

Chapter 9

Conclusions and Recommendations

9.1. Conclusions

This research project has focused on reactive distillation for ETBE production. Design and control aspects of the complex behaviours of the reactive distillation have been extensively investigated via steady state and dynamic simulations. A rigorous reactive distillation model, which is accurate and efficient, has been successfully developed using the equilibrium-stage approach. The model incorporated with appropriate height equivalent to a theoretical stage, which was written in Aspen Plus and Aspen CM environment, has been shown to satisfactorily and realistically represent the pilot scale of a packed reactive distillation column, which is available in the Department of Chemical Engineering, Curtin University of Technology.

The model was used to demonstrate the design of various reactive distillation columns for ETBE production. The effects of operating conditions on the product composition and conversion were investigated. The steady state simulations were employed to study the conflicting effects of integrating reaction and separation on the overall performance of the reactive distillation column. Models of side reactors were then integrated with the reactive distillation column. Several column configurations including single-feed and double-feed columns, with and without the presence of a pre-reactor and/or side reactors were considered.

The model was then extended to investigate dynamic behaviours, control aspect and optimisation. Adaptive controllers were implemented on a standard (LV) control scheme with respect to the operation and control of reactive distillation. Several control schemes including multivariable inferential control were then assessed for their effectiveness and appropriateness for reactive distillation. Open-loop, one-point (composition) and two-point (composition and conversion) controls were considered.

9.2. Key Contributions

The following specific key contributions are made and/or demonstrated from this research:

- the equilibrium stage-model with appropriate height equivalent to a theoretical stage is a satisfactory basis for packed reactive distillation simulation;
- the commercial simulation packages, Aspen Plus and Aspen CM, were extensively used and permitted accurate modelling of reactive distillation operations;
- effective dynamic simulation models of reactive distillation were implemented within the Aspen CM simulation environment;
- the response of reactive distillation columns to changes in operating conditions sometime does not follow that of conventional distillation columns (e.g. the pressure should be optimised to compromise the reaction and separation performance);
- conservative approach of adding a few extra stages can be implemented to reactive distillation columns and the column performance does not degrade if the operating conditions are chosen appropriately;
- side reactors are feasible to be integrated with the reactive distillation column for etherification to potentially reduce the capital costs and to offer more convenient ways for shut down operation and catalyst replacement;
- the control performance of nonlinear PI and model gain-scheduling controllers is clearly better than that of the standard PI controller in both set-point tracking and disturbance rejection;
- the switching scheme in the model gain-scheduling controller may cause instability of the system due to too large values of noise or changes in the operating conditions;
- although the inferential variable is tightly controlled using an advanced controller, the primary control variable (e.g. product purity) can not be reasonably maintained at its set-point due to feed composition changes;
- inferential model using several secondary variables is required for the estimates of the product purity and reactant conversion;

- control of both the product purity and reactant conversion is possible with simple linear controllers if a suitable control scheme is applied (e.g. cascade LV control scheme);
- multivariable inferential control can ensure the process performance remains acceptable following process disturbances and set-point changes, and improve the control performance,
- maximum profitability does not correspond to maximum product purity;
- dynamically operating conditions, which can satisfy the process constraints, were obtained by slightly paying an economic penalty compared to maximum profit design;
- set-point optimisation can be used to maximise profitability and provide a basis for a supervisory control system;

9.3. Recommendations

The research has met the objectives outlined in Chapter 1 and no further work is required to achieve them.

However, there is significant potential to continue the experimental aspects of this research using the reactive distillation pilot plant. In particular, the experimental data can demonstrate the viability of reactive distillation for ETBE production. It can serve for checking the process modelling, controlled development and advanced control algorithms proposed in this thesis.

Chapter 10

Cited Literature

- Abbas, A., 1997, 'A new set of controller tuning relations', *ISA Transactions*, vol. 36 (3), pp. 183-187.
- Agreda, V. H., Partin, L. R. and Heise, W. H., 1990, 'High purity methyl acetate via reactive distillation', *Chemical Engineering Progress*, vol. 2, pp. 40-46.
- Al-Arfaj, M. A. and Luyben, M. L., 2002a, 'Comparative control study of ideal and methyl acetate reactive distillation', *Chem. Eng. Sci.*, vol. 57, pp. 5039-5050.
- Al-Arfaj, M. A. and Luyben, W. L., 2000a, 'Comparison of alternative control structures for two-product reactive distillation column', *Ind. Eng. Chem. Res.*, vol. 39, pp. 3298-3307.
- Al-Arfaj, M. A. and Luyben, W. L., 2000b, 'Effect of Number of Fractionating Trays on Reactive Distillation Performance', *AIChE Journal*, vol. 46 (12), pp. 2417-2425.
- Al-Arfaj, M. A. and Luyben, W. L., 2002b, 'Control Study of Ethyl *tert*-Butyl Ether Reactive Distillation', *Ind. Eng. Chem. Res.*, vol. 41, pp. 3784-3796.
- Alejski, K. and Duprat, F., 1996, 'Dynamic Simulation of the Multicomponent Reactive Distillation', *Chem. Eng. Sci.*, vol. 51 (18), pp. 4237-4252.
- Alexander, C. A. and Trahan, R. E., 2001, 'A comparison of traditional and adaptive control strategies for systems with time delay', *ISA Transactions*, vol. 40, pp. 353-368.
- Andersen, H. W. and Kummel, M., 1992, 'Evaluating Estimation of gain directionality, Part 2: A Case Study of binary distillation', *J. Process Control*, vol. 2, pp. 66-86.
- Aspen Technology Inc., 2001, Aspen Engineering Suite 11.1, ver. 11.1, Cambridge, Massachusetts.
- Balasubramhanya, L. S. and Doyle III, F. J., 2000, 'Nonlinear model-based control of a batch reactive distillation column', *J. Process Control*, vol. 10, pp. 209-218.
- Banerjee, A., Arkun, Y., Ogunnaike, B. and Pearson, R., 1997, 'Estimation of Nonlinear Systems Using Linear Multiple Models', *AIChE Journal*, vol. 43, pp. 1204-1226.

