Chemical properties of solid biofuels – significance and impact

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Abstract

The chemical composition of solid biofuels (as defined in [1] and [2]) has manifold effects on their thermal utilisation. C, H and O are the main components of solid biofuels and are of special relevance for the gross calorific value, H in addition also for the net calorific value. The fuel N content is responsible for NO_x formation. NO_x emissions belong to the main environmental impact factors of solid biofuel combustion. Cl and S are responsible for deposit formation and corrosion and are therefore relevant for a high plant availability. Furthermore, Cl causes HCl as well as PCDD/F and S SO_x emissions and both elements are involved in the formation of aerosols (submicron particle emissions). The ash content influences the choice of the appropriate combustion technology and influences deposit formation, fly ash emissions and the logistics concerning ash storage and ash utilisation/disposal. Major ash forming elements (Al, Ca, Fe, K, Mg, Na, P, Si, Ti) are of relevance for the ash melting behaviour, deposit formation and corrosion. In addition, volatile elements such as Na and K are main constituents of aerosols. Volatile minor elements (As, Cd, Hg, Pb, Zn) play a major role in gaseous and especially aerosol emissions as well as in deposit formation, corrosion and ash utilisation/disposal. Either partly or non-volatile minor elements (Ba, Co, Cr, Cu, Mo, Mn, V) are of special relevance for ash utilisation. The present paper discusses the influence of chemical fuel properties on biomass combustion plants as well as possibilities and recommendations for controlling them.

1   Introduction

The whole process of thermal utilisation of solid biofuels (fuel supply, combustion system, solid and gaseous emissions) is influenced by the kind of

solid biofuel used, its physical characteristics (e.g. particle size, bulk density, moisture content, gross calorific value) and its chemical composition [3]. Two work packages of the EU project BioNorm (ENK6-CT-2001-00556) thus deal with the physical and chemical characteristics of solid biofuels. This paper focuses especially on chemical fuel properties. The work package concerned aims to develop analytical methods for the determination of (total) carbon (C) and hydrogen (H), sulphur (S), chlorine (Cl) and nitrogen (N) as well as major (Al, Ca, Fe, K, Mg, Na, P, Si, Ti) and minor elements (As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Tl, V, Zn) in solid biofuels. The present paper gives an overview of the influence and impact of these elements on combustion and points out technological and process control measures in order to deal with these fuel properties best. The fuels considered are all kinds of natural solid biofuels (as defined as biomass in [1] and as solid biofuels in [2]) and cover wood fuels, herbaceous fuels as well as other agricultural residues such as fruit stones and shells.

2 Principles of solid biofuel combustion and technologies applied

In the ideal case, combustion represents the complete oxidation of the solid organic part of the fuel into the gases CO_2 and H_2O. This conversion occurs in three steps: drying of the fuel (vaporising of water), pyrolysis/gasification (thermal degradation (devolatilisation) in the absence or presence of externally supplied oxygen (air), respectively) and the final oxidation of the charcoal and the flue gases (see Figure 1).

After drying, the main controlling parameter of the combustion process is the ratio between the amount of air added and the amount of air (oxygen) necessary for a complete combustion of the combustible parts of the fuel, the lambda (λ, excess air) factor.

At λ below 1, incomplete oxidation of the fuel (gasification) takes place and only a part of the fuel energy is converted into thermal energy. Adding too much air ($\lambda \gg 1$) will cool down the process, leading to incomplete combustion and thermal losses. Thus, the theoretical optimum of the combustion process is at lambda equal to 1. In reality however, this point is difficult to obtain due to mixing constraints between the fuel, flue gas and the air added. Thus, depending on the combustion technology utilised, a total λ between 1.1 – 1.8 in large-scale and 1.5 – 2.0 in small-scale applications is common in order to achieve complete combustion.

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A lower total λ can be achieved by separating the combustion stages into different locations in the furnace, thereby increasing the retention time for reactions and also the possibility of optimised control. This type of separation, so-called staged combustion, is shown in Figure 2 for fixed bed systems, where drying (I), pyrolysis/gasification (II) and char oxidation (III a) take place in different zones on and above the grate (primary combustion chamber). Subsequently, the flue gases are completely oxidised by addition of secondary air in the secondary combustion chamber (III b).

In order to achieve a combustion that is as efficient as possible and produces only low amounts of undesired products, each combustion step must be optimised taking into consideration the combustion technology applied and the kind of solid biofuel used.

The application of solid biofuel combustion comprises small-scale (domestic) application for domestic heating (with a nominal boiler capacity (NBC) up to around $100 \, kW_{th}$) as well as industrial application with NBC's in the MW_{th} range for district heating, process heating, electricity production as well as combined heat and power (CHP) production. The technologies used for small-scale applications include wood-stoves, fire-place inserts, heat storing stoves as well as boilers for wood logs, wood pellets and wood chips [3].

The furnaces for industrial applications are typically equipped with mechanical or pneumatic fuel-feeding systems and process control systems supporting fully automatic system operation. In general, the larger the combustion unit the more flexible it becomes in terms of the quality of the solid biofuels used. Thus, solid biofuels used in medium and large-scale biomass combustion units comprise not only wood, but also bark, energy crops, agricultural waste products and in some cases mixtures of these.

State of the art technologies applied for industrial combustion include fixed-bed (grate) furnaces, bubbling and circulating fluidised bed furnaces as well as dust burners.

The technologies applied for dust precipitation (which is the most relevant flue gas cleaning step for solid biofuel combustion) include settling chambers, cyclones/multi-cyclones, electrostatic precipitators, baghouse filters, scrubbers and panel bed filters, as well as flue gas condensation units (combination of heat recovery from the flue gas and dust precipitation).

