Flash Point Calculation by UNIFAC

Short Introduction and Tutorial

DDBSP - Dortmund Data Bank Software Package

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1 Introduction

This software calculates flash points of flammable liquid mixtures by the UNIFAC based methods "original UNIFAC"[1] and "modified UNIFAC (Dortmund)"[2]. Both methods are delivered with the latest published parameters.

The algorithm to calculate the flash points is described in a scientific paper[3] from 1982. The basic procedure is that from known pure component properties (flash point and heat of combustion) the real behavior of the mixture is estimated by the activity coefficients which are obtained from the predictive group contribution models orig. UNIFAC and modified UNIFAC (Dortmund). Additionally needed parameters are Antoine coefficients for the calculation of the saturated vapor pressures of pure components.

1.1 Theoretical Background

The flash point temperature of a pure combustible component is the temperature T_F for which the saturated pressure is equal to the lower flammability limit:

$$\frac{P_i^S}{L_i} = 1 \; or \; P_i^S = L_i$$

with

P_i^S Saturated vapor pressure of component *i*

L_i Lower flammability limit of component *i*

For mixtures this relation can be extended to

$$\sum_{i=1}^{N} \frac{P_i}{L_i} = 1$$

with

N Number of components

P_i Partial pressure of component *i* in a vapor-air mixture in equilibrium

L_i Partial pressure in a vapor-air mixture of component i corresponding to the lower flammability limit of the pure component.

The temperature dependence of the lower flammability limit is estimated by the function

$$L_i(t) = L_i(25°C) - 0.182\, t - 25/H_{ci}$$

with

$L_i(t)$ Lower flammability limit at temperature *t* in °C of component *i*

[1] Wittig R., Lohmann J., Gmehling J., "Vapor-Liquid Equilibria by UNIFAC Group Contribution. 6. Revision and Extension", Ind.Eng.Chem.Res., 42(1), 183-188, 2003

[2] Jakob A., Grensemann H., Lohmann J., Gmehling J., "Further Development of Modified UNIFAC (Dortmund): Revision and Extension 5", Ind.Eng.Chem.Res., 45(23), 7924-7933, 2006

[3] Gmehling J., Rasmussen P., "Flash Points of Flammable Liquid Mixtures Using UNIFAC.", Ind.Eng.Chem. Fundam., 21(2), 186-188, 1982

$L_i(25°C)$ Lower flammability limit at temperature 25 °C (tabulated, stored) of component *i*

H_{ci} Heat of combustion of component *i* in kJ/mol typically.

The partial pressures at vapor-liquid equilibrium conditions $P_i$can be calculated by

$$P_i = x_i \gamma_i P_i^S$$

when the vapor-air mixture behaves as an ideal gas.

x_i Mole fraction of component *i*

γ_i Activity coefficient of component *i* at a given temperature

P_i^S Saturated vapor pressure of component *i* at a given temperature

The activity coefficients $\gamma_i$are calculated by UNIFAC, the saturated vapor pressure of the pure components by the Antoine equation.

The flash point temperature T_F can now be calculated by iterating this equation to fulfill the condition

$\sum_{i=1}^{N} \frac{P_i}{L_i} = 1.$

1.1.1 Inert Components

Inert (non-combustible) components like water in the mixture reduce the partial pressures $P_i$of the combustible components. This leads to a higher flash point temperature because the vapor pressure needed for the ignition of the combustible components is obtained at higher temperatures. Additionally, inert components change the activity coefficients of the combustible components leading also to different partial pressures.

1.2 Available Parameters

The software comes with

- flash point temperatures for 210 components
- heats of combustion for 409 components
- flash point temperatures and heats of combustion for 146 components (both needed values are available)
- Antoine coefficients for approx. 4400 components
- original UNIFAC group assignments for approx. 12000 components
- mod. UNIFAC (Dortmund) group assignments for approx. 10900 components.

Flash points and heats of combustion can be entered directly in the program for every component. Antoine coefficients and group assignments are directly taken from data files and cannot be altered or added. Editable coefficients and group assignments will be added in future revisions of the software.

