School of Chemical Engineering

Simulation and Experimental Testing of Reactive Distillation Column for ETBE Synthesis

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ABSTRACT

Reactive distillation is a novel alternative to the sequential operation in reactor and distillation. It offers advantages in chemical reaction by shifting the chemical equilibrium and separation by overcoming distillation boundaries. Economic advantages also result from direct energy integration and reduction of equipment costs. Reactive distillation is accepted as a preferred technology for producing oxygenates, including ethyl *tert*-butyl ether (ETBE). The available reactive distillation column in School of Chemical Engineering, Curtin University of Technology was designed to produce ETBE. The mathematical models of the column written in Pro/II and SpeedUp Simulation Packages were significantly modified to study other aspects of reactive distillation phenomena, which were not previously considered by using steady state as well as dynamic simulations.

The ETBE reactive distillation column exhibits multiplicity phenomena, which influence the transient condition during start up and shut down operations. The input multiplicity region that depends on the operating condition is significant during start up operation. The input multiplicity could increase or decrease the overall process performance depending on the chosen operating condition. Regarding output multiplicity, different start up strategy results in different output conditions. This result implies that the column could be sent to an inappropriate operating condition due to the lack of understanding of the output multiplicity. Three scenarios for shut down operation were considered in order to maintain high isobutylene conversion as well as ETBE purity.

Since the multiplicity phenomena result from interaction between reaction and separation effects, the existence of multiplicity depends on the number of separation and reaction stages. Several columns were simulated to investigate the effects of different number of either separation or reaction stages on the multiplicity phenomena. It is speculated that input multiplicity always occurs in any reactive distillation column. This result implies that several reactive distillations may be designed to satisfy the same process requirements. On the other hand, output multiplicity region could be magnified by increasing the number of reactive and separation stages. Besides, output multiplicity could be found for low internal rates for high number of stages of the reactive distillation column.

The control schemes for the ETBE reactive distillation were also compared with respect to their disturbance rejection capabilities. One-point control schemes may be used to implicitly control the two main objectives of this reactive distillation column. It was found that disturbance gains resulting from steady state analysis could be used to predict the dynamic changes of the system resulting from the same disturbances. Among the control schemes studied, the LB scheme is the most suitable scheme to reject load disturbances at one-point scheme for this reactive distillation. The LB scheme also has excellent capability to change the steady state conditions through changes in the set-point temperature. Although the LV control scheme also has capability to reject load disturbances, the small step changes in the set-point temperature could destabilise the system. This results from the limitation in the reboiler sump, which is dry for step increases and floods for step decreases in the set-point temperature. It is recommended to use bigger reboiler sump in this reactive distillation. A detailed comparison for the LV and LB control schemes were investigated by using proportional-integral (PI) controllers with various values for the gains and reset times. It was found that the same values cannot satisfy both positive and negative disturbances. This results from the high degree of non linearity and bi-directionality of the system.

The Amberlyst-15 catalyst was first tested to determine the activity. The results show that the catalyst particles still have adequate activity to proceed the synthesis of ETBE. Experiments were then conducted under proposed batch operation to avoid any polymerisation of isobutylene. However, continuous operations could not be run due to pump failure. Other reasons for these difficulty and possible solutions to solve this problem are explained in the thesis. Efforts were also made to connect the controllers to a PC having SCAN 3000 through an interface converter, so that the rig can be used for control studies in future projects.

Keywords: reactive distillation, simulation, multiplicity, start up, shut down, control schemes, disturbance rejection.

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Brief Biography of the Author

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Nomenclatures

Abbreviations

AE	Algebraic Equation
DAE	Differential and Algebraic Equation
DIB	Di-isobutylene
ETBE	Ethyl tert-Butyl Ether
EtOH	Ethanol
HETP	Height Equivalent to a Theoretical Plate
IAE	Integrated Absolute Error
IBut	Isobutene
ITAE	Integrated Time-weighted Absolute Error
LMTD	Log Mean Temperature Difference
MON	Motor Octane Number
MTBE	Methyl tert-Butyl Ether
MSS	Multiple Steady States
NBP	Normal Boiling Point
NBut	n-Butenes
ODE	Ordinary Differential Equation
RON	Research Octane Number
RVP	Reid Vapour Pressure
TAME	*tert*-Amyl Methyl Ether
USEPA	US Environmental Protection Agency
VLE	Vapour Liquid Equilibrium

