

FREE ALKALI-INDEX FOR OPTIMIZING THE FUEL MIXTURE IN BIOMASS CO-FIRING

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ABSTRACT

Co-firing biomass with fossil fuels provides a cheap and efficient reduction of the CO₂ emissions in electricity generation. One of the main challenges in co-firing is the increased fouling and corrosion rates of the heat transfer surfaces when biomass is added to the fuel mixture. Optimization of the fuel mixture from the fouling and corrosion point of view would be an easier task, if some fuel properties would provide correlation with the fouling and corrosion rates. Currently there is no clear understanding of the most useful fuel indices. The fouling indices used in coal firing have proved to be less useful in biomass co-firing. Prediction of the fouling rate from the the (S/Cl) molar ratio or the (S/available alkali) molar ratio have shown some success. However, generally accepted threshold values for these are not available. The newly developed fouling indices in biomass co-firing are basically trying to predict the formation of alkali chlorides on the heat transfer surfaces. Alkali chlorides, especially KCl are believed to be the substances responsible for the high fouling and corrosion rates in biomass combustion and co-firing, whereas the formation of alkali sulfate seems to have a beneficial effect in the minimization of the fouling and corrosion rates. However, the mechanism of the formation of the alkali chlorides and sulfates on the heat transfer surfaces is not known in detail so the threshold values of the indices are based on empirical correlations found to fit the data of a particular experiment. In this paper, a new fouling index, $(x \cdot (Na+K) - 2 \cdot S) / LHV$, is presented. Theoretical background of the index is described and examples are given how to use the index in optimization of the fuel mixture in biomass co-firing. Finally, correlation of the index with available literature data is presented. Now the validation of the usefulness of the index requires further experimental work.

INTRODUCTION

Biomass combustion and co-firing causes fouling and corrosion of the heat transfer surfaces, especially if high heat transfer surface temperatures are used. Higher boiler efficiencies mean higher temperatures of the heat transfer surfaces, so if the efficiency of the biomass boilers is to be improved, the fouling and corrosion problems need to be

solved. In coal fired power plants, one of the major fouling and corrosion mechanisms is deposition of the essentially solid alkali sulfates, subsequent reaction of the iron oxides with SO₃ in the gas phase or released from the dissociation of alkali sulfates and finally the formation of a molten alkali-iron trisulfate phase. The melting point of the alkali-iron trisulfate depends on its composition. High alkali content in the deposit decreases the melting point, the minimum melting point being around 620 °C, which is why the coal fired power plants generally operate with maximum steam temperatures below 580 °C, although higher steam temperature have been achieved with low fouling coal and using corrosion resistant austenitic alloys. The most commonly used indices for the prediction of the fouling and slugging risk of the fuel in coal fired power plants are:

The alkali index:

$$\frac{mK_2O + mNa_2O}{HHV} \quad (1)$$

where mK₂O and mNa₂O are the weight concentrations in the fuel, calculated from the ash analysis and HHV is the higher heating value of the fuel.

The base to acid oxide ratio in the ash:

$$\frac{mFe_2O_3 + mCaO + mMgO + mK_2O + mNa_2O}{mSiO_2 + mTiO_2 + mAl_2O_3} \quad (2)$$

where all the values are weight concentrations in the ash. And the ash fusion temperature determined according to the ASTM E953 standard.

Several other empirical indices have been developed, but the usefulness of these in biomass combustion and co-firing is questionable (Winegartner 1974)¹. In pure biomass combustion, the fouling and corrosion mechanisms are different and extensive fouling and corrosion is observed already with substantially lower heat transfer and gas temperatures. In pure biomass boilers, the final superheat temperature is typically 480 °C, or even lower, and still the corrosion rates are typically higher than in coal fired plants. Long term field experience from Sweden suggest that when

the final steam temperature is higher than 480 °C, the superheater tubes last no longer than 4 years, even when fired with forest based biomass (Henderson et al. 2006)², which is considered less fouling and corrosive as the agricultural based biomass fuels. In biomass combustion and co-firing the high fouling and corrosion rates have been explained by several mechanisms. In the most common hypothesis found in the literature, KCl is believed to condense or otherwise deposit on the heat transfer surfaces. Solid potassium chloride is then believed to react with the protective oxide of the steel releasing corrosive Cl₂ gas near the metal-scale interface, possibly forming low melting eutectics with iron or chromium. Molten electrolyte would increase the corrosion rate and promote further sticking of the ash particles (Nielsen et al. 2000)³ (Cha and Spiegel 2006)⁴ (Montgomery et al. 2002)⁵ (Spiegel et al. 2003)⁶.

