CHAPTER IV

STEADY-STATE SIMULATION OF REACTIVE DISTILLATION COLUMN

4.1 Process Description and Assumption

The configuration of a reactive distillation column considered in this study is shown in Figure 4-1. There are three zones in the column. The rectification zone (Nr) and stripping zone (Ns) operates exactly as a nonreactive distillation column in order to purify top and bottom products, respectively. Butyl acetate (BuOAc) and water (H_2O) is formed in the reaction zone (Nrxn) from esterification of acetic acid (HOAc) and butanol (BuOH). The overhead vapor (with a composition close to that of the heterogeneous ternary azeotrope between H_2O, BuOH, and BuOAc) is condensed and than separated into aqueous and organic phases in the decanter. The aqueous phase is completely withdrawn whereas the organic phase is completely refluxed to the column. Pure BuOAc is withdrawn from the column bottom. The column specification is shown in Table 4-1.

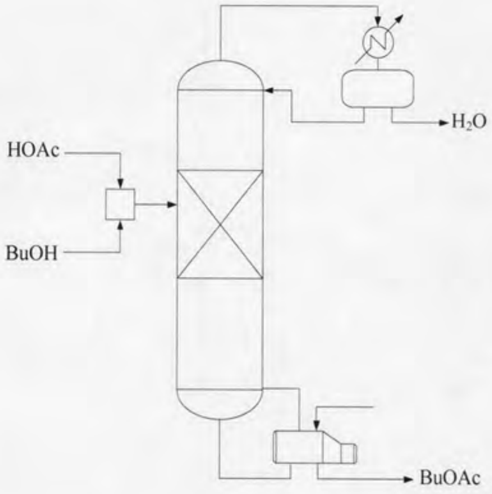

Figure 4-1 Configuration of reactive distillation column for BuOAc synthesis.

Table 4-1 Specifications of reactive distillation column.

Feed conditions		
Feed	HOAc	BuOH
Temperature (°C)	25	25
Pressure (atm)	1.2	1.2
Column specifications		
Rectification stages (Nr)		11
Reaction stages (Nrxn)		13
Stripping stages (Ns)		15
Overhead pressure (atm)		1
Column pressure drop (atm)		0.134
Holdup (m^3)		0.4909

A steady-state simulation for reactive distillation is developed based on the following assumption:

1) An equilibrium stage model is used.

2) The stages are numbered from top to bottom. Stage 1 represents the uppermost column tray, and stage N represents the partial reboiler. A total condenser is assumed between the column and the decanter.

3) Activity coefficients are calculated by the NRTL equation.

4) The forward rate constant and the reaction equilibrium constant are given by the following expression:

$$k_f = 6.1084 \times 10^4 \exp\left(-\frac{56.67 kJ/mol}{RT}\right) \tag{4-1}$$

$$K_{eq} = 0.6206 \exp\left(-\frac{10.99 kJ/mol}{RT}\right) \tag{4-2}$$

5) All simulations are carried out with the steady-state model from the process simulator HYSYS (version 3.1).

In order to study the effects of HOAc concentration in feed stream on design parameters (i.e., reboiler duty), the HOAc concentration are varied from 30 wt % to 100 wt % for the production of BuOAc with required purity of 99.5 wt %.

4.2 Model Validation

In order to use the three phase distillation model from HYSYS for simulating a reactive distillation with confidence, the reliability of the model is tested by comparing the simulation results obtained on this study with the experimental data from Steinigeweg and Gmehling (2002). With the same standard experimental conditions reported in their paper, results of the simulation run in comparison to the experimental data are shown in Table 4-2. It can be seen that the experimental data are in good agreement with the simulation results.

To ensure the most effective reactive distillation process, the influence of important design factors on the conversion of acetic acid has to be evaluated. This will be carried out in the following section.

4.3 Results and Discussion

Reactive distillation column behaves substantially differently from conventional distillation columns due to the interactions between the chemical reactions and vapor-liquid equilibrium. The specification of the reactive distillation column given in Table 4-1 for the synthesis of BuOAc is a preliminary configuration. The effects of the concentration of feed acetic acid and key design and operating variables are discussed in detail below. The major design parameters are the column pressure, reboiler duty, feed flow rates, number and location of feed position, and numbers of reactive and nonreactive stage. After investigating the influence of these parameters, a final configuration of the reactive distillation column will be determined and used for a dynamic simulation and control study.

Table 4-2 Comparison of experimental data and simulation results

	Experimental Data (Steinigeweg and Gmehling, 2002)	Simulation Results (HYSYS)
P_1 (mbar)	995.1	995.1
ΔP (mbar)	4.22	4.22
HOAc feed flow (mol/h)	34	34
BuOH feed flow (mol/h)	35	35
Bottom flow (mol/h)	42	41.9
Distillate flow (mol/h)	27	27.1
x_B (HOAc)	0.171	0.172
x_B (BuOH)	0.287	0.298
x_B (BuOAc)	0.517	0.527
x_B (H_2O)	0.025	0.003
x_D (HOAc)	0.143	0.1586
x_D (BuOH)	0	0
x_D (BuOAc)	0.008	0.0154
x_D (H_2O)	0.849	0.826
Reboiler Duty (Watt)	1070	950
X_{BuOH} (%)	64.58	64.31

4.3.1 Effect of Feed Mole Ratio

The mole ratio of the reactants (acetic acid and butanol) is an important role in determining the conversion and the relative weigh fraction of the top and bottom products. In this study, the mole ratio of HOAc to BuOH is varied as follows: 1:1, 1.5:1, 2:1, 1:1.5 and 1:2. Simulations are carried out at different concentration of acetic acid in feed stream (100 to 50 wt %). The results are shown in Tables 4-3 and 4-4. It can be seen that with an increase in mole ratio of HOAc to BuOH, the conversion of HOAc and the purity of BuOAc at bottom decreases in all simulations. The maximum conversion of HOAc, conversion of BuOH and mass fraction of BuOAc for all value of concentration of feed acetic acid are achieved at the mole ratio of HOAc to BuOH of 1:1. It is evident that feeding HOAc and BuOH at mole ratio of 1:1 is the optimum value and all the next simulations are carried out at this mole ratio.

