ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

PLANTWIDE CONTROL OF A COMPLEX PROCESS INVOLVING A REACTIVE DISTILLATION COLUMN

M.Sc. THESIS

Rojda Özgür BAKİ

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

REAKTİF KOLON İÇEREN KOMPLEKS PROSESİN FABRİKA ÖLÇEKLİ KONTROLÜ

YÜKSEK LİSANS TEZİ

Rojda Özgür BAKİ
(506081038)

Kimya Mühendisliği Anabilim Dalı

Kimya Mühendisliği Programı

Tez Danışmanı: Doç. Dr. Devrim B. KAYMAK

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Rojda Özgür BAKİ, a **M.Sc.** student of ITU **Institute of Science and Technology** student ID **506081038**, successfully defended the **thesis/dissertation** entitled "**Plantwide Control of a Complex Process Involving Reactive Distillation Column**'', which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below

Thesis Advisor :	**Assoc. Prof.Dr.Devrim B. KAYMAK** İstanbul Technical University	.....
Jury Members :	**Prof. Dr. Dursun Ali ŞAŞMAZ** İstanbul Technical University	.....
	Asst. Prof. Dr. Engin YEŞİL İstanbul Technical University	.....

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FOREWORD

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Rojda Özgür BAKİ
Chemical Engineer

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ABBREVIATIONS

ATV : Auto-tuning method
BuAc : Butyl acetate
CC : Capital cost
CE : Energy cost
CSTR : Continuous stirred tank reactor
DEC : Diethyl carbonate
EMC : Ethyl methyl carbonate
EtAc : Ethyl acetate
ETBE : Ethyl *tert*-butyl ether
EQ : Equilibrium state model
IPA : Isopropanol
MeAc : Methyl acetate
MESH : Material, equilibrium, summation and heat balance equations
MEOH : Methanol
MTBE : Methyl *tert*-butyl ether
NEQ : Non-equilibrium state model
P : Proportional
PI : Proportional-integral
RD : Reactive distillation
SISO : Singular input singular output
SVD : Singular value decomposition
TAC : Total annual cost
TAME : *Tert*-amyl methyl ether
VLE : Vapor liquid equilibrium

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A	Reactant component
a	Amplitude of output response
a_F	Preexponential factor for forward reaction ($kmol.s^{-1}.kmol^{-1}$)
A_C	Heat exchanger area for condenser (m^2)
A_R	Heat exchanger area for reboiler (m^2)
A_{VP}	Vapor pressure constant
B	Reactant component
B_{VP}	Vapor pressure constant
β_R	Time constant of rectifying section
β_{RXN}	Time constant of reaction section
β_S	Time constant of stripping section
C	Product component
D	Product component
d	Relay amplitude
E_F	Activation energy of the forward reaction ($cal.mol^{-1}$)
F_{0i}	Fresh feed flow rate of reactant *i* ($mol.s^{-1}$)
k_F	Specific reaction rate of the forward reaction ($kmol.s^{-1}.kmol^{-1}$)
K_C	Controller gain
K_{EQ}	Equilibrium constant
K_P	Steady-state gain
K_U	Ultimate gain
L_C	Length of the column (m)
L_i	Liquid flow rate from tray *i* (mol/s)
L_R	Liquid flow rate in the rectifying section (mol/s)
M_B	Liquid holdup in the column base (mol)
M_D	Liquid holdup in the reflux drum (mol)
M_i	Liquid holdup on tray *j* (mol)
M_{RX}	Liquid holdup on each tray in the reactive section (mol)
N_F	Location of feed tray
N_R	Number of rectifying trays
N_{RX}	Number of reactive trays
N_S	Number of stripping trays
N_T	Total number of trays in the column
P	Column pressure (bar)
P_U	Ultimate period (min)
$P^S_{j,i}$	Vapor pressure of component *i* on tray *j* (bar)
R	Reflux flow rate (mol/s)
$r_{j,i}$	Reaction rate of component *i* on tray *j* (mol/s)
T_j	Column temperature on tray *j* (K)
V_j	Vapor flow rate on tray *j* (mol/s)
V_{NT}	Vapor flow rate from the top of the column (mol/s)
V_S	Vapor boilup (mol/s)
U_C	Overall heat-transfer coefficient in condenser ($kJ.s^{-1}.K^{-1}.m^{-2}$)

U_R	Overall heat-transfer coefficient in the rebolier ($kJ.s^{-1}.K^{-1}.m^{-2}$)
U	Left singular vector matrix
$x_{B,i}$	Bottoms composition of component *i* in liquid
$x_{j,I}$	Vapor mole fraction of component *i* on tray *j*
$y_{j,I}$	Vapor mole fraction of component *i* on tray *j*
z_{0i}	Fresh feed mole fraction of component *i*
Greeksymbols	
A	Relative volatility
α_{ji}	Relative volatility of component *j* to component
β_{pay}	Payback period (year)
ΔH_V	Heat of vaporization, cal/mol
λ	Heat of reaction, cal/mol
v_i	Stoichometric coefficient of component *i*
$\sum$	Diagonal matrix of singular values
τ_I	Reset time (min)

PLANTWIDE CONTROL OF A COMPLEX PROCESS INVOLVING A REACTIVE DISTILLATION COLUMN

SUMMARY

Increasing energy demand and environmental considerations have forced industry to focus on process intensification. Reactive distillation columns combining reaction and seperation operations into a single vessel have been successful examples of process intensification. This have made the reactive distillation columns the subject of many papers in recent years. The vast majority of these papers dealt with the steady-state design and the dynamic behaviour of the individually operating reactive distillation columns. However, most of the chemical processes are multi-unit systems containing several reaction steps and multiple recycle streams. Thus, there is a lack of knowledge on the plantwide control of multi-unit complex processes involving reactive distillation columns.

In order to make up the deficit in this field, a simplified version of a real industrial process is modified as a test case. The original process contains two reaction steps, three distillation columns, two recycle streams and six chemical components. Since the chemistry and volatilities have been suitable, the second reaction and the third separation steps have combined into a reactive distillation column. By elimination of two reactors in series, the modified process consists of a reactor, two distillation columns and one reactive distillation column with two recycle streams. First, a steady-state design of the process has been developed using relaxation method for the reactive column and Wang-Henke method for the conventional columns. Next, several plantwide control strategies have been developed and tested in the face of different disturbances. In all control strategies, SISO structures have been used with tuning parameters based upon the recommendations of Tyreus and Luyben. Ultimate gains and frequencies have been found using relay-feedback test. Two of the composition control structures studied have been found workable among several alternatives. It has been realized that these workable control structures require composition control for the reactor and flow control in each recycle loop. In the next step, temperature-based inferential control structures have been designed, since temperature measurements are faster, cheaper and more reliable. Sensitive trays of conventional columns have been selected using the steepest slope criteria, while the most sensitive trays of reactive column have been determined with the aid of the sensitivity analysis and singular value decomposition (SVD) method. It has been observed that both composition and temperature-based control structures have effectively controled the system in the face of different disturbances. Results of the dynamic simulations show that the deviation in the product purities occurs in the temperature-based control structures. However, it has been seen that they are quite close to their specifications in single-end temperature control structures.

REAKTİF DİSTİLASYON KOLON İÇEREN KOMPLEKS PROSESİN FABRİKA ÖLÇEKLİ KONTROLÜ

ÖZET

Bir çok kimyasal prosesin en önemli parçalarından birini, ham maddeleri istenilen ürünlere dönüştüren kimyasal reaktörler oluşturmaktadır. Kimyasal reaksiyonlarda hammaddelerin ürünlere tamamen dönüşümü mümkün olmadığından, reaktör çıkış akımları reaksiyona giren hammaddeler, ürünler ve yan ürünlerden oluşmaktadır. Bu nedenle istenilen ürünleri istenilen saflıkta elde edebilmek için reaktör ünitelerini izleyen ayırma üniteleri endüstride çok yaygın olarak kullanılmaktadır. Giderek artan ekonomik ve çevresel kaygılar, endüstriyi, reaksiyon ve ayırma işlemlerini tek bir ünitede birleştiren reaktif distilasyon kolonları üzerinde yoğunlaşmaya teşvik etmiştir. Bu yüzden, reaktif distilasyon kolonları son yıllarda bir çok makalenin konusu olmuştur ve literatürdeki makalelerin büyük çoğunluğu, tek başına çalışan reaktif distilasyon kolonunun yatışkın hal tasarımını ve dinamik davranışını ele almıştır. Ancak, reaktif distilasyon kolonu içeren kompleks prosesin fabrika ölçekli kontrolünde önemli bir bilgi eksiği bulunmaktadır.

Bu alandaki eksikliği gidermek için, gerçek endüstriyel bir prosesin basitleştirilmiş hali, reaktif kolon içeren kompleks prosesin dinamik kontrol edilebilirliğini araştırma amacıyla kullanılmıştır. Basitleştirilmiş gerçek endüstriyel proses, iki reaksiyon basamağı, üç geleneksel distilasyon kolonu, iki geri dönüş akımı ve altı kimyasal bileşen içermektedir. Proses farazi bir sistem olarak düşünülmüş olup, altı kimyasal bileşeni A, B, C, D, E ve F olmaktadır. Prosesin ilk reaksiyon basamağını, sürekli karıştırmalı tank reaktörde meydana gelen $A+B \rightarrow C+D$ kimyasal reaksiyonu oluşturmaktadır. Bu reaksiyon sonucunda, istenilen ürün C elde edilmektedir. İkinci kimyasal reaksiyon, ikinci sürekli karıştırmalı tank reaktörde $D+E \rightarrow B+F$ reaksiyonu ile meydana gelmekte ve bu reaksiyon sonucunda istenilen ürün F bileşeni oluşmaktadır. Prosesteki bileşenlerin uçuculukları sırasıyla, $\alpha_A > \alpha_B > \alpha_C > \alpha_D > \alpha_E > \alpha_F$ şeklinde olmaktadır ve bileşenlerin uçuculukları arasındaki ilişki, birinci reaksiyon ünitesini takiben geleneksel distilasyon kolonuna beslenen çok bileşenli reaktör çıkış akımını, ilk reaksiyon basamağına ait reaksiyona girmemiş hammaddeleri kolonun üst akımından, ürünleri ise kolonun alt akımından olacak şekilde birbirlerinden ayrılmalarını sağlamaktadır. Birinci geleneksel distilasyon kolonunun üst akımından ayrılan reaksiyona girmemiş hammaddeler, reaksiyon verimini artırma amacıyla reaktöre geri dönüş akımı ile beslenmektedir. İlk geleneksel distilasyon kolonunun alt akımından ayrılan çoğunlukla C ve D ihtiva eden çok bileşenli karışım, hafif ürün C bileşenini, ağır D bileşeninden ayırmak için, ikinci geleneksel distilasyon kolonuna beslenmektedir. İkinci geleneksel distilasyon kolonu, istenilen ürün C bileşeninin, kolonun üst akımından, ağır D bileşeninin ise kolonun alt akımından ayrılmasını sağlamaktadır. Bu kolonun çoğunlukla D bileşeni içeren alt akımı ve saf E ihtiva eden eden taze besleme akımı, ikinci kimyasal reaksiyonu oluşturmak üzere, ikinci sürekli karıştırmalı tank reaktöre beslenmektedir. Burada ikinci kimyasal reaksiyon meydana gelmekte, B ve F bileşeni oluşmaktadır. Ardından çok bileşenli reaksiyon çıkış akımı, üçüncü ve prosesin son ünitesi olan geleneksel distilasyon kolonuna, istenilen ağır ürün F

bileşenini, hafif olan B bileşeninden ayırmak için beslenir. Prosesin bu kısmında, çoğunlukla B bileşeni içeren kolonun üst akımı, ilk reaktör ünitesine, ilk kimyasal reaksiyonu gerçekleştirmek üzere geri beslenmektedir. Bu basitleşitilmiş gerçek kimyasal proseste, B ve D bileşenlerinin, prosesin kendi içindeki reaksiyonlardan birinde üretilip bir diğerinde haracanan ara ürünler olmaları, sistemin hayati noktasını oluşturmaktadır. Bu sistemin en önemli noktasını ise, prosesin, ikinci reaksiyon ünitesinde ve üçüncü geleneksel distilasyon kolonunda meydana gelen kimyasal ve fiziksel değişimlere ait bileşen uçuculukları arasındaki ilişkinin, reaktif distilasyon kolonunun temel tasarım prensibini oluşturan yapı ile birebir örtüşmesi oluşturmaktadır. Bilindiği üzere reaktif kolonda bileşenlerin uçuculukları, reaksiyona giren hammadeler reaktif bölgede kalırken, oluşan ürünler ise distilasyon süreci ile reaktif bölmeden kolayca uzaklaşabilecek şekildedir. Böylece, bu çok üniteli kompleks proseste kimyasal yapının ve bileşenlerin uçuculukların uygun olması, ikinci reaksiyon basamağı ve üçüncü geleneksel distilasyon kolonunu, reaktif distilasyon kolonu olarak birleştirmeyi mümkün kılmıştır.

Bu amaçla çalışma, reaktörün, geleneksel distilasyon kolonlarının ve reaktif kolonun yatışkın hal değerlerinin hesaplanması, tüm sürecin dinamik simulasyonunun gerçekleştirilmesi, sistem için uygun kontrol yapılarının, fabrika ölçekli yapı göz önünde bulundurularak tasarlanması ve süreç için en uygun kontrol yapısının seçimi olmak üzere dört aşamada irdelenmiştir. Çalışmanın ilk kısmında, süreçteki ünitelerin yatışkın hal tasarımı ve bu tasarımlara ait başlangıç değerleri reaktif distilasyon kolonu için yatıştırma, geleneksel kolonlar için de Wang-Henke metodu kullanılarak hesaplanmıştır. Reaktif distilasyon kolonu ile basitleştirilen prosesin, toplam ekipman, enerji ve toplam yıllık maliyetleri hesaplanmış ve toplam yıllık ekipman maliyeti orijinal prosesteki toplam yıllık ekipman maliyetinden az, toplam enerji maliyeti ise orjinal prosesteki değerinden fazla ve sonuç olarak yıllık toplam maliyet değeri ise tüm sistem için optimizasyon çalışması yapılmamasına rağmen, orijinal prosesteki yıllık toplam maliyet değerinden daha az olarak bulunmuştur. Çalışmanın bir sonraki aşamasında, sürecin dinamik simulasyonu, sistemin kimyasal yapısı dikkate alınarak yatışkın hal simulasyonundan farklı bir yaklaşımla oluşturulmuştur. Çünkü prosesin ara ürünlerinin varlığı ve bu bileşenlerin kolonlardan tamamen ayrışamaması söz konusu olmaktadır, ayrıca prosesteki iki reaksiyon basamağındaki genel madde dengesi, değişen işletme koşulları ve bozan etkenler sebebiyle mükemmel bir şekilde sağlanamamaktadır. Bu nedenle, iki reaksiyon basamağındaki madde dengesini tam olarak sağlamak amacıyla, ara bileşenleri içeren saf akımların yatışkın ve dinamik halde sisteme ilavesi veya çıkarılması, sistemin fabrika ölçekli tasarımının ve kontrolünün de temel yapısını oluşturmaktadır. Sistemin yatışkın hal tasarımında ilave ara bileşen akımlarından biri reaktör ünitesine verilirken, sistemin dinamik simulasyonunda, aynı akımın, reaktif kolonun geri dönüş akımı haznesine eklenmesi veya çıkarılması, ayrıca sistemin bir diğer ara bileşenin ikinci geleneksel distilasyon kolonunun alt akımından eklenmesi veya çıkarılması söz konusu olmaktadır. Böylece çalışmanın ikinci kısmında, sürekli karıştırmalı tank reaktör ve yatışkın hal tasarımları yapılan kolonların tamamını ihtiva eden tüm prosesin dinamik simulasyonu, sistemdeki tüm madde dengesinin doğru olarak sağlanması amacıyla, ara bileşen akımlarının sisteme belirli ekipmanlardan eklenmesi veya çıkarılması ile gerçekleştirilmiştir. Çalışmanın kontrol aşamasında, fabrika ölçekli kontrol yapısı tasarlama gereklilikleri göz önünde bulundurularak, alternatif kontrol yapıları geliştirilmiştir. Bütün kontrol çevrimlerinde, Tyreus ve Luyben'ın tavsiyesine dayalı ayarlama parametreleri ile tek-giriş tek-çıkış (SISO) yapılı PI kontrol ediciler kullanılmıştır. Son kazançları ve

frekansları bulmak için relay-feedback testi kullanılarak, kontrol çevrimleri otomatik ayar yöntemi (ATV) yardımıyla ayarlanmıştır. Öncelikle, dört adet bileşen kontrolü içeren fabrika ölçekli kontrol stratejisi geliştirilmiş ve bunlar farklı bozan etkenler karşısında denenmiştir. Dört alternatiften, iki kompozisyon kontrol yapısı çalışabilir bulunmuştur. Çalışabilir kontrol yapılarının, reaksiyon için bileşen kontrolü ve her geri dönüş akımı için akış denetleyicisi bulundurmasını gerektirdiği fark edilmiştir. Bileşen kontrol edicileri, reaksiyon ünitesinde ara ürün B bileşenin kontrolüne, geleneksel distilasyon kolonlarının alt akımlarında veya üst akımlarında bulunan safsızlıkların kontrölüne, reaktif distilasyon kolonunda ise reaksiyona giren E bileşenin kontrolüne ve kolonun alt akımında bulunan safsızlığın kontrolü temellerine dayanmaktadır. Ayrıca ikinci geleneksel distilasyon kolonunun alt akımına eklenen saf ara ürün akımında ve reaktif distilasyon kolonunun geri besleme haznesine eklenen bir diğer saf ara ürün akımında bölme aralıklı seviye kontrol ediciler kullanılmaktadır. Bu bölme ayarlı seviye kontrol edicileri, dinamik simulasyonda değişen süreç şartlarına ve bozanetkenlere karşı, sürecin ihtiyacı olan ara ürünlerin gerekli miktarlarda sisteme ilavesi veya çıkarılması için kullanılmıştır. Kontrol yapılarının simülasyon sonuçları, bileşen kontrol yapılarının tüm prosesi etkin bir şekilde kontrol ettiğini ve bu kontrol yapılarının ürün saflıklarını değişen bozanetkenlere karşı istenilen değerlerde tutabildiğini göstermiştir. Tasarlanan fabrika ölçekli bileşen kontrol yapılarından birinin (CS4C) diğerinden (CS3C) daha hızlı cevap vermekte olduğu görülmüştür. Ayarlanan değişkenlerin yeni yatışkın haline daha çabuk ulaştığı bileşen kontrol yapısında (CS4C), hem iki ara ürün için ilave veya çıkarma akımları, hem de iki geri dönüş akımının her biri için iki ayrı akış denetleyicisi bulunması, bu yapının, diğer bileşen kontrol yapısından (CS3C) daha kısa sürede yeni yatışkın haline oturduğunu hissettirmektedir. Bir sonraki adımda, sıcaklık ölçümlerinin daha hızlı, daha ucuz ve daha gerçekçi olması sebebiyle, çalışabilir fabrika ölçekli bileşen kontrol yapıları kullanılarak tek-uçlu sıcaklığa dayalı dolaylı kontrol yapıları tasarlanmıştır. Sıcaklığa dayalı kontrol ediciler genellikle geleneksel distilasyon kolonları ve reaktif distilasyon kolonlarının en hassas rafları üzerine tasarlanmaktadırlar. Bu çalışmada da sıcaklığa dayalı kontrol ediciler kolonların en hassas oldukları raflar üzerine tasarlanmıştır. Geleneksel distilasyon kolonlarının hassas rafları, sıcaklık profilinin raftan rafa en çok değiştiği yeri ifade eden dik eğim kriteri kullanılarak seçilirken, reaktif kolonda, hassas raflar, tasarlanan kontrol yapılarındaki ayarlanan değişkenlerin kolon içerisindeki değişimlerine en duyarlı rafı belirlemeye yarayan hassaslık analizi ve ardından tekil değer ayrışması (SVD) metodu yardımıyla belirlenmiştir. Dinamik simulasyon sonuçları tek-uçlu sıcaklığa dayalı kontrol edicilerde ürün saflıklarında çok az miktarda sapma olduğunu gösterirken, ayarlanan değişkenlerin ve ürün saflıklarının bileşen kontrolü içeren yapılardan daha kısa sürede yeni yatışkın değerlerine oturduğunu göstermiştir. Ayrıca tasarlanan fabrika ölçekli kontrol yapılarından birinin (CS4ST) bir diğer kontrol yapısından (CS3ST) daha hızlı cevap verdiği görülmüştür. Daha sonra, ürün saflıklarında meydana gelen az miktardaki sapmayı önlemek için, geleneksel distilasyon kolonlarında, sıcaklık profilinin raftan rafa en çok değişiği ikincil noktalar bir diğer hassas raflar olarak belirlenmiş ve bu raflar üzerine de sıcaklık kontrol edicileri tasarlanarak iki-uçlu sıcaklığa dayalı kontrol yapıları (CS3DT ve CS4DT) elde edilmiştir. İki-uçlu sıcaklık kontrol yapılarının dinamik simulasyon sonuçları, ürün saflıklarında belirgin miktarda sapmalar olduğunu gösterirken, proses verilerinin yeni yatışkın hallerine gelmeleri için gerekli sürede önemli bir değişikliğin olmadığını göstermiştir.

Çalışmanın sonucunda, reaktif distilasyon kolonu içeren kompleks prosesin fabrika ölçekli kontrolünün, hem sıcaklık hem de bileşen kontrol yapıları tarafından, değişen bozanetkenlere karşı etkin bir şekilde gerçekleştirilebilirliği görülmüştür. Tek-uçlu sıcaklığa dayalı kontrol yapılarında ürün saflıklarında sapmalar meydana gelmelerine rağmen, ürünlerin spesifikasyonlarına oldukça yakın olmalarından dolayı sistem için en uygun fabrika ölçekli kontrol yapılarının, tek-uçlu sıcaklığa dayalı kontrol yapılarının olduğu görülmüştür.

1. INTRODUCTION

Since chemical reactors transform raw materials into desired product, they are one of the vital parts of many chemical processes. In general, reactor effluents contain not only products but also by-products and unconverted reactants. Because of the presence of these by-products and unconverted materials reactors followed by separation units are common in industry to obtain products with desired purities.

Primary method of separation in processing plants is distillation which is an ancient unit operation and has been widely practiced for thousands of years. This is a process of physically separating a mixture into two or more products those have different boiling points by preferentially boiling the more volatile components out of the mixture [1].