- Baur, R., Higler, A. P., Taylor, R. and Krishna, R., 2000, 'Comparison of equilibrium stage and nonequilibrium stage models for reactive distillation', *Chem. Eng. Journal*, vol. 76, pp. 33-47.
- Baur, R., Taylor, R. and Krishna, R., 2001a, 'Dynamic behaviour of reactive distillation columns described by a nonequilibrium stage model', *Chem. Eng. Sci.*, vol. 56 (6), pp. 2085-2102.
- Baur, R., Taylor, R. and Krishna, R., 2001b, 'Dynamic behaviour of reactive distillation tray columns described with a nonequilibrium cell model', *Chem. Eng. Sci.*, vol. 56, pp. 1721-1729.
- Beckmann, A., Nierlich, F., Popken, T., Reusch, D., Scala, C. v. and Tuchelenski, A., 2002, 'Industrial experience in the scale-up of reactive distillation with examples from C4-chemistry', *Chem. Eng. Sci.*, vol. 57, pp. 1525-1530.
- Bequette, B. W., 1991, 'Nonlinear Control of Chemical Processes: A Review', *Ind. Eng. Chem. Res.*, vol. 30, pp. 1391-1413.
- Bequette, B. W., 1998, 'Practical Approaches to Nonlinear Control: A Review of Process Application', ed. R. Berber and K. C., in *Nonlinear Model-based Process Control*, Kluwer, Dordrecht.
- Bezzo, F., Bertucco, A., Forlin, A. and Barolo, M., 1999, 'Steady-state analysis of an industrial reactive distillation column', *Separation and Purification Technology*, vol. 16, pp. 251-260.
- Bisowarno, B. H., 2000, *Simulation and Experimental Testing of Reactive Distillation Column for ETBE Synthesis*, MEng Thesis, Chemical Engineering, Curtin University of Technology, Perth-Australia.
- Bisowarno, B. H. and Tadé, M. O., 2000, 'Dynamic Simulation of Startup in Ethyl tert-Butyl Ether Reactive distillation with Input Multiplicity', *Ind. Eng. Chem. Res.*, vol. 39, pp. 1950-1954.
- Bisowarno, B. H. and Tadé, M. O., 2002, 'The Comparison of Disturbance Rejection Properties of One-Point Control Schemes for ETBE Reactive Distillation', *Chem. Eng. Comm.*, vol. 189 (1), pp. 85-100.
- Blagov, S., Bessling, B., Schoenmakers, H. and Hasse, H., 2000, 'Feasibility and multiplicity in reaction-distillation processes for systems with competing irreversible reactions', *Chem. Eng. Sci.*, vol. 55 (22), pp. 5421-5436.
- Brambilla, A., Chen, S. and Scali, C., 1990, 'Robust tuning of conventional controllers', *Hydrocarbon Processing*, vol. 69, pp. 53-58.
- Bravo, J. L., Pyhalathi, A. and Jaervelin, H., 1993, 'Investigations in a catalytic distillation pilot plant: Vapour/liquid equilibrium, kinetic and mass transfer issues', *Ind. Eng. Chem. Res.*, vol. 32, pp. 2220-2225.

- Buzad, G. and Doherty, M. F., 1994, 'Design of three component kinetically controlled reactive distillation systems using fixed-point method', *Chem. Eng. Sci.*, vol. 49, pp. 1947-1963.
- Cardoso, M. F., Salcedo, R. L., de Azevedo, S. F. and Barbosa, D., 2000, 'Optimization of Reactive Distillation Processes with Simulated Annealing', *Chem. Eng. Sci.*, vol. 55, pp. 5059-5078.
- Castier, M., Rasmussen, P. and Fredenslund, A., 1989, 'Calculation of simultaneous chemical and phase equilibria in nonideal systems', *Chem. Eng. Sci.*, vol. 44, pp. 237-248.
- Chen, C. L., 1989, 'A simple method for on-line identification and controller tuning', *AIChE Journal*, vol. 35, pp. 2037-2039.
- Chen, F., Huss, R. S., Malone, M. F. and Doherty, M. F., 2000, 'Simulation of kinetic effects in reactive distillation', *Comp. Chem. Eng.*, vol. 24, pp. 2457-2472.
- Cheung, T. F. and Luyben, W. L., 1980, 'Nonlinear and Nonconventional Liquid Level Controllers', *Ind. Eng. Chem. Fundam.*, vol. 19, pp. 93-98.
- Chiu, M. and Cui, S., 2000, 'Internal Model Control Design for Transition Control', *AIChE Journal*, vol. 46 (2), pp. 309-320.
- Ciric, A. R. and Gu, D., 1994, 'Synthesis of Nonequilibrium Reactive Distillation Processes by MINLP Optimization', *AIChE Journal*, vol. 40 (9), pp. 1479-1487.
- Davies, B. and Jeffreys, G. H., 1973, 'The continuous trans-esterification of ethyl alcohol and butyl acetate in a sieve plate column. Part III: Trans-esterification in a six plate sieve plate column', *Trans IChemE.*, vol. 51, pp. 272-280.
- DiGuilio, R. M. and McKinney, M. W., 2000, 'Selective production of diethanolamine', *US Patent*, 6,075,168.
- Doherty, M. F. and Buzad, G., 1992, 'Reactive Distillation by Design', *Trans IChemE.*, vol. 70 (Part A), pp. 448-457.
- Doherty, M. F. and Malone, M. F., 2001, 'Reactive Distillation', ed., in *Conceptual Design of Distillation Systems*, McGraw-Hill,
- Doyle III, F. J., 1998, 'Nonlinear inferential control for process applications', *J. Process Control*, vol. 8 (5-6), pp. 339-353.
- Engell, S. and Fernholz, G., 2003, 'Control of a reactive separation process', *Chem. Eng. And Processing*, vol. 42, pp. 201-210.
- Fite, C., Iborra, M., Tekero, J., Izquierdo, J. and Cunill, F., 1994, 'Kinetic of the Liquid Phase Synthesis of Ethyl tert-Butyl Ether (ETBE)', *Ind. Eng. Chem. Res.*, vol. 33, pp. 581-591.

