Simulation Studies of Reactive Distillation for Ethyl acetate Production through Esterification

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DECLARATION

I hereby declare that thesis entitled **"Simulation Studies of Reactive Distillation for Ethyl acetate Production through Esterification"** is an authentic record of my work carried out as per the requirements for the award of degree of **M.Tech. (Chemical Engineering)** at **Thapar University, Patiala**, under the guidance of **Dr. Raj Kumar Gupta**, (Assistant Professor) and **Mr. Rakesh Kumar Gupta**, (Assistant Professor) **Department of Chemical Engineering,** Thapar University, Patiala during **July 2010 to July 2011**. The matter embodied in this thesis has not been submitted in part or full to any other university or institute for the award of any degree.

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ABSTRACT

Reactive distillation (RD) is an integrated operation that combines a chemical reaction step with separation of the products in the same vessel. Reactive distillation is potentially attractive whenever a liquid phase reaction must be carried out with a large excess of one reactant. Under such circumstances, conventional processes incur large recycle costs for excess reactant. Reactive distillation, on the other hand can be carried out closer to stoichiometric feed conditions, thereby eliminating recycle costs. Both homogeneous and heterogeneous catalysed chemical reactions can be carried out in a reactive distillation column. Process development, design and operation of RD processes are highly complex tasks. The potential benefits of this intensified process come with significant complexity in process development and design.

Through RD implementation, chemical equilibrium limitation can be overcome, an equilibrium reaction can be driven to completion by separation of products from the reacting mixture (i.e., reaction conversion can approach 100%). Higher conversions are obtained due to shifting of the equilibrium to the right. Ethyl acetate is produced by the esterification reaction of ethyl alcohol and acetic acid using catalysts such as sulphuric acid, para toluene sulphonic acid or ion exchange resins. This equilibrium limited reaction and its process conditions are suitable for the RD implementation.

The system is strongly non-ideal due to the presence of ethanol, acetic acid, and water. The separation of pure components is very difficult due to the existence of five normal azeotropes, namely, ethanol–water; water–acetic acid, ethyl acetate–ethanol, ethyl acetate–water, and ethanol–ethyl acetate–water.

In this work, the simulation of reactive distillation of ethyl acetate production ($C_2H_5COOCH_3$), using acetic acid (CH_3COOH) and ethanol (C_2H_5OH), in a plate column are done using RADFRAC module of ASPEN Plus. The results show that the Wilson model for liquid phase activity with SRK model for vapor phase, and UNIQUAC model for liquid phase predict the experimental data most closely. However, the segmental model approach has improved the simulation predictions for the entire column.

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CHAPTER 1
INTRODUCTION

Distillation is one of the most important separation processes in chemical industry. All around the globe, in almost all the chemical industries a significant fraction of capital investment and operating cost involves distillation. As a result any kind of improvement of distillation operation can be very beneficial economically. Reactive distillation (RD) is one major step in the history of distillation in achieving these goals. Reactive distillation processes couple chemical reactions and physical separations into a single unit operation. These processes as a whole are not a new concept as the first patent dates back to the 1920s. While the concept existed much earlier, the first real-world implementation of reactive distillation took place in 1980s. The relatively large amount of new interest in reactive distillation is due to the numerous advantages it has over ordinary distillation.

Reactive distillation involves simultaneous chemical reaction and distillation. The chemical reaction usually takes place in the liquid phase or at the surface of a solid catalyst in contact with the liquid phase. General application of reactive distillation is the separation of a close-boiling or azeotropes. A second application of reactive distillation involves taking into account undesirable reaction that may occur during distillation but the most interesting application involves combining chemical reactions and separation by distillation in a single distillation apparatus.

Separation processes with simultaneous chemical reactions are gaining increased attention for a large number of reactive systems of industrial interest. Reactions limited by chemical equilibrium constraints will be favored if the products can be continuously removed from the reaction environment, thus shifting the direction of the equilibrium reaction towards the products side. Distillation processes with simultaneous chemical reaction would enhance the conversion of those equilibrium controlled reactive systems, which have a significant difference between the volatility of reactants and products. The reduction of total investment and operating cost, when reactions can be carried out simultaneously with the separation can be proven substantial. This is usually achieved through the reduction of the number of process units (reactors, intermediate

tanks), the elimination of large recycle streams and the heat integration between the reactor and the separation column.

In recent years, increasing attention has been directed toward reactive distillation processes as an alternative to conventional processes. This has led to the development of a variety of techniques for simulating reactive distillation columns. Meanwhile, the concept of reactive distillation is not new. The technique was first applied in the 1920s to etherification processes using homogeneous catalysts and was reviewed by Keyes in 1932.

Enhanced reaction rates, increased conversion, enhanced reaction selectivity, heat integration benefits and reduced operating costs are just to name a few. All these factors contribute to the growing commercial importance of reactive distillation. However, since heat transfer, mass transfer, and reactions are all occurring simultaneously, the dynamics which can be exhibited by catalytic distillation columns can be considerably more complex than found in regular columns. These result in an increase in the complexity of process operations and the control structure installed to regulate the process.

The principle of building a reactive distillation column is quite simple. A distillation column having a catalyst zone strategically placed in the column to carry out the desired reaction is a reactive distillation column. The catalyst may be in the same phase as that of the reacting species or it can be in the solid phase. The feed for the process is fed either above or below the reactive zone depending upon the volatility of the components and to carry out the desired reaction. The reaction occurs mainly in the liquid phase, in the catalyst zone.

Reactive distillation is potentially attractive whenever a liquid phase reaction must be carried out with a large excess of one reactant. Under such circumstances, conventional processes incur large recycle costs for excess reactant. Reactive distillation, on the other hand can be carried out closer to stoichiometric feed conditions, thereby eliminating recycle costs. Both homogeneous and heterogeneous catalysed chemical reactions can be carried out in a reactive distillation column. Process development, design and operation of RD processes are highly complex tasks. The potential benefits of this intensified process come with significant complexity in process development and design.

The non linear coupling of reactions, transport phenomena and phase equilibrium can give rise to highly system-dependent features, possibly leading to the presence of reactive azeotropes and the occurrence of steady-state multiplicities .Furthermore; the number of design decision variables for such an integrated unit is much higher than the overall design degrees of freedom of separate reaction and separation units.

RD has been successfully used and investigated in the past for several reactions such as etherification, esterification, hydrogenation, hydrodesulphurization and polymerization. Various reviews have been published on this aspect (Doherty and Buzad, 1992; Podrebarac et al., 1997; Taylor and Krishna, 2000; Mahajani and Chopade, 2001; Sharma and Mahajani, 2003). Figure 1.1 shows an updated version of the recently published statistics (Malone and Doherty, 2000), shows that there are around 180 papers and 100 patents published in the last two years on reactive distillation alone. This clearly reveals the increasing interest in this area.

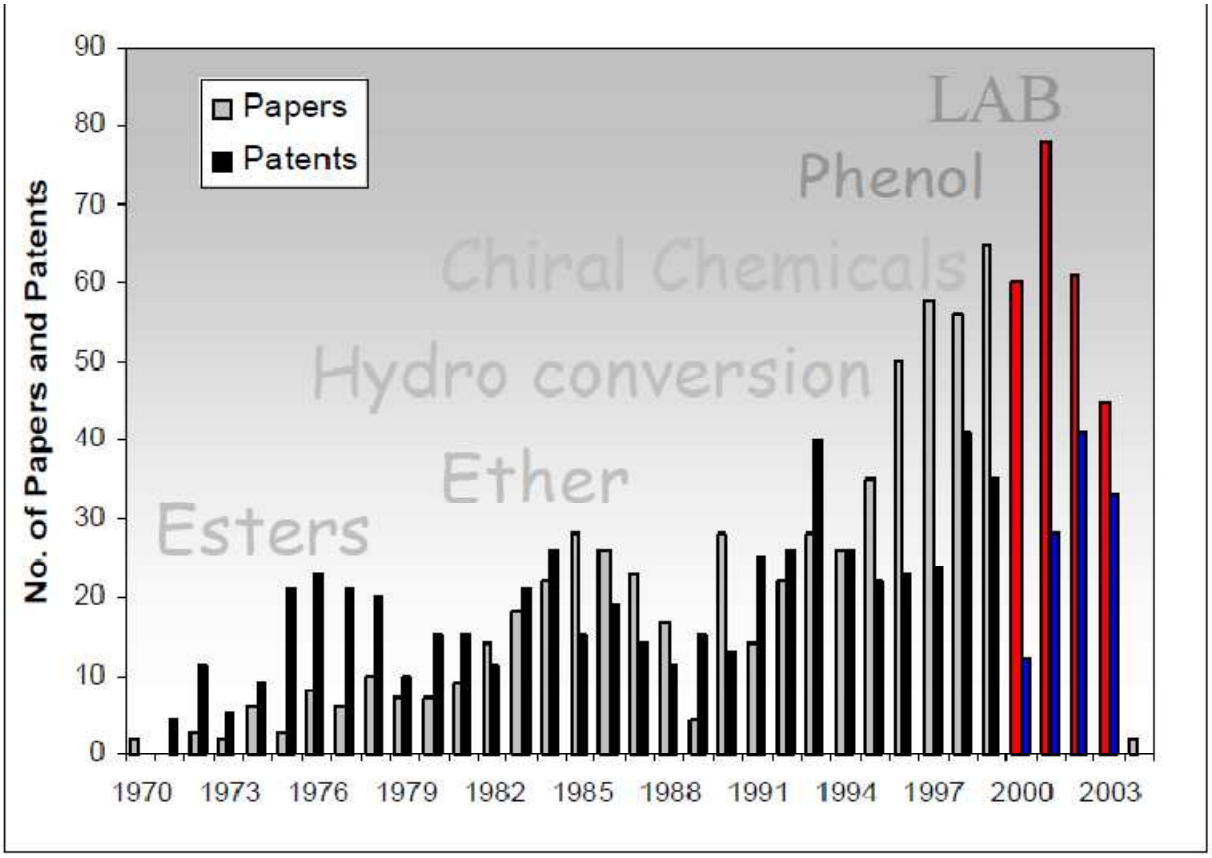

Figure 1.1: Statistics of patents and publications (Source: Harvey et al., 2004)

1.1 Basics of reactive distillation

Reactive distillation is a unit operation that combines a reactor as an integral part of the distillation column as depicted in Figure 1.2. It can be utilized for either equilibrium reactions or non-equilibrium (irreversible) reactions. In the first case, the withdrawal of products as they are formed results in an increase in the conversion that can be achieved. This increase is achieved through a shift in the equilibrium, based on Le Chatelier's principle.

