SYMPOSIUM SERIES NO. 152 © 2006 IChemE

DEVELOPMENT OF A NEW DISTILLATION BASED PROCESS FOR TRIOXANE PRODUCTION

Thomas Grützner[1], Neven Lang[2], Markus Siegert[2], Eckard Ströfer[2], Hans Hasse[1]*
[1]Institute of Thermodynamics and Thermal Process Engineering, University of Stuttgart, Germany
[2]Chemicals Research and Engineering – Process Development GCE/C, BASF AG, Ludwigshafen, Germany

This paper reports on the development of a new process for the production of trioxane ($C_3H_6O_3$), the cyclic trimer of formaldehyde (CH_2O). Trioxane is synthesized from aqueous formaldehyde solutions using concentrated sulfuric acid as a catalyst and is mainly used for producing the high performance polymer poly(oxymethylene) (POM). As the POM market is continuously growing trioxane producers are expanding their facilities. For new plants, it would be highly desirable to replace the existing complicated trioxane process is by a simpler, more economic one.

During the past two decades, powerful models were developed for describing vapor-liquid equilibria of aqueous formaldehyde solutions, the educt for trioxane synthesis. These solutions are complex reacting multicomponent mixtures that are neither experimentally nor theoretically easy to handle. The models give new opportunities for developing an improved trioxane process. In a first step, they were used in the present work for elucidating the phase behavior of the system formaldehyde/water/trioxane. Distillation line diagrams for that system were calculated for the first time. They show a complex topology, including several pressure dependent azeoptropes and distillation boundaries. α/α-analysis shows that pure trioxane can be obtained from by a pressure swing distillation so that the undesired extraction step of the conventional process can be totally avoided. The resulting new process was also simulated rigorously. Distillation experiments were carried out to validate the results. They prove the feasibility of the separations in each column and, hence, of the entire process.

For process design also reliable information on reaction kinetics is needed. Existing data on the trioxane synthesis is contradictory and unreliable. Therefore, experiments were carried out, in which the trioxane formation in highly concentrated formaldehyde solutions containing up to 0.1 g/g sulfuric acid was studied at temperatures up to 115 °C with quantitative ^{1}H NMR spectroscopy. Using that method, for the first time reliable data on the kinetics of the trioxane formation were obtained. They were used for developing the reaction kinetic model for the process simulation.

KEYWORDS: trioxane, process development, formaldehyde, chemical kinetics, fluid-phase-equilibria, NMR-spectroscopy

*corresponding author: Prof. Dr. Hans Hasse, Institut für Technische Thermodynamik und Thermische Verfahrenstechnik, Universität Stuttgart, D-70550 Stuttgart, Germany, Phone: ++49/711/685-6105, Fax: ++49/711/685-6140, E-mail: hasse@itt.uni-stuttgart.de,
Internet: http://www.itt.uni-stuttgart.de.

INTRODUCTION

Trioxane, the cyclic trimer of formaldehyde, is mainly used for the production of poly(oxymethylene) polymers (POM), which have excellent mechanical properties and high chemical resistance. Therefore POM is used for heavy duty gear, e.g. in valves or gear boxes. For POM synthesis ultra-clean trioxane is needed as educt [1].

The process presently used for trioxane production goes back to the 1960s and is shown in Figure 1. Aqueous formaldehyde solution with a formaldehyde mass fraction of approximately 0,50 g g^{-1} is used as feedstock. In a first distillation step, the formaldehyde is concentrated to reduce the water load of the following steps. The formaldehyde-rich stream is subsequently fed into the trioxane reactor where the conversion to trioxane is takes place. As the conversion is low, tedious downstream processing is necessary. First, trioxane is concentrated in a further distillation. In a following step, trioxane is extracted into a suitable solvent. Finally, the solvent and trioxane are separated in a subsequent distillation and further purification steps are necessary until in the end pure trioxane, containing only ppm-amounts of water, is obtained. The raffinate from the extraction and other side streams need to be treated in a number of additional units.

