Review of Ash Deposition Coefficients for Selected Biomasses

Waldemar Gądek and Sylwester Kalisz

Abstract Ambitious EU environmental policy decreasing $CO₂$ emissions from combustion of fossil fuels impact on whole EU economy. Utilization of biomass as carbon neutral fuel helps to address these challenges Combustion and co-combustion of biomass, especially agriculture residue biomass, is associated with many technical problems such us: bed agglomeration, slagging and fouling, chlorine corrosion, decreased boiler efficiency which do not occur in conventional fossil fuels combustion. In this study six fuels were investigated on their deposition ability (2 types of straw, Miscanthus and herbaceous pellets, RDF— Refuse-Derived Fuel and reference coal). Biomasses were selected as the most commonly used in Polish and German power industry. Analysis comprised chlorine and sulphur contents of the fuel, ash oxides analysis and ash fusion temperatures. The main objectives of this work were to predict ash deposition tendency of chosen fuels using ash deposition indices and compare it with reference fuel. Next weaknesses of selected indicators are pointed out.

Keywords Biomass \cdot Ash deposition \cdot Slagging \cdot Fouling \cdot Combustion

1 Introduction

Ambitious EU environmental policy decreasing $CO₂$ emissions from combustion of fossil fuels known as "2030 Framework for Climate and Energy" impact on whole EU economy [[1\]](#page-7-0). Utilization of biomass as carbon neutral fuel helps to address these challenges [\[2,](#page-7-0) [3\]](#page-7-0). However combustion and co-combustion of biomass, especially agriculture residue biomass, is associated with many technical problems

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W. Gądek (\boxtimes) · S. Kalisz

Silesian University of Technology, Institute of Power Engineering and Turbomachinery, Konarskiego 20, 44-100 Gliwice, Poland e-mail: waldemar.gadek@polsl.pl

S. Kalisz e-mail: sylwester.kalisz@polsl.pl

such as: bed agglomeration, slagging and fouling, chlorine corrosion, decreased boiler efficiency which do not occur in conventional fossil fuel combustion [[4\]](#page-7-0). Those problems are associated with high alkali metal (K and Na) contents in the fuel, especially potassium plays a negative role. In the presence of sulphur, chlorine and silica alkali silicate would be formed, these compound are characterized by low melting or softening point what may result in high deposit formation on boiler heat exchanger [\[5](#page-7-0)–[7](#page-7-0)]. Negative side effects of biomass combustion are as follows:

- slagging—this process mainly occurs in boiler combustion chamber, on furnace walls, platen steam superheater, burner areas [\[5](#page-7-0), [6](#page-7-0), [8](#page-7-0)]. Deposits are formed where ash is exposed on radiant heat of flames in high temperature range from 1050 to 800 °C [[8\]](#page-7-0). Slagging deposits consist often of an inner ash powdery layer covered by a molten or partly molten ash deposits followed by alkali and silicate compounds [[5,](#page-7-0) [7\]](#page-7-0). This dangerous phenomena results in overheating the steam superheaters.
- fouling—this process mainly occurs in convective passes of boiler on heat exchange surfaces such as: pendant superheters, reheaters, economizer and air preheters [[5,](#page-7-0) [6](#page-7-0), [8](#page-7-0)]. Fouling deposits are divided into two subgroups: high temperature fouling (temp. range $1300-900$ °C) and low temperature fouling (temp. range 900–300 °C) [\[6](#page-7-0), [8\]](#page-7-0). High temperature fouling is related with semi-fused sintered ash. On the other hand low temperature fouling is coupled with weakly sintered deposits. Previously vaporized in high temperature species are condensed at lower temperature in convective passes and the range of fouling depends on concentration of inorganic compounds in the stream of flue gases [\[6](#page-7-0)]. This actually results in the inner deposits layer on bank of tubes that is composed of condensed alkali salts with trap on its surface for non-sticky particles which influence increasing the deposit thickness [[6\]](#page-7-0).
- bed agglomeration—is also known as defluidization. This process is related with combustion of biomass in fluidized bed boilers. Biomass ashes with low melting point may surround and trap bed material (usually sand material). Alkali and silicate ash compounds create layer which carefully covers sand particles which results in increasing the sand particle size and weight [[9\]](#page-7-0). Moreover, covered particles can agglomerate together and create the ash—bridges between particles [\[9](#page-7-0)]. In the worst case the agglomerated ash and bed materials are too heavy for conditions of fluidization and stop the fluidization process.

