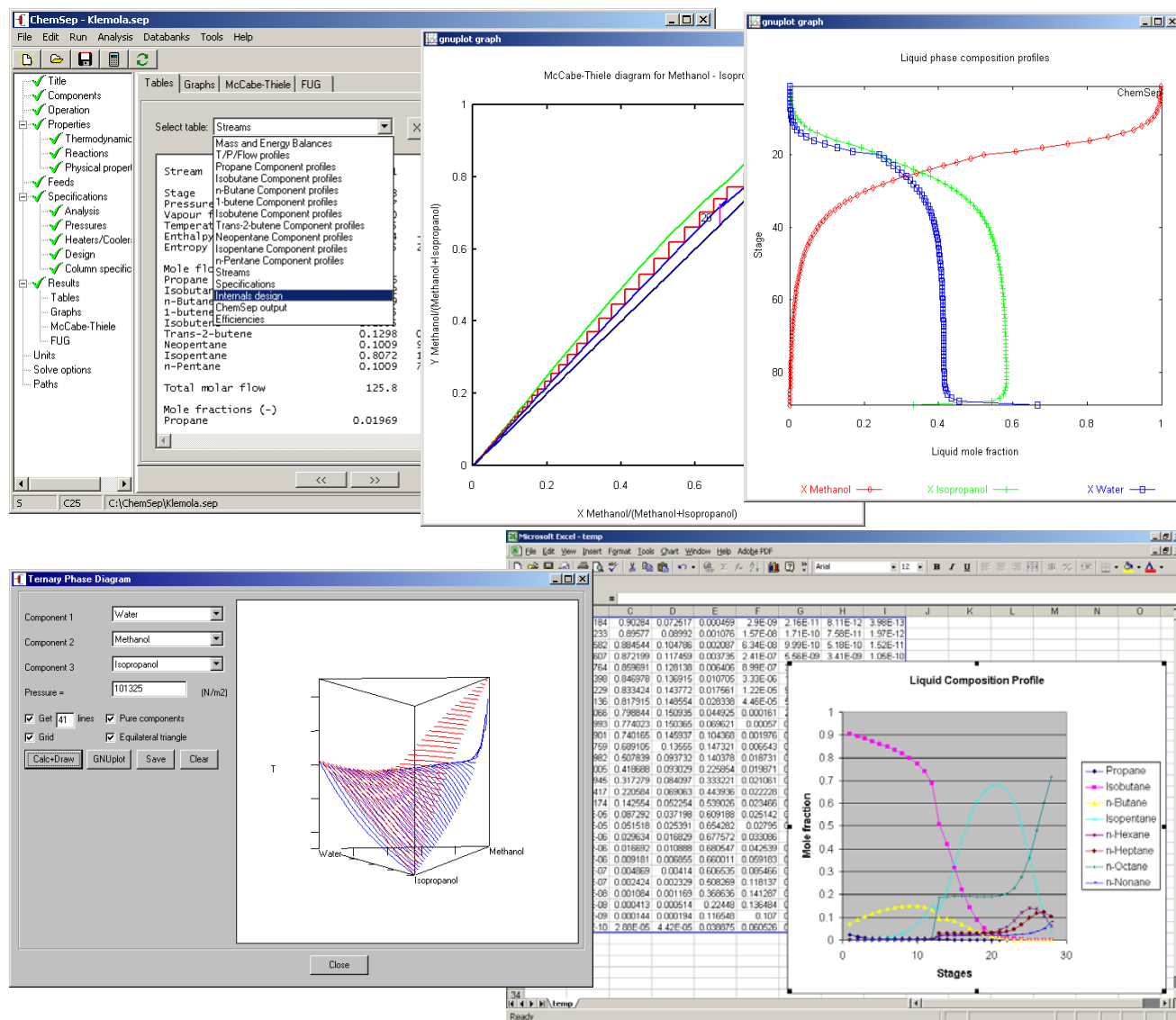# ChemSep 6

Harry Kooijman, Richard Baur, and Ross Taylor

ChemSep^{TM} is a program for performing multicomponent separation process calculations. **ChemSep** is designed for use in courses on thermodynamics and/or separation processes and features an easy to use interface for Windows, equilibrium and rate-based column models, integrated graphics (with GNUplot), and export capabilities (e.g. to Excel (see below), Word, and html).

