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Predicting Ash Deposit Tendency in Thermal Utilization of Biomass

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Abstract. In thermochemical utilization of biomass, ash produced during the process is a major problem that can result in decreased performance and increased in difficulty during operation. Preliminary assessment of potential ash related troubles prior to the use of a specific biomass is valuable, even if it is only a general guideline. In this work, tendency of ash slagging, fouling and agglomeration in thermal processing of biomass was evaluated. Reference peered reviewed data including mineral content and fusion temperature of selected biomass ash were used to calculate multiple indicators (base to acid ratio, slagging index, fouling index, agglomeration index, slag viscosity index, and ternary diagram of main biomass ash composition) adopted from coal research. Major ash forming elements (Fe, Ca, Mg, K, Na, Al, Si) were found to be of relevance to ash melting and deposit behavior. For conventional biomass available locally, woody biomass (wood and wood sawdust) may be combusted without slagging or fouling problem, while non-woody biomasses (bark, husk, straw) are highly probable to experience some of these problems. The ash fusibility predictive models for woody and non-woody biomass were found to be effective. Mitigation can then be designed possibly via fuel blending to avoid or minimize the impact of biomass ash related trouble.

Keywords: Ash fusion, fouling, inorganic matter, renewable energy, slagging tendency.

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1. Introduction

Biomass based resources were the predominant source of energy, chemicals, fuels and fibers in the previous century. Then, there was a swift transition to petroleum based resources which seemed to offer great promises. Presently, petroleum supplies most of the world demands for fuels and commodity chemicals, but biomass continues to play important roles in many emerging countries. The future use of fossil fuels is now in serious question due mainly to several key issues concerning rapidly depleted reserves, escalated costs, environmental pollutant emissions, and global climate change. It is inevitable that alternative sources are needed that reduce the current rates of fossil fuel usage and further contribute to meeting the future demand. A return to biomass based economy is viewed by many as a long-term solution and sustainable alternative to fossil resources [1, 2].

Biomass is a carbon based renewable fuel that can be utilized directly or through primary processing. There is a range of different processing technologies for biomass, but may generally be classified into three categories; thermochemical, biochemical and physicochemical processing. Thermochemical processing technology is by far the most popular method for converting biomass into thermal energy or upgraded fuels via combustion, gasification or pyrolysis [3-10]. Direct combustion produces hot flue gas that can be used for process heat or generation of electric power. Gasification of biomass yields mostly combustible gases suitable for subsequent heat or power generation, as well as synthesis of high quality gaseous or liquid fuels. Pyrolysis produces liquid fuel known as bio-oil which can be used for heat and power applications, or upgraded further to biofuels.

It is generally accepted that thermal utilization of solid biomass is well established, especially biomass combustion. Enormous R & D efforts have been put forwards, and resulted in a high level of development. However, there still remains one major challenge, namely ash related issue, which greatly affects plant performance, operation and maintenance [11-14]. Biomass ash is the solid residue, resulting from the combustion of biomass. It is a complex inorganic-organic mixture with multiple components, heterogeneous, and variable composition. It contains associated solid, liquid and gaseous phases with different origin [14, 15]. The most important ash related problems in thermal utilization of biomass include (i) formation of fused or partly fused agglomerates and slag deposits at high temperatures within furnaces and reactors, (ii) formation of bonded ash deposits and accumulations of ash materials at lower temperatures on surfaces in convective sections of boilers, (iii) accelerated metal wastage of furnace and boiler components due to gas side corrosion under ash deposits, and ash particle impact erosion, or ash abrasion, (iv) formation and emission of submicron aerosols and fumes, (v) biomass ash impacts on performance of flue gas cleaning equipment, and (vi) handling, disposal and utilization of ash residues from biomass firing/co-firing plants [13].

