



Combustion properties of biomass

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Abstract

Properties of biomass relevant to combustion are briefly reviewed. The compositions of biomass among fuel types are variable, especially with respect to inorganic constituents important to the critical problems of fouling and slagging. Alkali and alkaline earth metals, in combination with other fuel elements such as silica and sulfur, and facilitated by the presence of chlorine, are responsible for many undesirable reactions in combustion furnaces and power boilers. Reductions in the concentrations of alkali metals and chlorine, created by leaching the elements from the fuel with water, yield remarkable improvements in ash fusion temperatures and confirm much of what is suggested regarding the nature of fouling by biomass fuels. Other influences of biomass composition are observed for the rates of combustion and pollutant emissions. Standardized engineering practices setting out protocols of analysis and interpretation may prove useful in reducing unfavorable impacts and industry costs, and further development is encouraged. © 1998 Elsevier Science B.V.

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1. Introduction

The conversion of solar energy by plant photosynthesis yields the food energy supporting animal life on earth. Plant matter, or biomass, has also long served as one of the primary energy forms utilized by humans for essential activities aside from nutrition. It will continue to do so, in increasingly economic important ways, into the future. The energy invested by nature in the production of photosynthates is enormous; incident on the top of the atmosphere is a continuous radiant power of over 10^{17} W. Of this, plants collect and utilize 0.02%, producing a total annual energy storage of 10^{21} J. Plant

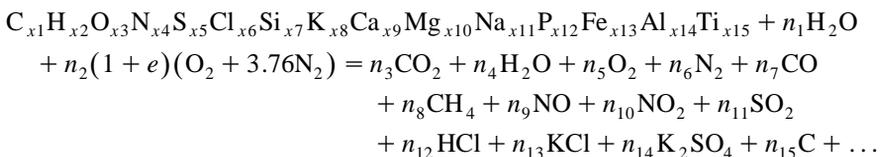
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photosynthesis also serves as the principal generator of atmospheric oxygen, critical to the respiration of plants and animals, as well as for the all important combustion reactions which drive modern human society. Prior to human industrialization, total energy in biomass was well in excess of human needs. Currently, the total is only a little better than three times the total human consumption of non-food commercial energy including all forms—fossil, nuclear, geothermal, gravitational, as well as solar. Biomass now contributes 6% of global non-food energy consumption, much of this through primitive low efficiency and highly polluting combustion in poorly controlled heating and cooking fires which support a major share of the world's population. Technical enhancements in the contribution of biomass to commercial energy needs are focused on improving both the efficiency and environmental impacts of biomass conversion. To this end, we seek a better understanding of the properties of biomass and their role in conversion. In this regard, we also seek an understanding of not only how the conversion technology can be adapted to fit the properties of the biomass fuel, but how properties of the fuel might be varied to suit the conversion technology of choice.

Plants rely on certain fundamental processes for growth and reproduction, yet have evolved to accommodate a great diversity of ecosystems and environmental conditions. Accordingly, they exhibit certain gross similarities in properties, yet with substantial specific variation. Many of these properties are critical for proper design and operation of conversion facilities, although not all properties are equally important for all conversion techniques. This paper attempts to briefly summarize some of the important properties for combustion, especially with respect to the use of biomass for electricity generation. As the biomass-fueled power generation industry has expanded in recent decades, the diversity of fuel types utilized has expanded as well, often with unanticipated and undesirable impacts on facility operation. Although the fundamental combustion behavior of biomass fuels has received increasing attention of late, there remains no comprehensive compilation of combustion properties, nor even a general recognition of the importance of certain properties for facility implementation and design. An objective of this paper is to stimulate the larger development of industry standards in the analysis, reporting, and interpretation of biomass properties.

2. Analytical methods

Combustion is a complex phenomenon involving simultaneous coupled heat and mass transfer with chemical reaction and fluid flow. Its prediction for the purposes of design and control requires knowledge of fuel properties and the manner in which these properties influence the outcome of the combustion process. A global reaction for the combustion of a biomass fuel in air might take the following form, where the first reactant compound is a biomass fuel:



		Hybrid poplar	Rice straw	Rice/Poplar
C	x_1	4.1916	3.2072	0.77
H	x_2	6.0322	5.1973	0.86
O	x_3	2.5828	2.8148	1.09
N	x_4	0.0430	0.0625	1.45
S	x_5	0.0006	0.0057	9.50
Cl	x_6	0.0003	0.0165	55.00
Si	x_7	0.0057	0.5000	87.72
K	x_8	0.0067	0.0592	8.84
Ca	x_9	0.0337	0.0141	0.42
Mg	x_{10}	0.0205	0.0135	0.66
Na	x_{11}	0.0002	0.0079	39.50
P	x_{12}	0.0012	0.0086	7.17
Fe	x_{13}	0.0007	0.0029	4.14
Al	x_{14}	0.0008	0.0073	9.13
Ti	x_{15}	0.0002	0.0004	2.00

The inclusion of 15 elements in the empirical formula for the fuel is incomplete. There are many more, some of which are important to the issue of biomass combustion. Heavy metals, for example, have a strong influence on ash disposal, but are not included in the elemental structure above. The second reactant term expresses the moisture in the fuel, which can be extremely variable, at least within limits. If too much moisture is present, the fuel will not spontaneously react. The third term represents air, although this again is a simplification, represented by the simple binary mixture of oxygen and nitrogen in the volume ratio of 21% to 79%. Air, of course, includes many more constituents, but these are not as important in a gross analysis (although it should not escape attention that the presence of certain gases at very low concentration, many contributed by biomass burning, has marked impact on the radiative properties of the atmosphere). The product side of the reaction is complex. The main products are those appearing first, but there are a host of products important to the successful operation of a commercial biomass combustion system, including criteria atmospheric pollutants such as CO, hydrocarbons (HC), oxides of nitrogen and sulfur, among others, as well as the reactions among inorganic species leading to fouling and slagging, such as the alkali chlorides, sulfates, carbonates and silicates. The detailed chemistry describing the simple global reaction above is far from understood. Making generalizations and engineering recommendations concerning the design of biomass combustion systems is made difficult by the variable composition of biomass, as indicated by the element coefficients for the wood from hybrid poplar and the herbaceous fuel, rice straw. Although there are many similarities, there are also many differences.

Biomass is similar to other fuel types in the need for standardized methods of analysis leading to accurate and consistent evaluations of fuel properties. Summarized in Table 1 are several methods frequently used to assess major properties of biomass fuels. A number of methods are also described by Milne et al. [3]. Some of these methods were developed for other fuels, such as coal, but are more generally applicable and have been found to be adequate for biomass as well. Other methods are less successful in

Table 1
Methods of biomass fuel analysis

Property	Analytical method
Heating value	ASTM ABBE
Particle size distribution	ASTM E828
Bulk density	ASTM E873
<i>Proximate composition</i>	
Moisture	ASTM E871
Ash	ASTM E830 (575°C) ASTM D1102 (600°C)
Volatiles	ASTM E872/E897
Fixed carbon	by difference
<i>Ultimate elemental</i>	
C,H	ASTM E777
N	ASTM E778
S	ASTM E775
Cl	ASTM E776
Ash elemental	ASTM D3682 ASTM D2795 various unnumbered methods ^a wet ashing preferred ASTM D4278 AOAC 14.7 microwave digest
Ash fusibility	ASTM E953/D1857 ^b Ash sinter test ^a Fuel pellet test ^c
Water soluble alkali	unnumbered method ^a
Chemical fractionation	unnumbered method ^a
Metals	ASTM E885

^aSee Ref. [1].

^bPyrometric cone test of questionable value.

^cSee Ref. [2].

their application to biomass and further development work is desirable. In particular, standard methods for evaluating the fouling and slagging behavior of biomass resulting from transformations among inorganic constituents, one of the most critical problems in biomass combustion, often fail in predicting such behavior in furnaces.

