

ANALYSIS OF SEPARATION OF WATER-METHANOL-FORMALDEHYDE MIXTURE

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The vacuum distillation of methanol from aqueous formaldehyde solution is an important step in the production of formaldehyde by silver process.

In this work the separation of this reactive threecomponent mixture is discussed. 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. Overall column efficiency was determined and compared with the efficiencies obtained from hydrodynamic conditions. The residence times of liquid on actual trays were compared with reaction times of most important chemical reactions in aqueous and methanolic formaldehyde solutions.

INTRODUCTION

Formaldehyde is an important raw material in the production of 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 2% production growth is expected for the next few years.

Formaldehyde is commercially available in the form of 37% 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. The first one, based on partial oxidation and reduction process at 600°C on silver grains, is working 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 is working 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 silver process is normally between 77% and 87%, while in some older production plants 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 both processes is the composition of the solution, leaving the absorber. Namely, the solution in silver process contains high fraction of unconverted methanol. It has to be removed by means of vacuum distillation and returned to the reaction stage.

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

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 $590^{\circ}C$ and $650^{\circ}C$. The reactor product gas stream is partially condensed and mixed gas-liquid stream with temperature around $115^{\circ}C$ is fed to the bottom of the absorber. The absorber is divided into two parts. At the top of the upper part enters water that serves for cooling and absorbing formaldehyde and water from 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, smaller stream is fed to the stripping column. The lower part of the absorber has two recycles. The bottom product (crude formalin) that consists of formaldehyde, methanol and water represents the main feed stream to the vacuum distillation column, where methanol is separated from formaldehyde-water mixture.

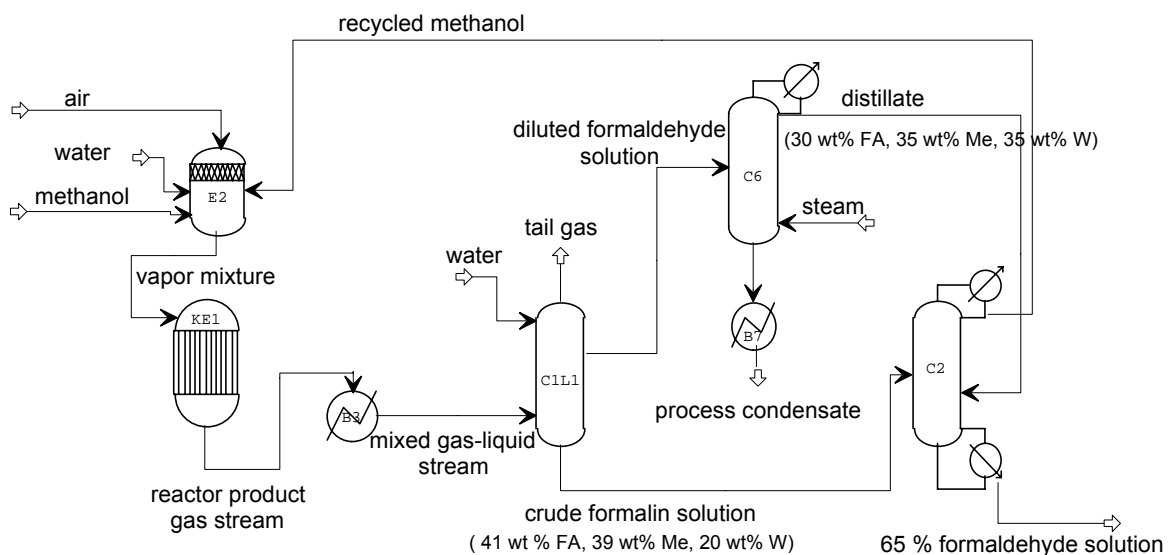


Figure 1. Process scheme of the formaldehyde production by silver process
Legend: E2- vaporizer, KE1- reactor, C1L1- absorber, C2- vacuum distillation column, C6- stripping column, B3- partial condenser, B7- condenser, FA- formaldehyde, Me- methanol, W- water

The modeling and simulation of industrial formaldehyde absorber was discussed by Winkelman et al. [1], where the system was simplified by neglecting the presence of methanol in the process. A differential model was used to simulate the performance of industrial absorber, taking into account chemical reactions in the liquid phase besides the diffusional transport.

