ASH MELTING TEMPERATURE PREDICTION FROM CHEMICAL COMPOSITION OF BIOMASS ASH

MICHAL HOLUBCIK, JOZEF JANDACKA, MILAN MALCHO

Faculty of Mechanical Engineering, University of Žilina, Žilina, Slovakia
　e-mail: michal.holubcik@fstroj.uniza.sk

Solid fuels, including biomass, consist of combustible, ash and water. Ash in fuel is result of reaction of minerals presented in the biomass. Minerals and other different substances which form ash got into biomass during growth. Ash is solid residue resulted from the perfect laboratory combustion of fuel. It is composed of minerals that are present in the fuel. Some species of biomass ash have low ash melting temperature and can cause various problems in combustion boilers. Ash slags and sinters can avoid heat transfer in heat exchangers, which can cause corrosion of heat transfer surfaces. Ash melting temperature can be determined on the basis of standard STN ISO 540 in some laboratory. Meltability of ash is characterized by the physical state of the ash, which occurs during the heating process under well-defined conditions in furnace. There exist 4 types of ash melting temperature - Shrinkage temperature (ST), Deformation temperature (DT), Hemisphere temperature (HT) and Flow temperature (FT). Experimental determination of ash melting temperature is quite expensive. In paper is described method of prediction ash melting temperature from known chemical composition of biomass ash. There is proposed mathematic model for determination of all ash melting temperatures. There is need to know the proportion of SiO_2, CaO, K_2O, MgO and Al_2O_3 in biomass ash. The mathematical model is relatively accurate with real ash melting temperatures and reaches accuracy about 90 % compared with ash melting temperatures obtained by STN ISO 540 method.
Key words: ash melting temperature, biomass, prediction, chemical composition.

Predviđanje temperature taljenja pepela iz kemijskog sastava pepela iz biomase. Kruta goriva, uključujući biomasu, sastoje se od zapaljive tvari, pepela i vode. Pepeo u gorivu je rezultat reakcijeprisutnihminerala u biomasi. Minerali i druge različite tvari koje tvore pepeo ulaze u biomasu tijekom rasta. Pepeo je zaostala krutinakoja proizlazi iz savršenog laboratorijskogizgaranja goriva. On se sastoji od minerala koji su prisutni u gorivu. Neke vrste pepela iz biomaseimaju nisku temperaturu taljenja pepela i mogu uzrokovati razne probleme u kotlovima pri izgaranju. Pepeo iz troske i sinteramože spriječiti prijenos topline u izmjenjivačima topline, što može uzrokovati površinsku korozijupri prijenosu topline. Temperatura taljenja pepela može se odrediti na temelju standarda STN ISO 540 u nekom laboratoriju. Taljivost pepela karakterizirana je fizikalnim stanjem pepela, koje se događatijekom procesa grijanja pod dobro utvrđenim uvjetima u peći. Postoje 4 vrste temperatura taljenja pepela–Temperatura skupljanja (ST), temperatura deformacije (DT), temperatura hemisfere (HT) i temperatura tečenja (FT). Eksperimentalno određivanje temperature taljenja pepela je vrlo skupo. U članku se opisuje metoda predviđanja temperature taljenjapepela iz poznatog kemijskog sastava pepela iz biomase. Predlaže se matematički model određivanja svih temperatura taljenja pepela. Potrebno je znati udio SiO_2, CaO, K_2O, MgO i Al_2O_3 u pepelu iz biomase. Matematički model je relativno precizan s realnom temperaturom taljenjapepela i doseže točnost oko 90% u usporedbi s temperaturom taljenja pepela dobivenih STN ISO 540 metodom.
Ključne riječi: temperatura taljenja pepela,　biomasa, predviđanje, kemijski sastav.