Many elementary properties of biomass have been determined for a wide range of fuel types. Summaries of various types appear in the literature (see, for example, Refs. [4–6,1,7] and references contained therein). These properties include moisture content, heating value, elemental composition, bulk density, specific gravity, thermal conductivity, and mechanical, acoustic, and electrical properties. Many such properties have only been determined for biomass in its original state at ambient temperature. The high temperature properties relevant to the modeling of biomass combustion are only partly developed. Difficulties arise in the determination of such properties because of the decomposition of the biomass under heating and reaction.

Rapid development in the biomass industry within the last decades has increased the available information substantially, and efforts continue in this area. Of recent critical concern, and serving as the focus of this discussion, are fuel composition and its effect on fouling, corrosion, and pollutant emissions, and on the prediction of the rate of reaction for scale-up and design.

3. Composition of biomass

Photosynthesis results in the production of structural and non-structural carbohydrates comprising the plant tissues. The components of biomass include cellulose, hemicelluloses, lignin, lipids, proteins, simple sugars, starches, water, HC, ash, and other compounds. The concentrations of each class of compound varies depending on species, type of plant tissue, stage of growth, and growing conditions. Cellulose is a linear polysaccharide of β -D glucopyranose units linked with (1–4) glycosidic bonds. Hemicelluloses are polysaccharides of variable composition including both five and six carbon monosaccharide units. The lignin is an irregular polymer of phenylpropane units [8–12]. Plants producing large amounts of free sugars, such as sugar cane and sweet sorghum, are attractive as feedstocks for fermentation, as are starch crops such as maize (corn) and other grains. Lignins are not yet generally considered fermentable, and thermochemical means are usually proposed for their conversion. Typically, 60–80% of the feedstock mass is ultimately fermentable. Combustion can be applied either to the direct conversion of the whole biomass, or to portions remaining following some sort of biochemical separation such as fermentation. Combustion, unlike the biochemical and some other thermochemical conversion strategies, is essentially non-selective in its use of the biomass, and intends to reduce the whole fuel to simple products. This is not to suggest that the complex structure of biomass does not have significant influences on its combustion behavior.

Due to the carbohydrate structure, biomass is highly oxygenated with respect to conventional fossil fuels including HC liquids and coals. Typically, 30 to 40 wt.% of the dry matter in biomass is oxygen. The principal constituent of biomass is carbon, making up from 30 to 60 wt.% of dry matter depending on ash content. Of the organic component, hydrogen is the third major constituent, comprising typically 5 to 6% dry matter. Nitrogen, sulfur, and chlorine can also be found in quantity, usually less than 1% dry matter but occasionally well above this. The latter are important in the formation of pollutant emissions and sulfur and chlorine in certain ash reactions leading to fouling and slagging. Nitrogen is a macronutrient for plants, and critical to their growth. Certain inorganic elements can be found in high concentration as well. In annual growth tissues, concentrations of the macronutrient potassium frequently exceed 1% dry matter. In some of the gramineae (grasses and straws), silica is the third largest component (in rice straw, silica is 10–15% of dry matter).

The compositions of selected biomass materials are listed in Table 2, including several fuel blends sampled from operating commercial biomass power plants. The compositions of some coals are included for comparison. The biomass fuels can be divided quite generally into four primary classes: (1) wood and woody materials, (2)

Table 2
Compositions, heating values, and alkali index for selected fuels [1]

	Alfalfa stems	Wheat straw	Rice hulls	Rice straw	Switch- grass	Sugar cane bagasse	Willow wood	Hybrid poplar
<i>Proximate analysis (% dry fuel)</i>								
Fixed carbon	15.81	17.71	16.22	15.86	14.34	11.95	16.07	12.49
Volatile matter	78.92	75.27	63.52	65.47	76.69	85.61	82.22	84.81
Ash	5.27	7.02	20.26	18.67	8.97	2.44	1.71	2.70
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
<i>Ultimate analysis (% dry fuel)</i>								
Carbon	47.17	44.92	38.83	38.24	46.68	48.64	49.90	50.18
Hydrogen	5.99	5.46	4.75	5.20	5.82	5.87	5.90	6.06
Oxygen (diff.)	38.19	41.77	35.47	36.26	37.38	42.82	41.80	40.43
Nitrogen	2.68	0.44	0.52	0.87	0.77	0.16	0.61	0.60
Sulfur	0.20	0.16	0.05	0.18	0.19	0.04	0.07	0.02
Chlorine	0.50	0.23	0.12	0.58	0.19	0.03	< 0.01	0.01
Ash	5.27	7.02	20.26	18.67	8.97	2.44	1.71	2.70
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
<i>Elemental composition of ash (%)</i>								
SiO ₂	5.79	55.32	91.42	74.67	65.18	46.61	2.35	5.90
Al ₂ O ₃	0.07	1.88	0.78	1.04	4.51	17.69	1.41	0.84
TiO ₂	0.02	0.08	0.02	0.09	0.24	2.63	0.05	0.30
Fe ₂ O ₃	0.30	0.73	0.14	0.85	2.03	14.14	0.73	1.40
CaO	18.32	6.14	3.21	3.01	5.60	4.47	41.20	49.92
MgO	10.38	1.06	< 0.01	1.75	3.00	3.33	2.47	18.40
Na ₂ O	1.10	1.71	0.21	0.96	0.58	0.79	0.94	0.13
K ₂ O	28.10	25.60	3.71	12.30	11.60	0.15	15.00	9.64
SO ₃	1.93	4.40	0.72	1.24	0.44	2.08	1.83	2.04
P ₂ O ₅	7.64	1.26	0.43	1.41	4.50	2.72	7.40	1.34
CO ₂ /other	14.80						18.24	8.18
Total	100.00	100.00	100.64	100.00	100.00	100.00	100.00	100.00
Undetermined	11.55	1.82	-0.64	2.68	2.32	1.39	8.38	1.91

Higher heating value (constant volume)

MJ/kg	18.67	17.94	15.84	15.09	18.06	18.99	19.59	19.02
Btu/lb	8025	7714	6811	6486	7766	8166	8424	8178

Alkali index (as oxide)

(kg alkali/GJ)	0.82	1.07	0.50	1.64	0.60	0.06	0.14	0.14
(lb alkali/MM Btu)	1.92	2.49	1.17	3.82	1.41	0.15	0.32	0.32

	Almond shells	Almond hulls	Pist. shells	Olive pitts	Demol. wood	Yard waste	Fir mill	Mixed paper	RDF
<i>Proximate analysis (% dry fuel)</i>									
Fixed carbon	20.71	20.07	16.95	16.28	12.32	13.59	17.48	7.42	0.47
Volatile matter	76.00	73.80	81.64	82.00	74.56	66.04	82.11	84.25	73.40
Ash	3.29	6.13	1.41	1.72	13.12	20.37	0.41	8.33	26.13
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
<i>Ultimate analysis (% dry fuel)</i>									
Carbon	49.30	47.53	50.20	52.80	46.30	41.54	51.23	47.99	39.70
Hydrogen	5.97	5.97	6.32	6.69	5.39	4.79	5.98	6.63	5.78
Oxygen (diff.)	40.63	39.16	41.15	38.25	34.45	31.91	42.10	36.84	27.24
Nitrogen	0.76	1.13	0.69	0.45	0.57	0.85	0.06	0.14	0.80
Sulfur	0.04	0.06	0.22	0.05	0.12	0.24	0.03	0.07	0.35
Chlorine	< 0.01	0.02	< 0.01	0.04	0.05	0.30	0.19		
Ash	3.29	6.13	1.41	1.72	13.12	20.37	0.41	8.33	26.13
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
<i>Elemental composition of ash (%)</i>									
SiO ₂	8.71	9.28	8.22	30.82	45.91	59.65	15.17	28.10	33.81
Al ₂ O ₃	2.72	2.09	2.17	8.84	15.55	3.06	3.96	52.56	12.71
TiO ₂	0.09	0.05	0.20	0.34	2.09	0.32	0.27	4.29	1.66
Fe ₂ O ₃	2.30	0.76	35.37	6.58	12.02	1.97	6.58	0.81	5.47
CaO	10.50	8.07	10.01	14.66	13.51	23.75	11.90	7.49	23.44
MgO	3.19	3.31	3.26	4.24	2.55	2.15	4.59	2.36	5.64
Na ₂ O	1.60	0.87	4.50	27.80	1.13	1.00	23.50	0.53	1.19