2 Using the Program

The graphical user interface contains four major parts:

- A tool bar with command buttons
- Several controls for the component management
- A panel with controls for the calculation, model selection, and data display
- A grid for the results

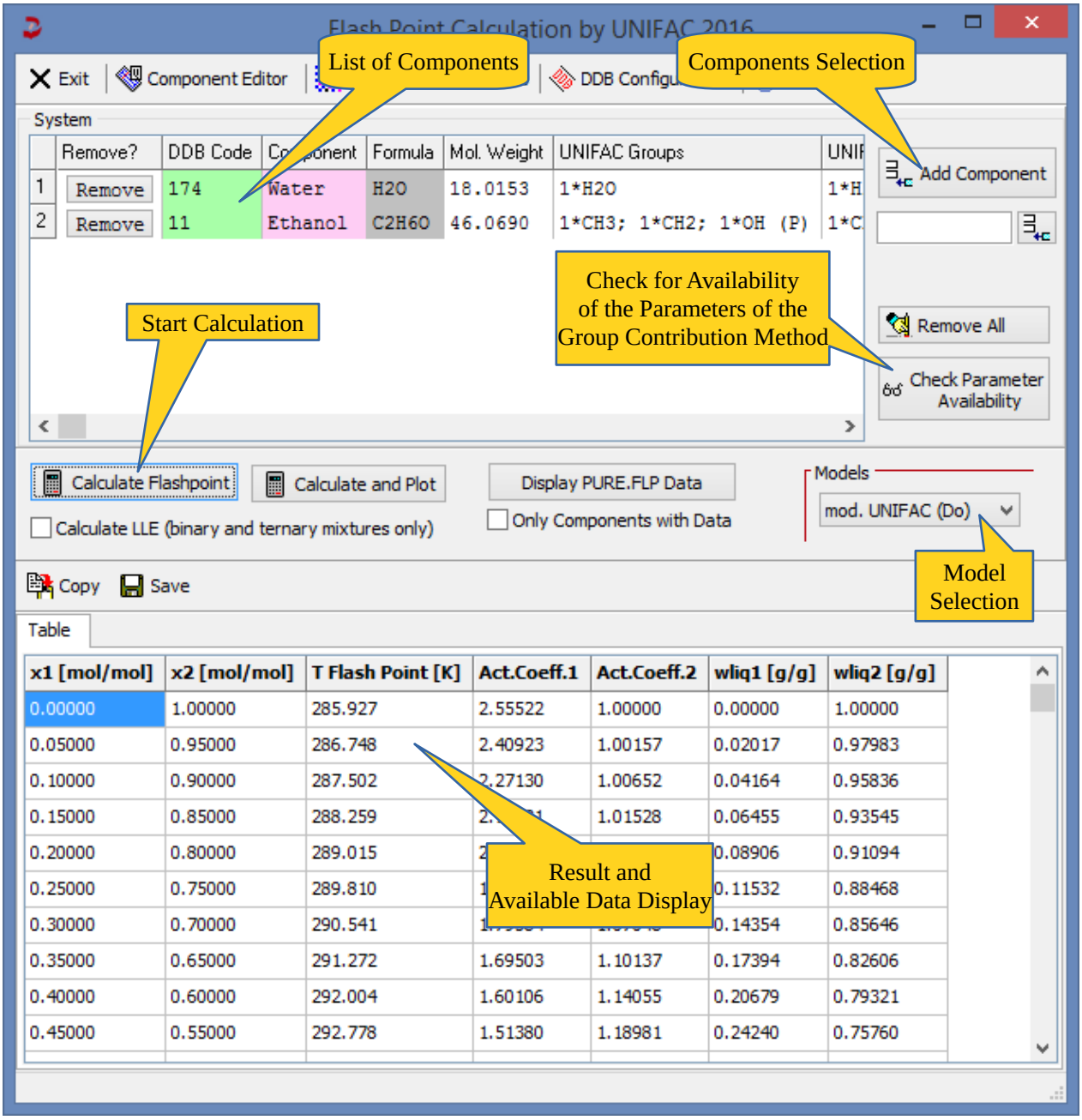
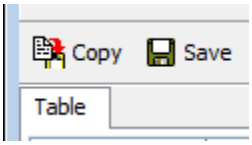


Figure 1: Graphical user interface

The result grid itself has a tool button bar which allows copying and saving the grid content.



