ProSim

PROSIMPLUS APPLICATION EXAMPLE

HETEROGENEOUS AZEOTROPIC DISTILLATION

EXAMPLE PURPOSE
This example illustrates a high purity separation process of an azeotropic mixture (ethanol-water) through heterogeneous azeotropic distillation. This process includes distillation columns. Additionally these rigorous multi-stage separation modules are part of a recycling stream, demonstrating the efficiency of ProSimPlus convergence methods. Specifications are set on output streams in order to insure the required purity. This example illustrates the way to set "non-standard" specifications in the multi-stage separation modules. Three phase calculations (vapor-liquid-liquid) are done with the taken into account of possible liquid phase splitting.

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CORRESPONDING PROSIMPLUS FILE	*PSPS_E05_EN – Heterogeneous Azeotropic Distillation.pmp3*

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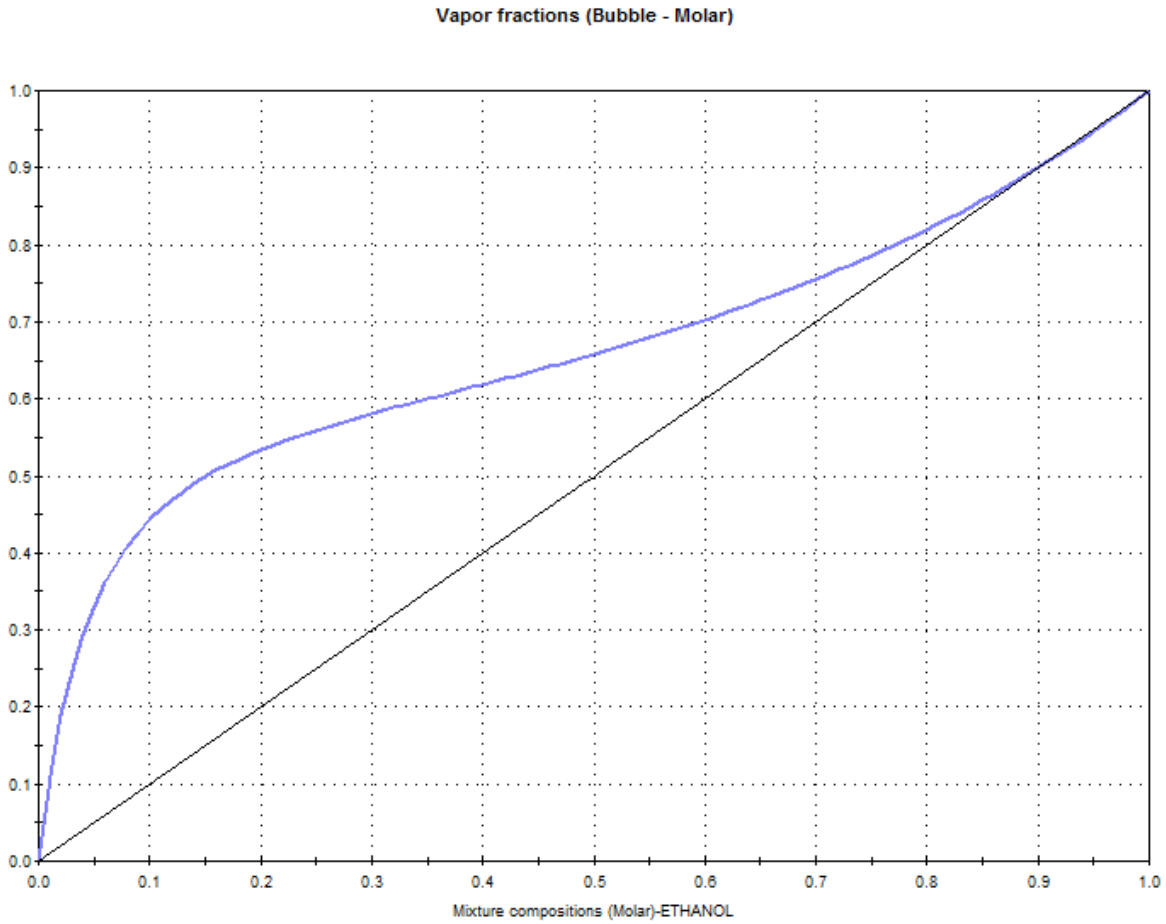
1. PROCESS MODELING