Elemental composition of ash (%)

SiO ₂	39.96	28.81	55.12	52.55	45.60	55.50	37.24	20.93
Al ₂ O ₃	12.03	8.47	12.49	13.15	10.75	9.37	23.73	13.78
TiO ₂	0.87	0.83	0.72	0.43	0.54	0.50	1.12	0.41
Fe ₂ O ₃	7.43	3.28	4.51	8.18	4.06	4.77	16.83	12.08
CaO	19.23	27.99	13.53	10.06	18.96	11.04	7.53	16.13
MgO	4.30	4.49	2.93	3.27	4.22	2.55	2.36	4.40
Na ₂ O	1.53	3.18	3.19	5.90	3.08	2.98	0.81	6.41
K ₂ O	5.36	8.86	4.78	5.04	6.26	6.40	1.81	0.22
SO ₃	1.74	2.00	1.92	2.10	2.06	1.80	6.67	24.27
P ₂ O ₅	1.50	2.57	0.88	1.90	1.47	1.04	0.10	0.00
CO ₂ /other	6.05	6.07						
Total	100.00	100.00	100.07	100.00	100.00	100.00	98.20	98.63
Undetermined	0.00	3.45	−0.07	−2.58	3.00	4.05	1.80	1.37

Higher heating value (constant volume)

MJ/kg	20.50	19.49	19.45	19.66	15.89	18.80	35.01	23.35
Btu/lb	8815	8379	8361	8450	6829	8083	15052	10040

Alkali index (as oxide)

(kg alkali/GJ)	0.15	0.15	0.23	0.29	0.40	0.41	0.03	0.39
(lb alkali/MM Btu)	0.34	0.36	0.53	0.66	0.93	0.95	0.08	0.90

^aLow volatile bituminous.

^bSee Ref. [13].

herbaceous and other annual growth materials such as straws, grasses, leaves, (3) agricultural by-products and residues including shells, hulls, pits, and animal manures and (4) refuse-derived fuels (RDF) and waste or non-recyclable papers, often mixed with plastics. The latter class is often excluded from the category of biomass, but the origin, with the exception of mixed plastics, is appropriate for inclusion as a biomass type. A fifth class, that of energetic materials including decommissioned rocket fuels, is emerging as part of the fuel mix for biomass facilities. The properties of these materials can be substantially different than those for conventional biomass materials. The distinctions among the first three classes—woods, herbaceous materials, and by-products—are largely based on the structural compositions for hemicellulose, cellulose, and lignin, and on the concentration and composition of inorganic materials.

The molar ratios of oxygen and hydrogen to carbon for a wide range of biomass fuels are shown in Fig. 1. The amount of variation is not particularly large considering the range of different materials examined. Biomass is compared with other fuels in the so-called coalification diagram [14] of Fig. 2. Illustrated in the figure are approximate boundaries between different classes of solid fuels. This type of diagram can be used to infer the chemical structure and some combustion and inorganic aspects of the fuels [7]. Inorganic material in biomass can be divided into two fractions, one of which is inherent in the fuel and the other of which is added to the fuel through processing steps. The latter, adventitious material such as dirt, often makes up a major fraction of the ash content of wood fuels used in power plants and originates from skidding and other operations whereby soil is incorporated into the fuel. Its composition is typically different from that of the inherent materials, as is the mode of occurrence of the elements (e.g., crystalline silicates and aluminum arising from the incorporation of

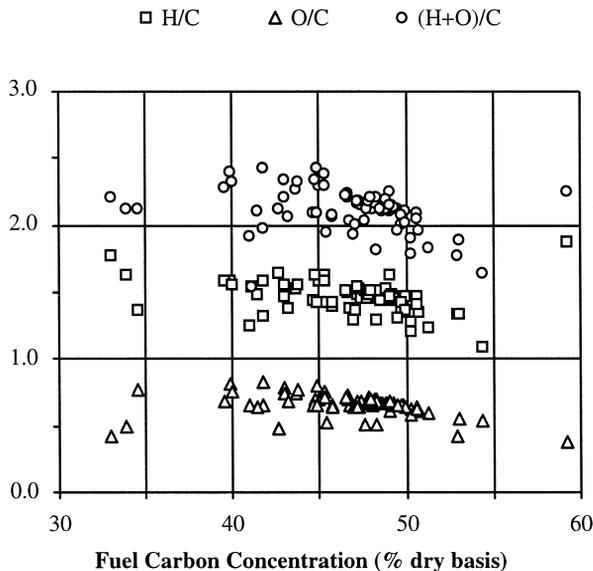


Fig. 1. Molar ratios of hydrogen and oxygen to carbon in biomass [5].

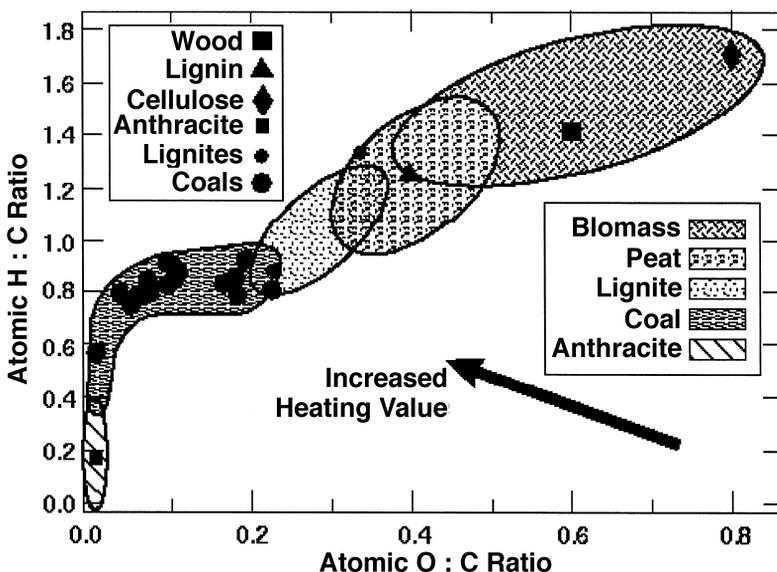


Fig. 2. Coalification diagram showing compositional differences among coals and biomass [14].

sands, clays and other soil particles, and potassium incorporated in feldspars with relatively little contribution to alkali reactions leading to fouling other than by inertial impaction and sticking of particles).

The inherent inorganic matter is more intimately distributed throughout the fuel, and is sometimes referred to as atomically dispersed material. Elements including Si, K, Na, S, Cl, P, Ca, Mg, Fe are involved in reactions leading to ash fouling and slagging, and the principal mechanisms describing these phenomena in biomass combustors are now reasonably well understood [14,15,1,7,16]. Descriptions of the detailed chemistry and means to control or mitigate these processes other than by fuel selection are, however, far from realization. More recent demonstrations of the impacts of removing certain elements from biomass on the fouling and slagging behavior [17,2] confirm much of what is perceived about the mechanisms involved.

