

Getting started with Simulis® Thermodynamics

Use Case 7: Plotting residue curves

Introduction

This document presents the different steps to follow in order to plot residue curves with Simulis Thermodynamics.

The steps are the following:

- Step 1: Set the thermodynamic system
- Step 2: Plot the ternary diagram
- Step 3: Plot the residue curves

The ternary system used in this example is a mixture of acetone, methanol and methyl-ethyl-ketone (MEK).



Before studying this case, it is recommended to consult *“Getting Started with Simulis Thermodynamics, Case 1”*

About residue curves...

Residue curves map (RCM) are useful, for example, to visualize and investigate entrainers that can facilitate distillation by breaking an azeotrope.

Because the choice of an entrainer determines the separation sequence, its selection is a critical step in the synthesis and conceptual design of azeotropic distillation processes.

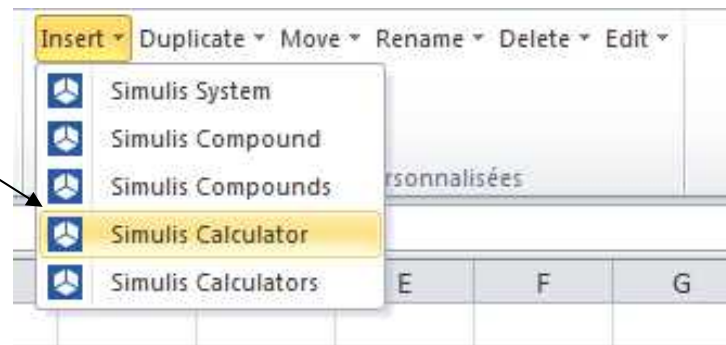
Residue curves are obtained by plotting the evolution through time of the composition of the liquid residue at vapor equilibrium for a simple batch distillation (Rayleigh distillation), starting with the initial composition of the boiler. The path of the liquid compositions starting from the initial point (charge composition) is called a *residue curve*.

Step 1: Set the thermodynamic system

ACCESS THE THERMODYNAMIC CALCULATOR EDITOR:

- If you are using Simulis Thermodynamics in Excel:

Create the calculator object in a spreadsheet



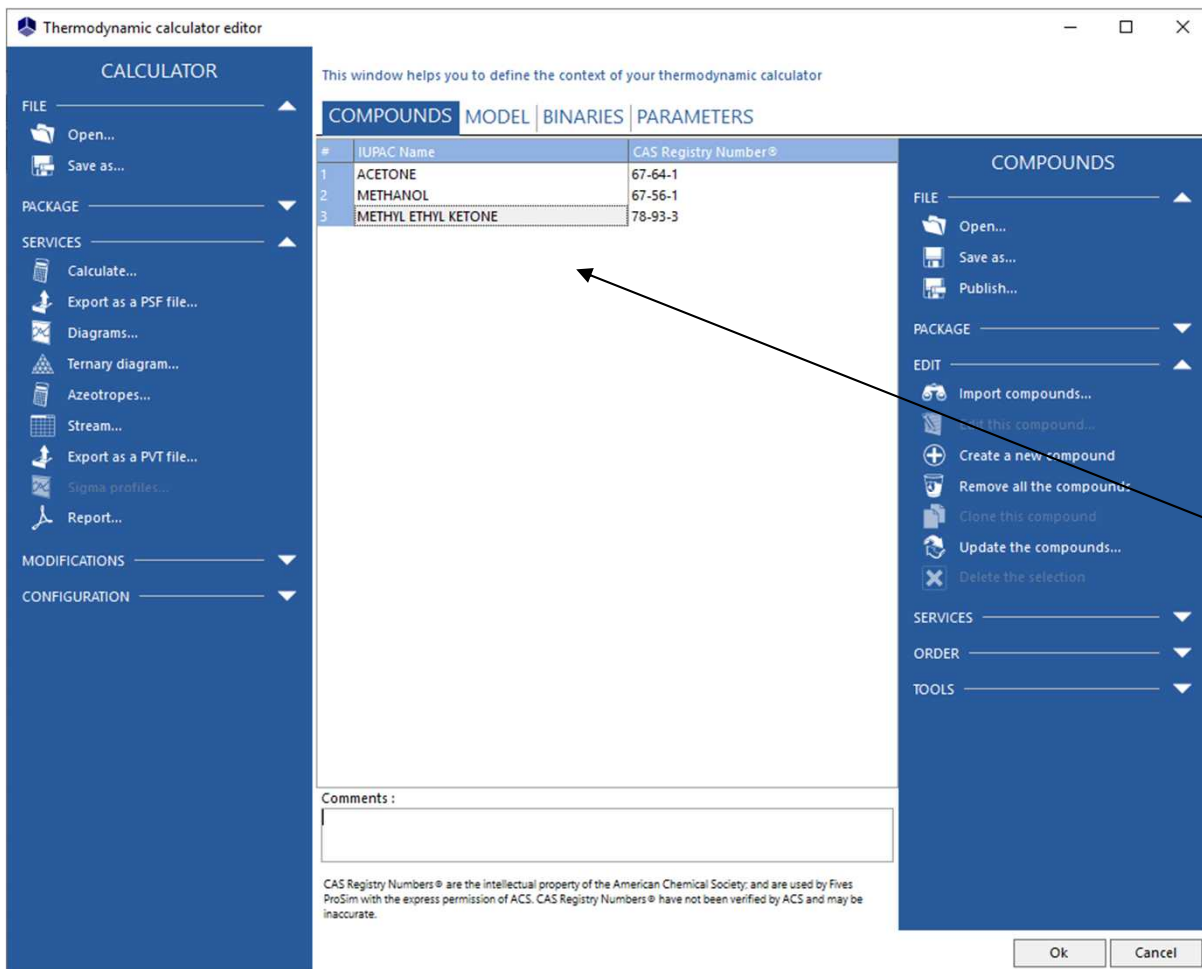
- If you are using Simulis Thermodynamics within another ProSim environment (ProSimPlus, BatchReactor, BatchColumn etc...):

Click on the thermodynamic icon to open the calculator editor:



Simulis Thermodynamics is a « software component » that you can integrate into different applications: ProSim software, Excel, Matlab, your own software, etc...

Step 1: Set the thermodynamic system



Select Acetone, Methanol and Methyl-Ethyl-Ketone in the standard pure components database (click on "Import compounds").