Different research groups were working on modeling of thermodynamic properties of formaldehyde mixtures, which are very complex, since formaldehyde reacts with water and methanol and forms different adducts. Very successful applied physico-chemical model was given by Maurer [2]. The model has been continuously improved and extended by including new experimental VLE data [3, 4, 5, 6, 7]. An enthalpy model was developed [8] and further improved [9, 5]. The reversible hydration of formaldehyde was studied by Zavitsas et al. [10], oligomer distribution of poly(oxymethylene) glycols, appearing in formalin solution was presented for the first time by Dankelman and Daemen [11] by using GC and NMR analysis. Kinetics of the desolvation of formaldehyde in aqueous and methanolic solutions was discussed by Rudnev et al. [12]. Rate constants for the formation of poly(oxymethylene) glycols in aqueous formaldehyde solutions were determined by Hasse and Maurer [13], measuring the density changes of 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 were studied by Hahnenstein et al. [14] using ^1H - and ^{13}C -NMR spectroscopy. The rate constants of formaldehyde polymer formation in water, deuterium oxide and methanol, obtained from NMR and high-resolution density data were shown as a function of temperature and pH [15].

Some authors [7,16] suggested that reaction and transport kinetics become important in the design of separation equipment at lower temperatures. Hahnenstein et al. [16] supposed that at higher temperatures successful design of separation equipment is possible with the presented equilibrium model and tray efficiencies can be predicted reliably as long as the temperatures are higher than the room temperature.

In the present work, the 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 are entering the simulated column. The first one represents the bottom product from the absorber with approximate temperature 64°C , 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 formaldehyde- water mixture. The allowed maximum concentration of methanol at the bottom of the distillation column is 1.5%. The column is that of the valve tray type.

METHODS

The method for the modeling of tray column was that of equilibrium type. The physico-chemical phase equilibrium model for multicomponent formaldehyde-containing mixtures of Maurer [2] was used with further extension and revision

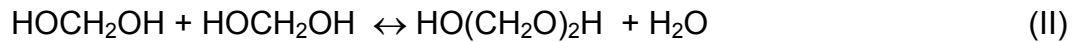
[3,4,5,8]. The enthalpies model was that presented by Hasse and Maurer [8], improved by Liu et al. [9] and Albert et al. [5].

The following reactions were considered in this work:

- the methylene glycol (HOCH₂OH) formation



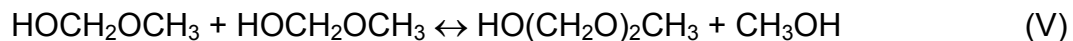
- the formation of di(oxymethylene) glycol and tri(oxymethylene) glycol



- the hemiformal (HOCH₂OCH₃) formation



- the formation of di(oxymethylene) hemiformal (HO(CH₂O)₂CH₃)



In order to check whether the process conditions are within the operating hydrodynamic limits of the tray and to find the type of flow regime at the operating conditions on the tray, empirical rules for valve trays summarized in a book by Lockett [17] and in the manual by Zuiderweg [18] were used.

RESULTS AND DISCUSSION

The simulation was carried out by using process simulator ASPEN PLUS[®]. The model accounted for the presence of eight components in the liquid phase, namely monomeric formaldehyde, water, methylene glycol, di- and tri(oxymethylene) glycol, methanol, hemiformal, di(oxymethylene) 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. Changing the operating conditions in the column, the simulation has shown that required separation (99.9% of methanol in top stream) in the vacuum distillation column can be achieved by using the reflux ratio 2 instead of 5.5, used on the actual column. In order to find the cause of using such high reflux ratios on the actual column, hydrodynamic limits of trays were checked along the column.