2.1 Toolbar Buttons

1. The button "Exit" closes the program.
2. "Component Editor" executes the separate program for editing basic component data.
3. "Interaction Parameters" execute the program that displays the interaction and other parameters for the models UNIFAC and modified UNIFAC.
4. "DDB Configuration" execute the program for the DDB configurations (paths and settings etc.).
5. The button "About" displays the accordant dialog.

2.2 Component Management

The component grid shows the DDB number, a typical name, the empirical formula, the molecular weight, and the group assignments (sub group numbers) of original UNIFAC and modified UNIFAC (Dortmund).

This component management uses the standard list of components in the Dortmund Data Bank. The component selection is done in the component selection program which is described in a separate PDF (see "ComponentManagement.pdf").

The "Add Component" button calls the component selection program:

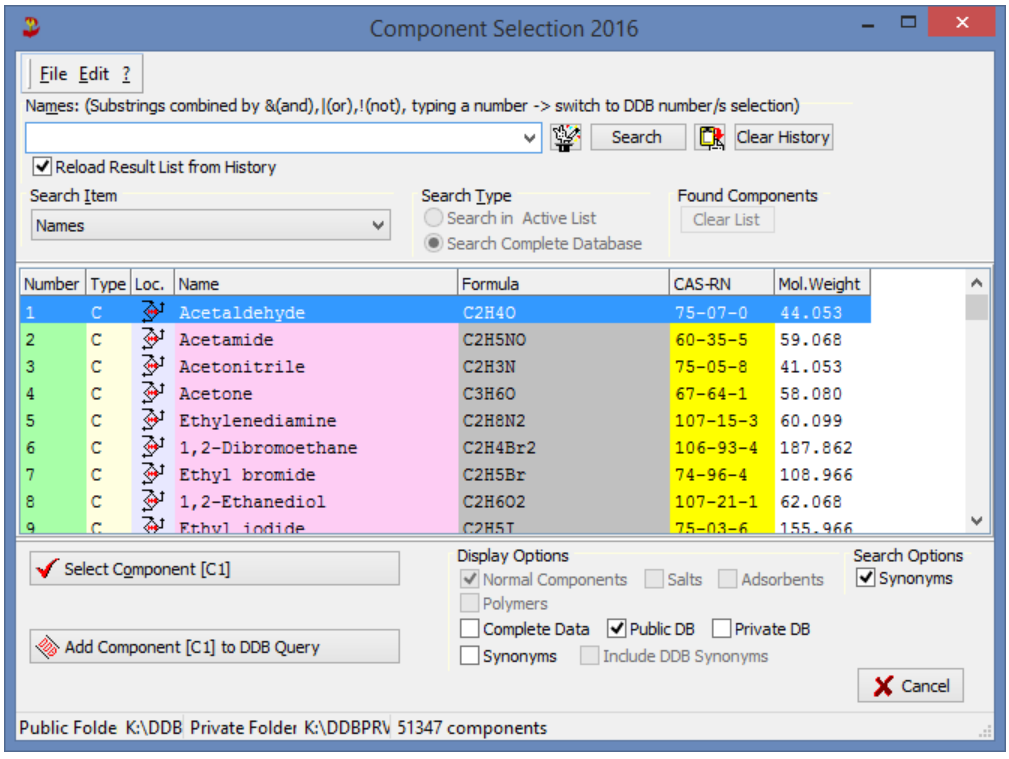


Figure 2: Component selection dialog.

Here it is possible to search the complete component file of the Dortmund Data Bank by names, formula, etc.

The edit field below the "Add Component" button allows the input of components by DDB numbers directly. This is useful after some experience with the DDB component list and the knowledge of the DDB numbers of the main components.