Possible and appropriate flue gas cleaning technologies for other emissions will be discussed in more detail in the following chapters.
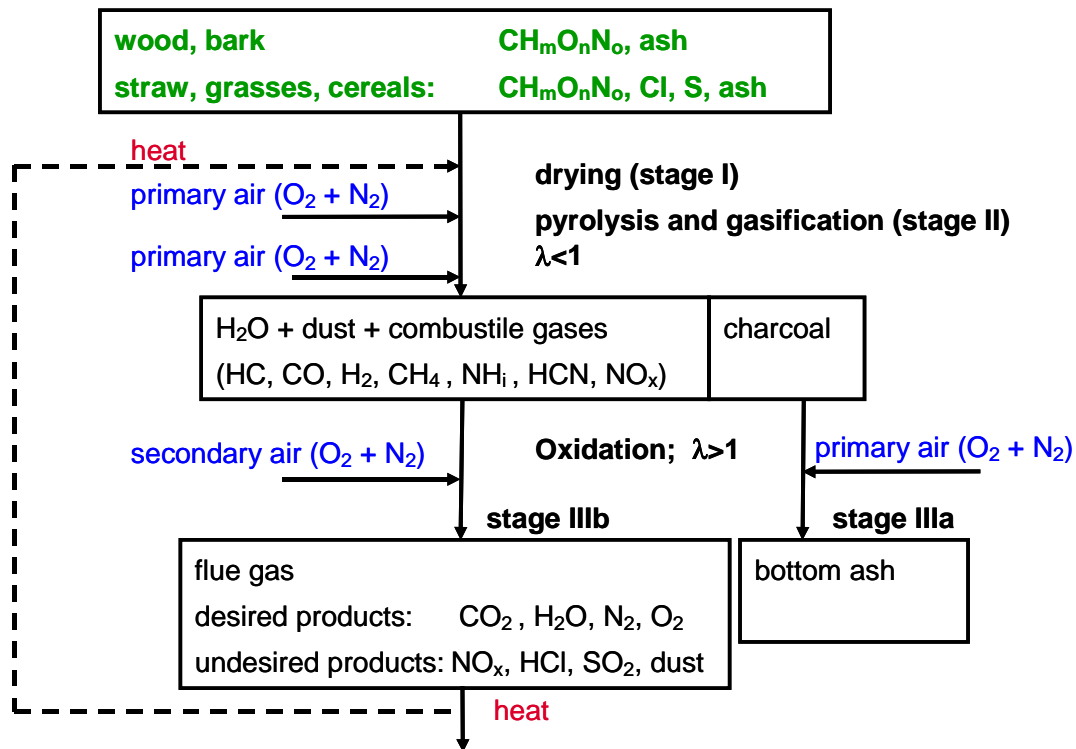
wood, bark $CH_mO_nN_o$, ash

straw, grasses, cereals: $CH_mO_nN_o$, Cl, S, ash

heat

primary air ($O_2 + N_2$)

primary air ($O_2 + N_2$)

drying (stage I)

pyrolysis and gasification (stage II)
$\lambda < 1$

H_2O + dust + combustile gases
(HC, CO, H_2, CH_4, NH_i, HCN, NO_x)

charcoal

secondary air ($O_2 + N_2$)

Oxidation; $\lambda > 1$

primary air ($O_2 + N_2$)

stage IIIb

stage IIIa

flue gas

desired products: CO_2, H_2O, N_2, O_2

undesired products: NO_x, HCl, SO_2, dust

bottom ash

heat

Figure 1:   Process of biomass combustion – principle
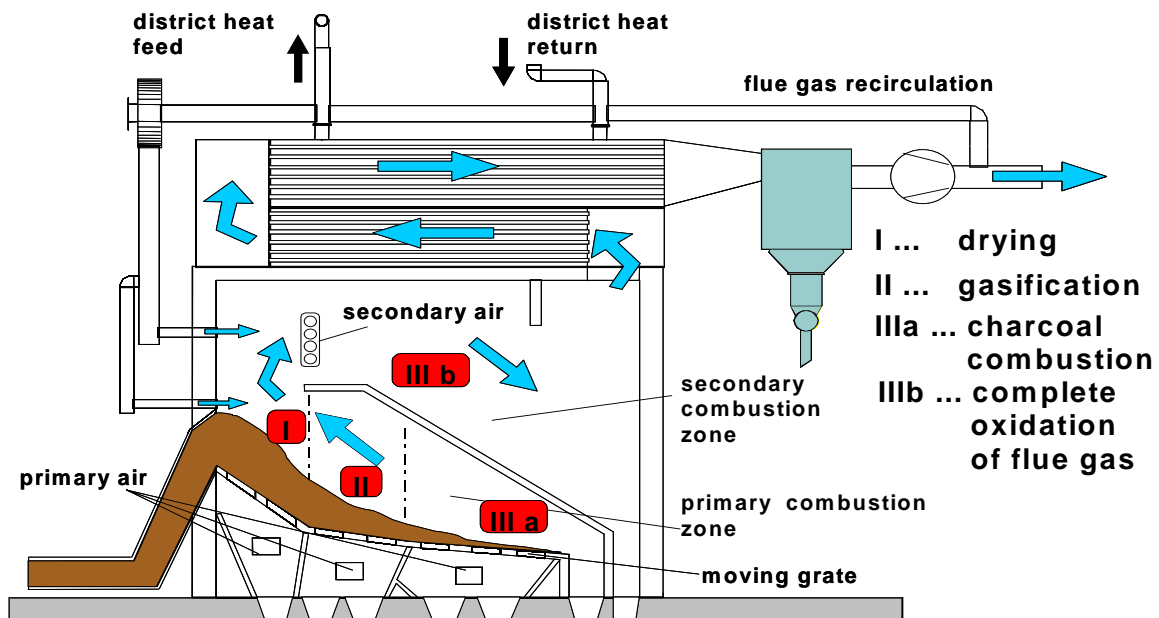
Explanations: data source [4]

Figure 2:   Process of biomass combustion –allocation of different stages of combustion in grate furnaces

Explanations: data source [4, 5]

3 Chemical composition of solid biofuels - influence on thermal utilisation

The elements are present in solid biofuels at varying concentrations depending on the origin and type of biomass. Table 1 and Table 2 contain guiding values for ash and element concentrations obtained from European research work [2]. In the following sub-chapters the influence of these elements on biomass combustion will be outlined and discussed in more detail.