ChemSep-Lite (a version with some limitations) is **available free from** www.chemsep.org.

New in **ChemSep** 6 (and demonstrated below):

- **Residue Curve Maps**
- **Ternary VLE diagrams** (see screen image below)
- **Parametric Study Mode**
- **CAPE OPEN (CO) compliance**
- **Constant relative volatility thermodynamic model**

Residue Curve Maps and *ChemSep*

Residue curve maps (RCMs) now are considered an established part of an undergraduate chemical engineering education with coverage in widely used textbooks on thermodynamics (Elliott & Lira, 1999), separation processes (Seader & Henley, 1998, 2005; Doherty & Malone, 2001), and design (Biegler, Grossman, & Westerberg, 1997; Seider, Seader, & Lewin, 1999).

The simple distillation of a liquid mixture is modeled by:

$$\frac{dx_i}{d\xi} = x_i - y_i$$

where ξ is a dimensionless time, x_i is the mole fraction of species *i* in the liquid phase, and y_i is the mole fraction of species *i* in the vapor phase. The liquid and vapor phase mole fractions are related through the familiar equations of phase equilibrium:

$$y_i = K_i x_i; \quad \sum_{i=1}^{c}(y_i - x_i) = 0$$

where K_i is the equilibrium ratio or K-value for species *i*.

These are the equations that describe residue curves in nonreacting systems and they have been very extensively studied (for reviews of the research literature see Pöllmann & Blass, 1994; Fien & Liu, 1994; Widago & Seider, 1996; Kiva, Hilmen & Skogestad, 2003). The (numerical) solution of these equations provides a family of curves known as a residue curve map, and they have become an important tool in separation process synthesis and design.

ChemSep now includes a tool for creating residue curve maps for ternary systems such as the one shown below for a simple ternary system with constant relative volatilities.
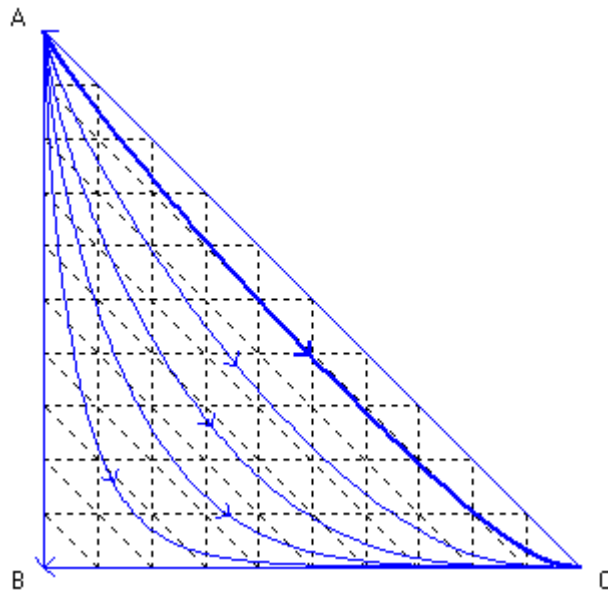

In what follows we demonstrate how to create these maps with ***ChemSep***.

As a first step to the creation of a residue curve map with **ChemSep** it is necessary to select components (in the series of illustrations to follow they will be acetone, chloroform, and methanol) and thermodynamic model (UNIFAC activity coefficients and Antoine vapor pressures in this example); it is *not* necessary first to solve a simulation problem (although that it is certainly possible). Then click on *Analysis* and select *Residue Curves* as shown in the screen shot below.
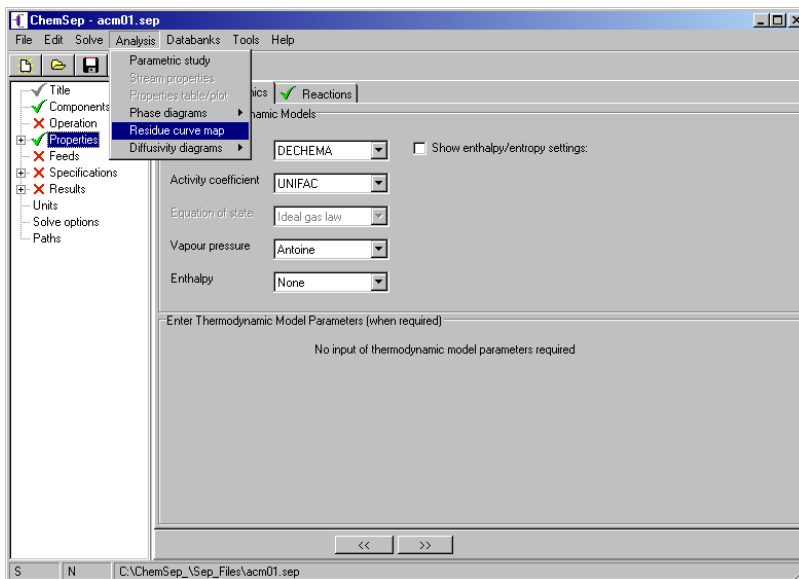