Increasing energy demand and environmental considerations have forced industry to focus on process intensification. So, the coupling of physical separation and chemical reaction in one unit operation is called reactive distillation (RD) column, and it has received increasing attention in recent years. RD columns with the combining reaction and separation operations in a single vessel become a successful example of process intensification.

Reactive distillation columns have several advantages as compared with conventional multi-unit reactor/separation processes, if it is used for suitable chemical systems. The main advantages of RD columns,

1. Reducing capital investment and operational costs by the elimination of reactor and separation units,
2. Increasing conversion since leaving of the product components drives the reaction toward the product side for reversible chemical reactions,
3. Eliminating the limitation of azeotropic mixture separation by the presence of reaction,
4. Improving energy efficiency by the internal heat integration between reaction and separation in the same vessel,

5. Increasing reaction selectivity with elimination of possible side reactions by continuously separation between products and reactants from the reaction zone [2,3].

However, RD can be effective for only a small class of chemical systems because of some inherent limitations. The relative volatilities of the reactants and products should be such that the while reactants remain in the column, the products are removed from the reactive zone of the column easily. The other important limitation is the need for a match between temperatures favorable for reaction and separation, because reaction ad separation occur in the single unit and at the same pressure. If the separation operation achieves in low temperatures, it causes low specific reaction rates, very large holdups or large amounts of catalyst. If the required temperatures to carry out the separation is high, this engenders to very small chemical constants with exothermic reversible reactions and it may be difficult to achieve the desired conversion. Also, high temperatures may promote undesirable side reactions. Therefore, both low and high-temperature cases, reactive distillation may not be economical. An other limitation of RD is that heats of reaction cannot be too large. If the heat of reaction is large, hydraulic problems such as weeping or flooding can occur [2, 3].

Although significant research has been done concerning the design and control of individual reactive distillation columns, the plantwide design and control of multi-unit processes which includes reactive distillation columns are still an advancing field. The aim of this study is to investigate the controllability of a multi-unit process including a reactive distillation column, which is a modified version of a process flow sheet given in the literature [4].

2. BACKGROUND

2.1 Reactive Distillation Columns

Reactive distillation occurs when a chemical reaction takes place within the liquid holdup of a distillation tray. This process was first proposed by Backus in 1921 and has become a popular approach for producing esters and gasoline oxidant MTBE (Methyl *tert*-butyl ether) [5]. Then, RD has been used and investigated for several reactions such as etherification, esterification, hydrogenation, hydrodesulfurisation and polymerization. Important etherification applications of RD are the production of ethyl tert-butyl ether (ETBE), methyl tert-butyl ether (MTBE) and tert amyl methyl ether (TAME) while the esterification applications are the production of ethyl acetate (EtAc), butyl acetate (BuAc) and methyl acetate (MeAc) [6].

However, a small number of industrial applications of reactive distillation had been around for many decades. One of the earliest was a DuPont process and in this plant, dimethyl terephthalate is reacted with ethylene glycol to produce methanol and ethylene terephthalate. In early 1980s, engineers at Eastman Chemical published a very influential paper [7]. The process developed by Eastman Kodak produces a high purity of MeAc (Methyl acetate) from methanol and acetic acid using a RD column. Along with this paper, interest in reactive distillation in both industry and academia has increased [3].

In the literature, numerical calculation procedures to solve the mass, equilibrium and energy balances rigorously in multicomponent, multistage reactive distillation columns have been reported since the 1970's [2]. Significant improvements in the conceptual design of RD had been achieved in the late 1990's. Then, dynamic behavior and control of reactive distillation processes start to get more attention.

A literature surveys presents a total of 236 different reaction systems for reactive distillation columns. These reaction systems are classified according to their reaction types:

1. 91 systems are the form of $aA + bB \leftrightarrow cC + dD$ class,

2. 60 of them belong to the $aA + bB \leftrightarrow cC$ class,
3. 21 sytems are the form of $aA \leftrightarrow bB + cC$,
4. 18 systems belong to the $aA \leftrightarrow bB$,
5. Two-stage reaction (e.g., ($A + B \leftrightarrow C + D$ and $B + C \leftrightarrow D + E$) or three-stage reaction ($A + B \leftrightarrow C$, $C + B \leftrightarrow D$, $D + B \leftrightarrow E$) occurs the the remaining 33 reaction systems [3].

2.1.1 Design of reactive distillation columns

In RD column, separation and reaction occurring simultaneously in the same unit result in complex interactions of vapor-liquid equilibrium, vapor-liquid mass transfer and chemical kinetics. Hence, the design and operation issues of RD columns are more complicated than those of conventional reactors and distillation columns.

For quaternary systems, reactive distillation columns consist of three sections as stripping, reactive and rectifying sections. Middle of the RD column is a reactive section and there is a catalyst which can be same phase with reactant or a solid phase. Here, the reactants are transformed into products which are separated out of reactive zone by distillation process. Location of the feed streams are determined considering the relative volatility of the reactants and desired compostions of the components [3].

In the literature, there are two main classes of modeling approaches regarding the design of RD. These are the equilibrium stage models and the non-equilibrium stage models. In equilibrium stage model, the vapor coming from the lower stages and liquid streams flowing from upper stages contact on a stage and leave this stage in equilibrium. In other words, bulk vapor and bulk liquid phases are in the thermodynamic equilibrium with each other. In the light of this equilibrium assumption, temperature gradient does not occur between the phases. In non-equilibrium stage model, it is assumed that only vapor and liquid interface is in equilibrium. Herewith, difference in temperatures takes place through the phases [8]. Therefore, the equilibrium stage model (EQ) contains the MESH (material balance, vapor-liquid equilibrium, summation of mole fraction and heat balance) equations, while the non-equilibrium stage model (NEQ) includes the MERQ (material balance, energy balance, rate equations for mass transfer, and phase equilibrium at vapor-liquid interface) equations. Most of reactive distillation model equations are based on EQ stage model with the extensions of MESH equations that has been derived for

conventional columns. To obtain the model equations for RD, the EQ stage model is modified by adding the reaction rate term into the material balance equations and by attaching the heat of reaction to the energy balance equations. [9-11].

The NEQ stage model for RD is based on the MERQ equations of conventional distillation columns. Rate equations for mass transfer and reaction kinetics increase the complexity of this approach. Hence, this model requires the thermodynamics properties for both phase equilibrium and chemical reactions. This model has been used for commercial RD column designs [12-15]. Since the NEQ stage model has more empirical parameters and is more complex than EQ stage model, EQ stage approach is more convenient for the design of ideal systems.

2.1.2 Control of reactive distillation columns

Estrada-Villagrana and co-workers investigated the controllability of a RD column for production of MTBE. Basically, the aim of that work was to establish the best control structure for reactive distillation column using the linear control tools. The analysis was made for the high conversion steady state. Three control objectives of the study are the purity of MTBE in the bottom stream and the levels of reflux drum and reboiler. Three control schemes were investigated to find the best one. In two control schemes, reflux drum level is controlled by manipulating the external flow (distillate flow), while in the other control scheme, reflux drum level is controlled by the manipulating internal flow (reflux flow). The base levels are controlled by manipulating the bottoms flows in all control loops. Also, reboiler duty is used to maintain the temperature as reference variable for the purity. They didn't analyse the influence of disturbances in the selection of inputs and outputs, but the results of the study showed that it is possible to use linear control for control structure design [16].

Sneesby and co-workers studied a two-point control structure to control both reactant conversion and product composition for a RD column of ethyl tert-butyl ether (ETBE). They developed control structure configuration with PI controllers as one-point and two-point control schemes. In one-point control structure, stripping section temperature is controlled to regulate the ether purity and to provide satisfied conversion of isobutylene, while in two-point control scheme, ether purity in the bottom composition is controlled manipulating the reboiler duty and isobutylene conversion is controlled the reflux flowrate. They demonstrated that the two-point

control scheme has superior disturbance rejection capability compared with the one–point control scheme [17].

In another study, Sneesby and co-workers designed three control structures for a RD column of ETBE by using only linear PI controllers. They showed that, despite the high-nonlinearity of the system, appropriate control objectives produced effective control loops satisfying the stability for a range of process disturbances. They emphasized that more complex control systems can be built on designed control structure [18].

Al-Arfaj and Luyben studied the design and control of ternary systems that is considered demonstrative example of metathesis of 2- pentene. They developed five control structures using dual composition, single-end composition, single-end temperature and dual temperature control loops. All the structures are SISO structures with PI controllers. They evidenced that column with a single feed, eliminates the internal composition analyzer, since there is no need to balance fresh feed streams. According to result of control studies, both dual composition and dual temperature control structures provide effective control [19].

Vora and Daoutidis studied the dynamics and control of a reactive distillation column for the production of ethyl acetate from acetic acid and ethyl alcohol. They designed the ethyl acetate RD column as distinct from conventional design. In this new design, reactants are fed to the column from different trays, while in the conventional column, they are fed to the column from the same tray. They showed that the new design gives a higher conversion and purity. Model based linear and nonlinear state feedback controllers along with conventional SISO PI controllers were designed on the control loop. It is shown that linear controllers give more appropriate responses than nonlinear controllers [20].

Al-Arfaj and Luyben investigated the design and control of methyl acetate (MeAc) RD column. Three control configurations using SISO structures with PI controllers were designed for both systems. They showed that a structure with one internal composition controller and one temperature controller provides effective control of both systems for both high and mid conversion designs while two-temperature control structure is effective only the RD column is redesign. On the other hand, nonlinearity and interaction make the direct composition control difficult, whereas control of the tray temperature prevents these problem [21].

In another study, Al-Arfaj and Luyben studied the controllability of two ETBE reactive distillation columns designed with two fresh feed streams and single mixed feed, respectively. They investigated four control structures using the SISO structures with PI controllers. Control structure results showed that the first design requires an internal composition control to balance the stoichiometry between the feed streams, while the second design operating with an excess of ethanol is effectively controlled with temperature controllers for a small disturbance range [22].

Kaymak and Luyben compared two different types of two-temperature control structures for quaternary RD columns. Two systems, an ideal and a methyl acetate, were studied. In the first structure, two tray temperatures in the column are controlled by manipulating two fresh feed streams, while in the second structure two tray temperatures are controlled by manipulating the fresh feed streams and vapor boilup. The effectiveness and robustness of the control structures were compared in the face of disturbances in the production rate and fresh feed compositions. One of the main conclusions of this study is that the selection of the manipulated fresh feed stream in the second structure has an important role in the stability of the system [23].

Kaymak and Luyben developed a two-temperature control structure for a two-reactant/ two-product reactive distillation column. In this study, conventional linear PI controllers in a decentralized (SISO) environment are used in all control structures. They purposed to explore the effectiveness of this two-temperature control structure for various column designs with different number of reactive trays to investigate the impact of design on controllability. They also show that two-temperature control structures can be used instead of a composition analyzer for the neat mode (without excess reactant). Two temperatures are controlled by manipulating the two fresh steams while reflux ratio is held constant. They emphasized that key criterion on the selection controlled temperatures is to having controllers with the same action to balance the stoichiometry [24].

Wang and Wong investigated process characteristics and control strategies for a RD column producing high-purity IPA (isopropanol). Because of the non-linearity between selected input and output pairs, variable transformation is a non-linear control technique was used to improve the control performance. They showed that the transformed temperatures and a composition control scheme provide rather good control performance [25].

Zeng and co-workers investigated the design and control of a RD unit for production of butyl acrylate from n-butanol and acrylate acid. They propesed a one-temperature control structure to obtain high purity of butyl acrylate from bottom of the column. In this control structure, while reboiler heat duty is held constant, ratio between feeds is controlled the temperature of tray. They also designed an alternative control configuration that includes two pure feeds at exact stoichiometric balance. They showed that, alternative control structure gives a worse control performance than the proposed control configuration. Namely, they found that exact stoechiometric balance between two feed streams is not a good choice of wide disturbance operability range for this type of RD unit due to the open-loop sensitivity. They emphasized that if the system operates with a slight imbalance of the stoichiometric feed ratio, a strong open-loop sensitivity is provided. Herewith, they showed that control performance gives a wider disturbance operability range [26].

Luyben studied the controllability of ternary reactive distillation columns with and without chemically inert components. It was observed that there are significant differences between these cases. Although the ternary system without inert is controlled effectively by a two-temperature control structure, the ternary system with inert does not work [27].

In their study, Kaymak and Luyben compared the controllability of a multi-unit reactor/column/recycle process and a RD column. According to the results of conventional multi-unit, dual temperature control structure process works as well as the control structure with a compositon analyzer. They featured that the controllability of RD column is more difficult and its operability region is much smaller, since RD columns have smaller number of control degrees of freedom than the conventional multi-unit systems. On the other hand, they showed that RD process have significantly lower capital and energy cost [28].

Kumar and Kaistha investigated the performance of two-temperature based inferential control structures for a RD column of MTBE. They improved two control structures using the temperature based inferential control structures. In the first control structure, reactive and stripping tray temperatures are controlled by the fresh feed acetic acid and methanol feeds, respectively and in the second control structue, reactive and stripping tray temperatures are controlled by the reboiler duty and methanol feed. They emphasized that choosing of tray temperatures suitably provides

to mitigate non-linearity between controlled and manipulated variable and improves robustness of control structures [29].

In another study, Kumar and Kaistha demonstrated the implications of output and input multiplicities on the control of a RD column of MTBE. They showed that controlling the most sensitive reactive tray temperature is not good choise because low rangeability cause wrong control action for large disturbances. However, controlling a reactive tray temperature with an acceptable sensitivity and larger rangeability gives better robustness. Thence, they showed that choosing suitable tray temperatures improved robustness of the control structures [30].

In their study, Kumar and Kaistha studied a two-point structure and a three-point temperature control structure for an ideal quaternary RD column. It was shown that two-point control structure give worse control performance in large throughput increases. They emphasized that reflux ratio must be adjusted, directly or indirectly, to force the escaping reactants back into the reactive zone. It was demonstrated that a tray temperature in the rectifying section is controlled by manipulating the reflux rate in the three-point control structure. They showed that controlled stripping and rectifying section tray temperatures in the three-point temperature control structure drive the product purities to their design values for large throughput changes in both directions [31].

Kumar and Kaistha also studied a two-temperature control structure for generic ideal RD column. They emphasized that controlling the most sensitive tray temperature makes the control structure susceptible to the nonlinear dynamic phenomena due to the input implicitiy. They showed that controlling a less sensitive reactive tray significantly improves the control systems robustness as the severity of input multiplicity [32].

In another study, Kumar and Kaistha studied a two-temperature control structure for RD column of methyl acetate. In this study, the control structure was modified to incorporate ratio controllers in three different configurations of column inputs. They showed that product purity control is effectively achieved when the two fresh feeds are kept in ratio with the reboiler duty [33].

2.2 Plantwide Process Control

In chemical and petroleum processes, unit operations approach has been traditionally used for control anaylsis and control systems design to simplify the plantwide control problem [34]. In this approach, all of the control loops are established individually for each piece of unit in the plant, then these units are combined together into an entire plant. So, the main assumption of this approach is that control system of the entire plant is consisted from sum of the individual control structures.

Most real chemical processes have complex flowsheets which include several recycle streams, energy integration and many different unit operations. Units in these flowsheets are arranged in series and each downstream unit simply sees disturbances from its upstream neighbor. Also, a feedback of material and energy among these units are carried by recycle streams and energy integration. Also, recycle streams attach seperation units and bring about a path for disturbance. Therefore, these streams alters the dynamic behavior of the plant. In the past, plant consisting recycle streams contained many surge tanks to prevent the integrating effect among the units and recycle streams. Since it increases both capital investment and operating costs, design engineers start to eliminate surge tanks by increasing the recycle streams and introducing energy integration. Thus, complex integrated chemical processes have three basic features which have to be considered for the control system of an entire plant: (1) the effect of material recycle, (2) the effect of energy integration, and (3) the need to account for chemical component inventories. Also, two basic effects of recycle stream are taken into account for the control structure of the entire plant. These are: (1) Since the overall time constant can be much different than the sum of the time constants of the individual units, recycle has an impact on the dynamics of the process. (2) A small change in throughput or feed composition can bring a large change in steady-state recycle stream flowrates. This is known as "snowball" effect. In the literature, dynamics and control of recycle streams have been investigated in series of paper [35-42]. To prevent the snowball effect, it is pointed that a stream somewhere in each liquid recycle loop should be flow controlled [43].

Fundamental features and properties of plantwide control problem explain how to design a control system from the viewpoint of an entire plant and not just by incorporating the control schemes of individual units. So, plantwide process control

comprises the systems and strategies needed to control an entire chemical plant consisting of many interconnected unit operations. Namely, base point of this procedure is to develop a control structure configuration for the entire plant and carry out a design objective of it. Thus, the plantwide control problem is quite complex and open-ended. There are lots of alternatives and feasible choices to develop control structure for complex flowsheets.

To satisfy an effective plantwide process control system, there is a plantwide control design procedure occurring from nine steps. These are (1) establishing the control objectives; (2) determining the control degrees of freedom; (3) establishing the energy management of the system; (4) setting the production rate; (5) controlling the product quality and handle safety; (6) fixing a flow in every recycle loop and control inventories; (7) checking of the component balance; (8) controlling the individual unit operations; (9) optimizing the economics and improve dynamic controllability [44,45]. These steps usually demand a plantwide perspective that often leads to control strategies that differ significantly from those devised by looking at isolated unit operations.

Also the effective plantwide process control system include (1) safe and smooth process operation; (2) tight control of product quality in the face of disturbances; (3) avoidance of unsafe process conditions; (4) a control system run in automatic, not manual; (5) rapid rate and product quality transitions and (6) zero unexpected environmental releases [44].

2.2.1 Control of multi-unit processes including reactive distillation columns

Bock and co-workers studied the design and control of a reactive distillation column that includes esterification of myristic acid with a recovery system. The recovery column is used to obtain high purity of by-product water and to complete the conversion of the acid. They showed that if temperature is used as a reference variable for purity, the effect on reaction to temperature has to be known. Because, they showed that there is no direct relation between temperature and purity as is usualin common distillation columns. So, they used this approach to design an effective control structure for esterification of myristic acid with a recovery system. Hence, they guaranteed the quality of the product streams using two SISO temperature control loops [46].

Luyben and co-workers studied the design and control of conventional and reactive distillation processes for the production of butyl acetate. They economically optimized each process and their results showed that the reactive distillation process has a 20% lower TAC than the conventional reactor/seperator process. Plantwide control structures were developed for each process using conventional PI controllers, and their effectiveness were demonstrated by dynamic simulations in the face of very large disturbances. They showed that both processes can be effectively controlled using conventional by using an appropriate plantwide control structure [47].

Wang and co-workers designed a RD column to produce dimethyl carbonate and ethylene glycol by the transesterification of ethylene carbonate and methanol. They found that a simple temperature control scheme is sufficient to maintain stoichiometric balance between the feed streams [48].

Hung and co-workers developed general design principles for controlling plantwide reactive distillation processes. To illustrate the application of the design principals, they studied the hydrolysis of methyl acetate, transesterification of methyl acetate and esterification of adipic acid with large recycle flow rates. They developed temperature and temperature-composition control structures for all RD process. They showed that control structures provide robust and stable responses in the face of different disturbances [49].

Wei and co-workers studied controllability of a RD process which produces diethyl carbonate (DEC) and methanol (MEOH) from dimethyl carbonate (DMC) and ethanol (EtOH) via two consecutive transesterification reactions. In this process, they used only a single-end temperature loop for both RD column and conventional column to hold product specifications. They showed that proposed control strategy works effectively when feed composition is changed [50].

3. FUNDAMENTALS OF STEADY- STATE DESIGN

This part presents the fundamentals of steady-state design for the system studied. The generic process is assumed with ideal vapor-liquid equilibrium, simple reaction kinetics and physical properties is used in this study. The simplified version of a real complex industrial process is utilized as the test case [4].

3.1 Process Studied

As shown in Figure 3.1, the process contains two reaction steps, three distillation columns, two recycle streams and six chemical components. There are two liquid-phase reactions taking place in the continuous stirred tank reactors (CSTR).

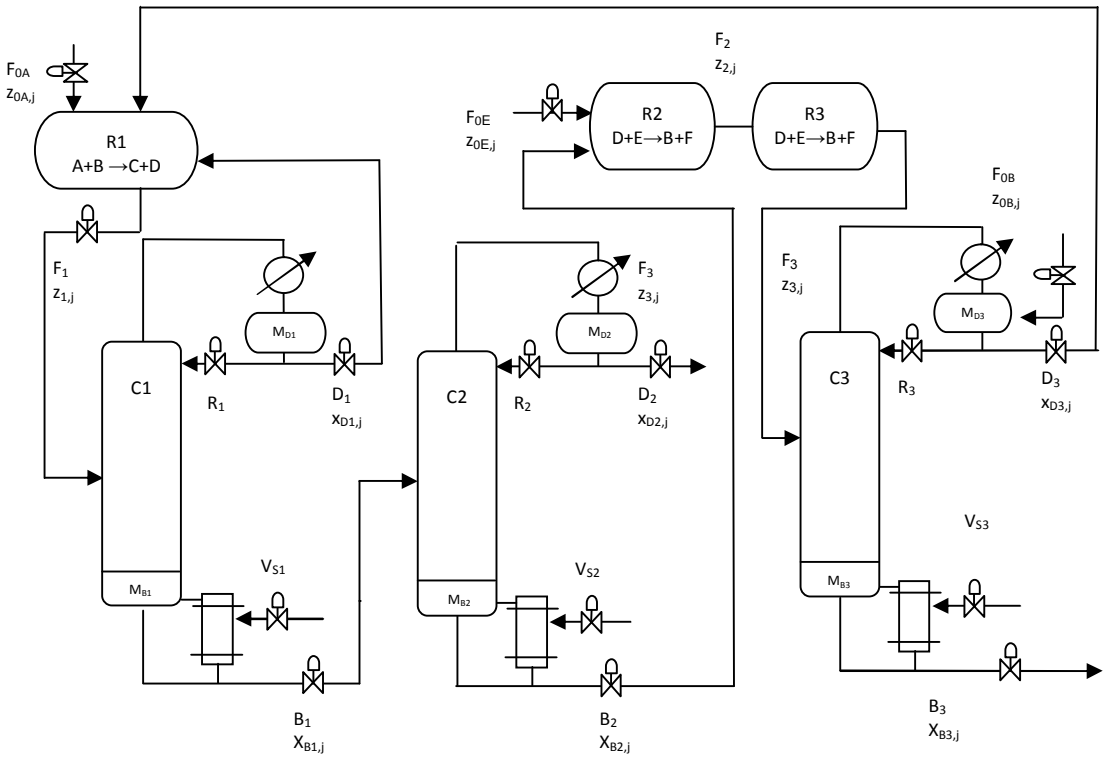

Figure 3.1 : Flowsheet of conventional multi-unit reactor/seperator/recycle system.