Table 4-3 Effect of mole ratio of HOAc to BuOH on the conversion of HOAc

Mole ratio	Conversion of HOAc (%)		
(HOAc : BuOH)	100 wt % HOAc	80 wt % HOAc	50 wt % HOAc
1:2	79.020	67.923	37.291
1:1.5	72.955	68.719	36.945
1:1	86.247	82.758	52.269
1.5:1	52.381	36.836	7.631
2:1	22.348	29.866	5.437

Table 4-4 Effect of mole ratio of HOAc to BuOH on the purity of BuOAc bottom product

Mole ratio	Mass fraction of BuOHc at bottom		
(HOAc:BuOH)	100 wt % HOAc	80 wt % HOAc	50 wt % HOAc
1:2	0.467	0.399	0.212
1:1.5	0.536	0.504	0.260
1:1	0.848	0.813	0.492
1.5:1	0.612	0.408	0.067
2:1	0.351	0.354	0.048

4.3.2 Effect of Feed Location

The feed position of HOAc and BuOH is also a very important parameter in the operation of the reactive distillation column. For the system to be operated optimally, provision should be made for maximum contact area between the reactants so that the column is more used as a reactor and not as a distillation unit only. Because of the boiling point difference between BuOH (117.7 ºC) and HOAc (117.9 ºC) is rather small, the idea of providing feed at two separated points is not very attractive. Therefore, in the following discussion, only a single feed case is considered.

In the following simulations, the mole ratio of feed reactant (HOAc: BuOH) is kept constant at 1:1 and reboiler duty is fixed at 1300, 2200, 4700 and 9300 kW for feed HOAc concentration of 100 wt %, 80 wt %, 50 wt % and 30 wt %, respectively. Figure 4-2 shows the effect of feed location on the HOAc conversion and mass fraction of BuOAc in the bottom stream at different concentration of feed acetic acid. While the feed tray is shifted down in the reactive section, the conversion of reactants decreases, leading to a decrease in the BuOAc concentration in the products. It can be found that feed location at stage 12 show the highest conversion of HOAc and bottom product purity. It can be concluded that the most effective approach is to feed both reactants into the column on the top of the reactive section. Therefore, all the next simulations are carried out by introducing the feed at this location.

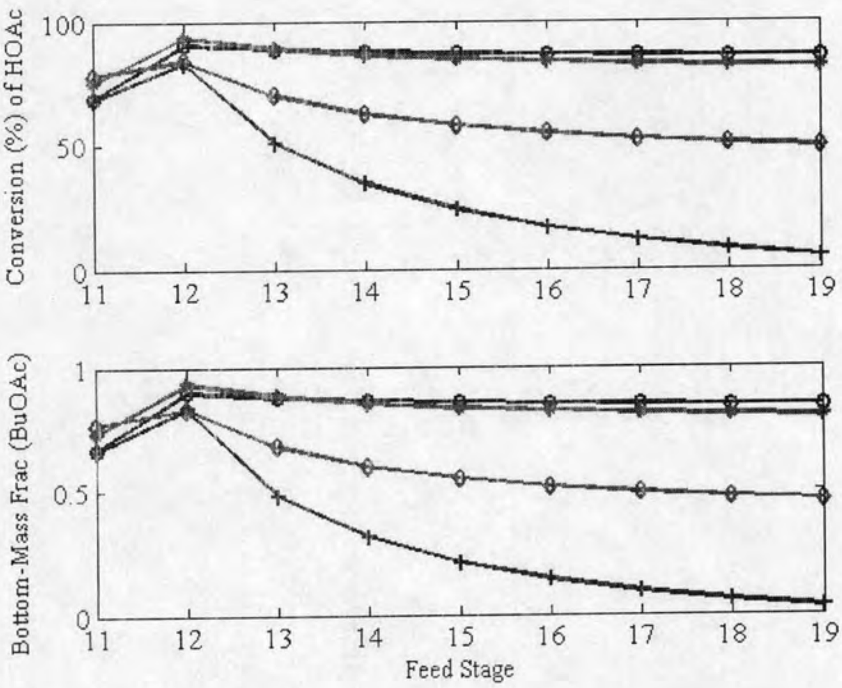

Figure 4-2 Effect of feed location on HOAc conversion at different concentrations of feed acetic acid (100 wt % (o); 80 wt % (*) 50 wt % (□) and 30 wt % (◊)).

4.3.3 Effect of Reboiler Duty

In this simulation, both of reactants are fed into column at 12th stage (the top of reactive zone). Figures 4-3 to 4-6 present the conversion of HOAc and the mass fraction of BuOAc in the bottom stream as a function of reboiler heat duty at feed HOAc concentration of 30, 50, 80, 100 wt %, respectively. Considering for case where 30 wt % acetic acid is fed to the column (Figure 4-3), it is observed that increasing the reboiler duty is directly to rise the BuOAc purity in the bottoms. It is even possible to get higher conversion of HOAc with an increase in reboiler duty. For other cases that use the feed acetic acid with different concentration, the conversion of HOAc and the mass fraction of BuOAc in the bottom stream show a similar trend. This is expected because increasing the heat duty increases the reactive section temperature. As the concentration of HOAc in feed stream decreases from 100 wt % to 30 wt %, the reboiler duty must be increased. Due to more water in fresh feed, the column requires higher heat duty in order to separate light reactant.

