

CALCULATION OF HEATING VALUES FOR THE SIMULATION OF THERMO-CHEMICAL CONVERSION PLANTS WITH ASPEN PLUS

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ABSTRACT. Flowsheet simulation is a prevalent tool to calculate mass- and energy balances of polygeneration plants for the production of fuels, heat and power. The results achieved by flowsheet modellings depend on the methods used for calculating material properties. A property of particular interest is the heating value because the calculation of energy balances is based on this value in many simulation programs. Regarding organic substances (e.g. coal, biomass), the heating value in general is determined with the help of empiric correlations depending on the elemental fuel composition. However, as the correlations used in flowsheet simulation programs are often developed for coal, calculations using solid biomass as feedstock (e.g. wood, straw) may lead to incorrect results. Against this background, empiric correlations for the calculations of heating values used in the flowsheet simulation program Aspen Plus for the component type “nonconventional solid” are analysed. The analysis focuses on the application of the correlations in case of wood and straw are defined with the help of the component type “nonconventional solid”. It is shown, that the correlation developed by Mott and Spooner achieves the best accordance to heating values of wood and straw from statistics, i.e. measurements.

Keywords: Flowsheet; Aspen; heating value; standard heat of formation; Boie; biomass

1 INTRODUCTION

The engineering and planning of power, heat and fuel production plants in general bases on the estimation of mass- and energy flows. An important tool to calculate mass- and energy balances are flowsheet simulation programs. However, the results achieved by flowsheet modellings depend on the methods used for calculating material properties. These methods either rely on empiric data or calculation approaches using substance specific chemical data (e.g. critical temperature, critical pressure). A material property of particular interest is the heating value as many flowsheet simulation programs use this value to calculate the energy balance of diverse unit operations. Heating values of common gaseous and liquid substances with defined chemical formulas can be found in different data bases [8]. But, there are some substances (e.g. coal, biomass) which are not characterised by a defined chemical formula. The properties of these substances in general are calculated with correlations depending on their elemental composition. As calculations in flowsheet simulation programs

often rely on correlations developed for coal, calculations using solid biomass as feedstock (e.g. wood, straw) may lead to larger deviations. Against this background it is the aim of this work to analyse different correlations used in the simulation program Aspen Plus for the calculation of heating values of the component type “nonconventional solid”. The analysis focuses on the identification of suitable correlations in case of wood and straw are modelled as “nonconventional solids”.

2 BASICS ON HEATING VALUE CALCULATION – GENERAL AND ASPEN PLUS APPROACH

This chapter firstly presents the general procedure of flow sheet simulation programs to calculate the heating values of solid fuels. Secondly, approaches (i.e. formulas and coefficients) used by the software Aspen Plus are described.

2.1 General calculation approach

In the following, the general approach of simulation programs to calculate heating values

based on the elemental fuel composition is presented.

The heating value of a fuel is defined as the amount of heat released by the combustion of a quantity of fuel. Heating value calculations in flow sheet simulation programs generally rely on empiric correlations (e.g. Boie formula [4]). These correlations use the elemental mass fractions of a fuel as variables. However, there are different reference states of the fuel (e. g. dry, dry and ash free, dry and mineral matter free), on which the mass fraction can be related to (Fig. 1). According to this, different reference states used for the calculation lead to different heating values.

The fractions in most empiric correlations refer either to a dry and mineral matter containing (d) or a dry and mineral matter free (dm) mass basis (reference state). Regarding organic fuels as coal and biomass, calculations of heating values done with help of mineral matter free mass fractions lead to more accurate results [7]. Therefore, the calculation procedure of heating values of these fuels generally comprises two main steps:

- calculation of a fuel's elemental composition referred to a dry and mineral matter free mass basis (e.g. by the modified Parr formula [10]) and
- calculation of the fuel's heating value based on the dry and mineral matter free elemental composition (e.g. by the Boie formula [4]).