All described issues are coupled with biomass combustion. The aim of this study is characterization of chosen fuels for assessment on deposit formation during combustion of biomass. To achieve that goal empirical, predictive ash deposition tendency coefficients were used. Study presented in this work is a starting point for large scale laboratory tests using 30 kWt slagging reactor.

1.1 Predictive Coefficients for Biomass Ash Deposition

For many years different ash behavior predictive coefficients were developed including: Silica content $(SiO₂)$, Chlorine content of the fuel (Cl), Basic to Acidic oxides (B/A), Bed Agglomeration Index (BAI), Babcock index (Rs), Ash Fusibility Index (AFI), Fouling index (Fu), Slag viscosity index (Sr) and Ash Fusion Temperatures AFT in oxidation conditions: Initial Deformation Temperature (IDT), Softening Temperature (ST). Indicators and their formulas used for calculations are widely described in Refs. $[9-12]$ $[9-12]$ $[9-12]$ $[9-12]$. However they not always show the real ash deposition tendency because they have been developed to verify coal ash rather than biomass ash deposition tendency $[10]$ $[10]$. Table 1 shows ranges of slagging and fouling indices.

2 Methodology

2.1 Materials

In this study six fuels were investigated such as: DS – cereal straw, SP-K—wheat straw, BZ—herbaceous pellets, DM—miscanthus, RDF—Refuse-Derived Fuel and WS—Polish Coal from Sobieski mine in order to compare fuels with non or intermediate slagging capabilities. Biomasses were selected as the most commonly used in Polish and German power industry which are characterized by high deposition tendency. Figure [1](#page-3-0) shows selected fuels in as received state. In the case of RDF fraction analysis shows that RDF consist of: 50.1% of plastics mixture, 28.6% textiles, 6.6% wood and 14.8% paper. In the case of RDF there was a great challenge to get uniform sample for further laboratory investigations. All fuels were milled in knife mill and sieved to fraction <0.2 mm.

Indicators	Low	Medium	High	Extremely high	
SiO ₂	<20	$20 - 25$	>25		
Cl in fuel	< 0.2	$0.2 - 0.3$	$0.3 - 0.5$	>0.5	
B/A	< 0.5	$0.5 - 1.0$	$1.0 - 1.75$		
BAI			< 0.15		
$\rm Rs$	< 0.6	$0.6 - 2.0$	$2 - 2.6$	>2.6	
AFI	>1342	1232-1342	1052-1232	< 1050	
Fu	< 0.6	$0.6 - 40$	>40		
Sr	>72	$65 - 72$	<65		
ST	>1390	1250-1390	1250		
IDT	>1100	$\sqrt{900-1100}$	< 900		

Table 1 Slagging and fouling indices with their ranges [\[10\]](#page-7-0)

Fig. 1 Pictures with investigated fuels: DS—cereal straw, SP-K—wheat straw, BZ—herbaceous pellets, DM—miscanthus, RDF—Refuse-Derived Fuel and WS—Polish Coal Sobieski

2.2 Experimental Section

For this study all selected fuels were analysed in certified laboratory using official procedures established by European Standard Technology Committee. Chlorine and sulphur contents of the fuel were analysed according to [[13](#page-7-0), [14\]](#page-7-0). For ash fusibility experiments and ash oxides analysis biomasses were ashed in muffle furnace at 550 °C in the case of RDF and coal, fuels were ashed at 815 °C according to [[15,](#page-7-0) [16](#page-7-0)]. For fusibility tests ash were formed into pyramids. Maximal temperature of experiments does not exceed 1500 °C under oxidizing conditions. Initial Deformation Temperature (ITD) Softening temperature (ST), Hemispherical temperature (HT), Fluid Temperature (FT) and its specific shapes were determined by camera and computer system according to procedure described in [\[17](#page-7-0)]. Major elements of ash Al, Ca, Fe, Mg, P, K, Si, Na, Ti, Mn, Sr were determined using procedure [[18\]](#page-7-0) by Plasma Spectrometer Thermo iCAP 6500 Duo ICP.