First reaction occurring in an isothermal CSTR produces one of the final products, C and one of the reactants of the second reaction steps, D.

$$A + B \rightarrow C + D \tag{3.1}$$

Second reaction which takes place in second reactor to produce the other final product, F and one of the reactants of the first reaction step, B.

$$D + E \rightarrow B + F \tag{3.2}$$

Reaction systems are irreversible, so there are only forward specific rate constants given by Arrhenius Law,

$$k = a_F \times e^{-Ef/RT} \tag{3.3}$$

The rate law is based on concentrations in mole fractions and liquid holdups in kmol. The first reaction rate is specified as 0.00278 kmol s^{-1} kmol $^{-1}$ at 366 K, while the second reaction rate is specified as 0.0139 kmol s^{-1} kmol $^{-1}$ at the same temperature and these parameters are given in Table 3.1.

Table 3.1 : Kinetic and physical parameters for ideal process.

Parameter		Value
Activation energy of reaction, E_f	cal / mol	30,000
Specific reaction rate 366 K		
k_1	(kmol)/(s kmol)	0,01389
k_2	(kmol)/(s kmol)	0,0028
Average heat of reaction, λ	cal / mol	10,000
Average heat of vaporization, ΔH_v,	cal / mol	6944
Molecular weight of the mixture , M_w	G / mol	50
Ideal gas constant , R,	cal / (mol K)	1,987

Ideal vapor-liquid equilibrium is assumed with constant volatilities. The relative volatilities of components are $\alpha_A > \alpha_B > \alpha_C > \alpha_D > \alpha_E > \alpha_F$, respectively. The vapor-liquid equilibrium parameters are taken from the literature [4] and given in Table 3.2.

Table 3.2 : Vapor pressure constants for ideal process.

Constants *	A	B	C	D	E	F
A_{VP}	13,04	12,75	12,34	11,65	11,14	10,96
B_{VP}	3862	3862	3862	3862	3862	3862
Relative volatilities	8	6	4	2	1.2	1

* $\ln P^S_J = A_{VP,J} - B_{VP,J}/T$ with temperature in K and vapor pressure in bar

To carry out the first reaction, fresh feed stream F_{0A} and component B which exists in recycle streams of D_1 and D_3 are fed in a continous stirred tank reactor (CSTR) that has an holdup of V_R. Since a complete one-pass conversion cannot be achived in this CSTR, its effluent contains a multi-component mixture.

This mixture is fed into first distillation column (C1) to separate the unreactanted reactants A and B from the products and they are recycled back to the reactor with a specific amount of product impurities to increase the yield. Bottoms stream of the first column is fed to the second distillation column (C2) to seperate the light product C from the heavy mixture which contains mostly component D. To achieve the second reaction, bottoms stream of this second distillation column and fresh feed of pure reactant E are fed into the second CSTR. Here, product B and F occur from the reactant component E and D. Then, multicomponent mixture of second CSTR are fed to the third conventional distillation column. Thus, product F with desired purity is removed from the bottom stream of the column and distillate stream D_3 with specific amount of component B is left from the distillate stream of the colum. And, this distillate streams D_3 which contains mostly component B is recycled back to the first CSTR to achieve the first reaction, as it is mentinod above.

As it is seen, components B and D are intermediates and exist ideally only within the process and any losses of these intermediate components must be accounted for both steady state design and in the plantwide control system. The losses of either intermadiate component occurs because it is impossible to obtain absolutely pure products from the columns and also it is probable to unbalance the two reaction sections by disturbances and changed operating conditions. Therefore, one of the important features of the plantwide control structure is based on the makeup and purge of the intermediate components. Because, there is a need for a make up or purge stream to satify the material balance of the entire plant. Hence, a pure make-up stream F_{0B} and makeup or purge stream of F_{0D} is essential to isolate the two reaction sections. In steady-state design**,** the pure makeup stream F_{0B} is added the to the first reactor while makeup stream F_{0B} enter the process from the reflux drum of the third distillation column in dynamic simulation.

In this process, combining the second reaction step and the third distillation column into a reactive distillation column is possible because the chemistry and volatilities are suitable. Herewith, the second reaction step and seperation occur simultaneously

in the RD column. By elimination of two reactors in series, the new process consists of a reactor, two distillation columns, one reactive distillation column and two recycle streams and as illustrated in Figure 3.2.

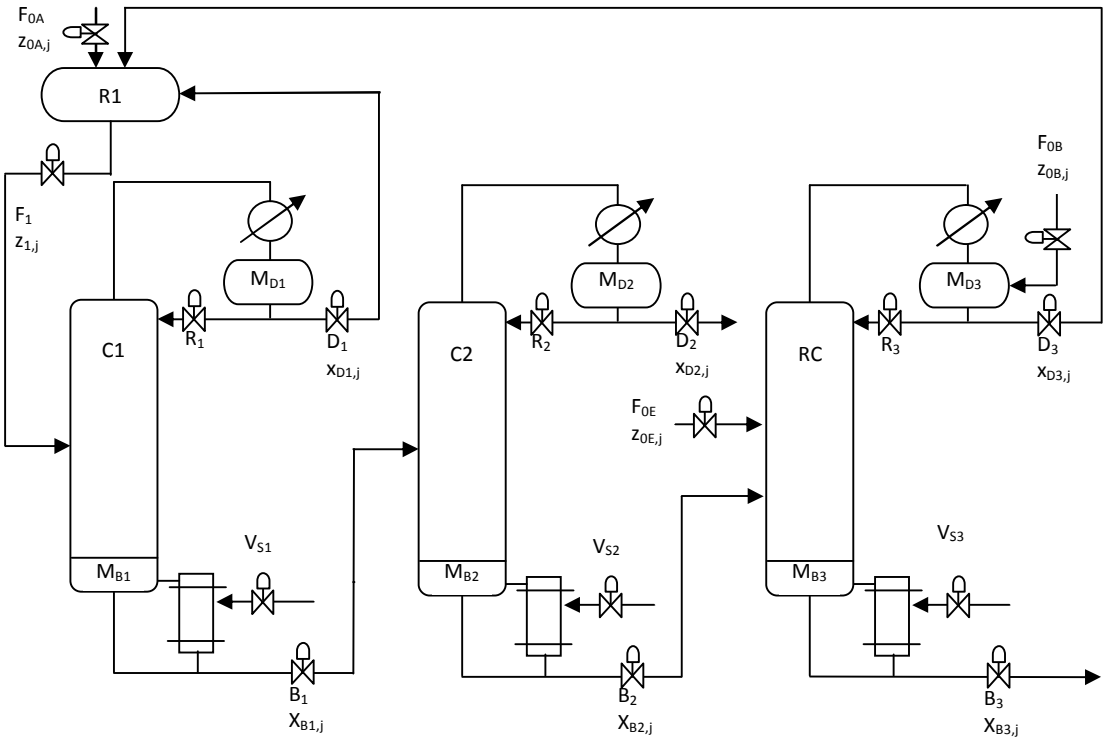

Figure 3.2 : Flowsheet of the RD process.

3.2 Assumptions and Specifications

Equimolal overflow is assumed in conventional distillation columns. According to this assumption, there is no need for energy and total mass balances on the trays during the steady state calculations. It means that vapor and liquid flow through the column are constant. Other assumptions for the conventional columns are the negligible vapor holdup, theoretical trays, total condensers and partial reboilers. Specifications for the steady state calculations of the entire process are given below:

i. It is convenient to set the amounts of components B, D, and E that leaving the process in the product streams. The amount of D in the product stream D_2 is constant at 0.063 mol/s, while the amount of E and D in the bottom stream B_3 is constant at 0.013 mol/s for each.

ii. Net production rate is set by fixing the fresh feed flow rate of F_{0A} at 12.6826 mol/s. Material balance of the process is achieved by a make-up stream of F_{0B} at 0.063 mol/s.

iii. Minimum reflux ratio RR_{min} is calculated using Underwood equation. Reflux ratio RR is 1.2 times bigger than the its minimum value.

iv. The number of stages N_T is twice the minimum number of stages N_{Tmin} that is calculated using Fenske equation.

v. Kirkbride's method is used to find the optimal feed tray location, N_F.

3.3 Steady- State Design of Reactive Distillation Columns

The column consists of three zones which are the stripping, reactive and rectifying sections starting from bottom with the N_S, N_{RX}, N_R tray, respectively. Reactant streams are fed into reactive zone. Since the location of the feeds entering the reactive zone is determined by considering the relative volatilities of the reactants, the heavy reactant E is fed from top of the reactive zone, while bottom stream of the second column that contains mostly D is fed to the bottom tray of the reactive zone. For the same reason, light by-product B leaves from the distillate and heavy product F is removed from the bottoms of the column.

RD columns can be represented by a set of algebraic and non-linear differential equations describing the physical and chemical properties of the studied process. To find a steady state design, number of design variables is reduced by the following assumptions and specifications:

i. Design objective is to obtain the product F with a purity of 0.9981

ii. Reflux and two fresh feed streams are saturated liquids.

iii. Equimolal overflow is assumed in the rectifying and stripping section.

iv. The holdups are constant on reactive trays at 1000 moles.

v. Pressure drops in the column are neglected.

In the literature, the development and application of the equilibrium stage models for conventional distillation column have been widely emphasized. The simulation of the RD columns is made standart MESH equations extented with chemical reactions.

The relaxation method is a reliable to solve this large set of equations [15]. It is used to calculate mole fractions and temperature profiles through the column. This is done by using the equilibrium stage model equations in an unsteady-state form and integrating them numerically till a steady-state solution is achived. Here, the liquid holdups on the trays are assumed constant. The net reaction rate $R_{j,i}$ (mol/s), for component i on tray j in the reactive zone can be expressed in terms of mole fractions ($x_{j,i}$) and the kinetic holdups M_j (mol) and given by,

$$R_{j,i} = M_j k_j x_{j,D} x_{j,E} \tag{3.4}$$

The kinetic holdup represents the molar amount of catalyst installed on reactive stage. The specific reaction rate on tray j is given by Arrhenius law,

$$k_{F_j} = a_F e^{-Ef/RT_j} \tag{3.5}$$

Because of the equimolal overflow the assumption, steady-state vapor and liquid rates are constant through the stripping and rectifying sections. But the presence of the exothermic reaction causes a change in these rates through the reactive zone. In that section, the heat of reaction vaporizes some of the liquid on each tray. Hence, the vapor rate increases up and liquid rate decreases down through the reactive zone.

$$V_j = V_{j-1} - \frac{\lambda}{\Delta H_V} R_j \tag{3.6}$$

$$L_j = L_{j+1} + \frac{\lambda}{\Delta H_V} R_j \tag{3.7}$$

where λ is the heat of reaction and ΔH_V is the latent heat of vaporization.

The total and component mass balance equations for each column section can be described as,

Reflux Drum:

$$\frac{dM_D}{dt} = V_{NT} - D(1+RR) + F_{0B} \tag{3.8}$$

$$\frac{dx_{NT,i}}{dt} = \frac{\left[V_{NT} y_{NT,i} - D(1+RR)x_{D,i} + F_{0B} z_{0B}\right]}{M_D} \quad \textbf{(3.9)}$$

Trays through the column:

$$\frac{dM_j}{dt} = L_{j+1} + V_{j-1} - L_j - V_j + F_j \quad \textbf{(3.10)}$$

$$\frac{dx_{j,i}}{dt} = \frac{\left[L_{j+1}x_{j+1,i} + V_{j-1}y_{j-1,i} - L_j, x_{j,i} - V_j y_{j,i} + R_{j,i} + F_j z_{j,i}\right]}{M_j} \quad \textbf{(3.11)}$$

(3.10) and **(3.11)** given in the above illustrate the general expression for the material balance around the each tray. $R_{j,i}$ term is eleminated if the reaction does not take place on the tray. Samely, F_j term is equal to zero throught the column except the trays where the fresh streams are fed.

Column Base:

$$\frac{dM_B}{dt} = L_1 - B - V_S \quad \textbf{(3.12)}$$

$$\frac{dx_{B,i}}{dt} = \frac{\left[L_1 x_{1,i} - B x_{B,i} - V_S y_{B,j}\right]}{M_B} \quad \textbf{(3.13)}$$

According to Rault's Law, the vapor pressure of the pure component multiplied by its mole fraction is equal to the vapor pressure of a component in an ideal solution, and the total pressure of the solution is the sum of the vapor pressures of the individual components. Temperature T_j and vapor compositions $y_{j,i}$ on the tray can be calculated by Newton- Raphson iterative converge method for a given pressure P and liquid compositions $x_{j,i}$,

$$P = \sum_{i=1}^{NC} x_{j,i} P^S{}_{j,i}(T) \quad \textbf{(3.14)}$$

$$y_{j,i} = \frac{P^S{}_{j,i} x_{j,i}}{P} \quad \textbf{(3.15)}$$

Following steps are used in the design procedure of reactive distillation column;

i. Fix the column pressure, the number of trays in each section and the flowrates of the feed and product streams .

ii. Manipulate the vapor boilup V_S with a P-only controller to control the level in the column base.

iii. Manipulate the reflux flow rate R with a PI controller to achieve the desired compostion of product F in the bottoms.

iv. By using bubble-point calculations with **(3.14)** and **(3.15),** compute the temperatures and vapor compositions on each tray.

v. Compute the reaction rates by using **(3.4)** and **(3.5).**

vi. Compute the vapor and liquid rates in the reactive zone using **(3.6)** and **(3.7).**

vii. Evaluate the time derivatives of component material balances using **(3.8)**-**(3.13)**.

viii. Integrate all ODEs using Euler algorithm.

ix. Repeat these steps till the desired steady state solution is found.

3.4 Sizing and Economic Basis

Total annual cost (TAC) is calculated from the sums the energy and capital costs of the system assuming a payback period (β pay) of 3 years for capital cost. It is defined as,

$$TAC = Energy\ Cost + \frac{Capital\ Investment}{\beta_{pay}} \qquad \textbf{(3.16)}$$

The economic parameters and basis of the equipment sizing calculations are given in Table 3.3. The capital costs of individual equipments and the energy cost are calculated using the following equations [28].

$$Column\ \cos t = 17640\ D_c^{1.066} L_c^{0.802} \qquad \textbf{(3.17)}$$

$$Tray\ \cos t = 229\ D_c^{1.55}\ N_T \qquad \textbf{(3.18)}$$

$$Heat \text{ exchanger cost} = 7296\ (A_R^{0.65} + A_C^{0.65}) \quad \textbf{(3.19)}$$

$$Energy \text{ cost} = 0.6206\ \Delta H_V V_S \quad \textbf{(3.20)}$$

Following set of assumptions and guidelines are used for terms in the TAC ;

The diameter of reactor is calculated from,

$$D_R = (0.00003977 V_R)^{0.3333} \quad \textbf{(3.21)}$$

The reactor length is assumed to be twice of diameter ,

$$L_R = 2D_R \quad \textbf{(3.22)}$$

The diameter of column is calculated from,

$$D_C = 1.735 \times 10^{-2} \left(\frac{M_W T}{P}\right)^{0.25} V_{NT}^{0.5} \quad \textbf{(3.23)}$$

The column height is calcualted assuming a 0.61m (2-ft) tray sapcing and allowing 20% more height for base-level volume.

$$L_C = 0.73152 N_T \quad \textbf{(3.24)}$$

The heat-transfer areas of reboiler and condenser are calculated using the steady-state vapor flow rates and heat of vaporization.

$$A_R = 0.0042 \frac{V_S \Delta H_V}{U_R \Delta T_R} \quad \textbf{(3.25)}$$

$$A_C = 0.0042 \frac{V_{NT} \Delta H_V}{U_C \Delta T_c} \quad \textbf{(3.26)}$$

The vapor flow rate in the top tray V_{NT} is different than the vapor flow rate in the reboiler V_S because of the liquid vaporized through the reactive section. Thus, the heat transfer areas of the reboiler and the condenser are calculated using two different vapor flow rates.

Lastly, the process is assumed to be equally reliable and operates for 365 days per year.

Table 3.3 : Sizing and economic basis.

Parameter	Value	
Reboiler		
heat transfer coefficient, $U_{R,}$	0.5678	kJ / (s.K.m^2)
Temperature difference, $T_{R,}$	34.8	K
Condenser		
Heat transfer coefficient, U_C	0.8517	kJ / (s.K.m^2)
Temperature difference, $T_{C,}$	13.9	K
Energy cost	4.740	\$ / 10^6 kJ
Payback period, $\beta_{pay,}$	3.0	Year

4. FUNDAMENTALS OF DYNAMIC CONTROL

The dynamic models of reactor, RD column and conventional distillation columns are given in this section. This part presents the fundamentals of control work required for the entire plant. Tuning procedure of controllers, use of steepest slope criteria, sensitivity analysis and the use of singular value decomposition method for controlled variable selection are also defined in this part.

4.1. Dynamic Models

4.1.1. Reactor

The dynamic model of the reactor is derived by a set of ordinary differential equations: total and component mass balances for components.

$$\frac{dV_R}{dt} = F0_A + D_1 + D_3 - F_1 z_{1,i} \tag{4.1}$$

$$\frac{d(V_R z_i)}{dt} = F0_A z_{0A,i} + D_1 x_{D1,i} + D_3 x_{D3,i} - F_1 z_{1,i} + v_i V_R k_F z_{1,A} z_{1,B} \tag{4.2}$$

4.1.2 Columns

Equimolal overflow assumption is valid for both conventional columns in the process. Hence, there is no requirement for energy equations for the trays. Vapor and liquid stream flows are constant along the conventional columns. Because of the negligible vapor holdup, the vapor rate through the column does not change in a dynamic column. But, the liquid rates through the column depend on the fluid mechanics of the tray. Conventional distillation columns of the process have multicomponent single feed streams and this streams are fed into tray N_F. In RD column, reactant streams B_2 and pure fresh stream of E, F_{0E} are fed into reactive zone where the location of the feeds are the N_{S+1} and N_R trays, respectively. Columns have

total condensers and reflux drums with a liquid molar holdup M_D. They have partial reboilers with a base molar holdups is M_B.

From the known liquid compositions and pressure, the temperature and vapor compositions of each tray are calculated using Newton-Raphson method. In dynamic similation, liquid flowrates are calculated by using the linearized version of the Francis weir formula. In this formula, M_j is the liquid holdup of the tray, L_j is the liquid flow rate leaving the tray and β is the hydraulic time constant.

$$L_j = L_{ss,j} + \frac{M_j - M_{ss,j}}{\beta} \tag{4.3}$$

The differential equations defining different sections of the columns are as follow:

Reflux Drum:

$$\frac{dM_D}{dt} = V_{NT} - D(1+RR) + F_{0B} \tag{4.4}$$

$$\frac{dx_{NT,i}}{dt} = \frac{\left[V_{NT}y_{NT,i} - D(1+RR)x_{D,i} + F_{0B}z_{0B}\right]}{M_D} \tag{4.5}$$

(4.4) and **(4.5)**, F_{0B} term is equal to the zero for conventional columns.

Trays through the column:

$$\frac{dM_j}{dt} = L_{j+1} + V_{j-1} - L_j - V_j + F_j \tag{4.6}$$

$$\frac{dx_{j,i}}{dt} = \frac{\left[L_{j+1}x_{j+1,i} + V_{j-1}y_{j-1,i} - L_j, x_{j,i} - V_j y_{j,i} + R_{j,i} + F_j z_{j,i}\right]}{M_j} \tag{4.7}$$

$R_{j,i}$ term is neglected in the conventional columns and also it is eliminated if the reaction does not take place in the tray of RD column. F_j term is equal to zero throught the columns except the trays where the fresh streams are fed.

As it is mentioned in the section 3.1, there is a make up or purge stream F_{0D} in the bottom of second column while an other make up stream F_{0B} is used on the reflux drum of RD to supply the material balance of the process.

Column Base :

$$\frac{dM_B}{dt} = L_1 - B - V_S + F_{0D} \tag{4.8}$$

$$\frac{d(x_{B,i}M_B)}{dt} = L_1 x_{1,i} - Bx_{B,i} - V_S y_{B,i} + F_{0D} z_{0D} \tag{4.9}$$

F_{0D} term in **(4.8)** and **(4.9)**, only exist in the second conventional distillation column.

Steady-state initial condition of heuristic design is taken from the motivated study [4]. In dynamic simulation, steady-state initial condition of RD column is obtained getting help from the relaxation method and the rigorous steady-state Wang-Henke method is used to find initial condition for conventional columns.

The tridiagonal matrix method that is explored by Wang and Henke is a fast and exact technique for computing the component and total flow rates. To create the tridiagonal matrix, the total material balance equations are used. In these equations, the tridiagonal matrix coefficients is occurred by using the vapor and liquid flow rates. Then, coefficients of the matrix are calculated. Herewith, vapor and liquid flow rates are found. To find the stage temperatures, the bubble-point (BP) equations are solved. Component and flow rates are calculated by updating these temperatures till the temperatures are not changed between the iterations.

4.2 Controller Tuning

In this work, temperature, composition control loops are SISO structures with PI controllers. Since reactor level impacts the reaction rates, tight control of this level is required. Hence, it is required to use PI controller for reactor level. P-only and split ranged level controllers are used for other levels.

Multi-loop SISO controllers (single input-single output) is explained as one controlled variable paired with one manipulated variable.

In this study, negative feedback is used to design controller because negative feedback systems are more stable than positive feedback systems and this also makes systems more proof to random variations in component values and inputs. Output of a process might be a composition, a tray temperature or a liquid level.

Figure 4.1 shows a block diagram of a control system which is called a feedback system. A feedback system is a synonym with a closed-loop system. In closed-loop system, the measured value of the controlled variable (T_M) is fed back to the comparator. In here, the desired variable of the controlled variable is a set point which is shown with the T_R. The load might lead to change of controlled variable of the process. Then, the measured output variable (T_M) is compared with the set point (T_R).

