SIMULATION AND CONTROL OF A REACTIVE DISTILLATION COLUMN FOR THE HYDROGENATION OF BENZENE IN A REFORMATE STREAM

[1]Akpa, Jackson Gunorubon, Uchendu, James[2]

Department of Chemical/Petrochemical Engineering

Rivers State University, Port-Harcourt, Rivers State, Nigeria

[1](corresponding author: akpa.jackson@ust.edu.ng), [2](jameslordsuchendu@yahoo.com)
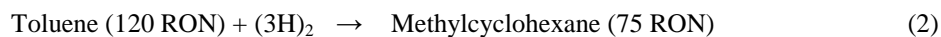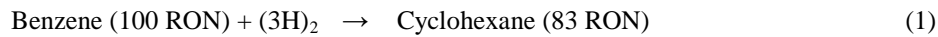
Abstract

The Dynamic models of an N stage reactive distillation column for the hydrogenation of benzene in a reformate feed was developed. The developed models were simulated to obtain optimum number of trays (74), a benzene mass fraction in the bottom product (0.0056) and feed entry point (24th tray) as process conditions of the column. The developed models were tested using industrial plant data from Charkrabaty, (2004) and a benzene mass fraction from the first tray (bottom) of 0.00589 (0.0061 vol. %) was obtained compared to 0.00599 (.0062 vol. %) obtained by Charkrabaty, (2004). Open loop response of the column to step changes (±) in disturbances such as feed composition, flowrate and temperature showed fluctuations and linear response/relationship between the outputs (re-boiler mass fraction of benzene, condenser liquid hold-up, re-boiler liquid holdup) and the disturbances with stability attained over a long time. Column control was studied by performing Closed loop response of the column to a multiple input-multiple output (MIMO) feedback control configuration with proportional controllers using the re-boiler heat duty, reflux and distillate flow rates as manipulated variables. Results showed a great reduction in fluctuations with stability attained in 30 and 900 seconds respectively for the condenser liquid hold up and re-boiler benzene mass fraction compared to 8750 seconds obtained for both variables in the open loop response.

Keywords: Reactive Distillation model, Hydrogenation of reformate, open and close loop response.

1. Introduction

Gasoline is upgraded to increase its octane number through the reforming process; a process that produces high octane aromatics (one of which is benzene) by converting straight/linear hydrocarbons (paraffin) into branched alkanes (iso-paraffin) and cyclo napthenes into aromatics had been reported to contain benzene a known casino-gene (Colwell, 2008), with typical composition of gasoline hydrocarbons (% volume) been: 4-8% alkanes; 2-5% alkenes; 25-40% isoalkanes; 3-7% cycloakanes; 1-4% cycloalkenes; 20-50% aromatics and 0.5-2.5% benzene (Hoekman, 1992). The presence of benzene in gasoline also causes environmental pollution and contamination of air quality through automotive emissions. These adverse effects necessitated the enactment of regulations on acceptable composition limits of benzene in gasoline, thus balancing the need for gasoline to meet high engine performance requirements of automobiles without jeopardizing human and environmental safety. One of such regulations is the United States Environmental Protection Agency, (2007) specification of a concentration limit of below 0.62 volume % for benzene in gasoline. Catalytic reforming has been reported by Rock, et al., (2008) to be the source of 50- 80% of the benzene in the gasoline pool; with other sources being: the FCC gasoline, Coker and straight-run gasoline. Hence the benzene limit requirement can be attained by the removal of benzene/reduction of the benzene concentration in the reformate stream. Conventional methods adopted by refiners include: Preventing benzene formation in the reforming unit by removing benzene precursors (C6 content) from the naphtha feed to the reforming unit (Pre-fractionation) using a reformate splitter and

downstream removal of benzene from the reformate produced (Post fractionation). However, more recent methods of benzene removal in the reformate stream are: reformate benzene saturation (benzene is hydrogenated to cyclohexane), alkylation, reformate splitting and benzene extraction. This study investigates benzene removal via hydrogenation to cyclohexane. In the conventional hydrogenation process, other valuable components of the reformate with high octane rating especially toluene are also hydrogenated to lower octane rating products as the catalyst used is not selective for benzene hydrogenation only as shown below (Mahindrakara & Hahn, 2014):

Benzene (100 RON) + (3H)$_2$ →   Cyclohexane (83 RON)   (1)

Toluene (120 RON) + (3H)$_2$ →   Methylcyclohexane (75 RON)   (2)

Therefore, various methods of minimizing or eliminating the hydrogenation of valuable products such as toluene are being developed. One of such methods is the reactive distillation (a combination of chemical reaction and separation occurring in the same column), where one of the component is non condensable under the operating conditions; thus effecting separation and ensuring the selective reaction of one component in a specified region of the column while suppressing unwanted reactions of other components.

Reactive Distillation had been successfully used in the following processes: Ethyl acetate production (Kumar and Daoutidis, 1999); Biodiesel production (He et al., 2006; Kiss et al., 2008) and synthesis of fatty esters (Kiss, 2011). The advantages of this process over conventional sequential system of reaction followed by separation through distillation or other separation techniques includes (Harmsen, 2007) improved selectivity, increased conversion, thus higher product yield due to continuous removal of the products from the zone by distillation, effective utilization of the heat of the reaction resulting in lower energy costs and lower capital investment, however; the simultaneous presence of reaction and separation phenomena can result in complex dynamic behavior leading to complex interactions between vapor–liquid equilibrium, vapor–liquid mass transfer and intra-catalyst diffusion (Taylor and Krishna, 2000).

As with conventional distillation processes, reactive distillation had been modeled as: a batch process (Bollyn and Wright, 1998), Steady state equilibrium stage model with and without stage efficiencies (Baur, 2000), Dynamic equilibrium model (Espinosa et al., 1994; Peng et al., 2003) and non-equilibrium model (Higler et al., 1999). Models for the control of reactive distillation columns also abound: servo control (Giwa et al., 2015); Nonlinear model predictive control (NMPC), (Kumar and Daoutidis, 1999); Linear model predicative control (LMPC) (Sneesby et al., 1999) and coupled PI control by Zalten and Klein, (2007). However, works on reformate hydrogenation through reactive distillation were few: Chakrabarty, (2004) developed dynamic models and use feedback PID controllers to effect control in feed disturbances while Mahindrakara & Hahn (2014) developed equilibrium models and use a combination of feedback and feedforward control to effect control in feed disturbances.