The release of atomically dispersed inorganic material from a fuel particle is influenced both by its inherent volatility and the reactions of the organic portions of the fuel. Material that is inherently volatile at combustion temperatures includes derivatives of some of the alkali and alkaline earth metals, most notably potassium and sodium. Other, non-volatile material can be released by convective transport during rapid pyrolysis. The amount of fuel lost during the pyrolysis stage of combustion increases with increasing hydrogen to carbon ratio and, to a lesser extent, with increasing oxygen to carbon ratio. Whereas anthracite coals typically lose less than 10% of their mass by pyrolysis, and bituminous coals lose between 5 and 65% of their mass, lignites, peats, and biomass can lose over 90% of their mass in this first stage of combustion. Typically, the volatile loss during early pyrolysis of biomass is about 75%. The combination of high oxygen content and high organic volatile matter in biomass indicates a potential for

creating large amounts of inorganic vapors during combustion. Alkali elements are also directly vaporized at normal furnace operating temperatures, as evidenced by differences between standard ash content determinations conducted at 575°C (as recommended for RDF) and at 750°C (the standard temperature for coal). Upon heating, ash from wheat straw has been observed to lose up to 40% weight between 575°C and 1000°C [2].

Herbaceous fuels contain silicon and potassium as their principal ash-forming constituents. They are also commonly high in chlorine relative to other biomass fuels. These properties portend potentially severe ash deposition problems at high or moderate combustion temperatures. The primary sources of these problems are (1) the reaction of alkali with silica to form alkali silicates that melt or soften at low temperatures (can be lower than 700°C, depending on composition), and (2) the reaction of alkali with sulfur to form alkali sulfates on combustor heat transfer surfaces. Alkali material plays a central role in both processes. Potassium is the dominant source of alkali in most biomass fuels. Differences among fuel types are displayed in Fig. 3, which plots percent K_2O in ash against the fuel ash content. The hyperbolic lines plotted in the figure are lines of constant K_2O in the fuel. Wood fuels tend to reside in the region below 0.5% K_2O in the fuel, whereas straws and grasses reside in the region between 1 and 3%. The scatter suggests that as the ash content increases for woods, the fraction of potassium in the ash decreases, consistent with soil derived matter accounting for the increasing ash. For straws, an increasing potassium concentration in the fuel tends to accompany an

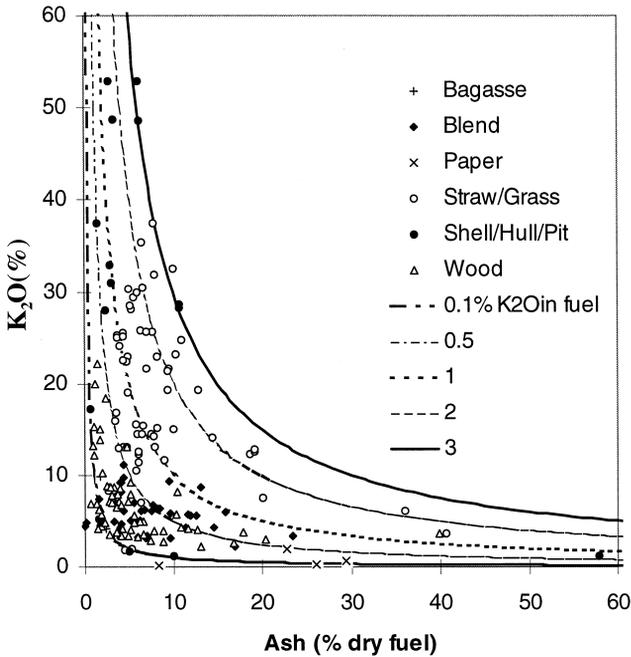


Fig. 3. Potassium oxide concentrations in relation to the ash content of biomass. The curves are isopleths of concentration for potassium oxide in the fuel.

increasing ash content, indicating an inherent source of potassium. Sugar cane bagasse is substantially depleted in potassium relative to the parent material due to washing of the cane during processing. Similar results have been obtained for wet extraction of straws [2]. Non-biologically derived alkali is present as soil contaminants and additives to the fuels, such as clay fillers used in paper production. This non-biogenic alkali exhibits far lower mobility during combustion than the biological fraction as determined by chemical fractionation analyses. As a result, some traditional indicators of deposit behavior, most notably ash fusion temperatures, poorly predict ash behavior.

Many of the agricultural by-products also contain high potassium concentrations (see Fig. 3, Table 2) with equally high potassium mobility. Some woods, on the other hand, contain far less ash overall, differing by as much as a factor of 40 from high-ash straws, for example. In addition, the ash-forming constituents contain greater amounts of calcium with less silicon. Although the total amount of potassium in wood is typically much lower than in straws, the fraction in the ash may be higher. Calcium reacts with sulfur to form sulfates in ways somewhat analogous to potassium, but the mobility of calcium and the properties of the deposits it forms are both more favorable to sustained

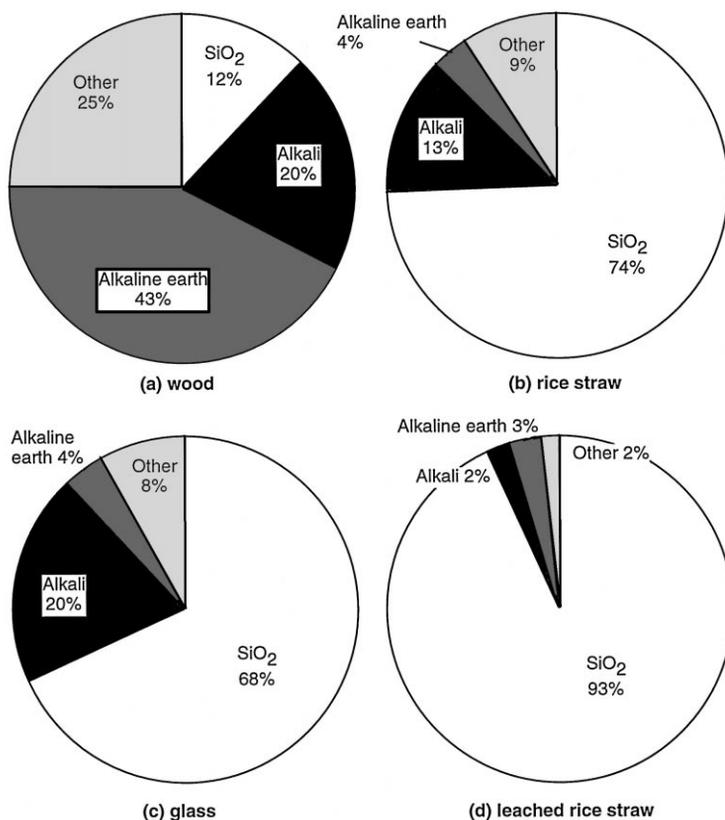


Fig. 4. Inorganic compositions for (a) Douglas fir wood (California), (b) rice straw (variety M202, California), (c) ordinary soda-lime glass, (d) water leached rice straw (same original straw as in (b)).

furnace operation than the ashes formed from straws and grasses. The composition of rice straw ash is compared against that of Douglas fir wood in Fig. 4. The composition of the straw ash is remarkably similar to that of an ordinary glass (also shown in Fig. 4), helping to explain the rapid sintering, slagging, and fouling observed when burning straws in most power boilers designed for wood.

Chlorine is a major factor in ash formation. Chlorine facilitates the mobility of many inorganic compounds, in particular potassium. Potassium chloride is among the most stable high-temperature, gas-phase, alkali-containing species. Chlorine concentration often dictates the amount of alkali vaporized during combustion as strongly as does the alkali concentration. In most cases, the chlorine appears to play a shuttle role, facilitating the transport of alkali from the fuel to surfaces, where the alkali often forms sulfates. In the absence of chlorine, alkali hydroxides are the major stable gas-phase species in moist, oxidizing environments, i.e., combustion gases [7].