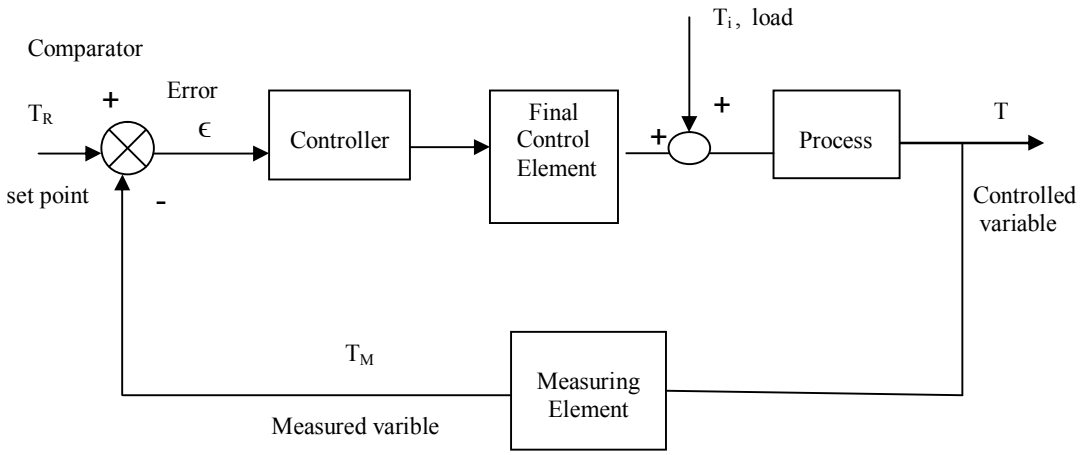

Figure 4.1 : Block diagram of a simple control system.

Difference between the measured variable and set point occurs and this is called as a control error. This error enters to the controller as a signal. According to this signal, the controller output is calculated. Thence, the manipulated variable is adjusted by a final control element.

The P-only controller is defined by the following equation,

$$u(t) = K_c e(t) \tag{4.10}$$

The conventional linear PI controllers are used with the equation,

$$u(t) = K_c \left[e(t) + \frac{1}{\tau_I} \int e(t) d(t) \right] \tag{4.11}$$

In here, u is the control signal, e (T_R-T_M) is the control error, K_c is the controller gain, τ_I is the integral (or reset) time [51].

The other gains are 1 for all P-only controllers. All temperature loops have two first-order measurement lags of 60-second while 3 minutes dead-time is used for the composition analyzer.

Relay-feedback method is used to tune these control loops. This method has been presented by Astrom and Hagglund (1984) and developed as an attractive alternative to the continous cycling method. In this method, simple test is used to determine K_{cu} and P_u As shown in Figure 4.2 [52].

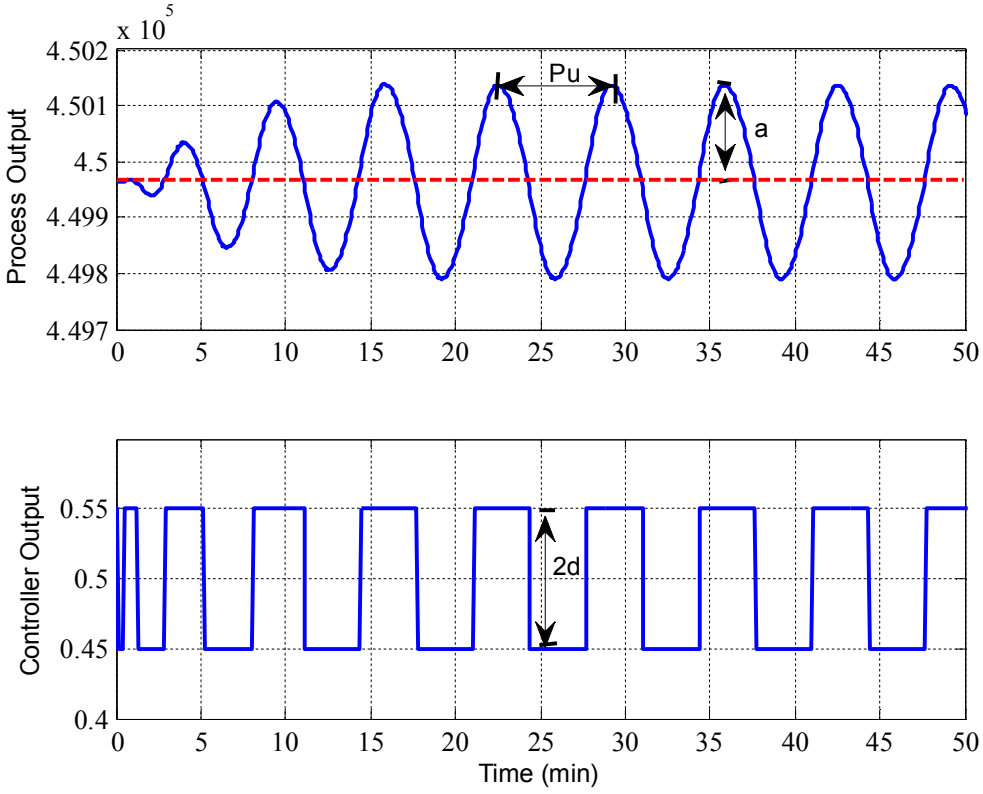

Figure 4.2 : Typical relay feedback response.

$$K_{cu} = \frac{4d}{\pi a} \tag{4.12}$$

where a is the measured amplitude of the process oscillation and d is the relay amplitude. These parameters are enough to calculate the controller settings. It is known that Ziegler-Nichols tuning equations are to aggressive for many chemical. Thence Tyreus-Luyben tuning method is used for all PI control loops in this study [52].

$$K_c = \frac{K_u}{3.2} \tag{4.13}$$

$$\tau_i = 2.2P_u \tag{4.14}$$

To make controller gains dimensionless, temperature transmitter spans are defined as 50K and composition transmitter spans are determined as 0.5 mol fraction for control loops where reaction takes place. For other composition loops, the span is set as 0.1 mol fraction. All the valves are designed to be half open at steady-state.

4.2.1 Singular value decomposition

Due to the fact that presence of strong interactions in the columns, choosing of the appropriate controlled variables cannot be find easily. Therefore, in two-temperature controlled distillation column, fundamental issue is the selection of tray temperature that must be controlled. So, the singular value decomposition method (SVD) is used to determine the most sensitive trays as controlled variable. In this method, the gain matrix between the inputs and the outputs is calculated numerically from the rigorous steady-state simulation.

$$K_P = U\Sigma V^T \tag{4.15}$$

Here, the steady-state gains K_P is the product of three matrices: a U matrix, a Σ diagonal matrix, and a V^T matrix. First, very small changes are made in the inputs to obtain linearized gains of the process. Then, decomposition of the gain matrix K_P give the component matrix of its. Here, the biggest component of U matrix give the most sensitive process output (controlled variable) to the input changes (manipulated variable) applied [53].

4.3 Disturbance

The effectiveness of control structures studied in this work is demonstrated by using dynamic simulations and subjecting the processes to changes on production-rate handles, reaction temperature in CSTR by changing the specific reaction rate (k_1) and feed compositions.

5. RESULTS AND DISCUSSION

5.1 Results of Steady-State Design

At the end of the design calculations, it is seen that two reaction series and one distillation column in the conventional multi-unit process is successfully combined into an appropriate size of RD unit. Also, there is a significant difference in capital costs of conventional multi-unit reactor/separator/recycle system and process simplified with a RD column. Detailed design results are given in Table 5.1.

Table 5.1 : Summary of Design.

C1		C2		C3	
D_1[a]	10,05	D_2[a]	12,97	D_3[a]	17,78
R_1[a]	42,94	R_2[a]	36,16	R_3[a]	77,95
RR_1	4,27	RR_2	2,79	RR_3	4,39
B_1[a]	30,46	B_2[a]	17,41	B_3[a]	12,46
V_1[a]	52,99	V_2[a]	49,12	V_3[a]	77,43
N_1	30	N_2	30	N_3	30
N_{F1}	15	N_{F2}	15	$N_{F31,2}$	11 15
$x_{B1,i(i=A,B,C,D,E,F)}$	0,0002	$x_{B2,I}$	0,0000	$x_{B3,I}$	0,0000
	0,0052		0,0000		0,0000
	0,4182		0,0037		0,0000
	0,5763		0,9962		0,0019
	0,0000		0,0000		0,0000
	0,0000		0,0000		0,9981
$x_{D1,i}$	0,7569	$x_{D2,i}$	0,0005	$x_{D3,I}$	0,0000
	0,2018		0,0122		0,7218
	0,0413		0,9776		0,0037
	0,0000		0,0096		0,2745
	0,0000		0,0000		0,0000
	0,0000		0,0000		0,0000
z_{F1}	0,1879				
	0,0540				
	0,3247	F_{0A}[a]	12,68	V_R[b]	450.10^3
	0,4333	F_{0B}[a]	0,39	Energy Cost[c]	782.10^3
	0,0000	F_{0D}[a]	0,09	Capital Cost[c]	2334.10^3
	0,0000	F_{0E}[a]	12,44	TAC[c]	1560.10^3

[a] Unit : mol/s , [b] Unit : mol , [c] Unit : $ / year

Using the modified process, total annual cost is decreased significantly. Capital cost of the modified design are calculated as 2334.10^3 $/year while capital cost of the conventional process is 3262.10^3 $/year. But, energy cost of the RD process is found 782.10^3 $/year, while energy costs of the conventional flowsheet is 589.10^3 $/year.

At the end, the total annual cost is computed as 1560.10^3 \$/year for modified design, while it is 1677.10^3 \$ /year for conventional multi-unit process. The column molar holdups and hydraulic time constants the trays are listed in Table 5.2. These values are used in the dynamic simulation. Holdups for the base of second column (M_B) and reflux drum of RD (M_D) are set 20 min on the basis of inflow rates, while the other bases and drums are set at 5 min.

Table 5.2 : Hydraulic time constant and molar holdups for dynamic simulations.

Parameters	C1	C2	RD
β_S [a]	3,07	3,55	2,63
β_{RXN} [a]			2,78
β_R [a]	3,75	4,36	2,93
M_D [b]	16000	15000	115000
M_S [b]	800	900	400
M_{RXN} [b]			1000
M_R [b]	650	775	400
M_B [b]	25000	80000	27000

[a] Unit : s , [b] Unit : mol

5.2 Results of Dynamic Simulation

The control objective in this study is to maintain the purities of the product C in the distillate of the second column and the product F in the bottoms of the reactive column at their desired set points in the face of different disturbances.

To design a control structure for the entire plant, first the control degrees of freedom has to be defined. This is the number of variables that can be controlled in a process. Since the control degress of freedom is equal to the number of control valves, this degrees of freedom can be simply found for a complex multi-unit process [54]. There are 17 control valves in this proces. These are the valves for fresh feed streams (F_{0A}, F_{0B}, F_{0E}, F_{0D}), reactor effluent (F_1), vapor boilup (V_1, V_2, V_3), bottoms (B_1, B_2, B_3), reflux (R_1, R_2, R_3) and distillate (D_1, D_2, D_3) flow rates of each column as shown in the Figure 5.1. At least 9 variables must be controlled including two product purities and levels of the reactor, reflux drums and column bases.

The process is subjected to three disturbances to check the control structure: (1) step change in production rate handle (±20%), (2) step change in specific reaction rate k_1 in reactor (+50%) to change the reaction temperature and (3) step change in fresh

feed compostion z_{0A} (from 100%A to 80%A - 20%B and from 100%A to 90% A - 10%B).

5.2.1 Structures using composition controllers

5.2.1.1 Control structure CS1C

Control structure CS1C is given in Figure 5.1. In this structure, the production is set by controlling the flow rate of fresh feed of component A (F_{0A}). The reactor effluent (F_1) is manipulated to control the holdup of the reactor. The concentration of component B (z_{1B}) in the reactor is controlled by manipulating the recycle stream D_3. The base levels of all columns are controlled by bottoms flow rates. For conventional distillation columns (C1 and C2), distillate flow rates are manipulated to control the reflux drum levels, while a split-ranged controller on the reflux drum of reactive distillation column manipulates the make-up/purge stream F_{0B}. Reflux flow rates are flow controlled in all columns.

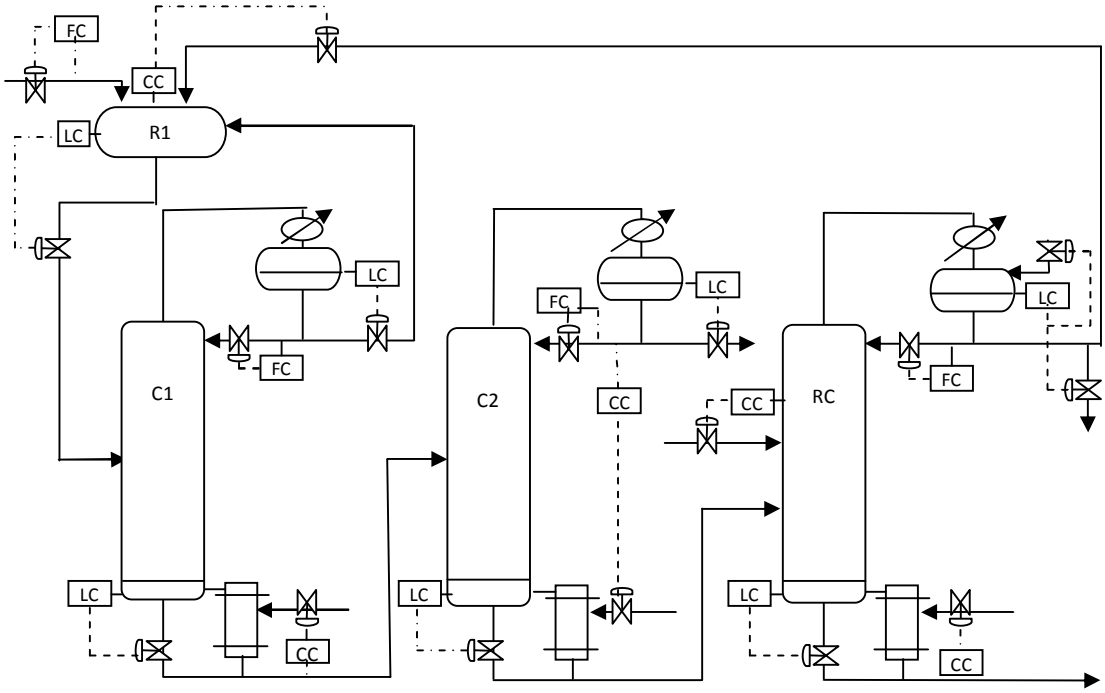

Figure 5.1 : Control Structure CS1C.

Composition of component E on the feed stage ($x_{2,E}$) is controlled by the fresh feed stream F_{0E} to set the stoichiometry of the reaction in reactive distillation column. The impurities of product streams ($x_{D2,D}$ and $x_{D3,D}$) are controlled by manipulating the vapor boilups of columns C2 and RD V_{S2} and V_{S3}, respectively. There is also

omposition controller for the concentration of component B ($x_{B1,B}$) in the bottoms of column C1. Table 5.3 presents the controller gains and reset times for CS1C.

Table 5.3 : Controller gains and reset times (min) for CS1C.

Control Loop	K_U	P_U[a]	K_c	τ_I[a]
z_{1B} - D_3	76,89	11,5	23,83	25,30
V_{R1} - F_1	324,57	6,67	100,62	14,67
x_{B1B} - D_3	3,63	19,75	1,13	43,45
x_{D2D} - V_2	1,83	35,33	0,57	77,73
X_{2E} - F_{0E}	8,95	6,17	2,77	13,57
x_{D3D} - V_{S3}	4,61	12,83	1,43	28,23

[a] Unit: min

Figure 5.2 shows the results for a +20% step change in production rate handle F_{0A}. In this control structure, the streams in both recycle loops are used for level control. Since none of these streams has a flow controller, a snowball growth produce large changes in recycle flow rates. The gradual increase of recycle flow rate D_3 until it saturates can be seen in the figure. Thus, it is observed that CS1C cannot handle this disturbance.

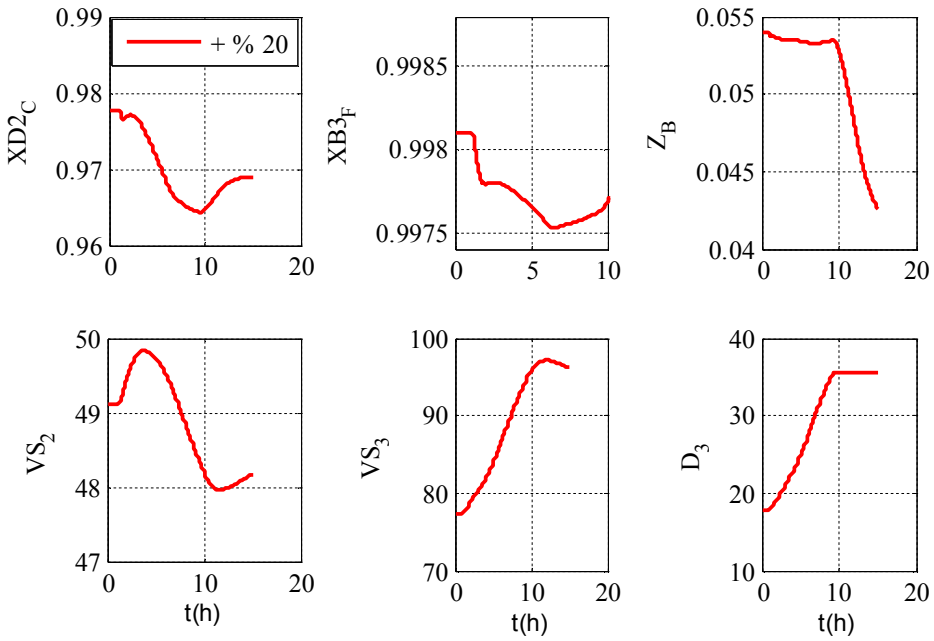

Figure 5.2 : + 20% step change in F_{0A} for CS1C.

5.2.1.2 Control structure CS2C

Figure 5.3 shows the control structure CS2C. In this case, the production rate is fixed by controlling the flow rate of fresh feed F_{0A}. Recycle stream D_3 is flow controlled

and adjusted to give a constant ratio with F_{0A}. However, there is not any composition controller for component B in the reactor. All other control loops of this structure are same with those of control structure CS1C. The controller gains and reset times for CS2C are given in Table 5.4.

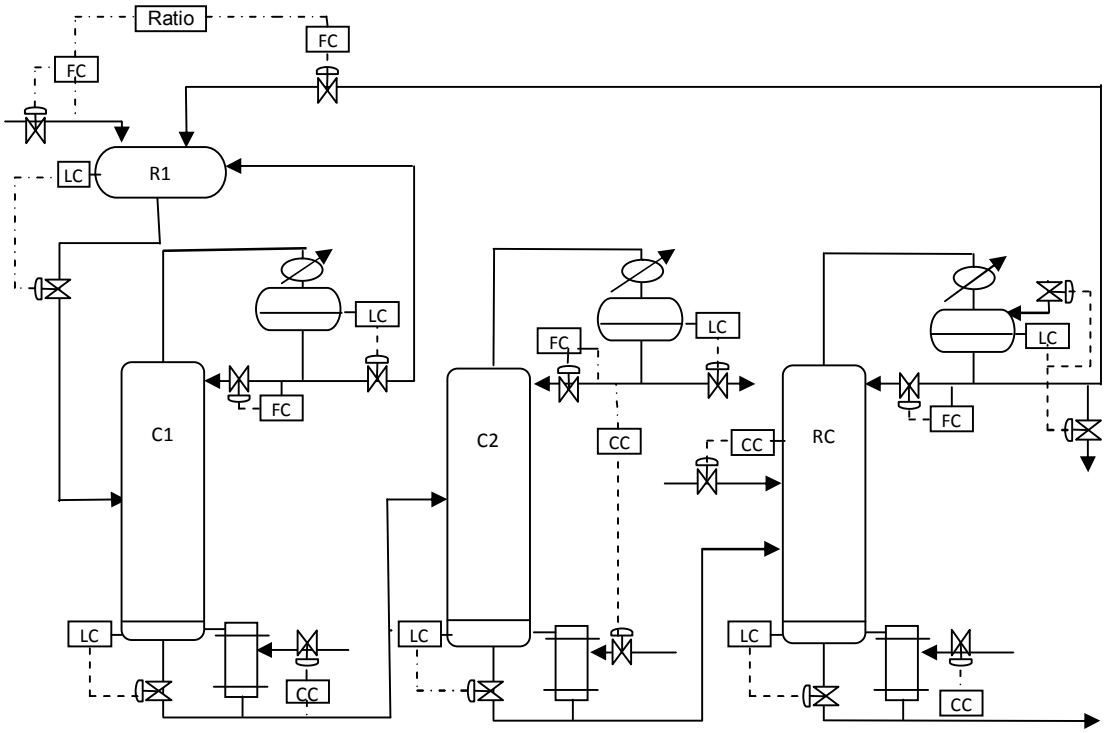

Figure 5.3 : Control Structure of CS2C.

Table 5.4 : Controller gains and reset times (min) for CS2C.

Control Loop	K_U	P_U[a]	K_c	τ_I[a]
V_{R1} - F_1	324, 57	6,67	100,62	14,67
x_{B1B} - V_{S1}	3,63	19,75	1,13	43,45
x_{D2D} - V_2	0,35	35,33	0,11	77,73
X_{2E} - F_{0E}	8,95	6,17	2,77	13,57
x_{D3D} - V_{S3}	4,61	12,83	1,43	28,23

[a] Unit: min

Figure 5.4 gives the results for a +20% step change in production rate handle F_{0A}. Since the reactant B is the intermediate component of the plant, controlling of this component in the reactor is the vital part of the plantwide control structure. It is seen that the ratio control does not help to regulate the inventory of component B without a composition controller in the reactor. The amount of components B in the reactor starts to decrease dramatically after the recycle flow rate D_3 saturates in about 10 hours. Thus, the product purity of D_2 cannot be maintained at its desired value.