1.1.   Process Description

The liquid feed from the reforming unit enters the reactive distillation column at some trays below the reactive stages, where it is separated, toluene in the feed being heavier than most of the other components in the feed remains a liquid, while benzene and other lighter feed components vaporizes and flows upwards into the reactive zone (filled with Nickel catalysts supported on a mixture of Titanium dioxide and Zirconium dioxide), where it reacts with hydrogen feed which enters above the feed tray and is hydrogenated to cyclohexane. The products from the column are the vapor stream from the condenser containing unreacted hydrogen; the top liquid products (lighter components of the reformate and cyclohexane) and the bottom product which is the main product stream containing de-benzenized reformate with the desired octane properties (high percentage of toluene and very low concentration of benzene) from the re-boiler.

The process variables of this system change/fluctuate in the course of operations, causing its output variables to

change and fluctuate for some time before attaining new steady state values. These process variables called disturbances include: the amount of benzene in the feed (ranges from 3% to 15% weight fraction) and the composition of the heavier components (ranges from 40% to 80%). Since the frequency and magnitude of these fluctuation cannot be ascertained, the need for effective process control becomes paramount. This involves the installation of appropriate equipment (controllers) which returns the output variables back to their set point values whenever there are disturbances (changes in the inlet variables) in the process. Hence this work studies the behavior of the reactive distillation column particularly to fluctuations in the feed conditions and develop appropriate closed loop models with proportional controllers capable of bringing the system back/close to its original set point and ensure the attainment of stability in a reasonably short time.

2.   Model Development

The models of the reactive distillation column were based on the principles governing the various chemical engineering operations occurring in the column. The operations and principles are: Chemical Reaction in the reactive trays based on the principles of chemical reaction kinetics; Mass and Heat transfer in the column based on the law of conservation of mass and energy. The models were developed with the following assumptions: The bulk vapor and liquid in the column are in thermodynamic equilibrium with each other. This means that the vapor composition is a function of the liquid composition; there is no temperature gradient within the region where the equilibrium assumption is valid. This implies that the temperature of each stage is uniformly distributed; there is no interphase mass transfer between the liquid and vapor. This means that no transport phenomena occurs across the vapor and liquid films; hence the effects of interphase mass transfer was neglected. In a typical equilibrium stage reactive distillation column, the stage is characterized by temperature T, Pressure P, Molar hold up M and component molar hold up M_i. The feed F enters the stage j with feed composition Z_f and feed enthalpy H_f.

2.1.   Kinetic Model

The benzene hydrogenation reaction: $C_6H_6 + 3H_2 \longleftrightarrow C_6H_{12}$ (3)

is considered to be an equilibrium-limited chemical reaction (Almeida-River and Grievink, 2001). For typical reactions of this type, the expression for the rate of reaction as given by Perry and Green, (2008) are: The reaction kinetics has been considered by Chakrabarty, (2004) to be first order in the two reactants with the rate of reaction expression (r) given as;

$$r = KC_{BZ}C_{H_2}$$ (4)

Equation (4) through a series of substitution and mathematical manipulations can be expressed in terms of fractional conversion of benzene (X_{BZ}) and partial pressure of hydrogen (P_{H_2}) as:

$$r = K_{BZ}X_{BZ}P_{H_2}$$ (5)

Where: $$K_{BZ} = \frac{KP}{(RT)^2}$$ (6)

where $\quad K = k_0 e \dfrac{E}{RT}$ $\hspace{6cm}$ (7)

2.2. Open Loop Process Model

2.2.1 Mass Transfer and Mole Balance Equation

Mass transfer occurring from stage to stage within the column was described using the principle of conservation of mass/moles applied on an equilibrium stage to yield the model equation for predicting the mass flow at any time (t) on tray j of the column as:

$$\frac{dM_j}{dt} = F_j + L_{j+1} + V_{j-1} - L_j - V_j + r_j \varepsilon_j \hspace{4cm} (8)$$

r_j is rate of reaction on stage j and ε_j represent the reaction volume on the jth stage.

Similarly, a component balance for any component i on tray j yields the model equation for predicting the amount (mass) of component i at any time (t) on tray j of the column as:

$$\frac{dM_j X_{i,j}}{dt} = F_j Z_i + L_{j+1} x_{i,j+1} + V_{j-1} y_{i,j-1} - L_j x_{i,j} - V_j y_{i,j} - k_B X_{BZ}, _j P_{H_2} \varepsilon_j \hspace{1cm} (9)$$

The equilibrium assumption between the vapor and liquid gives:

$$y_{i,j} = k_{i,j} x_{i,j} \hspace{5cm} (10)$$

Substituting eqn. (10) into (9); the component model equation can be written for the component benzene, without the subscript *i* or *BZ* since benzene is the reacting component of interest as:

$$\frac{dM_j X_j}{dt} = F_j z + L_{j+1} x_{j+1} + V_{j-1} k_{j-1} x_{j-1} - L_j x_j - V_j k_j x_j - k_B X_j P_{H_2} \varepsilon_j \hspace{2cm} (11)$$

Equation (11) is the dynamic model equation of the column which predicts the amount of benzene at any time (t) on each tray/stage of the reactive distillation column.

2.2.2 Heat Transfer and Heat/Enthalpy Balance

The principle of conservation of energy was used to describe the heat transfer occurring on each stage/tray and gives the model equation for predicting the temperature on each stage/tray of the column as:

$$\frac{C_P d(M_j T_j)}{dt} = F_j C_P T_j^F + V_{j-1} C_P T_{j-1}^V + L_{j+1} C_P T_{j+1}^L - V_j C_P T_j^V - L_j C_P T_j^L + \Delta H_R k_B X_j P_{H_2} \varepsilon_j$$

$$(12)$$

Expanding the derivative term; substitution of the derivative $\dfrac{dM_j}{dt}$ from equation (8) and rearranging gives:

$$M_j C_p \frac{dT_j}{dt} = F_j C_p T_j^F + V_{j-1} C_p T_{j-1}^V + L_{j+1} C_p T_{j+1}^L - V_j C_p T_j^V - L_j C_p T_j^L + \Delta H_R k_B X_{BZ}, _j P_{H_2} \varepsilon_j -$$

$$T_j C_p(F_j + L_{j+1} + V_{j-1} - L_j - V_j - k_B X_{BZ,j} P_{H_2} \varepsilon_j) \hspace{3cm} (13)$$