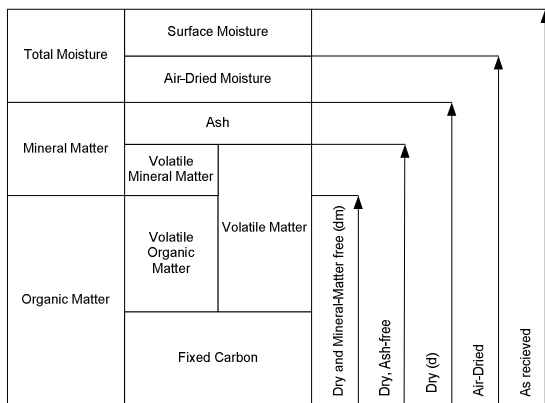


Fig. 1 Reference states of organic fuel compositions (adapted from [10]) – the deviation between ash and mineral matter content is related to volatile substances which are incorporated in the structure of minerals like carbon present in carbonates [5]

2.2 Calculation approaches from Aspen Plus

In the following, calculation approaches used by the software Aspen Plus are presented. Formulas used to describe nonconventional solids (i.e. substances which cannot be expressed by a specific chemical formula or molar weight) [2] are the focus. According to the general approach

for heating value calculations, firstly, formulas to calculate the mass fractions referred to a dry and mineral matter free mass basis are explained. Secondly, empiric formulas to calculate the heating value from that dry and mineral matter free basis are described.

Calculation of the elemental fuel composition referred to the dry and mineral matter free basis.

To determine the mass fraction x_i^{dm} of an element i referred to dry and mineral matter free basis, in addition to the mass fraction of the element referred to a dry and mineral matter containing basis x_i^d , the mineral matter content of the fuel x_{MM} and an element specific correction number Δx_i^d is required [2] (equation (1)).

$$x_i^{dm} = \frac{x_i^d - \Delta x_i^d}{1 - x_{MM}} \quad (1)$$

For the calculation of the fuel's mineral matter content, Aspen Plus uses the modified Parr formula [10]. Thereby, the mineral matter content of a fuel is estimated by the weight fractions of ash x_A , pyritic sulphur $x_{S,pyr}$ and chlorine x_{Cl} (equation (2)).

$$x_{MM} = 1.13 x_A + 0.47 x_{S,pyr} + x_{Cl} \quad (2)$$

Whereas the correction numbers of carbon Δx_C^d and the correction number of hydrogen Δx_H^d used in equation (1) are calculated according to equations (3) and (4).

$$\Delta x_C^d = 0.014 x_A^d + 0.005 x_{S,pyr}^d \quad (3)$$

$$\Delta x_H^d = 0.013 x_A^d - 0.020 x_{S,pyr}^d \quad (4)$$

The dry and mineral matter free fraction of oxygen results by the difference of the mass fractions of carbon, hydrogen, nitrogen and organic sulphur – the dry and mineral matter free fraction of sulphur by the difference of the mass fractions of the total, pyritic and organic sulphur (equation (5) and (6)).

$$x_O^{dm} = 1 - x_C^{dm} - x_H^{dm} - x_N^{dm} - x_{S,org}^{dm} \quad (5)$$

$$x_s^{dm} = x_{S,tot}^{dm} - x_{S,pyr}^{dm} - x_{S,org}^{dm} \quad (6)$$

Calculation of the heating value based on the dry and mineral matter free elemental fuel composition. Regarding the heating value of organic fuels as coal several formulas relying on the elemental composition of the fuel have been developed [6]. The flowsheet simulation program Aspen Plus uses five different correlations developed for coal or other organic fuels [2].

Boie correlation. This correlation was published by Boie in 1952 [4]. It is a generic correlation developed by the analysis of the heating value of a multitude of different organic fuels [6] (equation (7)).

$$H_s^{Boie} = 100 \cdot (a_1 x_C^{dm} + a_2 x_H^{dm} + a_3 x_S^{dm} + a_4 x_O^{dm} + a_5 x_N^{dm}) + a_6 \quad (7)$$

Dulong correlation. The correlation developed by Dulong around 1880 bases on the assumption of a complete fuel combustion [9] (equation (8)).

$$H_s^{Dulong} = 100 \cdot (a_1 x_C^{dm} + a_2 x_H^{dm} + a_3 x_S^{dm} + a_4 x_O^{dm} + a_5 x_N^{dm}) + a_6 \quad (8)$$