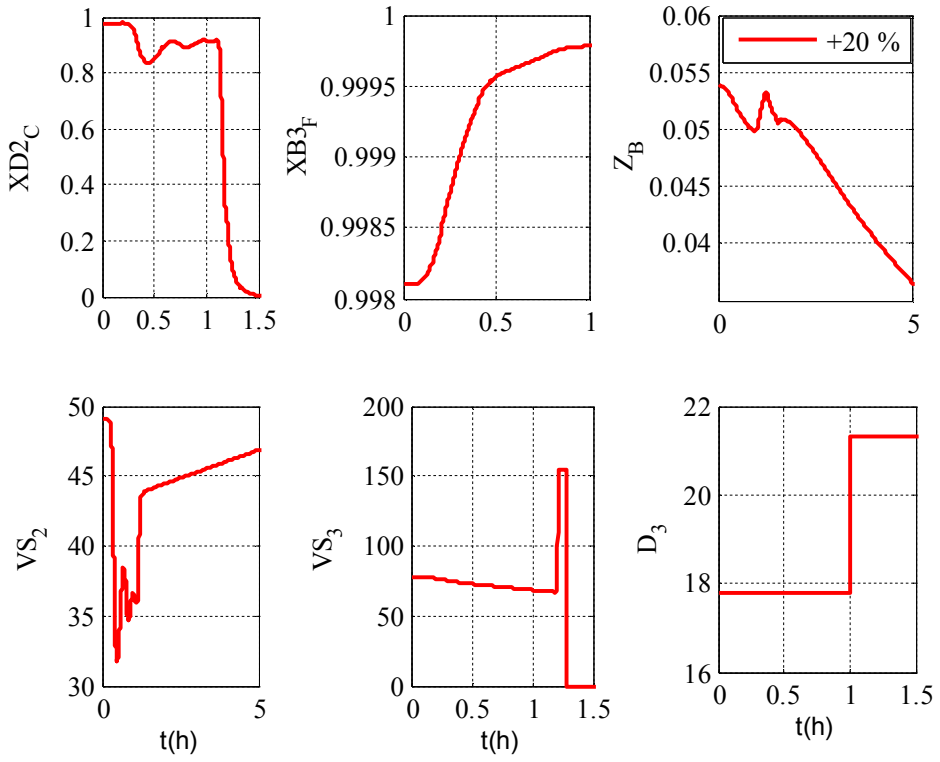

Figure 5.4 : + 20% step change in F_{0A} for CS2C.

5.2.1.3 Control structure CS3C

Control structure CS3C is given in Figure 5.5. The main difference of this structure is the production rate handle. In this case, the production rate is set by controlling the reactor effluent (F_1). Recycle stream D_3 is used to control the concentration of component B (z_{1B}) in the reactor. In addition, the holdup of the reactor is controlled by fresh feed stream of component A (F_{0A}). The rest of the control structure is same with that of CS1C. It should be noted that there is no direct handle on the production rate. The controller gains and reset times for CS2C are given in Table 5.5.

Table 5.5 : Controller gains and reset times (min) for CS3C.

Control Loop	K_U	P_U[a]	K_c	τ_I[a]
Z_{1B} - D_3	76,89	11,5	23,83	25,30
V_{R1} - F_{0A}	991, 99	6,67	307,52	14,67
x_{B1B} - V_{S1}	3,63	19,75	1,13	43,45
x_{D2D} - V_{S2}	0,35	35,33	0,11	77,73
X_{2E} - F_{0E}	8,95	6,17	2,77	13,57
x_{D3D} - V_{S3}	4,61	12,83	1,43	28,23

[a] Unit: min

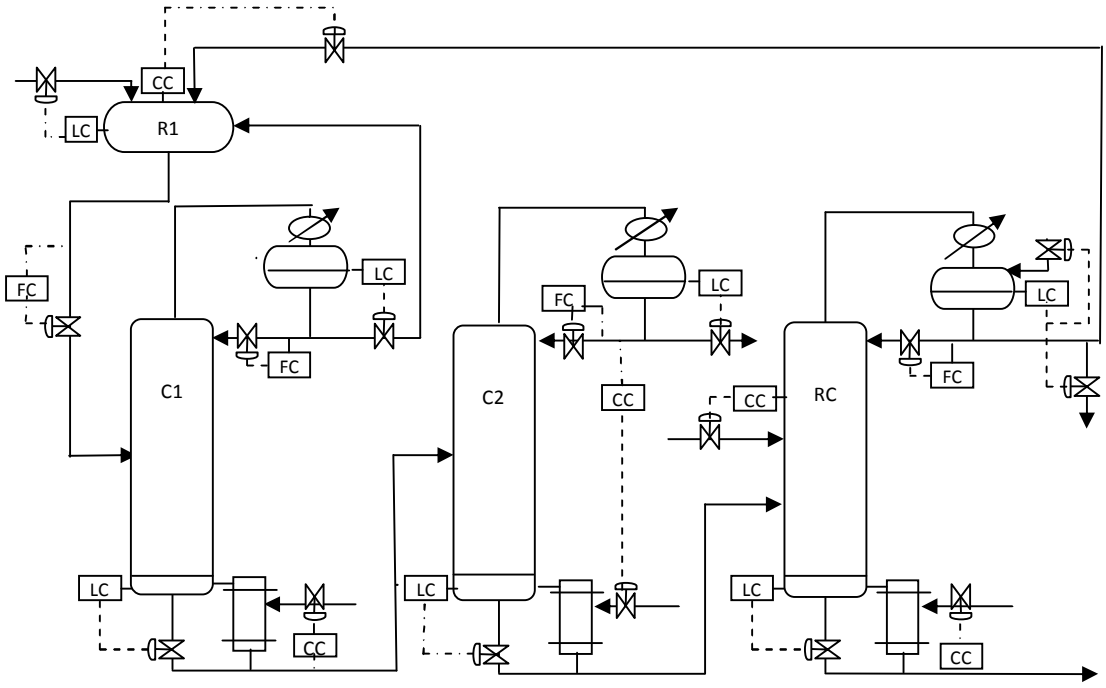

Figure 5.5 : Control Structure CS3C.

Figure 5.6 presents the response of CS3C for ±20% step changes in the production rate handle F_1. For the positive change in F_1, the purity of bottoms product $x_{B3,F}$ recovers back to its specified value. However, there is more of an offset in the distillate composition $x_{D2,C}$, but this small change in product purity is quite acceptable. The amount of vapor boilup slightly decreases in the second column, while there is a significant increase in the vapor boilup of the reactive column. The control performance for the negative change in F_1 is essentially the same observed for the positive disturbance.

Figure 5.7 illustrates the effects of an increase in k_1. This control structure successfully handles this large disturbance. Figure 5.8 shows what happens when the composition z_{0A} of the fresh feed F_{0A} is changes from pure A to a mixture of A and B. The increse in the amount of component B introduced by the fresh feed stream F_{0A} results in an increase of z_{1B}. Thus, there is a decrease in the recycle flow rate D_3. Although there is a small increase in the product purity of second column, the product purity in the bottoms of reactive column is fairly tight controlled. The responses of step change in feed composition z_{0A} is shown in the Figure 5.8. These disturbance changes are easily handled by CS3C.

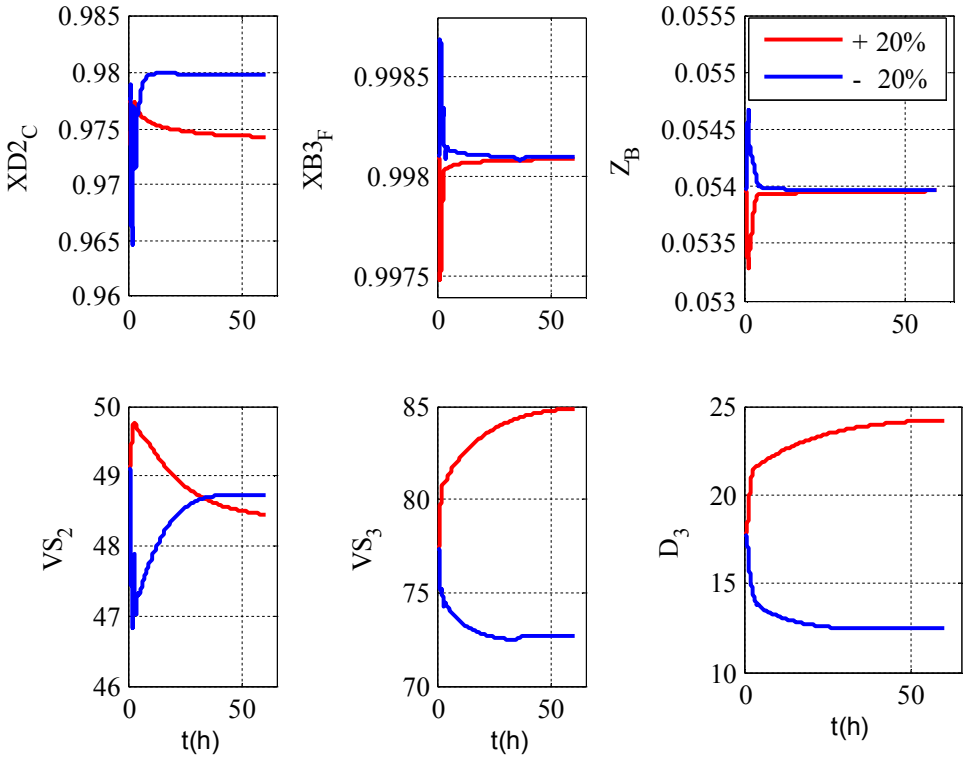

Figure 5.6 : ±20% step change in F_1 for CS3C.

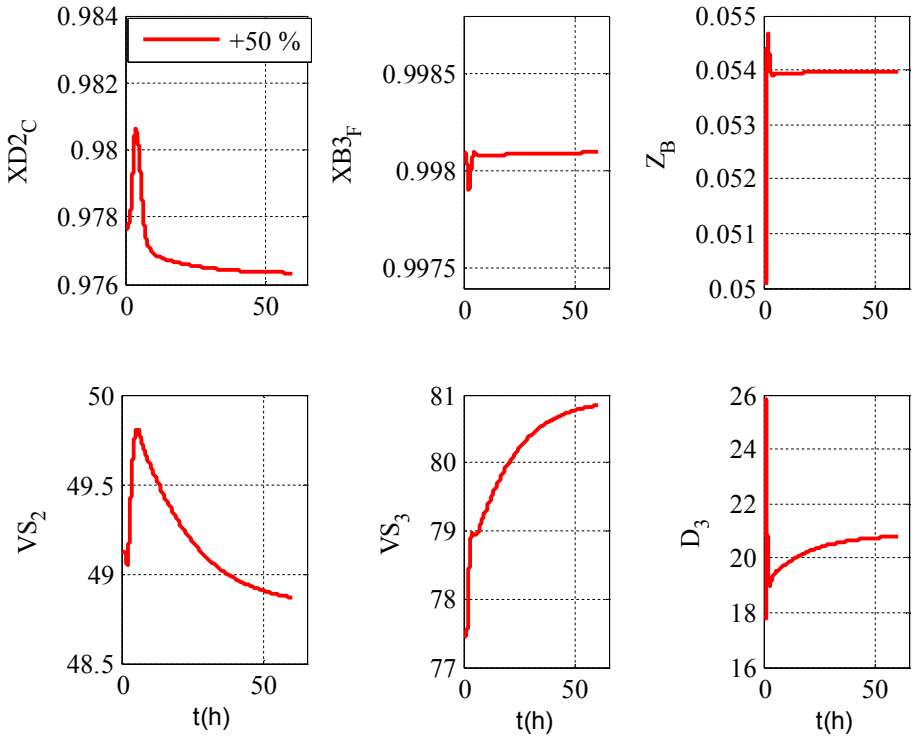

Figure 5.7 : +50% step change k_1 for CS3C.

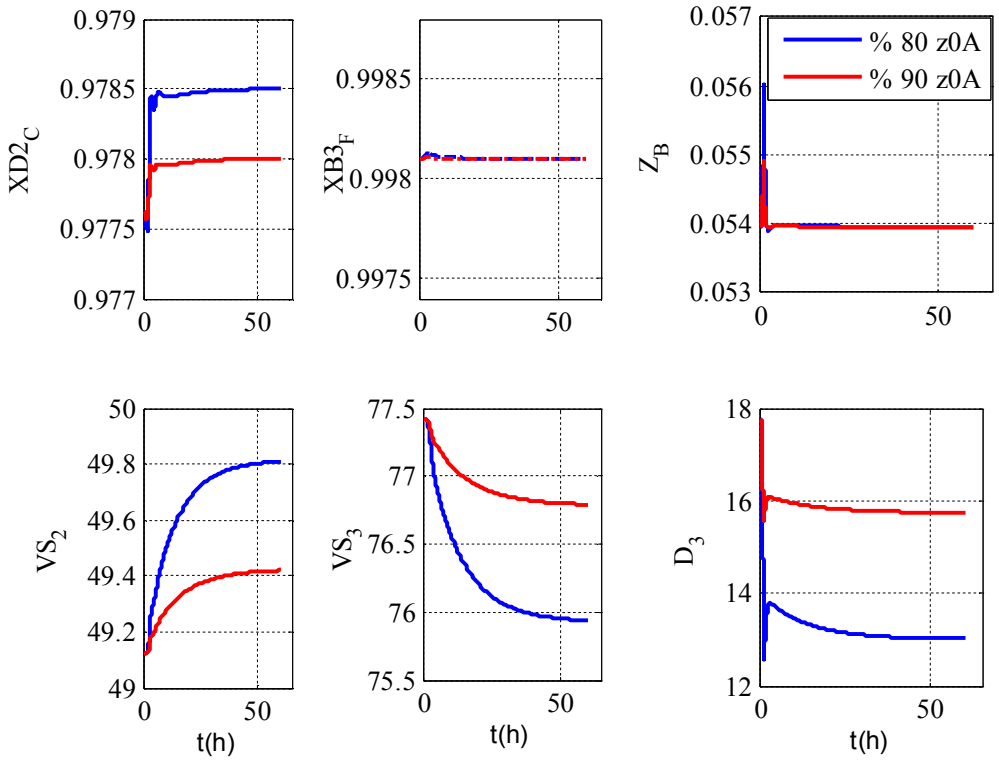

Figure 5.8 : Step change in fresh feed composition z_{0A} for CS3C.

In summary, control structure CS3C provides a stable base-level regulatory control for any type of disturbances. However, it requires a long settling time for both controlled and manipulated variables.

5.2.1.4 Control structure CS4C

Control structure CS4C is given in Figure 5.9. In this structure, the holdup of the reactor is controlled by fresh feed stream of component A (F_{0A}). Recycle stream D_3 is used to control the concentration of component B (z_{1B}) in the reactor. Although the control loops for reflux drum levels are same with those of the previous structures, there is a difference for the base level loop of the second column. In this case, a split-ranged controller is used on the base of column C2 with the make-up/purge stream F_{0D}. In this structure, there is no direct handle on the production rate. Reactor effluent (F_1) and feed to reactive column (F_R) streams are flow controlled. Thus, production rate can be changed by adjusting these flow rates. It means that there is a flow-controlled stream somewhere in each recycle loop. Table 5.6 presents the controller gains and reset times for CS4C.

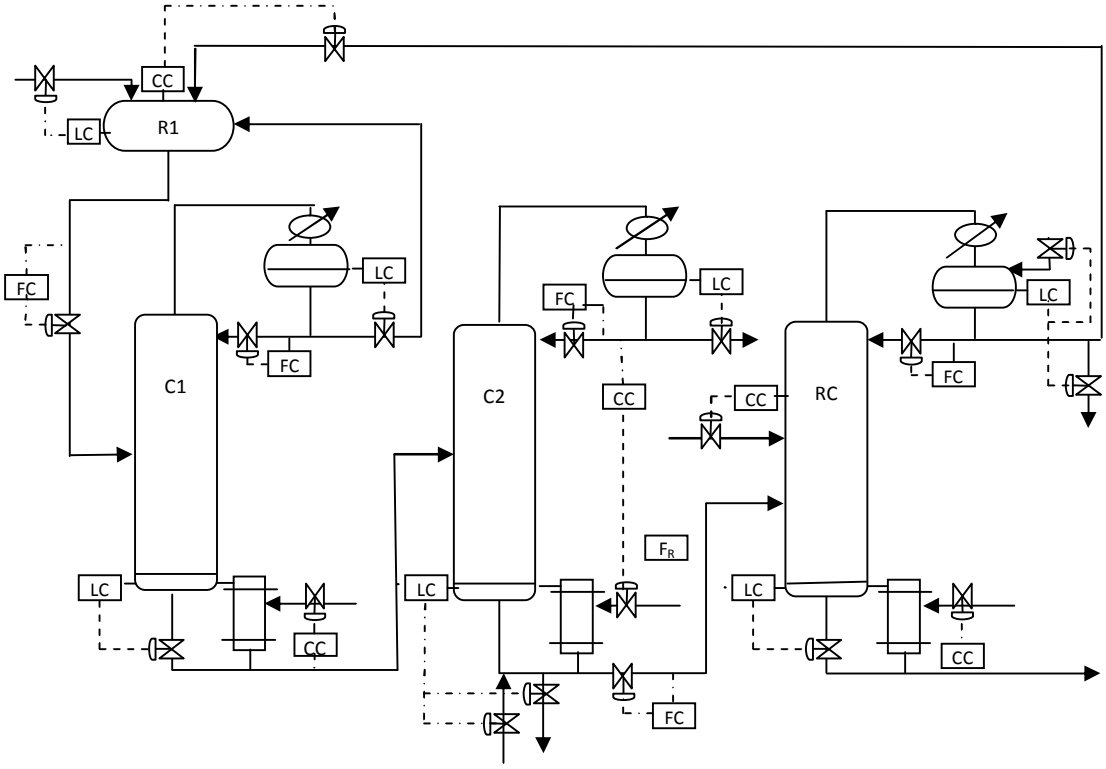

Figure 5.9 : Control structure CS4C.

Table 5.6 : Controller gains and reset times (min) for CS4C.

Control Loop	K_U	P_U[a]	K_c	τ_I[a]
z_{1B} - D_3	76,89	11,5	23,83	25,30
V_{R1} - F_{0A}	991, 99	6,67	307,52	14,67
x_{B1B} - V_{S1}	3,63	19,75	1,13	43,45
x_{D2D} - V_{S2}	1,83	35,33	0,57	77,73
x_{2E} - F_{0E}	8,95	6,17	2,77	13,57
x_{D3D} - V_{S3}	4,61	12,83	1,43	28,23

[a] Unit: min

Figure 5.10 gives the results of CS4C for ±20% step changes in the production rate handles F_1 and F_R. For the positive change in production rate handle, the product purities settle down to their final steady-state values in less than 5 hours. Here, the purity of bottoms product $x_{B3,F}$ recovers back to its specified value, while a small offset is observed in the distillate composition $x_{D2,C}$. An increase in the production rate results in more vapor boilup requirement for the columns, but the increase in the vapor boilup of reactive column is smaller than that of CS3C. The control performance for the negative changes in F_1 and B_2 are essentially the same observed for the positive disturbance. However, there is a sustained oscillation in the product purity of second column $x_{D2,C}$ and its manipulated variable V_{S2}, which might be improved by detuning this control loop.

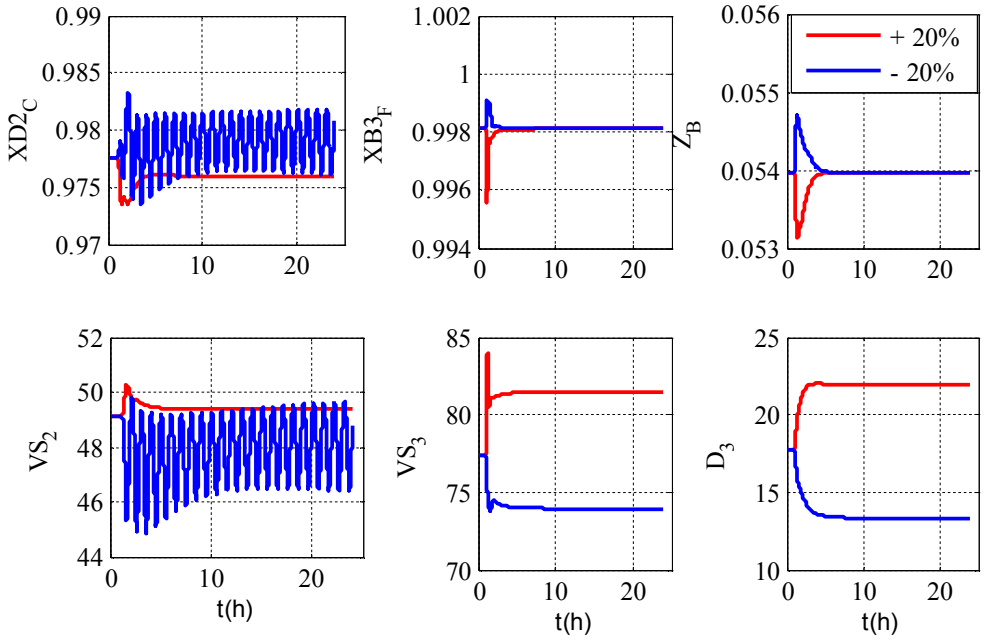

Figure 5.10 : ±20% step change in F_1 & F_R for CS4C.

Figure 5.11 shows the performance of control structure CS4C for a +50% step change in specific reaction rate. Dynamic result of step change in specific reaction rate shows that increasing the reaction temperature in reactor does not effect the purity of component F leaving the process from the bottoms of reactive column. On the other hand, it takes about 8 hours for component C in the distillate of second column to settle down in a new steady-state, which is quite close to its specification. It is observed that CS4C easily handles the this disturbance change

As shown in Figure 5.12, the change in the purity of fresh feed stream F_{0A} does not effect the results significantly. It is seen that the recycle flow rate D_3 decreases with the increse of component B in the fresh feed stream F_{0A}. There is a slight increase in the product purity of the second column. This deviation from the set point increases as the purity of fresh feed stream decreases. Even in the worst case, the product purity $x_{D2,C}$ settles down in less than 10 hours

In summary, control structure CS4C is dynamically stable for any type of disturbances. In addition, the required settling time for product purities is significantly shorter than that of control structure CS3C. The CS4C has two flow controller that are on streams of F_1 and F_R for each recycle loop, so it is predicted that the response of structure CS4C is more quickly for this reason.