Another mechanism originating from the studies of recovery boiler corrosion postulates that the melt is formed prior to the reaction of KCl with the tube by formation of low melting point mixtures in the (K,Na)Cl-(K,Na)₂CO₃-(K,Na)₂SO₄ system and then a molten phase attack towards the protective oxide is initiated (Isaak et al. 1986)⁷ (Backman et al. 1987)⁸ (Tran et al. 1999)⁹. Recently, a deposit growth initiation mechanism based on the condensation of KOH has been proposed, postulating that KOH condensing from the flue gases forms the initial molten phase, followed by a heterogeneous reaction with HCl or SO₂. This promotes the dissolution of the protective oxide and further sticking of the ash particles (Blomberg et al. 2004)¹⁰ (Blomberg 2006)¹¹.

Regardless of the mechanisms involved in the fouling and corrosion, and their relative importance in the deposit build up, it has been shown that feeding sulfur based additives in the combustion chamber reduces the fouling and corrosion rate (Henderson et al. 2006)² (Skrifvars et al. 2004)¹² (Robinson et al. 2002)¹³. Similarly, aluminium silicate or SiO₂ based additives that are reactive towards the gaseous alkali species (KCl(g), KOH(g), NaCl(g), NaOH(g)) have shown to reduce the fouling rate in the superheater area (Aho et al. 2005)¹⁴ (Tran et al. 2004)¹⁵. The lower fouling and corrosion rates in co-firing, compared to pure biomass combustion, can be explained by these mechanisms. Fossil fuels have higher sulfur content and the ashes contain alkali getter minerals thus reducing the gaseous alkali species in the flue gas further downstream in the superheater area.

The molar S/Cl ratio in the fuel mixture has been proposed as an index predicting the severity of fouling and corrosion (Bryers 1996)¹⁶. Values higher than 4 indicate no KCl formation on the superheater surfaces and thus low corrosion rate. Some other tests, however, show that S/Cl ratio of the fuel mixture is not a good indicator of the fouling tendency and the S/Cl molar ratio in the flue gases

should be used instead (Vainikka et al. 2004)¹⁷. Instead of the S/Cl ratio, the S/(K+Na) molar ratio has also been used. Here K and Na represent the available alkali in the fuel, determined by the amount of alkali soluble in water or ammonium acetate. The threshold value of this index is also 4-5 and the underlying principle of it is, that when the chloride content of the fuel is higher than the available alkali, the amount of alkali chloride in the flue gases is limited by the available alkali and not by the chloride content and thus this index should be used instead of the S/Cl ratio.

Advanced fuel analysis combined with thermodynamic equilibrium predictions of the fraction of the melt in the alkali deposit has also been used to predict the fouling tendency of the fuel. Threshold values, T₁₅ and T₇₀ have been proposed as ash particle temperature limits, between of which fouling is inevitable (Backman et al. 1987)⁸. T₁₅ means the temperature of the alkali particle in which the fraction of melt is 15 % and T₇₀ means the fraction of melt is 70 %. The underlying principle of this classification is that when the fraction of melt is under 15 %, the ash particles do not stick to the tube, and when the fraction of melt is more than 70 %, the viscosity of the particle is so low that the deposit flows freely away from the tube surface with gravitational force and thus does not promote further deposit growth. The downside of these indices is that the calculation of them requires fractionating analysis of the fuel as well as complicated Gibbs energy minimization calculations of the melting points of the alkali mixtures.

In the earlier work by the author, another fouling mechanism in biomass boilers was proposed. The importance of KCl as the initiator for deposit growth was challenged. It was postulated instead that primarily KOH condenses on the superheater tubes and acts as a 'glue' promoting further sticking of the ash particles (Blomberg et al. 2004)¹⁰ (Blomberg 2006)¹¹. Furthermore, the melting point of KOH is only 406 °C instead of the 774 °C for KCl, which could explain the formation of melt at significantly lower heat transfer surface temperatures and consequently high corrosion rates at low superheat temperatures.