The ash problems are mainly rooted from its deposits via slagging, fouling and sintering/agglomeration. It is therefore essential to predict ash related problems in a thermal environment, particularly when variety of biomass materials is used. These ash deposition problems are influenced by ash fusibility which, in turns, associated with ash composition [11-16]. So far, there have been a number of works on biomass related ash slagging and deposition tendency [11-28], but, there is no directly available tool that predicts ash slagging from biomass. Usually, ash fusibility correlations from coal research are used instead. Vassilev et al. [16] sorted out distribution of biomass ash, its oxide contents, oxide combinations and ash fusion temperatures. It was confirmed that most of inorganic trends in natural biomass ash were found in coals [17]. Hence, correlations between ash fusion characteristics and ash mineral composition found in coal research may be applicable and equally valid to biomass. Several research studies were conducted for the relationship between biomass ash fusibility and its ash composition [18-24, 26]. Only a handful of these works were directly about slagging indices [19, 20, 22-24, 26]. These empirical ash related indices can potentially be useful as a general guideline for operators and designers in subsequent utilization of biomass. In the present work, the multiple indices developed for coal ash were adopted and applied to give indication if troubles may be expected from use of conventional biomass.

2. Methodology

The present study adopted data from the literature in which the mineral compositions in biomass ash were investigated using X-ray fluorescence and the fusion temperatures of biomass ash were determined using sintering instrument [16-18]. The reference peered reviewed data of biomass ash composition in Table 1 were used to analyze slagging factors that influence the slag potential (base to acid ratio, slagging index, fouling index, agglomeration index, slag viscosity index, and ternary diagram of main biomass ash composition). Ash flow temperatures (AFT) of selected biomass consist of four temperatures: initial deformation temperature (IT), softening temperature (ST), hemispherical temperature (HT) and fluid temperature (FT). The selected reference peered reviewed AFT data was shown in Table 2. They were also used to analyze ash fusibility. From the data, it was generally observed that woody biomasses has beneficial properties for combustion, namely high Ca, low Si and K content, compared to non-woody materials. Their ash fusion temperatures are generally higher, as a result. Non-woody biomasses normally have high contents of Si and K, hence more likely to form potassium silicates which potential formation of deposits. The predictive models were generated from the relationship of main biomass ash composition and ash fusibility index. The correlation coefficient between measured and predicted values from the model was considered by Eq. (1).

$$r = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2 \cdot (\sum_{i=1}^{n}(y_i - \bar{y})^2}} \tag{1}$$

Table 1. Mineral composition of selected biomass ash [17, 18].

Biomass	**Composition (%)**										
	SiO_2	CaO	K_2O	P_2O_5	Al_2O_3	MgO	Fe_2O_3	SO_3	Na_2O	TiO_2	total
Wood	11.1	64.5	0.2	-	0.1	1.2	3.3	2.0	8.9	0.1	92.4
Wood residue	53.2	11.7	4.85	1.37	12.6	3.06	6.24	1.99	4.47	0.57	100
Pine	39.0	25.5	6.0	-	14.0	6.5	3.0	0.3	1.3	0.2	95.8
Pine bark	9.2	56.8	7.78	5.02	7.2	6.19	2.79	2.83	1.97	0.19	100
Eucalyptus bark	10.0	57.7	9.3	2.4	3.1	10.9	1.1	3.5	1.9	0.1	100
Forest residue	20.6	47.6	10.2	5.05	2.99	7.2	1.42	2.91	1.6	0.4	100
Rice husk	94.5	1.0	2.29	0.54	0.21	0.19	0.22	0.92	0.16	0.02	100
Rice straw	52.0	7.7	17.8	2.5	0.9	2.3	0.8	6.5	1.0	-	92.9
Corn stalk	45.2	9.6	21.4	8.5	2.8	3.7	0.9	4.6	0.6	-	98.0

Table 2. Fusion temperatures of selected biomass ash [17, 18].