2.2.1 Adding Missing Flash Point Data

	Remove?	DDB Code	Component	Formula	Mol. Weight	UNIFAC Groups	UNIFAC(Do) Groups	T(Flashpoint) [K]	Heat of Combustion [kcal/mol]
1	Remove	11	Ethanol	C2H6O	46.0690	1*CH3; 1*CH2; 1*OH (P)	1*CH3; 1*CH2; 1*OH (P)	285.93	-1368.50
2	Remove	21	Ethyl acetate	C4H8O2	88.1063	1*CH3; 1*CH2; 1*CH3COO	1*CH3; 1*CH2; 1*CH3COO	268.71	-2250.41

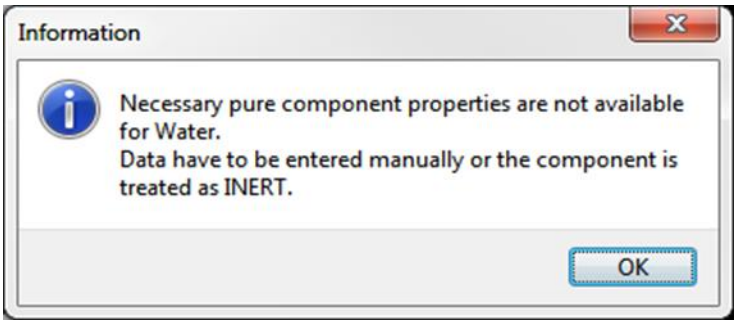
The component grid displays information about

1. The DDB code number
2. A typical component name
3. The empirical formula
4. The molecular weight
5. UNIFAC group assignment
6. mod. UNIFAC (Do) group assignment
7. Flash point temperature in [K]
8. Heat of combustion in [kcal/mol]

The last both cells are editable and allow entering new values for both the pure components flash point temperature and the heat of combustion.

2.2.2 Inert Components

Inert components are added like normal components. Inert components are recognized by the missing flash point temperature and heat of combustion. When adding components without these two values a message



is shown. A possible pitfall here is that a combustible component without data will be treated as inert.

2.3 Check Interaction Parameter Availability

This function checks if the activity coefficients of the defined mixture can be calculated with the group contribution models. The dialog has two pages – the first with an overview if the calculation is possible or not

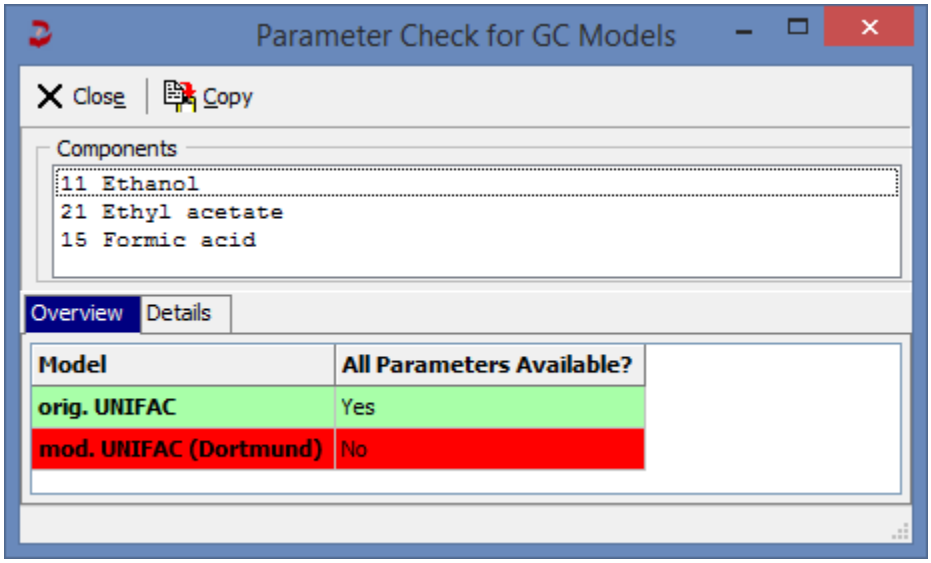


Figure 3: Check for available interaction parameters and group assignments.

and the second page with a details about the group assignments (sub and main groups) and the interaction parameters.

