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JUDUL : DYNAMIC MODELING OF A REACTIVE DISTILLATION COLUMN

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DYNAMIC MODELING OF A REACTIVE DISTILLATION COLUMN

BERT CHIN KIEN CHUNG

Thesis submitted in partial fulfillment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical and Natural Resources Engineering
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JANUARY 2012

SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

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STUDENT'S DECLARATION

I hereby declare that the work in this thesis entitled "Dynamic Modeling of A Reactive Distillation Column" is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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Special thanks to my family for their love,

Dear loving person for your moral support,

Lots of thanks to my friends, who guided and helped me,

Last but not least, to my supervisor, thanks a lot.

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ABSTRACT

This research focuses on white box modeling of the dynamics of a reactive distillation column, precisely, one that is used for the commercial production of MTBE (methyl-tert-butyl-ether) by the reaction between methanol and isobutylene. The motivation for this study is mainly the process complexity posed by simultaneous reaction and separation which complicates the design and control of the column. In this study, an equilibrium model of reactive distillation column is developed in MATLAB by putting together the MESH equations and other equations like Francis weir formula and reaction rate law. Subsequently, the developed model is validated by comparison of simulation results with industrial data. Finally, the dynamic behaviour of the system is studied by applying step changes to each of the input variables, one at a time. The model of reactive distillation column is successfully developed. It is also proven to be a good representation of the column in the industry because model predictions and plant data come to a good agreement.

ABSTRAK

Kajian ini memberi tumpuan kepada pemodelan kotak putih dinamik kolum penyulingan reaktif, secara tepatnya, kolum yang digunakan untuk pengeluaran komersial MTBE (metil-tert-butil-eter) oleh tindak balas antara metanol dan isobutena. Motivasi untuk kajian ini ialah kerumitan proses yang disebabkan oleh tindak balas dan pemisahan serentak yang merumitkan perekaan dan kawalan kolum. Dalam kajian ini, model keseimbangan kolum penyulingan reaktif diterbitkan dalam MATLAB dengan mengumpulkan persamaan MESH dan persamaan lain seperti formula empang dasar Francis dan persamaan kadar tindak balas. Selepas itu, model yang diterbitkan telah disahkan melalui perbandingan keputusan simulasi dengan data industri. Akhir sekali, tingkah laku dinamik sistem dikaji dengan melakukan perubahan langkah untuk setiap pemboleh ubah dimanipulasi, satu pada satu-satu masa. Model kolum penyulingan reaktif berjaya diterbitkan. Ia juga terbukti bahawa model tersebut mampu mewakili kolum dalam industri dengan baiknya kerana keputusan simulasi dengan data industri adalah mirip.

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r	Rate of reaction per unit mass of catalyst
q	Number of equivalent acid groups on one unit mass of catalyst
a	Activity of different components
k_f	Rate constant of the forward reaction
K_{eq}	Equilibrium constant
T	Temperature
E_n	Murphree tray efficiency
y_n	Actual vapour composition
y_{n-1}	Actual composition of vapour received from the tray below
y^*_n	Equilibrium vapour composition that corresponds to the bulk liquid composition on the tray
x_i	Initial value of variable x
y_i	Initial value of variable y
y_{i+1}	New value of variable y
h	Step size
i	Dummy that represents components
j	Dummy that represents stages
m	Dummy that represents reactions
M_j	Molar holdup on stage j
M_c	Molar holdup in condenser
M_b	Molar holdup in reboiler
V_j	Vapour flow rate from stage j
L_j	Liquid flow rate from stage j
F_j	Feed flow rate to stage j
$\sum$	Summation notation
$v_{i,m}$	Reaction coefficient of component i in reaction m
$r_{m,j}$	Rate of reaction m on stage j per unit mass of catalyst
W_j	Weight of catalyst on stage j
$z_{i,j}$	Composition of component i in feed to stage j
$x_{i,j}$	Composition of component i in liquid flow from stage j
$y_{i,j}$	Composition of component i in vapour flow from stage j

h_j	Enthalpy of liquid flow from stage *j*
H_j	Enthalpy of vapour flow from stage *j*
$h_{F,j}$	Enthalpy of liquid feed to stage *j*
$H_{F,j}$	Enthalpy of vapour feed to stage *j*
q	Degree of superheat or liquid fraction in feed
$\Delta H_{m,j}^{R}$	Heat of reaction of reaction *m* on stage *j*
R	Reflux flow rate
D	Distillate flow rate
Q_C	Condenser duty
B	Bottom product flow rate
Q_B	Reboiler duty
P	Pressure
γ_i	Activity Coefficient
P_i^{sat}	Vapour pressure of component *i*
l_w	Weir length
H_{ow}	Weir height
t	Time
F_L	Liquid flow rate over weir

LIST OF ABBREVIATIONS

RDC	Reactive distillation column
PID	Proportional, integral and derivative
MTBE	Methyl tert-butyl-ether
MeOH	Methanol
IB	Isobutylene
MESH	Mass balance, equilibrium relation, summation equation and heat balance
EQ	Equilibrium
NEQ	Nonequilibrium
UNIQUAC	Universal Quasichemical

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CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Reactive distillation is a process in which catalytic reactions and separation by distillation are carried out simultaneously in a column. A schematic diagram of reactive distillation column is shown in figure 1.1. Industrial applications of the process include the production or decomposition of esters, ethers and alcohols, selective hydration of olefins or aromatics and isomerization reactions (Moritz *et al.*, 2003).

Amongst the benefits of employing such operation is that the process simplification by combining reaction and separation reduces capital costs, this is because plant owners need not purchase reactors and distillation columns separately as they come in a ‘package’. Next, it improves conversion for reversible reactions as the built-in separation enables product species to be taken away from the reaction zone, in this way, the system equilibrium shifts towards the right according to Le Chatelier’s principle and more reactants will be consumed to form products. For the same reason, reactive distillation improves selectivity and minimizes side reactions. Finally, if the reaction taking place in the column is exothermic, heat integration benefits can be derived because the liberated heat can be utilized for the heat of vaporization and reduce reboiler duty (Taylor and Krishna, 2000).

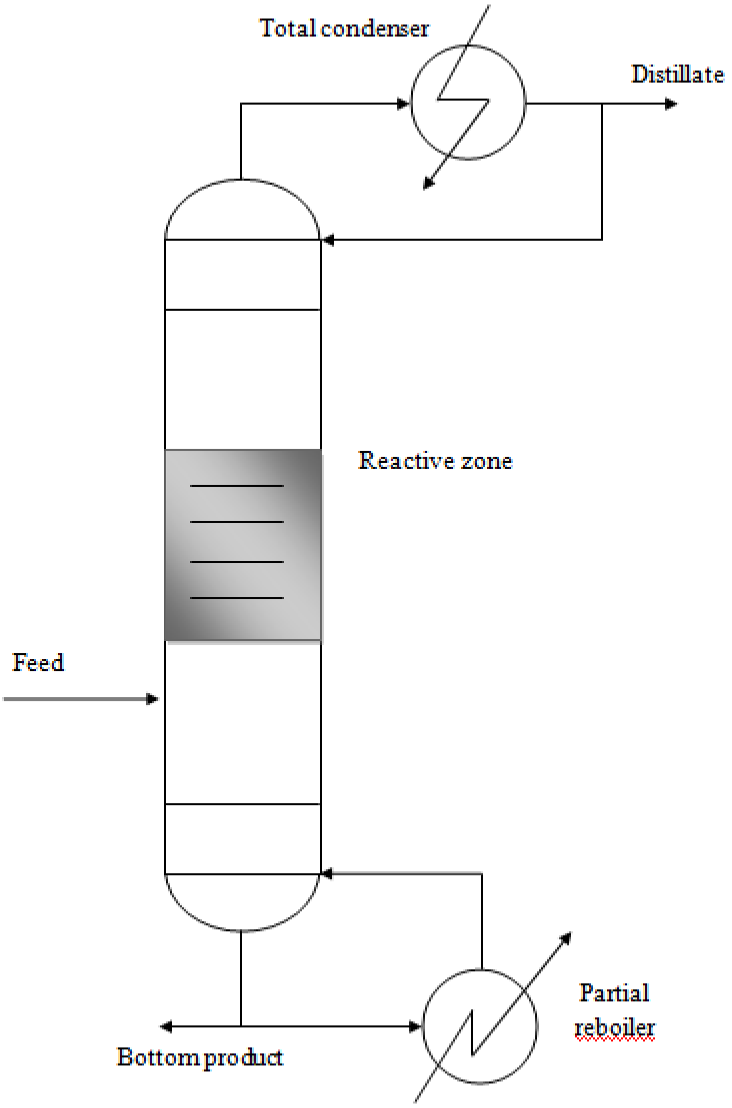


Figure 1.1: A schematic diagram of reactive distillation column

Despite having numerous advantages, reactive distillation does have some drawbacks. Firstly, it is not practical for reactions that require long residence time as a large column and tray holdup would be needed, hence it is likely more economic to resort to the conventional reaction-followed-by-separation setup. Besides, for cases where the optimum operating conditions of reaction and distillation are far from each other, it simply defeats the purpose of the combination. Moreover, it is not suitable for large flow rates due to liquid distribution problems in packed section, too large a flow rate will cause liquid to accumulate at different parts of the packing or even flood it, this situation impedes the up bound flow of vapor and renders the entire column ineffective. Lastly, the reactants and products must have suitable volatilities, if they have similar volatilities, they would vaporize to the same extent and would not achieve a good extent of separation (Taylor and Krishna, 2000).

1.2 PROBLEM STATEMENT

The reactive distillation column is associated with complex processing configurations which complicate the design procedures and considerations. Precisely, there exists multiplicity and nonlinear interactions between reaction kinetics, intra-catalyst diffusion, vapor-liquid equilibrium and mass transfer (R. Taylor & R. Krishna, 2000). Moreover, in most chemical industries, where more often than not, products of high purity, processes of high selectivity and conversion are desired, the process nonlinearity is amplified. Distillation systems become highly nonlinear as the purity exceeds 98% (Olanrewaju and Al-Arfaj, 2005). A good dynamic model is also necessary to verify the design of the column.

Next, the dynamics and control of RDC are poorly understood as there lacks publications in the literature (Peng *et al.*, 2003). The nonlinearity of the system also poses problems to the control aspects of the reactive distillation column. Standard PID tuning with fixed parameters is inadequate for handling such processes (Bisowarno *et al.*, 2004). For complex processes such as this, advanced control strategies like model based controllers should be employed and this can only be made possible by a thorough understanding of the dynamics of the reactive distillation column. In addition, most of the published works appear to be steady-state models (Peng *et al.*, 2003).

1.3 OBJECTIVES

This research aims to attain the objectives below as part of the requirements for its success.

i. To develop an equilibrium model for reactive distillation column.

ii. To validate the model with industrial data.

iii. To study the dynamic performance of developed model.

1.4 SCOPE OF STUDY

The scope of this study is chosen in order to set the limit to where this research will explore, and also to ensure that the research objectives can be achieved without deviations. This study focuses on the white box modeling of the commercial MTBE (methyl tert-butyl ether) production by the reaction of methanol and isobutylene in a reactive distillation column.

1.5 SIGNIFICANCE OF RESEARCH

The developed process model for reactive distillation column will contribute to the following aspects (Seborg *et al.*, 2004):

i. Design of the reactive distillation column; the model allows dynamic and steady-state behavior of the system to be detailed and understood. This information will greatly ease the design.

ii. Development of control strategies; with the knowledge about the system behavior at disposal, various control methods can be proposed and tested. The effectiveness of different control strategies can be compared and the best method determined and implemented.

iii. Optimization of operating conditions; owners of the column can utilize the model to estimate the optimum operating conditions from time to time. In this way, the owner is subjected to benefits in yield, profit and rate of product manufacture.

iv. Training for plant operating personnel; the model can be developed into a simulation software to provide a realistic situation that imitates the circumstances when the reactive distillation column is to be operated. With that, plant workers can learn to operate and get familiar with the equipment before they are actually put on duty.

CHAPTER 2

LITERATURE REVIEW

2.1 MTBE

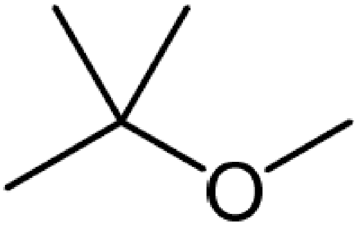


Figure 2.1: Skeletal Structure of MTBE

The above figure shows the skeletal structure of MTBE (or methyl tert-butyl ether in full). MTBE is an organic compound with molecular formula $C_4H_9OCH_3$ and a molecular weight of 88.15 g/mol. It is a colourless liquid with an ether-like smell and is extremely volatile and flammable. It is widely used around the globe as a gasoline oxygenate to increase the octane number. High purity MTBE is utilized as a solvent in labs as well as pharmaceutical industries (Hatermann, n.d.)

2.2 REACTION KINETICS

The reversible reaction between methanol (MeOH) and isobutylene (IB) to produce MTBE can be represented by the following equation:

$$MeOH + IB \leftrightarrow MTBE \tag{2.1}$$

The reaction is heterogeneously catalyzed by Amberlyst 15. The rate of the liquid phase reaction can be described by the rate equation as shown below (Rehfinger and Hoffmann, 2001; Eldarsi and Douglas, 1998):

$$r = qk_f\left(\frac{a_{IB}}{a_{MeOH}} - \frac{a_{MTBE}}{K_{eq}\, a_{MeOH}^2}\right) mol/s\,.kg \tag{2.2}$$

r represents the rate of reaction per unit mass of catalyst while q is the number of equivalent acid groups on one unit mass of catalyst resin (4.9 equiv/kg for Amberlyst 15), a is the activity of different components, k_f is the rate constant of the forward reaction, K_{eq} is the equilibrium constant. The expressions for k_f and K_{eq} are as follows:

$$k_f = 3.67 \times 10^{12} \exp\left(\frac{-11110}{T}\right) mol/s\,.kg \tag{2.3}$$

$$K_{eq} = 284 \exp[f(t)] \tag{2.4}$$

$$f(t) = A_1\left(\frac{1}{T} - \frac{1}{T_0}\right) + A_2 \log\left(\frac{T}{T_0}\right) + A_3(T - T_0) + A_4(T^2 - T_0^2) + A_5(T^3 - T_0^3) + A_6(T^4 - T_o^4) \tag{2.5}$$

where

$T_o = 298.15\ K$

$A_1 = -1.49277 \times 10^3\ K$

$A_2 = -77.4002$

$A_3 = 0.507563\ K^{-1}$

$A_4 = -9.12739 \times 10^{-4}\ K^{-2}$

$A_5 = 1.10649 \times 10^{-6}\ K^{-3}$

$A_6 = -6.27996 \times 10^{-10}\ K^{-4}$

2.3 TYPES OF MATHEMATICAL MODELS

2.3.1 White Box Model

A white box model is a list of equations that represents a system or process; it is developed from theories of science, namely, conservation principles that apply to mass, energy and momentum as well as relations that govern the equilibrium between liquid and vapor. What differentiates a white box model from the other types is that it provides details about the insights of a system (Seborg *et al.*, 2004). The followings are equations that constitute a white box model of a reactive distillation column:

$$\frac{\mathrm{d}U_j}{\mathrm{d}t} = V_{j+1} + L_{j-1} + F_j - (1 + r_j^V)V_j - (1 + r_j^L)L_j + \sum_{m=1}^{r} \sum_{i=1}^{c} v_{i,m} R_{m,j} \varepsilon_j.$$

$$y_{i,j} = K_{i,j} x_{i,j}$$

$$\sum_{i=1}^{c} x_{i,j} = 1, \quad \sum_{i=1}^{c} y_{i,j} = 1$$

$$\frac{\mathrm{d}U_j x_{i,j}}{\mathrm{d}t} = V_{j+1} y_{i,j+1} + L_{j-1} x_{i,j-1} + F_j z_{i,j} - (1 + r_j^V)V_j y_{i,j} - (1 + r_j^L)L_j x_{i,j} + \sum_{m=1}^{r} v_{i,m} R_{m,j} \varepsilon_j$$

$$\frac{\mathrm{d}U_j H_j}{\mathrm{d}t} = V_{j+1} H_{j+1}^V + L_{j-1} H_{j-1}^L + F_j H_j^F - (1 + r_j^V)V_j H_j^V - (1 + r_j^L)L_j H_j^L - Q_j$$

Figure 2.2: An example of white box model

Source: Taylor and Krishna (2000)

2.3.2 Black Box Model

Unlike in a white box model, the system under consideration is treated like an opaque box, that is, only the input and output for the system are considered but the inner workings are not known. The development of a black box model is based on regression to find the relations between the input and output (Seborg *et al.*, 2004). A black box model which represents the temperature increase due to heat liberation by thermogenin, a mitochondrial membrane protein is shown below:

$$\dot{N} = Nr\left(1 - \frac{N}{K}\right)$$

$$\dot{G} = -\beta_1 N$$

$$\dot{H} = \alpha \frac{\left(\frac{G}{K_1}\right)^n}{1 + \left(\frac{G}{K_1}\right)^n} - \beta_2 H + \gamma$$

$$\dot{T} = -k(T - T_a) + \xi H$$

Figure 2.3: An example of black box model

Source: IGEM (2008)

2.3.3 Grey Box Model

In a grey box or hybrid model, fundamental principles from a white box model is combined into a black box model, hence it gives better physical meaning than a complete black box model. In this approach, the model is defined partly by physical knowledge while the remaining unknown parts are described by a black box model. An example of a grey box model representing a reactive distillation column is as follows:

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} S_1 \\ S_2 \\ A \\ D \\ E \\ G \end{pmatrix} = \begin{bmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 2 & 1 & -1 & -1 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 1 & -1 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{pmatrix} r_1 \\ r_2 \\ r_3 \\ r_4 \end{pmatrix}$$

$$+\frac{1}{V}\begin{pmatrix} F_{S1,in} & S_{1,in} & -F_l S_1 \\ F_{S2,in} & S_{2,in} & -F_l S_2 \\ & & -F_l A \\ F_{D,in} & D_{in} & -F_l D \\ & & -F_l E \\ & & -F_l G \end{pmatrix} - \frac{F_v}{V}\begin{pmatrix} 0 \\ 0 \\ 0 \\ f_D \\ f_E \\ f_G \end{pmatrix} \quad \dot{Y} = -\frac{F_l}{V}Y + \frac{F_{D,in}D_{in}}{V}(U-1) - r_4 + \frac{F_v}{V}f_D - \frac{1}{V}(F_l S_2 - F_l D)$$

Figure 2.4: An example of grey box model

Source: Chen *et al.* (2004)

2.4 DEVELOPMENT OF EQUILIBRIUM MODEL

The schematic diagram of an equilibrium stage in a reactive distillation column is shown below:

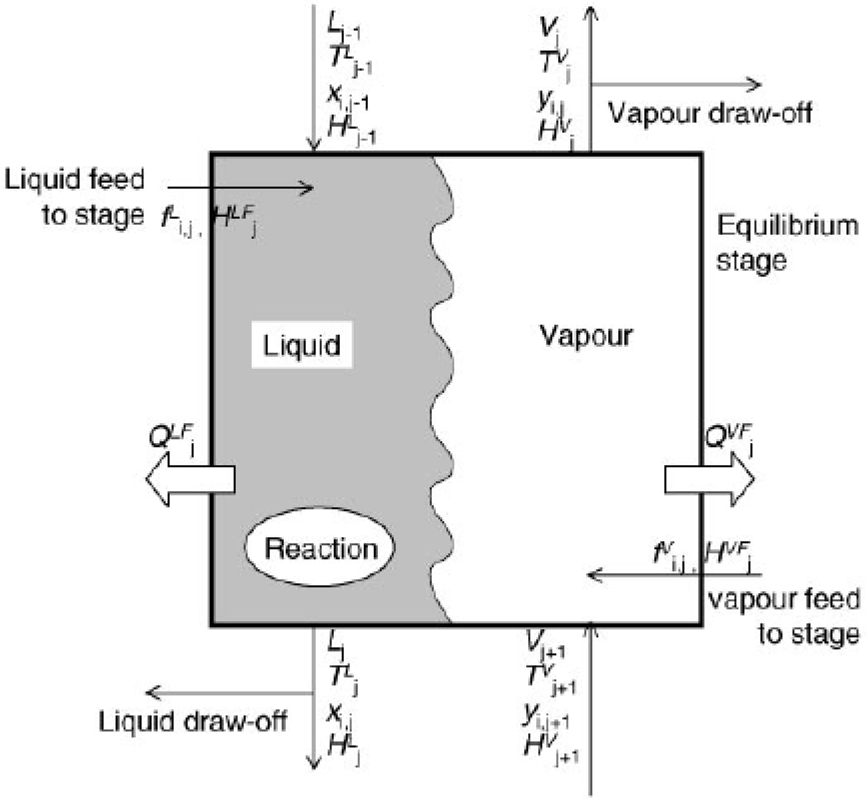


Figure 2.5: Schematic diagram of an equilibrium stage

Source: Taylor and Krishna (2000)

Liquid from the stage above and vapour from the stage below as well as fresh or recycle feed, are all brought into contact in a stage. In an equilibrium model, the liquid and vapour streams that leave the stage are assumed to be in equilibrium. The elements that constitute the model are collectively known as MESH equations. ‘M’ and ‘H’ refer to mass and heat balances respectively, they are written for each stage of separation including the reboiler and condenser. ‘E’ refers to equilibrium relations that govern the contacting vapor and liquid properties like composition, fugacity coefficient and activity coefficient. ‘S’ refers to summation equations such as those that dictate the total mass fraction of the components in the same phase equals unity (Taylor and Krishna, 2000).