Biomass	**Temperature (^{o}C)**			
	IT	ST	HT	FT
Wood	1050	-	1190	> 1190
Wood residue	1175	1205	1230	1250
Pine	1190	1200	1220	1280
Pine bark	1231	1425	1519	1527
Eucalyptus bark	1200	-	1250	1275
Forest residue	1320	-	1380	1395
Rice husk	1427	-	1605	> 1620
Rice straw	1020	1140	1196	1246
Corn stalk	995	1102	1242	1276

2.1. Base-to-acid Ratio

The ash content is a good indicator of the problematic nature of biomass. The oxides in ash can be classified into acidic (i.e. SiO_2, Al_2O_3, TiO_2) and base (i.e. Fe_2O_3, CaO, MgO, Na_2O, K_2O) oxides. Ash deposition potential may be evaluated in terms of base-to-acid (B/A) ratio using Eq. (2) [15]. The B/A ratio is an indication of the fusion characteristics and slagging potential of ash and ash-containing metals to combine in the combustion process to produce low temperature melting salts. The main ash compositions are used to calculate B/A ratio.

$$\frac{B}{A}=\frac{Fe_2O_3+CaO+MgO+Na_2O+K_2O}{SiO_2+Al_2O_3+TiO_2} \tag{2}$$

2.2. Slagging Index

Slagging refers to deposit formation from adhering of sticky, melted or softened ash particles on heat transfer surfaces exposed to radiant heat. The slagging index (*R_s*) of a solid fuel has been taken as a measure of the slagging propensity of the ash [25]. This value gives indication of slagging tendency, similar to the B/A ratio, and is calculated from Eq. (3).

$$R_s=\frac{B}{A}\cdot Fe_2O_3 \tag{3}$$

2.3. Fouling Index

Fouling refers to dry deposition of ash particles or condensation of volatile inorganic components on heat transfer surfaces. The fouling index (*R_f*) of a solid fuel is a measure of the fouling propensity of the ash. This value gives indication of fouling tendency, and is calculated from Eq. (4).

$$R_f=\frac{B}{A}\cdot\left(Na_2O+K_2O\right) \tag{4}$$

2.4. Agglomeration Index

Because of sintering process, loosely bound particles can become denser and form compact and hard particles. Bed sintering/ agglomeration index gives indication of ash sintering and agglomeration during thermal conversion processes. This parameter is calculated in from Eq. (5).

$$R_a=\frac{Fe_2O_3}{Na_2O+K_2O} \tag{5}$$

2.5. Ash Fusibility Index

Ash fusibility can indicate ash agglomeration and clinkering during high temperature thermal conversion processes. This parameter is calculated in terms of representative fusion temperature, from Eq. (6).

$$T_{AFI}=\frac{4\,IT+HT}{5} \tag{6}$$

2.6. Slag Viscosity Index

Slag Viscosity is one of index to predict the slagging tendency because it leads to a better understanding of the structure of slag. The slag viscosity is related to the ash and defined as, in Eq. (7).

$$G = \frac{SiO_2}{SiO_2 + Fe_2O_3 + CaO + MgO} \times 100 \quad (7)$$

2.7. Ternary Diagram

The ternary diagram method is refereed to chemical equilibrium calculations to show the liquidus isotherms. The compositional triangle (weight percent) in the silicon (SiO_2)-alkali (K_2O+Na_2O)-alkaline earth (CaO+MgO) system can be used to predict the slagging tendency [26]. The biomass ash tends to fuse at a certain temperature below the the liquidus isotherms.

2.8. Modeling Ash Fusibility Index

Ash fusibility index (T_{AFI}) may be predicted based on the content of oxides in ash [19]. This is calculated from Eq. (8). For woody biomass materials, a characteristic index is acquired from Eq. (9). For non-woody ones, a characteristic index is referred to Eq. (10).

$$T_{AFI} = f(x) \quad (8)$$

where

$$X = \frac{CaO + MgO}{SiO_2 + Al_2O_3 + K_2O + Fe_2O_3} \quad (9)$$

$$X' = \frac{SiO_2 + K_2O + Na_2O}{CaO + Al_2O_3 + Fe_2O_3} \quad (10)$$

3. Results and Discussion

In this work, the biomass materials are divided into two types, woody and non-woody plants. Woody plants are from shrubs, tree, and lianas. Non-woody or herbaceous plants are annual plants which have no persistent woody stem above ground and die at the end of the growing season.