- Flato, J. and Hoffmann, U., 1992, 'Development and Start-up of a Fixed Bed Reaction Column for Manufacturing Antiknock Enhancer MTBE', *Chem. Eng. Technol.*, vol. 15, pp. 193-201.
- Frey, T. and Stichlmair, J., 1999A, 'Review: Thermodynamic Fundamentals of Reactive Distillation', *Chem. Eng. Technol.*, vol. 22 (1), pp. 11-18.
- Georgiadis, M. C., Schenk, M., Pistikopoulos, E. N. and Gani, R., 2002, 'The interaction of design and control in reactive distillation systems', *Comp. Chem. Eng.*, vol. 26, pp. 735-746.
- Giessler, S., Danilov, R. Y., Pisarenko, R. Y., Serafimov, L. A., Hasebe, S. and Hashimoto, I., 1999, 'Feasible Separation Modes for Various Reactive Distillation Systems', *Ind. Eng. Chem. Res.*, vol. 38, pp. 4060-4067.
- Giessler, S., Danilov, R. Y., Pisarenko, R. Y., Serafimov, L. A., Hasebe, S. and Hashimoto, I., 2001, 'Systematic structure generation for reactive distillation processes', *Comp. Chem. Eng.*, vol. 25 (1), pp. 49-60.
- Gonzalez, J. A. and Fair, J. R., 1997, 'Preparation of tertiary amyl alcohol in a reactive distillation column. 1. Reaction kinetics, chemical equilibrium, and mass-transfer issues', *Ind. Eng. Chem. Res.*, vol. 36, pp. 3833-3844.
- Gonzalez, J. A., Subawalla, H. and Fair, J. R., 1997, 'Preparation of tert-amyl alcohol in a reactive distillation column. 2. Experimental demonstration and simulation of column characteristics', *Ind. Eng. Chem. Res.*, vol. 36, pp. 3845-3853.
- Gruner, S., Mohl, K. D., Kienle, A., Gilles, E. D., Fernholz, G. and Friedrich, M., 2003, 'Nonlinear Control of a reactive distillation column', *Chemical Engineering Practice*, vol. 11, pp. 915-925.
- Güttinger, T. E., Dorn, C. and Morari, M., 1997, 'Experimental Study of Multiple Steady State in Homogeneous Azeotropic Distillation', *Ind. Eng. Chem. Res.*, vol. 36, pp. 794-802.
- Güttinger, T. E. and Morari, M., 1999a, 'Predicting Multiple Steady States in Equilibrium Reactive Distillation. 1. Analysis of Nonhybrid Systems', *Ind. Eng. Chem. Res.*, vol. 38, pp. 1633-1648.
- Güttinger, T. E. and Morari, M., 1999b, 'Predicting Multiple Steady States in Equilibrium Reactive Distillation. 2. Analysis of Hybrid Systems', *Ind. Eng. Chem. Res.*, vol. 38, pp. 1649-1665.
- Han, M., Lin, H., Wang, L. and Jin, Y., 2002, 'Characteristics of the reactive distillation column with a novel internal', *Chem. Eng. Sci.*, vol. 57, pp. 1551-1555.
- Hanika, J., Kolena, J. and Smejkal, Q., 1999, 'Butylacetate via reactive distillation - modelling and experiment', *Chem. Eng. Sci.*, vol. 54 (21), pp. 5205-5209.

