Flash Point Estimation

Short Introduction and Tutorial

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1 Introduction

This software calculates flash points of flammable liquid mixtures by the UNIFAC based methods “original UNIFAC”[1], “modified UNIFAC (Dortmund)”[2], “NIST modified UNIFAC”[3], and other activity coefficient models.

The algorithm to calculate the flash points is described in a scientific paper[4] 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. Additional 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

[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] Constantinescu D., Gmehling J., "Further Development of Modified UNIFAC (Dortmund): Revision and Extension 6", J.Chem.Eng.Data, 61(8), 2738-2748, 2016.

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

$L_i(t)$	Lower flammability limit at temperature *t* in °C of component *i*
$L_i(25°C)$	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 γ_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

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 can be altered or added for private components.

2 Using the Program

The graphical user interface contains four major parts:

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

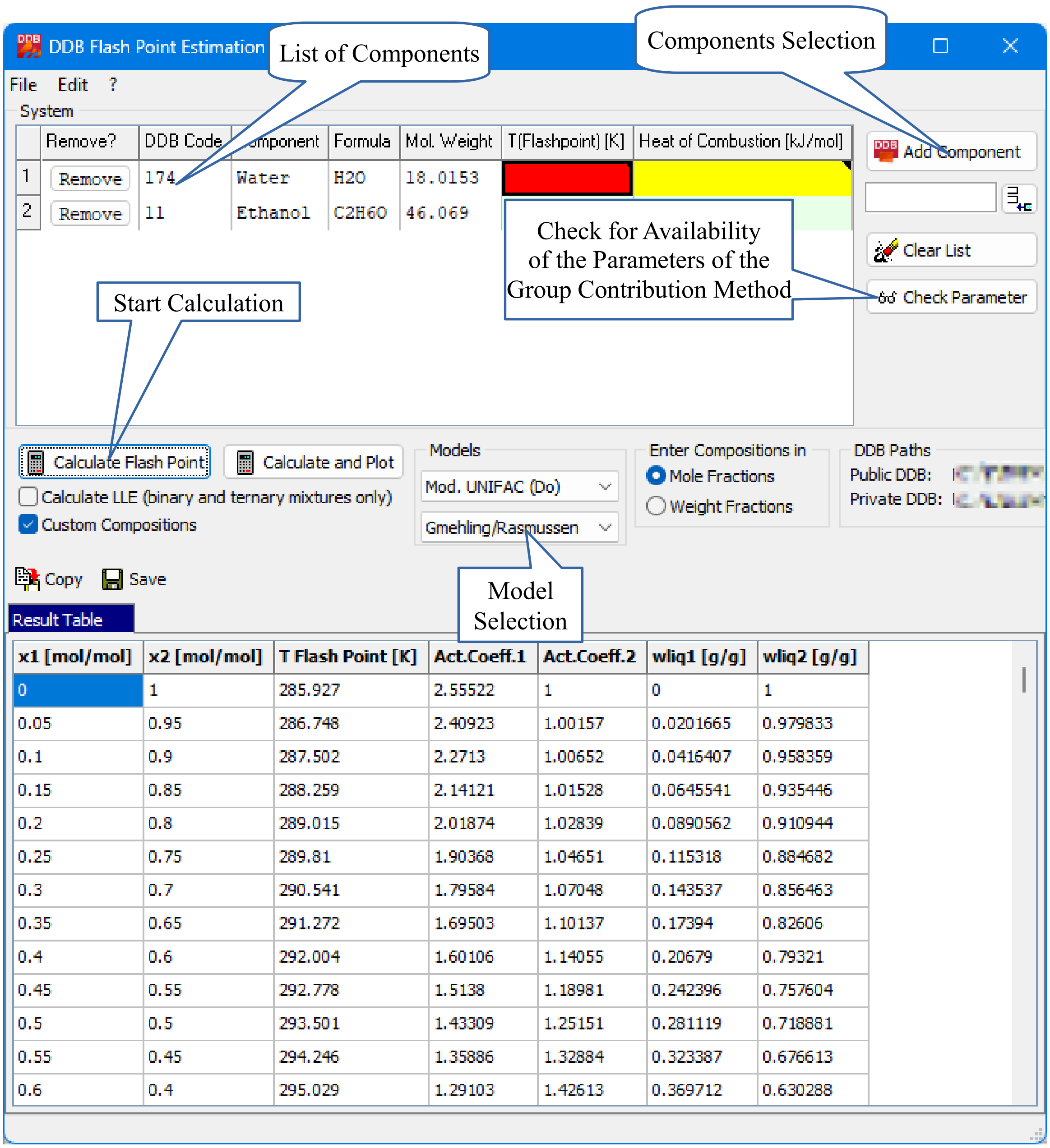

Figure 1: Graphical user interface

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

2.1 Menu bar

- The “Load Component List” and “Save Component List” option in the file menu allows loading and saving a component list from a DDB conformed file.
- The button “Exit” in the file menu closes the program.
- The edit menu contains the following selections
  - “Component Editor” executes the separate program for editing basic component data.
  - “Interaction Parameters” execute the program that displays the group interaction parameters for the models.
  - “Parameter DDB Organizer” executes the program that manages parameters like Antoine vapor pressure parameters.
  - “Regression Pure” fits parameters for a large variety of equations for pure component properties.
- The “?” contains a link to the manual, the “About” button displays an information dialog.

2.2 Component Management

The component grid shows the DDB number, a typical name, the empirical formula, the molecular weight, flash point and heat of combustion of the different components.

The component management uses the standard list of components of the Dortmund Data Bank. The component selection is done in DDB Components which is described in a separate PDF (see “Components.pdf”) and is opened by the “Add Component” button.

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 if you have 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	T(Flashpoint) [K]	Heat of Combustion [kJ/mol]
1	Remove	11	Ethanol	C2H6O	46.069	285.93	-1368.5
