

**DYNAMIC MODELLING
OF A
REACTIVE DISTILLATION COLUMN**

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REAKTİF DİSTİLASYON KOLONUNUN DİNAMİK MODELLEMESİ

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To my father and mother,

FOREWORD

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ABBREVIATIONS

EQ	: Equilibrium
NEQ	: Non Equilibrium
ODE	: Ordinary Differential Equation
RD	: Reactive Distillation
VLE	: Vapor/Liquid Equilibrium
F	: Feed stream
L	: Liquid phase
V	: Vapor phase

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DYNAMIC MODELLING OF A REACTIVE DISTILLATION COLUMN

SUMMARY

There is a great interest for separation processes in chemical industry. Common separation technologies are distillation, extraction, pervaporation, crystallization, etc. Distillation is the most used and known process between all these technologies for last years. In the separation processing industry, there is the need to approach the operation of industrial equipment so they increase their energy efficiency, leading to more-economical and environmentally oriented processes. A feasible way to achieve these purposes lies in the optimal dynamic operation of industrial operations. Reactive distillation (RD) is the process in which vapor-liquid separation and one or more chemical reactions occur simultaneously.

Separation of the product from the reaction mixture does not need a separate distillation step, which saves energy (for heating) and materials. In this way, only one piece of equipment (the RD column) is used, possibly reducing investment and operation costs.

This technique is especially useful for equilibrium-limited reactions such as esterification and ester hydrolysis reactions. Conversion can be increased far beyond what is expected by the equilibrium due to the continuous removal of reaction products from the reactive zone. This helps reduce capital and investment costs and may be important for sustainable development due to a lower consumption of resources.

Being a relatively new field, research on various aspects such as modeling and simulation, process synthesis, column hardware design, non-linear dynamics and control is in progress. The suitability of RD for a particular reaction depends on various factors such as volatilities of reactants and products along with the feasible reaction and distillation temperature. Hence, the use of RD for every reaction may not be feasible. Exploring the candidate reactions for RD, itself is an area that needs considerable attention to expand the domain of RD processes. Although invented in 1921, the industrial application of reactive distillation did not take place before the 1980s.

The esterification of acetic acid with alcohols like *n*-butanol, ethanol, isobutyl alcohol and amyl alcohol fall in a typical class of reacting systems. Butyl acetate is an industrially important chemical with wide applications as a versatile solvent. *n*-Butyl acetate is manufactured by the esterification of acetic acid with *n*-butanol in the presence of suitable acid catalyst. The alcohol is sparingly soluble in water and the ester is almost insoluble. Another interesting feature of this system is that it is associated with the formation a minimum boiling ternary azeotrope of ester, alcohol and water, which is heterogeneous in nature. Hence, in a typical reactive distillation column that consists of both reactive and non-reactive zones, the heterogeneous azeotrope or a composition close to the azeotrope can be obtained as the distillate product. Moreover, the aqueous phase that forms after the condensation of the vapor

is almost pure water. Depending on the requirement either of the phases can be withdrawn as a product and the other phase can be recycled back as reflux. The pure ester i.e. butyl acetate is the least volatile component in the system is realized as a bottom product.

RD columns have a tendency to be difficult to control. To operate distillation columns, the design of the column will likely be based on a mathematical model of the process. Because there are strong nonlinearities (through mass, energy and chemical kinetic couplings), the modeling and design problem could be difficult to handle, which means that simulation and design tasks will be rather complicated.

The main goal of this project is to obtain new insights on systematic dynamic modeling of a reactive distillation with the aim to use it for optimization and control. This model gives a good idea to figure out the RD concept but it should be reduced dynamic model that can be used to optimize a grade transition a reactive distillation system.

In this study, the dynamic mass and energy balances, basic kinetics and basic thermodynamics (MESH equations) have been set up using equilibrium model. The dynamic modeling begins with those equations implemented on MATLAB in a toy problem (3 stages distillation) until a model that works for a 5 stages reactive distillation column with a reaction such as $A + B \leftrightarrow C + D$.

While being developed this model, it has been applied for different stages. Composition profiles and resolutions of these stages were observed step by step. It was shown on diagrams how we could gain step response while we were changing the feed flow and feed compositions. The best ODE function was selected for reactive distillation column. The issues covered include the liquid – vapor equilibrium, mass – energy balances, reaction rate equations, feed compositions, feed flows, step changes and step responses, ODE functions, linearization. It works with for $A + B \leftrightarrow C + D$ reaction in 5 stages RD.

REAKTİF DİSTİLYASYON KOLONUNUN DİNAMİK MODELLEMESİ

ÖZET

Kimya endüstrisinde ayırma işlemlerine karşı sürekli artan ve çok büyük bir ilgi bulunmaktadır. Bu endüstride kullanılan en yaygın ayırma işlemleri ise distilasyon, ekstraksiyon, evaporasyon ve kristallendirmedir. Artan ilgiyle birlikte son yıllarda bu teknolojiler arasında en çok kullanılan ve bilinen işlem distilasyon olmuştur.

Ayırma işlemleri endüstrisinde, enerji verimini artırarak daha ekonomik ve de daha çevreci işlemler gerçekleştirecek ekipmanların kullanılacağı yaklaşımlara ihtiyaç duyulmaktadır. Bu amaçları gerçekleştirebilecek en makul yol ise endüstriyel operasyonlar için en uygun dinamik sistemin seçilmesidir. Reaktif distilasyon hem sıvı buhar ayırımının hem de bir veya daha fazla kimyasal reaksiyonun aynı anda gerçekleştiği bir prosestir. Böylece, sadece bir adet reaktif distilasyon kolonu kullanarak hem yatırım için hem de operasyon için kullanılan maliyetler azalmakta ve böylece kullanılma oranları artmaktadır.

Geleneksel yöntemlere baktığımızda reaksiyon karışımından elde ettiğimiz ürünü ayrı bir distilasyon kolonunda saflaştırmak için ayırma işlemine sokmamız gerekirdi; ancak reaktif distilasyon sistemi ile beraber reaksiyon karışımından elde etmek istediğimiz ürünü çekmek için ayrı bir distilasyon basamağına ihtiyacımız bulunmamaktadır. Dolayısıyla ısıtma için enerji tasarrufu ve daha fazla madde kazanımı sağlanmakta, ayrıca daha az ekipman kullanılmaktadır. Bu şekilde reaktif distilasyon sistemiyle sadece bir ekipman kullanarak (reaktif distilasyon kolonu) yatırım ve operasyonel maliyetleri azaltmak mümkün olmaktadır.

Bu sistem ve teknik özellikle esterifikasyon ve ester hidroliz reaksiyonları gibi denge – limitli reaksiyonlarda çok fazla yarar sağlamakta ve kullanılmaktadır. Dönüşüm, reaksiyon bölgesinden reaksiyon ürünlerinin sürekli olarak çekilmesi sayesinde beklenenin çok üzerinde bir artış göstermektedir. Bu oran, sermaye ve yatırım maliyetlerinin azalmasını sağlayarak, kaynakların tüketiminin azaltılması için çok önemli bir sürdürülebilir gelişme olabilir.

Bu teknoloji oldukça yeni alanların açılmasını sağlayarak, modelleme, simülasyon, proses sentezi, kolonun donanımsal dizaynı, non-lineer dinamik ve kontrol gibi çok çeşitli dallarda sürekli bir gelişme ve ilerlemenin olmasını, böylece daha fazla araştırma yapılması için yeni kapılar açmaktadır. Seçtiğimiz bir reaksiyon için reaktif distilasyon sisteminin uygunluğu mümkün olan en uygun reaksiyon ve ayırma sıcaklığıyla beraber reaktan ve ürünlerin uçuculuğu gibi çok çeşitli faktörlere bağlıdır. Bu nedenle, reaktif distilasyon sistemi kullanımı her reaksiyon için mümkün olamamaktadır. Reaktif distilasyon sistemine uygun aday reaksiyonlar keşfederken, baskın reaktif distilasyon proseslerini genişletmek için dikkate değer bir ilgi ihtiyacı meydana gelmektedir. Reaktif distilasyon sistemi 1921’ de icat edilmesine rağmen, reaktif distilasyonun endüstriyel uygulamaları 1980’ den önce çok fazla yer almamıştır.

Endüstriyel anlamda çok fazla kullanım alanı olan reaktif distilasyon sistemi, özellikle asetilasyon, aldol kondenzasyonu, alkilleşme, aminleşme, dehidrasyon, esterleşme, eterleşme, hidroliz, izomerleşme, oligomerleşme, transesterifikasyon ve hidrodesülfürasyon gibi reaksiyon sistemlerinde sıklıkla tercih edilmekte ve uygulanmaktadır.

Asetik asidin n-bütanol, etanol, isobutil alkol and amil alkol gibi alkollerle esterleşmesi sanayide ve laboratuarlarda kullanılan tipik bir reaksiyon sınıfını oluşturmaktadır. Bütil asetat çok çeşitli uygulamaları olan bir çözücü olarak endüstriyel anlamda önemli bir kimyasaldır. n – bütül asetat, asetik asidin uygun bir katalizör varlığında n-bütanol ile esterleşmesi sonucu üretilir. Alkoller suda çok az bir şekilde çözünür ve esterler hemen hemen hiç çözünmezler.

Bu sistemin bir diğer ilginç özelliği ise doğada heterojen olarak bulunan su – alkol – ester üçlü azeotrop karışımının minimum kaynama noktasıyla olan ilişkisidir. Bu nedenle, tipik bir reaktif distilasyon kolonu hem reaktif, hem de reaktif olmayan bölgeleri içermektedir. Heterojen azeotrop ya da azeotrop olmaya yakın bir bileşim distilat ürünü olarak, bu sistemden elde edilebilmektedir. Dahası, buharın yoğunlaşmasından sonra oluşan sulu faz tamamen saf su içermektedir. Fazlardan biri isteğe bağlı olarak ürün olarak çekilebilir ve diğer faz reflüks olarak sisteme geri döndürülebilir. Sistemdeki relatif uçuculuğu en az olan bütil asetat gibi saf bir ester alt ürün olarak düşünülür.

Reaktif distilasyon kolonlarının kontrolü zor olmaktadır. Distilasyon kolonlarını çalıştırmak için, kolonların tasarımı matematiksel bir modeli esas almaktadır. Çünkü kütle, enerji ve kimyasal kinetik eşitlikleri gibi modelleme ve dizayn problemini çözmeyi zorlaştıracak ve bu nedenle simülasyon ve dizayn işlemini oldukça karmaşık hale getirecek bir çok lineer olmayan bağlantı bulunmaktadır.

Bu projedeki temel amacımız reaktif distilasyon işlemini yeni bir sistematik dinamik modelleme yaklaşımıyla optimizasyon ve kontrol işlemlerinde kullanmaya hazır hale getirmektir. Bu model reaktif distilasyon uygulamasını anlamak için iyi bir fikir vermektedir; ama optimizasyon ve kontrol uygulamaları için bazı kısıtlamalar getirilmesi uygun olacaktır.

Bu çalışmada dinamik kütle ve enerji dengesi, temel kinetik ve temel termodinamik (MESH eşitlikleri) denklemleri kurularak, denge modelimizin oluşturulmasında kullanılmıştır. Dinamik model ilk olarak 3 raflı bir kolonda, MATLAB kullanılarak test edilmiş, daha sonra yine aynı program 3, 5, 10 raflı kolonlar için denenmiş ve bu model, $A + B \leftrightarrow C + D$ gibi bir reaksiyon için, 5 raflı reaktif bir distilasyon kolonuna genişletilmiştir.

Bu model geliştirilirken, farklı raf sayılarında uygulanarak (3, 5, 10 raflı reaktif distilasyon kolonu) test edilmiştir. Bileşim profilleri ve bu raflardaki çözümleri adım adım gözlenmiştir. Çıktılarımızın olduğu kısımdaki grafiklerde görüleceği üzere besleme akımında ya da besleme bileşiminde herhangi bir değişim uyguladığımızda sistemimizin buna nasıl cevap vereceği de tespit edilmiştir.

Ayrıca, çeşitli adi diferansiyel eşitlikler kullanarak (ODE 23, 23s, 15s, 45), sistemimiz için en uygun profili verecek adi diferansiyel eşitliğin ne olabileceği MATLAB’ da uygulanarak belirlenmiştir.

Bunlara ek olarak reaktif distilasyon sisteminde özellikle modelleme, kontrol ve optimizasyon çalışmaları için, MATLAB paket programının, sistemimizi tanımlamada kullandığımız modelin çıktıları ve profilleri göz önüne alındığında ne kadar uygun bir program olduğunu da söyleyebiliriz.

1. INTRODUCTION

1.1 Purpose of the Thesis

The main goal of this project is to obtain new insights for systematic dynamic modeling of a reactive distillation with the aim to use it for optimization and control. Therefore, we should design a modeling strategy and we should have test and development with cases study;

- Dynamic behavior
- Inverse response
- Equilibrium
- Nonlinear

1.2 Background

Reactive distillation (RD) is receiving increased interest in the chemical process industry and academia in the last years. In RD, chemical reaction and multi-component distillation are combined in a single unit. When a solid catalyst is used to accelerate the reaction, the process is referred to as catalytic distillation (CD).

These processes as a whole are not a new concept as the first patent dates back to the 1920s. The initial publications deal with homogeneous self-catalyzed reactions such as esterification and hydrolysis. Heterogeneous catalysis in reactive distillation is a more recent development. While the concept existed much earlier, the first real-world implementation of reactive distillation took place in 1980s [11].

Combining reaction and distillation may have several advantages over conventional process systems consisting of separate reactor and distillation units, including: a) shift of the chemical equilibrium and an increase of reaction conversion by simultaneous separation of the products, b) suppression of side reactions and c) utilization of the heat of reaction for the mass transfer operation. These synergistic effects may result in significant economic benefits of reactive distillation compared to a conventional design: a) lower capital investment, b) lower energy cost and c)

higher product yields. Examples for successful applications of reactive distillation have, among others, been reported for esterifications, etherification, alkylation and isomerizations [4].

1.2.1 Industrial applications of reactive distillation: recent trends

Reactive distillation can be used in many variety chemical applications;

- Acetylation
- Aldol condensation
- Alkylation
- Amination
- Dehydration
- Esterification
- Etherification
- Hydrolysis
- Isomerization
- Oligomerization
- Transesterification
- Hydrodesulfurization of light oil fractions

The reactions in reactive distillation considered include heterogeneous catalysis reactions, homogeneous catalysis reactions, and thermal (non-catalyst) reactions.

As reactive distillation is the most widely applied process intensification technique today, lessons learned for implementation of other process intensification techniques are derived.

Sulzer reports the following industrial commercial scale applications: synthesis of ethyl, butyl and methyl acetates, hydrolysis of methyl acetate, synthesis of methylal, removal of methanol from formaldehyde, formation of fatty acid esters [7] with their regional spread.

Eastman's first methyl acetate reactive distillation tower started up in 1980. It is more than 80 m tall with a diameter of about 4 m. The process (including condenser and reboiler) is made of five different materials of construction (ranging to zirconium). It has an annual capacity significantly in excess of 200,000 metric tonnes

per year methyl acetate [17]. The second plant, built 7 years later with the benefit of operating experience, is virtually identical (geometry, staging, dimensions, capacity) except for some sieve tray details in the upper non-reactive zones [17]. It contains five functions in one column resulting in capital expenditure and energy reductions by a factor 5 relative to conventional unit operation design [17].

1.2.1.1 Esterification

Esterification of acetic acid with alcohols like *n* - butanol, isobutyl alcohol, amyl alcohol and hexanol fall in a typical class of the reacting systems (Eq. 1.1). The alcohols are sparingly soluble in water and the ester is almost insoluble. Another interesting feature of this system is that it is associated with the formation a minimum boiling azeotrope, which is heterogeneous in nature. Hence, in a typical reactive distillation column that consists of both reactive and non-reactive zones, the heterogeneous azeotrope can be removed as the top product. Moreover, the aqueous phase that forms after the condensation of the vapor is almost pure water. It can be conveniently withdrawn as a product and the organic phase can be recycled back as reflux. The bottom product is also a pure ester, which is the least volatile component in the system [5]. A typical reactive distillation column used for these reacting systems is shown in Figure 1.1.

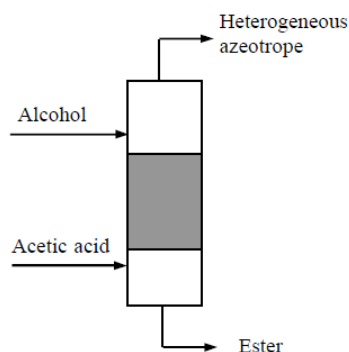
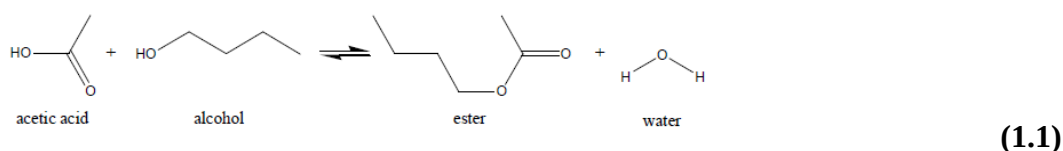


Figure 1.1: Synthesis of $C_4 - C_5$ acetates with reactive distillation.