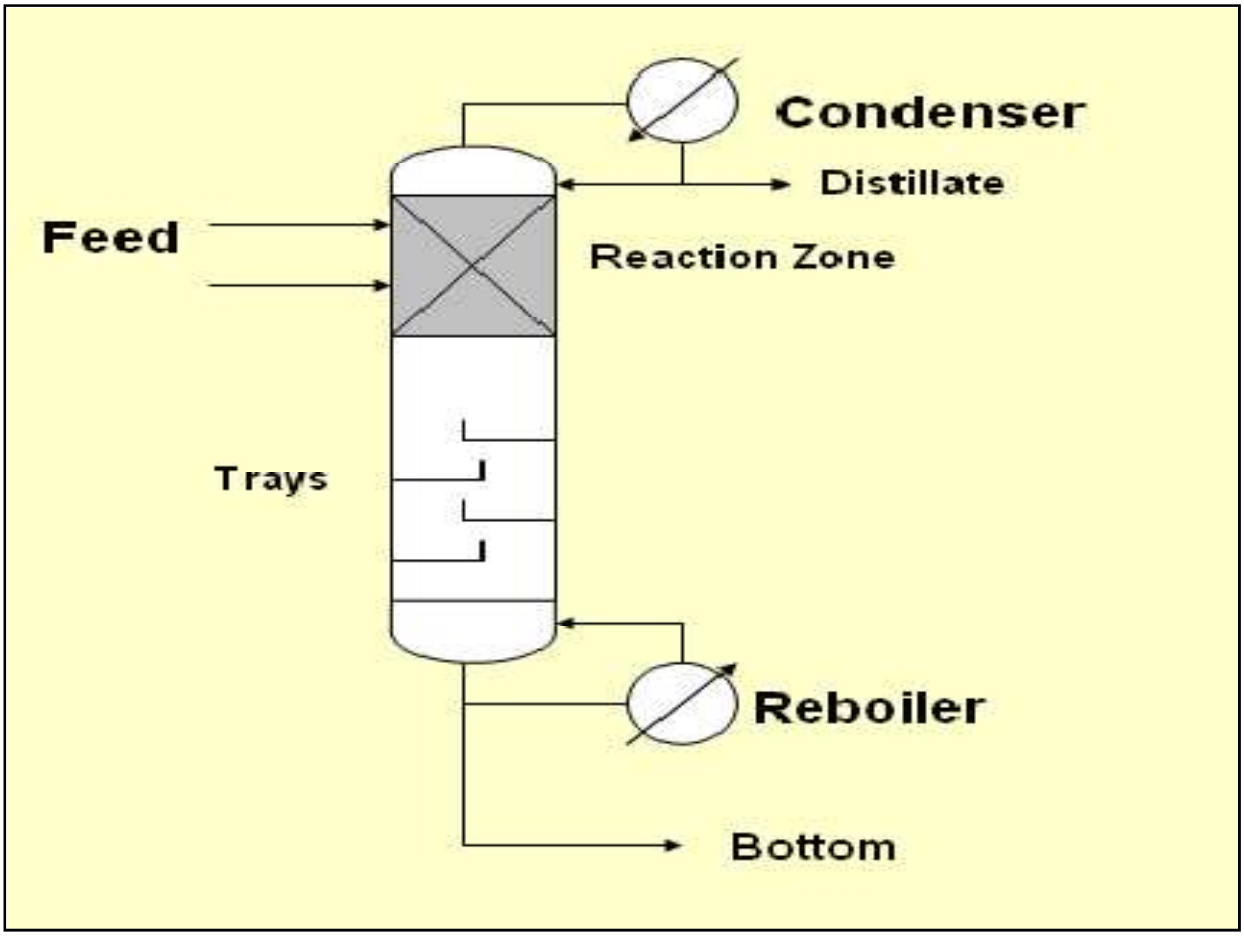

Figure 1.2: Simple reactive distillation

In the second case, it is generally applied to systems where products may react with reactants, causing a decrease in product yield in conventional reactors The term catalytic distillation is also used for such systems where a catalyst (homogeneous or heterogeneous) is used to accelerate the reaction.

1.2 Importance of RD

The potential benefits of applying RD processes are taxed by significant complexities in process development and design. For reactions that are irreversible, it is more economical to take the reaction to completion in a reactor and then separate the products in a separate distillation column (Harvey et al., 2004). The principles may be illustrated when we look for an example process for the production of chemical C out of A and B according the following reaction scheme:

A+ B ⇔C+ D, where the boiling points of the components follow the sequence A, C, D and B.

In addition some undesired side reactions are assumed, for example:

A+ C ⇔E, 2C⇔F

This reaction can be carried out in a conventional process setup as sketched on the left side of Figure 1.3 the objective is to produce C out of reactants A and B, thereby making byproduct D. In addition, there are undesired side and consecutive reactions, so that the exit stream of the reactor will be a mixture of all components. A and B have to be separated and recycled, C has to be separated and purified to separation, and D, E, and F have to be disposed of. Normally, this will require more than the single distillation column that is given in Figure 1.3. Shown on the right hand side of Figure 1.3 is a typical setup for reactive distillation column. The reactions will take place in the reactive section.

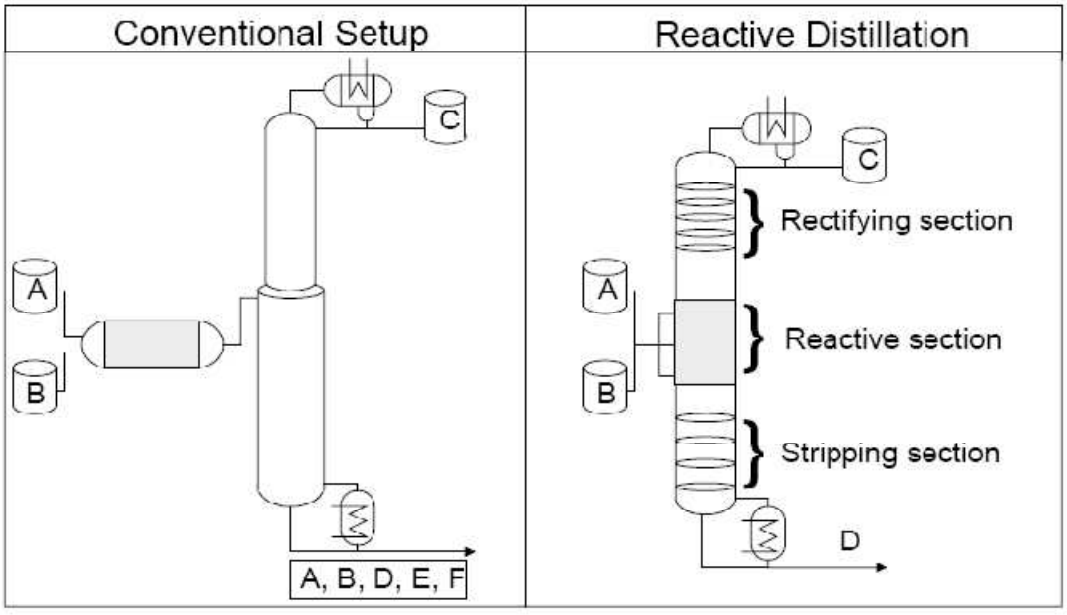

Figure 1.3: Schematic representation of a conventional and reactive distillation process (Source: Around, 1999)

In case of a heterogeneous reaction, this section can consist of reactive packing elements but also of trays that are covered with a teabag type. For homogeneous reactions, the location of the reactive section is defined by the feed location of a homogeneous liquid catalyst. The non-reactive rectifying and stripping section take care of additional product separation. In this kind of setup there is in-situ product removal of desired product C, which will pull the equilibrium of the main reaction towards the right hand side, thereby increasing the overall conversion. This way one can overcome a bad equilibrium constant. In addition, lowering the concentration of C due to the in-situ separation will also reduce the rates of side reactions, there will be less conversion of C to undesired side products, and this illustrates how reactive distillation may be applied to systems where selectivity is important.

The non-reactive section in the column play an important role in product separation and reactants recycle. In the ideal case, the non-reactive zones separate the products from the reactant in such a way that the reactants are automatically flushed back into the reactive zone, while pure products may be obtained as product stream. The design and operation issues for reactive distillation (RD) system are considerable more complex than those involved for either conventional reactor or conventional distillation column.

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The most spectacular example of the benefits of RD is in the production of methyl acetate. The acid catalyzed reaction MeOH + AcOH ⇔ MeOAc +H2O was traditionally carried out using the processing scheme shown in Figure 1.4 (a), which consists of one reactor and a train of nine distillation columns .In the RD implementation (Figure 1.4 (b)) only one column is required and nearly 100 % conversion of the reactant is achieved. The capital and operating costs are significantly reduced.

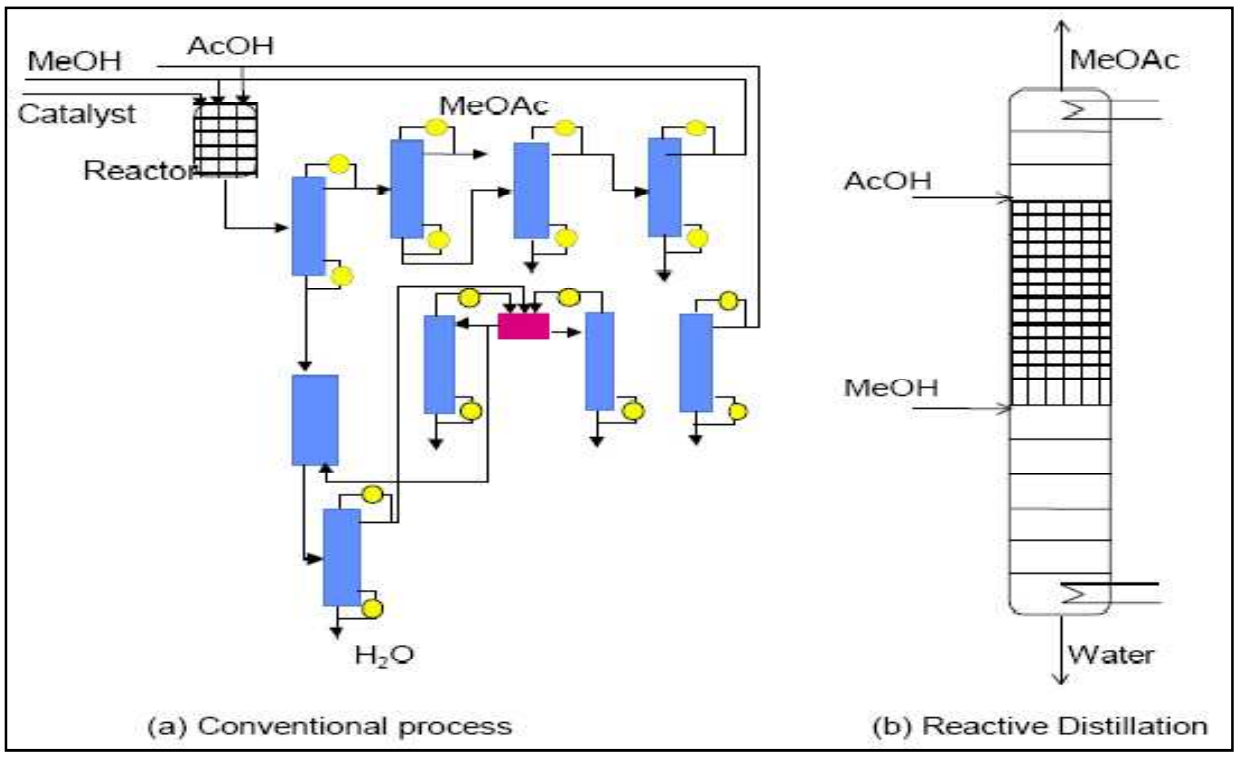

Figure 1.4: (a) Conventional distillation columns (b) The reactive distillation configuration (Source: Taylor and Krishna, 2000)

For the acid catalyzed reaction between iso-butene and methanol to form methyl tert-butyl ether, isobutylene + MeOH ⇔ MTBE, the traditional reactor-followed-by-distillation concept is particularly complex because the reaction mixture leaving the reactor forms three minimum boiling azeotropes. The RD implementation requires only one column to which the butenes feed (consisting of a mixture of n-butene, which is non-reactive, and iso- butene which is reactive) and methanol is fed near the bottom of the reactive section.

The RD concept shown in Figure 1.5 (a) is capable of achieving close to 100% conversion of iso-butene and methanol, along with suppression of the formation of the unwanted dimethyl ether. Also, some of the azeotropes in the mixture are "reacted away". For the hydration of ethylene oxide to mono-ethylene glycol: EO + H2O ⇔ DEG, the RD concept, shown in Figure 1.5 (b) is advantageous for two reasons. Firstly, the side reaction EO+EG ⇔ DEG is suppressed because the concentration of EO in the liquid phase is kept low because of its high volatility. Secondly, the high heat of reaction is utilized to vaporize the liquid phase mixtures on the trays. To achieve the same selectivity to EG in a conventional liquid phase plug flow reactor would require the use

of 60% excess water. Similar benefits are also realized for the hydration of iso-butene to tert-butanol and hydration of 2-methyl-2-butene to tert-amyl alcohol.

