What's New in *ChemSep*™ 6.9

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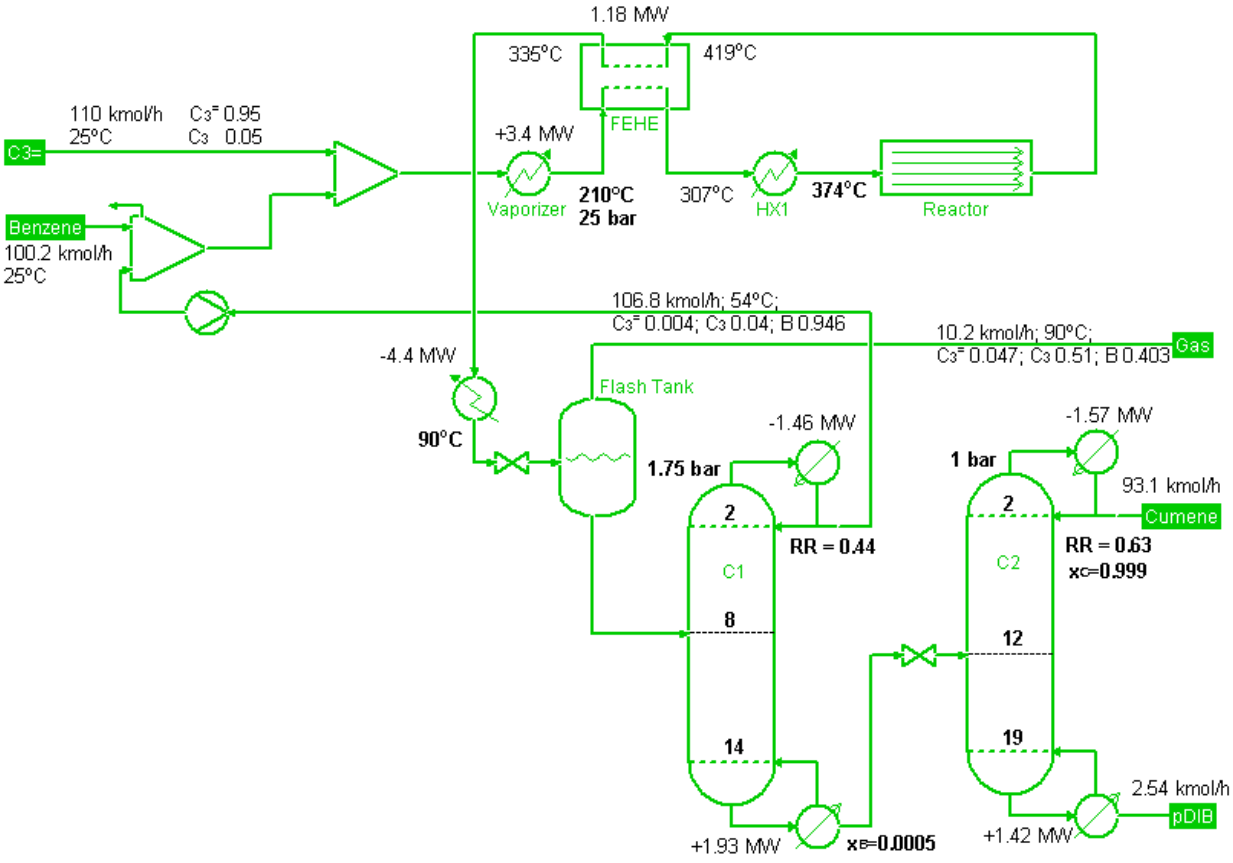
In this document we identify and describe the most important new features in ***ChemSep***.



Process Flowsheet for manufacture of Cumene
Inspired by work of W.L. Luyben (*Ind. Eng. Chem. Res. 2010,* **49**, 717-734).

New: *ChemSep* Lite now allows more compounds and more stages

New in Version 6.9 of *ChemSep* Lite is an increase in both the maximum number of compounds and the maximum number of stages allowed in a simulation. The maximum number of compounds has increased from 10 to 40 and the maximum number of stages has increased from 150 to 300.

ChemSep Lite is available free from http://chemsep.com.