The superscripts indicate the liquid and vapor properties. However, the equilibrium stage assumption stipulates that the vapor and liquid are in thermodynamic equilibrium; hence the liquid and vapor are at the same temperatures on each stage thus the model equation can be written without the superscripts as:

$$M_j C_p \frac{dT_j}{dt} = F_j C_p T_j^F + V_{j+1} C_p T_{j+1} + L_{j-1} C_p T_{j-1} - V_j C_p T_j - L C_{pj} T_j + \Delta H_R k_B X_{BZ,j} P_{H_2} \varepsilon_j -$$

$$T_j C_p (F_j + L_{j-1} + V_{j+1} - L_j - V_j - k_B X_{BZ,j} P_{H_2} \varepsilon_j) \tag{14}$$

Equation (14) is the dynamic model of the column which predicts the temperature progression on each tray.

2.2.3.   Re-boiler and Condenser

The principles and procedures used in modeling the column were also followed to model the mass (total and component (benzene)) and heat transfer within the re-boiler and condenser. The resulting model equations are:

$$\frac{dM_b^l}{dt} = L_1 - B_F - V_b - r_B \varepsilon_B \tag{15}$$

$$\frac{dM_b^l x_{i,b}}{dt} = L_1 x_1 - B_F x_b - V_b y_b + \Delta H_R k_B X_b P_{H_2} \varepsilon_b \tag{16}$$

$$M_b^l C_p \frac{dT_b}{dt} = L_1 C_p T_1 - B_F C_p T_{bf} - V_b C_p T_b + \Delta H_R k_B X_{BZ,j} P_{H_2} \varepsilon_b - C_p T_b (L_1 - B_F - V_b - k_B x_b P_{H_2} \varepsilon_b)$$

$$\tag{17}$$

$$\frac{dM_c^l}{dt} = V_N - D_F - L_C + r_C \varepsilon_C \tag{18}$$

$$\frac{dM_b^l x_{i,C}}{dt} = V_N k_N x_N - D_F x_{i,C} - L_C x_{i,C} + k_B X_C P_{H_2} \varepsilon_C \tag{19}$$

$$M_C^l C_P \frac{dT_C}{dt} = V_N C_P T_N - D_F C_P T_{df} - L_C C_P T_C + \Delta H_R k_B X_{BZ,j} P_{H_2} \varepsilon_C - Q_C - C_P T_C (V_N - D_F - L_C + k_B X_C P_{H_2} \varepsilon_C)$$

$$\tag{20}$$

Where subscripts b and c represents the re-boiler and condenser respectively.

2.3. Closed Loop Process Model

The control objectives were to ensure that the benzene composition in the bottom product was maintained below the specified limit and that the system returns quickly to its new steady state (stability of the system). These were achieved by suppressing the effects of the identified disturbances. The variables measured in order to monitor the operational performance of the column were the benzene mass fraction in the re-boiler, condenser liquid hold-up and re-boiler liquid hold-up. The disturbances affect the following variables: mass fraction of benzene in the

bottom (reboiler), condenser liquid hold-up and re-boiler liquid hold-up. These variables were controlled by manipulating the following variables: re-boiler heat duty (Q_B), distillate flow rate (D), and bottom flow rate from the re-boiler (B) respectively. Proportional controllers were used to effect the control action. The controller equations for each of the manipulated variables were developed from the general actuating output equation of the controller which is proportional to the error signal. These equations were obtained as:

$$Q_B = Q_{BS} + (M_{QB} - M_{QBS})K_{CQB} \tag{21}$$

$$D = D_S + (M_D - M_{DS})K_{CD} \tag{22}$$

$$B = B_S + (M_B - M_{BS})K_{CB} \tag{23}$$

The subscript (s) stand for steady state values while the others stand for the measured and set point/desired values of the variables. $K_{(subscript)}$ stands for the corresponding proportional controller constant.

2.4. Methods

A hypothetical N stage reactive distillation column was proposed. The developed models written for the N stages/trays were used to perform a simulation of the reactive distillation column to determine the feed tray and the optimum number of trays to achieve desired/specified composition of Benzene in the reformate stream. The developed models were validated using the column configuration and process data from the work of Charkrabaty, (2004). Haven established the feed tray and optimum number of tray/stages, the developed models were used for simulation and control studies. The open loop model of the reactive distillation column was simulated to determine the effects of step changes ($\pm$) of commonly occurring disturbances (the feed stream, being downstream of the reforming unit was usually prone to fluctuations; hence the feed composition, rate and temperature were considered as disturbances of the process) on key performance indicators of the column - mass fraction of benzene in bottom (reboiler), condenser liquid hold-up and re-boiler liquid hold-up (controlled variables). The feedback control configuration with proportional (P) controllers was adopted for control studies of the column. Direct measurements of the controlled variables were used to adjust the manipulated variables (re-boiler heat duty, Distillate flow rate and bottom flow rate from re-boiler respectively). Hence the control system is a Multiple Input - Multiple Output (MIMO) system with three different controlled variables (outputs) requiring three different manipulated variables. The developed proportional controller output equation for the three manipulated variables were substituted in the open loop model equations (instead of the fixed values) to obtain the closed loop model equations. Controller tuning method based on known process model as described in Perry and Green, (2008) was adopted. In this method, the process parameters were specified, then the controller settings iterated until the desired response were obtained. The controller settings which gave the minimum absolute error were taken as the optimum controller settings.   These equations were then used to simulate the close loop response of the column to step changes in the disturbances. Hence determine the effect of the controllers on the key performance indicators of the column,

2.5. Determination of Operating Parameters

The various models developed contain certain process parameters and constants which have to be determined before the model equations can be solved. These parameters were determined as follows:

2.5.1.   Heat Capacity

The heat capacity (a thermodynamic property) of reformate which is a mixture of organic liquids was calculated using the principles of pseudo properties (Sinnott, 2005).

$$C_{P(reformate)} = X_a C_{pa} + X_b C_{pb} + X_C C_{pc} + ... \tag{24}$$

The heat capacity of an organic liquid as a function of temperature is: (Perry and Green, 2008).

$$C_{P_L} = C_1 + C_2 T + C_3 T^2 + C_4 T^3 + C_5 T^4 + ...\tag{25}$$

Where T is temperature in Kelvin and C_{PL} is in J/kmol K.

