

# What's New in ChemSep™ 8.4

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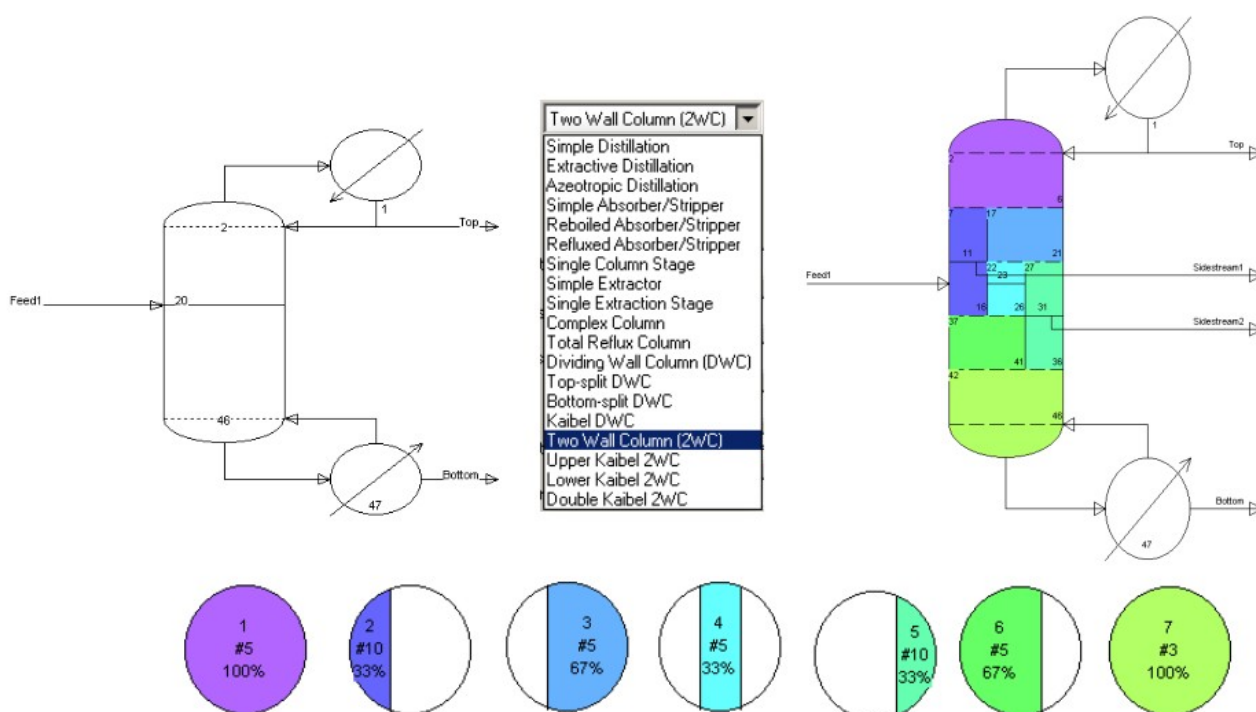
Two features were added in this version:

- Improved setup of Dividing Wall Columns (DWCs)
- Enthalpy liquid path for better sensible heats
- Improved Matthias-Copeman parameters (for cubic EOS)

In addition we discuss how to add new compounds to user PCD libraries

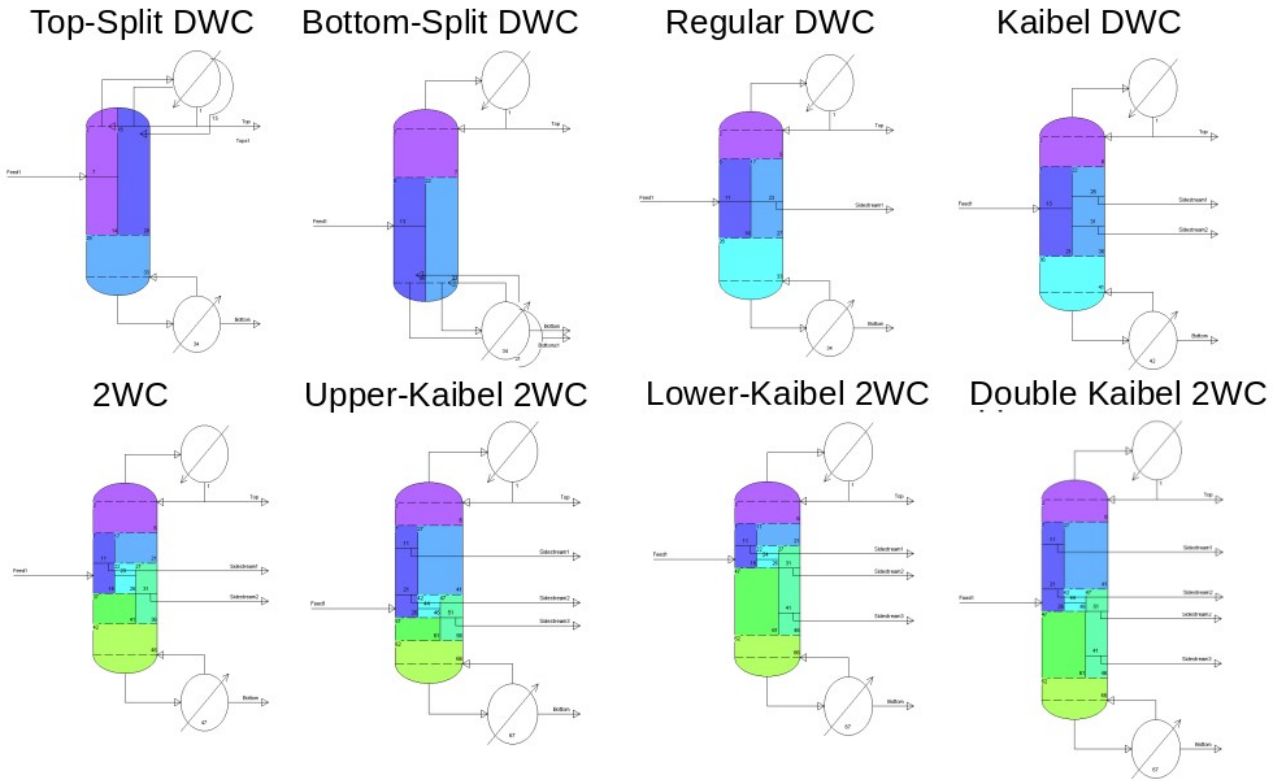
## Easy (& Fast) Dividing Wall Column Setup