2.5 INCORPORATION OF TRAY EFFICIENCIES INTO EQUILIBRIUM MODEL

Some equilibrium models incorporate tray efficiency factors in the phase equilibrium equations as a modification (Taylor and Krishna, 2000). Ramesh K. *et al.* (2005) incorporated Murphree vapour phase efficiencies to account for departure from equilibrium between the vapour and liquid streams leaving a stage. The Murphree efficiency of tray *n* for component *j* can be calculated with the formula:

$$E_{n,j} = \frac{y_{n,j} - y_{n-1,j}}{y_{nj}^{*} - y_{n-1,j}} \qquad (2.5)$$

where $y_{n,j}$ represents actual vapour composition, $y_{n-1,j}$ is actual composition of vapour received from the tray below while $y*_{n,j}$ is the equilibrium vapour composition that corresponds to the bulk liquid composition on the tray. $y*_{n,j}$ can be determined by conducting bubble point calculations.

2.6 VALIDATION OF MODEL WITH EXPERIMENTAL/INDUSTRIAL DATA

Bhatia *et al.* (2007) developed two types of models for simulation of a catalytic distillation column that produces isopropyl palmitate, they were equilibrium model and rate-based model. Subsequently, the models were used to predict the conversion of palmitic acid and liquid composition for comparison with experimental data. It was shown that the results obtained from the rate-based model were in good agreement with the experimental data. On the other hand, the equilibrium model could only describe the column behaviour qualitatively.

2.7 STUDY OF DYNAMIC PERFORMANCE

An MTBE case study was done by Švandová *et al.* (2009) to investigate the dynamic behaviour of the reactive distillation column as predicted by both the equilibrium (EQ) and nonequilibrium (NEQ) models. A step increase was applied on butenes feed flow rate at time 1 h and it was held until time reached 11 h when it was returned to its original value. The dynamic response given by both models are depicted by the following figures:

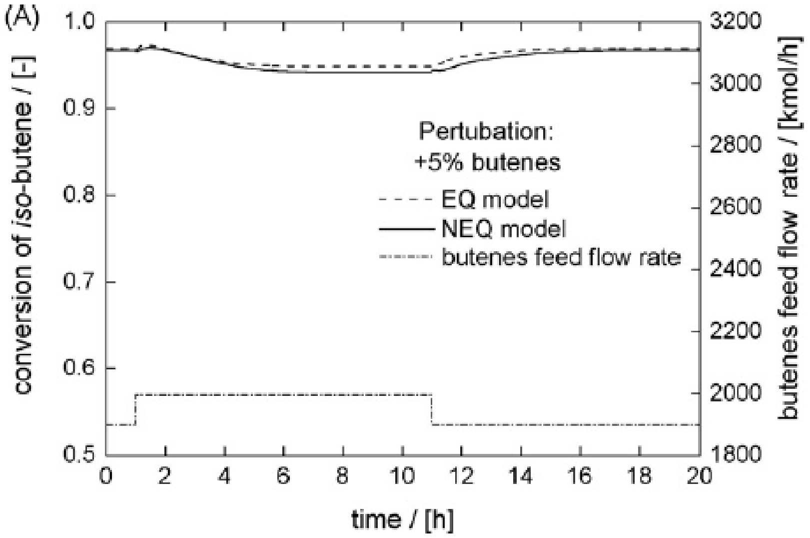


Figure 2.6: Dynamic response given by EQ and NEQ models following 5 % step increase of butenes feed flow rate and back

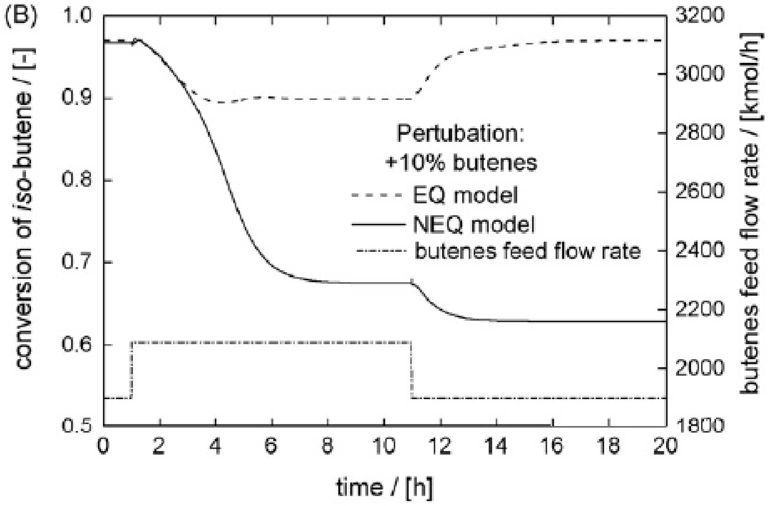


Figure 2.7: Dynamic response given by EQ and NEQ models following 10 % step increase of butenes feed flow rate and back

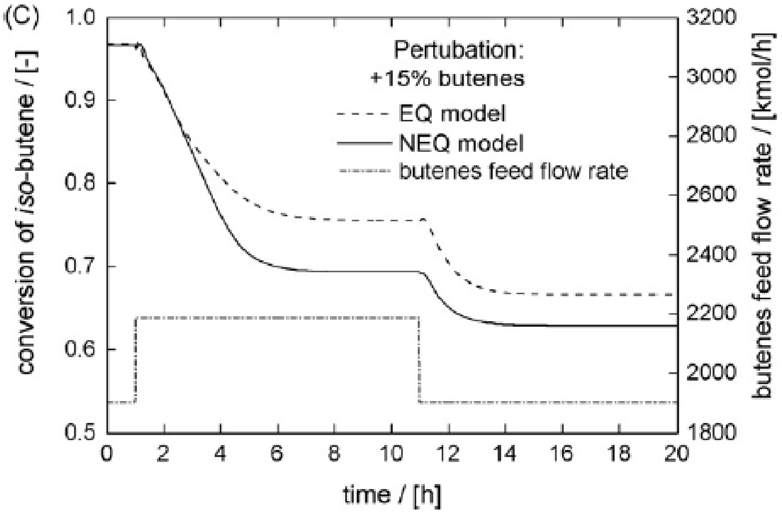


Figure 2.8: Dynamic response given by EQ and NEQ models following 15 % step increase of butenes feed flow rate and back

Source: Švandová *et al.* (2009)

Similar response were obtained from both models except for the case of 10 % step increase of butenes feed flow rate.

Muhammad *et al.* (2011) studied the dynamic performance of an i-butane/n-butane nonreactive distillation column. 2 % step changes of reboiler duty, reflux flow rate, feed flow rate and feed composition of n-butane were made, one at a time, while the response of top and bottom product composition were observed. The following figures show the response of the said variables:

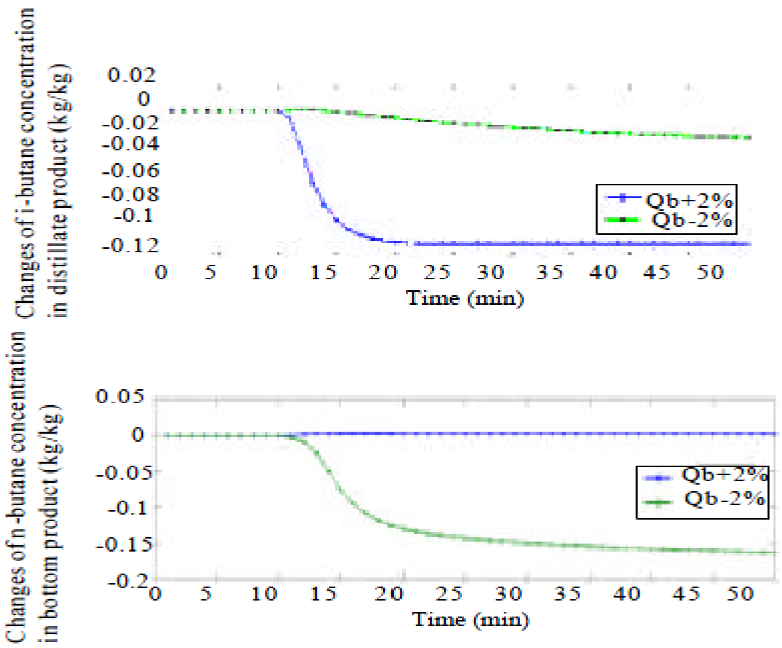


Figure 2.9: The response of top and bottom product composition with 2 % step changes in reboiler duty

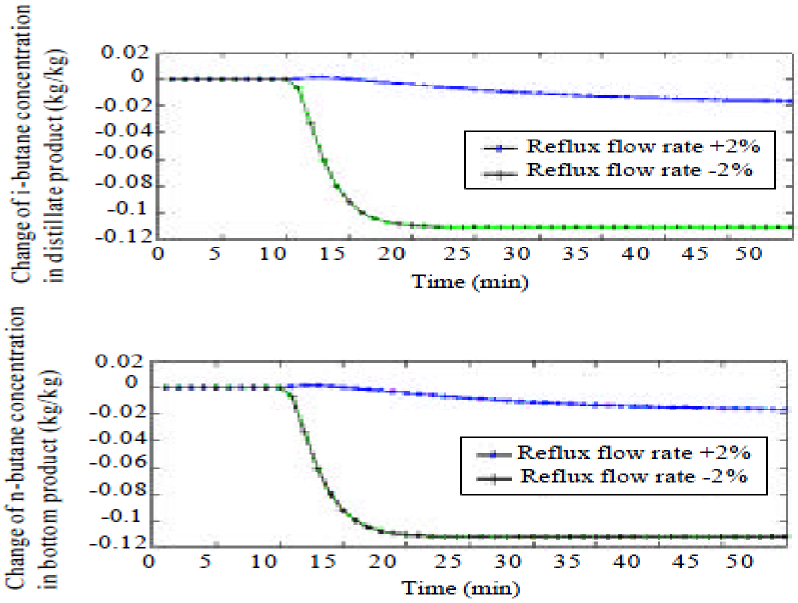


Figure 2.10: The response of top and bottom product composition with 2 % step changes in reflux flow rate

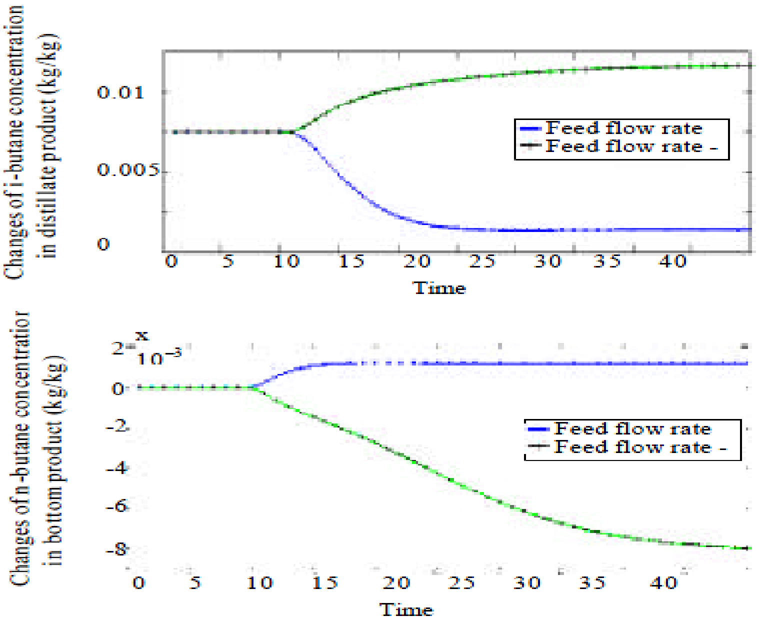


Figure 2.11: The response of top and bottom product composition with 2 % step changes in feed flow rate

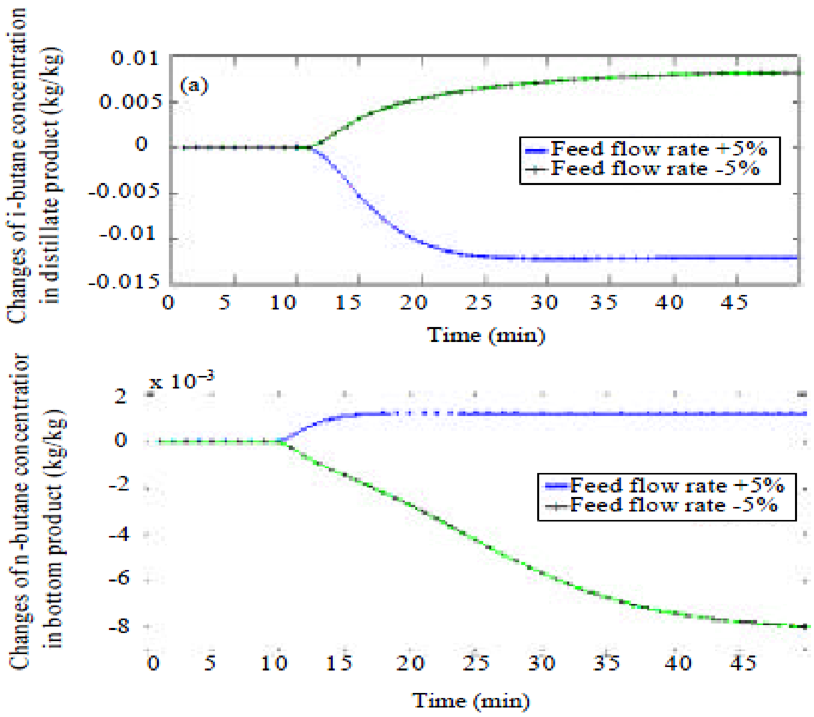


Figure 2.12: The response of top and bottom product composition with 2 % step changes of feed composition in n-butane

Source: Muhammad *et al.* (2011)

The system was classified as being mildly nonlinear as the responses given were asymmetrical.

CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

This chapter highlights the steps taken to conduct this research. Firstly, an equilibrium model for reactive distillation column is developed in MATLAB environment, the numerical method chosen to solve the sets of differential equations is Euler’s method. Next, industrial data is used to validate the developed model. Lastly, simulations are performed to study the column dynamics behavior, in this step, step changes are performed on input variables and changes of output variables with time are observed. The following figure depicts the overall process flow of this study:

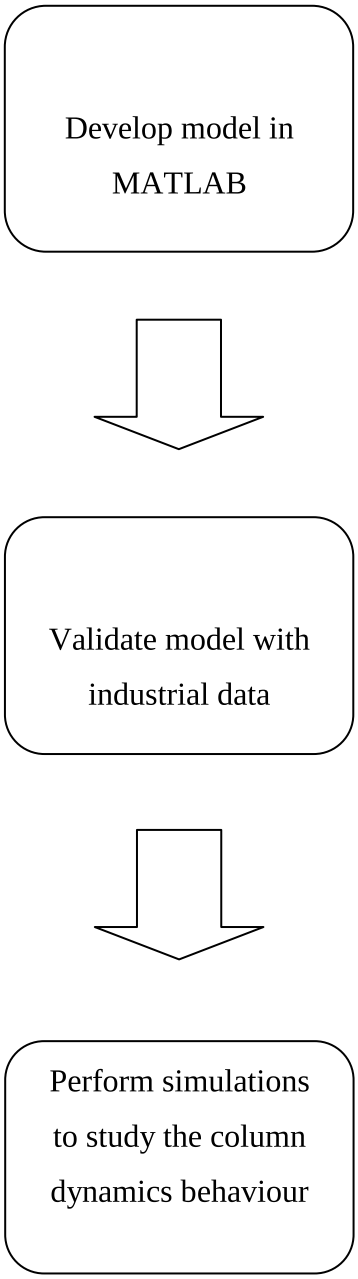


Figure 3.1: Overall process flow of the study

3.2 DEVELOPMENT OF MODEL IN MATLAB

An equilibrium model for reactive distillation column is developed in MATLAB environment. The model consists mainly of MESH equations. Mass and heat balances (M and H) are written for each stage of separation including the reboiler and condenser. Equilibrium relations (E) are used to relate the vapour and liquid compositions on a stage and calculate activity coefficients with UNIQUAC method (Smith *et al.*, 2005) to account for liquid phase nonideality. Besides, the summation (S) of compositions of different components in the same phase on a stage must equal unity. Other equations necessary to complete the model are the Francis weir formula and reaction rate law. Furthermore, Murphree tray efficiencies are incorporated into the model as well.

3.2.1 Basis of Model Development

An industrial reactive distillation column for the commercial production of MTBE is used as the basis of model development. Its configurations and specifications are shown in the following figure:

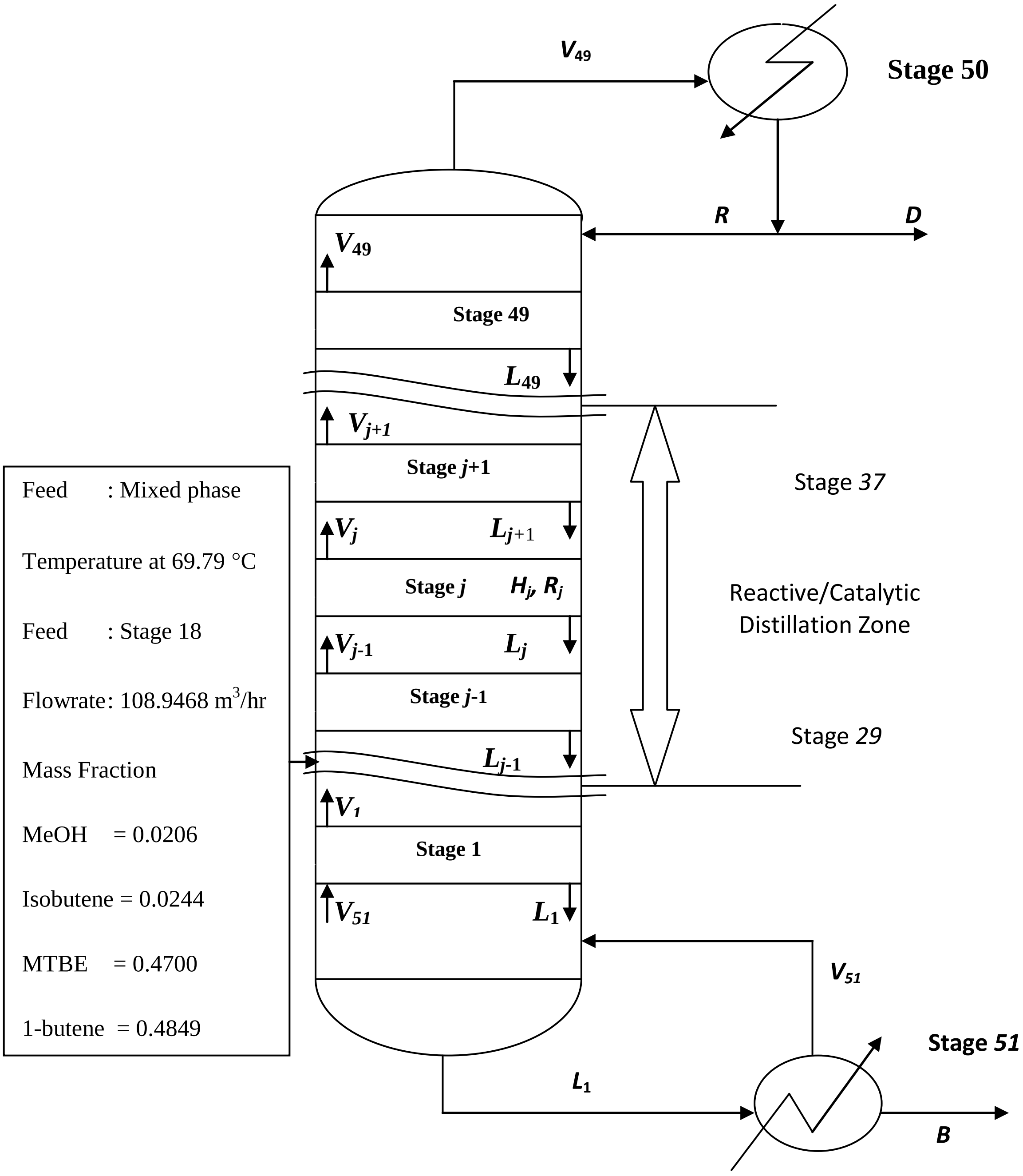


Figure 3.2: Column configurations and specifications used as model development basis

3.2.2 Model Assumptions

The following assumptions are made to simplify the model:

1. The vapour and liquid leaving a stage are in thermal equilibrium
2. Heat of mixing of vapour and liquid mixtures are negligible
3. Negligible vapour holdup on trays
4. Liquid on each stage is perfectly mixed
5. The column does not lose heat to the surroundings and is adiabatic
6. Vapour phase throughout the column is assumed to be ideal

3.2.3 Simulation Algorithm

Firstly, all the column specifications, required constants and parameters are specified. Secondly, with the feed composition, liquid compositions throughout the column are initialized. Then, vapour compositions and temperature throughout the column are computed with bubble point calculations. Subsequently, previously obtained values are used to calculate liquid and vapour enthalpy and flow rates throughout the column. Next, mass balance derivatives and their residuals are calculated. If the residual is not less than the specified error of tolerance, integration routine is called and then the calculations are repeated starting at bubble point calculations, otherwise, the temperature and composition profile of the column is generated. The steps described are summarized in the flowchart below:

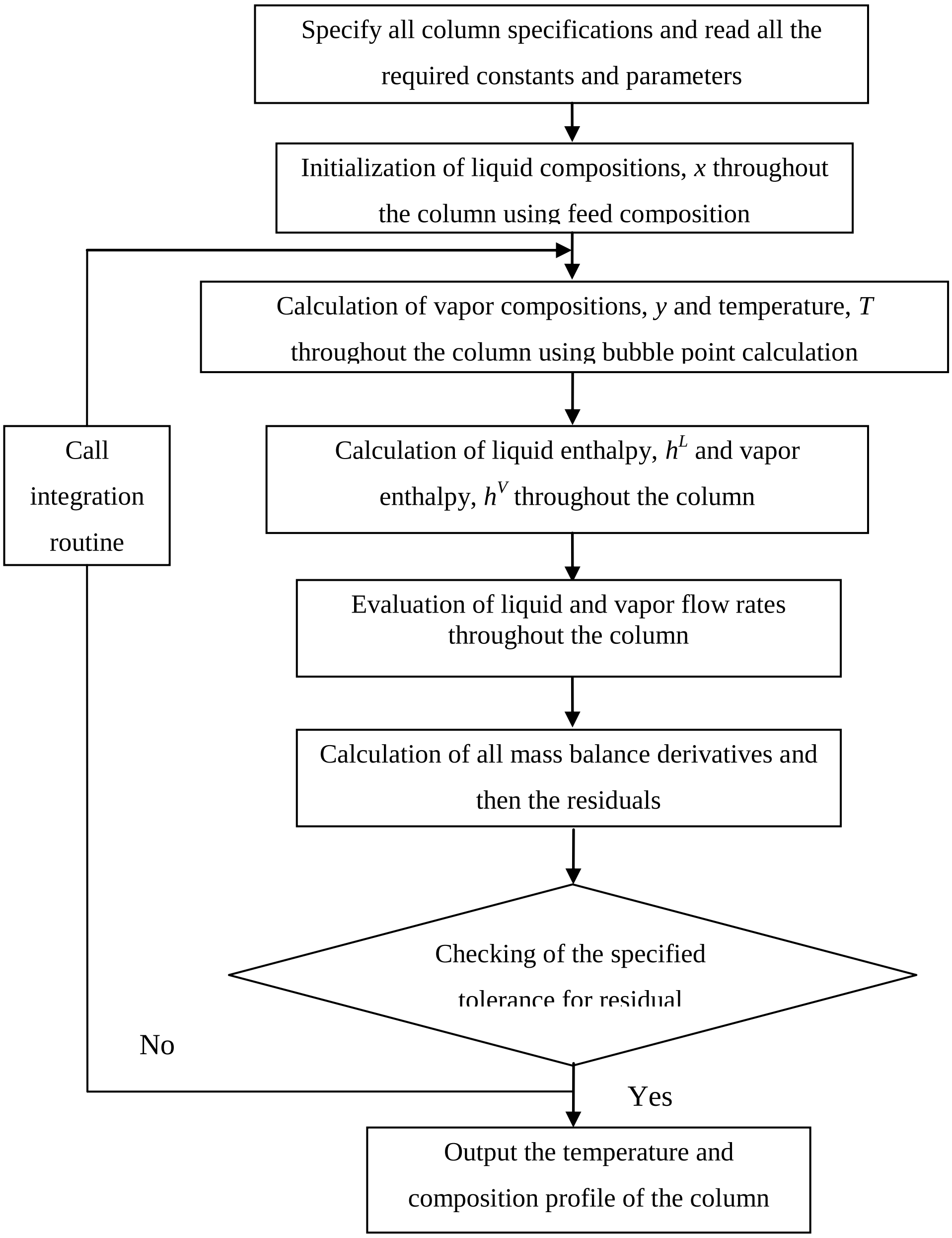


Figure 3.3: Flowchart of simulation algorithm

3.2.4 Numerical Method for the Solution of Differential Equations

In order to solve the sets of differential equations, Euler's method or the point-slope method is employed. This method uses equations of the form:

$$y_{i+1} = y_i + f(x_i, y_i)h \tag{3.1}$$

$f(x_i,y_i)$ has the same expression as the derivative in a differential equation to be solved and it is computed using the initial values of variables x and y. Upon substitution of $f(x_i,y_i)$ into the formula above, the initial value of variable y is extrapolated linearly over step size h and result in a new value of y (Chapra and Canale, 2006).

3.3 VALIDATION OF MODEL WITH INDUSTRIAL DATA

After the model is developed, comparison with industrial data is necessary to ensure its validity. Input variables like feed flow rate, feed composition, reflux flow rate and reboiler duty are extracted from plant data and are incorporated into the model. The input variables are utilized by the model to generate output variables like tray temperature, top and bottom product composition. The results generated by the model are then compared with the corresponding values of the plant data to determine if they are in close agreement.

3.4 STUDY OF COLUMN DYNAMIC BEHAVIOUR

The developed model is used to study the dynamic behaviour of the reactive distillation column. Simulations are conducted to study the effects of change of input variables (feed flow rate, feed composition, reflux flow rate and reboiler duty) on output variables. With the system initially at steady-state, positive and negative 5% step changes are applied on one of the input variables with the others held constant. The changes of MTBE composition in top and bottom product with time are then observed.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 INTRODUCTION

This chapter presents all the important results and findings of this study, as well as the equations that constitute the developed model.

4.2 MODEL EQUATIONS

The total mass, component and energy balance for a generic tray

$$\frac{dM_j}{dt} = V_{j-1} + L_{j+1} + F_j - L_j - V_j + \sum_{m=1}^{r}\sum_{i=1}^{c} v_{i,m} r_{m,j} W_j \qquad (4.1)$$

$$\frac{dM_j x_{i,j}}{dt} = V_{j-1} y_{i,j-1} + L_{j+1} x_{i,j+1} + F_j z_{i,j} - L_j x_{i,j} - V_j y_{i,j} + \sum_{m=1}^{r} v_{i,m} r_{m,j} W_j \qquad (4.2)$$

$$\frac{dM_j h_j}{dt} = V_{j-1}H_{j-1} + L_{j+1}h_{j+1} + F_j\left[qh_{F,j} + (1-q)H_{F,j}\right]$$
$$-L_j h_j - V_j H_j + \sum_{m=1}^{r} \Delta H_{m,j}^{R} r_{m,j} W_j \tag{4.3}$$

The total mass, component and energy balance for condenser

$$\frac{dM_C}{dt} = V_{49} - (R + D) \tag{4.4}$$

$$\frac{dM_C x_D}{dt} = V_{49}y_{49} - (R + D)x_D \tag{4.5}$$

$$\frac{dM_C h_D}{dt} = V_{49}H_{49} - (R + D)h_D - Q_C \tag{4.6}$$

The total mass, component and energy balance for reboiler

$$\frac{dM_B}{dt} = L_1 - (V_{51} + B) \tag{4.7}$$

$$\frac{dM_B x_B}{dt} = L_1 x_1 - (V_{51}y_{51} + Bx_B) \tag{4.8}$$

$$\frac{dM_B h_N}{dt} = L_1 h_1 - (V_{51}H_{51} + Bh_B) + Q_B \tag{4.9}$$

The vapour and liquid composition on a stage must sum to unity

$$\sum_{i=1}^{c} x_{i,j} = 1 \tag{4.10}$$

$$\sum_{i=1}^{c} y_{i,j} = 1 \tag{4.11}$$

The activity coefficient of liquid is calculated with UNIQUAC method

$$y_{i,j}P = \gamma_i x_{i,j} P_i^{sat} \tag{4.12}$$

Francis weir formula to calculate liquid flow rate in each tray

$$F_L = 1.8385 l_w H_{ow}^{1.5} \tag{4.13}$$

Reaction kinetics

Methanol (MeOH) + Isobutene (IB) ⇔MTBE

$$r = qk_f\left(\frac{a_{IB}}{a_{MeOH}} - \frac{a_{MTBE}}{K_{eq}\, a_{MeOH}^2}\right) \tag{4.14}$$

4.3 RESULTS OF MODEL VALIDATION

4.3.1 Validation with Temperature Profile

The following figures give the temperature profiles of reactive trays predicted by the model and that given by plant data respectively:

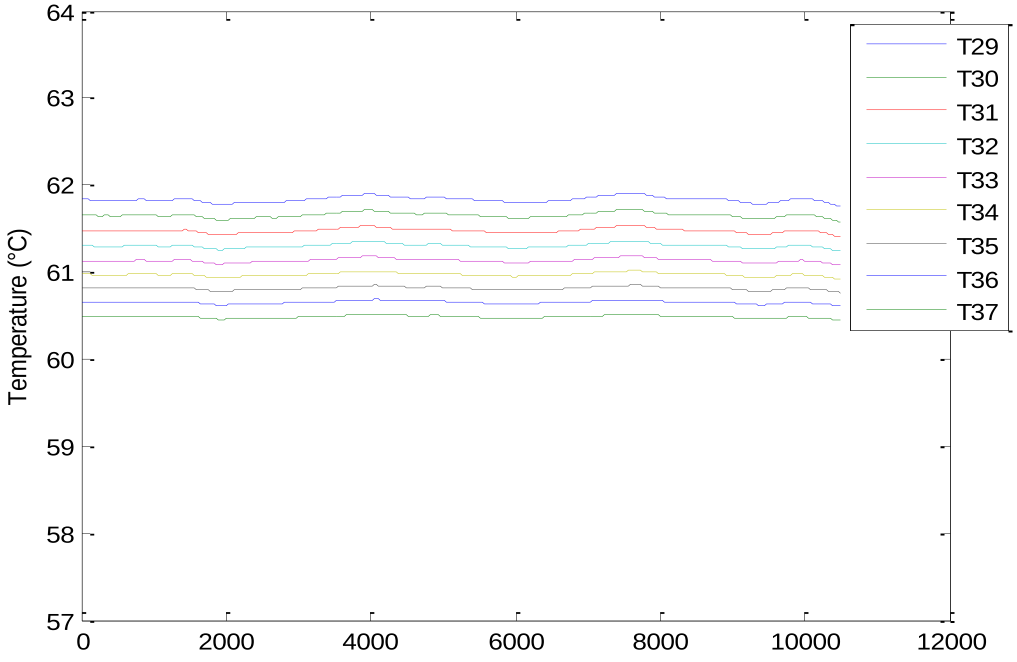


Figure 4.1: Model temperature profile

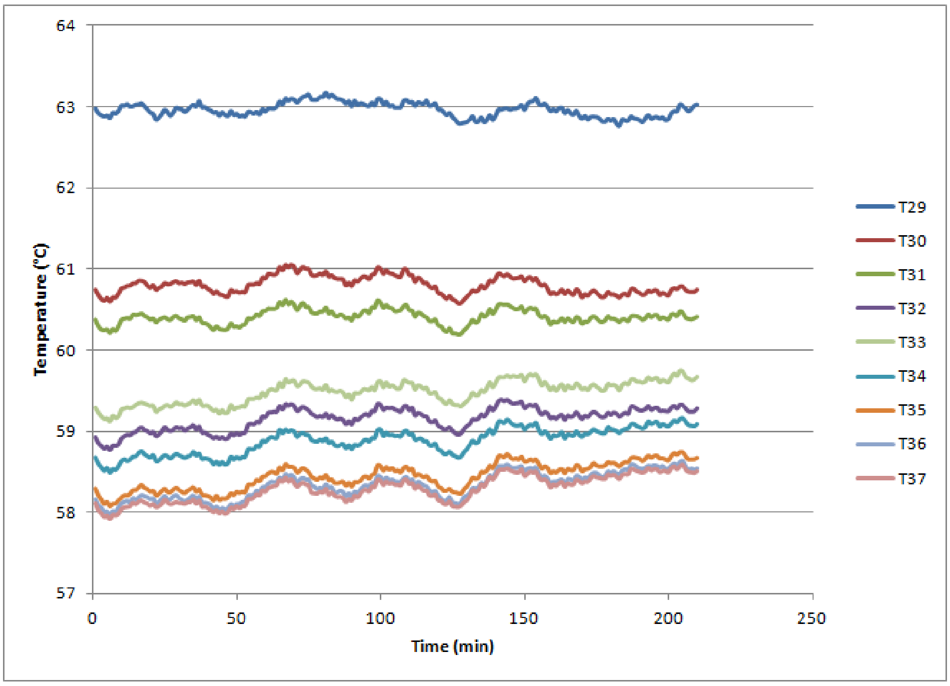


Figure 4.2: Plant temperature profile

Upon comparison, it can be said that the model and plant temperature profiles show good agreement as the results given for each tray only differ by about 2 or 3 ℃ at most.

4.3.2 Validation with Distillate and Bottom Product Composition

The distillate and bottom product compositions of different components at the end of the simulation and the corresponding values from the plant data are summarized in the following table for comparison:

Table 4.1: Comparison of distillate and bottom product composition of plant data and model prediction

Components	Distillate Composition (wt %)			Bottom Composition (wt %)		
	Plant	Model	% error	Plant	Model	% error
Methanol	1.2515	1.3025	4.08	0.7733	0.8535	10.37
Isobutylene	0.6007	0.6657	10.82	0.5815	0.6345	9.11
MTBE	0.0000	0.0068	-	96.0794	94.0650	2.10
Isobutane	98.1479	98.0250	0.13	2.5658	4.4474	73.33

The compositions predicted by the model are in good agreement with that of the plant data except for bottom composition of isobutane. These deviations are because of the presence of at least 8 other components in the system as impurities and side products which are not taken into consideration in this study (Bao *et al.*,2002).

4.4 RESULTS OF DYNAMIC STUDY

4.4.1 5 % Increase in Feed Flow Rate

The dynamic responses of the top and bottom product compositions of MTBE with 5 % step increase in feed flow rate are shown as follows:

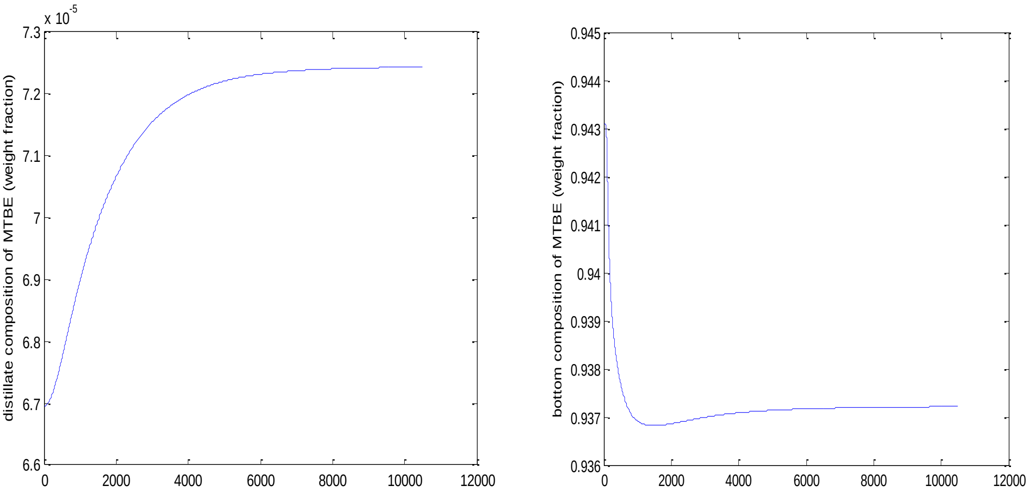


Figure 4.3: Dynamic responses of the top and bottom product compositions of MTBE with 5 % step increase in feed flow rate

The MTBE composition in top product increases by 8.21 % while in the bottom product, it decreases by 0.62 %.

Since the feed to the column is in mixed vapour and liquid phase, the increase in feed flow rate brings about the increase of vapour flow rates towards the top of the column, this increased vapour flow rate signifies that MTBE in the vapour phase has less residence time on trays and less contact time to condense and diffuse into the liquid phase, therefore more MTBE reaches the condenser and that explains the increasing trend of MTBE composition in top product.

The increase in feed flow rate also brings about the increase of liquid flow rates towards the bottom of the column, this increased liquid flow rate signifies that the reboiler whose duty is kept constant is subjected to an increase of liquid feed, as such, the extent to which the more volatile components (methanol, isobutylene and isobutane) vapourise decreases, therefore more of those components stay in the liquid phase with MTBE and that explains the decreasing trend of MTBE composition in bottom product.

4.4.2 5 % Decrease in Feed Flow Rate

The dynamic responses of the top and bottom product compositions of MTBE with 5 % step decrease in feed flow rate are shown as follows:

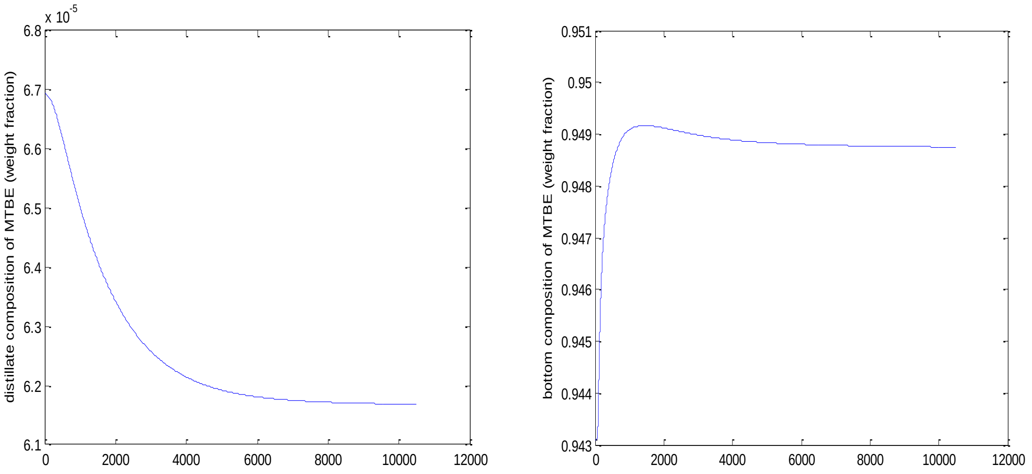


Figure 4.4: Dynamic responses of the top and bottom product compositions of MTBE with 5 % step decrease in feed flow rate

The MTBE composition in top product decreases by 7.86 % while in the bottom product, it increases by 0.60 %.

Since the feed to the column is in mixed vapour and liquid phase, the decrease in feed flow rate brings about the decrease of vapour flow rates towards the top of the column, this decreased vapour flow rate signifies that MTBE in the vapour phase has more residence time on trays and more contact time to condense and diffuse into the liquid phase, therefore less MTBE reaches the condenser and that explains the decreasing trend of MTBE composition in top product.

The decrease in feed flow rate also brings about the decrease of liquid flow rates towards the bottom of the column, this decreased liquid flow rate signifies that the reboiler whose duty is kept constant is subjected to a decrease of liquid feed, as such, the extent to which the more volatile components (methanol, isobutylene and isobutane) vapourise increases, therefore less of those components stay in the liquid phase with MTBE and that explains the increasing trend of MTBE composition in bottom product.

4.4.3 5 % Increase in Reflux Flow Rate

The dynamic responses of the top and bottom product compositions of MTBE with 5 % step increase in reflux flow rate are shown as follows:

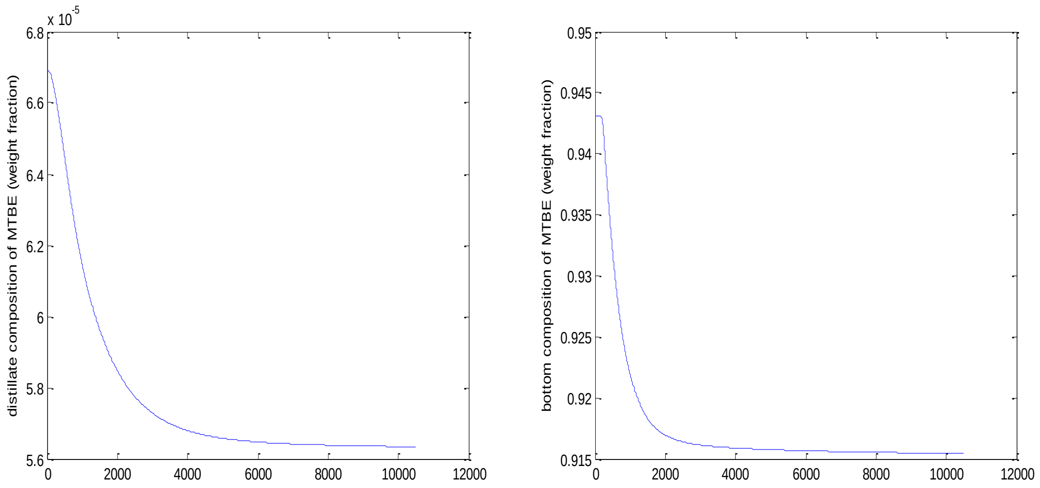


Figure 4.5: Dynamic responses of the top and bottom product compositions of MTBE with 5 % step increase in reflux flow rate

The MTBE composition in top product decreases by 15.84 % while in the bottom product, it decreases by 2.93 %.

The increase in reflux flow rate brings about the increase of liquid flow rates towards the bottom of the column, this means MTBE in the vapour phase has more chances to be in contact with liquid for condensation and diffusion into the liquid phase, therefore less MTBE reaches the condenser and that explains the decreasing trend of MTBE composition in top product.

The increase of liquid flow rates towards the bottom of the column signifies that the reboiler whose duty is kept constant is subjected to an increase of liquid feed, as such, the extent to which the more volatile components (methanol, isobutylene and isobutane) vapourise decreases, therefore more of those components stay in the liquid phase together with MTBE and that explains the decreasing trend of MTBE composition in bottom product.

4.4.4 5 % Decrease in Reflux Flow Rate

The dynamic responses of the top and bottom product compositions of MTBE with 5 % step decrease in reflux flow rate are shown as follows:

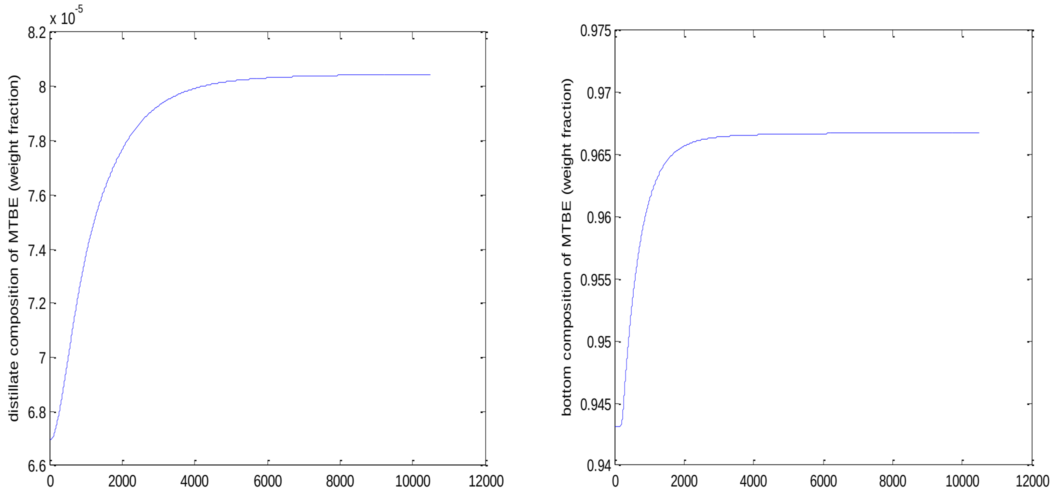


Figure 4.6: Dynamic responses of the top and bottom product compositions of MTBE with 5 % step decrease in reflux flow rate

The MTBE composition in top product increases by 20.18 % while in the bottom product, it increases by 2.51 %.

