

Development of Dynamic Models for a Reactive Packed Distillation Column

Abdulwahab GIWA

*Engineering/Chemical Engineering/Process
Systems Engineering
Ankara University
Ankara, 06100, Turkey*

agiwa@ankara.edu.tr

Süleyman KARACAN

*Engineering/Chemical Engineering/Process
Systems Engineering
Ankara University
Ankara, 06100, Turkey*

karacan@eng.ankara.edu.tr

Abstract

This work has been carried out to develop dynamic models for a reactive packed distillation column using the production of ethyl acetate as the case study. The experimental setup for the production of ethyl acetate was a pilot scale packed column divided into condenser, rectification, acetic acid feed, reaction, ethanol feed, stripping and reboiler sections. The reaction section was filled with Amberlyst 15 catalyst while the rectification and the stripping sections were both filled with Raschig rings. The theoretical models for each of the sections of the column were developed from first principles and solved with the aid of MATLAB R2011a. Comparisons were made between the experimental and theoretical results by calculating the percentage residuals for the top and bottom segment temperatures of the column. The results obtained showed that there were good agreements between the experimental and theoretical top and bottom segment temperatures because the calculated percentage residuals were small. Therefore, the developed dynamic models can be used to represent the reactive packed distillation column.

Keywords: Reactive Distillation, Dynamic Models, MATLAB, Ethyl Acetate, Percentage Residual.

1. INTRODUCTION

There are three main cases in the chemical industry in which combined distillation and chemical reaction occur: (1) use of a distillation column as a chemical reactor in order to increase conversion of reactants, (2) improvement of separation in a distillation column by using a chemical reaction in order to change unfavourable relations between component volatilities, (3) course of parasitic reactions during distillation, decreasing yield of process [1].

Distillation column can be used advantageously as a reactor for systems in which chemical reactions occur at temperatures and pressures suitable to the distillation of components. This combined unit operation is especially useful for those chemical reactions for which chemical equilibrium limits the conversion. By continuous separation of products from reactants while the reaction is in progress, the reaction can proceed to a much higher level of conversion than without separation [1]. This phenomenon is referred to as "reactive distillation".

Reactive distillation has been a focus of research in chemical process industry and academia in the last years (e.g., [2]; [3]; [4]; [5]). Combining reaction and distillation has several advantages, including: a) shift of chemical equilibrium and an increase of reaction conversion by simultaneous reaction and separation of products, b) suppression of side reactions and c) utilization of heat of reaction for mass transfer operation. These synergistic effects may result in significant economic

benefits of reactive distillation compared to a conventional design. These economic benefits include: a) lower capital investment, b) lower energy cost and c) higher product yields [6]. Though there are economic benefits of reactive distillation, the combination of both reaction and separation in a single unit has made the design and modelling of the process very challenging.

The design issues for reactive distillation (RD) systems are considerably more complex than those involved for either conventional reactors or conventional distillation columns because the introduction of an in situ separation function within the reaction zone leads to complex interactions between vapour-liquid equilibrium, vapour-liquid mass transfer, intra-catalyst diffusion (for heterogeneously catalysed processes) and chemical kinetics. Such interactions have been shown to lead to phenomena of multiple steady states and complex dynamics [7] of the process.

In designing a reactive distillation column, the model of the process is required. Broadly speaking, two types of modelling approaches are available in the literature for reactive distillation: the equilibrium stage model and the non-equilibrium stage model [8].

The equilibrium model assumes that the vapour and liquid leaving a stage are in equilibrium. The non-equilibrium model (also known as the "rate-based model"), on the other hand, assumes that the vapour-liquid equilibrium is established only at the interface between the bulk liquid and vapour phases and employs a transport-based approach to predict the flux of mass and energy across the interface. The equilibrium model is mathematically much simpler and computationally less intensive. On the other hand, the non-equilibrium one is more consistent with the real world operations [9]. According to the information obtained from the literature, different studies have been carried out on the two types of models.