To the best of our knowledge, ChemSep is the only available column simulation tool that can model Dividing Wall Columns (DWCs) as a single column. (The usual approach is to model such columns using a modular approach multiple linked independent column sections. Our single-column approach required us to develop a novel way to define the structure of a DWC that was sufficiently flexible to cover all realistic DWC configurations. However, using that scheme has been found to be a challenge. To make it easier to model a DWC in Chemsep, we have added a set of predefined DWC configurations; they can be seen in the extended list of configurations available:

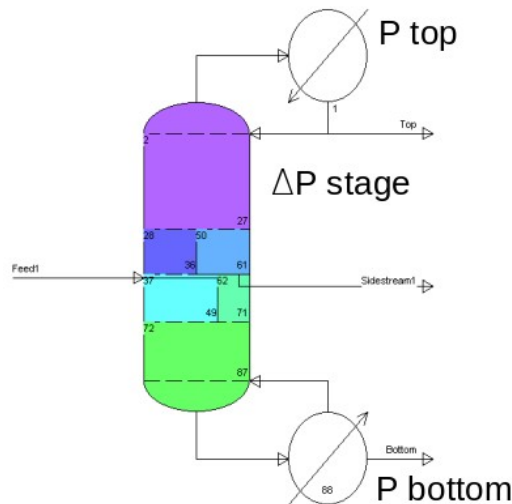


Following the selection of a particular DWC, the column drawing is color-coded to identify the different sections created by the walls. When hovering over a section, the user interface displays the number of stages and cross sectional vapor flow area. The user can adapt the number of stages with a simple left-click on the partition to adapt the number of stages, and a right-click to adjust

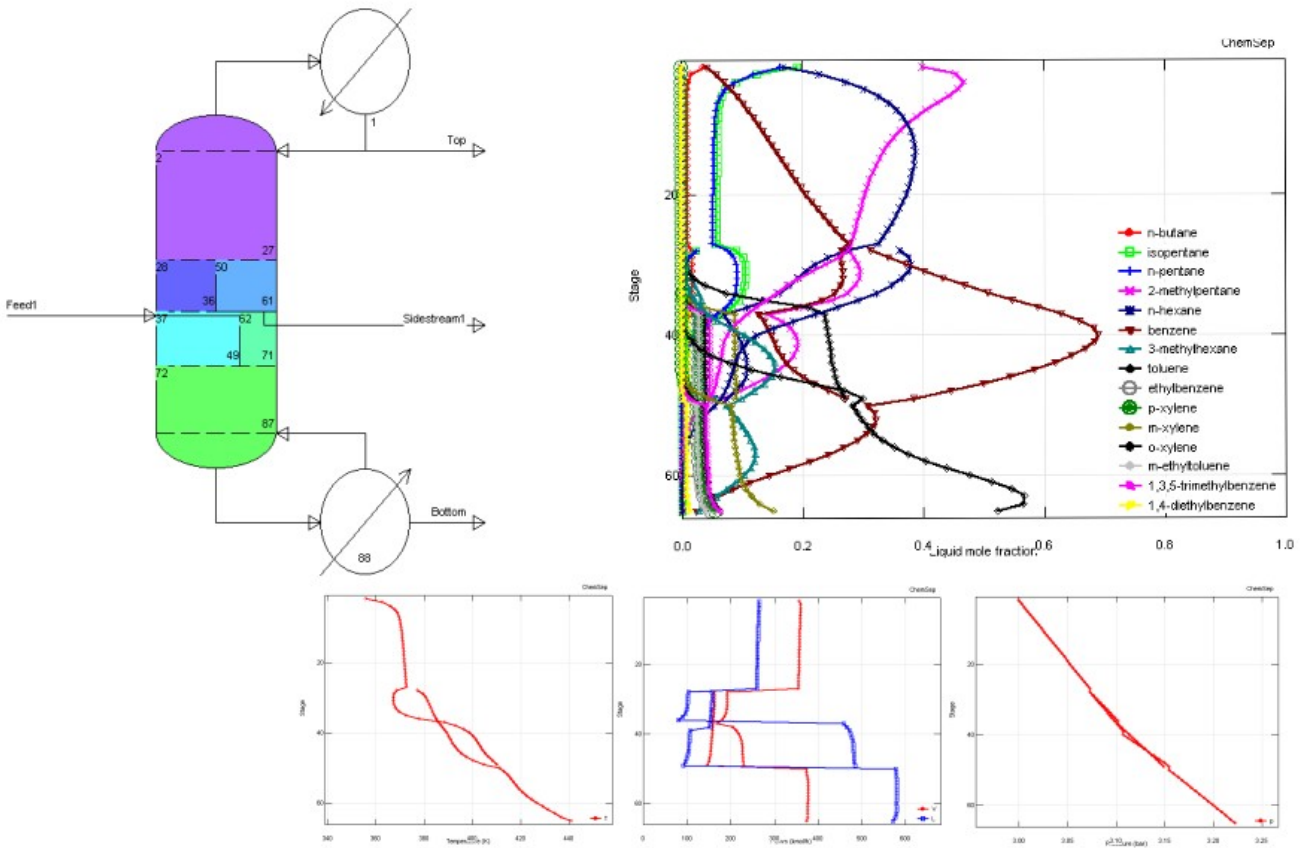
the vapor cross-sectional area. To set the liquid split-ratio the user can click on the top of a wall. The vapor split-ratio is set automatically to the area ratio on the bottom of a wall. This makes it trivially simple to setup a new DWC. We have created predefined configurations with one or two walls (2WC). For single wall columns, we added top- and bottom-split configurations.