This brings up the Residue Curve Map window:
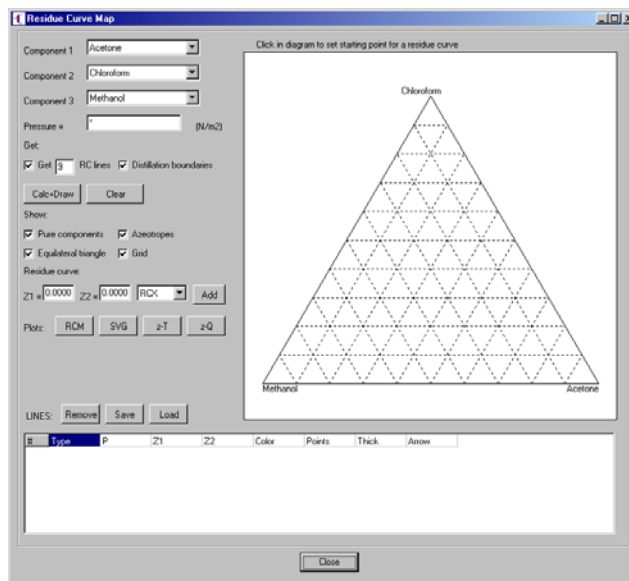
The composition triangle is shown in the top right of this panel. To the left is the list of components (the first three if more than that number was included in the list if components selected earlier). The component selection (and order) can be changed here if desired. There is a cell to enter the pressure (showing a * in the illustration above), and two cells lower down to enter mole fractions. Next to the composition cells is a pull down menu for selecting the type of composition line that is to be drawn; more on this below. Above the composition cells are various control buttons and check boxes that are used to indicate what is to be calculated and/or displayed on the diagram (more on some of these below as well).

The next step is to set the pressure in the empty cell provided. We may then do nothing more than click on the *Calc+Draw* button for ChemSep to initiate the calculations needed to draw a map with the number of lines equal to that set in the cell above the *Calc+Draw* button (the default is 9). Since this does not always produce a visually appealing diagram (the lines may not be well spaced) we do not do that here. Instead, we set the number of lines to zero, click off the distillation boundaries checkbox and click on the *Calc+Draw* button. This leads to the calculation of the boiling points of the pure components, and any binary azeotropes and the diagram shown below.
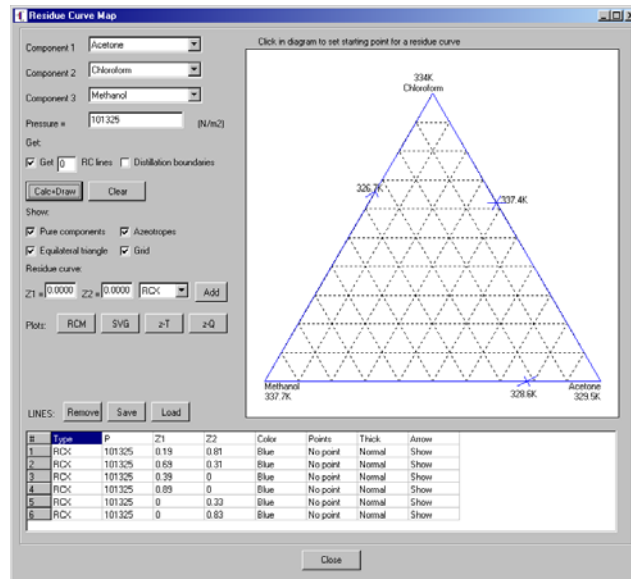

The portion of the window below the triangle provides the details of each curve shown in the triangle. The list includes the details of the computations used to determine the boiling points of the pure component and binary azeotropes.

