Department of Chemical Engineering

Process Design and Advanced Control Strategies for Model-based Reactive Distillation Columns

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Abstract

Reactive distillation, which is a novel alternative to the sequential operation in reactor and distillation for certain reactive systems, is gradually becoming an important unit operation in chemical process industries. It offers advantages in chemical reaction through lifting the chemical equilibrium limitations and separation by overcoming the distillation boundaries. Economic advantages can also result from the direct energy integration and the reduction of the number equipments due to simpler production flow sheet. Therefore, it can reduce in investment and operational costs

Reactive distillation is a highly non-linear system due to the interactions between vapour-liquid phase equilibrium, chemical kinetics, vapour-liquid mass transfer and diffusion inside the particle catalysts. It causes the existence of multiplicity phenomena and complex dynamics, which have been verified using experimental laboratory and pilot plant unit.

A high quality-rigorous mathematical process model is required to investigate and obtain the optimal design and control of the reactive distillation. For modelling the reactive distillation, a rate-based model can represent physically closer to the real system. However, it requires estimation of more empirical and semi-empirical parameters and offers no improvement in accuracy for most reactive systems. An equilibrium-stage model with proper efficiency (for tray column) or height equivalent to a theoretical stage, HETP (for packed column) is satisfactory and still a preferable alternative model.

This work focuses on the application of reactive distillation for ethyl *tert*-butyl ether (ETBE) production. Compared to methyl *tert*-butyl ether (MTBE) reactive distillation, the ETBE reactive distillation is still limited and yet to be commercialised. Current research has focused on MTBE, while recent studies reveal

that MTBE has severe ingress problem, which pollutes underground water. The pilot scale of reactive distillation column for ETBE production, which is available in the Department of Chemical Engineering, provides experimental data to verify the mathematical model and serve as the case study for control design and optimisation.

The conceptual design of reactive distillation estimates the number of separation and reactive stages, feed flows and locations, energy loads, catalyst requirements, etc. It has been investigated extensively and several methods are proposed. However, reactive distillation design is still an open research area due to the complex interactions between the vapour-liquid transfers and reaction rates. Some unusual responses have been reported and should be fully understood to avoid poor design and sub-optimal performances. Besides, the market price of the products, the costs of the reactants, and the utility costs determine the optimisation process. A rapid method, which can optimise a reactive distillation column, is challenging to develop.

Despite the presence of multiplicity phenomena and complex dynamics, conservative approach of adding a few extra stages to the calculated theoretical stages can be applied in designing reactive distillation columns. The additional stages do not degrade the column performance if the operating conditions are chosen appropriately. However, shorter columns are recommended for both single-feed and double-feed because they can produce comparable performance with less energy consumptions. If related problems of the internal catalyst such as flexibility for loading and unloading and supporting techniques for adequate liquid-vapour contacts can be overcome, a pre-reactor can be eliminated from the ETBE production flowsheet employing a reactive distillation column. The concept of side reactors is introduced to overcome hardware design limitations especially those in the reactive section. The side reactor can reduce the requirement of catalyst loading in the reactive section. The reactive section can be shortened, leading to potential reduction of the costs of the column if the amount of catalyst forces a decrease in the diameter or height of the column. The side reactor also offers convenient procedure for shut down operation and catalyst replacement.

