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Research paper

## Impacts of acidic gas components on combustion of contaminated biomass fuels

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### ABSTRACT

The formation of high concentrations of acid gases; in combustion with large variations in fuel qualities, represents a major challenge for energy production from contaminated biomass fuels. This paper provides a comprehensive evaluation of the effects of acid gas formation and retention in the combustion of recycled wood fuels. A model has been developed based on the chemical reactions involved and empirical correlations from plant monitoring and testing. The model has been used to study the behaviour of acidic gas components in critical stages of a bubbling fluidised bed boiler process. Results indicate that the variation in type of fuel contamination is the most important issue to deal with in the combustion of recycled wood fuels. Peaks in the flue gas chlorine concentrations cannot be suppressed easily by conventional flue gas cleaning measures. Upon applying ammonium sulphate dosing for the protection of chlorine induced corrosions, it is sometimes difficult to maintain the required S/Cl ratio when large variations of fuel chlorine occur. Moreover, a high level of chlorine in the fuel can also indirectly affect the emission control of sulphur dioxide because it would require an increased level of ammonium sulphate decomposition, which results in a high level of SO<sub>2</sub> in flue gas. The study also shows a beneficial effect of the recirculation of quench water from the flue gas condenser to the boiler. It offers opportunities for the optimisation of flue gas cleaning and flue gas condensation, for improving the efficiencies of water and wastewater treatment, as well as for emission reduction with a sustainable way.

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### 1. Introduction

The use of biomass as energy fuels for heat and power production has significantly increased over the past decades in the Nordic and other EU countries, due to their energy policy for supporting renewable energy production. Currently bioenergy is the largest energy source of renewable energy, which accounts for 61.2% of all renewable energy consumption in Europe. Biomass contributed to more than 32% of the national energy consumption in Sweden in 2013 [1]. It is estimated that the share of biomass in the global energy supply could range from 100 EJ y<sup>-1</sup> to 400 EJ y<sup>-1</sup> in comparison to a global primary energy consumption of 420 EJ in 2001 [2]. Wood fuels such as primary forest fuels (PFF) are major

resources for renewable energy production in the majority of EU countries [3]. It is expected that the competition for biomass fuels on the international market will be increased in the coming decade [4–6]. On the other hand, considerable amounts of used wood materials are potentially available as an energy source [7]. It is estimated that 4.3 million tonnes of waste wood was generated in UK in 2010 [8]. Recycled (waste) wood as biomass fuel has been introduced into the wood fuel market in Sweden and EU countries due to the improved recycle/separation of sources for waste-to-energy, and relatively low fuel costs [9]. It was estimated that the use of waste wood as fuel increased from 10% to 40% of the total fuel for district heating from 1980 to 2009 in Sweden [10]. Recycled wood (also called waste wood) fuels are wood that has been used for various purposes such as furniture, packaging and construction, and has finally ended up in the waste stream to be recycled as biofuels. The recycled woods have been contaminated during the usage and collection processes. The contaminations can be introduced from other materials (<1–2%) and chemicals (agents etc.

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used for wood treatment) [11]. Table 1 shows a general comparison of recycled wood chips (fuels) with clean wood chips in terms of major chemical components.

Fuel contamination is a general concern for recycled wood materials used as biomass fuels. The contamination of biomass fuels has been discussed by Edo et al. [12] for waste wood fuels, and Strömberg and Svärd [11] for other biomass fuels. The contents of different kinds of contaminations, such as surface treatment chemicals, wood preservatives and non-wood components like plastics and metals, could be up to 1–2% in chemical composition [13]. The contaminated biomass fuels are characterised with high variability and heterogeneity in chemical composition by several investigations [14–17]. In comparison to conventional wood fuels such as virgin biomass fuels, recycled wood fuels are often enriched with certain contaminants, e.g. chlorine, sulphur and nitrogen. The contamination can vary in a significant range depending on sources [11]. The common contamination sources of solid biomass fuels and original forms of main contaminants were discussed for acidic components [18,19] and heavy metals et al. [20,21].

As a consequence of fuel contamination, the formation of high concentrations of acidic gases in the combustion has the most significant influence on boiler operation, emission control and the costs of energy production. The variation of fuel quality may give remarkable negative impacts in a very short time, which may not be easily identified by common monitoring procedures. These are considered as an essential challenge for the utilisation of contaminated biomass fuels [22]. Therefore, it is necessary to have a comprehensive characterisation of the formation and retention of acidic gas components in different locations of biomass-fired utility boilers. This can provide a deep understanding of the impacts of the fuel contamination and the variation of fuel quality in specific locations and time periods.

A large percentage of chlorine contained in wastes is associated with plastics (e.g. PVC) or from salts. The majority of chlorine is quickly released in the gasification stage of biomass combustion [23,24]. The formation of HCl is dominant in oxidation conditions [25,26]. Chlorine could also form alkali chlorides like KCl, NaCl and metal chlorides such as SbCl<sub>3</sub> or SbCl<sub>5</sub>, CuCl or CuCl<sub>2</sub> [19] depending on the fuel composition and combustion conditions.