- Hasse, H., Hahnentien, I. and Maurer, G., 1990, 'Revised vapour liquid equilibrium model for multi-component formaldehyde mixtures', *AIChE Journal*, vol. 36, pp. 1807-1814.
- Hauan, S., Hertzberg, T. and Lien, K. M., 1997, 'Multiplicity in Reactive Distillation of MTBE', *Comp. Chem. Eng.*, vol. 21 (10), pp. 1117-1124.
- Hauan, S. and Lien, K. M., 1998, 'A Phenomena Based Design Approach to Reactive Distillation', *Tans IChemE*, vol. 76 (Part A, March), pp. 396-407.
- Hauan, S., Westerberg, A. W. and Lien, K. M., 2000, 'Phenomena-based analysis of fixed-points in reactive separation systems', *Chem. Eng. Sci.*, vol. 55, pp. 1053-1075.
- Heath, J. A., Kookos, I. K. and Perkin, J. D., 2000, 'Process control structure selection based on economics', *AIChE Journal*, vol. 46 (10), pp. 1998-2016.
- Hendriksen, D. E., Lattner, J. R. and Janssen, M. J. G., 1999, 'Alkylation process using zeolite beta', *US Patent*, 6,002,057.
- Higler, A., Taylor, R. and Krishna, R., 1998, 'Modelling of a Reactive Separation Process using a Nonequilibrium Stage Model', *Comp. Chem. Eng.*, vol. 22 (Supp.), pp. S111-S118.
- Higler, A., Taylor, R. and Krishna, R., 1999a, 'The influence of mass transfer and mixing on the performance of a tray column for reactive distillation', *Chem. Eng. Sci.*, vol. 54, pp. 2873-2881.
- Higler, A., Taylor, R. and Krishna, R., 1999b, 'Nonequilibrium Cell Model for Multicomponents (Reactive) Separation Processes', *AIChE Journal*, vol. 45 (11), pp. 2357-2370.
- Higler, A. P., Taylor, R. and Krishna, R., 1999c, 'Nonequilibrium Modelling of Reactive Distillation: Multiple steady states in MTBE synthesis', *Chem. Eng. Sci.*, vol. 54, pp. 1389-1395.
- Holmgren, J. S., Galloway, D. B., Galperin, L. B. and Willis, W. R., 1999, 'Selective aromatics disproportionation/transalkylation', *US Patent*, 6,008,423.
- Hoyme, C. A. and Holcombe III, E. F., 2003, 'Reactive distillation process for hydrolysis of esters', *US Patent*, 6,518,465.
- Isidori, A., 1989, *Nonlinear Control System*, Springer, Berlin, Germany.
- Jackson, J. R. and Grossmann, I. E., 2001, 'A disjunctive programming approach for the optimal design of reactive distillation columns', *Comp. Chem. Eng.*, vol. 25 (11-12), pp. 1661-1673.
- Jacobs, R. and Krishna, R., 1993, 'Multiple Solution in Reactive Distillation for Methyl *tert*-Butyl Ether Synthesis', *Ind. Eng. Chem. Res.*, vol. 32, pp. 1706-1709.



- Jacobsen, E. W. and Skogestad, S., 1991, 'Multiple Steady States in Ideal Two-Product Distillation', *AIChE Journal*, vol. 37 (4), pp. 499-511.
- Jacobsen, E. W. and Skogestad, S., 1995, 'Multiple Steady States and Instability in Distillation. Implication for Operation and Control', *Ind. Eng. Chem. Res.*, vol. 34 (12), pp. 4395-4405.
- Jakobsson, K., Pyhalathi, A., Pakkanen, S., Keskinen, K. and Aittamaa, J., 2002, *Modelling of a Side Reactor Configuration Combining Reaction and Distillation*, Retrieved: 1 November 2002, <http://www.dechema.de/veranstaltung/ecce/cd/pages/487.htm>.
- Jensen, K. L. and Datta, R., 1995, 'Ethers from Ethanol. 1. Equilibrium Thermodynamic Analysis of the Liquid Phase Ethyl *tert*-Butyl Ether Reaction', *Ind. Eng. Chem. Res.*, vol. 34, pp. 392-399.
- Jimenez, L. and Costa-Lopez, J., 2002, 'The Production of Butyl Acetate and Methanol via Reactive and Extractive Distillation. II. Process Modelling, Dynamic Simulation, and Control Strategy', *Ind. Eng. Chem. Res.*, vol. 41, pp. 6735-6744.
- Jimenez, L., Wanhschafft, O. M. and Julka, V., 2001, 'Analysis of residue curve maps of reactive and extractive distillation units', *Comp. Chem. Eng.*, vol. 25 (4-6), pp. 635-642.
- Jung, C. W., Garrou, P. E. and Streckler, G. R., 1987, 'Disproportionation of Alkenes', *US Patent*, 4,709,115.
- Jutan, A., 1989, 'A Nonlinear PI(D) controller', *Can. J. Chem. Eng.*, vol. 67, pp. 485-493.
- Kano, M., Miyazaki, K., Hasebe, S. and Hashimoto, I., 2000, 'Inferential control system of distillation compositions using dynamic partial least squares regression', *J. Process Control*, vol. 10, pp. 157-166.
- Kenig, E. Y., Bader, H., Gorak, A., Beßling, B., Adrian, T. and Schoenmakers, H., 2001a, 'Investigation of ethyl acetate reactive distillation processes', *Chem. Eng. Sci.*, vol. 56, pp. 6185-6193.
- Kenig, E. Y., Schneider, R. and Gorak, A., 2001b, 'Reactive absorption: Optimal process design via optimal modelling', *Chem. Eng. Sci.*, vol. 56, pp. 343-350.
- Keyes, D. B., 1932, 'Esterification Processes and Equipment', *Ind. Eng. Chem.*, vol. 24, pp. 1096.
- Kister, H. Z., 1990, *Distillation Operation*, McGraw-Hill Pub. Co., New York.
- Kitchaiya, P. and Datta, R., 1996, 'Ethers from Ethanol. 6 Kinetics of Simultaneous *ter*-Amyl Ether Synthesis and Isoamylene Isomerisation', *Ind. Eng. Chem. Res.*, vol. 34 (4), pp. 1092-1101.