THEORETICAL BASIS OF THE FREE ALKALI-INDEX

Recently published studies of the alkali release in biomass combustion have shown that in fact KCl(g) is not the major gaseous alkali compound in the flue gases. Instead, it seems that primarily all the gaseous alkali is in the form of KOH(g), at least in the gas temperature higher than 900 °C (Jiménez and Ballester 2004)¹⁸ (Jiménez and Ballester 2006)¹⁹ (Westberg et al. 2003)²⁰ (Lind et al. 2006)²¹. Potassium chloride forms either homogeneously or

heterogeneously from the reaction of KOH(g) with HCl(g) as the flue gases are cooled (Jiménez and Ballester 2005)²². In the superheater area, plenty of surface area exists to promote the heterogeneous reaction on the tube surfaces, but of course it is also possible that KCl(g) forms homogeneously first and then condenses on the tube. However in pure biomass fuels, the sulfur and chlorine contents are typically significantly lower than the alkali content, so there is likely always a surplus of KOH(g) compared to the concentrations of HCl (g) and SO₂(g).

Adding sulfur to the flue gas environment promotes the formation of K₂SO₄ from KOH(g). Potassium sulfate has a very low saturation vapor pressure and thus K₂SO₄ nucleates already at high gas temperatures (~1000 °C) getting effectively the KOH(g) before the superheater area (Jiménez and Ballester 2005)²³.

This forms the theoretical basis of the free alkali index. In the earlier work of the author, free alkali index was derived as follows (Blomberg et al. 2004)¹⁰ (Blomberg 2006)¹¹.

$$A_f = \frac{Na + K - (2 \cdot S + Cl)}{LHV} \quad (3)$$

As explained above it has now been shown that the HCl(g) is not capable of capturing KOH(g) at gas temperatures typical before the inlet of the convection superheaters (Jiménez and Ballester 2004)¹⁸ (Jiménez and Ballester 2006)¹⁹ and because KCl(g) can be considered an equivalent source of condensing alkali (Schofield 2003)²⁴, it is reasonable to modify the free alkali index slightly:

$$A_f = \frac{Na + K - 2 \cdot S}{LHV} \quad (4)$$

Further modification of the index can be suggested based on the interaction of the alkali with the other components in the fuel ash:

$$A_f = \frac{x \cdot (Na + K) - 2 \cdot S}{LHV} \quad (5)$$

For example fuels with very high silica content in the ash can effectively capture the fuel alkali and reduce the conversion of fuel alkali to vaporized alkali. On the other hand, high Ca content in the fuel will capture part of the fuel sulfur thus making it unavailable for alkali capture.

This will reduce the beneficial effect of fuel sulfur and increase the apparent conversion of fuel alkali to vaporized alkali. Therefore, with high Ca fuels this parameter can have values even higher than unity. The same would occur if Ca based additives are used in the boiler. Additionally, this parameter can be a complicated function of the oxygen content in the boiler, the temperature profile of the boiler, the gas residence time in the boiler and the goodness of mixing of the flue gases, because these will have an effect on the alkali release from the fuel and the sulfur capture by the ash or additive. Due to the complexity of determining the relative importance of these detailed effects, it is probably more useful for engineering purposes to determine this parameter with experimental fouling rate measurements.

RESULTS

Use of the index is straightforward. Only the heating value and the molar concentrations of sodium, potassium, and sulfur of the individual fuel in the fuel mixture need to be analyzed. However, one must keep in mind that calculating these concentrations backwards from the ash content and the elemental analysis of the ash is not valid. These elements are partly loosed in the sample preparation of the ashing process and also the ash content of some biomass fuels is very low. This makes the backwards calculation very inaccurate and prone to errors. Therefore the analysis should be made directly from the fuel sample.

The maximum biomass share of the fuel mixture is then optimized by selecting the biomass-fossil fuel mixture so that the free alkali index of the fuel mixture is slightly below zero. For example:

$$a \cdot A_f(1) + b \cdot A_f(2) + c \cdot A_f(3) \dots \leq 0 \quad (6)$$

Typical free alkali indices of different fuels and an example of the co-firing calculation are presented in Table 1.

Unfortunately, alkali concentrations in the fuels are rarely reported and thus experimental results for testing the correlation of the free alkali index with the fouling/corrosion tendency are scarce. The calculated fouling rate is also heavily dependent on the duration of the experiment. Typically short exposure times lead to higher fouling rates, because in the beginning of the deposit growth, the rates of condensation and sticking of the ash particles are higher. Later in the deposit formation process, the fouling rate is governed by the adhesion of the deposit towards the tube surface. Therefore, when comparing the

measured fouling rates in the boilers, values calculated from short term and long term exposure times should not be compared together. Most realistic fouling rate calculations

are expected from the long term tests with exposure times measured at least in days. Figure 1 presents the calculation applied to the experiments by Theis et al.²⁵

Table 1. An example of free alkali indices of different fuels. Fuel analyses from (Kurkela 1996)²⁶.