Next, we simply move the mouse over the triangle and click on a point (this will enter the coordinates directly in the composition cells to the left of the triangle). Then click on the *Add* button. This will lead to the calculation of the residue curve that passes through those coordinates.

Click on *Done* and the curve will be displayed in the composition triangle. To add lines we simply repeat the process of locating a starting point as described above and clicking on the *Add* button each time. The illustration below shows the map after 11 lines have been drawn. Single lines can be highlighted (as can be seen below)
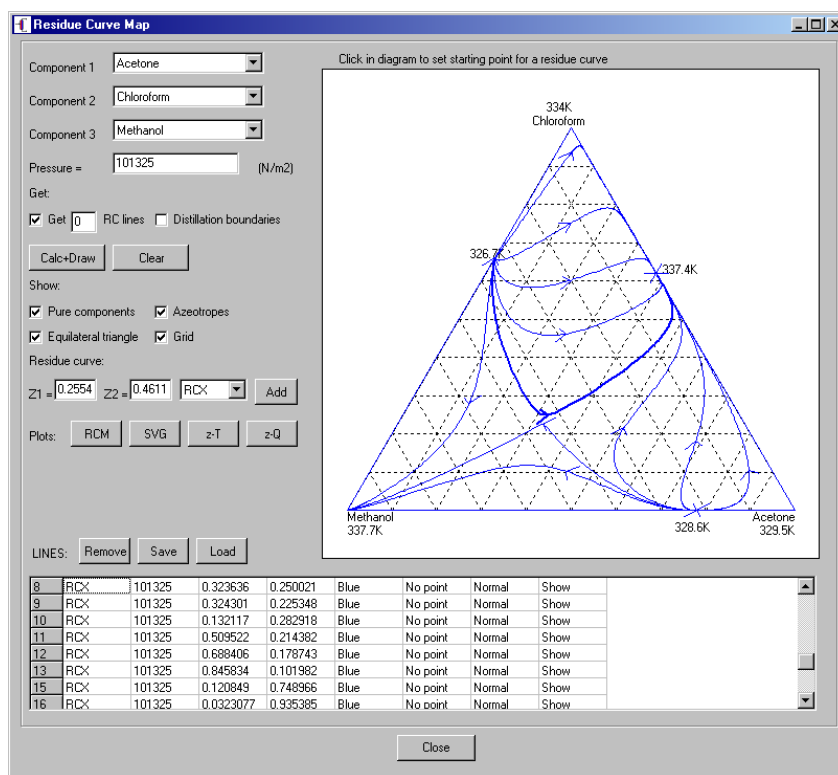
Further Reading about Residue Curves:

Biegler, L.T., I.E. Grossmann, & A.W. Westerberg, *Systematic Methods of Chemical Process Design*, Prentice-Hall, Upper Saddle River, N.J. (1997).

Doherty, M.F.; Malone, M.F. *Conceptual Design of Distillation Systems,* McGraw-Hill, New York (2001).

Elliott, J.R. & C.T. Lira, *Introductory Chemical Engineering Thermodynamics*, Prentice-Hall, Upper Saddle River, N.J. (1999).

Pöllmann, P.; Blass, E. Best products of homogeneous azeotropic distillations. *Gas Separation and Purification*, (1994) *8*, 194–228.

Fien, G-J.A.F.; Liu, Y.A. Heuristic Synthesis and Shortcut Design of Separation Processes Using Residue Curve Maps: A Review (1994) *Ind. Eng. Chem. Res. 33*, 2505-2522.

Widagdo, S.; Seider, W.D. Azeotropic Distillation, *AIChE J.* (1996) *42*, 96.

Kiva, V.N.; Hilmen, E.K.; Skogestad, S. Azeotropic Phase Equilibrium Diagrams: A Survey, *Chemical Engineering Science* (2003) *58*, 1903-1953.