Grummel and Davis correlation. This correlation was published in 1933 and bases on the assumption that the heat released by the complete combustion of a fuel is proportional to the oxygen consumed for the combustion [6] (equation (9)) (Note that the correlation of Grummel and Davis is reported incorrect in the Aspen Plus documentation (state 2009 [2]) but correctly implemented in the program).

$$H_s^{GD} = \left(\frac{a_2 x_H^{dm}}{1 - x_A^d} + a_5 \right) \cdot 100 \cdot (a_1 x_C^{dm} + x_H^{dm} + a_3 x_S^{dm} + a_4 x_O^{dm}) \quad (9)$$

Mott and Spooner correlation 1 ($x_O^d < 0.15$). Around 1940 Mott and Spooner developed a correlation for the heating value calculation of coal based on the assumption that two third of the oxygen consumed for complete combustion reacts with the coal's hydrogen and one third with the coals carbon [6]. Thereby, a formula for coals with an oxygen content below 15 % (equation (10)) and a formula for coals with an oxygen content above 15 % (equation (11)) can be distinguished. The formula for coals with an

oxygen content below 15 % does not consider the coal's ash content (equation (10)).

$$H_s^{MS1} = 100 \cdot (a_1 x_C^{dm} + a_2 x_H^{dm} + a_3 x_S^{dm} - a_4 x_O^{dm}) + a_7 \quad (10)$$

Mott and Spooner correlation 2 ($x_O^d > 0.15$). The formula for coals with an oxygen content above 15 % incorporates the coal's ash content (equation (11)).

$$H_s^{MS2} = 100 \cdot (a_1 x_C^{dm} + a_2 x_H^{dm} + a_3 x_S^{dm} - \left(a_6 - \frac{a_5 x_O^{dm}}{1 - x_A^d} \right) x_O^{dm}) + a_7 \quad (11)$$

IGT correlation. The correlation of the Institute of Gas Technology developed in 1978 bases on a comparison of different other correlations [7] and the analysis of a wide range of coals [6] (equation (12)).

$$H_s^{IGT} = 100 \cdot (a_1 x_C^d + a_2 x_H^d + a_3 x_S^d + a_4 x_A^d) + a_5 \quad (12)$$

The coefficients a_i used within these five correlations have been determined by measurements of a multitude of different fuels (mainly coal [7]) and complemented over the years. Coefficients used by the flowsheet simulation program Aspen Plus are shown in Tab. 1.

The use of these coefficients leads to results expressed in btu/lb. For the calculation in this analysis the conversion to kJ/kg is done using a factor of 2.326.

Tab. 1 Coefficients of different formulas for heating value calculation

	Unit	a_1	a_2	a_3	a_4	a_5
Boie	Btu/lb	151.20	499.77	45.00	-47.70	27.00
Dulong	Btu/lb	145.44	620.28	40.50	-77.54	-16.00
Grummel and Davis	Btu/lb	0.3333	654.30	0.125	-0.125	424.62
Mott and Spooner 1	Btu/lb	144.54	610.20	40.30	62.45	-
Mott and Spooner 2	Btu/lb	144.54	610.20	40.30	-	30.96
IGT	Btu/lb	198.11 ¹	620.31	80.93	44.95	-5153.00

¹ Parameter in Aspen Plus database is 178.110; in literature generally 198.11 is reported (e.g. [7])

3 RESULTS – HEATING VALUES BASED ON DIFFERENT CALCULATION APPROACHES FROM ASPEN PLUS

To analyse the validity of the formulas for wood / wheat straw, in the following exemplary elemental compositions of wood / wheat straw are regarded. The compositions and the statistical value for the higher heating value with the related standard deviation are shown in Tab. 2.

Tab. 2 Elemental composition biomass [3]

	Unit	Wood	Straw
x_C (dry)	wt. %	50.63	44.33
x_H (dry)	wt. %	6.02	5.32
x_O (dry)	wt. %	41.52	42.93
x_S (dry)	wt. %	0.03	0.14
x_N (dry)	wt. %	0.35	0.57
x_{Cl} (dry)	wt. %	0.02	0.50
x_A (dry)	wt. %	1.43	6.21
$H_{s,d}$	kJ/kg	20263	17821
$\Delta H_{s,d}$	kJ/kg	±640	±1038

Based on the elemental composition shown in Tab. 2 each formula leads to a different heating value. These heating values are compared with statistical values taken from the Biobib database [3] (Fig. 2). In the database a set of 30 data points for wood and 17 for straw results in a mean heating value of 20263 kJ/kg for wood and 17821 kJ/kg for wheat straw, respectively. The standard deviation of the data sets is indicated as an error bar in the diagram.