Table 3 shows resultant slagging factors (base to acid ratio, slagging index, fouling index, agglomeration index, and slag viscosity index) for woody and non-woody biomass. The slagging potential in terms of the B/A ratio may be determined from where the lower range of the slag is defined at B/A less than 0.2. Values between 0.2-1.0 indicate medium deposition tendency and those greater than 1.0 indicate high potential [15]. The results of non-woody materials were not found to be over 1.0, meaning that they have lower medium slagging potential. While the values of some members (wood, pine bark, eucalyptus bark, and forest residue) in the woody type were over 1.0, implying that they may probably be very high deposition tendency. High slagging index values increased slagging potential [15]. The woody type showed higher probability for slagging tendency than the non-woody type. Fouling index value showed similar trend with slagging index, except for Eucalyptus bark and forest residue. The biomass materials that have high B/A ratio and high Na_2O appeared to have high fouling tendency. They are wood, pine bark, eucalyptus bark, and forest residue. For all biomass considered, the agglomeration index values were not found to exceed 1.0. There was no clear indication of agglomeration behavior.

For ash fusibility index, a value in the range of 1052-1232°C refers to high slagging potential. If it is less than 1052°C, severe slagging potential is very likely to occur [27]. The fusibility indices of wood, wood residue, pine, eucalyptus bark, rice husk, and rice straw were in the range of 1052-1232°C, indicating that they have high deposition tendency. For slag viscosity index, a value in the range of 72-80 is expected to show slight deposition tendency. A value between 65-72 may show moderate slag tendency, and that in the range of 50-65 indicates possibility of severe slagging problem [28]. All of the woody biomass type showed high probability for severe slagging to occur. Pine bark and eucalyptus bark were the most serious cases.

It should be noted that empirical indices from coal research may have limitations when predicting the slagging potential of biomass combustion. Although the mineral composition of biomass ash is as broad as that of coal ash, the ash loading from biomass is generally lower than that of coal. It was known that biomass slagging was also closely related to Cl, which was not considered here. Additionally, the fuel properties, together with thermal conditions and potential chemical interactions can also influence slagging and fouling behavior [20-22, 24].

Table 3. Slagging factors of woody and non-woody biomass.

Biomass	Index	Base-to-acid Ratio	Slagging Index	Fouling Index	Agglomeration Index	Ash Fusibility Index	Slag Viscosity Index
Woody	Wood	6.9	22.8	62.9	0.4	1078	13.9
	Wood residue	0.5	2.9	4.3	0.7	1186	71.7
	Pine	0.8	2.4	5.8	0.4	1196	52.7
	Pine bark	4.6	12.7	44.4	0.3	1289	12.3
	Eucalyptus bark	6.1	6.7	68.6	0.1	1210	12.5
	Forest residue	2.8	4.0	33.5	0.1	1332	26.8
Non-Woody	Rice husk	0.0	0.0	0.1	0.1	1463	98.5
	Rice straw	0.6	0.4	10.5	0.0	1055	82.8
	Corn stalk	0.8	0.7	16.6	0.0	1044	76.1