1.1. Process description

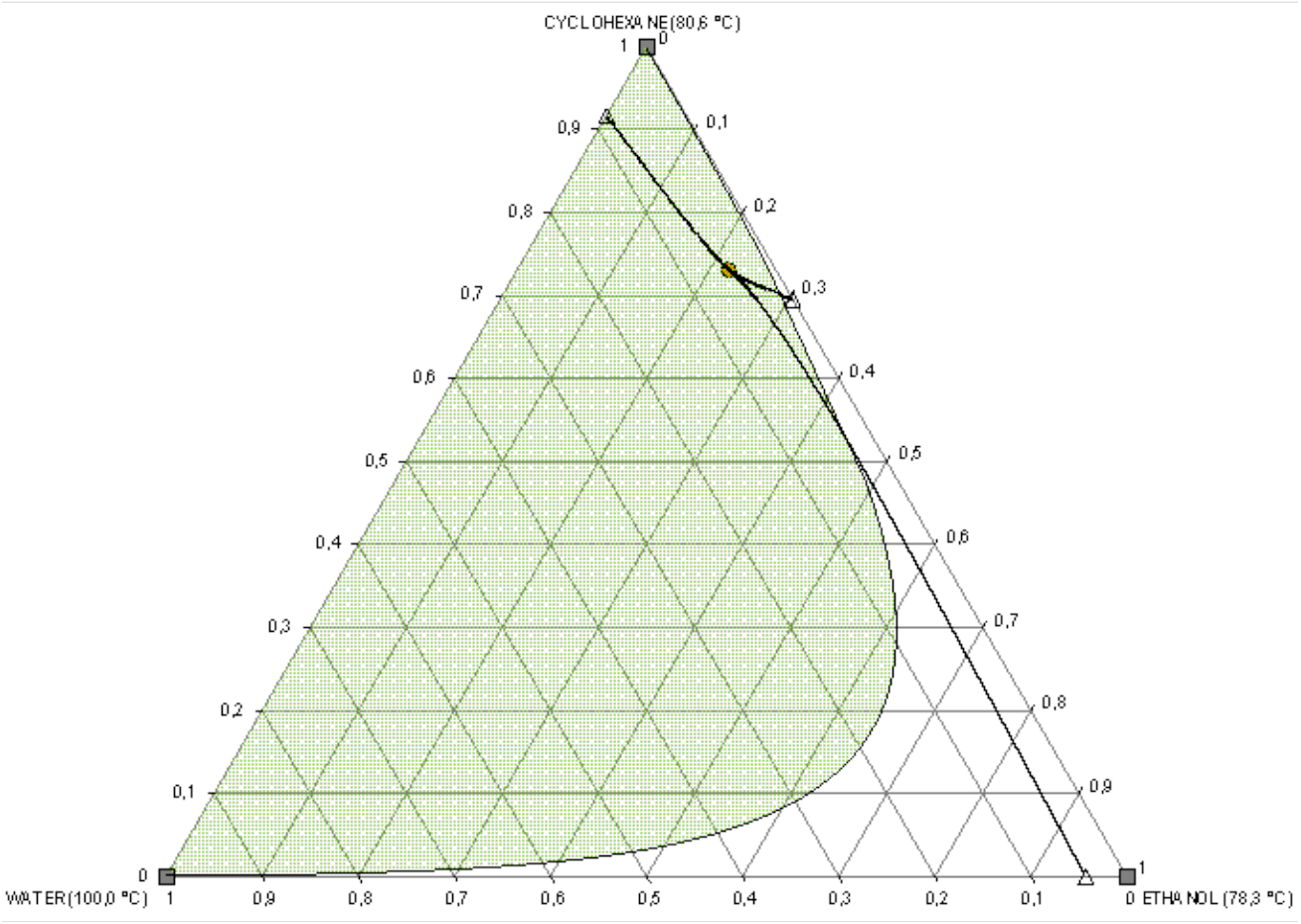
As shown by the equilibrium diagram below (generated for example with the mixture properties calculation service in ProSimPlus), the ethanol-water binary mixture is particularly difficult to separate due to the presence of an azeotropic point and the very low relative volatility of the two components on the pure ethanol side.