1.2.1.2 Etherification

The C₄ fraction of hydrocarbon generally contains 1-butene, 2-butene, *n*-butane, butadiene and isobutene. Butadiene is separated by extractive distillation. However, the separation of remaining components is economically not favored because of small difference in the boiling points. The existing process for the isolation of isobutene is based on reacting C₄ stream with primary C₃ or C₄ alcohol in the presence of ion exchange resins to give corresponding tertiary ether. The reaction is conducted in a cascade of three reactors with an excess of primary alcohol to achieve satisfactory conversions. The ether formed is then separated from the remainder of C₄ stream by distillation. Isobutene is obtained after catalytic cleavage of the ether (Eq. 1.2).

A modified process combines the reaction and the separation steps in a single column by employing reactive distillation (Fig. 1.2). The C₃ or C₄ alcohol and C₄ hydrocarbon mixture are fed to the column above and below the reaction zone respectively. The reaction zone contains Bayer Levatit. R ion exchange resins. The remaining C₄ stream and ether are separated from isobutanol in the rectification and stripping zone respectively. The top and the bottom products contain < 1.5% and 0.3% by weight of isobutene respectively. The separated ether is then cleaved to subsequent alcohol and isobutene by the conventional process [14].

The possibility of using etherification as separation tool for the C₄ streams has also been explored recently by Baur et al. [2]. In the first column, isobutene and methanol react to form MTBE hence separating the inert C₄ component, while in the second column MTBE splits back to methanol and isobutene. Methanol is recycled back to MTBE formation column and isobutene is obtained as a pure product. This coupled reaction would be useful if no side reactions occur. The side products liked isobutene, *di*-methyl ether and water; if present; these affect the purity of methanol. Thus, the outlet of the splitting column must first be separated before recycling. Selectivity of the product is also affected by factors like reflux ratio. If reflux ratio increases, the amount of byproducts formed increases thus affecting the selectivity of isobutene. Even though RD could increase the selectivity of the desired product by selective reaction, this is not so always.

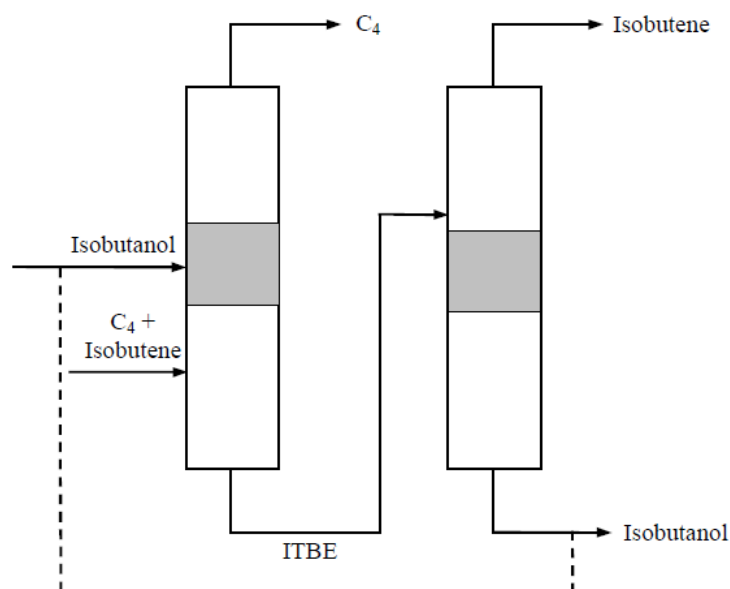
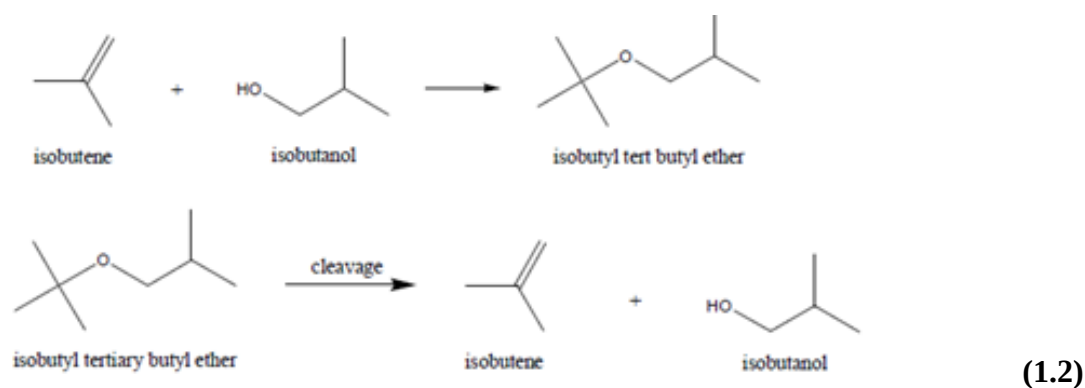


Figure 1.2: Separation of isobutene from hydrocarbon mixture [16].

1.2.1.3 Hydrogenation

Cyclohexane being the main precursor for the production of nylon products, its demand will always remain on the rise. It was first obtained by the direct fractional distillation of suitable crude petroleum refinery streams. Hydrogenation of benzene (Eq. 1.3) was carried out at moderate temperature and pressure conditions in a RD column using heterogeneous catalyst to produce almost pure (99.9%) cyclohexane [7]. Group VIII metals on suitable support is the preferred catalyst system. Reactive distillation facilitates efficient contact of hydrogen with benzene, proper utilization of the heat of reaction, and good temperature control. Higher conversion (90%) of benzene and almost 100% selectivity to cyclohexane has been reported. The schematic of the process is shown in Fig. 1.3. Moreover, the “washing effect” due to the internal reflux, reduces the possibility of polymer build-up and coking.

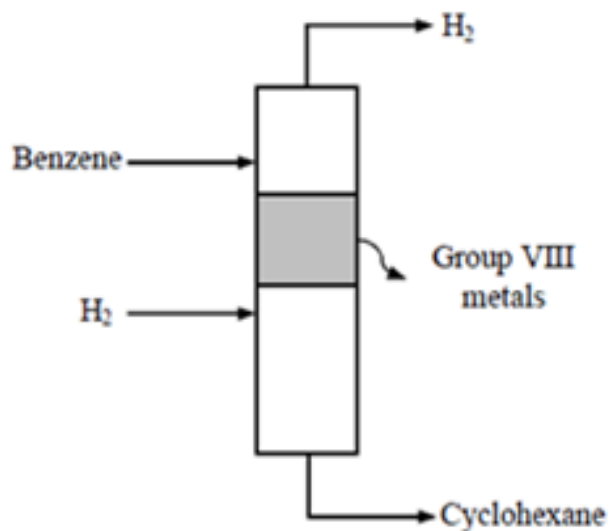
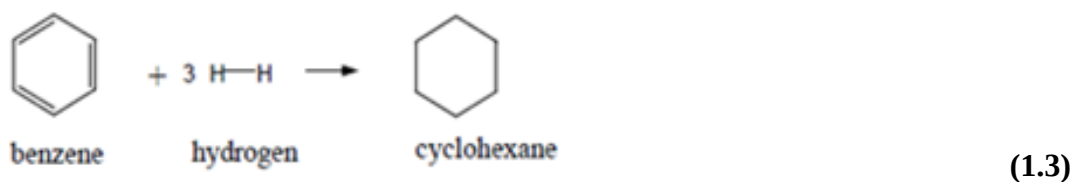


Figure 1.3: Hydrogenation of benzene to cyclohexane [15].

1.2.1.4 Ethylene Glycol

If we consider the reaction of ethylene oxide (EO) with water to produce ethylene glycol (EG) in a reactive distillation column, the reaction is irreversible (Eq. 1.4-1.5) and proceeds in the presence of a catalyst (Fig. 1.4).

In addition to this, we have an unwanted side reaction in which ethylene glycol reacts with ethylene oxide to di – ethylene – glycol (DEG).



Ethylene glycol is the major product of these reactions, and diethylene glycol is a waste byproduct.

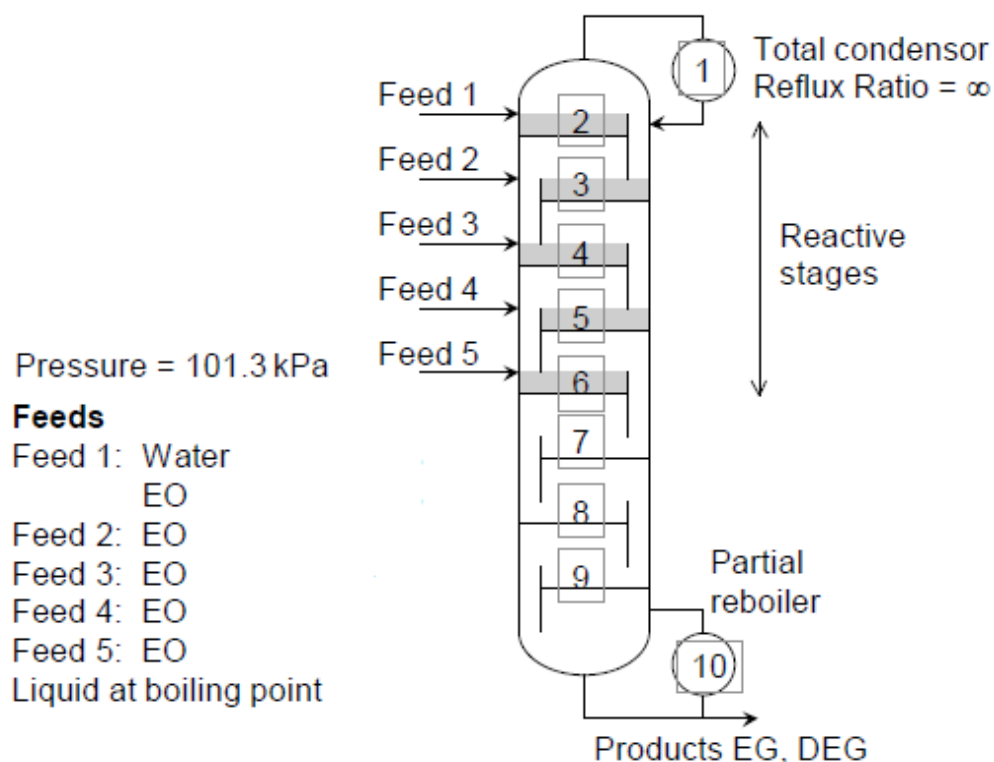


Figure 1.4: Configuration of reactive distillation column for hydration of ethylene oxide to ethylene glycol.

1.2.2 Advantages of reactive distillation

Reactive distillation (RD) is an innovating process which combines both distillation and chemical reaction into a single unit, which saves energy (for heating) and materials. Therefore, the RD technology offers many benefits as well as restrictions over the conventional process of reactor followed by distillation or other separation approaches. Reducing capital cost, higher conversion, improving selectivity, lower energy consumption, the reduction or elimination of solvents in the process and avoidance of azeotropes are a few of the potential advantages offered by RD. This technique is especially useful for equilibrium-limited reactions such as esterification and transesterification reactions. Conversion can be increased far beyond what is expected by the equilibrium due to the continuous removal of reaction products from the reactive zone. This helps to reduce capital and investment costs and may be important for sustainable development due to a lower consumption of resources [13].

In addition to this, the heat which produced in the exothermic reaction can be used in separation. In comparison with conventional methods, less process equipments are

used in the RD system (less units, pumps, valves, sensors). Therefore, less voluminous process reduces the catalyst and reactants storage, and then minimizes the environmental impact if an accident happens.

1.2.3 Disadvantages of reactive distillations

Although the reactive distillation which combines reaction and separation brings some advantages, it has complexity in according to its steady and dynamic situation;

- Incompatibility of process conditions for reaction and separation,
- Residence time requirements,
- Volatility constraints for the reactants and products in the reaction zone of the distillation column and,
- Most importantly, the lack of well-established design methods.

2. MODELING OF REACTIVE DISTILLATION

Reactive distillation is attractive (Fig.2.1):

- If the reaction is so exothermic, that cooling in the conventional reactor is required.
- If there is an undesired consecutive reaction and the production is a light boiler.
- If the conventional separation is expensive due to azeotrope formation and the azeotrope is prevented by reaction.

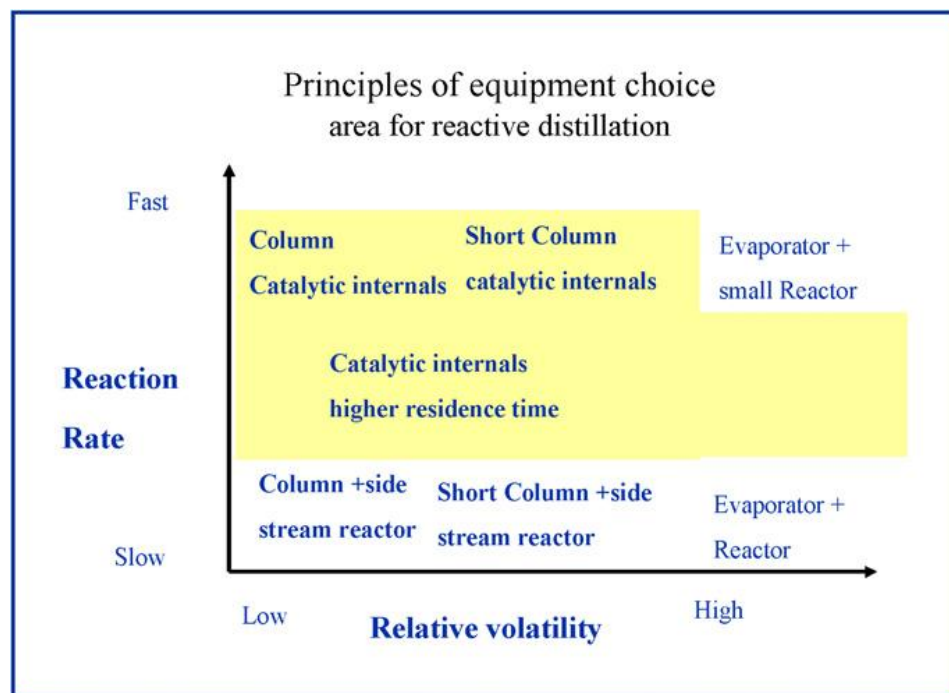


Figure 2.1 : Principles of equipment choice reactor and distillation [15].

It can be said that there are many variety of models in the literature for design RD columns. They can be classified in the following types (Fig.2.2);

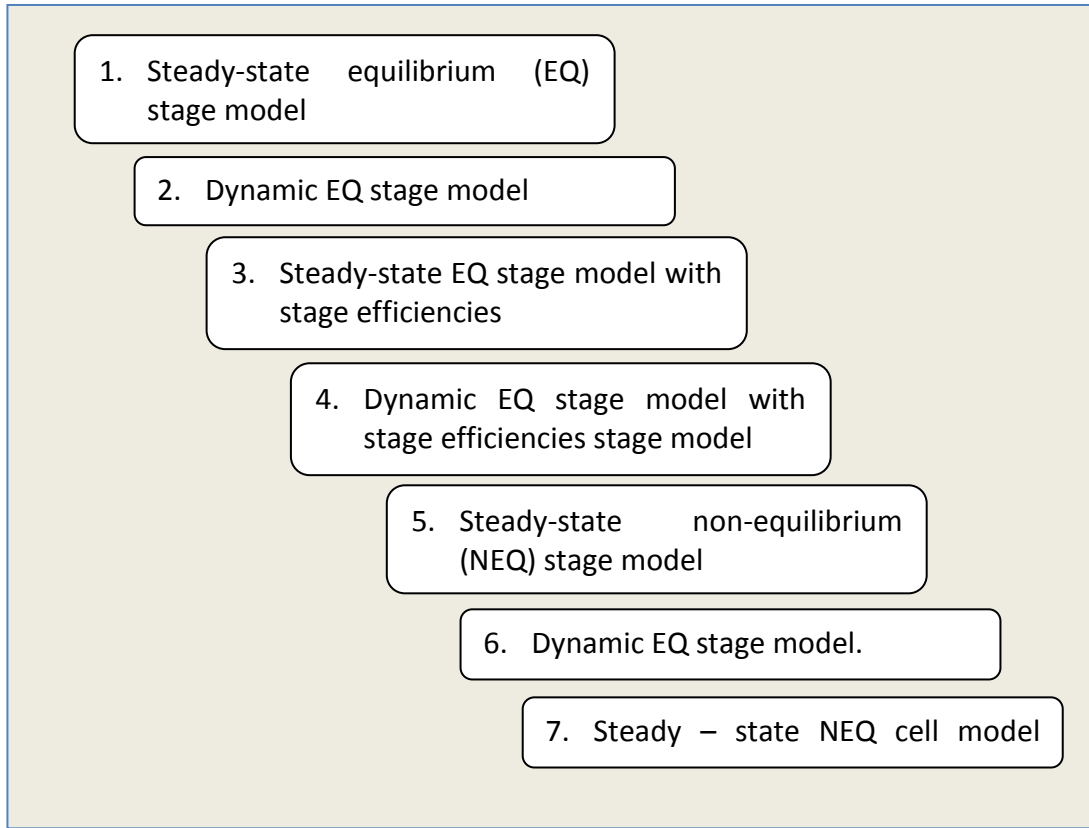


Figure 2.2 : Types of RD model

2.1 Steady State Behavior

It is established that the steady-state behavior of most real distillation columns, both trayed and packed columns, can be modeled well using a equilibrium staged model. The critical factor is usually to obtain a good description of the vapor-liquid equilibrium.