The compositions of biomass are complex, involving six major elements in the organic phase and at least 10 other elements, not including heavy metals, in the inorganic phase important to ash characterization. Some of the trends described above can be more formally elucidated through the application of multivariate statistical techniques. Figs. 5–7 give results of PCA using 177 separate observations of complete ultimate elemental analyses (C, H, N, S, Cl, O, and Ash as % dry fuel) and 230 complete observations of 10 ash elements (Si, Al, Ti, Fe, Ca, Mg, Na, K, S, P) as oxides (note sulfur accounted for as the element in the ultimate analysis and as sulfate in the ash analysis). The chemical analyses were conducted using consistent methods and most

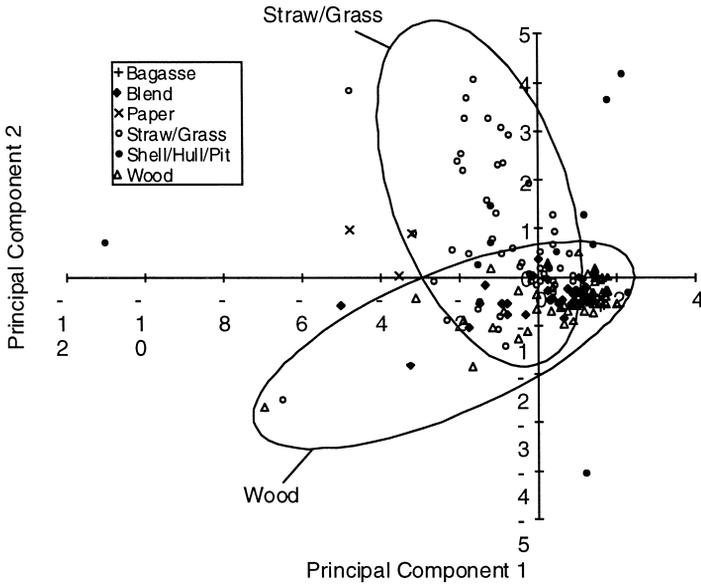


Fig. 5. Component plot for principal components 1 and 2 from a principal components analysis (PCA) on the ultimate elemental composition of biomass. P1 is largely associated with the major organic elements (C, H, O) of the fuel and P2 with N, S, and Cl.

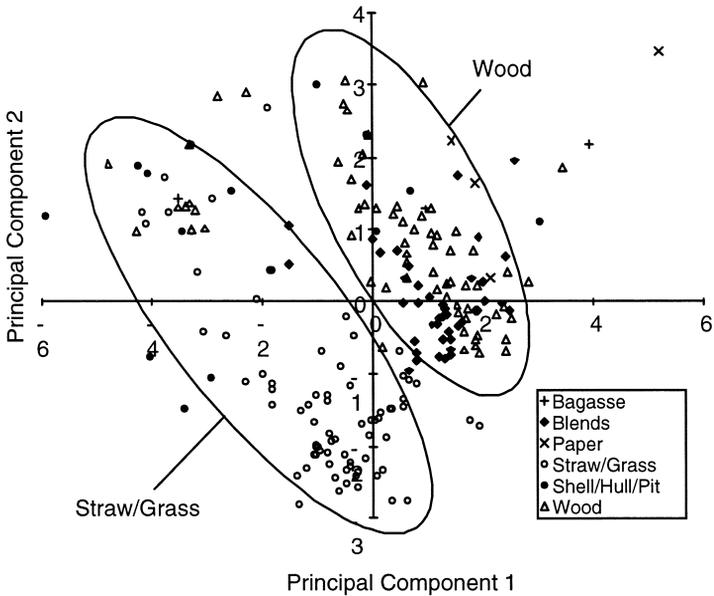


Fig. 6. Component plot for principal components 1 and 2 from a PCA on the elemental ash composition of biomass. P1 is largely associated with the elements Si, Al, Ti, and Fe, P2 with the alkaline earth metals Ca and Mg.

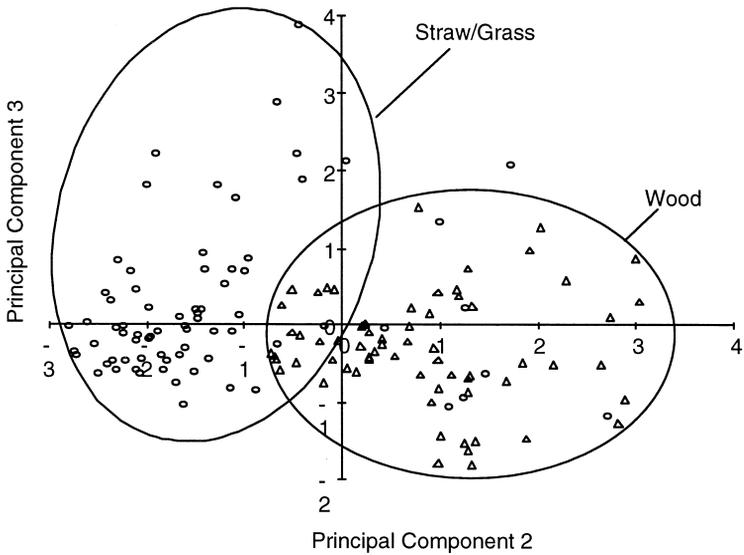


Fig. 7. Component plot for principal components 2 and 3 from a PCA on the elemental composition of biomass. P2 is largely associated with the alkaline earth metals Ca and Mg (same P2 as in Fig. 6), P3 with the elements Na and S. P2 is also negatively correlated with Si.

were completed by a single laboratory as part of an alkali deposits investigation for biomass fuels [1]. The majority of the analyses are for straws, grasses, and woods, many of the latter as urban wood fuels and blends obtained from operating power plants. Other classes are represented as indicated in figures. Differences between the two main classes have been highlighted in the figures. Fig. 5 is a plot of the first principal component (P1) against the second principal component (P2). Together, these two components account for 67% of the total variance in the data. P1 has a strong positive correlation to the organic elements C, H, and O, with a strongly negative correlation to ash concentration (as is to be expected—as ash content increases, the organic fraction must decline). P2 shows a strongly positive correlation to N, S, and Cl. For straws, as P1 decreases, P2 increases, indicating that as ash content increases, the concentrations of N, S, and Cl also increase, consistent with a predominantly inherent ash. The trend is reversed for woods, consistent with an ash of increasing adventitious origin (i.e., greater levels of dirt).

For the ash PCA, the first three components, P1, P2, and P3, account for 68% of variance. In this case, P1 has a strong positive correlation to the concentrations of Si, Al, Ti, and Fe, suggesting it represents ash of soil origin. P2 has a strong negative correlation to Si (which immediately implies that as P1 increases, P2 should decrease), but a strong positive correlation to the alkaline earths, Ca and Mg. P3 is strongly correlated with Na and S concentrations. Again, distinct differences appear between woods and straws/grasses. Fig. 6 gives results for P1 against P2. Here, as P1 increases, P2 decreases, indicating that as Si, Al, Ti, and Fe increase in concentration, they dilute the concentrations of Ca and Mg. This is again consistent with an adventitious origin for increasing levels of ash. The straws and grasses exhibit a similar trend in slope, but are shifted in the component space, suggesting less adventitious material. The trend is towards diminished amounts of alkaline earths with increasing silica concentrations. In Fig. 7, P3 is plotted against P2. The woods show relatively little sensitivity in response to increasing alkaline earth concentrations (and decreasing soil borne ash) for Na and S concentrations. The straws and grasses, again shifted in component space towards lower levels of alkaline earths and higher silica concentrations compared to woods, tend to add more sodium and sulfur along with the alkaline earths. The trends observed in these data are not necessarily general, as the nature of the sample set bears substantial influence on the results.