The decrease in reflux flow rate brings about the decrease of liquid flow rates towards the bottom of the column, this means MTBE in the vapour phase has less chances to be in contact with liquid for condensation and diffusion into the liquid phase, therefore more MTBE reaches the condenser and that explains the increasing trend of MTBE composition in top product.

The decrease of liquid flow rates towards the bottom of the column signifies that the reboiler whose duty is kept constant is subjected to a decrease of liquid feed, as such, the extent to which the more volatile components (methanol, isobutylene and isobutane) vapourise increases, therefore less of those components stay in the liquid phase with MTBE and that explains the increasing trend of MTBE composition in bottom product.

4.4.5 5 % Increase in Reboiler Duty

The dynamic responses of the top and bottom product compositions of MTBE with 5 % step increase in reboiler duty are shown as follows:

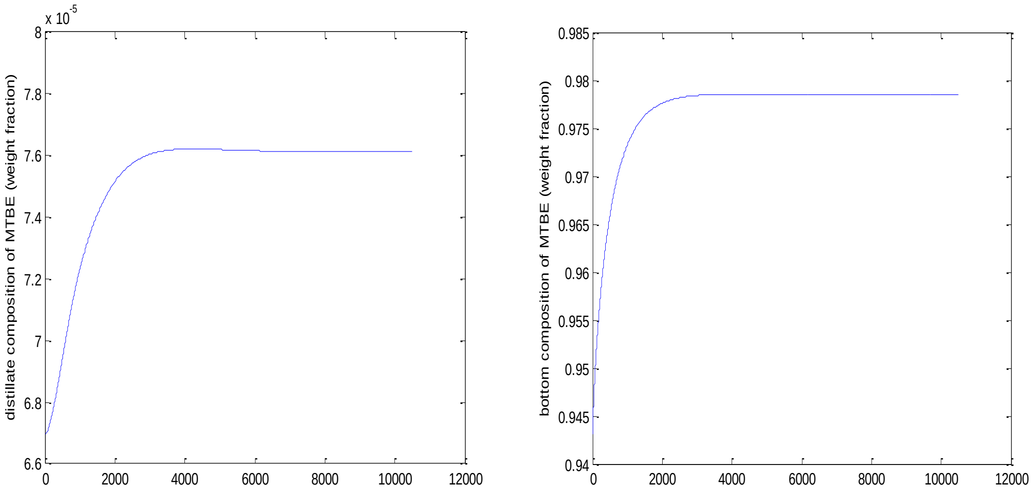


Figure 4.7: Dynamic responses of the top and bottom product compositions of MTBE with 5 % step increase in reboiler duty

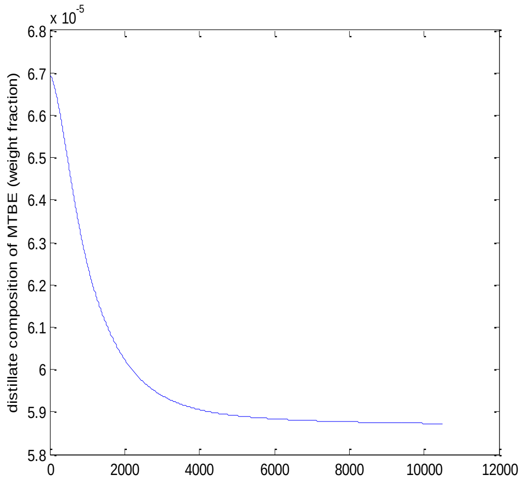
The MTBE composition in top product increases by 13.70 % while in the bottom product, it increases by 3.75 %.

The increase in reboiler duty brings about the increase of vapour flow rates towards the top of the column, this increased vapour flow rate signifies that MTBE in the vapour phase has less residence time on trays and less contact time to condense and diffuse into the liquid phase, therefore more MTBE reaches the condenser and that explains the increasing trend of MTBE composition in top product.

The increase of reboiler duty signifies that the extent to which the more volatile components (methanol, isobutylene and isobutane) vapourise increases, therefore less of those components stay in the liquid phase with MTBE and that explains the increasing trend of MTBE composition in bottom product.

4.4.6 5 % Decrease in Reboiler Duty

The dynamic responses of the top and bottom product compositions of MTBE with 5 % step decrease in reboiler duty are shown as follows:



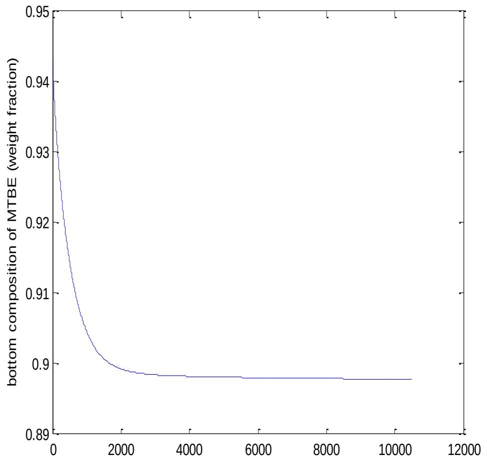


Figure 4.8: Dynamic responses of the top and bottom product compositions of MTBE with 5 % step decrease in reboiler duty

The MTBE composition in top product decreases by 12.27 % while in the bottom product, it decreases by 4.80 %.

The decrease in reboiler duty brings about the decrease of vapour flow rates towards the top of the column, this decreased vapour flow rate signifies that MTBE in the vapour phase has more residence time on trays and more contact time to condense and diffuse into the liquid phase, therefore less MTBE reaches the condenser and that explains the decreasing trend of MTBE composition in top product.

The decrease of reboiler duty signifies that the extent to which the more volatile components (methanol, isobutylene and isobutane) vapourise decreases, therefore more of those components stay in the liquid phase with MTBE and that explains the decreasing trend of MTBE composition in bottom product.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

In this study, an equilibrium model of a reactive distillation column for the commercial production of MTBE is developed in MATLAB by putting together the MESH equations and other equations like Francis weir formula and reaction rate law. Subsequently, the developed model is validated by comparison of simulation results with industrial data. Finally, the dynamic behaviour of the system is studied by applying step changes to each of the input variables, one at a time.

The model of reactive distillation column is successfully developed. It is also proven to be a good representation of the column in the industry because model predictions and plant data come to a good agreement. From the responses to step changes of input variables, the dynamic behaviour of the system is more clearly understood. In conclusion, all three objectives of this research are successfully achieved.

5.2 RECOMMENDATIONS

The followings are some recommendations that can be useful for future researchers. The model developed in this research can be modified to enable usage with other processes in reactive distillation column, for instance, the production of isopropyl palmitate. One should replace the reaction rate law and equilibrium relations if one wishes to modify the model.

Another type of model commonly used to represent reactive distillation columns is the nonequilibrium or rate-based model. The nonequilibrium model is based on the rate and coefficient of heat and mass transfer across the vapour-liquid film (Ramesh K. *et al.*, 2005). It is more rigorous than the equilibrium model and may be more accurate.

Other numerical methods can also be used to solve the sets of differential equations. Unlike Euler's method which assumes a constant slope over each step size, Huen's method and midpoint method use more accurate means to estimate new values of the variables to be calculated (Chapra and Canale, 2006). Usage of the suggested methods can possibly result in models which represent the industrial columns better.

For the study of column dynamic behavior, not just step changes, other kinds of disturbances like ramp change and sinusoidal change also can be applied on the system. In this way, the dynamic performance of the column can be further detailed and understood.

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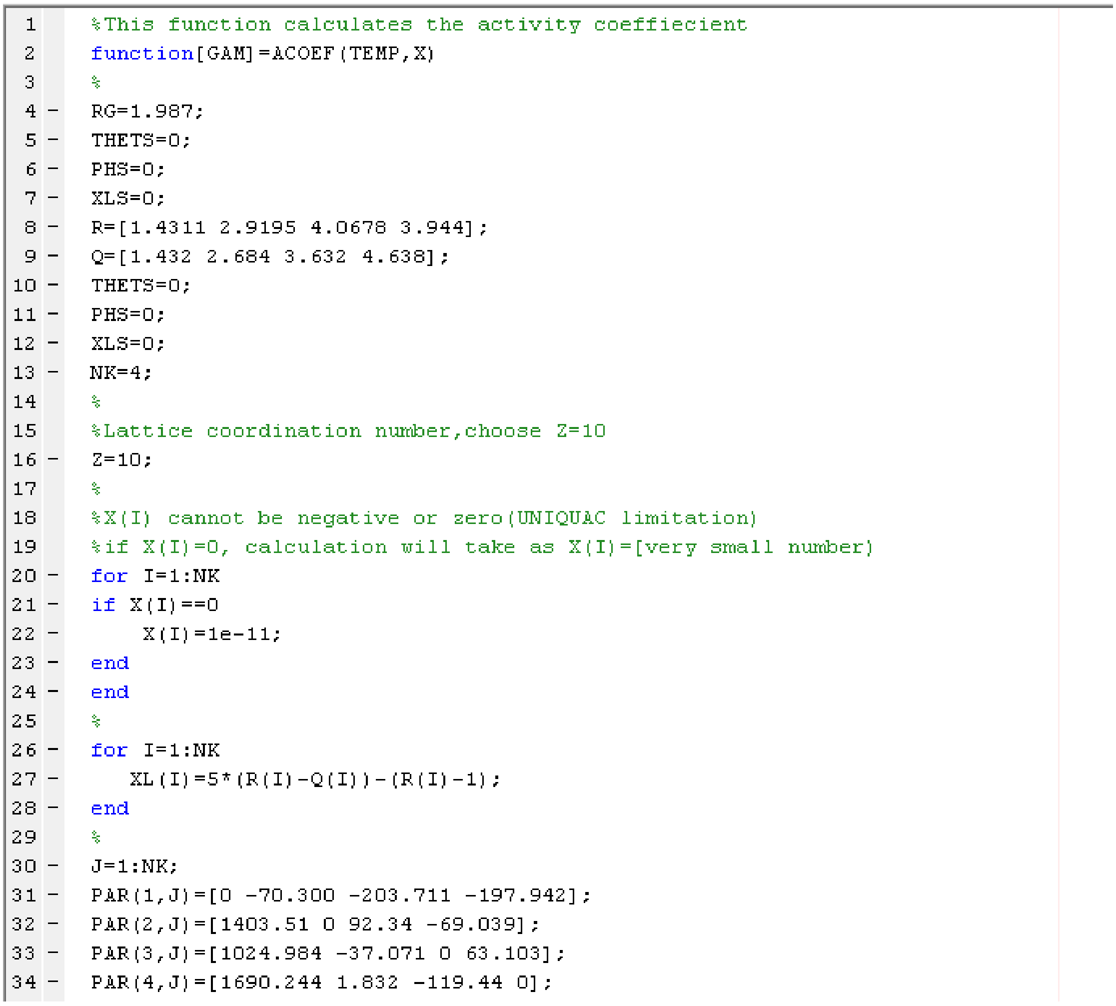
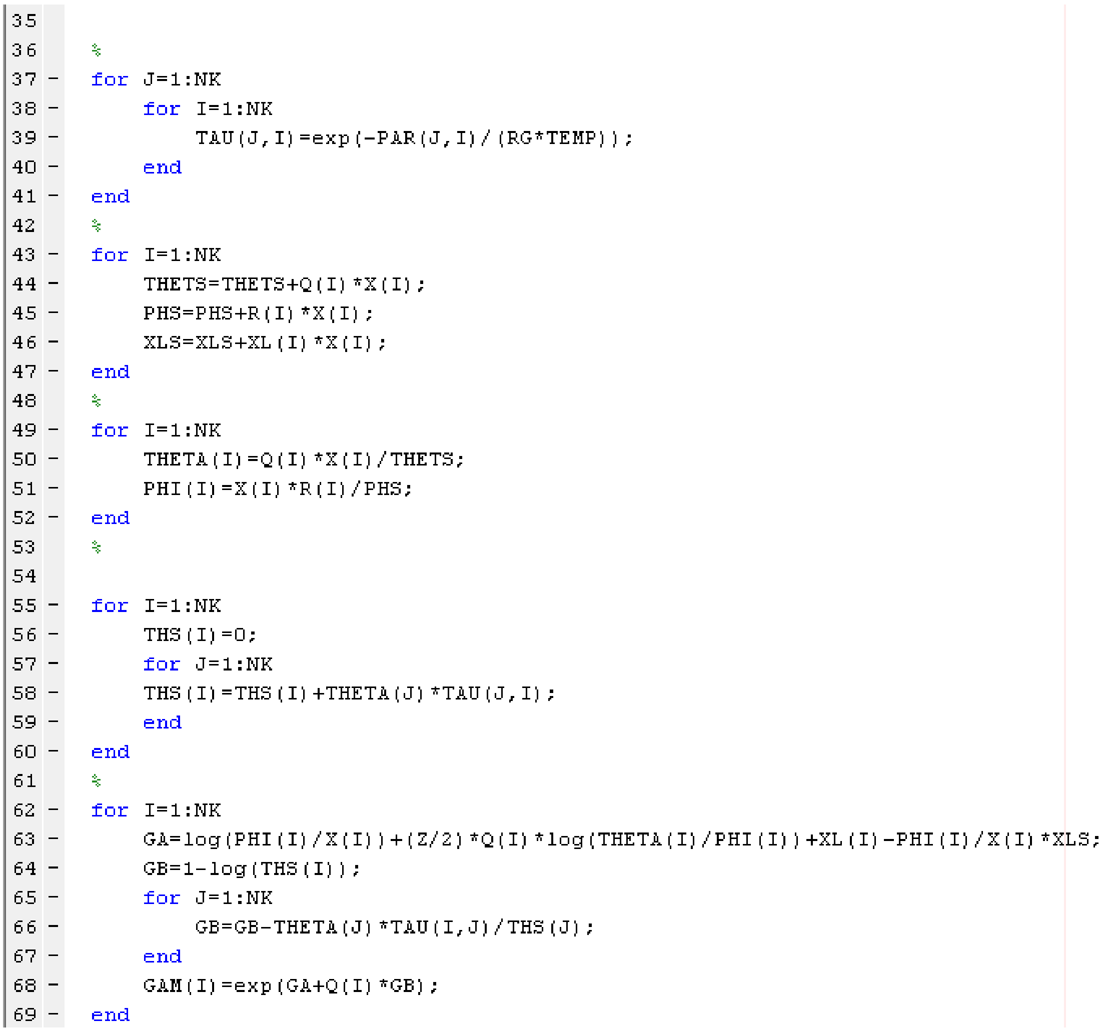
APPENDIX A

Program for Calculations of Activity Coefficient



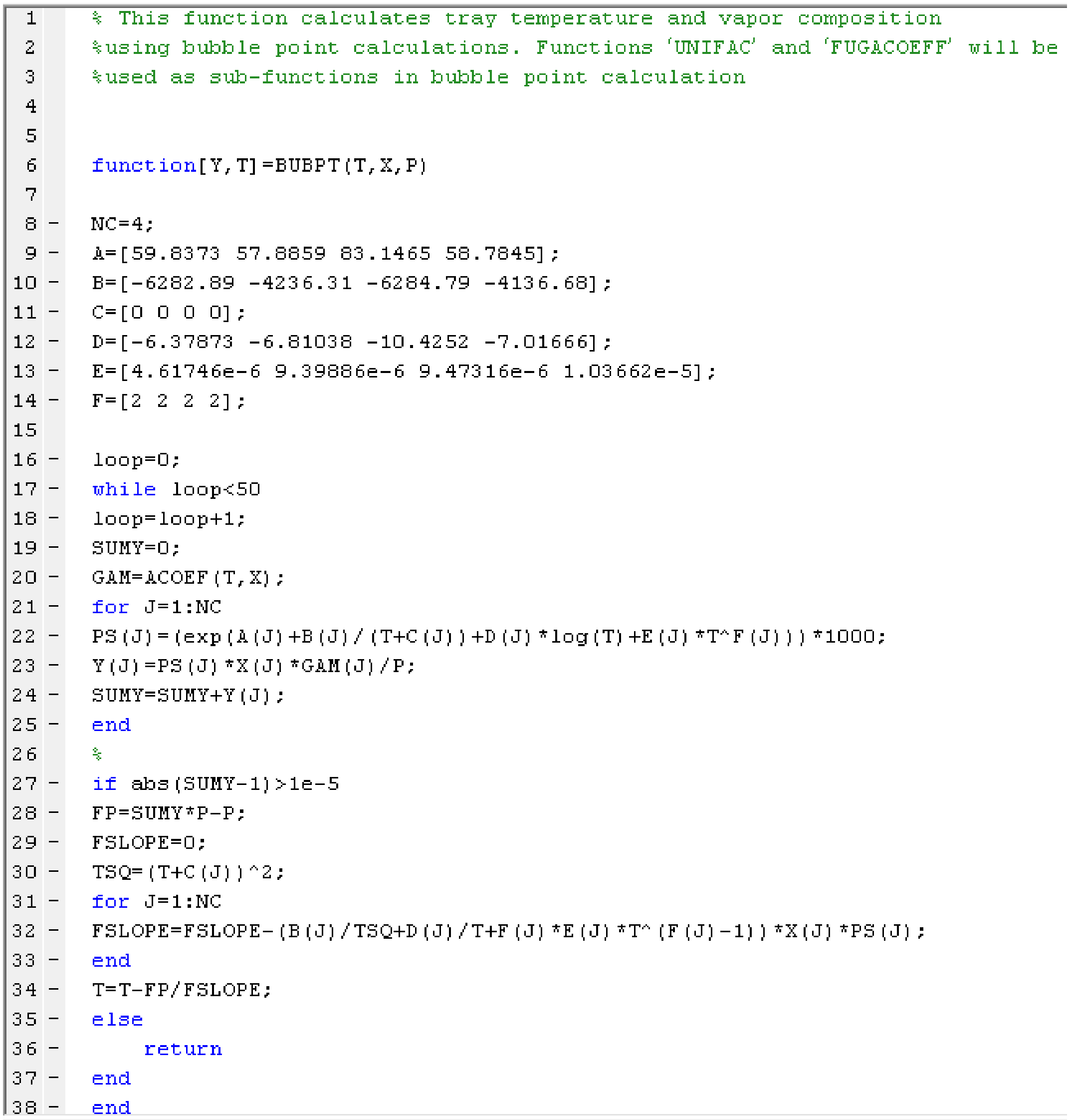
```
%This function calculates the activity coeffiecient
function[GAM]=ACOEF(TEMP,X)
%
RG=1.987;
THETS=0;
PHS=0;
XLS=0;
R=[1.4311 2.9195 4.0678 3.944];
Q=[1.432 2.684 3.632 4.638];
THETS=0;
PHS=0;
XLS=0;
NK=4;
%
%Lattice coordination number,choose Z=10
Z=10;
%
%X(I) cannot be negative or zero(UNIQUAC limitation)
%if X(I)=0, calculation will take as X(I)=[very small number)
for I=1:NK
if X(I)==0
    X(I)=1e-11;
end
end
%
for I=1:NK
   XL(I)=5*(R(I)-Q(I))-(R(I)-1);
end
%
J=1:NK;
PAR(1,J)=[0 -70.300 -203.711 -197.942];
PAR(2,J)=[1403.51 0 92.34 -69.039];
PAR(3,J)=[1024.984 -37.071 0 63.103];
PAR(4,J)=[1690.244 1.832 -119.44 0];
```



```

%
for J=1:NK
    for I=1:NK
        TAU(J,I)=exp(-PAR(J,I)/(RG*TEMP));
    end
end
%
for I=1:NK
    THETS=THETS+Q(I)*X(I);
    PHS=PHS+R(I)*X(I);
    XLS=XLS+XL(I)*X(I);
end
%
for I=1:NK
    THETA(I)=Q(I)*X(I)/THETS;
    PHI(I)=X(I)*R(I)/PHS;
end
%

for I=1:NK
    THS(I)=0;
    for J=1:NK
    THS(I)=THS(I)+THETA(J)*TAU(J,I);
    end
end
%
for I=1:NK
    GA=log(PHI(I)/X(I))+(Z/2)*Q(I)*log(THETA(I)/PHI(I))+XL(I)-PHI(I)/X(I)*XLS;
    GB=1-log(THS(I));
    for J=1:NK
        GB=GB-THETA(J)*TAU(I,J)/THS(J);
    end
    GAM(I)=exp(GA+Q(I)*GB);
end
```