INTRODUCTION

Solid fuels, including biomass, consist of combustible, ash and water [1]. Combustible substance is the part of fuel which releases heat by oxidation, i.e.energy is chemically bounded in fuel. Ballast of fuel is ash and water. Ballast is undesirable proportion of the fuel. [2, 3, 4]

Ash in fuel is result of from reaction of minerals presented in the biomass. Minerals and other different substances which form ash got into biomass during growth. Ash is solid residue resulted from the perfect laboratory combustion of fuel. It is composed of minerals that are present in the fuel. In published work [5, 6] it was found that the highest concentration of diversity to make up the ash biomass reaches silicon, aluminium and iron. Chemically, the ash from biomass is mainly composed of a mixture of oxides of inorganic elements K_2O, Na_2O, CaO, MgO, Fe_2O_3, Al_2O_3, SiO_2, P_2O_5. Amount of ash depends on the combustion conditions [7, 8, 9] The presenceof ash forming elements of biomass is the result of chemical processes, intake of minerals from the soil and method of transporting biomass. Some of these elements are necessary for plant growth. Constituent parts of ash biomass are divided into macronutrients (potassium, calcium, magnesium, phosphorus and sulphur) and micronutrients (iron, manganese and chlorine). Silicon, aluminium and sodium are essential for plant growth. [10]

Ash in combustion boilers can cause various problems. It can avoid heat transfer in heat exchangers, which can cause corrosion of heat transfer surfaces. For biofuels is monitored in potassium, sodium, sulphur, chlorine and the various compounds, as the burning they comprise a molten phase in which the particles become sticky ash, thereby adhering to the heat exchange surface [10]. For certain types of plant biomass, such as straw, whole plant cereals and hay combustion chamber temperature is higher than 800 to 900° C. Therefore, they must be regarded as technically complicated combustible fuels [11, 12]. Maintaining the temperature in the combustion chamber in temperature under ash melting temperature and avoid creating of sinter deposits and slags are quite complex, but it is possible to control the combustion temperature at least within certain limits, so that the formation of sediments and sinters is significantly limited. [13]

Possible solution problems of low ash melting temperature of biomass may be the addition of additives to the fuel during its production or addition of additives just before combustion of fuel. Additives change chemical composition of ash and it cause changing of ash melting temperature. Ash melting temperature testing before combustion of each fuel with differential additives can be very expensive because it has to be performed in special conditions. This is the main reason for searching of some ash melting temperature prediction method.

This paper deals about method of prediction of ash melting temperature by using of chemical composition of ash.

MATERIALS AND EXPERIMENTAL METHODS

As additive is considered a substance (ingredient) added to some material (product) in order to improve some of its properties [13]. Usually it happens in practice, that with the improving some characteristics are beginning to discover new deficiencies. Because of this is necessary for each used ingredient to analyse its effects to properties of fuel. 6 types of additives were used: kaolin, talc, limestone, lime, dolomite, bentonite and were added to basic fuel.
They were used 3 types of basic fuels:

- Spruce wood – was crushed to 4 mm fractionin accordance with the recommendation of works [14, 15] – wood sawdust. Relative humidity was 10 %, calorific value was 18,8 MJ.kg^{-1}. Chemical composition: 49,8 % C, 6,3 % H$_2$,43,2 % O$_2$, 0,13 % N$_2$, 0,01 % S, 0,005 % Cl. Ash melting (deformation) temperature 1170 °C.
- Miscanthusgiganteus - was crushed to 4 mm fraction –miscanthus mash. Relative humidity was 10 %, calorific value was 17,6 MJ.kg^{-1}. Chemical composition: 47,5 % C, 6,2 % H$_2$, 41,7 % O$_2$, 0,73 % N$_2$, 0,15 % S, 0,22 % Cl. Ash melting (deformation) temperature 940 °C.
- Wheat straw - was crushed to 4 mm fraction –wheat straw mash. Relative humidity was 12 %, calorific value was 16,35 MJ.kg^{-1}. Chemical composition: 45,6 % C, 5,8 % H$_2$, 42,4 % O$_2$, 0,48 % N$_2$, 0,082 % S, 0,19 % Cl. Ash melting (deformation) temperature 915 °C.

Biomass samples with additives were ashed at 550 °Con the basis of standard STN EN 14775 [16]. Ashes were tested to determine melting temperature and chemical composition of ash.

Ash melting temperature of produced wood pellets samples was determined on the basis of standard STN ISO 540 [17].