The fate of certain inorganic constituents in a combustion system can be traced through an analysis of fuel, ash, and deposits. Fig. 8 displays the normalized compositions for some fuels, slags, and deposit samples acquired from operating commercial biomass power plants. Full compositions are listed by Miles et al. [1]. Two main trends are apparent. For the grate furnaces and the bubbling fluidized bed combustor (FBC), superheater deposits were enriched in alkali relative to the fuel. For the circulating fluidized bed combustors (CFB) examined, the deposits were enriched in both alkali and alkaline earth metals. All deposits were also enriched (not shown) in sulfur, especially for the units firing wood fuels, and chlorine (for European units firing straw). To some extent, the enrichment in calcium in the deposits from the CFB units is due to the addition of limestone (CaCO_3) to help control bed agglomeration and to control sulfur emissions.

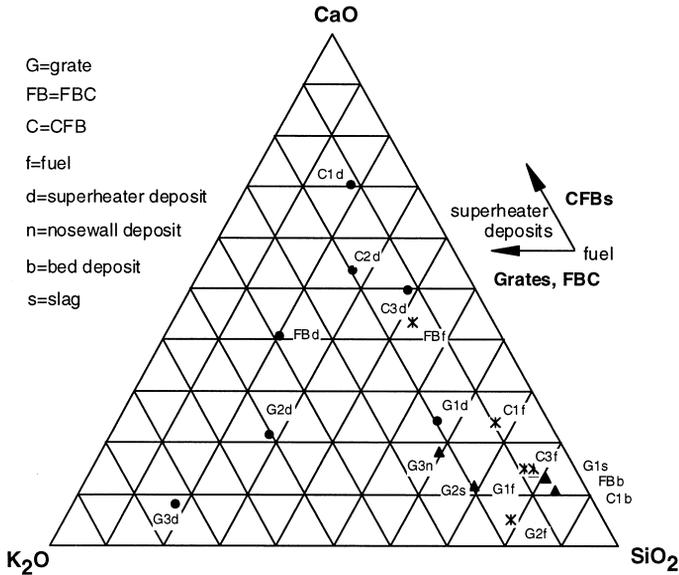


Fig. 8. Normalized compositions of fuels and various deposits and slags from commercial biomass power plants in the three component oxide system Si–K–Ca. Each corner of the diagram represents a composition consisting entirely of the compound shown at that corner. Intermediate values are mass concentrations of the oxides. The grid spacing is 10%. The first letter of the designation refers to the type of combustion unit, the number following refers to individual units. The lower case letter refers to the type of material as shown in the legend.

A number of indices have been developed for coal and other fuels relating composition to fouling and slagging behavior. These have proved for the most part to be of limited value as predictors for biomass. One simple index, the alkali index, has become popular in recent years as a threshold indicator for fouling and slagging, although all biomass fuels exhibit fouling behavior, but at different rates depending on composition and ash content (woods tend not to foul at as high a rate as straws because at the same fuel firing rate, there is less ash entering the combustor in the same time, and because woods have more favorable ash compositions). The alkali index expresses the quantity of alkali oxide in the fuel per unit of fuel energy (kg alkali GJ^{-1} or $\text{lb alkali MMBtu}^{-1}$). It is computed as:

$$(1/Q)Y_f^a(Y_{K_2O}^a + Y_{Na_2O}^a) \tag{1}$$

in which Q is the heating value (either GJ kg^{-1} or MMBtu lb^{-1} as appropriate) of the fuel (the value obtained from a bomb calorimeter, the higher heating value at constant volume, dry basis, is commonly used), Y_f^a is the mass fraction (dimensionless) of ash in the fuel, $Y_{K_2O}^a$ and $Y_{Na_2O}^a$ are the mass fractions (dimensionless) of K_2O and Na_2O in the ash. Miles et al. [1] have suggested that above $0.17 \text{ kg alkali GJ}^{-1}$ ($0.4 \text{ lb alkali MMBtu}^{-1}$) fouling is probable, and above 0.34 kg GJ^{-1} ($0.8 \text{ lb MMBtu}^{-1}$), fouling is virtually certain to occur. The threshold levels are determined principally on the basis of experience. Fig. 9 gives the alkali index (kg GJ^{-1}) in rank order for selected biomass

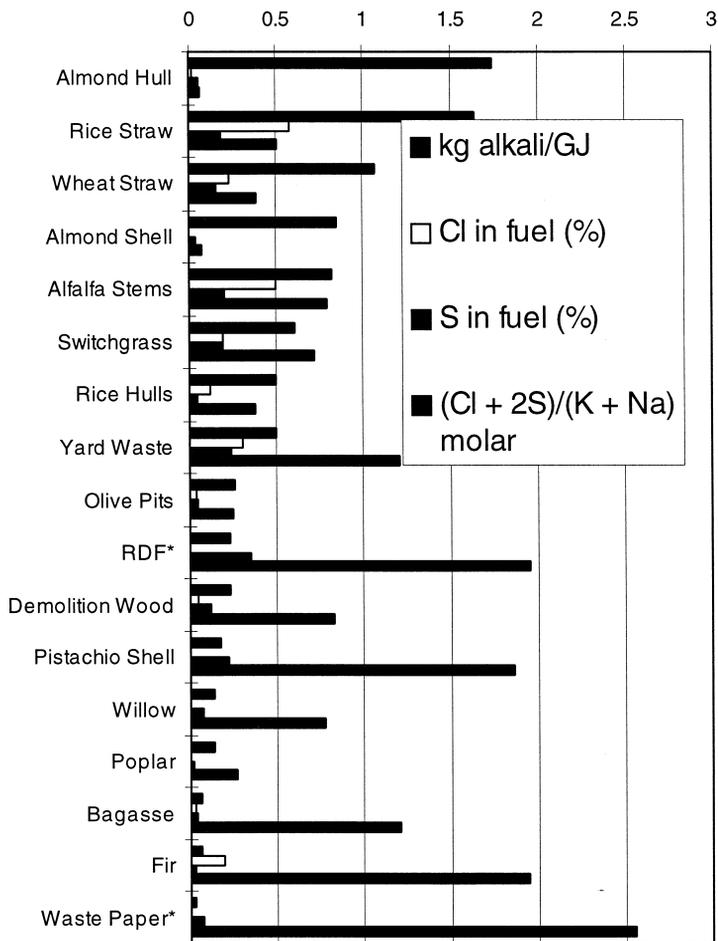


Fig. 9. Alkali index, chlorine and sulfur concentrations, and chloride–sulfate ratios for biomass.

fuels (see also Table 1). The alkali index is incomplete as a descriptor of fouling behavior, however, and is useful principally as a general guide. Also shown in Fig. 9 are the Cl and S concentrations in the fuel, as well as an indicator expressing the stoichiometric ratios of Cl and S to K and Na in the fuel. This latter value represents a theoretical potential fraction of alkali that could be reacted as chloride and sulfate by Cl and S originating with the fuel (note that 2 mol of alkali metal are required for each mole of sulfur in the formation of the sulfate). A value of 1 indicates that there is sufficient Cl and S in the fuel to completely react the alkali, although this is not likely to occur due to the complexity of the combustion reactions and variable mineral state of the elements. Values in excess of unity are not meaningful, and serve only to indicate that potentially more than enough Cl and S are present to completely react the alkali. Values less than unity express an excess of alkali. Low alkali fuels tend to have high

chloride and sulfate ratios, whereas high alkali fuels exhibit lower ratios, with Cl and S concentrations limiting. The straws and grasses have relatively high alkali indexes as well as higher chloride and sulfate ratios, consistent with the higher rates of fouling and slagging observed for these fuels. Both almond hull and almond shell are regarded as high fouling fuels. Although they contain large quantities of alkali, they have lower chlorine and sulfur concentrations compared with many other fuels. Almond hulls and shells are also known to contribute to rapid corrosion of boiler surfaces, but the role of Cl and S in corrosion for these fuels has not been detailed.