3.1 Carbon (C), hydrogen (H) and oxygen (O)

C, H and O are the main components of solid biofuels (Table 1, Table 2). C and H are oxidised during combustion by exothermic reactions (formation of CO_2 and H_2O). The content of C and H contributes positively to the gross calorific value (GCV), the content of O negatively. H also influences the net calorific value (NCV) due to the formation of water. The C contents of wood fuels (including bark) are higher than those of herbaceous biofuels, which explains the slightly higher GCV of wood fuels. CO_2 is formed and emitted as a major product of complete combustion. However, CO_2 emissions from biomass combustion are regarded as being CO_2-neutral with respect to the greenhouse gas effect if a sustainable utilisation is assumed [3]. Incomplete combustion can lead to emissions of unburnt carbon based pollutants such as carbon monoxide, hydrocarbons, polycyclic aromatic hydrocarbons, tar and soot. An effective reduction of these pollutants can be achieved by an optimised combustion process, providing good mixing between fuel and air, sufficient retention time (>1.5 s) at high temperatures (>850°C) and a low total λ. In modern furnaces with effective process control systems the concentrations of unburned pollutants can be reduced to levels close to zero (e.g. CO < 50 mg/Nm³ and C_XH_Y < 5 mg/Nm³ at 11% O_2 [6].

3.2 Nitrogen (N)

According to [2], coniferous and deciduous wood has the lowest N content. Higher concentrations are found in bark, logging residues, short rotation coppice (willow and poplar) and straw from wheat, rye and barley. The concentrations are usually still higher in rape straw (wheat, rye and barley straw can also have N contents in this range), miscanthus and fruit residues (e.g. olive or grape cakes, kernels, shells). Grains and grasses usually show the highest values (Table 1, Table 2).

Table 1: Typical mean values for the chemical composition of wood fuels

Explanations: data source [2], daf…dry basis, ash free, d.b…dry basis; ash content measured according to ISO 1171 (1997) at 550°

Parameter /	Unit	Wood without bark Coniferous wood	Wood without bark Deciduous wood	Bark Coniferous wood	Bark Deciduous wood	Logging residues Coniferous wood	Logging residues Deciduous wood	Short rotation coppice Willow
Ash	w-% d.b.	0.3	0.3	4.0	5.0	2.0	1.5	2.0
C	w-% daf	51	49	54	55	52	52	49
H	w-% daf	6.3	6.2	6.1	6.1	6.1	6.1	6.2
O	w-% daf	42	44	40	40	41	41	44
N	w-% daf	0.1	0.1	0.5	0.3	0.5	0.5	0.5
S	w-% daf	0.02	0.02	0.1	0.1	0.04	0.04	0.05
Cl	w-% daf	0.01	0.01	0.02	0.02	0.01	0.01	0.03
F	w-% daf	< 0.0005	< 0.0005	0.001				0.01
Al	mg/kg d.b.	100	20	800	50			-
Ca	mg/kg d.b.	900	1,200	5,000	15,000	5,000	4,000	5,000
Fe	mg/kg d.b.	25	25	500	100			100
K	mg/kg d.b.	400	800	2,000	2,000	2,000	1,500	3,000
Mg	mg/kg d.b.	150	200	1,000	500	800	250	500
Mn	mg/kg d.b.	147	83	500	190	251	120	97
Na	mg/kg d.b.	20	50	300	100	200	100	-
P	mg/kg d.b.	60	100	400	400	500	300	800
Si	mg/kg d.b.	150	150	2,000	10,000	3,000	150	-
Ti	mg/kg d.b.	< 20	< 20					10
As	mg/kg d.b	< 0.1	< 0.1	1		0.3		< 0.1
Cd	mg/kg d.b	0.1	0.1	0.5	0.5	0.2	0.1	2
Cr	mg/kg d.b	1	1	5	5			1
Cu	mg/kg d.b	2	2	5	5			3
Hg	mg/kg d.b	0.02	0.02	0.05	< 0.05	0.03	0.02	< 0.03
Ni	mg/kg d.b	0.5	0.5	10	10			0.5
Pb	mg/kg d.b	2	2	4	5	3	5	0.1
V	mg/kg d.b	< 2	< 2	1				
Zn	mg/kg d.b	10	10	100	50			70

Table 2: Typical mean values for the chemical composition of herbaceous fuels and fuels from fruit residues

Explanations: data source [2], daf…dry basis, ash free ; d.b…dry basis; [1]…values for C, H, O, N, S, Cl, F in w-% d.b.; ash content measured according to ISO 1171 (1997) at 550°