The POM market has continuously been growing in the last decade with about 5 % p.a. [2]. Therefore, trioxane producers are expanding their production facilities in order to be able to satisfy the growing demand a competitive basis. For new plants, it would be highly desirable to replace the existing trioxane process is by a simpler, more economic one.

The aim of the present work is the development of such a new trioxane process which overcomes the intrinsic disadvantages of the existing one. The development of that new process became possible by the progress in understanding the complex chemical and physical behaviour of aqueous formaldehyde solutions during the past two decades. That progress was triggered by the introduction of NMR spectroscopy for analyzing aqueous formaldehyde solutions. No other analytical technique allows the quantification of the different formaldehyde species that is necessary for the model development.
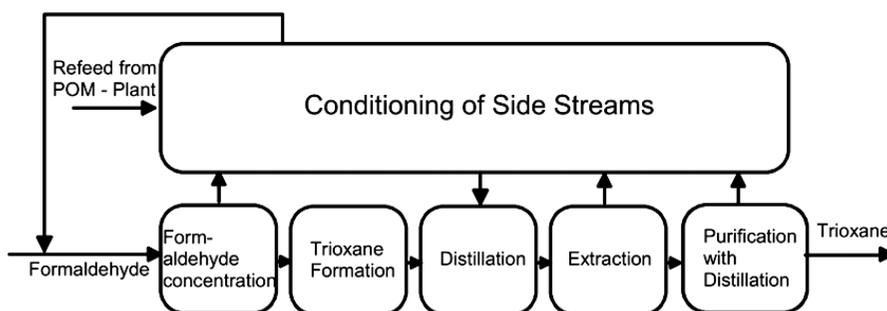
Figure 1. Simplified flow sheet of the state of the art process for trioxane production

Formaldehyde and water react forming methylene glycol (MG_1) and poly(oxy-methylene) glycols (MG_n) as shown in equations Ia, b. Therefore aqueous formaldehyde solutions are complex multicomponent reacting mixtures.

$$CH_2O + H_2O \rightleftharpoons HOCH_2OH \qquad\qquad (Ia)$$

$$HO(CH_2O)_{n-1}H + CH_2O \rightleftharpoons HO(CH_2O)_nH \qquad\qquad (Ib)$$

Trioxane is formed from aqueous formaldehyde solutions using a strong acid as a catalyst, normally concentrated sulfuric acid with mass fractions over 0.1 g g^{-1}. The most probable mechanism by which trioxane is formed is an intramolecular ring formation of the linear methylene glycol containing three CH_2O units (MG_3) according to reaction (II). In the past the trioxane formation was usually described more formally by reaction (III) [3, 4].

$$HO(CH_2O)_3H \rightleftharpoons (CH_2O)_3 + H_2O \qquad\qquad (II)$$

$$3CH_2O \rightleftharpoons (CH_2O)_3 \qquad\qquad (III)$$
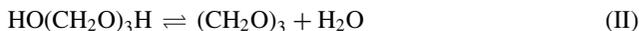
VLE-MODELING AND PHASE BEHAVIOUR

Much work has been devoted to developing physico-chemical vapor-liquid equilibrium (VLE) models for aqueous formaldehyde solutions, especially in the group of Maurer, who, after his pioneering work [5] continuously improved the model [6, 7, 8]. The VLE-model used in the present work is the latest one of that series and stems from Kuhnert [9]. As the model is presented in detail in [9], only the basic model assumptions are briefly presented here (cf. Figure 2).