2	Remove	21	Ethyl acetate	C4H8O2	88.1063	268.71	-2250.41

The component grid displays information about

- The DDB code number
- A typical component name
- The empirical formula
- The molecular weight
- Flash point temperature in [K]
- Heat of combustion in [kJ/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. These modifications are non-permanent.

For permanent modifications you have to use private components. To create or edit private components run the *DDB Components* application (“Component Editor” in the edit menu). There you can use the “Clone substance to Private DDB” entry in the pop-up menu for existing components or “New substance” for own components.

Within *DDB Components* you can edit the flash point and the heat/temperature of combustion. The phase of combustion can be selected as follows: enter 1 for liquid, 2 for gas, 3 for solid, 4 for liquid or gas.

Group assignments can be changed with the “Group Editor” which is available within the application run by “Interaction Parameters” in the edit menu.

Existing Antoine coefficients for components can be found, modified or entered by the “Parameter DDB Organizer” application.

Use the “Regression Pure” application to fit Antoine parameters from a vapor pressure curve.

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.

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

3 Calculating Flash Points

The button “Calculate Flashpoint” will calculate the flash points for given composition. If ‘Custom composition’ is selected, a dialog pops up where compositions can be entered.

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.

The created data points will be displayed in the data grid 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.

3.1 Standard or Custom Compositions

☑ Custom Compositions

It is possible to calculated just 21 points in 5 mole-% steps and without specifying the compositions manually by switching the option “Custom Compositions” off.

3.2 Calculation Result

The data grid contains three parts.

Result Table

x1 [mol/mol]	x2 [mol/mol]	T Flash Point [K]	Act.Coeff.1	Act.Coeff.2	wliq1 [g/g]	wliq2 [g/g]
0	1	285.927	2.55522	1	0	1
0.11862	0.88138	287.784	2.22195	1.00931	0.0499979	0.950002
0.22127	0.77873	289.398	1.9689	1.03544	0.100002	0.899998
0.31095	0.68905	290.701	1.77317	1.07661	0.15	0.85
0.38999	0.61001	291.857	1.61933	1.13196	0.200003	0.799997
0.46016	0.53984	292.923	1.49687	1.20125	0.249999	0.750001
0.52289	0.47711	293.838	1.39831	1.28474	0.300001	0.699999
0.5793	0.4207	294.699	1.31833	1.38309	0.350005	0.649995
0.63029	0.36971	295.578	1.25305	1.49726	0.400002	0.599998
0.67661	0.32339	296.4	1.19952	1.6286	0.449997	0.550003
0.71888	0.28112	297.271	1.15556	1.77884	0.499998	0.500002
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

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 file.