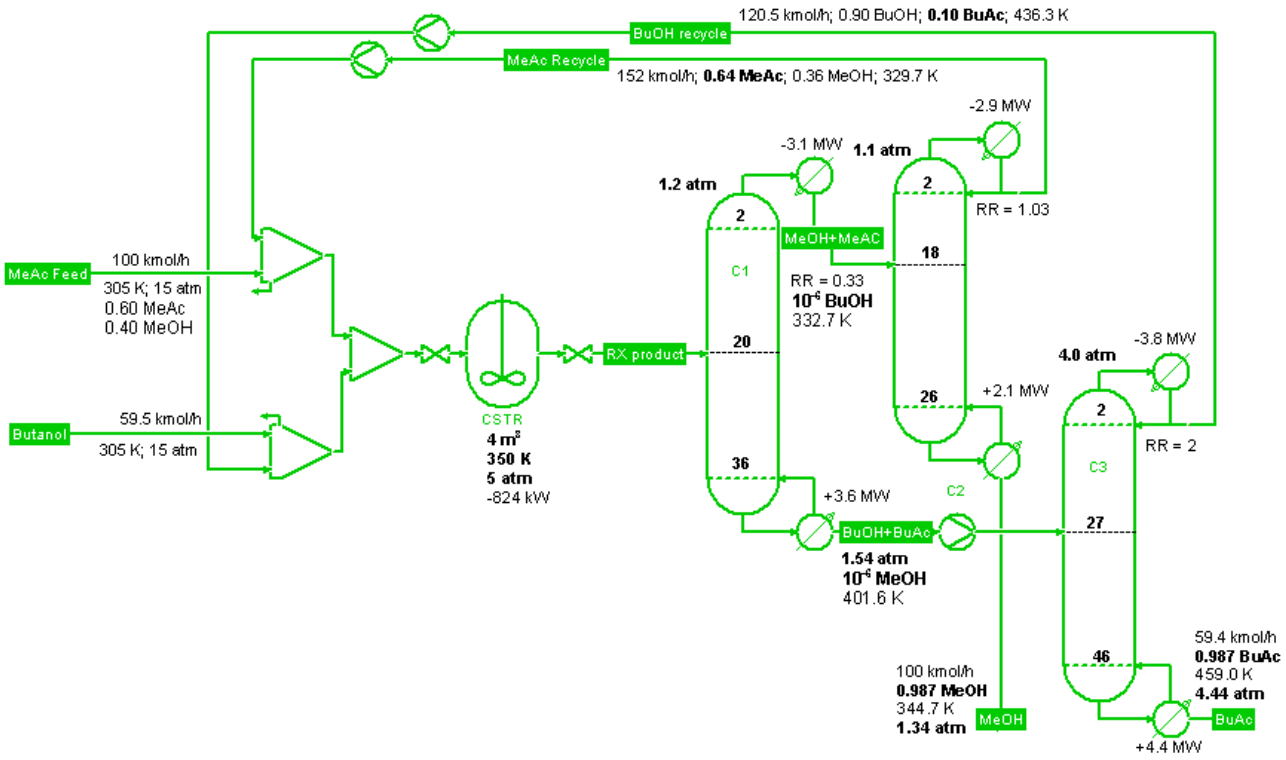
New: Process Flowsheets with COCO and *ChemSep*

We have used the COCO flowsheet simulator created by Jasper van Baten (and available free from www.cocosimulator.org) to model a series of chemical process flowsheets. The new flowsheet simulation files are available on the *ChemSep* web site (http://chemsep.com/downloads/index.html). More information is available by clicking on the graphic image on the home page of the web site.

The new flowsheets represent the following processes:

1. THF-water heat integrated separation process
2. Cumene process (shown on page 1)
3. Methanol from Syngas
4. Butyl acetate process (shown below)

Several of the older flowsheets appearing on the same page have also been updated.



Process Flowsheet for manufacture of Butyl Acetate.
Inspired by work of W.L. Luyben (*Ind. Eng. Chem. Res.* 2011, **50**, 1247–1263).

New: Peng-Robinson (1978) Model and the PPR78 Equation of State

The Peng-Robinson Equation of State (EOS) is a modification of the concepts pioneered by Soave with a view towards improving the estimates of liquid density provided by the basic EOS.

The Peng-Robinson EOS is:

$$P=\frac{RT}{V-b}-\frac{a}{V(V+b)+b(V-b)}$$

where:

$$a=a(T_c)\alpha$$
$$a(T_c)=\frac{\Omega_A R T_c^2}{P_c}$$
$$b=\frac{\Omega_B R T_c}{P_c}$$
$$\sqrt{\alpha}=1+(0.37464+1.5422\,\omega-0.26992\,\omega^2)(1-\sqrt{T_r})$$
$$\Omega_A=0.45724 \qquad \Omega_B=0.07880$$

In 1978 Peng and Robinson published a revision (shown below) to their model that now is also available in *ChemSep* (as a separate model).

$$\sqrt{\alpha}=\begin{cases} 1+(0.37464+1.5422\,\omega-0.26992\,\omega^2)(1-\sqrt{\mathrm{T_r}}) & \text{if } \omega\le 0.491 \\ 1+(0.379642+1.48503\,\omega-0.164423\,\omega^2+0.01666\,\omega^3)(1-\sqrt{\mathrm{T_r}}) & \text{if } \omega>0.491 \end{cases}$$