- Klatt, K. U. and Engell, S., 1998, 'Gain-scheduling trajectory control of a continuous stirred tank reactor', *Comp. Chem. Eng.*, vol. 22 (4/5), pp. 491-502.
- Knapp, J. P. and Doherty, M. F., 1994, 'Minimum Entrainer Flows for Extractive Distillation: A Bifurcation Theoretical Approach', *AIChE Journal*, vol. 40 (2), pp. 243-.
- Knifton, J. F., Sanderson, J. R. and Stockton, M. E., 1998, 'Use of reactive distillation in the dehydration of tertiary butyl alcohol', *US Patent*, 5,811,620.
- Kresta, J. V., Marlin, T. E. and MacGregor, J. F., 1994, 'Development of Inferential Process Models Using PLS', *Comp. Chem. Eng.*, vol. 18 (7), pp. 597-611.
- Kreul, L. U., Gorak, A., Dittrich, C. and Barton, P. I., 1998, 'Dynamic Catalytic Distillation: Advanced Simulation and Experimental Validation', *Comp. Chem. Eng.*, vol. 22 (Supp.), pp. S371-S378.
- Krishna, R., 2002, 'Reactive separations: more ways to skin a cat', *Chem. Eng. Sci.*, vol. 57, pp. 1491-1504.
- Krishna, R. and Wesselingh, J. A., 1997, 'The Maxwell-Stefan Approach to Mass Transfer', *Chem. Eng. Sci.*, vol. 52, pp. 861-911.
- Krishnamurthy, R. and Taylor, R., 1985, 'Nonequilibrium stage model of multicomponent separation processes', *AIChE Journal*, vol. 32, pp. 449-465.
- Kuhlmann, A. and Bogle, I. D. L., 2001, 'Controllability Evaluation for Nonminimum Phase-Processes with Multiplicity', *AIChE Journal*, vol. 47 (11), pp. 2627-2632.
- Kumar, A. and Daoutidis, P., 1999, 'Modeling, Analysis and Control of Ethylene Glycol Reactive Distillation Column', *AIChE Journal*, vol. 45 (1), pp. 51-68.
- Lebas, E., Jullian, S., Travers, C., Capron, P. B., Joly, J. and Thery, M., 1999, 'Paraffin isomerisation process using reactive distillation', *US Patent*, 5,948,945.
- Lee, J. and Dudukovic, M. P., 1998, 'A comparison of the equilibrium and nonequilibrium models for a multicomponent reactive distillation column', *Comp. Chem. Eng.*, vol. 23, pp. 159-172.
- Lee, J. W., Huan, S. and Westerberg, A. W., 2000a, 'Extreme Conditions in Binary Reactive Distillation', *AIChE Journal*, vol. 46 (1), pp. 2225-2236.
- Lee, J. W., Huan, S. and Westerberg, A. W., 2000b, 'Graphical Methods for Reactive Distribution in a Reactive Distillation Column', *AIChE Journal*, vol. 46 (1), pp. 1218-1233.
- Lee, W. J. and Westerberg, A. W., 2001, 'Graphical Design Applied to MTBE and Methyl Acetate Reactive Distillation Processes', *AIChE Journal*, vol. 47 (1333-1345), pp.

- Lerou, J. L. and Ng, K. M., 1996, 'Chemical Reaction Engineering: A Multiple Approach to A Multiobjective Task', *Chem. Eng. Sci.*, vol. 51 (10), pp. 1595-1614.
- Loperena, R. M., Cisneros, E. P. and Ramirez, J. A., 2000, 'A robust PI control configuration for a high-purity ethylene glycol reactive distillation column', *Chem. Eng. Sci.*, vol. 55, pp. 4925-4937.
- Loperena, R. M. and Ramirez, J. A., 1999, 'On the steady state multiplicities for an ethylene glycol reactive distillation column', *Ind. Eng. Chem. Res.*, vol. 38, pp. 451-455.
- Loperena, R. M. and Ramirez, J. A., 2000, 'Output-feedback control of reactive batch distillation columns', *Ind. Eng. Chem. Res.*, vol. 39, pp. 378-386.
- Loperena, R. M., Cisneros, E. P. and Ramirez, J. A., 2000, 'A robust PI control configuration for a high-purity ethylene glycol reactive distillation column', *Chem. Eng. Sci.*, vol. 55, pp. 4925-4937.
- Luo, H. P. and Xiao, W. D., 2001, 'A reactive distillation process for a cascade and azeotropic reaction system: Carbonylation of ethanol with dimethyl carbonate', *Chem. Eng. Sci.*, vol. 56, pp. 403-410.
- Luyben, W. L., 1990, *Process Modelling, Simulation, and Control for Chemical Engineers*, McGraw-Hill Pub. Co., New York.
- Luyben, W. L., 2000, 'Economic and dynamic impact of the use of excess reactant in reactive distillation systems', *Ind. Eng. Chem. Res.*, vol. 39, pp. 2935-2946.
- Luyben, W. L. and Luyben, M. L., 1997, *Essentials of Process Control*, McGraw Hill, New York.
- Malone, M. F. and Doherty, M. F., 2000, 'Reactive Distillation', *Ind. Eng. Chem. Res.*, vol. 39, pp. 3953-3957.
- Marker, T. L., Funk, G. A., Barger, P. T. and Hammershaimb, H. U., 1998, 'Two-stage process for producing diisopropyl ether using catalytic distillation', *US Patent*, 5,744,645.
- Meeuse, F. M. and Tousain, R. L., 2002, 'Closed-loop controllability analysis of process design: application to distillation column design', *Comp. Chem. Eng.*, vol. 26, pp. 641-647.
- Mejdell, T. and Skogestad, S., 1991a, 'Composition estimator in a pilot plant distillation column using multiple temperatures', *Ind. Eng. Chem. Res.*, vol. 30, pp. 2555-2564.
- Mejdell, T. and Skogestad, S., 1991b, 'Estimation of distillation composition from multiple temperature measurements using partial-least-squares regression', *Ind. Eng. Chem. Res.*, vol. 30, pp. 2543-2555.

