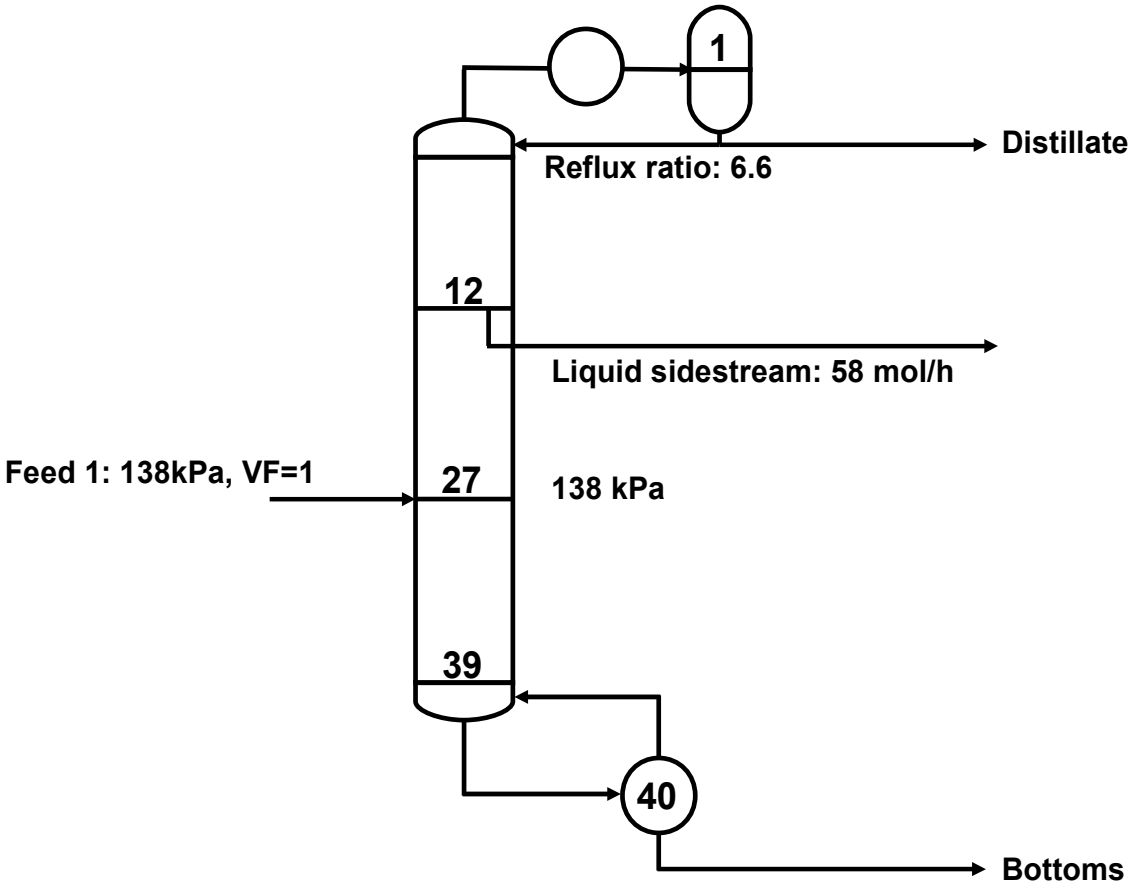
# ChemSep Tutorial: Distillation with Hypothetical Components

Harry Kooijman and Ross Taylor

Here we use *ChemSep* to solve a complex multicomponent distillation problem presented in a paper entitled *Multistage Multicomponent Separation Calculations using Thermodynamic Properties Evaluated by the SRK/PR Equation of State*, by M.K. Shah and P.R. Bishnoi (*Canadian Journal of Chemical Engineering*, **56**, pp478-486).

The specifications for this problem provided in the paper cited are summarized in the figure below.




This column is used to recover a paraffin cut from straight kerosene. The feed is a mixture of "hypothetical" compounds with the following flowrates:

| Mole flows (mol/h) | |
|---|---|
| Hyp-A | 12.900 |
| Hyp-B | 11.600 |
| Hyp-C | 5.550 |
| Hyp-D | 5.200 |
| Hyp-E | 10.500 |
| Hyp-F | 10.030 |
| Hyp-G | 9.650 |
| Hyp-H | 9.370 |
| Hyp-I | 8.770 |
| Hyp-J | 5.080 |
| Hyp-K | 3.340 |
| Hyp-L | 7.980 |

Shah and Bishnoi do not actually specify a time unit in their paper; all flows are given in mol. We have assumed a time unit of one hour here, but note that all relative flows are unchanged by this arbitrary choice.

The specifications made in this case are summarized in the table below:

| Variable | Number | Value |
|---|---|---|
| Number of stages | 1 | 40 |
| Feed stage locations | 1 | 27 |
| Component flows in feed 1 | $c = 12$ | See table above |
| Feed 1 pressure | 1 | 138 kPa |
| Feed 1 vapor fraction | 1 | 1 |
| Pressure on all stages | $N = 40$ | 138 kPa |
| Heat duty on all other stages except reboiler and condenser | $N - 2 = 38$ | 0 |
| Reflux ratio | 1 | 6.6 |
| Liquid sidestream flow from stage 3 | 1 | 58 mol/h |
| Total | 96 | |

In addition, we have assumed that the pressure of the reflux divider is the same as the pressure of the condenser, the heat loss from the reflux divider is zero, and the reflux temperature is the boiling point of the condensed overhead vapor.

The number of variables specified above is one less than is actually required to satisfy the total number of degrees of freedom for this column. Shah and Bishnoi do not state their final specification; we have, therefore chosen to specify the bottoms flow rate to be consistent with the values given in their stream table.

**Property Data Creation**

To proceed we must first create a databank of the properties of the various hypothetical compounds that make up the mixture to be separated in this column. Shah and Bishnoi tell us that the feed mixture is divided into twelve hypothetical components based on its True Boiling Point (TBP) curve and these components have the derived properties shown in the table below.

| Name | Tb (C) | API Gravity | Tb (K) | SG |
|---|---|---|---|---|
| Hyp-A | 126 | 56.92 | 399.15 | 0.75 |
| Hyp-B | 156 | 53.23 | 429.15 | 0.77 |
| Hyp-C | 170 | 51.08 | 443.15 | 0.78 |
| Hyp-D | 178 | 50.14 | 451.15 | 0.78 |
| Hyp-E | 186 | 48.98 | 459.15 | 0.78 |
| Hyp-F | 198 | 47.61 | 471.15 | 0.79 |
| Hyp-G | 212 | 46.26 | 485.15 | 0.8 |
| Hyp-H | 224 | 44.71 | 497.15 | 0.8 |
| Hyp-I | 238 | 44.06 | 511.15 | 0.81 |
| Hyp-J | 245 | 42.33 | 518.15 | 0.81 |
| Hyp-K | 257 | 40.64 | 530.15 | 0.82 |
| Hyp-L | 280 | 38.16 | 553.15 | 0.83 |

The first three columns of this table are directly from the paper by Shah and Bishnoi, the fourth column represents the conversion of the normal boiling point in Celcius (column 2) to Kelvin. The fifth column contains the results of the conversion of the API gravity in column 3 to the specific gravity from the formula:

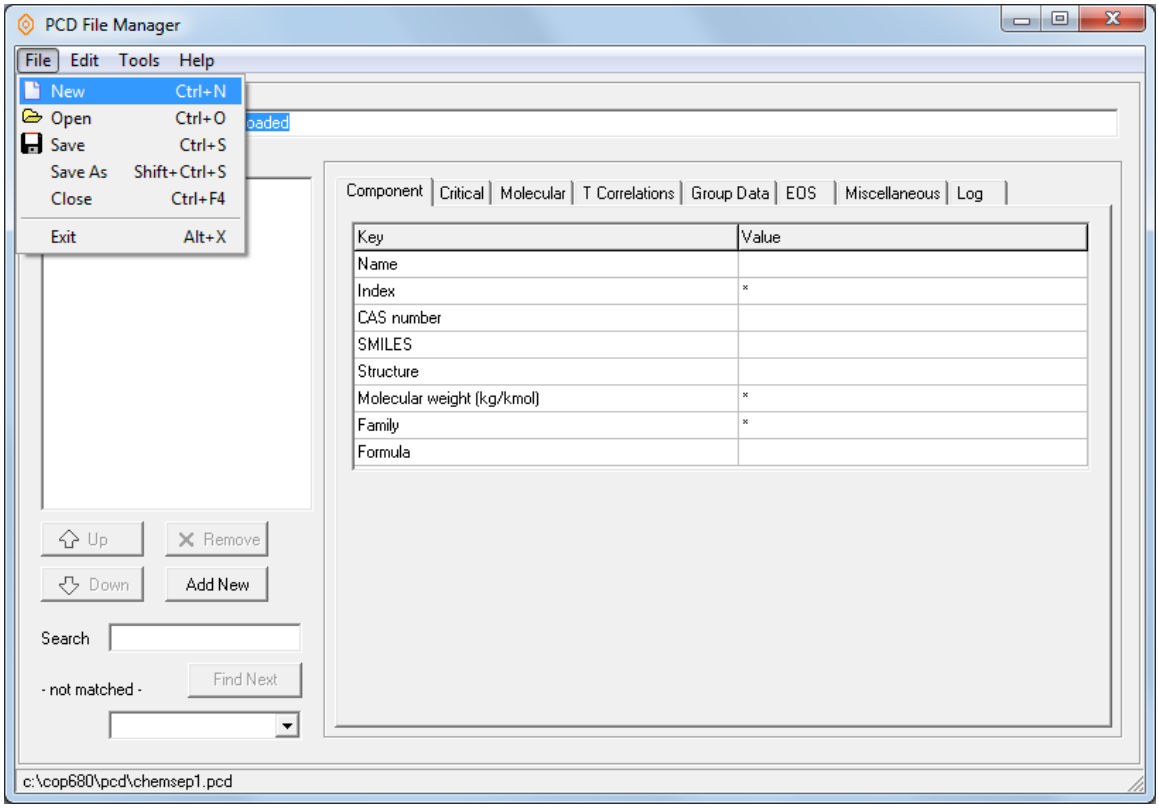
$$SG = \frac{141.5}{API + 131.5}$$

The reasons for carrying out this conversion will soon become clear.

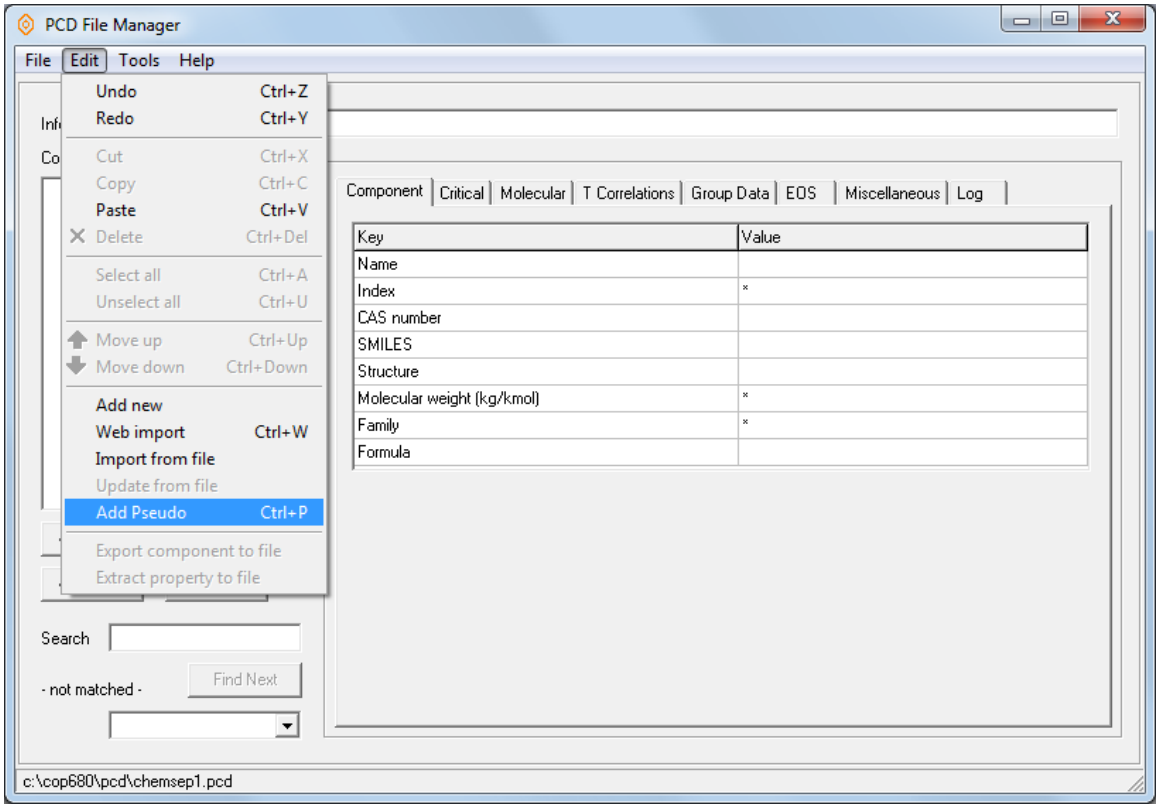
Modeling a system such as this using the Peng-Robinson or SRK equations of state – which is what we are about to do – requires the creation of a databank with the necessary physical properties. This includes the critical temperature and pressure, the acentric factor, and the ideal gas heat capacity, for example.