For mixtures the parameters are obtained from the following simple "mixing rules":

$$a=\sum_{i=1}^{c}\sum_{j=1}^{c} x_i x_j a_{i,j}$$
$$b=\sum_{i=1}^{c} x_i b_i$$

where

$$a_{i,j}=\sqrt{a_i a_j}(1-k_{i,j})$$

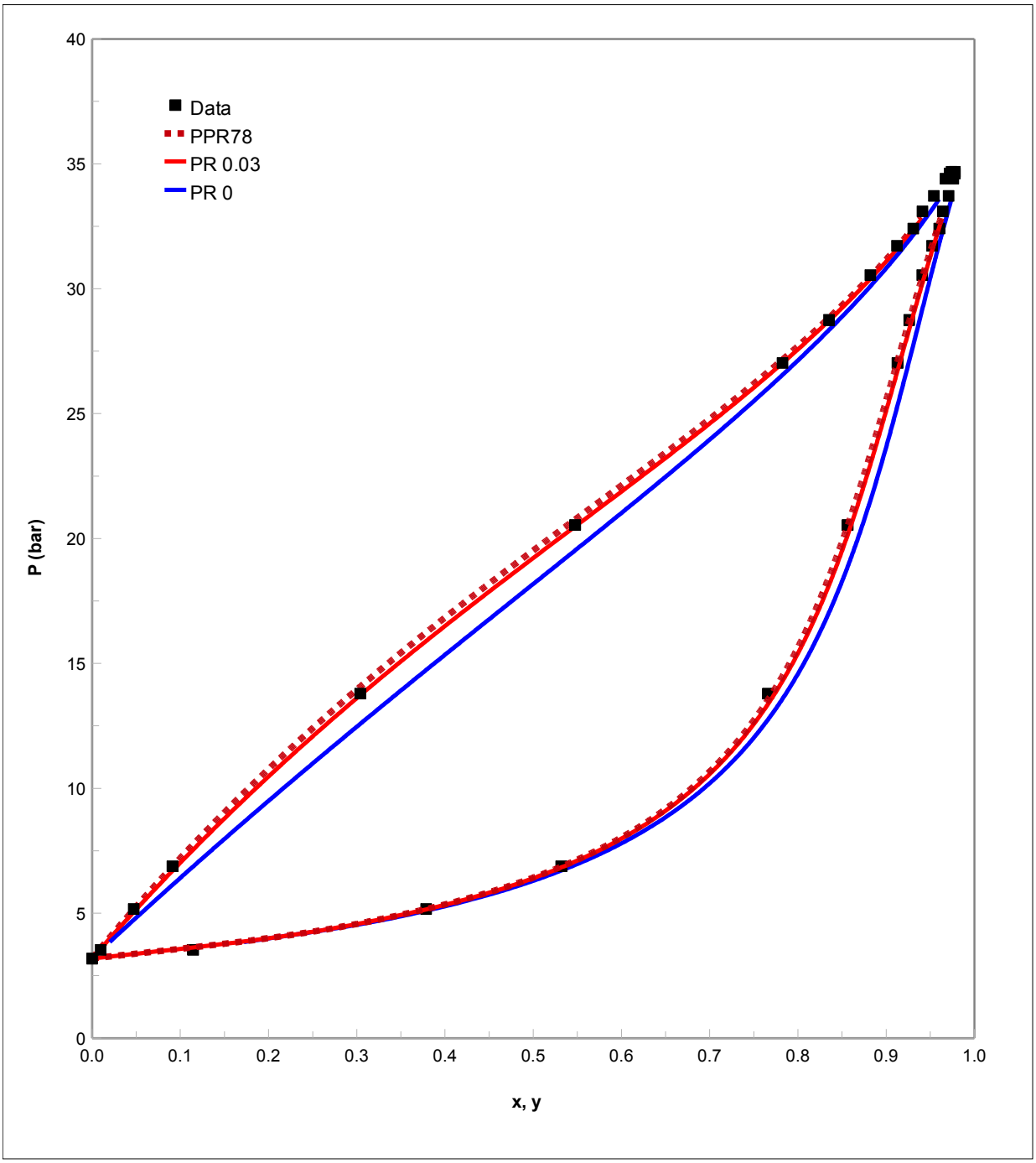
$k_{i,j}$ is the binary interaction parameter for the i-j pair of compounds.