Noeres et al. (2003) gave a comprehensive overview of basics and peculiarities of reactive absorption and reactive distillation modelling and design. Roat et al. (1986) discussed dynamic simulation of reactive distillation using an equilibrium model. Ruiz et al. (1995) developed a generalized equilibrium model for the dynamic simulation of multicomponent reactive distillation. A simulation package called REActive Distillation dYnamic Simulator (READYS) was used to carry out the simulations. Several test problems were studied and used to compare the work with those of others. Perez-Cisneros et al. (1996) proposed a different approach to the equilibrium model by using chemical elements rather than the real components. Alejski and Duprat (1996) developed a dynamic equilibrium model for a tray reactive distillation column. A similar dynamic equilibrium model was developed by Sneesby et al. (1998) for a tray reactive distillation column for the production of ethyl tert-butyl ether (ETBE). In their work, chemical equilibrium on all the reactive stages and constant enthalpy were assumed to simplify the model. The model was implemented in SpeedUp and simulated. Kreul et al. (1998) developed a dynamic rate-based model for a reactive packed distillation column for the production of methyl acetate. All the important dynamic changes except the vapour holdup were considered in the model developed in their study. The dynamic rate-based model was implemented into the ABACUSS large-scale equation-based modelling environment. Dynamic experiments were carried out and the results were compared to the simulation results. Baur et al. (2001) proposed a dynamic rate-based cell model for reactive tray distillation columns. Both the liquid and vapour phases were divided into a number of contacting cells and the Maxwell–Stefan equations were used to describe mass transfer. Liquid holdup, vapour holdup, and energy holdup were all included in the model. A reactive distillation tray column for the production of ethylene glycol was used to carry out dynamic simulations. Vora and Daoutidis (2001) studied the dynamics and control of a reactive tray distillation column for the production of ethyl acetate from acetic acid and ethyl alcohol. Schneider et al. (2001) studied reactive batch distillation for a methyl acetate system, using a two-film dynamic rate-based model. In their study, pilot plant batch experiments were carried out to validate the dynamic model and the agreement was found to be reasonable. Peng et al. (2003) developed dynamic rate-based and equilibrium models for a reactive packed distillation column for the production of tert-amyl methyl ether (TAME). The two types of models, consisting of differential and algebraic equations, were implemented in gPROMS and dynamic simulations were carried out to study the dynamic behaviour of the reactive distillation of the TAME system.

Heterogeneous reactive distillation in packed towers is of special interest because the catalyst does not have to be removed from the product and different reactive and non-reactive sections can be realized. At the same time, the interactions of reaction and separation increase the complexity of the process and, thus, a better understanding of the process dynamics is required [20].

Therefore, this work is aimed to develop dynamic models for a heterogeneous reactive packed distillation column using the production of ethyl acetate (desired product) and water (by-product) from the esterification reaction between acetic acid and ethanol as the case study.

2. PROCEDURES

The procedures used for the accomplishment of this work are divided into two, namely experimental procedure and modelling procedure.

2.1 Experimental Procedure

The experimental pilot plant in which the experiments were carried out was a reactive packed distillation column (RPDC) set up as shown in Figures 1a (pictorially) and b (sketch view) below. The column had, excluding the condenser and the reboiler, a height of 1.5 m and a diameter of 0.05 m. The column consisted of a cylindrical condenser of diameter and height of 5 and 22.5 cm respectively. The main column section of the plant was divided into three subsections of approximately 0.5 m each. The upper, middle and lower sections were the rectifying, the reaction and the stripping sections respectively. The rectifying and the stripping sections were packed with raschig rings while the reaction section was filled with Amberlyst 15 solid catalyst (the catalyst had a surface area of 5300 m²/kg, a total pore volume of 0.4 cc/g and a density of 610 kg/m³). The reboiler was spherical in shape and had a volume of 3 Litre. The column was fed with acetic acid at the top (between the rectifying section and the reaction section) while ethanol was fed at the bottom (between the reaction section and the stripping section) with the aid of peristaltic pumps that were operated with the aid of a computer via MATLAB/Simulink program. All the signal inputs (reflux ratio (R), feed ratio (F) and reboiler duty (Q)) to the column and the measured outputs (top segment temperature (T_{top}), reaction segment temperature (T_{rxn}) and bottom segment temperature (T_{bot})) from the column were sent and recorded respectively on-line with the aid of MATLAB/Simulink computer program and electronic input-output (I/O) modules that were connected to the equipment and the computer system.

The esterification reaction, for the production of ethyl acetate and water, taking place in the column is given as shown in Equation (1):



The conditions used for the implementation of the experiment of this study are as tabulated below.

TABLE 1: Conditions for the experimental study

Parameter	Value
Reflux ratio (R)	3
Acetic acid flow rate (F _a), cm ³ /min	10
Ethanol flow rate (F _e), cm ³ /min	10
Reboiler duty (Q _{reb}), W	630

It can be seen from Table 1 above that the feed ratio was chosen to be 1 (volume basis) for the experimental study of this particular work.