There can be two simplifying assumptions;

1. **Constant relative volatility.** In this case the vapor-liquid equilibrium between any two components is given by Eq. 2.1;

$$\alpha = \frac{y_L/x_L}{y_H/x_H} = \frac{y_L/y_H}{x_L/x_H} \quad (2.1)$$

This assumption holds well for the separation of similar components, for example, for alcohols or for hydrocarbons. Obviously, this assumption does not hold for non-ideal mixtures such as azeotropes. For a *binary mixture* (Eq. 2.2) yields [19];

$$\alpha = \frac{y/(1-y)}{x/(1-x)} \Rightarrow y = \frac{\alpha x}{1 + (\alpha - 1)x} \quad (2.2)$$

2. **Constant molar flows.** In this case the molar flows of liquid and vapor along the column do not change from one stage to the next, that is, if there is no feed or product removal between stages I and I+1, then at steady-state (Eq. 2.3);

$$L_I = L_{I+1} \quad V_I = V_{I+1} \quad (2.3)$$

Again, this assumption usually holds well for similar components if their heats of vaporization do not differ too much [19].

2.2 Mathematical Model of a RD Column

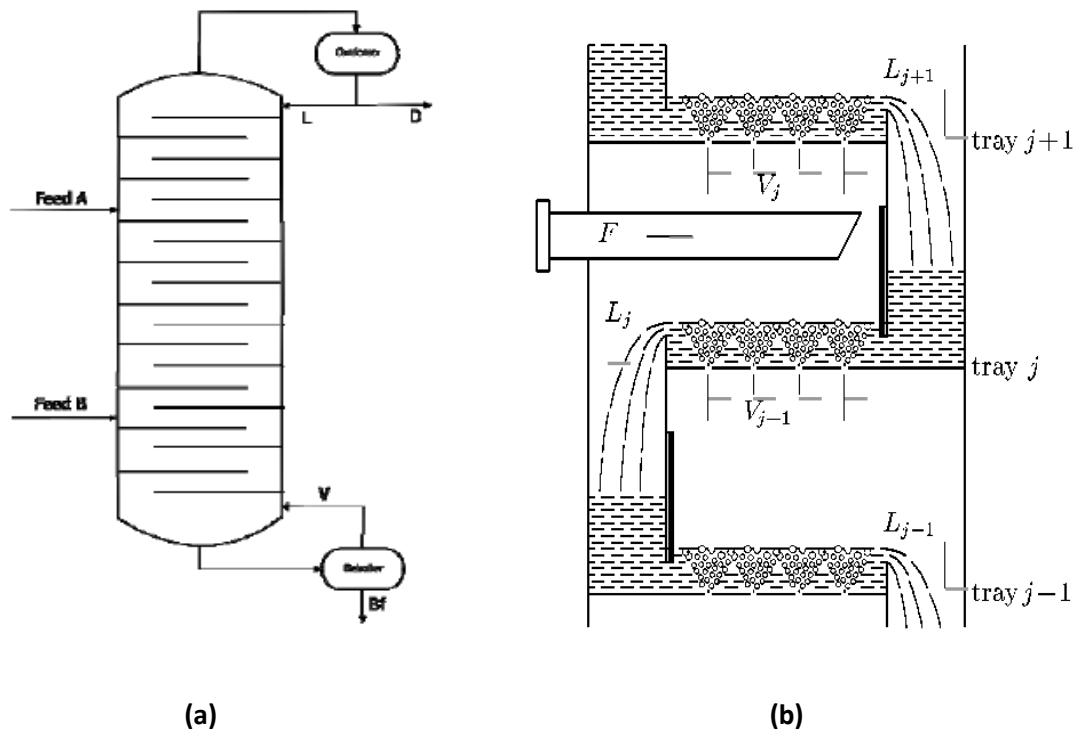


Figure 2.3 : (a) Reactive Distillation Column, (b) Tray – by - tray model of the column.

The simple way to study the models of reactive distillation is included of two feeds of components and two products on basis of mathematical representation, where a reaction of the form;



takes place in the liquid phase. The feeds of components A and B enter the column in a selected tray, the products C and D are removed as top and bottom products, respectively. The main object of this process is maximizing the conversion of the reactants and separation of the products. The reboiler vapor flow and the liquid reflux in the condenser are used as manipulated variables. The distillate flow and the bottom liquid flow are used to control the total liquid holdup in the reboiler and the condenser, respectively (Fig.2.3). The reaction is assumed to take place only in the liquid phase.

2.2.1 Equilibrium stage models (EQ)

Those models are based on well-known equilibrium stage models. The description of the transport processes is usually a film model. Respective film profiles for homogeneous systems are shown in Fig. 2.4 (a), and for heterogeneous systems in Fig. 2.4 (b). The mass transfer can be described by either assuming equilibrium or applying a kinetic model.

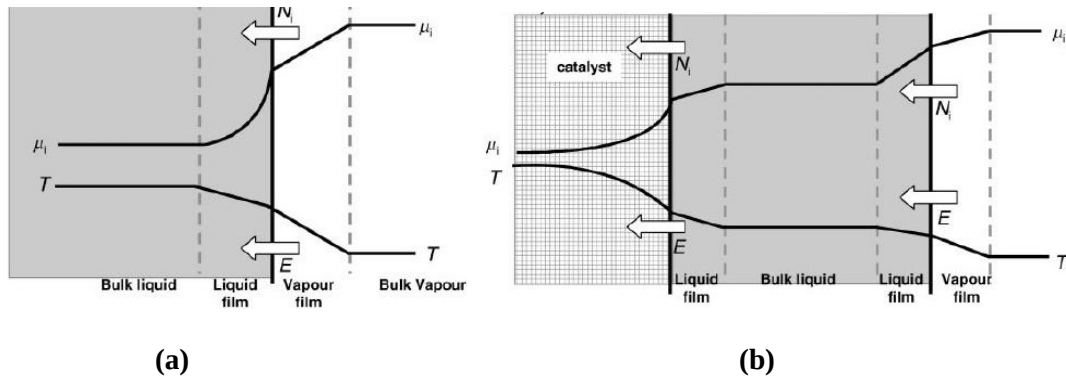


Figure 2.4 : Transport processes in RD. **(a)** homogeneous liquid-phase reaction.
(b) Heterogeneous catalyzed reactions [20].

Vapor from the stage below and liquid from the stage above are brought into contact on the stage together (Fig. 2.5). The vapor and liquid streams leaving the stage are assumed to be in equilibrium with each other.

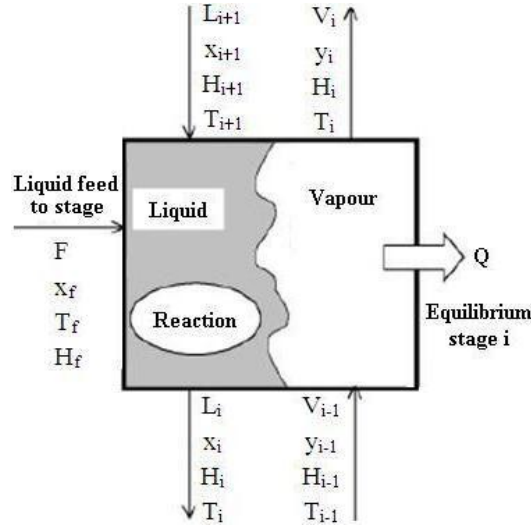


Figure 2.5 : The equilibrium stage [20].

The equations that model equilibrium stages are known as the MESH equations (MESH name coming from different types of equation), assuming no side streams.

M stands for material balanced equations for i stages, j components:

$$\frac{dM_i x_{i,j}}{dt} = V_{i-1} y_{i-1,j} + L_{i+1} x_{i+1,j} - V_i y_{i,j} - L_i x_{i,j} + V_c r_{i,j} + F x_{f,i} \quad (2.5)$$

where M_i is the liquid holdup (the vapor holdup is only taken into account for high pressures) and V_c is the average reaction volume.

E equations which are related to vapor/liquid equilibrium

$$y_{i,j} = K_{i,j}^I x_{i,j} \quad (2.6)$$

$K_{i,j}^I$ is the interface vapor-liquid equilibrium constant of component j on stage i .

For binary mixture, ratio of K is the relative volatility α such as

$$\alpha = \frac{K_1}{K_2} = \frac{y_1/x_1}{y_2/x_2} \quad (2.7)$$

or

$$\alpha = \frac{K_1}{K_2} = \frac{y_1/x_1}{y_2/x_2} \quad (2.8)$$

Also, Raoult's law can be used to solve VLE

$$P_1 = x_1 P_1^0 \quad (2.9)$$

Where P_i is the partial pressure of the component 1 in the mixture (in the solution), P_i^0 is the vapor pressure of the pure component 1, x_i is the mole fraction of the component 1 in the mixture (in the solution).

S for summation equations

$$\sum_{j=1}^{nc} x_{i,j} = 1 \quad \text{Liquid fraction} \quad (2.10)$$

$$\sum_{j=1}^{nc} y_{i,j} = 1 \quad \text{Vapor fraction} \quad (2.11)$$

H is the enthalpy/heat balance

$$\frac{dM_i H_i}{dt} = V_{i-1} H_{i-1,j}^V + L_{i+1} H_{i+1,j}^L - V_i H_{i,j}^V - L_i H_{i,j}^L + F H_i^F - Q_i \quad (2.12)$$

2.3 MATLAB ODE Solvers

There are several different ode solvers supplied by Matlab.

ODE45 (an explicit Runge-Kutta method) is efficient, but can become unstable with stiff systems. This will manifest itself by the solver taking shorter and shorter time steps to compensate. The solution will either take a long time, or the time step will be reduced to the point where machine precision causes the routine to fail.

ODE23 is used for problems with crude error tolerances or for solving moderately stiff problems.

In addition to the ODE solvers, ode23 and ode45, which are both based on the Runge-Kutta scheme, MATLAB has several additional solvers, listed below along with MATLAB's help-file suggestions regarding when to use them (Table 2.1).

Table 2.1: Usage of some ODE functions

ODE FUNCTION	USAGE
Multiple step Solvers	
Ode113	If using stringent error tolerances or solving a computationally intensive ODE file.
Stiff Problems	
Ode15s	If ode45 is slow because the problem is stiff.
ode23s	If using crude error tolerances to solve stiff systems and the mass matrix is constant.
ode23t	If the problem is only moderately stiff and you need a solution without numerical damping.
ode23tb	If using crude error tolerances to solve stiff systems

3. DYNAMICS & CONTROL OF RD

A RD column must be operated so that the product purity and reaction conversion are maintained close to their design values for major disturbances entering the column. A robust control system needs to put in place that can regulate the column for anticipated production rate changes and changes in the feedstock composition, the principal disturbances into a column. In the design of such a control system, the selection of the control structure is the most crucial decision. A control structure refers to the number of control loops and the specific input-output pairing used in the loops. Potential input variables are the reflux rate, reflux ratio, reboiler duty, reboils ratio, distillate rate, bottoms rate and the fresh feeds. Potential output variables are easily measurable variables such as tray / stream temperatures and compositions. There are thus several possible input (manipulated) variables and output (controlled) variables even in a simple RD column. The various permutations and combinations lead to a large number of possible control structures from which a small set of “good” control structures must be chosen. Evidently, the key to successful column operation is this screening of control structures to zero in on the most appropriate controlled variables and effective handles to manipulate them so that by maintaining the controlled variables at their set-points, the purity and conversion of the column remain near the design specifications. Indeed, for a good control structure, other control system design decisions such as the choice between sophisticated versus simple control algorithms becomes obvious in that simple PI control should suffice. On the other hand, no amount of sophistication in the control algorithm can compensate for an inherently poor control structure [16].

A good control structure is one that rejects disturbances effectively. In order to do so, controlled variables that are sensitive to the occurrence of the primary disturbances should be chosen so that timely control action can be initiated [12]. Also, the manipulated variables used for control should affect the controlled variables in a substantial and easily predictable way. Such a choice assures enough “stick” for column regulation even for large disturbances. At steady state, linear or nearly linear

input-output relationships are certainly desirable so that the process gain does not change appreciably. In case multiple control loops are used, the input output pairings should not cause stability problems due to interaction between the loops. Last but not least, since sensor measurements are never exact, the column performance should be robust to typical measurement errors or errors in the set-point inputs [16].

Systematic steady state analyses can be conducted to reveal the control structure/s that provides effective column regulation for the primary disturbances into a column. These analyses include sensitivity studies for obtaining potential controlled variables that are sensitive to disturbances and manipulated variables. For different control structures, the column response in terms of performance variables such as steady state product purity and conversion, and the steady state input-output relationship that a controller sees, can be studied for the major anticipated disturbances. From these analyses, good control structures are obtained as the ones that ensure product purity and conversion within acceptable limits while avoiding steady state multiplicities with nearly linear input-output relations [16].

3.1 A simple example control study for three compositions

Fig. 3.1 gives control structure in which three components are measured and controlled. The purities of the distillate and bottoms are controlled by manipulating reflux and reboiler heat-input, respectively. A composition inside the reactive zone of the column is measured and controlled by manipulating one of the fresh feeds. This loop permits the “neat” operation of the column (no excess of one of the reactants is used). Exact stoichiometric amounts of the two reactants must be fed, and this can only be achieved by some type of feedback of composition information about the amounts of the reactant components in the system. Any imbalance in the inflow of the two reactants will result in a gradual buildup of the reactant that is in excess. This will lead to an unavoidable drop in product purity when one or more of the manipulated variables hits a constraint.

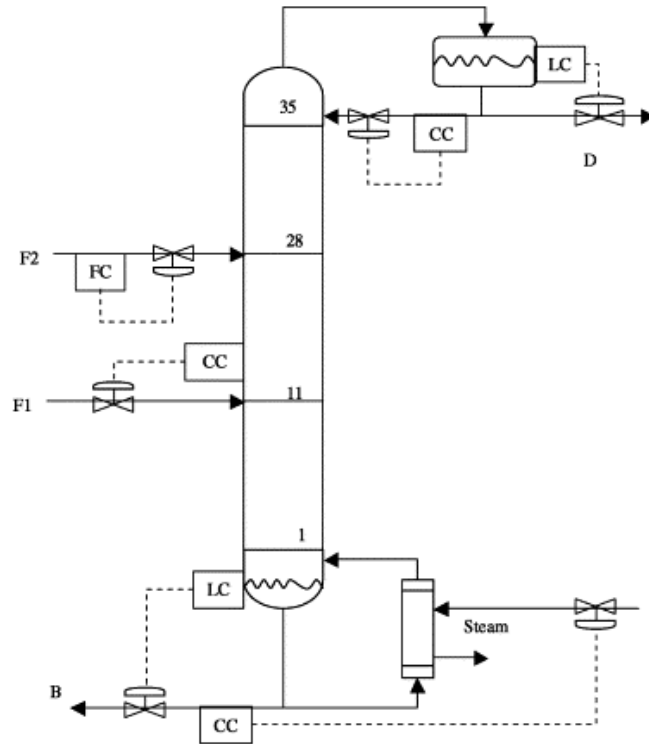


Figure 3.1 : Control structure

In practical applications, it is impossible to simply ratio the two feed streams, as has been proposed in some of the literature papers. Flow measurement inaccuracies and feed composition changes doom to failure any ratio structure that does not somehow incorporate information about compositions inside the system and feed this information back to adjust fresh feed [1].

3.2 Inverse response

A few processes exhibit a behavior where for a step change in input, the output initially changes in a direction that is opposite to the final direction it will have taken when the process has fully responded to the input change. Such a process response is shown below and is characterized as an inverse response (Fig 3.2).

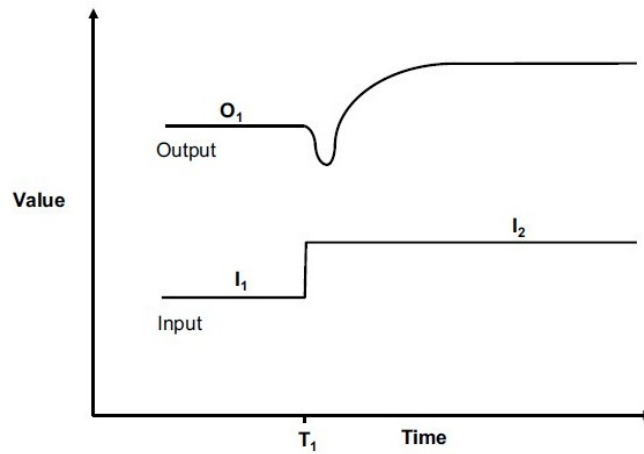


Figure 3.2 : Inverse response process

Often a process will only exhibit an inverse response to a step change in one direction of change but not in the opposite direction. The reason for this behavior may be understood when the source of the inverse response is better understood. For example, the level in the bottom of the distillation column illustrated below may show an inverse response to a step change increase in heat input [3].