The last few years have seen the development of what has been called the Predictive Peng-Robinson Model or PPR78 by Jaubert and Colleagues from Nancy in France. The PPR78 model uses the 1978 version of the Peng-Robinson EOS as the basis to which is added a group contribution method for estimating the binary interaction parameters as a function only of temperature. The equations are too complicated to be summarized here; readers are referred the original literature for details. The PPR78 model may be selected from the Equation of State pull down menu on the Thermodynamics panel.

Note that the PPR78 model can predict binary interaction parameters only for mixtures containing the following compounds (or groups of compounds):

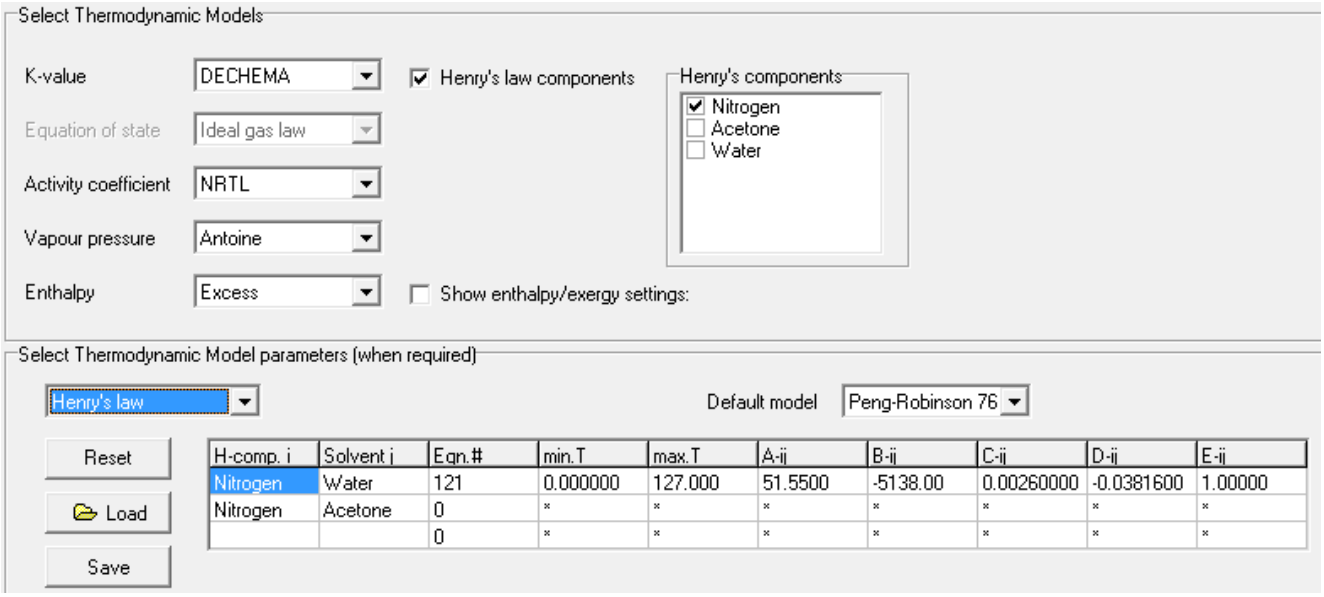
1. Aliphatic hydrocarbons including methane and branched chain alkanes.
2. Aromatic and cyclic hydrocarbons.
3. Mercaptans
4. Nitrogen and carbon dioxide

The illustrations below shows a phase envelope for a mixture of nitrogen and methane predicted by the PPR78 model alongside the standard PR equation of state. The numbers next to the letters PR refer to the value of the binary interaction parameter used for that particular calculation.



New: Henry's Law

While it was always possible to use Henry's law in older versions of ChemSep, it was never explicitly clear to users exactly how to do this. Thus, starting with version 6.9 and, as shown with the blue highlight in the screen image above, we have added a way to identify those compounds that are to be treated using Henry's law. Click in the checkbox to the left of words *Henry's law components* to bring up a checklist of all of the compounds in the system:



To select those compounds to be treated using Henry's law simply click in the check box to the left of each Henry's compound. The illustration also shows that we have loaded coefficients for the estimation of the Henry's law "constant" for nitrogen in water (but not yet for nitrogen in acetone).