ChemSep can create the necessary databank for us given the information in the table above.

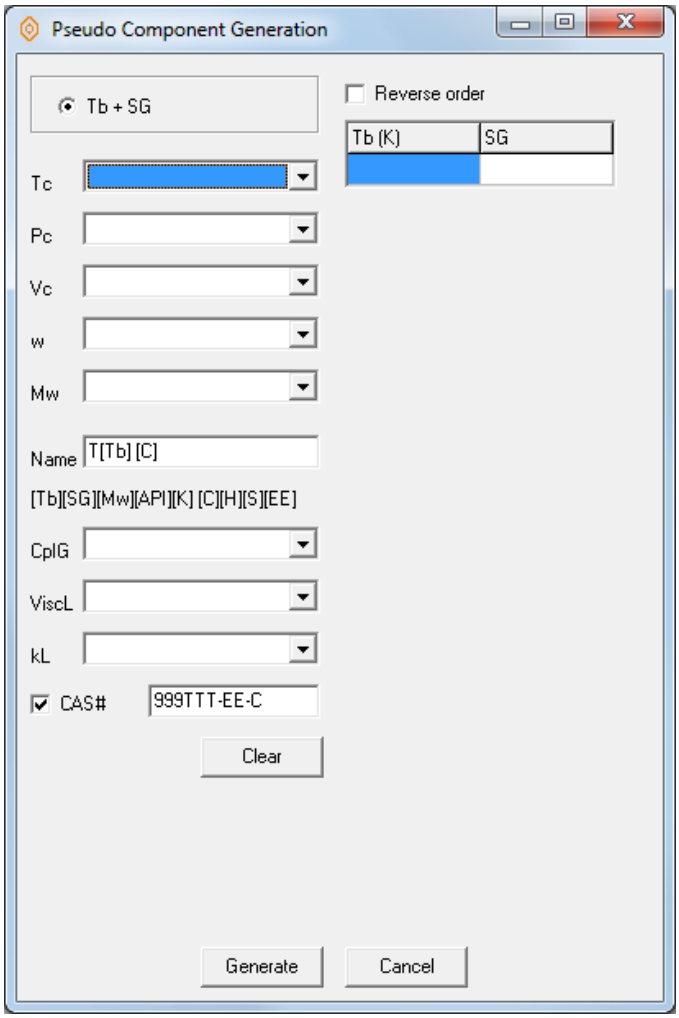
Start the Pure Compound Data (PCD) manager by clicking on the PCD manager icon (the benzene ring). Click on *File* and then click *New* to create a completely new databank (we do not advocate adding hypothetical compounds to the existing databank of data for real compounds).




Next, click on ***Edit*** and then on *Add Pseudo*:

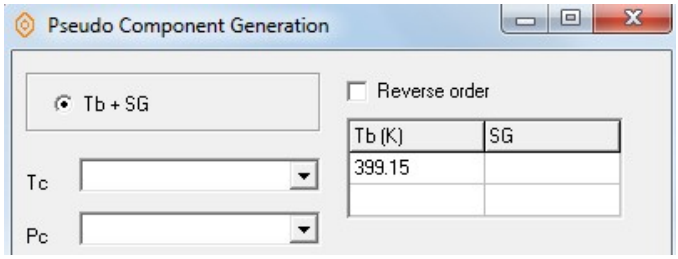


This brings up a separate panel that will allow us to add pseudo-compounds or hypothetical compounds to the databank:




Now we need to record the normal boiling point and specific gravity of our collection of hypothetical compounds given in the table above (now it will be clear why it was necessary to convert the boiling point data to Kelvin and the API gravity to specific gravity).

To enter this information click in the table to the upper right of the panel shown above and start typing. Every time you type something new in the first line a new line will appear below it, ready for the data for the next hypothetical compound:

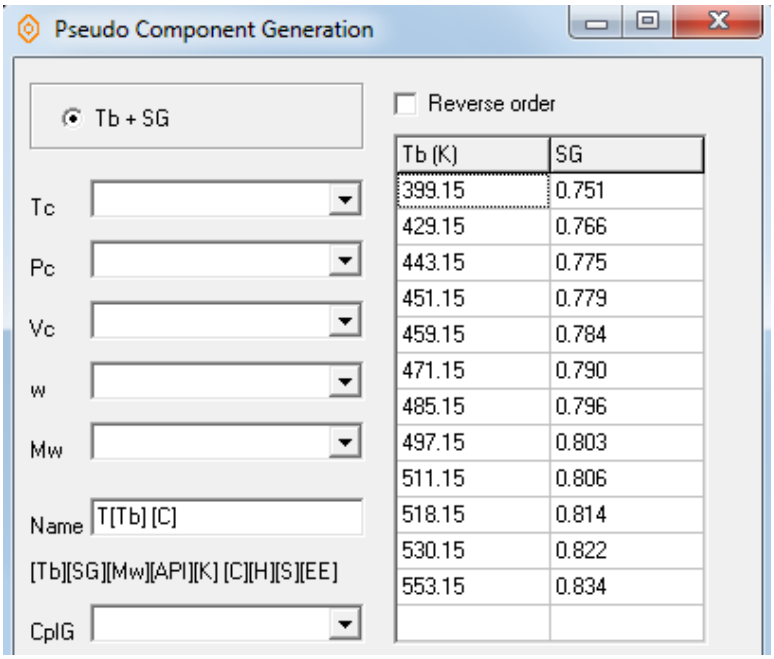


There is, however, a quicker way to record the data if we have used a spreadsheet program to record the basic data and do any necessary data conversions (as we have for this problem).

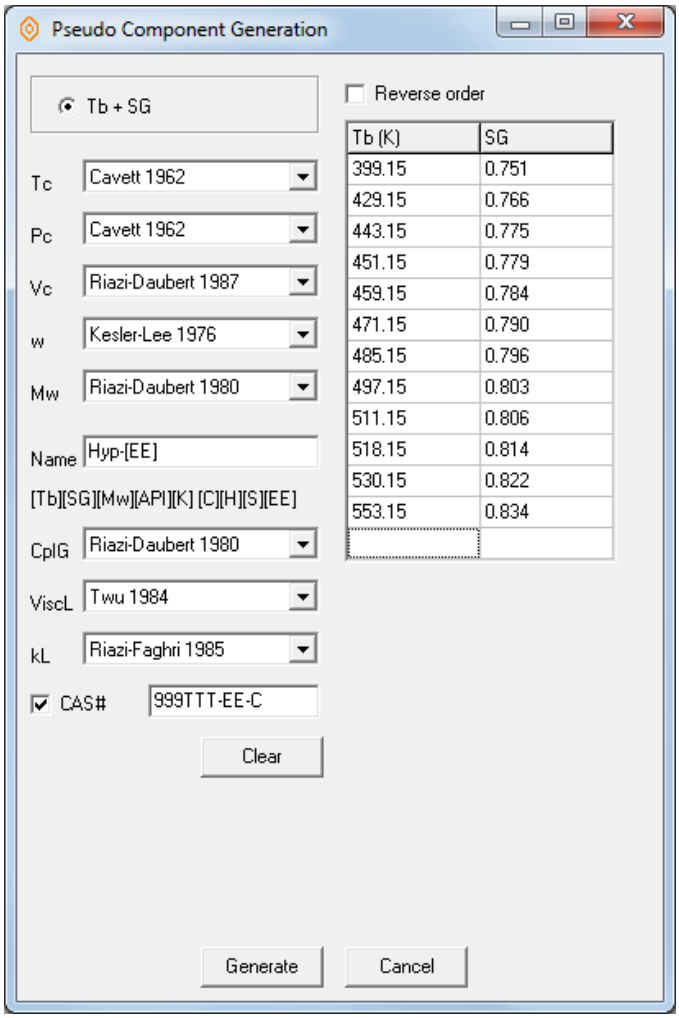
Highlight the block of relevant data in the spreadsheet:

| | A | B | C | D | E |
|---|---|---|---|---|---|
| 1 | | | | | |
| 2 | | Tb(C) | API | Tb (K) | SG |
| 3 | Hyp-A | 126.0 | 56.92 | 399.15 | 0.751 |
| 4 | Hyp-B | 156.0 | 53.23 | 429.15 | 0.766 |
| 5 | Hyp-C | 170.0 | 51.08 | 443.15 | 0.775 |
| 6 | Hyp-D | 178.0 | 50.14 | 451.15 | 0.779 |
| 7 | Hyp-E | 186.0 | 48.98 | 459.15 | 0.784 |
| 8 | Hyp-F | 198.0 | 47.61 | 471.15 | 0.790 |
| 9 | Hyp-G | 212.0 | 46.26 | 485.15 | 0.796 |
| 10 | Hyp-H | 224.0 | 44.71 | 497.15 | 0.803 |
| 11 | Hyp-I | 238.0 | 44.06 | 511.15 | 0.806 |
| 12 | Hyp-J | 245.0 | 42.33 | 518.15 | 0.814 |
| 13 | Hyp-K | 257.0 | 40.64 | 530.15 | 0.822 |
| 14 | Hyp-L | 280.0 | 38.16 | 553.15 | 0.834 |
| 15 | | | | | |

Press *Ctrl-C* and click in the first cell of the table to the top right of the *Pseudo Component Generation* panel. Then press *Ctrl-V.*



The next task is to select the methods to be used to estimate the properties listed on the left hand half of this panel. Shah and Bishnoi report using the method of Cavett for the critical temperature and pressure, but they do not tell us what they used for the acentric factor or for any of the other properties. The image below shows what we used for this exercise:

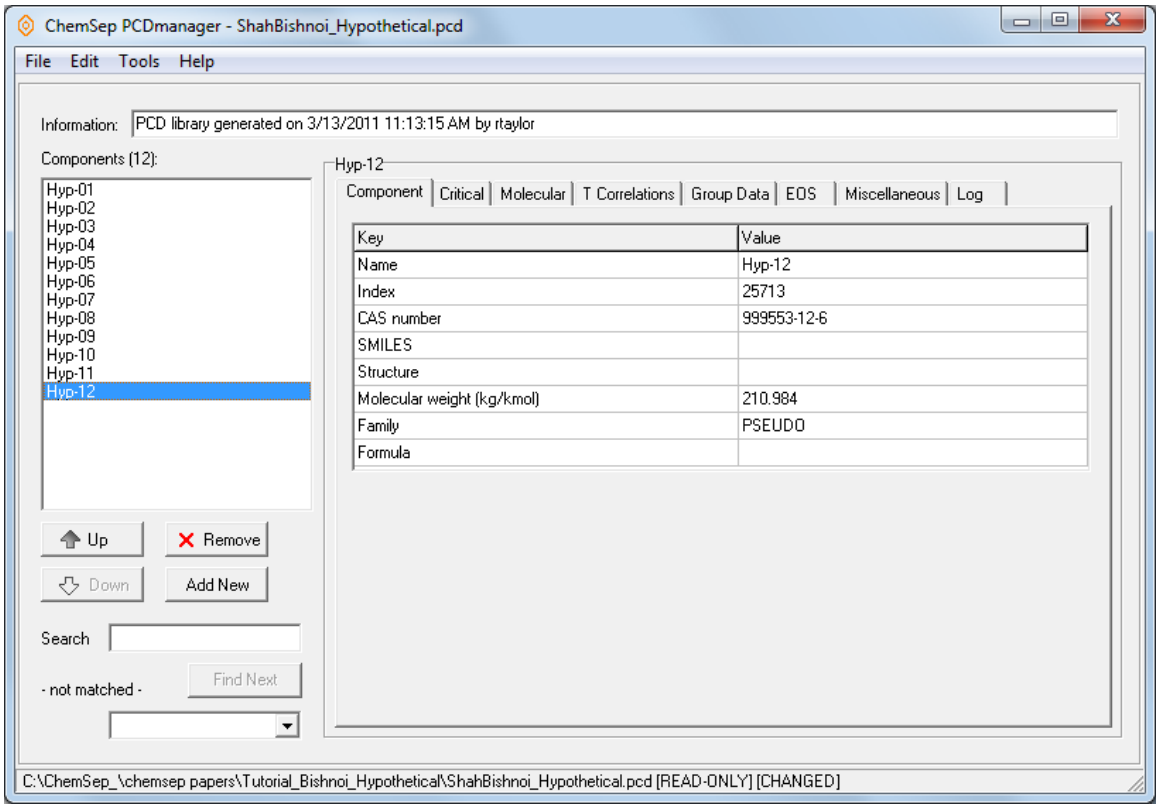



Note, in particular, the cell labeled *Name*. This cell specifies how the hypothetical compounds will be named in the data file soon to be created. Compound names can be generated using a variety of labels including:

Normal boiling point – [Tb]
Specific gravity – [SG]
Molecular weight – [Mw]
API gravity – [API]
Numerical exponent (01, 02, etc) – [EE]

In this case we have elected to name the compounds Hypo-EE where the EE is the sequence of numbers starting at 01.