Parameter	Unit	Straw from wheat, rye, barley	Straw from oilseed rape	Grains from wheat, rye, barley	Grains from rape	Virgin reed canary grass Summer harvest	Grass, in general	Miscanthus (China reed)	Exhausted olive cake[1]
Ash	w-% d.b	5.0	5.0	2.0	5.0	6.4	7.0	4.0	2.0 - 7.0
C	w-% daf	49	50	46	63	49	49	49	48 - 50
H	w-% daf	6.3	6.3	6.6	7.5	6.1	6.3	6.4	5.5 - 6.5
O	w-% daf	43	43	45	25	43	43	44	
N	w-% daf	0.5	0.8	2	4	1.4	1.4	0.7	0.5 - 1.5
S	w-% daf	0.1	0.3	0.1	0.1	0.2	0.2	0.2	0.07 - 0.17
Cl	w-% daf	0.4	0.5	0.1		0.6	0.8	0.2	0.08 - 0.15
F	w-% daf	0.0005					0.001	< 0.0005	
Al	mg/kg d.b.	50	50				200	-	
Ca	mg/kg d.b.	4,000	15,000	500		3,500	3,500	2,000	
Fe	mg/kg d.b.	100	100				600	100	
K	mg/kg d.b.	10,000	10,000	5,000		12,000	15,000	7,000	
Mg	mg/kg d.b.	700	700	1,500		1,300	1,700	600	
Na	mg/kg d.b.	500	500			200	1,000	-	
P	mg/kg d.b.	1,000	1,000	4,000		1,700	3,000	700	
Si	mg/kg d.b.	10,000	1,000			12,000	15,000	-	
As	mg/kg d.b.	< 0.1	< 0.1	< 0.1		0.1	0.1	0.2	
Cd	mg/kg d.b.	0.1	0.1	0.05		0.04	0.2	0.1	
Cr	mg/kg d.b.	10	10	0.5			1	1	
Cu	mg/kg d.b.	2	2	4			5	2	
Hg	mg/kg d.b.	0.02	0.02	< 0.02		0.03	< 0.02	0.03	
Ni	mg/kg d.b.	1	1	1			2	2	
Pb	mg/kg d.b.	0.5	2	0.1		1	1	2	
V	mg/kg d.b.	3					3	< 1	
Zn	mg/kg d.b.	10	10	30			25	10	

During combustion the fuel N is almost entirely converted to gaseous N_2 and nitric oxides (NO_x [NO, NO_2]).The amount of nitrous oxide (N_2O) is very low in modern solid biofuel furnaces. Only an insignificant amount of N is incorporated in the ash. Recent investigations have shown that one of the main environmental impacts of solid biofuel combustion is caused by NO_x emissions [6]. NO_x can be formed via three different reaction pathways:

Thermal NO_x is formed from the reaction of airborne N with oxygen radicals at temperatures above ~1,300°C. The amount increases with increasing temperature. Prompt NO_x is formed from airborne N at temperatures above ~1,300°C under low oxygen conditions in the presence of hydrocarbons [7, 8]. Due to the comparatively low furnace temperatures in solid biofuel combustion plants (around 800-1,200°C), thermal and prompt NO_x formation is only of minor importance. NO_x formation from the oxidation of fuel N (during a series of elementary reaction steps) is the most important mechanism in biomass combustion units [9, 10, 11, 12]. The NO_x emissions thus increase with increasing fuel N content, as shown by [13, 14, 15]. Furthermore, the air supply, the geometry of the furnace, the combustion temperature and the type of combustion technology applied are major influencing variables for NO_x formation [3].

Comprehensive investigations on the combustion behaviour of solid biofuels have resulted in guiding values and ranges for concentrations of combustion relevant elements in solid biofuels and ashes for unproblematic combustion. These values are summed up in [18], together with the parameters affected, the types of solid biofuels potentially concerned and appropriate technological countermeasures (see Table 3 and Table 5). According to this, emission related problems (exceeding of emission limits) for solid biofuels can be expected at fuel N concentrations above 0.6 w-% (d.b.). This could especially occur for straw, cereals, grasses, grains and fruit residues (see also Table 1, Table 2). The technological possibilities for NO_x emission reduction include primary and secondary measures.

Primary measures include air staging (see primary and secondary combustion zones in Figure 2) in combination with a primary λ around 0.7, temperatures between 900 – 1,100°C and a flue gas residence time of 0.5 s in the primary combustion chamber. With these measures a 30 to 50% reduction in NO_x emissions compared to conventional combustion, is possible [16] (see also Figure 3). The effect of a staged combustion can also be achieved by a staged addition of fuel. This technique shows a slightly larger reduction potential but is limited in its application to solid biofuels with lower particle sizes (e.g. sawdust, wood dust) [18]. Moreover, the furnace concept and operation is more complex due to the need for two independent fuel feeding systems. For
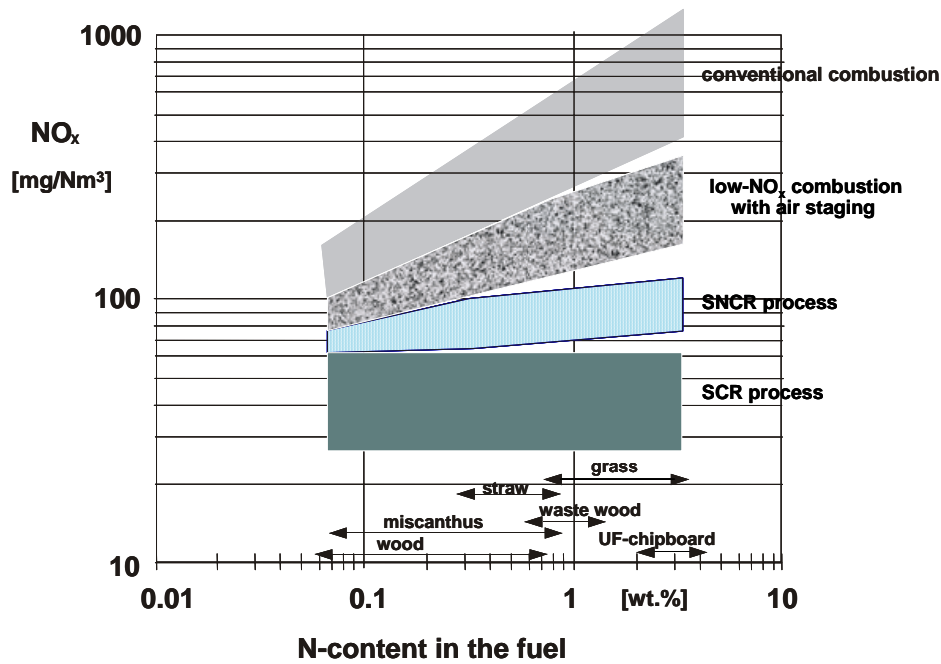
Figure 3: NO$_x$ emissions and emission reduction potentials for different solid biofuels and flue gas cleaning technologies

