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 and "NIST modified UNIFAC"³. All methods are delivered with the latest published parameters.

The algorithm to calculate the flash points is described in a scientific paper⁴ 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). 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:

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

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

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

with

¹Wittig 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

²Jakob 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.

⁴Gmehling 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
$L_i(25^{\circ}C)$	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

🥦 DDB Flash F File Edit ?	Point Estimatio	on 2(Lis	t of Co	mponents]	(Component	ts Selection	n 🗆	×
System		7								
Remove?	DDB Code C	or onent	Formula	Mol. Weight	T(Flashpoint	t) [K] H	leat of Combus	tion [kJ/mol]	Add Comp	onent
1 Remove	174 W	ater	H20	18.0153						
2 Remove	11 E	thanol	C2H60	46.069	of the H	Param	Availability neters of the pution Meth	e 🗌	స్లో Clear List రింి Check Par	amete
Calculate Fla	ash Point	-	e and Plot ires only)	Models Mod. UNI	FAC (Do)	~ (Enter Composi Mole Fraction Weight Fraction	ons P	DDB Paths Public DDB:	
Custom Comp	positions			Gmehling/	Rasmussen	~				
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Custom Comp	ave x2 [mol/mo	-	h Point [K] Act.Coe	fodel lection		wliq1 [g/g]	wliq2 [g/g]		
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Custom Comp Copy S copy S cesult Table x1 [mol/mol] 0.05 0.1 0.15 0.2 0.25 0.3	x2 [mol/mo 1 0.95 0.9 0.85 0.8 0.75	285.92 286.74 287.50 288.25 289.01 289.81	27 48 02 59 15 1 41	K] Act.Coe 2.55522 2.40923 2.2713 2.14121 2.01874 1.90368	Iodel lection 1 1.0015 1.0065 1.0152 1.0152 1.0283 1.0465	7 2 8 9 1 8	0 0.0201665 0.0416407 0.064554 0.0890561 0.115318	1 0.979833 0.958359 0.935446 0.910944 0.884682		
Custom Comp Copy S cesult Table x1 [mol/mol] 0.005 0.1 0.15 0.2 0.25 0.3 0.35	x2 [mol/mo 1 0.95 0.9 0.85 0.8 0.75 0.7	285.92 285.92 286.74 287.50 288.25 289.01 289.81 290.54	227 48 02 59 15 1 1 41 72	K] Act.Coe 2.55522 2.40923 2.2713 2.14121 2.01874 1.90368 1.79584 1.79584	Iodel lection 1 1.0015 1.0065 1.0152 1.0283 1.0465 1.0704	7 2 8 9 1 1 8 8 7	0 0.0201665 0.0416407 0.064554 0.0890561 0.115318 0.143537	1 0.979833 0.958359 0.935446 0.910944 0.884682 0.856463		
Custom Comp Copy S cesult Table x1 [mol/mol] 0 0.05 0.1 0.15 0.2 0.25 0.3 0.35 0.4	x2 [mol/mo 1 0.95 0.9 0.85 0.8 0.75 0.7 0.65	285.92 286.74 287.50 288.25 289.01 289.81 290.54 291.27	27 18 12 15 1 1 11 72 14 14 10 14	N Se 2.55522 2.40923 2.2713 2.14121 2.01874 1.90368 1.79584 1.69503	Iodel lection 1 1.0015 1.0065 1.0152 1.0283 1.0465 1.0704	7 2 8 99 11 8 8 77 5	0 0.0201665 0.0416407 0.064554 0.0890561 0.115318 0.143537 0.17394	1 0.979833 0.958359 0.935446 0.910944 0.884682 0.856463 0.82606		
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Custom Comp	x2 [mol/mo 1 0.95 0.9 0.85 0.75 0.7 0.65 0.6 0.55	285.92 285.92 286.74 287.50 288.25 289.01 289.81 290.54 291.27 292.00 292.77	27 18 10 15 1 1 1 1 1 1 1 1 1 1 1 1 1	N Se 2.55522 2.40923 2.713 2.14121 2.01874 1.90368 1.79584 1.60503 1.60106 1.5138	Iodel lection 1 1.0015 1.0055 1.0152 1.0283 1.0465 1.0704 1.1013 1.1405 1.1898	7 2 8 9 1 1 8 8 7 7 5 5 1 1 1	0 0.0201665 0.0416407 0.064554 0.0890561 0.115318 0.143537 0.17394 0.20679 0.242395	1 0.979833 0.958359 0.935446 0.910944 0.884682 0.856463 0.82606 0.79321 0.757605		