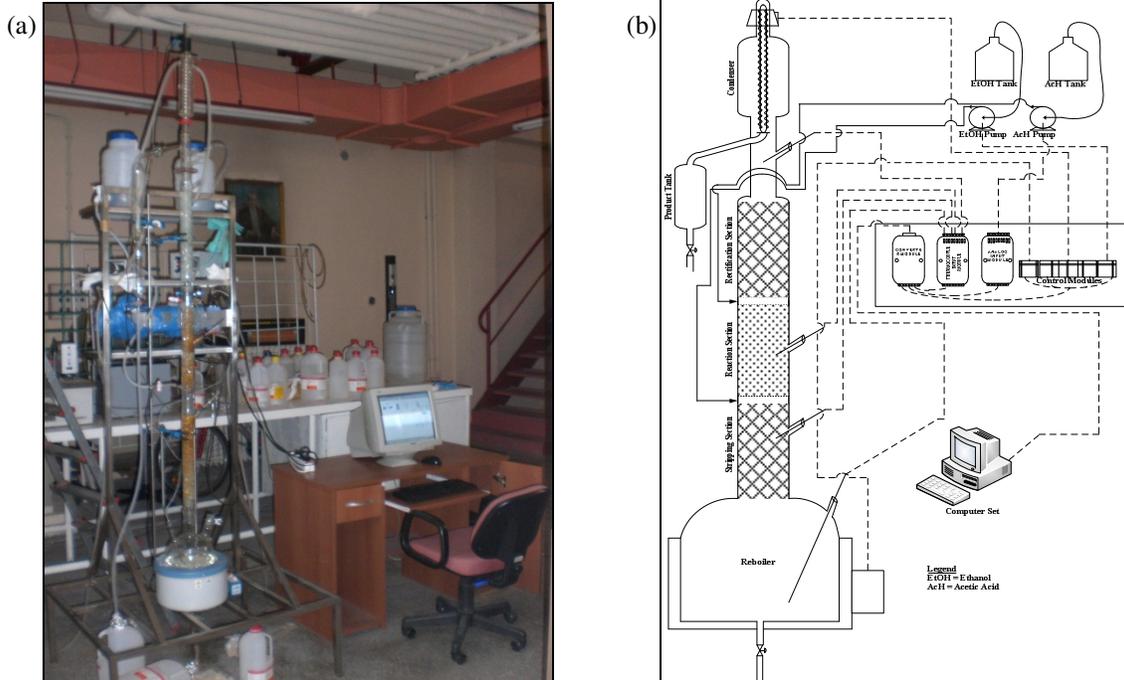


FIGURE 1: Reactive packed distillation pilot plant: (a) Pictorial view; (b) Sketch view

2.2 Modelling Procedure

The development of the models of the reactive packed distillation column of this work was carried out using first principles approach. That is, the models developed were theoretical ones.

2.2.1 Assumptions

In the course of developing the theoretical models for the reactive packed distillation column, the following assumptions were made:

- i. Occurrence of proper mixing at each stage.
- ii. Equilibrium condenser, reboiler and feed stages.
- iii. Constant vapour flow in the column.
- iv. Constant total molar hold-up at each stage.
- v. Constant liquid flow at each section.

2.2.2 Model Equations

For the condenser section, that is, for $j = 1$,

$$\frac{dx_j}{dt} = \frac{V_{j+1}y_{j+1} - (L_d + L_R)x_j}{M_j} \quad (2)$$

For the rectifying section, that is, for $j = 2 : n_{fa} - 1$, for the liquid phase,

$$\frac{\partial x}{\partial t} = \frac{1}{M_j} \left(L_j \frac{\partial x_j}{\partial z} - k_y a A_c (y_j^* - y_j) \right) \quad (3)$$

and for the vapour phase,

$$\frac{\partial y_j}{\partial z} = \frac{k_y a A_c}{V_j} (y_j^* - y_j) \quad (4)$$

For the acetic acid feed section, that is, for $j = n_{fa}$,

$$\frac{dx_j}{dt} = \frac{L_{j-1}x_{j-1} + V_{j+1}y_{j+1} + F_a x_{fa} - L_j x_j - V_j y_j}{M_j} \quad (5)$$

For the reaction section, that is, for $j = n_{fa} + 1 : n_{fe} - 1$, for the liquid phase,

$$\frac{\partial x_j}{\partial t} = \frac{1}{M_j} \left(L_j \frac{\partial x_j}{\partial z} - k_y a A_c (y_j^* - y_j) + r_j' W_j \right) \quad (6)$$

and for the vapour phase,

$$\frac{\partial y_j}{\partial z} = \frac{k_y a A_c}{V_j} (y_j^* - y_j) \quad (7)$$