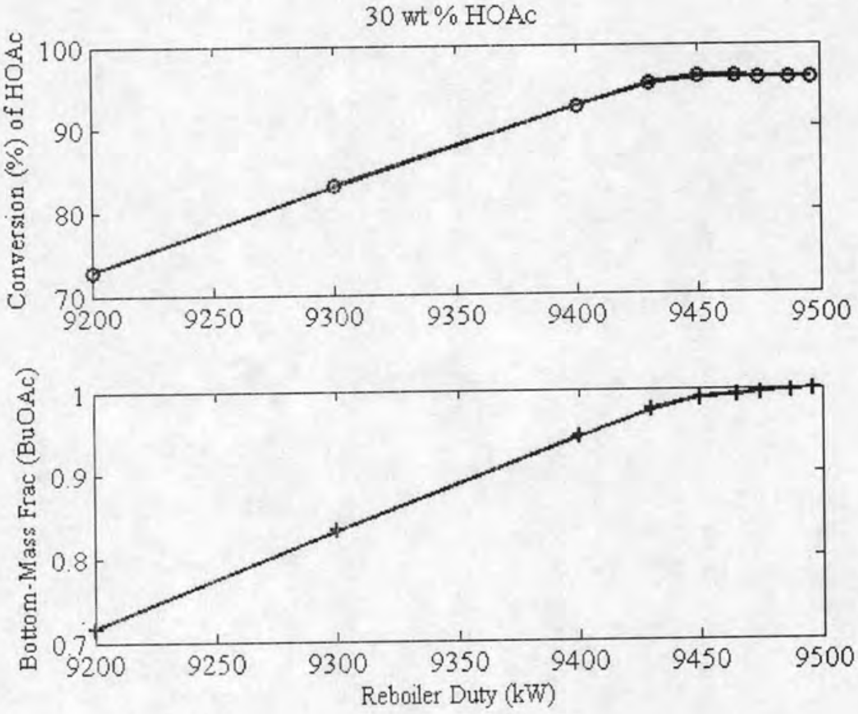

Figure 4-3 Effect of reboiler duty on the conversion of HOAc and mass fraction of BuOAc at 30 wt % HOAc in feed stream.

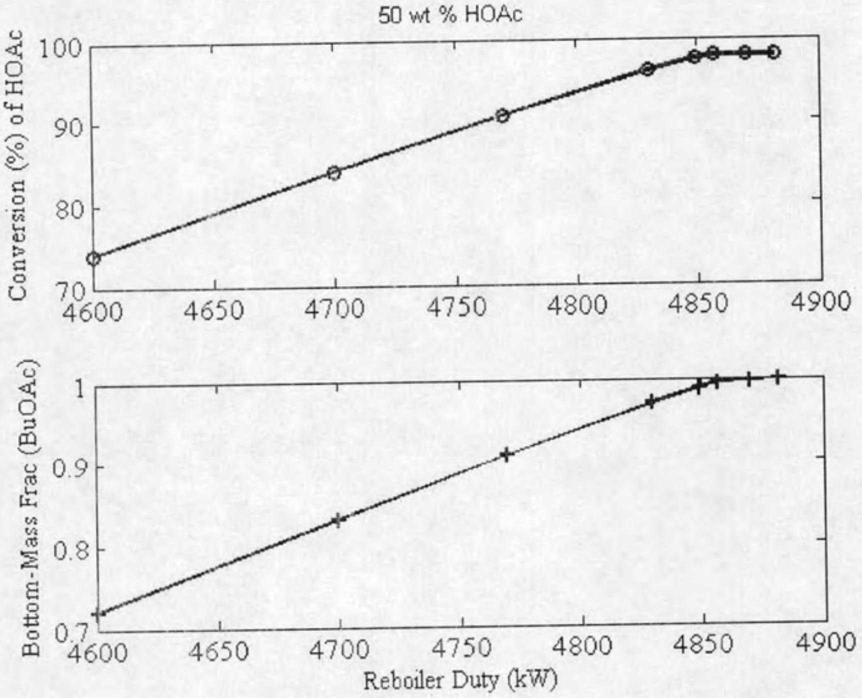

Figure 4-4 Effect of reboiler duty on the conversion of HOAc and mass fraction of BuOAc at 50 wt % HOAc in feed stream.

