World Applied Sciences Journal 7 (5): 574-581, 2009
ISSN 1818-4952

Shock-Control Study in Ethyl Acetate Production Process in a Reactive Distillation Column: Experimental and Simulation

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Abstract: In this article, the dynamics and shock-control in a Reactive Distillation Column (RDC) for the transesterification of ethanol and acetic acid was studied and simulated. The dynamic behavior of the process was experimentally analyzed. The reactants were conducted in a fifteen stages RDC in a single feed stream. An appropriate strategy was chosen and performed for column start up to achieve the steady state condition. The temperature, pressure, mass flow rates (TPF) and mole fractions effects in feed were considered in the column until a new steady state condition was obtained. For top flow of the column, the simulated results were compared with the experimental data. It concluded that there were errors less than 8% for the mole fraction shock results. Furthermore, there were errors less than 3.5% for the feed temperature shock results. Therefore, the simulation method applied in the current research could simulate a RDC well.

Key words: Dynamics . transesterification . ethyl acetate . reactive distillation . simulation

INTRODUCTION

There are several researches on design of steady state and Dynamic Equilibrium (EQ) Reactive Distillation (RD) processes but a few papers have studied the dynamic non-equilibrium (NEQ) behavior of RD column and its controlling.

Georgiadis *et al.* used a rigorous dynamic EQ stage model and optimized the process design (via two different approaches: sequentially and simultaneously) and controlled the system [1]. They could considerably control the system and showed that the simultaneously optimization leading to a better control and save much more money.

Tang *et al.* studied a system containing two columns (RD and stripping columns), a decanter and two recycles [2]. They showed an optimum design of equilibrium RD process and its controlling. Tang *et al.* studied plant-wide control with four alternative control schemes (CS1 to CS4) [3]. According to this study, the changes of both feed streams containing acetic acid and ethanol as well as the changes of ethanol feed flow rate are treated as disturbance items which are used for testing the closed-loop performance of each control scheme. Furthermore, in product stream, based on weight percentages, ethyl acetate 99.5%, acetic acid with less than 0.01% and ethanol impurities of less than 0.02% are treated as the control targets and in these conditions the process response became more alternative.

Lee *et al.* studied plant-wide control for the production of ethyl acetate using RD with the developed control schemes [4]. They considered four important items containing economics, steady state deviation of key product purities, controllability in terms of oscillation, settling time and feasible region for effective control.

Scenna *et al.* studied three cases using EQ model and showed how a given start up policy can be better or worse for the overall process. They also showed that different steady state conditions are obtained using the reasonable strategies in start up procedures [5]. Further, the time for reaching steady state would be decreased to half of the others by using these strategies.

Bisowarno *et al.* studied the dynamic simulation and showed the effects of a start up policy on ETBE reactive distillation [6].

Al-Arfaj *et al.* considered control structures for ETBE equilibrium reactive distillation with two process configuration designs: one with two reactant streams (double-feed) and the other with a single mixed feed stream [7]. They showed that the single-feed case with an excess of ethanol was effectively controlled with only a temperature controller for not too large disturbances.

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Reepmeyer *et al.* developed a rigorous process model to simulate the start up of a cold and empty RDC and also presented new alternative strategies to minimize the necessary start up time [8].

Al-Arfaj *et al.* reported the synthesis and control of a plantwide flowsheet to produce TAME which consists of a reactor, a RDC and two conventional distillation columns [9]. The RD was run with an excess methanol. The proposed control structure is able to handle feed disturbances up to ±20%.

There are four types of models for reactive distillation column in the literature involving equilibrium stage model [5], equilibrium stage model with fixed stage efficiencies [10], non-equilibrium stage model [11] and non-equilibrium cell model [12].

The applied model in this study was a non-equilibrium cell model [12]. It was selected for the following benefits:

- The molar transfer rate (N_i) is related to the chemical potential (μ_i) gradients by use of the Maxwell-Stefan theory for describing mass transfer between liquid and vapor phases [13].
- Chemical reactions occur in the liquid phase only, both within the diffusion layer and in the bulk.
- The coupling between mass transfer and chemical reactions within the diffusion layer is accounted for.