Control system design basically include the selection of control algorithms and control schemes. The concepts of established linear control were initially applied for reactive distillation column studied in this thesis. The linear controllers with proper standard control schemes can be successfully implemented to avoid control problems associated with the presence of multiplicity and complex dynamics while achieving the control objectives. However, the nonlinear-multivariable nature of the reactive distillation combined with higher product competitiveness, tighter safety and environmental regulations would certainly increase the growing nonlinear control applications on reactive distillation. Therefore, advanced control algorithms such as adaptive controllers, which are based on a linear controller integrated with a tuning method, were considered. Firstly, nonlinear PI controller was designed allowing its controller gain to vary to accommodate the nonlinearity of the process gain. Secondly, model gain-scheduling controller was designed using multi-simplified models, which cover relevant operating conditions and cope with nonlinear characteristics, and a switching scheme to integrate the models. The results clearly show that the proposed adaptive controllers can improve the control performance for both set-point tracking and disturbance rejection. However, the model gain-scheduling controller may destabilise the reactive distillation due to fast switching resulting from large values of noise. An estimator is also recommended for controlling the primary controlled variable (product purity) especially due to changes in the feed composition. Multivariable inferential controller was then designed to overcome the limitations. The inferential models were constructed using steady state least square regression method for the estimation of the product purity and reactant conversion from multi-secondary variables. The models were then implemented on reactive distillation using several control schemes employing standard linear controllers. The results indicate that a proper control scheme (cascade two-point control scheme) with an appropriate controller tuning can offer an alternative of model-based nonlinear controller for reactive distillation.

Operability and optimisation of the existing reactive distillation column were investigated using set-point optimisation method. Despite a fixed column configuration (number of stages and feed point) and a fixed control configuration (pairing of controlled and manipulated variables), the operating conditions were

optimised to maximise profitability while a set of safety, operating and product quality constraints and specifications are satisfied. The set-point optimisation framework was then used to provide a basis for a supervisory control system.

Keywords: reactive distillation, process simulation, process design, complex interaction, side reactor, process control, adaptive control, nonlinear PI, gain-scheduling, multivariable control, inferential control, operability, optimisation.

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Brief Biography of the Author

Budi H. Bisowarno completed a Bachelor (Sarjana) of Chemical Engineering degree at Bandung Institute of Technology (ITB), Indonesia in 1993. He then worked as an associate lecturer and researcher at the Department of Chemical Engineering, Parahyangan Catholic University, Indonesia for three year. He obtained his Master of Chemical Engineering degree from Curtin University of Technology in 1999. He commenced Doctor of Philosophy in Chemical Engineering studies at the same University in 2000 with the assistance of the Australian Government through the International Postgraduate Research Scholarship (IPRS).

The journal papers in support of this thesis:

1. Bisowarno, B. H., Tian, Y. C. and Tadé, M. O., 2003, Interaction of separation and reactive stages on ETBE reactive distillation columns, accepted in *AIChE Journal*.
2. Bisowarno, B. H., Tian, Y. C. and Tadé, M. O., 2003, Model gain-scheduling control of an ETBE reactive distillation column, accepted in *Ind. Eng. Chem. Res.*.
3. Bisowarno, B. H., Tian, Y. C. and Tadé, M. O., 2003, Adaptive control of an ETBE reactive distillation column, *Journal of Chemical Engineering of Japan*, in print.
4. Bisowarno, B. H., Tian, Y. C. and Tadé, M. O., 2003, Application of side reactors on ETBE reactive distillation, submitted to *The Chemical Engineering Journal*.
5. Bisowarno, B. H., and Tadé, M. O., 2003, Multivariable inferential control for composition and conversion of an ETBE reactive distillation column, submitted to *Ind. Eng. Chem. Res.*.
6. Bisowarno, B. H., and Tadé, M. O., Operability and optimisation of ETBE reactive distillation systems, in preparation.

One journal paper, which has been contributed by providing the significant data:

1. 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.

Related conference papers in support of this thesis:

1. Bisowarno, B. H., Tian, Y. C. and Tadé, M. O., 2003, 'Modelling and Control of Reactive Distillation Systems', accepted for *ADCHEM 2003*.
2. Bisowarno, B. H., Tian, Y. C. and Tadé, M. O., 2003, 'Combined gain-scheduling and multimodel of a reactive distillation column', accepted for *ADCHEM 2003*.
3. Bisowarno, B. H., Tian, Y. C. and Tadé, M. O., 2003, 'Multivariable inferential control of an ETBE reactive distillation column', accepted for *Chemeca 2003*.
4. Bisowarno, B. H., Tian, Y. C. and Tadé, M. O., 2002, 'Adaptive control of an ETBE reactive distillation column', *9th APCChE Congress and Chemeca 2002*, Christchurch-New Zealand, CD-ROM.
5. Bisowarno, B. H., Tian, Y. C. and Tadé, M. O., 'Effects of Separation Stages on Reactive Distillation of Etherification Processes', *9th APCChE Congress and Chemeca 2002*, Christchurch-New Zealand, CD-ROM.
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In addition, there are papers resulting from the previous research in support to his Master Thesis entitled Simulation and Experimental Testing of Reactive Distillation Column for ETBE Synthesis, which was completed in the Department of Chemical Engineering, Curtin University of Technology, in 1999.