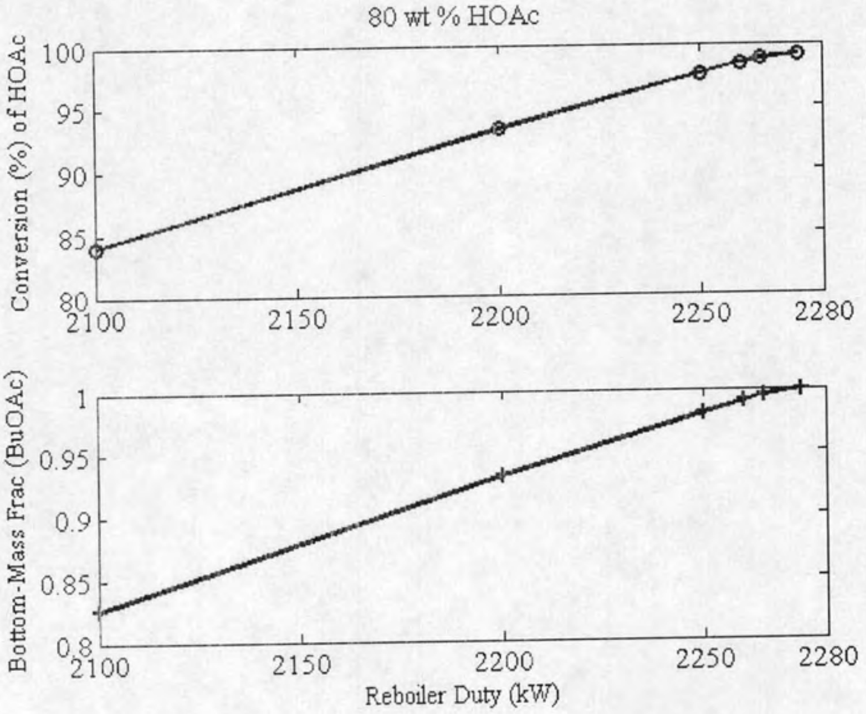

Figure 4-5 Effect of reboiler duty on the conversion of HOAc and mass fraction of BuOAc at 80 wt % HOAc in feed stream.

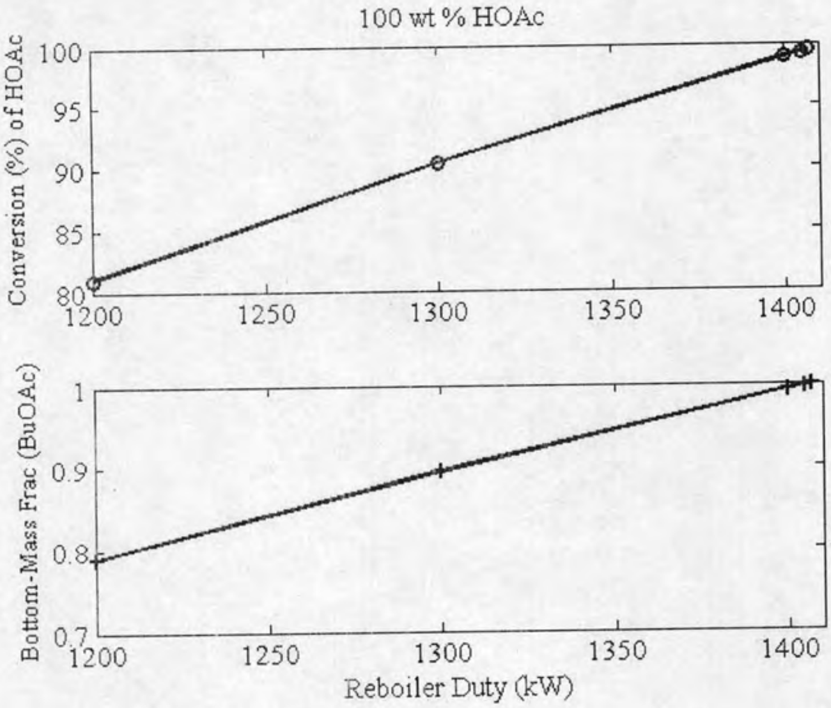

Figure 4-6 Effect of reboiler duty on the conversion of HOAc and mass fraction of BuOAc at 100 wt % HOAc in feed stream.

4.3.4 Effect of Number of Reactive Stages

In order to increase the product purity the optimum number of catalytic stages should be provided in the reactive section (Nrxn). In all simulations presented in this section, the number of rectification (Nr) and stripping stages (Ns) is fixed at 11 and 15 stages, respectively. The numbers of reactive zone (Nrxn) is varied from 6 to 14 stages for the specification of BuOAc product purity of 99.5 wt %. Figures 4-7 to 4-10 show the influence of the number of reactive stages on the conversion of HOAc and the required reboiler heat duty at different HOAc feed concentrations. For all case studies, increasing Nrxn is insensitive to the conversion of HOAc and reboiler duty; however, this leads to an increase in the bottom flowrate. Therefore, increasing Nrxn offers no significant change in all of the conversion of HOAc and reboiler duty.

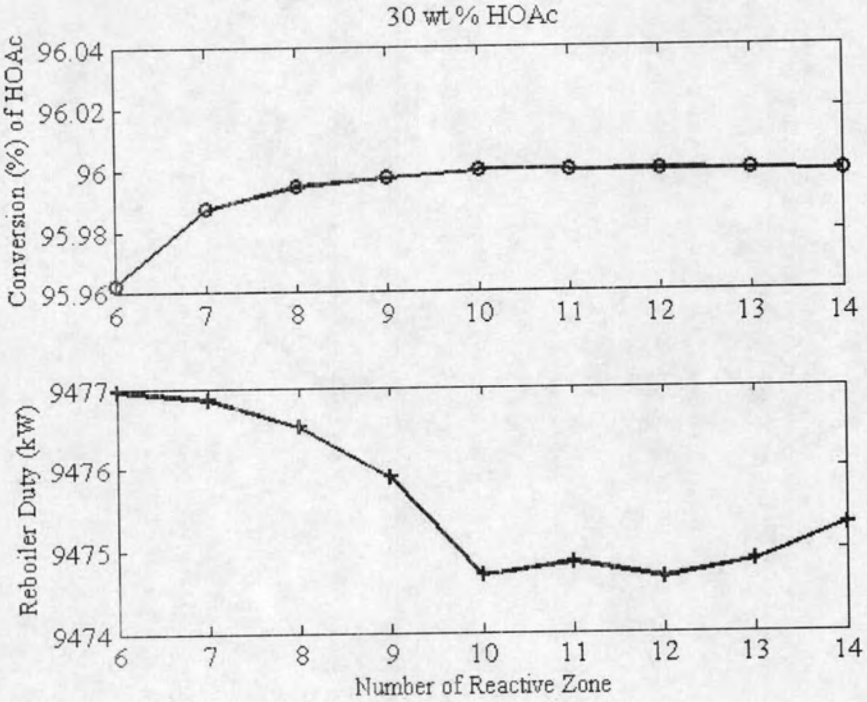

Figure 4-7 Effect of the number of reactive section at 30 wt % HOAc concentration.