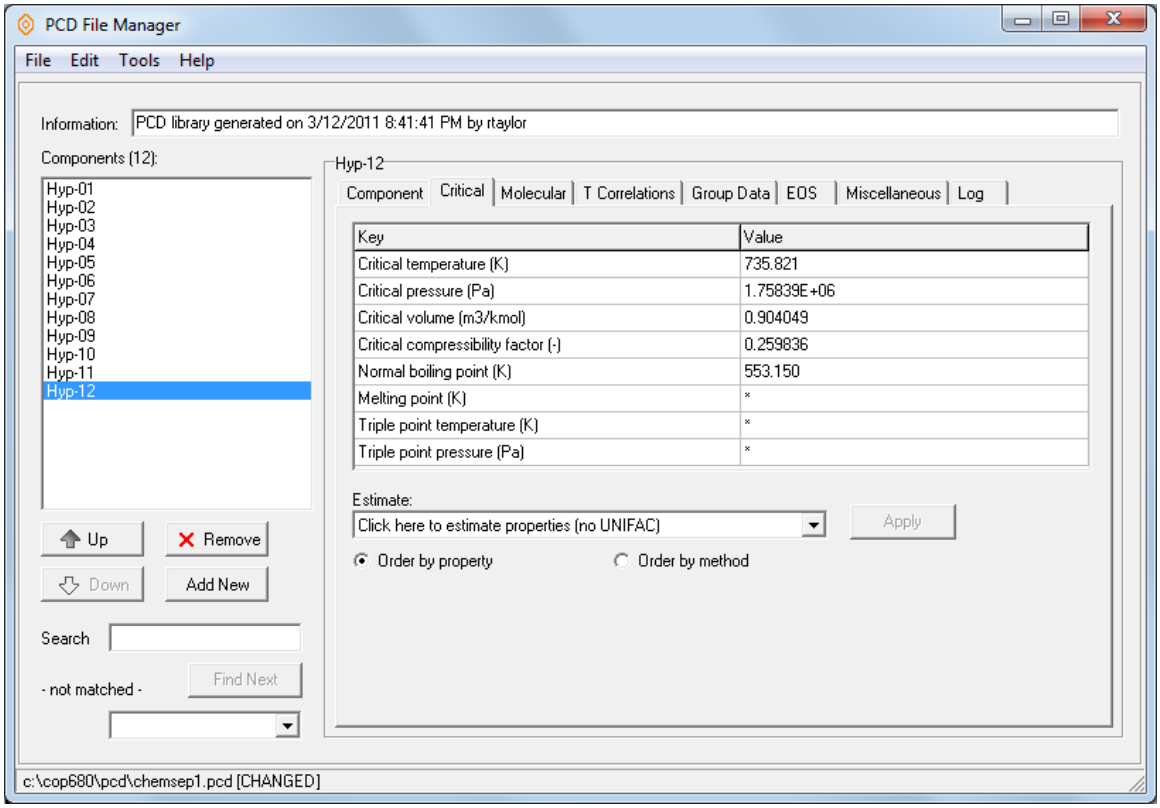
Click on the button *Generate* to close this window and create the compound data records which will appear in *PCDmanager* as shown below:

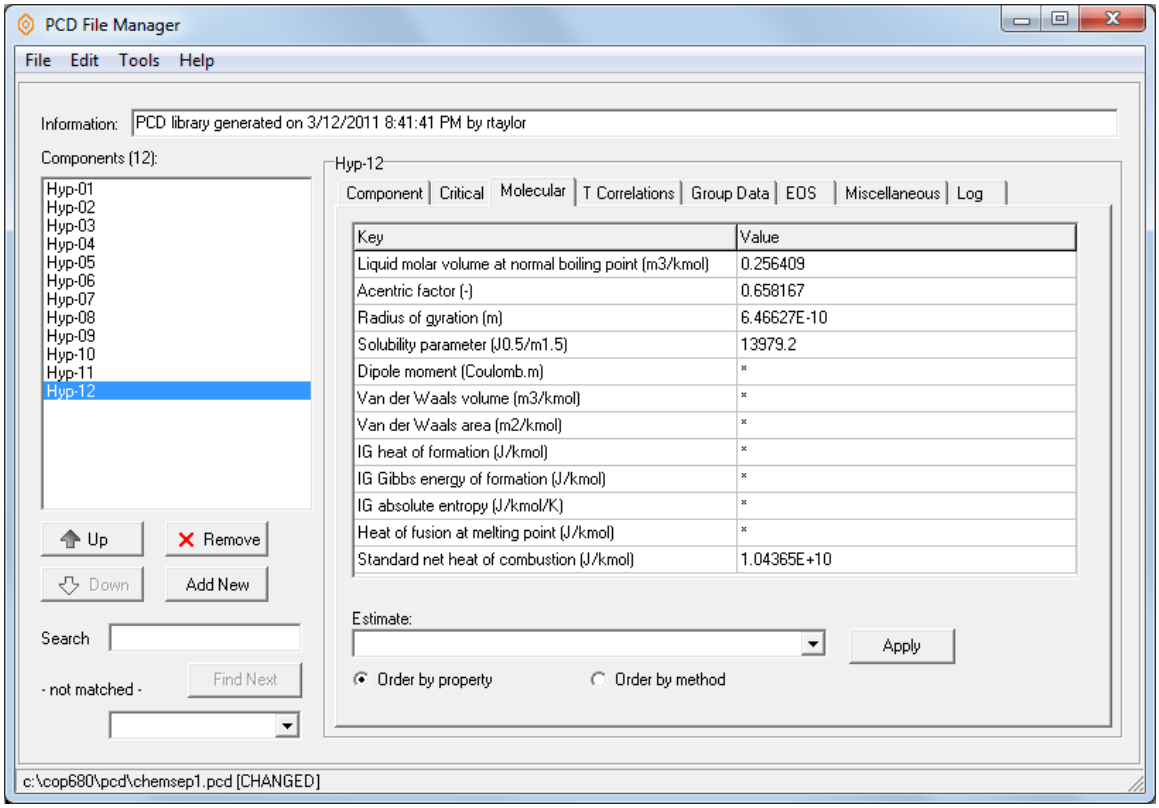


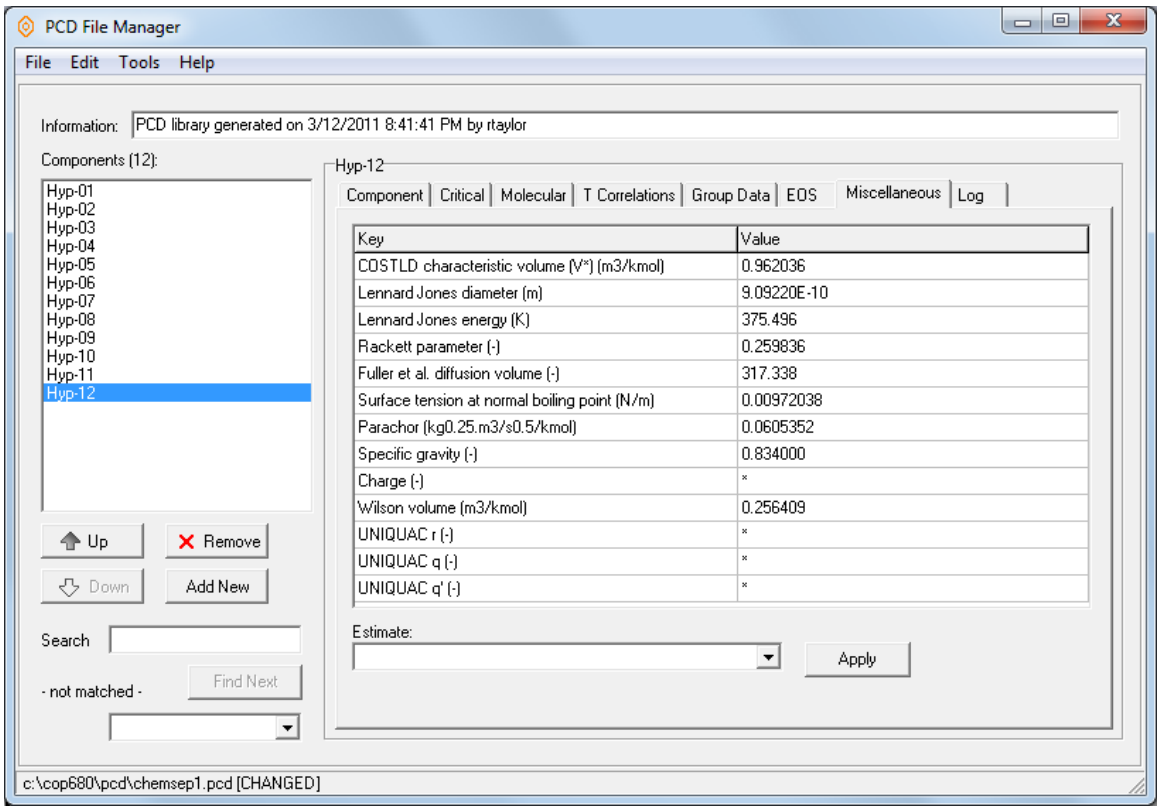

Note the list of compound names in the panel to the left of the screen above. To the right appears the first tab showing compound name, index number, CAS number, molecular weight, and compound family, all generated using the methods selected earlier or designated automatically by the compound data manager. All compounds generated in this way are automatically defined as belonging to the family of *pseudo-compounds.* The CAS number is created automatically according to the formula shown on the pseudo-compound generation panel shown above. Pseudo-compounds do not normally have a genuine CAS number, but this number is used for internal purposes by *ChemSep*, so it is necessary to create one here.

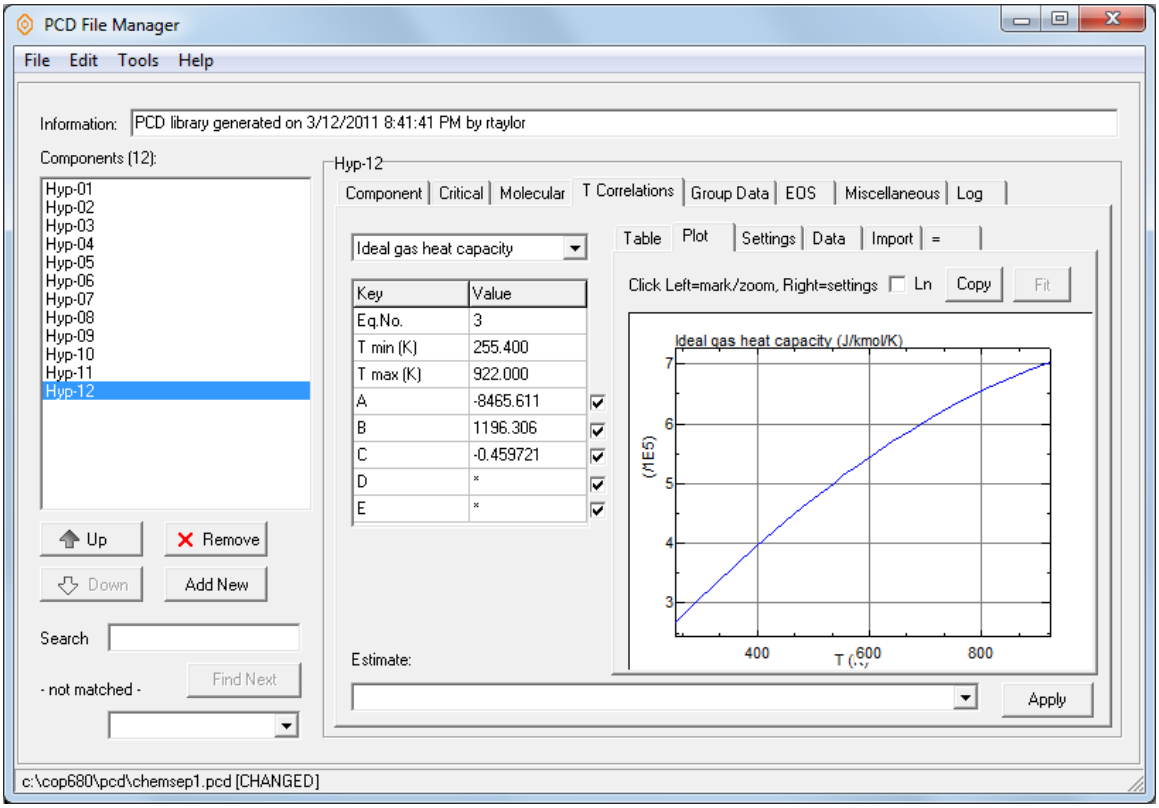
The entire set of molecular weights is in reasonable agreement with those given by Shah and Bishnoi although they do not specify exactly how those were calculated. The method used here (that of Riazi and Daubert (1980) was not available to Shah and Bisnoi because their paper was published was published two years before. We leave it as an exercise for our readers to see how much difference there is with the other methods of estimating the various properties.