Design graphs, constructed by Zuiderweg [18], which cover both the entrainment and the bed expansion limits and operating diagrams by Fair [19], 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 a tray was determined. Using the

correlations of Ramm [17] and Hofhuis [17], the mixed-froth subregime was detected, where at higher gas velocities gas jets and channels occur. Flooding-gas velocities on valve trays were determined from Fair's [19] operating diagrams, using capacity factor and flow parameter. In order to determine the downcomer hydraulics, the downcomer backup (h_{fd}) was calculated from a pressure balance. The wet tray pressure drop (h_{wt}) was calculated taking into account the dry tray pressure drop, aeration factor and the clear liquid height (h_{cl}). For obtaining dry pressure drop, correlation presented by Lockett [17] and drop coefficients given by Brambila and Nencetti [17] were used. Pressure drop through the aerated liquid (βh_{cl}) on the valve tray was calculated as the sum of two contributions. The first contribution h_{ow} , height of crest over weir, was obtained by using Francis weir equation. The second one h_{udc} , the pressure drop under the downcomer, as millimeters of liquid, was estimated from the correlation $h_{udc} = 165.2 (Q_L/A_{da})^2$.

Based on hydrodynamic conditions on the trays (gas phase kinetic energy term or load factor λ_s), tray efficiencies were determined, according to diagram presented in Perry [19] and given by Zuiderweg [18].

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

Table 1. Hydraulic conditions along the column

D= 76.1 kmol/h

R	2		5		5.5	
	top	bottom	top	bottom	top	bottom
Tray position						
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_L (l/min)	106.9	137.1	267.1	218.5	293.8	231.3
Q_V (l/s)	3384.7	4272.9	6783.8	8158.1	7350.3	8775.0
ρ_L (kg/m ³)	770.4	1064.5	770.4	1004.5	770.4	999.3
ρ_V (kg/m ³)	0.6055	0.3192	0.6055	0.3174	0.6055	0.3172
FP (l)	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
$U_{vn, flood}$ (m/s)	2.60	3.26	2.60	3.17	2.61	3.16
$Q_{v, flood}$ (l/s)	9070.5	11373.1	9070.5	11054.2	9108.3	11025.8
$U_{vn, actual}$ (m/s)	1.065	1.344	2.134	2.566	2.312	2.761
$U_{s, a}$ (m/s)	1.065	1.344	2.134	2.566	2.312	2.761
$(Q_L/L_W) \cdot 1000$ (m ³ m ⁻¹ s ⁻¹)	1.179	1.513	2.949	2.411	3.243	2.553
σ/ρ_V (m ³ s ⁻²)	0.0336	0.1852	0.0336	0.1885	0.0336	0.1888
$\rho_L - \rho_V$ (kg/m ³)	769.79	1064.22	769.79	1004.18	769.79	999.03
$U_{s, Hofhuis}$ (m/s)	0.748	0.738	0.799	0.771	0.807	0.776

$Q_L/L_W, max = 0.01 \text{ m}^3 \text{ m}^{-1} \text{ s}^{-1}$

$U_{s, Ramm} = 0.582 \text{ m/s}$

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 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 flow rate due to Fair [17] 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 on Figure 2 together with the total pressure drop on the wet tray.

From hydrodynamic conditions tray efficiencies were determined (Figure 3) depending on the capacity factor [19] and load factor λ_s given by Zuiderweg [18].