For the ethanol feed section, for $j = n_{fe}$,

$$\frac{dx_j}{dt} = \frac{L_{j-1}x_{j-1} + V_{j+1}y_{j+1} + F_e x_{fe} - L_j x_j - V_j y_j}{M_j} \quad (8)$$

For the stripping section, that is, for $j = n_{fe} + 1 : n - 1$, for the liquid phase,

$$\frac{\partial x_j}{\partial t} = \frac{1}{M_j} \left(L_j \frac{\partial x_j}{\partial z} - k_y a A_c (y_j^* - y_j) \right) \quad (9)$$

and for the vapour phase,

$$\frac{\partial y_j}{\partial z} = \frac{k_y a A_c}{V_j} (y_j^* - y_j) \quad (10)$$

For the reboiler section, that is, for $j = n$,

$$\frac{dx_j}{dt} = \frac{L_{j-1}x_{j-1} - L_j x_j - V_j y_j}{M_j} \quad (11)$$

The equilibrium relationships for any concerned stage are also given as:

$$y_i = K_i x_i \quad (12)$$

$$\sum_{i=1}^m y_i = 1 \quad (13)$$

$$\sum_{i=1}^m x_i = 1 \quad (13)$$

Since the model equations developed in this work for the reactive packed distillation column composed of both ordinary and partial differential equations, the partial differential equations were converted to ordinary differential equations using the backward difference approach, as found in Fausett (2003), to make the model equations uniform in nature. The resulting ordinary differential equations were then solved using the *ode15s* command of MATLAB R2011a.

3. RESULTS AND DISCUSSIONS

In this study, the temperature and compositions of the top segment were taken as the points of interest because they were the ones used to determine the nature of the desired product (ethyl acetate) obtained, but the temperature of the bottom segment was also considered in validating the developed model equations. However, due to the fact the compositions of the mixture could not be measured on-line while performing the experiments, the quality of the top product was inferred from the top temperature.

Using the conditions shown in Table 1 to carry out experiments in the pilot plant shown in Figure 1, the dynamics of the process was studied experimentally and it was revealed from the experiment that the steady state top segment temperature was 76.52 °C. The steady state temperature of the bottom segment was also obtained from the experimental dynamics to be 91.96 °C.

Using the same data (Table 1) used for the experimental study to simulate the developed model equations with the aid of MATLAB R2011a, the dynamic responses obtained for the top segment and the bottom segment compositions as well as the steady state temperature and composition profiles of the column are as shown in Figures 2 – 5 below.

Figure 2 shows the dynamic responses of the mole fractions of components in the top segment of the column and Figure 3 shows that of the mole fractions of the components in the bottom segment. As can be seen from Figure 2, the dynamic response of the mole fraction of ethyl acetate tended towards unity in the condenser while those of the other components were very negligible there.