Name	K, ppm	Na, ppm	Cl, ppm	S, ppm	Ca, % in ash	Si, % in ash	LHV, MJ/kg	Ca/Si	X	Af, mol/GJ	Af _{max} , mol/GJ	X _{max}	Af, mol/tonne	Price, €/GJ	Price, €/tonne
Straw (wheat)	10910	230	2890	800	5.8	27.2	17.2	0.2	0.5	5.5	16.8	1.2	94.6	-0.58	-10
Forest residue	2110	110	240	400	20.0	12.0	19.7	1.7	2.0	4.7	3.0	1.4	92.5	0.51	10
Eucalyptus	890	670	940	200	n/a	n/a	18.5	n/a	2.0	4.9	2.8	1.2	91.3	0.54	10
Bark (pine)	1120	50	110	300	29.0	0.6	20.1	48.3	2.0	2.1	1.5	1.6	42.9	1.00	20
Sawdust (pine)	500	40	15	100	30.0	3.9	19.0	7.7	2.0	1.2	0.8	1.4	22.8	1.58	30
Wood chips (pine)	1060	30	75	300	n/a	n/a	18.9	n/a	2.0	2.0	1.5	1.7	38.1	1.59	30
Peat, surface	690	380	180	1000	7.2	24.5	18.5	0.3	0.5	-2.4	1.8	2.8	-45.3	2.70	50
Peat, carex	440	330	270	2000	12.3	20.1	21.0	0.6	0.5	-5.3	1.2	5.9	-112.0	2.38	50
Rhein brown coal	140	300	250	3000	32.0	6.4	24.1	5.0	2.0	-6.4	0.7	12.3	-153.9	2.07	50
lowan Rawhide coal	570	1140	25	5000	16.6	16.2	26.0	1.0	2.0	-7.1	2.5	5.9	-183.6	1.92	50
Polish bituminous coal	1420	450	760	7000	5.0	19.8	29.2	0.3	0.5	-14.0	1.9	8.8	-408.7	1.71	50
Columbian bituminous coal	2600	440	130	10000	1.3	28.0	28.4	0.0	0.5	-20.5	3.0	8.3	-581.0	1.76	50
Illinois no 6, bituminous coal	3610	1420	1210	29000	3.3	25.0	25.2	0.1	0.5	-68.7	6.1	12.7	-1732.1	1.98	50

Optimized fuel mixture

Af	Price
-0.17 mol/GJ	30.00 €/tonne
	1.50 €/GJ

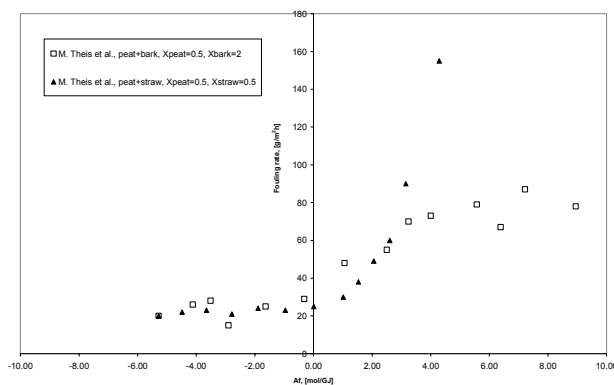


Fig. 1. The correlation of the free alkali index, $(x \cdot (K+Na) - 2 \cdot S) / LHV$, with the fouling rate in co-firing. The experiments from Theis et al. are from entrained flow reactor (EFR) tests with exposure times of 40 min.

DISCUSSION

As mentioned before, the x parameter depends both on the fuel and on the combustion device. In the EFR test runs by Theis et al. the combustion device is the same for both fuel mixtures, so from the value of the x parameter, some assumptions on the alkali capture mechanism with different fuels can be made. Values higher than unity mean that the fuel sulfur is not fully utilized in the alkali capture. Values lower than unity means that the fuel ash captures part of the alkali and thus the amount of vaporized alkali is reduced. If a similar percentage of the fuel alkali and sulfur are released in the gas phase the parameter will have a value of unity. With peat and straw this value was set to 0.5 indicating that only 50 % of the fuel bound alkali is released to the gas

phase as these fuel have a high Si/Ca ratio. With bark, it was set to 2 indicating high sulfur capture by calcium, because bark has a high Ca/Si ratio. With these x parameter values for the fuels used, a good indication of the starting point of the increase in the fouling rate is when the alkali index is higher than zero.