In this study, a RD column was used to carry out chemical reaction and distillation processes together in a tower although in the conventional method a separate reactor after distillation process is required. The significant benefit of RD in comparison with the conventional method is the products collection from reaction zone which it moves reaction direction to the right hand to prevent an undesired reaction between reactants and products. RD columns have the other advantages such as lower costs (capital and operational ones), faster and easier separation, products higher purity, lower reboiler duty (reaction heat recovery is achieved for liquid vaporization in the column trays) and the azeotrope production avoidance. Therefore, RDCs are more economic than the conventional method [13]. In the present work, the dynamic behavior and shock control of the RDC for ethyl acetate production was experimentally studied and the column was simulated. These shock controlling processes and their short required times show another benefit for the dynamic RDC in comparison with the conventional one. Furthermore, by combining reactor and separating columns in one tower, the capital and operational costs decrease with low off-specification products by shortening the start up and shock controlling times.

EXPERIMENTAL

Column set up: The reactive distillation column set up used for this work is located in Kimia Gostar Company (Arak, Iran) and is fabricated by Taghtiran Kashan

Table 1: RDC properties

Parameter	Value	Unit
Number of stages	15.000	-
Tray diameter	91.440	cm
Tray height	182.880	cm
Reboiler duty	615.237	kw
Condenser duty	497.285	kw
Feed tray	7.000	-
Feed properties:		
Acetic acid mole fraction	0.5	-
Acetic acid mole flow rate	0.013889	kmol.s^{-1}
Ethanol mole fraction	0.5	-
Ethanol mole flow rate	0.013889	kmolg.s^{-1}
Pressure	100000.00	N.m^{-2}
Temperature	50.00	°C
Total mole flow rate	0.0277778	kmole.s^{-1}
Total mass flow rate	1.473911	kg.s^{-1}

Table 2: Experimental and simulated steady state data and relative error percentages for stream 2

Specification	Sim.		Exp.		Relative error (%)	
Temperature (°C)	67.5396		64.2162		-5.2	
Pressure (N.m^{-2})	100000		99620		-0.4	
Mole flow rate (kmole.s^{-1})	0.008333		0.0079		-5.5	
Mass flow rate (kg.s^{-1})	0.393627		0.3732		-5.5	
Mass and mole percents:	Mole (%)	Mass (%)	Mole (%)	Mass (%)	Mole (%)	Mass (%)
Acetic acid	0.003732	0.47	0.0035	0.44	-6.6	-6.82
Ethanol	0.271210	26.44	0.2591	24.73	-4.7	-6.91
Ethyl acetate	0.306096	57.09	0.3227	58.93	-4.1	3.12
Water	0.418962	15.98	0.4255	15.89	1.5	-0.57

