



Determination of the optimal ratio of coal to biomass in the co-firing process: feed mixture properties

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Abstract

This study presents research that was conducted to determine the impact of biomass chemical composition on the characteristic ash melting behaviour of a biomass–coal blend made for use in the co-firing of power plants. It was conducted using two different types of biomass: wood biomass—pine (*Pinus sylvestris* L.) residue from sawmill, and agrarian biomass—miscanthus (*Miscanthus giganteus*). The design-of-experiments matrix was prepared using the simplex–lattice design method with four independent variables (i.e. coal A and B and biomass A and B). The characteristic melting points of ash (ash fusibility temperatures, i.e. the sintering, softening, melting and flowing temperatures) were used as the dependent variables, which were analysed under two atmospheres (e.g. oxidative and reductive). The analysis of the ash fusibility temperatures in oxidized and reduced atmospheres was conducted under accredited standards and test procedures using a PR-25/1750 furnace that was capable of reaching a maximum temperature of 1650 °C at a heating rate of 30 K min⁻¹ to 1200 °C and 10 K min⁻¹ between 1200 and 1650 °C, which provided an adequate zone of uniform temperature. In addition to the analyses of the ash melting point, full characterization of the physico-chemical properties of the applied fuels and their mixtures was performed. Based on the results of these analyses, the ash deposit behaviour was calculated, and its impact was discussed.

Keywords Ash melting behaviour · Biomass co-firing · Design of experiments · Slagging hazard determination

Introduction

Global-warming-related CO₂ emissions into the atmosphere and shrinking fossil fuel resources are increasing the importance of the search for new technologies that could use environmentally friendly renewable fuels. Therefore, basic raw material (i.e. biomass) is being used more often as an energy source and is currently the third largest natural and renewable source of energy in the world. Biomass samples are burnt and co-fired with coal and are increasingly being used for thermal processes (e.g. torrefaction, pyrolysis and gasification; Kalisz et al. 2015). Based on a report from the

International Energy Agency, the world's bioenergy sources are sufficient to ensure the supply of biomass and biofuels for energy purposes without the need to compete with food production (World Energy Outlook 2012).

Currently, firing and co-firing in fluidized bed technology is increasingly important, especially in the case of biomass–coal co-combustion for high-efficiency steam generators in power plants. This method has the benefit of reducing greenhouse gas emissions. Adding biomass to coal reduces SO₂ emissions, and a reduction in NO_x emissions is also possible due to the low sulphur and nitrogen contents present in biomass (Savolainen 2003; Baxter 2005; Al-Mansour and Zuwala 2010; The European Bioenergy Networks (EUBIONET 2017). The co-firing of biomass–coal blends can provide a reasonably attractive option for the utilization of biomass for power generation. Biomass–coal co-firing in most countries is one of the most economical technologies available for providing significant CO₂ reductions. Biomass has zero net CO₂ emissions, while coal represents the most intensive CO₂ emissions per kWh of electricity production. Unfortunately, biomass is typically characterized by a high moisture content, relatively low calorific value, low bulk

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density compared to coal, low ash melting point and different chemical compositions. Often, biomass has a high chlorine content, which increases its corrosivity and can thus influence deposit formation (i.e. slagging and fouling), agglomeration, corrosion and/or erosion, and ash utilization.

The impacts of these difficulties depend on the quality and concentration of biomass used in the fuel blend; the type of combustion that occurs; the co-firing configuration of the system; and the properties of the coal used (Sajdak et al. 2015; NIST/SEMATECH 2017).

For these reasons, it is important to conduct research on the suitability of biomass–coal mixtures and determine their relative proportions in a mass fuel stream to minimize the possible adverse impacts of using biomass. This type of study has been conducted with different scales of experiments (Grammelis et al. 2006; Theis et al. 2006a, b; Wigley et al. 2007). These studies are focused on the co-combustion of coal with different types of biomass. Some types, such as sawdust, have relatively low deposition rates, which means they are relatively safe, since co-firing with coal would not significantly influence or even decrease the ash deposition rate. Experiments on the behaviour of ash deposition for biomass co-fired with different types of coal in an electrically heated entrained pulverized fuel flow experimental reactor (Kazagic and Smajevic 2007) showed no significant difference in the ash deposition characteristics of the coal–biomass ash against the single coal ash samples at temperatures up to 1250 °C. Above this temperature, fouling was significant for the coal–biomass blends. However, a better understanding of the burning characteristics of these types of blends requires special attention.

In this paper, a slightly different approach to this issue has been presented. To describe slagging and fouling behaviours of ash from the co-combustion of coal with different types of biomass, the design-of-experiments method was applied. This approach showed the effects of biomass in the fuel feed blends on the ash fusibility temperatures and slagging hazard in a clear way. The ANOVA prepares a nonlinear regression (in this case) to calculate the optimal ratio for biomass and coal to obtain the lowest values for the slagging hazard parameters.

All presented experiments, analysis and data were obtained in 2016 in Institute for Chemical Processing of Coal in Poland.

Materials and methods

Proximate and ultimate analysis

In this study, two hard coals (KWK Murcki-Staszic [coal 1] and KWK Mysłowice Wesola [coal 2]) and two different

types of commercially available biomass: wood biomass (*Pinus sylvestris L.*), which was composed of sawmill wood waste [biomass 1], and agrarian biomass, i.e. miscanthus (*Miscanthus giganteus*) [biomass 2], were used. Technical analyses of the selected materials were performed using the classical method. First, all raw samples were subjected to basic analyses, including measurements of ash content (Ash) and volatile matter content (VM) and ultimate analysis. All materials for analysis were ground to pass through a 212- μm sieve. A portion of the sample was separated for moisture measurements in parallel with VM measurements. For the volatile matter analysis, 1 g of each sample was heated out of contact with ambient air at 900 °C for 7 min. The percentage of volatile matter was calculated based on the loss of mass from the sample due to moisture reduction. The ash contents of the samples were determined via incineration by placing the sample in a muffle furnace, heating it in air at a specific rate to a temperature of 815 ± 10 °C and maintaining this temperature until a constant weight was reached.

Ultimate analysis: determination of the carbon, hydrogen, nitrogen and sulphur contents

The samples were then analysed using automatic quantitative combustion in an oxygen stream at 1350 °C for sulphur determination and 950 °C for carbon, hydrogen and nitrogen content determination. The combustion products were transferred through a quartz bridge into a reduction tube where the sulphur and nitrogen oxides were reduced to SO_2 and N_2 . When measuring sulphur content, the gas steam passed through traps of glass wool and magnesium perchlorate. Then, the gas steam passed through a cell in which SO_2 was measured by an infrared absorption detector. Analysis of the combustion gases (e.g. N_2 , CO_2 and H_2O) was conducted using a thermal conductivity detector. Elemental analysis was performed on a LECO TruSpec CHN device (LECO, USA) and a LECO SC632 device (LECO, USA; Procedure of Institute for Chemical Processing of Coal).

