J. King Saud Univ., Vol.15, *Eng. Sci* (1), pp. 13-27, Riyadh (1423/2002)

Simulation of Distillation of a Large Relative Volatility Mixture

Anis H. Fakeeha
Chemical Engineering Dept., College of Engineering,
King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia

(Received 19 June, 2001, accepted for publication 05 November, 2001)

Abstract. In this paper, difficulties relating to the simulation of distillation columns for separating mixtures containing components with large relative volatility between the light and heavy key components are discussed. The system used for the study is ethylene o-xylene mixture. The relative volatility is not only large but its change with temperature is also large. This makes the system model equations highly non-linear. Great difficulty is met to obtain converged solution using packages like Hysis and Pro/II. Attempts have been made to obtain optimum design and a method suggested to enhanced convergence.

Nomenclature

d_j.D	Distillate molar flow rate of component j and of total flow respectively,
F_j	Component j flow rate at feed trays.
$H_{s,j}$	Vapour enthalpy of a component j at a tray s.
$h_{s,j}$	Liquid enthalpy of a component j at a tray s.
$h_{f.j}$	Enthalpy of component j in a feed to a tray s.
$L_{s,j}$	Liquid molar flow rate of a component j at a tray s.
L_s	Total liquid molar flow rate at a tray s.
m	Number of components.
q	Amount of heat added in reboiler or the negative heat lost in a condenser.
$V_{s,j}$	Vapour molar flow rate of component j at a tray s.
V_s	Total vapour molar flow rate at a tray s.

Introduction

A process was suggested by Mehra [1] to separate methane from the gases coming out of a hydrocarbon cracker using o-xylene as a solvent for ethane, ethylene, propylene and higher hydrocarbons. This replaces the demethanizer in a conventional ethylene cracking plant. The gases are then separated from o-xylene by distillation. During economic evaluation of the process difficulties had been met in obtaining converged solutions due to the high non-linearity of the modeling equations. In addition the reboiler heat duty is so large that a large diameter column is required in simulating the distillation column which separates the C^+_2 from o-xylene using commercial simulation packages such as Pro/II and Hysis. A simplified system consisting of mixture of ethylene and o-xylene was studied. Having gained experience with this system, a multi-component mixture that could represent an actual industrial case was studied and results are presented here.

Seader and Henley [2] summarized the present status of numerical methods for rigorous solution of distillation column as follows:

(1) The bubble point method [3] is generally restricted to distillation problems involving narrow boiling feed mixtures. There a new set of stage temperatures is computed during each iteration from bubble point equations. The mass balance equation for each component is set in a tridiagonal matrix form which simplifies calculation.

(2) The inside out method [4] is often the method of choice. In this method, a simple thermodynamic model is used in an inner loop to obtain an approximate solution which is then improved in an outer loop which has rigorous thermodynamic set

.

(3) The simultaneous correction procedure [5] is generally slower than the inside-out method and is the second choice if the inside-out method fails. It depends on the simultaneous solution of all equations using Newton-Raphson method.

(4) Relaxation method [6] is very slow and will be the last choice if other methods fail. The relaxation method depends on following the column transients until it reaches steady state.

In the next section we present methods used in commercial packages.

In this paper, it is intended to find out a sub-optimum design to industrial distillation column separating ethylene from o-xylene and suggest a mathematical formulation for the modeling equations which could be helpful when we have convergence problems.

Methods Used for Distillation Simulation in Pro II and Hysis Package

The packages have built-in schemes or algorithms for solving problems in order to allow efficient ways to solve industrial problems such as distillation or liquid-liquid extraction.

Five methods are used for distillation in Pro II package with the inside-out method as default method [7].

1. **Inside-Out Method:** same as that described above by Seader and Henley. This method is insensitive to the initial estimate and allows simultaneously solution of side columns with the main column. It converges fast but it allows the usage of one liquid phase only and has difficulty in solving highly non-ideal thermodynamics. The method does not allow total pump around.

2. **Enhanced Inside-out Method:** This method applies a new solution technique that extends the application of the previous inside-out method to applications such as total pump around.

3. **Sure Method:** The method is based on using Newton-Raphason technique with matrix partitioning. It depends on the simultaneous solution of all equations. It is useful for non-ideal chemical applications and for hydrocarbon application. It needs long time in calculation and requires accurate initial estimates especially for flow.

4. **Chemical Method:** The method uses Naphtali-Sandholm algorithm with matrix solver developed by SimSci. It is used with highly non-ideal distillation. It uses only advanced equation of state or liquid activity thermodynamic systems.