The gas phase is treated as a reacting mixture of ideal gases, containing formaldehyde, water, methylene glycol and trioxane. In the liquid phase the chemical reactions leading to poly(oxymethylene) glycols (cf. equations Ia and Ib) are taken into account. The vapor pressure of the poly(oxymethylene) glycols with more than one formaldehyde block (MG_n with $n > 1$) is negligible, and hence physical equilibria have to be considered only for formaldehyde, water, methylene glycol and trioxane:

$$p_i^s \cdot x_i \cdot \gamma_i = p \cdot y_i \qquad i = FA, \ Wa, \ MG_1, \ Tri \qquad\qquad (1)$$

The activity coefficients are calculated using the UNIFAC group contribution method. The chemical equilibria are modeled in a thermodynamically consistent manner using activities. The model allows accurate descriptions of VLE of the studied system [9].

The first step in conceptual distillation process design is the calculation of the phase behaviour. For that purpose, the VLE-model of Kuhnert [9] was implemented into ASPEN PLUS [10]. The distillation lines in the system formaldehyde/water/trioxane were calculated for the first time in the present work. Some results are shown in Figure 3. Only overall concentrations are depicted, i.e. those that would be obtained if all formaldehyde
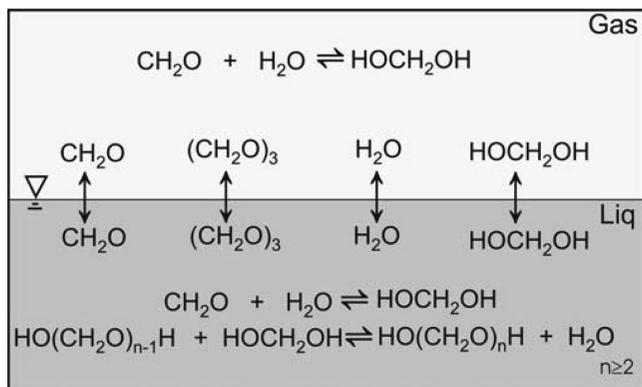
Figure 2. Vapor-liquid equilibrium model for the system formaldehyde/water/trioxane

species would decompose into formaldehyde and water. It is also overall concentrations that are determined with conventional analytics like titration. Note, that for the calculation of the VLE all species were explicitly taken into account and assumed to be in chemical equilibrium. Hence, the distillation lines shown in Figure 3 are in fact reactive distillation lines. The shaded area in Figure 3 indicates qualitatively the region at high formaldehyde concentrations where solid precipitation occurs.
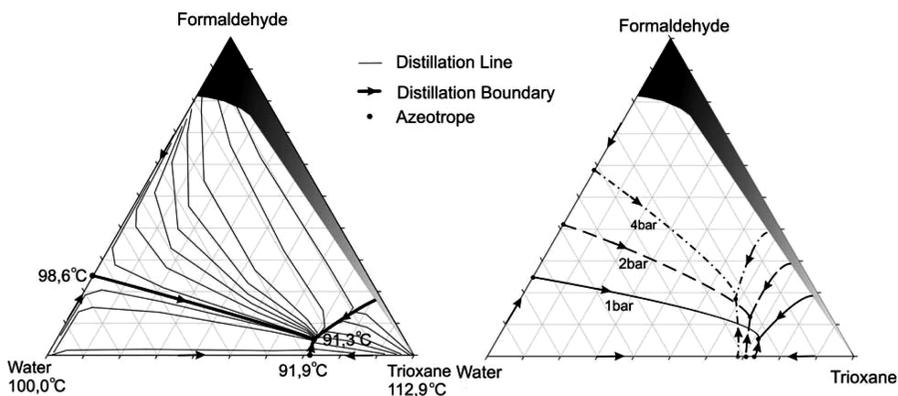
Figure 3. VLE-topology of formaldehyde/water/trioxane. Left: reactive distillation lines at $p = 1$ bar. Right: Pressure dependence of azeotropes and distillation boundaries at $p = 1$; 2; and 4 bar. All units in g g^{-1}. Shaded area: solid precipitation (qualitatively)

The system formaldehyde/water/trioxane has a complex VLE-topology. At the pressures shown in Figure 3, there is a low boiling azeotrope in the binary system for-maldehyde/water, and another in the binary system water/trioxane. Furthermore, there is a ternary azeotrope, which is the overall low boiling node in the system. The resulting distillation boundaries separate the system into three distillation areas and cannot be overcome in a simple distillation process. However, the calculations show a signifi-cant pressure dependence of the separatrices that can be exploited in a pressure swing distillation (cf. Figure 3b).