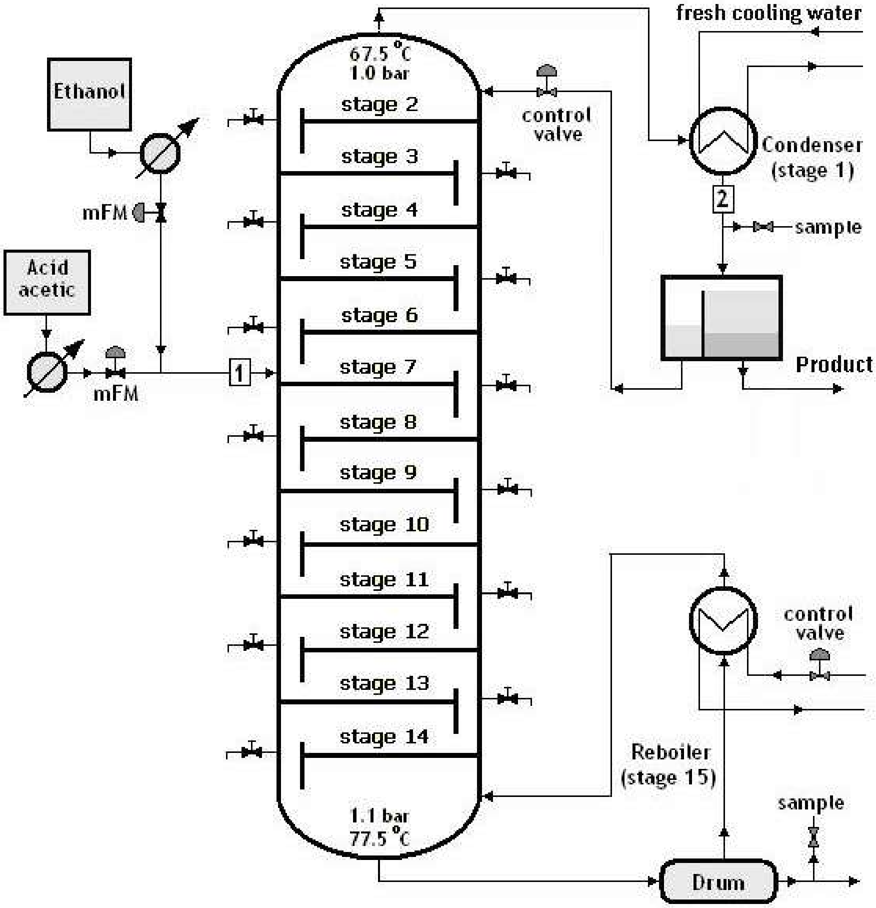

Fig. 1: RDC schematic diagram

Company (Kashan, Iran). Its configuration is shown in Fig. 1 and the stages are numbered from top to bottom. This column is a tray tower including fifteen stages (condenser is stage 1, reboiler is stage 15 and thirteen sieve trays are stages 2 to 14) and each stage equipped with a valve for sampling. Furthermore, some details of this apparatus are tabulated in Table 1. Stream 1 is a single feed flow which is containing ethanol and acetic acid mixture. It is entered into the column from the tray 7. Stream 2 is outlet flow in top of the column. The column is made of stainless steel 316 and its height and diameter are 28.1 m and 91.44 cm, respectively. The sensors are installed in reflux section, condenser, reboiler and in top and bottom of the column. All control loops are Programmable Logic Control (PLC) type. Both pressure and temperature are controlled by digital indicators up to seven places. The precisions of temperature and pressure controllers are 1 and 0.5% in full scales, respectively.

Column start up: Ethanol and acetic acid streams are initially flown at 1 bar and 50°C at rates of 0.834063 and 0.639848 kg.s^{-1}, respectively. The feed stream is flown at a rate of 1.473911 kg.s^{-1} to the column while the condenser is in total reflux situation. For column start up, the heater of the reboiler is turned on until the temperature is distributed in all of the units and then by increasing 10% in feed mass flow. Therefore, the stream 2 mass flow (which is equal to this enhancement) is gradually changed to the desired value until the steady state condition is obtained. The required time for start up is about 9 h and after this time the shocks are made and the dynamic RDC behaviors are studied. The experimental and simulated steady state specifications obtained in stream 2 are presented in Table 2. The temperature controllers for condenser (total one) and reboiler (kettle one) are set at 67.5°C and 77.5°C, respectively.

Sample analysis: The samples are taken from the sample lines as shown in Fig. 1. The samples are analyzed using a gas chromatograph (SHIMADZU, GC-14A) and one chromatogram (for feed mole fraction shock curves of 2.5 h) as an example is shown in Fig. 2. The time increments used are shown in Figs. 3 to 7.