Substituting equation (25) into (24) and truncating after the second order, the heat capacity of the reformate mixture was obtained as:

$$C_{P(reformate)} = \sum_{i=1}^{n} X_i (C_1 + C_2 T + C_3 T^2)_i \tag{26}$$

Where n is the total number of components i in reformate.

Equation (26) with the reformate composition given in Chakrabarty, (2004) and component constants given by Perry and Green, (2008) were used to obtain the specific heat capacity of reformate as a function of temperature as:

$$C_{P\,reformate} = 114946 - 33T + 0.685792209T^2 \tag{27}$$

2.5.2.   Calculation of Heat of Reaction for Benzene Hydrogenation

The heat of reaction was calculated as the difference between the heats of formation of the products and the reactants thus:

$$\Delta H_r = \sum_{i-1}^{n} \Delta H_F \Pr oducts - \sum_{i-1}^{n} \Delta H_F \operatorname{Re} ac \tan ts \tag{28}$$

The heat of formation of hydrogen gas is zero; hence equation (26) reduces to:

$$\Delta H_r = \Delta H_{Formation} CycloHexane - \Delta H_{Formation} Benzene \tag{29}$$

The heat of formation for cyclohexane and benzene were obtained from Perry and Green (2008).

2.5.3.   Calculation of Benzene Composition

The Benzene composition in gasoline expressed in percentage by volume (vol %) was expressed in mass fraction using the relationship:

$$\% \text{ Vol. Benzene} = \frac{\text{Vol. of Benzene in Reformate}}{\text{Total Vol. of Reformate}} = \frac{V_B}{V_R} \tag{30}$$

$$\text{Where: } V_B = \frac{M_B}{\rho_B}; \qquad V_R = \frac{M_R}{\rho_R} \tag{31}$$

M_B and M_R are benzene and reformate Molecular weight.

Substituting equation (29) into (28) and rearranging gives the benzene composition in terms of mass fraction as:

$$\frac{M_B}{M_R} = \% \, vol. \, \frac{\rho_B}{\rho_R} \tag{32}$$

This was used to obtain the benzene mass fraction of the bottom product.

2.5.4.   Calculation of Average Molecular Weight of Reformate

The feed composition in terms of weight percent (mass fraction) and the mole fractions were calculated using the molecular weights of the components and the mass fraction. With these, the average molecular weight of reformate was obtained.

2.5.5.   Determination of Equilibrium Stage K-Values

The combined Dalton's and Raoult's equations were used to obtain a relationship for the equilibrium stage K values in terms as pressure from:

$$y_i P = x_i P_i^{sat} \tag{33}$$

At equilibrium:

$$y_i = k_i x_i \tag{34}$$

Substituting equation (34) in (33) and rearranging gives:

$$k_i = \frac{P_i^{sat}}{P} \tag{35}$$

P_i^{sat} for benzene in any tray j; $\left(P_j^{sat}\right)$ was obtained in terms of temperature of the tray using the Antoine's equation since the feed temperature (456 K) falls within the temperature range where the Antoine equation is valid (Perry and Green, 2008) as:

$$ln P_j^{sat} = C_1 + \frac{C_2}{T_j} + C_3 ln T_j + C_4 T_j^{C_5} \tag{36}$$

The values of these constants were obtained from Perry and Green, (2008) for benzene. Substitution of P_j^{sat} obtained from equation (36) into equation (35) gives the equilibrium stage K value as a function of temperature of any tray as:

$$K_i = \frac{exp\left(83.107 - \frac{6486.2}{T_j} - 9.2194 \, Ln T_j + 6.9844 x 10^{-6} T_j^2\right)}{P} \tag{37}$$

2.5.6.   Operational Data

The operational data for this column were based on projected Nigerian gasoline production considering the amount of reformates used in blending. The Port Harcourt refinery produces 3,080,380,000 Kg per annum of gasoline. (PHRC, 2006). A typical gasoline blend consists of about 32% reformate (WRPC, 2010). The column is to process half of this. Other relevant operational data were obtained from the works of Charkrabarty (2004), Perry and Green (2008), assumed based on distillation principles and rule of thumb.

2.6. Solution Techniques

The model equations developed were a system of N (number of trays used) coupled ordinary differential equations (ODE) each for the general mass, component mass and energy balances on each of the N stages making a total of 3N equations. There were also N algebraic equations (AE) for the component K-values. Hence a total of 3N ODEs and N AEs were solved for the open and closed loop models. The fourth order Runge-Kutta algorithm was adapted to develop a visual basic program to solve these equations and perform the simulations.