The gross calorific value was analysed using 1 g of each sample via burning in high-pressure oxygen at a constant volume at the reference temperature of 25 °C in a bomb calorimeter that was calibrated by the combustion of certified benzoic acid. The combustion heating values were measured using a LECO AC500 apparatus (LECO, USA; Procedure of Institute for Chemical Processing of Coal). The results from the proximate and ultimate analyses are given in Table 1.

Chemical composition of ash

Quantification of the major components of the samples was conducted using an ICP-OES device (iCAP6500 Duo, Thermo Fisher Scientific, USA). Because this ICP-OES



Table 1 Properties of selected biomass and coal materials

Parameter	Unit	Coal 1	Coal 2	Biomass 1	Biomass 2
<i>Proximate analysis</i>					
M ^a	wt%	1.7 ± 0.1	2.2 ± 0.1	2.5 ± 0.1	3.1 ± 0.1
A ^d		3.7 ± 0.2	3.8 ± 0.2	0.5 ± 0.2	4.6 ± 0.2
VM ^d		32.03 ± 0.17	31.94 ± 0.17	84.02 ± 0.45	78.72 ± 0.45
FC		62.5 ± 0.3	62.0 ± 0.3	13.0 ± 0.3	13.6 ± 0.3
LHV _a	MJ kg ⁻¹	32.76 ± 0.83	32.04 ± 0.83	19.960 ± 0.148	18.810 ± 0.148
LHV _r		31.41 ± 0.83	30.33 ± 0.83	17.08 ± 0.14	16.12 ± 0.14
<i>Ultimate analysis</i>					
C _t ^d	wt%	83.01 ± 0.63	81.70 ± 0.6	50.00 ± 0.7	45.90 ± 0.7
H _t ^d		4.82 ± 0.27	4.58 ± 0.27	6.06 ± 0.32	5.86 ± 0.32
N ^d		1.33 ± 0.15	1.32 ± 0.25	0.30 ± 0.16	0.47 ± 0.16
S _t ^a		0.22 ± 0.04	0.21 ± 0.04	0.03 ± 0.03	0.12 ± 0.03
O _t ^a		6.95 ± 0.69	8.41 ± 0.69	43.11 ± 0.76	43.05 ± 0.76

M moisture, A ash, VM volatile matter, LHV_a low heating value in the analytical state, LHV_r low heating value in the “as-received” state

^aAnalytical state, ^ddry basis

Table 2 Chemical composition of ashes from the studied fuels

Parameters	Coal 1 (%)	Coal 2 (%)	Biomass 1 (%)	Biomass 2 (%)
SiO ₂	17.64 ± 1.85	22.94 ± 1.92	13.54 ± 1.05	57.97 ± 1.28
Al ₂ O ₃	13.15 ± 1.23	17.46 ± 1.32	9.36 ± 0.23	1.13 ± 0.32
Fe ₂ O ₃	13.59 ± 0.48	14.18 ± 0.41	14.76 ± 0.28	0.55 ± 0.25
CaO	18.79 ± 0.18	14.28 ± 0.15	22.88 ± 0.87	8.64 ± 0.71
MgO	10.68 ± 0.09	8.90 ± 0.06	11.22 ± 0.09	3.65 ± 0.10
P ₂ O ₅	0.87 ± 0.04	0.27 ± 0.18	1.11 ± 0.15	3.24 ± 0.18
SO ₃	17.95 ± 0.18	13.86 ± 0.20	3.81 ± 0.08	2.33 ± 0.06
Mn ₃ O ₄	0.24 ± 0.02	0.33 ± 0.02	0.3 ± 0.01	0.62 ± 0.01
TiO ₂	0.47 ± 0.04	0.81 ± 0.03	0.32 ± 0.02	0.08 ± 0.03
BaO	0.41 ± 0.01	0.36 ± 0.01	0.23 ± 0.01	0.06 ± 0.01
SrO	0.25 ± 0.01	0.15 ± 0.01	0.12 ± 0.01	0.03 ± 0.01
Na ₂ O	2.94 ± 0.03	4.76 ± 0.03	1.51 ± 0.04	0.24 ± 0.03
K ₂ O	0.84 ± 0.05	0.97 ± 0.06	1.77 ± 0.61	11.06 ± 0.51

SiO₂ silica dioxide, Al₂O₃ aluminium(III) oxide, Fe₂O₃ iron(III) oxide, CaO calcium oxide, MgO magnesium oxide, P₂O₅ diphosphorus pentoxide, SO₃ sulphur trioxide, Mn₃O₄ trimanganese tetraoxide, TiO₂ titanium dioxide, BaO barium oxide, SrO strontium oxide, Na₂O disodium oxide and K₂O dipotassium oxide

device requires the sample to be in the form of a solution, acid digestion of the solid ash residue was performed. For each sample, at least three digestion replicates and three ICP-OES instrumental replicates were performed (Table 2).

Ash fusibility temperatures

The analysis of the ash fusibility temperatures in an oxidized and reduced atmosphere were conducted using a

PR-25/1750 furnace (PIE/ITR, Poland) that was capable of reaching a maximum temperature of 1650 °C at a heating rate of 30 K min⁻¹ to 1200 °C and 10 K min⁻¹ between 1200 and 1650 °C, which provided an adequate zone of uniform temperature. The analysis of the fusibility of ash was performed under two different types of atmosphere: reducing (i.e. a mixture of carbon monoxide and carbon dioxide at a ratio of 3:2) and oxidizing (i.e. air and carbon dioxide). The temperatures at which characteristic changes in the shape occurred are described as follows:

1. Sintering temperature (t_s)—first signs of rounding of the tip or edges of the test piece;
2. Softening temperature (t_A)—height and length of the test piece are equal to the width of its bottom, the edges of the test piece are round, and its length does not change;
3. Melting temperature (t_B)—the height of the test piece is equal to half its base diameter based on visual observations; and
4. Flowing temperature (t_C)—the temperature at which ash is spread over the supporting tile in a layer of one-third of the height of the t_C temperature.

Determination of the characteristic melting temperature of ash is performed in oxidizing (when air is used in the process) and reducing (when the process is carried out in a gas mixture of carbon monoxide and carbon dioxide at a ratio of 3:2) atmosphere. The study of the characteristic melting temperature is carried out in two different atmospheres because the results can be applied to the real conditions existing during the combustion of solid fuels in power plants. The melting temperature of ash observed in both



atmospheres was monitored to avoid adverse results from the slagging process in the boilers.