Heterogeneous azeotropic distillation is generally used to separate non-ideal mixtures. This technique utilizes an “entrainer” (also called “liquid separating agent”) to form a ternary azeotrope with minimum boiling temperature. In addition, the presence of this entrainer must create a demixion zone which will make it possible to overcome the traditional distillation frontiers.

The “entrainer” selected to separate the water-ethanol mixture is here the cyclohexane.

The ternary diagram of the water / ethanol / cyclohexane system at atmospheric pressure is shown below (this diagram was generated with ProSimPlus).



Thermodynamic analysis of the ternary system water / ethanol / cyclohexane

The analysis of this diagram reveals the presence of 3 binary azeotropes (represented by triangles on the ternary diagram). The temperature of each of these azeotropes is lower than the bubble temperatures of the mixture pure substances. In addition, the three components form a ternary azeotrope (represented by a circle on the ternary diagram) whose temperature is lower than the bubble temperatures of the pure substances and than the temperatures of binary azeotropes. Consequently, the ternary azeotrope is an unstable node, the binary azeotropes are “saddles” points and the pure substances are the stable nodes of the system.

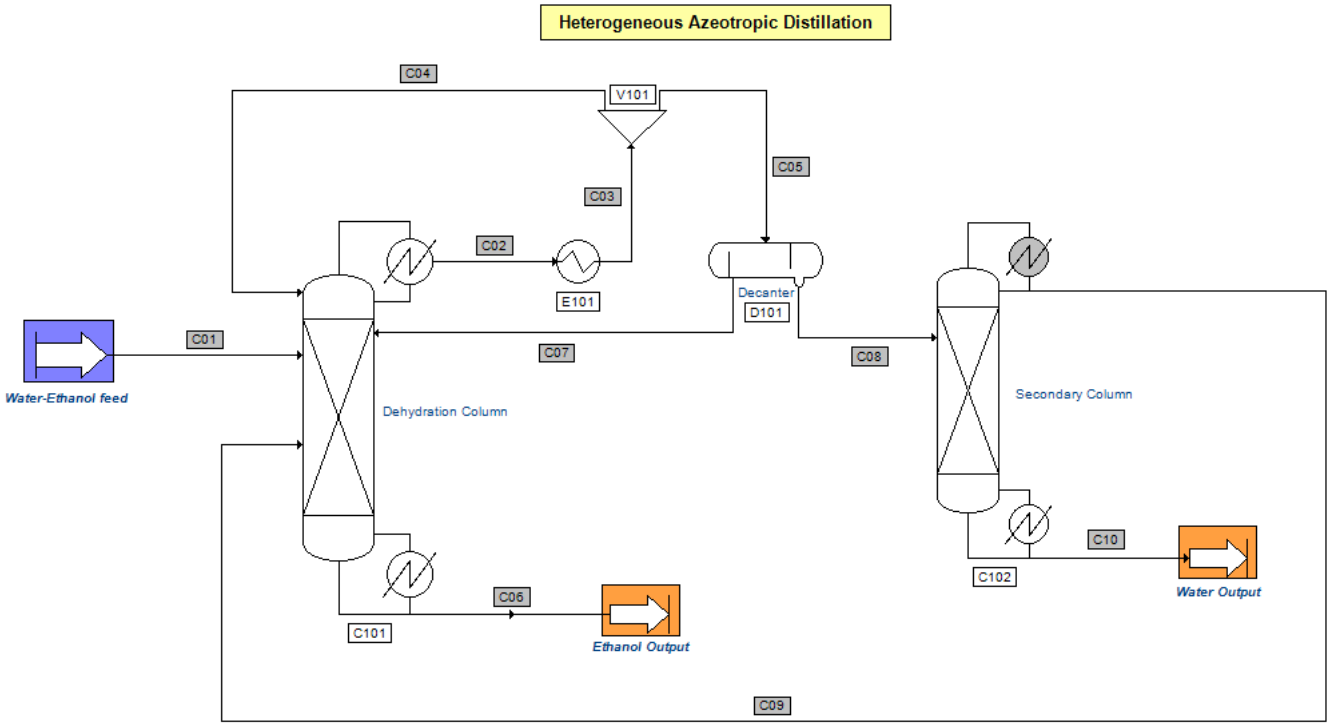
The ternary diagram breaks up into three zones, separated by frontiers that cannot be crossed by traditional distillation. This means that in a column fed with a given mixture of these three components,