3.3 Diagrams

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

3.3.1 Ternary Mixtures

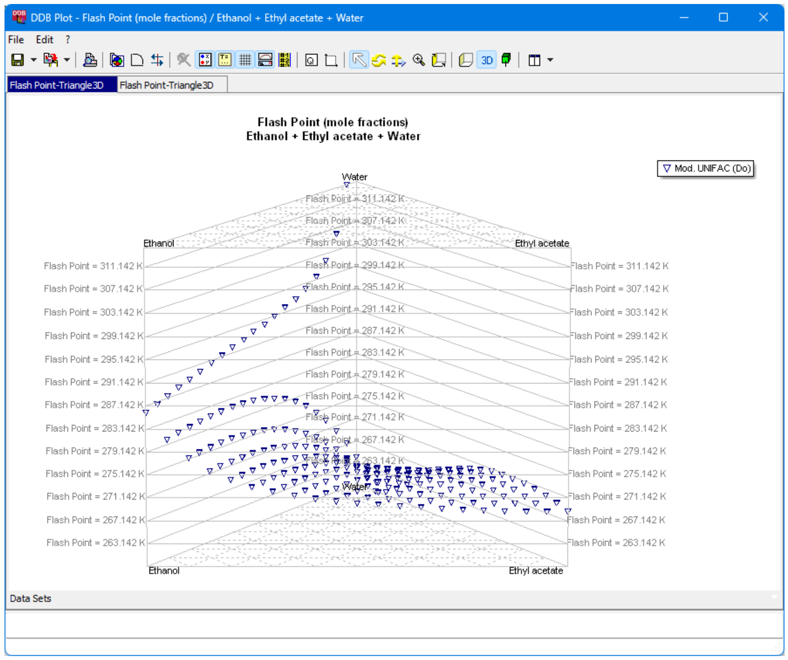

Figure 2: Flashpoint diagram of a ternary mixture.

3.3.2 Binary Mixtures

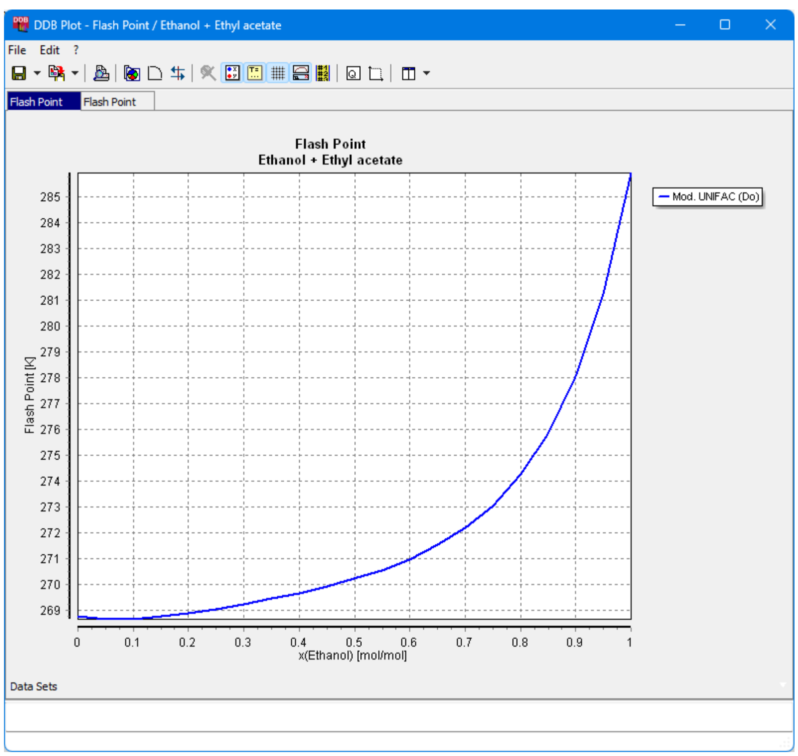

Figure 3: Flashpoint diagram of a binary mixture.

A description of the plot program is available separately ("DDBPlot.pdf").

3.4 LLE Calculation

The program allows the calculation of miscibility gaps (liquid-liquid equilibria) for binary mixtures only. If an LLE is found, no flash point is calculated and the compositions in the data grid are set to light red.