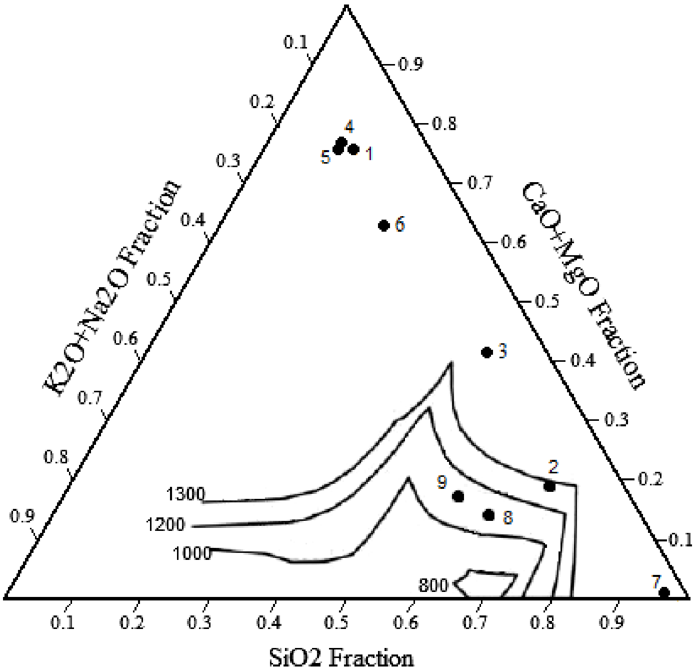

Fig. 1. Liquidus temperature of biomass in ternary diagram from CaO(+MgO)- K_2O(+Na_2O)-SiO_2 system, (Solid point 1 = Wood, 2 = Wood residue, 3 = Pine, 4 = Pine bark, 5 = Eucalyptus bark, 6 = Forest residue, 7 = Rice husk, 8 = Rice straw, and 9 = Corn stalk).

Figure 1 shows the isothermic curves representing the liquidus temperature from the CaO(+MgO)-K_2O(+Na_2O)-SiO_2 system. Also plotted in the diagram are solid points corresponding to each biomass material considered in this work. It was shown that the region whose SiO_2 fraction of around 0.7 and the value of CaO(+MgO) fraction close to zero probably had the lowest liquidus temperature (800°C). It was found that rice straw (point 8) and corn stalk (point 9) appeared to have the lowest liquidus temperature, according to AFT and ash fusibility index. Wood residue (point 2) showed the lowest liquidus temperature (~ 1300°C) among the woody biomass type. It was clear that the liquidus temperature was dependent on biomass ash compositions, not directly related to the biomass type.

From the data distribution and curve fitting, the relationships between the characteristic index (X , X') and ash fusibility index for the biomass ash considered in this work can be obtained. They are shown in Fig. 2. The isolated points show processed data from measured values, while the continuous curve is an empirical formula representing the relationship. For woody plants, it can be seen that ash fusibility temperature initially increases, exhibit a peak, and then decreases with the increasing index *X*. The predictive model can be obtained as Eq. (11), where its correlation coefficient is 0.92 and mean square deviation is 29.1°C.

$$T_{AFI} = -34.5X^2 + 133.3X + 1159.8 \tag{11}$$

For non-woody plants, the empirical formula is shown in Eq. (12). Its correlation coefficient and mean square deviation are about 1.0 and 4.4 °C, respectively.

$$T_{AFI} = 0.04X'^2 + 3.9X' + 1023.8 \tag{12}$$

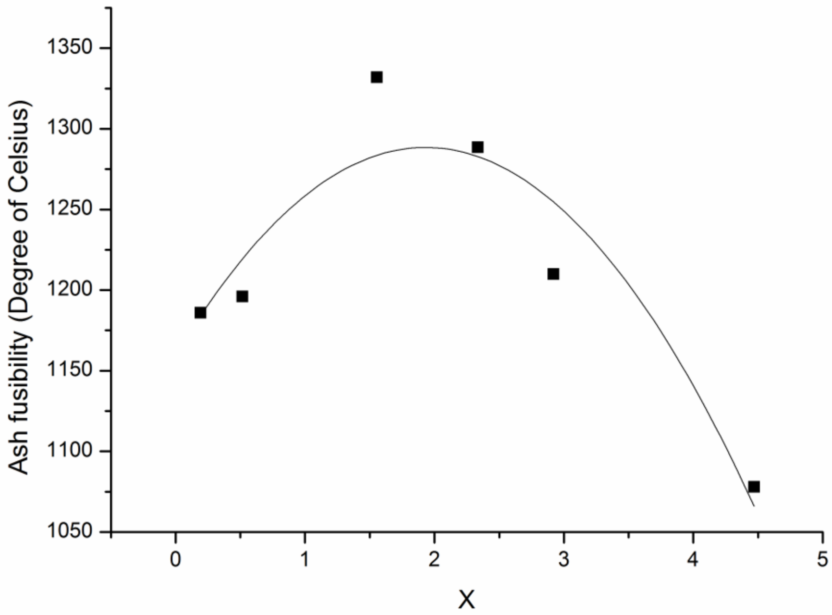

Fig. 2. The scattered distribution and fitting curve between woody biomass characteristic index and ash fusibility index.