UNIFAC

```
Component     11: Ethanol
                  Subgroups:    1 (CH3     )    2 (CH2     )   14 (OH      )
Component     21: Ethyl acetate
                  Subgroups:    1 (CH3     )    2 (CH2     )   21 (CH3COO  )
Component     15: Formic acid
                  Subgroups:   43 (HCOOH   )

List of Main Groups
Maingroups:    1 (CH2     )    5 (OH      )   11 (CCOO    )   20 (COOH    )

Interaction parameters
  1 -   5: 1 parameter/s
  1 -  11: 1 parameter/s
  1 -  20: 1 parameter/s
  5 -  11: 1 parameter/s
  5 -  20: 1 parameter/s
 11 -  20: 1 parameter/s

System has all parameters available.
```

mod. UNIFAC (Dortmund)

```
Component     11: Ethanol
                  Subgroups:    1 (CH3     )    2 (CH2     )   14 (OH (P)  )
Component     21: Ethyl acetate
                  Subgroups:    1 (CH3     )    2 (CH2     )   21 (CH3COO  )
Component     15: Formic acid
                  Subgroups:   43 (HCOOH   )

List of Main Groups
Maingroups:    1 (CH2     )    5 (OH      )   11 (CCOO    )   44 (HCOOH   )

Interaction parameters
  1 -   5: 3 parameter/s
  1 -  11: 3 parameter/s
```

```
  1 -  44: 1 parameter/s
  5 -  11: 3 parameter/s
  5 -  44: 0 parameter/s
 11 -  44: 1 parameter/s

Parameters are missing.
```

This example shows that original UNIFAC could be used to calculate activity coefficients but the calculation with modified UNIFAC will fail because of missing interaction parameters between the main group 5 (OH) and 44 (HCOOH).

Trying to start a calculation will lead to the error message

3 Calculating Flash Points

The button “Calculate Flashpoint” will calculate the flash points for given composition. A dialog pops up where compositions can be entered:

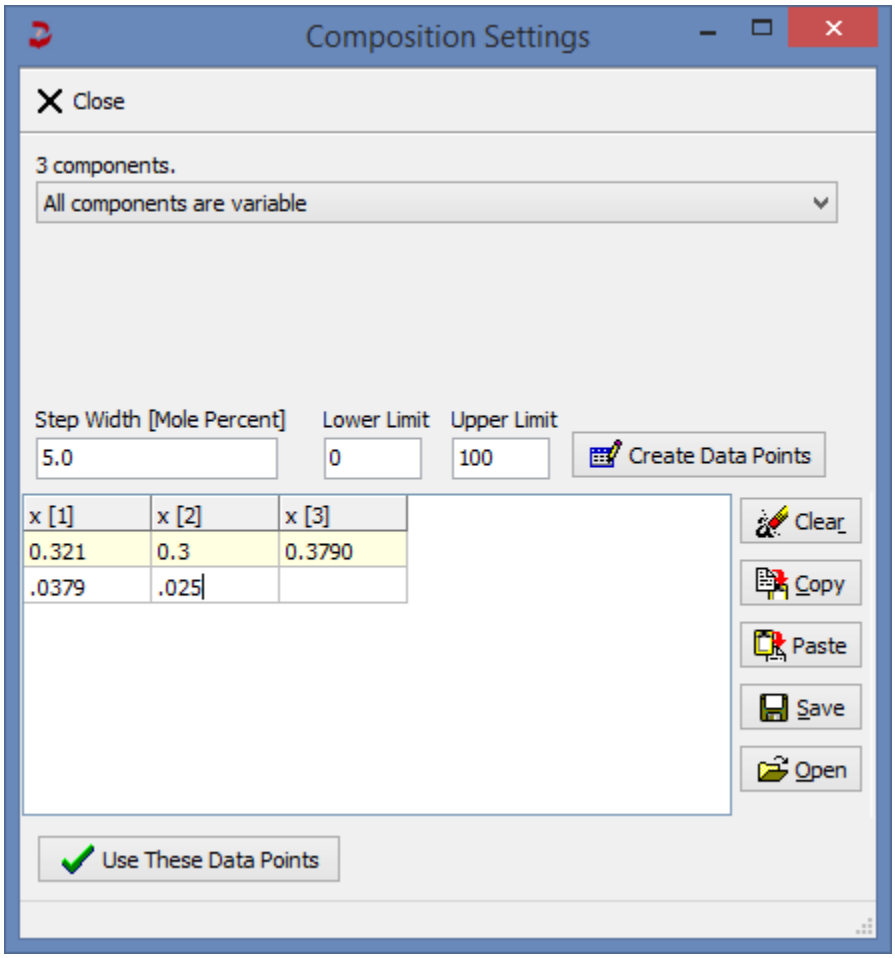


Figure 4: Composition

Wanted compositions can either be entered directly in the data grid or automatically created by the “Create Data Points” button.