3.   Discussion of Results

The simulation of the developed N stage column to determine optimum process conditions (feed entry point and number of trays/stages that satisfies gasoline specification of less than 0.0062 vol. % (0.00599 mass fraction) of benzene) gave: an optimum number of 74 trays/stages, with the feed entering at the 24th tray produced a bottom product with a benzene mass fraction of 0.0056. The developed models were validated with process parameters, column operating data/conditions of Charkrabaty, (2004); (a 72 tray column, the feed introduced on the 25th tray) the benzene mass fraction of the bottom was 0.00589 (0.0061 vol. %). This shows a deviation of 4.92%, hence the developed model results compared favorably with the plant/literature values and satisfies the stipulated EPA benzene concentration in gasoline of 0.00599 (mass fraction) (.0062 vol. %). The developed models were therefore used for simulation of the reactive distillation column. The open loop transient behavior of the benzene mass fraction in the gasoline withdrawn on the first tray (the bottom) is shown in Figure 1.
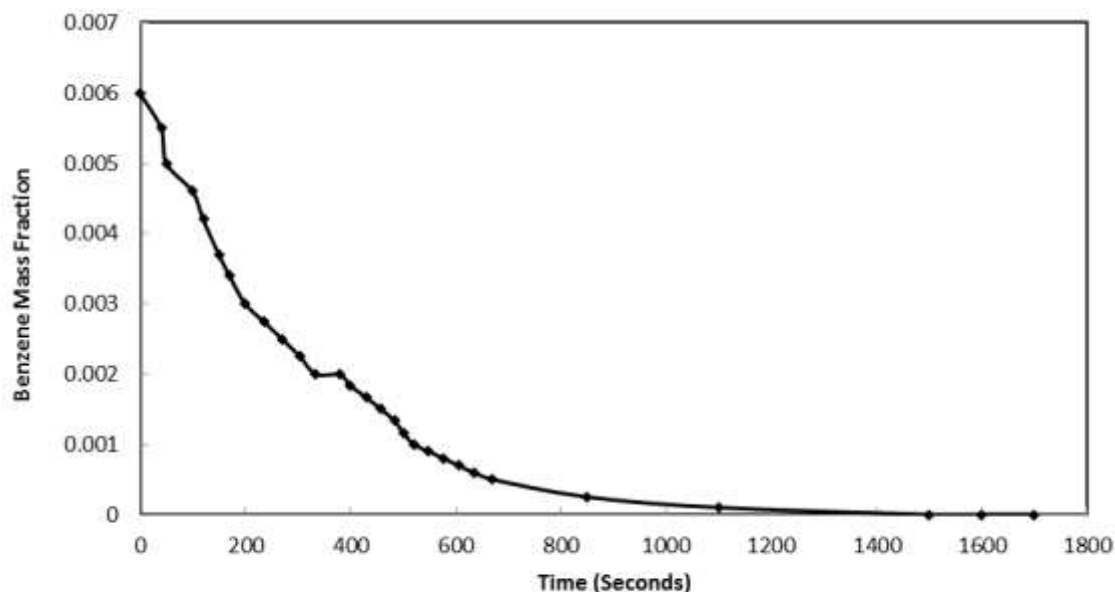

Figure 1: Variation of Benzene Mass Fraction of The First Tray With Time

The benzene mass fraction approaches values less than 0.005986 at less than 100 seconds operation of column. There was a continuous decrease of the benzene mass fraction in the bottom product and it gradually attained a steady state value of 0.0000167 in about 1500 seconds.

3.1. Open Loop Responses

The response of the column without controllers (open loop response) was studied by simulating the behavior of the open loop model equations to fluctuations/changes in the disturbances (the feed flow rate, composition and temperature). The open loop response of the following outputs/controlled variables: reboiler liquid holdup,

reboiler benzene mass fraction and condenser liquid holdup to changes in these disturbances are hereby presented.

3.1.1.   Response of Re-boiler (Column Base) Liquid Hold Up to Change in Feed Rate

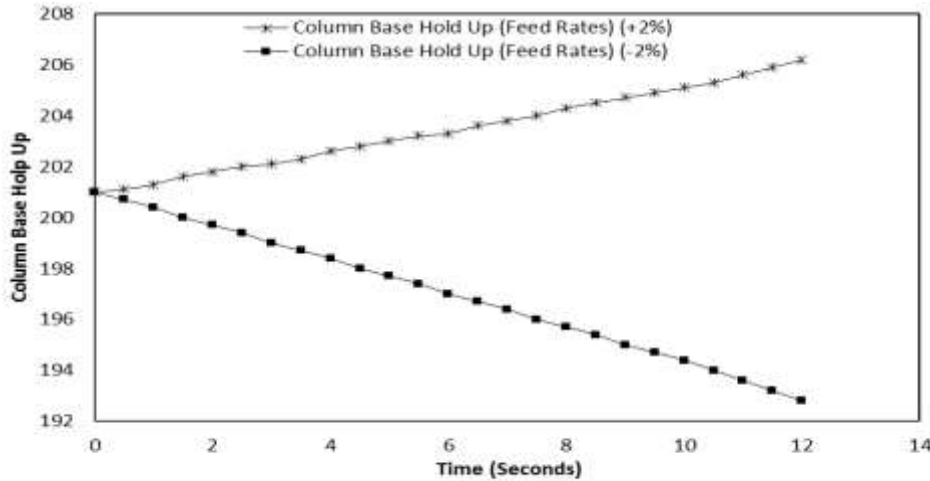The response of the column to step changes (increase and decrease) in the feed rate are shown in Figure 2.

Figure 2: Column Base Hold-Up Response to step change in feed rate

An increase in the feed rate results in an increase in the quantity of liquid in the column. Thus more liquid flow in and cascade down the trays accumulating at the column base with time. The column base hold up will therefore continuously increase as shown in Figure 2.   If this trend (increase in column base hold up) continues, the column begins to flood, causing a significant decrease in separation efficiency thus requiring an infinitely large column. A decrease in the feed rate gives an opposite trend as shown in Figure 2, a continuous reduction in the column base hold up.

3.1.2 Response of Re-Boiler Benzene Mass Fraction to Change in Feed Composition

The effects of step changes in the feed composition of benzene ($\pm$ 25%) on the benzene mass fraction in the re-boiler are shown in Figure 3.
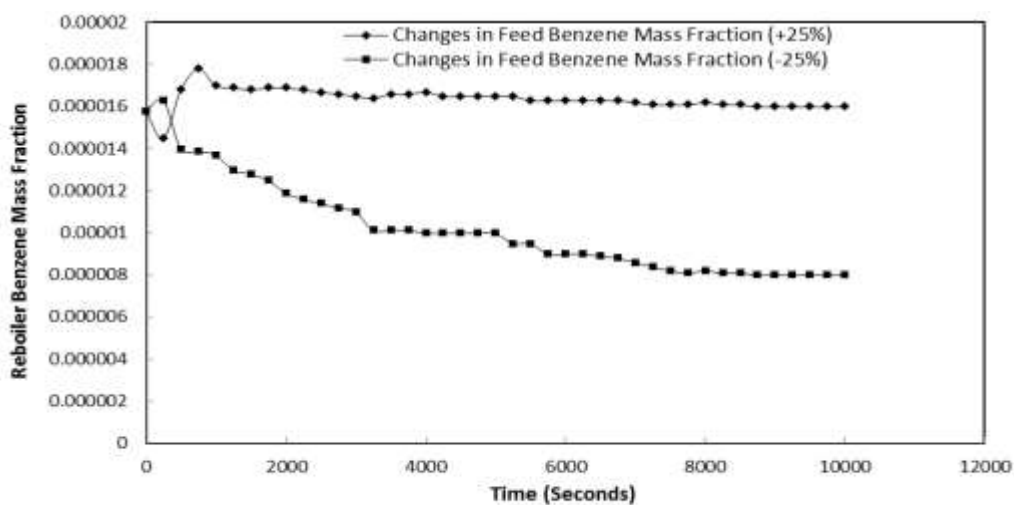

Figure 3: Response of Reboiler Benzene Mass Fraction to Changes in feed composition

Increase or decrease of the benzene composition in the feed means a decrease or increase in the composition of some other components of the feed.