Regarding the results for wood, values within the standard deviation of the statistical value can be achieved by Mott and Spooner, the IGT correlation as well as the Boie correlation.

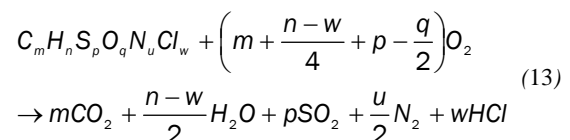
For wheat straw only the Mott and Spooner correlation leads to reasonable results compared to the statistical value.

In general, the higher heating value is underestimated by most correlations. The best results are achieved applying the Mott and Spooner correlation, whereas the Dulong formula leads to the highest deviation compared to the statistical value.

4 DISCUSSION – INFLUENCE OF THE CALCULATION APPROACHES ON THE STANDARD HEAT OF FORMATION

In the flowsheet simulation program Aspen Plus the energy balancing of unit operations relies on the standard heat of formation of the participating substances. Thereby, the standard heat of formation of nonconventional solids is directly calculated from the heating value of the substances. Hence, incorrect heating values influence the results of the energy balancing. The influence of the heating value on the standard heat of formation calculation is discussed in the following.

The standard heat of formation of a substance is defined as the change of energy that is related to the formation of a substance from its elements at standard pressure and temperature. Amongst others, the standard heat of formation of a fuel can be calculated based on its stoichiometric combustion balance and the fuel's heating value. By the combustion, an organic fuel composed of carbon, hydrogen, sulphur, oxygen, nitrogen and chlorine is ideally converted to the products carbon dioxide, water, sulphur dioxide, nitrogen and hydrogen chloride (equation (13)).



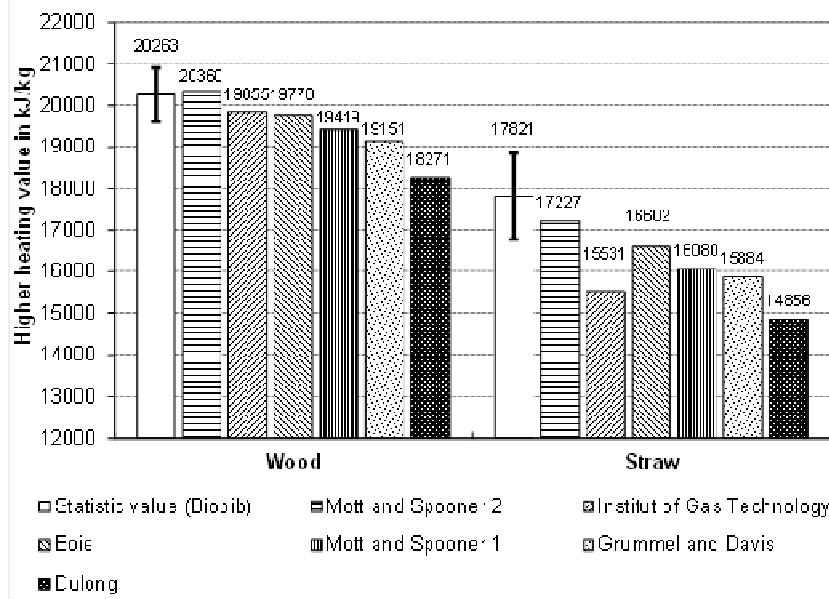


Fig. 2 Higher heating values calculated based on different correlations used in the software Aspen Plus

Based on the equation characterising the stoichiometric combustion, the specific heat released by the combustion can be determined with help of the molar standard heat of formation $\Delta h_i^{f,0}$ of the participating molecules i . The amount of this heat related to the molar quantity of fuel corresponds to the fuel's molar heating value (equation (14)).