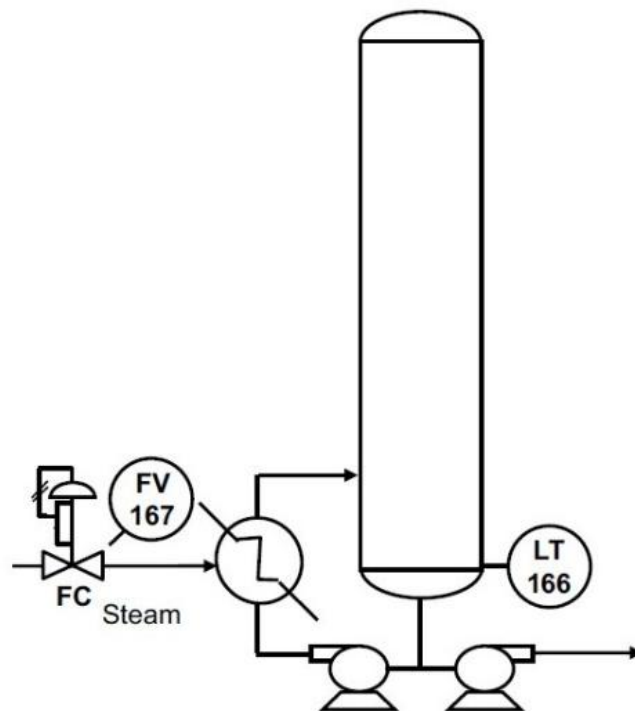


Figure 3.3 : Distillation process with inverse response.

As a result of a large step change increase in heat input to the column, a lot of bubbling and froth may temporarily result in a false level indication (Fig.3.3). However, long term, the increased energy input will boil away more material at a faster rate and the actual level will drop at a faster rate than previously. An inverse response has been observed on an increase in energy input. On a decrease in energy input, the same disruption of the level measurement will not be observed. A similar inverse response may be seen in boiler drum level control and other applications. The size and direction of an input change will often determine whether an inverse response is observed for a change in the process input [3].

3.3 Steady-state multiplicities

Reactive distillation columns are highly nonlinear, and multiple steady-state solutions have been reported by many researchers [8]. The control of unstable systems is more difficult than controlling stable systems.

There are some different types of multiplicities such as output multiplicity, output multiplicity, input multiplicity etc.

4. RESULTS AND DISCUSSION

Until now, we tried to obtain equilibrium stage model - MESH equations. The next step will be developed a suitable program for RD in MATLAB. Then program will be enhanced and studied to obtain step changes of flow and feed compositions.

At first, it will be started to develop simple 3 stage model with mass and vapor–liquid equilibrium (VLE) equations and then it will be extended to models including 5, 10 and more stages with more components and energy-reaction equations. At the end, a four component model with all MESH equations will be generated.

In the reactive distillation column, the reaction of four components and the separation of four components are simulated at the end. As described above, this reaction is hypothetical. The simulation is executed with the following physical data in according with the last developed program (Table 4.1):

Table 4.1 Physical datas of the reactive distillation system

alpha = [2.34 1.1 3.5 0.44];	% Assume constant relative volatility
N = 5;	% Number of stages
NR = N-2;	% Number of reactive stages
zF = [0.4 0.6 0 0];	% Feed composition
M = [375;50;50;50;750];	% Molar holdup, mol
F = 40;	% Feed flow, mol/s
% Reaction A+B => C + D	
k = 40000;	% Rate constant, mol/s
Ea = 20000;	% Activation energy, mol/J
Ru = 8.3145;	% Universal gas constant, J/mol.K
ksi = [-1 -1 1 1];	% Stoichiometric coefficients
% Flows in the column:	

B = 15;	% Bottoms product from the column, mol/s
D = F-B;	% Over head product of the column, mol/s
L1 = 125;	% Liquid molar flows, mol/s (assume constant molar flows)
L2 = L1;	% Liquid molar flows, mol/s (assume constant molar flows)
L3 = 165;	% Liquid molar flows, mol/s (assume constant molar flows)
L4 = L3;	% Liquid molar flows, mol/s (assume constant molar flows)
V = 150;	% Vapor molar flows; mol/s (assume constant molar flows)
V _C = 5;	% Average Reaction Volume (m ³)
% Energy	
T _f = 350;	% Feed temperature, K

4.1 Program Development

4.1.5 3- Stages Model – Test Problem

The beginning part of stage models is a 3–stage distillation (Fig. 4.1).

Assumptions of the model:

- Distillation column (no reaction yet)
- 3 stages
- Mass balances
- VLE

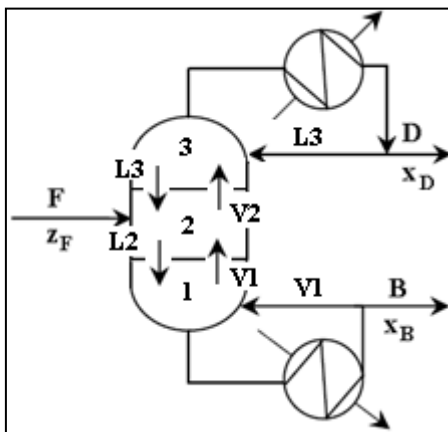


Figure 4.1: 3 stage distillation column

We assume a binary separation at constant pressure and negligible vapour holdup, the liquid holdup M at each stage being 1 kmol. The distillation is set up with a LV configuration (perfect control of levels using D and B) and constant molar flows (which replace the energy balance). The vapour-liquid equilibrium is on all stages with relative volatility and constant liquid holdup (i.e. neglect flow dynamics). With

these assumptions the only variables are the mole fraction of x_i of light component on each stage (i is the stage number).

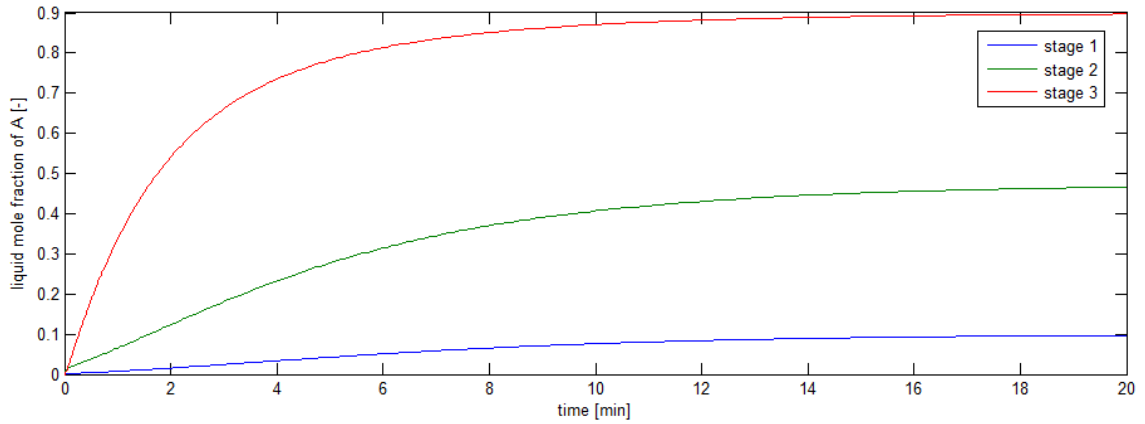


Figure 4.2: The profile of liquid mole fraction of A for 3 stages.

Given the initial conditions $x_{i0} = 0, \forall i$, the resulting Ordinary Differential Equation (ODE) system is used to simulate and create the composition profiles. The main program can be found in the appendix A.3.1.

So if you analyze the program appendix A.3.1, you can see that there are two separate sections. The upper one deals with the resolution of the equations (VLE and component balances) which are located at the lower part of the program. An explanation of the resolution and the settings of the odesolver are given in the appendix A.3.2.

4.1.2 5 – Stages Model

This model consists of 5 stages. In this model, mass balances and VLE equations are also used. There is no reaction and energy balances. Only mass balance of A component is used and then liquid mole fraction of A is composed. The only difference from former example is two more stages.

Assumptions of the model:

- Distillation column (no reaction yet)
- 5 stages
- Mass balances
- VLE

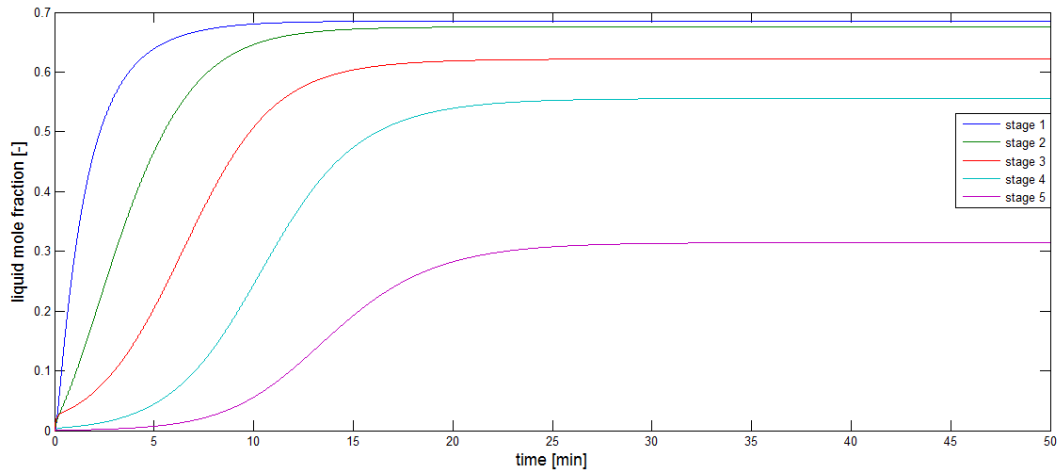


Figure 4.3: The profile of liquid mole fraction of A for 5 stages on Graph.

In this case, the composition of A and equilibrium equations for 5 stages is obtained stage by stage (Fig. 4.2).

4.1.5 10 – Stages Model

This model consists of 10 stages. In this model, mass balances and VLE equations are also used. There is no reaction and energy balances. Only mass balance of A component is used and then liquid mole fraction of A is composed.

Assumptions of the model:

- Distillation column (no reaction yet)
- 10 stages
- Mass balances
- VLE

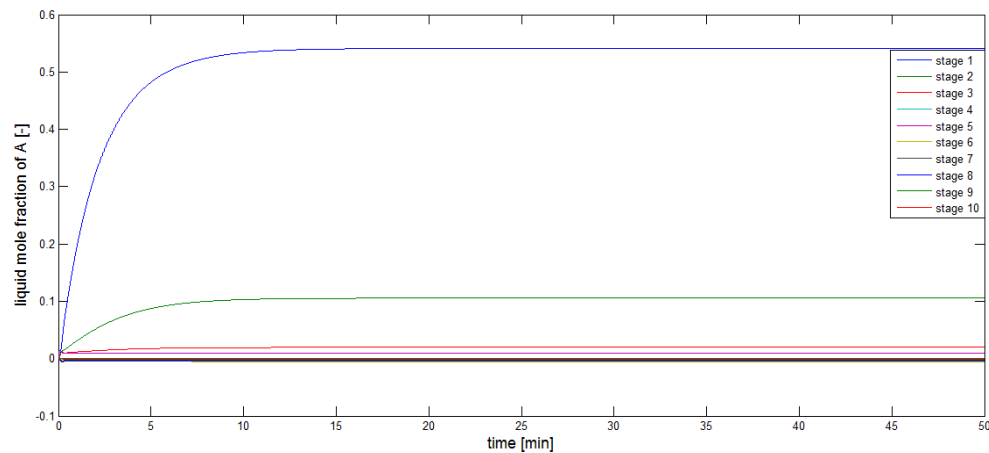


Figure 4.4 : The profile of liquid mole fraction of A for 10 stages on Graph.

The only difference from former model is more five stages (Fig. 4.4).

While we are comparing the results for different simple stage models with different ODE functions, we can see 15s function which is the most suitable function for RD. It can be easily checked the following Table 4.2 :

Table 4.2 The comparison results of different stages (3, 5, 10 stages) from command window.

ELAPSED TIME(S)			
ODE FUNCTION	3 STAGES	5 STAGES	10 STAGES
45	0.402796	0.551904	0.765053
23	0.586743	1.537274	1.044841
113	0.294743	0.412594	0.978608
15s	0.360815	0.603210	0.627705
23s	4.726069	9.834710	7.446546
SUCCESSFUL STEPS			
ODE FUNCTION	3 STAGES	5 STAGES	10 STAGES
45	738	1035	1227
23	2523	4089	3387
113	486	725	2555
15s	378	640	602
23s	5886	10213	4434
FUNCTION EVALUATION			
ODE FUNCTION	3 STAGES	5 STAGES	10 STAGES
45	4435	6217	8401
23	7579	12277	5235
113	985	1472	16022
15s	605	1253	1138
23s	35319	81707	57645

4.1.5 5 – Stages Model with Two More Component, Reaction Rate and Energy Balances ($A+B \leftrightarrow 2C$)

This model consists of 5 stages as well as reaction and energy balances. Our case is studied with $A + B \leftrightarrow 2C$ reaction, then liquid mole fractions of A, B and C are composed.

Assumptions of the model:

- RD column
- 5 stages
- Mass balances
- VLE
- $A + B \leftrightarrow 2C$
- Energy balances
- Reaction rate

A separation of three components (A, B and C) takes place at constant pressure and negligible vapour holdup, the liquid holdup for each stage is $M_i = [375, 50, 50, 50, 75]^T$ (mol) and constant (i.e. neglect flow dynamics). The control of levels is perfect using D and B (LV configuration, Fig. 4.5), adiabatic conditions, vapour-liquid equilibrium on all stages with constant relative volatility.

Therefore, with these assumptions the only variables are the mole fraction of $x_{i,j}$ of light components on each i stage for j component.

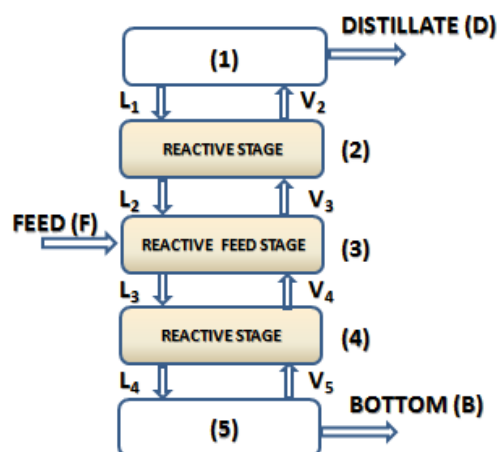


Figure 4.5: 5 stages reactive distillation column.

The column separates a ternary mixture with relative volatilities of $\alpha_j = [2.34, 1.00, 0.44]^T$ and has four theoretical stages ($N = 4$), plus a total condenser. This condenser is the first stage with $D = 25$ mol/s, the liquid feed F (40 mol/s) enters on stage 3, with a composition $z_{fj} = [0.5, 0.5, 0]^T$ and a temperature $T_F = 350$ K, and the stage 5 is the reboiler ($B = 15$ mol/s). The vapour flows for each stage at the same, $V_i = 150$ mol/s and the liquid flows are given as follows $L1 = L2 = 125$ mol/s and $L3 = L4 = 165$ mol/s (appendix A.3.3).

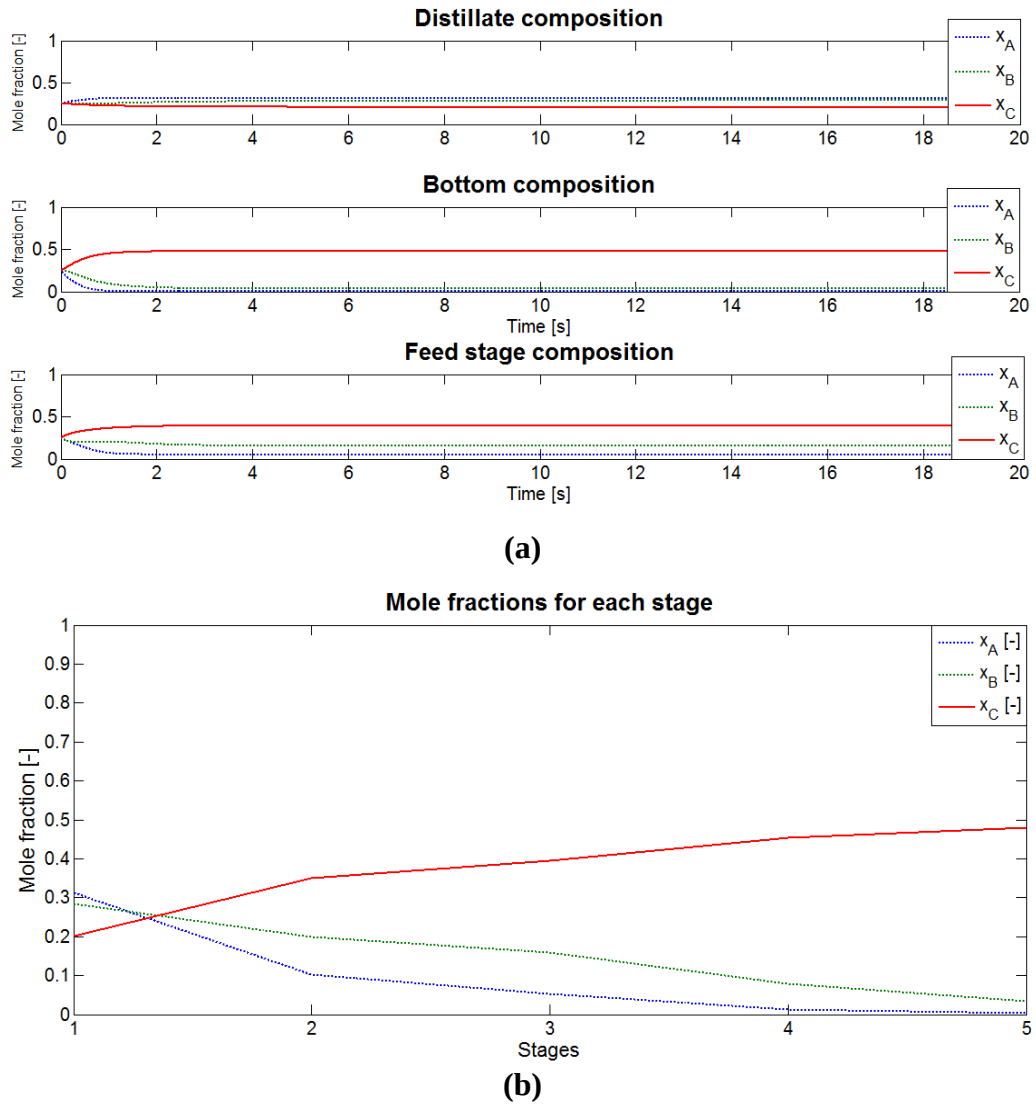


Figure 4.6 : (a) Liquid mole fractions of A, B, C for 5 stages. (b) Mole fractions of A, B and C for each stages.