- one of the three pure substances (depending on the zone in which is located the feed) is obtained at the bottom of the column,
- a mixture close to ternary azeotrope is obtained at the top of the column.

It should be noted that the distillation frontiers calculated by the software are curved and not linear. The demixion area, represented by the hatched surface, was calculated at 25°C.

1.2. Process flowsheet

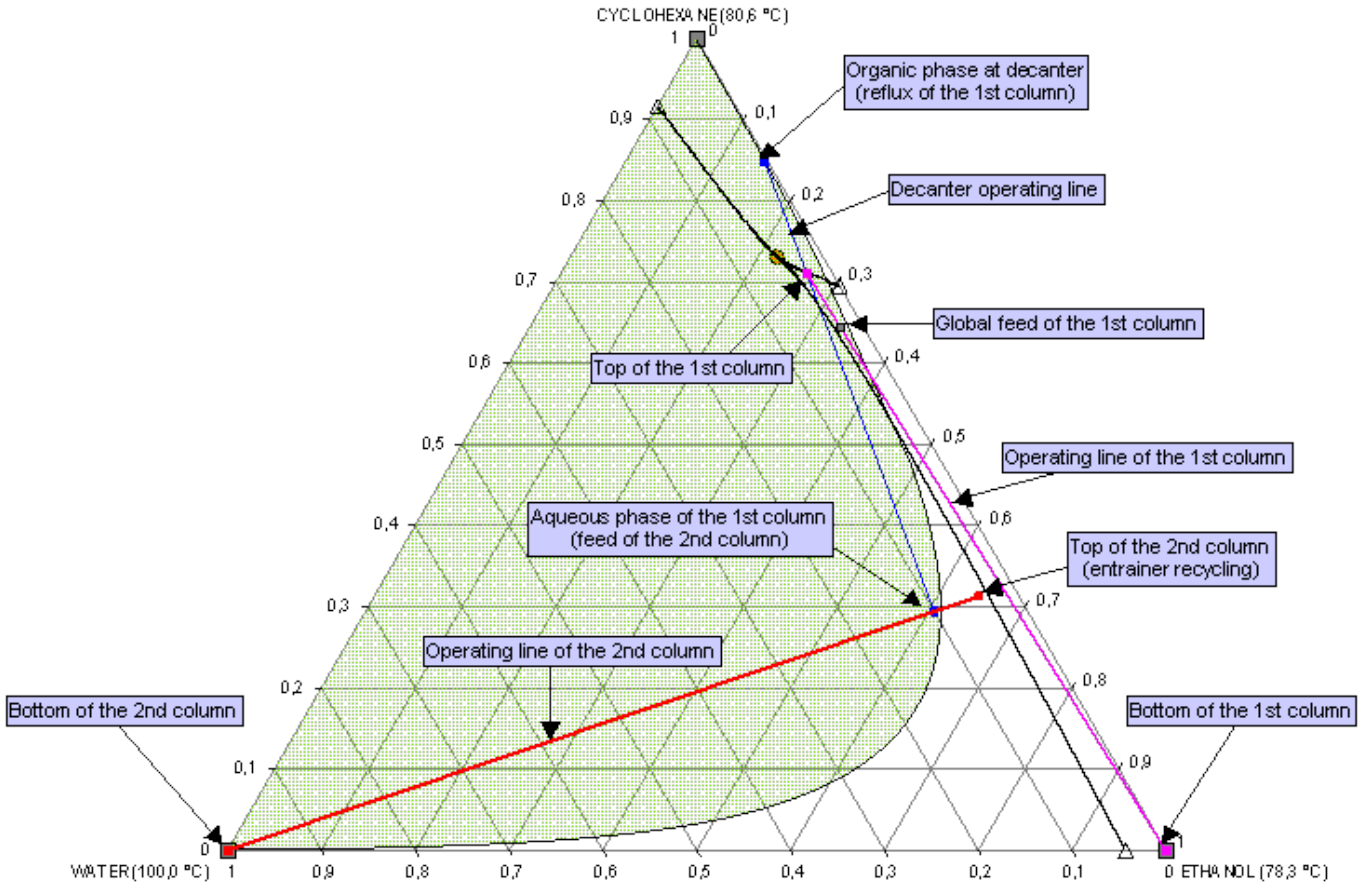
The principle process flowsheet for the separation of the binary mixture considered is as follows:



Process flowsheet of heterogeneous azeotropic distillation

The total feed of the column (C101) must be located in the area that makes it possible to obtain the ethanol at the bottom of the column (area delimited by the points pure ethanol - binary azeotrope water-ethanol - ternary azeotrope - binary azeotrope cyclohexane-ethanol). The vapor distillate of this column is condensed in a cooler heater (E101, from stream C02) and sub-cooled so as to increase demixion effect. This stream is sent in a decanter (D101, from stream C05), the light phase leaving this equipment (organic phase rich in ethanol) constitutes the reflux flow of the column (stream C07) and the heavy phase (aqueous phase) feeds the second column (C102, stream C08) which will make it possible to purify water and to recycle the entrainer.

The following ternary diagram illustrates the analysis of the mass balances obtained by the simulation and presented in the paragraphs hereafter. The total feed of the first column, made up of the feed of the process and the recycling stream of entrainer, is located on the operating line of the first column.



Analysis of simulation results

1.3. Specifications

The process specifications are as follow:

- At the bottom of column C101, ethanol must have a purity of 99.9999% mass
- At the bottom of column C102, ethanol must have a purity of 99.99% mass.

1.4. Components

Components taken into account in the simulation are taken from the ProSimPlus standard database:

- Water
- Ethanol
- Cyclohexane

1.5. Thermodynamic model

The thermodynamic model used for this process is based on an activity coefficient approach. The UNIFAC modified Dortmund [1] [2] has been selected for this simulation. Furthermore, in order to take into account the possible liquid phase splitting in the calculations, the corresponding option has to be activated in the thermodynamic model selection window.

1.6. Operating conditions

✓ Process feed

Parameters	*Value*
Total flowrate (kg/h)	330
Mass fraction	
Water	0.065
Ethanol	0.935
Temperature (°C)	20
Pressure (atm)	1.05

✓ Column C101

Operating parameters	*Value*
Type of column	Distillation with partial condenser
Number of theoretical stages	45
Feed stage C01	14
Feed stage C04	1
Feed stage C09	17
Feed stage C07	14
Top pressure (atm)	1
Pressure drop in the column (atm)	0.15
Vapor distillate flowrate (kmol/h) for a feed flowrate of 1 kmol/h	0.88
Condenser duty (W)	0

Additional specifications for column C101:

Specification		*Product type*	*Component*	*Value*	*Phase*	*Type*	*Action*
1 :	Mass fraction	Bottom liquid product	Ethanol	0.999999	Liq.	Mass.	Vapor distillate flowrate