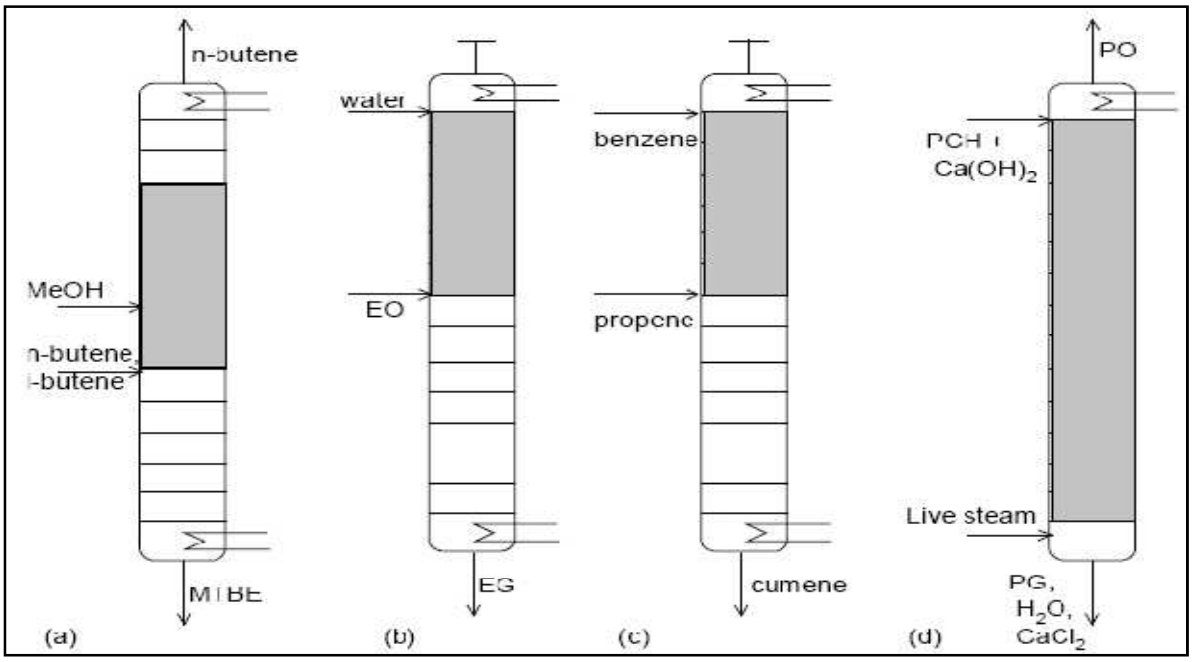

Figure 1.5: Reactive distillation concept for synthesis of (a) MTBE (b) Ethylene glycol (c) Cumene (d) Propylene oxide (Source: Taylor and Krishna, 2000)

Several alkylation reactions, Aromatic + Olefin ⇔ Alkylaromatic, are best carried out using the RD concept not only because of the shift in the reaction equilibrium due to in-situ Separation but also due to the fact that the undesirable side reaction, Alkyl Aromatic+Olefin ⇔ dialkyl aromatic, is suppressed. The reaction of propene with benzene to form cumene, Benzene+Propene ⇔ Cumene (Figure 1.5 (c)), is advantageously carried out in a RD column because not only is the formation of the undesirable di-isopropylbenzene suppressed, but also the problems posed by high exothermicity of the reaction for operation in a conventional packed bed reactor are avoided. Hot spots and runaway problems are alleviated in the RD concept where liquid vaporization acts as a thermal flywheel. The alkylation of Isobutane to iso-octane, isobutene+ n-butane ⇔ iso-octane, is another reaction that benefits from a RD implementation because in-situ separation of the product The reaction between propylene chlorohydrin (PCH)

and $Ca(OH)_2$ to produce propylene oxide (PO) is best implemented in an RD column, as shown in Figure 1.5 (d).

1.3 Advantages of RD

- Chemical equilibrium limitation can be overcome, an equilibrium reaction can be driven to completion by separation of products from the reacting mixture (i.e., reaction conversion can approach 100%). Higher conversions are obtained due to shifting of the equilibrium to the right. This is exemplified by the production of methyl acetate. (Stankiewicz, 2003; Agreda et al., 1990) and tertiary amyl ether (Bravo et al., 1993).

- Higher selectivity can be achieved elimination of possible side reaction by removal of the product from the reaction zone. This can serve to increase selectivity. In some applications particularly in cases when thermodynamic reaction prevents high conversion the coupling of distillation to remove reaction product from reaction zone can improve the overall conversion and selectivity significantly, for example in the production of propylene oxide from propylene chlorohydrins (Carra et al., 1979) and for alkylation of benzene to produce cumene (Shoemaker and Jones, 1987).

- The heat of reaction can be used in-situ for distillation, saving associated energy costs, through use of energy released by exothermic reaction for vaporization. This reduces the reboiler heat duty which is supplied normally by steam. Benefits of heat integration are obtained because the heat generated in chemical reaction is used for vaporization, this particularly advantageous for situation involving heat of reaction such the hydration of ethylene oxide (Circ et. al., 1994).

- Reduction of hotspot, because the liquid vaporization provides a sink for thermal energy. This is beneficial in, for example, the hydrolysis of ethylene oxide to ethylene glycol (Ciric et al., 1994).

- Increasing process efficiently and reducing of investment and operational cost are direct result of this approach (Cristhain et al., 2008).

- Effecting distillation and reaction simultaneously reduces the capital cost and includes benefits such as reduction of recycle, optimization of separation, lower requirements of pump, instrument and piping.

- Improved product quality–reducing opportunity for degradation because of less heat; heat duty can be reduced by utilizing the heat of reaction (if present) in situ.

- Avoidance of azeotropes. RD is particularly advantageous when the reactor product is a mixture of species that can form several azeotropes with each other. RD conditions can allow the azeotropes to be reacted away in a single vessel.

- Heat integration benefits. If the reaction is exothermic, the heat of reaction can be used to provide the heat of vaporization and reduce the reboiler duty.

1.4 Constraints and disadvantages of RD

In spite of above stated benefits of reactive distillation, cannot be used for every process that requires reaction and separation in a single unit. It has some constraints. In general, reactive distillation is not attractive for supercritical condition, for gas-phase reaction, and for reaction that must take place at high temperature and pressures, or that involves solid reactants or product.

RD is considered as an alternative to the use of separate reactor and distillation vessel whenever the following holds:

- Reactive distillation is not suitable for every process where reaction and separation steps occur. Operating conditions, such as pressure and temperature of reactive and separation process and perhaps other requirement, must overlap in order to assure the feasibility of combined process. In some processing the optimum conditions of temperature and pressure for distillation may be far from optimal condition for reaction and vice versa. This limitation can be overcome by fixing adequate operating conditions in the cases where this is possible.

- Difficulties in providing proper residence time characteristics. If the residence time for the reaction is long, it may require a large column size and a large hold-up leading to the process becoming uneconomical compared with standard separate reactor and distillation column setup.

- Scale up to large flows. It is difficult to design RD process for very large flow rates because of liquid distribution problems in packed RD columns.

- A very stable catalyst is required for heterogeneous system. Catalyst deactivation may have a marked effect on column performance and is not easily overcome.

- Higher requirements on the quality of the design and control systems including more sophisticated controller designs and more complicated control structures.

- A very stable catalyst is required for heterogeneous system. Catalyst deactivation may have a marked effect on column performance and is not easily overcome.

1.5 Transport processes in RD

The design and operation issues for RD systems are considerably more complex than those involved for either conventional reactors or conventional distillation columns. The introduction of an in-situ separation function within the reaction zone leads to complex interactions between vapour-liquid equilibrium, vapour-liquid mass transfer, intra-catalyst diffusion (for heterogeneously catalysed processes) and chemical kinetics. Figure 1.6 shows the various transfer processes in homogeneous and heterogeneous RD.

In heterogeneous RD the problem is exacerbated by the fact that these transfer processes occur at length scales varying from 1 nm (pore diameter in gels, say) to say a few meters (column dimensions).The timescales vary from 1 ms (diffusion within gels) to say a few hours (column dynamics). The phenomena at different scales interact with each other. Such interactions, along with the strong non-linearity introduced by the coupling between diffusion and chemical kinetics in counter-current contacting, have been shown to lead to the phenomenon of multiple steady

states and complex dynamics, which have been verified in experimental laboratory and pilot plant units.

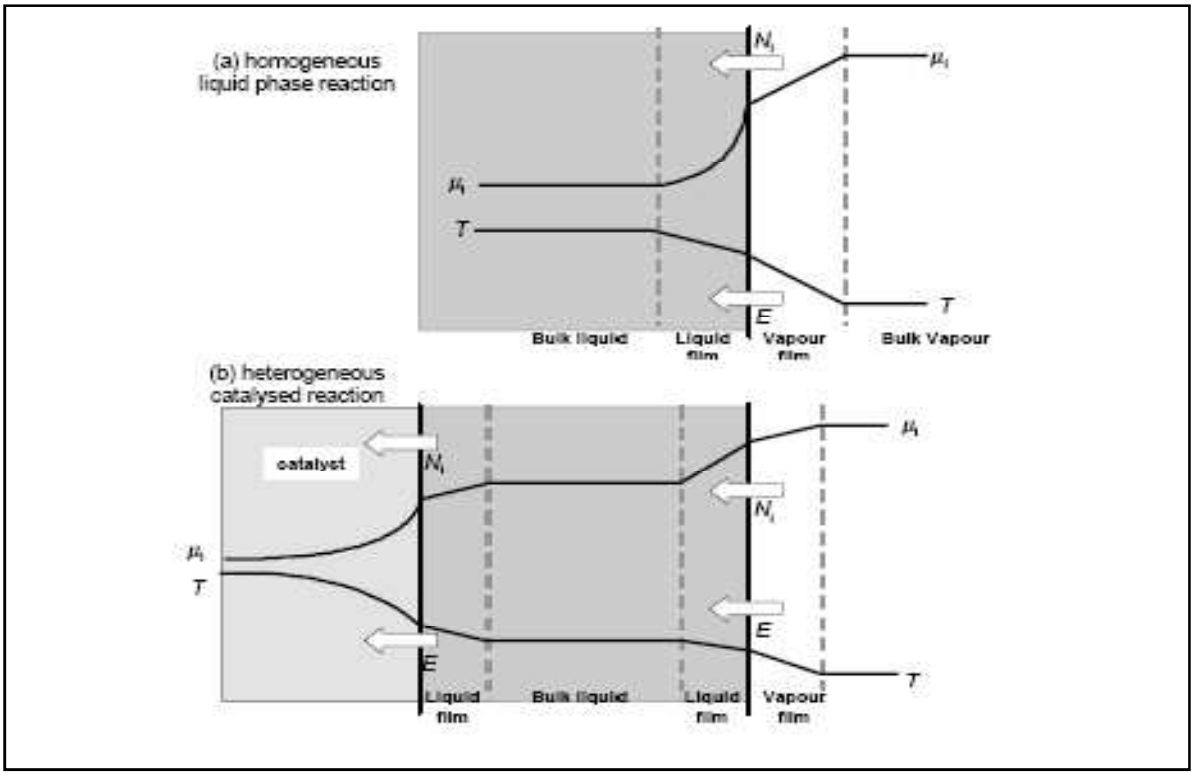

Figure 1.6 Transport process for (a) Homogeneous liquid phase reaction, and
(b) Heterogeneous catalyzed reaction.(Source: Taylor and Krishna, 2000)

1.6 Application of RD

The most important application of reactive distillation is the production of fuel ethers because the success of the MTBE process was boosted by phase out of lead based anti-knock agents in gasoline. These octane enhancers are nowadays mainly replaced by MTBE or similar oxygenates like ethyl tertiary butyl ether (ETBE) and tertiary amyl methyl ether (TAME). For some time, MTBE has been the fastest growing chemical (Ainsworth, 1991), and over the last two decade a considerable number of plants for production of these oxygenate were built, many based on reactive distillation technology.

1.7 Production of ethyl acetate

Ethyl acetate is produced by the esterification reaction of ethyl alcohol and acetic acid using catalysts such as sulphuric acid, para-toluene sulphonic acid or ion exchange resins. The reaction

of ethanol (EtOH) with acetic acid (AcOH) towards ethyl acetate (EtAc) and water (H_2O) is an equilibrium reaction.

$$CH_3COOH + C_2H_5OH \Leftrightarrow C_2H_5COOCH_3 + H_2O$$

(Acetic Acid) (Ethanol) (Ethyl Acetate) (Water)

The system is strongly non-ideal due to the presence of ethanol, acetic acid, and water. The separation of pure components is very difficult due to the existence of five normal azeotropes, namely, ethanol–water; water–acetic acid, ethyl acetate–ethanol, ethyl acetate–water, and ethanol–ethyl acetate–water. Suzuki et al., (1971), also determined the phase equilibrium for the system taking the reaction into account (they fitted 16 coefficients in Modified Margules equations, for calculating the VLE-model of this mixture). The normal boiling point of ethyl acetate, ethanol, water and acetic acid is 77.1, 78.4, 100 and 118.1 in °C respectively. The order of volatility is ethyl acetate, ethanol, water and acetic acid. Ethanol and water do not differ greatly in volatility, making it difficult to move ethanol up the column. The minimum-boiling binary homogeneous azeotrope is formed by ethanol–water at 78.2°C.