Seader, J.D. & E.J. Henley, *Separation Process Principles*, Wiley, New York (1998, 2005).

Seader, J.D., W.D. Seider, & D. Lewin, *Process Design Principles*, Wiley, New York (1999).

Parametric Study

We illustrate the new *Parametric Study* feature of **ChemSep** with the help of a butane-pentane spliiter from Seader and Henley (1998) and shown below.
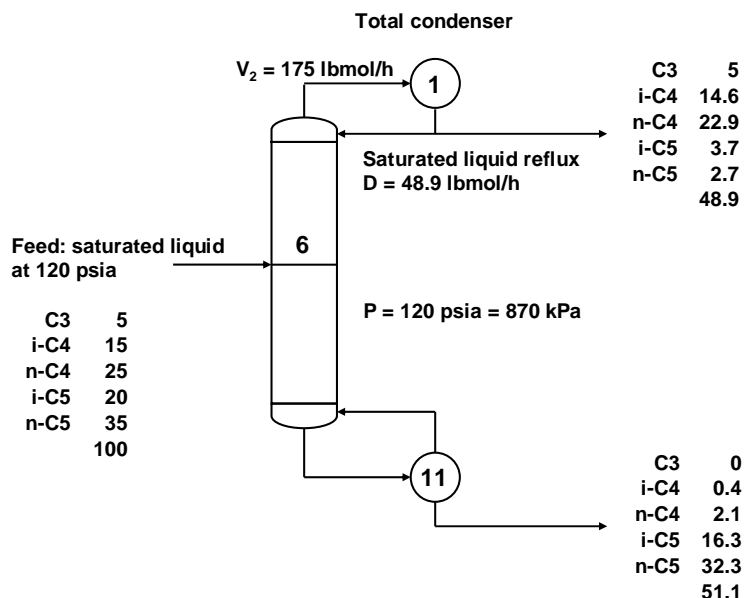
Specifications and calculated product stream flows for butane- pentane splitter. Flows are in lbmol/h.

The Peng-Robinson equation of state was used to estimate K-values and enthalpy departures.

With 11 stages and 5 components the equilibrium stage model has 143 equations to be solved for 143 variables (the unknown flow rates, temperatures, mole fractions). **ChemSep** solved this problem in just 4 iterations. Computed product flows are shown in the figure above.
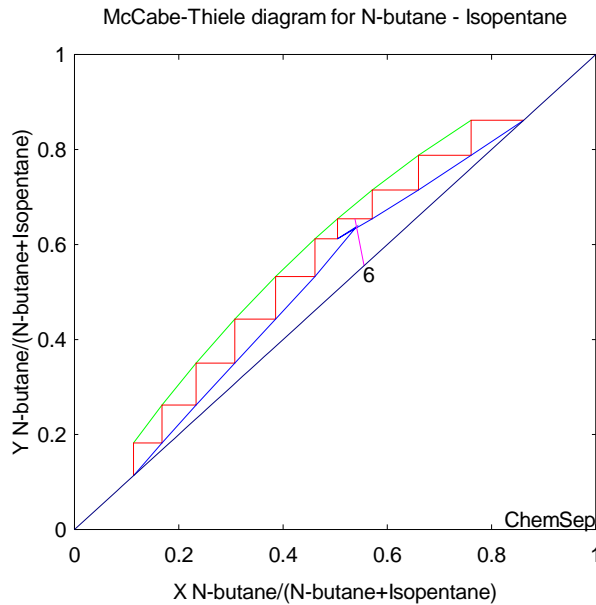
A McCabe-Thiele diagram for this multicomponent system is shown below. For systems with more than two components these diagrams can only be computed from the results of a computer simulation. The axes are defined by the relative mole fractions:

$$X = \frac{x_{lk}}{x_{lk} + x_{hk}}; \; Y = \frac{y_{lk}}{y_{lk} + y_{hk}}$$

where the subscripts *lk* and *hk* refer to light and heavy key respectively.

The fact that the staircase of triangles visible fails to come close to the corners of the diagram where $X = Y = 1$ and $X = Y = 0$ shows that the separation is not especially sharp. In addition, we can see that the feed is not in the best possible location.