Equilibrium for a Henry's law compound may be represented by:

$$P\, y_i \phi_i^V = H_i x_i \gamma_i^*$$

where the unsymmetrical activity coefficient is defined by:

$$\gamma_i^* = \gamma_i / \gamma_i^\infty$$

where γ_i^∞ is the activity coefficient at infinite dilution. In terms of the conventional K-value:

$$K_i = \frac{y_i}{x_i} = \frac{H_i \gamma_i^*}{\phi_i^V P} = \frac{H_i \gamma_i / \gamma_i^\infty}{\phi_i^V P}$$

The Henry's law constant for a mixed solvent *ChemSep* uses the model implemented by Zhang and Chen:

$$\ln\left(\frac{H_i}{\gamma_i^\infty}\right) = \sum_A w_A \ln\left(\frac{H_{i,A}}{\gamma_{i,A}^\infty}\right)$$

where w_A is a volume fraction and the summation is taken over the solvent species only.
The Henry's law coefficients in pure solvents (on the right hand side of the above) are given by:

$$H_{i,a}(T,P) = H_{i,A}(T,P_A^{sat}) \ \exp\left(\frac{1}{RT}\int_{P_A^{sat}}^{P} \bar{V}_{i,A} \ dp\right)$$

The Henry's law constants are evaluated at the vapor pressure of the pure solvents and then corrected by the Poynting factors (the exponential term on the right hand side above). In practice the Henry's law coefficients on the right hand side are most often correlated as a function only of temperature, the form shown below being most common:

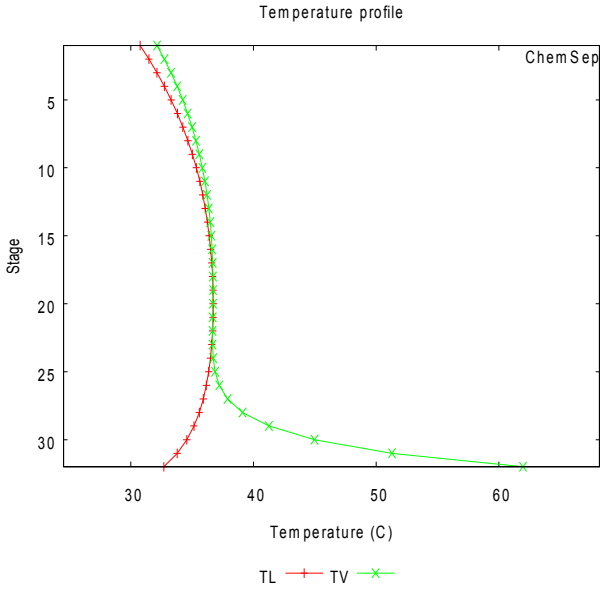
This fairly general form of Henry's law simplifies considerably in many cases. For example, if there is only one solvent (often the case), the activity coefficient for the solute (nitrogen in this case) is assumed to be unit, and the Poynting factor is ignored then:

$$K_i = \frac{y_i}{x_i} = \frac{H_i}{P}$$

This is the form of Henry's law used most often in practice. The Henry's law coefficients can be estimated from any of the many different temperature dependent functions in *ChemSep.* A commonly used representation of Henry's law data is:

$$\ln H = A + B/T + C\ln T + DT^E$$

Below we show the temperature profiles in a packed acetone absorber. The column is 4.5m in height and is filled with IMTP 25 packing. It should be noted that the shape of the temperature profiles is a strong function of the water (solvent) flow rate.