Other properties (including the very important critical temperature and pressure and the ideal gas heat capacity are shown in the series of screen images below that illustrate other tab panels in *PCDmanager*.

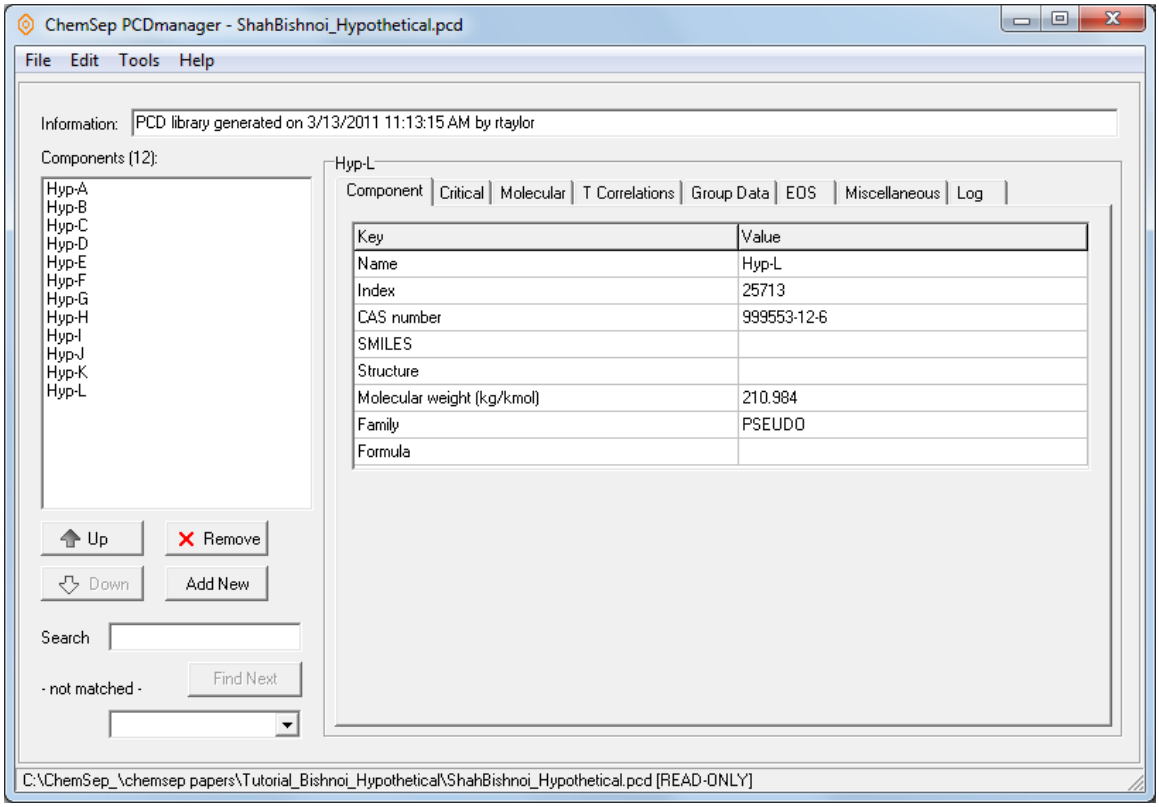

PCD File Manager
File Edit Tools Help
Information: PCD library generated on 3/12/2011 8:41:41 PM by rtaylor
Components (12):
Hyp-01
Hyp-02
Hyp-03
Hyp-04
Hyp-05
Hyp-06
Hyp-07
Hyp-08
Hyp-09
Hyp-10
Hyp-11
Hyp-12
Up
Remove
Down
Add New
Search
- not matched -
Find Next
Hyp-12
Component Critical Molecular T Correlations Group Data EOS Miscellaneous Log
Key
Value
Critical temperature (K)
735.821
Critical pressure (Pa)
1.75839E+06
Critical volume (m3/kmol)
0.904049
Critical compressibility factor (-)
0.259836
Normal boiling point (K)
553.150
Melting point (K)
*
Triple point temperature (K)
*
Triple point pressure (Pa)
*
Estimate:
Click here to estimate properties (no UNIFAC)
Apply
Order by property
Order by method
c:\cop680\pcd\chemsep1.pcd [CHANGED]


PCD File Manager
File Edit Tools Help
Information: PCD library generated on 3/12/2011 8:41:41 PM by rtaylor
Components (12):
Hyp-01
Hyp-02
Hyp-03
Hyp-04
Hyp-05
Hyp-06
Hyp-07
Hyp-08
Hyp-09
Hyp-10
Hyp-11
Hyp-12
Up
Remove
Down
Add New
Search
- not matched -
Find Next
Hyp-12
Component Critical Molecular T Correlations Group Data EOS Miscellaneous Log
Key
Value
Liquid molar volume at normal boiling point (m3/kmol)
0.256409
Acentric factor (-)
0.658167
Radius of gyration (m)
6.46627E-10
Solubility parameter (J0.5/m1.5)
13979.2
Dipole moment (Coulomb.m)
*
Van der Waals volume (m3/kmol)
*
Van der Waals area (m2/kmol)
*
IG heat of formation (J/kmol)
*
IG Gibbs energy of formation (J/kmol)
*
IG absolute entropy (J/kmol/K)
*
Heat of fusion at melting point (J/kmol)
*
Standard net heat of combustion (J/kmol)
1.04365E+10
Estimate:
Apply
Order by property
Order by method
c:\cop680\pcd\chemsep1.pcd [CHANGED]

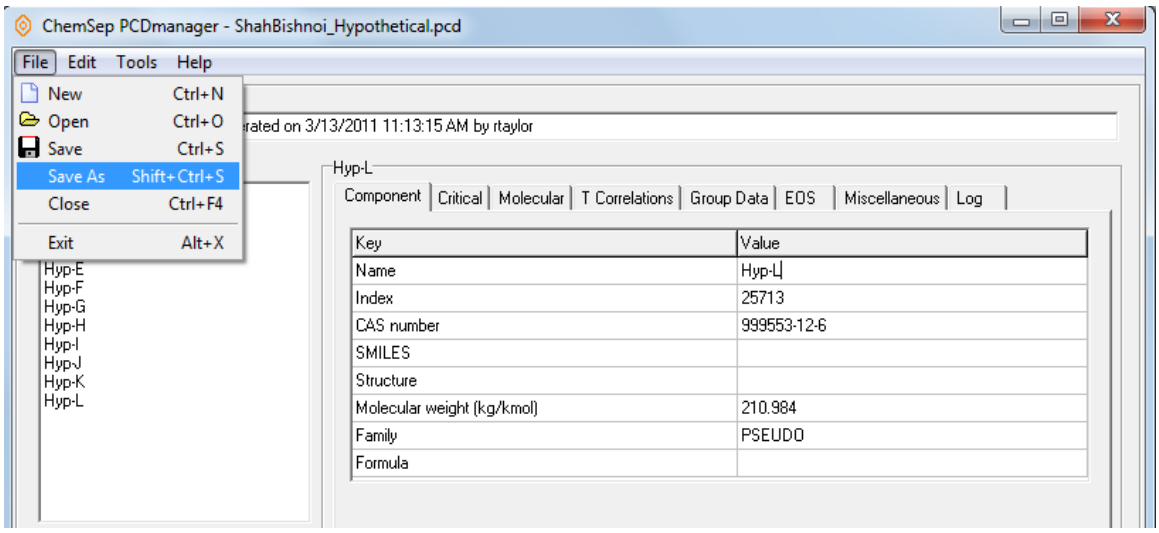

PCD File Manager
File Edit Tools Help
Information: PCD library generated on 3/12/2011 8:41:41 PM by rtaylor
Components (12):
Hyp-01
Hyp-02
Hyp-03
Hyp-04
Hyp-05
Hyp-06
Hyp-07
Hyp-08
Hyp-09
Hyp-10
Hyp-11
Hyp-12
Up
Remove
Down
Add New
Search
- not matched -
Find Next
Hyp-12
Component Critical Molecular T Correlations Group Data EOS Miscellaneous Log
Key Value
COSTLD characteristic volume (V*) (m3/kmol) 0.962036
Lennard Jones diameter (m) 9.09220E-10
Lennard Jones energy (K) 375.496
Rackett parameter (-) 0.259836
Fuller et al. diffusion volume (-) 317.338
Surface tension at normal boiling point (N/m) 0.00972038
Parachor (kg0.25.m3/s0.5/kmol) 0.0605352
Specific gravity (-) 0.834000
Charge (-) *
Wilson volume (m3/kmol) 0.256409
UNIQUAC r (-) *
UNIQUAC q (-) *
UNIQUAC q' (-) *
Estimate:
Apply
c:\cop680\pcd\chemsep1.pcd [CHANGED]


PCD File Manager
File Edit Tools Help
Information: PCD library generated on 3/12/2011 8:41:41 PM by rtaylor
Components (12):
Hyp-01
Hyp-02
Hyp-03
Hyp-04
Hyp-05
Hyp-06
Hyp-07
Hyp-08
Hyp-09
Hyp-10
Hyp-11
Hyp-12
Up
Remove
Down
Add New
Search
- not matched -
Find Next
Hyp-12
Component Critical Molecular T Correlations Group Data EOS Miscellaneous Log
Ideal gas heat capacity
Key Value
Eq.No. 3
T min (K) 255.400
T max (K) 922.000
A -8465.611
B 1196.306
C -0.459721
D *
E *
Table Plot Settings Data Import =
Click Left=mark/zoom, Right=settings Ln Copy Fit
Ideal gas heat capacity (J/kmol/K)
(*1E5)
7
6
5
4
3
400
600
800
Estimate:
Apply
c:\cop680\pcd\chemsep1.pcd [CHANGED]

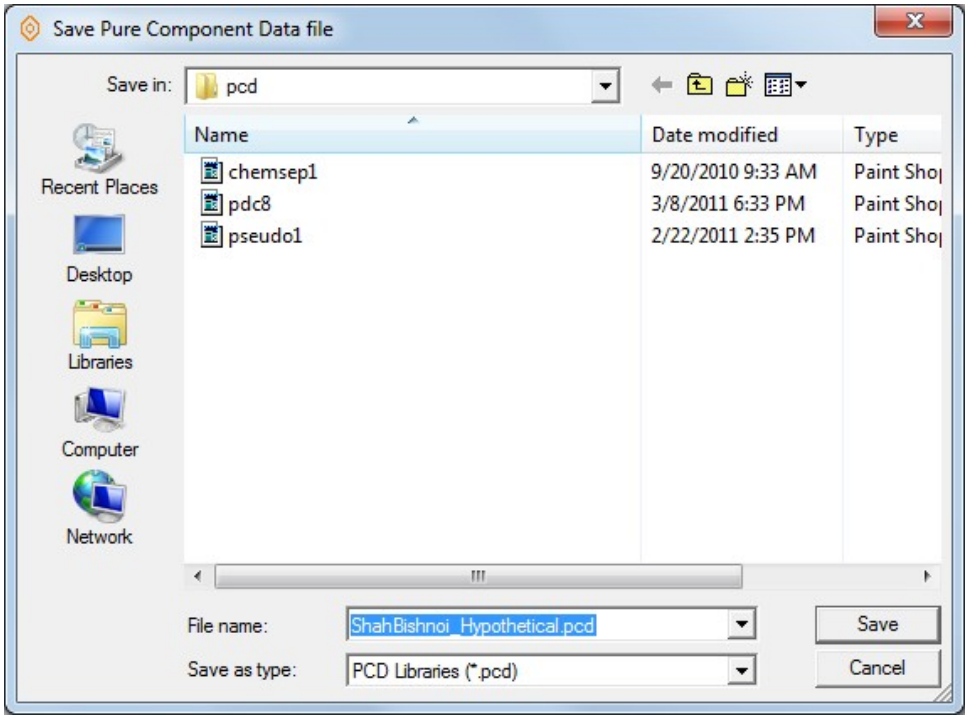
One last change, before we save the file is shown below. Here we have renamed the compounds so that they are identified by the sequence of letters starting with *A*. This change is not necessary and is done here solely to be consistent with the names used by Shah and Bishnoi.