Refer to "Getting Started with Simulis Thermodynamics, use case 1" for details on these operations

Step 1: Set the thermodynamic system

Select the NRTL profile
in the "MODEL" tab

The screenshot shows the 'Thermodynamic calculator editor' window. The left sidebar contains a 'CALCULATOR' menu with options like FILE, PACKAGE, SERVICES, and MODIFICATIONS. The main area has tabs for COMPOUNDS, MODEL, BINARIES, and PARAMETERS. The 'MODEL' tab is active, showing a form to define the thermodynamic model. The 'Name' field is set to 'NRTL', and the 'Profile' dropdown is also set to 'NRTL'. Other settings include 'Approach type' (From activity coefficients), 'Equation of state' (Perfect gas), 'Activity coefficient model' (NRTL), and 'Enthalpy calculation' (H*=0, ideal gas, 25°C, 1 atm). A right sidebar titled 'THERMODYNAMIC MODEL' contains links for documentation and help. At the bottom right are 'Ok' and 'Cancel' buttons.



Refer to "Getting Started with Simulis Thermodynamics, use case 1" for details on these operations

Step 1: Set the thermodynamic system

Thermodynamic calculator editor

CALCULATOR

FILE

- Open...
- Save as...

PACKAGE

SERVICES

- Calculate...
- Export as a PSF file...
- Diagrams...
- Ternary diagram...
- Azeotropes...
- Stream...
- Export as a PVT file...
- Sigma profiles...
- Report...

MODIFICATIONS

CONFIGURATION

This window helps you to define the context of your thermodynamic calculator

COMPOUNDS | MODEL | **BINARIES** | PARAMETERS

These parameters correspond to the general values and are used if the user has not provided specific parameters (buttons to the right of each option in the thermodynamic profile)

Binaries view: ☒ Grid ☐ Matrix

Formulation : $g_{ij} - g_{ij}^0 = C_{ij}^0 + C_{ij}^1(T - 273.15)$, $a_{ij} = a_{ij}^0 + a_{ij}^1(T - 273.15)$

Compound	Compound	C_{ij}^0	C_{ij}^1	a_{ij}^0	C_{ij}^1
ACETONE	METHANOL	184,701	222,645	0,3084	0
ACETONE	METHYL ETHYL KETC	0	0	0	0
METHANOL	METHYL ETHYL KETC	307,427	217,91	0,3003	0

Not supplied Supplied Imported Estimated Error

Comments :

BINARIES

ACTIONS

- Import binaries...
- Clear all binaries
- Estimate binaries...
- Save the binaries...

OPTIONS

Unit

cal/mole

☐ parameters will be ignored

☒ parameters are automatically loaded

Ok Cancel

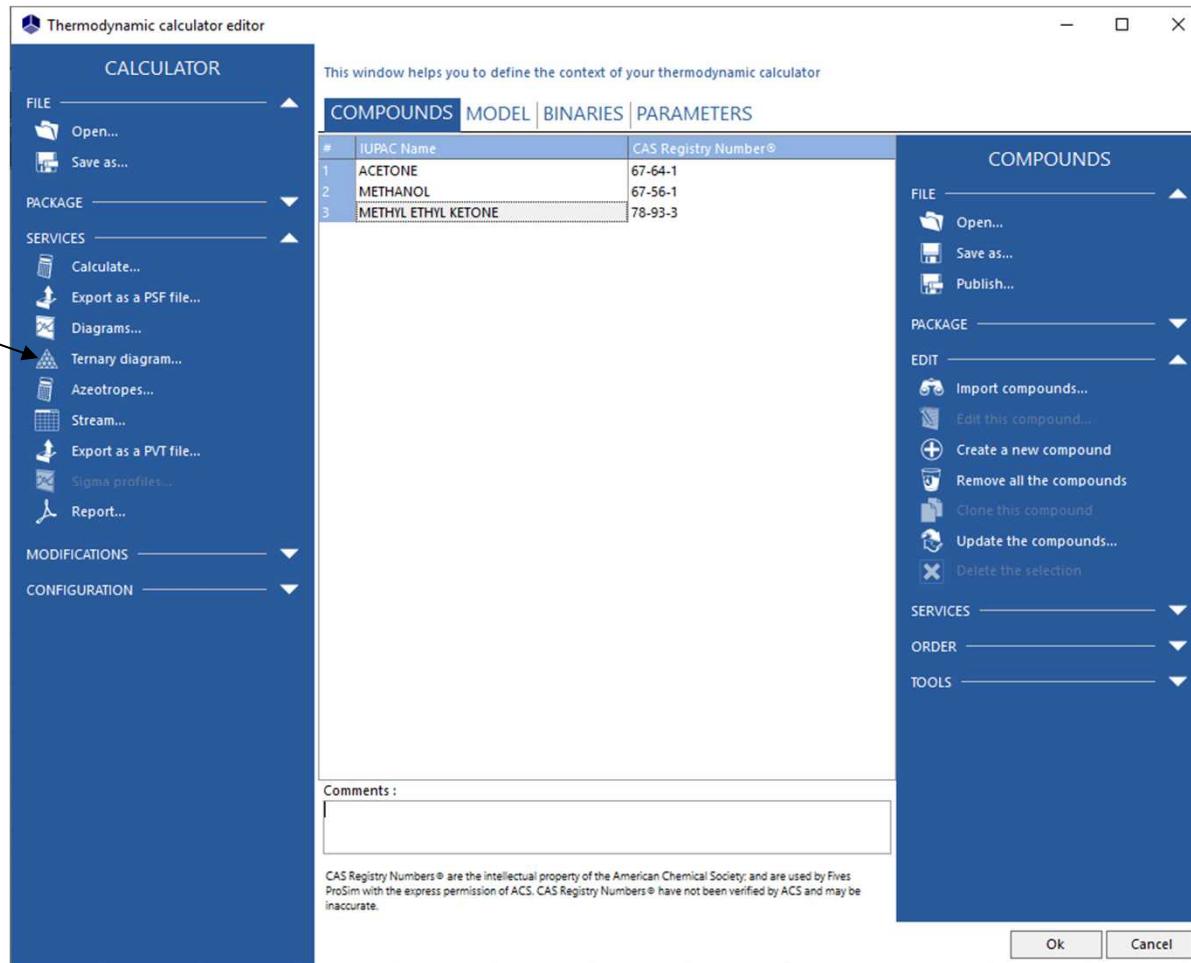
Click on the "**BINARIES**" tab (which appears when you select the NRTL model). The binaries interaction parameters (BIPs) available in the Standard database are automatically loaded.