The main problems encountered in achieving high purity products in the ethyl acetate reactive distillation system are:

• Unfavorable reactant conversion

• Similar K-values of ethanol, water, and ethyl acetate

• Temperature profile in the column

1.8 Steady state models available for design of RD columns

Successful commercialization of RD technology requires careful attention to the modeling aspects, including column dynamics, even at the conceptual design stage. In some cases the reactor and distillation paradigms do not translate easily to RD. The potential advantages of RD could be nullified by improper choice of feed stage, reflux, amount of catalyst, boilup rate, etc. Thus, it is possible to decrease conversion by increasing the amount of catalyst under certain circumstances. Increased separation capability could decrease process performance.

A variety of models exist in the literature for design of RD columns. They can be classified in the following manner.

- Steady-state equilibrium (EQ) stage model

- Steady-state EQ stage model with stage efficiencies
- Steady-state nonequilibrium (NEQ) stage model, where the interphase
- Mass transfer is described by rigorous Maxwell-Stefan diffusion equations
- Steady-state NEQ cell model, developed by Higler 1999, in order to account for staging of the vapour and liquid phases during cross-current contacting on a distillation tray.

Aspen plus software

In 1970s the researchers at MIT's Energy Laboratory developed a prototype for process simulation. They called it Advanced System for Process Engineering (ASPEN). This software has been commercialized in 1980's by the foundation of a company named AspenTech. This sophisticated software package can be used in almost every aspect of process engineering from design stage to cost and profitability analysis. It has a built- in model library for distillation columns, separators, heat exchangers, reactors, etc. Custom or propriety models can extend its model library. These user models are created with FORTRAN subroutines or Excel worksheets and added to its model library. It has a built- in property databank for thermodynamic and physical parameters. During the calculation of the flow sheet any missing parameter can be estimated automatically by various group contribution methods. Aspen Plus can interactively change specifications such as, flow sheet configuration, operating conditions, and feed compositions, to run new cases and analyze process alternatives.

In the present work RADFRAC module of Aspen Plus is used to carry out the steady state simulations for the esterification of acetic acid with ethanol for the production of ethyl acetate in a RD column.

CHAPTER 2

LITERATURE REVIEW

The combination of chemical reaction with distillation in only one unit is called reactive distillation. The performance of reaction with separation in one piece of equipment offers distinct advantages over the conventional, sequential approach. In reactive distillation (RD) chemical reactions occur within the distillation column to achieve specific goals, such as to obtain high conversions and high purity products as well to minimize side reactions. Reactive distillation is being used in industrial applications with more frequency because of increasing research and development of this technology, a result of commercial and academic experience and success.

So far, there is no generally accepted method for the design of distillation with reaction. Most of the systematic methods available possess limitations because of their simplified assumptions. Moreover, these methods have rarely been proven with a variety of reactive distillation processes and they do not consider the design in detail.

In spite of the advances in separation with reaction processes, reactive distillation still relies on intuition and expertise. A reactive distillation problem can be studied using different approaches including: feasibility, simulation modeling, design and experimental studies in the laboratory and the pilot plant. A combination of all of these methods gives rise to the most accurate solution to the problem. One very important aspect of predicting the behavior in these systems is the model used to design and simulate the reactive distillation process. In the literature, the most common models that have been developed and proven are the equilibrium stage model and the non-equilibrium stage model. The equilibrium stage model is based on the conventional equilibrium stage model of a distillation column with the addition of the reaction terms in the mass and energy balances. The non-equilibrium stage model for reactive distillation, also known as the rate-based model, is an extension of the conventional rate based model for distillation. In this chapter, a discussion of the important aspects of modeling, simulation, design and analysis of reactive distillation is provided.

Much of the early literature on RD modeling is concerned primarily with the development of methods for solving the steady-state equilibrium (EQ) stage model. For the most part such methods are more or less straightforward extensions of methods that had been developed for

solving conventional distillation problems. The number of examples that illustrate most of the early papers usually is limited (most often it is an esterification reaction). More and more of the recent modeling studies are carried out using one or other commercial simulation package: Aspen Plus, Pro/II, and HYSYS (Taylor and Krishna, 2000).

The design of reactive distillation processes requires the simultaneous study of the physical and chemical phenomena that occur. The task is further complicated when kinetically controlled reactions are involved. Barbosa and Doherty (1988 a, b) developed a methodology for the design of reactive distillation columns for reactions in chemical equilibrium. Their method is based on the introduction of a new composition coordinate transformation that allows the use of existing methods for conventional distillation in the design of reactive distillation processes. Multiple reactions were considered by Ung and Doherty (1995) where residue curve maps, expressed in terms of the transformed composition coordinates, determine the feasibility region for the separation.

Matthias et al.(1983) presented a conceptual design methodology for the reactive distillation columns, the method assesses feasibility of a proposed reactive distillation, designs the column and allows evaluation of the design for both fully reactive and "hybrid" column configurations. Stage composition lines are used to represent all possible liquid compositions in a column section for specified product compositions and for all reflux or reboiler ratios. Reaction equilibrium is assumed on each reactive stage and vapor-liquid equilibrium is assumed on all stages. The methodology is illustrated by application to an ideal reactive system and for MTBE production.

There are several classes of computer-based methods that have been developed for solving the EQ stage model equations. Tearing methods involve dividing the model equations into groups to be solved separately. A brief description of computer based tray-to-tray calculations for the RD of ethylene oxide and water was given by Corrigan and Miller (1968).

Tray-to-tray calculations and parametric studies for the simulation and optimization of an RD column for trioxane synthesis are described by Hu, Zhou and Yuan (1999). The bubble-point method of Wang and Henke (1966) was extended by Suzuki et al. (1971) to be able to deal with chemical reactions. The θ method developed for conventional distillation columns by Holland and his many collaborators (Holland 1963) was extended to RD operations by Komatsu and

Holland (1977) and named the multi-θ-η method. The method is applied to the esterification of acetic acid. Savkovic et al. (1992) used the θ method to model an esterification of acetic acid and ethanol carried out in a glass column that was 33 mm in diameter and 1000 mm tall. The calculated temperature profile and product compositions are in good agreement with the measured quantities. Short-cut methods discussed above involve a number of simplifying assumptions that are made in order to derive simple approximate equations that can be used for rapid computations. It is quite difficult to develop generic short-cut procedures for RD because of the many ways in which chemical reactions influence the process (Taylor and Krishna 2000). Bock and Wozny (1997) show that the assumption of chemical equilibrium, often made in developing short cut methods, is inappropriate for many RD processes.

The Computational methods used for reactive distillation are extensions to the algorithms developed for the solution of the equations for conventional distillation. The first attempts to model reactive distillation were by using the simplified plate-to-plate calculations. Rigorous mathematical models for Computer simulation was not developed until the 1970's. Since that time, various techniques have been developed that allow the rigorous solution of the equations. These techniques include equation partitioning methods, and Newton-Raphson based methods.

Nelson (1971) modified the Tierny-Bruno (1968) algorithm based on tray-by tray calculation, by taking into consideration the non-ideal vapor liquid equilibrium. Which represented in material balance equations no longer linear in composition.

Suzuki et al. (1971) applied the successive iteration method to reactive distillation problems, and concluded that it converges rapidly and it is stable. However, difficulties with convergence arise for systems with non-ideal solutions, because of non linearity of the equations. In addition, successive iteration methods have the disadvantage that as the solution is approached, the progress of iteration calculations decelerates.

Murthy (1984) considered an extension of the Newton-Raphson algorithm to columns in which chemical reactions occur, while Venkataraman et al. (1990). Jelinek and Hlavacek (1976) applied the relaxation method to solve steady state countercurrent equilibrium stage separation with chemical reaction problems. They confirmed the suitability of this method where azeotropes exist.

Teirney and Riquelme (1982) proposed a correction algorithm which gives quadratic convergence near the solution. Its use was demonstrated on a sample problem of the separation of meta-and para-xylene using experimental results from an earlier study done by Satio et al. (1971). They found that their solution agree well with the numerical solution obtained by Satio et al. (1971), but not with Saito's experimental data. Teirney and Riquelme (1982) claimed the equilibrium in the reaction is not satisfied in each stage. This contradicts the experimental results of Satio et al. (1971), showing that the equilibrium constant is almost constant in the range of operating temperature between (50-100°C).

Reactive Distillation (RD) is state-of-the-art multifunctional reactor concept that integrates reaction and distillation in a single process unit. Some recent reactions that have been proposed to utilize RD technology involve non condensable species like hydrogen which proposed by Kamath et al. (2005). Reactions involving liquid phase splitting have also been examined in RD.

Okur and Bayramoglu (2001) have worked on the effect of the liquid-phase activity model on the simulation of ethyl acetate production by reactive distillation. Reactive distillation is an attractive way of improving process economics by combining distillation and reaction, especially for equilibrium-limited reactions such as esterification. Reactive systems are more nonideal than conventional ones; thus, they need elaborate models that consider the non ideality of the vapor and liquid phases. Among abundant liquid-phase activity models, modified versions of UNIFAC are cited as being well-suited for this purpose. In this paper, four activity models are compared by means of a simulation model applied to the production of ethyl acetate. It is found that the two versions of UNIFAC give similar results their work deals with the development of an equilibrium reactive distillation model that takes into account the non ideality of both the vapor and liquid phases. The simulation model is applied to the production of ethyl acetate. The research is focused especially on the influence of liquid-phase activity models on the simulation results. The results obtained with four liquid-phase activity models. At low reflux ratios, discrepancies between various model results are as high as 10%, whereas at high reflux ratios with low conversions, the results become increasingly closer. The highest conversion is obtained with the UNIQUAC model the other model estimations are more or less similar. The two versions of UNIFAC give similar distillate compositions, especially for water and acetic acid. The ethyl acetate distribution ratio, expressed as the ratio of the number of moles of ethyl acetate

in the distillate to the total number of moles of ethyl acetate produced, and the conversion as functions of the reflux ratio. On the other hand, the temperature profiles in the column for a reflux ratio of 1.5 .The profiles obtained with the two versions of UNIFAC are almost equal, with the empirical model giving the most dissimilar temperature profile.

Venkatraman et al. (1990) describe the inside-out algorithm known as RADFRAC that is part of the commercial program Aspen Plus. Inside-out methods involve the introduction of new parameters into the model equations to be used as primary iteration variables. Four examples demonstrate that RADFRAC can be applied to a wide variety of reactive separation processes. RADFRAC is able to handle both equilibrium reactions as well as kinetically limited reactions. Simandl and Svrcek (1991) provide more details of their own implementation of an inside-out method for RD simulation.

The Non-equilibrium (NEQ) stage model for RD follows the philosophy of rate-based models for conventional distillation (Krishnamurthy and Taylor, 1985; Taylor and Krishna, 1993; Kooijman and Hung, 1994; Seader and Henley, 1998).Sawistowski and Pilavakis, 1979, 1988) modeled a packed RD column for the esterification of methanol and acetic acid to methyl acetate. They used an effective diffusivity method for their mass transfer model. The system of differential equations that constitute their model was solved numerically. Their second paper includes parametric studies that show how conversion changes as a function of catalyst flow rate, pressure, feed composition, reflux ratio, reboiler ratio, feed flow rates, and feed position. In 1990 Aspen Technology Inc. introduced the RATEFRAC model for rate-based multicomponent separation modeling (Sivasubramanian and Boston, 1990). RATEFRAC is based on the NEQ model of Krishnamurthy and Taylor (1985) with the addition of equations to account for the effect of reaction on mass transfer, and chemical equilibrium constraints. The influence of homogeneous reaction kinetics on chemical phase equilibria and reactive azeotropes was discussed by Venimadhavan et al. (1994) and Rev (1994).

Schenk et al. (1999) describe in considerable detail a hybrid-modeling environment in which distillation-type processes can be simulated using a combination of steady-state, dynamic, EQ stage, and/or rate-based models. Two of the three examples that are given in their paper concern RD (ethyl acetate production and an MTBE column). The models are compared to experimental data of Suzuki et al. (1971). The agreement between the profiles obtained with the rate-based

model and the data is very encouraging. The authors do, however, demonstrate a sensitivity of the computed profiles to the activity coefficient model used. A novel feature of their paper is the introduction of Gibbs energy profiles in the column.

Zhu and Shen (1995) discussed the modification of the NEQ model of Krishnamurthy and Taylor (1985) to handle RD. Simulation results appear to show reasonable agreement with temperature and liquid composition profiles measured for the esterification of ethanol and acetic acid carried out in an Oldershaw column.