APPENDIX B

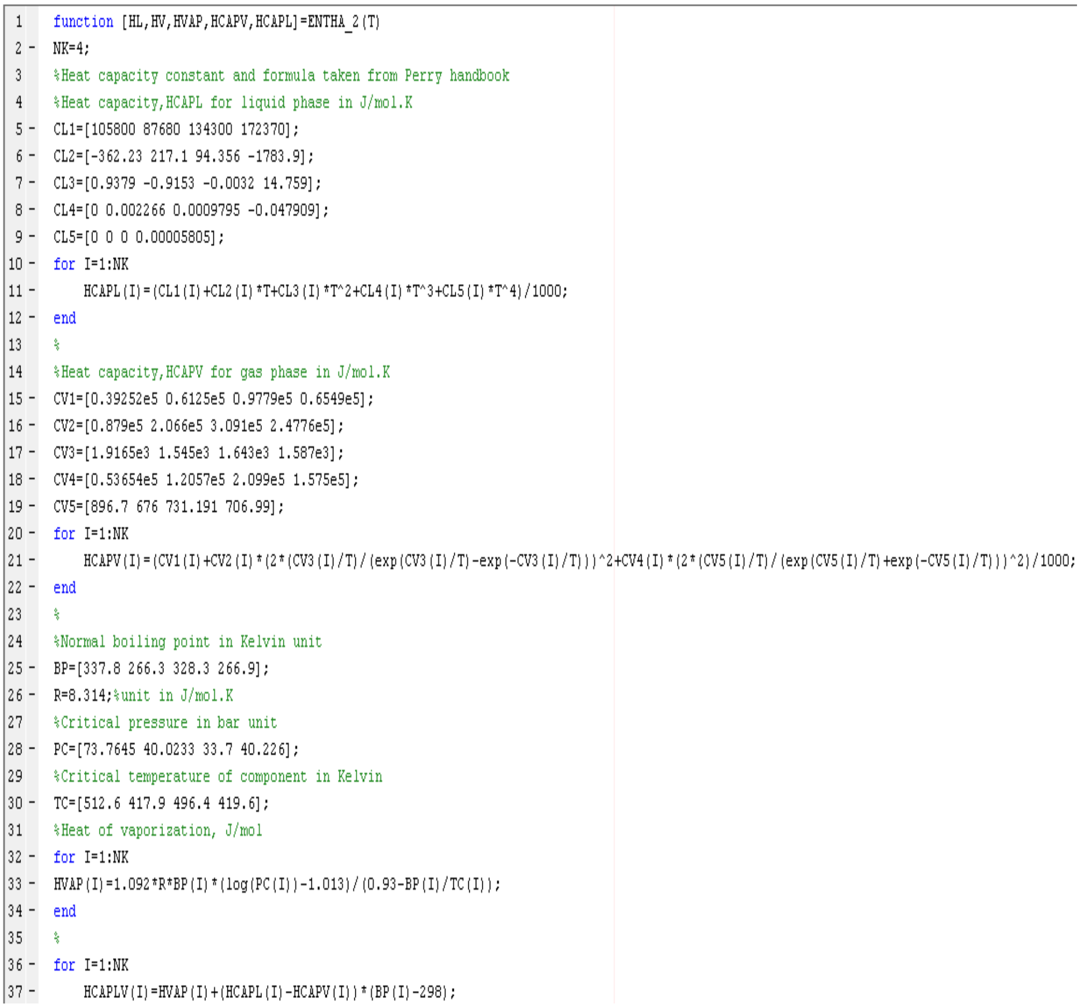
Program for Bubble Point Calculations



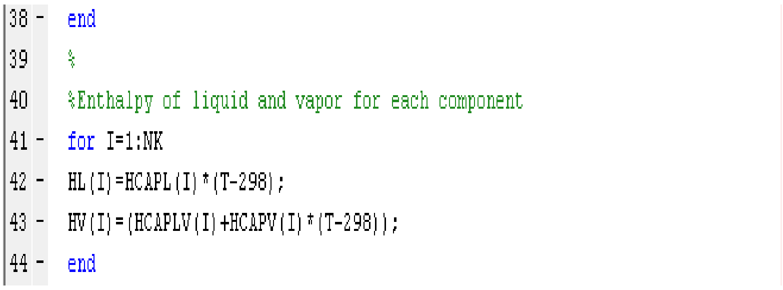
```
% This function calculates tray temperature and vapor composition
%using bubble point calculations. Functions ‘UNIFAC’ and ‘FUGACOEFF’ will be
%used as sub-functions in bubble point calculation


function[Y,T]=BUBPT(T,X,P)

NC=4;
A=[59.8373 57.8859 83.1465 58.7845];
B=[-6282.89 -4236.31 -6284.79 -4136.68];
C=[0 0 0 0];
D=[-6.37873 -6.81038 -10.4252 -7.01666];
E=[4.61746e-6 9.39886e-6 9.47316e-6 1.03662e-5];
F=[2 2 2 2];

loop=0;
while loop<50
loop=loop+1;
SUMY=0;
GAM=ACOEF(T,X);
for J=1:NC
PS(J)=(exp(A(J)+B(J)/(T+C(J))+D(J)*log(T)+E(J)*T^F(J)))*1000;
Y(J)=PS(J)*X(J)*GAM(J)/P;
SUMY=SUMY+Y(J);
end
%
if abs(SUMY-1)>1e-5
FP=SUMY*P-P;
FSLOPE=0;
TSQ=(T+C(J))^2;
for J=1:NC
FSLOPE=FSLOPE-(B(J)/TSQ+D(J)/T+F(J)*E(J)*T^(F(J)-1))*X(J)*PS(J);
end
T=T-FP/FSLOPE;
else
    return
end
end
```

APPENDIX C

Program for Heat Capacity Calculations



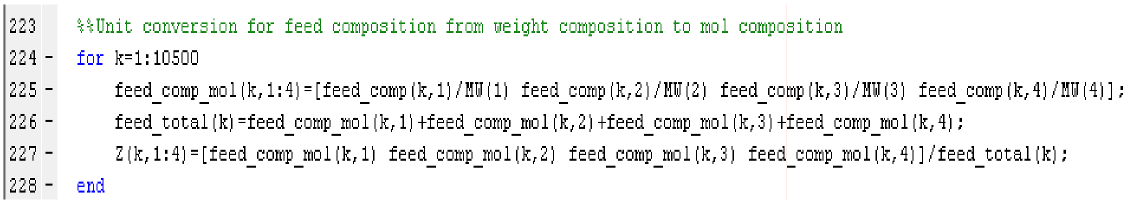
```
function [HL,HV,HVAP,HCAPV,HCAPL]=ENTHA_2(T)
NK=4;
%Heat capacity constant and formula taken from Perry handbook
%Heat capacity,HCAPL for liquid phase in J/mol.K
CL1=[105800 87680 134300 172370];
CL2=[-362.23 217.1 94.356 -1783.9];
CL3=[0.9379 -0.9153 -0.0032 14.759];
CL4=[0 0.002266 0.0009795 -0.047909];
CL5=[0 0 0 0.00005805];
for I=1:NK
    HCAPL(I)=(CL1(I)+CL2(I)*T+CL3(I)*T^2+CL4(I)*T^3+CL5(I)*T^4)/1000;
end
%
%Heat capacity,HCAPV for gas phase in J/mol.K
CV1=[0.39252e5 0.6125e5 0.9779e5 0.6549e5];
CV2=[0.879e5 2.066e5 3.091e5 2.4776e5];
CV3=[1.9165e3 1.545e3 1.643e3 1.587e3];
CV4=[0.53654e5 1.2057e5 2.099e5 1.575e5];
CV5=[896.7 676 731.191 706.99];
for I=1:NK
    HCAPV(I)=(CV1(I)+CV2(I)*(2*(CV3(I)/T)/(exp(CV3(I)/T)-exp(-CV3(I)/T)))^2+CV4(I)*(2*(CV5(I)/T)/(exp(CV5(I)/T)+exp(-CV5(I)/T)))^2)/1000;
end
%
%Normal boiling point in Kelvin unit
BP=[337.8 266.3 328.3 266.9];
R=8.314;%unit in J/mol.K
%Critical pressure in bar unit
PC=[73.7645 40.0233 33.7 40.226];
%Critical temperature of component in Kelvin
TC=[512.6 417.9 496.4 419.6];
%Heat of vaporization, J/mol
for I=1:NK
HVAP(I)=1.092*R*BP(I)*(log(PC(I))-1.013)/(0.93-BP(I)/TC(I));
end
%
for I=1:NK
    HCAPLV(I)=HVAP(I)+(HCAPL(I)-HCAPV(I))*(BP(I)-298);
```



```
end
%
%Enthalpy of liquid and vapor for each component
for I=1:NK
HL(I)=HCAPL(I)*(T-298);
HV(I)=(HCAPLV(I)+HCAPV(I)*(T-298));
end
```

APPENDIX D

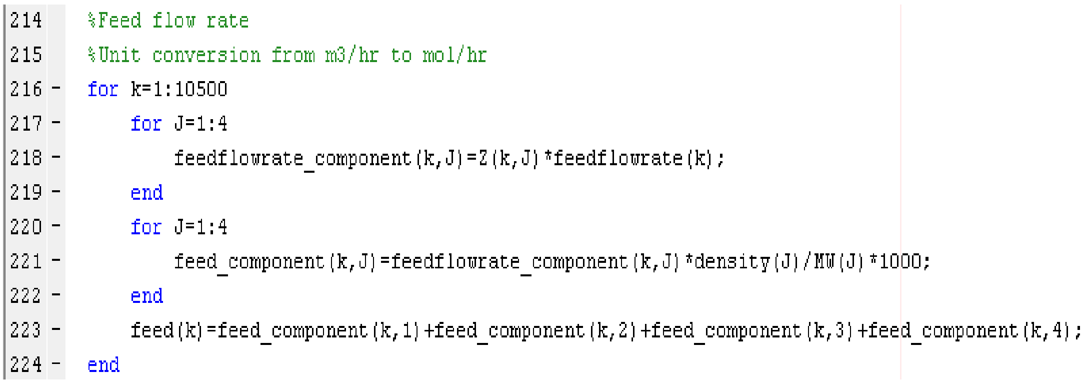
Program for Feed Composition Calculations



```
%%Unit conversion for feed composition from weight composition to mol composition
for k=1:10500
    feed_comp_mol(k,1:4)=[feed_comp(k,1)/MW(1) feed_comp(k,2)/MW(2) feed_comp(k,3)/MW(3) feed_comp(k,4)/MW(4)];
    feed_total(k)=feed_comp_mol(k,1)+feed_comp_mol(k,2)+feed_comp_mol(k,3)+feed_comp_mol(k,4);
    Z(k,1:4)=[feed_comp_mol(k,1) feed_comp_mol(k,2) feed_comp_mol(k,3) feed_comp_mol(k,4)]/feed_total(k);
end
```

APPENDIX E

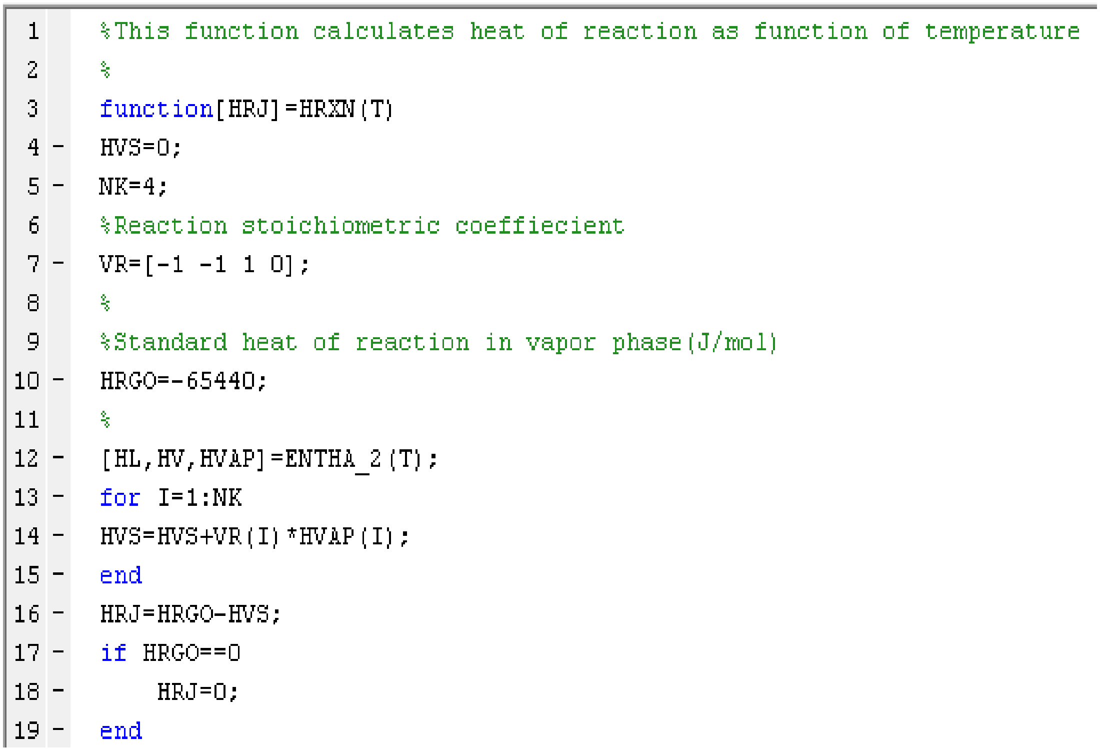
Program for Feed Flow Rate Calculations



```
%Feed flow rate
%Unit conversion from m3/hr to mol/hr
for k=1:10500
    for J=1:4
        feedflowrate_component(k,J)=Z(k,J)*feedflowrate(k);
    end
    for J=1:4
        feed_component(k,J)=feedflowrate_component(k,J)*density(J)/MW(J)*1000;
    end
    feed(k)=feed_component(k,1)+feed_component(k,2)+feed_component(k,3)+feed_component(k,4);
end
```

APPENDIX F

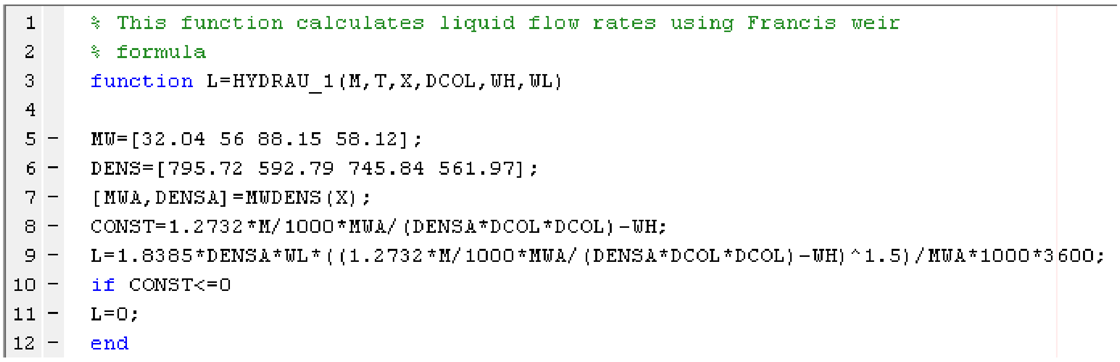
Program for Heat of Reaction Calculations



```
%This function calculates heat of reaction as function of temperature
%
function[HRJ]=HRXN(T)
HVS=0;
NK=4;
%Reaction stoichiometric coeffiecient
VR=[-1 -1 1 0];
%
%Standard heat of reaction in vapor phase(J/mol)
HRGO=-65440;
%
[HL,HV,HVAP]=ENTHA_2(T);
for I=1:NK
HVS=HVS+VR(I)*HVAP(I);
end
HRJ=HRGO-HVS;
if HRGO==0
    HRJ=0;
end
```

APPENDIX G

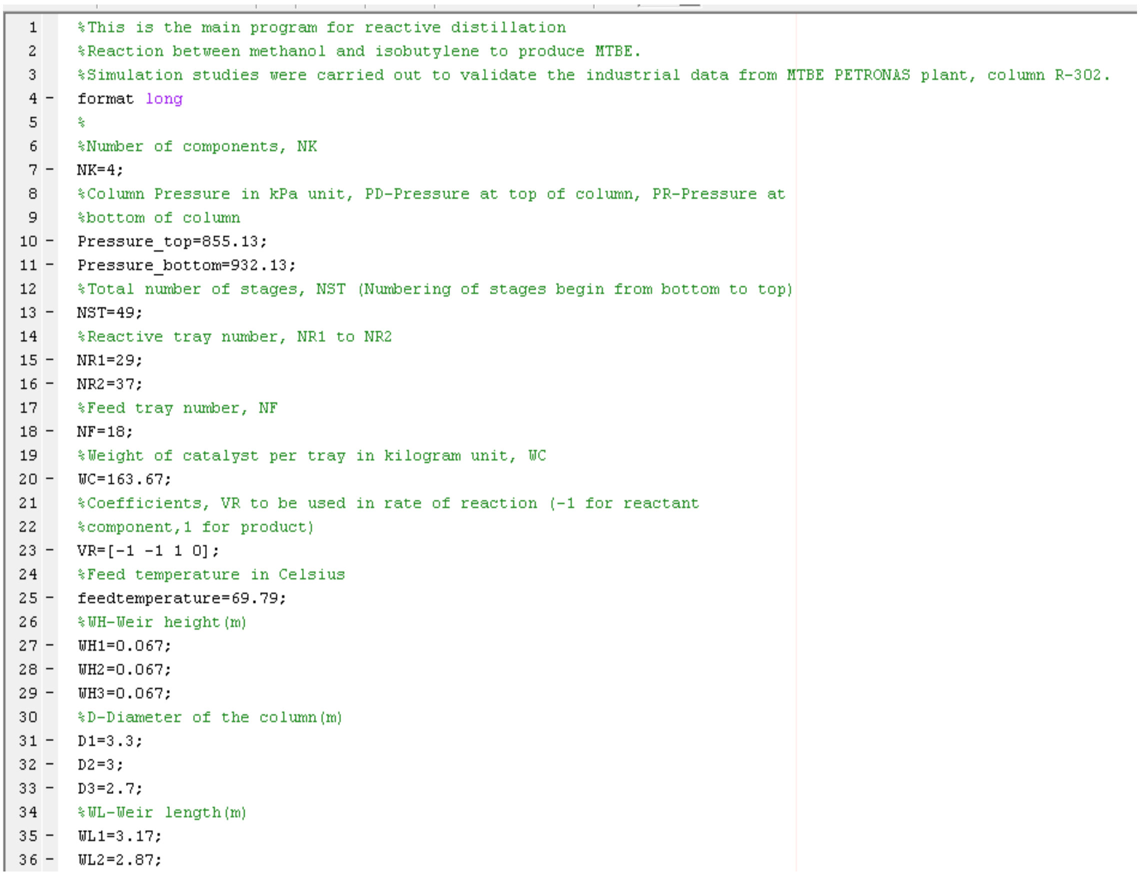
Program for Liquid Flow Rates Calculations with Francis Weir Formula



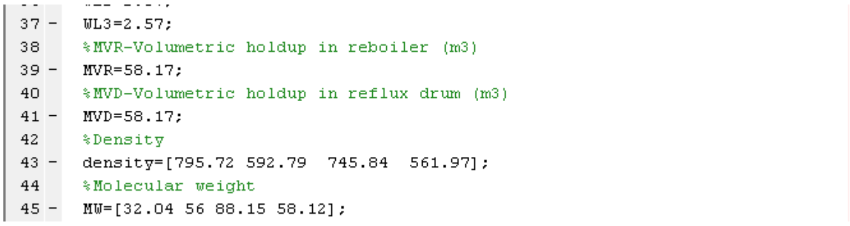
```
% This function calculates liquid flow rates using Francis weir
% formula
function L=HYDRAU_1(M,T,X,DCOL,WH,WL)

MW=[32.04 56 88.15 58.12];
DENS=[795.72 592.79 745.84 561.97];
[MWA,DENSA]=MWDENS(X);
CONST=1.2732*M/1000*MWA/(DENSA*DCOL*DCOL)-WH;
L=1.8385*DENSA*WL*((1.2732*M/1000*MWA/(DENSA*DCOL*DCOL)-WH)^1.5)/MWA*1000*3600;
if CONST<=0
L=0;
end
```