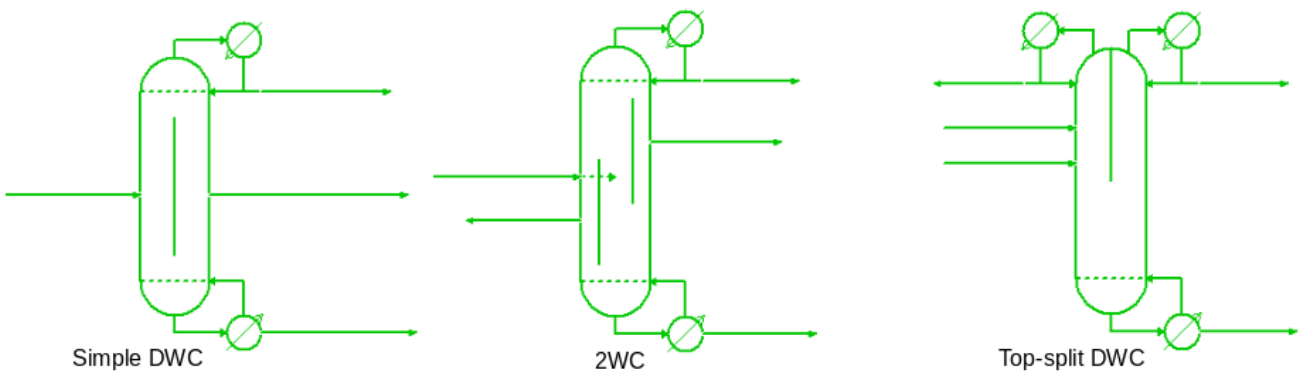
We have simplified the specification of the pressures in the column by automatically calculating pressures on all the stages on both sides of any wall. The only thing the user has to specify is the pressure in the top and bottom of the column or the pressure in the top and a pressure drop per stage:



The results of the simulation are plotted such that the values on adjacent stages on either side of the wall are side by side, easing the understanding how components distribute on either side of the wall:



Finally, when using the column in COCO, the columns icons are displayed with the same wall and feed configuration:



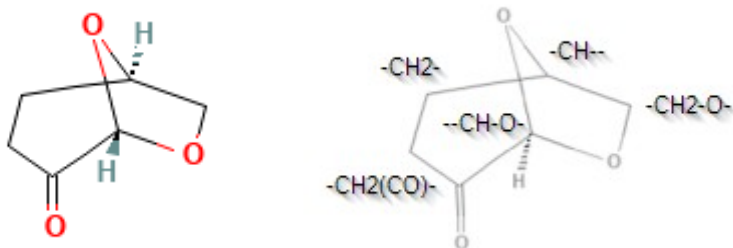
The feed stage positions can also be shown so that it is very clear when these are changed.

## Adding New Compounds to User PCD Libraries

ChemSep stores Pure Component Data (PCD) in binary formatted libraries. Users can add to the existing libraries or add their own. If all the data is known, this is not so difficult. However, when this is not the case, it is important to know what parameters are required to get reasonable simulation results for distillation columns. Of course, this will depend on what thermodynamic models were selected. Also for obtaining the physical properties that are needed for actual column internals design, such as densities, viscosities, and surface tensions the simulator requires certain PCD parameters. Here we want to give you a primer as to how to go about finding the right PCD information. We do this on the hand of adding a new compound, Dihydrolevoglucosenone, which is also being referred to as Cyrene in [Inter.J.Thermophysics, Vol 40, 102 \(2019\)](#).

Since distillation separates by means of boiling temperature differences the most important step is finding experimental vapour pressure for our new component. Here the above mention publication provides the this as well as the normal boiling temperature (499 K), its chemical structure, liquid density (as function of temperature), and its CAS registry number. We begin by opening the PCD manager from the Tools menu in ChemSep. By default the PCD manager loads the default PCD library. However, we want to create a new file. Thus, select the "New" option in the file-menu.

We create a new compound with the "Add New" option in the Edit Menu. We will be prompted for the name and enter "Cyrene". This will add the component under this name and perform a check if there is already a DIPPR number associated with this component. If not, as is the case, a new library index number is automatically generated based on the name. In this case the generated index is 2450. We then enter the CAS number 53716-82-8. This helps us in finding information on the web for information. Using the PubChem option in the Tools menu you will now find the isomeric SMILES string for Cyrene. To enter it in the PCD manager you must remove the @ characters: C1CC(=O)[CH]2OC[CH]1O2. Click the image of the compound to understand its structure (left). We can then decode its structure (right) in UNIFAC groups as (CHO)(CH<sub>2</sub>CO)(CH<sub>2</sub>)(CH)(CH<sub>2</sub>O):