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.
 - \circ "Parameter 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 besides 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	T(Flashpoint) [K]	Heat of Combustion [kJ/mol]
1	Remove	11	Ethanol	C2H60	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

🚸 Parameter Check for GC	м — 🗆 🗙							
🛱 Сору								
Components 11 Ethanol 21 Ethyl acetate								
Overview Details								
Model	All Parameters Available?							
orig. UNIFAC	Yes							
mod. UNIFAC (Dortmund)	Yes							
NIST-mod. UNIFAC	Yes							

Figure 2: Check for available interaction parameters and group assignments.

and the second page with 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)
List of Main G Maingroups:	-	(ОН)	11 (CCOO)	
Interaction par 1 - 5: 1 p	rameters parameter/s (CH2	/ ОН)		

	parameter/s (CH2 parameter/s (OH	/ CCOO / CCOO			
System has all	parameters availa	ble.			
mod. UNIFAC	C (Dortmund)				
Component	11: Ethanol Subgroups:) 2 (CF	12)	14 (OH (P))
Component	21: Ethyl acetate Subgroups:) 2 (CH	12)	21 (CH3COO)
List of Main G Maingroups:	1	(OH)	11 (CCOC)	
1 - 11: 3	rameters parameter/s (CH2 parameter/s (CH2 parameter/s (OH	/ OH / CCOO / CCOO	,		
System has all	parameters availa	ble.			
NIST-mod. U	JNIFAC				
Component	<pre>11: Ethanol Subgroups: 21. Ethyl agotato</pre>) 2 (CF	12)	14 (OH prim)
Component	21: Ethyl acetate Subgroups:	1 (CH3) 2 (CH	12)	21 (CH3COO)

List of Main Groups 5 (OH 11 (CCOO Maingroups: 1 (CH2))) Interaction parameters 1 - 5: 3 parameter/s (CH2 / OH) 1 - 11: 3 parameter/s (CH2 / CCOO) 5 - 11: 3 parameter/s (OH / CCOO)

System has all parameters available.

This example shows that all models can be used to calculate activity coefficients.

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:

🇞 Composition Settings		□ ×
2 components. All components are variable		~
Step Width [Mole Percent] Lower Limit Upper Limit 5.0 0 100 Image: Compare the second se	🖌 Create D	ata Points
x [1] x [2]		🖌 Clea <u>r</u>
		Сору
		Paste
		i <u>⊇</u> ave i <u>⊃</u> open
Use These Data Points		

Figure 3: 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.

3 components.	
All components are variable	~
All components are variable	
Constant mole fraction for /1/	
Constant mole fraction for /2/	
Constant mole fraction for /3/	
Constant mole fraction RATIO for /1/2/	
Constant mole fraction RATIO for /1/3/	
Constant mole fraction RATIO for /2/3/	
Sten Width [Mole Percent] Lower Limit	Unner Limit

Figure 4: Options for the automatic data point creation.