1. 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.
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Nomenclature

Abbreviations

AE	Algebraic equation
DAE	Differential and algebraic equation
DIB	di-isobutylene
ETBE	Ethyl *tert*-Butyl Ether
EtOH	Ethanol
FC	Flow control
HETP	Height equivalent to a theoretical plate
IAE	Integrated absolute error
iBut	Isobutene
ITAE	Integrated time-weighted absolute error
LC	Level control
LMTD	Log mean temperature difference
MTBE	Methyl *tert*-Butyl Ether
MSS	Multiple steady states
NBP	Normal boiling point
NPI	Nonlinear proportional-integral
nBut	n-Butenes
ODE	Ordinary differential equation
PC	Pressure control
PI	Proportional-integral
PID	Proportional-integral-derivative
RE	Rectification section
RX	Reactive section
RVP	Reid vapour pressure
SISO	Single input single output
SR	Side reactor
ST	Stripping section
TAME	*tert*-Amyl Methyl Ether
TC	Temperature control

USEPA	US Environmental Protection Agency
VLE	Vapour liquid equilibrium

Symbols

α	Free design parameter for switching scheme
β	Free design parameter for switching scheme
Δ	Change in parameter value
ε	Reaction volume
γ_i	Activity of component, I
μ	Chemical potential
η	Distance along diffusion path
λ	Closed loop time constant
θ	Time delay
Γ	Thermodynamic factor
a	Interfacial area
B	Bottoms rate
C	Total concentration
D	Distillate rate **or** Diameter
Da	Damköhler number
E	Energy transfer rate
F	Feed or flow rate
H	Vapour molar enthalpy **or** reaction enthalpy
h	Heat transfer coefficient
K	Reaction equilibrium constant **or** process gain **or** controller gain
K_A	Adsorption equilibrium constant
$k.a$	Maxwell-Stefan diffusivity
k_{rate}	Reaction rate constant
L	Molar liquid flow **or** reflux rate
M	Molar holdup
MGS	Model gain scheduling
m_{cat}	Mass of catalyst
N	Mass transfer rate
P	Pressure

P^{vap}	Vapour pressure
Q	Heat duty
R	Gas constant **or** electrical resistance
r_i	Reaction rate of component, i
S	Separation factor **or** side stream flow rate
t	Time
T	Temperature **or** open-loop time constant **or** integral time
U	Heat transfer coefficient
u	Primary manipulated variable
V	Molar vapour flow **or** boilup rate **or** voltage
v	Secondary manipulated variable
w	Disturbance variables
X	Conversion of reactant
X_i	Molar liquid concentration of component, i
Y_i	Molar vapour concentration of component, i

Sub Scripts

i, j, k	"ith", "jth", "kth" reacting component, stage, variable or parameter
R	Reboiler
C	Condenser
a	Ambient

Super Scripts

L	Liquid phase
V	Vapour phase
S	Saturated
I	Interface condition

Chapter 1

Introduction

1.1. Historical Background

Reactive distillation, which combines the functionality of a continuous reactor with a distillation column, has received a crucial attention since the 1980s. The total numbers of literature and patents recently increase dramatically (Taylor and Krishna, 2000). The advantages of reactive distillation result from the improvement in separation by using reaction such as overcoming azeotropes and the improvement in reaction by using separation via overcoming reaction equilibrium limitations and increasing selectivity (Malone and Doherty, 2000). The advantages lead to the reduction on investment and operational costs compared to conventional series of reactor and separator.