For the automatic creation it is possible to specify lower and upper limits of compositions and the step width. For mixture with three or more components it is possible to specify constant compositions or constant mole fraction ratios.

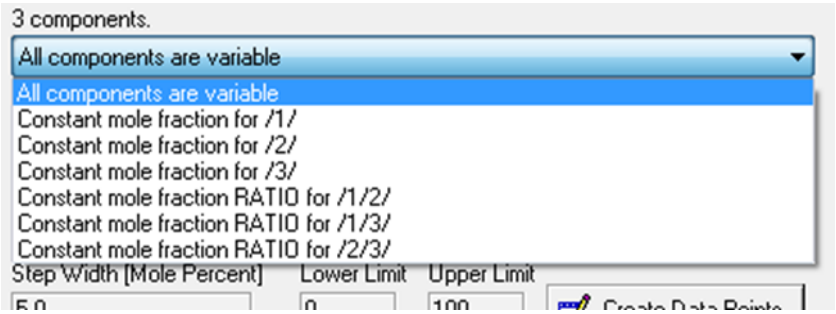


Figure 5: Options for the automatic data point creation

The created data points will be displayed in the data grid

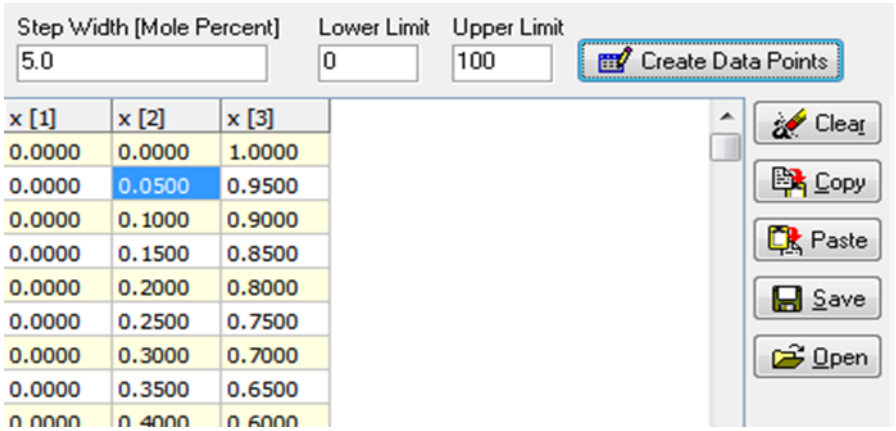


Figure 6: Automatically created compositions.

and can be copied to the Windows clipboard or saved as CSV files (**C**omma **S**eparated **V**alues). If data are available in other programs (like spread sheets) or on disk the data table can be pasted or loaded.

The "Use These Data Points" button closes this dialog and starts the calculation, the "Close" also closes this dialog but does not start the calculation (like "Cancel").

3.1 Calculation Result

The data grid contains three parts.

Table

x1 [mol/mol]	x2 [mol/mol]	x3 [mol/mol]	T Flash Point [K]	Act.Coeff.1	Act.Coeff.2	Act.Coeff.3
0.00000	0.00000	1.00000	342.109	3.31374	5.11514	1.00000
0.00000	0.05000	0.95000	296.186	2.92677	3.76158	1.00822
0.00000	0.10000	0.90000	288.499	2.43467	2.92973	1.02818
0.00000	0.15000	0.85000	284.698	2.11817	2.43377	1.05493

The compositions are the composition either entered manually or created automatically. The flash point temperatures and the activity coefficients are calculated values.