Result Table

x1 [mol/mol]	x2 [mol/mol]	T Flash Point [K]	Act.Coeff.1	Act.Coeff.2	wliq1 [g/g]	wliq2 [g/g]
0.05	0.95	306.694	18.3552	1.02075	0.178003	0.821997
0.1	0.9	306.694	9.801	1.07329	0.313734	0.686266
0.15	0.85	306.694	6.03535	1.14959	0.420652	0.579348
0.2	0.8	306.694	4.12635	1.24529	0.507052	0.492948
0.25	0.75	306.694	3.0549	1.35782	0.578322	0.421678
0.3	0.7	306.694	2.4052	1.48557	0.638118	0.361882
0.35	0.65	306.694	1.98705	1.62755	0.689003	0.310997
0.4	0.6	306.694	1.70518	1.7831	0.732832	0.267168
0.45	0.55	306.694	1.50828	1.95181	0.770976	0.229024
0.5	0.5	306.694	1.36699	2.13338	0.804475	0.195525
0.55	0.45	306.694	1.2636	2.32761	0.834128	0.165872
0.6	0.4	306.694	1.18698	2.53434	0.860562	0.139438
0.65	0.35	306.612	1.12985	2.75344	0.884274	0.115726
0.7	0.3	306.07	1.08728	2.98479	0.905664	0.0943364
0.75	0.25	305.672	1.05587	3.22824	0.925056	0.0749439

Figure 4: Result table with marked LLE.

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

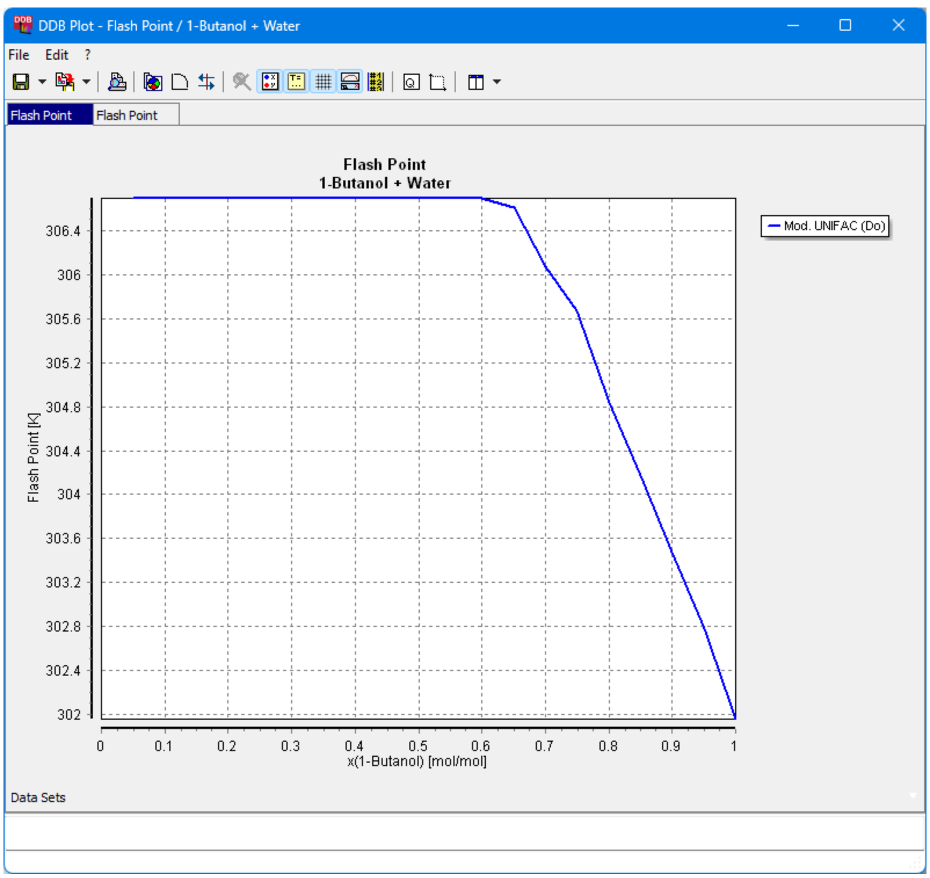

Figure 5: Plot of the calculation results.

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