Flash Point Calculation by UNIFAC

Short Introduction and Tutorial

DDBSP - Dortmund Data Bank Software Package
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 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 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

\(p_i^S\) \quad Saturated vapor pressure of component \(i\)

\(L_i\) \quad 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

\(N\) \quad Number of components

\(P_i\) \quad Partial pressure of component \(i\) in a vapor-air mixture in equilibrium

\(L_i\) \quad 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

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

with


\( L_i(t) \) 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 \( i \)

\( \gamma_i \) 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 includes

- flash point temperatures for 965 components
- heats of combustion for 1550 components
- flash point temperatures and heats of combustion for 439 components (both needed values are available)
- Antoine coefficients for approx. 5,500 components
- original UNIFAC group assignments for approx. 25,300 components
- mod. UNIFAC (Dortmund) group assignments for approx. 25,000 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 can be altered or added for private components.
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

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

- The button “Exit” closes the program.
- “Component Editor” executes the separate program for editing basic component data.
- “Interaction Parameters” execute the program that displays the interaction and other parameters for the models.
- “DDB Configuration” execute the program for the DDB configurations (paths and settings etc.).
- 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, flash point and heat of combustion of the different components.

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:

![Component selection dialog](image)

**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

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Remove</td>
<td>11</td>
<td>Ethanol</td>
<td>C2H6O</td>
<td>46.0690</td>
<td>235.53</td>
<td>-1965.50</td>
</tr>
<tr>
<td>Remove</td>
<td>21</td>
<td>Ethyl acetate</td>
<td>C4H8O2</td>
<td>88.1063</td>
<td>268.71</td>
<td>-2356.41</td>
</tr>
</tbody>
</table>

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. Fragmentation and Antoine coefficients for private components can be changed / fitted by pressing the “Component Editor” button. A new window pops up and shows the pure component properties of the marked component:

![Figure 3: View and edit pure component properties.](image-url)
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.

![Parameter Check for GC Models](image)

**Figure 4:** Check for available interaction parameters and group assignments.

**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 Groups**  
Maingroups: 1 (CH2) 5 (OH) 11 (CCOO)

**Interaction parameters**

1 - 5: 1 parameter/s (CH2 / OH)
1 - 11: 1 parameter/s (CH2 / CCOO)
5 - 11: 1 parameter/s (OH / CCOO)

*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)

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

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.*

**NIST-mod. UNIFAC**

Component 11: Ethanol  
Subgroups: 1 (CH3) 2 (CH2) 14 (OH prim)

Component 21: Ethyl acetate  
Subgroups: 1 (CH3) 2 (CH2) 21 (CH3COO)

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

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. A dialog pops up where compositions can be entered:

![Composition Settings](image)

**Figure 5:** 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.

![Options for the automatic data point creation](image)

**Figure 6:** Options for the automatic data point creation.
The created data points will be displayed in the data grid

![Figure 7: Automatically created compositions.](image)

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 Calculation Result

The data grid contains three parts.

<table>
<thead>
<tr>
<th>Result Table</th>
<th>Antoine Parameters</th>
<th>PURE_FLIP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00000</td>
<td>0.05000</td>
<td>0.95000</td>
</tr>
<tr>
<td>0.00000</td>
<td>0.10000</td>
<td>0.80000</td>
</tr>
<tr>
<td>0.00000</td>
<td>0.15000</td>
<td>0.85000</td>
</tr>
<tr>
<td>0.00000</td>
<td>0.20000</td>
<td>0.80000</td>
</tr>
</tbody>
</table>

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 8: Flashpoint diagram of a ternary mixture.]

3.2.2 Binary Mixtures

![Figure 9: Flashpoint diagram of a binary mixture.]

A description of the plot 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.

**Figure 10:** Result table with marked LLE.

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

**Figure 11:** 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.