- Mejdell, T. and Skogestad, S., 1993, 'Output estimation using multiple secondary measurements: high purity distillation', *AIChE Journal*, vol. 39 (10), pp. 1641-1653.
- Melles, S., Grievink, J. and Schrans, S. M., 2000, 'Optimisation of the conceptual design of reactive distillation columns', *Chem. Eng. Sci.*, vol. 55, pp. 2089-2097.
- Mohl, K. D., Kienle, A., Gilles, E. D., Rapmund, P., Sundmacher, K. and Hoffmann, U., 1999, 'Steady-state multiplicities in reactive distillation columns for the production of fuel ethers MTBE and TAME: theoretical analysis and experimental verification', *Chem. Eng. Sci.*, vol. 54, pp. 1029-1043.
- Mohl, K. D., Kienle, A., Sundmacher, K. and Gilles, E. D., 2001, 'A theoretical study of kinetic instabilities in catalytic distillation processes: influence of transport limitations inside the catalyst', *Chem. Eng. Sci.*, vol. 56, pp. 5239-5254.
- Moritz, P. and Hasse, H., 1999, 'Fluid dynamic in reactive distillation packing Katapak-S', *Chem. Eng. Sci.*, vol. 54, pp. 1367-1374.
- Narendra, K. S., Balakrishnan, J. and Ciliz, M. K., 1995, 'Adaptation and Learning Using Multiple Models, Switching, and Tuning', *IEEE Control Systems*, vol. 15 (June), pp. 37-51.
- Nijhuis, S. A., Kerkhof, F. P. J. M. and Mak, A. N. S., 1993, 'Multiple Steady States during Reactive Distillation of Methyl tert-Butyl Ether', *Ind. Eng. Chem. Res.*, vol. 32 (11), pp. 2767-2774.
- Noeres, C., Hoffmann, A. and Gorak, A., 2002, 'Reactive Distillation: non-ideal flow behaviour of the liquid phase in structured catalytic packings', *Chem. Eng. Sci.*, vol., pp.
- Ogunnaike, B. and Ray, W., 1994, *Process Dynamics, Modelling and Control*, Oxford University Press, Oxford.
- Okasinski, M. J. and Doherty, M. F., 1998, 'Design Method for Kinetically Controlled Staged Reactive Distillation Columns', *Ind. Eng. Chem. Res.*, vol. 37, pp. 2821-2834.
- Oudshoorn, O. L., Janissen, M., van Kooten, W. E. J., Jansen, J. C., van Bekkum, H., van de Bleek, C. M. and Calis, H. P. A., 1999, 'A novel structured catalyst packing for catalytic distillation of ETBE', *Chem. Eng. Sci.*, vol. 54, pp. 1413-1418.
- Pilavachi, P. A., Schenk, M., Cisneros, E. P. and Gani, R., 1997, 'Modelling and Simulation of Reactive Distillation Operations', *Ind. Eng. Chem. Res.*, vol. 36 (8), pp. 3188-3197.
- Pisarenko, R. Y. and Efremov, D., 2000, *Reactive distillation: history, theory, practice, personalia, references*, Retrieved: 20 April 2003, Reactive distillation group of Russia, <http://reactive-distillation.org/>.
- Podrebarac, G. G., Ng, F. T. T. and Rempel, G. L., 1997, 'More Uses for Catalytic Distillation', *ChemTech*, vol. 5 (May), pp. 37-45.

- Popken, T., Steinigeweg, S. and Gmehling, J. A., 2001, 'Synthesis and Hydrolysis of Methyl Acetate by Reactive Distillation Using Structure Catalytic Packings: Experiments and Simulation', *Ind. Eng. Chem. Res.*, vol. 40, pp. 1566-1574.
- Pottmann, M., Unbehauen, H. and Seborg, D. E., 1993, 'Application of a General Multi-Model Approach for Identification of Highly Nonlinear Processes - a Case Study', *Int. J. of Control*, vol. 57, pp. 97-120.
- Rapmund, P., Sundmacher, K. and Hoffmann, U., 1998, 'Multiple Steady States in a Reactive Distillation Column for the Production of the Fuel Ether TAME, II. Experimental Validation', *Chem. Eng. Technol*, vol. 21 (2), pp. 136-139.
- Rock, K., Gildert, G. R. and Guirk, T., 1997, 'Catalytic Distillation Extends its Reach', *Chem. Eng.*, vol. (July), pp. 78-84.
- Rugh, W. J., 1987, 'Design of Nonlinear PID Controllers', *AIChE Journal*, vol. 33, pp. 1738-1742.
- Rugh, W. J. and Shamma, J. S., 1999, 'A Survey of Research on Gain Scheduling', vol., pp.
- Ruiz, C. A., Basualdo, M. S. and Scenna, N. J., 1995, 'Reactive Distillation Dynamic Simulation', *Tans IChemE*, vol. 73 (Part A, May), pp. 263-378.
- Sågfors, M. F. and Waller, K. V., 1995, 'Dynamic Low-Order Models for Capturing Directionality in Nonideal Distillation', *Ind. Eng. Chem. Res.*, vol. 34, pp. 2038-2050.
- Sawitoski, I. L. and Pilavakis, P. A., 1988, 'Performance of Etherification in a Reactive-Distillation Column', *Chem. Eng. Sci.*, vol. 43, pp. 355-.
- Scenna, N. J., Ruiz, C. A. and Benz, S. J., 1998, 'Dynamic Simulation of Start-up Procedures of Reactive Distillation Columns', *Comp. Chem. Eng.*, vol. 22 (Supp.), pp. S719-S722.
- Schenk, M., Gani, R., Bogle, D. and Pistikopoulos, E. N., 1999, 'A hybrid modelling approach for separation systems involving distillation', *Chem. Eng. Res. Des., Trans. IChemE*, vol. 77 (Part A), pp. 519-534.
- Schrans, S. and Wolf, S. D., 1996, 'Dynamic Simulation of Reactive Distillation: An MTBE Case Study', *Comp. Chem. Eng.*, vol. 20 (Supp.), pp. S1619-S1624.
- Seader, J. D., 1989, 'The Rate-based Approach for Modelling Stage Separations', *Chem. Eng. Prog.*, vol. (October), pp. 41-49.
- Seborg, D. E., Edgar, T. F. and Mellichamp, D. A., 1989, *Process Dynamics and Control*, John Wiley & Sons, New York.