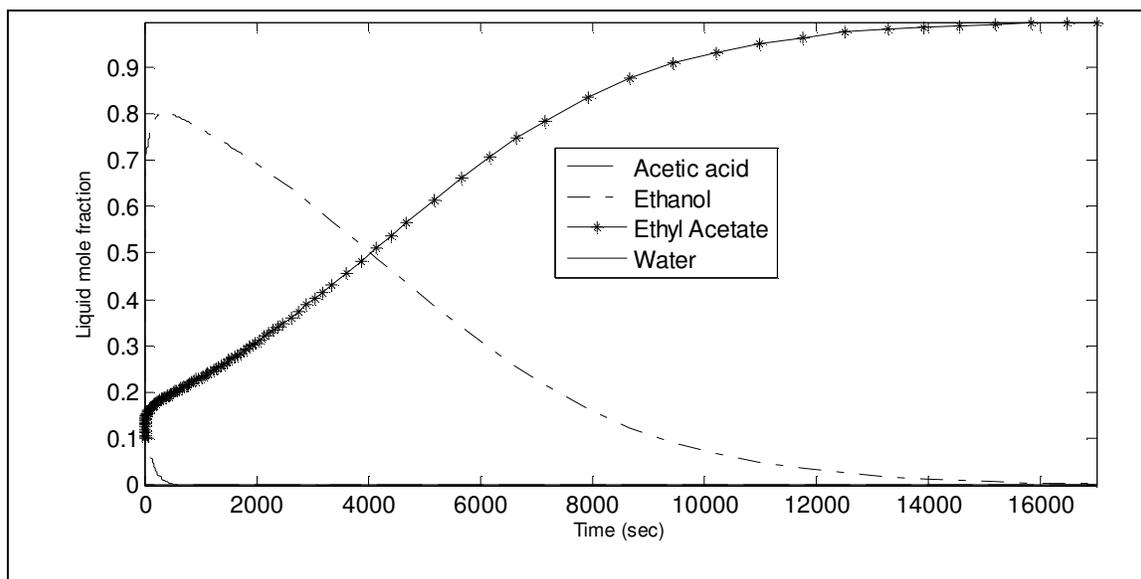


FIGURE 2: Theoretical dynamic responses of mole fractions of components in the condenser

Considering Figure 3, it was discovered that the mole fraction of ethyl acetate was low in the reboiler compared to the one present in the condenser. This is an indication that good reaction conversion and separation occurred in the column. Apart from the ethyl acetate that was present in the reboiler, it was also discovered that there were some acetic acid and ethanol still present there too. The reason for the presence of these two components (acetic acid and ethanol) in the reboiler was due to the fact that acetic acid, after being fed into the column at the acetic acid feed section, was moving down the column towards the reboiler while ethanol, being more volatile, was finding its way upwards and the two reactants were meeting at the reaction section where the reaction was taking place. The unreacted portions of these two reactants were definitely

moving downwards to the reboiler and settling there before they were boiled to move up again as a mixed vapour. It was also discovered that the presence of acetic acid and ethanol in the reboiler gave rise to the occurrence of reaction there too. That is to say that the reboiler also served, to some extent, as a reactor in a reactive distillation process.

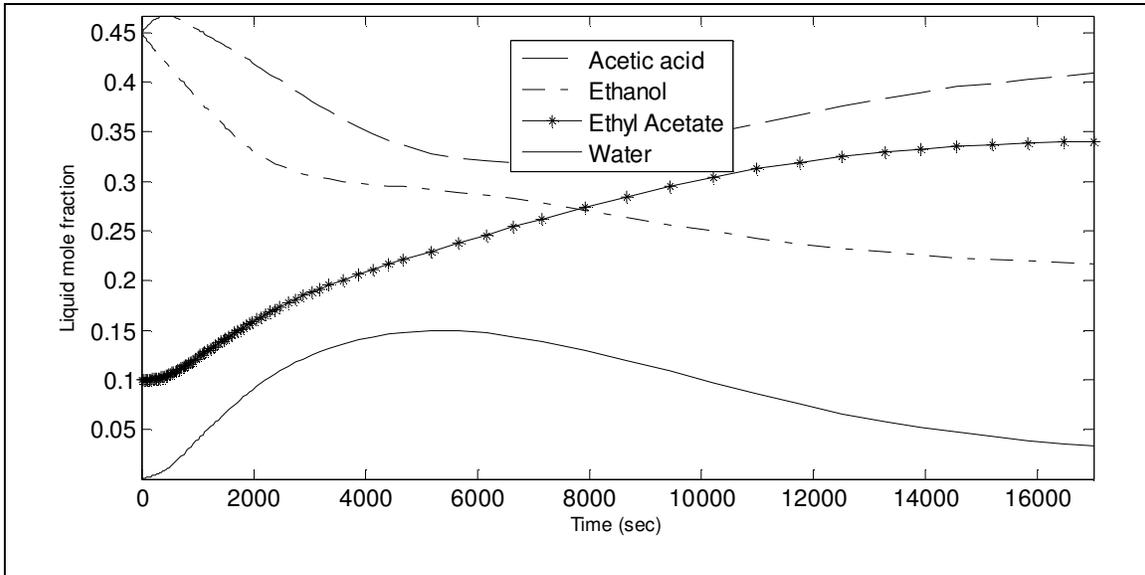


FIGURE 3: Theoretical dynamic responses of mole fraction of components in the reboiler

Figures 4 and 5 show the steady-state temperature and composition profiles respectively. As can be seen from Figure 4, the temperature profile tended to be constant from the condenser down the column up to the reaction section where a sharp increase in the temperature was observed. The reason for the increase in the temperature at this section was as a result of the exothermic nature of the reaction taking place at the section. However, for the ethanol feed section, due to the fact that ethanol was fed at room temperature into the column, there was a slight decrease in the temperature of the segment near the point where it (the ethanol) was fed into the column.