It is worth asking what can be done to improve the separation obtained with this column. The parameters that have a significant effect on the separation are the numbers of stages in the sections above and below the feed, the reflux ratio, and a product flow rate (or reflux flow). We can use the parametric study option of **ChemSep** to investigate the influence of these parameters on the separation.

McCabe-Thiele diagram for N-butane - Isopentane

Multicomponent McCabe-Thiele diagram for butane – pentane splitter.

Click on the *Analysis* menu and select *Parametric Study* to bring up the window. Then add specification variables from the pull down menu to the list of parameters that will be varied. Here we have selected the reflux ratio and specified that it be varied from 1.5 to 6 over 21 steps. In the center section we select results that we wish to monitor from another pull down list. In this illustration we have selected the mole fractions of isopentane in the overhead and n-butane in the bottoms, and the reboiler duty.
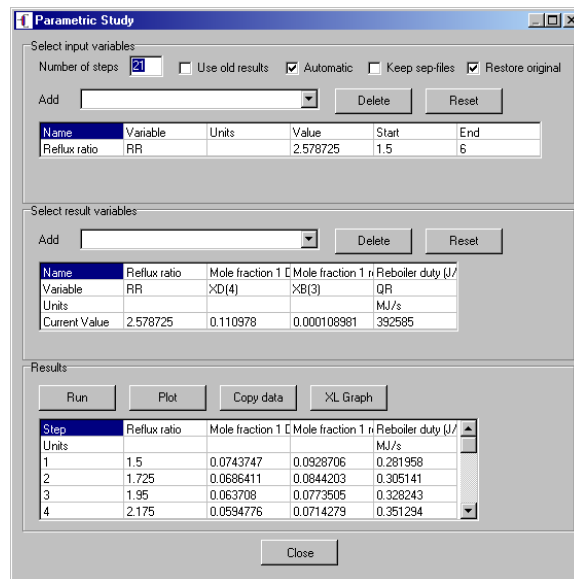
After we click the *Run* button **ChemSep** will execute 21 simulations at different reflux ratios and the values of the select output parameters will be tabulated in the bottom part of the parametric study panel as can be seen in the screen image shown above.

ChemSep can export these results to Excel, or to the plotting package provided with the program. Below left we show the results of our calculations after formatting the graph (with ***ChemSep***) so that the mole fractions use the left vertical axis and the reboiler duty the right vertical axis.
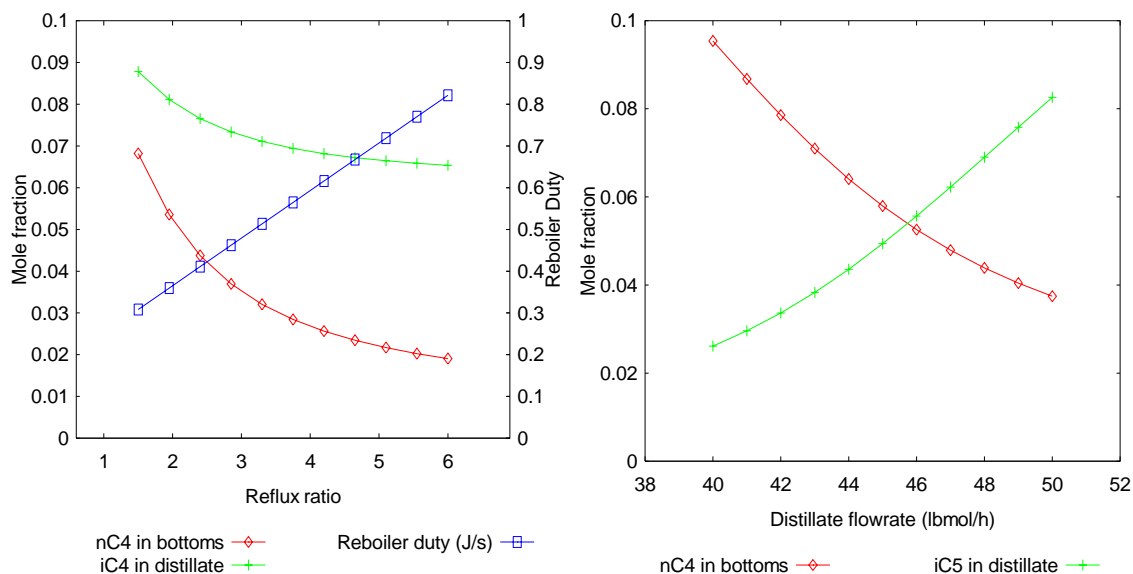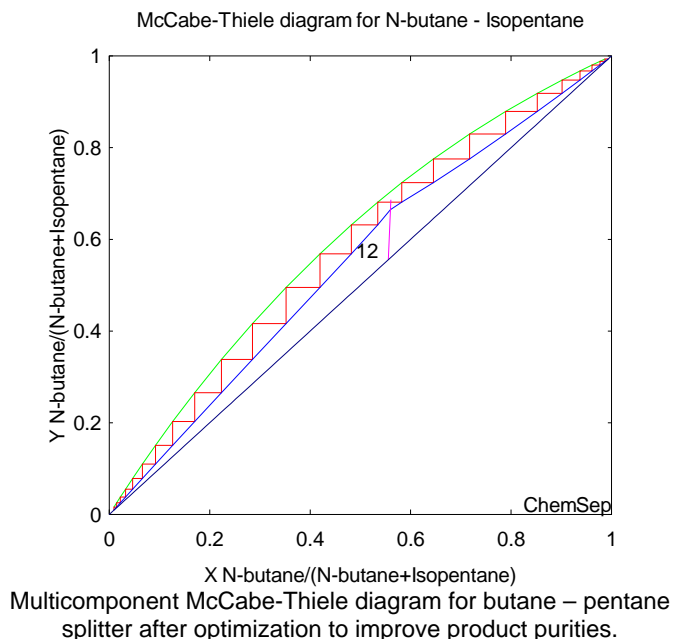