In order to use this new compound data bank in column simulations we must save it. Click on *File* and then select *Save As:*



This will bring up the file save window where we give the file a name and find somewhere to save it:

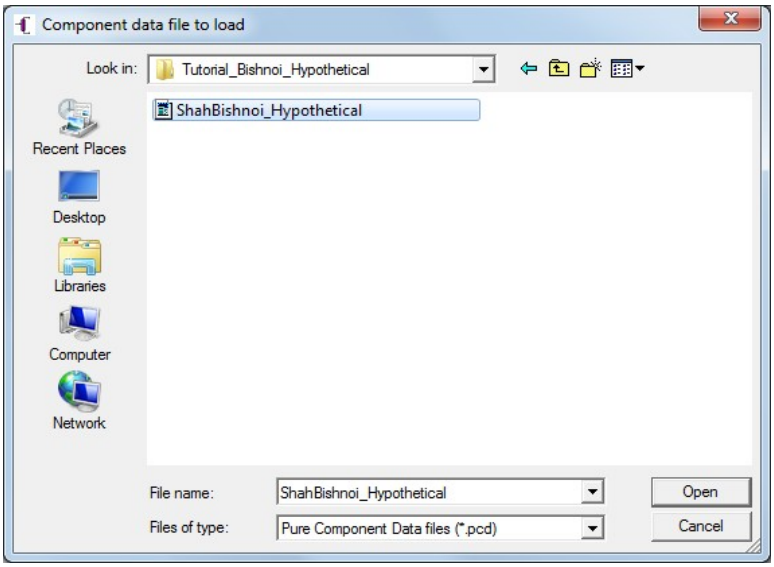



*ChemSep* pure compound data banks use the extension *pcd*. These three letters are sometimes used as the extension for files used by the program *Paint Shop*. It is for this reason that we see in the image above that our databank files appear to be associated with *Paint Shop*. We can always use the facilities of Windows to re-assign our *pcd* file to *ChemSep*, but we have not bothered to do that here.

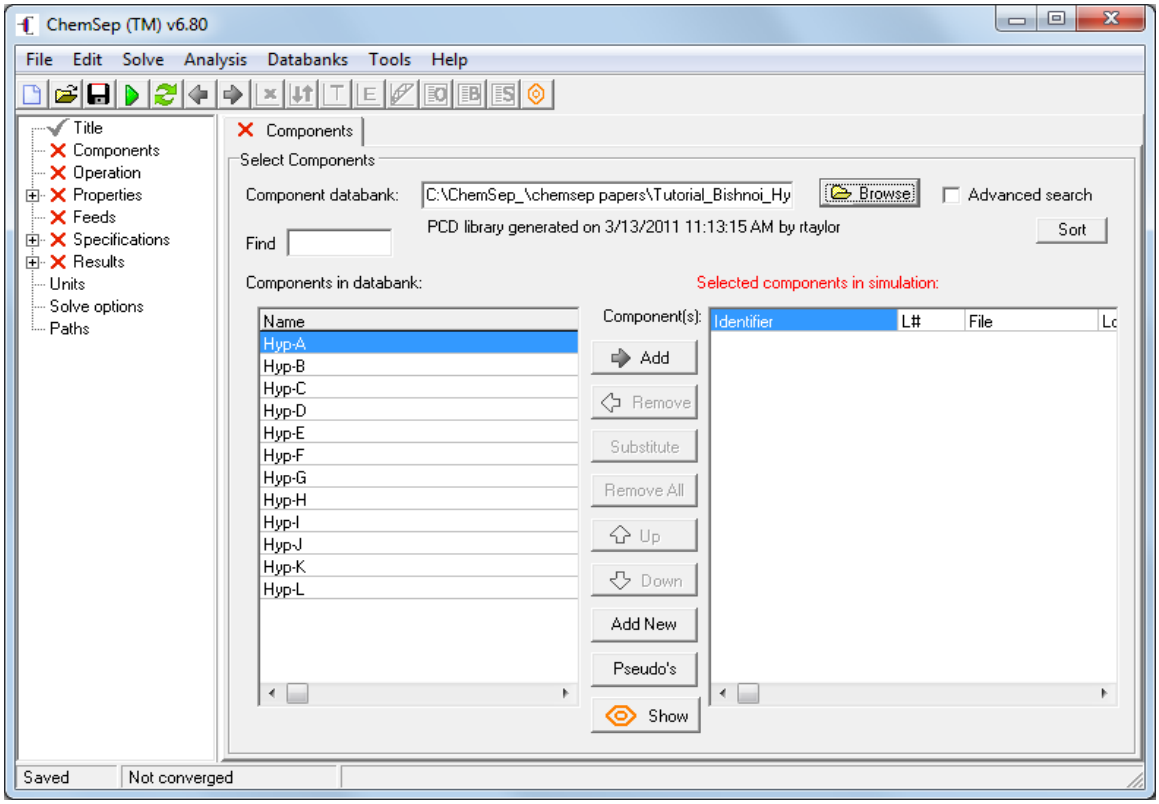
The new data bank now is ready for use and we can proceed to model the column described in the paper by Shah and Bishnoi.

## Compound Selection

We begin by returning to *ChemSep* and selecting compounds. Click on *Components* in the list on the left. Then, use the *Browse* button to locate the compound data file that we have just created:



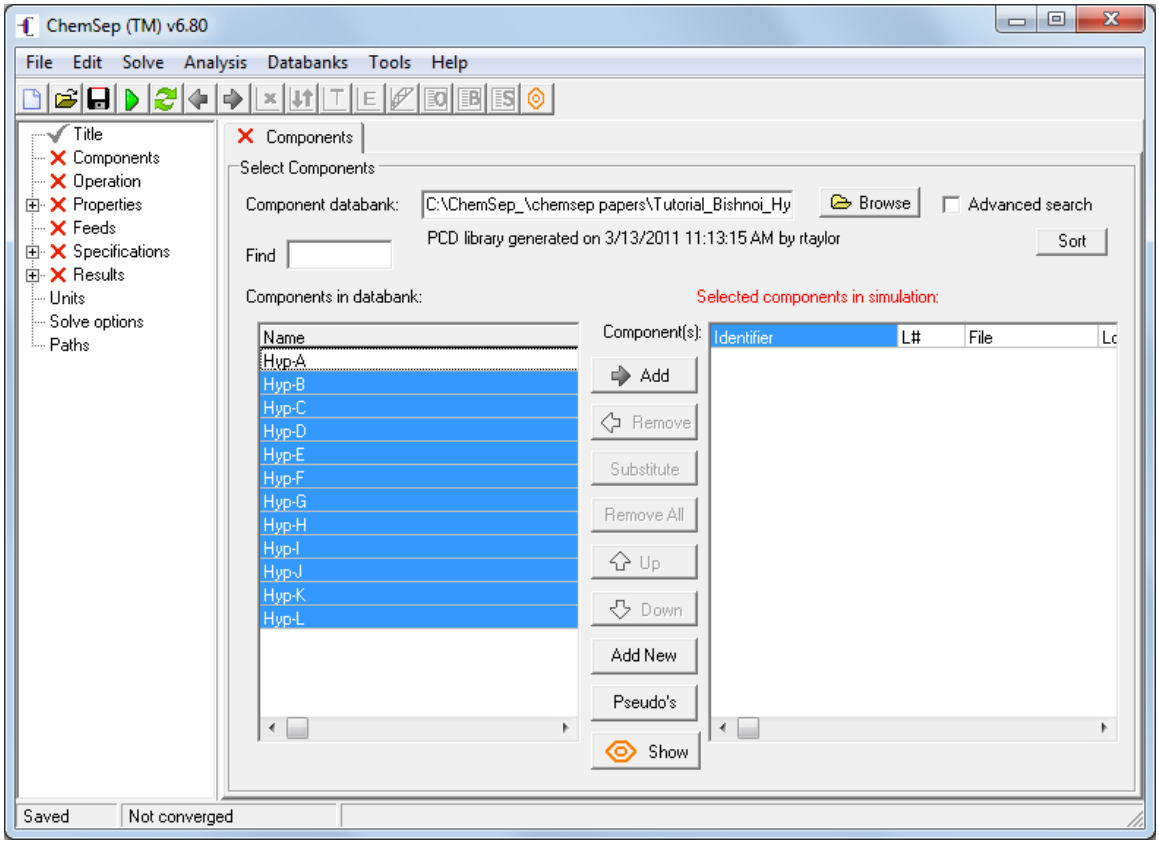

Select this file (this will return us to the *ChemSep* component selection panel which should now look something like this:



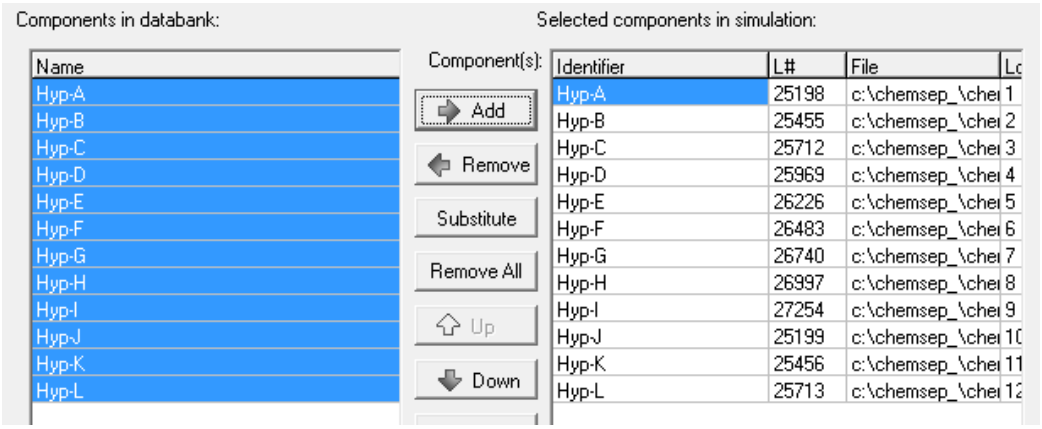
We can select all of these compounds in one go by proceeding as follows:

Click on the first compound in the list to the left of the compounds panel.
Hold down the *Shift* key
Click on the name of the last compound in the list.