Refer to "Getting Started with Simulis Thermodynamics, use case 1" for details on these operations

Step 2: Plot the ternary diagram

Click on “Ternary diagram” to open the residue curve calculation service



The residue curve calculation service is only available when 3 components at least are present in the list. If more than 3 components are present, a complementary window will allow to select only 3.

Step 2: Plot the ternary diagram

Set the pressure to 1 atm
(default value)

Change the temperature
units from Kelvin to
Celsius in the unit system

Click on “Azeotropes” to
identify the possible
azeotropes in the mixture

Residue curve...

RESIDUE CURVE

DATA

Pressure 1 atm

Edit the calculator

Extractive profiles

Extractive profiles data

RESULTS

Fractions Molar

Unit system

CALCULATIONS

Azeotropes

Boundaries

Isovolatilities

Liquid-Liquid equilibrium

Residue curve

OPTIONS

Numerical parameters

Graphic styles

Export to MS Excel

Sketch...

This window helps you to determine azeotropes and to plot the residue curves.

Project Acetone-Methanol-MEK ternary diagram

Azeotropes Isovolatilities Liquid-Liquid equilibrium Residue curve Ternary diagram

Sampling compositions (Molar)

ACETONE	METHANOL	METHYL ETHYL KETONE
0,06667	0,06667	0,86666
0,06667	0,86666	0,06667
0,86666	0,06667	0,06667

Add

Delete

Move up

Move down

Azeotropes

Pure ?	Name	Binary	Ternary	System	Temperatu...	ACETONE	METHANOL	METHYL E...
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Sampling compositions are automatically initialized, therefore it is not mandatory to provide values

Step 2: Plot the ternary diagram

The following table appears and displays boiling points of pure components as well as binary and ternary azeotropes

Residue curve...

RESIDUE CURVE

DATA

Pressure: 1 atm

Project: Acetone - Methanol - MEK residue curve calculation

Azeotropes | Boundaries | Isovolatilities | Liquid-Liquid equilibrium | Residue curve | Ternary diagram

Sampling compositions (Molar)

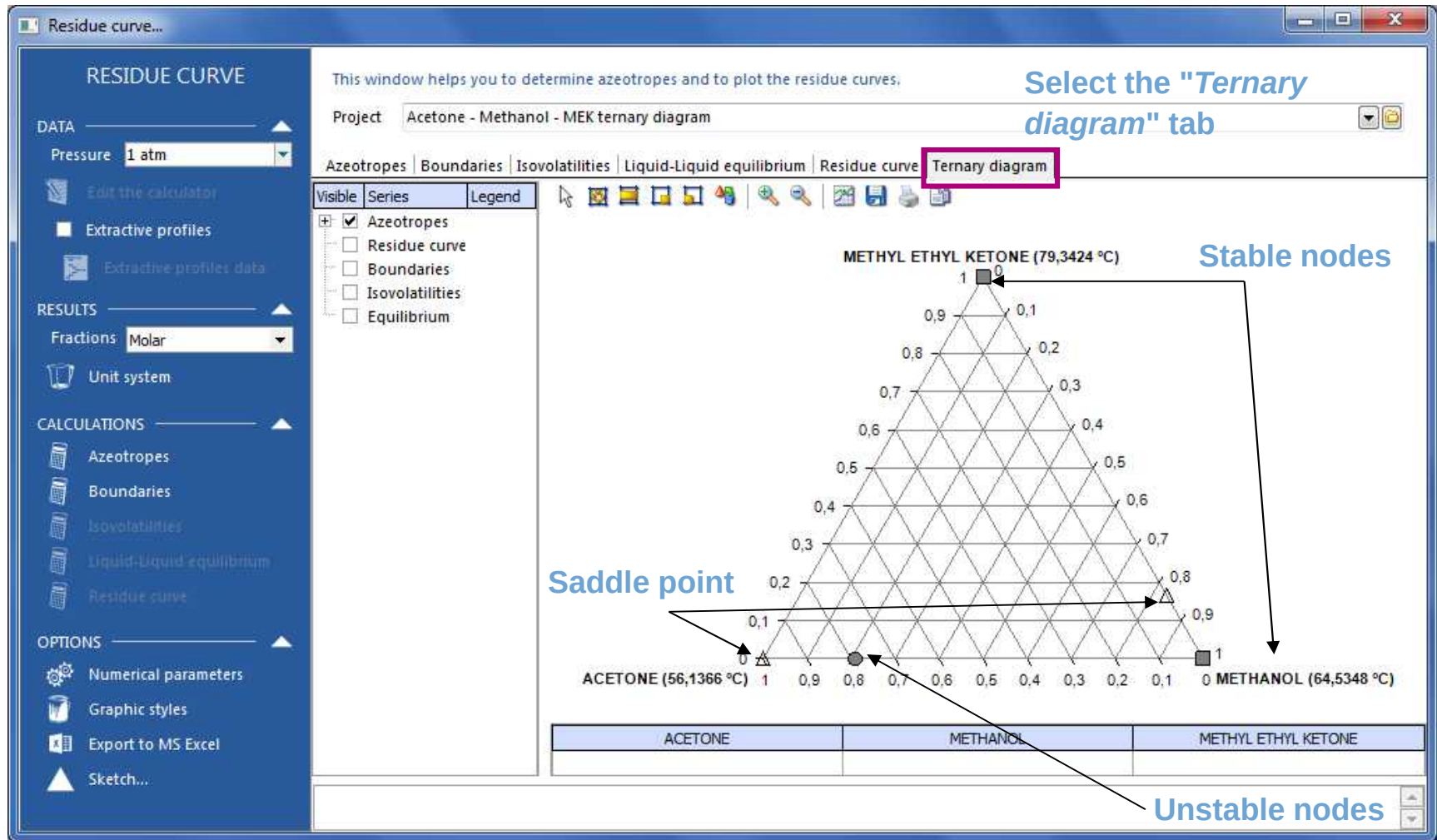
ACETONE	METHANOL	METHYL ETHYL KETONE
0,06667	0,06667	0,86666
0,06667	0,86666	0,06667
0,86666	0,06667	0,06667