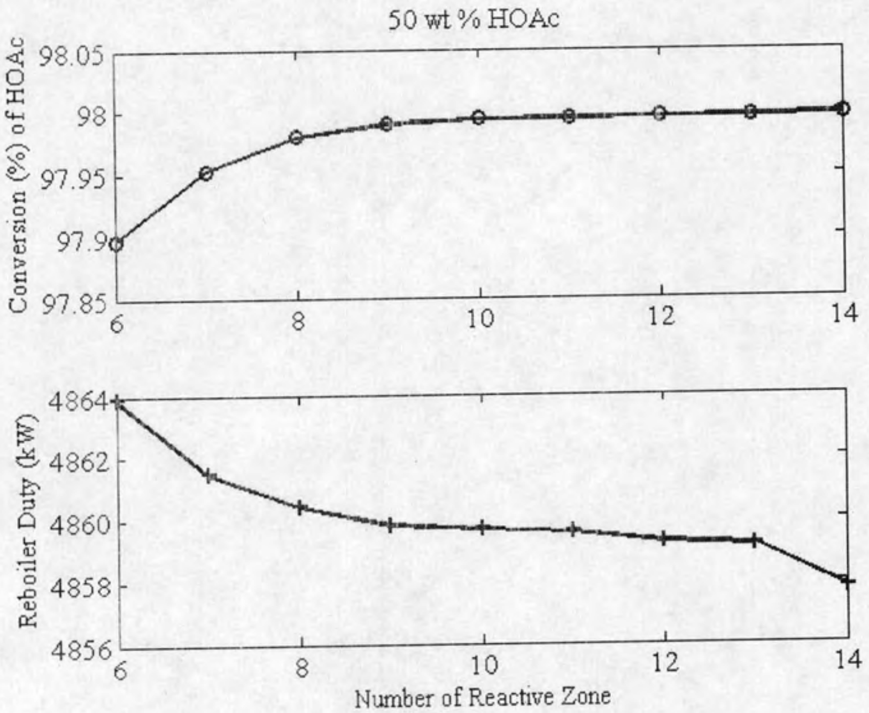

Figure 4-8 Effect of the number of reactive section at 50 wt % HOAc concentration.

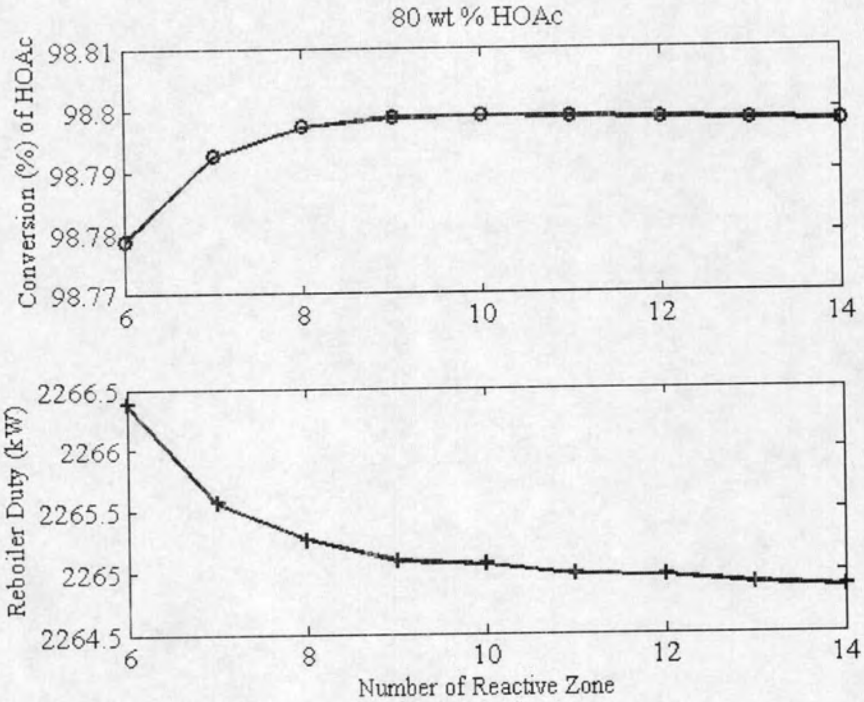

Figure 4-9 Effect of the number of reactive section at 80 wt % HOAc concentration.