Symbols

A_I	Activity of component, I
B	Bottoms rate
D	Distillate rate ***or*** Diameter
F	Feed rate
h	Liquid Molar enthalpy
H	Vapour Molar enthalpy
K	Reaction equilibrium constant **or** Process gain
K_A	Adsorption equilibrium constant
k_{rate}	Reaction rate constant
L	Molar liquid flow ***or*** Reflux rate
M	Molar holdup
m_{cat}	Mass of catalyst
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
t	Time
T	Temperature
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

Greek Characters

γ_i	Activity of component, '
ρ	Density

Subscripts and Superscripts

0	Initial condition **or** degree Celcius
C	Condenser
L	Liquid phase
p	Stage number
R	Reboiler
T	Temperature
u	Primary manipulated variable
V	Vapour phase
v	Secondary manipulated variable
w	Disturbances variable
x	Conversion

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Chapter 1

Introduction

The tighter environmental regulations have driven not only the increasing demand of environmentally compatible products but also the development of chemical engineering processes. For example, the Clean Air Act (CAA) which was amended in November 1990 has established a permanent role for oxygenates in the US gasoline. On the other hand, reactive distillation has also received more interests in recent years. It combines chemical reaction and multistage distillation simultaneously (De Garmo *et al.*, 1992) that offers a reduction in the capital investment as well as the operating costs. 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).

1.1 Background

1.1.1 Ethyl *tert*-butyl ether

Recently there are two main oxygenates, ethanol and tertiary ethers, which can be blended into gasoline to improve its performance. In general, ethers such as methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE) are preferred to ethanol due to their blending properties, which are more like conventional gasoline hydrocarbon constituents (Kyle and Datta, 1995). The demand for MTBE rose very fast in this decade and may reach 540,000 bpd by the end of 2000 (Thomas, 1994). Although MTBE is used widely at this time, ETBE will be a more important oxygenate due to its better properties.

ETBE has some more advantages compared to MTBE. First, the properties of ETBE are better than MTBE. It has a slightly higher octane rating and a lower volatility. As a result, ETBE can raise combustion temperature and improve engine efficiency (Thiel *et al.*, 1997). Therefore, the level of carbon monoxide emission and unburned hydrocarbon can be minimised. Besides, ETBE is less hydrophilic than MTBE so that ETBE can less permeate and pollute groundwater surface. ETBE is synthesised from isobutylene and ethanol, which can be produced from biomass such as agricultural wastes. In other words, ETBE is a semi renewable oxygenate. The comparison properties between ETBE and MTBE were summarised by Sneesby *et al.* (1997a) as shown in Table 1.1. It can be seen that ETBE slightly has a lower oxygen content, therefore unburned fuel and carbon monoxide emissions are slightly higher.

Table 1.1 The comparison properties between ETBE and MTBE*

No	Properties	MTBE	ETBE
1	Molecular weight	88	102
2	Oxygen content (wt%)	18.2	15.7
3	Normal boiling point (°C)	55	73
4	Blending RVP (kPa)	55	27
5	Octane ((RON+MON)/2)	110	111
6	Energy content (MJ/kg)	35.3	36.3
7	Relative cost	low	moderate
8	Renewable source?	no	yes

* Source: Sneesby *et al.* (1997a)

The oxygenates, especially MTBE are one of the fastest growing chemicals in the nineties. Global MTBE capacity has reached about 30 millions of tons/year in 1995, US consumed around 53% of them (Ancillotti and Fattore, 1998). However, ETBE may become a major oxygenate in the future because it has some better advantages compared to MTBE. Besides, the increasing contamination of water resources of MTBE has become a major public concern in US. MTBE that dissolves in the water resources is resistance to microbial decomposition and is difficult to remove in water treatments. Furthermore, the US Environmental Protection Agency (USEPA) has classified MTBE as a potential human carcinogen (USGS, 1999). Besides, the price of ETBE can be reduced by the improvements in design, operating and control technologies.

1.1.2 Reactive distillation

Research and development in chemical reaction engineering should be directed to meet such demands as process and product safety, environmentally compatible products, minimisation of waste generation, minimisation of investment, minimisation of energy consumption and operability and control (Lerou and Ng, 1996). The first three demands relate to tighter environmental regulation. Besides, a new process should not only be safe and environmentally friendly but also economically competitive compared to other processes. In this regard, globalisation of the world economy will increase economic pressure. Thus, it is important to develop a process that can minimise investment and energy consumption. Finally, some processes that tend to be most severe and complex should be designed for smooth start up and shut down, and for optimal steady state operation through process control.