The created data points will be displayed in the data grid

Step Wid 5.0	th [Mole Pe	rcent]	Lower Limit	Upper Limit 100	📑 Create I	Data Points
x [1]	x [2]	x [3]				^ 📝 Clear
0.0000	0.0000	1.0000				
0.0000	0.0500	0.9500				E Copy
0.0000	0.1000	0.9000				
0.0000	0.1500	0.8500				📴 Paste
0.0000	0.2000	0.8000				Save
0.0000	0.2500	0.7500				
0.0000	0.3000	0.7000				😅 Open
0.0000	0.3500	0.6500				

Figure 5: Automatically created compositions.

and can be copied to the Windows clipboard or saved as CSV files (Comma Separated Values). 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 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

Result Table							
x1 [mol/mol]	x2 [mol/mol]	T Flash Point [K]	Act.Coeff.1	Act.Coeff.2	wliq1 [g/g]	wliq2 [g/g]	^
0.00000	1.00000	285.927	2.55522	1.00000	0.00000	1.00000	
0.11862	0.88138	287.784	2.22194	1.00931	0.05000	0.95000	
0.22127	0.77873	289.398	1.96891	1.03544	0.10000	0.90000	
0.31095	0.68905	290.701	1.77317	1.07661	0.15000	0.85000	
0.38999	0.61001	291.857	1.61934	1.13196	0.20000	0.80000	
0.46016	0.53984	292.923	1.49687	1.20125	0.25000	0.75000	
0.52289	0.47711	293.838	1.39831	1.28474	0.30000	0.70000	
0.57930	0.42070	294.699	1.31834	1.38308	0.35000	0.65000	
0.63029	0.36971	295.578	1.25305	1.49725	0.40000	0.60000	1
0.67661	0.32339	296.400	1.19952	1.62861	0.45000	0.55000	1
0.71888	0.28112	297.271	1.15556	1.77885	0.50000	0.50000	
0 75760	0.04040	200,200	1 11047	1.05010	0.55000	0.45000	×

The data grid contains three parts.

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").

3.3 Diagrams

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

3.3.1 Ternary Mixtures

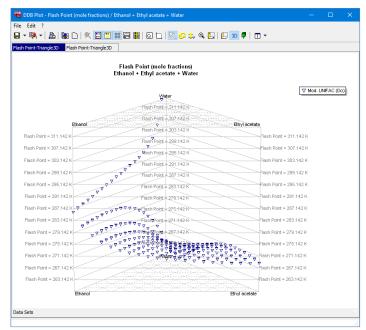


Figure 6: Flashpoint diagram of a ternary mixture.

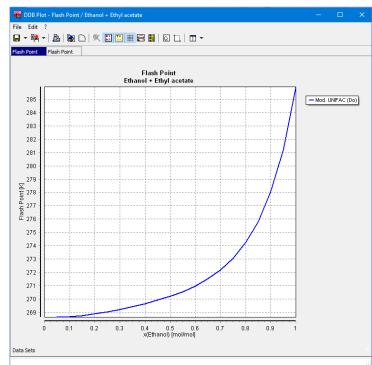


Figure 7: Flashpoint diagram of a binary mixture.

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

3.3.2 Binary Mixtures

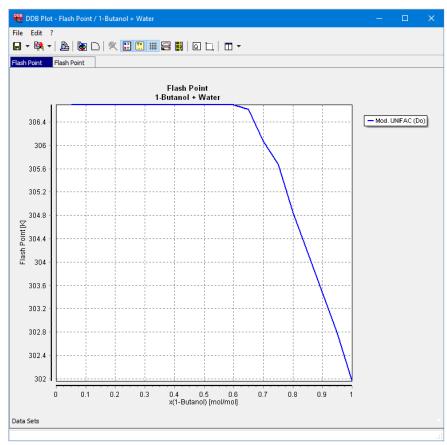
3.4 LLE Calculation

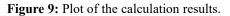
The program allows the calculation of miscibility gaps (liquid-liquid equilibria) for binary mixtures only. If a LLE is found, no flash point is calculated and the compositions in the data grid are set to light red.

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
~ ~		22.4.022	1 00045	0.40067	0.040740	0.0575044

Figure 8: Result table with marked LLE.

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





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