The content of this data table can either be copied to the Windows clipboard or saved as Microsoft Excel 2007 files (extension "xls").

3.2 Diagrams

Diagrams are available for binary and ternary mixtures. Typical results are shown in this chapter.

3.2.1 Ternary Mixtures

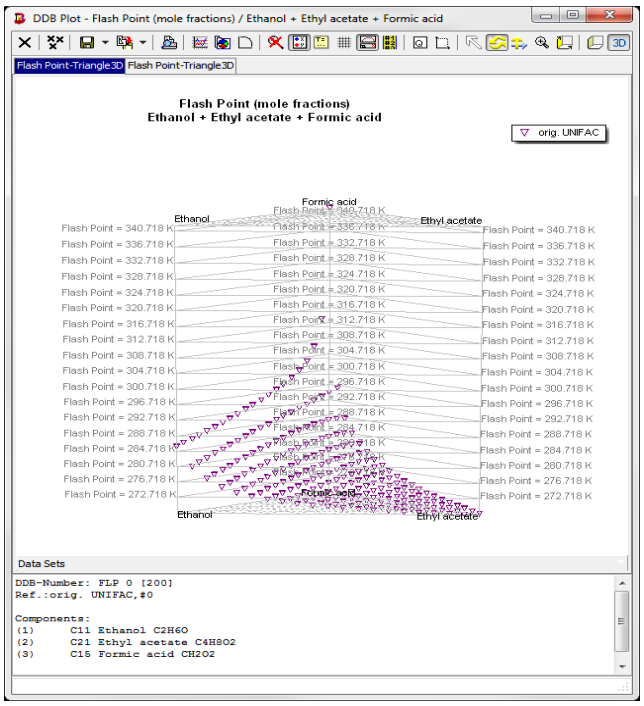


Figure 7: Flashpoint diagram of a ternary mixture.

3.2.2 Binary Mixtures

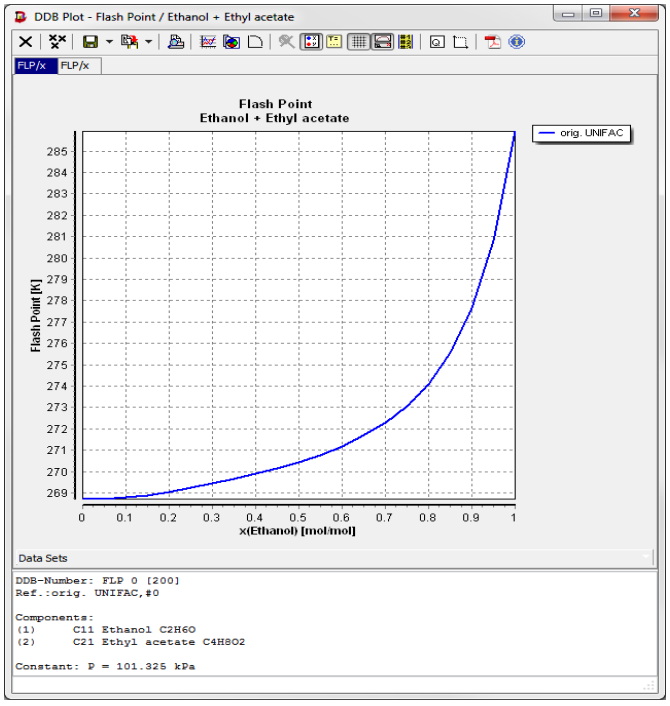


Figure 8: Flashpoint diagram of a binary mixture.

A description of this diagram program is available separately (“DDBPlot.pdf”).