In this case, we obtain the profiles of liquid mole fraction of A, B, C for each stage (Fig. 4.4 and Fig. 4.5).

The equations for B and C are the same, just replace A by B or C and the number of dxdt, x and y. As MATLAB only allows 1 ODE to be solved at the same time, consider dxdt from 1 to 5 (from condenser to reboiler) to be for component A as dxdt from 6 to 10 is for component B and from 11 to 15 for component C. A table gathering dxdt information can be found in appendix A.1.

Compared to the previous case, the stages 2, 3 and 4 are reactive stages at which the $A + B \leftrightarrow 2C$ chemical reaction takes place that can be found in appendix A.2.

For the **LVE**, we consider the equilibrium equations such as:

$$y_1 = x_1, \text{ for the total condenser (i = 1)} \quad (3.1)$$

$$y_{j,i} = \frac{\alpha_j x_{j,i}}{\sum_{i=1}^3 \alpha_j x_{j,i}} \quad \text{For the other stages} \quad (3.2)$$

As an example, for the component A at 2nd stage, it gives:

$$y_{A,2} = \frac{\alpha_A x_{A,2}}{\alpha_A x_{A,2} + \alpha_B x_{B,2} + \alpha_C x_{C,2}} \quad (3.3)$$

For this case, the **energy/heat balance** are added and compared to the EQ energy balance equation (2.13) enthalpy H is replaced by the corresponding temperature. So H becomes $C_p T$ but then c_p (specific heat capacity) gets removed. Also, no boiler heat duty is taken into account and we consider the temperatures of vapour and liquid on a stage are the same (well stirred flow).

So, equation (2.13) becomes;

$$\frac{dT_i}{dt} = (V_{i+1}T_{i+1,j} + L_{i-1}T_{-1,j} - V_iT_{i,j} - L_iT_{i,j} + F.T_{F,i}) / M_i \quad (3.4)$$

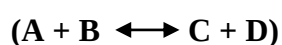
And as you cannot have several ODEs solved at the same time, the energy balances have to follow the previous mass balances. Then, the heat balances will be displayed as dxdt from 16 to 20 as follow:

Table 4.3: Heat balances for MATLAB.

```
% Energy balance
dxdt(16) = ( V*x(17)-L1*x(16)- D*x(16))/M(1);           % Stage 1, Condenser
dxdt(17) = (L1*x(16)+V*x(18)- V*x(17)-L2*x(17))/ M(2);   % Stage 2
dxdt(18) = ( L2*x(17)+V*x(19)- V*x(18)-L3*x(18)+F*Tf ) / M(3); % Stage 3, Feed stage
dxdt(19) = (L3*x(18)+V*x(20)- V*x(19)-L4*x(19) ) / M(4);  % Stage 4
dxdt(20) = ( L4*x(19)-V*x(20)- B*x(20) ) / M(5);          % Stage 5, Reboiler
```

Note that the summation equations aren't added yet as they are not necessary to get results. When they are used in the model, the results are the same. The model isn't given for this case but will be released for incoming case.

4.1.5 5 – Stages Model with Four Components for Last Conditions



This model is just slightly different from the previous one: a fourth component is added to the reaction. Also, the relative volatilities are changed such as: $\alpha_j = [2.34, 1.1, 3.5, 0.44]^T$ which means the component D should go out from the bottom whereas C leaves the column at the top. Moreover, the summation equation is added for component B to get a lighter model.

Basically, the model is the same as before, just that the summation is added after the ode resolution and feed steps are available by making a loop during the resolution. The point is to split the resolution into different time ranges with corresponding feed flows. In the model, three feed flows are available but more can be made (Appendix A.3.4).

Assumptions of the model:

- RD column
- 5 stages
- Mass balances
- VLE
- Energy balances
- Summation equations
- $A + B \leftrightarrow C + D$

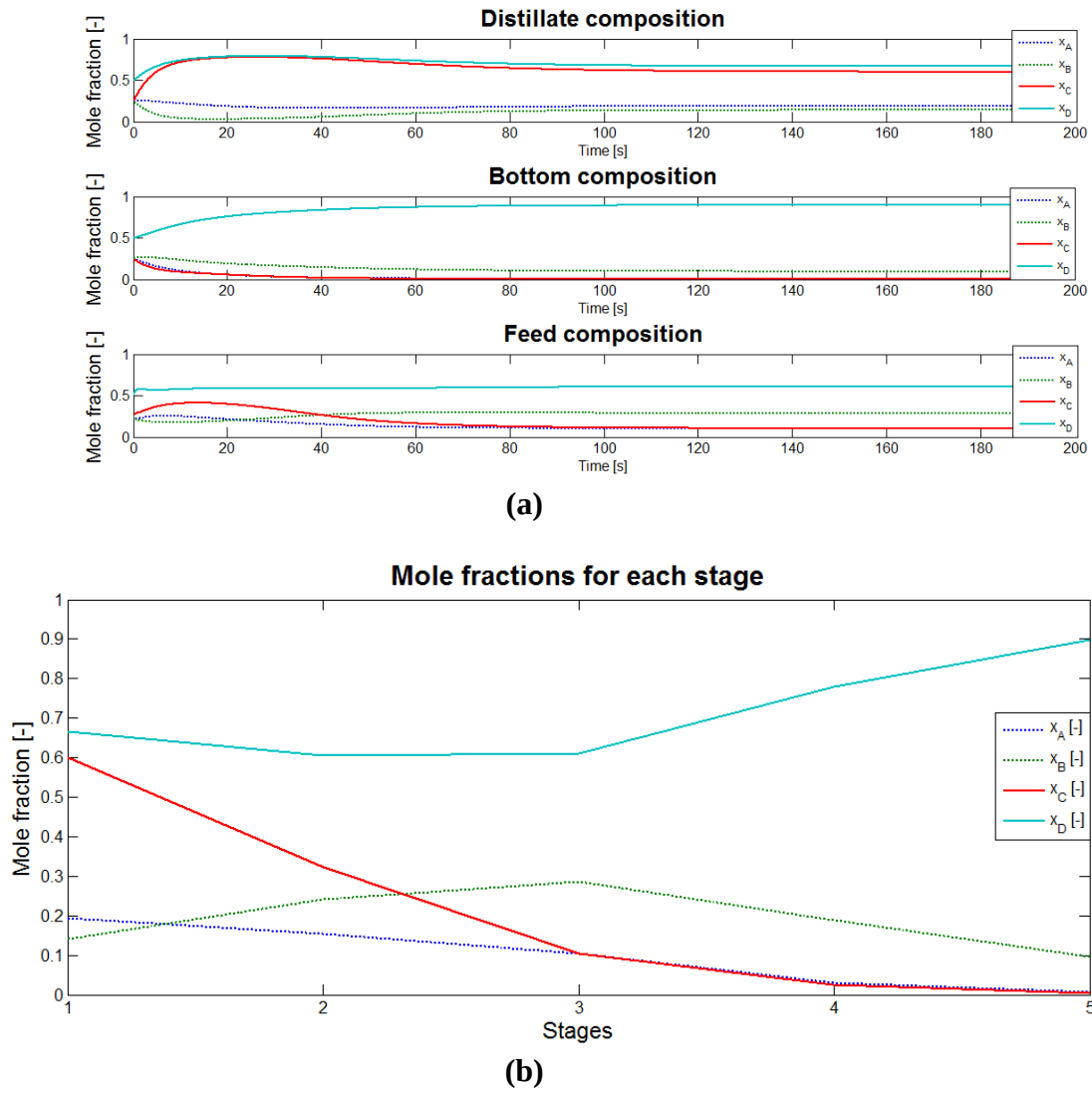


Figure 4.7 : (a) Distillate, bottom and feed stage composition for 5 stages RD, **(b)** Mole fractions of A, B and C for each stages.

Note that the numbers and notations for mass and energy balances are the same as written on previous model. For the component D the molar fractions X corresponds to numbers between 21 (stage 1: $x_{D,1}$) to 25 (stage 5 $x_{D,5}$).

Table 4.4 : Comparison of ODEs for the 5 stages model.

ELAPSED TIME(S)			
ODE FUNCTION	3 Components With Only Mass and Energy Balances (A+B $\longleftrightarrow$ 2C)	3 Components With All MESH Equations (A + B $\longleftrightarrow$ 2C)	4 Components With All MESH Equations (A + B $\longleftrightarrow$ C + D)
45	10.296876	17.400615	7.117727
23	7.078800	7.398557	5.315441
15s	10.103515	10.495013	10.081094
23s	54.750002	50.711496	32.617695
SUCCESSFUL STEPS			
6	10	10	10
23	10	10	10
15s	10	10	12
23s	10	12	10
FUNCTION EVALUATIONS			
45	61	61	61
23	31	31	31
15s	42	51	51
23s	232	282	282

After we analyzed the resolution of different ODEs, we tried to figure out which function gives the fastest resolution for 5 stages RD with MESH equations. All things considered, ODEs 15s function is selected as a best choice. Thus, we will use the ODEs 15s function for the whole dynamic modeling.

4.1.6 Feed Steps, Feed Flows and The Changes of the Distillate, Bottom and Feed Compositions

Feed step profiles give that we get a good overview for the behavior after a step change in the feed flows. It is so hard to make a real column because of the experimental conditions and times. On the other hands, it is available to see with a model how the system is going on if we have useful datas.

The point of the feed steps profiles is to get a quick overview of what happens after a change in the feed. It can't be made on a real column as heating up the column and preparing an experiment takes few hours whereas it is easy to see what is going on with a model. Thus, 2 feed steps are made with the latest model: flow, temperature and outlet compositions and column temperature for each stages are plotted. The case configuration is the 5 stages RD with $A + B \rightarrow C + D$. Of course, as this is only a 5 stages RD column, this will not represent an industrial case but it will allow to have an idea of what should happen in a larger scale.

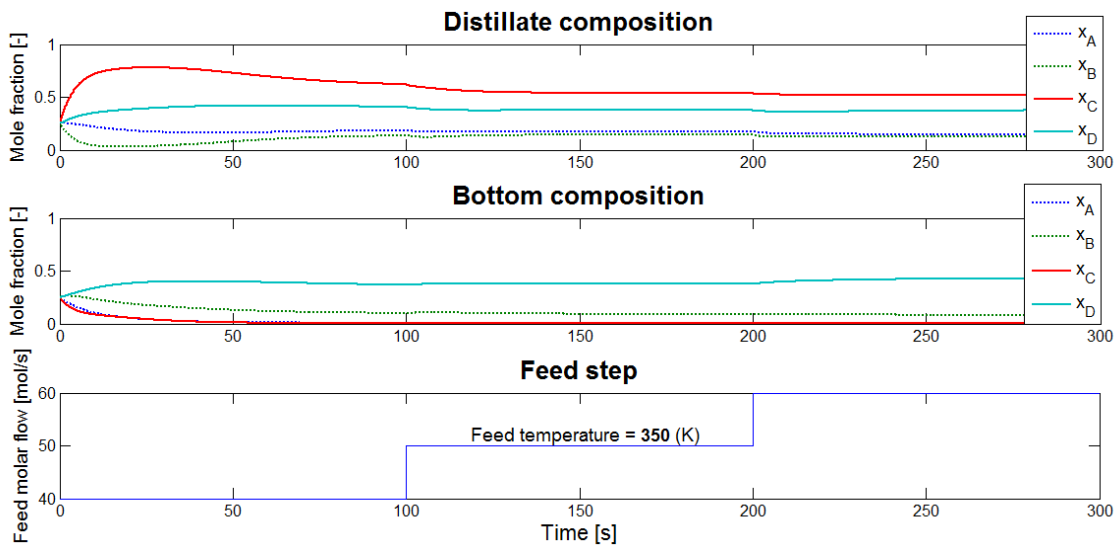


Figure 4.8 : Feed composition profiles with step changes of feed flow for 5 stages RD.

In this case, the feed flow is 40 mol/s so two step changes are made, starting from this standard flow which give one feed step profile of 40/50/60 mol/s (Fig. 4.8).

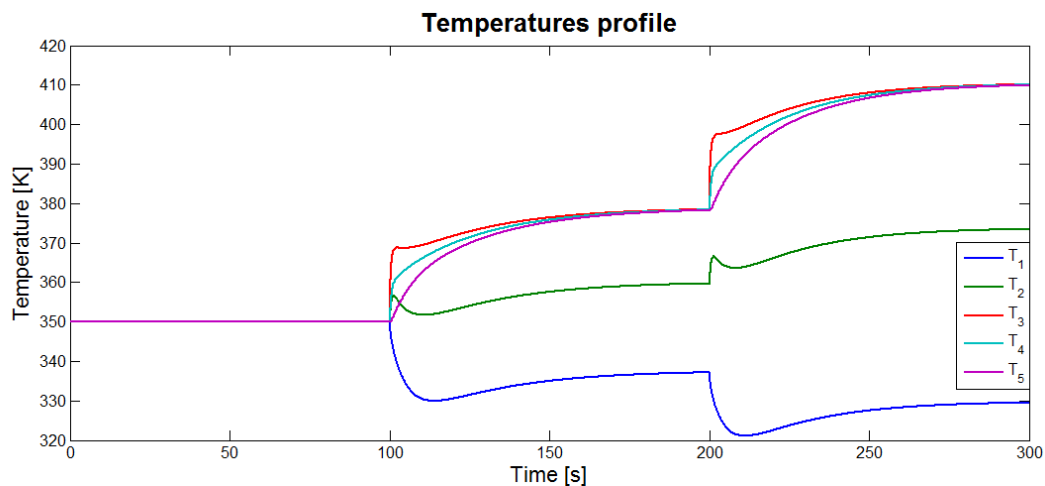


Figure 4.9: Effect of feed steps on temperature.

When the feed flow increases, it does not affect the bottom or distillate composition consistently (Fig 4.8). But the temperature profiles show some different results stage by stage (Fig. 4.9).

On the graph below (fig 4.10) are displayed the mole fractions for each stage and the temperatures on 5 stages, T1 being the condenser temperature and T5 the reboiler temperature (appendix A.3.5).

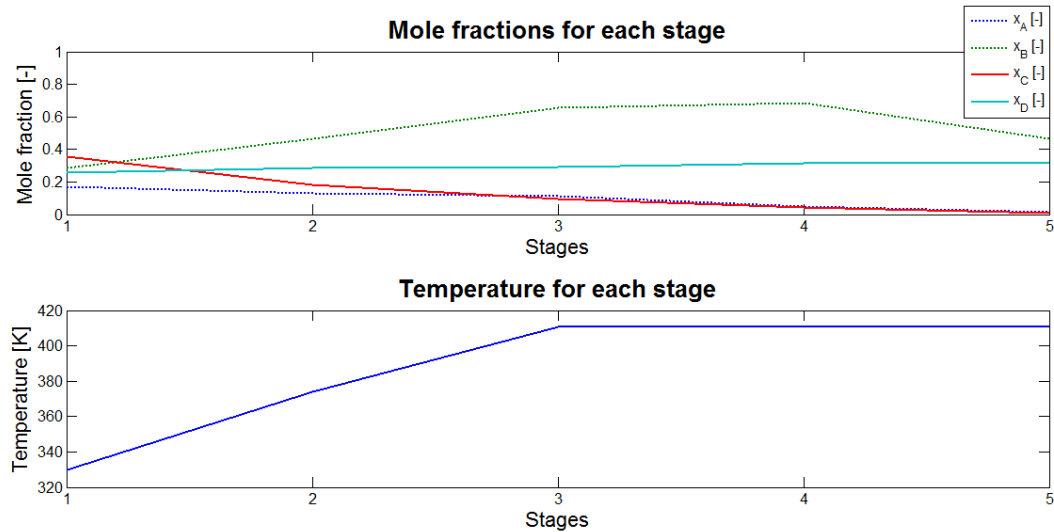


Figure 4.10 : Feed composition profiles with step changes of feed flow for 5 stages RD.

On the other hand, if we apply the step change of feed composition (appendix A.3.6), we can recognize that this step change doesn't effect the distillate and the bottom compositions (fig. 4.11).