Seferlis, P. and Grievink, J., 2001, 'Process design and control structure screening based on economic and static controllability criteria', *Comp. Chem. Eng.*, vol. 25 (1), pp. 177-188.

Sharma, M. M. and Mahajani, S. M., 2003, 'Industrial applications of reactive distillation', ed. K. Sundmacher and A. Kienle, in *Reactive Distillation: Status and Future Directions*, Wiley-VCH, Weinheim.

Shinsky, F. G., 1988, *Process Control Systems*, McGraw-Hill, New York.

Shoemaker, J. D. and Jones, E. M. J., 1987, 'Cumene by catalytic distillation', *Hydrocarbon Processing*, vol. 66 (6), pp. 57-58.

Simandl, J. and Svrcek, W. Y., 1991, 'Extension of the Simultaneous-Solution and Inside-Out Algorithms to Distillation with Chemical Reactions', *Comp. Chem. Eng.*, vol. 15 (5), pp. 337-348.

Smejkal, Q. and Soos, M., 2002, 'Comparison of computer simulation of reactive distillation using ASPEN PLUS and HYSYS software', *Chem. Eng. Proc.*, vol. 41, pp. 413-418.

Smith, L. A., 1980a, 'Catalytic Distillation Process and Catalyst', *Eur. Pat. Appl.*, EP8860.

Smith, L. A., 1980b, 'Catalytic Distillation Process and Catalyst', *Eur. Pat. Appl.* EP8860,

Smith, L. A., 1984, 'Catalytic distillation structure', *US Patent*, 4,443,559.

Smith, L. A., 1993, 'Method for operating catalytic distillation process', *US Patent*, 5,221,441.

Sneesby, M. G., 1998, *Simulation and Control of Reactive Distillation*, PhD Thesis, Chemical Engineering, Curtin University of Technology, Perth-Australia.

Sneesby, M. G., Tadó, M. O. and Datta, R., 1995, 'tert-Butyl Ethers - A Comparison of Properties, Synthesis Techniques and Operating Conditions for High Conversions', *Dev. Chem. Eng. Miner. Process*, vol. 3, pp. 89-.

Sneesby, M. G., Tadó, M. O., Datta, R. and Smith, T. N., 1997a, 'ETBE Synthesis via Reactive Distillation: 1. Steady-State Simulation and Design Aspects', *Ind. Eng. Chem. Res.*, vol. 36, pp. 1855-1869.

Sneesby, M. G., Tadó, M. O., Datta, R. and Smith, T. N., 1997b, 'ETBE Synthesis via Reactive Distillation: 2. Dynamic Simulation and Control Aspects', *Ind. Eng. Chem. Res.*, vol. 36, pp. 1870-1881.

Sneesby, M. G., Tadó, M. O., Datta, R. and Smith, T. N., 1998a, 'Detrimental Influence of Excessive Fractionation on Reactive Distillation', *AIChE Journal*, vol. 44 (2), pp. 388-393.

- Sneesby, M. G., Tadó, M. O. and Smith, T. N., 1997c, *Implication of Steady-State Multiplicity for Operation and Control of Etherification Column*, Proc. of Distillation and Absorption '97, Maastricht.
- Sneesby, M. G., Tadó, M. O. and Smith, T. N., 1998b, 'Mechanistic Interpretation of Multiplicity in Hybrid Reactive Distillation - Physically Realisable Cases', *Ind. Eng. Chem. Res.*, vol. 37, pp. 4424-4433.
- Sneesby, M. G., Tadó, M. O. and Smith, T. N., 1998c, 'Multiplicity and Pseudo-Multiplicity in MTBE and ETBE Reactive Distillation', *Trans IChemE*, vol. 76 (Part A), pp. 525-531.
- Sneesby, M. G., Tadó, M. O. and Smith, T. N., 1999, 'Two-Point Control of a Reactive Distillation Column for Composition and Conversion', *J. Process Control*, vol. 9, pp. 19-31.
- Sneesby, M. G., Tadó, M. O. and Smith, T. N., 2000, 'A Multi-Objective Control Scheme for ETBE Reactive Distillation Process', *Trans IChemE.*, vol. 78 (Part A), pp. 283-292.
- Song, W., Huss, R., Doherty, M. F. and Malone, M. F., 1997, 'Discovery of a reactive azeotrope', *Nature*, vol. 388, pp. 561-563.
- Sorensen, S. and Skogestad, S., 1994, 'Control strategies for reactive batch distillation', *J. Process Control*, vol. 4, pp. 205-217.
- Spes, H., 1966, 'Katalytische Reaktionen in Ionenaustauscherkolonnen unter Verschiebung des chemische Gleichgewichts', *Chemiker Atg/Chemische Apparatur.*, vol. 90, pp. 443-446.
- Steinigeweg, S. and Gmehling, J. A., 2002, 'n-Butyl acetate synthesis via reactive distillation: thermodynamic aspects, reaction kinetics, pilot-plant experiments, and simulation studies', *Ind. Eng. Chem. Res.*, vol. 41, pp. 5483-5490.
- Stichlmair, J. and Frey, T., 1999B, 'Review: Reactive Distillation Processes', *Chem. Eng. Technol*, vol. 22 (2), pp. 95-102.
- Stichlmair, J. and Frey, T., 2001, 'Mixed- Integer Nonlinear Programming Optimization of Reactive Distillation Processes', *Ind. Eng. Chem. Res.*, vol. 40, pp. 5978-5982.
- Stitt, E. H., 2002, 'Reactive distillation for toluene disproportionation: a technical and economic evaluation', *Chem. Eng. Sci.*, vol. 57 (9), pp. 4537-1543.
- Sundmacher, K. and Hoffmann, U., 1994, 'Multicomponent mass and energy transport on different length scales in a packed reactive distillation column for heterogeneously catalysed fuel ether production', *Chem. Eng. Sci.*, vol. 51, pp. 4443.