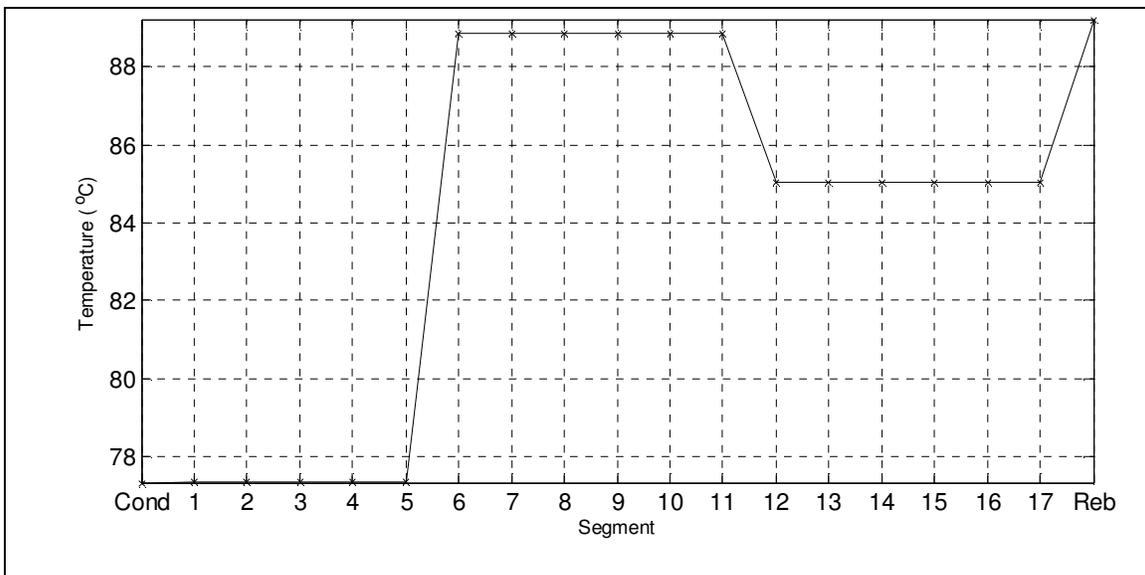


FIGURE 4: Steady state temperature profile obtained from the simulation of theoretical models

It is worth mentioning at this point that no such decrease in temperature was witnessed in the case of acetic acid feed segment owing to the fact the heat liberated from the reaction and the heat carried by the vapour moving upward was able to counter the decreasing effect that the acetic acid feed fed into the column at room temperature might have had on the temperature profile of the column. The temperature profile was also noticed to be approximately constant in the stripping section but later increased towards the reboiler section where the maximum temperature of the column was observed. All in all, the steady state temperatures of the top and bottom segments estimated from the dynamic simulation of the theoretical models were found to be 77.33 and 89.22 °C respectively.

Also obtained from the simulation of the theoretical models were the composition profiles shown in Figure 5 below. As can be seen from the figure, the steady state mole fraction of the desired product (ethyl acetate) from the liquid obtained at the top segment of the column was discovered to be 0.9963. It is a motivating result having almost pure ethyl acetate as the top product theoretically, especially if the theoretical models are able to represent the real plant very well.