$$\begin{aligned}
 -H_s &= -\Delta h_{C_m H_n S_p O_q N_r Cl_w}^{f,0} \\
 &- \left(m + \frac{n-w}{2} + p - \frac{q}{2} \right) \Delta h_{O_2}^{f,0} \\
 &+ m \Delta h_{CO_2}^{f,0} + \frac{n}{2} \Delta h_{H_2O}^{f,0} \\
 &+ p \Delta h_{SO_2}^{f,0} + \frac{r}{2} \Delta h_{N_2}^{f,0} + w \Delta h_{HCl}^{f,0}
 \end{aligned} \quad (14)$$

Vice versa, the standard heat of formation of a fuel can be calculated based on its heating value and the standard heat of formation of all participating molecules (equation (15)).

$$\begin{aligned}
 \Delta h_{C_m H_n S_p O_q N_r Cl_w}^{f,0} &= H_s \\
 &- \left(m + \frac{n-w}{2} + p - \frac{q}{2} \right) \Delta h_{O_2}^{f,0} \\
 &+ m \Delta h_{CO_2}^{f,0} + \frac{n}{2} \Delta h_{H_2O}^{f,0} + p \Delta h_{SO_2}^{f,0} \\
 &+ \frac{r}{2} \Delta h_{N_2}^{f,0} + w \Delta h_{HCl}^{f,0}
 \end{aligned} \quad (15)$$

As the composition of organic fuels generally is characterised by the elemental composition and not by a chemical formula, for calculations in flowsheet simulation programs equation (15) is

commonly written based on the elemental mass fractions x_i^{dm} of the fuel (equation (16)).

$$\begin{aligned}
 \Delta h_{C_m H_n S_p O_q N_r Cl_w}^{f,0} &= H_s + x_C \frac{\Delta h_{CO_2}^{f,0}}{M_C} \\
 &+ x_H \frac{\Delta h_{H_2O,l}^{f,0}}{M_{H_2}} + x_S \frac{\Delta h_{SO_2}^{f,0}}{M_S} \\
 &+ x_N \frac{\Delta h_{N_2}^{f,0}}{M_{N_2}} + x_{Cl} \frac{\Delta h_{HCl}^{f,0}}{M_{Cl_2}}
 \end{aligned} \quad (16)$$

To simplify equation (16) the standard heat of formation and molar mass M_i of a molecule i are summarised to the coefficients a_i (equation (17)).

$$\begin{aligned}
 \Delta h_{C_m H_n S_p O_q N_r Cl_w}^{f,0} &= H_s + a_1 x_C^d \\
 &+ a_2 x_H^d + a_3 x_S^d + a_4 x_N^d + a_5 x_{Cl}^d
 \end{aligned} \quad (17)$$

The result of equation (17) is the standard heat of formation in kJ/kg. The higher heating value has to be taken into account in kJ/kg.

Coefficients a_i for the calculation of the standard heat of formation from the heating value are shown in Tab. 3.

Tab. 3 Coefficients for the calculation of the standard heat of formation of organic fuels

	Unit	Value ¹
a_1	kJ/kg	$-3.276 \cdot 10^4$
a_2	kJ/kg	$-1.418 \cdot 10^5$
a_3	kJ/kg	$-9.257 \cdot 10^3$
a_4	kJ/kg	0
a_5	kJ/kg	$-1.302 \cdot 10^3$

¹ Coefficients reported by Aspen Plus [2] slightly differ from these values (based on equation 16)

To emphasise the influence of the heating value deviation on the standard heat of formation, the latter is calculated based on the different heating values shown in Fig. 2. The results are presented in Fig. 3.

In accordance to the calculations of the higher heating values, the standard heat of formation calculated based on the higher heating value corresponding to the correlation from Mott and Spooner shows the lowest deviation from the

standard heat of formation calculated based on the statistical higher heating value /3/. Accordingly, the standard heat of formation based on the higher heating value corresponding to the Dulong formula /7/ shows the highest deviation from the database value. Comparing the relative deviation of the higher heating value and standard heat of formation relative to the statistical value one can conclude that a small error in the calculation of the higher heating value (0.5 % for Mott and Spooner 2) leads to significantly larger deviations regarding the related standard heat of formation (2.0 % for Mott and Spooner 2). Regarding the Boie correlation the error of 2.4 % in the heating value leads to 9.9 % deviation calculating the standard heat of formation. This emphasises the need for accurate correlations describing the higher heating value especially if it is used as a basis to calculate the standard heat of formation.