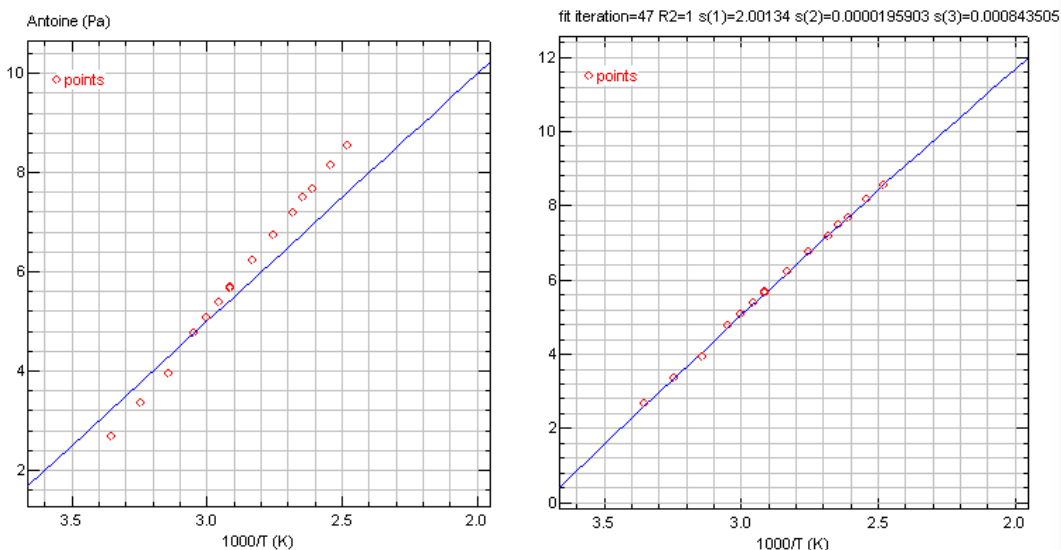
Enter this string as the chemical formula and the PCD manager offers to enter the computed mole weight of 128.126 and sets the formula C<sub>6</sub>H<sub>8</sub>O<sub>3</sub>. Now we select "Other polyfunctional C, H, O" as family. This all the information required for the tab "Component". The next step is to enter group information as it will allow you to perform estimation of parameters.

Click on the tab “Group Data” to continue. The default group method is UNIFAC. Enter for all five of the groups the number of occurrences, in this case a 1 for each CH2, CH, CH2CO, CH2O, and CH-O (you need to scroll down the list to find them all). Now switch to the UNIFAC-LLE method and repeat these entries. Similarly enter the information for all the other group methods (except PPR78).

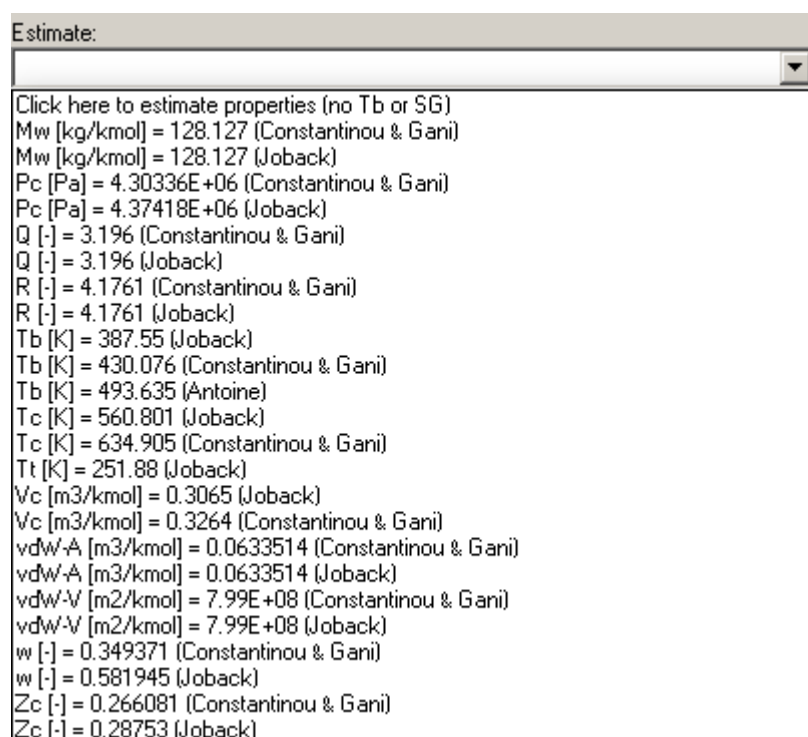
Next we click the “T correlations” tab to enter the vapor pressure. On this page we select “Antoine” as property, which is the most effective type of correlation for the vapour pressures. Now select the “Import” sub-tab sheet and mark the following lines (including the description) with data from the publication:

T (K)	p* (Pa)
298.26	14.4
308.31	28.2
318.24	51.5
328.27	116.9
333.32	157.3
338.27	219.4
343.26	294
343.26	288
353.25	506.1
363.26	842
373.24	1324
378.23	1780
383.26	2133
393.18	3490
403.16	5170
499.0	101325

Then set the Equation Number to #10 and set the values for A to 20 (a guess), for B to  $333(20 - \ln(157)) \approx 5000$  (157 is the vapor pressure at T=333 K) and C=0. For the minimum temperature we use 273 K, and set the maximum temperature to 1 degree above the normal boiling point, 500 K. With these parameters the PCD manager can plot the vapor pressure with the data we entered. Use the “Ln” and “1000/T” check boxes to get a log plot with an appropriate temperature axis for vapor pressures (left). Click the Fit button to get a better correlation (right):