We should not see all (except the first) compounds highlighted:

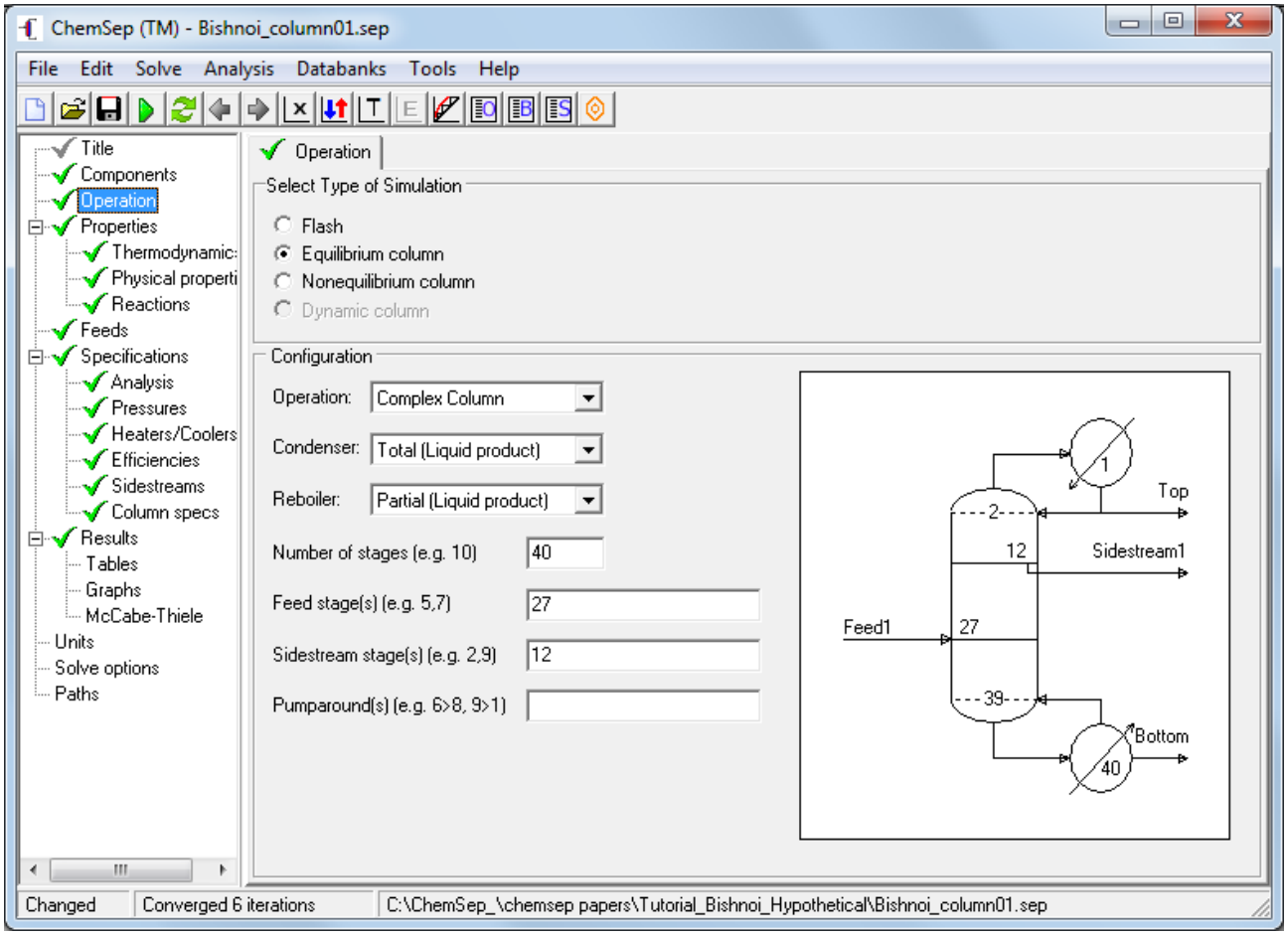



Click on the *Add* button to include all of these compounds in the simulation.



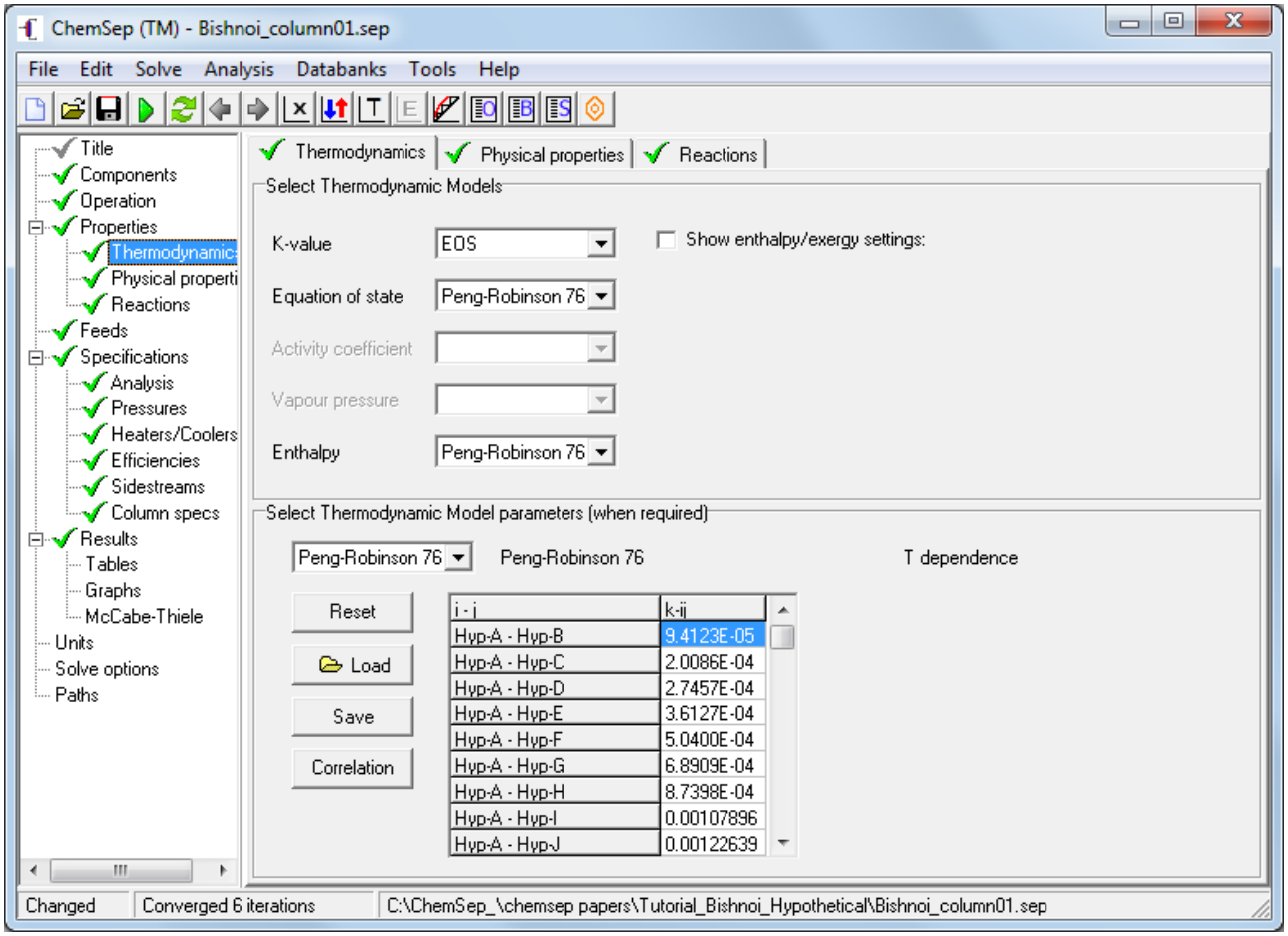
## Operation

We select an *Equilibrium Column* and create a column configuration to match that shown above.



**Thermodynamic Model Selection**

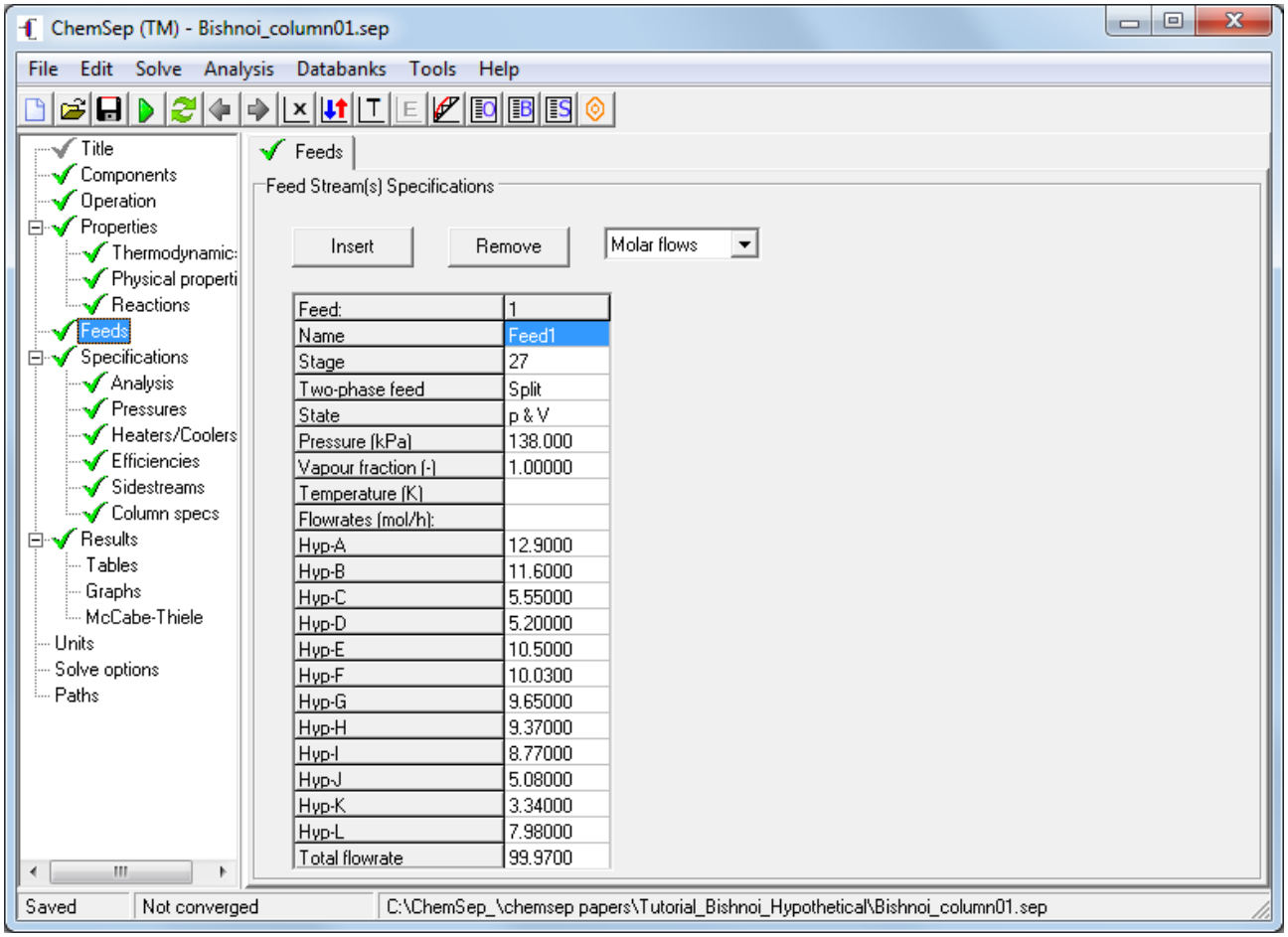
In their paper, Shah and Bishnoi use the SRK, PR EOS models as well as the Chao-Seader method to model a series of columns, one of which is the subject of this tutorial. For this tutorial we will make the selections shown below:




We have selected the Peng-Robinson EOS for this exercise.

Since binary interaction parameters are not available for this system from experimental data we have used the *Correlation* button to estimate them. Most of these interaction parameters are small and will not have a significant impact on the results of a simulation.

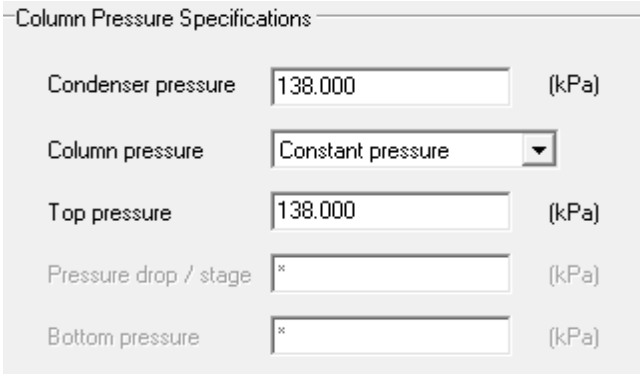
**Feeds**




The feed vapor fraction is set to unity to match the specification by Shah and Bishnoi that the feed is at its dew point.

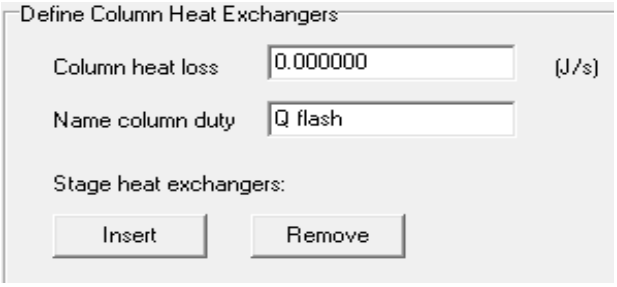
**Pressures**

The column pressure is constant at 138 kPa:



**Heaters and Coolers**

There are no heaters and coolers other than the condenser and reboiler:

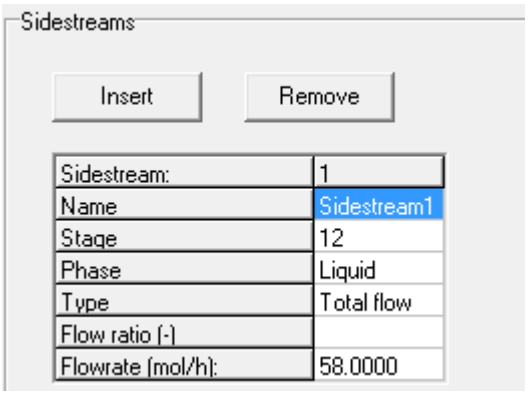



**Efficiencies**

The efficiencies are set to their default value of unity and so this panel is not shown here.