Lee and Dudukovic (1998) described an NEQ model for homogeneous RD in tray columns. The Maxwell-Stefan equations are used to describe interphase transport, with the AIChE correlations used for the binary (Maxwell-Stefan) mass transfer coefficients. Newton's method and homotopy continuation are used to solve the model equations. A close agreement between the predictions of EQ and NEQ models was found only when the tray efficiency could be correctly predicted for the EQ model. Kreul et al. (1999) used an NEQ model of homogeneous RD and studied the importance of various model simplifications. They found little difference between the full MS description of multicomponent mass transfer and the simpler effective diffusivity models. However, they also conclude that there can be significant differences between EQ and NEQ models, and that the additional effort of the more complicated NEQ approach is justified.

Taylor and Krishna (2000) presented a detailed review concerning design and operation issues during the modeling of reactive distillation.

Jianhua and Fu (2003) have proposed a generalized model of reactive distillation using rate based approach. The homotopy-continuation method was employed to solve the complicated non-linear model equation. Variations of various simulation parameters were studied and the pitfalls in experimental design were obtained.

Alfradique and Castier (2005) used Thermath for the simulation of steady-state reactive distillation columns. Authors suggest that using Thermath, it is possible to develop complete Fortran subroutines for the calculation of thermodynamic properties with relatively little effort compared to what a manual implementation would usually require. They included the example of the simulation of esterification of acetic acid with ethanol and compared the results with experimental data of Komatsu (1977).

Tang et al. (2005) have presented the esterification of the acetic acid with five alcohols ranging from ethanol (EtOH) to amyl alcohol (AmOH) are intended to gain insight for the design of reactive distillation by varying the chemical species discretely. Here, qualitative relationships between macroscopic process flowsheet and microscopic phase equilibria are established. Next, a systematic design procedure is devised to optimize the design, based on the total annual cost (TAC). Finally, the economic potentials of these three different flowsheet are explored. His results clearly indicate that it is possible to systemize the design of reactive distillation by qualitatively generating flowsheet from phase equilibria and by quantitatively completing the process flow diagram from a sequential design procedure.

Markus et al. (2005) proposed the ethyl-acetate synthesis via reactive distillation is studied theoretically and experimentally using different catalytic packing. Experiment are carried out at laboratory scale in a 50 mm diameter column, packing height of 3m, and semi-industrial scale of 162 mm diameter column, with packing height of 12 m. Sulzer KATAPAK and Montz MUTLIPAK-1 was used as packing .Modeling was performed using Aspen custom modeler with rate based simulation module.

Dalaouti and Seferlis (2006) proposed the NEQ/OCFE process model formulation involving the rigorous description of mass and heat transfer phenomena, phase equilibrium relations and chemical reactions in both gas and liquid phases in a limited but number of collocation points. In addition, the authors implemented polynomial approximation as implemented in the OCFE techniques that transforms the staged column domain into a continuous analog and tested the proposed formulation in the reactive distillation column under static and dynamic conditions and compared it with the corresponding full-order tray-by-tray model for reactive absorption of NO_x and ethyl acetate production via reactive distillation using ethanol and acetic acid.

Khaledi and Bishnoi (2006) developed an algorithm for the steady-state simulation of two- and three-phase multistage reactive distillation processes with equilibrium chemical reactions. In this algorithm, the phase stability, phase equilibrium, and chemical reaction equilibrium calculations are preformed simultaneously. Apart from other examples; the authors included the modeling of two-phase reactive distillation example of the esterification of methanol with acetic acid.

Singh et al. (2007) has presented a parametric study for the design of a reactive distillation column used to recover acetic-acid from dilute aqueous solution (30% w/w) through the formation of methyl acetate. The parameters such as feed molar ratio, feed location, reflux ratio, and reboiler ratio are varied by a one-parameter continuation method, and the best possible configuration is suggested. Close to quantitative recovery may be obtained by a proper choice of parameters, and reactive distillation can be successfully used for the recovery process. An experimental support is provided to the recommended configuration.

Toikka et al. (2009) has presents a review of phase equilibrium data for four-component systems involving ester synthesis and hydrolysis reactions (acid–alcohol–ester–water) systems. Data for the 14 best ester synthesis systems were selected; however, these data are incomplete and contradictory to a considerable extent. In particular, he noted the discrepancies between the data of different authors even for comparatively simple and commercially significant reactive systems, such as the propyl-acetate and iso-propyl acetate synthesis systems. Sometimes, the results of simulation are not verified against experimental data.

Zhixian et al. (2010) has developed a reactive distillation (RD) column with packing where a cation exchange resin as a catalyst is applied. Mathematical models of reactive distillation are based on the conventional distillation process with supplementary equations added to model the reactions present. Column simulations performed here using Aspen Plus show excellent agreement with experimental data for the EtAc system. A sensitive analysis was performed to determine the effects of key design and operating variables on column performance and, subsequently, an optimal column configuration was obtained.

CHAPTER 3

MATHEMATICAL MODELING OF REACTIVE DISTILLATION

In the reactive distillation system selected for the proposed work, ethanol and acetic acid form ethyl acetate through an exothermic liquid-phase esterification reaction (reversible) in the presence of sulfuric acid/para-toluene sulfonic acid (PTSA) that acts as the catalyst. The reaction is:

$CH_3COOH + C_2H_5OH \Leftrightarrow C_2H_5COOCH_3 + H_2O$

(Acetic Acid) (Ethanol) (Ethyl Acetate) (Water)

Ethanol and acetic acid are fed into the column that operates near atmospheric pressure. At these conditions acetic acid as the heaviest of the components moves towards the bottom of the column. The lighter components Ethyl Acetate, Ethanol and water moves towards the top of the column. The rate of reaction is generally low and is therefore favored by a large residence time in each column stage. Ethanol has relatively high volatility and prefers the vapor phase rather than the liquid phase where the reaction takes place. This necessitates the maintenance of low ethanol composition in the liquid phase thereby reducing the overall production rate of ethyl acetate.

The simulations are carried out by using Aspen Plus. The RADFRAC module, based on a rigorous equilibrium stage model for solving the mass balance, phase equilibrium, summation and energy balance (MESH) equations, was used in this study to describe a multistage vapour-liquid separation in the distillation column.

Model Assumptions:

1. Each stage is a perfectly mixed i.e. liquid composition at each stage is homogeneous and equal to the composition of liquid leaving the stage.
2. The vapor and liquid leaving any stage are in physical equilibrium.
3. Entrainment of liquid drops in vapor and occlusion of vapor bubbles in liquid are negligible.
4. Vapor molar holdup and vapor-phase chemical reactions were neglected.

5. Homogeneous esterification reaction $CH_3COOH+C_2H_5OH \Leftrightarrow C_2H_5COOCH_3+H_2O$ is assumed to be occurring in the liquid phase only.

The extent of liquid-phase reaction at each stage is governed by reversible kinetic rate expressions. For the modeling of equilibrium stage in reactive distillation MESH (material balance, energy balance, summation, and enthalpy balance) equations with reaction term are used. An equilibrium stage, in the column, with feed stream is shown in the Figure 3.1.

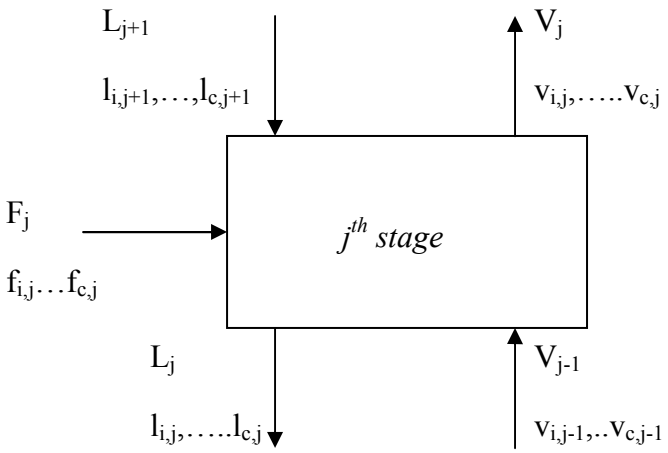

Figure 3.1: General equilibrium stage

The model equations in terms of the vapor and liquid molar flow rates are as follows:

Total Condenser (j=1; i = 1 to C):

$v_{i,2} - d_{i,1}(R+1) + \alpha_i V_C r_{2,1} = 0$

$l_{i,1} - d_{i,1}R = 0$

$V_2H_2 - D(R + 1)\, h_1 - Q_C = 0$

Non-catalyzed reaction section (j=1…. N_R; i = 1 to C):

$l_{i,j-1} + v_{i,j+1} + f_{i,j} - l_{i,j} - v_{i,j} + \alpha_i V_j r_{2,j} = 0$

$L_{j-1}h_{j-1} + V_{j+1}H_{j+1} + F_jh_{fj} - L_jh_j - V_jH_j = 0$

$$K_{i,j}l_{i,j}\frac{\sum_{i=1}^{C} v_{i,j}}{\sum_{i=1}^{C} l_{i,j}} - v_{ij} = 0$$

Catalyzed reaction section ($j=N_R+1\ldots..N-1$; i = 1 to C):

$l_{i,j-1} + v_{i,j+1} + f_{i,j} - l_{i,j} - v_{i,j} + \alpha_i V_j r_{1,j} = 0$

$L_{j-1}h_{j-1} + V_{j+1}H_{j+1} + F_jh_{fj} - L_jh_j - V_jH_j = 0$

$$K_{i,j}l_{i,j}\frac{\sum_{i=1}^{C} v_{i,j}}{\sum_{i=1}^{C} l_{i,j}} - v_{ij} = 0$$

Reboiler (j=N; i = 1 to C)

$l_{i,\,N-1} - l_{i,N} - v_{i,\,N} + \alpha_i V_R r_{1,N} = 0$

$L_{N-1}h_{N-1} - L_N h_N - V_N H_N + Q_R = 0$

$$K_{i,N}l_{i,N}\frac{\sum_{i=1}^{C} v_{i,N}}{\sum_{i=1}^{C} l_{i,N}} - v_{iN} = 0$$

Where,

$$L_j = \sum_{i=1}^{C} l_i$$

$$V_j = \sum_{i=1}^{C} v_i$$

$K_{i\,j} = K_{i,\,j}\{T_j, P_j, x_j, y_j\}$

$H_j = H_j\{T_j, P_j, y_j\}$

$h_j = h_j\{ T_j, P_j, x_j\}$

Various correlations are available in literature for the prediction of thermodynamic properties. Liquid phase and vapour phase enthalpies may be predicted using Missenard group contribution method and modified Peng-Robinson respectively. The liquid mixture under consideration is known to be highly non ideal and liquid phase activity coefficients may be predicted using Wilson/NRTL/UNIQUAC/Empirical (Suzuki) model. Pure component vapour pressure may be predicted using Antoine equation. RADFRAC has these models in the physical properties routines. Empirical models may be supplied to the RADFRAC through user subroutines.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter the simulation of reactive distillation of ethyl acetate production ($C_2H_5COOCH_3$), using acetic acid (CH_3COOH) and ethanol (C_2H_5OH), in a plate column are done using RADFRAC module of ASPEN PLUS. The reaction is catalysed by sulfuric acid and is assumed to be occurring in the liquid phase only. A constant-pressure adiabatic column, a total condenser, and a partial reboiler are assumed. RADFRAC representation of the RD column with a single feed is shown in Figure 4.1.