Meltability of ash is characterized by the physical state of the ash, which occurs during the heating process under well-defined conditions in furnace. [3, 8] During melting of ash were monitored following temperatures [8]:

1. Shrinkage temperature (ST) – is temperature at which first symptoms occur rounded edges or the edges of the test specimen due to melting.
2. Deformation temperature (DT) – is temperature at which the edges of the test specimen completely rounded, without changing the amount.
3. Hemisphere temperature (HT) – is temperature at which test specimen creates hemisphere, the amount of which is equal to about half the base.
4. Flow temperature (FT) - is temperature at which the ash pitch on a base in such a layer, the amount of which is approximately one third of the test specimen at the melting temperature.

Chemical composition of ash by using of inductively coupled plasma atomic emission spectroscopy (ICP-AES) in extern laboratory. Sample was melted to measure the required elements. ICP-AES analysis requires adhibition of elements to be analyzed in argon plasma induced by high frequency, where the temperature is about 8000 to 10,000 °C. The sample in aerosol form was put into the plasma where it was excited. Each excited particle of an element emits a characteristic spectrum of light (qualitative analysis), which is captured by the optical system of the spectrometer and further processed electronically. The intensity of the emitted radiation is directly proportional to the amount of this element in the sample (quantitative analysis). There were determined amounts of calcium oxide (CaO), silicon dioxide (SiO$_2$), magnesium oxide (MgO), aluminium oxide (Al$_2$O$_3$) and potassium oxide (K$_2$O). [6]

RESULTS AND DISSCUSION

Ash melting temperatures ranges of various biomass samples with addition of different types of additives are given in table 1. Impact of used additives to ash melting temperatures was very high and various (concrete results are in [8]).

Table 1. Ash melting temperatures ranges of various biomass samples with addition of different types of additives
Tablica 1. Raspon temperatura taljenja pepela različitih uzoraka biomase s dodatkom različitih tipova aditiva

Type ofbiomass	DT [•C]	ST [•C]	HT [•C]	FT [•C]
Sprucewood	1129 - 1361	1157 - 1452	1187 - 1560	1231 - 1638
Miscanthusgiganteus	940 - 1187	980 - 1231	1170 - 1240	1190 - 1319
Wheatstraw	915 - 1193	914 - 1227	1111 - 1261	1126 - 1337

Chemical composition of ash ranges of various biomass samples with addition of different types of additives are given in table 2. Addition of different additives to biomass influenced chemical composition of ash according to the chemical composition of additives. Values of chemical composition were very various (concrete results are in [8]).

Table 1. Chemical composition of ash ranges of various biomass samples with addition of different types of additives
Tablica 2. Rasponi kemijskog sastava pepela različitih uzoraka biomase s dodatkom različitih tipova aditiva

Type ofbiomass	SiO$_2$ [%]	CaO [%]	MgO [%]	Al$_2$O$_3$ [%]	K$_2$O [%]
Sprucewood	8,2 –49,5	8,7 – 67,3	1,59 – 18,35	2,08 – 20,41	2,36 – 7,8
Miscanthusgiganteus	17,3 – 54,4	4,7 – 14,9	1,85 – 8,23	4,5 - 19,8	5,0 – 20,4
Wheatstraw	38,3 – 64,3	5,4 – 18,5	1,8 - 9,94	11,74 - 21,34	8,6 – 17,0

From obtained results of ash melting temperatures and chemical composition of ash was made mathematic model for prediction of ash melting temperature under reducing atmosphere based on chemical composition of biomass ash. Concrete it is necessary to know the relative weight content of compounds SiO_2, CaO, K_2O, MgO and Al_2O_3 of the total ash.To obtain a correlation for calculating biomass ash melting temperatures was used multiple linear regression [18], which examines the relationship between several variables.It was necessary to choose the method of least squares using so as to minimize the sum of squares of residues.