3 Results and Discussion

3.1 Ash Fusibility Experiments

Ash fusibility experiments are basic ash characterisation tests. This procedure may simply identify melting behaviour of ash. Figure [2](#page-4-0) shows fusion points of ash according to ash fusibility analysis. The greatest importance for the process of slagging and fouling play two first characteristic temperatures: Initial Deformation

Fig. 2 Results of ash fusibility experiments

Temperature and Softening Temperature. The highest melting curve of WS coal, shows that reference fuel with IDT—1200 $^{\circ}$ C and ST—1270 $^{\circ}$ C is on range with non or small danger of slagging and fouling. Next BZ is characterized by intermediate potential of deposit formation, IDT—1100 °C and ST—1110 °C. The melting of BZ ash occur rapidly, achieving FT—at 1140 °C. Three another agricultural biomasses DM, DS and SP-K achieve IDT in the range of 750–790 °C and ST 940– 1080 °C. In Fig. 2 fusion curves of these biomasses are located close to each other. On this basis, one can conclude that these biomasses are described by high potential of ash deposition tendency. ST of RDF achieve temperature 700 °C, and IDT were not captured because of experiments range (700–1500 °C). Investigated RDF is described by highest potential of ash deposition tendency. It is extremely unstable fuel and results of experiments (ash oxides analysis, ash fusibility) depend on proper mixing and milling of different fractions of the fuel. From ash fusibility experiments fuels can be ranked from the smallest to the greatest potential of ash deposition tendency as follow: $WS < BZ < DS < DM < SPK < RDF$.

3.2 Ash Oxides Analysis and Deposition Indices

Ash oxides analysis is one of the most common method for ash characterization. In Table [2](#page-5-0) results of ash oxides analysis are shown. The conducted study clearly indicates agriculture biomasses are characterized by high potassium content K_2O 14.02%—BZ, 16.75%—DM, 18.09%—DS, 18.59%—SP-K compared to coal

Fuel	SiO ₂ $(\%)$	CaO $(\%)$	$K2O$ (%)	P_2O_5 (%)	Al_2O_3 $(\%)$		$Fe2O3$ (%)
DS	55.50	9.59	18.09	2.79	4.13	2.85	1.84
BZ	45.58	15.49	14.04	4.41	4.86	4.28	2.04
DM	61.83	9.43	16.75	4.47	1.03	1.50	0.77
SP-K	61.22	7.51	18.59	3.29	1.23	2.17	0.83
WS	54.94	1.95	2.39	0.18	24.99	1.37	9.93
RDF	33.56	9.02	0.87	0.22	34.73	1.99	3.14
Fuel	$SO_3(\%)$	Na ₂ O $(\%)$	TiO ₂ $(\%)$	Cl in ash $(\%)$	BaO $(\%)$	SrO (%)	Mn_3O_4 $(\%)$
DS.	2.18	0.95	0.22	1.69	0.05	0.04	0.07
BZ	4.06	1.02	2.47	1.26	0.13	0.05	0.30
DM	2.53	0.33	0.08	1.13	0.03	0.02	0.09
SP-K	2.43	0.32	0.10	1.98	0.08	0.02	0.22
WS	0.80	2.47	0.87	n.m.	0.07	0.03	0.02
RDF	2.28	12.72	1.04	n.m.	0.22	0.03	0.19
Fuel	$SO_3(\%)$	Na_2O (%)	$TiO2(\%)$	Cl in ash $(\%)$	BaO $(\%)$	SrO $(\%)$	Mn_3O_4 (%)
DS.	2.18	0.95	0.22	1.69	0.05	0.04	0.07
BZ	4.06	1.02	2.47	1.26	0.13	0.05	0.30
${\rm DM}$	2.53	0.33	0.08	1.13	0.03	0.02	0.09
SP-K	2.43	0.32	0.10	1.98	0.08	0.02	0.22
WS	0.80	2.47	0.87	n.m.	0.07	0.03	0.02
RDF	2.28	12.72	1.04	n.m.	0.22	0.03	0.19