NEW TRIOXANE PROCESS

For the evaluation of process alternatives using the distillation line diagrams presented above, computer aided infinity/infinity analysis was used. The resulting basic process concept is shown in Figure 4. It consists of a reactor in which the trioxane synthesis takes place, followed by a downstream column train with three distillation columns run at different pressures.

The separations in each column are shown in Figure 5. Aqueous formaldehyde sol-ution is fed to the reactor. As the conversion is low, the reactor product contains only small amounts of trioxane (Stream 3). Column K1 produces a trioxane rich overhead product (Stream 5) with a composition close to the ternary azeotrope. The bottom product of column K1 (Stream 4), which contains high amounts of formaldehyde is recycled to the reactor. The separation in column K1 is carried out at low pressures, e.g., 1 bar, which must be chosen so that the temperature is high enough to avoid solid precipitation. The top product of column K1 is fed into column K2 which is operated at a higher pressure, e.g. 4 bar. The pressure in column K2 is limited by formaldehyde decomposition at high
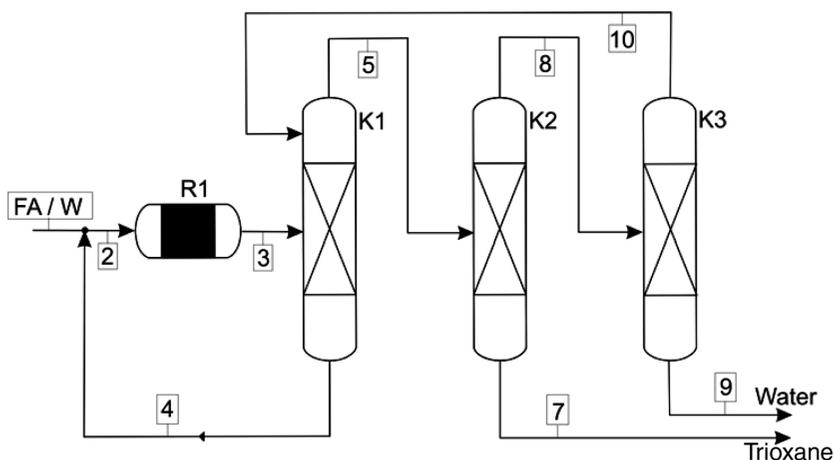
Figure 4. Flow sheet of the new distillation based trioxane process
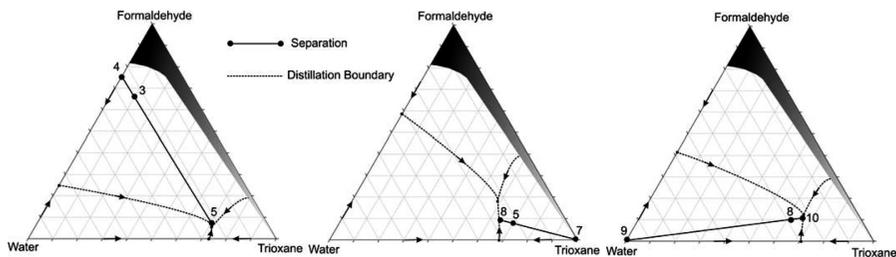
Figure 5. Separations in the three distillations of the new trioxane process: Left: K1, 1 bar; Middle: K2, 4 bar, and Right: K3, 2 bar. Numbers refer to streams in Figure 4

temperatures. Due to the increased pressure Stream 5 lies now in the distillation area where trioxane can be reached as a bottom product (Stream 7). The overhead product of column K2 (Stream 8) is separated in a third column K3 that is operated at intermediate pressure into pure water withdrawn as bottom product (Stream 9) and an overhead product (Stream 10) with a composition close to the ternary azeotrope that is recycled to K1.