An increase in benzene concentration in the feed means an increase in the reactant concentration for the hydrogenation reaction. This causes an increase in the rate of reaction during which more of the reactant benzene is consumed; resulting in less/a decrease in the benzene concentration in the bottom. However, this increased rate of reaction results in the release of more heat (hydrogenation reaction is exothermic) resulting in an increase in reaction temperature. This may cause the equilibrium to shift in the reverse direction viz: a reduction in the rate of reaction with less benzene being consumed leading to an increase in the concentration of benzene in the re-boiler.   A decrease in benzene concentration gives an opposite trend. A decrease in rate of reaction resulting in more benzene in the bottom; however, the decrease reaction rate means less heat is generated and lower temperatures on the trays. This may cause the equilibrium to shift in the reverse direction leading to increase reaction rate and less benzene in the bottom. These dynamics continues in both situations until stability is attained.

3.1.3 Response of Condenser Liquid Holdup to Change in Feed Temperature

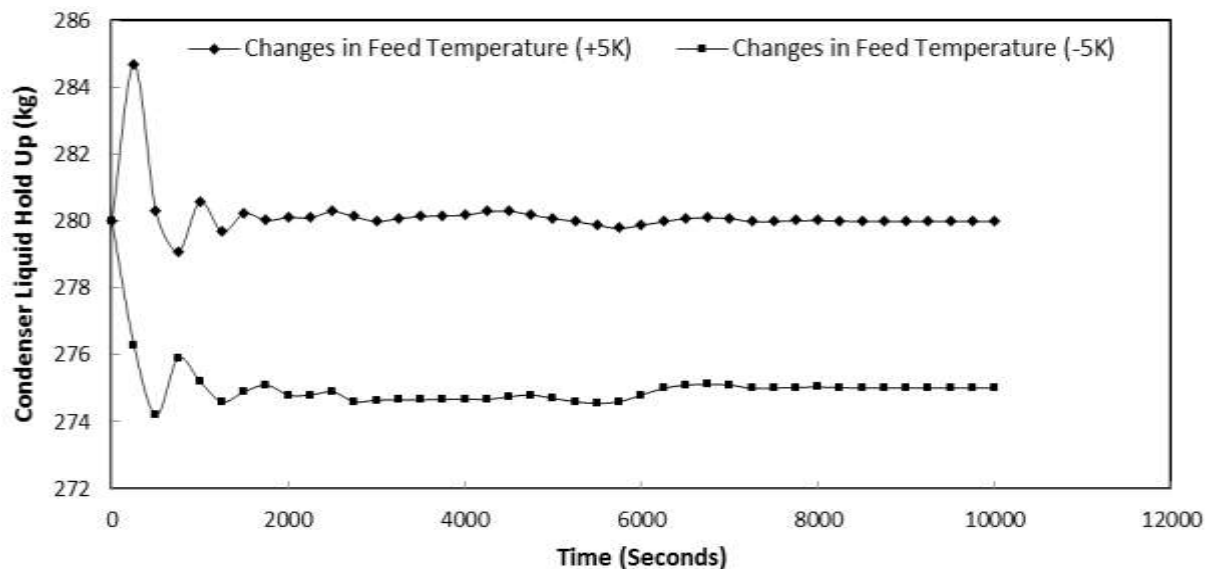The responses of the column to a $\pm 3K$ step changes in the feed temperature are shown in Figure 4.

Figure 4: Response of Condenser Liquid hold-up due to feed temperature

An increase in feed temperature would cause an increase in column temperature resulting in increased vapor flow; hence the liquid hold-up in the condenser suddenly increases. This increase occurred for a short period due to the instability caused by this disturbance, followed by a period of fluctuations (increase and decrease) until the condenser liquid holdup eventually attained new steady state at values slightly higher than the initial hold up. A reduction in the feed temperature gives a response in the reverse direction; a sudden decrease followed by fluctuations (increase and decrease) until new steady state was attained at lower values than the initial hold-up. The new steady states were attained after 8750 seconds.

3.2. Closed Loop Response

The effectiveness of controllers to meet the control objectives; particularly to ensure faster stability of the column were ascertained by studying the behavior of the closed loop model equations (responses of the controlled variables) to fluctuations in the disturbances and changes in the manipulated variables as inputs to the

column.

A   The response of two controlled variables: condenser liquid holdup and reboiler benzene mass fraction to fluctuations of a disturbance - the feed temperature is hereby presented.

The closed loop response of the condenser liquid hold-up and reboiler benzene mass fraction to changes in feed temperature are shown in Figures 5 and 6 respectively.
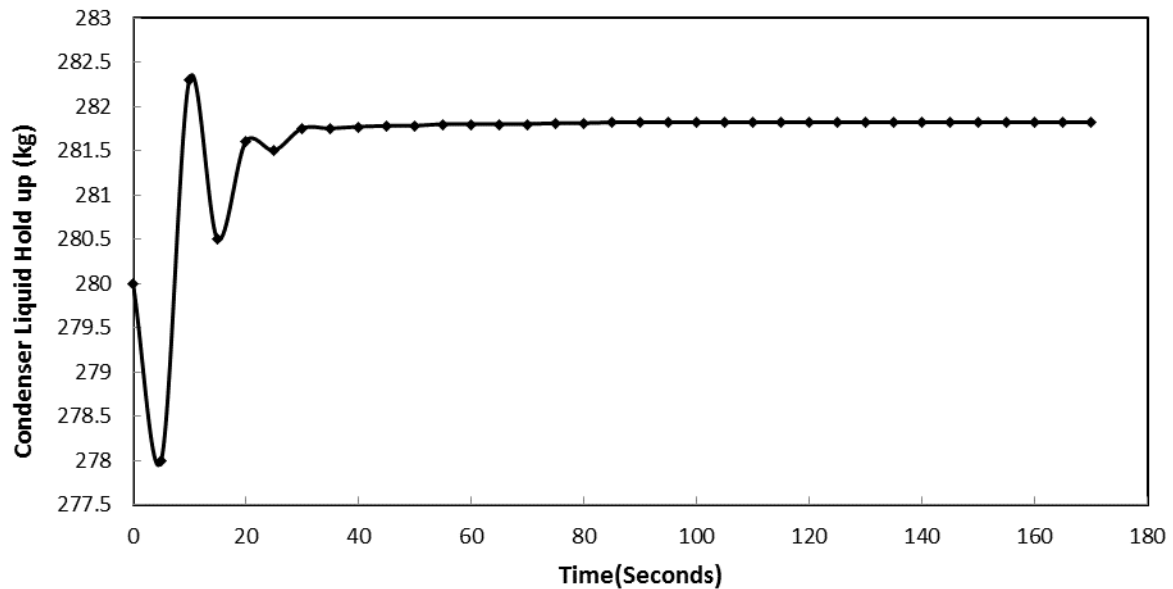