APPENDIX H

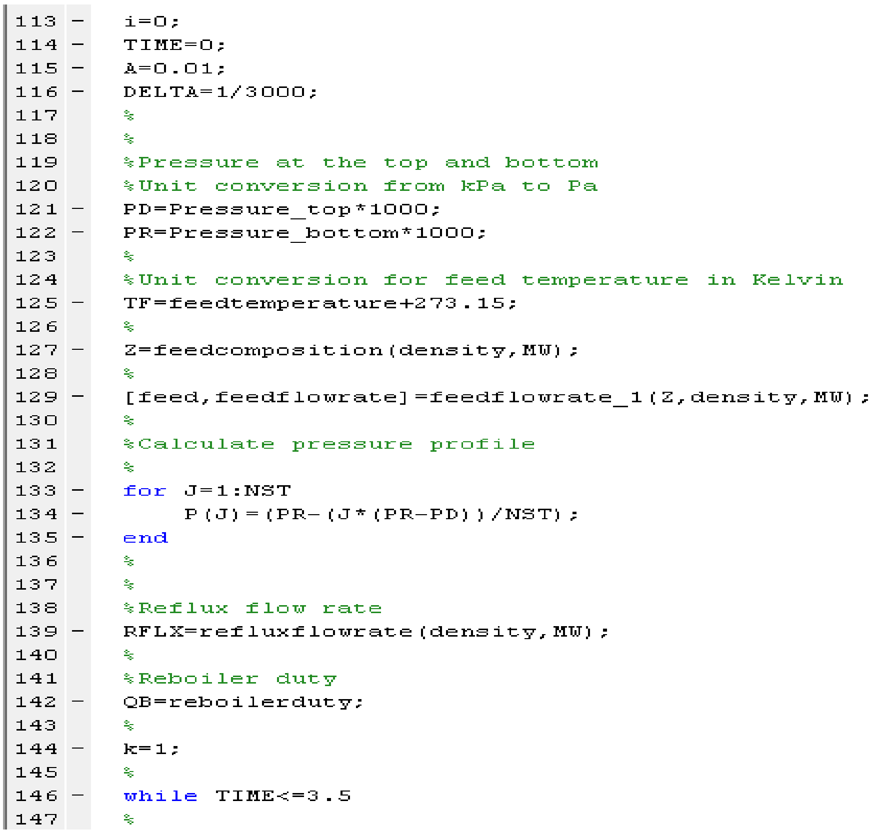
Main Program



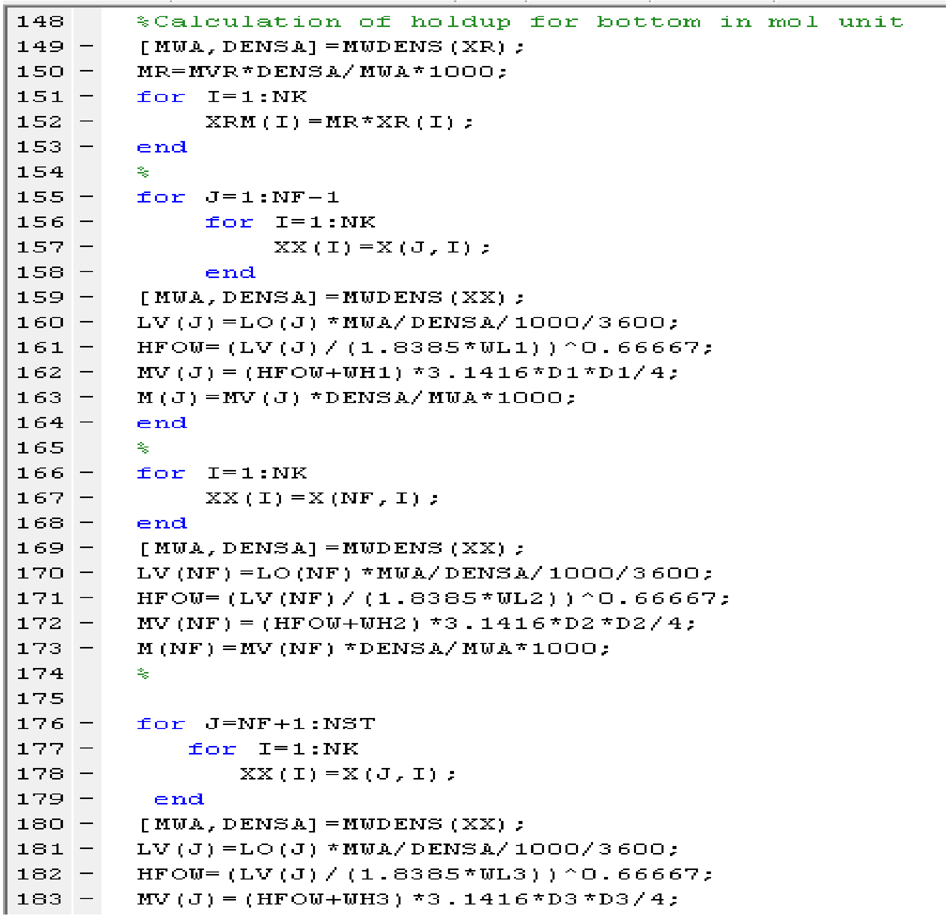
```
%This is the main program for reactive distillation
%Reaction between methanol and isobutylene to produce MTBE.
%Simulation studies were carried out to validate the industrial data from MTBE PETRONAS plant, column R-302.
format long
%
%Number of components, NK
NK=4;
%Column Pressure in kPa unit, PD-Pressure at top of column, PR-Pressure at
%bottom of column
Pressure_top=855.13;
Pressure_bottom=932.13;
%Total number of stages, NST (Numbering of stages begin from bottom to top)
NST=49;
%Reactive tray number, NR1 to NR2
NR1=29;
NR2=37;
%Feed tray number, NF
NF=18;
%Weight of catalyst per tray in kilogram unit, WC
WC=163.67;
%Coefficients, VR to be used in rate of reaction (-1 for reactant
%component,1 for product)
VR=[-1 -1 1 0];
%Feed temperature in Celsius
feedtemperature=69.79;
%WH-Weir height(m)
WH1=0.067;
WH2=0.067;
WH3=0.067;
%D-Diameter of the column(m)
D1=3.3;
D2=3;
D3=2.7;
%WL-Weir length(m)
WL1=3.17;
WL2=2.87;
```



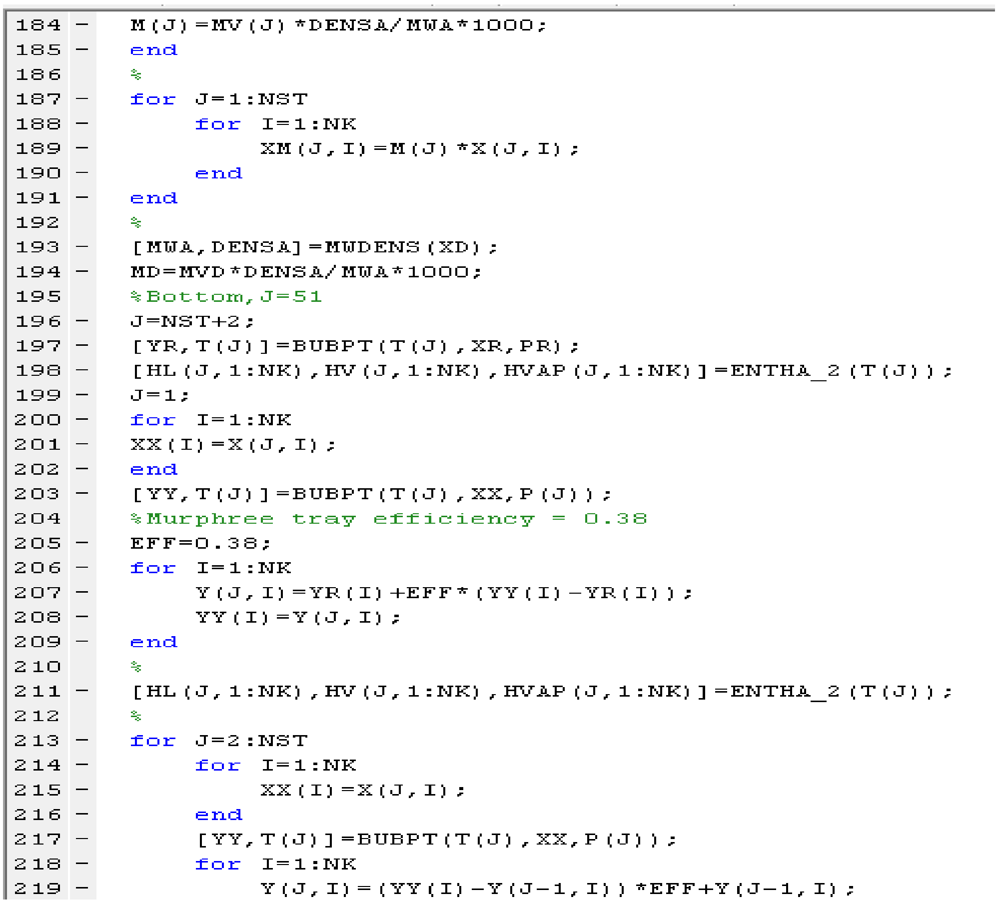
```
WL3=2.57;
%MVR-Volumetric holdup in reboiler (m3)
MVR=58.17;
%MVD-Volumetric holdup in reflux drum (m3)
MVD=58.17;
%Density
density=[795.72 592.79  745.84  561.97];
%Molecular weight
MW=[32.04 56 88.15 58.12];
```



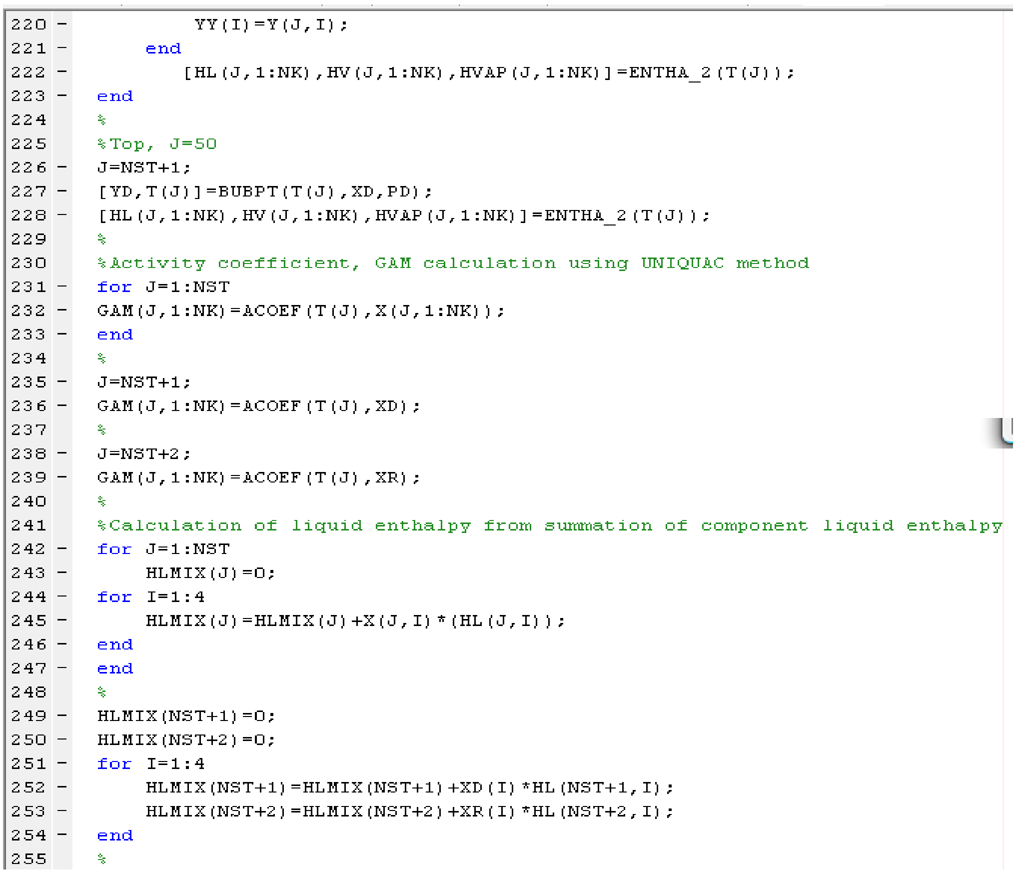
```
i=0;
TIME=0;
A=0.01;
DELTA=1/3000;
%
%
%Pressure at the top and bottom
%Unit conversion from kPa to Pa
PD=Pressure_top*1000;
PR=Pressure_bottom*1000;
%
%Unit conversion for feed temperature in Kelvin
TF=feedtemperature+273.15;
%
Z=feedcomposition(density,MW);
%
[feed,feedflowrate]=feedflowrate_1(Z,density,MW);
%
%Calculate pressure profile
%
for J=1:NST
    P(J)=(PR-(J*(PR-PD))/NST);
end
%
%
%Reflux flow rate
RFLX=refluxflowrate(density,MW);
%
%Reboiler duty
QB=reboilerduty;
%
k=1;
%
while TIME<=3.5
%
```



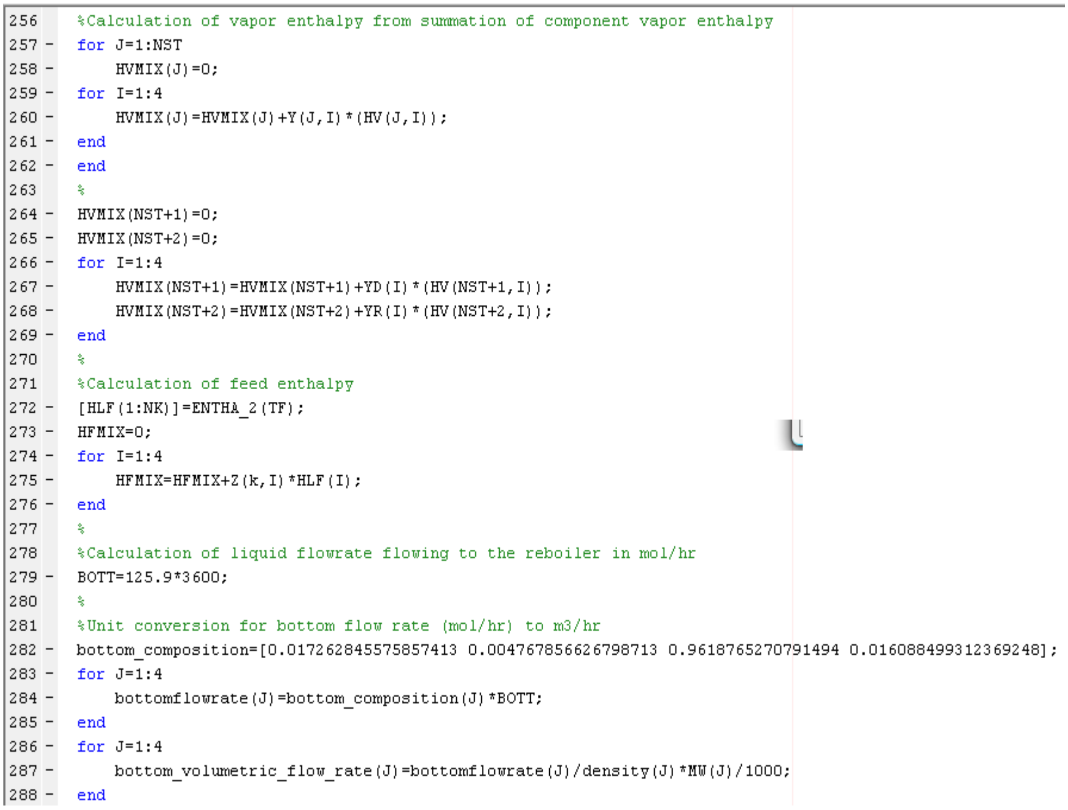
```
%Calculation of holdup for bottom in mol unit
[MWA,DENSA]=MWDENS(XR);
MR=MVR*DENSA/MWA*1000;
for I=1:NK
    XRM(I)=MR*XR(I);
end
%
for J=1:NF-1
    for I=1:NK
        XX(I)=X(J,I);
    end
[MWA,DENSA]=MWDENS(XX);
LV(J)=LO(J)*MWA/DENSA/1000/3600;
HFOW=(LV(J)/(1.8385*WL1))^0.66667;
MV(J)=(HFOW+WH1)*3.1416*D1*D1/4;
M(J)=MV(J)*DENSA/MWA*1000;
end
%
for I=1:NK
    XX(I)=X(NF,I);
end
[MWA,DENSA]=MWDENS(XX);
LV(NF)=LO(NF)*MWA/DENSA/1000/3600;
HFOW=(LV(NF)/(1.8385*WL2))^0.66667;
MV(NF)=(HFOW+WH2)*3.1416*D2*D2/4;
M(NF)=MV(NF)*DENSA/MWA*1000;
%

for J=NF+1:NST
   for I=1:NK
      XX(I)=X(J,I);
 end
[MWA,DENSA]=MWDENS(XX);
LV(J)=LO(J)*MWA/DENSA/1000/3600;
HFOW=(LV(J)/(1.8385*WL3))^0.66667;
MV(J)=(HFOW+WH3)*3.1416*D3*D3/4;
```



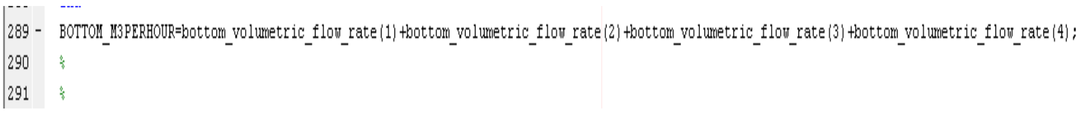
```
M(J)=MV(J)*DENSA/MWA*1000;
end
%
for J=1:NST
    for I=1:NK
        XM(J,I)=M(J)*X(J,I);
    end
end
%
[MWA,DENSA]=MWDENS(XD);
MD=MVD*DENSA/MWA*1000;
%Bottom,J=51
J=NST+2;
[YR,T(J)]=BUBPT(T(J),XR,PR);
[HL(J,1:NK),HV(J,1:NK),HVAP(J,1:NK)]=ENTHA_2(T(J));
J=1;
for I=1:NK
XX(I)=X(J,I);
end
[YY,T(J)]=BUBPT(T(J),XX,P(J));
%Murphree tray efficiency = 0.38
EFF=0.38;
for I=1:NK
    Y(J,I)=YR(I)+EFF*(YY(I)-YR(I));
    YY(I)=Y(J,I);
end
%
[HL(J,1:NK),HV(J,1:NK),HVAP(J,1:NK)]=ENTHA_2(T(J));
%
for J=2:NST
    for I=1:NK
        XX(I)=X(J,I);
    end
    [YY,T(J)]=BUBPT(T(J),XX,P(J));
    for I=1:NK
        Y(J,I)=(YY(I)-Y(J-1,I))*EFF+Y(J-1,I);
```



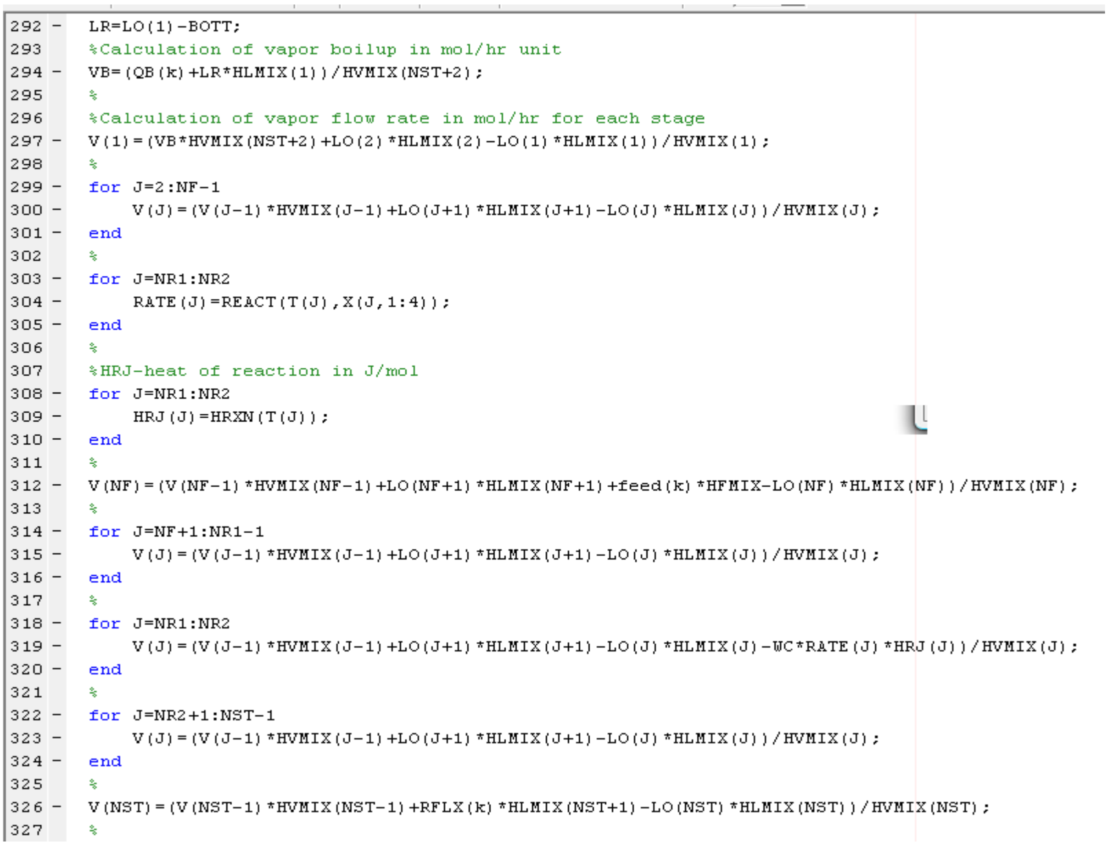
```
        YY(I)=Y(J,I);
    end
       [HL(J,1:NK),HV(J,1:NK),HVAP(J,1:NK)]=ENTHA_2(T(J));
end
%
%Top, J=50
J=NST+1;
[YD,T(J)]=BUBPT(T(J),XD,PD);
[HL(J,1:NK),HV(J,1:NK),HVAP(J,1:NK)]=ENTHA_2(T(J));
%
%Activity coefficient, GAM calculation using UNIQUAC method
for J=1:NST
GAM(J,1:NK)=ACOEF(T(J),X(J,1:NK));
end
%
J=NST+1;
GAM(J,1:NK)=ACOEF(T(J),XD);
%
J=NST+2;
GAM(J,1:NK)=ACOEF(T(J),XR);
%
%Calculation of liquid enthalpy from summation of component liquid enthalpy
for J=1:NST
    HLMIX(J)=0;
for I=1:4
    HLMIX(J)=HLMIX(J)+X(J,I)*(HL(J,I));
end
end
%
HLMIX(NST+1)=0;
HLMIX(NST+2)=0;
for I=1:4
    HLMIX(NST+1)=HLMIX(NST+1)+XD(I)*HL(NST+1,I);
    HLMIX(NST+2)=HLMIX(NST+2)+XR(I)*HL(NST+2,I);
end
%
```



