| BULETINUL | Vol. LXI | 235 - 242 | Seria Tehnică |
|--|------------|-----------|---------------|
| Universității Petrol – Gaze din Ploiești | No. 3/2009 | | |

Modeling and Simulating Reactive Distillation from Control Perspective

Ioana-Luiza Georgescu

Petroleum – Gas University of Ploiești, 39 București Blvd., Ploiești, ROMÂNIA e-mail: igeorgescu@upg-ploiesti.ro

Abstract

Reactive distillation (RD) combines a chemical reactor and a distillation column into a single operating unit. Even if the idea of combining the reaction and separation processes is quite old, it has been successfully applied in the last years, due to the advanced research made in this field. This paper presents a brief overview of modeling and simulation of reaction column. As specific application example, a methyl acetate column is considered. A simple dynamic model is given and first results of the dynamic simulation with the simulation environment DIVA are shown. The conclusions regarding simulation results will be used as support for implementing future advanced control structures for RD column.

Key words: reactive distillation, mathematical model, dynamic simulation, control.

Introduction

RD process, compared to classical distillation processes, has a high complexity, compensated by infrastructure simplification and costs reduction, as inside the reactive distillation column both reaction and separation take place. Because the processes needs less equipments, maintenance costs are also reduced – compared to classical distillation processes.

Because of the advanced research made in this field, RD has been successfully applied in the last years and it covers a wide area of commercial processes [1].

Due to the strong interaction between reaction and separation, RD processes can sometimes show an intricate nonlinear dynamic behavior including steady state multiplicities, bi-stability and self sustained nonlinear oscillation [2, 16]. Understanding all these phenomena represents not only a scientific interest, but also a necessary condition for improved process design and control of industrial processes.

During the research stage made by the author at Max Planck Institute for Dynamics of Complex Technical from Magdeburg¹, the production of methyl acetate process was investigated.

The acid catalyzed reaction was traditionally carried out using one reactor and a train of nine distillation columns. Eastman Kodak developed a RD process for producing high-purity methyl acetate [6, 17]. The process requires only one column and nearly 100% conversion of the reactant is achieved. By flashing off the methyl acetate from the reactant mixture, conversion is increased without using excess reactants. The RD has stoichiometrically balanced feeds and is

¹ http://www.mpi-magdeburg.mpg.de

designed so that the lighter reactant methanol is fed at the bottom and the heavier acid is fed at the top [17]. A single Eastman Kodak's Tennessee plant produces 180 000 tons/year of high-purity methyl acetate [17].

The capital and operating costs are significantly reduced (costs one-fifth of the capital investment of the conventional process, and consumes only one-fifth of the energy).

Dynamic RD model

Two different approaches are available in the literature for modeling RD process: the EQuilibrium stage model (EQ), where both the vapor and the liquid phases are assumed to be in thermodynamic equilibrium with each other, and the NonEQuilibrium stage models (NEQ) which follow the philosophy of rate-based models for conventional distillation [3]. In addition, the NEQ models require thermodynamic and physical properties, detailed in Taylor and Krishna's paper [4].

The model of a RD column will involve 3 parts: the column top (meaning the condenser and the reflux tank), a regular tray and the column bottom (the reboiler).

In this paper a simple model, good for further studies is presented. The basic assumptions for having a good and robust model are the following:

- the column has NSTAGE theoretical stages, including the condenser, decanter and the reboiler;
- there is constant holdup on trays (no tray hydraulics);
- constant pressure is assumed;
- negligible heat effects;
- deviations from thermodynamic equilibrium are modeled with the tray efficiency η ;
- the vapor and liquid phases on each tray are in equilibrium;
- the reaction takes place only in the liquid phase, where there is a perfect mixture between reactants and catalyst.

Taking into consideration all mentioned before, the equations specific to the sections mentioned above are the following:

A. The column top is described by the following equations:

Component material balance is described by the next equations:

$$U_{1} \frac{dx_{i,1}}{dt} = V_{2} \cdot K_{i,2} \cdot x_{i,2} - L_{1} \cdot x_{i,1} - V_{1} \cdot K_{i,1} \cdot x_{i,1} + v_{i} \cdot R(x_{1,1}, ..., x_{NC,1}) \cdot V_{1}$$
, i=1,...,NC - 1. (1)

The reactive term $v_i \cdot R_1(x_{1,1},...,x_{NC,1}) \cdot V_1$ is written separately, because it represents the only difference between the non-reactive and RD models.