Azeotropes

Pure ?	Name	Binary	Ternary	System	Temperature (K)	ACETONE	METHANOL	METHYL ETHYL K...
☒	ACETONE	Unknown	Saddle	Homogeneous	329,287	1	0	0
☒	METHANOL	Unknown	Stable	Homogeneous	337,685	0	1	0
☒	METHYL ETHYL KETO	Unknown	Stable	Homogeneous	352,492	0	0	1
☐	Azeotrope - 1	Unstable	Unstable	Homogeneous	328,543	0,791229200979475	0,208770799020525	0
☐	Azeotrope - 2	Unstable	Saddle	Homogeneous	337,142	0	0,833992231081272	0,166007768918728

This system presents two homogeneous azeotropes (acetone-methanol and methanol-MEK) and no ternary azeotrope

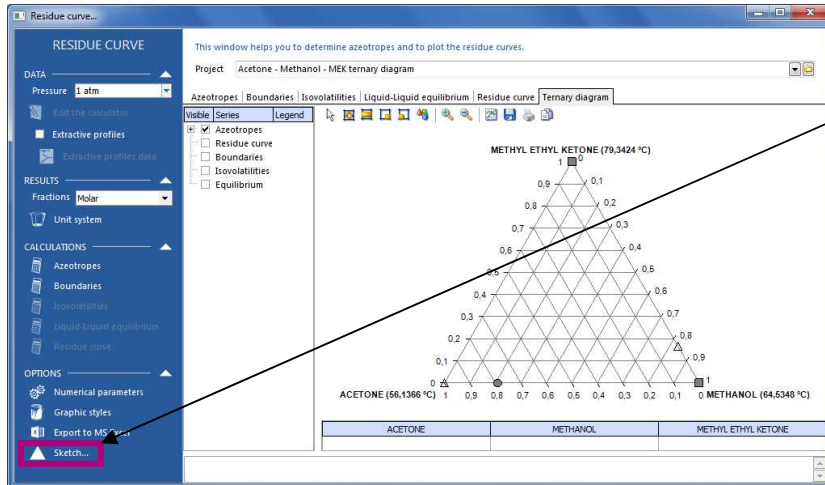
Step 2: Plot the ternary diagram



- Stable nodes are represented by a square (MEK and methanol)
- Unstable nodes are represented by a circle (acetone-methanol azeotrope)
- Saddle points are represented by a triangle (MEK-methanol azeotrope and acetone)

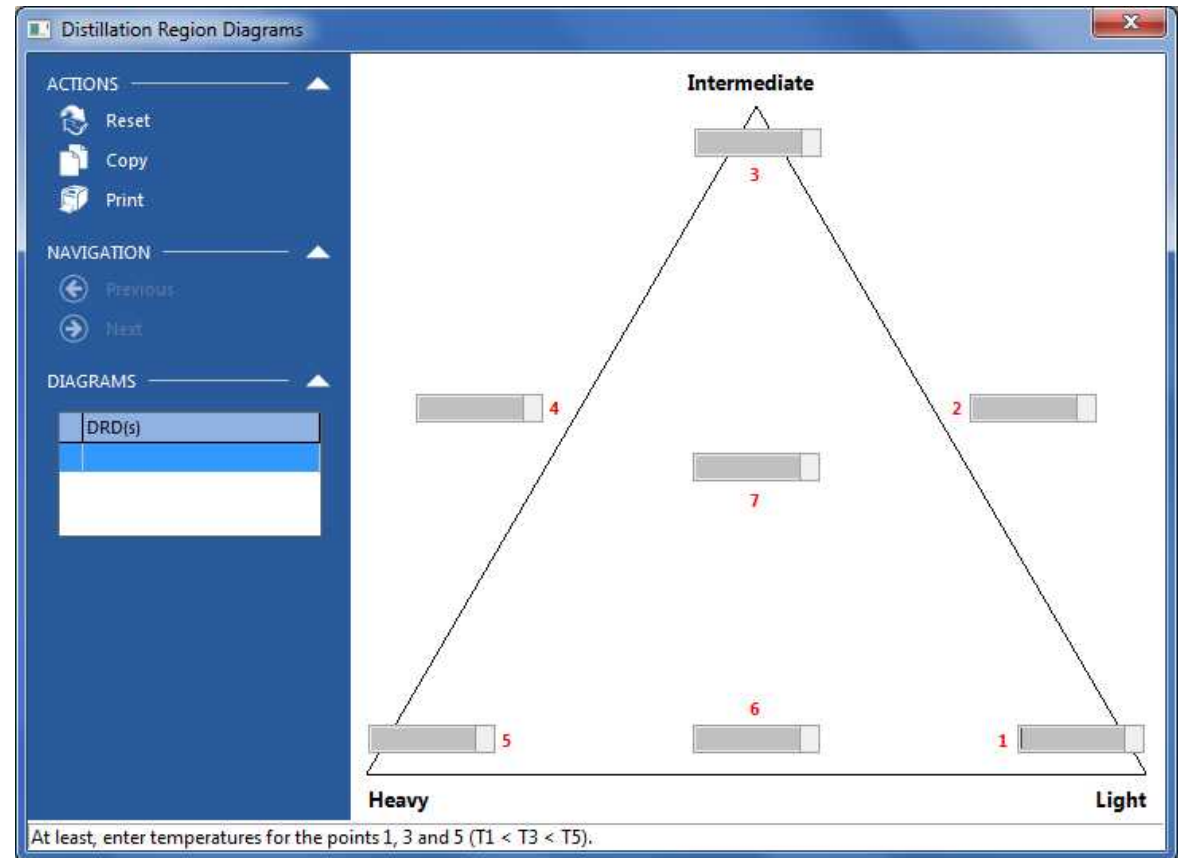
Step 2: Plot the ternary diagram

Click on "*Sketch...*".



This graph gives a simplified representation of the ternary diagram.

In each relevant cells, enter the temperatures calculated in the previous table. In this example there is no ternary azeotrope (cell #7) and no binary azeotrope between heavy and light (cell #6). All other cells can be filled.