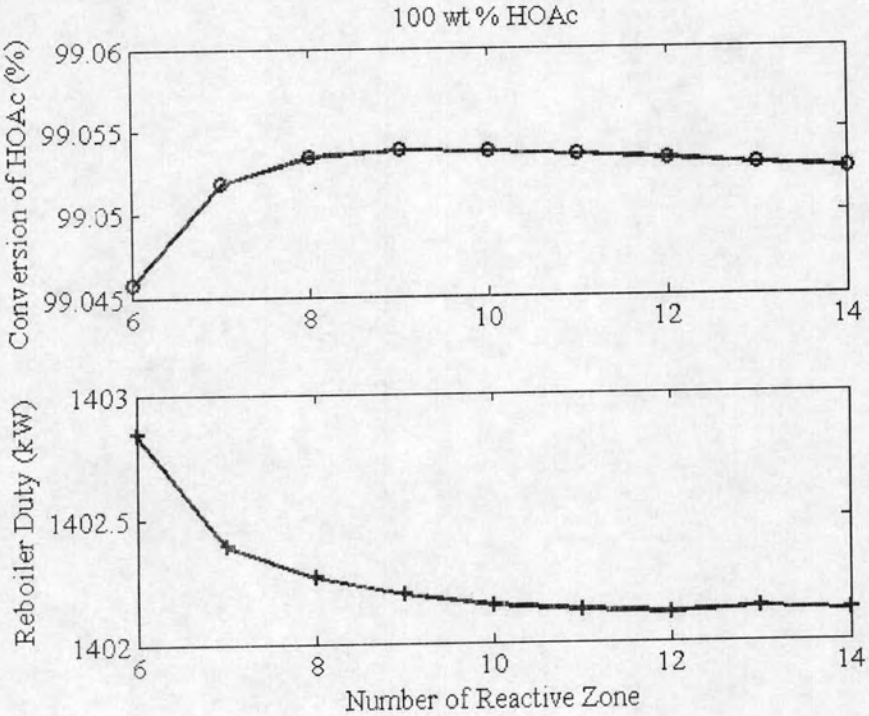

Figure 4-10 Effect of the number of reactive section at 100 wt % HOAc concentration.

4.3.5 Effect of Number of Non-Reactive stages

In all simulations, the number of reactive section is fixed at 13 stages and product specification at the bottom is set to 99.5 wt % of BuOAc. Figures 4-11 to 4-14 show the influence of the number of non-reactive stages on conversion, reboiler duty and product stream at each concentration of HOAc in feed stream. For 100 wt %, 80 wt % and 50 wt % of HOAc, increasing the number of rectification stages (Nr) increases both the conversion of HOAc and the reboiler duty. However, for 30 wt % of HOAc (Figure 4-11), an increase in Nr results in the decreased conversion of HOAc and the increased reboiler duty. Considering the influence of the number of stripping stages (Ns), it is found that increasing the number of stripping stages (Ns) has no significant effect on the conversion of HOAc and reboiler duty for all values of feed HOAc concentration. From the results, it is indicated that no further separation stages at the top are required because the decanter ensures a sufficient separation of water from the organic compounds because of the low solubilities of BuOH and BuOAc in water.

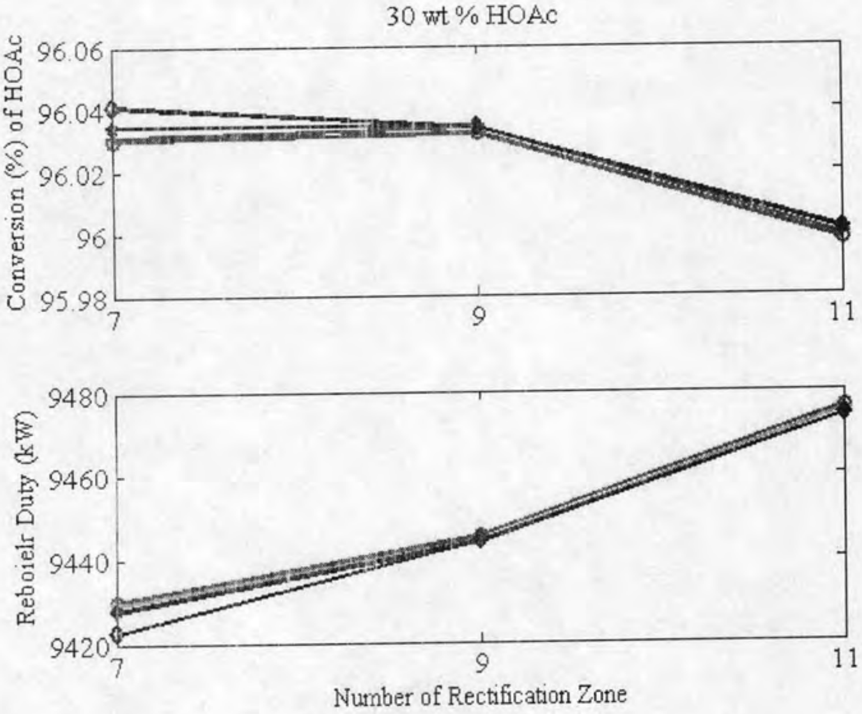

Figure 4-11 Effect of the number of non-reactive stages at 30 wt% of HOAc in feed stream.