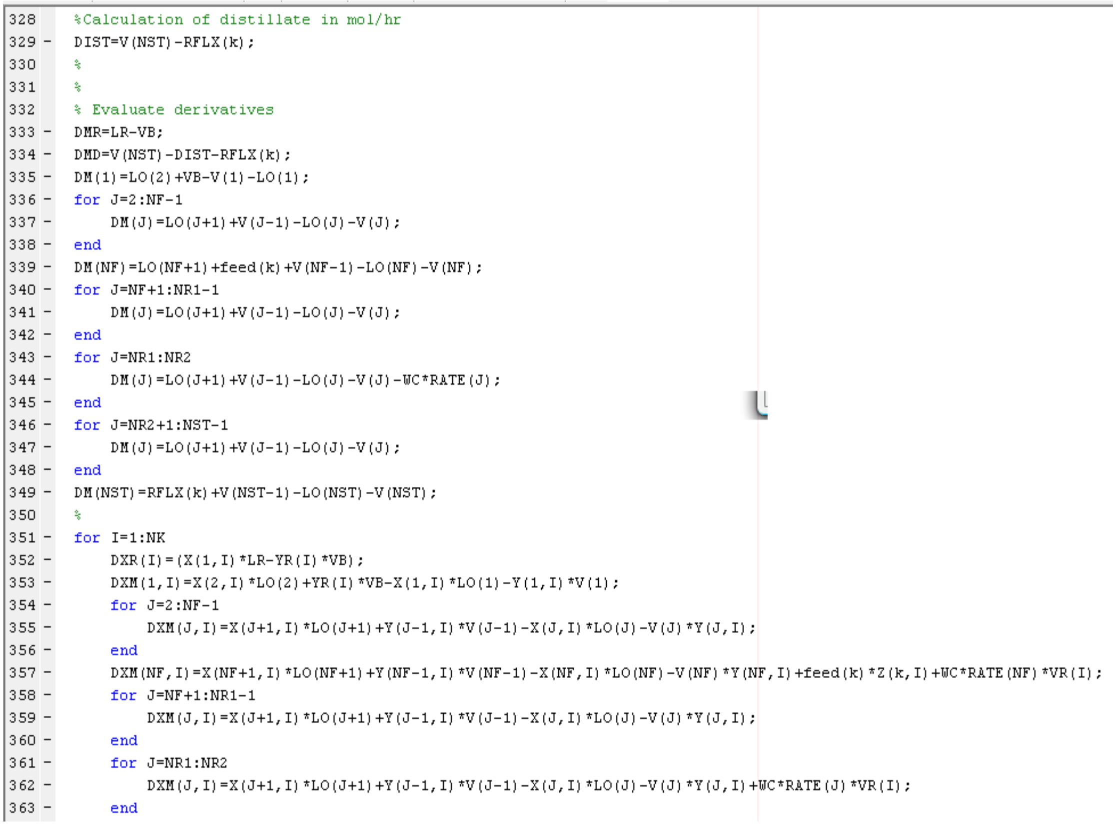
```
%Calculation of vapor enthalpy from summation of component vapor enthalpy
for J=1:NST
    HVMIX(J)=0;
for I=1:4
    HVMIX(J)=HVMIX(J)+Y(J,I)*(HV(J,I));
end
end
%
HVMIX(NST+1)=0;
HVMIX(NST+2)=0;
for I=1:4
    HVMIX(NST+1)=HVMIX(NST+1)+YD(I)*(HV(NST+1,I));
    HVMIX(NST+2)=HVMIX(NST+2)+YR(I)*(HV(NST+2,I));
end
%
%Calculation of feed enthalpy
[HLF(1:NK)]=ENTHA_2(TF);
HFMIX=0;
for I=1:4
    HFMIX=HFMIX+Z(k,I)*HLF(I);
end
%
%Calculation of liquid flowrate flowing to the reboiler in mol/hr
BOTT=125.9*3600;
%
%Unit conversion for bottom flow rate (mol/hr) to m3/hr
bottom_composition=[0.017262845575857413 0.004767856626798713 0.9618765270791494 0.016088499312369248];
for J=1:4
    bottomflowrate(J)=bottom_composition(J)*BOTT;
end
for J=1:4
    bottom_volumetric_flow_rate(J)=bottomflowrate(J)/density(J)*MW(J)/1000;
end
```



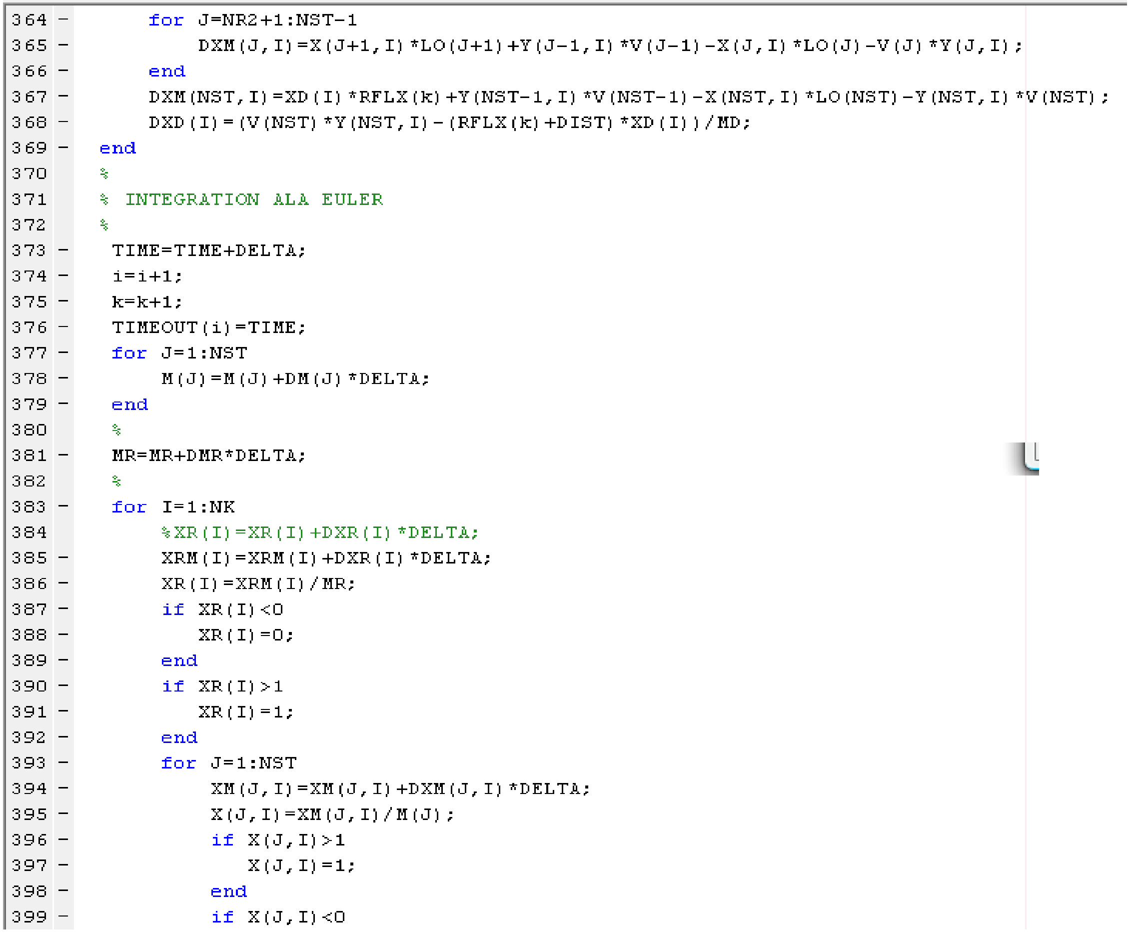
```
BOTTOM_M3PERHOUR=bottom_volumetric_flow_rate(1)+bottom_volumetric_flow_rate(2)+bottom_volumetric_flow_rate(3)+bottom_volumetric_flow_rate(4);
%
%
```



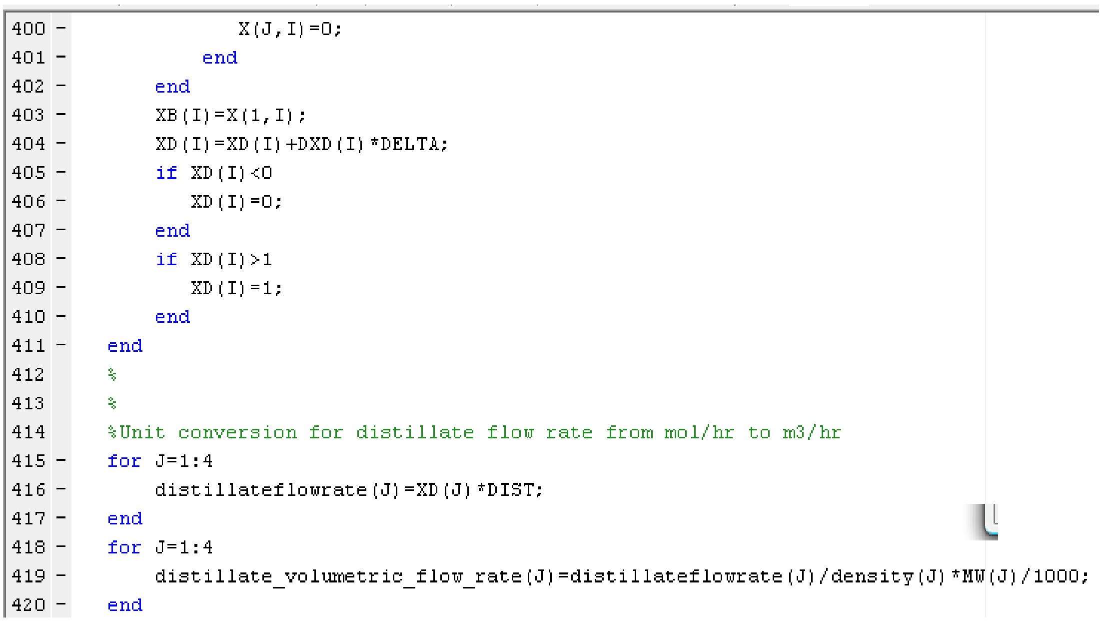
```
LR=LO(1)-BOTT;
%Calculation of vapor boilup in mol/hr unit
VB=(QB(k)+LR*HLMIX(1))/HVMIX(NST+2);
%
%Calculation of vapor flow rate in mol/hr for each stage
V(1)=(VB*HVMIX(NST+2)+LO(2)*HLMIX(2)-LO(1)*HLMIX(1))/HVMIX(1);
%
for J=2:NF-1
    V(J)=(V(J-1)*HVMIX(J-1)+LO(J+1)*HLMIX(J+1)-LO(J)*HLMIX(J))/HVMIX(J);
end
%
for J=NR1:NR2
    RATE(J)=REACT(T(J),X(J,1:4));
end
%
%HRJ-heat of reaction in J/mol
for J=NR1:NR2
    HRJ(J)=HRXN(T(J));
end
%
V(NF)=(V(NF-1)*HVMIX(NF-1)+LO(NF+1)*HLMIX(NF+1)+feed(k)*HFMIX-LO(NF)*HLMIX(NF))/HVMIX(NF);
%
for J=NF+1:NR1-1
    V(J)=(V(J-1)*HVMIX(J-1)+LO(J+1)*HLMIX(J+1)-LO(J)*HLMIX(J))/HVMIX(J);
end
%
for J=NR1:NR2
    V(J)=(V(J-1)*HVMIX(J-1)+LO(J+1)*HLMIX(J+1)-LO(J)*HLMIX(J)-WC*RATE(J)*HRJ(J))/HVMIX(J);
end
%
for J=NR2+1:NST-1
    V(J)=(V(J-1)*HVMIX(J-1)+LO(J+1)*HLMIX(J+1)-LO(J)*HLMIX(J))/HVMIX(J);
end
%
V(NST)=(V(NST-1)*HVMIX(NST-1)+RFLX(k)*HLMIX(NST+1)-LO(NST)*HLMIX(NST))/HVMIX(NST);
%
```



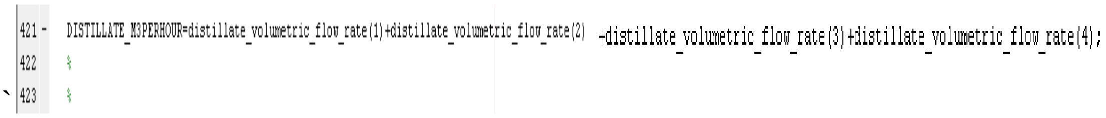
```
%Calculation of distillate in mol/hr
DIST=V(NST)-RFLX(k);
%
%
% Evaluate derivatives
DMR=LR-VB;
DMD=V(NST)-DIST-RFLX(k);
DM(1)=LO(2)+VB-V(1)-LO(1);
for J=2:NF-1
    DM(J)=LO(J+1)+V(J-1)-LO(J)-V(J);
end
DM(NF)=LO(NF+1)+feed(k)+V(NF-1)-LO(NF)-V(NF);
for J=NF+1:NR1-1
    DM(J)=LO(J+1)+V(J-1)-LO(J)-V(J);
end
for J=NR1:NR2
    DM(J)=LO(J+1)+V(J-1)-LO(J)-V(J)-WC*RATE(J);
end
for J=NR2+1:NST-1
    DM(J)=LO(J+1)+V(J-1)-LO(J)-V(J);
end
DM(NST)=RFLX(k)+V(NST-1)-LO(NST)-V(NST);
%
for I=1:NK
    DXR(I)=(X(1,I)*LR-YR(I)*VB);
    DXM(1,I)=X(2,I)*LO(2)+YR(I)*VB-X(1,I)*LO(1)-Y(1,I)*V(1);
    for J=2:NF-1
        DXM(J,I)=X(J+1,I)*LO(J+1)+Y(J-1,I)*V(J-1)-X(J,I)*LO(J)-V(J)*Y(J,I);
    end
    DXM(NF,I)=X(NF+1,I)*LO(NF+1)+Y(NF-1,I)*V(NF-1)-X(NF,I)*LO(NF)-V(NF)*Y(NF,I)+feed(k)*Z(k,I)+WC*RATE(NF)*VR(I);
    for J=NF+1:NR1-1
        DXM(J,I)=X(J+1,I)*LO(J+1)+Y(J-1,I)*V(J-1)-X(J,I)*LO(J)-V(J)*Y(J,I);
    end
    for J=NR1:NR2
        DXM(J,I)=X(J+1,I)*LO(J+1)+Y(J-1,I)*V(J-1)-X(J,I)*LO(J)-V(J)*Y(J,I)+WC*RATE(J)*VR(I);
    end
```



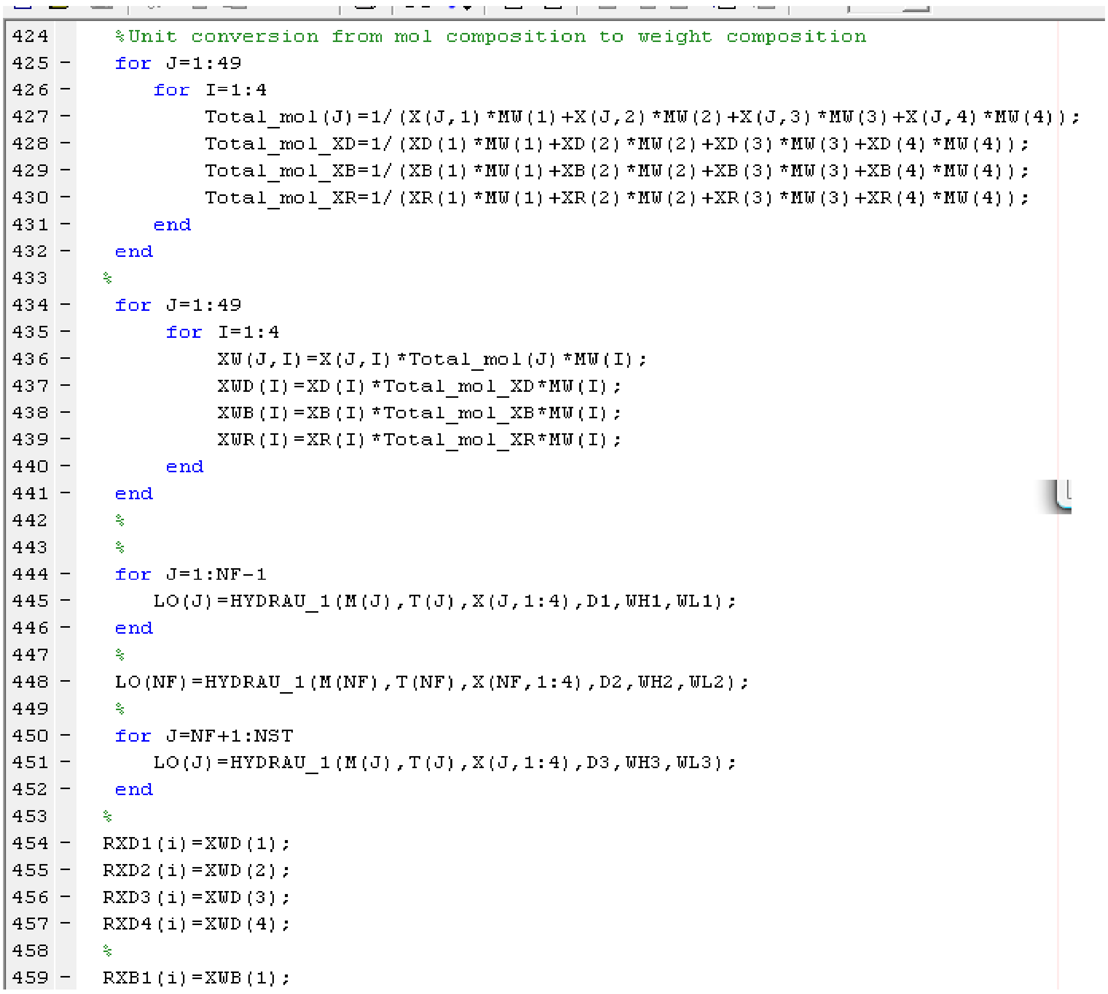
```
    for J=NR2+1:NST-1
        DXM(J,I)=X(J+1,I)*LO(J+1)+Y(J-1,I)*V(J-1)-X(J,I)*LO(J)-V(J)*Y(J,I);
    end
    DXM(NST,I)=XD(I)*RFLX(k)+Y(NST-1,I)*V(NST-1)-X(NST,I)*LO(NST)-Y(NST,I)*V(NST);
    DXD(I)=(V(NST)*Y(NST,I)-(RFLX(k)+DIST)*XD(I))/MD;
end
%
% INTEGRATION ALA EULER
%
 TIME=TIME+DELTA;
 i=i+1;
 k=k+1;
 TIMEOUT(i)=TIME;
 for J=1:NST
     M(J)=M(J)+DM(J)*DELTA;
 end
 %
 MR=MR+DMR*DELTA;
 %
 for I=1:NK
     %XR(I)=XR(I)+DXR(I)*DELTA;
     XRM(I)=XRM(I)+DXR(I)*DELTA;
     XR(I)=XRM(I)/MR;
     if XR(I)<0
        XR(I)=0;
     end
     if XR(I)>1
        XR(I)=1;
     end
     for J=1:NST
         XM(J,I)=XM(J,I)+DXM(J,I)*DELTA;
         X(J,I)=XM(J,I)/M(J);
         if X(J,I)>1
            X(J,I)=1;
         end
         if X(J,I)<0
```



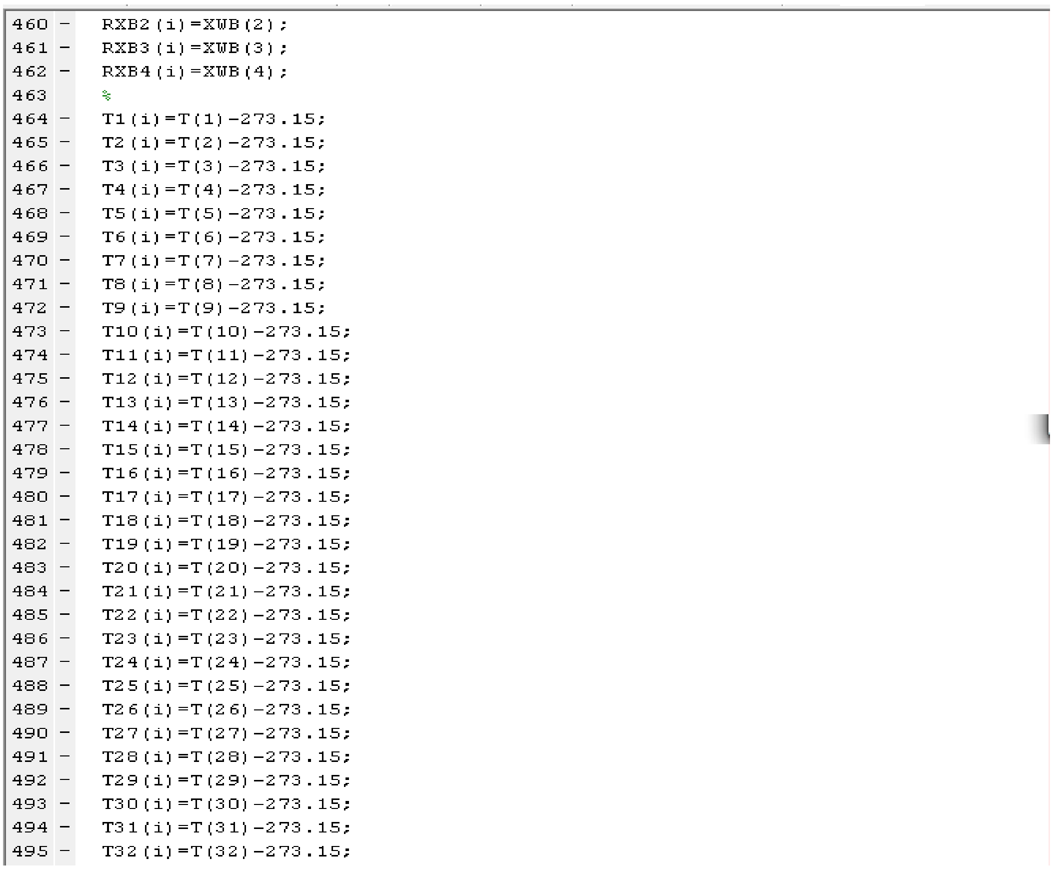
```
            X(J,I)=0;
        end
    end
    XB(I)=X(1,I);
    XD(I)=XD(I)+DXD(I)*DELTA;
    if XD(I)<0
       XD(I)=0;
    end
    if XD(I)>1
       XD(I)=1;
    end
end
%
%
%Unit conversion for distillate flow rate from mol/hr to m3/hr
for J=1:4
    distillateflowrate(J)=XD(J)*DIST;
end
for J=1:4
    distillate_volumetric_flow_rate(J)=distillateflowrate(J)/density(J)*MW(J)/1000;
end
```