5. **Electrolytic Method:** The method uses Newton-Raphason method to solve non-ideal aqueous electrolytic distillation columns containing ionic species. It cannot be used to solve problems with side column or pump around.

For Hysis package [8], five methods are also used to solve problems.

1. Hysis inside-out which is used for general purpose with two loops, that use simple model in the inside loop, which is refined in the outside loop.

2. Modified Hysis inside-out: This method is used to extend the applicability of the previous method to application such as mixer and heat exchanger inside the column sub flow sheet.

3. Newton-Raphson Inside-out: This method is applicable for general purpose with capability of calculation of liquid phase kinetic reaction.

4. Sparse Continuation Solver: The method is used for highly non-ideal and reactive distillation calculation.

5. Simultaneous Correction: This method uses dogleg method, suitable for chemical systems and reactive distillation.

Comparison of Results Obtained for Simulation of Similar Operating and Design Conditions by Using Pro II and Hysis Packages

The separation of ethylene from o-xylene is performed by using the Pro/II and Hysis packages under similar operating and design conditions. In simulation the following parameters are specified:

1. Feed pressure and temperature.
2. Column pressure.
3. Number of trays.
4. Feed tray.
5. Reboiler and condenser duties.

In comparing the simulation results of the two packages the gas feed to the distillation column with ethylene mole fraction of 0.3 with inlet pressure and temperature of 2800 kPa and 310 °K respectively, the pressure inside the column was chosen as 1000 kPa. Five trays are assumed and the feed is introduced to the third tray. The first tray is the condenser and the fifth tray is the reboiler. Thermodynamic properties are generated using Soave Redlick Kwong method.

Comparison of the results obtained from the process of simulation using the two packages are shown in Table 1 for temperature distribution, Table 2 for the K-value of both ethylene and o-xylene and Table 3 for the composition distribution.

Table 1. Temperature distribution predicted by Pro/II and Hysis package in °K

Tray	Pro/II	Hysis
1	221.2	221.1
2	221.2	221.1
3	255.6	264.6
4	427.6	455.5
5	523.0	524.8

Table 2. K-value distribution predicted by Pro/II and Hysis package

Tray	K-Value for Ethylene		K-Value for o-xylene		Relative Volatility from Pro/II
	Pro/II	Hysis	Pro/II	Hysis	
1	1	1	$1.706*10^{-5}$	$2.678*10^{-5}$	58616
2	1	1	$1.705*10^{-5}$	$2.673*10^{-5}$	58651

3	3.1237	4.177	$8.4352*10^{-5}$	$1.763*10^{-4}$	37032
4	18.708	20.8	0.15685	0.2972	119.3
5	19.184	17.44	0.91835	0.9442	20.9

Table 3. Composition predicted by the two packages

Tray	Ethylene Composition			
	Pro II		Hysis	
	Vapor	Liquid	Vapor	Liquid
1	1	1	1	1
2	1	0.9999	1	0.9998
3	0.9999	0.3201	0.9999	0.2394
4	0.8503	0.0454	0.713	0.0343
5	0.0857	0.0045	0.0586	0.003

The two packages do not predict results with the same value. There is a difference of 1.8, 27.9, 9 °K in temperature prediction of the 5th, 4th, and 3rd tray respectively. Similarly there are differences in K-value and composition prediction by the two packages as seen in the Tables 1,2,3. The difference in the results is due to the differences in estimating the thermodynamic properties of the components.

The feed pressure is changed by selecting values of 2500, 1800 and 1000 kPa. The column pressure for most of cases are selected 1000 kPa except one case where a pressure of 2500 kPa is chosen.

For Pro II, the Sure method converges in all cases. For the case of inlet pressure of 1800 kPa the chemidist converges. For the case of inlet pressure 1000 kPa all methods converge.

For Hysis, the Hysis modified inside-out algorithm works for all cases except the case of inlet pressure 1000 kPa. The Hysis-inside out algorithm converges in this case only. Other methods do not work at all.

Initial attempts to determine the optimum design and operating conditions were dictated by cases that converge since great difficulty in finding out convergent solution is met. The results of these initial attempts are given in Table 4. We notice the following:

1. In most cases, the top tray is not needed since the two top trays have almost equal liquid and vapour composition as in table (3).

2. In most cases, the tower has impractically large diameter, high reflux ratio and high boil up rate.

3. The best case is that of case 3.

In case three with lower condenser and boiler duties, reflux ratio obtained is lower than the other cases. This will reflect on minimizing energy needed in boiler and condenser as well as pumping power required for the reflux. It is noticed that this case is reached by increasing the inlet temperature of feed and lowering the column pressure.