Four variables were evaluated – ash melting temperatures (ST, DT, HT, FT) under reducing conditions (ISO 540).
For increasing the accuracy of the mathematic model were created 3 factors:

- Dolomite index - determines the proportion of dolomitic compounds (CaO and MgO) to the sum of the amounts of SiO_2, CaO, K_2O, MgO and Al_2O_3 in biomass ash.

$$D_{IX} = \frac{\%CaO + \%MgO}{\%SiO_2 + \%CaO + \%K_2O + \%MgO + \%Al_2O_3}$$

(1)

- Factor CMK - the ratio of the sum of CaO and MgO content to K₂O content in biomass ash.

$$f_{CMK} = \frac{\%CaO + \%MgO}{\%K_2O} \quad (2)$$

- Factor PH - the ratio of the sum of basic (CaO, K2O, MgO) and acidic (SiO₂, Al₂O₃) compounds in biomass ash.

$$f_{PH} = \frac{\%CaO + \%K_2O + \%MgO}{\%SiO_2 + \%Al_2O_3} \quad (3)$$

The equation for ash melting temperatures (ST, DT, HT, FT) predictionunder reducing atmosphere is

$$t = b_0 + b_1.SiO_2 + b_2.CaO + b_3.K_2O + b_4.MgO + b_5.Al_2O_3 + \\ + b_6.D_{IX} + b_7.f_{CMK} + b_8.f_{PH}$$

$$(4)$$

Constant b_0 [°C], the regression coefficients b_1 - b_8 [°C], standard deviation σ and correlation index R forprediction of ash melting temperatures of DT, ST, HT and FT in the table 3.

Table 3. Regression coefficientsfor prediction of ash melting temperatures
Tablica 3. Regresijski koeficijenti predviđanja temperature taljenja pepela

Indication.	Variables	DT	ST	HT	FT
b_0 [°C]	constant	854,7001827	959,5514381	1005,429562	1172,865022
b_1 [°C]	SiO_2	-10,20767818	33,12852889	161,6122538	300,0681685
b_2 [°C]	CaO	368,138734	285,9113051	-361,8976417	-855,8003084
b_3 [°C]	K_2O	35,4651134	-400,6882542	-42,36404369	-921,9924019
b_4 [°C]	MgO	115,2004821	134,6911578	-216,323586	-359,0323222
b_5 [°C]	Al_2O_3	1043,827256	977,8195132	749,4195645	682,7742762
b_6 [°C]	D_{IX}	762,9269328	640,5533142	588,3611569	411,2205704
b_7 [°C]	f_{CMK}	1,229534564	-3,27701975	0,023970513	3,064078364
b_8 [°C]	f_{PH}	-67,61601605	-32,84441128	24,72771191	69,24627947
σ [°C]		51,62	52,11	59,32	59,80
R		0,935	0,937	0,892	0,914

Calculated values of ash melting temperatures obtained using the equation (4) with using the correlation coefficients in table 3 are very accurate because the standard deviation σ all biomass ash melting temperatures are less than 60° C, which is below the limit value of the reproducibility of the experiment [17]. High accuracy of the mathematic model confirm high levels of correlation index R higher than the value of 0.9, except one temperature (HT determination, R = 0.892).

The high accuracy of the model also shows fig. 1, where is comparison of real values of biomass ash melting temperatures from experimental measurements with values obtained from mathematic model.
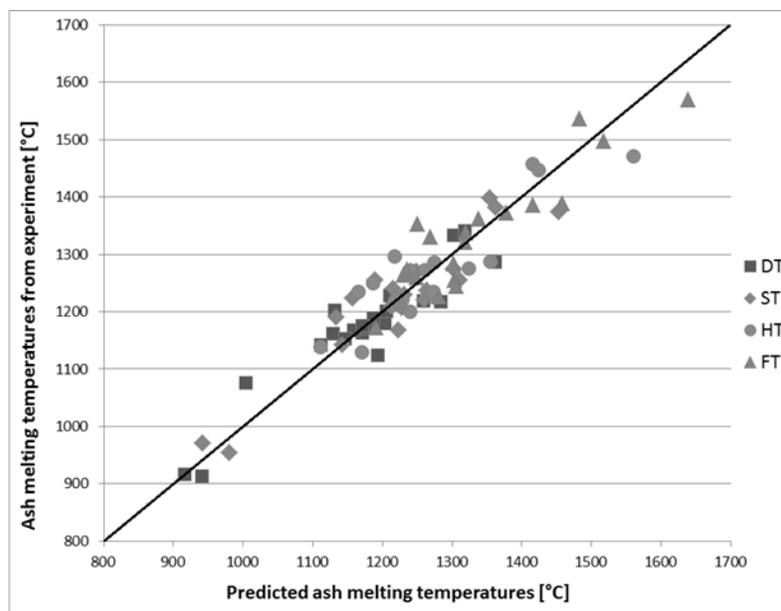
Figure 1. Comparison of ash melting temperatures from experiment and predicted ash melting temperatures
Slika 1. Usporedba eksperimentalne i predviđene temperature taljenja pepela