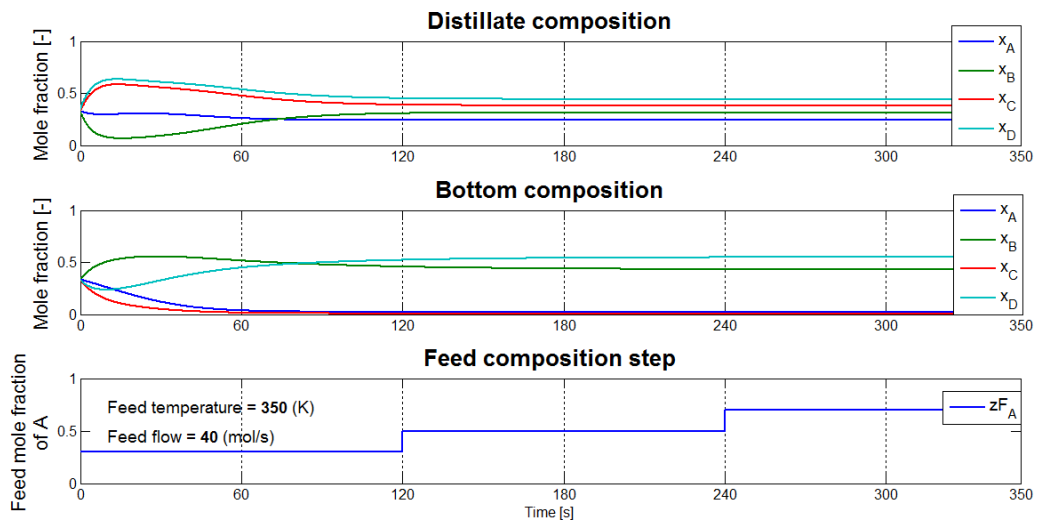


Figure 4.11: Distillate and bottom compositions with feed composition steps.

5. CONCLUSION

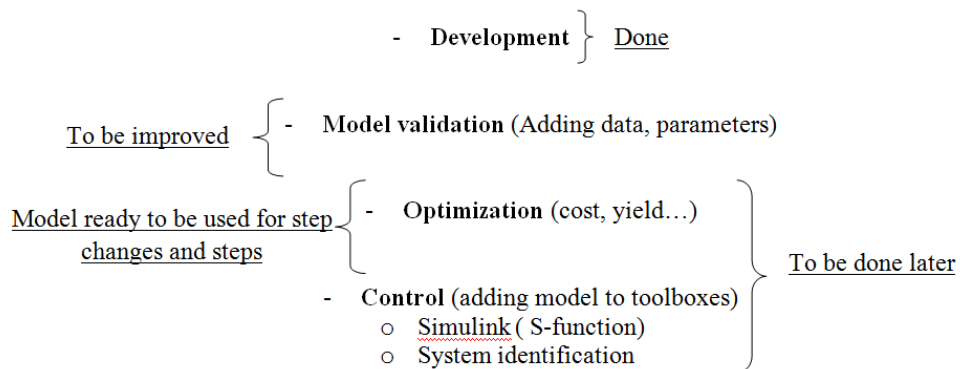
In this report, we have presented some important topics for models and dynamics of the reactive distillation columns including a treatment of steady-state operation. The issues covered include the liquid – vapor equilibrium, mass – energy balances, reaction rate equations, feed compositions, feed flows, step changes and step responses, ODE functions, linearization. It works with for $A + B \rightleftharpoons C + D$ reaction in 5 stages RD.

The thing to tell in the report is that ODE 15s function gives good approximation to solve reactive distillation equations. It is extremely easier to make such kind of profiles with MATLAB than in reality.

6. RECOMMENDATIONS

This model gives a good idea to figure out the RD concept but it should be reduced dynamic model that can be used to optimize a grade transition a reactive distillation system.

The model has been almost validated as it gives same results as simpler model. So it needs to be finished like the development of an optimization tool that can be used to determine dynamic feed-change profiles over time that minimize the product transition time.



The development has been done in this report as there is now a functional model that can work for 5 stages with a reaction $A + B \rightleftharpoons C + D$, VLE and heat and mass balances. Thus, the model will be taken to end the whole project with the optimization and control to be made.

For optimization, it would be a good thing to determine the time needed to reach the steady state after each step. So then, we would see the influence of high or low steps on the steady step and that is the main point of the project.

The control is all about using the model effectively and in other MATLAB toolboxes. It could be added to Simulink in order to use it as a black box in a large case with many processes. Also, system identification could be used to simulate the graphs obtained with time constants and process gains.

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APPENDICES

APPENDIX A.1 : Table of Notation

APPENDIX A.2 : Reaction Equations

APPENDIX A.3 : Matlab Codes For Reactive Distillation Columns

APPENDIX A.3.1 : 3- Stages Model – Test Problem

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APPENDIX A.3.3 : Model for 5 stages with 3 components

APPENDIX A.3.4 : 5 – Stages Model with Four Components for Last Conditions

APPENDIX A.3.5 : Feed Step for 5 – Stages Model with Four Components

APPENDIX A.3.6 : Feed Composition Step for 5 – Stages Model with Four Components

APPENDIX A.1

Stage 1	$dx_{A,1}dt = dxdt(1);$ $x_{A,1} = x(1);$	$dx_{B,1}dt = dxdt(6);$ $x_{B,1} = x(6);$	$dx_{C,1}dt =$ $dxdt(11);$ $x_{C,1} = x(11);$	$dT_1dt = dxdt(16);$ $T_1 = x(16);$
Stage 2	$dx_{A,2}dt = dxdt(2);$ $x_{A,2} = x(2);$	$dx_{B,1}dt = dxdt(7);$ $x_{B,2} = x(7);$	$dx_{C,2}dt =$ $dxdt(12);$ $x_{C,2} = x(12);$	$dT_2dt = dxdt(17);$ $T_2 = x(17);$
Stage 3	$dx_{A,3}dt = dxdt(3);$ $x_{A,3} = x(3);$	$dx_{B,1}dt = dxdt(8);$ $x_{B,3} = x(8);$	$dx_{C,3}dt =$ $dxdt(13);$ $x_{C,3} = x(13);$	$dT_3dt = dxdt(18);$ $T_3 = x(18);$
Stage 4	$dx_{A,4}dt = dxdt(4);$ $x_{A,4} = x(4);$	$dx_{B,1}dt = dxdt(9);$ $x_{B,4} = x(9);$	$dx_{C,4}dt =$ $dxdt(14);$ $x_{C,4} = x(14);$	$dT_4dt = dxdt(19);$ $T_4 = x(19);$
Stage 5	$dx_{A,5}dt = dxdt(5);$ $x_{A,5} = x(5);$	$dx_{B,1}dt = dxdt(10);$ $x_{B,5} = x(10);$	$dx_{C,5}dt =$ $dxdt(15);$ $x_{C,5} = x(15);$	$dT_5dt = dxdt(20);$ $T_5 = x(20);$

APPENDIX A.2

The stages 2, 3 and 4 are reactive stages at which the $A + B \leftrightarrow C + D$ chemical reaction takes place.

With the following kinetics:

Stoichiometric coefficient: $\xi_A = -1, \xi_B = -1, \xi_C = 1, \xi_D = 1$

Rate constant: $k = 40\,000 \text{ mol/s}$

Activation energy: $Ea = 20\,000 \text{ J/mol}$

Universal gas constant: $R = 8,314 \text{ J/mol.K}$

Initial temperature at each stage: $T = 350 \text{ K}$

$$r_{i,j} = \xi_j \cdot k \cdot x_{i,A} \cdot x_{i,B} \cdot e^{\frac{-Ea}{RT}} \quad (1)$$

APPENDIX A.3: Matlab Codes for Reactive Distillation Columns

APPENDIX A.3.1: 3- Stages Model – Test Problem

```
function distilrun3
%% Run and simulate the dynamic model
% We first define the settings for the solver.

% Initial conditions at each stage
x0 = [0 0 0];

% Timespan
Timespan = [0 20];

% Setting the odesolver options
options=odeset('RelTol',1e-10, 'AbsTol',[1e-10 1e-10 1e-10], 'Stats','on');

% Solve the ODE's system
[T,X] = ode15s(@distil3,Timespan,x0,options);

% Plotting the results
figure
plot(T,X);
xlabel('time [min]');
ylabel('liquid mole fraction of A [-]');
legend('stage 1','stage 2','stage 3');

function dxdt = distil3(t,x)
%% Formulation of the dynamic model

% Vapor-liquid equilibrium (assuming constant relative volatility)
y(1) = alpha*x(1)/(1+(alpha-1)*x(1));
y(2) = alpha*x(2)/(1+(alpha-1)*x(2));
y(3) = x(3); % Total condenser (no equilibrium stage)

% Component balances
dxdt = zeros(N,1); % Preallocate the vector
dxdt(1) = L2*x(2)-V1*y(1)-B*x(1); % Reboiler
dxdt(2) = L3*x(3)+V1*y(1)-L2*x(2)-V2*y(2)+F*zF; % Feed stage
dxdt(3) = V2*y(2)-L3*x(3)-D*x(3); % Condenser
```

Equation
Resolution

Equations
to solve

APPENDIX A.3.2: Explanation of the resolution

Initial Value Problems for Ordinary Differential Equations (ODEs) is the most popular type of problems solved using MATLAB ODE solvers. An initial value problem is an ODE $\frac{dy}{dt} = f(y)$ with a specified value, initial condition $y(t_0) = y_0$, of the function at a given point in the domain of the solution. Initial value problems are usually solved with ODE45 for nonstiff cases, and with ODE15s for stiff cases.

A stiff ODE is a differential equation for which certain numerical methods for solving the equation are numerically unstable, unless the step size is taken to be

extremely small. It is difficult to formulate a precise definition of stiffness. Though, the main idea is that some terms of the equation can lead to rapid variation in the solution. An important characteristic of a stiff system is that the equations are always stable: they converge to a solution.

The options display different stats that help to see how the ODEs are solved. Also, the RelTol and AbsTol are:

- Relative error tolerance allowed (Default = .001 or .1 %.). If the ratios of successive values in iteration are within 'Relative tolerance' of one, it considers this value has converged.
- Absolute error tolerance allowed (Default = .000001 or .0001 %.). A scalar tolerance applies to all components of the solution vector. If successive values in iteration are within 'absolute tolerance' of each other, it considers this value has converged"

Then in the model, some ode functions were tested for this case in order to find the best one that would fit to the problem. We figured out that the ode15s was the function which gave quickest resolution. Thus, we decided to keep it for the whole dynamic modeling.

APPENDIX A.3.3: Model for 5 stages with 3 components

```
% SIMULATION OF A 5-STAGE REACTIVE DISTILLATION COLUMN

function [T,X]=four5()

%% Run and simulate the dynamic model
tic
clear all; close all; clc;
% We first define the settings for the solver.

% Initial conditions at each stage
x0=[0.25*ones(15,1);350*ones(5,1)];

% Timespan, s
Tspan = [0:20];

% Feed values
F = 40; % Feed molar flow (mol/s)
Tf = 350; % Feed temperature (mol/s)
% Feed composition step (xA and xB)
zF1 = [0.5*ones(21)];

% Setting the odesolver options
options=odeset('RelTol',1e-10, 'AbsTol',1e-10*ones(20,1), 'Stats','on');

% Solve the ODE's system
T = [];
X = [];

for i = 1:length(Tspan)-1
    [t,x] = ode15s(@Rdistillation,Tspan(i):Tspan(i+1),x0,options,zF1(i));
    T=[T; t];
    X=[X; x];
    x0 = x(end,:);
end

for k = 1:5
    X(:,k+20) = 1 - X(:,k) - X(:,k+5) - X(:,k+10);
end
toc

%% Make graphs

% Figure 1
FigHandle = figure('units','normalized');set(FigHandle, 'Position', [ 0, 0, 1, 1 ]);

% Full screen

% Composition Distillate

figure(1)
subplot(3,1,1,'FontSize',15)
plot(T,X(:,1),':',T,X(:,6),':',T,X(:,11),'LineWidth',2) % 0<x<1
ylim([0 1]);
title('Distillate composition','FontWeight','bold','FontSize',20);
ylabel('Mole fraction [-]','FontSize',18);
legend1 = legend('x_A','x_B','x_C');
set(legend1,'Location','NorthEast','FontSize',16);

% Composition Bottom product

figure(1)
subplot(3,1,2,'FontSize',15)
plot(T,X(:,5),':',T,X(:,10),':',T,X(:,15),'LineWidth',2) % 0<x<1
ylim([0 1]);
title('Bottom composition','FontWeight','bold','FontSize',20);
ylabel('Mole fraction [-]','FontSize',18);xlabel('Time [s]');
legend1 = legend('x_A','x_B','x_C');
set(legend1,'Location','NorthEast','FontSize',16);
```



```

% Composition Feed stage

figure(1)
subplot(3,1,3,'FontSize',15)
plot(T,X(:,3),'-',T,X(:,8),'-',T,X(:,13),'LineWidth',2)
ylim([0 1]); % 0<x<1
title('Feed stage composition','FontWeight','bold','FontSize',20);
ylabel('Mole fraction [-]','FontSize',18);xlabel('Time [s]');
legend1 = legend('x_A','x_B','x_C');
set(legend1,'Location','NorthEast','FontSize',16);

% Figure 3

FigHandle = figure('units','normalized');set(FigHandle, 'Position', [ 0, 0, 2, 2 ]);

% Full screen

% X for each stage,F1
figure(2)
subplot(1,1,1,'FontSize',15)
plot(1:5,X(end,1:5),'-',1:5,X(end,6:10),'-',1:5,X(end,11:15),'LineWidth',2);
title('Mole fractions for each stage','FontWeight','bold','FontSize',20);
ylim([0 1]);
xlabel('Stages','FontSize',16);ylabel('Mole fraction [-]','FontSize',17);
legend3=legend('x_A [-]','x_B [-]','x_C [-]','FontSize',16);
set(legend3,'Location','Best');
set(gca,'XTick',0:1:5)

function dxdt = Rdistillation(t,x,zF1)

%% Formulation of the dynamic model

% Datas and assumptions:

alpha = [2.34 1.1 0.44]; % Assume constant relative volatility
N = 5; % Number of stages
NR = N-2; % Number of reactive stages
M = [375;50;50;50;75]; % Molar holdup, mol

% Reaction A+B => C
k = 400000; % Rate constant, mol/s
Ea = 20000; % Activation energy, mol/J
Ru = 8.3145; % Universal gas constant, J/mol.K
ksi = [-1 -1 2]; % Stoichiometric coefficients

% Flows in the column:

F=40;
B = 15; % Bottoms product from the column, mol/s
D = F-B; % Over head product of the column, mol/s
L1 = 125; % Liquid molar flows, mol/s (assume constant molar flows)
L2 = L1; % Liquid molar flows, mol/s (assume constant molar flows)
L3 = 165; % Liquid molar flows, mol/s (assume constant molar flows)
L4 = L3; % Liquid molar flows, mol/s (assume constant molar flows)
V = 150; % Vapor molar flows; mol/s (assume constant molar flows)
Vc = 5; % Average Reaction volume(m^3)

% Energy
Tf = 350;

% Vapor-liquid equilibrium (assuming constant relative volatility)

y = zeros(15,1); % Preallocate the vector
for j = 1:1:15
    if j==1 || j==6 || j==11 % Total condenser (no equilibrium stage)
        y(j)=x(j);
    elseif j>=2 && j<=5
        y(j) = ( alpha(1)*x(j) ) / ( alpha(1)*x(j) + alpha(2)*x(j+5) + alpha(3)*x(j+10) );
    % Component A
    elseif j>=7 && j<=10
        y(j) = ( alpha(2)*x(j) ) / ( alpha(1)*x(j-5) + alpha(2)*x(j) + alpha(3)*x(j+5) );
    % Component B
    elseif j>=12
        y(j) = ( alpha(3)*x(j) ) / ( alpha(1)*x(j-10) + alpha(2)*x(j-5) + alpha(3)*x(j) );
    % Component C
    end
end
end

```

```

% Kinetics
rA=zeros(NR,1);rB=zeros(NR,1);rC=zeros(NR,1); % Preallocate the vector
for j = 2:4
    rA(j) = Vc * ksi(1) * k * x(j) * x(j+5) * exp( -Ea / (Ru*x(15+j)) ); % Component A
    rB(j) = Vc * ksi(2) * k * x(j) * x(j+5) * exp( -Ea / (Ru*x(15+j)) ); % Component B
    rC(j) = Vc * ksi(3) * k * x(j) * x(j+5) * exp( -Ea / (Ru*x(15+j)) ); % Component C
end

% Component balances
dxdt = zeros(20,1); % Preallocate the vector

% Component A
dxdt(1) = ( V*y(2) - L1*x(1) - D*x(1) ) / M(1); % Stage 1, Condenser
dxdt(2) = ( L1*x(1) + V*y(3) - V*y(2) - L2*x(2) + rA(2) ) / M(2); % Stage 2,
dxdt(3) = ( L2*x(2) + V*y(4) - V*y(3) - L3*x(3) + rA(3) + F*zF1 )/M(3); % Stage 3,
Feed stage
dxdt(4) = ( L3*x(3) + V*y(5) - V*y(4) - L4*x(4) + rA(4) ) / M(4); % Stage 4,
dxdt(5) = ( L4*x(4) - V*y(5) - B*x(5) ) /M(5); % Stage 5, Reboiler

% Component B
dxdt(6) = ( V*y(7) - L1*x(6) - D*x(6) ) / M(1); % Stage 1, Condenser
dxdt(7) = ( L1*x(6) + V*y(8) - V*y(7) - L2*x(7) + rB(2) ) / M(2); % Stage 2,
dxdt(8) = ( L2*x(7) + V*y(9) - V*y(8) - L3*x(8) + rB(3) + F*(1-zF1))/M(3); % Stage 3
Feed stage
dxdt(9) = ( L3*x(8) + V*y(10) - V*y(9) - L4*x(9) + rB(4) ) / M(4); % Stage 4,
dxdt(10) = ( L4*x(9) - V*y(10) - B*x(10) ) / M(5); % Stage 5, Reboiler

% Component C
dxdt(11) = ( V*y(12) - L1*x(11) - D*x(11) ) / M(1); % Stage 1, Condenser
dxdt(12) = ( L1*x(11) + V*y(13) - V*y(12) - L2*x(12) + rC(2) ) / M(2); % Stage 2,
dxdt(13) = ( L2*x(12) + V*y(14) - V*y(13) - L3*x(13) + rC(3) ) / M(3); % Stage 3
Feed stage
dxdt(14) = ( L3*x(13) + V*y(15) - V*y(14) - L4*x(14) + rC(4) ) / M(4); % Stage 4,
dxdt(15) = ( L4*x(14) - V*y(15) - B*x(15) ) / M(5); % Stage 5, Reboiler

% Energy balance
dxdt(16) = ( V*x(17) - L1*x(16) - D*x(16) ) / M(1); % Stage 1, Condenser
dxdt(17) = ( L1*x(16) + V*x(18) - V*x(17) - L2*x(17) ) / M(2); % Stage 2,
dxdt(18) = ( L2*x(17) + V*x(19) - V*x(18) - L3*x(18) + F*Tf ) / M(3); % Stage 3
Feed stage
dxdt(19) = ( L3*x(18) + V*x(20) - V*x(19) - L4*x(19) ) / M(4); % Stage 4,
dxdt(20) = ( L4*x(19) - V*x(20) - B*x(20) ) / M(5); % Stage 5, Reboiler