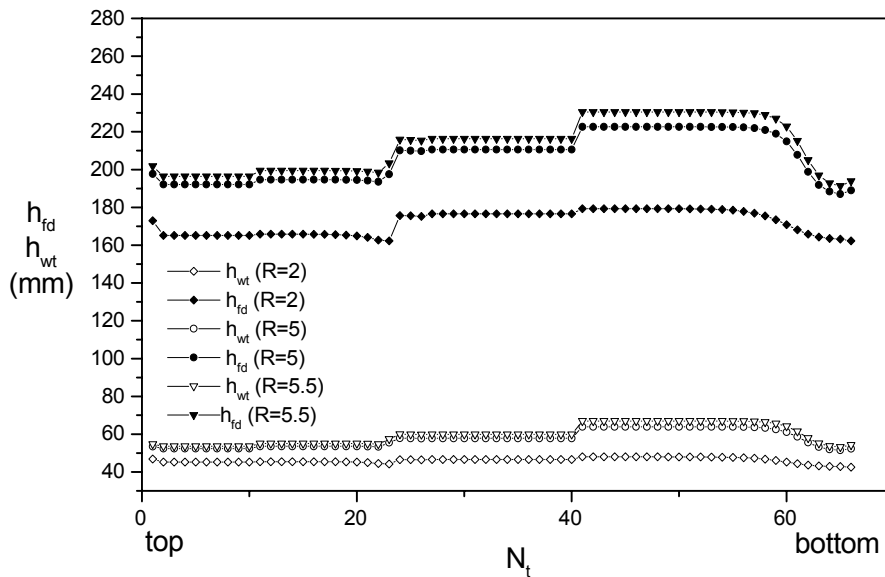


Figure 2. The calculated total pressure drop on the wet tray and downcomer backup along the column

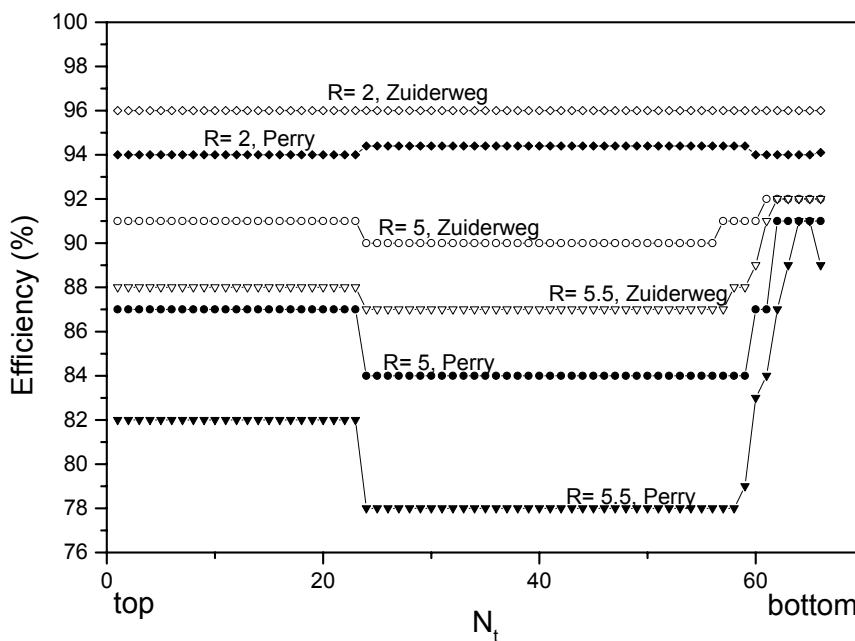


Figure 3. Efficiencies obtained from hydrodynamic conditions along the column using two sources

It can be noticed that tray efficiencies are quite high according to both sources. At highest reflux ratio there is a decrease in efficiency, mainly due to higher entrainment fraction. Tray efficiencies as well as downcomer backup (liquid height in the

downcomer is well below the tray spacing) imply, that the vacuum distillation column is working in a stable region even at highest reflux ratio.

The calculation of the number of theoretical plates needed for separation that obeys required specification has shown, that only 12 equilibrium stages are needed. The overall column efficiency using ad hoc procedure in this case does not exceed 20% average plate efficiency. This efficiency is far away from those obtained from hydrodynamic conditions.

Although we know that the efficiency concept in multicomponent mixture is extremely confusing [20], it was used to obtain a rough experience on trays. The discrepancies in efficiencies as pointed out by several authors, are due to departure from equilibrium state that can be caused by mass transfer and chemical reaction kinetics. The residence times of liquid on actual trays were calculated at different reflux ratios (Figure 4) and compared with the approximate reaction times of most important reactions.