Explanations: data source [17]; NO$_x$ calculated as NO$_2$ and related to dry flue gas and 11 vol.% O$_2$

Table 3: Guiding values and guiding ranges for N, Cl and S in solid biofuels for unproblematic combustion

Explanations: data source [18]; d.b….dry basis; solid biofuels in brackets can exceed guiding values in special cases but usually keep them

element	guiding concentr. in the fuel w-% (d.b.)	limiting parameter	if guiding concentr. ranges are not kept problems can occur for	technological possibilities if the guiding values are not fulfilled
N	< 0.6	NO$_x$ emissions	straw, cereals, grasses, grains, fruit residues	primary measures (air staging, fuel staging) secondary measures (SNCR and SCR process)
Cl	< 0.1	corrosion	straw, cereals, grasses, fruit residues, (grains)	against corrosion: - fuel leaching - automatic heat exchanger cleaning systems - coating of boiler tubes - appropriate material selection
	< 0.1	HCl emissions	straw, cereals, grasses, fruit residues, (grains)	against HCl emissions: - dry sorption - scrubbers - fuel leaching
	< 0.3	PCDD/F emissions	straw, cereals, grasses	against PCDD/F-emissions: - sorption with activated carbon
S	< 0.1	corrosion	straw, cereals, grasses, fruit residues, (bark, grains)	see Cl
	< 0.2	SO$_x$ emissions		see HCl emissions

both types of staged combustion, accurate process control is needed to ensure an operation at the λ needed in the different zones. If primary measures are not effective enough to achieve the required limiting values, secondary measures must be applied but should always be combined with primary measures.

Secondary measures include selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR). In both techniques ammonia (NH_3) or urea ($CO(NH_2)_2$) is injected to reduce NO_x to N_2, without or with a catalyst, respectively. In the case of SNCR, the reducing agent is injected into a reduction chamber of the furnace at operating temperatures between 850 to 950°C at a stoichiometric coefficient (NH_3/NO_x [mol/mol] or $CO(NH_2)_2/NO_x$ [mol/mol]) of approx. 2.2. The residence time of the flue gas in the furnace after ammonia/urea injection should be between 0.3 to 0.5 s. On average a 60 to 70% NO_x reduction can be achieved with SNCR. When urea is used as reducing agent, an increase of CO emissions by approx. 10 to 20 ppm is to be expected. In case of the SCR, ammonia or urea is injected into the flue gas (downstream the boiler) at a stoichiometric coefficient of approx. 1.0. This technique needs a platinum, titanium or vanadium oxide based catalyst to initiate the reduction reactions. SCR works optimally at temperatures between 220 and 270°C using ammonia and 400 to 450°C using urea. An average NO_x reduction between 80 to 95% can be achieved by SCR. In comparison to SNCR the investment costs of SCR are considerably higher, whereas the operating costs concerning the reducing agent are lower. A major problem of SCR is the likelihood of catalyst deactivation by alkali metals contained in the flue gas of biomass combustion systems [18].

3.3 Chlorine (Cl)

The Cl content of wood is generally very low, while significantly higher amounts are present in herbaceous biofuels, grains and fruit residues (Table 1, Table 2).

During combustion, the Cl contained in the biofuel mainly forms gaseous HCl, Cl_2 or alkali chlorides such as KCl and NaCl. Due to the subsequent cooling of the flue gas in the boiler section of the combustion plant, a large part of the Cl condenses as salts on the heat exchanger surfaces or on fly ash particles in the flue gas. Investigations have shown that 40 to 80% of the total Cl released are integrated in the ash in the case of wood chip or bark combustion, or 80 to 85% in the case of straw or cereals (whole crop) combustion if baghouse filters are applied. The integration of Cl in the ash depends mainly on the concentration of alkali and earth-alkali metals as well as Si in the fuel, which react with Cl.

The main effect of Cl are the corrosive effect of chloride salts and HCl on metal parts in the furnace and boiler [19, 20, 21, 22, 23], HCl and particulate (KCl, $NaCl$, $ZnCl_2$, $PbCl_2$) emissions as well as the influence of HCl on the formation of PCCD (polychlorinated dibenzo-p-dioxins) and PCDF (polychlorinated dibenzofurans) [24, 25, 26, 27].

According to [18] (Table 3) Cl induced corrosion and HCl emission problems are to be expected at fuel concentrations above 0.1 w-% (d.b.) and can therefore be of relevance for straw, cereals, grasses and fruit residues (see also Table 1, Table 2). Measures against corrosion include automatic heat exchanger cleaning systems, coating of the boiler tubes, appropriate material selection as well as optimised combustion and process control technologies. Washing of the fuel in order to decrease its Cl content (leaching) is an additional measure that can also be applied to reduce HCl emissions. HCl emissions can also be reduced by scrubbing the flue gas with limestone or by dry sorption with calcium hydroxide ($Ca(OH)_2$), or, to a smaller extend by dry sorption with fly ash on baghouse filter surfaces.