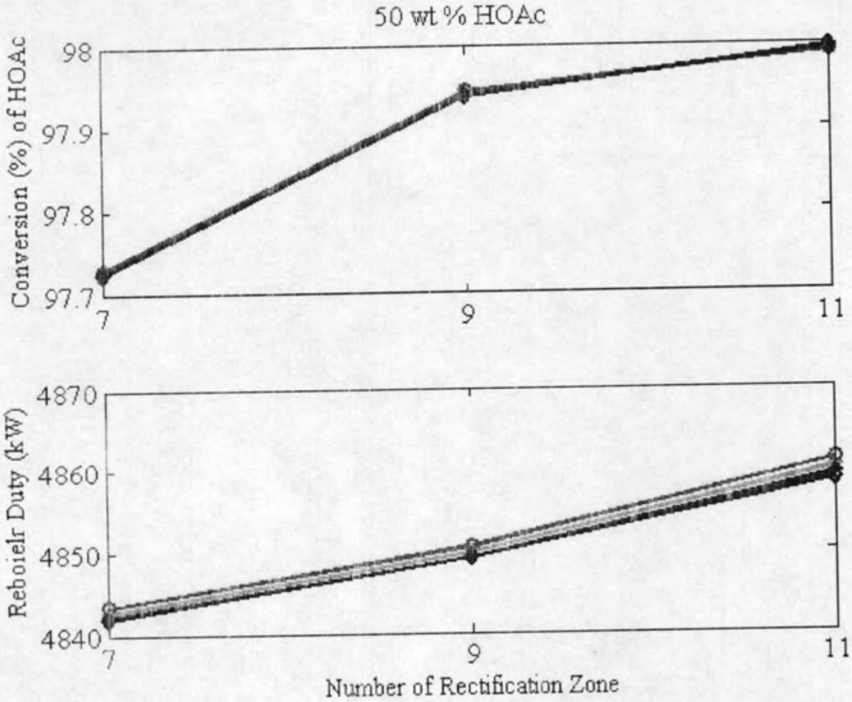

Figure 4-12 Effect of the number of non-reactive stages at 50 wt% of HOAc in feed stream.

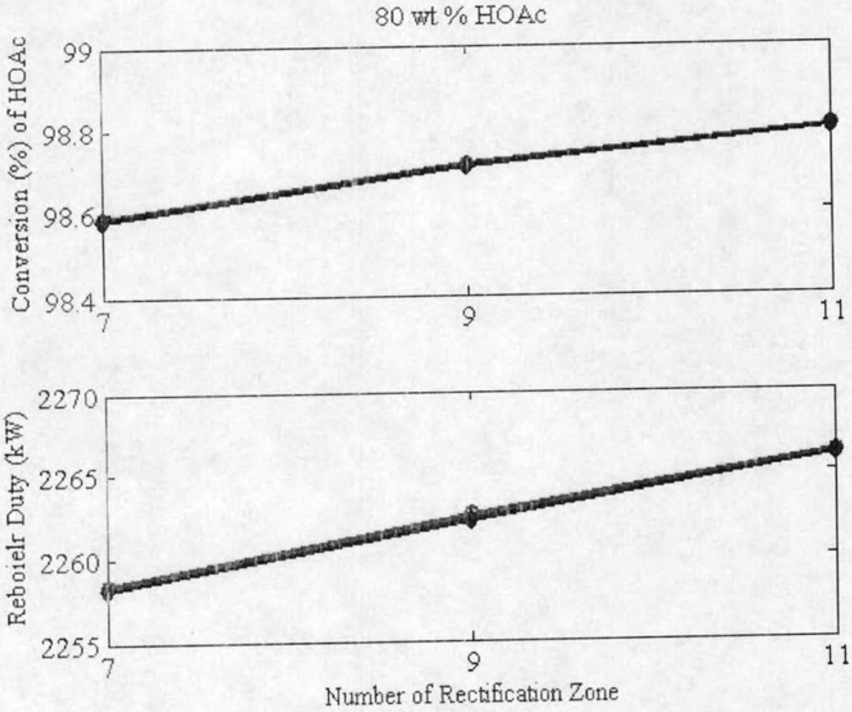

Figure 4-13 Effect of the number of non-reactive stages at 80 wt% of HOAc in feed stream.

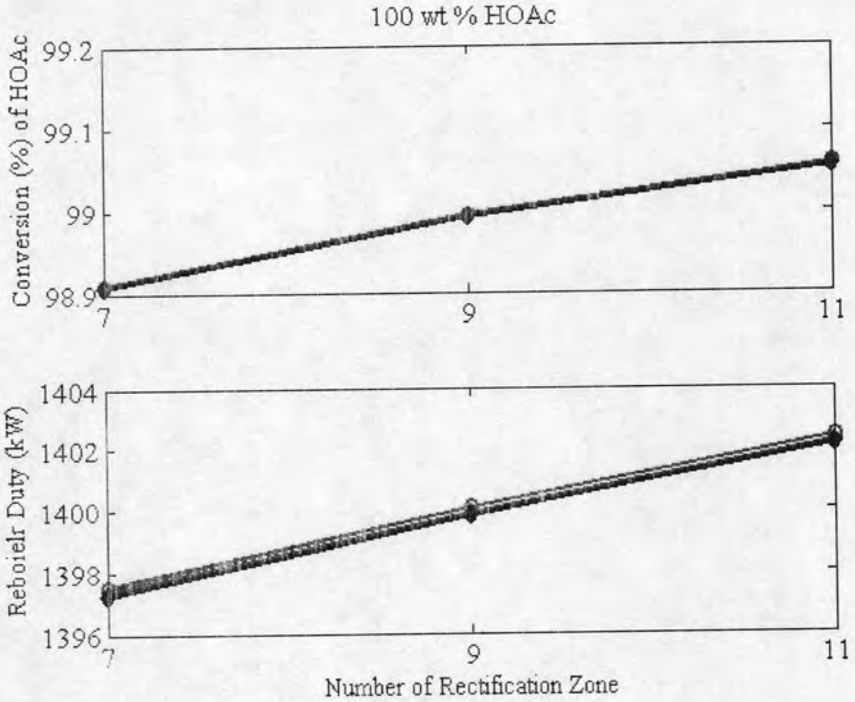

Figure 4-14 Effect of the number of non-reactive stages at 100 wt% of HOAc in feed stream.