The weakness of the index is the prediction the conversion (x) of fuel alkali to vaporized alkali, because both the combustion conditions and ash chemistry will influence it. It would be more useful for plant operators if this parameter would be known beforehand. In the literature, 50 % or higher conversions have been determined experimentally, (Knudsen et al., Okuno et al.)^{27,28}. One possibility could be to use the Ca/Si ratio in the ash as a first approximation:

$$x_i \approx \frac{Ca_i}{Si_i} \quad (7)$$

However, this leads to excessively large x values for high Ca fuels (Table 1). Obviously the maximum x value cannot be higher than the one leading to the maximum free alkali index (=standard alkali index on molar basis):

$$A_{f_{\max}} = \frac{Na + K}{LHV} \quad (8)$$

$$x_{\max} = \frac{LHV \cdot A_{f_{\max}} - 2 \cdot S}{Na + K} \quad (9)$$

Therefore, with high Ca/Si ratio fuels the x_{\max} could be used instead of the Ca/Si ratio in the ash. Figure 2 shows the correlation using this methodology for the experiments by Theis et al.

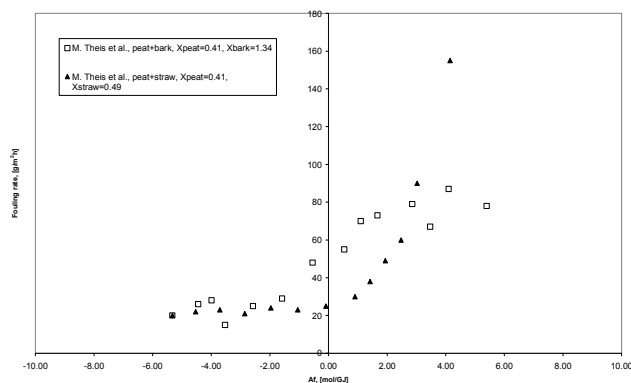


Fig. 2. The correlation of the free alkali index, $(x \cdot (K+Na) - 2 \cdot S) / LHV$, with the fouling rate in co-firing. The Ca/Si mass ratio in the ash was used as the x parameter for peat and straw and the x_{\max} was used for bark. The experiments from Theis et al. are from entrained flow reactor (EFR) tests with exposure times of 40 min.

There is still reasonable correlation with the fouling rate and with this methodology all the required parameters can be estimated beforehand.

Other mechanisms can influence the fouling rate as well, such as erosion effect of solid ash particles or difference in the ash loading on the surface. For the situations, where mechanisms other than sulfation of gaseous alkali species are the governing factors of the fouling rate, the free alkali index may fail to predict the fouling tendency, because these effects are not included in the derivation of the index.

CONCLUSIONS

Free alkali-index, a simple index calculated from the fuel chemical analysis was shown to correlate with the fouling rate of the biomass-fossil fuel mixture. This index can be used to optimize the fuel mixture in biomass co-firing. The index is based on the fouling mechanism where the amount of $(K,Na)OH(g)$ plus $(K,Na)Cl(g)$ before the superheater area is considered as the limiting factor in the growth process of the deposits. With a single adjustable parameter in the index it was possible to predict the fouling tendency of very different fuel mixtures. Further experimental work is needed to verify the usefulness of the index in co-firing

NOMENCLATURE

A_f	free alkali index, mol/MJ, mol/GJ
$A_{f\max}$	maximum free alkali index (standard alkali index on molar basis), mol/MJ, mol/GJ
Na	acetic acid soluble, or total sodium, mol/kg
K	acetic acid soluble, or total potassium, mol/kg
S	sulfur content of the fuel, mol/kg
Cl	chlorine content of the fuel, mol/kg
Si	Silicon content of the fuel ash, w-%
Ca	Calcium content of the fuel ash, w-%
LHV	lower heating value of the fuel, MJ/kg
HHV	higher heating value of the fuel, MJ/kg
X	conversion of fuel alkali to vaporized alkali before the superheater area
X_{\max}	maximum conversion of fuel alkali to vaporized alkali before the superheater area (with the assumption that all the sulfur has reacted with calcium)
a,b,c...	share of fuel 1,2,3... in the fuel mixture on energy basis

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