The two characteristics indices (*X* and *X'*) were found to be correlated well with ash fusibility index temperature for both types of biomass ash. Both prediction models are rational because of good correlation and low mean square deviation values, below 30°C. The results of prediction models are shown in Table 4. The measured values and the predicted ash fusibility indices were compared. The absolute errors for woody and non-woody biomass considered in this paper were found to be less than 50°C. The relative errors between them were within 4%. In comparison with the results predicted by using the empirical formula in ref. [19] also shown in Table 4, their results appeared to be inferior to our results, based on absolute and relative errors obtained. The prediction models proposed in this paper seemed to have high accuracy.

Nonetheless, it should be noted that number of data considered here was rather small. Greater number of data should be included in the future study.

Table 4. Results of the prediction models

Type of biomass	Sample	Fusion temperature (°C)	Prediction results		
			Predictive value (°C)	Error (°C)	Relative error (%)
Woody	Wood	(T_{AFI}) 1078	1066.4	11.6	1.1
	Wood residue	(T_{AFI}) 1186	1184.1	1.9	0.2
	Pine	(T_{AFI}) 1196	1219.4	-23.4	2.0
	Pine bark	(T_{AFI}) 1289	1282.9	5.7	0.4
	Eucalyptus bark	(T_{AFI}) 1210	1254.9	-44.9	3.7
	Forest residue	(T_{AFI}) 1332	1283.7	48.3	3.6
	Pine [18]	(ST) 1226	1160.8	65.2	5.3
	Phoenix tree wood1 [18]	(ST) 1145	1181.5	-36.5	3.2
	Phoenix tree wood2 [18]	(ST) 1185	1177.9	7.2	0.6
Non-Woody	Rice husk	(T_{AFI}) 1463	1472.1	-9.5	0.6
	Rice straw	(T_{AFI}) 1055	1055.4	-0.2	0.0
	Corn stalk	(T_{AFI}) 1044	1044.5	-0.1	0.0
	Peanut shell [18]	(ST) 1170	1213.0	43	3.7
	Poplar sawdust [18]	(ST) 1193	1259.1	-63.1	5.3
	Chaff [18]	(ST) 1190	1177.8	12.2	1.0
	Pepper rod 1 [18]	(ST) 1221	1242.4	-21.4	1.8
	Pepper rod 2 [18]	(ST) 1202	1256.7	-54.7	4.6

4. Conclusion

Oxides in different types of biomass ash vary significantly. They may be formulated to give useful correlations with or indication for ash deposit tendency. Various oxides related indicators (B/A ratio, slagging index, fouling index, agglomeration index, slag viscosity index, ternary diagram of main biomass ash composition and AFT) derived from coal research were useful in preliminary assessment of occurrence and probability of slagging, fouling and agglomeration. Woody biomass materials containing low silica ash seemed to be used successfully as solid fuel without slagging or fouling problems. Non-woody biomass materials containing high silica ash may experience some slagging and fouling during thermal processes. This tendency can be mitigated by co-firing with appropriate amount of woody biomass or coal.

Applicability of indices developed from coal (base to acid ratio, slagging index, fouling index, agglomeration index, and slag viscosity index) should be evaluated with caution, when applied to biomass. Nonetheless, they allow rapidly initial realization of slagging and fouling potential of solid fuel. From the chemical equilibrium calculations, it was conclusive that the liquidus temperature depends on the quantity of biomass ash compositions. The prediction models were found to show good correlation with ash fusibility index. This can be useful for predicting ash fusibility of biomass. For future works, study of blended biomass materials and the use of additives to reduce slagging and fouling tendency may be carried out. Use of thermochemical software such as FactSage is also of great interest to predict liquidus temperature, proportions of solids, mineral formation, and phase equilibria of ash samples.

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