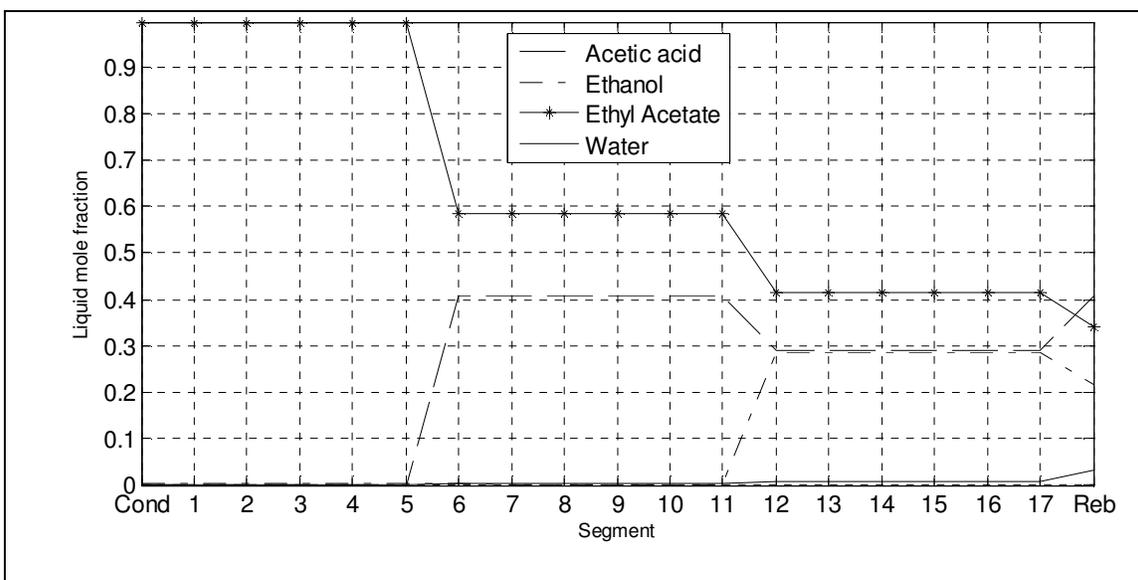


FIGURE 5: Steady state composition profiles obtained from the simulation of theoretical models

In order to know how well the developed models could represent the plant, comparisons between the experimental and the theoretical top and bottom segment temperatures of the column were made as shown in Table 2 below. It was observed from the results, as can be seen from the table, that good agreements existed between the experimental and the theoretical results because the percentage absolute residual of the top segment temperatures was calculated to be 1.06% while that of the bottom segment temperature was also calculated to be 2.98%. The percentage residuals were found to be low enough to say that the developed theoretical model is a good representation of the reactive packed distillation column.

TABLE 2: Comparisons between experimental and theoretical temperatures

Description	Values	
	Top Segment	Bottom Segment
Experimental temperature (°C)	76.52	91.96
Theoretical temperature (°C)	77.33	89.22
Absolute residual (°C)	0.81	2.74
Percentage absolute residual (%)	1.06	2.98

4. CONCLUSIONS

The results obtained from this study have shown there were good agreements between the top and bottom segment temperatures estimated from the experimental study and the one obtained from the simulation of the theoretical models developed for the reactive packed distillation column because their percentage absolute residuals were less than 5.00% that was set as the criterion for the validity of the model equations. Therefore, the developed models have been found to be suitable in representing the reactive packed distillation column very well.

5. NOMENCLATURES

Symbols

A_c	Column cross sectional area (m^2)
A_{cat}	Catalyst specific surface area (m^2/kg)
C_p	Specific heat capacity ($J/(kmol K)$)
F	Feed ratio ($mL s^{-1}$ acetic acid/ $mL s^{-1}$ ethanol)
F_a	Acetic acid feed molar rate ($kmol/s$)
F_e	Ethanol feed molar rate ($kmol/s$)
K	Phase equilibrium constant
K_{eq}	Equilibrium reaction rate constant
$k_{y,a}$	Mass transfer coefficient ($kmol/(m^2 s)$)
L	Liquid molar flow rate ($kmol/s$)
M_i	Molar hold up ($kmol$)
M	Molar hold per segment ($kmol/m$)
Q	Reboiler duty (kJ/s)
r'	Reaction rate ($kmol/(kg s)$)
R	Reflux ratio ($kmol s^{-1}$ recycled liquid / $kmol s^{-1}$ distillate)
t	Time (s)
T	Temperature ($^{\circ}C$)
V	Vapor molar flow rate ($kmol/s$)
W	Catalyst weight (kg_{cat})
x	Liquid mole fraction
y	Vapor mole fraction
z	Flow length (m)

Abbreviations

MATLAB	Matrix Laboratory
RPDC	Reactive Packed Distillation Column

Subscripts

a	Acetic acid
cat	Catalyst
e	Ethanol
fa	Acetic acid feed
fe	Ethanol feed
i	Component
j	Column segment
L	Liquid phase
m	Component number
n	Segment number

Superscript

*	Equilibrium
---	-------------

6. ACKNOWLEDGEMENTS

Abdulwahab GIWA wishes to acknowledge the support received from The Scientific and Technological Research Council of Turkey (TÜBİTAK) for his PhD Programme. In addition, this

research was supported by Ankara University Scientific Research Projects under the Project No 09B4343007.