Summation condition:

$$\sum_{k=1}^{NC} x_{k,1} = 1 \tag{2}$$

Phase equilibrium equation is:

$$K_{i,1} \cdot x_{i,1} \cdot p = \eta \cdot psp_{i,1} \cdot \gamma_{i,1} \cdot x_{i,1} \qquad i = 1, ..., NC$$
(3)

Summation condition is represented by the equation:

$$\sum_{k=1}^{NC} K_{k,1} x_{k,1} = 1$$
(4)

Total material balance equation is:

$$0 = -L_{1} + V_{2} - V_{1} + \sum_{k=1}^{NC} \left[V_{k} \cdot R(x_{1,1}, ..., x_{NC,1}) \cdot V_{1} \right]$$
(5)

The free variables are the distillate, the reflux or the reflux ratio. Being part of the total material balance equation means they can't be given by the user in the same time.

B. For the normal tray ("j" tray) the next equations are considered:

$$U_{j} \frac{dx_{i,j}}{dt} = L_{j-1} \cdot x_{i,j-1} + V_{j+1} \cdot K_{i,j+1} \cdot x_{i,j+1} - L_{j} \cdot x_{i,j} - V_{j} \cdot K_{i,j} \cdot x_{i,j} + F_{j} \cdot x_{F_{ij}} - D_{j} \cdot x_{i,j} + v_{i} \cdot R_{j} (x_{1,j}, \dots, x_{NC,j}) \cdot V_{R_{j}}$$

i=1,...,NC – 1. (6)

Summation condition is described by the following equation:

$$\sum_{k=1}^{NC} x_{k,j} = 1$$
(7)

Phase equilibrium equation is:

$$K_{i,k} \cdot x_{i,k} \cdot p = \eta \cdot psp_{i,k} \cdot \gamma_{i,k} \cdot x_{i,k} \qquad i = 1, \dots, NC$$
(8)

Summation condition equation is:

$$\sum_{k=1}^{NC} K_{k,j} x_{k,j} = 1$$
(9)

Total material balance for the liquid phase equation is:

$$0 = L_{j-1} - L_j + F_j - D_j + \sum_{k=1}^{NC} \left[\nu_k \cdot R(x_{1,j}, ..., x_{NC,j}) \cdot V_j \right]$$
(10)

Total material balance for the vapor phase equation is:

$$V_j = V_{j+1} \tag{11}$$

For a regular distillation tray there are no degrees of freedom (no free variables).

C. For the column bottom the equations are the following:

$$U_{NSTAGE} \frac{dx_{i,NSTAGE}}{dt} = L_{NSTAGE-1} \cdot x_{i,NSTAGE-1} - L_{NSTAGE} \cdot x_{i,NSTAGE} - V_{NSTAGE} \cdot K_{i,NSTAGE} \cdot x_{i,NSTAGE} + , + v_i \cdot R(x_{1,NSTAGE}, ..., x_{NC,NSTAGE}) \cdot V_{NSTAGE}$$

 $i = 1, ..., NC - 1$
 $i = 1, ..., NC - 1$ (12)

Summation condition is represented by the equation:

$$\sum_{k=1}^{NC} x_{k,NSTAGE} = 1 \tag{13}$$

Phase equilibrium equation is:

1.

$$K_{i,NSTAGE} \cdot x_{i,NSTAGE} \cdot p = \eta \cdot psp_{i,NSTAGE} \cdot \gamma_{i,NSTAGE} \cdot x_{i,NSTAGE} \quad i = 1, \dots, NC \quad (14)$$

Summation condition equation is:

$$\sum_{k=1}^{NC} K_{k,NSTAGE} x_{k,NSTAGE} = 1$$
(15)

Free variables are V_{NSTAGE} , reacting rate or L_{NSTAGE} . As the variables are part of the total material balance, they are not independent.

RD column details

Modeling and simulations were made on a methyl acetate RD column, which has 27 trays in all, it is a lab scale column and consists of three sections: from 1 to 6 trays is the stripping section, 7 to 17 represents reactive section and from 18 to 27 is the rectifying section (see fig. 1).