✓ Heat exchanger E101

Operating parameters	*Value*
Type	Cooler/heater
Output temperature (°C)	45

✓ Decanter D101

Operating parameters	*Value*
Temperature (°C)	45
Pressure (atm)	1

✓ Column C102

Operating parameters	*Value*
Type of column	Distillation with total condenser
Type of condenser	total
Number of theoretical stages	25
Feed stage C08	7
Pressure Top (atm)	1.01

Additional specifications for column C102:

Specifications		*Product type*	*Component*	*Value*	*Phase*	*Type*	*Action*
1 :	Mass fraction	Bottom liquid product	Water	0.9999	Liq.	Mass.	Liquid distillate flowrate

✓ Splitter V101

Operating parameters	*Value*
Splitting rate for stream C04	50%

1.7. "Hints and Tips"

This process includes a recycle stream which must take into account the fact that the feed stream does not contain the entrainer (cyclohexane) and that the columns are three-phase columns. This increases the complexity of the convergence. ProSimPlus only requires initialization of one stream. In this case, only stream C03 has been initialized. This makes it possible to calculate the decanter, then the distillation column C102 and then the distillation column C101.

Initialization parameters do not require to be close to the solution. The following values were used:

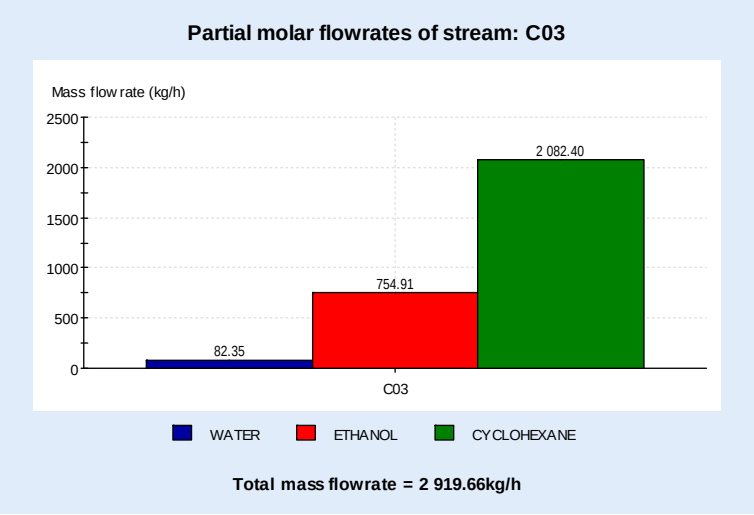
- Temperature: 45 °C
- Pressure: 1 atm
- Flowrate: 2 740 kg/h
- Mass composition: Water: 7% - Ethanol: 17 % - Cyclohexane: 76 %

2. RESULTS

2.1. Comments on results

Convergence of both columns is reached at the first try and the recycle loop convergence is reached in very few iterations.

It has to be noted that the resulting flowrate and composition of stream C03 are relatively far from the values given as initialization.



It is possible to reach the required purities (in particular for the ethanol production) with this process configuration and the proposed operating parameters. The loss in entrainer is very low and very few ethanol is lost.

At the first column (C101), the reboiler duty is 420 000 kcal/h.

At the second column (C102), the heat duty to be supplied at the reboiler is higher than for column C101: about 1 000 000 kcal/h.

The entrainer recycling flowrate (stream C09) is equivalent to the process feed flowrate.