Table 2 Ash oxides analysis of selected fuels normalized at 100 wt%

n.m. not measured

2.39%—WS. Potassium is mainly responsible for slagging and fouling phenomena. Silica content in all investigated fuels is higher or on similar level, exception is RDF where $SiO₂$ content is 33.56%. All investigated fuels are in high range of silica content in high deposit range. Silica in the presence of chlorine, alkali metals, sodium, potassium affect on formation of eutectics with low temperature melting point $[10, 19, 20]$ $[10, 19, 20]$ $[10, 19, 20]$ $[10, 19, 20]$ $[10, 19, 20]$. Coal WS is characterized by the high Na₂O content of 2.47% so it seems to have high tendency for deposition compared to biomasses. But in fact the selected reference fuel has moderate or low deposition tendency. On the other hand RDF Na₂O content is on extremely high level at 12.72% compared to other fuels. One can conclude RDF is described by high potential of slagging/fouling tendency. A great convenience is to use a ash deposition indices which are presented in Table [1.](#page-2-0) Using only ash oxides analysis it is hard to conclude which fuels are described by high ash deposition tendency.

From ash oxides analysis several predictive ash deposition indices may be evaluated [[9](#page-7-0)–[12\]](#page-7-0). Results are shown in Table [3](#page-6-0). The indices have been highlighted with gray scale in order to increase readability as follows: high slagging and fouling range—black, intermediate—gray, weak—light gray. The selected indicators do not

Fuel	S^a $(\%)$	SiO ₂ $(\%)$	Cl^b $(\%)$	B/A	BAI	Rs	AFI	Fu	Sr	IDT $(^\circ C)$	ST $(^\circ C)$
DS	0.43	55.5	0.43	0.60	0.10	0.261	862	11.5	79.5	790	1080
BZ	0.10	45.5	0.09	0.78	0.14	0.078	1106	11.7	67.6	1100	1110
DM	0.06	61.8	0.09	0.53	0.04	0.032	858	9.0	84.1	780	940
$SP-K$	0.09	61.2	0.19	0.52	0.04	0.047	814	9.9	85.3	750	960
WS	1.52	54.9	0.36	0.23	2.04	0.344	1226	1.1	80.6	1200	1270
RDF	0.44	33.5	0.63	0.40	0.23	0.177	≤ 70 Ω	5.5	70.4	< 700	700

Table 3 Results of ash deposition coefficients for selected fuels

a Sulphur content of fuel in db—dry basis

^bChlorine content of fuel in db

coincide with ash fusibility experiments, and they do not show always the correct tendency. However, some of them: B/A , $SiO₂$, BAI , AFI , Fu , IDT , ST are partly consistent with ash fusibility experimental studies.

4 Conclusions

In this study several biomasses, one refused derive fuel and coal were examined in order to determine ash deposition tendency using experimental procedure and deposition indices. Phenomena of ash deposition tendency during combustion and co-combustion of biomasses affects negatively utilization of these fuels. The increasing accuracy of the ash deposition prediction methodology allows for selection of fuels that can be used in power industry. Research conducted in this study categorize investigated agricultural biomasses as fuel with high potential of ash deposition tendency. However biomasses would be more accurately examined on large scale laboratory test stands. Methodology of evaluation deposition tendency of biomasses during combustion and co-combustion will be further developed.

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