The molar fee flows of MeAc and AcH are 8.4033×10^{-4} kmol/min, respectively 8.1667×10^{-4} kmol/min, on the stages 7 and 21. The reflux ratio is set at 1.68. The column operates at a pressure of 1 atm. The reaction is catalyzed by sulfuric acid, added to the liquid phase [18].

The reaction equilibrium is due to Agreda et al. [17] and vapour-liquid equilibrium is calculated according to Doherty & Barbosa [7].

Feed rates, reboiler rate, reaction rate and measured temperatures are inputs and outputs of the model for controller synthesis and implementation purposes.

From the possible candidates for manipulated variables, for the investigated methyl acetate process, the molar fee flow of methyl acetate F_{AcH} and molar fee flow rate of methanol F_{MeOH} , reboiler duty Q_r , and reaction rate R were chosen (see fig. 2, on the next page).

238

Fig. 1. Reactive distillation column.

The measured variables are represented by two reaction temperatures T_{16} and T_{21} , one stripping temperature T_{25} and a difference between two temperatures T_{16} - T_{21} .



Fig. 2. Manipulated and measured variables for the investigated process.

Open loop simulations

The dynamic simulation is useful in understanding the behavior of the process. The simulations were made with DIVA simulator (Dynamische Simulation Verfahrenstechnischer Anlagen), developed at the Stuttgart University. This simulation environment runs under Linux operating system and integrates some sets of high-level routines to solve/integrate complex algebraic and differential equation systems [10, 14]. For details about the simulator, the reader may consult the references [5, 8, 9, 10, 11, 13, 14, 15].

The steady-state variations of T_{16} (reactive tray temperature) and T_{25} (stripping tray temperature), both measured in K, with respect to F_{AcH} and Q_r are plotted in figure 3 and figure 4. The inputs are changed by $\pm 5\%$ and $\pm 10\%$ around the base case.



Fig. 3. Step responses of reactive temperature T_{16} in input and reboiler rate step changes. a) F_{AcH} , b) Q_r .



Fig. 4. Step responses of stripping temperature T_{25} in input and reboiler rate step changes. a) F_{AcH} , b) Q_r .

Figure 3 shows the process's nonlinearity, an inverse response being illustrated in fig. 3 a), at 10% step change in disturbance F_{AcH} . This requires a suitable control strategy, which will be investigated in a future paper. For a ±5% step disturbance in F_{AcH} (from fig. 4) the responses are symmetrical.

Conclusions

RD combines both reaction and distillation in a single unit, offering significant economic benefits when compared to conventional process designs (reaction followed by separation). Its application area became wider in the last years due to researches that had been made in this field. This paper briefly presented the actual state of reactive distillation modeling and simulation.

A simple dynamic model was given and some first results of the dynamic simulation with the simulation environment DIVA were shown. The obtained results lead to the necessity of using advanced control techniques, for example a model predictive control strategy.

Future work will focus on the synthesis of suitable control strategies which will take into account the strong nonlinearity of the system.

Acknowledgements

The author wants to thank Prof. Dr. -Ing. Achim Kienle for making possible my research stage at Max-Planck Institute and for his permanent guidance, suggestions and kind way of leading my research work. Also, my deepest gratitude to Dr. -Ing. habil. Michael Mangold for his permanent help and support during my research stage and to all the colleagues from Process Synthesis and Process Dynamics group for creating a friendly working environment.

Nomenclature

| AcH – acetic acid | L – internal liquid molar flowrate | |
|---|--|--|
| MeOH – methanol | V – volumetric liquid holdup on tray | |
| MeAc – methyl acetate | U – molar liquid holdup on tray | |
| F_{AcH} – acetic acid flow fee | Q _r – heating rate | |
| F _{MeOH} – methanol flow fee | p – pressure | |
| R – reaction rate | psp – saturation pressure in the vapor phase | |
| T – temperature | x – mole fraction, liquid | |
| NC – number of components | γ – activity coefficient | |
| K – liquid-vapor equilibrium constant | η – tray efficiency | |
| F – external liquid feed molar flowrate | v – stoichiometric coefficient | |
| D – liquid sidedraw molar flowrate | i - component indices | |
| V – internal vapor molar flowrate | j – tray number | |