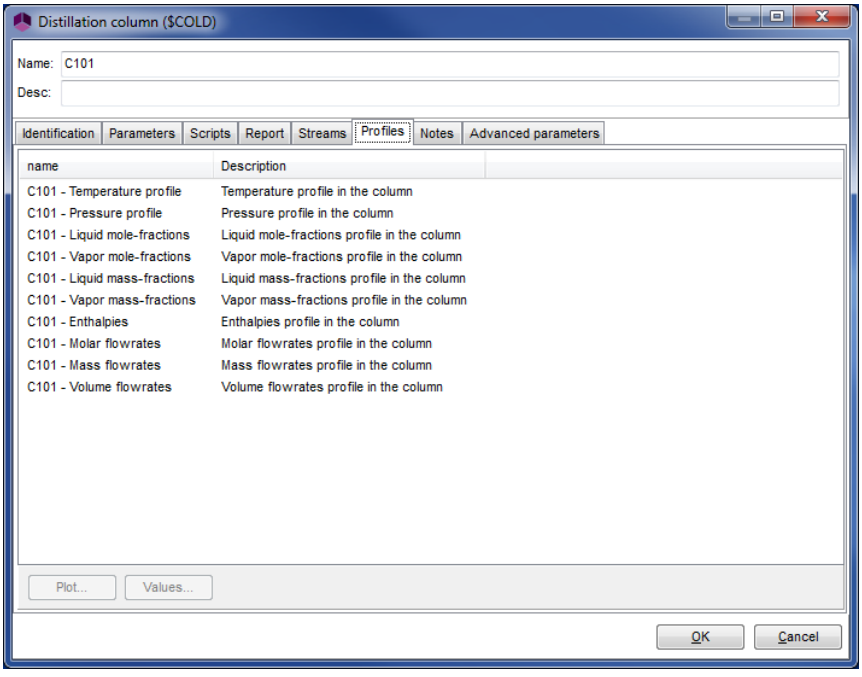
2.2. Mass and energy balances

This document presents only the most relevant stream results. In ProSimPlus, mass and energy balances are provided for every stream. Results are also available at the unit operation level (result tab in the configuration window).

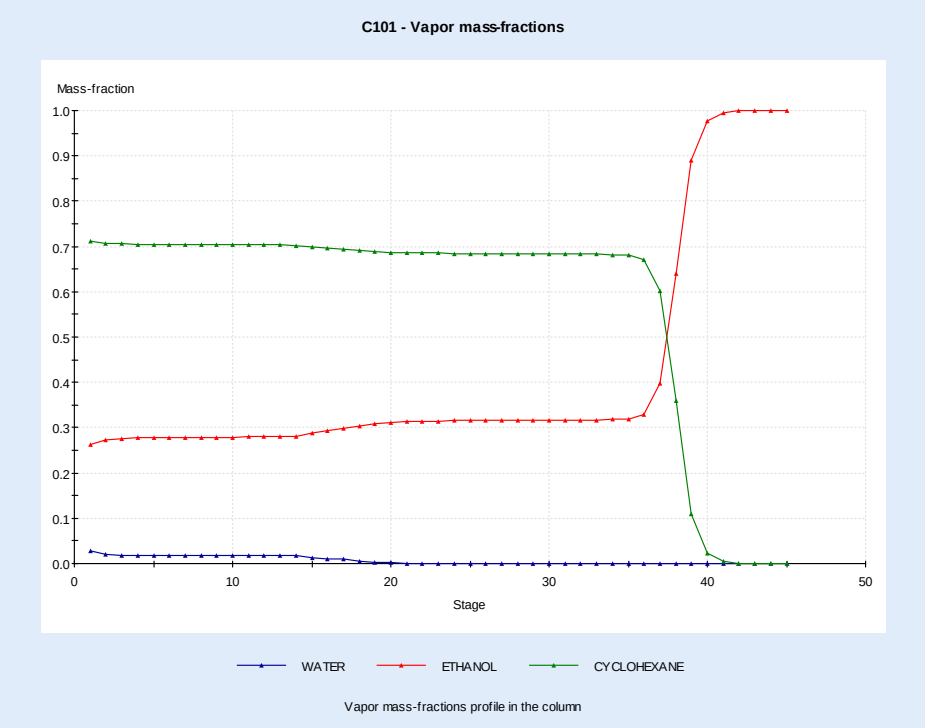
Streams		C01	C04	C06	C09	C10
From		Process Feed	V101	C101	C102	C102
To		C101	C101	Process Ou...	C101	Process Ou...
Partial flows		kg/h	kg/h	kg/h	kg/h	kg/h
WATER		21.45	41.177	0.00011214	19.377	21.45
ETHANOL		308.55	377.46	308.53	331.05	0.0021452
CYCLOHEXANE		0	1041.2	0.00019639	178.69	0
Total flow	kg/h	330	1459.8	308.53	529.12	21.452
Mass fractions						
WATER		0.065	0.028207	3.6347E-007	0.036621	0.9999
ETHANOL		0.935	0.25856	1	0.62567	0.0001
CYCLOHEXANE		0	0.71323	6.3653E-007	0.33771	0
Physical state		Liquid	Liquid	Liquid	Liquid	Liquid
Temperature	°C	20	45	81.904	65.439	100.28
Pressure	atm	1.05	1	1.15	1.01	1.01
Enthalpic flow	kcal/h	-80454	-1.8729E005	-55530	-87102	-10887
Vapor molar fraction		0	0	0	0	0