Parametric studies of product compositions as a function of reflux ratio (left) and distillate flow rate (right).

It is clear that increasing the reflux ratio has the desired effect of improving product purity. This improvement in purity is, however, accompanied by an increase in both the operating cost, indicated by the increase in reboiler duty, and capital cost, because a larger column would be needed to accommodate the increased internal flow. Note, however, that the curves that represent the mole fractions of the keys in the overhead and bottoms appear to flatten showing that product purity will not increase indefinitely as the reflux ratio increases. Further improvement in product purity can only be made by changing a different specification.

Our next step is to examine what happens to product purity when we change the specified distillate flow rate, maintaining all other specifications at the values specified in the base case. We carry out a separate parametric study (window not shown) that leads to the graph shown above right. We see that the best overall product purity is obtained when the distillate rate is 45 lbmol/h. This should not come as a surprise since the flow rate of the light key (*n*-butane) and all components with a higher volatility is 45 lbmol/h. However, even with the distillate flow rate set to 45 lbmol/h there remains room for improvement in the separation.

The other key design specifications here are the total number of stages and the location of the feed stage. In most cases, increasing the number of stages will improve the separation. On increasing the number of stages to 26, with the feed to stage 12, increasing the overhead vapor flow to 195 lbmol/h and decreasing the distillate rate to 45 lbmol/h we obtain the McCabe-Thiele diagram shown below in which the feed now appears to be in the optimum location; the product purities also have significantly improved.

McCabe-Thiele diagram for N-butane - Isopentane

Multicomponent McCabe-Thiele diagram for butane – pentane
splitter after optimization to improve product purities.

CAPE OPEN *ChemSep*

Despite considerable interest for many years, *ChemSep* has not been widely used in industry. The primary reason for the lack of commercial users is that **ChemSep** did not function well with major commercial flowsheet simulation programs. The main requirement for an industrial user is for *ChemSep* to use the thermodynamic models available in the flowsheet simulator. The protocols developed under the CAPE OPEN movement have made it possible to link make **ChemSep** function as a user model in any CAPE OPEN compliant process simulation system. This includes the ability to use the thermodynamic property packages of the favored simulation system, but ANY CAPE OPEN compliant thermodynamics package could be used with *ChemSep*. The illustration at the end of this article shows *ChemSep* used to replace a distillation column model in an HDA flowsheet in Aspen Plus.

ChemSep-Lite Now Available for Nothing!