The analysis of the ash fusibility temperatures was conducted under accredited standards and test procedures. It is a graphical method that uses image analysis to interpret the results while carrying out the analysis. In order to ensure the quality of measurements and for continuous monitoring, laboratories participate in domestic and foreign inter-laboratory studies, e.g. DCC Delta Coal Control GmbH. The analyser—a furnace-type PR-25/1750 (made by ITR), which is used for the analysis, was subjected to cyclic calibration by noble metals with sufficient purity, having a defined melting point: silver (960.5 °C), gold (1064 °C) and palladium (1554 °C), with a maximum difference of ± 10 °C (according ISO 540 standard).

Results for each material are given in Table 3.

Mixture design: simplex–lattice method

To optimize the melting temperature of the mixture of biomass and coal ash, the concept of mixture design was used. The design method was applied to the studied coal-and-biomass mixture ratio in order to determine the characteristic melting temperature and furnace slagging and fouling properties of the blend (Sajdak et al. 2015; NIST/SEMATECH 2017).

The mixture can be described by the following equation:

$$\sum_{i=1}^n x_i = x_1 + x_2 + \dots + x_n = 1.0, \quad (1)$$

$$x_i > 0; \quad i = 1, 2, 3, \dots, n, \quad (2)$$

Table 3 Characteristic melting temperature of ashes from the studied fuels

Parameters	Mu ^a (°C)	Coal 1	Coal 2	Biomass 1	Biomass 2
<i>Oxidizing atmosphere</i>					
$t_{s(O)}$	30	1060	1190	1280	680
$t_{A(O)}$	20	1340	1270	1360	840
$t_{B(O)}$		1350	1310	1360	1220
$t_{C(O)}$		1350	1320	1370	1280
<i>Reducing atmosphere</i>					
$t_{s(Or)}$	30	850	1070	1110	670
$t_{A(Or)}$	20	1310	1160	1310	810
$t_{B(Or)}$		1320	1200	1320	1290
$t_{C(Or)}$		1330	1210	1340	1360

^aMeasurement uncertainty

where n is the number of components in the study (e.g. type of fuels) and x_i is the proportion of the i th component in the mixture.

The first step in this method is to define the so-called useful area and the mathematical model to predict the properties of the mixture (e.g. in the case of a change in the ratio of different types of fuel ashes). This step is critical to design the properties and composition of the studied mixture. If the composition mixture must be modified, then the selected method (as a standard design-of-experiments method—DOE) can solve the problem. If the mixture consists of three or four components, then the usable space can be shown on the side of a triangle (Appendix A), where the vertices of the triangle determine the amount of pure components present.

The number of experiments was calculated by simplex–lattice method (NIST/SEMATECH 2017). For example, if $p = m = 3$, then the number of experiments equals 10 (Fig. 1b), and $x_i = 0, \frac{1}{3}, \frac{2}{3}, 1$. The same values of factor numbers ($p = 3$) and numbers of factor levels ($m = 3$) were applied in experiments.

Each of the three sides of the triangle represents a part of the mixture and defines part of one of the three components. In this study, the characteristic melting points of the studied samples were considered to be dependent variables, while the blends of ash from the coal and biomass were considered to be independent variables. The detailed mass ratios of the coal and biomass are given in Appendix B. In each test, the test sample was formed into a cylinder, and the measurement was taken three times.

Determination of slagging hazard

Biomass co-firing with hard coal can have a negative impact on slagging, fouling and corrosion. High biomass concentrations (e.g. straw) can cause chlorine corrosion in boilers (Pronobis 2005; Dahl et al. 2010; Zuwala and Sciazko 2010). During the combustion process, alkali chlorides can be converted into silicates and sulphates and can therefore minimize corrosion damage. Another aspect of large-scale biomass co-firing is the hazard of surface slagging, which strongly depends on the properties of the ash. The hazard of surface slagging can be described by the characteristic ash fusion temperatures of sintering, softening, melting and flowing. Ashes over the softening temperature can be strongly adhesive. For the precise prediction of ash fusibility, various correlations between the fusion temperatures and the standardized chemical composition of ashes, which are given in the form of oxides, have been proposed (Pronobis 2005; Dahl et al. 2010; World Energy Outlook 2012).

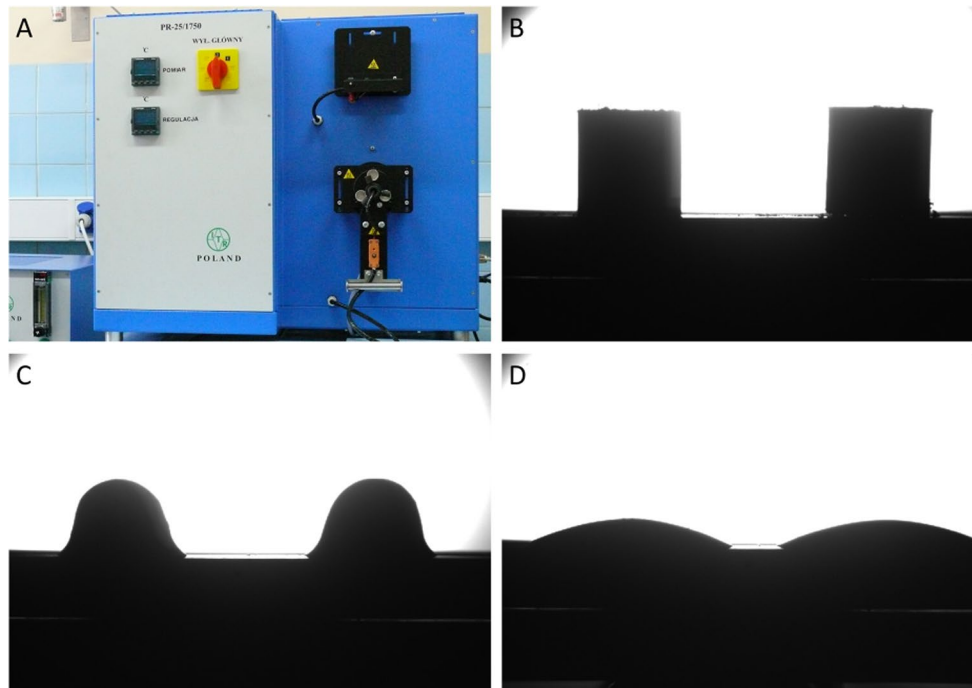


Fig. 1 Analysis of the ash fusibility temperatures, **a** PR-25/1750 furnace PIE/ITR and examples of the behaviour for each sample: **b** sample before heating, **c** melting temperature (1399 °C) and **d** flowing temperature (1405 °C)

The most frequently applied parameters used for slagging hazard determination are described below (Couch 1994; Bryers 1996; Ots and Zelkowski 2000; Öhman et al. 2004; Zuwała and Sciazko 2010; Pawlak-Kruczek et al. 2013; Ji et al. 2016; Shi et al. 2016):

- the ratio of the amount of basic compounds present to the amount of acidic compounds present:

$$B/A = \frac{\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2}; \quad (3)$$