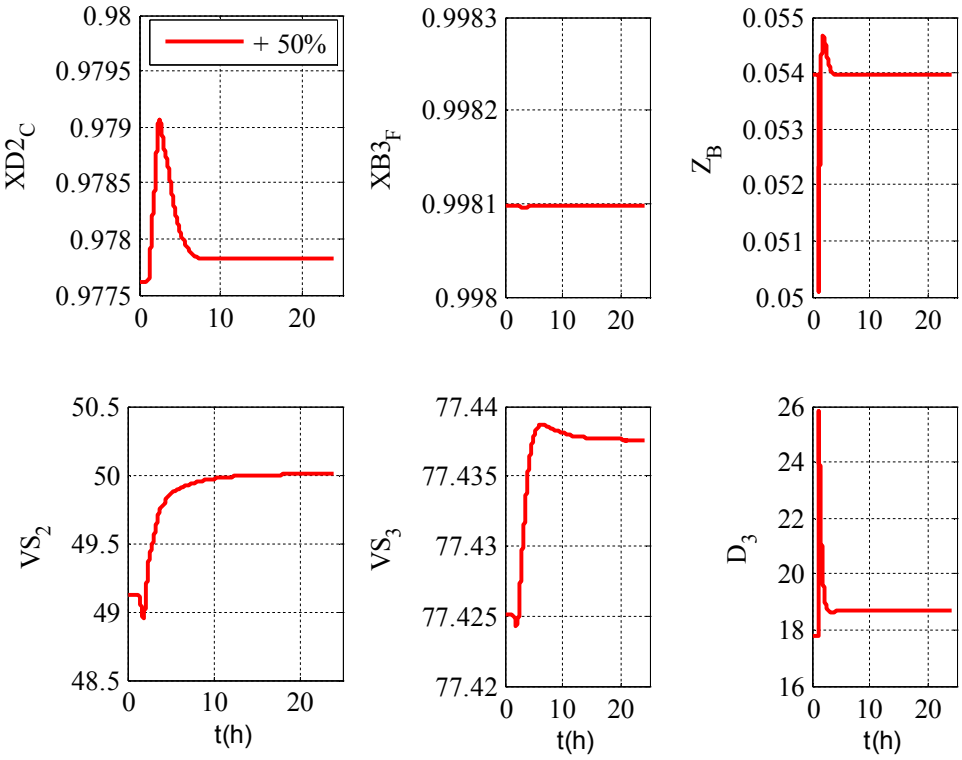

Figure 5.11 : + 50% step change in k_1 for CS4C.

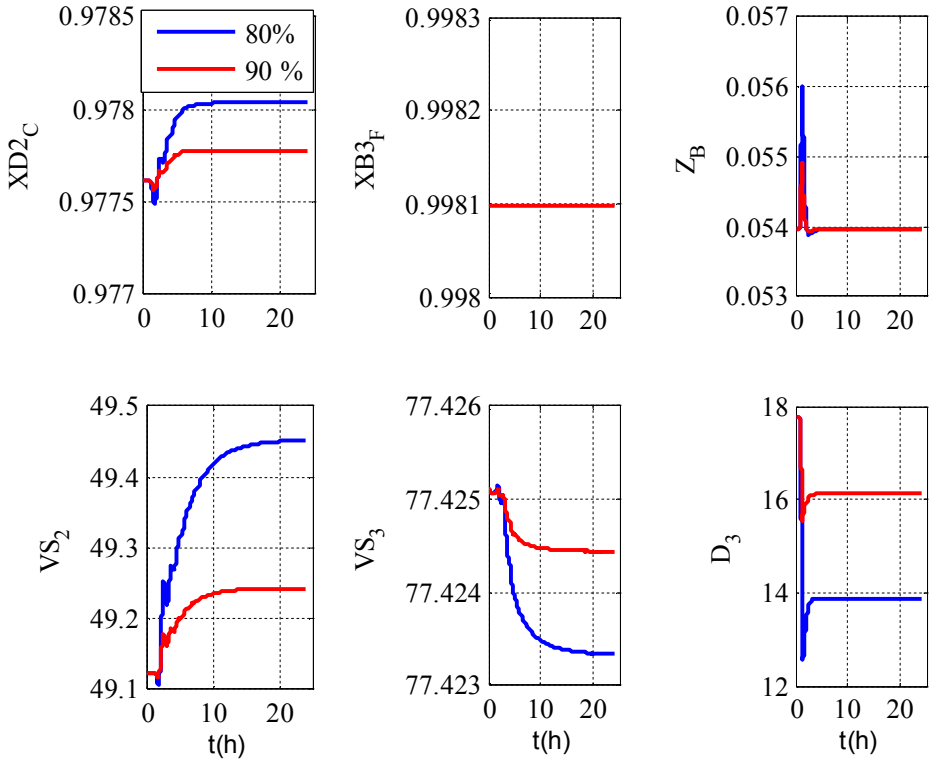

Figure 5.12 : Step change in fresh feed composition z_{0A} for CS4C.

5.2.2 Structures using single-end temperature control

A number of control strategies are constructed and tested in the face of different disturbances using composition controllers. Two of the control structures given in the previous section are found workable. However, composition analyzers are expensive and unreliable with large dead times. On the other hand, temperature measurement is very fast, reliable and cheap. Thus, many industrial columns prefer to use inferential temperature control instead of direct composition control if it is possible. In this section of the study, composition controllers of distillation columns are replaced with temperature controllers for two workable control structures of the previous section.

Selection of the trays to temperature control is the main issue to develop the temperature control structure. Hence, Luyben investigated that criteria of selecting temperature control trays in distillation column. In literature, there are number of criteria for selecting which trays to hold at constant temperature. They are; (1) using slope of the temperature profile, (2) choosing sensivite tray temperature for changing in the manipulated variable, (3) using the singular values analysis (SVD), (4) selecting the tray where the temperature does not change as feed composition changes, (5) choosing the tray that produces the smallest changes in product purities. It is mentioned that SVD analysis provided a simple and effective method for selecting temperature control tray location. In this study, sensitivity analysis and Singular Value Decomposition (SVD) method are used to determine the most sensitive tray in the RD column and most sensitive tray for the conventional columns are selected using the temperature profile which is changing the most from tray to tray [55]. Inferential single-end temperature control structure design is based on these sensitive tray, and it have studied in the face of different disturbance.

As shown in the Figure 5.13, most sensitive tray in the first conventional distillation column is found tray 13 and the other sensitive tray is determined as tray 26 by using the steepest slope criteria.

As it seen from the Figure 5.14, temperature profile is change most where the tray is around the tray 21 and other sensitive tray is found as tray 10.

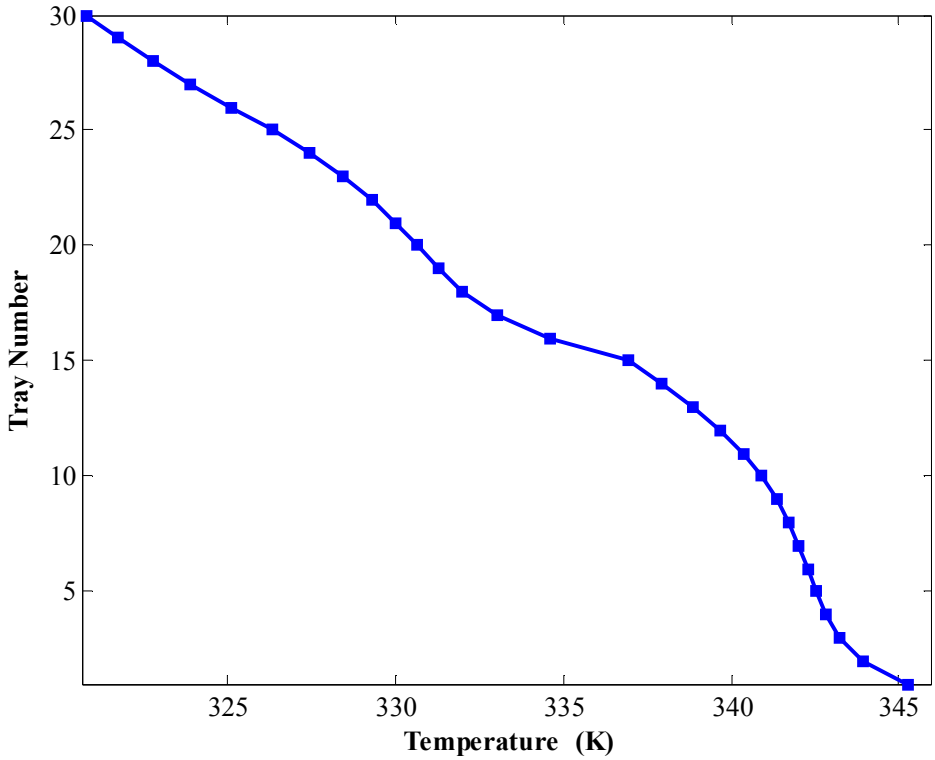

Figure 5.13 : Temperature profile of the first conventional distillation column.

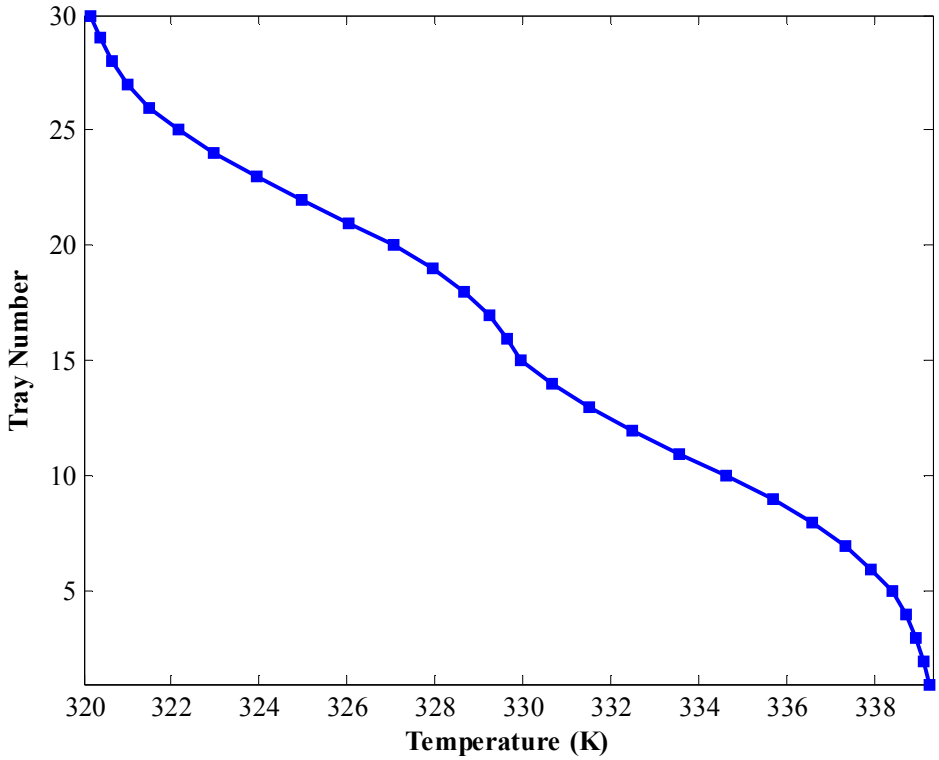

Figure 5.14 : Temperature profile of the second conventional distillation column.

To find the sensitive trays in the RD column, U matrix is obtained from the decomposition of the the steady-state gains K_P. As it seen from the Figure 5.15, the biggest component of U matrix give the most sensitive trays as tray 19 and tray 22 for the manipulated variables V_S and F_{0E}, respectively.

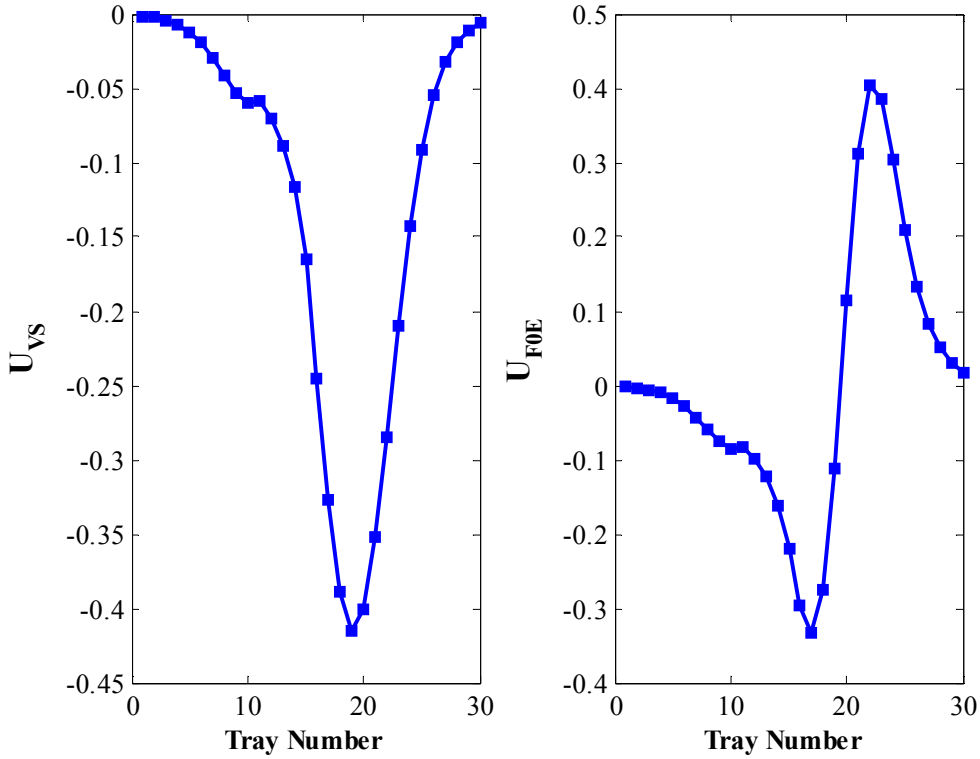

Figure 5.15 : SVD analysis results of reactive distillation column.

5.2.2.1 Control structure CS3ST

The control structure that is shown in the Figure 5.16, the holdup of the reactor is controlled by manipulating the fresh feed stream $F_{0A,}$ while concentration of component B (z_{1B}) in the reactor is controlled by the recycle stream D_3. This configuration attempts to fix the production rate by controlling the reactor effluent (F_1). The base levels of all columns are controlled by bottoms flow rates. Distillate flow rates are manipulated to control the reflux drum levels for C1 and C2, while a split-ranged controller on the reflux drum of RD manipulates the make-up/purge stream $F_{0B.}$ Reflux flow rates are flow controlled in all columns. Most sensitive trays for the first and second columns are tray 13 and tray 21, respectively. The temperatures of these trays are controlled by manipulating the vapor boilup of

corresponding columns. According to the results of SVD method, tray 19 is paired with fresh feed stream F_{0E}, while the temperature of tray 22 is matching vapor boilup V_{S3}. Controller gains and reset times are listed in Table 5.7.

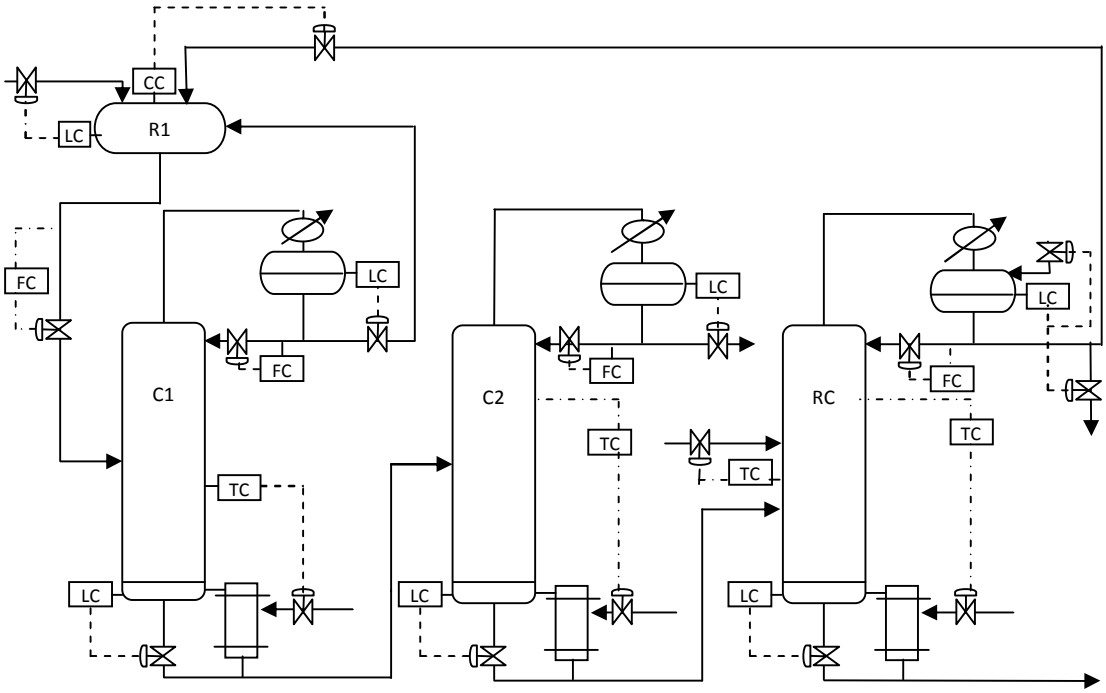

Figure 5.16 : Control Structure CS3ST.

Table 5.7 : Controller gains and reset times for CS3ST.

Control Loop	K_U	P_U[a]	K_c	τ_I[a]
Z_{1B} - D_3	76,89	11,5	23,83	25,30
V_{R1} - F_{0A}	991, 99	6,67	307,52	14,67
$T_{1,13}$ - V_{S1}	11,12	5,33	3,45	11,73
$T_{2,21}$ - V_{S2}	12,99	7,17	4,03	15,77
$T_{3,19}$ - F_{0E}	3,12	12,83	0,97	28,23
$T_{3,22}$ - V_{S3}	10,05	3,67	3,12	8,07

[a] Unit: min

Figure 5.17 presents the response of CS3ST for ±20% step changes in the production rate handle F_1. Although the temperatures on the selected trays settle down to their set points in a short time, it takes a longer period for the product purities. In addition, the product purities $x_{D2,C}$ and $x_{B3,F}$ are not held as close to their specifications as with the control structure CS3C.On the other hand, there is a significant decrease in the settling time compared to CS3C.

The performance of control structure CS3ST for the %50 step change in specific reaction rate is given in Figure 5.18.

It is seen that the purities of both products are affected by this disturbance. The decrease is more significant in the purity of component C in the distillate of second column. It is realized that, the temperature measurements bring the plant more sensitive to reaction temperature of the reactor. Because the dynamic result of this disturbance shows that the increasing the reaction temperature of the reactor causes the deviation in product purities, and this deviations are more significant than those of composition control structures. But, final steady state values of the product purities are still close to their steady state values and control structure of CS3ST overcomes the change of reaction temperature. Also, it is clearly seen that response of the CS3ST is more quickly than response of the CS3C.

Figure 5.19 illustrates the response of CS3ST for step change in fresh feed composition z_{0A} .The control structure of CS3ST easily handles the both disturbance changes of feed composition. Although manipulated variables settles down in long time, there is no remarkable difference between initial steady-state and final steady state values.

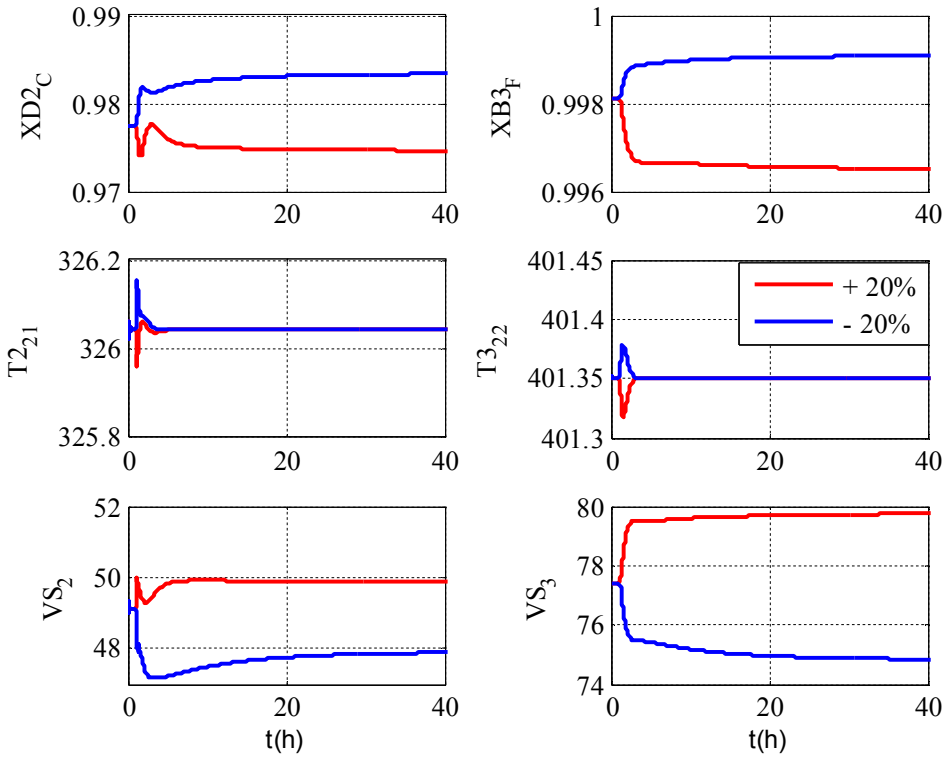

Figure 5.17 : ±20% F_1 step change in for CS3ST.

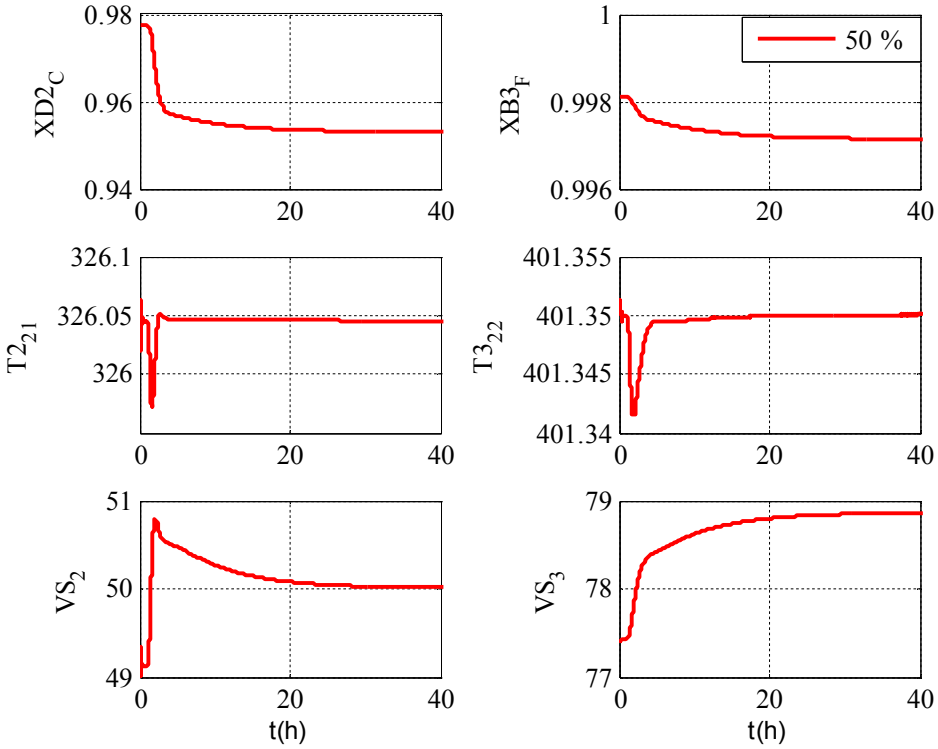

Figure 5.18 : + 50% step change in k_1 for CS3ST.