DISTILLATION EXPERIMENTS AND PROCESS SIMULATION

The separations in all columns were studied in laboratory experiments. The experiments were run under infinite and finite reflux in a 50 mm vacuum column equipped with structured packing and a 30 mm tray column under elevated pressure. The experimental results verified the position of azeotropic points, their pressure dependence as well as the feasibility of all separations and, hence, the validity of the conceptual considerations discussed above and the feasibility of the new process.

The different separations were also simulated based on a stage model using the VLE model presented above, that allows taking into account the kinetics of the formation of the poly(oxymethylene) glycols. For a detailed discussion of the influence of reaction kinetics on such simulations, see Ott [10, 11, 12]. The entire process with all recycle streams was successfully simulated. For these simulations, CHEMASIM was used.

REACTION KINETIC DATA FOR TRIOXANE FORMATION

For process design also reliable information on reaction kinetics is needed. Existing data on the trioxane synthesis is contradictory and unreliable [3, 13, 14]. Therefore, experiments were carried out, in which the trioxane formation at reactor conditions was studied. ^{1}H NMR spectroscopy was used for reaction monitoring [15]. Using that method, for the first time reliable data on the kinetics of the trioxane formation were obtained. They were used for developing the reaction kinetic model for the process simulation.

The experiments are extremely challenging as highly concentrated formaldehyde solutions with large amounts of sulfuric acid have to be handled at high temperatures.
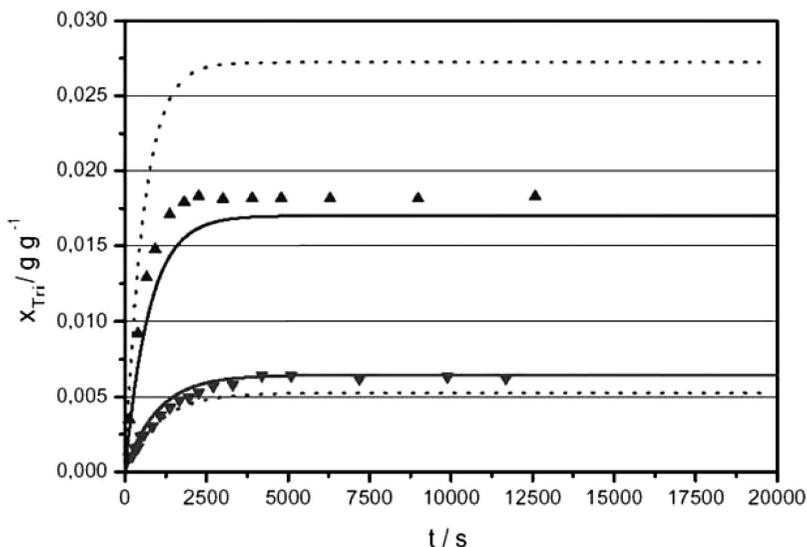
Figure 6. Reaction kinetics of the trioxane formation in an aqueous formaldehyde solution at $t = 110°C$ with 0.04 g g^{-1} sulfuric acid (initial overall formaldehyde composition ▲: 0.50 g g^{-1}; ▼: 0.30 g g^{-1}). Experimental results obtained by ^1H NMR spectroscopy and reaction kinetic model based on equation II (solid lines) and equation III (dotted lines)

Figure 6 shows a typical result. In Figure 6, also results from the reaction kinetic model are shown. That model is based on equation II, and, hence, on the knowledge of the true composition of the formaldehyde containing species. It can also be seen from Figure 6 that the alternative kinetic description based on equation III using overall concentrations does not give satisfactory results.

CONCLUSION

A new trioxane process was developed in an industrial – academic cooperation [16]. The new process is substantially simplified compared to the existing one. Its development was only possible by combining methods from conceptual process design with reliable models for the complex physico-chemical behaviour of the system formaldehyde/water/trioxane. The feasibility of the new process has been proven in laboratory experiments. Pilot plant studies are under way.