- the slagging (Babcock) index R_s :

$$R_s = B/A \cdot S^d, \quad (4)$$

where S^d is the percentage of S in the dry fuel;

- the fouling index F_u :

$$F_u = R_s \cdot \frac{\text{Na}_2\text{O} + \text{K}_2\text{O}}{S^d} = B/A \cdot (\text{Na}_2\text{O} + \text{K}_2\text{O}); \quad (5)$$

- the slag viscosity index:

$$S_R = \frac{\text{SiO}_2}{\text{SiO}_2 + \text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO}}; \quad (6)$$

- the iron–calcium ratio:

$$\text{Fe} - \text{Ca}_{\text{ratio}} = \frac{\text{Fe}_2\text{O}_3}{\text{CaO}}; \quad (7)$$

- the amount of iron plus calcium present:

$$\sum \text{Fe\&Ca} = \text{Fe}_2\text{O}_3 + \text{CaO}. \quad (8)$$

Based on the chemical properties of coal, biomass and its blend ashes can be used as input data to determine the correlations of the fusibility, slagging and corrosion hazards. The limiting values for the relevant slagging factors are given in Appendix G.

Results and discussion

The results of this study were analysed using an analysis of variance (i.e. ANOVA) to determine the nature of the change in individual ash fusibility temperatures depending on the quantitative fuel mass ratio (Massart et al. 1997; Sajdak and Słowik 2014). As given in Table 4, changes in temperature exhibit quadratic characteristics with a relatively low p value in an oxidizing and reducing atmosphere, which indicates that these changes are statistically significant. In the case of an oxidizing atmosphere, the changes in the ash fusibility temperatures may be affected by the coexistence of oxides

Table 4 Results from the multivariate analysis of the fusibility temperatures of the studied ashes and mixtures in oxidizing and reducing atmospheres

	Oxidizing atmosphere				Reducing atmosphere			
	$t_{s(O)}$	$t_{A(O)}$	$t_{B(O)}$	$t_{C(O)}$	$t_{s(Or)}$	$t_{A(Or)}$	$t_{B(Or)}$	$t_{C(Or)}$
Effect	Q	Q	Q	Q	Q	L	Q	Q
Interaction	AD, CD	AD, CD	AD, BD, CD	AB, BD, CD	CD	CD	BD, CD	AD, BD, CD
<i>p</i> value	0.0007	0.0034	0.0062	0.0050	0.0205	0.0001	0.0221	0.0066
<i>F</i> value	135.71	275.43	30.37	16.58	18.59	53.34	15.46	19.71
<i>R</i> ²	0.989	0.995	0.950	0.909	0.919	0.918	0.903	0.923
<i>SS</i>	370,893.3	20,440.0	27,493.33	23,600.00	344,373.31	212,640.01	35,573.33	44,173.33
<i>df</i>	14	14	14	14	14	14	14	14
<i>MS</i>	26,492.38	14,950.00	1963.81	1685.71	24,598.10	15,188.57	2540.95	3155.24

t_s sintering temperature, t_A softening temperature, t_B melting temperature, t_C flowing temperature, *O* reducing atmosphere, *Or* oxidizing atmosphere, *L* linear effect, *Q* quadratic effect, *SS* sum of squares, *df* degrees of freedom and *MS* mean square

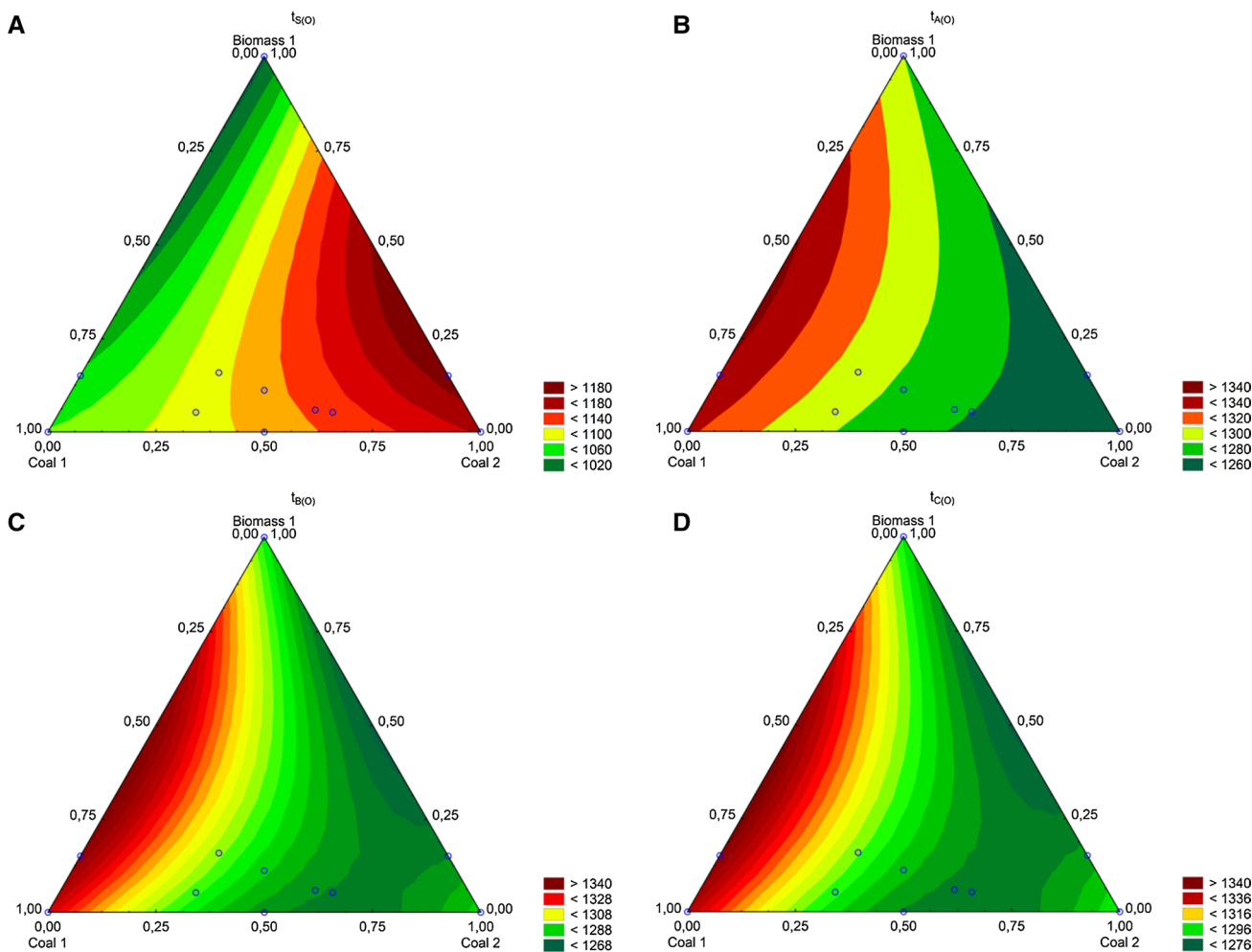


Fig. 2 Change in the ash fusibility temperatures in an oxidizing atmosphere as a function of coal. **a** sintering temperature $t_{s(O)}$, **b** softening temperature $t_{A(O)}$, **c** melting temperature $t_{B(O)}$ and **d** flowing temperature $t_{C(O)}$