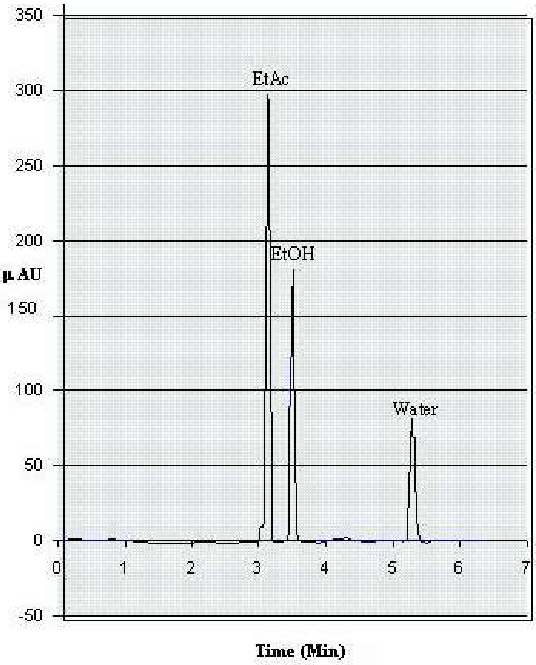

Fig. 2: A chromatogram mole fractions of stream 2 for a shock of +20% in acetic acid mole flow rate in feed

The calculations for the mass percentage of component *i* and relative error percentage were carried out using the following equations:

$$(m\%)_i = \frac{M_i x_i}{\sum_{n=1}^{4} M_n x_n} \times 100 \quad (1)$$

$$\text{Error\%} = \frac{\text{Exp.} - \text{Sim.}}{\text{Exp.}} \times 100 \quad (2)$$

where,

$(m\%)_i$: Mass percentage of component i
M_i: Molecular weight of component i
x_i: Mole fraction of component i
Error%: Relative error percentage

DYNAMIC SIMULATION

Dynamic study of the RDC was carried out using the ASPEN 11.1 software including two important modules; ASPEN PLUS and ASPEN DYNAMIC. It is very important to input all parameters (such as RDC elements and streams specifications, kinetic rate, physical, chemical and thermodynamic properties) in correct formats as ASPEN PLUS module. ASPEN is run firstly till the steady state is reached and then the entire shock is made in feed specifications in ASPEN DYNAMIC module and it is run for dynamic study.

The esterification reaction of acetic acid with ethanol (using sulfuric acid as hemogen catalyst) and its rate are:

$$CH_3COOH + C_2H_5OH \leftrightarrow H_2O + CH_3\ COOC_2H_5$$

$$r = K_1 C_{ACAC} C_{EtOH} - (K_1 / K_c) C_{EtAC} C_W \quad (3)$$

$$K_1 = (4.19 C_k + 0.08815) \exp(-6500.1/T) \quad (4)$$

$$K_c = 7.558 - 0.012T \quad (5)$$

where, C_k is the catalyst volume percent [14, 15].

RESULTS AND DISCUSSION

The shocks for the system analyzing were created by changing the steady state feed properties such as TPF and mole fractions. The effects and results of these shocks on top flow (stream 2) are explained as following:

Feed mole fraction shocks were made by increasing 5, 10, 20 and 50 percents in acetic acid inlet flow rate and the simulated results are shown in Fig. 3(a-d) and among them, the obtained experimental (and also simulated) results for 20% shock are shown in Fig. 4 where the mole fractions of water, ethyl acetate and acetic acid show a constant trend at mole fractions of 0.42, 0.31 and 0.0 versus time. Furthermore, ethanol mole fractions show a descending

Table 3: Ethyl acetate mass and mole flow rates and relative error percentages in stream 2 for a feed shock of +20% in acetic acid flow rate

Time	Sim.		Exp.		Relative error (%)	
(h)	Mole (%)	Mass (%)	Mole (%)	Mass (%)	Mole (%)	Mass (%)
0.0	30.60	57.11	32.50	60.36	5.85	5.38
0.5	30.60	57.46	33.01	61.45	7.30	6.49
1.5	32.14	59.41	33.50	62.10	4.06	4.33
2.5	32.14	59.41	33.01	61.63	2.64	3.60
3.5	32.14	59.41	33.01	61.63	2.64	3.60