The Antoine parameters A and B increased to 23.7826 and 5685.04, respectively, where C decreased to -29.7962. Now the Antoine parameters have been set, we want to switch to the tab “Critical”. First, since we know the normal boiling point is 499 K, we enter this value. Then we need to determine the critical constants for Cyrene. Since we entered the UNIFAC groups we can estimate these using the Joback or the Constantinou & Gani (C&G) group contribution methods. To see these estimates, click on the selector under “Estimate”. You will see the following listing of estimated values:



When we inspect this list, we see that the normal boiling point of Cyrene is under-predicted by a good 69 degrees (16%) by C&G, and even more by Joback. As such, it likely the critical temperature is under-predicted as well. So, how do we pick a value? Looking at the critical pressures, we see the two methods give very similar predictions. Therefore, select the value estimated by C&G, and apply it. Now with the critical pressure known we can estimate the critical temperature from the Antoine correlation. This is why we fitted the Antoine first! Click the estimate option again and you see an estimated value of 698 K. This is 10% over the C&G estimated critical temperature. This looks consistent. So, accept this value by clicking the apply button.

Similarly, with Tc & Pc known, we can use the Antoine and the Ambrose-Walton method to estimate the acentric factor. The estimated value is 0.585. Accept it and switch to the EOS tab. There it is reported that the SRK vapor pressures deviate only 0.5% from those of the Antoine correlation. This means that for VLE at higher pressures we can use the SRK Equation of State, with little loss in accuracy. The same page lists for the PR EOS 2.3% error. To use the PR it is advised to use Matthias-Copeman parameters (under Edit, Estimate property estimate to file). This will reduce the error < 0.1%.

Now select “vapour pressure” on the “T correlations tab” and pick equation #200 with  $T_{min}=273$ ,  $T_{max}=500$ , and the Ambrose-Walton values  $A=-8.5$ ,  $B=C=D=0$  and set to  $P_c=4.3e6$ . The A value is a guess. Press the “Fit” button and you obtain a very good fit. Now that the vapor pressures are well represented, switch back to the “Critical” tab and estimate the critical volume using C&G. The program will offer to enter also the critical compressibility.

In order to predict duties of heat exchangers we need to have the ideal gas heat capacities, named CpIG in ChemSep. With the UNIFAC groups defined we can estimate these. Click the Estimate selector and select “CpIG” using “Harrison-Seaton exponential with fixed slope”. Next we are going to fit the liquid density, for which there are experimental data in the article:

T	rhoL
293.15	1250.75
298.15	1245.77
323.15	1221.30
348.15	1196.86
373.15	1172.28
398.16	1147.60
423.15	1122.77

Typically the correlation #105 is used for liquid densities. This correlation has 4 parameters of which the parameter C is the critical temperature and B and D are usually around 0.25. Select liquid density, set the minimum and maximum temperatures to 273 and 500 K. Enter  $A=0.73$ ,  $C=736$  and  $B=D=0.25$ . Here the value of A is a guess. Unselect the fitting of the C parameter (with the checkbox next to the parameter) and perform a fit. You now have a very accurate density.

Select the “Miscellaneous” tab and use the estimate option. With our density function we can estimate the Specific Gravity (SG) at 60 F. Select the estimated SG value by T correlation and apply it. Similarly, we can apply the estimated R and Q values from UNIFAC. Do the same with the Fuller diffusion volume and the COSTALD  $V^*$  and the Rackett (from liquid density) estimates. To estimate the Parachor select the Quayle method with elemental contributions, and for the Wilson volume use the Tyn-Calus method.

Now select the “Molecular” tab and estimate the molar volume again with Tyn-Calus method. Then estimate  $G_f$ ,  $H_c$ ,  $H_f$ ,  $R_{gyr}$ ,  $S_0$ ,  $SoIP$ ,  $vdW-A$  and  $vdW-V$  all using the C & G + Perry method. Save the PCD file. You are now ready to use the new compound Cyrene.

To verify the new compound we will try to reproduce the VLE as published in Brouwer and Schuur, Green Chemistry 22 p. 5369 (2020). Start ChemSep and start a new problem. Select Cyrene, MethylCycloHexane, and Toluene as compounds. Chose the DECHEMA K-model with UNIFAC activity coefficient model and the Antoine vapor pressure correlation. This will suffice. Select metric units and define the feed at 0.8 bar and 0.5, 0.25, and 0.25 mol/s. This creates a Solvent to Feed rate of  $0.5 / (0.25+0.25) = 1$ . For the flash specifications perform the calculations at the given feed pressure and  $V/F=0$ . The flash solves and gives a vapor MCH mole fraction of ~72%.



Now select the parametric study from the Analysis menu. Add variables to vary and provide the ranges such that the S/F remains 1 all the time:

Select input variables

Number of steps:   Use old results  Automatic  Keep sep-files  Restore original

Add

Name	Variable	Units	Value	Start/Valuelist	End
Feed1 compone	F1F1	mol/s	0.5	0.5	0.5
Feed1 compone	F1F2	mol/s	0.25	0.5	0
Feed1 compone	F1F3	mol/s	0.25	0	0.5

