH equal 3 are given in Table 2.

**Table 2.** The estimated average reaction times along the column.

type of aduct	formation		degradation	
	upper part	lower part	upper part	lower part
MG	27 ms	23 ms	8 s	6 s
HF	10 ms	9.6 ms	90 s	64 s
MG <sub>2</sub>	27 s	15 s	158 s	85 s
MG <sub>3</sub>	27 s	15 s	102 s	55 s
HF <sub>2</sub>	149 min	75 min	22 min	11 min

MG- methylene glycol, HF- hemiformal, MG<sub>2</sub>, MG<sub>3</sub>- di- and tri(oxymethylene) glycol, HF<sub>2</sub>- di(oxymethylene) hemiformal.

Both hemiformal formation and methylene glycol formation are fast compared to typical residence times in separation equipment. The degradation reaction of hemiformal is slower compared to the residence time in the vacuum distillation column, while the degradation reaction of methylene glycol falls within the residence time scale. Poly(oxymethylene) glycol formation is also fast compared to residence time, while the corresponding degradation reactions are a bit slower. Since the residence time of the liquid on the tray is shorter compared to the reaction time of poly(oxymethylene) hemiformal formation, the fraction of formaldehyde bound in higher hemiformals is small. This implies that the fractions of formaldehyde bound in different adducts differ considerably from those calculated at equilibrium state in the vacuum distillation column.

## Conclusions

The separation of the ternary mixture water-formaldehyde-methanol in the vacuum distillation column was studied by using the physico-chemical phase equilibrium model of Maurer. The accounted number of species in the simulation was eight and might be too low to give a good agreement with vapor-liquid equilibrium data in the concentration range of interest. The overall column efficiency, expected to be 80% considering hydrodynamic conditions on the trays, does not exceed 20% when the equilibrium model is applied. The discrepancies in efficiencies can be due to departure from the equilibrium state caused by chemical reaction kinetics and mass transfer.

The comparison of residence times of the liquid on actual trays with the estimated reaction times of the most important chemical reactions in aqueous and methanolic formaldehyde solutions suggested that reaction and transport kinetics is important also in designing of a vacuum distillation column working at temperatures higher than the room temperature.

## Notes

CF'	capacity parameter, ft/s	R	reflux ratio
D	distillate flow rate, kmol/h, kg/h	U <sub>s,a</sub>	superficial vapor velocity based on active area, ms <sup>-1</sup>
FP	flow parameter	U <sub>v,n</sub>	linear gas velocity based on net area, ms <sup>-1</sup>
h <sub>fd</sub>	downcomer backup, mm of liquid	V	vapor flow rate, kgh <sup>-1</sup>
h <sub>wt</sub>	wet tray pressure drop, mm of liquid	λ <sub>s</sub>	load factor, ms <sup>-1</sup>
L	liquid flow rate, kgh <sup>-1</sup>	ρ <sub>L</sub>	liquid density, kgm <sup>-3</sup>
L <sub>w</sub>	weir length, m	ρ <sub>v</sub>	vapor density, kgm <sup>-3</sup>
N <sub>t</sub>	number of theoretical stages	σ	surface tension, N m <sup>-1</sup>
Q <sub>L</sub>	liquid flow rate, m <sup>3</sup> /s	τ <sub>L</sub>	residence time of liquid, s
Q <sub>v</sub>	gas or vapor flow rate, m <sup>3</sup> /s		

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### Povzetek

Prispevek obravnava separacijo reaktivne trikomponentne mešanice voda-metanol-formaldehid z vakuumsko destilacijo, ki nastopa pri proizvodnji formaldehida s srebrovim procesom. Za modeliranje smo uporabili fizikalno-kemijski ravnotežni model z namenom ugotoviti vpliv nekaterih obratovalnih parametrov na ločitev metanola iz trikomponentne mešanice. Z modelom dobljeno empirično učinkovitost kolone smo primerjali z učinkovitostmi, izračunanimi pri določenih hidrodinamskih pogojih. Napravljena je bila tudi primerjava zadrževalnih časov tekoče faze na prekatih z reakcijskimi časi najpomembnejših reakcij v vodnih in metanolnih raztopinah formaldehida.