```

APPENDIX A.3.4: 5 – Stages Model with Four Components for Last Conditions

```
% SIMULATION OF A 5-STAGE REACTIVE DISTILLATION COLUMN

function [T,X]=RDensum()

%% Run and simulate the dynamic model
tic
clear all; close all; clc;

% We first define the settings for the solver.

% Initial conditions at each stage
x0=[0.25*ones(20,1);350*ones(5,1)];

% Timespan
Tspan = [0:200];

Tf = 350;
% Feed molar flow step (mol/s)
F = [40*ones(200,1)];

% Setting the odesolver options
options=odeset('RelTol',1e-10, 'AbsTol',1e-10*ones(25,1), 'Stats','on');

% Solve the ODE's system
T = [];
X = [];

for i = 1:length(Tspan)-1
    [t,x] = ode113(@nonRdistillation,Tspan(i):Tspan(i+1),x0,options);
    T=[T; t];
    X=[X; x];
    x0 = x(end,:);
end

% Summation equation for component C

for k = 1:5
    X(:,k+15) = 1 - X(:,k) - X(:,k+5);
end
toc

%% Make graphs

% Figure 1
FigHandle = figure('units','normalized');set(FigHandle, 'Position', [ 0, 0, 1, 1 ]);
% Full screen

% Composition Distillate
figure(1)
subplot(3,1,1,'FontSize',12)
plot(T,X(:,1),':',T,X(:,6),':',T,X(:,11),T,X(:,16),'LineWidth',2)
ylim([0 1]);
title('Distillate composition','FontWeight','bold','FontSize',20);
ylabel('Mole fraction [-]','FontSize',16);xlabel('Time [s]');
legend1 = legend('x_A','x_B','x_C','x_D');
set(legend1,'Location','NorthEast','FontSize',14);

% Composition Bottom product
figure(1)
subplot(3,1,2,'FontSize',12)
plot(T,X(:,5),':',T,X(:,10),':',T,X(:,15),T,X(:,20),'LineWidth',2)
ylim([0 1]);
title('Bottom composition','FontWeight','bold','FontSize',20);
ylabel('Mole fraction [-]','FontSize',16);xlabel('Time [s]');
legend1 = legend('x_A','x_B','x_C','x_D');
set(legend1,'Location','NorthEast','FontSize',14);
```

```

% Composition Feed Stage
figure(1)
subplot(3,1,3,'FontSize',12)
plot(T,X(:,3),'-',T,X(:,8),'-',T,X(:,13),T,X(:,18),'LineWidth',2) % 0<x<1
ylim([0 1]);
title('Feed composition','FontWeight','bold','FontSize',20);
ylabel('Mole fraction [-]','FontSize',16);xlabel('Time [s]');
legend1 = legend('x_A','x_B','x_C','x_D');
set(legend1,'Location','NorthEast','FontSize',14);

% Figure 3
FigHandle = figure('units','normalized');set(FigHandle, 'Position', [ 0, 0, 1, 1 ]);

% Full screen

% X for each stage,F1
figure(2)
subplot(2,1,1,'FontSize',12)
plot(1:5,X(end,1:5),'-',1:5,X(end,6:10),'-',1:5,X(end,11:15),1:5,X(end,16:20),'LineWidth',2);
title('Mole fractions for each stage','FontWeight','bold','FontSize',20);
ylim([0 1]);
xlabel('Stages','FontSize',16);ylabel('Mole fraction [-]','FontSize',16);
legend3=legend('x_A [-]','x_B [-]','x_C [-]','x_D [-]','FontSize',14);
set(legend3,'Location','SouthEast');
set(gca,'XTick',0:1:5)

function dxdt = nonRdistillation(t,x)

%% Formulation of the dynamic model
% Datas and assumptions:

alpha = [2.34 1.1 3.5 0.44]; % Assume constant relative volatility
N = 5; % Number of stages
NR = N-2; % Number of reactive stages
zF = [0.5 0.5 0 0]; % Feed composition
M = [375;50;50;50;750]; % Molar holdup, mol

% Reaction A+B => C
k = 40000; % Rate constant, mol/s
Ea = 20000; % Activation energy, mol/J
Ru = 8.3145; % Universal gas constant, J/mol.K
ksi = [-1 -1 1 1]; % Stoichiometric coefficients

% Flows in the column:
F = 40;
B = 15; % Bottoms product from the column, mol/s
D = F-B; % Over head product of the column, mol/s
L1 = 125; % Liquid molar flows, mol/s (assume constant molar flows)
L2 = L1; % Liquid molar flows, mol/s (assume constant molar flows)
L3 = 165; % Liquid molar flows, mol/s (assume constant molar flows)
L4 = L3; % Liquid molar flows, mol/s (assume constant molar flows)
V = 150; % Vapor molar flows; mol/s (assume constant molar flows)
Vc = 5; % Average Reaction volume(m^3)

% Energy
Tf = 350;

% Vapor-liquid equilibrium (assuming constant relative volatility)
y = zeros(20,1); % Preallocate the vector
for j = 1:1:20
    if j==1 || j==6 || j==11 || j == 16
        y(j)=x(j); % Total condenser (no equilibrium stage)
    elseif j>=2 && j<=5
        y(j) = ( alpha(1)*x(j) ) / ( alpha(1)*x(j) + alpha(2)*x(j+5) + alpha(3)*x(j+10) +
alpha(4)*(1-x(j)-x(j+5)-x(j+10) ) ); % Component A
    elseif j>=7 && j<=10
        y(j) = ( alpha(2)*x(j) ) / ( alpha(1)*x(j-5) + alpha(2)*x(j) + alpha(3)*x(j+5) +
alpha(4)*(1-x(j-5)-x(j)-x(j+5) ) ); % Component B
    elseif j>=12 && j<=15
        y(j) = ( alpha(3)*x(j) ) / ( alpha(1)*x(j-10) + alpha(2)*x(j-5) + alpha(3)*x(j) +
alpha(4)*(1-x(j-10)-x(j-5)-x(j) ) ); % Component C
    elseif j>=17
        y(j) = ( alpha(4)*x(j) ) / ( alpha(1)*x(j-15) + alpha(2)*x(j-10) + alpha(3)*x(j-5) +
alpha(4)*(1-x(j-15)-x(j-10)-x(j-5) ) ); % Component D
    end
end
end

```

```

% Kinetics
rA=zeros(NR,1);rB=zeros(NR,1);rC=zeros(NR,1);rD=zeros(NR,1); % Preallocate the
vector
for j = 2:4
    rA(j) = Vc * ksi(1) * k * x(j) * x(j+5) * exp( -Ea / (Ru*x(20+j)) ); % Component A
    rB(j) = Vc * ksi(2) * k * x(j) * x(j+5) * exp( -Ea / (Ru*x(20+j)) ); % Component B
    rC(j) = Vc * ksi(3) * k * x(j) * x(j+5) * exp( -Ea / (Ru*x(20+j)) ); % Component C
    rD(j) = Vc * ksi(4) * k * x(j) * x(j+5) * exp( -Ea / (Ru*x(20+j)) ); % Component D
end

% Component balances
dxdt = zeros(25,1); % Preallocate the vector

% Component A
dxdt(1) = ( V*y(2) - L1*x(1) - D*x(1) ) / M(1); % Stage 1, Condenser
dxdt(2) = ( L1*x(1) + V*y(3) - V*y(2) - L2*x(2) + rA(2) ) / M(2); % Stage 2
dxdt(3) = ( L2*x(2) + V*y(4) - V*y(3) - L3*x(3) + rA(3) + F*zF(1) )/M(3); % Stage 3,
Feed stage
dxdt(4) = ( L3*x(3) + V*y(5) - V*y(4) - L4*x(4) + rA(4) ) / M(4); % Stage 4
dxdt(5) = ( L4*x(4) - V*y(5) - B*x(5) ) /M(5); % Stage 5, Reboiler

% Component B
dxdt(6) = ( V*y(7) - L1*x(6) - D*x(6) ) / M(1); % Stage 1, Condenser
dxdt(7) = ( L1*x(6) + V*y(8) - V*y(7) - L2*x(7) + rB(2) ) / M(2); % Stage 2
dxdt(8) = ( L2*x(7) + V*y(9) - V*y(8) - L3*x(8) + rB(3) + F*zF(2) )/M(3); % Stage 3,
Feed stage
dxdt(9) = ( L3*x(8) + V*y(10) - V*y(9) - L4*x(9) + rB(4) ) / M(4); % Stage 4
dxdt(10) = ( L4*x(9) - V*y(10) - B*x(10) ) / M(5); % Stage 5, Reboiler

% Component C
dxdt(11) = ( V*y(12) - L1*x(11) - D*x(11) ) / M(1); % Stage 1, Condenser
dxdt(12) = ( L1*x(11) + V*y(13) - V*y(12) - L2*x(12) + rC(2) ) / M(2); % Stage 2
dxdt(13) = ( L2*x(12) + V*y(14) - V*y(13) - L3*x(13) + rC(3) + F*zF(3) )/M(3); % Stage 3,
Feed stage
dxdt(14) = ( L3*x(13) + V*y(15) - V*y(14) - L4*x(14) + rC(4) ) / M(4); % Stage 4
dxdt(15) = ( L4*x(14) - V*y(15) - B*x(15) ) / M(5); % Stage 5, Reboiler

% Component D
dxdt(16) = ( V*y(17) - L1*x(16) - D*x(16) ) / M(1); % Stage 1, Condenser
dxdt(17) = ( L1*x(16) + V*y(18) - V*y(17) - L2*x(17) + rD(2) ) / M(2); %Stage 2
dxdt(18) = ( L2*x(17) + V*y(19) - V*y(18) - L3*x(18) + rD(3) + F*zF(4) )/M(3); %Stage 3,
Feed stage
dxdt(19) = ( L3*x(18) + V*y(20) - V*y(19) - L4*x(19) + rD(4) ) / M(4); % Stage 4
dxdt(20) = ( L4*x(19) - V*y(20) - B*x(20) ) / M(5); % Stage 5, Reboiler

% Energy balance
dxdt(21) = ( V*x(22) - L1*x(21) - D*x(21) ) / M(1); % Stage 1, Condenser
dxdt(22) = ( L1*x(21) + V*x(23) - V*x(22) - L2*x(22) ) / M(2); % Stage 2
dxdt(23) = ( L2*x(22) + V*x(24) - V*x(23) - L3*x(23) + F*Tf ) / M(3); % Stage 3,
Feed stage
dxdt(24) = ( L3*x(23) + V*x(25) - V*x(24) - L4*x(24) ) / M(4); % Stage 4
dxdt(25) = ( L4*x(24) - V*x(25) - B*x(25) ) / M(5); % Stage 5, Reboiler

```

APPENDIX A.3.5: Feed Step for 5 – Stages Model with Four Components

```
% SIMULATION OF A 5-STAGE REACTIVE DISTILLATION COLUMN

function [T,X]=RDsumstepD()

%% Run and simulate the dynamic model
tic
clear all; close all; clc;

% We first define the settings for the solver.
% Initial conditions at each stage
x0=[0.25*ones(20,1);350*ones(5,1)];

% Timespan
Tspan = [0:300];
Tf = 350;

% Feed molar flow step (mol/s)
F = [40*ones(100,1);50*ones(100,1);60*ones(101,1)];

% Setting the odesolver options
options=odeset('RelTol',1e-10, 'AbsTol',1e-10*ones(25,1), 'Stats','off');

% Solve the ODE's system
T = [];
X = [];

for i = 1:length(Tspan)-1
    [t,x] = ode15s(@Rdistillation,Tspan(i):Tspan(i+1),x0,options,F(i));
    T=[T; t];
    X=[X; x];
    x0 = x(end,:);
end
toc
%% Make graphs

% Figure 1
FigHandle = figure('units','normalized');set(FigHandle, 'Position', [ 0, 0, 1, 1 ]);
% Full screen
% Composition Distillate
figure(1)
subplot(3,1,1,'FontSize',12)
plot(T,X(:,1),':',T,X(:,6),':',T,X(:,11),T,X(:,16),'LineWidth',2)
ylim([0 1]);
% 0<x<1
title('Distillate composition','FontWeight','bold','FontSize',20);
ylabel('Mole fraction [-]','FontSize',16);
legend1 = legend('x_A','x_B','x_C','x_D');
set(legend1,'Location','NorthEast','FontSize',14);
% Composition Bottom product
figure(1)
subplot(3,1,2,'FontSize',12)
plot(T,X(:,5),':',T,X(:,10),':',T,X(:,15),T,X(:,20),'LineWidth',2)
ylim([0 1]);
% 0<x<1
title('Bottom composition','FontWeight','bold','FontSize',20);
ylabel('Mole fraction [-]','FontSize',16);
legend1 = legend('x_A','x_B','x_C','x_D');
set(legend1,'Location','NorthEast','FontSize',14);
% Feed step
figure(1)
subplot(3,1,3,'FontSize',12)
stairs(Tspan,F);xlabel('Time [s]','FontSize',16);ylabel('Feed molar flow
[mol/s]','FontSize',16);
title('Feed step','FontWeight','bold','FontSize',20);
text(100,50.2,['Feed temperature = \bf',num2str(Tf),'\rm (K)'],'FontSize',14);
```

```

% Figure 2
FigHandle = figure('units','normalized');set(FigHandle, 'Position', [ 0, 0, 1, 1 ]);
% Full screen

% Temperature
figure(2)
subplot(1,1,1,'FontSize',12)
plot(T,X(:,21:25),'LineWidth',2)
title('Temperatures profile','FontWeight','bold','FontSize',20);
xlabel('Time [s]','FontSize',16);ylabel('Temperature [K]','FontSize',16);
text(100,150,['Feed temperature = \bf',num2str(Tf),' \rm (K)'],'FontSize',14);
text(100,151,['Feed flows = \bf',num2str(F(1)),' - ',num2str(F(100)),' - ',num2str(F(300)),' \rm (mol/s)'],'FontSize',14);
legend2 = legend('T_1','T_2','T_3','T_4','T_5','FontSize',14);
set(legend2,'Location','SouthEast');

% Figure 3
FigHandle = figure('units','normalized');set(FigHandle, 'Position', [ 0, 0, 1, 1 ]);
% Full screen
% X for each stage,F1
figure(3)
subplot(2,1,1,'FontSize',12)
plot(1:5,X(end,1:5),'-',1:5,X(end,6:10),'-',1:5,X(end,11:15),1:5,X(end,16:20),'LineWi
dth',2);
title('Mole fractions for each stage','FontWeight','bold','FontSize',20);
ylim([0 1]);
xlabel('Stages','FontSize',16);ylabel('Mole fraction [-]','FontSize',16);
legend3=legend('x_A [-]','x_B [-]','x_C [-]','x_D [-]','FontSize',14);
set(legend3,'Location','SouthEast');
set(gca,'XTick',0:1:5)

% T for each stage
figure(3)
subplot(2,1,2,'FontSize',12)
plot(1:5,X(end,21:25),'LineWidth',2);
title('Temperature for each stage','FontWeight','bold','FontSize',20);
xlabel('Stages','FontSize',16);ylabel('Temperature [K]','FontSize',16);
set(gca,'XTick',0:1:5)
function dxdt = Rdistillation(t,x,F)

%% Formulation of the dynamic model
% Datas and assumptions:

alpha = [2.34 1.1 3.5 0.44]; % Assume constant relative volatility
N = 5; % Number of stages
NR = N-2; % Number of reactive stages
zF = [0.5 0.5 0 0]; % Feed composition
M = [375;50;50;50;750]; % Molar holdup, mol

% Reaction A+B => C
k = 40000; % Rate constant, mol/s
Ea = 20000; % Activation energy, mol/J
Ru = 8.3145; % Universal gas constant, J/mol.K
ksi = [-1 -1 1 1]; % Stoichiometric coefficients

% Flows in the column:

B = 15; % Bottoms product from the column, mol/s
D = F-B; % Over head product of the column, mol/s
L1 = 125; % Liquid molar flows, mol/s (assume constant molar flows)
L2 = L1; % Liquid molar flows, mol/s (assume constant molar flows)
L3 = 165; % Liquid molar flows, mol/s (assume constant molar flows)
L4 = L3; % Liquid molar flows, mol/s (assume constant molar flows)
V = 150; % Vapor molar flows; mol/s (assume constant molar flows)
Vc = 5; % Average Reaction Volume(m^3)

% Energy
Tf = 350;