Reactive distillation is an example of a unit operation that can meet these demands. This unit combines chemical reaction and multistage distillation simultaneously (De Garmo *et al.*, 1992). Two main advantages result from reactive distillation. First, there is a reduction in capital investment (De Garmo *et al.*, 1992), due to the integration of the reactor and the distillation column into one unit reactive distillation column. It also leads to a reduced number of pumps, piping and instrumentation. Next, the operating costs can be minimised (Bock *et al.*, 1997), due to the ability of reactive distillation to overcome thermodynamic and kinetic restrictions. This ability results from utilising the high degree of internal recycle present in a reactive distillation system, which creates reaction conditions suitable for high conversion (Sneesby *et al.*, 1997a). In addition, it also offers direct energy integration between the reaction system and separation system in the process (Ung and Doherty, 1995). It results from exothermic heat of reaction that is used for evaporation of liquid-phase. In addition, reactive distillation may also reduce downstream processing.

Although there are advantages in using reactive distillation column, some unusual phenomena are still unclear due to the interaction of many variables. As a result, "the interaction between variables in reactive distillation generates some unusual responses to changes in operating condition" (Sneesby *et al.*, 1997a). This generates unusual control problems that may not be understood without detailed simulation results. Furthermore, it may create unusual design in catalyst bed. It should provide a surface for condensing the vapour and allowing hot vapour to rise through the column and liquid to trickle down (Nathan, 1997). Besides, the catalyst has to be located in the best suitable temperature for reaction.

In recent years, the application of reactive distillation is quite attractive for both heterogeneously catalysed etherification such as MTBE and ETBE and homogenously catalysed esterification or hydration (Thiel *et al.*, 1997). Podrebarac *et al.* (1997) reviewed some of reactions that could benefit from the application of reactive distillation. Stichmair and Frey (1999) presented similar work by discussing the possibility of reactive distillation through the comparison of conventional processes and reactive distillation processes. The knowledge of reactive distillation lines and potential reactive azeotrope were used for systematic design of reactive distillation in the latter one. Another computational approach, which was based on the concept of "Static Analysis", was developed as a new systematic method for the feasibility study of the reactive distillation (Geissler *et al.*, 1998).

There are now few commercial applications, for examples, the Eastman Kodak process for the production of methyl acetate and the Smith's catalytic distillation of MTBE (Lerou and Ng, 1996). CD tech is the leader in this technology with some 70 units which are operated around the world (Nathan, 1997). Besides, this research area is still growing in international scale, for example, European Union has sponsored a research consortium project which costs around Ecu4m (some £2.3m) (Nathan, 1997). This project is led by Nestle which includes BP, BASF, Hoechst, Snamprogetti and the Universities of Aston, Bath, Essen, Dortmund, Clausthal and Helsinki. This consortium has announced the achievement that provides a predictive tool (named SYNTHESISER), a process simulator (named DISIGNER), and an integrated tool (named PREDICTOR) (Kenig *et al.*, 1999). The SYNTHESISER is used for a fast evaluation of whether reactive distillation is suitable for certain chemical systems and then provides a basic design for further development of the process. The DESIGNER is used for modelling, designing and understanding of the complex behaviour of the reactive distillation column and then integrated into industrial process design. Furthermore, the PREDICTOR is used for synthesis and design of reactive distillation processes using a special common user interface.

1.2 Research Objectives and Contributions

The principal objective of the research is to enrich the study of reactive distillation control for ETBE synthesis. The research includes the dynamics of start up and shut down operations to obtain more stable steady state operations. Further efforts focus on the multiplicity phenomena and comparison of the control configurations. The available model as discussed in Sneesby *et al.* (1997a, b), which are written in Pro/II and SpeedUp were assessed and expanded further as the basis of reactive distillation control studies. At the current time, there are very few published results on how this can be done.

The secondary objective focuses on completing instrumentation of the pilot scale reactive distillation unit, which is available in the School of Chemical Engineering. Progeny CTX temperature controllers was connected to a PC having SCAN 3000 through an interface converter. The reactive distillation unit is expected to be run for collecting experimental data, which can be used to validate the simulation results. At this time, there are no published experimental results.

1.3 Thesis Outline

The thesis discusses the application of reactive distillation for ETBE synthesis. It is divided into four main topics: the effects of the multiplicity phenomena during start up and shut down operation (Chapter 3); the effects of number of stages in reactive distillation on multiplicity phenomena (Chapter 4); the comparison of one-point scheme for controlling ETBE purity (Chapter 5); and the discussion of the characteristics of the reactive distillation unit (Chapter 6). Supplemental to this core are the literature review (Chapter 2), the conclusions and recommendations (Chapter 7) and the list of cited literature (Chapter 8).

Program listings for the simulation models (Chapters 3-5) have not been included in the thesis in order to conserve space. These are available from the School of Chemical Engineering, Curtin University of Technology, on request.