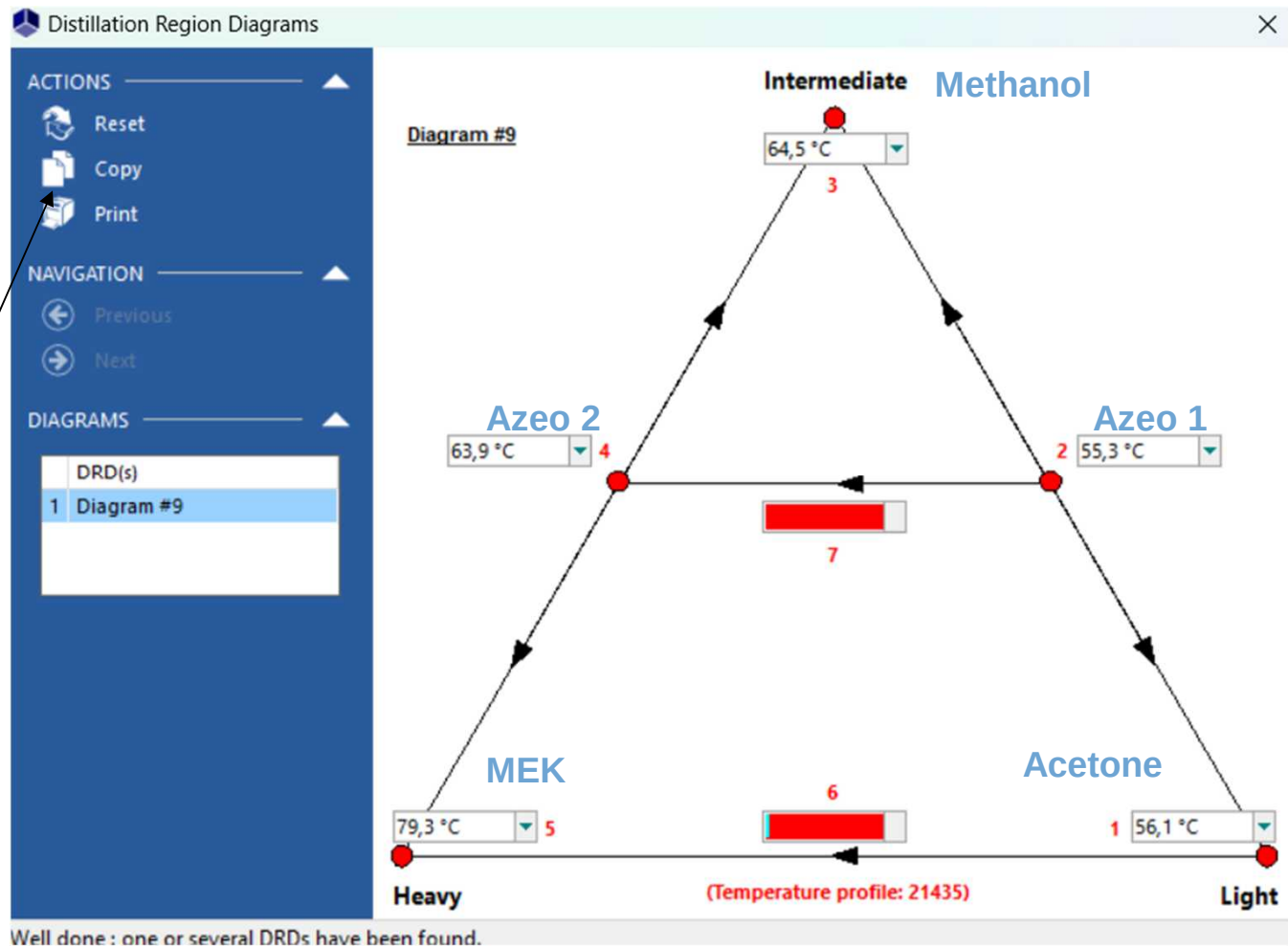
Step 2: Plot the ternary diagram

Azeotropes

Pure ?	Name	Binary	Ternary	System	Temperature (°C)	ACETONE	METHANOL	METHYL ETHYL K...
☒	ACETONE	Unknown	Saddle	Homogeneous	56,1366	1	0	0
☒	METHANOL	Unknown	Stable	Homogeneous	64,5348	0	1	0
☒	METHYL ETHYL KETC	Unknown	Stable	Homogeneous	79,3424	0	0	1
☐	Azeotrope - 1	Unstable	Unstable	Homogeneous	55,3933	0,791229200979474	0,208770799020526	0
☐	Azeotrope - 2	Unstable	Saddle	Homogeneous	63,9921	0	0,833992231081272	0,166007768918721

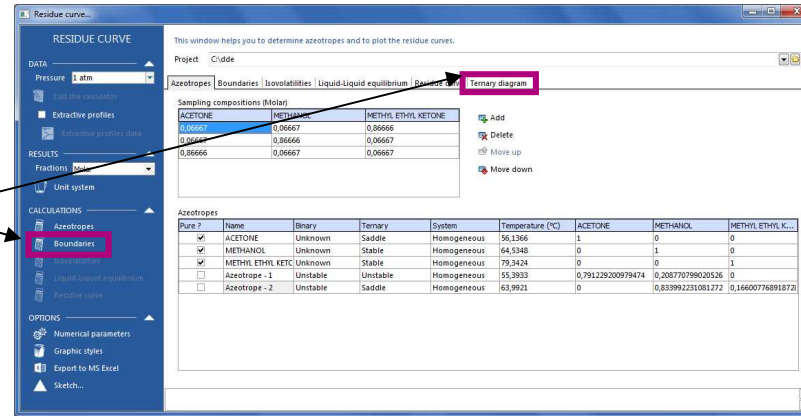
As soon as temperatures are provided, arrows appear between the binaries. It shows the direction of residue composition when increasing the temperature.