However, reactive distillation creates considerably complicated problems in the design and control aspects. These result from the complex interactions between vapour-liquid equilibrium, chemical kinetics, vapour-liquid mass transfer and diffusion inside the particle catalysts (Baur et al., 2000). The interactions cause the existence of multiplicity phenomena and complex dynamics, which have been verified using experimental laboratory and pilot plant unit (Bravo et al., 1993; Rapmund et al., 1998; Mohl et al., 1999).

Design and control of such complex behaviours as reactive distillation requires a high-quality of mathematical process model. Most models were based on equilibrium-stage approach, which assumes that vapour and liquid leaving each stage is in thermodynamic equilibrium (Nijhuis et al., 1993; Hauan et al., 1997; Pilavachi et al., 1997). Some models also consider the column dynamic behaviour while keeping the assumption of vapour-liquid phase equilibrium (Ruiz et al., 1995; Schrans and Wolf, 1996; Scenna et al., 1998). For packed reactive distillation columns, the equilibrium-stage models require height equivalent to a theoretical plate (HETP), which is difficult

or impossible to estimate. The same difficulty also occurs for calculating tray efficiency of tray reactive distillation columns because the reaction alters the composition profiles and consequently the mass transfer coefficient. The efficiency can have positive, zero and negative values without changing the hydrodynamic conditions (Higler et al., 1998). These limitations would lead to the significance of a rate-based model. Although the rate-based model is gaining in popularity due to advances in the available computational power, it is much more complex and requires the estimation of more empirical parameters. Besides, the model does not offer improvement in accuracy for most systems (Luo and Xiao, 2001; Popken et al., 2001; Jimenez and Costa-Lopez, 2002). Therefore, the equilibrium-stage approach with proper efficiency (for tray column) or HETP (for packed column) is still a preferable alternative for modelling reactive distillation.

The conceptual design of reactive distillation estimates number of separation and reactive stages, feed flows and locations, energy loads, catalyst requirements, etc. It has been investigated extensively and several methods are proposed. Geometric method (Okasinski and Doherty, 1998), different-point method (Lee and Westerberg, 2001), and mathematical programming (Ciric and Gu, 1994; Cardoso et al., 2000) can be used to provide the basis for the economic evaluation of reactive distillation designs. However, reactive distillation design is still an open research area due to the complex interaction between vapour-liquid transfer and reaction rates. Some conflicting reports can be found in the open literature. For example, the effects of additional separation stages on the overall column performance are contentious (Sneesby et al., 1998a; Al-Arfaj and Luyben, 2000b). Therefore, the conservative approach of adding a few stages to the calculated theoretical stages may not be applicable to the reactive distillation design. The interaction between control and process design is also an important area for investigation. Therefore, an optimal reactive distillation design can also have a good control performance.

Reactive distillation presents many challenging control problems due to its complex dynamics as shown by the existence of multiplicity phenomena (Sneesby et al., 1998c). The stability of one-point control of reactive distillation with input multiplicity could not be maintained using linear control with integral action (Bisowarno, 2000). As in a particular distillation column (Zhu, 1998), reactive

distillation is also characterized by multivariable interactions between manipulated and controlled variables, which results in nonlinear dynamic responses. Constraints in the manipulated and state variables should always be taken into account in the optimisation of reactive distillation.

The conventional PID algorithm with fixed parameters is not generally sufficient for nonlinear characteristics, which is actually inherent in most chemical processes. For reactive distillation, its changing sign and directionality of the process gain complicates the design of a control system. In some cases, the changing sign of the gain can be overcome by employing an inferential control such that the relationship between the control variable and the manipulated variable is always monotonic. However, the directionality of the gain, which may result from the inferential control system, cannot be handled well by using the PID algorithms with fixed parameters. It needs to be re-tuned adequately over a wide range of the operating conditions. Limited number of reports has discussed the control aspects of reactive distillation. Among these reports are investigations on control strategies of batch reactive distillations (Wajge and Reklaitis, 1999; Balasubramhanya and Doyle III, 2000; Loperena and Ramirez, 2000), continuous reactive distillation for glycol production (Kumar and Daoutidis, 1999; Loporena et al., 2000), esterification (Vora and Daoutidis, 2001), and etherification (Sneesby et al., 1997b; Sneesby et al., 2000). Therefore, control of reactive distillation, especially which employs advanced control strategies, is still an open research area.