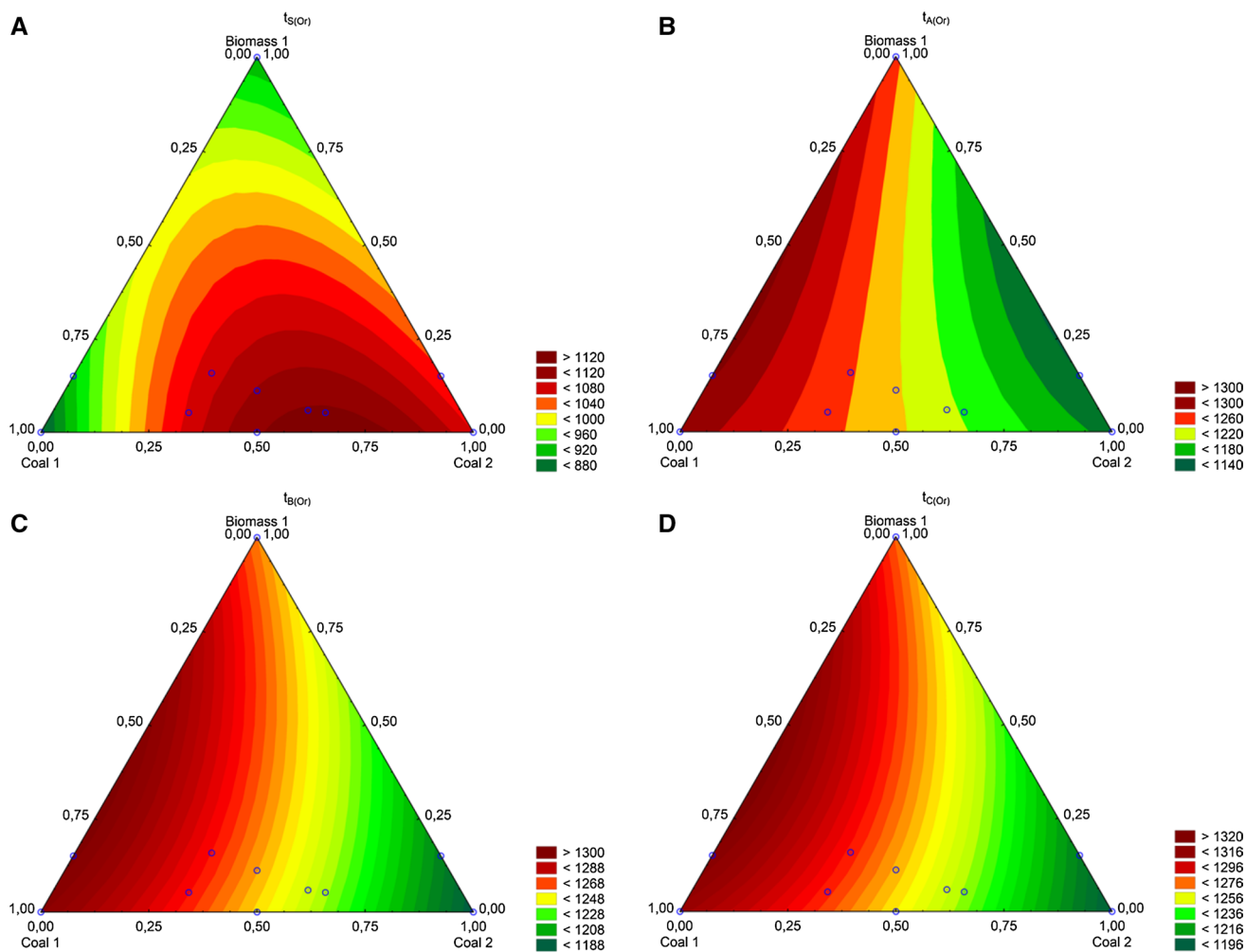


Fig. 3 Change in the ash fusibility temperatures in a reducing atmosphere as a function of coal. **a** sintering temperature $t_{s(O_2)}$, **b** softening temperature $t_{A(O_2)}$, **c** melting temperature $t_{B(O_2)}$ and **d** flowing temperature $t_{C(O_2)}$

in both tested biomasses, which may be closely related to the fact that the study used two different compositions and characteristics of oxide biomass samples.

The data show that the chemical composition of biomass 2 (miscanthus) has a markedly stronger negative effect on the ash fusibility temperature (Appendix H) than of biomass 1 (sawmill waste). This effect is also strong under a reducing atmosphere, where the interactions primarily occur between biomass 2 (miscanthus) and biomass 1. This effect is associated with a significantly higher content of potassium oxide in the ash of biomass 2 (Appendix I)

Figures 2 and 3 show the response surface for each ash fusibility temperature, which depends on the quantitative ratio of the ash used in the test fuel. The sintering

temperatures $t_{s(O_2, OR)}$ in both cases show different characteristics compared to the softening, melting and flowing properties. This behaviour of the sample is related to the different chemical compositions of the coal ash used for the tests. The results of the response surface for the ash fusibility temperatures of biomass 2 blends are given in Appendices H and I.

In the conditions studied, adding coal 1 (C_1), biomass 1 (B_1) and biomass 2 (B_2) showed a negative effect on the sintering temperature. In the case of the combustion of tested coal blends under an oxygen atmosphere in a 51:49 ratio (%), which yields an ash mass ratio of 1:1, the sintering temperature was 1100 °C. Considering the other characteristic temperatures of the physical changes, there

was a small (i.e. 30–50 °C) decline in the test values (softening temperature $t_{A(O)} = 1290$ °C, melting temperature $t_{B(O)} = 1310$ °C and flowing temperature $t_{C(O)} = 1320$ °C) compared to the temperatures for clean coal. Both of these fuels are different as to the content of silicon oxide, aluminium oxide, calcium oxide and sodium oxide by an average of 2–6%. Similar characteristic temperatures were obtained with the mixture of ashes with a mass fraction for $C_1/C_2/B_1/B_2$ of 70:10:10:10. For this mixture, the characteristic temperatures of the ash were as follows: melting temperature $t_{s(O)} = 1100$ °C, softening temperature $t_{A(O)} = 1300$ °C, melting temperature $t_{B(O)} = 1310$ °C and flowing temperature $t_{C(O)} = 1310$ °C. To obtain a fuel mixture with the mass ratio of ash described above, the tested fuel should be prepared with the dry weight ratios 44:6:45:5. Using the right type of biomass for co-combustion in a power plant could increase its participation in the fuel stream to more than 40% without a radical change in the ash fusibility temperature. Under a reducing atmosphere, the characteristic fusibility temperatures of this mixture ($C_1/C_2/B_1/B_2$ of 70:10:10:10) showed much higher values (melting temperature $t_{s(Or)} = 1130$ °C, softening temperature $t_{A(Or)} = 1260$ °C, melting temperature $t_{B(Or)} = 1290$ °C and flowing temperature $t_{C(Or)} = 1300$ °C).