PCDD/F (dioxins) can be formed in very small amounts from all solid biofuels containing Cl. In general, the PCDD/F emission levels of modern biomass combustion applications using virgin wood as fuel are well below the health risk limit. According to the guiding values specified in Table 3, emission related problems are to be expected for materials with Cl concentration above 0.3 w-% (d.b.) and can therefore be of relevance for herbaceous biofuels (see also Table 1 and Table 2). PCDD/F are formed at high oxygen concentrations on the surface of unburned fly ash particles in a temperature window between 180 to 500°C. In addition to Cl, carbon, oxygen and catalysts (Cu) are necessary for PCDD/F formation. These emissions can thus be significantly reduced by reducing the entrainment of unburned fuel particles, by ensuring a complete combustion of the flue gas and a complete burnout of the fly ash particles at low excess air ratios as well as by low heavy metal contents in the solid biofuel. Efficient fly ash precipitation at low temperatures (<200°C) is a secondary measure designed to reduce PCDD/F emissions in the flue gas, since the greater part of PCDD/F is normally bound on the surface of the fly ash particles due to their formation process [28, 29]. Further secondary measures include dry sorption with activated carbon or catalytic converters.

3.4 Sulphur (S)

Like Cl, the S contained in the solid biofuel (see Table 1 and Table 2) forms mainly gaseous SO_2 (to a certain extent also SO_3) and alkali as well as earth-alkali sulphates. Due to the subsequent cooling of the flue gas in the boiler

section of the combustion plant, SO_x forms sulphates and condenses on the heat exchanger surfaces or forms fine fly ash particles, or reacts directly with fly ash particles deposited on heat exchanger surfaces (sulphation).

Investigations have shown that 40 to 70% or 60 to 90% of the fuel S were integrated in the ash in the case of wood chip or bark combustion. In the case of (wheat) straw or cereal combustion (plants equipped with baghouse filters) only 40 to 55% were integrated in the ash. The efficiency of S fixation in the ash depends on the concentration of alkali and earth-alkali metals (especially Ca) in the fuel (fuels like wood chips and bark can contain high Ca contents and therefore cause a high S fixation) [4].

The residual S remains in the flue gas as aerosols and in gaseous form as SO_2 (in minor quantities as SO_3). Emissions of SO_2 are usually not significant for wood combustion due to the typically low concentrations of S in the fuel, and, especially in the case of wood chips and bark utilisation, because of the relatively high embedment in the ash. According to [18] (Table 3) emission related problems are to be expected at S concentrations above 0.2 w-% (d.b.). This can be of relevance for rape straw and grasses. Technological possibilities to reduce SO_x emissions are the same as already outlined for Cl emissions (see chapter 3.3).

The importance of S does not primarily result from SO_2 emissions but from its role in corrosion processes. Higher SO_2 concentrations in the flue gas cause sulphation of alkali and earth-alkali chlorides with decreasing flue gas temperature (Figure 4). This leads to the release of Cl. If these reactions take place in ash particles precipitated on the surface of heat exchanger tubes, the released Cl can cause corrosion by $FeCl_2$ or $ZnCl_2$ formation at the heat exchanger surfaces [4, 30]. Technological measures against corrosion have already been stated in chapter 3.3.

3.5 Ash content

The ash content of the fuel (see Table 1, Table 2) is essential for the choice of the appropriate combustion and gas cleaning technologies. Furthermore, fly ash formation, ash deposit formation as well as logistics concerning ash storage and ash utilisation/disposal (see also 3.6) depend on the ash content of the fuel [4]. Fuels with low ash content are therefore preferable. Wood usually contains relatively low amounts of ash, while significantly higher values are typically found in bark, straw, grasses, grains and fruit residues (Table 1, Table 2).

Grate or fluidised bed combustion are suitable technologies for ash-rich fuels. Underfeed stokers are not suitable for ash-rich fuels due to the formation of

ash layers on the surface of the fuel bed which can cause irregular breakthroughs of the gas and combustion air resulting in increased emissions [4].

The composition, density, size and amount of the fly ash emissions formed are influenced by the amount of ash forming elements in the fuel as well as by the combustion technology and process control applied. A more detailed insight into ash formation and particulate formation processes is given in chapter 3.6.

3.6 Major and minor elements

Major (Al, Ca, Fe, K, Mg, Na, P, Si, Ti) and minor (As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Tl, V, Zn) elements form, together with Cl and S, the ash components. These elements are of relevance for ash melting, deposit formation, fly ash and aerosol emissions as well as corrosion (together with S and Cl) and the utilisation/disposal of the ashes.

Typical concentrations of major and minor elements in different solid biofuels are given in Table 1 and Table 2. Table 4 shows concentration ranges for selected major and minor elements in solid biofuel ashes.

As already mentioned major and minor elements influence the ash melting behaviour. Ca and Mg usually increase the ash melting point, while K decreases it [3, 4]. Chlorides and low melting alkali- and alumosilicates may also significantly decrease the ash melting point [31]. This can cause sintering or slag formation in the combustion chamber (reduced plant availability and lifetime). In addition, melts occurring in fly ash particles may cause hard deposit formation on cooled furnace walls or heat exchanger tubes [4]. Hard deposit formation due to sticky fly ash particles can be accelerated by alkali and heavy metal salt mixtures (mixtures of alkali chlorides and sulphates with Zn and Pb chlorides) [30].

Straw, cereal, grass and grain ashes, which contain low concentrations of Ca and high concentrations of Si and K (see Table 4), start to sinter and melt at significantly lower temperatures than wood fuels. This fact must be considered when selecting the appropriate combustion and temperature control technology [3].

Together with Cl and S, K and Na play a major role in corrosion mechanisms (see chapters 3.3 and 3.4). Moreover, low melting mixtures of alkali and heavy metal chlorides can also cause corrosion by sulphation reactions.