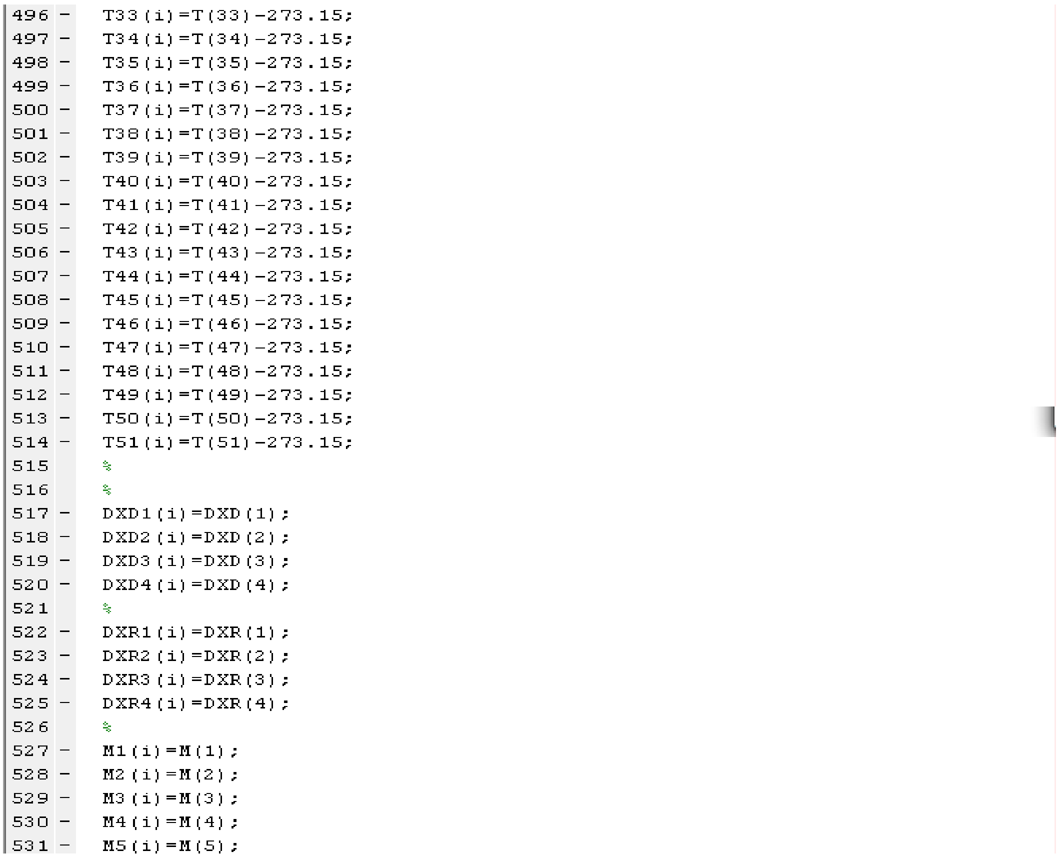
```
DISTILLATE_M3PERHOUR=distillate_volumetric_flow_rate(1)+distillate_volumetric_flow_rate(2) +distillate_volumetric_flow_rate(3)+distillate_volumetric_flow_rate(4);
%
%
```



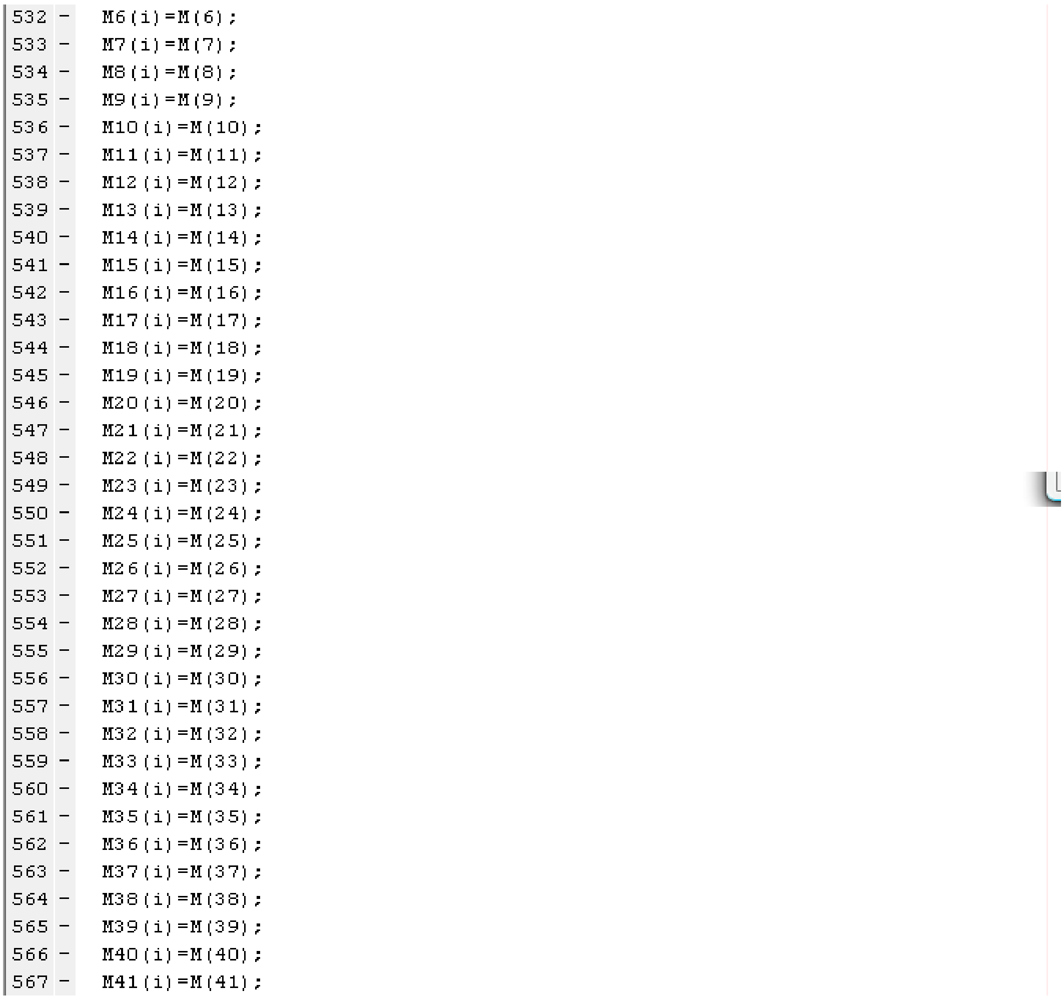
```
 %Unit conversion from mol composition to weight composition
 for J=1:49
    for I=1:4
        Total_mol(J)=1/(X(J,1)*MW(1)+X(J,2)*MW(2)+X(J,3)*MW(3)+X(J,4)*MW(4));
        Total_mol_XD=1/(XD(1)*MW(1)+XD(2)*MW(2)+XD(3)*MW(3)+XD(4)*MW(4));
        Total_mol_XB=1/(XB(1)*MW(1)+XB(2)*MW(2)+XB(3)*MW(3)+XB(4)*MW(4));
        Total_mol_XR=1/(XR(1)*MW(1)+XR(2)*MW(2)+XR(3)*MW(3)+XR(4)*MW(4));
    end
 end
%
 for J=1:49
     for I=1:4
         XW(J,I)=X(J,I)*Total_mol(J)*MW(I);
         XWD(I)=XD(I)*Total_mol_XD*MW(I);
         XWB(I)=XB(I)*Total_mol_XB*MW(I);
         XWR(I)=XR(I)*Total_mol_XR*MW(I);
     end
 end
 %
 %
 for J=1:NF-1
    LO(J)=HYDRAU_1(M(J),T(J),X(J,1:4),D1,WH1,WL1);
 end
 %
 LO(NF)=HYDRAU_1(M(NF),T(NF),X(NF,1:4),D2,WH2,WL2);
 %
 for J=NF+1:NST
    LO(J)=HYDRAU_1(M(J),T(J),X(J,1:4),D3,WH3,WL3);
 end
%
RXD1(i)=XWD(1);
RXD2(i)=XWD(2);
RXD3(i)=XWD(3);
RXD4(i)=XWD(4);
%
RXB1(i)=XWB(1);
```



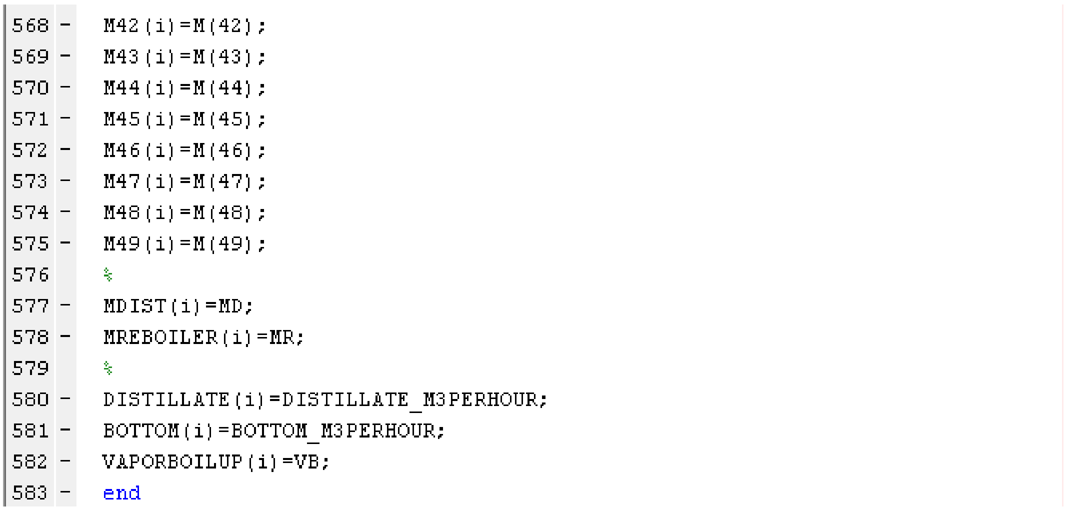
```
RXB2(i)=XWB(2);
RXB3(i)=XWB(3);
RXB4(i)=XWB(4);
%
T1(i)=T(1)-273.15;
T2(i)=T(2)-273.15;
T3(i)=T(3)-273.15;
T4(i)=T(4)-273.15;
T5(i)=T(5)-273.15;
T6(i)=T(6)-273.15;
T7(i)=T(7)-273.15;
T8(i)=T(8)-273.15;
T9(i)=T(9)-273.15;
T10(i)=T(10)-273.15;
T11(i)=T(11)-273.15;
T12(i)=T(12)-273.15;
T13(i)=T(13)-273.15;
T14(i)=T(14)-273.15;
T15(i)=T(15)-273.15;
T16(i)=T(16)-273.15;
T17(i)=T(17)-273.15;
T18(i)=T(18)-273.15;
T19(i)=T(19)-273.15;
T20(i)=T(20)-273.15;
T21(i)=T(21)-273.15;
T22(i)=T(22)-273.15;
T23(i)=T(23)-273.15;
T24(i)=T(24)-273.15;
T25(i)=T(25)-273.15;
T26(i)=T(26)-273.15;
T27(i)=T(27)-273.15;
T28(i)=T(28)-273.15;
T29(i)=T(29)-273.15;
T30(i)=T(30)-273.15;
T31(i)=T(31)-273.15;
T32(i)=T(32)-273.15;
```



```
T33(i)=T(33)-273.15;
T34(i)=T(34)-273.15;
T35(i)=T(35)-273.15;
T36(i)=T(36)-273.15;
T37(i)=T(37)-273.15;
T38(i)=T(38)-273.15;
T39(i)=T(39)-273.15;
T40(i)=T(40)-273.15;
T41(i)=T(41)-273.15;
T42(i)=T(42)-273.15;
T43(i)=T(43)-273.15;
T44(i)=T(44)-273.15;
T45(i)=T(45)-273.15;
T46(i)=T(46)-273.15;
T47(i)=T(47)-273.15;
T48(i)=T(48)-273.15;
T49(i)=T(49)-273.15;
T50(i)=T(50)-273.15;
T51(i)=T(51)-273.15;
%
%
DXD1(i)=DXD(1);
DXD2(i)=DXD(2);
DXD3(i)=DXD(3);
DXD4(i)=DXD(4);
%
DXR1(i)=DXR(1);
DXR2(i)=DXR(2);
DXR3(i)=DXR(3);
DXR4(i)=DXR(4);
%
M1(i)=M(1);
M2(i)=M(2);
M3(i)=M(3);
M4(i)=M(4);
M5(i)=M(5);
```



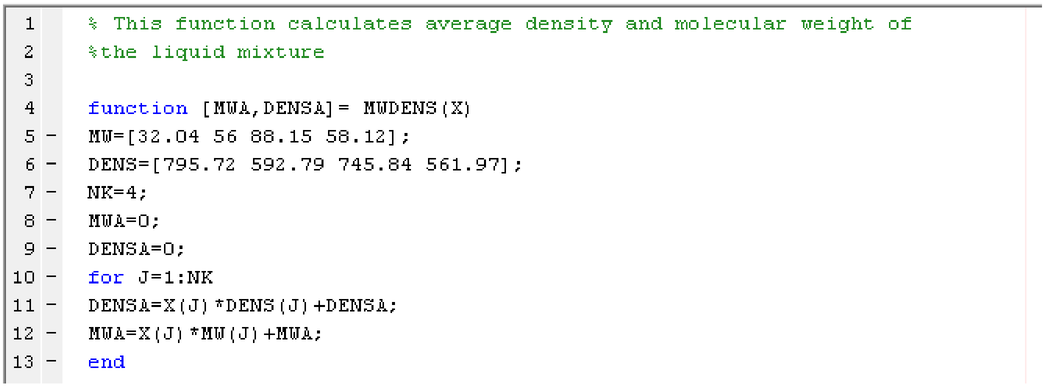
```
M6(i)=M(6);
M7(i)=M(7);
M8(i)=M(8);
M9(i)=M(9);
M10(i)=M(10);
M11(i)=M(11);
M12(i)=M(12);
M13(i)=M(13);
M14(i)=M(14);
M15(i)=M(15);
M16(i)=M(16);
M17(i)=M(17);
M18(i)=M(18);
M19(i)=M(19);
M20(i)=M(20);
M21(i)=M(21);
M22(i)=M(22);
M23(i)=M(23);
M24(i)=M(24);
M25(i)=M(25);
M26(i)=M(26);
M27(i)=M(27);
M28(i)=M(28);
M29(i)=M(29);
M30(i)=M(30);
M31(i)=M(31);
M32(i)=M(32);
M33(i)=M(33);
M34(i)=M(34);
M35(i)=M(35);
M36(i)=M(36);
M37(i)=M(37);
M38(i)=M(38);
M39(i)=M(39);
M40(i)=M(40);
M41(i)=M(41);
```



```
M42(i)=M(42);
M43(i)=M(43);
M44(i)=M(44);
M45(i)=M(45);
M46(i)=M(46);
M47(i)=M(47);
M48(i)=M(48);
M49(i)=M(49);
%
MDIST(i)=MD;
MREBOILER(i)=MR;
%
DISTILLATE(i)=DISTILLATE_M3PERHOUR;
BOTTOM(i)=BOTTOM_M3PERHOUR;
VAPORBOILUP(i)=VB;
end
```

APPENDIX I

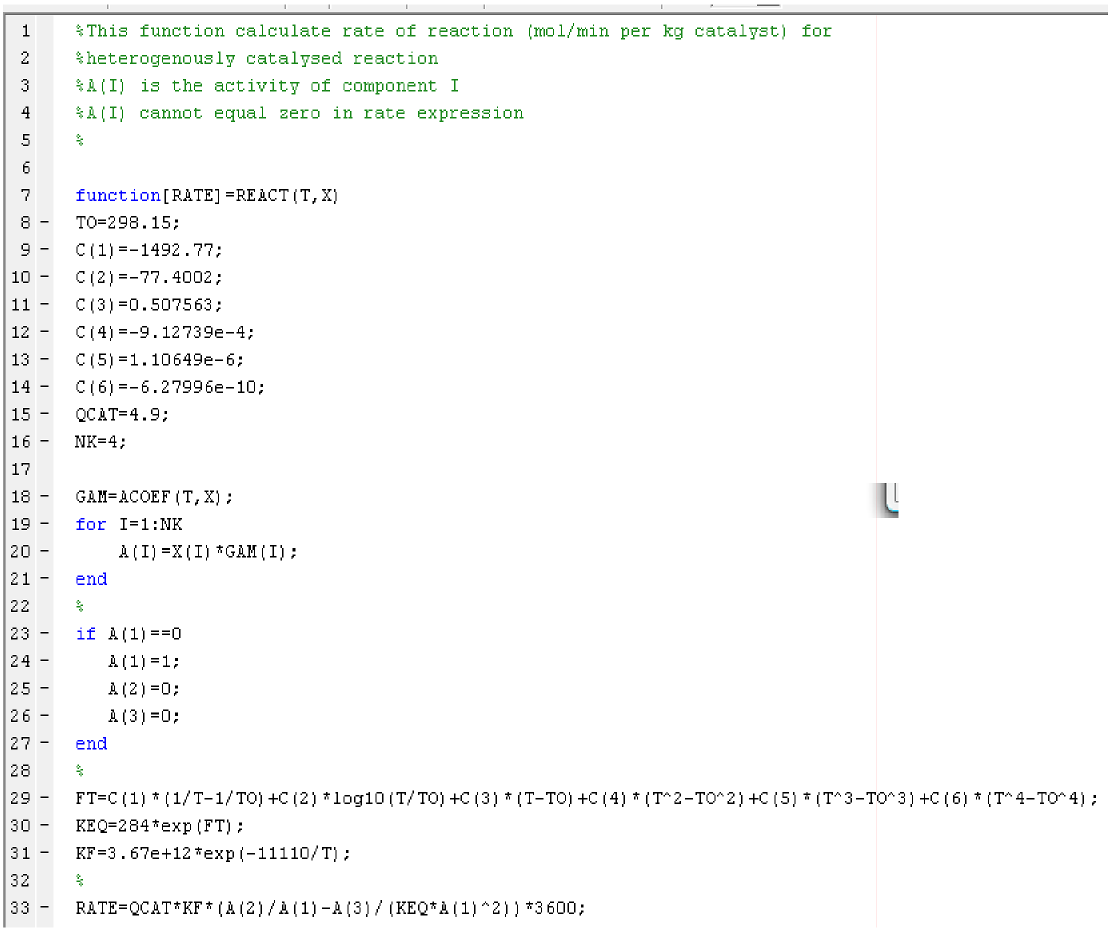
Program for Average Density and Molecular Weight Calculations



```
% This function calculates average density and molecular weight of
%the liquid mixture

function [MWA,DENSA]= MWDENS(X)
MW=[32.04 56 88.15 58.12];
DENS=[795.72 592.79 745.84 561.97];
NK=4;
MWA=0;
DENSA=0;
for J=1:NK
DENSA=X(J)*DENS(J)+DENSA;
MWA=X(J)*MW(J)+MWA;
end
```

APPENDIX J

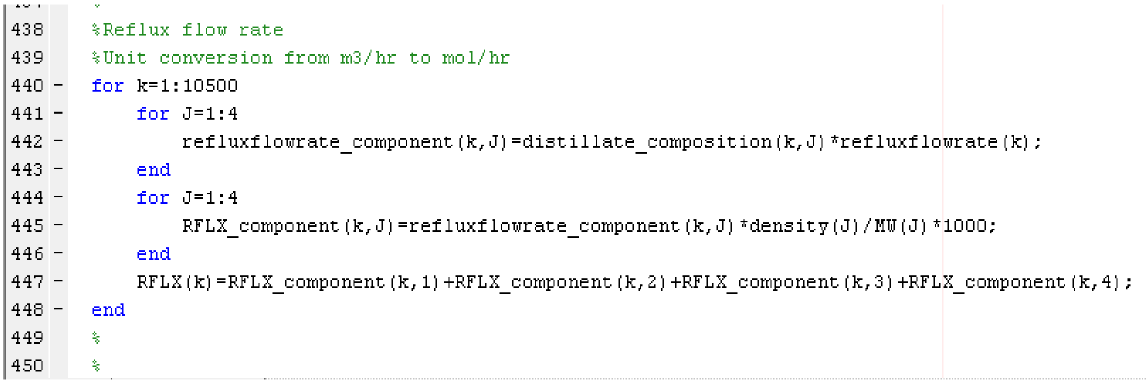
Program for Rate of Reaction Calculations



```
%This function calculate rate of reaction (mol/min per kg catalyst) for
%heterogenously catalysed reaction
%A(I) is the activity of component I
%A(I) cannot equal zero in rate expression
%

function[RATE]=REACT(T,X)
TO=298.15;
C(1)=-1492.77;
C(2)=-77.4002;
C(3)=0.507563;
C(4)=-9.12739e-4;
C(5)=1.10649e-6;
C(6)=-6.27996e-10;
QCAT=4.9;
NK=4;

GAM=ACOEF(T,X);
for I=1:NK
    A(I)=X(I)*GAM(I);
end
%
if A(1)==0
   A(1)=1;
   A(2)=0;
   A(3)=0;
end
%
FT=C(1)*(1/T-1/TO)+C(2)*log10(T/TO)+C(3)*(T-TO)+C(4)*(T^2-TO^2)+C(5)*(T^3-TO^3)+C(6)*(T^4-TO^4);
KEQ=284*exp(FT);
KF=3.67e+12*exp(-11110/T);
%
RATE=QCAT*KF*(A(2)/A(1)-A(3)/(KEQ*A(1)^2))*3600;
```

APPENDIX K

Program for Reflux Flow Rate Calculations



```
%Reflux flow rate
%Unit conversion from m3/hr to mol/hr
for k=1:10500
    for J=1:4
        refluxflowrate_component(k,J)=distillate_composition(k,J)*refluxflowrate(k);
    end
    for J=1:4
        RFLX_component(k,J)=refluxflowrate_component(k,J)*density(J)/MW(J)*1000;
    end
    RFLX(k)=RFLX_component(k,1)+RFLX_component(k,2)+RFLX_component(k,3)+RFLX_component(k,4);
end
%
%
```