LITERATURE

1. *Ullmanns Encyclopedia of Industrial Chemistry*, 6th edition, Wiley-VCH, Weinheim, 2002.
2. N. Katalenic, M. Weber: Increased Demand: Polyoxymethylens (Polyacetals, POM), *Kunststoffe – Plast Europe*, 10, **2004**, 102–108.

3. E. Bartholomé, W. Köhler, H.-G. Schecker, G. Schulz, Reaktionstechnische und kinetische Untersuchung zur Trioxan-Synthese, *Chem. Ing. Tech.*, 43 (10), **1971**, 597–644.

4. M. Albert, *Thermodynamische Eigenschaften formaldehydhaltiger Mischungen*, Dissertation Universität Kaiserslautern, 1999.

5. G. Maurer, Vapor-Liquid Equilibrium of Formaldehyde- and Water-Containing Multicomponent Mixtures, *AIChE Journal*, 32 (6), **1986**, 932–947.

6. H. Hasse, I. Hahnenstein, G. Maurer, Revised Vapor-Liquid Equilibrium Model for Multicomponent Formaldehyde Mixtures, *AIChE Journal*, 36 (12), **1990**, 1807–1814.

7. M. Albert, B. C. Garcia, C. Kreiter, G. Maurer, Vapor-Liquid Equilibrium of Formaldehyde Mixtures: New Data and Model Revision, *AIChE Journal*, 42 (6), **1996**, 1741–1752.

8. M. Albert, I. Hahnenstein, H. Hasse, G. Maurer, Vapor-Liquid and Liquid-Liquid Equilibria in Binary and Ternary Mixtures of Water, Methanol and Methylal, *J. Chem. Eng. Data*, 46 (4), **2001**, 897–903.

9. C. Kuhnert: *Dampf-Flüssigkeits-Gleichgewichte in mehrkomponentigen formaldehydhaltigen Systemen;* Dissertation, Universität Kaiserslautern, 2004.

10. M. Ott, *Reaktionskinetik und Destillation formaldehydhaltiger Mischungen*, Dissertation, Universität Stuttgart, 2004.

11. M. Ott, H. H. Fischer, M. Maiwald, K. Albert, H. Hasse, Kinetics of Oligomerisation Reactions in Formaldehyde Solutions: NMR Experiments up to 373 K and Thermodynamically Consistent Model, *Chem. Eng. Pro.*, 44, **2005**, 653–660.

12. M. Ott, H. Schoenmakers, H. Hasse, Distillation of Formaldehyde Containing Mixtures: Laboratory Experiments, Equilibrium Stage Modeling and Simulation, *Chem. Eng. Pro.*, 44, **2005**, 687–694.

13. A. G. Gruznov, E. F. Oreshenkova, V. N. Klyuchinkov, Kinetic Study of the Formation of Methanol and Formic Acid in Aqueous Formaldehyde Solutions in the Pressence of Acids, *Plasticheskie Massy*, 4, **1996**, 12–15.

14. P. Petrov, D. Elenkov, D. Tokarev, Chemische Kinetik der Trioxan-Herstellung aus sauren konzentrierten Formaldehyd-Lösungen, *Chem. Ing. Tech.*, 42, **1970**, 549–548.

15. M. Maiwald, H. Fischer, Y.-K. Kim, K. Albert, H. Hasse, Quantitative high-resolution online NMR spectroscopy in reaction and process monitoring, *Journal of Magnetic Resonance*, 166, **2004**, 135–146

16. M. Siegert, N. Lang, E. Ströfer, A. Strammer, T. Friese, H. Hasse, Verfahren zur Abtrennung von Trioxan aus einem Trioxan/Formaldehyd/Wasser – Gemisch mittels Druckwechsel-Rektifikation, Deutsches Patent, DE10361516, 2005.