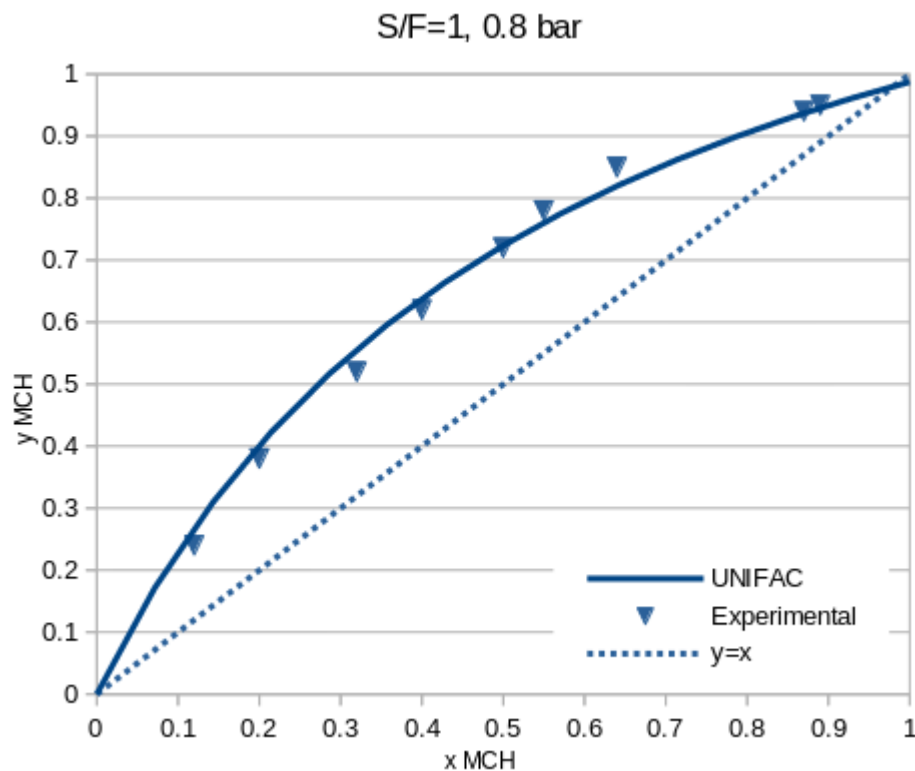
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Select result variables

Add

Name	Feed1 compone	yMCH	yTOL	xMCH	xTOL
Variable	F1F1	TOPS1Y(2)	TOPS1Y(3)	BOTS1X(2)/0.5	BOTS1X(3)/0.5
Units	mol/s				
Current Value	0.5	0.723487	0.262376	0.5	0.5

Then select the result variables as above to generate x,y for the VLE parity plot as published by Brouwer and Schuur:



The match validates the vapor pressures and the UNIFAC selection of groups. We leave it to the reader to reproduce the same parity plots for the experimental data at 0.5 and 1 bar pressure. The UNIFAC model seems certainly accurate enough to predict the extractive distillation with Cyrene.



Brouwer and Schuur, *Sust.Chem.Eng.* 39 p. 14807 (2020) also report Liquid-Liquid Equilibrium data for the same mixture. For this we need to switch to the LL (gamma) K-model. Select the UNIFAC for computing the activities. For the flash specification select the LL flash temperature and set it to 298.15 K. Solve to be able to select the parametric study option under Analysis. Define the following varying input variables, and set the results for the reporting variables:

Select input variables

Number of steps   Use old results  Automatic  Keep sep-files  Restore original

Add

Name	Variable	Units	Value	Start/Valuelist	End
Feed1 compone	F1F1	kmol/s	0.5	0.5	0.5
Feed1 compone	F1F2	kmol/s	0.5	0.5	0
Feed1 compone	F1F3	kmol/s	0	0	0.5

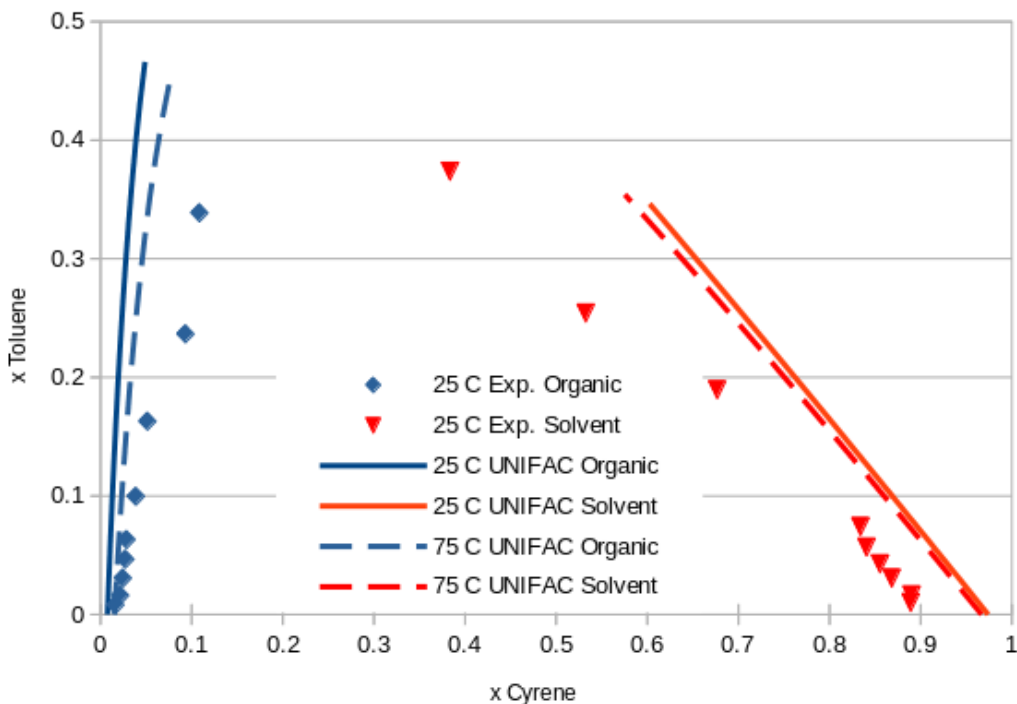
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Select result variables