Figure 5: Response of Condenser Liquid hold up to change in feed Temperature
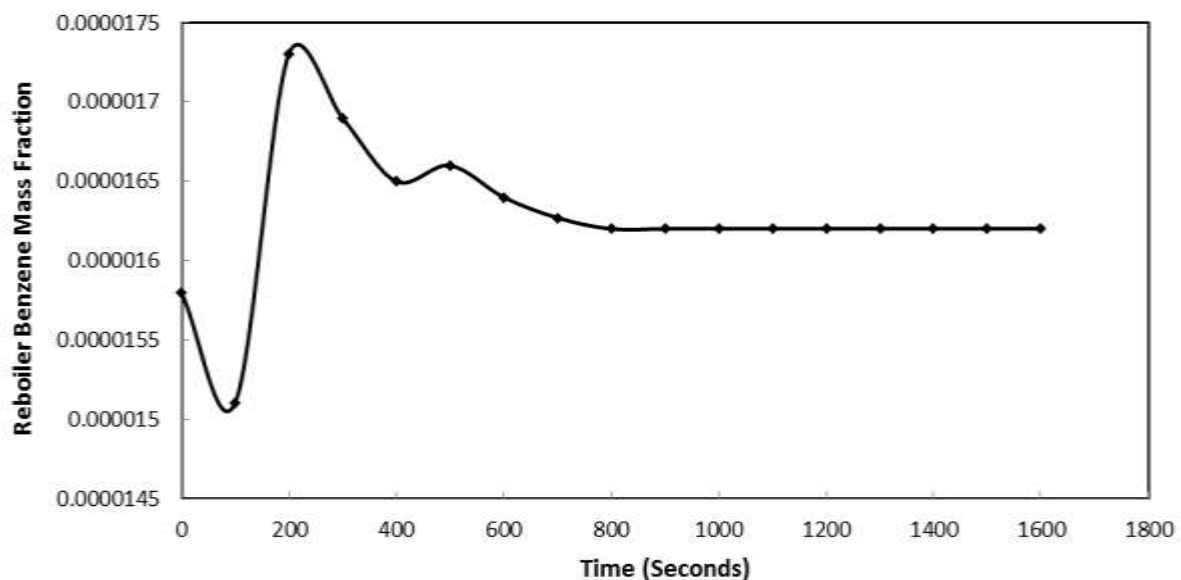

Figure 6: Closed Loop Response of the Reboiler Benzene Mass Fraction to Changes in Feed Temperature

The trend of the closed loop response of the condenser liquid hold up to changes in feed temperature is similar to that of the open loop response however; a new steady state was quickly attained for the close loop model/system after 30 seconds as shown in Figure 5 compared to a time of 8750 seconds of the open loop model in Figure 4. This showed that the effect of this input disturbance was quickly eliminated in the column due to the proportional

control action effected.

An increase in feed temperature increases column temperature and the rate of benzene hydrogenation reaction resulting in a reduction in the benzene concentration in the bottom. Also as reaction proceeds, increase in feed temperature for an exothermic reaction may shift the equilibrium in the reverse direction. These dynamics continues until stability was attained. Hence figure 6 shows an initial drop in benzene mass fraction in the reboiler, a sharp increase and some fluctuations until new steady state was attained after 800 seconds with a benzene mass fraction of 0.0000162 far less than 0.005986 (i.e. 0.62% by Volume) compared to a steady state value of 0.0000167 attained in about 8750 seconds in the open loop process.

B   The response of a controlled variable: the reboiler benzene mass fraction to changes in the following manipulated variables; reboiler heat duty and distillate flow rate are shown in Figures 7 and 8.
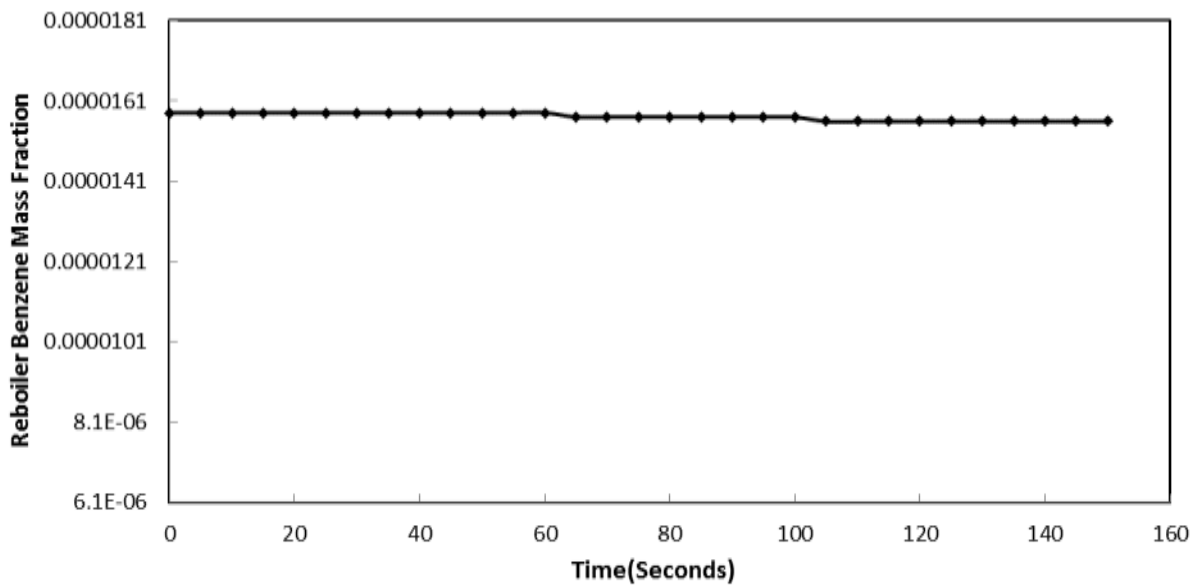