For co-combustion with a high proportion of coal C_2 (10:70:10:10), the characteristic temperatures of the physical transformations were: melting temperature $t_{s(O)} = 1120$ °C, softening temperature $t_{A(O)} = 1260$ °C, melting temperature $t_{B(O)} = 1270$ °C and flowing temperature $t_{C(O)} = 1280$ °C. Under a reducing atmosphere, the 70:10:10:10 mix was compared to the degraded properties of the 10:70:10:10 mixture (melting temperature $t_{s(Or)} = 1080$ °C, softening temperature $t_{A(Or)} = 1190$ °C, melting temperature $t_{B(Or)} = 1220$ °C and flowing temperature $t_{C(Or)} = 1230$ °C).

In addition to analysing the ash fusibility temperatures of the studied mixtures of ashes, calculations for selected

Table 6 Constant values for multiple regressions used in Eq. 4 with the interaction among the studied variables for the slagging parameter

Material	Y			
	B/A	Fe/Ca	F_u	S_R
C_1	1.50	0.97	5.55	29.32
C_2	1.03	1.21	5.65	38.38
B_1	2.26	0.65	7.55	21.43
B_2	0.40	2.05	5.18	82.12
C_1C_2	–	–	2.67	–3.95
C_1B_1	–	–	–	–
C_1B_2	–0.99	–1.29	–	13.15
C_2B_1	–0.58	–	–	–
C_2B_2	–	–0.84	–	–
B_1B_2	–1.65	–2.068	3.35	9.08

B/A basic–acidic compounds ratio, Fe/Ca iron–calcium ratio, F_u fouling index and S_R slag viscosity index

slagging hazard parameters of ash were also done, including the following:

- the ratio of the amount of basic compounds present to the amount of acidic compounds present;
- the slagging (Babcock) index R_s ;
- the fouling index F_u ;
- the slag viscosity index;
- the iron–calcium ratio; and
- the amount of iron present plus the amount of calcium present.

Based on the chemical composition of ash and according to Eqs. 3–8, the parameters used for slagging hazard determination were calculated and then subjected to an analysis of variance (ANOVA). The results of this analysis are given in Tables 5 and 6.

Table 5 Effect of biomass parameters on selected slagging hazard parameters for the studied blends

	B/A	R_s	Fe/Ca	Fe + Ca	F_u	S_R
Effect	Q	L	Q	L	Q	Q
Interaction	AD, BC, CD	AD	AD, BD, CD	AB	AB	AB, AD, CD
<i>p</i> value	0.0006	0.0000	0.00001	0.0000	0.0048	0.0002
<i>F</i> value	1022.54	70.68	1444.87	108.05	7.64	1713.16
R^2	0.998	0.972	0.998	0.991	0.913	0.999
SS	2.26	0.09	1.41	782.43	5.91	2784.22
<i>df</i>	14	14	14	14	14	14
MS	0.16	0.006	0.11	55.89	0.42	198.93

t_s sintering temperature, t_A softening temperature, t_B melting temperature, t_C flowing temperature, *O* reducing atmosphere, *O_r* oxidizing atmosphere, *L* linear effect, *Q* quadratic effect, *SS* sum of squares, *df* degrees of freedom and *MS* mean square

An analysis of variance was used to determine the changes in the characteristics of the slagging parameter depending on the ratio of the mass of ashes from the fuel. As given in Table 5, only two of the calculated variables are linear: the sum of the iron oxide and the calcium oxide. The analysis shows that the content of calcium oxide and iron in biomass 2 (*miscanthus*; $\text{Fe}_2\text{O}_3 = 0.54\%$, $\text{CaO} = 8.63$) is sufficiently low in the studied range, that is, does not have a statistically significant effect (p value = 0.315, for a specified level of significance $\alpha = 0.05$) on the calculated parameter. Therefore, in the case under examination, this relationship can be written as:

$$\sum_{\text{Fe}_2\text{O}_3}^{\text{CaO}} = 25.97C_1 + 30.35C_2 + 24.00B_1. \quad (9)$$

The coefficient of determination $R^2 = 0.959$ and p value = 0.000.

The R_s ratio indicates a statistically significant (negative) interaction between coal 1 (C_1) and biomass (B_2) *miscanthus*. This relationship can be written as:

$$R_s = 0.31C_1 + 0.21C_2 + 0.07B_1 + 0.05B_2 - 0.41C_1B_2. \quad (10)$$

The coefficient of determination $R^2 = 0.937$ and p value = 0.000.

With the other parameters, only changes in a square characteristic with variable amounts of the interaction between the test samples are observed when the mass ratio of ash changes. The relationships of each of the tested slagging hazard parameters in the tested range can be described by Eq. 4.

The general equation for each of the studied slagging hazard parameters, which vary based on the test conditions (i.e. chemical characterization of ash in the test fuel), can be used only for the analysis of fuels that are similar to those investigated in this study.

Neither fuel exhibited low slagging parameters compared to other fuels (e.g. measurements from a Polish power plant in Skawina—1532 MW; Zuwała and Sciazko 2010). In these studies of the co-combustion of coal and biomass, the coal added into the boiler was characterized by the following slagging parameters: (1) the ratio of the amount of basic compounds present to the amount of acidic compounds present— $B/A = 0.18$, (2) the slagging (Babcock) index— $R_s = 0.13$, (3) the iron–calcium ratio— $\text{Fe}/\text{Ca} = 4.36$, (4) the amount of iron and calcium— $\text{Fe} + \text{Ca} = 36.47$, (5) the fouling index— $F_u = 0.65$, and (6) the slag viscosity index— $S_R = 82.66$.

However, based on that study, there are no contraindications for the co-firing of biomass B_1 when burning a 1:1 blend of coals C_1 and C_2 . At specific weight ratios of biomass 1 and the studied coals, the addition will not affect the deterioration of the slagging hazard parameters.

For coal ash 1:1 ratio (coal 1 and coal 2), comparable values of the ratio of the amount of basic compounds present to the amount of acidic compounds (B/A) can be obtained for a mixture of ashes with biomass B_1 ash additions with a ratio of $C_1/C_2/B_1$ equal to 15:70:15 (Fig. 4a).