The base-to-acid ratio has often been used as a measure of the fouling tendency of a fuel ash, although its interpretation for biomass appears to be different from that for coal [18]. This ratio takes the form:

$$R_{b/a} = (\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O}) / (\text{SiO}_2 + \text{TiO}_2 + \text{Al}_2\text{O}_3) \quad (2)$$

where the label for each compound makes reference to its weight concentration in the ash. The melting temperature of ash tends to be parabolic with respect to $R_{b/a}$, reaching a minimum at intermediate values. For coal, a minimum is frequently located in the vicinity of $R_{b/a} = 0.75$, but for biomass the minimum tends to appear at lower values. There are many similar empirical indices of ash behavior (see, for example, Ref. [19]). No single index has so far been developed that reliably describes the behavior of the ash under all combustion conditions. A good knowledge of the combustion conditions as well as the fuel and ash compositions is needed for any prediction of the fouling characteristics of a biomass fuel.

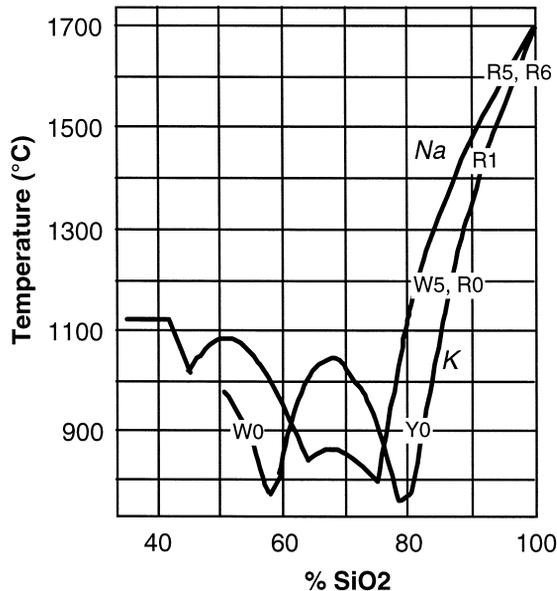


Fig. 10. Binary phase diagram for the alkali oxides Na_2O and K_2O with silica (SiO_2). Also shown are the locations for the normalized compositions (including only alkali and silica) for three cereal straws: R is rice straw, W is a high alkaline wheat straw, Y is a low alkaline wheat straw. Numbers following letter designations refer to treatments: 0 is untreated, 5 is laboratory water leached straw, 6 is rain washed straw [2].

Although the detailed chemistry of ash slagging and fouling is not yet fully developed, removal of alkali and other elements is known to increase the fusion temperature of the ash. Sugar cane bagasse is an example. In recent experiments, the leaching of alkali metals plus chlorine by simple water washing has shown dramatic improvements in the fusion temperatures for straw ash [2]. This technique removes 80% or more of the alkali, and better than 90% of the chlorine, an advantage in terms of reducing corrosion and acid gas emissions as well as reducing the chlorine facilitation in ash deposition. These rates exceed, in some cases, those measured by chemical fractionation (Table 1), which suggests further development is needed in the standard methods for evaluating such properties.

The impact of leaching is illustrated in Fig. 10 by means of a binary alkali–silica phase diagram giving the liquidus temperatures for sodium-silicate and potassium-silicate from 40 to 100% silica concentration. The points indicated on the graph represent treatments of three different straw materials: rice straw (R), a high alkaline wheat straw (W), and a low alkaline wheat straw (Y). The number following the letter is the treatment: 0 is untreated (as received from the field), 5 is laboratory washed, and 6 is rain washed. Washing has in all cases increased the melting temperature of the ash. The potential for decreasing the fusion temperature also exists. The fusion temperature for the high alkaline wheat straw (W0) can decrease if insufficient leaching occurs to shift the composition above about 85% silica. The increase in fusion temperature is very steep above 80% silica, indicating the substantial improvements available with even minor amounts of leaching. There are other impacts of leaching on the combustion behavior, as noted below.

4. The energy value of biomass

The standard measure of the energy content of a fuel is its heating value, sometimes called the calorific value or heat of combustion. In fact, there are multiple values for the heating value, depending on whether it measures the enthalpy of combustion, the internal energy of combustion, and whether, for a fuel containing hydrogen, product water is accounted for in the vapor phase or the condensed (liquid) phase. The enthalpy of combustion is determined at constant pressure, and so includes flow work. With water in the vapor phase, the lower heating value at constant pressure measures the enthalpy change due to combustion. The higher heating value at constant pressure measures the enthalpy change of combustion with water condensed. If the combustion is carried out at constant volume, the internal energy change due to combustion with water in the condensed state is the higher heating value at constant volume (the standard value measured with a bomb calorimeter), while the lower heating value at constant volume measures the internal energy change with product water in the vapor phase. In addition, moisture in the fuel reduces the heating value compared to a dry weight determination. Determinations of thermal efficiency are often difficult to interpret because the basis for the heating value determination is not reported. Thermal efficiencies must be reduced to the same basis for direct comparison.

Fuel moisture is a limiting factor in biomass combustion due to its effect on heating value. The combustion reaction is exothermic, the evaporation of water strongly

endothermic. The autothermal limit (self-supporting combustion) for most biomass fuels is around 65% moisture content wet basis (mass of water per mass of moist fuel). Above this point, insufficient energy is liberated by combustion to satisfy evaporation and product heating. Practically, most combustors require a supplemental fuel, such as natural gas, when burning biomass in excess of 50 to 55% moisture wet basis, and CO and other products of incomplete combustion may be emitted in greater quantities depending on combustor design.

There have been many attempts at correlating the heating value with the composition. Formulas developed for coal, such as the Dulong equation, typically do not do well at predicting for biomass. Some rough approximations can be made on single component analyses. The heating value of biomass can be partially correlated with ash concentration, for example. Woods with less than 1% ash typically have heating values near 20 MJ kg^{-1} (8600 Btu lb^{-1}). Each 1% increase in ash translates roughly into a decrease of 0.2 MJ kg^{-1} [4], because the ash does not contribute substantially to the overall heat released by combustion, although elements in the ash may be catalytic to the thermal decomposition (see later under kinetics).

Heating values can also be correlated with carbon concentration, with each 1% increase in carbon elevating the heating value by approximately 0.39 MJ kg^{-1} [4], a result identical to that found by Shafizadeh [20] for woods and wood pyrolysis products. The heating value relates to the amount of oxygen required for complete combustion, with $14,022 \text{ J}$ (13.3 Btu) released for each g of oxygen consumed [20]. Cellulose has a smaller heating value (17.3 MJ kg^{-1}) than lignin (26.7 MJ kg^{-1}) because of its higher degree of oxidation. Other compounds, such as HC in the fuel with lower degrees of oxidation, tend to raise the heating value of the biomass. Coals and HC liquids in general have heating values greater than those for biomass because of the lower degree of oxidation. Some lower rank coals have heating values nearly identical to biomass, however.

There has been some confusion as to how the heating value of a fuel relates to the ‘quality’ of the fuel as an energy source. One misinterpretation is that the efficiency of a power cycle can be interpreted solely on the basis of the heating value of the fuel. A common mistake is to assume that because the heating value of biomass is lower than most conventional fuels, the efficiency of a system using it will be lower by an equal amount. Such is not the case. A standard measure of the energy value or ‘quality’ of fuel is another thermodynamic property known as the availability of combustion. This essentially measures the maximal work available from the fuel, and incorporates the entropy effects of the second law as an ingredient of the measure, which the heating values described above do not. This can also be viewed effectively from the standpoint of the maximum temperature, the adiabatic flame temperature, attained under ideal combustion. For a heat engine, the maximum possible efficiency is that of the Carnot cycle (although practical Carnot cycles cannot be built). The efficiency of the Carnot cycle, η_C , is:

$$\eta_C = 1 - (T_L/T_H) \quad (3)$$

where T_L and T_H are the low and high temperatures between which the cycle operates.