(Table No. 4)

Now we would like to improve on the results of this case. First, it is desirable that the pressure in the tower be kept at 2500 kPa, since the pressure is needed in the down stream operation. To determine a suitable feed temperature, Gani and Pedersen [9] analysis will be used. This requires plotting [y-x] against x. For the case of a pressure 2500 kPa, the graph is shown in Fig. 1. According to this method, if the feed plate is located at a point where the driving force [y-x] is maximum the resulting design could correspond to near minimum cost of operation. If the feed composition is higher than the value of x corresponding to a maximum driving force, then it should enter the tower as mixed vapor. The maximum driving force [y-x] occurs at x values of about 0.25. Since the feed is at x = 0.3, it is desirable that the feed enters as saturated or vapour mixed feed. Thus inlet temperature should be raised above 310 °K.

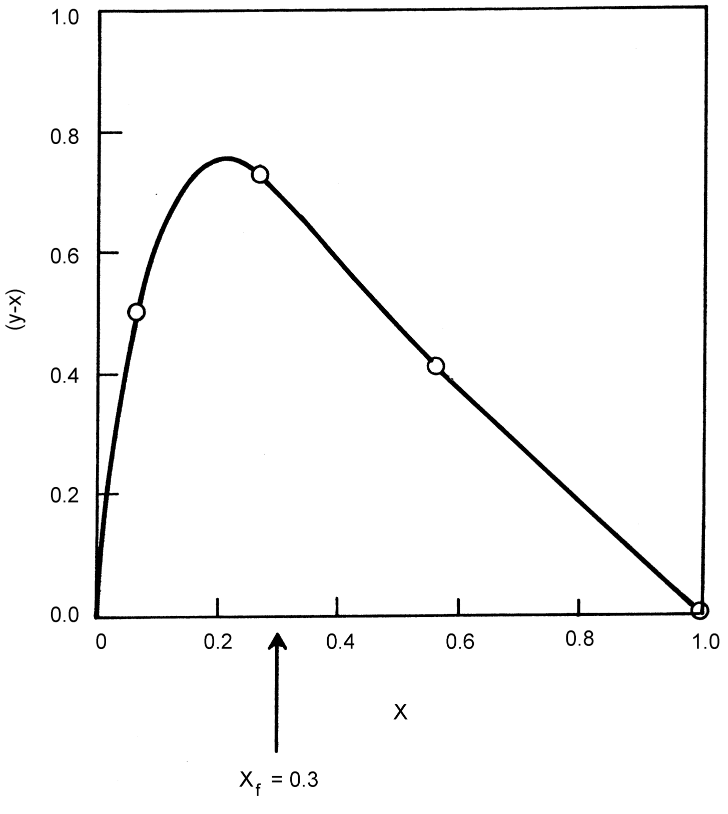

Fig. 1. Driving forced as function liquid molefraction at 310^{o}k and 2500 KPa

Pro/II package is used arbitrarily to simulate cases where the feed temperature is changed from 350 to 360 K with column pressure of 2500 kPa and inlet pressure of 2800 kPa. The feed is introduced in the second tray. The results are shown in Table 5.

(Table No. 5)

When the inlet temperature is increased to 360 K the ethylene mole fraction at the bottom improves to 0.0388 but the diameter increases to 4.22 m. This indicates how sensitive this system is to changes in inlet temperature. At 360 °C and heat duties of reboiler $7.5*10^8$ kJ/hr the bottom product is much lean in ethylene at the expense of using much larger diameter.

Fixing the reboiler and condenser duties, trays number, feed tray and pressure, the effect of changing the feed temperature is further studied at 340, 350, 360 K. At 340 C the tower diameter is increased with respect to case 6 at 350 K as shown in table (5) to 3.91 and ethylene mole fraction in the bottom increased to 0.0528.

Finally to get an estimate of the diameter of the tower for actual case with actual industrial mixture, a simulation is performed at feed temperature of 350 K and inlet pressure of 2800 kPa and column pressure of 2500 kPa. The result of simulation is shown in Table 5 with feed, top and bottom composition shown in Table 6.

Table 6. Simulation of actual industrial feed composition

Parameter	**Feed**	**Bottom Product**	**Top Product**
Flow rate in kg.mole/hr.			
Total	17177	12535.37	4641.63
Ethylene	3120	306.72	2813.28
o-xylene	11900	11899.76	0.24
Hydrogen	98	0.06	97.94
Methane	129	1.92	127.08
Acetylene	14	2.0	12.0
Ethane	1860	298.69	1561.31
Propylene	56	26.23	29.77
Temperature, °K	350	533.8	264.3

Suggested Method for Convergence

Different packages use algorithms for solution which is not known to the user and some of these algorithms do not converge. As an alternative that can be used in commercial package for simulations that are difficult to converge [10], the following method is suggested for solving the material, enthalpy balances and equilibrium relations. First we write down the material, enthalpy balances, equilibrium relations.