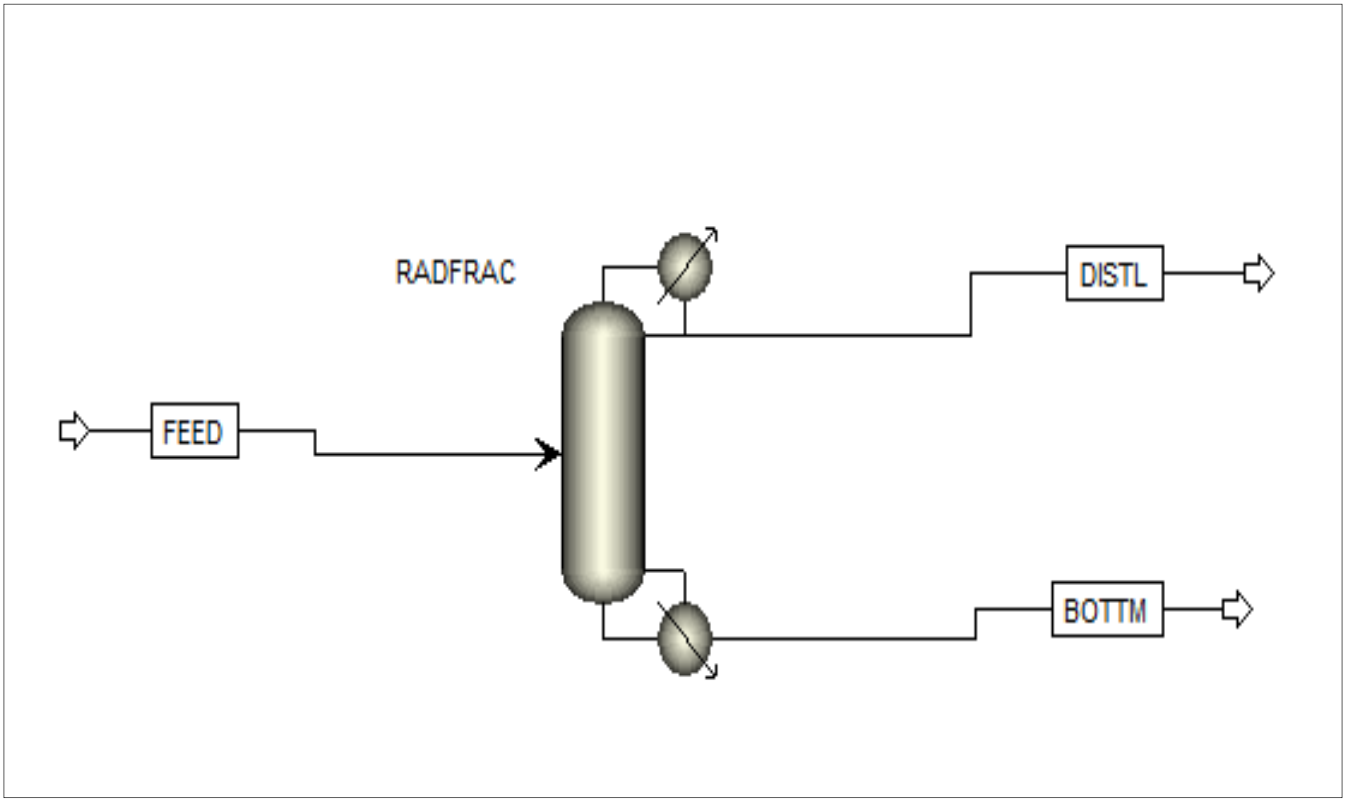

Figure 4.1: RADFRAC representation of the RD column used in the present work

Table 4.1: Column specifications and other parameters used for RADFRAC simulations

Feed Temperature		340 K
Pressure		1 atm
Total Stages		13 (including Reboiler and condenser)
Feed Stages		6 (from top)
Feed rate (mol/min)		0.1076
Distillate Rate(mol/min)		0.0208
Holdup		1 l for reboiler, 0.3 l for each stage
Component mole fraction	Acetic Acid	0. 4963
	Ethanol	0.4808
	Water	0.0229
	Ethyl acetate	0.0
Reaction		$CH_3COOH+C_2H_5OH \Leftrightarrow C_2H_5COOCH_3+H_2O$ (A) + (B) $\Leftrightarrow$ (C) + (D)
Reflux Ratio		10
Reaction Kinetics		$r_A = k_1C_AC_B - k_2C_CC_D$ (lit·mol/s) $k_1 = 483.33\exp(-5.94451E7/RT)$ $k_2 = 123\ \exp(-5.94451E7/RT)$ where R = 8314 J/kmol
Convergence		Non-ideal

Okur and Bayramoglu (2001) in their simulation of the ethyl acetate production by RD have used UNIQUAC, UNIFAC (Dortmund), UNIFAC (Lyngby) and empirical methods for the liquid phase activity. Pilavachi et al. (1997) in their simulations used UNIQUAC (with ideal and SRK vapor phase models), UNIFAC (with ideal, SRK, virial equation for vapor phase model), and Wilson (with SRK model for vapor phase). Therefore, in the present work, simulations are run for various activity models and the results for ethyl acetate composition are compared with the experimental data of Suzuki et al. (1971). The results are presented in Figure 4.2.

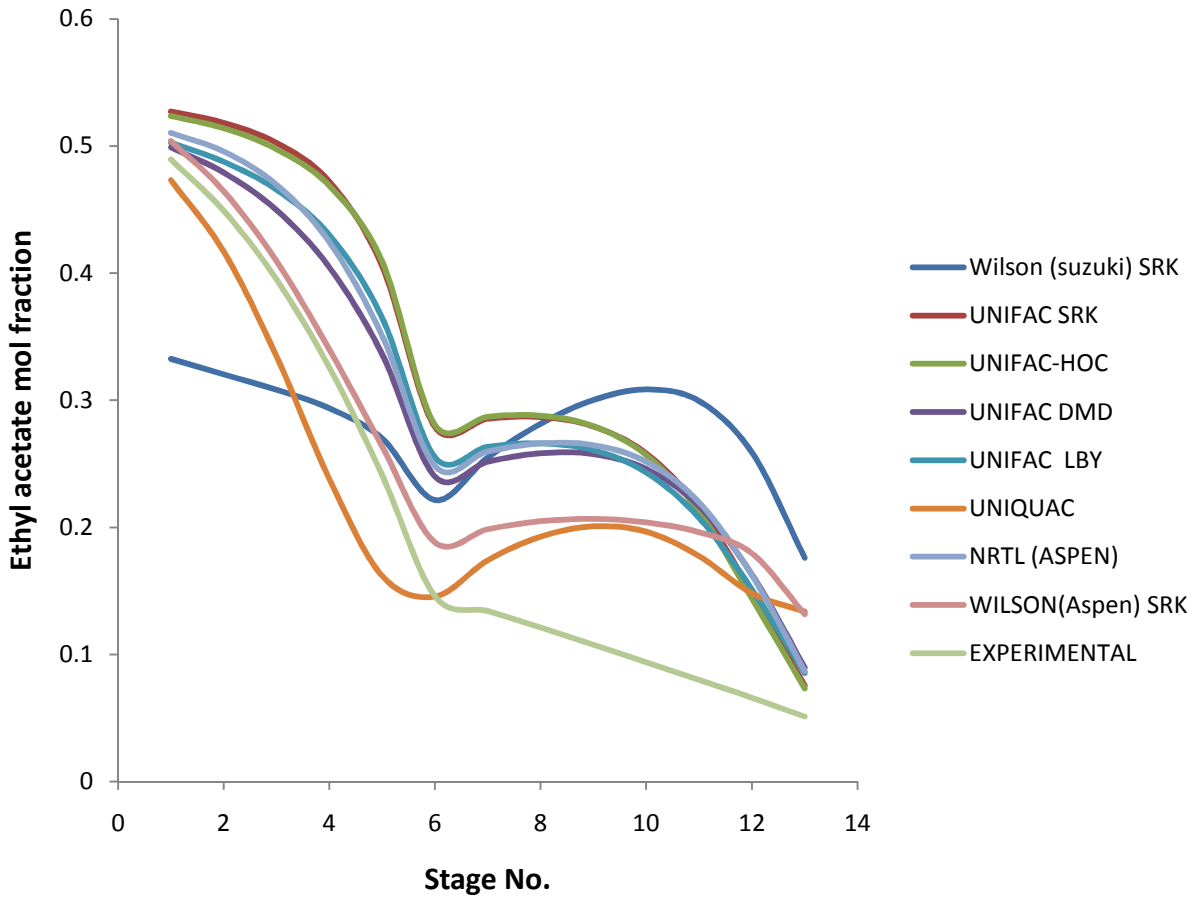

Figure: 4.2 Comparison of simulation results with the experimental data

The results show that the Wilson model for liquid phase activity with SRK model for vapor phase, and UNIQUAC model for liquid phase predict the experimental data most closely. However, in the lower part of the column even these models do not match with the experimental data.

The causes of this mismatch of experimental data with the simulation results are (i) highly non-ideal behavior of the liquid mixture and (ii) the interaction between the physical and chemical steps. Figures 4.3 to 4.6 show the comparison of simulation predicted K values with the experimental data of Suzuki et al. (1971).

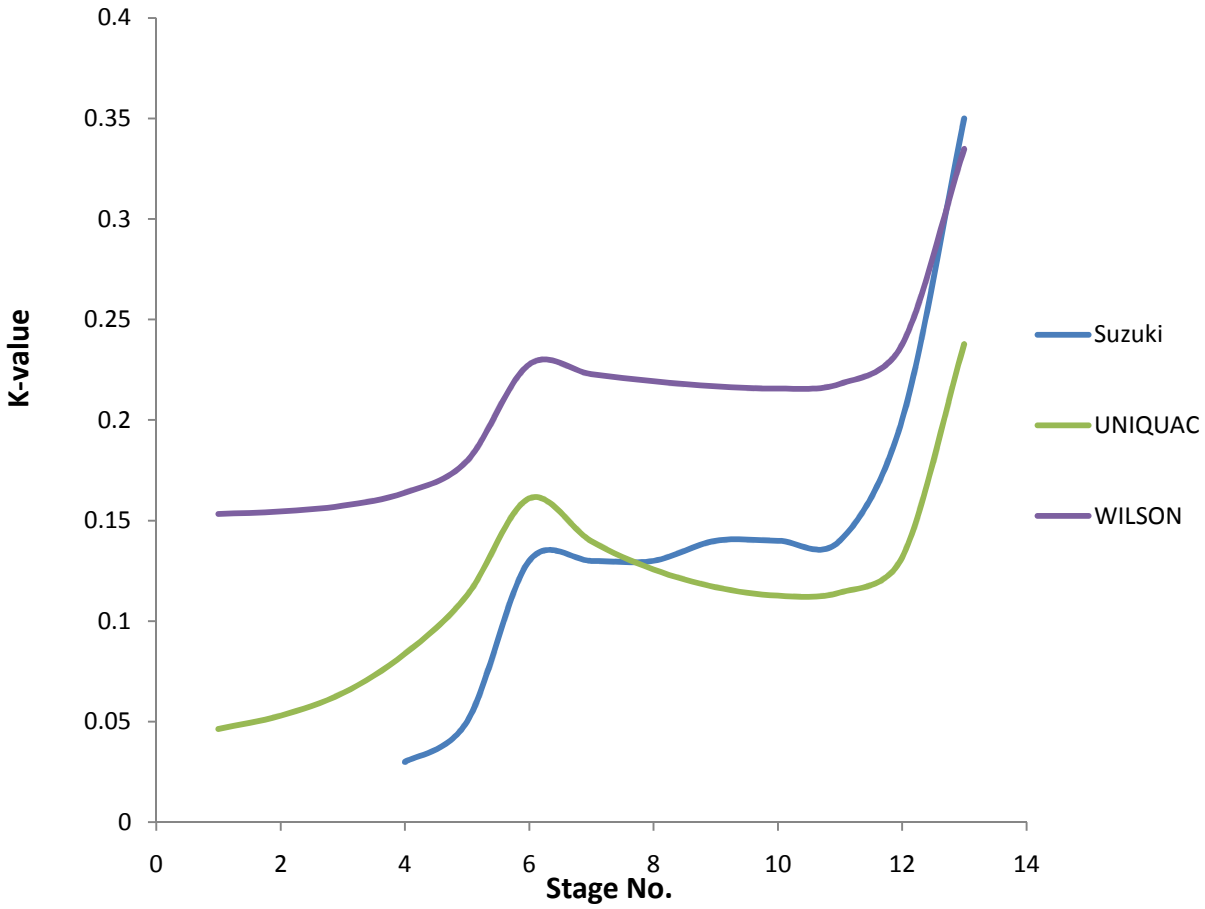

Figure 4.3: Acetic acid K values (simulation Vs experimental)