You can copy this graph into other applications



Step 2: Plot the ternary diagram

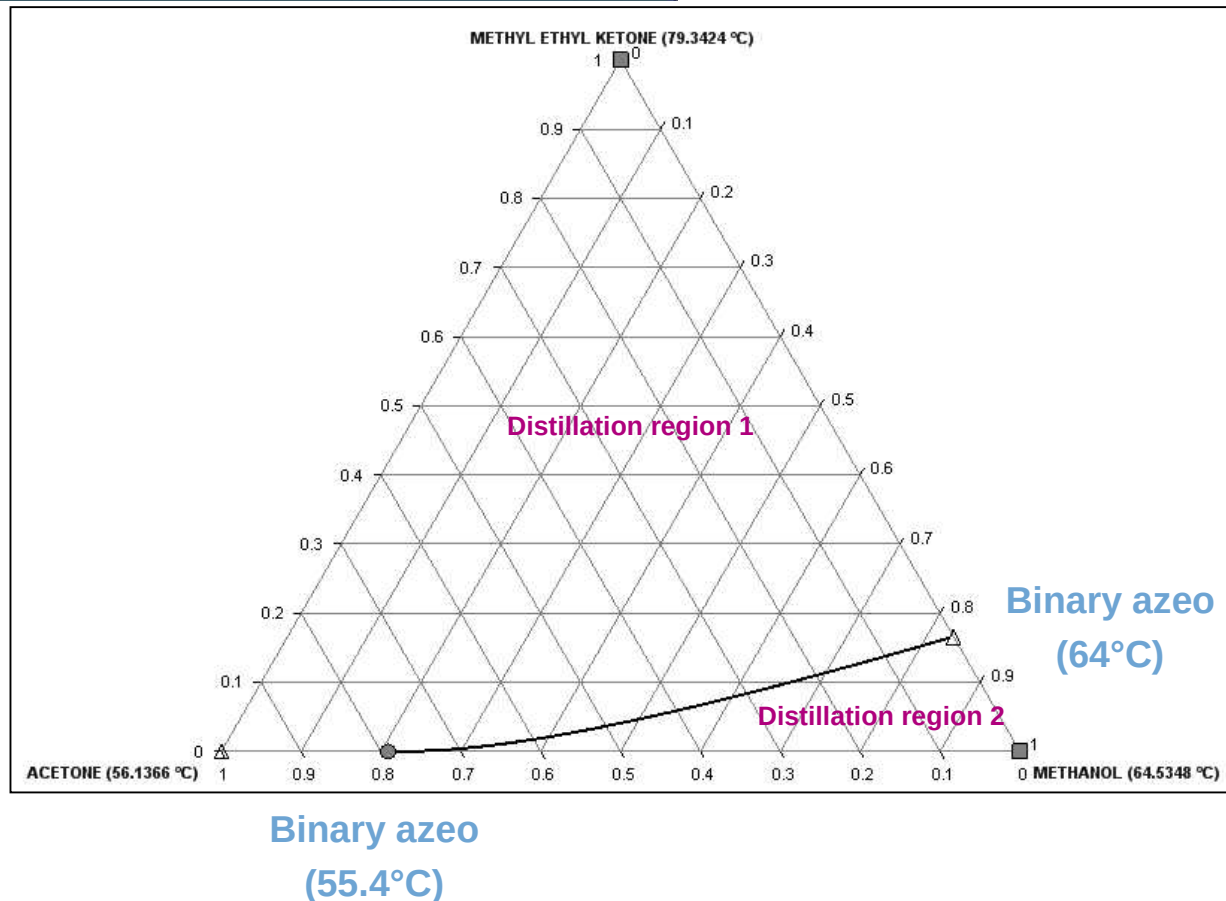
Close the sketch window to go back to the main interface. Click on "**Boundaries**" and then on the "**Ternary diagram**" tab.



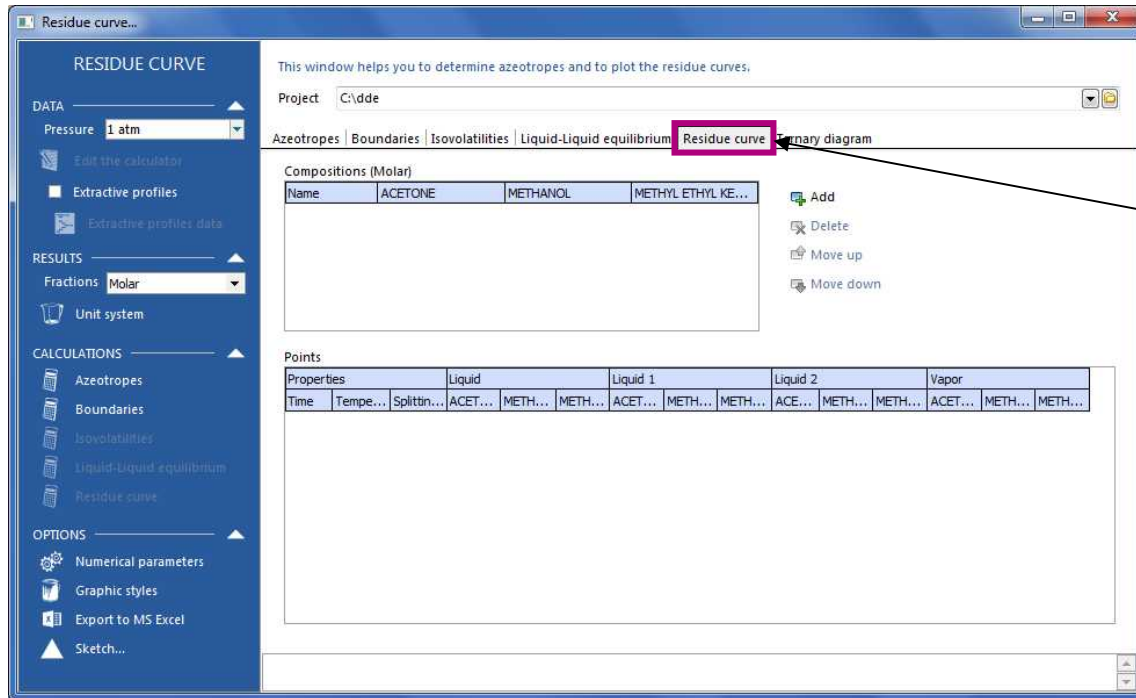
This diagram shows the distillation dividing curve which is called *distillation boundary*.

A *distillation boundary* corresponds to a frontier that cannot be crossed by distillation.

The presence, location and structure of the distillation boundaries are crucial to evaluate the distillation feasibility. For each distillation column, the distillate and the bottom products must be in the same distillation region.