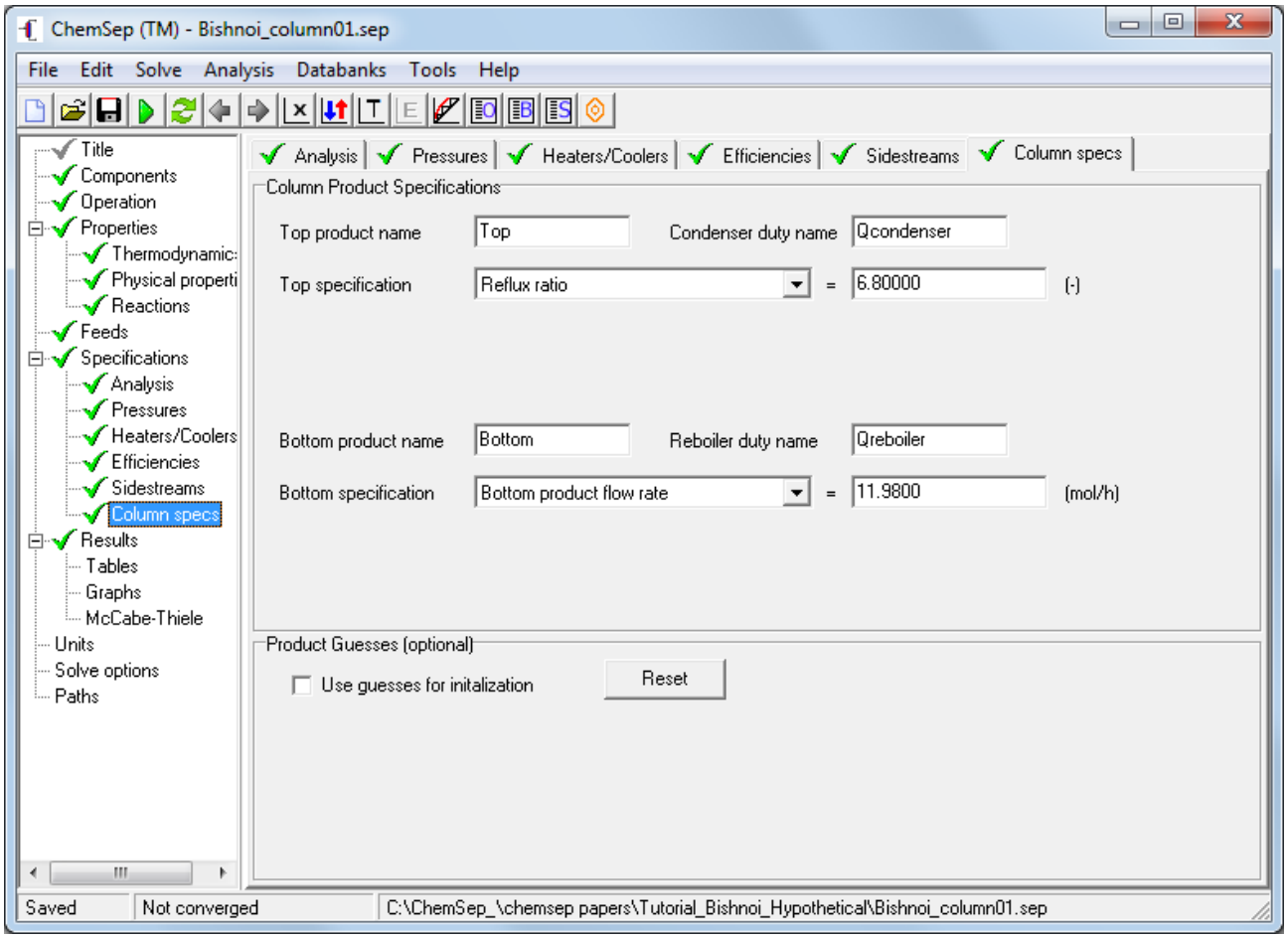
**Sidestreams**

The sidestream is specified as shown in the next image:



**Column Specifications**

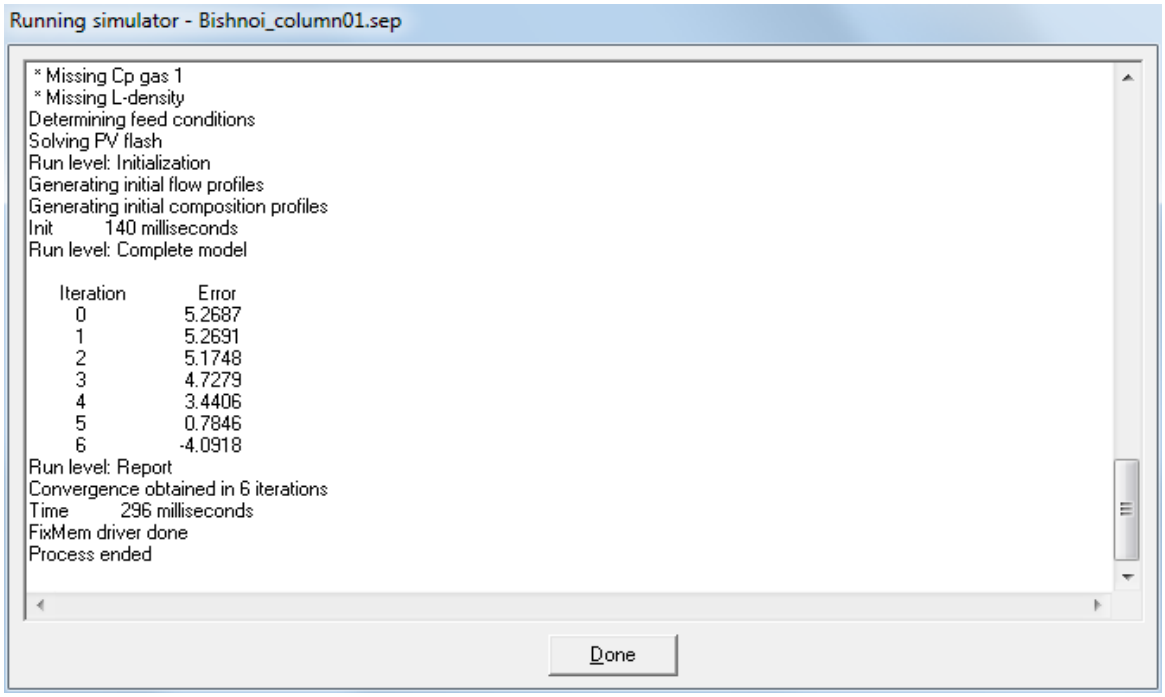
Shah and Bishnoi specified the reflux flow ratio (with a value of 6.6). However, as noted above, they do not state what "other" variable was specified to completely account for the number of degrees of freedom for this column. (As an aside we note that Shah and Bisnoi are similarly vague in their descriptions of four other test problems. Interestingly, they do tell us that they modeled the total condenser as a partial condenser with a very small vapor flow rate. This was the only way their computer program could model columns with a total condenser and does not complete the missing degree of freedom.) The tables of results given in the original paper of Shah and Bisnoi allow one to invent several possible additional specifications (such as the bottoms flow rate, component recoveries or purities in the top or bottom products, reboiler or condenser heat duties and so on). We have selected the bottoms rate and the column specifications are then as follows:




This completes the entry of the problem specifications. Save the file.

**Solving the Simulation**

With 40 stages and 12 components the equilibrium stage model has 1080 equations to be solved for 1080 variables (the unknown flow rates, temperatures, mole fractions). Convergence was obtained in just 7 iterations.




**Results**

The stream table is shown below:

| Stream | Feed1 | Top | Bottom | Sidestream |
|---|---|---|---|---|
| Stage | 27 | 1 | 40 | 12 |
| Pressure (kPa) | 138.000 | 138.000 | 138.000 | 138.000 |
| Vapour fraction (-) | 1.00000 | 0.000000 | 0.000000 | 0.000000 |
| Temperature (K) | 507.775 | 431.416 | 558.795 | 488.847 |
| Enthalpy (J/mol) | 62116.2 | -8430.38 | 55276.6 | 13519.2 |
| Entropy (J/mol/K) | 173.084 | 3.74263 | 163.185 | 73.7289 |
| Mole flows (mol/h) | | | | |
| Hyp-A | 12.9000 | 11.9401 | 2.8686E-14 | 0.959895 |
| Hyp-B | 11.6000 | 9.75401 | 2.6559E-11 | 1.84599 |
| Hyp-C | 5.55000 | 3.92998 | 4.0392E-10 | 1.62002 |
| Hyp-D | 5.20000 | 2.50186 | 2.8998E-09 | 2.69814 |
| Hyp-E | 10.5000 | 1.75079 | 4.7124E-08 | 8.74921 |
| Hyp-F | 10.0300 | 0.110428 | 1.1242E-06 | 9.91957 |
| Hyp-G | 9.65000 | 0.00276555 | 5.3835E-05 | 9.64718 |
| Hyp-H | 9.37000 | 1.0416E-04 | 0.00175358 | 9.36814 |
| Hyp-I | 8.77000 | 1.9676E-06 | 0.130785 | 8.63921 |
| Hyp-J | 5.08000 | 1.3466E-07 | 0.749787 | 4.33021 |
| Hyp-K | 3.34000 | 2.1666E-10 | 3.11787 | 0.222135 |
| Hyp-L | 7.98000 | 2.6057E-16 | 7.97976 | 2.4612E-04 |
| Total molar flow | 99.9700 | 29.9900 | 11.9800 | 58.0000 |

The component flows differ slightly from those given by Shah and Bishnoi, but the essential nature of the component split is preserved. Note that the sidestream flow is significantly greater than either the top or bottom product flow rate.

The material and energy balance table shows the main mass and energy flows into and out of the column:

Mass and Energy Balances

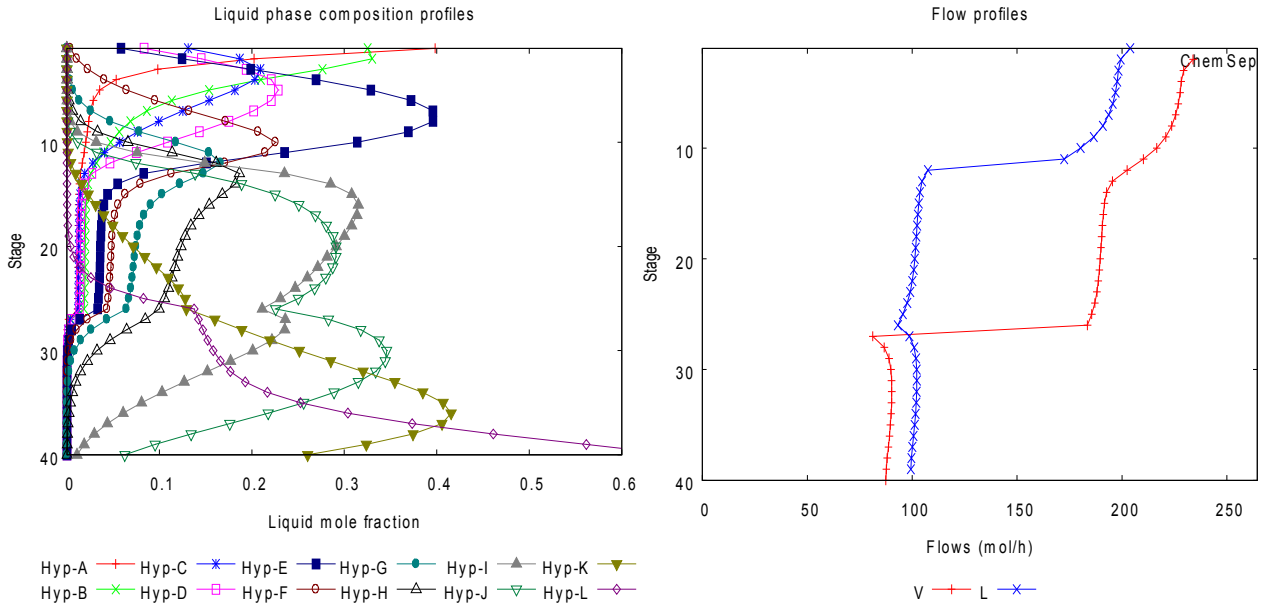
| Stream / Apparatus | Mass (mol/h) | Energy (J/s) | Exergy (J/s) |
|---|---|---|---|
| Feed1 | 99.9700 | 1724.93 | 291.891 |
| Top | -29.9900 | 70.2299 | 79.5256 |
| Bottom | -11.9800 | -183.948 | -22.0400 |
| Sidestream1 | -58.0000 | -217.810 | 136.349 |
| Qcondenser | | -2629.55 | -812.278 |
| Qreboiler | | 1236.35 | 576.684 |
| Balance | 0.000000 | 0.199951 | 250.133 |