```

```

% Vapor-liquid equilibrium (assuming constant relative volatility)
y = zeros(20,1); % Preallocate the vector
for j = 1:1:20
    if j==1 || j==6 || j==11 || j == 16
        y(j)=x(j); % Total condenser (no equilibrium stage)
    elseif j>=2 && j<=5
        y(j) = ( alpha(1)*x(j) ) / ( alpha(1)*x(j) + alpha(2)*x(j+5) + alpha(3)*x(j+10) +
alpha(4)*(1-x(j)-x(j+5)-x(j+10) ) ); % Component A
    elseif j>=7 && j<=10
        y(j) = ( alpha(2)*x(j) ) / ( alpha(1)*x(j-5) + alpha(2)*x(j) + alpha(3)*x(j+5) +
alpha(4)*(1-x(j-5)-x(j)-x(j+5) ) ); % Component B
    elseif j>=12 && j<=15
        y(j) = ( alpha(3)*x(j) ) / ( alpha(1)*x(j-10) + alpha(2)*x(j-5) + alpha(3)*x(j) +
alpha(4)*(1-x(j-10)-x(j-5)-x(j) ) ); % Component C
    elseif j>=17
        y(j) = ( alpha(4)*x(j) ) / ( alpha(1)*x(j-15) + alpha(2)*x(j-10) + alpha(3)*x(j-5)+
alpha(4)*(1-x(j-15)-x(j-10)-x(j-5) ) ); % Component D
    end
end

% Kinetics
rA=zeros(NR,1);rB=zeros(NR,1);rC=zeros(NR,1);rD=zeros(NR,1); % Preallocate the vector
for j = 2:4
    rA(j) = Vc * ksi(1) * k * x(j) * x(j+5) * exp( -Ea / (Ru*x(20+j)) ); % Component A
    rB(j) = Vc * ksi(2) * k * x(j) * x(j+5) * exp( -Ea / (Ru*x(20+j)) ); % Component B
    rC(j) = Vc * ksi(3) * k * x(j) * x(j+5) * exp( -Ea / (Ru*x(20+j)) ); % Component C
    rD(j) = Vc * ksi(4) * k * x(j) * x(j+5) * exp( -Ea / (Ru*x(20+j)) ); % Component D
end

% Component balances
dxdt = zeros(25,1); % Preallocate the vector

% Component A
dxdt(1) = ( V*y(2) - L1*x(1) - D*x(1) ) / M(1); % Stage 1, Condenser
dxdt(2) = ( L1*x(1) + V*y(3) - V*y(2) - L2*x(2) + rA(2) ) / M(2); % Stage 2
dxdt(3) = ( L2*x(2) + V*y(4) - V*y(3) - L3*x(3) + rA(3) + F*zF(1) ) / M(3); % Stage 3,
Feed stage
dxdt(4) = ( L3*x(3) + V*y(5) - V*y(4) - L4*x(4) + rA(4) ) / M(4); % Stage 4
dxdt(5) = ( L4*x(4) - V*y(5) - B*x(5) ) / M(5); % Stage 5, Reboiler

% Component B
dxdt(6) = ( V*y(7) - L1*x(6) - D*x(6) ) / M(1); % Stage 1, Condenser
dxdt(7) = ( L1*x(6) + V*y(8) - V*y(7) - L2*x(7) + rB(2) ) / M(2); % Stage 2
dxdt(8) = ( L2*x(7) + V*y(9) - V*y(8) - L3*x(8) + rB(3) + F*zF(2) ) / M(3); % Stage 3,
Feed stage
dxdt(9) = ( L3*x(8) + V*y(10) - V*y(9) - L4*x(9) + rB(4) ) / M(4); % Stage 4
dxdt(10) = ( L4*x(9) - V*y(10) - B*x(10) ) / M(5); % Stage 5, Reboiler

% Component C
dxdt(11) = ( V*y(12) - L1*x(11) - D*x(11) ) / M(1); % Stage 1, Condenser
dxdt(12) = ( L1*x(11) + V*y(13) - V*y(12) - L2*x(12) + rC(2) ) / M(2); % Stage 2
dxdt(13) = ( L2*x(12) + V*y(14) - V*y(13) - L3*x(13) + rC(3) + F*zF(3) ) / M(3); % Stage 3,
Feed stage
dxdt(14) = ( L3*x(13) + V*y(15) - V*y(14) - L4*x(14) + rC(4) ) / M(4); % Stage 4
dxdt(15) = ( L4*x(14) - V*y(15) - B*x(15) ) / M(5); % Stage 5, Reboiler

% Component D
dxdt(16) = ( V*x(17) - L1*x(16) - D*x(16) ) / M(1); % Stage 1, Condenser
dxdt(17) = ( L1*x(16) + V*x(18) - V*x(17) - L2*x(17) + rD(2) ) / M(2); % Stage 2
dxdt(18) = ( L2*x(17) + V*x(19) - V*x(18) - L3*x(18) + rD(3) + F*zF(4) ) / M(3); % Stage 3,
Feed stage
dxdt(19) = ( L3*x(18) + V*x(20) - V*x(19) - L4*x(19) + rD(4) ) / M(4); % Stage 4
dxdt(20) = ( L4*x(19) - V*x(20) - B*x(20) ) / M(5); % Stage 5, Reboiler

% Energy balance
dxdt(21) = ( V*x(22) - L1*x(21) - D*x(21) ) / M(1); % Stage 1, Condenser
dxdt(22) = ( L1*x(21) + V*x(23) - V*x(22) - L2*x(22) ) / M(2); % Stage 2
dxdt(23) = ( L2*x(22) + V*x(24) - V*x(23) - L3*x(23) + F*Tf ) / M(3); % Stage 3, Feed stage
dxdt(24) = ( L3*x(23) + V*x(25) - V*x(24) - L4*x(24) ) / M(4); % Stage 4
dxdt(25) = ( L4*x(24) - V*x(25) - B*x(25) ) / M(5); % Stage 5, Reboiler

```


APPENDIX A.3.6: Feed Composition Step for 5 – Stages Model with Four Components

```
% SIMULATION OF A 5-STAGE REACTIVE DISTILLATION COLUMN

function [zF1,X]=RDenergysumxstep()

%% Run and simulate the dynamic model
tic
close all; clear all; clc;

% We first define the settings for the solver.
% Initial conditions at each stage
x0=[0.33*ones(20,1);350*ones(5,1)];

% Timespan
Tspan = [0:350];

% Feed values
F = 40; % Feed molar flow (mol/s)
Tf = 350; % Feed temperature (mol/s)

% Feed composition step (xA and xB)
zF1 = [ 0.3*ones(120,1) ; 0.5*ones(120,1) ; 0.7*ones(111,1)];

% Setting the odesolver options
options=odeset('RelTol',1e-10, 'AbsTol',1e-10*ones(25,1), 'Stats','off');

% Solve the ODE's system
T = [];
X = [];

for i = 1:length(Tspan)-1
    [t,x] = ode15s(@Rdistillation,Tspan(i):Tspan(i+1),x0,options,zF1(i));
    T=[T; t];
    X=[X; x];
    x0 = x(end,:);
end

% Summation equation for component C

for k = 1:5
    X(:,k+15) = 1 - X(:,k) - X(:,k+5);
end
toc

%% Make graphs

FigHandle = figure;set(FigHandle, 'Position', [ 0, 0, 1280, 1024 ]);
% Full screen

% Composition Distillate
figure(1)
subplot(3,1,1,'FontSize',12)
plot(T,X(:,1),T,X(:,6),T,X(:,11),T,X(:,16),'LineWidth',2)
ylim([0 1]);
% 0<x<1
title('Distillate composition','FontWeight','bold','FontSize',20);
ylabel('Mole fraction [-]','FontSize',16);
legend1 = legend('x_A','x_B','x_C','x_D');
set(legend1,'Location','NorthEast','FontSize',14);

% Composition Bottom product
figure(1)
subplot(3,1,2,'FontSize',12)
plot(T,X(:,5),T,X(:,10),T,X(:,15),T,X(:,20),'LineWidth',2)
ylim([0 1]);
% 0<x<1
title('Bottom composition','FontWeight','bold','FontSize',20);
ylabel('Mole fraction [-]','FontSize',16);
legend2 = legend('x_A','x_B','x_C','x_D');
set(legend2,'Location','NorthEast','FontSize',14);
```

```

% Feed composition step
figure(1)
subplot(3,1,3,'FontSize',12)
stairs(Tspan,zF1);
ylim([0 1]);
xlabel('Time [s]');ylabel('Feed mole fraction','FontSize',16);
title('Feed composition step','FontWeight','bold','FontSize',20);
legend2 = legend('zF_A','FontSize',14);
set(legend2,'Location','NorthEast','FontSize',14);
text(10,0.4,['Feed flow = \bf',num2str(F),' \rm (mol/s)'],'FontSize',14);
text(10,0.5,['Feed temperature = \bf',num2str(Tf),' \rm (K)'],'FontSize',14);

FigHandle = figure;set(FigHandle, 'Position', [ 0, 0, 1280, 1024 ]);

% Full screen

% Temperature

figure(2)
subplot(1,1,1,'FontSize',12)
plot(T,X(:,21:25),'LineWidth',2)
title('Temperatures profile','FontWeight','bold','FontSize',20);
xlabel('Time [s]','FontSize',16);ylabel('Temperature [K]','FontSize',16);
text(40,352,['Feed composition (zF_A - zF_B) = \bf',num2str(zF1(1)), ' - ',num2str(1-zF1(1)), ' ', ' ',num2str(zF1(150)), ' - ',num2str(1-zF1(150)), ' ', ' ',num2str(zF1(300)), ' - ',num2str(1-zF1(300)), ' \rm'],'FontSize',14);
text(40,356,['Feed flow = \bf',num2str(F),' \rm (mol/s)'],'FontSize',14);
text(40,359,['Feed temperature = \bf',num2str(Tf),' \rm (K)'],'FontSize',14);
legend2 = legend('T_1','T_2','T_3','T_4','T_5','FontSize',14);
set(legend2,'Location','SouthEast');

function dxdt = Rdistillation(t,x,zF1)

%% Formulation of the dynamic model

% Datas and assumptions:

alpha = [2.34 1.1 3.5 0.44]; % Assume constant relative volatility
N = 5; % Number of stages
NR = N-2; % Number of reactive stages
zF = [0.4 0.6 0 0]; % Feed composition
M = [375;50;50;50;750]; % Molar holdup, mol

% Reaction A+B => C
k = 40000; % Rate constant, mol/s
Ea = 20000; % Activation energy, mol/J
Ru = 8.3145; % Universal gas constant, J/mol.K
ksi = [-1 -1 1 1]; % Stoichiometric coefficients

% Flows in the column:

F = 40; % Feed flow, mol/s
Tf = 350; % Feed temperature (mol/s)
B = 15; % Bottoms product from the column, mol/s
D = F-B; % Over head product of the column, mol/s
L1 = 125; % Liquid molar flows, mol/s (assume constant molar flows)
L2 = L1; % Liquid molar flows, mol/s (assume constant molar flows)
L3 = 165; % Liquid molar flows, mol/s (assume constant molar flows)
L4 = L3; % Liquid molar flows, mol/s (assume constant molar flows)
V = 150; % Vapor molar flows, mol/s (assume constant molar flows)
Vc = 35; % Average Reaction volume(m^3)

% Energy
Tf = 350;

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```

% Vapor-liquid equilibrium (assuming constant relative volatility)
y = zeros(20,1); % Preallocate the vector
for j = 1:1:20
    if j==1 || j==6 || j==11
        y(j)=x(j); % Total condenser (no equilibrium stage)
    elseif j>=2 && j<=5
        y(j) = ( alpha(1)*x(j) ) / ( alpha(1)*x(j) + alpha(2)*x(j+5) + alpha(3)*x(j+10) +
alpha(4)*x(j+15) ); % Component A
    elseif j>=7 && j<=10
        y(j) = ( alpha(2)*x(j) ) / ( alpha(1)*x(j-5) + alpha(2)*x(j) + alpha(3)*x(j+5) +
alpha(4)*x(j+10) ); % Component B
    elseif j>=12 && j<=15
        y(j) = ( alpha(3)*x(j) ) / ( alpha(1)*x(j-10) + alpha(2)*x(j-5) + alpha(3)*x(j) +
alpha(4)*x(j+5) ); % Component C
    elseif j>=17
        y(j) = ( alpha(4)*x(j) ) / ( alpha(1)*x(j-15) + alpha(2)*x(j-10) + alpha(3)*x(j-5) +
alpha(4)*x(j) ); % Component C
    end
end

% Kinetics
rA=zeros(NR,1);rB=zeros(NR,1);rC=zeros(NR,1);rD=zeros(NR,1); % Preallocate the vector
for j = 2:4
    rA(j) = Vc * ksi(1) * k * x(j) * x(j+5) * exp( -Ea / (Ru*x(20+j)) ); % Component A
    rB(j) = Vc * ksi(2) * k * x(j) * x(j+5) * exp( -Ea / (Ru*x(20+j)) ); % Component B
    rC(j) = Vc * ksi(3) * k * x(j) * x(j+5) * exp( -Ea / (Ru*x(20+j)) ); % Component C
    rD(j) = Vc * ksi(4) * k * x(j) * x(j+5) * exp( -Ea / (Ru*x(20+j)) ); % Component C
end

% Component balances
dxdt = zeros(25,1); % Preallocate the vector

% Component A
dxdt(1) = ( V*y(2) - L1*x(1) - D*x(1) ) / M(1); % Stage 1, Condenser
dxdt(2) = ( L1*x(1) + V*y(3) - V*y(2) - L2*x(2) + rA(2) ) / M(2); % Stage 2
dxdt(3) = ( L2*x(2) + V*y(4) - V*y(3) - L3*x(3) + rA(3) + F*zF(1) ) / M(3); % Stage 3,
Feed stage
dxdt(4) = ( L3*x(3) + V*y(5) - V*y(4) - L4*x(4) + rA(4) ) / M(4); % Stage 4
dxdt(5) = ( L4*x(4) - V*y(5) - B*x(5) ) / M(5); % Stage 5, Reboiler

% Component B
dxdt(6) = ( V*y(7) - L1*x(6) - D*x(6) ) / M(1); % Stage 1, Condenser
dxdt(7) = ( L1*x(6) + V*y(8) - V*y(7) - L2*x(7) + rB(2) ) / M(2); % Stage 2
dxdt(8) = ( L2*x(7) + V*y(9) - V*y(8) - L3*x(8) + rB(3) + F*zF(2) ) / M(3); % Stage 3,
Feed stage
dxdt(9) = ( L3*x(8) + V*y(10) - V*y(9) - L4*x(9) + rB(4) ) / M(4); % Stage 4
dxdt(10) = ( L4*x(9) - V*y(10) - B*x(10) ) / M(5); % Stage 5, Reboiler

% Component C
dxdt(11) = ( V*y(12) - L1*x(11) - D*x(11) ) / M(1); % Stage 1, Condenser
dxdt(12) = ( L1*x(11) + V*y(13) - V*y(12) - L2*x(12) + rC(2) ) / M(2); % Stage 2
dxdt(13) = ( L2*x(12) + V*y(14) - V*y(13) - L3*x(13) + rC(3) + F*zF(3) ) / M(3); % Stage 3,
Feed stage
dxdt(14) = ( L3*x(13) + V*y(15) - V*y(14) - L4*x(14) + rC(4) ) / M(4); % Stage 4
dxdt(15) = ( L4*x(14) - V*y(15) - B*x(15) ) / M(5); % Stage 5, Reboiler

% Component D
dxdt(16) = ( V*x(17) - L1*x(16) - D*x(16) ) / M(1); % Stage 1, Condenser
dxdt(17) = ( L1*x(16) + V*x(18) - V*x(17) - L2*x(17) + rD(2) ) / M(2); % Stage 2
dxdt(18) = ( L2*x(17) + V*x(19) - V*x(18) - L3*x(18) + rD(3) + F*zF(4) ) / M(3); % Stage 3,
Feed stage
dxdt(19) = ( L3*x(18) + V*x(20) - V*x(19) - L4*x(19) + rD(4) ) / M(4); % Stage 4
dxdt(20) = ( L4*x(19) - V*x(20) - B*x(20) ) / M(5); % Stage 5, Reboiler

% Energy balance
dxdt(21) = ( V*x(22) - L1*x(21) - D*x(21) ) / M(1); % Stage 1, Condenser
dxdt(22) = ( L1*x(21) + V*x(23) - V*x(22) - L2*x(22) ) / M(2); % Stage 2
dxdt(23) = ( L2*x(22) + V*x(24) - V*x(23) - L3*x(23) + F*Tf ) / M(3); % Stage 3, Feed
stage
dxdt(24) = ( L3*x(23) + V*x(25) - V*x(24) - L4*x(24) ) / M(4); % Stage 4
dxdt(25) = ( L4*x(24) - V*x(25) - B*x(25) ) / M(5); % Stage 5, Reboiler

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CURRICULUM VITA



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