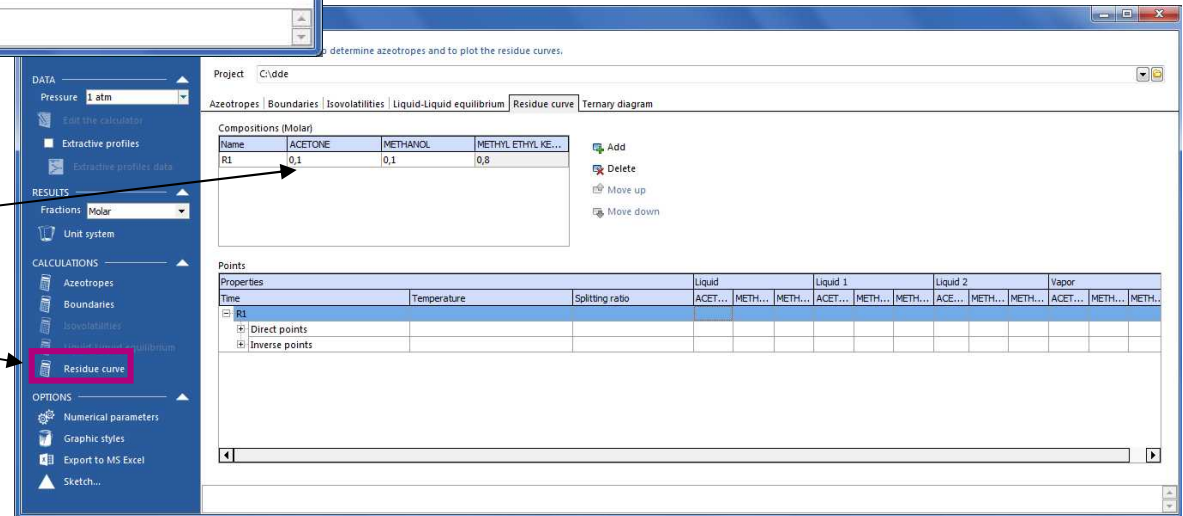
Step 3: Plot the residue curves



Click on the "Residue curve" tab

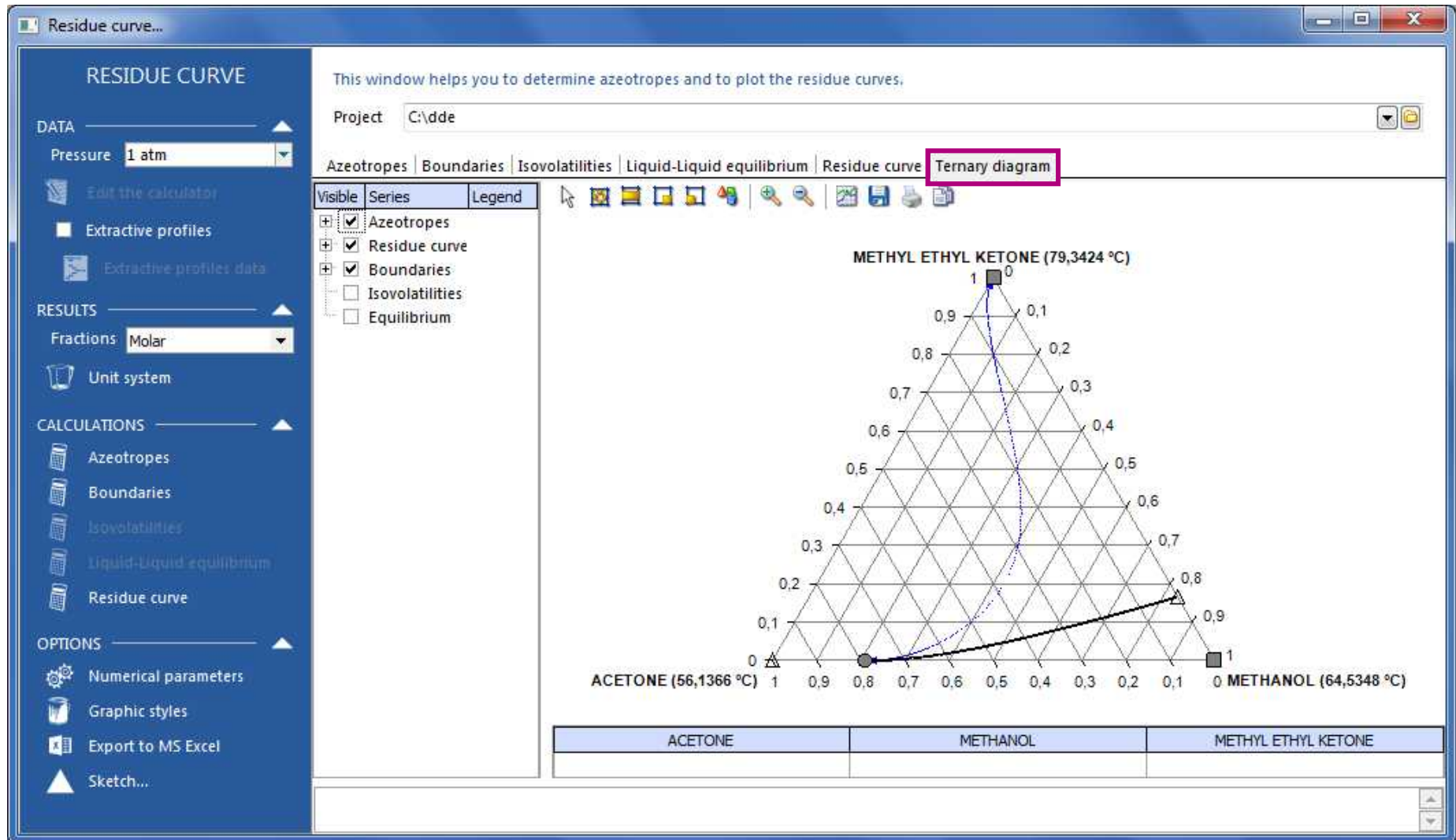
Create a table with one line in which you will enter a mixture composition

Click on "Residue curve" to run the calculation



Step 3: Plot the residue curves

Click on the "*Ternary diagram*" tab to view the graph



Step 3: Plot the residue curves

Compositions (Molar)

Name	ACETONE	METHANOL	METHYL ETHYL KE...
R1	0,1	0,1	0,8
R2	0,1	0,8	0,1
R3	0,8	0,1	0,1
R4	0,2	0,2	0,6
R5	0,2	0,6	0,2
R6	0,6	0,2	0,2