References

- 1. Harmsen, G.J. Reactive distillation: The front-runner of industrial process intensification A full review of commercial applications, research, scale-up, design and operation. Chemical Engineering and Processing 46, 774–780, 2007.
- 2. Kienle, A., Sundmacher, K. *Reactive Distillation Status and Future Directions*, 217 240, Wiley-VCH Verlag GmbH & Co. KGaA, ISBN: 3-527-30579-3 (Hardback), 2002.
- 3. Baur, R., Higler, A. P., Taylor, R., Krishna, R. Comparison of equilibrium stage and nonequilibrium stage models for reactive distillation. Chemical Engineering, 76, 33-47, 2000.
- 4. Taylor, R., Krishna, R. *Modeling reactive distillation*. Chemical Engineering Science, 55, 5183-5229, 2000.
- 5. Gilles, E. D., Holl, P., Marquardt, W., Mahler, R., Schneider, H., Brinkmann, K., Will, K.H. – Ein Trainingssimulator zur Ausbildung von Betriebpersonal in der chemischen Industrie. Automatisierungstechnische Praxis, 32, 1990.
- 6. *** Internal Reports. Max-Planck Institut Magdeburg, Germania.
- 7. Barbosa, D., and Doherty, M., F. *The influence of equilibrium chemical reactions* on vapor liquid phase diagrams. Chemical Engineering Science, 43, 529 540, 1988.
- 8. Kröner, A., Holl, P., Marquardt, W., Gilles, E. D., DIVA An open architecture for dynamic simulation. Computers Chem. Engng., 14, 1990.
- 9. Marquardt, W., Holl, P., Gilles, E. D. DIVA A dynamic process flowsheet simulator. III World Congress of Chemical Engineering, Tokyo, 1986.
- 10. Mangold, M., Kienle, A., Mohl, K, D., Gilles, E. D. Nonlinear computation using DIVA Methods and applications. Chem. Engng. Science, 55, 2000.
- 11. Mohl, K. D., Spieker, A., Köhler, R., Gilles, E. D., Zeitz, M. DIVA – A simulation environment for chemical engineering applications. ICCS-97, Donetsk, Ukraine, 1997.
- 12. Spieker, A., Burg, W., Robeller, T. Die Kurzanleitung für die neue DIVA-MATLAB-Graphik. Universität Stuttgart, 1995.
- 13. Marquardt, W., Holl, P., Butz, D., Gilles, E. D. DIVA A flowsheet oriented dynamic process simulator. Chemical Engineering Technology, 10, 1987.

- 14. Häfele, M., Kienle, A., Klein, E. User manual DIVA 3.9. Universität Stuttgart, Max-Planck Institut Magdeburg, 2001.
- 15. Kröner, A., Helget, A., Majer, C., Mangold, M. DIVA Simulator V3 command reference manual. Universität Stuttgart, 1999.
- Rădulescu, G., Gangadwala, J., Kienle, A., Steyer, F., Sundmacher, K. – Dynamic simulation of reactive distillation processes with liquid-liquid phase splitting, Symposium on Process Control – SPC2006.
- 17. Agreda, V.H., Partin, L.R., Heise, W.H. *High-purity methyl acetate via reactive distillation*. Chemical Engineering Prog., 40-46, 1990.
- 18. Doherty, M.F., Malone, M.F. Conceptual design of distillation systems. Mc-Graw Hill, New York, 2001.

Abordarea modelării matematice dinamice a procesului de distilare reactivă din perspectiva conducerii acestuia

Rezumat

În cadrul acestui articol este prezentat pe scurt conceptul de distilare reactivă, precum și o apreciere a stadiului actual al cercetărilor din domeniul distilării reactive. Ca aplicație practică este ales procesul de obținere a metil acetatului. Pentru acest proces s-a implementat un model matematic simplificat, în acest sens fiind prezentate câteva rezultate obținute prin simularea dinamică în buclă deschisă a procesului, cu ajutorul mediului de simulare DIVA. Aceste rezultate reprezintă baza pentru viitoarele studii privind controlul proceselor de distilare reactivă, în special cel pentru obținerea metil acetatului.