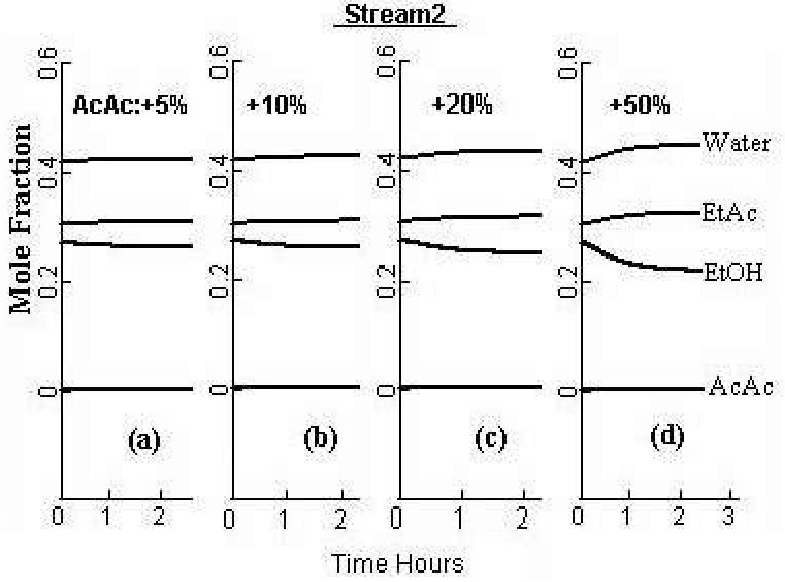

Fig. 3: Simulated mole fraction diagrams in stream 2 for shocks in acetic acid mass flow rate as: a) +5%, b) +10%, c) +20%, d) +50%

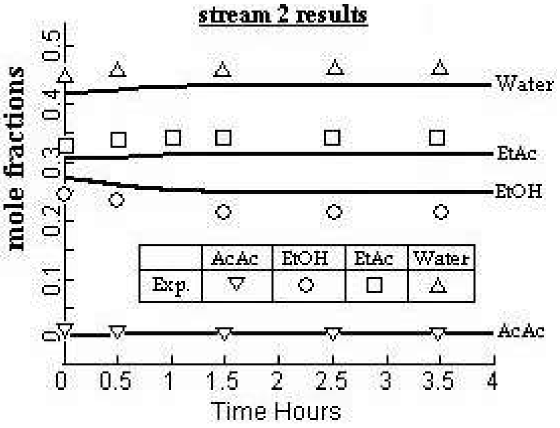

Fig. 4: Simulated and experimental mole fraction diagrams in stream 2 for +20% change in acetic acid mole flow rate in feed

trend. It decreases from mole fractions of 0.27 to 0.25 from initial time to time of 1.35 h, respectively. Then, it follows as a constant trend versus time up to end of process (time of 4 h). Ethyl acetate mole and mass fractions and their relative error percentages are presented in Table 3.

Temperature shocks are created by 20% decreasing and increasing in feed temperature and the results are shown in Fig. 5 (a and b). By 20% decreasing shock in feed temperature as shown in Fig. 5(a), the temperature varies from an initial value of 64.070°C to a maximum of 64.120°C at 0.4 h and then rapidly decreases to 64.080°C (time of 2 h) and finally smoothly reaches a constant value of 64.075°C at 5.3 h (while experimental result reaches a constant temperature of 62.520°C at 6 h). Furthermore, the pressure rapidly varies from an initial value of 99600 N.m^{-2} to a constant value of 100000 N.m^{-2} at 1.2 h. For this shock, the experimental and simulated results and their relative error percentages are presented in Table 4. By 20% increasing shock in feed temperature as shown in Fig. 5(b), the temperature varies from an initial value of 64.370°C to a minimum of 64.300°C at 0.6 h and then with a few increase reaches 64.310°C (time of 2.3 h). The pressure rapidly decreases from an initial value of 100650 N.m^{-2} to a constant value of 100000 N.m^{-2} at 1.3 h.