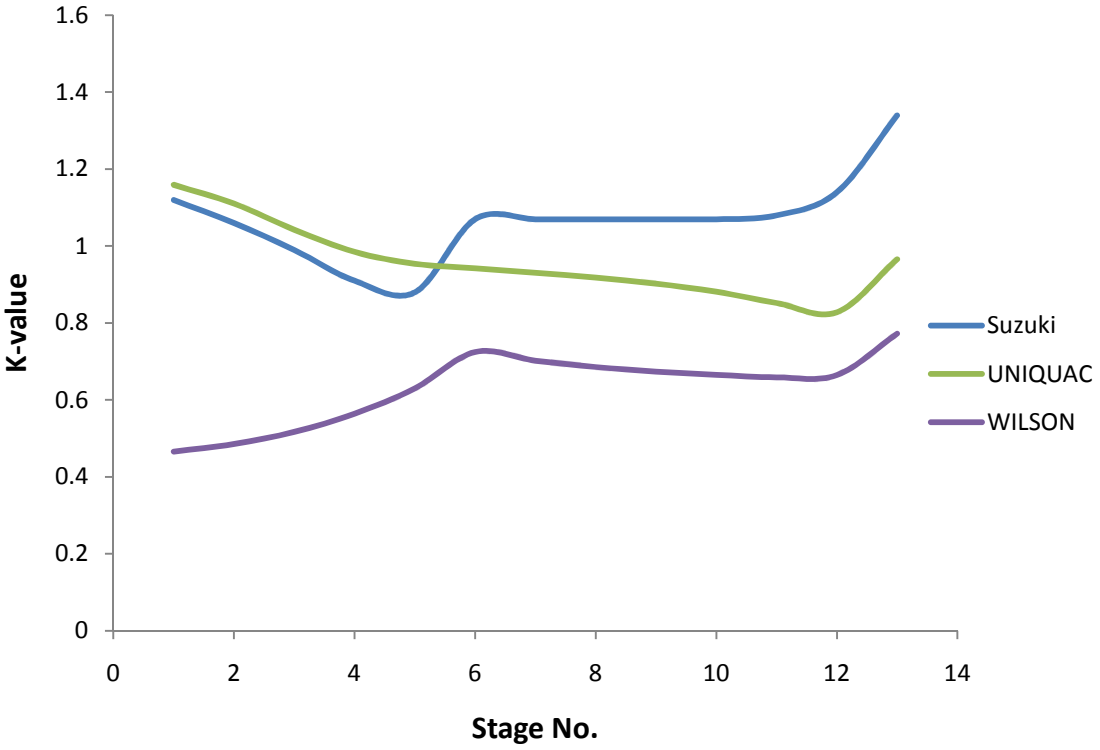

Figure 4.4: Water K values (simulation Vs experimental)

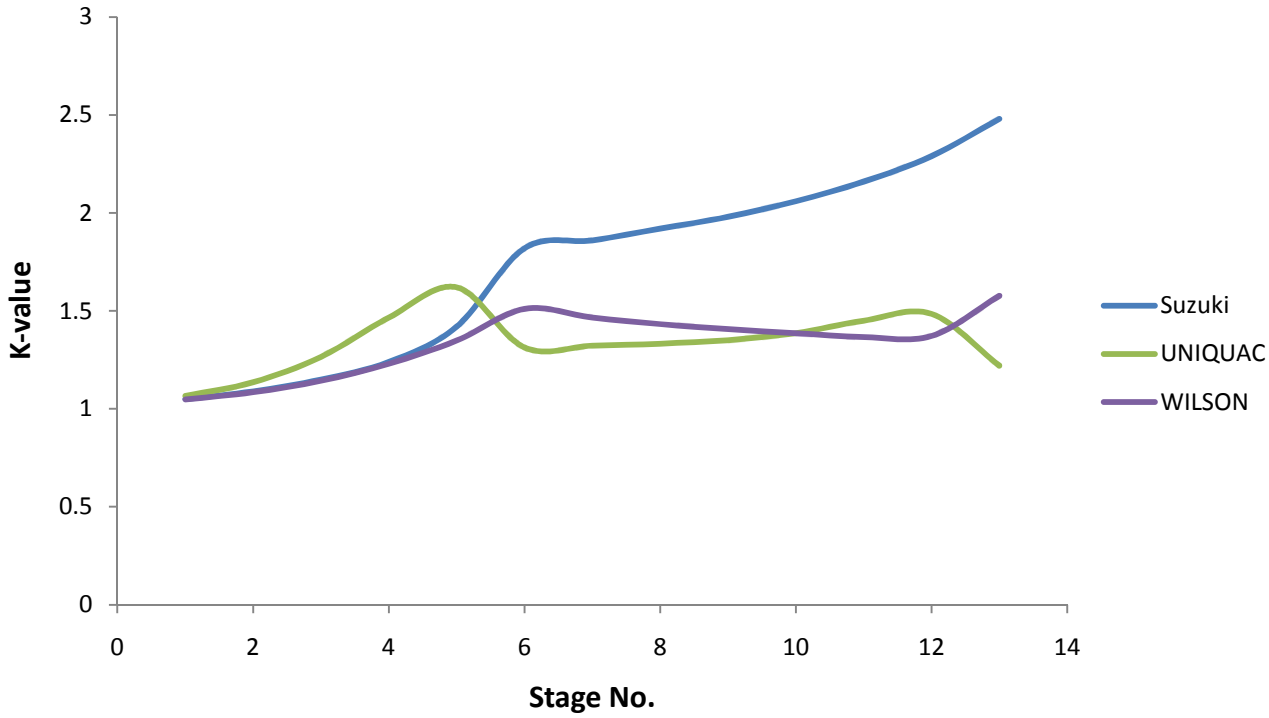

Figure 4.5: Ethyl acetate K values (simulation Vs experimental)

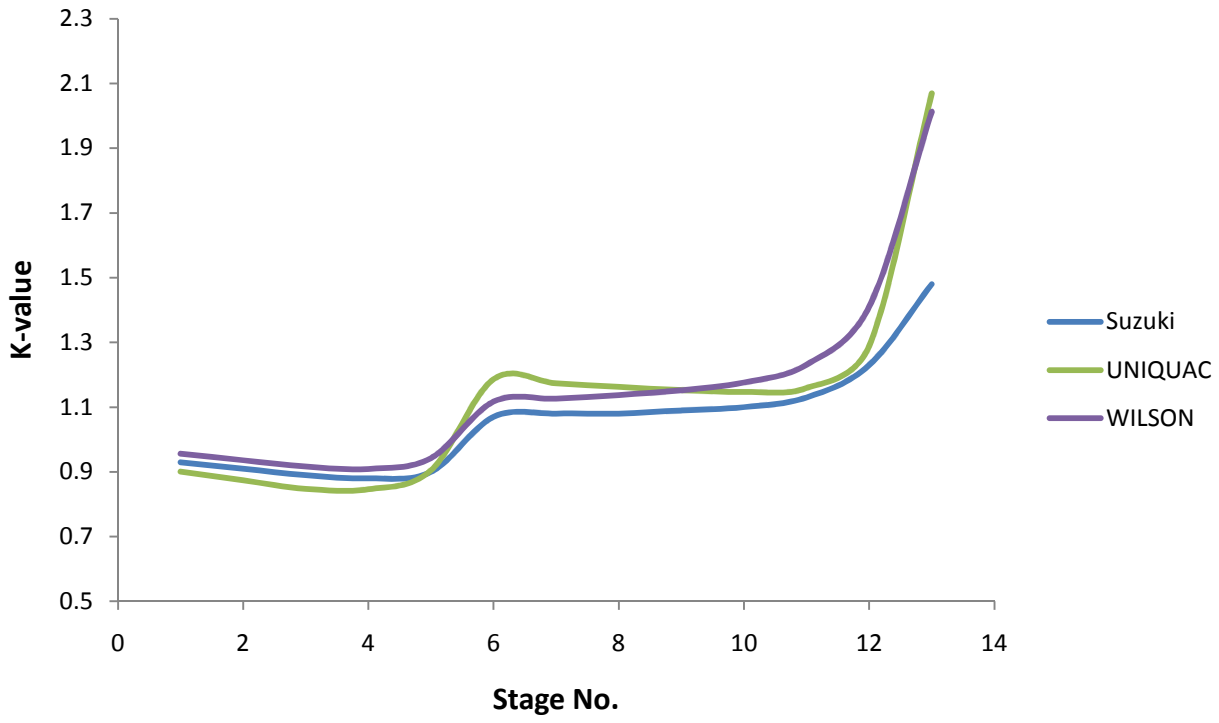

Figure 4.6: Ethanol K values (simulation Vs experimental)

The results show that the K values for acetic acid and water are better predicted by UNIQUAC model and K values of ethanol and ethyl acetate are better predicted by the Wilson model. However, the match is poor in the lower portion of the column for both the models. This explains the poor match of ethyl acetate composition in the lower portion of the column shown in Figure 4.2.

Tables 4.2 shows the comparison of liquid phase composition for the UNIQUAC and Wilson model results with the data of Suzuki et al. (1971). Column temperature and flow rate profiles are compared with the experimental data in Table 4.3.

Table 4.2 Comparison of simulation results with experimental data for liquid phase composition profiles

Stage no.	Acetic acid (mol/mol)			Ethanol (mol/mol)			Ethyl acetate (mol/mol)			Water (mol/mol)		
	a	b	c	a	b	c	a	b	c	a	b	c
1	0.000	0.001	0.000	0.450	0.442	0.491	0.489	0.473	0.504	0.057	0.084	0.005
2	0.000	0.001	0.000	0.494	0.506	0.491	0.449	0.417	0.464	0.054	0.076	0.011
3	0.000	0.002	0.002	0.548	0.588	0.491	0.395	0.334	0.409	0.055	0.075	0.020
4	0.001	0.006	0.009	0.611	0.678	0.491	0.326	0.238	0.340	0.061	0.079	0.034
5	0.027	0.031	0.045	0.663	0.722	0.491	0.241	0.162	0.263	0.068	0.085	0.049
6	0.193	0.178	0.189	0.598	0.587	0.491	0.146	0.146	0.188	0.063	0.089	0.059
7	0.193	0.167	0.178	0.597	0.548	0.491	0.134	0.174	0.198	0.076	0.111	0.076
8	0.193	0.157	0.169	0.595	0.519	0.491	0.121	0.193	0.205	0.092	0.130	0.094
9	0.193	0.150	0.161	0.589	0.500	0.491	0.108	0.201	0.207	0.111	0.149	0.114
10	0.196	0.144	0.154	0.576	0.489	0.491	0.094	0.197	0.204	0.135	0.171	0.138
11	0.211	0.143	0.157	0.545	0.480	0.491	0.080	0.177	0.196	0.165	0.200	0.173
12	0.276	0.178	0.198	0.468	0.431	0.491	0.066	0.148	0.179	0.190	0.243	0.229
13	0.447	0.368	0.363	0.320	0.243	0.491	0.051	0.134	0.132	0.183	0.256	0.279

a = Suzuki data; b= Uniquac model; c= Wilson model

Table 4.3 Comparison of simulation results with experimental data for temperature and flow rate

Stage no.	Temperature (^{0}C)			Liquid flow rate (kmol/hr)			Vapor flow rate (kmol/hr)		
	a	b	c	a	b	c	a	b	c
1	72.8	71.2	71.1	0.012	0.012	0.012	0.000	0	0
2	72.9	71.5	71.3	0.012	0.012	0.012	0.014	0.014	0.014
3	73.2	72.0	71.7	0.012	0.012	0.012	0.014	0.014	0.014
4	73.5	73.0	72.3	0.012	0.012	0.012	0.014	0.013	0.013
5	74.7	74.8	73.9	0.012	0.012	0.012	0.013	0.013	0.013
6	80.1	79.6	78.2	0.018	0.018	0.019	0.013	0.013	0.013
7	80.3	78.8	78.0	0.018	0.018	0.018	0.013	0.013	0.013
8	80.6	78.2	77.9	0.018	0.018	0.018	0.013	0.013	0.013
9	80.9	77.8	77.9	0.018	0.018	0.018	0.013	0.013	0.013
10	81.3	77.6	78.0	0.018	0.018	0.018	0.013	0.013	0.013
11	82.2	77.8	78.6	0.018	0.018	0.018	0.013	0.013	0.013
12	85.0	79.6	80.6	0.018	0.017	0.018	0.013	0.012	0.012
13	92.1	88.5	87.9	0.005	0.005	0.005	0.013	0.012	0.012

a= Suzuki data; b= Uniquac model; c= Wilson model

We further tried to improve the simulation results by using **a**nother approach in which the RD column is divided into two segments and different activity models in each segment was tried. Segment 1 was from stage 1 to 6 and segment 2 was from stage 7 to 13. The combination of UNIFAC model for the top segment and Wilson model for the bottom segment gave the best results. In these simulations HOC model is used for the vapor phase. The simulation results for ethyl acetate composition are compared with the experimental data (Figure 4.7). The results show that the segmental model approach has improved the simulation predictions in the lower portion of the column. The overall ethyl acetate composition profile is better predicted by this approach as compared to the single activity model approach for the entire column.

Table 4.4 shows the comparison of simulation results with the experimental data for column temperature profiles and K values. The segmental model approach has improved the simulations prediction for K values and for temperature also.