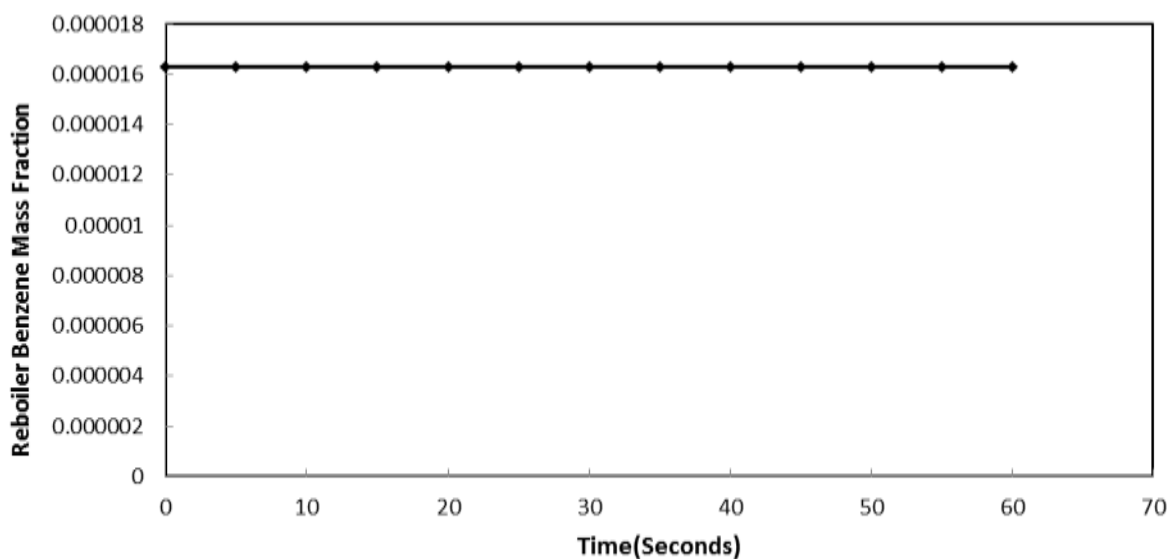Figure 7: Closed Loop Response of Reboiler Benzene Mass Fraction to Changes in Reboiler Heat Duty

Figure 8: Closed Loop Response of the Reboiler Benzene Mass Fraction to Change in Distillate flow rate

As the re-boiler heat duty and distillate flow rate are manipulated respectively; the re-boiler benzene mass fraction is expected to quickly return close to its set point (initial steady state), that is, reduce the error/offset (difference between final and initial stead state values). Figure 7 shows that as the re-boiler heat duty is manipulated, the fluctuations of the benzene mass fraction is greatly reduced and new steady state value of 0.0000156 was attained in 105 seconds compared to initial value of 0.0000158 giving an error of 0.0000002. However, when the re-boiler heat duty was not manipulated; Figure 6 showed that a new steady state of 0.0000162 was attained in 900 seconds, giving an error of -0.000004. Figure 8 however showed that the distillate flow rate had no effect on the re-boiler benzene mass fraction. Hence the re-boiler Heat duty should be the manipulated variable to control the re-boiler benzene mass fraction.

4.   Conclusion

Dynamic models of an N stage reactive distillation column for the hydrogenation of benzene in a reformate have been developed. The developed models were used to obtain optimum number of trays and mass fraction of benzene in the bottom product of the column. The developed models were tested using plant data from Charkrabaty, (2004) and a benzene mass fraction on the first tray (bottom) of 0.00589 (0.0061 vol. %) was obtained compared to 0.00599 (0.0062 vol. %) obtained by Charkrabaty, (2004). The developed models were therefore used for simulation of the reactive distillation column. The open loop models were simulated to determine the effects of commonly occurring disturbances (the composition, flow rate and temperature of the feed stream) on key performance indicators of the column - mass fraction of benzene in bottom, condenser liquid hold-up and re-boiler liquid hold-up (controlled variables). The results showed linear relationships (mirror images of step changes) between the disturbances and controller/output variables with upset conditions (fluctuations) persisting for a maximum of 8750 seconds before stability was attained. A Multiple Input - Multiple Output (MIMO) feedback control configuration with proportional (P) controllers was adopted for control studies of the column using the re-boiler heat duty, reflux flow rate, Distillate flow rate and bottom flow rate from re-boiler as manipulated variables. After appropriate tuning, the close loop responses of the column to step changes in the disturbances were investigated. The results showed that stability was quickly attained with upset conditions disappearing in 30 – 900 seconds.

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Nomenclature

C_i =   Concentration of Component i (mol/m^3)

C_P =   Heat Capacity (J/kg K)

F_j =   Feed Flowrate on Tray j (kg/s)

K   =   Reaction rate constant (s^{-1})

K_O =   Pre-exponential Constant

L_j =   Liquid Flowrate on Tray j (kg/s)

M_j =   Mass on Tray j (kg)

M_R =   Mass of Reformate (kg)

P   =   Total Pressure of Column (N/m^3)

P_{H_2} =   Partial Pressure of Hydrogen (N/m^3)

R   =   Universal Gas Constant

r   =   Rate of Reaction (kgm^{3}s^{-1})

r_j =   Rate of Reaction on Tray j (kgm^{3}s^{-1})

T   =   Temperature (K)

T_j =   Temperature on Tray j (K)

X_i =   Mole Fraction of Component i

V_j =   Vapor Flowrate on Tray j (kg/s)

Z_j =   Mass of Component in Feed on Tray j (kg)

ΔH_r =   Heat of Reaction (J/kg)

ε_j =   Reaction volume on Tray j (m^3)