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Table 4: Concentration ranges of combustion relevant elements in various biomass ashes

Explanations: data source [3]; d.b…dry basis

ash/element	wood chips (spruce)	bark (spruce)	straw (wheat, rye)	cereals (wheat, triticale)
	[w-% d.b.]	[w-% d.b.]	[w-% d.b.]	[w-% d.b.]
Si	4.0 - 11.0	7.0 - 17.0	16.0 - 30.0	16.0 - 26.0
Ca	26.0 - 38.0	24.0 - 36.0	4.5 - 8.0	3.0 - 7.0
Mg	2.2 - 3.6	2.4 - 5.6	1.1 - 2.7	1.2 - 2.6
K	4.9 - 6.3	3.5 - 5.0	10.0 - 16.0	11.0 - 18.0
Na	0.3 - 0.5	0.5 - 0.7	0.2 - 1.0	0.2 - 0.5
	mg/kg d.b.	mg/kg d.b	mg/kg d.b	mg/kg d.b
Zn	260 - 500	300 - 940	60 - 90	120 - 200
Cd	3.0 - 6.6	1.5 - 6.3	0.1 - 0.9	0.1 - 0.8

During combustion, a fraction of the ash-forming compounds in the fuel is volatilised (especially K, Na, S, Cl, Zn, Pb, Cd, to some degree also refractory species like Ca, Mg and Si) and released to the gas phase (see Figure 4). The volatilised fraction depends on the chemical composition of the fuel, the surrounding gas atmosphere, the local temperature and the combustion technology in use. For instance, high combustion temperatures and a reducing atmosphere enhance the volatilisation of the environmentally relevant heavy metals Zn, Pb and Cd. By subsequent nucleation or condensation, these volatiles, together with solid phase sub-micron particles released from the fuel bed, form fine fly ash particles (aerosols) with sizes between 1nm to 1μm. They mainly consist of K, Na, S and Cl. Due to the high volatility of Cd, Zn and Pb amounts of these heavy metals can also be present in the aerosol fraction depending on the heavy metal concentration in the fuel.

The non-volatile compounds remaining in the charcoal form, by coalescence or melting, ash particles with a wide range of compositions, shapes and sizes, related to the characteristics of the parent material. They consist mainly of refractory species such as Ca, Mg and Si as well as of smaller amounts of bound volatile compounds such as K, Na and Al. The major part of this ash usually remains on the grate and forms the bottom ash, while the rest gets entrained with the flue gas and forms the coarse part of fly ash with particle sizes between some μm to some 100μm. Coarse fly ash particles can cause depositions on furnace walls and heat exchanger surfaces and contribute to particulate emissions.
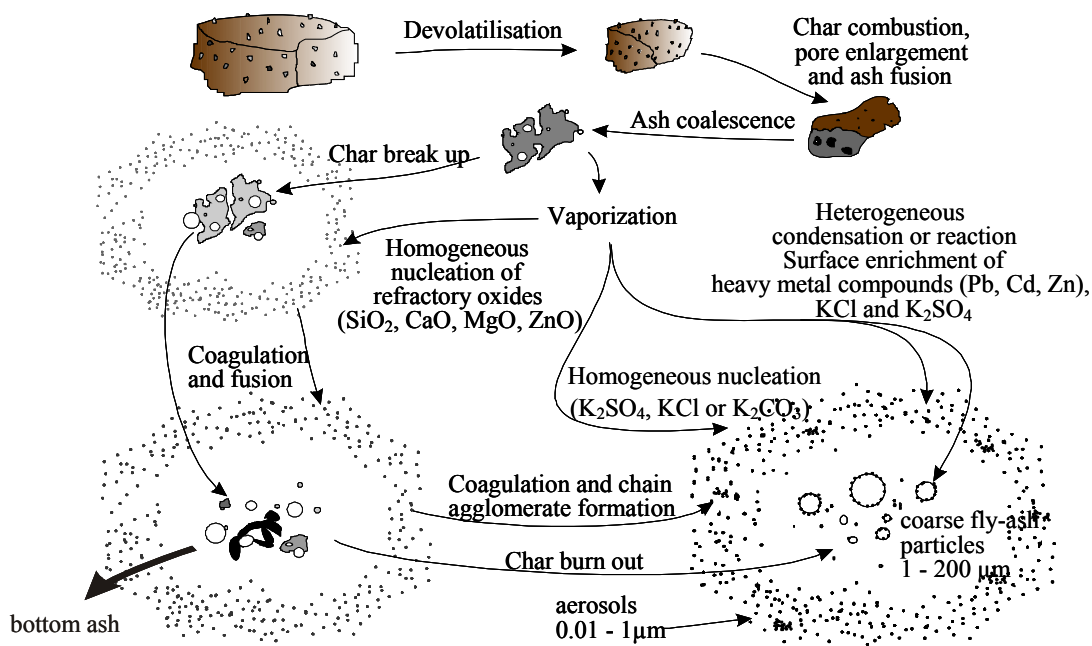
Figure 4   Mechanisms involved in ash formation during biomass combustion

Explanations: adapted from [32]

Upon cooling the flue gas in the convective heat exchanger section, vapours of volatilised compounds can condense or react on the surface of existing fly ash particles. Due to the much larger specific surface of the fine fly ash particles in comparison to the coarse fly ash particles, the concentrations of condensing or reacting ash forming elements (K, Na, S, Cl, Zn, Pb) increase with decreasing particle size. This also explains the very high heavy metal concentrations found in aerosol particles from biomass combustion plants [33, 34, 35]. Particulate emissions, together with NO_x emissions, are considered as one of the main environmental impacts from biomass combustion [6].

Efficient dust precipitation and treatment of the resulting condensates from flue gas condensation units are recommended to control particulate and heavy metal emissions [18].