Both homogeneous and heterogeneous catalysed reaction can be carried out in reactive distillation (Sundmacher et al., 1994). Simulation and experimental results of reactive distillation can be found in published papers discussing different applications such as esterification (Agreda et al., 1990; Vora and Daoutidis, 2001), alkylation for cumene (Shoemaker and Jones, 1987), synthesis of ethylene glycol (Loporena et al., 2000) and the formation of fuel oxygenates (Smith, 1980a; Sneesby, 1998; Beckmann et al., 2002). Recently, reactive distillation has been selected by more than a hundred operators for various applications including more than 60 ether units (Rock et al., 1997).

Reactive distillation has been widely accepted as a preferred technology for producing ethers. Methyl *tert*-butyl ether (MTBE), which increases the octane rating of the fuel and adds oxygen to promote cleaner burning, is a valuable and mostly used gasoline additive. It is now commercially produced through the application of reactive distillation. However, recent researches show that MTBE has severe water ingress problem and therefore pollute underground water (USGS, 1999). Ethyl *tert*-butyl ether (ETBE) is an alternative to MTBE, which offers less water contaminant. Besides, ETBE has better fuel properties such as lower volatility with higher octane rating. ETBE is a semi-renewable product because it can be synthesised from ethanol. On the other hand, reactive distillation has been found feasible for ETBE production (Sneesby, 1998). Reactive distillation columns for ETBE production are still limited and are yet to be commercialised.

1.2. Motivation and Objectives of this work

This research was motivated by several fundamental and technical problems relating to reactive distillation applications. This relatively new technology needs to be fully understood particularly concerning its nonlinear characteristics and complex dynamics, which affect both design and control strategies.

This research focuses on a relatively wide area so that it permits significant contributions. In the design aspects, an improved understanding of the reactive distillation behaviours will help in the design of an optimal reactive distillation column. The effects of interaction between separation and reactive stages, which causes multiplicity phenomena, require more investigations. Unlike most conventional distillation, reactive distillation produces some counter-intuitive behaviours, which may prevent the application of a conservative approach by adding a few stages to the calculated theoretical stages.

In the control aspects, the development of advanced control strategies will allow for safer and profitable operation of this technology. This current research leads to directly implement advanced control strategies and compare them to that of the

conventional PID algorithm. The interaction between design and control aspects is also significant for investigation.

This thesis was undertaken with the objective of making significant contributions to the body of knowledge. Reactive distillation columns for ETBE production was extensively studied in the following areas:

1. modelling techniques for both steady state and dynamic simulation of reactive distillation columns;
2. the understanding of reactive distillation characteristics, which contribute to the complex design and control of reactive distillation columns;
3. general design considerations especially for heterogeneous reactive distillation columns for ether productions, including the application of side reactors;
4. implementation of such advanced control strategies as adaptive control, multivariable inferential control for reactive distillation columns having multiple steady state phenomena;
5. interaction between design and control, operability and optimisation of reactive distillation columns.

1.3. Thesis Outline

Although reactive distillation is a very broad topic, this thesis focuses extensively on reactive distillation that consists of separation and reactive stages. Production of ethyl *tert*-butyl ether (ETBE) is used as a study case in which the simulation study was conducted to illustrate many of the important points.

The thesis can be subdivided into two main topics: steady state simulation and its implementation for design including the application of side reactor and optimisation (Chapters 4, 5, 8) and dynamic simulation and its application for advanced control strategies (Chapters 6-8). Supplemental to this core is the literature review (Chapter 2), the modelling of reactive distillation (Chapter 3), conclusions and recommendations (Chapter 9) and the list of cited literature (Chapter 10).

Program listings for the simulation models have not been included in the thesis to conserve space. They are available from the Department of Chemical Engineering, Curtin University of Technology, on request.