Pressure shocks are created by 10% decreasing and increasing in feed pressure and the results are shown in Fig. 6 (a and b). By 10% decreasing shock in feed pressure as shown in Fig. 6(a), the temperature varies from an initial value of 64.2162°C to a minimum of 64.2160°C at 0.1 h and then gradually increases to a constant value of 64.2163°C in time of 3.7 h (while experimental result shows a time of 4 h). Furthermore, the pressure rapidly decreases from an initial value of 100000.05 N.m^{-2} to 99999.8 N.m^{-2} at 0.1 h and then it smoothly increases to a constant value of 100000 N.m^{-2} at 1.3 h (while experimental result shows a time of 1.5 h). By 10% increasing in feed pressure as shown in Fig. 6(b), the temperature varies from an initial value of 64.2163°C to a minimum value of 64.2161°C at 0.2 h and then rapidly increases to a constant value of 64.21637°C at 3.3 h (while experimental result shows a time of 4 h). The pressure rapidly decreases from an initial value of 100000.3 N.m^{-2} to a constant value of

Table 4: Temperature and pressure relative error percentages in stream 2 for a shock of -20% in feed temperature

Time	Pressure ($N.m^{-2}$)			Temperature (°C)		
(h)	Sim.	Exp.	Error (%)	Sim.	Exp.	Error (%)
0	99600	97990	-1.64	64.0850	62.6	-3.50
0.2	99670	98000	-1.07	64.1120	62.6	-2.41
0.5	99970	98500	-1.49	64.1170	64.3	0.28
1	99990	99400	-0.59	64.1000	63.8	-0.47
2	100000	99800	-0.20	64.0810	63.2	-1.39
3	100000	100200	0.20	64.0740	63.0	-1.63
4	100000	100300	0.30	64.0730	62.7	-2.19
5	100000	100300	0.30	64.0720	62.5	-2.51
6	100000	100300	0.30	64.0715	62.4	-2.67