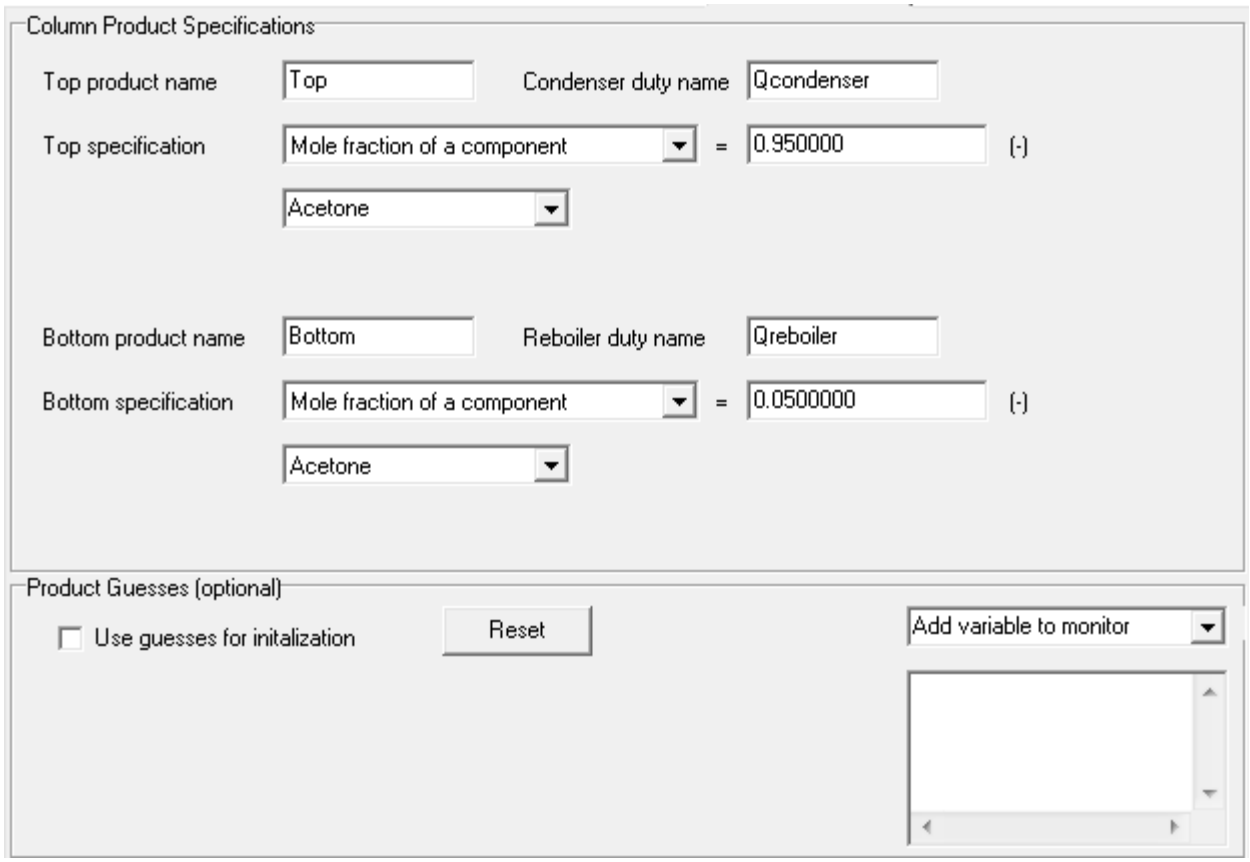


A more comprehensive demonstration of the application of Henry's law to model an acetone absorber, along with a discussion of the shape of the temperature profiles seen in the above illustration is available in a tutorial on the *ChemSep* web site.

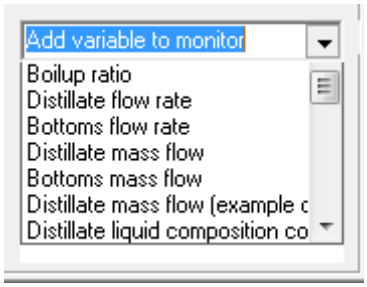
New: Variable Monitor

In *ChemSep* 6.9 it is possible to monitor the values of any column variable (flow rate, mole fraction, temperature, pressure, on any stage) as well as the values of certain key specified parameters such as the reflux ratio that are defined combinations of specified variables.

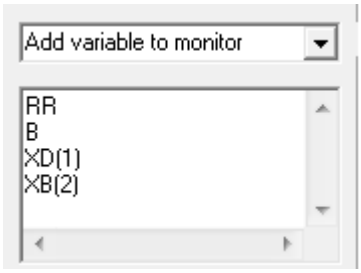
The selection of the monitored variables can be made on the *Column Specifications* panel, an example of which is shown below:



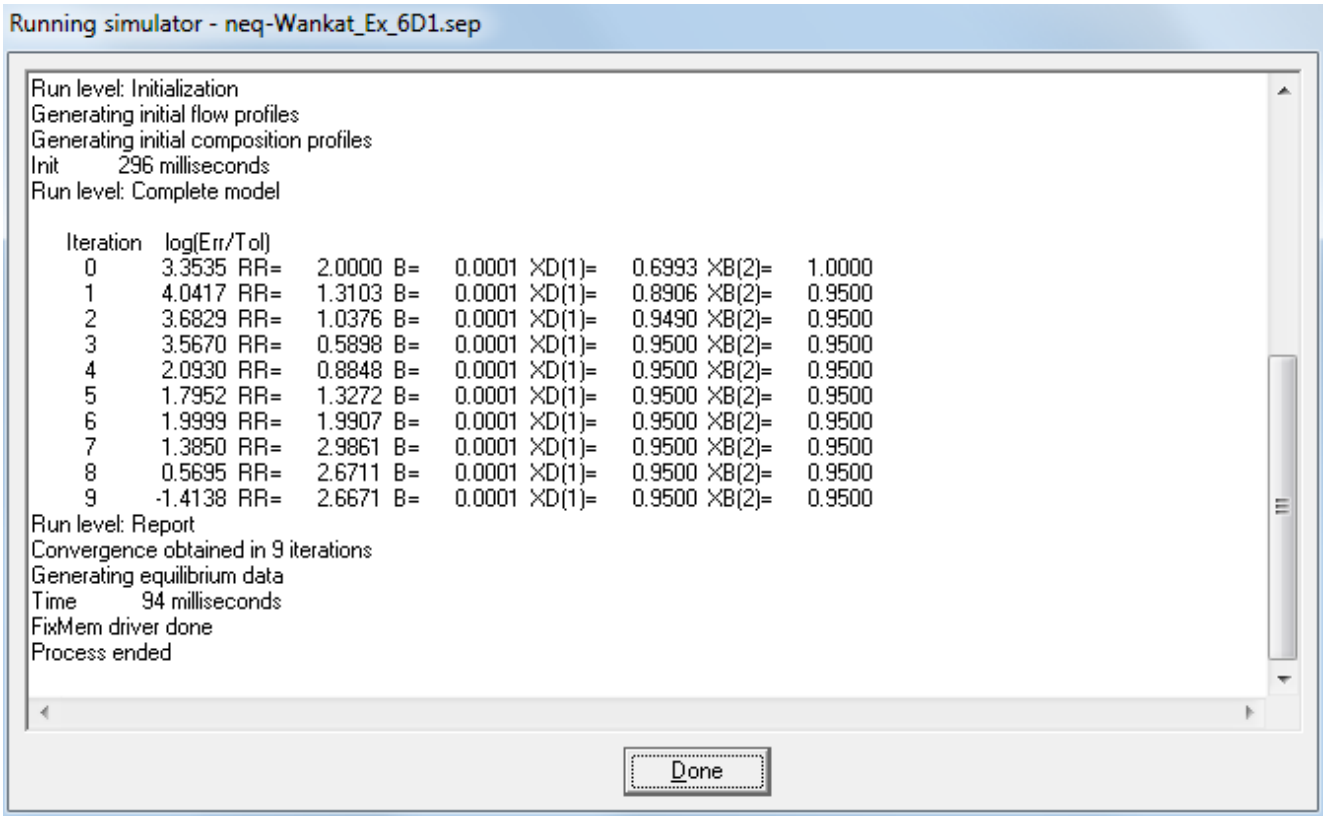
Click on the pull down arrow in the lower-right quadrant to select from a list of variables:



It is possible to select up to four variables to display during the solution. Here we have chosen the reflux ratio, the bottoms flow rate and the mole fraction of acetone in the distillate (which is one of the target specifications as shown above) and the mole fraction of isopropanol in the bottoms (which is the other – by implication anyway):



Now, when the file is executed you will see something similar to that shown below:



Each of the monitored variables appears following the = sign, to the left of which is some indication of the variable displayed. Thus, RR = Reflux Ratio, B = Bottoms flow rate, XD(1) is the mole fraction of component 1 in the distillate, and XB(2) is the mole fraction of component 2 in the bottoms product.

Monitoring variables in this way is instructive, as well as providing a useful tool to help diagnose what is happening in a simulation that is hard (or impossible) to converge.

New: 400+ Compound Database

The number of compounds in the database has been increased from 194 (in versions up to 6.8) to 423. A complete list of the compounds that have been added to the ChemSep databank appears below.