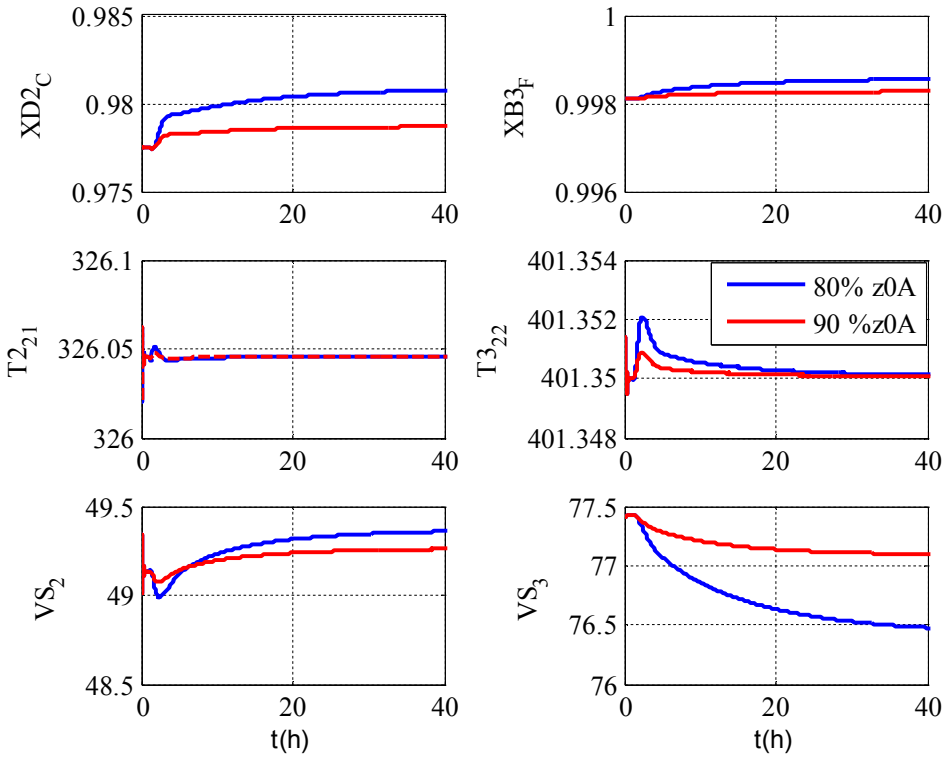

Figure 5.19 : Step change in fresh feed composition z_{0A} for CS3ST.

5.2.2.2 Control structure CS4ST

As shown in the Figure 5.20, Tray 13 and tray 21 are selected as the most sensitive trays for the first and second columns, respectively. Tthe temperatures of these trays are controlled by manipulating the vapor boilup of corresponding columns. In the reactive column, tray 19 is paired with the fresh feed stream F_{0E}, while the temperature of tray 22 is controlled by vapor boilup V_{S3}. Table 5.8 illustrates the controller gain and reset times for control structure CS4ST.

Table 5.8 : Controller gains and reset times (min) for CS4ST.

Control Loop	K_U	P_U[a]	K_c	τ_I[a]
Z_{1B} - D_3	76,89	11,5	23,83	25,30
V_{R1} - F_{0A}	991, 99	6,67	307,52	14,67
$T_{1,13}$ - V_{S1}	11,12	5,33	3,45	11,73
$T_{2,21}$ - V_{S2}	12,99	7,17	4,03	15,77
$T_{3,19}$ - F_{0E}	3,12	12,83	0,97	28,23
$T_{3,22}$ - V_{S3}	10,05	3,67	3,12	8,07

[a] Unit: min

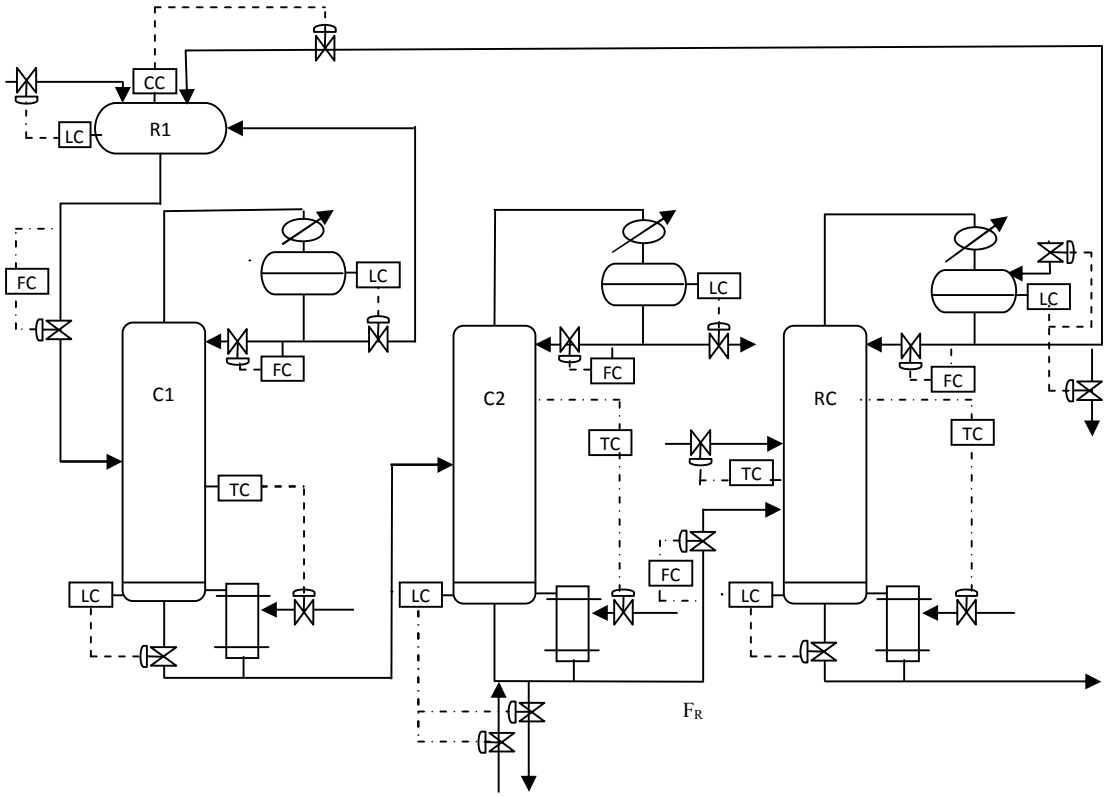

Figure 5.20 : Control Structures of CS4ST.

Figure 5.21 shows the results of CS4ST for ±20% step changes in production rate handles. The increase of the throughput results in an increase of vapor boilup, and

the opposite is true for the decrease of the throughput. It is seen that the controlled temperatures recover back to their set points in less than 5 hours. On the other hand, the product purities settle down in less than 8 hours. Since the compositions are not directly measured, there is no guarantee that they are held exactly at their specifications. Thus, there is an offset in the product purities. These deviations are bigger than those of CS4C, but these small drops are quite acceptable.

Figure 5.22 shows the performance of control structure CS4ST for a %50 step change in specific reaction rate. This disturbance does not effect the purity of component F leaving the process from the bottoms of reactive column. On the other hand, although it settles down in less than 5 hours, there is a significant decrease in the purity of component C in the distillate of second column. This occurs even though the temperatures recover back to their specified values easily.

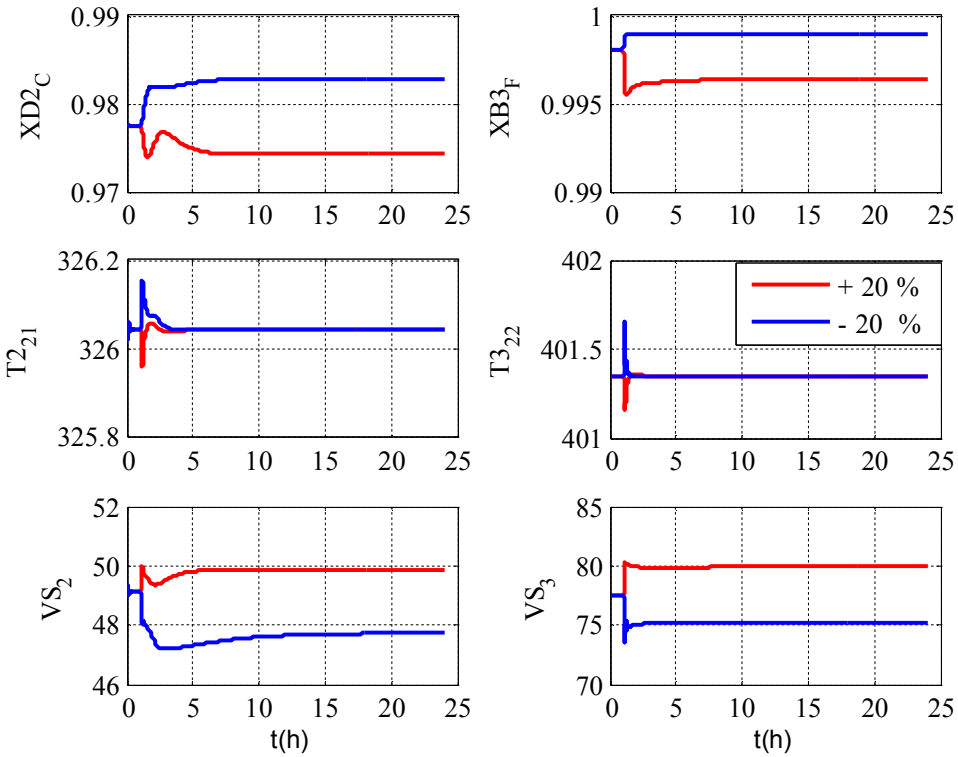

Figure 5.21 : ±20% step change in F_1 & F_R for CS4ST.

As it seen in Figure 5.23, there is an offset in the purity of component C in the distillate of second column, while the controlled temperature recovers back to its set point in around 3 hours. Although this deviation is bigger than the deviation of CS4C, it is quite close to its specification.

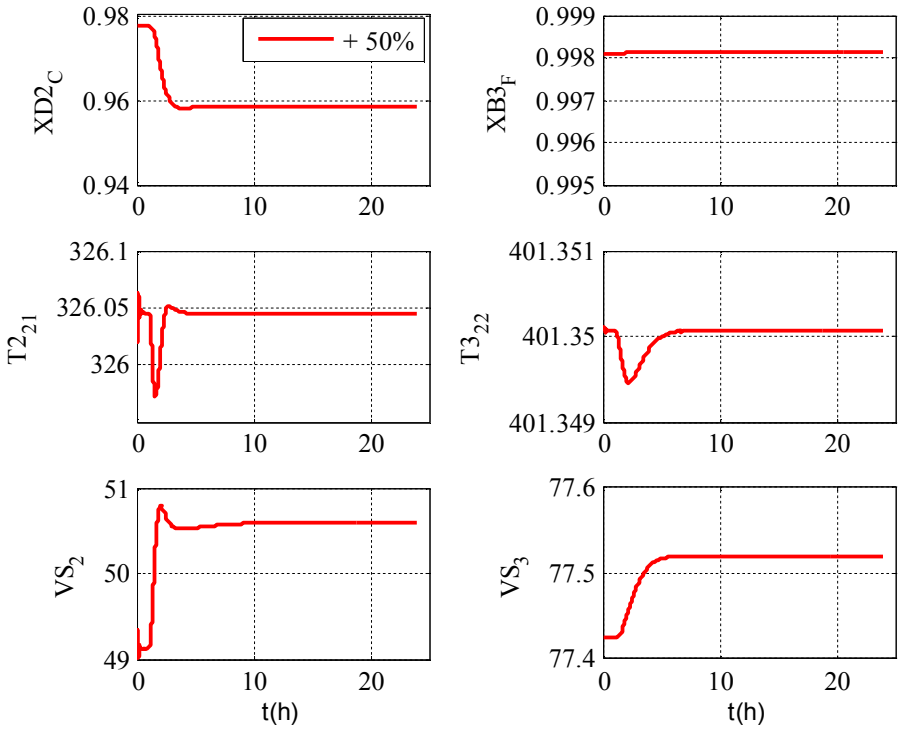

Figure 5.22 : + 50% step change in k_1 for CS4ST.

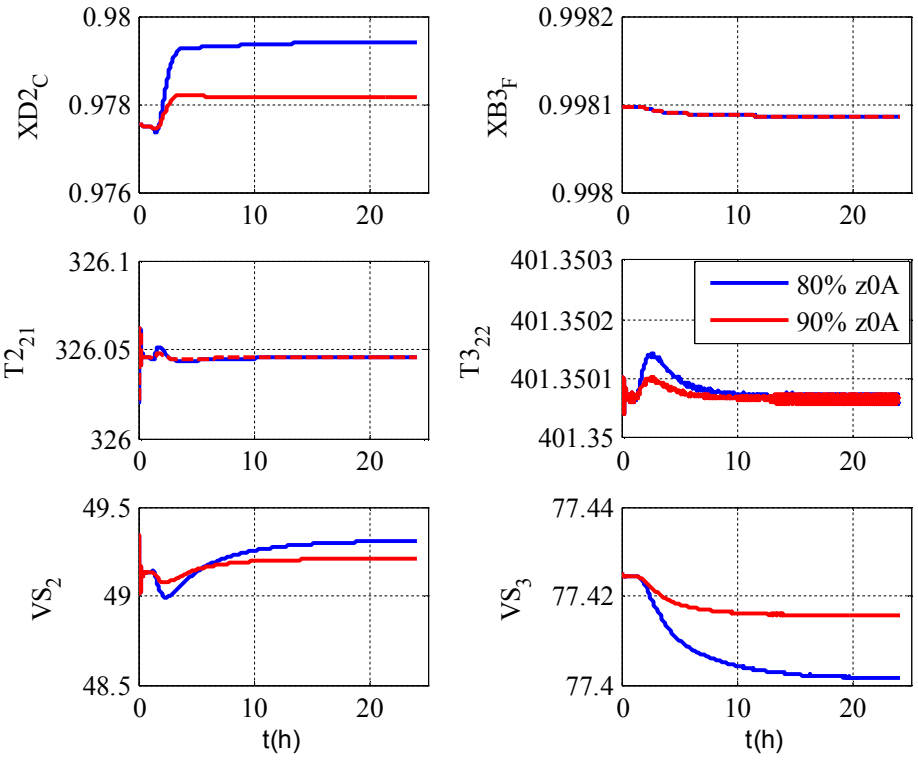

Figure 5.23 : Step change in fresh feed composition z_{0A} for CS4ST.

5.2.3 Structures using two-temperature control

In this multi-unit process, it is important to recognize that both distillate and also bottom compositions have to be in specific amount. Also, when conventional columns are controlled with inferential single-end temperature structure, it is seen that offset occurs in desired product purities. Thus, to developed more effective temperature control structures, an inferential dual-temperature control structure is designed based on most sensitive trays.

5.2.3.1 Control structure CS3DT

In the two-temperature control structure, pairing of the controlled tray temperature and manipulated variables are the key issue for columns to design effective and robust control structure. Since determining the most sensitive trays in the conventional columns are based on steepest slope criterion, most sharpest of two points in the temperature profile are selected as control temperature trays to design a dual-temperature control structure. Sharp point in the stripping section is matched with vapor boilup, while sharp point in the rectifying section is paired with reflux flow rate, as shown in the Figure 5.24.

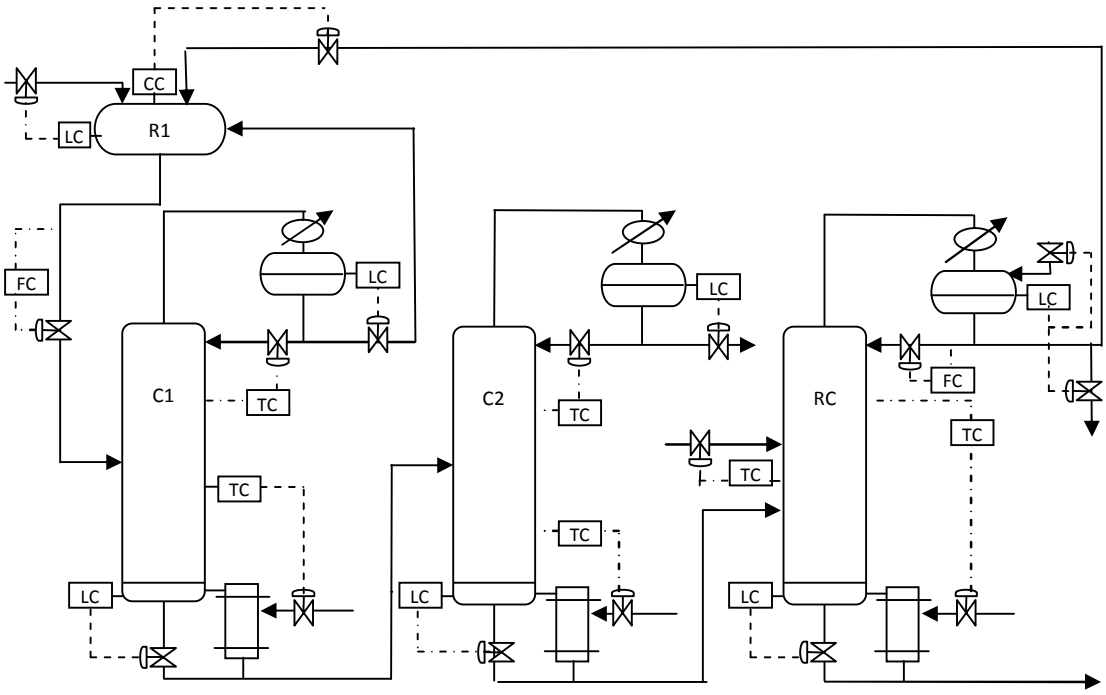

Figure 5.24 : Control Structures of CS3DT.

With the basis as mentioned above, temperature tray 13 and temperature tray 10 are controlled by manipulating the vapor boilups; reflux flow rate control the temperature tray 26 and temperature tray 21 for C1 and C2, respectively. Other control loops are the same with CS3ST. Controller gains and reset times (min) of CS3DT structure are given Table 5.9.

Table 5.9 : Controller gains and reset times (min) for CS3DT.

Control Loop	K_U	P_U[a]	K_c	τ_I[a]
Z_{1B} - D_3	76,89	11,5	23,83	25,30
V_{R1} - F_{0A}	991, 99	6,67	307,52	14,67
$T_{1,13}$ - V_{S1}	11,12	5,33	3,45	11,73
$T_{1,26}$ - R_1	8,87	7,00	2,75	15,4
$T_{2,10}$ - V_{S2}	9,52	6,50	14,30	14,30
$T_{2,21}$ - R_2	7,05	10,17	2,19	22,37
$T_{3,19}$ - F_{0E}	3,12	12,83	0,97	28,23
$T_{3,22}$ - V_{S3}	10,05	3,67	3,12	8,07

[a] Unit: min

Figure 5.25 presents the response of CS3DT for ±20% step changes in the production rate handle F_{0A} and F_R. Although the controlled temperatures settle down to their set points in a short time, product purities need a longer time to reach final steady-state.

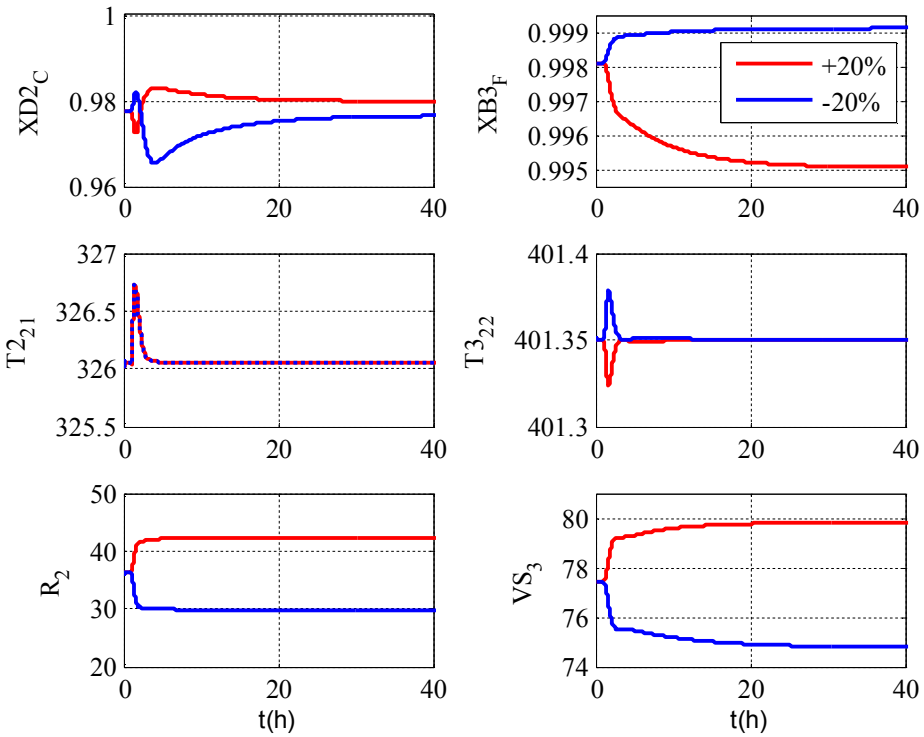

Figure 5.25 : ±20% step change in F_{0A} & F_R for CS3DT.