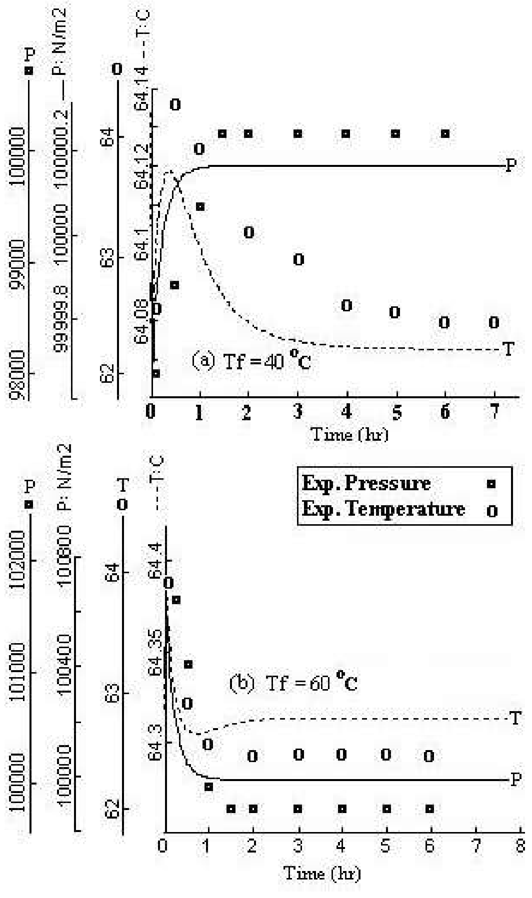

Fig. 5: Results in stream 2 for feed temperature shocks: (a)-20%, (b) +20%

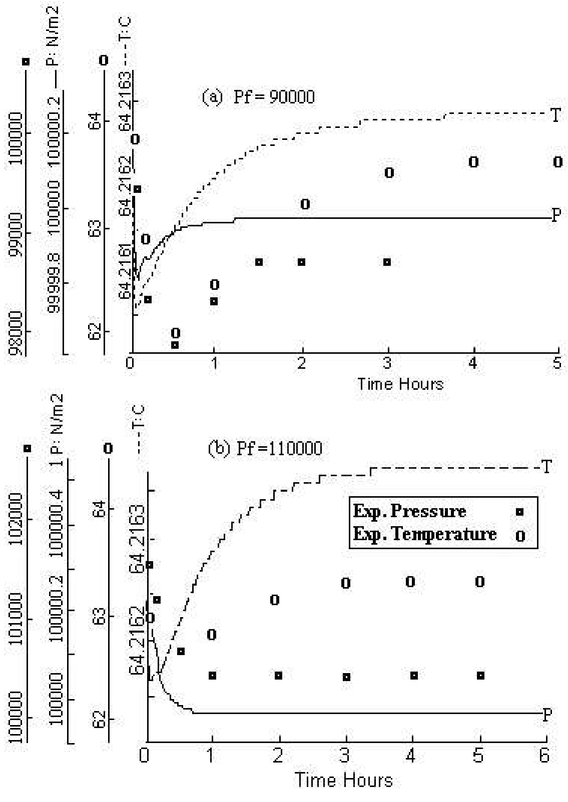

Fig. 6: Results in stream 2 for feed pressure shocks: (a)-10%, (b) +10%

99870 $N.m^{-2}$ at 0.7 h (while experimental result shows a time of 1 h).

Flow rate shocks are created by 20% decreasing and increasing in feed flow rate and the experimental and simulated results are shown in Fig. 7 (a and b). By 20% decreasing shock in feed flow rate as shown in Fig. 7(a), the temperature varies from an initial value of 64.2162°C to a minimum of 64.2161°C at 0.1 h and then it increases to a constant value of 64.2163°C at 5.2 h (while experimental result shows a time of 6 h). The pressure rapidly decreases from an initial value of 100000.4 $N.m^{-2}$ to 99999.7 $N.m^{-2}$ at 1.2 h (while experimental result shows a time of 1.5 h). By 20% increasing in feed flow rate as shown in Fig. 7(b), the temperature increases from an initial value of 64.1°C to a constant value of 64.43°C at 2.7 h (while experimental result shows a time of 3 h). The pressure rapidly increases from an initial value of 99620 $N.m^{-2}$ to

Table 5: Final experimental and simulated data, their ending times and relative error percentages for different shocks in stream 2

Feed shock type	Shock value	Stream 2 property	Sim. Time (h)	Sim. Value	Exp. Time (h)	Exp. Value	Error (%) Time (h)	Error (%) Value
Mole (%)	+20%	EtAc mole%	0.9	31%	1.0	34%	10.00	8.82
Feed Temp.	-20%	T (°C)	5.3	64.075	6.0	62.52	11.67	-2.48
		P (N.m^{-2})	1.2	100000.150	1.5	100150.00	20.00	0.15
	+20%	T (°C)	2.3	64.310	3.0	62.48	23.30	-2.93
		P (N.m^{-2})	1.3	100000.000	1.5	99750.00	13.33	0.25
Feed Press	-10%	T (°C)	3.7	64.21628	4.0	63.65	7.50	-0.89
		P (N.m^{-2})	1.3	100000.00000	1.5	98650.00	13.33	1.37
	+10%	T (°C)	3.3	64.21640	4.0	63.41	17.50	-1.27
		P (N.m^{-2})	0.7	100000.00000	1.0	100500.00	30.00	0.50
Feed mFR	-20%	T (°C)	5.2	64.21634	6.0	64.51	13.30	0.46
		P (N.m^{-2})	1.2	99999.90000	1.5	98700.00	20.00	-1.32
	+20%	T (°C)	2.7	64.42000	3.0	65.31	10.00	1.36
		P (N.m^{-2})	1.7	100000.00000	2.0	101600.00	15.00	1.57