Add

Name	xF1CYR	xF1MCH	xF1TOL	x1CYR	x1TOL	x2CYR	x2TOL
Variable	F1F1/F1FT	F1F2/F1FT	F1F3/F1FT	TOPS1Z(1)	TOPS1Z(3)	BOTS1Z(1)	BOTS1Z(3)
Units							
Current Value	1	0	0	0.00766217	0	0.974033	0

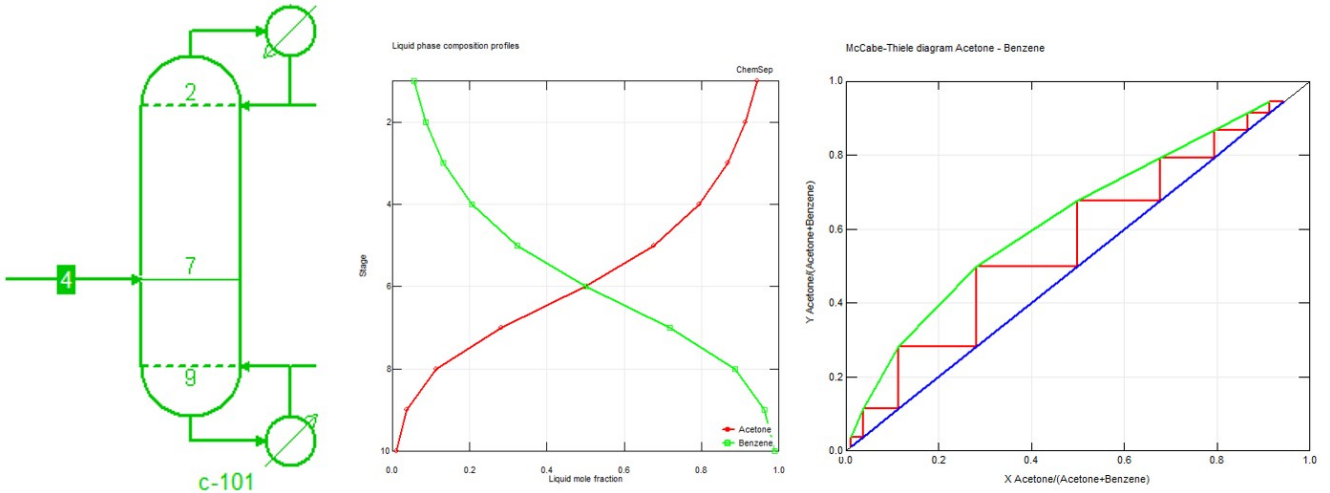
Press the Run button to obtain the results. Below you see that the UNIFAC-LLE model matches the experimental data as reported by Brouwer and Schuur qualitatively. Though the temperature dependency of the UNIFAC is in the right direction, it is not good enough to use it for the design of LL extraction columns. As such we need tweak the interactions, or we need to fit the LLE e.g. using UNIQUAC as Brouwer did.



# Total Reflux Operation

ChemSep has had the ability to simulate operations at total reflux for a very long time. Now, that capability has been extended so that total reflux operations can be modelled in a CAPE-OPEN compliant simulator.

Here, we show a ChemSep total reflux simulation in the (free) CAPE-OPEN simulator COFE.

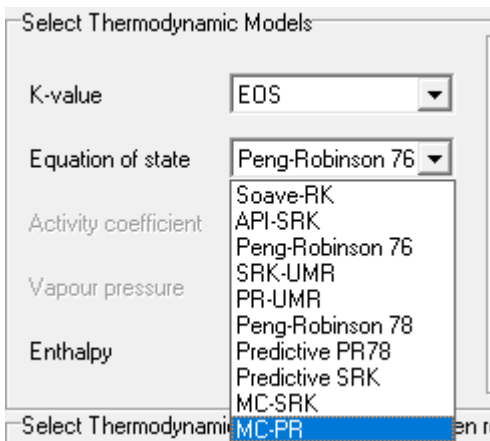


Total reflux operation implies no product withdrawal and, therefore, no feed. Thus, to model such an operation in a simulator requires some computational sleight-of-hand.

The ability to model total reflux operations is particularly useful for interpreting the experimental work of Fractionation Research Incorporated.

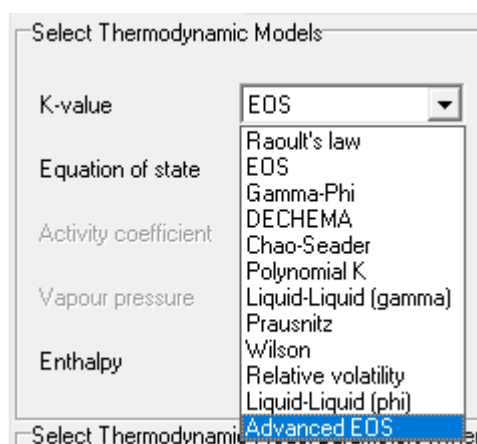
## New Equation of State Options (some coming soon)

Long time users may have noticed two new Equation of State (EOS) models on the Thermodynamics tab:



Here we can see two new entries at the bottom of this list: MC-SRK and MC-PR. These are, respectively, the SRK and PR Equations of state that employ the Mathias-Copeman (MC)  $\alpha$ -function instead of the traditional Soave  $\alpha$ -function that is used in the implementations of the SRK and PR equations that appear higher up this list. (As noted elsewhere in this document, the SRK-UMR, PR-UMR and PSRK models also use the MC  $\alpha$ -function.) The necessary parameters are loaded automatically when these models are selected.

At a level above, there is an entirely new K-value model: The Advanced EOS.