4.3.6 Suitable Configuration of Reactive Distillation Column

From previous studies on the influence of feed acetic acid concentration and key design and operating variables, it is found that the HOAc concentration in feed stream is very important variable to design reactive distillation column. It has many effects on design parameters, i.e., feed location, reboiler duty and total stages of column. As HOAc concentration is decreased from 100 wt % to 30 wt %, the reboiler duty have to be increased for the production of BuOAc with purity at 99.5 wt %. For example, at 30 and 50 wt % HOAc, reboiler heat duty of 9400 and 4800 kW is required. By considering the required heat duty, the use of 80 wt % HOAc as a reactant for the synthesis of BuOAc in a reactive distillation column seems to be practical. Figure 4-15 and 4-16 shows temperature and composition profiles. It found that BuOAc is formed in reaction zone. And top of column, heterogeneous azeotropic mixture between water, BuOH and BuOAc, is formed and then separated into aqueous and organic phases in reflux drum. The aqueous phase is completely withdrawn, whereas the organic phase is completely refluxed to the column. It can be seen from Table 4-5 that distillate rate mostly contains water (94.9 wt %) whereas, the majority component of bottom stream is BuOAc (99.5 wt %). Table 4-6 shows a suitable configuration of the reactive distillation column which is further used for control study presented in Chapter V.

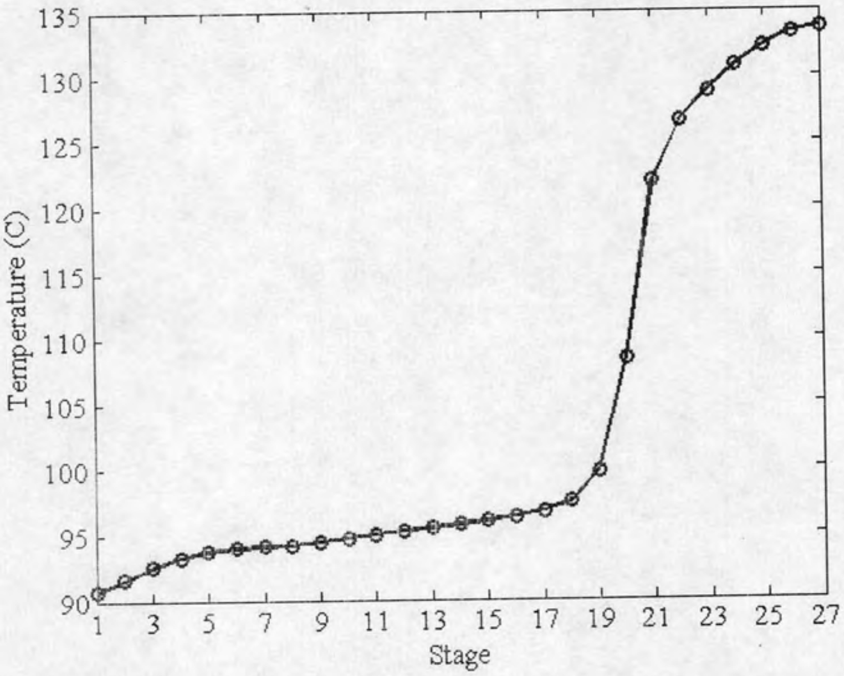

Figure 4-15 Temperature profile at nominal operating condition

Table 4-5 Compositions and flowrate of distillate and bottom streams

	Bottom	**Distillate**
Flowrate (kmol/h)	49.5113	92.1637
Composition (Mass Fraction)		
H_2O	0	0.9490
HOAc	0.0017	0.0183
BuOH	0.0031	0.0190
BuOAc	0.9953	0.0137

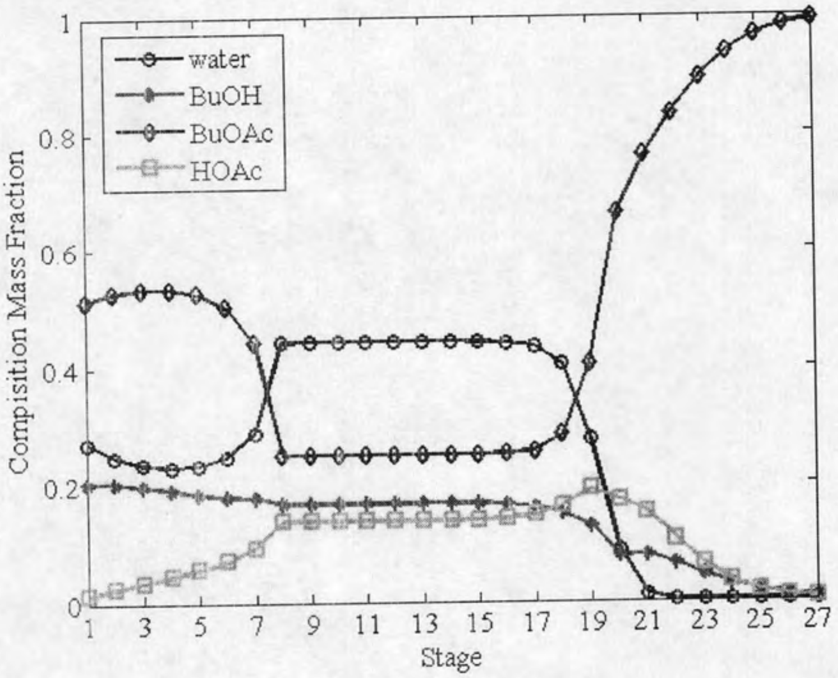

Figure 4-16 Composition profile at nominal operating condition

Table 4-6 Optimal steady-state operating conditions for the reactive distillation fed by 80 wt % HOAc

Feed conditions at 80 wt % HOAc		
Feed	HOAc	BuOH
Temperature (°C)	25	25
Pressure (atm)	1.259	1.259
Feed flow (kmol/h)	91.67	50
Feed stage	8	8
Column specifications		
Rectification stages (Nr)		7
Reaction stages (Nrxn)		13
Stripping stages (Ns)		7
Overhead pressure (atm)		1
Column pressure drop (atm)		0.248
Holdup (m^3)		0.4909