Compounds Added to ChemSep Database

2-methyl-2-butanol
Nitrogen trioxide
Nitrogen tetroxide
Helium-4
Fluorine
Krypton
Xenon
Ozone
Carbonyl sulfide
Sulfur hexafluoride
Dimethyl sulfoxide
N-heptadecane
N-octadecane
N-nonadecane
N-heneicosane
N-docosane
N-tricosane
N-tetracosane
N-pentacosane
N-hexacosane
N-heptacosane
N-octacosane
N-nonacosane
Squalane
2-methylhexane
3-methylhexane
3-ethylpentane
2,2-dimethylpentane
2,3-dimethylpentane
2,4-dimethylpentane
3,3-dimethylpentane
2,2,3-trimethylbutane
2-methylheptane
3-methylheptane
4-methylheptane
3-ethylhexane
2,2-dimethylhexane
2,3-dimethylhexane
2,4-dimethylhexane
2,5-dimethylhexane
3,3-dimethylhexane
3,4-dimethylhexane
2-methyl-3-ethylpentane
3-methyl-3-ethylpentane
2,2,3,3-tetramethylbutane
2,2,5-trimethylhexane
2,4,4-trimethylhexane
3,3-diethylpentane
2,2,3,3-tetramethylpentane
2,2,3,4-tetramethylpentane
2,2,4,4-tetramethylpentane
2,3,3,4-tetramethylpentane
2-methyloctane
3-methyloctane
4-methyloctane
3-ethylheptane
2,2-dimethylheptane
3,3,5-trimethylheptane
2,2-dimethyloctane
3-methylnonane
2-methylnonane
4-methylnonane
5-methylnonane
Cis-2-hexene
Trans-2-hexene
1-octene
1-nonene
1-undecene
2-methyl-1-pentene
4-methyl-cis-2-pentene
4-methyl-trans-2-pentene
Cyclohexene
1,1-dimethylcyclopentane
Cis-1,2-dimethylcyclopentane
Trans-1,2-dimethylcyclopentane
Cis-1,3-dimethylcyclopentane
Trans-1,3-dimethylcyclopentane
Isopropylcyclopentane
1-methyl-1-ethylcyclopentane
N-butylcyclopentane
1,1-dimethylcyclohexane
Cis-1,2-dimethylcyclohexane
Trans-1,2-dimethylcyclohexane
Cis-1,3-dimethylcyclohexane
Trans-1,3-dimethylcyclohexane
Cis-1,4-dimethylcyclohexane
Trans-1,4-dimethylcyclohexane
Tert-butylcyclohexane
O-ethyltoluene
M-ethyltoluene
P-ethyltoluene
1,2,3-trimethylbenzene
1,2,4-trimethylbenzene
Mesitylene
Isobutylbenzene
Sec-butylbenzene
Tert-butylbenzene
O-cymene
M-cymene
P-cymene
O-diethylbenzene
M-diethylbenzene
P-diethylbenzene
1,2,3,4-tetramethylbenzene
1,2,3,5-tetramethylbenzene
1,2,4,5-tetramethylbenzene
2-ethyl-m-xylene
2-ethyl-p-xylene
4-ethyl-m-xylene
4-ethyl-o-xylene
1-methyl-3-n-propylbenzene
1-methyl-4-n-propylbenzene
P-diisopropylbenzene
Methyl isobutyl ketone
3-heptanone
4-heptanone
3-hexanone
2-pentanone
2-hexanone
2-heptanone
5-methyl-2-hexanone
3,3-dimethyl-2-butanone
Diisobutyl ketone
Diisopropyl ketone
Propanal
Butanal
Pentanal
Hexanal
Heptanal
Diisopropyl ether
Di-n-butyl ether
Di-sec-butyl ether
Methyl ethyl ether
Methyl n-propyl ether
Isopropyl butyl ether
Methyl isobutyl ether
Methyl isopropyl ether
Tert-butyl ethyl ether
Ethyl tert-pentyl ether
Butyl vinyl ether
Anisole
Isopropyl acetate
N-butyl acetate
Isobutyl acetate
N-pentyl acetate
Vinyl acetate
N-hexyl acetate
1-pentanol
2-pentanol
2-methyl-1-butanol

2,2-dimethyl-1-propanol
1-hexanol
1-heptanol
1,4-butanediol
Methyl mercaptan
N-propyl mercaptan
Tert-butyl mercaptan
Isobutyl mercaptan
Sec-butyl mercaptan
N-hexyl mercaptan
Methyl ethyl sulfide
Methyl n-propyl sulfide
Methyl t-butyl sulfide
Methyl t-pentyl sulfide
Di-n-propyl sulfide
Diethyl sulfide
Diethyl disulfide
Dimethyl disulfide
Di-n-propyl disulfide
Di-tert-butyl disulfide
Ethyl methyl disulfide
Ethyl propyl disulfide
Diphenyl disulfide
Monoethanolamine
Diethanolamine
Triethanolamine
Ethylenediamine
Diisopropylamine
N-aminoethyl piperazine
Diethylenetriamine
N-aminoethyl ethanolamine
P-phenylenediamine
Piperazine
Methylethanolamine
Dimethylethanolamine
Nitromethane
Nitroethane
1-nitropropane
2-nitropropane
1-nitrobutane
O-nitrotoluene
P-nitrotoluene
M-nitrotoluene
2,4-dinitrotoluene
2,6-dinitrotoluene
3,4-dinitrotoluene
2,5-dinitrotoluene
3,5-dinitrotoluene
2,4,6-trinitrotoluene
Oxalic acid
Acrylic acid
Methacrylic acid
Benzoic acid
O-toluic acid
P-toluic acid
Salicylic acid
Adipic acid
Phthalic acid
Maleic acid
Terephthalic acid
Acetic anhydride
Maleic anhydride
Ketene
Methyl methacrylate
Dimethyl terephthalate
1,2-propylene oxide
Cumene hydroperoxide
Propionitrile
Dimethyl carbonate
DiEthyl Carbonate
Methyl Ethyl Carbonate
Methyl Phenyl Carbonate
Ethyl Phenyl Carbonate
DiPhenyl Carbonate
Ethylene carbonate
Propylene carbonate
2-methyl-1-heptene
2-Methoxy-2-Methyl-Heptane
2-Methyl-2-Heptanol
Methylal