Currently this menu option serves only as a place-holder for what will be the most flexible cubic equation of state available in ChemSep. Knowledgeable readers will know of the tcPR variant of Privat and Jaubert and their co-workers (see Piña-Martinez, A., Privat, R., Nikolaidis, I.K., Economou, I.G., Jaubert, J.-N., 2021. What Is the Optimal Activity Coefficient Model To Be Combined with the translated-consistent Peng–Robinson Equation of State through Advanced Mixing Rules? Cross-Comparison and Grading of the Wilson, UNIQUAC, and NRTL aE Models against a Benchmark Database Involving 200 Binary Systems. *Ind. Eng. Chem. Res.* 60, 17228–17247 <https://doi.org/10.1021/acs.iecr.1c03003>). The advanced EOS option in ChemSep is a step towards the level of flexibility envisaged in this paper; it will allow the use to select their choice of  $\alpha$ -function and mixing rule.

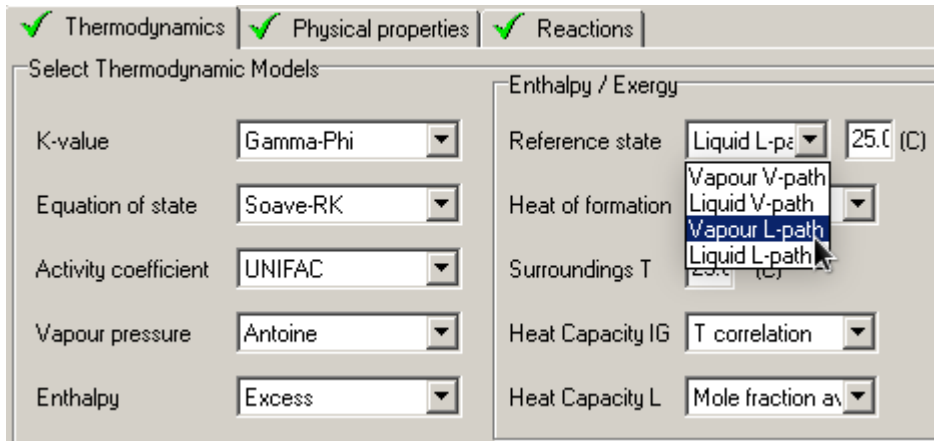
We emphasize that the Mathias-Copeman based versions of the SRK and PR equations are available now; the more flexible Advanced EOS remains a work in progress.

## Improved Matthias-Copeman (MC) parameters

To improve the accuracy of vapor pressures of pure component, the Matthias-Copeman parameters in our ChemSep libraries were re-fitted. This will affect all simulations that use the PSRK and the SRK-UMR equation of state models. In generic terms this improved predicted VLE by a few percent for most systems, but a few components will see drastic improvements. Since the PR-UMR now has MC parameters that we fitted for the Peng-Robinson EOS specifically, the results may for this method may have improved drastically such that the method performs equally well as the PSRK and SRK-UMR.

## Enthalpy liquid path for better sensible heats

ChemSep used the ideal gas heat capacities to compute the enthalpy of streams. Unfortunately, this frequently provides inaccurate heat duties for heat exchangers of liquid streams. As such we now feature “Liquid path” enthalpies which use the liquid heat capacities instead:



## Miscellaneous Updates

Version 8.4 also includes many small improvements such as:

- Improved Antoine parameters of various components
- Recognize the InChiKey component identifier
- Support accessing various databases found on the internet
- Added new estimation methods in the PCD manager for the critical temperature and acentric factor, given Antoine vapor pressure correlation
- Estimation of the melting point temperature from a group contribution model
- Editing PSRK and UNIFAC-NIST group contributions
- Allow for more than six groups per molecule in the group contribution methods
- Improved estimation of binary interaction parameters (BIPs) for NRTL and Wilson models
- Tweaks to TP flash algorithm for when vapor fraction is within machine precision of the edge of the allowed range
- Setting a limit for non-zero mole fractions in the report
- Support for X-files
- Minor updates to some plots
- Export the McCabe-Thiele diagram to Veusz

## New Compounds

As usual we added some new components to our library ChemSep2.pcd which will be automatically searched when you select the wild card \*.pcd in the search box of ChemSep. The following compounds were added:

95-15-8	Benzothiophene	123-63-7	Paraldehyde
108-98-5	Phenyl mercaptan	109-06-8	2-methylpyridine
811-97-2	1,1,1,2-tetrafluoroethane	108-99-6	3-methylpyridine
623-36-9	2-methyl-2-pentenal	108-89-4	4-methylpyridine
123-38-6	Propanal	108-48-5	2,6-dimethylpyridine
124-19-6	Nonanal	589-93-5	2,5-dimethylpyridine
112-44-7	Undecanal	75-09-2	Dichloromethane
10486-19-8	Tridecanal	120-82-1	1,2,4-trichlorobenzene
4394-85-8	4-formylmorpholine	87-61-6	1,2,3-trichlorobenzene
506-30-9	Arachidic acid	108-70-3	1,3,5-trichlorobenzene
127-27-5	Pimaric acid	578-58-5	2-methylanisole
1945-53-5	Palustric acid	1004-66-6	2,6-dimethylanisole
5835-26-7	Isopimaric acid	4028-66-4	2,4,6-trimethylanisole
514-10-3	Abietic acid	90-00-6	o-ethylphenol
1740-19-8	Dehydroabietic acid	496-16-2	2,3-dihydrobenzofuran
471-77-2	Neoabietic acid	107-19-7	Propargyl alcohol
83-46-5	Sitosterol	110-65-6	2-butyne-1,4-diol
98-55-5	Alpha-terpineol	57-55-6	Cis-3-Hexene
99-86-5	Alpha-terpinene		
80-56-8	Alpha-pinene		