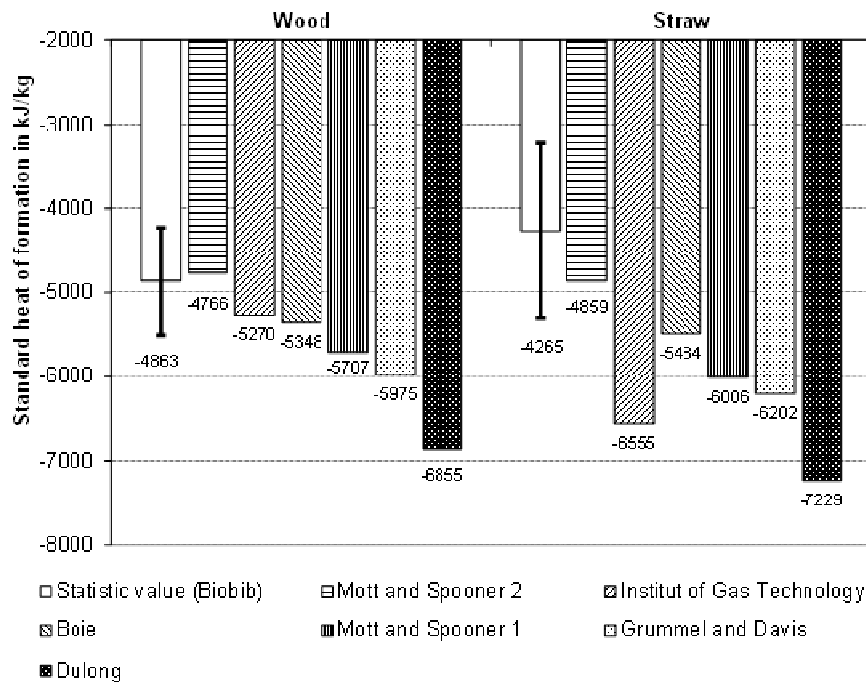


Fig. 3 Standard heat of formation calculated based on different heating value correlations used in the software Aspen Plus

5 CONCLUSIONS

Regarding the calculation results, the following conclusions can be outlined:

- In general, most correlations (developed for coal) underestimate the higher heating value for straw and wood compared to their statistical values.
- For the calculation of the higher heating value the correlation developed by Mott and Spooner ($x_o^d > 0.15$) seems to be

most suitable for wood as well as for straw.

- Alternatively, the formula developed by Boie can be used. However, a higher deviation from the statistical value than by the formula of Mott and Spooner has to be taken into account (especially for straw).
- Other correlations (e.g. developed by Dulong, Grummel and Davis) are not suitable to calculate the higher heating value of wood and straw.

- In general, the results for straw show a higher deviation from the statistical value than the results obtained for woody biomass.
- A deviation between calculated and statistical heating values leads to an increased deviation regarding the standard heat of formations calculated from the heating values.

6 NOMENCLATURE

Symbols

Δ	Standard deviation
a	coefficients
h	standard heat of formation
m	stoichiometric index of carbon
n	stoichiometric index of hydrogen
p	stoichiometric index of sulphur
q	stoichiometric index of oxygen
u	stoichiometric index of nitrogen
w	stoichiometric index of chlorine
x	mass fraction
M	molar weight
H	heating value

Abbreviations

GD	Grummel and Davis
IGT	Institute of Gas Technology
MS	Mott and Spooner

Indices

l	liquid
d	dry
dm	dry and mineral matter free
f	formation
org	organic
pyr	pyritic
s	superior
sp	pyritic sulphur
tot	total
A	ash
C	carbon
Cl	chlorine
CO ₂	carbon dioxide
H	hydrogen
HCl	hydrogen chloride
MM	mineral matter content
N	nitrogen
O	oxygen
S	sulphur
SO ₂	sulphur dioxide
0	standard conditions

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