The performance of control structure CS3DT for a %50 step change in specific reaction rate is given in Figure 5.26. Temperatures on selected trays quickly recover back to their steady state value and also manipulated variables settles down to their new steady-state values easily, nevertheless offsets occur in both product purities Specially, final steady-state value of the reflux flow rate of C2 is significantly different from the its original steady-state value. Control structure of CS3DT can handle the increasing the reaction temperature in reactor, but the deviation in the product purities occur. Although deviation in the product purity C is bigger than that of CS3ST, deviation in the product purity F is smaller.

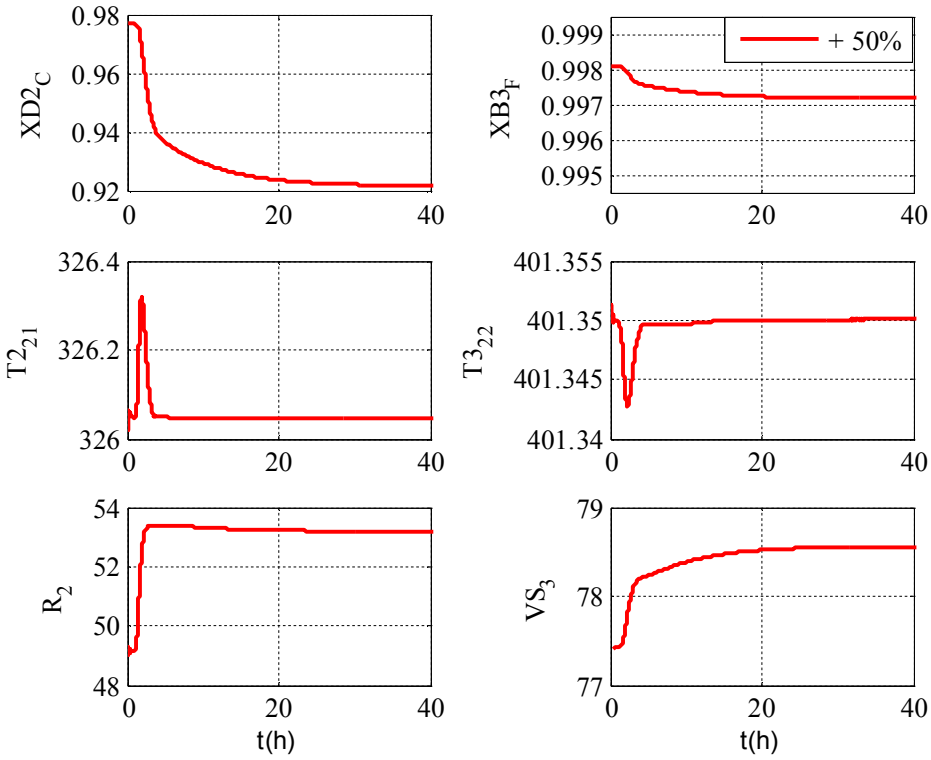

Figure 5.26 : +50% step change in k_1 for CS3DT.

The results for a step change in the fresh feed composition are given in Figure 5.27 In this control structre, there are offset in the purity of component C in the distillate of second column and purity of the product F which obtains from the bottom stream of RD column. Manipulated variables settle down quickly and temperatures recovers back to its set point within 3 hours.

Despite using the dual-temperature control structure in the conventional columns, it is seen that there is no sigficicant difference in responses of CS3ST and CS3DT.

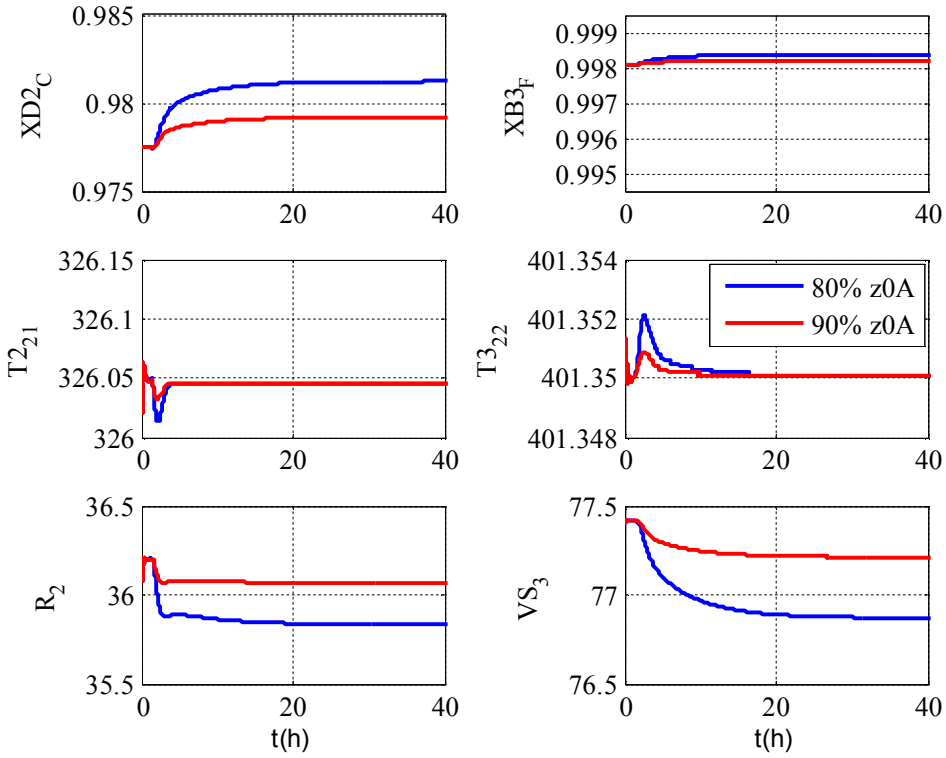

Figure 5.27 : Step change in fresh feed composition z_{0A} for CS3DT.

5.2.3.2 Control structure CS4DT

Control structure CS4DT given in the Figure 5.28, shows that there is the additional make-up/purge stream F_{0B} on the bottom flow of C2. Hence, F_R is flow controlled. The holdup of the reactor is controlled by fresh feed stream of component A (F_{0A}). Recycle stream D_3 is used to control the concentration of component B (z_{1B}) in the reactor. Other control loops are the same with CS3DT. Table 5.10 presents the controller gains and reset times for CS4DT.

Table 5.10 : Controller gains and reset times (min) for CS4DT.

Control Loop	K_U	P_U[a]	K_c	τ_I[a]
Z_{1B} - D_3	76,89	11,5	23,83	25,30
V_{R1} - F_{0A}	991, 99	6,67	307,52	14,67
$T_{1,13}$ - V_{S1}	11,12	5,33	3,45	11,73
$T_{1,26}$ - R_1	8,87	7,00	2,75	15,4
$T_{2,10}$ - V_{S2}	9,59	6,33	4,03	15,77
$T_{2,21}$ - R_2	7,05	10,17	2,19	22,33
$T_{3,19}$ - F_{0E}	3,12	12,83	0,97	28,23
$T_{3,22}$ - V_{S3}	10,05	3,67	3,12	8,07

[a] Unit: min

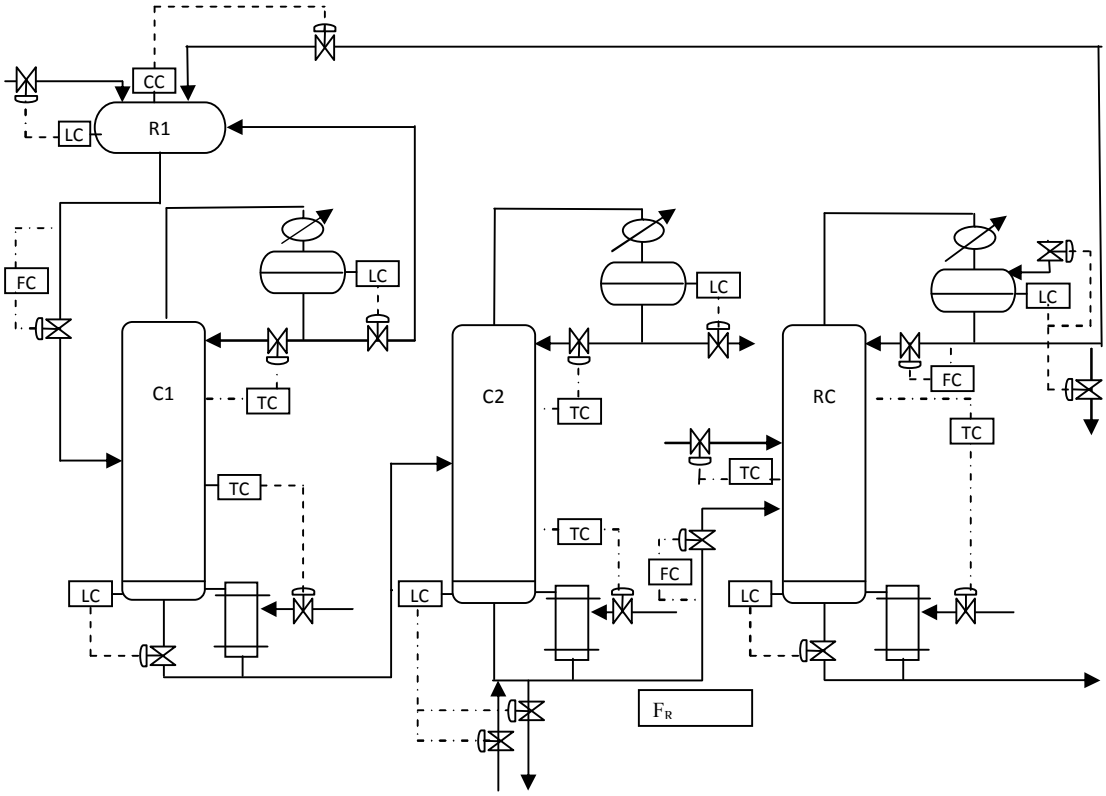

Figure 5.28 : Control Structures of CS4DT.

The system of scheme CS4DT in Figure 5.29 gives the results for ±20% step changes in the production rate handles F_1 and F_R. The increase of the throughput results in an increase of reflux flow rate and vapor boilup, and the opposite is true for the decrease of the throughput. It is seen from the Figure 5.29 that purities of the products settle down approximately 10 hour. Controlled temperatures recover back to their set points within the 5 hours. On the other hand, there is an offset in the product purities. These deviations are bigger than those of single-end temperature control structure of CS4ST. Performance of control structure CS4ST for a %50 step change in specific reaction rate is given in Figure 5.30. Although the temperature in the distillate of second column recover back to their specified values easily, there is a significant decrease in the purity of component C. Figure 5.31 shows the results for a step change in the fresh feed composition. It is seen that component F leaving the process from the bottoms of reactive column remains at its original value, but there is an offset in the purity of component C in the distillate of second column for both feed composition changes. Although control structure CS4DT handles all disturbances easily, the deviations in the product purities are bigger than both control structures of CS4ST and CS4C.

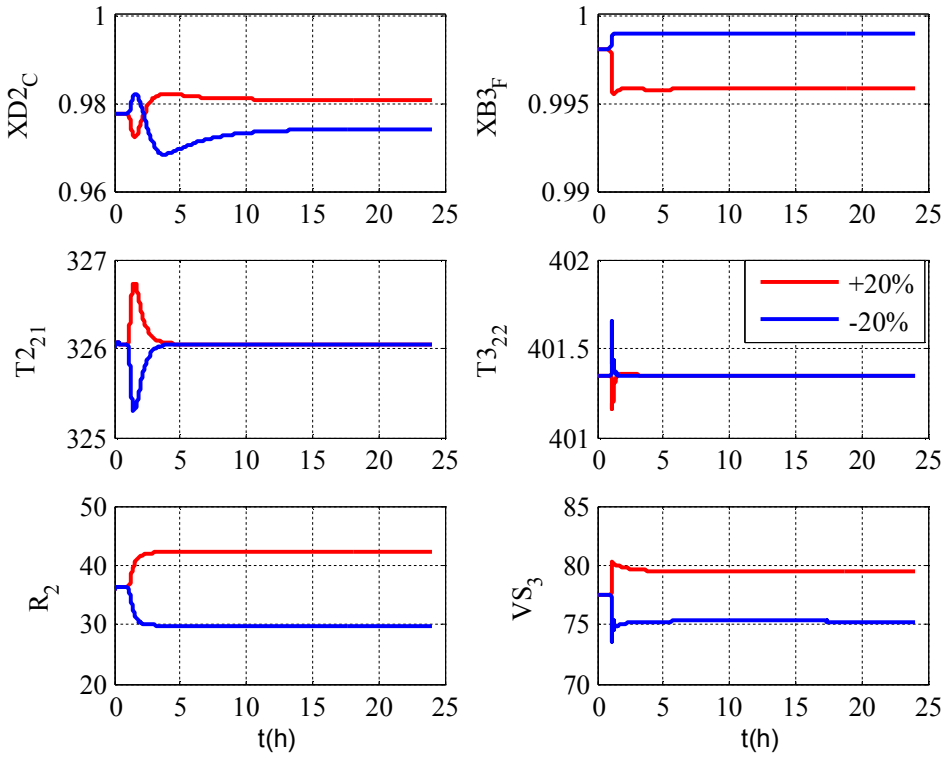

Figure 5.29 : ±20% step change in F_{0A} & F_R for CS4DT.

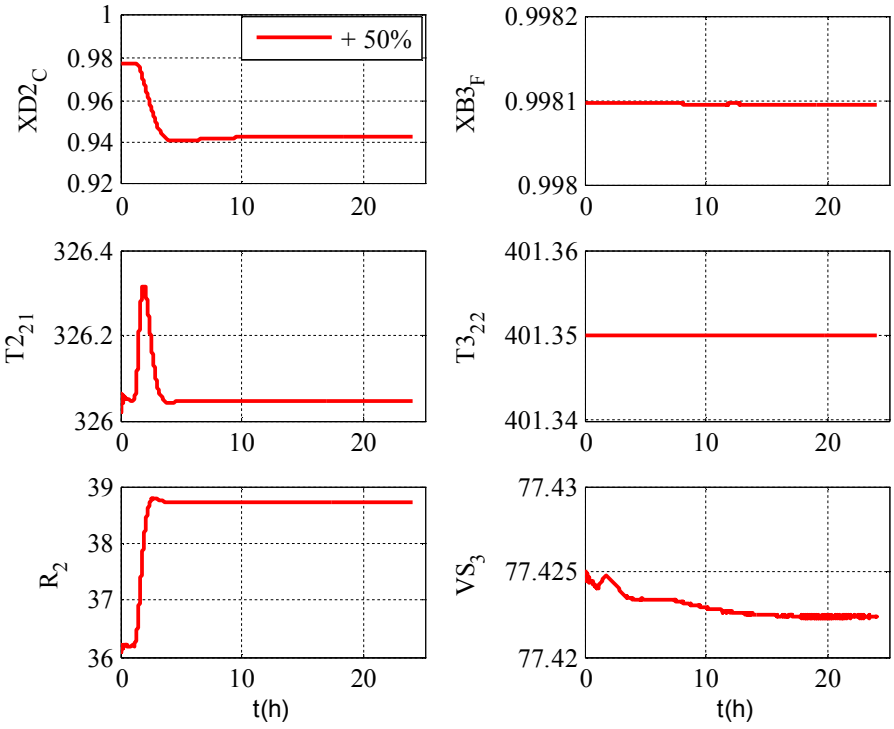

Figure 5.30 : + 50% step change in k_1 for CS4DT.

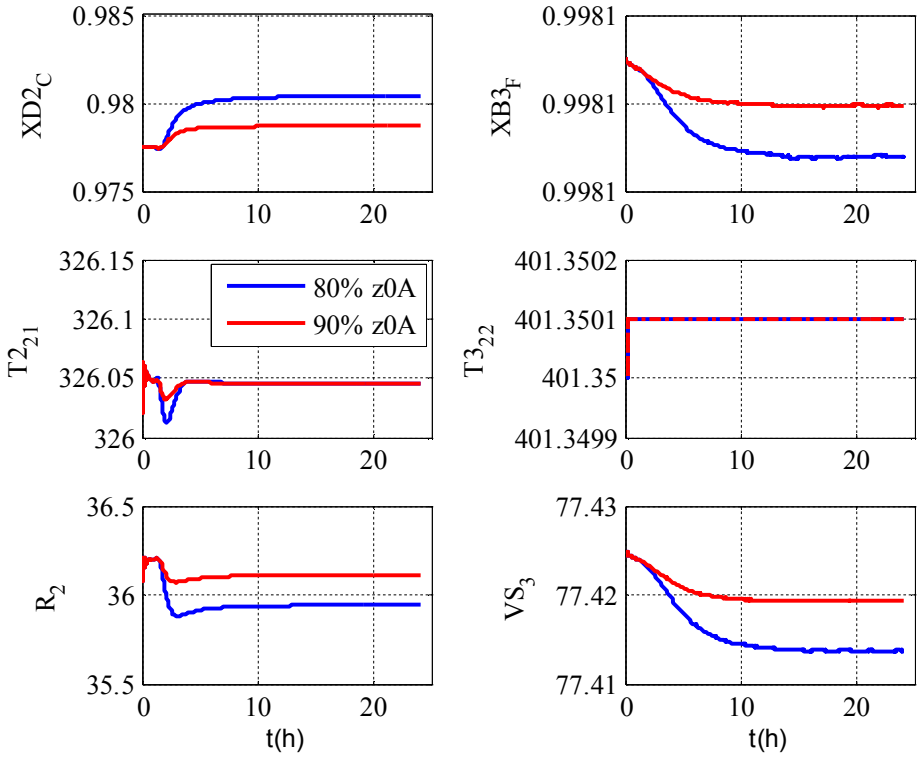

Figure 5.31 : Step change in fresh feed composition z_{0A} for CS4DT.

5.2.3 Discussion

The steady state deviations of workable control structures are given in Table 5.11. After dynamic simulation, from the four composition control structures, two of them are found as workable. It is observed that composition control structures provide stable responses in the face of different disturbances. In single-end temperature control structure, it is obtained that there is a little deviation in product purities. But, response of the single-end temperature control structures are faster than the composition control structures. In dual-temperature control structures, significant deviation in product purities is seen. Also, there is no remarkable change in the settling times when it compares the other control structures.

Consequently, although deviations of control structures using temperature controllers are bigger compared to those of control structures using composition control, results illustrate in the previous figures show that the system settles down faster with control structures including temperature control. In the single-end temperature control structures, it should be noted that the deviation of the product purities can be tolerable because product purities are quite close to their specifications.

Table 5.11 : Steady state deviations of product purities.

Control Structures	Disturbance	$\|\Delta x_{D2,C}\|$	$\|\Delta x_{B3,F}\|$
CS3C	+20% in PRH*	0,0033	0,0000
	-20% in PRH	0,0022	0,0000
	+50% in k_1	0,0013	0,0000
	80% in z_{0A}	0,0009	0,0000
	90% in z_{0A}	0,0004	0,0000
CS4C	+20% in PRH	0,0015	0,0000
	-20% in PRH	0,0032	0,0000
	+50% in k_1	0,0002	0,0000
	80% in z_{0A}	0,0004	0,0000
	90% in z_{0A}	0,0002	0,0000
CS3ST	+20% in PRH	0,0030	0,0016
	-20% in PRH	0,0058	0,0010
	+50% in k_1	0,0246	0,0010
	80% in z_{0A}	0,0032	0,0005
	90% in z_{0A}	0,0011	0,0002
CS4ST	+20% in PRH	0,0033	0,0017
	-20% in PRH	0,0053	0,0009
	+50% in k_1	0,0191	0,0000
	80% in z_{0A}	0,0018	0,0000
	90% in z_{0A}	0,0001	0,0000
CS3DT	+20% in PRH	0,0023	0,0030
	-20% in PRH	0,0010	0,0010
	+50% in k_1	0,0554	0,0009
	80% in z_{0A}	0,0036	0,0003
	90% in z_{0A}	0,0016	0,0001
CS4DT	+20% in PRH	0,0033	0,0023
	-20% in PRH	0,0034	0,0009
	+50% in k_1	0,0349	0,0000
	80% in z_{0A}	0,0028	0,0000
	90% in z_{0A}	0,0011	0,0000

* production rate handle

6. CONCLUSION

In this study, simplified version of a real complex industrial process that includes two reaction steps, three conventional distillation column and two recycle stream is used. Combining the second reaction step and the third distillation column into a reactive distillation, the modified process consists of a reactor, two conventional distillation columns, one reactive distillation column and two recycle streams.

According to the steady-state design results, the capital, energy and total annual cost of the modified design is significantly less than that of the original design. Capital cost of the modified design are calculated as 2334.10^3 \$/year while capital cost of the conventional process is 3262.10^3\$/year. Also, energy cost of the RD process is found 782.10^3 \$/year, while energy costs of the conventional flowsheet is 589.10^3\$/year. Therefore, the total annual cost of the process-intensified design is 1560.10^3 \$/year, while it is 1677.10^3\$/year for the conventional design. This result emphasizes that even without doing optimization study, modifying this conventional process using a reactive distillation column is successful example of process intensification in terms of the costs.

Because of the losses of intermadiate component B and D, plantwide control structure focus on the makeup and purge of the intermediate components. So, pure makeup stream F_{0B} and makeup/purge stream of F_{0D} are essential to isolate the two reaction sections by disturbances and changed operating conditions.

Next, several plantwide control structures including composition controllers are designed to investigate the dynamic controllability of the process, two of them are found workable. It is seen that control of the composition control for the reactor is the essential to prevent the accumulation or depletion of the intermediate component of B. It is found that workable composition control structures require composition controllers for the reactor and also flow controllers in each recycle loops.

Then, the direct composition controllers of distillation columns are replaced with inferential temperature controllers for workable control structures. It is found that deviations of control structures using temperature controllers are bigger compared to

those of control structures using composition control. But, the settling time of control structures using temperature controllers are shorter than control structures including composition control. Since product purities are rather close to their specifications in the single-end temperature control structures, it is appropriate to chose these control structures for controlling the entire plant. In single-end temperature control structures, it is observed that there is no significant deviation in product purities, but the response of CS4ST is faster than CS3ST.

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CURRICULUM VITAE

Candidate's full name: Rojda Özgür BAKİ

Place and date of birth: Bingöl, 15.11.1986

Permanent Address: Cumhuriyet Mahallesi, Söğütlü Çayır Caddesi, Dinçer Sokak , No:2, D:5, Üsküdar /Istanbul

Universities and Colleges attended:

B.Sc.: Gazi University, Chemical Engineering, (2004-2008)

M.Sc.: Istanbul Technical Univesity, Chemical Engineering, (2009-2012)