7. REFERENCES

- [1] K. Alejski, F. Duprat. "Dynamic simulation of the multicomponent reactive distillation". *Chemical Engineering Science*, 51(18): 4237-4252, 1996.
- [2] V.H. Agreda, L. R. Partin and W.H. Heise. "High purity methyl acetate via reactive distillation". *Chemical Engineering Progress*, 86(2): 40-46, 1990.
- [3] D. Barbosa, M.F. Doherty. "The simple distillation of homogeneous reactive mixtures". *Chemical Engineering Science*, 43: 541-550, 1988.
- [4] B. Bessling, G. Schembecker and K.H. Simmrock. "Design of processes with reactive distillation line diagrams". *Industrial and Engineering Chemistry Research*, 36: 3032-3042, 1997.
- [5] B. Bessling, J.M. Loning, A. Ohligschläger, G. Schembecker and K. Sundmacher. "Investigations on the synthesis of methyl acetate in a heterogeneous reactive distillation process". *Chemical Engineering Technology*, 21: 393-400, 1998.
- [6] P. Moritz, H. Hasse. "Fluid dynamics in reactive distillation packing Katapak®-S". *Chemical Engineering Science*, 54: 1367-1374, 1999.
- [7] R. Baur, R. Taylor and R. Krishna. "Development of a dynamic nonequilibrium cell model for reactive distillation tray columns". *Chemical Engineering Science*, 55: 6139-6154, 2000.
- [8] R. Baur, A.P. Higler, R. Taylor and R. Krishna. "Comparison of equilibrium stage and nonequilibrium stage models for reactive distillation". *Chemical Engineering Journal*, 76: 33-47, 2000.
- [9] A.M. Katariya, R.S. Kamath, S. M. Mahajani and K.M. Moudgalya. "Study of Non-linear dynamics in Reactive Distillation for TAME synthesis using Equilibrium and Non-equilibrium models". In Proceedings of the 16th European Symposium on Computer Aided Process Engineering and 9th International Symposium on Process Systems Engineering. Garmisch-Partenkirchen, Germany, 2006.
- [10] C. Noeres, E.Y. Kenig and A. Górak. "Modelling of reactive separation processes: reaction absorption and reactive distillation". *Chemical Engineering and Processing*, 42: 157-178, 2003.
- [11] S.D. Roat, J. J. Downs, E.F. Vogel and J.E. Doss. "The integration of rigorous dynamic modeling and control system synthesis for distillation columns: An industrial approach." In M. Morari, & T. J. McAvoy, Chemical process control, CPC III. New York: Elsevier. 1986.
- [12] C.A. Ruiz, M.S. Basualdo and N.J. Scenna. "Reactive distillation dynamic simulation". *Chemical Engineering Research and Design, Transactions of the Institution of Chemical Engineers, Part A*, 73: 363-378, 1995.
- [13] S. Pérez-Correa, P. González and J. Alvarez. "On-line optimizing control for a class of batch reactive distillation columns". In Proceedings of the 17th World Congress the International Federation of Automatic Control. Seoul, Korea, 2008
- [14] M.G. Sneesby, M.O. Tade and T.N. Smith. "Steady-state transitions in the reactive distillation of MTBE". *Computers and Chemical Engineering*, 22(7-8): 879-892, 1998.

- [15] L.U. Kreul, A. Górak, C. Dittrich, and P.I. Barton. "Dynamic Catalytic Distillation: Advanced Simulation and Experimental Validation". *Computers and Chemical Engineering*, 22: 371-378, 1998.
- [16] R. Baur R. Taylor and R. Krishna. "Dynamic behaviour of reactive distillation tray columns described with a nonequilibrium cell model". *Chemical Engineering Science*, 56: 1721-1729, 2001.
- [17] N. Vora, P. Daoutidis. "Dynamics and control of an ethyl acetate reactive distillation column". *Industrial and Engineering Chemistry Research*, 40: 833-849, 2001.
- [18] R. Schneider, C. Noeres, L.U. Kreul and A. Górak. "Dynamic modeling and simulation of reactive batch distillation". *Computers and Chemical Engineering*, 25: 169–176, 2001.
- [19] J. Peng, T.F. Edgar and R.B. Eldridge. "Dynamic rate-based and equilibrium models for a packed reactive distillation column". *Chemical Engineering Science*, 58: 2671-2680, 2003.
- [20] F. Forner, M. Meyer, M. Döker, J. Repke, J. Gmehling and G. Wozny. "Comparison of the startup of reactive distillation in packed and tray towers". In Proceedings of the 16th European Symposium on Computer Aided Process Engineering and 9th International Symposium on Process Systems Engineering. Garmisch-Partenkirchen, Germany, 2006.
- [21] L.V. Fausett. Numerical Methods: Algorithms and Applications. Pearson Education, Inc., 2003, pp. 407-443.