The material balance equation in distillation column (Fig. 2) for tray s is written as:

$$L_{s,j} + V_{s,j} = L_{s-l,j} + V_{s+l,j} + F_j \qquad (1)$$

The enthalpy balance round the same plate is:

$$\sum_{j=1}^{m} L_{s,j}\, h_{s,j} + \sum_{j=1}^{m} V_{s,j}\, H_{s,j} = \sum_{j=1}^{m} L_{s-1,j}\, h_{s-1,j} + \sum_{j=1}^{m} V_{s+1,j}\, H_{s+1,j} + \sum_{j=1}^{m} F_j\, h_{F,j} + q \qquad (2)$$

where m is the number of components.

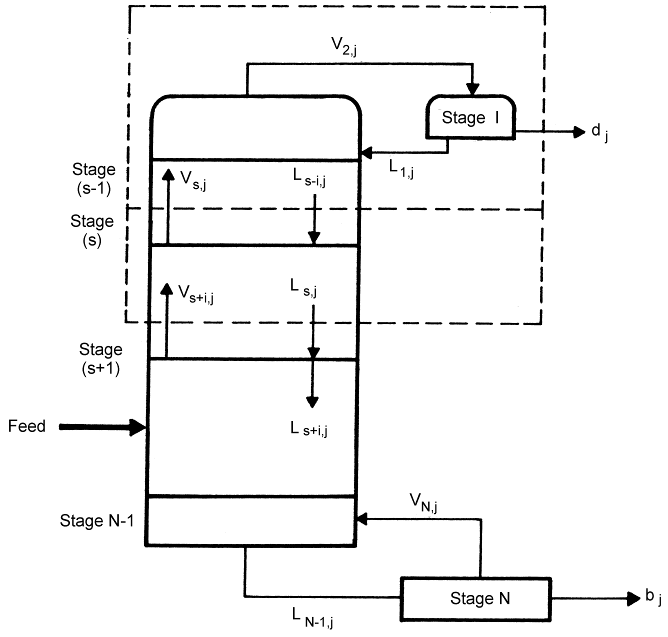

Fig. 2. Distillation column configuration.

The term F_j will have a value only at the feed plate q will have a value only in a condenser, or reboiler and it is the amount of heat added in a reboiler or is the negative of the heat lost in a condener.

Assuming the liquid and vapour phases are in equilibrium, we obtain for stage s the following equilibrium relationship:

$$\frac{V_{s,j}}{\sum_{j=1}^{m} V_{s,j}} = K_{s,j}\left(\frac{L_{s,j}}{\sum_{j=1}^{m} L_{s,j}}\right) \tag{3}$$

Additional component material and heat balances and equilibrium relationships are established round the condenser, feed plate and reboiler. Secondly, we reformulate the equations as follows:

The equation which express the overall material balance around stages in the rectifying section in the column are written in the form:

$$\sum_{j=1}^{m} V_{s+l,j} = \sum_{j=1}^{m} L_{s,j} + \sum_{j=1}^{m} d_j \tag{4}$$

$$\sum_{j=1}^{m} V_{s,j} = \sum_{j=1}^{m} L_{s-l,j} + \sum_{j=1}^{m} d_j \tag{5}$$

Equilibrium relationship gives:

$$\frac{V_{s+1,j}}{\sum_{j=1}^{m} V_{s+1,j}} = K_{s+1,j}\left(\frac{L_{s+1,j}}{\sum_{j=1}^{m} L_{s+1,j}}\right) \tag{6}$$

Substituting for $\sum_{j=1}^{m} V_{s+1,j}$ from (4) we obtain:

$$V_{s+1,j} = K_{s+1,j}\left(\frac{L_{s+l,j}}{\sum_{j=1}^{m} L_{s+l,j}}\right)\left(\sum_{j=1}^{m} L_{s,j} + \sum_{j=1}^{m} d_j\right) \tag{7}$$

Similarly, we obtain a relationship for $V_{s,j}$:

$$V_{s,j} = K_{s,j} \left(\frac{L_{s,j}}{\sum_{j=1}^{m} L_{s,j}} \right) \left(\sum_{j=1}^{m} L_{s-1,j} + \sum_{j=1}^{m} d_j \right) \tag{8}$$

Thus, the vapour component flow rates entering and leaving stages have been expressed in terms of liquid component flow rates. After substitution of (7) and (8) into (1), the component material balance equations will no longer contain vapour flow rates. This procedure eliminates the need to include the vapour approximating profile from the solution algorithm.