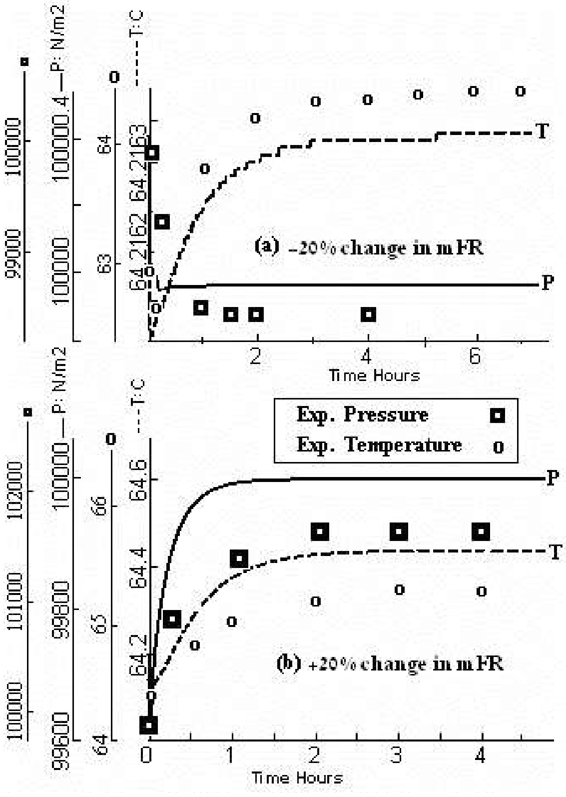

Fig. 7: Results in stream 2 for feed flow rate shocks: (a)-20%, (b) +20%

a constant value of 100000 N.m^{-2} at 1.7 h (while experimental result shows a time of 2 h).

The experimental and simulated results are shown in Table 5 for different shocks, including TPF and feed molar percentage. The maximum relative error percentage between experimental and simulated data for ethyl acetate molar percentage was around 8.82% while the error percentages for temperature and pressure were less than 3%. By 10% decreasing in feed flow rate, the related shock affected error less than 3.5% for either the temperature or pressure between experimental and simulated data as shown in Table 4. Table 3 shows that the relative error percentages for mass and molar flow rates of ethyl acetate were less than 8% for 20% increasing in acetic acid flow rate. However, at steady state condition, the relative error percentages for TPF were less than 6% as shown in Table 2. Meanwhile, the corresponding error values for all applied components in this study were less than 7%.

CONCLUSIONS

A RDC for esterification of ethanol and acetic acid was used to produce ethyl acetate in a fifteen non-equilibrium stages column. The dynamic behavior of column was studied and the effects of different feed shocks (TPF and mole fraction) were investigated. The obtained results showed a good agreement between experimental and simulated data where a relative error was less than 8% for either the temperature or pressure of stream 2.

This study showed that the simulation technique can be applied to analyze the dynamic behavior of RDC used in the similar systems. According to the experiment and simulation the mass percentage of ethyl acetate produced in the RDC was around 60% based on the current research. Furthermore, this percentage can be increased by changing in the RDC configuration such as the number of trays increment, a change in the feed tray position, using a double feed streams (ethanol and acetic acid streams enter into the different trays) and using a packed column instead of a sieve tray column.

ACKNOWLEDGMENTS

The authors thank Kimia Gostar and Hallal Pouyan Companies, Arak, Iran for the facilities provided to accomplish this research.

Nomenclature

Symbol	Description	Units
AcAc	Acetic acid	-
E	Activation energy	Joule.mole^{-1}
EQ	Equilibrium	-
EtAc	Ethyl acetate	-
EtOH	Ethanol	-
Exp.	Experimental	-
GC	Gas chromatography	-
k	Rate constant	m^{3}.mole^{-1}.s^{-1}
mFR	Mass flow rate	kg.s^{-1}
$(m\%)_i$	Mass percentage of component i	-
M_i	Molecular weight of component i	kg.kgmole^{-1}
N	Mass transfer rate	mole.s^{-1}
NEQ	Non-equilibrium	-
P	Pressure	N.m^{-2}
Pf	Feed pressure	N.m^{-2}
PLC	Programmable Logic Control	-
R	Gas constant	Joule.mole^{-1}.K^{-1}
r	Rate of reaction	mole.m^{-3}.s^{-1}
RDC	Reactive distillation column	-
Sim.	Simulated	-
T	Temperature	°C
Tf	Feed temperature	°C
x_i	Mole fraction of component i	-
μ	Chemical potential	Joule.mole^{-1}

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