This ratio was calculated on the amount of raw dry fuel, and the mass ratio of the fuel directed to co-firing may be up 7:37:56 m/m ($C_1/C_2/B_1$). In the case of biomass B_2 , the additive has a positive effect on the value of values of the ratio of the amount of basic compounds present to the amount of acidic compounds (B/A), which is given in Appendix J: B/A C_1/C_2 —1:1 ≈ 1.3 , the values of the ratio of the amount of basic compounds present to the amount of acidic compounds (B/A) for $C_1/C_2/B_1$ —15:70:15 m/m ≈ 1.1 . With the slagging index (R_s) when the test coal ash mass ratio for C_1/C_2 is 1:1, comparable values can be obtained for a mixture of coal ashes with biomass B_1 ash additions in the ratio of $C_1/C_2/B_1$ —15:70:15 (Fig. 3b), for which the amount of fuel directed to the co-mass ratio (of raw dry fuels) was 7:37:56 m/m. The results were similar for biomass B_2 . For the other parameters (i.e. the sum and quotient of iron trioxide and calcium oxide— Fe/Ca , $\text{Fe} + \text{Ca}$), the addition of biomass caused decreased values, but the values were too high based on the limits specified in Appendix G and thus contributed to an increased risk of slagging. As shown in the enclosed diagrams (Fig. 4 and Appendix J), the addition of biomass from sawmill waste does not affect the fouling index F_u in the studied case. Biomass from Giant Miscanthus (*Miscanthus giganteus*) was found to marginally improve this ratio, where lower values yield better performance. With the slag viscosity index, the addition of biomass had a positive effect, which is best seen in the case of biomass B_2 (*Miscanthus giganteus*), as in the other cases tested in this study; thus, larger quantities of B_2 increase the ratio S_R .

Conclusion

In this study, the design-of-experiments approach very easily showed the effects of biomass additions to fuel feed blends with coal on the ash fusibility temperatures and slagging hazard. Based on the collected experimental data, the response surface graphs of the fusibility temperatures in two

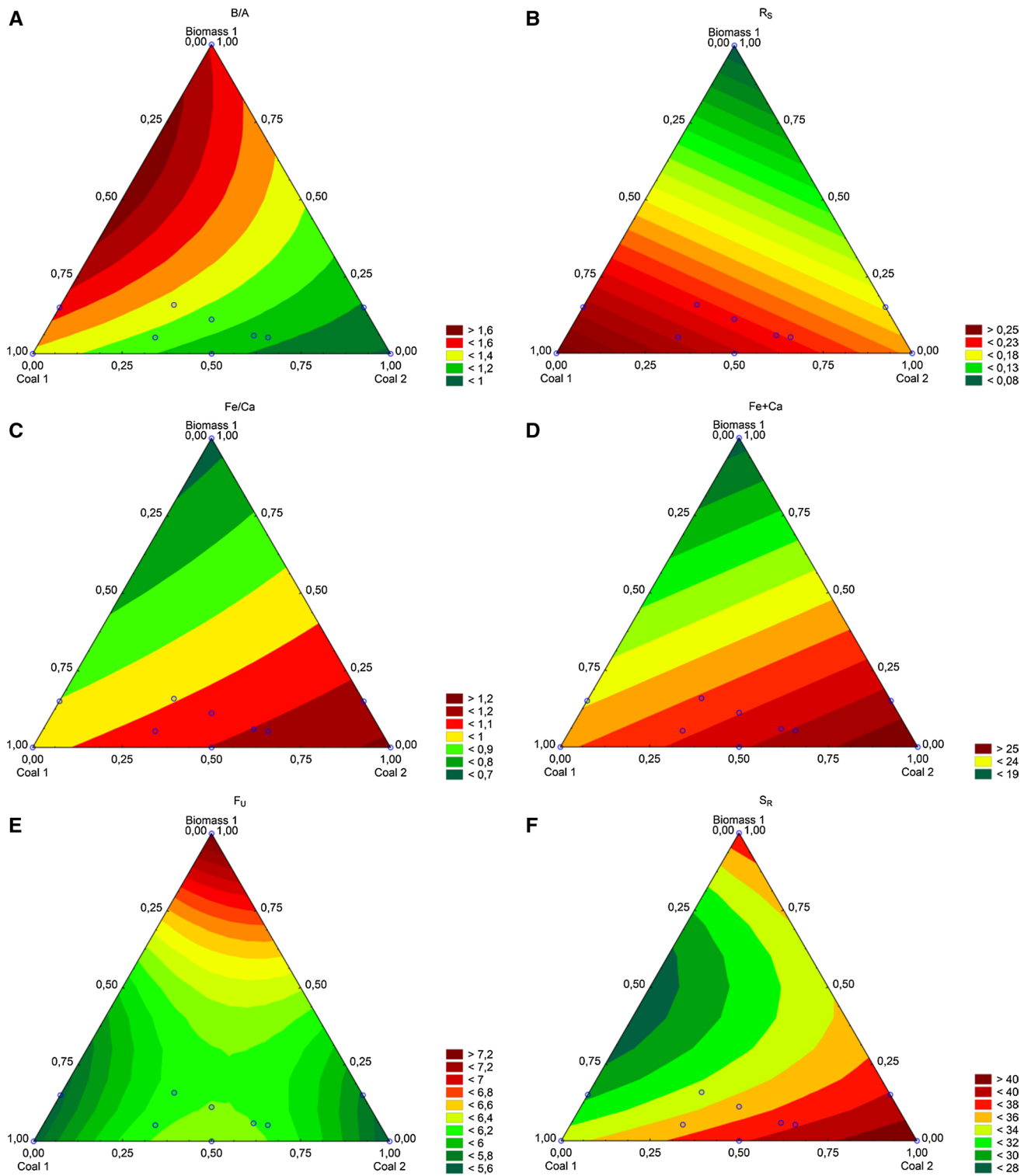


Fig. 4 Change in the characteristic slagging hazard coefficients of fuel depending on the amount of coal present. **a** ratio of the amount of basic compounds present to the amount of acidic compounds pre-

sent, **b** slagging (Babcock) index R_s , **c** fouling index F_u , **d** slag viscosity index, **e** iron–calcium ratio and **F** iron plus calcium



atmospheres (i.e. an oxidizing atmosphere and a reducing atmosphere) were presented.

Using response surface graphs and nonlinear regression equations obtained based on the ANOVA allowed to calculate the optimal biomass–coal ratio in the feed mixture. This leads to maximize the amount of biomass and reduce the slagging hazard to the limit accepted in the process used or low and medium values for slagging factors of ash (Appendix G).

