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Review article

An overview of the behaviour of biomass during combustion: Part I. Phase-mineral transformations of organic and inorganic matter

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ABSTRACT

An extended overview of the phase-mineral transformations of organic and inorganic matter that occur during biomass combustion was conducted. Some general considerations and particularly problems associated with the composition of biomass and biomass ash (BA) and behaviour of biomass during burning were discussed initially. Then, reference peer-reviewed data plus own investigations were used to organise and describe systematically the above topics. It was demonstrated that the phase composition of BA is polycomponent, heterogeneous and variable and includes: (1) mostly inorganic matter (IM) composed of non-crystalline (amorphous) and crystalline to semi-crystalline (mineral) constituents; (2) subordinatedly organic matter (OM) consisting of char and organic minerals; and (3) some fluid matter associated with both IM and OM. Approximately 291 phases or minerals were identified in BA. These species have primary, secondary or tertiary origin in the combustion residue and they are generated from natural (authigenic and detrital) and technogenic phases or minerals originally present in biomass. Afterwards, common issues related to the composition, occurrence, transformation and origin of common constituents in biomass and BA such as: (1) OM, namely cellulose, hemicellulose, lignin, char and other organic phases plus organic minerals; and (2) IM such as silicates, oxides and hydroxides, phosphates, sulphates (plus sulphides, sulphosalts, sulphites and thiosulphates), carbonates (plus bicarbonates), chlorides (plus chlorites and chlorates), nitrates, glass, amorphous (non-glass) material and other inorganic phases; were described and compared to coal ash. As a final point, a systematization of physico-chemical transformations during biomass combustion is given. It was found that the original OM and IM in biomass during combustion transform: (1) initially to devolatilization of OM and burning of combustible gases and char with formation of intermediate and less stable oxalates, nitrates, chlorides, hydroxides, carbonates, sulphates and inorganic amorphous (non-glass) material; (2) subsequently to more stable silicates, phosphates and oxides; (3) then to melting accompanied by dissolution of the refractory minerals; with increasing combustion temperatures in the system; and (4) followed by crystallisation of melt and formation of glass accompanied by some salt condensation and hydroxylation, hydration and carbonation of newly formed phases during cooling of BA. Finally, some post-combustion transformations of the newly formed minerals and phases to stable during weathering species among silicates, hydroxides, phosphates, sulphates, carbonates, chlorides and nitrates also occur due to their hydration, hydroxylation and carbonation by moisture and CO₂ in the air through storage of BA. Certain major associations related to the occurrence, content and origin of elements and phases were identified in the BA system and they include: (1) Si–Al–Fe–Na–Ti (mostly glass, silicates and oxyhydroxides); (2) Ca–Mg–Mn (commonly carbonates, oxyhydroxides, glass, silicates and some phosphates and sulphates); and (3) K–P–S–Cl (normally phosphates, sulphates, chlorides, glass and some silicates and carbonates). These associations were applied for classification of BAs to four types and six sub-types. It was found that such systematic relationships have a key importance in both fundamental and applied aspects related to innovative and sustainable processing of biomass and BA. The ash formation mechanisms and ash fusion behaviour, as well as some indications of potential technological problems and environmental risks during combustion of biomass types and sub-types and application of their BAs will be described in Part II of the present work.

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Nomenclature

A	ash yield	MM	marine macroalgae
AFTs	ash fusion temperatures	MP	melting point
BA	biomass ash	OM	organic matter
BC	beech wood chips	PP	plum pits
CC	corn cobs	R ²	correlation coefficient
daf	dry, ash-free basis	RH	rice husks
db	dry basis	SG	switchgrass
DTA	differential-thermal analysis	SS	sunflower shells
DWR	dry water-soluble residue	TGA	thermo-gravimetric analysis
FC	fixed carbon	VM	volatile matter
FT	fluid temperature	WS	walnut shells
HTA	high-temperature ash (≥ 500 °C)	XRD	X-ray powder diffraction
IM	inorganic matter	%	weight%
LTA	low-temperature ash (100–250 °C)		

1. Introduction

It is widely accepted that biofuel combustion does not contribute to the greenhouse effect due to the CO₂ neutral conversion thanks to the renewability of biomass. The focus on bioenergy as an alternative to fossil energy has increased tremendously in recent times because of global warming problems originating mostly from fossil fuels combustion. Therefore, extensive investigations have been carried out worldwide recently to enhance biomass use instead of fossil fuels for energy conversion ([1–4] and references therein). In total about 95–97% of the world's bioenergy is currently produced by direct combustion of biomass [5–8]. As a result of that, it was estimated that approximately 480 million tonnes of biomass ash (BA) could be generated worldwide annually if the burned biomass is assumed to be 7 billion tonnes [3]. Hence, this quantity is comparable to that of coal ash, namely 780 million tonnes [9]. The perspective of increasing large-scale combustion of natural biomass and its co-combustion with semi-biomass (con-

taminated biomass such as municipal solid waste, refuse-derived fuel, sewage sludge, demolition wood and other industrial organic wastes) and solid fossil fuels (coal, peat, petroleum coke) seems to be one of the main drivers for biofuel promotion in many countries worldwide in the near future ([3] and references therein).

Numerous biomass varieties with large biological diversity and distinct source and origin can be used as solid biofuel resources (Table 1). Two fundamental aspects related to the use of biomass and BA are: (1) to extend and improve the basic knowledge on composition and properties; and (2) to apply this knowledge for their most innovative and sustainable utilisation. The systematic identification, quantification and characterization of chemical and phase composition of a given solid fuel are the initial and most important steps during the investigation and application of such fuel. This composition is a unique fundamental code that depends on various factors and determines or predicts properties, quality and application perspectives, as well as technological and environmental problems related to any fuel. There is a huge amount of

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