Fuel-S occurs in biomass with different forms including organic and inorganic compounds. A two-step sulphur release mechanism can be observed, in which organically associated sulphur is released

at low temperature, while inorganic sulphur retained in the ash can reach up to combustion temperatures of 900 °C [26,27]. In biomass combustion, fuel-S could form H<sub>2</sub>S with a minor amount of SO<sub>2</sub> and COS at reducing conditions, but fuel-S or sulphur components are mainly oxidised to SO<sub>2</sub> in combustion of biomass. The formation of SO<sub>3</sub> is limited by reaction kinetics at normal combustion conditions, and could be not dominated as major sulphur component in flue gas [28–30]. SO<sub>3</sub> is more activated in comparison to SO<sub>2</sub> and therefore it easily reacts with other alkaline components in boiler processes. Metal sulphides (e.g., ZnS, PbS and FeS) or sulphates could be formed under different redox and temperature conditions, which may represent small fractions of sulphur components but have an influence on deposition and furnace corrosion in biomass combustion [19].

The oxidation of fuel-N is considered as the main mechanism of NO<sub>x</sub> formation in the combustion of biomass [31]. The fuel-N mainly consists of cyclic N-compounds in biomass fuels, which may results in a similar fuel-N dependent NO<sub>x</sub> formation in biomass combustion [32]. The mechanisms of NO<sub>x</sub> formation in biomass combustion are complicated, especially for industrial scale utility facilities. Although the factors affecting NO<sub>x</sub> formation are not fully understood [33], there are some experiences on NO<sub>x</sub> emissions and reduction approaches from combustion of different types of biomass fuels in utility boilers [34].

Emissions of HCl, SO<sub>x</sub> and NO<sub>x</sub> from contaminated biomass fuels are affected by the fuel chemistry, combustion conditions (such as boiler type, combustion temperature, excess O<sub>2</sub> levels etc.), interactions with other components, and flue gas cleaning [35]. As indicated by Laryea-Goldsmith et al. [36], there are certain relationships among the acidic gas emissions, fuel mixing and interactions with other components such as ashes and sorbents for flue gas cleaning, which could be used to minimise the acidic gas emissions from combustion.

Chlorine is a well-known corrosive component that causes corrosion problems in the boilers firing biomass and waste fuels [37,38]. Chlorine induced high temperature corrosions have been observed from boiler water-walls [39,40] and superheaters [41,42]. Sulphur components like SO<sub>2</sub> and SO<sub>3</sub> have had a positive effect in the sulphation of gaseous alkali chlorides (mainly KCl) to reduce the chloride induced high temperature corrosions on the surface of heat exchangers [43]. Low temperature corrosions may also appear as in the formation of hygroscopic salts (e.g. CaCl<sub>2</sub>) and deposit on

**Table 1**  
Comparison of the chips (fuels) from recycled wood with the chips from clean wood in chemical compositions.

		The chips of recycled wood			The chips of clean wood		
		Average	Max	Min	Average	Max	Min
Moisture	% (105 °C, as received)	25.15	36.50	13.00	45.00	55.00	30.00
Ash	% (550 °C, dry basis)	4.23	10.70	1.20	2.60	4.70	1.30
C	% (dry basis)	48.78	50.1	46.30	51.00	54.10	42.80
H	% (dry basis)	5.95	6.20	5.60	6.10	6.60	5.00
O	% (dry basis)	39.37	41.40	35.20	42.40	38.40	52.10
N	% (dry basis)	1.07	1.84	0.41	0.40	0.80	0.10
S	% (dry basis)	0.05	0.09	0.02	0.04	0.05	0.01
Cl	% (dry basis)	0.13	0.70	0.03	0.02	0.04	0.01
Al	mg kg <sup>-1</sup> (dry basis)	1383	6810	381	434	1133	145
Ca	mg kg <sup>-1</sup> (dry basis)	4149	8760	2170	4654	6982	2484
Fe	mg kg <sup>-1</sup> (dry basis)	1053	4830	324	296	675	111
K	mg kg <sup>-1</sup> (dry basis)	927	1710	575	1843	3000	1158
Mg	mg kg <sup>-1</sup> (dry basis)	596	1270	289	580	720	323
Mn	mg kg <sup>-1</sup> (dry basis)	84	193	61	254	640	44
Na	mg kg <sup>-1</sup> (dry basis)	1121	3920	339	174	300	24
P	mg kg <sup>-1</sup> (dry basis)	98	215	47	461	626	178
Si	mg kg <sup>-1</sup> (dry basis)	7638	25700	1520	3093	4705	622
Ti	mg kg <sup>-1</sup> (dry basis)	1113	2580	127	21	73	10

Note: % - a mass fraction.

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