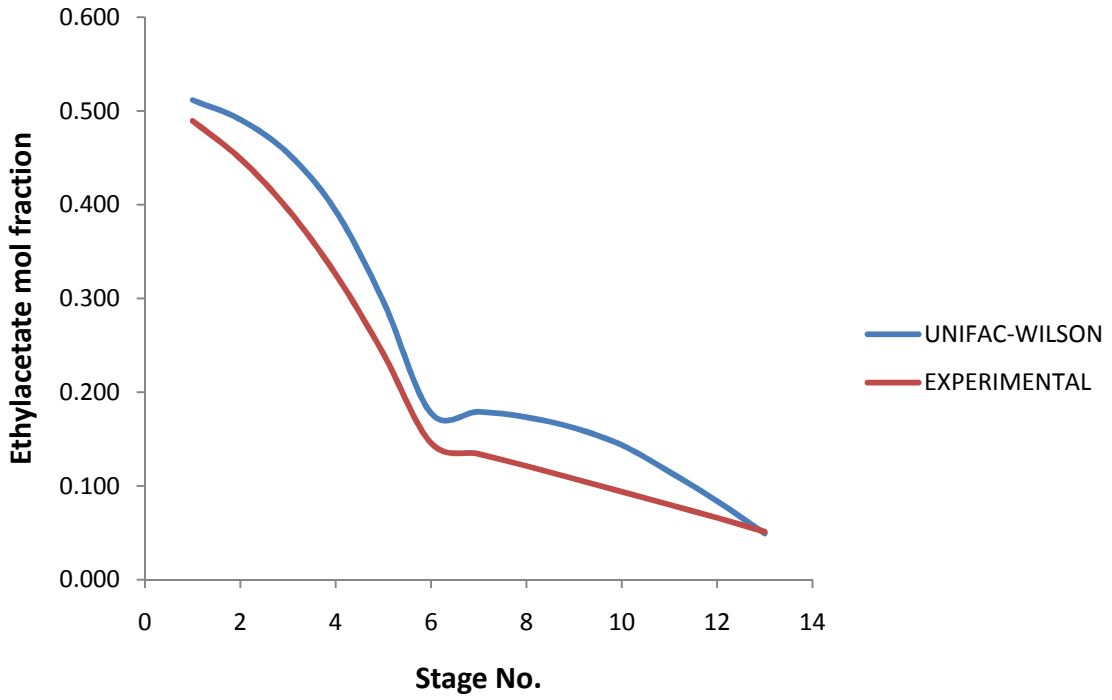

Figure 4.7: Comparison of simulation results for segmented column with experimental data

Table 4.4: Comparison of simulation results with experimental data for temperature and K- values

Stage no.	Temperature (C)		$K_{acetic\ acid}$		$K_{ethanol}$		$K_{ethyl\ acetate}$		K_{water}	
	a	b	a	b	a	b	a	b	a	b
1	72.8	70.8	-	0.057	0.930	0.965	1.050	1.021	1.120	1.062
2	72.9	70.8	-	0.056	0.910	0.948	1.090	1.042	1.060	1.038
3	73.2	70.9	-	0.055	0.890	0.921	1.150	1.084	0.990	1.000
4	73.5	71.1	0.030	0.054	0.880	0.886	1.240	1.169	0.910	0.947
5	74.7	72.2	0.050	0.060	0.900	0.869	1.420	1.362	0.880	0.903
6	80.1	77.6	0.130	0.122	1.070	1.029	1.820	1.779	1.070	0.989
7	80.3	79.4	0.130	0.117	1.080	1.106	1.860	1.563	1.070	0.831
8	80.6	79.4	0.130	0.115	1.080	1.117	1.920	1.536	1.070	0.816
9	80.9	79.5	0.140	0.113	1.090	1.133	1.960	1.518	1.070	0.807
10	81.3	79.9	0.140	0.113	1.100	1.154	2.060	1.512	1.070	0.807
11	82.2	81.0	0.140	0.126	1.130	1.200	2.160	1.551	1.080	0.843
12	85.0	84.3	0.200	0.182	1.230	1.329	2.290	1.669	1.140	0.946
13	92.1	92.3	0.35	0.359	1.48	1.597	2.45	1.983	1.34	1.235

a= Suzuki data; b= Simulation results

Another set of simulations of reactive distillation of ethyl acetate production ($C_2H_5COOCH_3$), using acetic acid (CH_3COOH) and ethanol (C_2H_5OH), in an eight plate column is carried out. The column specifications taken from Alejski et al. (1988), given in Table 4.5, are used for the simulations. The reaction is assumed to be occurring in the liquid phase only. A constant pressure adiabatic column, a total condenser, and a partial reboiler are assumed.

Table 4.5: Eight plate RD column specifications (Alejski et al. (1988))

Feed Temperature		340 K
Pressure		1 atm
Total stages		8 (including Reboiler and condenser)
Feed stages		3 (from top)
Feed rate (mol/min)		0.2584
Distillate rate (mol/min)		0.0425
Holdup		0.6 l for reboiler, 0.4 l for each stage
Component mole fraction	Acetic Acid	0. 2559
	Ethanol	0.6159
	Water	0.0743
	Ethyl acetate	0.0539
Reaction		$CH_3COOH+C_2H_5OH \Leftrightarrow C_2H_5COOCH_3+H_2O$ (A) + (B) $\Leftrightarrow$ (C) + (D)
Reflux Ratio		2.1
Reaction kinetics		$r_A = k_1C_AC_B - k_2C_CC_D$ (lit·mol/s) $k_1 = 4.76\times10^{-4}$ mol/min $k_2 = 1.63\times10^{-4}$ mol/min
Convergence		Non-ideal

The UNIQUAC liquid phase model and HOC vapour phase model is used for the simulations. The simulation results for liquid phase compositions are compared with the simulation results Alejski et al. (1988) and are plotted in Figure 4.8. The column temperature and K value profiles are compared with Alejski's results in Table 4.6. The results are matching well with those of Alejski et al. (1988).

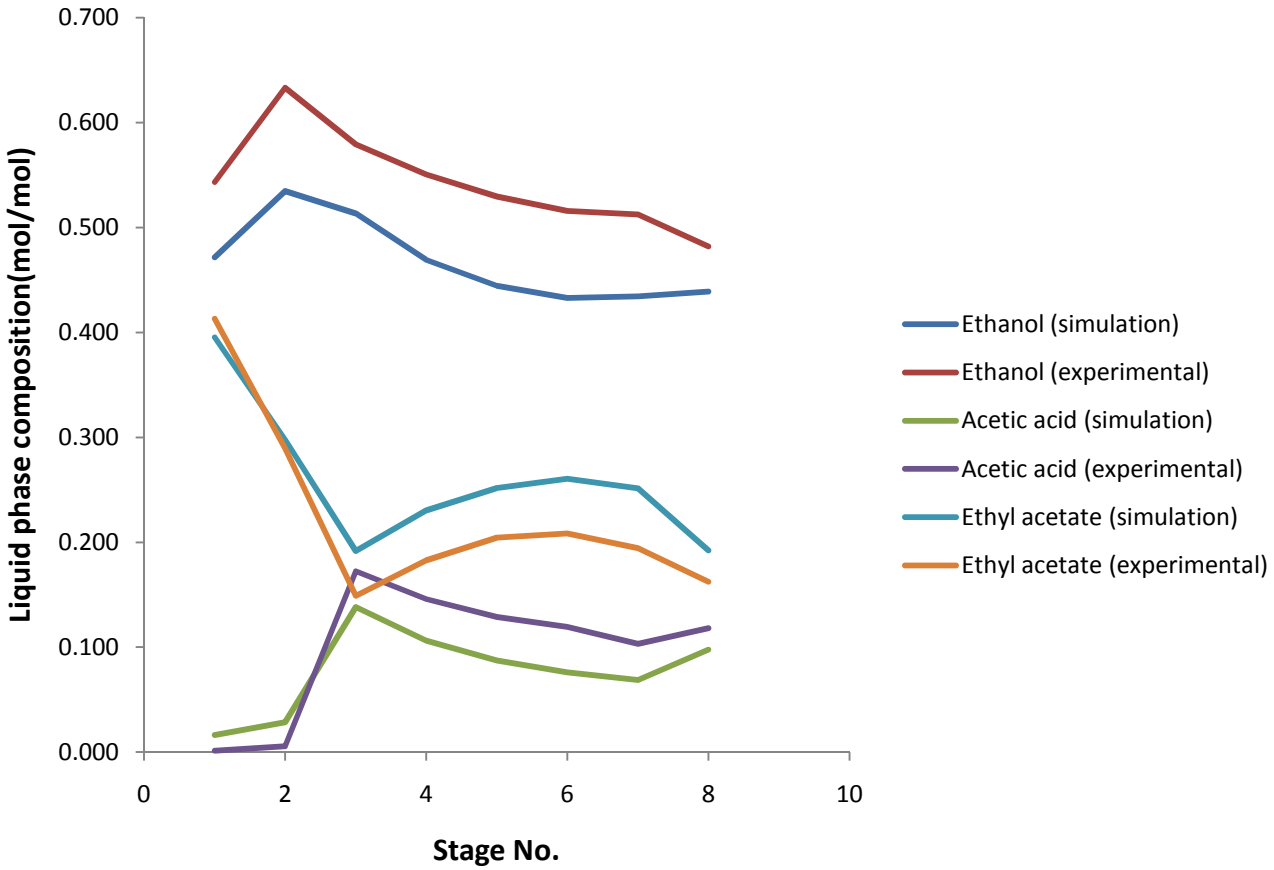

Figure 4.8: Comparisons of liquid phase compositions with the results of Alejski et al. (1988)

Table 4.6: Column temperature and flow rate profiles

Stage no.	Temperature (C)		Liquid flow rate (mol/min)		Vapor flow rate (mol/min)	
	a	b	a	b	a	b
1	344.8	345.6	0.089	0.089	0.000	0.000
2	345.7	346.9	0.086	0.090	0.132	0.132
3	349.9	351.9	0.353	0.322	0.128	0.110
4	348.2	351.1	0.351	0.326	0.137	0.108
5	347.3	350.6	0.351	0.322	0.135	0.108
6	346.9	350.5	0.350	0.318	0.135	0.102
7	346.7	350.4	0.347	0.345	0.134	0.100
8	348.3	351.2	0.216	0.216	0.132	0.128

a =Simulation results; b= Alejski et al. (1988)

CONCLUSIONS AND FUTURE RECOMMENDATIONS

Conclusions:

The reactive distillation of ethyl acetate production ($C_2H_5COOCH_3$), using acetic acid (CH_3COOH) and ethanol (C_2H_5OH), in a plate column are done using RADFRAC module of ASPEN PLUS. The results show that the Wilson model for liquid phase activity with SRK model for vapor phase, and UNIQUAC model for liquid phase predict the experimental data most closely. However, in the lower part of the column even these models do not match with the experimental data.

The segmental model approach has improved the simulation predictions in the lower portion of the column. The overall ethyl acetate composition profile is better predicted by this approach as compared to the single activity model approach for the entire column.

Future recommendations:

There is a strong influence of the thermodynamic activity models on the simulation results, and it is of crucial importance to use the right liquid phase activity model. However, the influence of kinetics on phase equilibrium demands that the user model (empirical) should be used to get the better results for this system.

NOMENCLATURE:

D	distillate component molar flow rate (mol/s)
D	distillate molar flow rate (mol/s)
f	feed component molar flow rate (mol/s)
F	feed total molar flow rate (mol/s)
h	liquid-phase enthalpy (kJ/mol)
h_f	feed enthalpy (kJ/mol)
H	vapor-phase enthalpy (kJ/mol)
I	component number (i = 1, 2, …, C)
J	tray number (j = 1, 2, …., N)
k	reaction rate constant [m^3/(mol.s)]
K_c	constant of reaction equilibrium
$K_{i,j}$	vapor-liquid equilibrium coefficient
l	liquid-phase component molar flow rate (mol/s)
L	liquid-phase total molar flow rate (mol/s)
P	pressure (atm)
Q_C	condenser heat duty (kJ/mol)
Q_R	reboiler heat duty (kJ/mol)
r_1	rate of catalyzed reaction [mol/(s m^3)]
r_2	rate of non catalyzed reaction [mol/(s m^3)]
R	reflux ratio
T	temperature (K)
v	vapor-phase component molar flow rate (mol/s)
V	vapor-phase total molar flow rate (mol/s)
V_C	reaction volume in condenser (m^3)
V_j	reaction volume on j^{th} tray (m^3)
V_R	reaction volume in reboiler (m^3)
x	liquid-phase mole fraction
y	vapor-phase mole fraction
α_i	stoichiometric coefficient; for reactant < 0; for product > 0

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