Sundmacher, K., Rihko, L. K. and Hoffmann, U., 1994, 'Classification of Reactive Distillation Processes by Dimensionless Numbers', *Chem. Eng. Comm.*, vol. 127, pp. 151-157.

Sundmacher, K., Uhde, G. and Hoffmann, U., 1999, 'Multiple reactions in catalytic distillation processes for the production of fuel oxygenates MTBE and TAME: Analysis by rigorous model and experimental validation', *Chem. Eng. Sci.*, vol. 54, pp. 2839-2847.

Tadé, M. O. and Tian, Y. C., 2000, 'Conversion inference for ETBE reactive distillation', *Separation and Purification Technology*, vol. 19, pp. 85-91.

Taylor, R. and Krishna, R., 1993, *Multicomponent Mass Transfer*, Wiley, New York.

Taylor, R. and Krishna, R., 2000, 'Modelling Reactive Distillation', *Chem. Eng. Sci.*, vol. 55 (22), pp. 5421-5436.

Thiel, C., Sundmacher, K. and Hoffmann, U., 1997, 'Synthesis of ETBE: Residue Curve Maps for the Heterogenously Catalysed Reactive Distillation Process', *Chemical Engineering Journal*, vol. 66, pp. 181-191.

Tian, Y. C. and Tadé, M. O., 2000, 'Inference of Conversion and Purity for ETBE Reactive Distillation', *Brazilian J. of Chem. Eng.*, vol. 17 (4-7), pp. 617-625.

Tian, Y.-C., Zhao, F., Bisowarno, B. H. and Tadé, M. O., 2003, 'Pattern-based predictive control for ETBE reactive distillation', *J. Process Control*, vol. 13 (1), pp. 57-67.

Towler, G. P. and Frey, S. J., 2002, 'Reactive Distillation', ed. S. Kulprathipanja, in *Reactive Separation Process*, Taylor and Francis, New York.

Tuchelenski, A., Beckmann, A., Reusch, D., Düssel, R., Weidlich, U. and Janowsky, R., 2001, 'Reactive distillation - industrial applications, process design and scale-up', *Chem. Eng. Sci.*, vol. 56 (2), pp. 387-394.

Tuchlenski, A., Beckmann, A., Reusch, D., Düssel, R., Weidlich, U. and Janowsky, R., 2001, 'Reactive distillation - industrial applications, process design and scale-up', *Chem. Eng. Sci.*, vol. 56 (2), pp. 387-394.

Ung, S. and Doherty, M. F., 1995, 'Synthesis of reactive distillation systems with multiple equilibrium chemical reactions', *Ind. Eng. Chem. Res.*, vol. 34, pp. 2555-2565.

USGS, 1999, *Methyl tert-Butyl Ether*, Retrieved: August 1999, <http://www.wr.usgs.gov/mtbe>.

Venimadhavan, G., Malone, M. F. and Doherty, M. F., 1999, 'Bifurcation study of kinetic effects in reactive distillation', *AIChE Journal*, vol. 45, pp. 546-556.

- Venkataraman, S., Chan, W. K. and Boston, J. F., 1990, 'Reactive Distillation using ASPEN PLUS', *Chem. Eng. Prog.*, vol. 86 (8), pp. 45-54.
- Vora, N. and Daoutidis, P., 2001, 'Dynamic and Control of an Ethyl Acetate Reactive Distillation Column', *Ind. Eng. Chem. Res.*, vol. 40, pp. 833-846.
- Wajge, R. M. and Reklaitis, G. V., 1996, *Campaign optimization of multicomponent reactive batch distillation*, AIChE Spring Meeting, New Orleans.
- Wajge, R. M. and Reklaitis, G. V., 1999, 'RBD OPT: a general-purpose object-oriented module for distributed campaign optimization of reactive batch distillation', *Chem. Eng. Journal*, vol. 75, pp. 57-68.
- Ward, D. J., 1993, 'Etherification of isoamylenes by catalytic distillation', *US Patent*, 5,196,612.
- Zhao, F., Tian, Y. C. and Tade, M. O., 2002, 'A time delay compensation strategy for chemical processes with uncertainties', *Comp. Chem. Eng.*, vol. 26 (10), pp. 1437 - 1447.
- Zheng, A. and Mahajanam, R. V., 1999, 'A Quantitative Controllability Index', *Ind. Eng. Chem. Res.*, vol. 38, pp. 999-1006.
- Zhu, Y., 1998, 'Multivariable process identification for MPC: the asymptotic method and its applications', *J. Process Control*, vol. 8 (2), pp. 101-115.
- Zoeiler, J. R., Lane, D. W. C., Eleanor, H., Fuller Jr., D. W. and Barnicki, S. D., 1998, *US Patent*, 5,821,384.