Thermodynamic efficiency = 0.485033

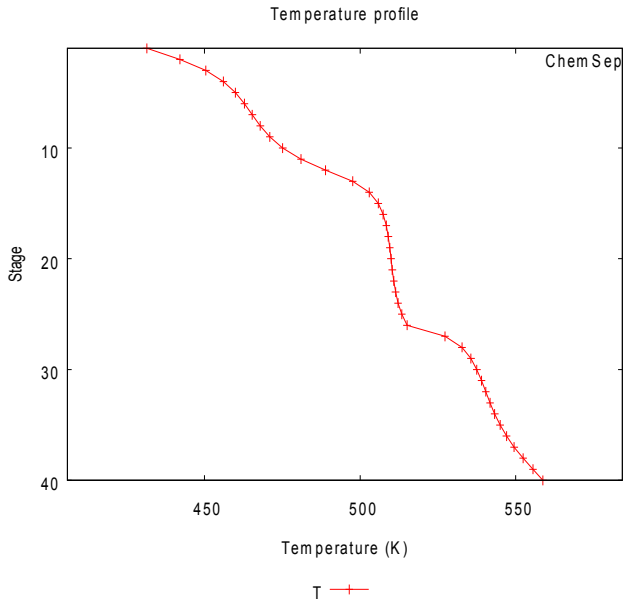
Component discrepancies: absolute (mol/h), relative ( )

| | | |
|---|---|---|
| Hyp-A | -2.609E-07 | -2.022E-08 |
| Hyp-B | -2.642E-07 | -2.278E-08 |
| Hyp-C | -4.796E-09 | -8.642E-10 |
| Hyp-D | 2.6892E-07 | 5.1717E-08 |
| Hyp-E | 4.4314E-07 | 4.2204E-08 |
| Hyp-F | 7.5176E-07 | 7.4951E-08 |
| Hyp-G | -6.832E-07 | -7.079E-08 |
| Hyp-H | -5.826E-07 | -6.218E-08 |
| Hyp-I | 5.6736E-07 | 6.4693E-08 |
| Hyp-J | 2.7893E-07 | 5.4908E-08 |
| Hyp-K | 6.1380E-08 | 1.8377E-08 |
| Hyp-L | 3.5933E-07 | 4.5029E-08 |

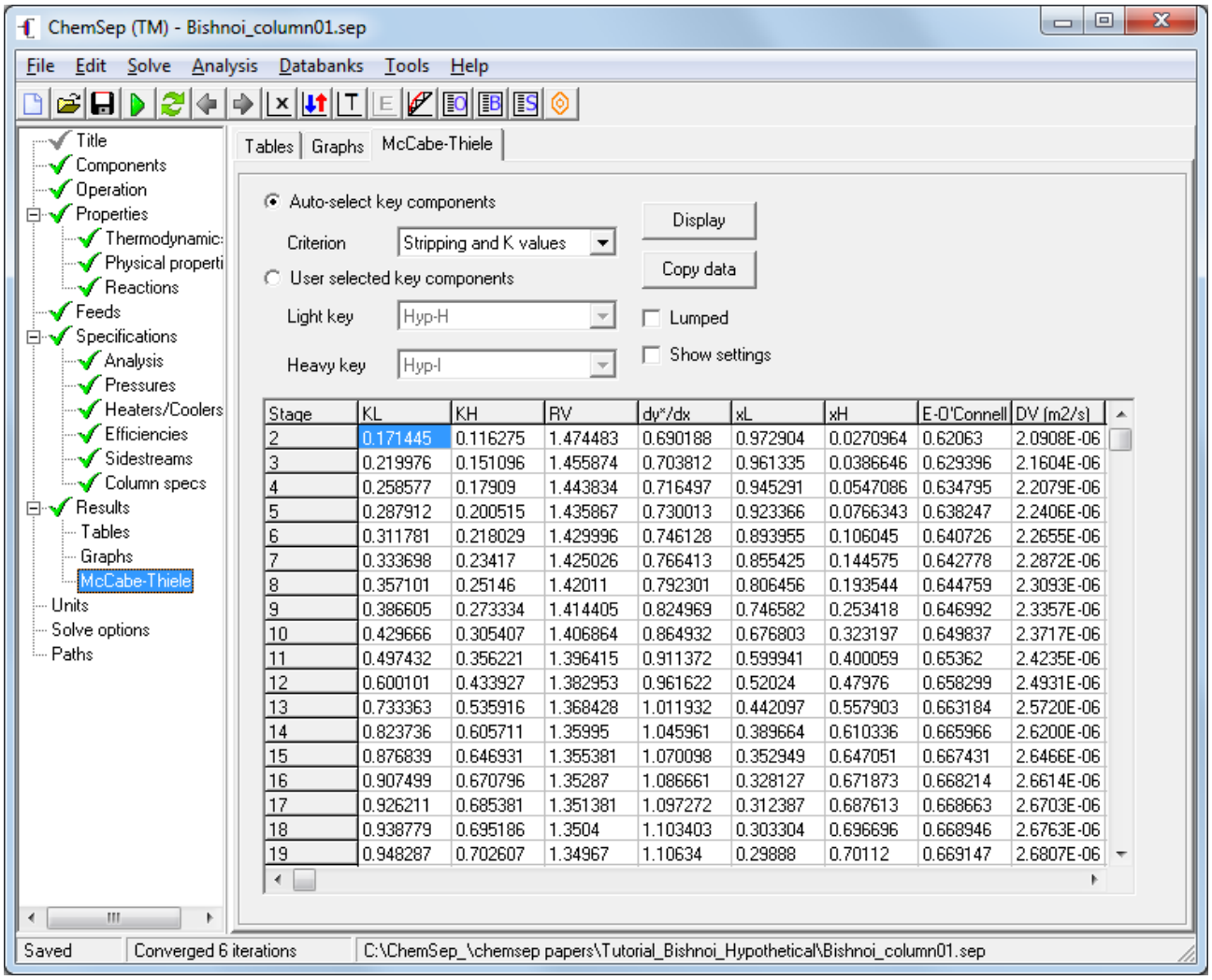
The composition and flow profiles is obtained by clicking on the appropriate icons on the button bar.



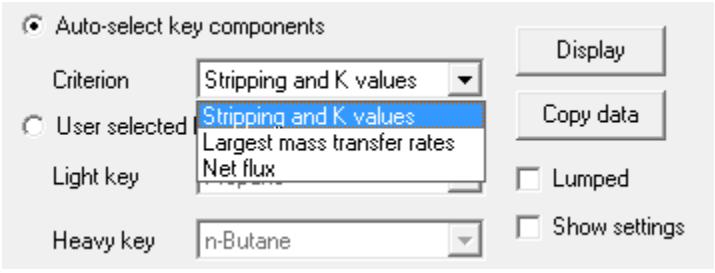

The temperature profile is shown below.



A McCabe-Thiele diagram can be obtained by clicking on the McCabe-Thiele icon on the button bar. We may also elect to select the McCabe-Thiele panel:

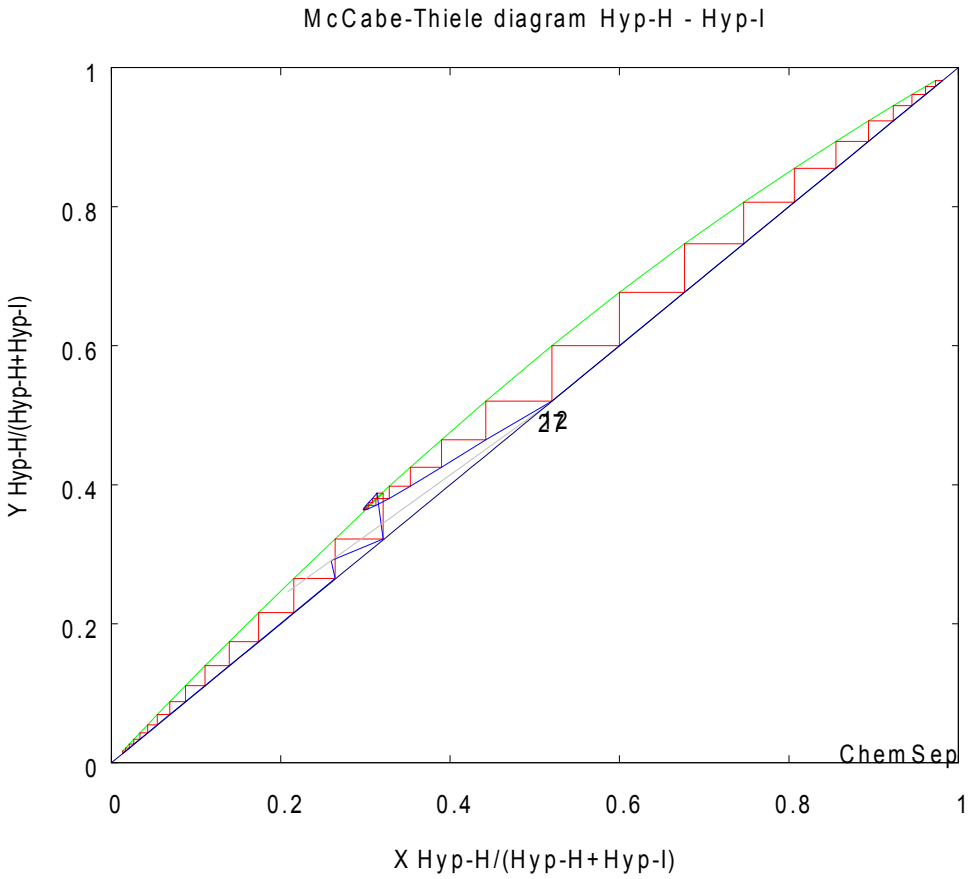



*ChemSep* will select the key components to be used in this diagram, but it does not always make the best choice. The program contains three different criteria on which to base its selection of the keys:




In this particular case the best choice is given by using the *Stripping and K-values* as the criterion. The other options lead (in this case) to a different pair of compounds. Alternatively, one can select the key components directly.

Click on the *Display* button to see the actual McCabe-Thiele diagram shown below:




**Discussion**

The original paper of Shah and Bishnoi was ostensibly to describe how a computational method for solving column simulation problems developed by Y. Ishii and F.D. Otto (*Can. J. Chem. Eng.*, **51**, 601, 1973) could be improved so that it could be used to solve systems where the thermodynamic properties were obtained from cubic equations of state. They also documented some other improvements to the original method and illustrated its use by solving 5 example problems of which the one solved here was number 5. Shah and Bishnoi used a CDC CYBER 172 computer and they report that their computer program needed 6 iterations to solve this example in slightly less than 41 seconds. *ChemSep* also needed 6 iterations (although the methods are not exactly the same so any comparison is somewhat lacking in context) and less than one third of one second on a 1.8 GHz Dell Precision Laptop Computer. These numbers only provide a measure of how much computer technology has advanced from 1978 to 2011 when this tutorial was written.

More interesting, perhaps, is that Shah and Bishnoi reported that the Chao-Seader model failed to solve this particular problem. *ChemSep* will solve this simulation using the Chao-Seader model in the same number of iterations (6) and in about the same amount of computer time as is needed for the Peng-Robinson EOS. Shah and Bishnoi report that for columns at low temperatures the

results from the Chao-Seader model are very different from those with the SRK or PR equations of state. This conclusion does not appear to be valid In this particular case.

**Exercises**

Repeat this simulation with the following changes:

1. The SRK EOS.

2. The Chao-Seader model.

3. Recreate the pure compound data bank but use other methods to estimate the various properties noted on the pseudo-compound generation panel. Do the simulaiton results differ very much if an alternative method was used for estimating the crtical temperature and pressure and the ideal gas heat capacity?