3.3 LLE Calculation

The program allows the calculation of miscibility gaps (liquid-liquid equilibria) for binary mixtures only. If a

LLE is found, no flash point is calculated and the compositions in the data grid are set to light red.

x1 [mol/mol]	x2 [mol/mol]	T Flash Point [K]	Act.Coeff.1	Act.Coeff.2
0.00000	1.00000	284.268	6.24264	1.00000
0.05000	0.95000	272.977	5.35390	1.00406
0.10000	0.90000	267.963	4.63927	1.01597
0.15000	0.85000	265.050	4.05841	1.03578
0.20000	0.80000	263.266	3.57927	1.06398
0.25000	0.75000	262.096	3.17889	1.10151
0.30000	0.70000	261.312	2.84064	1.14979
0.35000	0.65000	260.786	2.55224	1.21088
0.40000	0.60000	260.441	2.30442	1.28767
0.45000	0.55000	260.223	2.09010	1.38429
0.50000	0.50000		1.90376	1.50659
0.55000	0.45000		1.74109	1.66318
0.60000	0.40000		1.59866	1.86705
0.65000	0.35000		1.47377	2.13852
0.70000	0.30000		1.36431	2.51092
0.75000	0.25000		1.26871	3.04219
0.80000	0.20000		1.18595	3.84069
0.85000	0.15000		1.11568	5.12953
0.90000	0.10000	260.119	1.05857	7.43068
0.95000	0.05000	260.365	1.01737	12.19907
1.00000	0.00000	262.033	1.00000	24.44590

Figure 9: Result table with marked LLE.

In binary diagrams the LLE area is shown as a straight horizontal line:

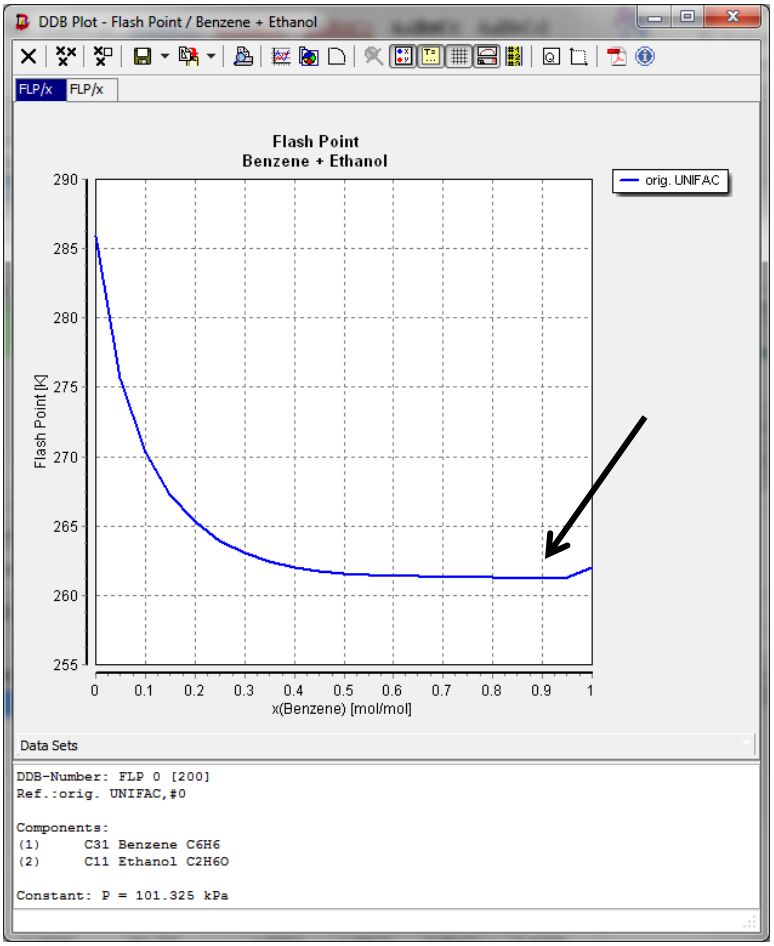


Figure 10: Plot of the calculation results.

The LLE is not determined exactly. Instead all given compositions are tested if they are inside the miscibility gap.

4 The UNIFAC Consortium

The UNIFAC Consortium has been founded at the University of Oldenburg for the further revision, extension and development of the group contribution methods UNIFAC, mod. UNIFAC (Dortmund), and the predictive equation of state PSRK.

The consortium examines and improves model parameters; it fills gaps in the existing parameter tables, introduces new groups, and modifies existent groups.

Consortiums made parameters are not publicly available – at least not for several years – and can be used only by consortium members. Members pay a yearly fee to support the future work of the consortium.

This software is prepared to use Consortium-made parameter files.