The equations were characterized by determination coefficients above 0.97 for the slagging index and the sum of iron and calcium oxide and above 0.99 for the other examined factors. In the presented case, the slagging hazard parameters had quadratic characteristics, except for the fouling index (R_S) and the sum of iron and calcium oxide, as in the case of the fusibility temperatures.

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References

- Al-Mansour F, Zuwala J (2010) An evaluation of biomass co-firing in Europe. *Biomass Bioenergy* 34:620–629. <https://doi.org/10.1016/j.biombioe.2010.01.004>
- Baxter L (2005) Biomass–coal co-combustion: opportunity for affordable renewable energy. *Fuel* 84:1295–1302. <https://doi.org/10.1016/j.fuel.2004.09.023>
- Bryers RW (1996) Fireside slagging, fouling, and high-temperature corrosion of heat-transfer surface due to impurities in steam-raising fuels. *Prog Energy Combust* 22:29–120. [https://doi.org/10.1016/0360-1285\(95\)00012-7](https://doi.org/10.1016/0360-1285(95)00012-7)
- Couch G (1994) Understanding slagging and fouling in pf boilers. IEA-Consolidated Contractors Company, London
- Dahl O, Nurmesniemi H, Pöykiö R, Watkins G (2010) Heavy metal concentrations in bottom ash and fly ash fractions from a large-sized (246 MW) fluidized bed boiler with respect to their Finnish forest fertilizer limit values. *Fuel Process Technol* 91:1634–1639. <https://doi.org/10.1016/j.fuproc.2010.06.012>
- Grammelis P, Skodras G, Kakaras E (2006) Effects of biomass co-firing with coal on ash properties. Part I: characterisation and PSD. *Fuel* 85:2310–2315. <https://doi.org/10.1016/j.fuel.2006.01.036>
- Ji S, Li F, Li J, Fang Y (2016) Adjustment behaviors of blending coal on the ash fusion characteristics of coal with a high ash fusion temperature. *J Therm Anal Calorim* 125:45–52. <https://doi.org/10.1007/s10973-016-5372-3>
- Kalisz S, Ciukaj S, Mroczek K, Tymoszek M, Wejkowski R, Pronobis M, Kubiczek H (2015) Full-scale study on halloysite fireside additive in 230 t/h pulverized coal utility boiler. *Energy* 92:33–39. <https://doi.org/10.1016/j.energy.2015.03.062>
- Kazagic A, Smajevic I (2007) Experimental investigation of ash behavior and emissions during combustion of Bosnian coal and biomass. *Energy* 32:2006–2016. <https://doi.org/10.1016/j.energy.2007.03.007>
- Massart DL, Vandeginste BG, Buydens LMC, De Jong S, Lewi PJ, Smeyers-Verbeke J (1997) Handbook of chemometrics and quality metrics. Part A. Elsevier, Amsterdam
- NIST/SEMATECH (2017) E-handbook of statistical methods. NIST/SEMATECH. <http://www.itl.nist.gov/div898/handbook/>. Accessed 14 April 2017
- Öhman M, Boman C, Hedman H, Nordin A, Boström D (2004) Slagging tendencies of wood pellet ash during combustion in residential pellet burners. *Biomass Bioenergy* 27:585–596. <https://doi.org/10.1016/j.biombioe.2003.08.016>
- Ots A, Zelkowski J (2000) Abschätzung der Kohleneigung zur Verschlackung und Verschmutzung auf Grund von Kohleladedaten und erweiterter Laboruntersuchungen. Evaluation of coal tendency to slagging and fouling basing on coal data and laboratory investigation, vol XXXII. Kraftwerkstechnisches Kolloquium, Dresden, pp 47–58
- Pawlak-Kruczek H, Ostrycharczyk M, Baranowski M, Czerep M, Zgóra J (2013) Co-firing of biomass with pulverised coal in oxygen enriched atmosphere. *Chem Process Eng* 34:215–226. <https://doi.org/10.2478/cpe-2013-0018>
- Pronobis M (2005) Evaluation of the influence of biomass co-combustion on boiler furnace slagging by means of fusibility correlations. *Biomass Bioenergy* 28:375–383. <https://doi.org/10.1016/j.biombioe.2004.11.003>
- Sajdak M, Słowik K (2014) Use of plastic waste as a fuel in the co-pyrolysis of biomass: part II. Variance analysis of the co-pyrolysis process. *J Anal Appl Pyrol* 109:152–158. <https://doi.org/10.1016/j.jaap.2014.07.001>
- Sajdak M, Muzyka R, Hrabak J, Słowik K (2015) Use of plastic waste as a fuel in the co-pyrolysis of biomass: part III: optimisation of the co-pyrolysis process. *J Anal Appl Pyrol* 112:298–305. <https://doi.org/10.1016/j.jaap.2015.01.008>
- Savolainen K (2003) Co-firing of biomass in coal-fired utility boilers. *Appl Energy* 74:369–381. [https://doi.org/10.1016/S0306-2619\(02\)00193-9](https://doi.org/10.1016/S0306-2619(02)00193-9)
- Shi T, Wan T, Zhang Z, Yang X, Yang L, Zhong B, Kong X, Wang X (2016) Effect of SiO₂ on the melting characteristics of reaction between phosphogypsum and calcium sulfide. *J Therm Anal Calorim* 123:1601–1609. <https://doi.org/10.1007/s10973-015-5032-z>
- The European Bioenergy Networks (EUBIONET) (2017) Biomass co-firing—an efficient way to reduce greenhouse gas emissions. EUBIONET. <http://projects.mcrit.com/foresightlibrary/attachment/s/BioMass.pdf>. Accessed 14 April 2017



- Theis M, Skrifvars B, Zevenhoven M, Hupa M, Tran H (2006a) Fouling tendency of ash resulting from burning mixtures of biofuels. Part 2: deposit chemistry. *Fuel* 85:1992–2001. <https://doi.org/10.1016/j.fuel.2006.03.015>
- Theis M, Skrifvars B, Zevenhoven M, Hupa M, Tran H (2006b) Fouling tendency of ash resulting from burning mixtures of biofuels. Part 3. Influence of probe surface temperature. *Fuel* 85:2002–2011. <https://doi.org/10.1016/j.fuel.2005.12.011>
- Wigley F, Williamson J, Malmgren A, Riley G (2007) Ash deposition at higher levels of coal replacement by biomass. *Fuel Process Technol* 88:1148–1154. <https://doi.org/10.1016/j.fuproc.2007.06.015>
- World Energy Outlook (2012) IEA, France. ISBN Print 978-92-64-18084-0
- Zuwała J, Sciazko M (2010) Full-scale co-firing trial tests of sawdust and bio-waste in pulverized coal-fired 230 t/h steam boiler. *Biomass Bioenerg* 34:1165–1174. <https://doi.org/10.1016/j.biombioe.2010.03.003>