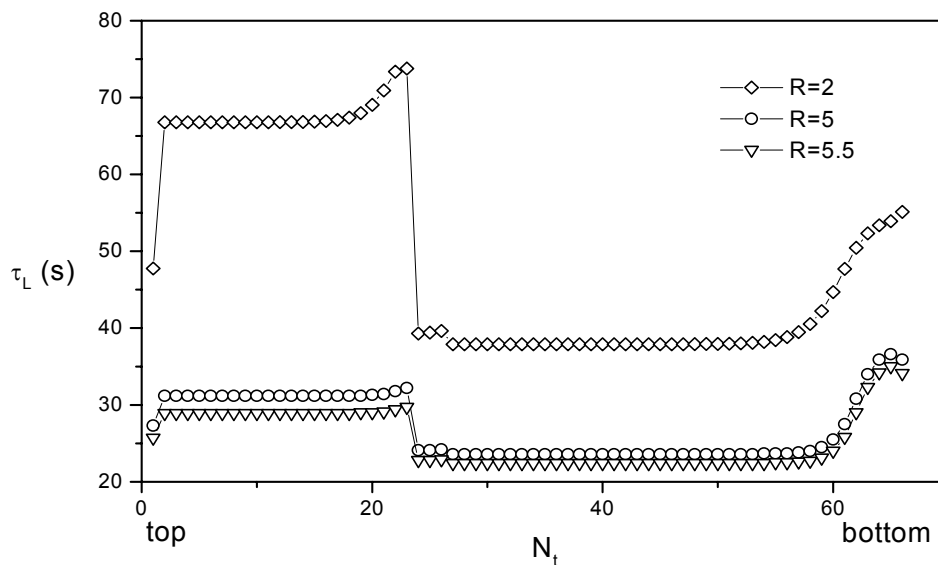


Figure 4. The residence times of liquid along the column

The formation of methylene glycol and hemiformal is very fast. The former reaction time along the column is estimated on 20 ms for formation and 6 s for degradation, the latter on 9 ms for formation and 60-90 s for degradation. As can be seen, the residence times of liquid on trays are at higher reflux ratio 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 residence times of liquid are di- and tri(oxy)methylene glycol formation and degradation, while reaction time to form di(oxy)methylene hemiformal is much longer (expressed in min). The estimated average reaction times for formation and degradation of some relevant reactions using the temperature profile along the column at 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 ₂	27 s	15 s	158 s	85 s
MG ₃	27 s	15 s	102 s	55 s
HF ₂	149 min	75 min	22 min	11 min

MG- methylene glycol, HF- hemiformal, MG₂, MG₃- di- and tri(oxymethylene) glycol, HF₂- di(oxymethylene) hemiformal

As pointed out by Hahnenstein et al. [15], 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 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, corresponding degradation reactions are a bit slower. Since the residence time of liquid on the tray is shorter compared to reaction time of poly(oxymethylene) hemiformal formation, the fraction of formaldehyde bound in higher hemiformals is small.

This implies that the fractions of formadehyde bound in different aducts differ much from those calculated at equilibrium state not only in separation equipment operated at around room temperature, but also in vacuum distillation column.

SUMMARY

The separation of the ternary mixture water-formaldehyde-methanol in the vacuum distillation column was studied by using physico-chemical phase equilibrium model of Maurer with some further extensions and revisions. The calculated overall column efficiency differed considerable from those obtained from hydrodynamic conditions in the column with actual trays. Overall column efficiency turned out not to exceed 20% average plate efficiency. The discrepancies in efficiencies can be due to departure from equilibrium state caused by chemical reaction kinetics and mass transfer.

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

NOTES

A_{da} - minimum area of flow under the downcomer apron, m²

CF- capacity parameter, ft/s

FP- flow parameter

h_{cl} - clear liquid height, mm of liquid

h_{fd} - downcomer backup, mm of liquid

h_{ow} - height of crest over wire, mm of liquid

h_{udc} - pressure drop under the downcomer, mm of liquid

h_{wt} - wet tray pressure drop, mm of liquid

L- liquid flow rate, kg h^{-1}
 L_w- weir length, m
 Q_L- liquid flow rate, m^3/s
 Q_V- gas or vapor flow rate, m^3/s
 U_d- liquid velocity in downcomer on vapor-free basis, ms^{-1}
 U_{s,a}- superficial vapor velocity based on active area, ms^{-1}
 U_{Vn}- linear gas velocity based on net area, ms^{-1}
 V- vapor flow rate, kg h^{-1}
 β- aeration factor
 λ_s- load factor, ms^{-1}
 ρ_L- liquid density, kg m^{-3}
 ρ_V- vapor density, kg m^{-3}
 σ- surface tension, N m^{-1}

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