A version of *ChemSep* with limited functionality is available for free download from www.chemsep.org/downloads/index.html. *ChemSep* Lite is limited to no more than five components, a databank with a limited number of components, no more than 50 stages in a column simulation, and no nonequilibrium model. A CAPE OPEN compliant version of ChemSep-Lite will be available from January 2006.
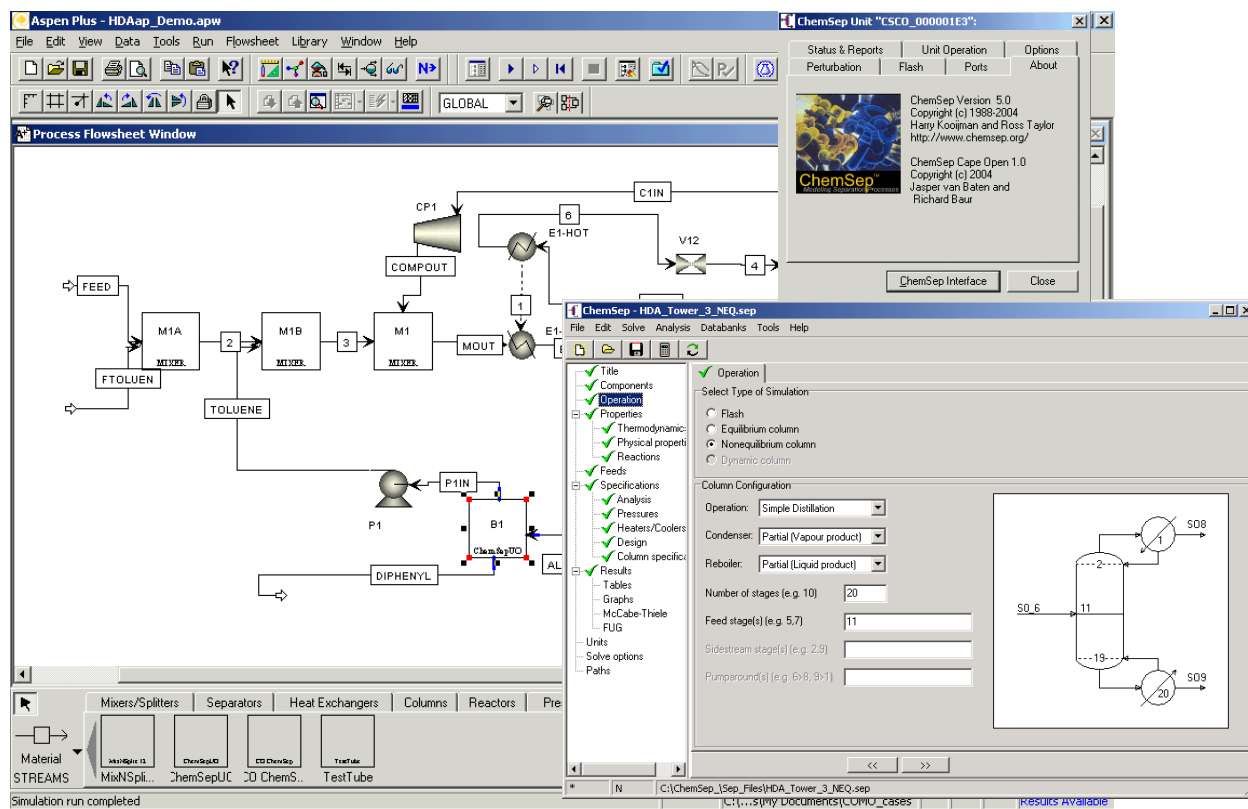
ChemSep used to replace a distillation column in an HDA flowsheet in Aspen-Plus. Background is the Aspen-Plus screen. Top right is the CAPE OPEN **ChemSep** interface through which Aspen-Plus and **ChemSep** communicate. Bottom right is the **ChemSep** program for the column that appears as a tagged square labeled ChemSepUO in the lower center of the Aspen Plus flowsheet.

Availability

ChemSep is available for educational use from the CACHE corporation (www.cache.org). For licenses for non-educational use please contact the authors.

Further Information

Additional information about the program can be found at www.chemsep.org. The authors can be contacted at kooijman@chemsep.org and taylor@chemsep.org. For more information on CAPE OPEN visit www.colan.org.