Particles larger than 5 μm (coarse fly ash particles) can be precipitated by cyclone separators, while effective precipitation of particles smaller than 1 μm (aerosols) requires electrostatic precipitators or baghouse filters [36, 37]. Electrostatic precipitators and baghouse filters are cost intensive and thus economically viable only for medium and large-scale combustion units [37]. If no dust precipitation technology is applied or if the precipitation technology used is characterised by a limited efficiency, as in the case of

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small-scale solid biofuel combustion units, only fuels with low ash content and low concentrations of volatile ash forming elements (like K, Na, S, Cl, Zn and Pb) are recommended for use (such as wood pellets and wood chips).

According to Table 5, problems in respect to ash melting are to be expected at Ca concentrations below 15 w-% (d.b.) and K concentrations above 7 w-% (d.b.) in the ash and can therefore be of relevance for straw, cereals, grasses and grains. Technological countermeasures include appropriate temperature control on the grate and in the furnace as well as in the boiler section. Measures against emissions include efficient dust precipitation, appropriate fuel selection or fuel pre-treatment (e.g. fuel leaching).

Table 5: Guiding values and guiding ranges for elements in biomass ashes for unproblematic combustion

Explanations: data source [18]; guiding values for ashes related to the solid biofuels ashed according to ISO 1171 (1997) at 550°C; d.b....dry basis

element	guiding concentr. in the ash w-% (d.b.)	limiting parameter	if guiding concentr. ranges are not kept problems can occur for	technological possibilities if the guiding values are not fulfilled
Ca	15 - 35	ash melting point	straw, cereals, grasses grains	temperature control on the grate and in the furnace
K	< 7.0	ash melting point, depositions, corrosion	straw, cereals, grasses, grains	against ash melting: see Ca against corrosion: see Cl
	--	formation of aerosols	straw, cereals, grasses, grains	efficient dust precipitation, fuel leaching
Zn	< 0.08	ash recycling, ash utilisation	bark, wood chips, sawdust, grains	fractionated heavy metal separation, ash treatment
	--	formation of aerosols	bark, wood chips, sawdust; grains	efficient dust precipitation, treatment of condensates
Cd	< 0.0005	ash recycling, ash utilisation	bark, wood chips, sawdust	see Zn
	--	formation of aerosols	bark, wood chips, sawdust	see Zn

The ash from (chemically non-treated) solid biofuels should, in favour of a sustainable utilisation, be recycled to agricultural or forest soils in order to close the natural cycles of mineral nutrients. The environmental pollution of the last decades, however, has led to higher concentrations of heavy metals in solid biofuels. Of special importance in this respect are the ecologically relevant elements Cd, Zn and Pb. Problems with ash utilisation for recycling purposes are to be expected at Zn and Cd concentrations above 0.08 and 0.0005 w-% (d.b.), respectively (according to present Austrian guiding values for solid biofuel ash utilisation). This is mainly of relevance for fuels such as bark, wood chips and sawdust (ashes from grains can contain relatively high amounts of Zn). Ashes from straw, cereals (whole crop) and grasses usually contain significantly lower amounts of heavy metals (see Table 4).

For fuels where high ash concentrations of environmentally relevant heavy metals are to be expected appropriate primary and secondary measures are necessary in order to ensure an efficient and environmentally friendly ash utilisation. These include the following procedures:

The heavy metals are fractionated during combustion. This is achieved by air staging and an appropriate combustion temperature (> 800°C), which cause evaporation of volatiles including the environmentally relevant heavy metals (Zn, Cd, Pb). Only small quantities of heavy metals remain in the bottom ash, the major portion is contained in the fine fly ash. The fly ash is precipitated in a two stage process. The coarse fly ash particles are separated by a cyclone/multi-cyclone; this ash fraction can be mixed with the bottom ash ("usable ash mixture") and be used on agricultural land or in forests as secondary raw material with fertilising and liming effects. The heavy metal rich aerosols are precipitated in fine filters (filter fly ash); this fraction must be separately collected and disposed of or industrially treated.

Between 85 to 95% of the plant nutrients in solid biofuel ashes (Ca, Mg, K, P) occur in the "usable ash" mixture of bottom and cyclone fly ash. In modern biomass combustion plants it is possible to retain 30 to 60 w-% of the total Cd input and 25 to 50 w-% of the total Zn input in the filter fly ash, which, in the case of wood and bark combustion, forms only 2 to 15% of the total ash produced.

Wood ashes, in general, contain higher heavy metal concentrations than ashes from herbaceous biofuels due to the lower pH and higher heavy metal depositions as well as the higher lifetime of biomass in forests [4].

4   Summary and conclusions

The chemical properties of the different kinds of solid biofuels affect their thermal utilisation and thus the combustion and flue gas cleaning technologies needed.

Wood fuels (coniferous and deciduous wood, bark, logging residues and short rotation coppice) contain usually relatively low amounts of N, S and Cl. With the exception of bark they are also characterised by a low ash content. Their ash usually contains comparatively high concentrations of heavy metals, which is of importance in respect to the utilisation/disposal of ashes but also in respect to aerosol formation and fine particulate emissions. Straw, cereals, grasses, grains and fruit residues can contain relatively high levels of N, Cl and S, which is of special relevance in respect to NO_x, HCl, PCDD/F and SO_x emissions as well as corrosion. They are usually also characterised

by a high ash content. Therefore grate combustion should be applied for the thermal utilisation of these fuels preferably. There ashes contain comparatively low Ca but high K and Si contents and therefore start to sinter and melt at significantly lower temperatures than wood fuels.

The varying chemical properties of the different solid biofuels mentioned emphasise the necessity of reliable methods for their characterisation as well as of the standardisation of these methods and of the fuels themselves. Moreover, an appropriate fuel characterisation is of great relevance in order to be able to adapt the combustion and flue gas cleaning technology to the fuel accordingly and to be able to define and also control acceptable quality deviations for a certain solid biofuel.

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