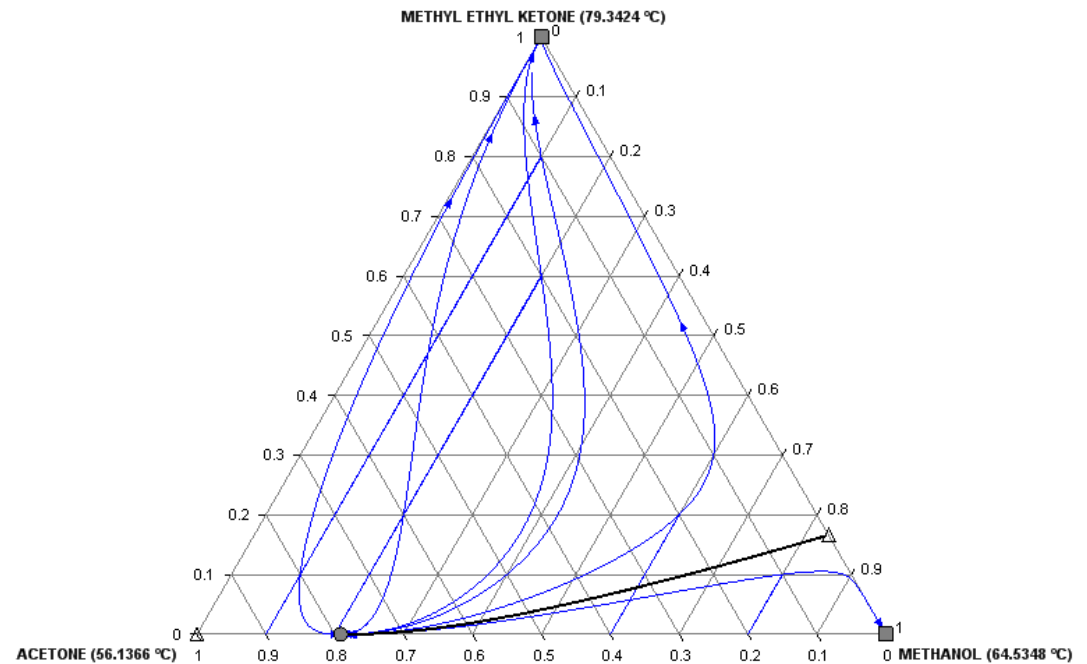
 Add
 Delete
 Move up
 Move down

You can add more composition samples in order to have additional residue curves and a more comprehensive analysis of the system

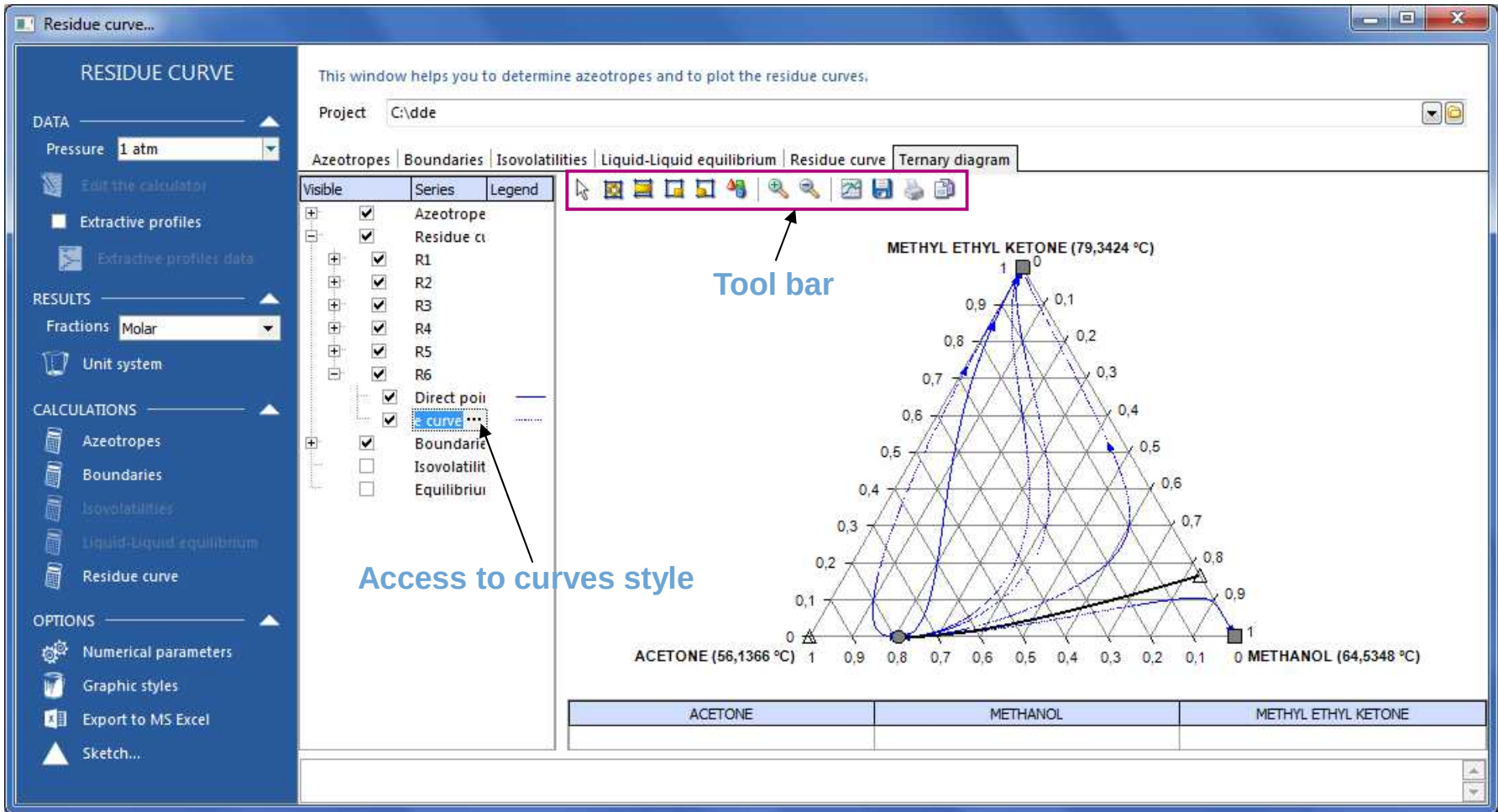
Here, we enter 6 different compositions corresponding to 6 different residue curves R1 to R6

The direction of the residue curves goes from the lightest boiling point (acetone-methanol azeotrope) toward MEK or methanol, depending on the initial composition

The location of the feed point determines the distillation region of the potential distillate and product



Step 3: Plot the residue curves



You can switch the diagram summitts and modify the graphical properties of the diagram and the curves. You can also copy the diagram into other documents or save it as a picture.



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