2.3. Composition profiles

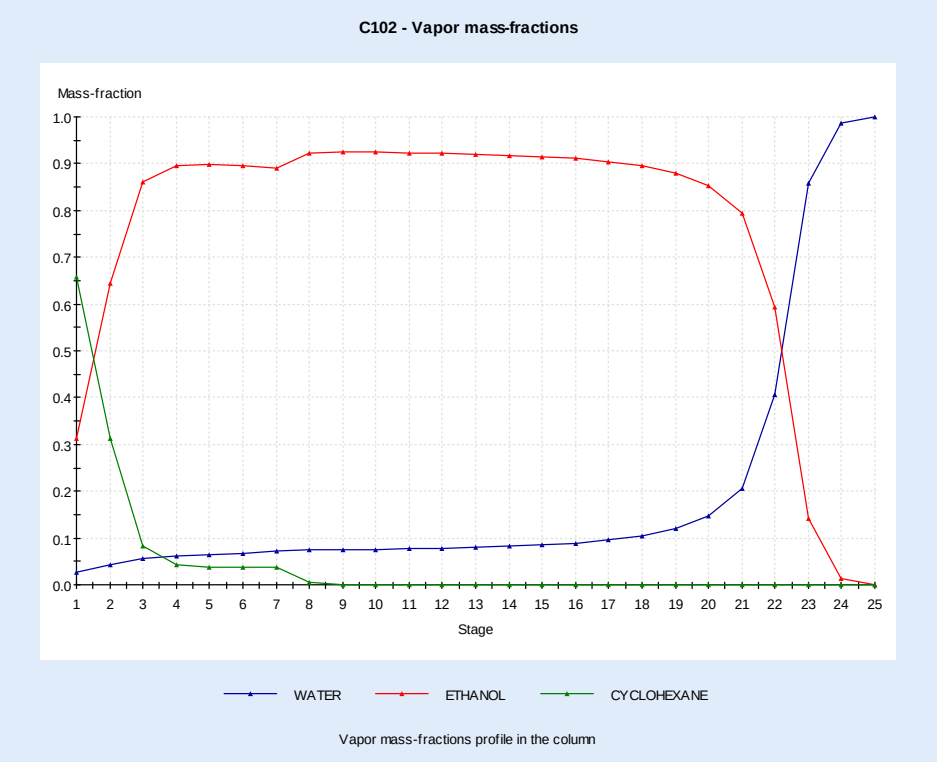
Composition profiles can be accessed after the simulation in each column configuration window, in the “Profiles” tab. Double clicking on the profile will generate the corresponding graph.



Column C101



Column C102



3. REFERENCES

[1] WEIDLICH V., GMEHLING J

"A Modified UNIFAC Model: 1. Prediction of VLE, h^E and γ^{∞}"

Ind. Eng. Chem. Res., 26, 1372-1381 (1987)

[2] GMEHLING J., JIDING L., SCHILLER M.

"A modified UNIFAC model. 2. Present parameter matrix and results for different thermodynamic properties"

Ind. Eng. Chem. Res., 32, 178-193 (1993)