CONCLUSION

Empirical equations in proposed mathematical model have been derived to relate biomass ash melting temperature under reducing atmosphere. Mathematic model can be used with small standard deviation for various types of biofuels with various ash chemical compositions. It can be also used for prediction of ash melting temperature biomass with addition of various types of additives with known chemical composition.

Using of proposed mathematical model can save a lot of finances for workplaces with equipment for chemical composition determination and without equipment for ash melting temperature determination.

REFERENCES

[1]   P. Nemec, J. Hužvár: Proposal of heat exchanger in micro cogeneration unit, configuration with biomass combustion, Materials Science and Technology, special issue, pp. 66 – 76, 2011.

[2]   R. Buczyński, R. Weber, A. Szlek, R. Nosek: Time-dependent combustion of solid fuels in a fixed-bed: Measurements and mathematical modelling, Energy and Fuels, 26(2012)8, 4767-4774.

[3]   J. Jandačka et al., Wood pellets and additives, JurajŠtefuň – Georg, 2011, p. 130.

[4]   L. Šooš, M. Koleják, F. Urban: Biomass - Renewable energy source. Vert Bratislava, 2012.

[5]   M. Zevenhoven: Ash-Forming Matter in Biomass Fuels. Ábo/Turku: Faculty of Chemical Engineering, ÁboAkademi University, 2001, 88.

[6]   M. Zevenhoven: Co-Firing in FBC a challenge for fuel characterization and modelling. Proceedings of the international conference on fluidized bed combustion, 2003.

[7]   M. Holubčík, R. Nosek, J. Jandačka: Optimization of the production process of wood pellets by adding additives, International Journal Of Energy Optimization And Engineering, 2012, 20-40.

[8]   M. Holubčík: Possibilities of increasing ash melting temperature of biomass, PhD thesis, University of Zilina, 2013.

[9]   R. Nosek J. Jandačka, M. Holubčík: Effect of additives to wood pellets properties, Power Control And Optimization, Kuching, Malaysia, 2010.

[10] J. Werkelin, B. Skrifvars, M. Hupa: Ash-Forming Elements In Four Scandinavian Wood Species, Biomass And Bioenergy, Vol. 29(2005) 6, 451–466.

[11] J. Malaťák, M. Kučera: Determination of some properties of solid biofuels from the pyrolysis technology. In: Acta Facultatis Xylologiae Zvolen., 55(2013)1, 119-127.

[12] D. Tarasov, Ch. Shahi, M. Leitch: Effect Of Additives On Wood Pellet Physical And Thermal Characteristics: A Review, Isrn Forestry, Volume 2013.

[13] J. Jandačka, R. Nosek, M. Holubčík: Effect of selected additives to properties of wood pellets and their production, Acta Facultatis Xylologiae Zvolen, 2011.

[14] L. Dzurenda, J. Slovák: Energy properties of pellets made from spruce sawdust. In: ActaMechanicaSlovaca. Vol. 5(2001)3, 201 - 206.

[15] L. Dzurenda: Combustion of wood and bark, Vydanie I. Vydavateľstvo TUvo Zvolene, 2005

[16] STN EN 14775, 2009: Solid biofuels. Determination of ash content

[17] STN ISO 540, 2008: Hard coal and coke: Determination of ash fusibility

[18] M. Carnogurska, M. Prihoda, T. Brestovic: Modelling of nitrogen oxides formation applying dimensional analysis. Chemical and Process Engineering, 32(2011)3, 175-184.