In the stripping section the overall component balances include the bottom component flow rates instead of the distillates. The material balance equations are included in the enthalpy balance equations to improve convergence.

At a trays s, eliminating the components vapour flow rate from equations (1,2) using equations (7,8), the following equations are obtained:

$$\begin{gathered} L_{s-1,j} + K_{s+1,j} \frac{L_{s+1,j}}{L_{s+1}} \left[L_s + D \right] + F_j \\ = L_{s,j} + K_{s,j} \frac{L_{s,j}}{L_s} \left[L_{s-1} + D \right] \end{gathered} \tag{9}$$

$$\begin{gathered} \sum L_{s-1,j} h_{s-1,j} + \frac{\sum K_{s+1,j} L_{s+1,j}}{L_{s+1}} \left[L_s + D \right] H_{s+1,j} + \sum F_j h_{Fj} + q \\ = \sum L_{s,j} h_{s,j} + \sum \left\{ \left[L_{s-1,j} + K_{s+1,j} \frac{L_{s+1,j}}{L_{s+1}} \left[L_s + D \right] - L_{s,j} \right] H_{s,j} \right\} \end{gathered} \tag{10}$$

Notice that the enthalpy balance as written above is obtained by the substitution of material balance in the enthalpy balance of the original equations. This manipulation is found to improve the convergence of the resulting non-linear equation to the solution.

Any non-linear equation solver can be used to solve for liquid components flow rates and trays temperature using equations (9,10).

In the present case, the non-linear equations are solved using ZSPOW subroutine of the IMSL. This subroutine is based on a Newton-Raphson method in which the Jacobean is evaluated numerically.

A computer program was prepared which uses the above algorithm and uses equilibrium data from the converged case no. 4. Gas and liquid enthalpies are obtained from reference [11]. Heat of mixing is assumed to be negligible. The effect of pressure on enthalpies is also neglected. The initial guess is the same as that used for running simulations packages.

The results are shown in Table 7. There are some differences in temperatures and flow rates due to the above assumptions made.

Table 7. Comparison of results of suggested methods and simulation of case 4

	Temperature, °K		**Liquid flow Rate kg.mol/hr.**	
Tray No.	**Case No. 4**	**Our Work**	**Case No. 4**	**Our Work**
1	252.3	252.3	36210	33574
2	252.3	254.9	32630	32453
3	265	268.2	30980	36447
4	314.3	314.9	20540	22110
5	517.3	516.8	12800	12797

Thus if one has a problem of convergence with existing commercial package, the above algorithm could be tried.

Conclusion

The difficulties that could be encountered when simulating the distillation with a mixture of large relative volatilities between the light and heavy key components are discussed. The steps taken to get a sub-optimum design for a column that separates ethylene from o-xylene are indicated. The mathematical formulation for the column that could converge when there are difficulties with commercial simulation packages is presented.

References

[1] Mehra, Y.R. *US Patent*, 4, 617, 0.38, Oct. 14 (1986).

[2] Seader, J.D. and Henley, E.J. *Separation Process Principle*, New York: John Wiley, 1998.

[3] Friday, J.R. and Smith, B.D. "An Analysis of the Equilibrium Stage Separation Problem Formulation and Convergence". *AIChE J.*, 10 (1964), 698-707.

[4] Boston, J.F. and Sullivan, S.L. "A New Class of Solution Methods for Multicomponent, Multistage Separation Processes". *Can. J. Chem. Eng.*, 52 (1974), 56-63.

[5] Naphthali, L.M. and Sandholm, D.P. "Multicomponent Separation Calculation by Linearization". *AIChE J.*, 17 (1971), 148-153.

[6] King, C.J., *Separation Processes*, USA: McGraw Hill, 1980.

[7] Pro II Manual, 2000.

[8] *Hysis Mannual*, Version 2.1, (1998).

[9] Gani, R.and Bek-Pedersen, E. "Simple New Algorithm for Distillation Column Design". *AIChE J*. 46, No. 6 (2000), 1271-1274.

[10] Wagialla, K.M. and Soliman, M.A. "Distillation Column Simulation by Orthogonal Collocation: Efficient Solution Strategy" *J. King Saud Univ., Eng. Sci.* 5, No. 1 (1993), 17-40.

[11] G.V. Reklaitis, *Introduction to Material and Energy Balances*, N.Y.: John Wiley, 1983.

(Arabic Abstract)