The efficiency is increased with increased T_H . The higher the flame temperature, the higher the theoretical maximum efficiency. Maximal efficiencies can therefore be compared on the basis of the flame temperature, which depends not only on the heating value, but on the composition as well, as the composition dictates the theoretical quantity of air needed for combustion. The less air needed for reaction, the less diluent in the form of atmospheric nitrogen must be heated along with combustion products to achieve the adiabatic flame temperature (since nitrogen does not participate in the primary oxidation reactions, although it is important for the production of thermal NO_x). Stoichiometric air fuel ratios for HC fuels are typically between 14 and 17, for biomass they are 4 to 7, the lower values due largely to the higher oxygen contents of biomass. Adiabatic flame temperatures for biomass (dry basis) lie typically in the range of 2000 to 2700 K (3100 to 4400°F) [5,21]. For comparison, the adiabatic flame temperature of methane, CH_4 , in air, is approximately 2300 K (3700°F). The higher heating value of methane is 55.6 MJ kg^{-1} ($23,900 \text{ Btu lb}^{-1}$), or almost three times that of wood.

A simple computational procedure representing this idea is to normalize the heating values by the total mass of products (or reactants). This modified heating value is more useful in evaluating fuel quality in the sense of potential conversion of thermal energy to work in idealized heat engines. Fig. 11 illustrates both the traditional and modified heating values for a variety of fuels with values all being normalized to those of one of the bituminous coals. Pure compounds, coals, biomass fuels, biomass pyrolysis oils, and energetic materials are all represented in the figure. The values designated HHV are traditional higher heating values (dry basis), and those designated EC are the modified heating values, or energy contents. As illustrated, the relative values of these two quantities can differ by factors of up to two within coal and biomass fuels and factors of

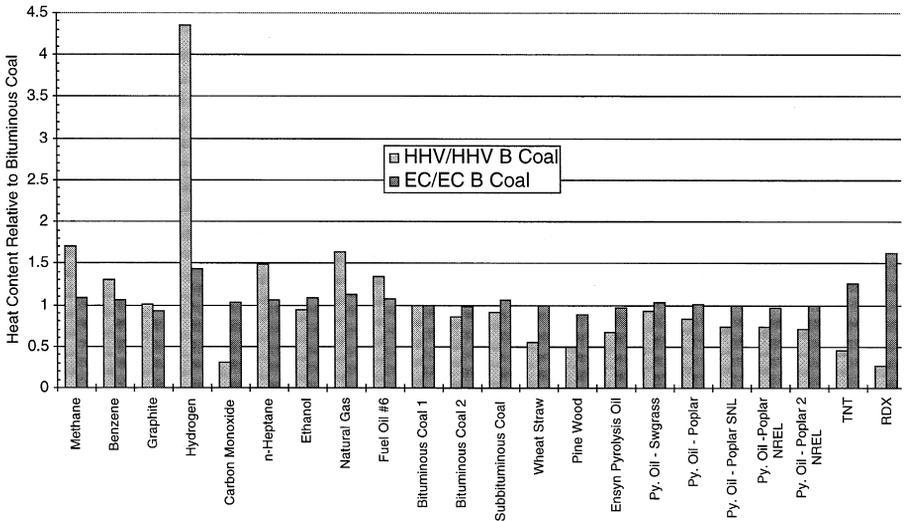


Fig. 11. Relative values of the standard heating value and the modified heating value (heating value divided by the mass of products, or equivalently the mass of air and fuel). The values shown are relative to a bituminous coal (Bituminous Coal 1).

over 20 when considering highly oxygenated fuels such as energetic materials (e.g., nitrocellulose).

5. Rates of combustion

In addition to the energy released by combustion, the rate of combustion is also important in the design of combustion systems. Occasionally, biomass combustion power plants have been observed to be underdesigned in terms of boiler volume and grate area for the rated capacity. Typical design heat release rates (expressed per unit grate area) for a stoker fired travelling grate combustor are in the range of 2 to 4 MW (thermal) m^{-2} . A whole tree combustion concept (not yet built) utilizes a design based on a heat release rate of 6 MW m^{-2} , but this also uses a very deep fuel bed [22]. Some circulating fluidized bed furnaces firing biomass have heat release rates approaching 10 MW m^{-2} . The rates at which biomass fuels burn depends on a number of physical phenomena which have been set out in some detail by Kanury [23]. Two predominant factors are the rates of heat transfer and the kinetic rates of reaction. Particle size dominates the influence of heat transfer, with small, thin (thermally thin) particles heating rapidly and coarser, thicker (thermally thick) particles heating more slowly. Combustion occurs both in the gas phase with the burning of volatile materials released through pyrolysis of the fuel upon heating, and heterogeneously in the solid phase as char oxidation. The burning of volatiles is generally quite rapid and follows as fast as volatiles are released, the oxidation of the char occurs much more slowly. The residence time of the particle in the furnace and the environment of the particle are therefore important to the total conversion attained through combustion, as well as the emissions from the combustor.

Fundamental to the combustion rate are the rates of fuel pyrolysis and char oxidation. The standard method of measuring these rates is via dynamic thermogravimetric analysis (TGA), whereby a small sample of the fuel (5–15 mg typically) is heated at a controlled rate in a controlled atmosphere while simultaneously recording weight, time, and temperature. Other techniques are also employed. The resulting thermogram has a characteristic shape for biomass.

Starting from room temperature, the sample is observed to dry (if the sample contains moisture which is normally the case, biomass being hygroscopic, and extreme care needed in handling to achieve a bone dry sample in the TGA) with a small weight loss up to about 150°C. Between about 200 and 400°C there is a very rapid loss of weight due to the evolution of volatile material, which in an oxidative environment (e.g., air) will ignite and burn. Following the release of volatiles, there is a slow loss of weight as the residual char decomposes. The conversion of a biomass fuel (rice straw) in an inert atmosphere (nitrogen) is shown as a function of temperature in Fig. 12 (refer to experimental curve).¹ In this case, the weight loss has been converted to the dimensionless conversion fraction by normalizing with respect to the total mass loss over the

¹ A.S. Bining, A study of reaction kinetics for thermochemical conversion of rice straw, Unpublished PhD dissertation, University of California, Davis, 1996.

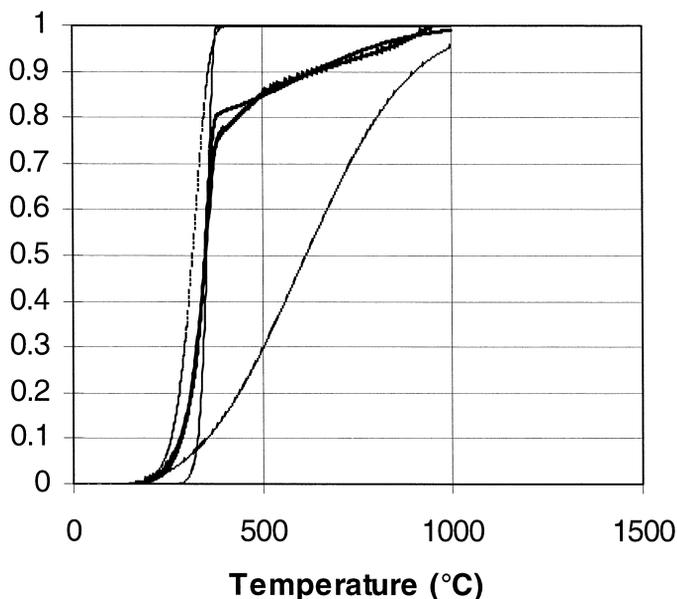


Fig. 12. Conversion of rice straw in nitrogen at 1.7 K s^{-1} by dynamic TGA. Experimental data (thick dashed line), three component model (thick solid line), individual components (narrow lines).

experiment. The shape of the thermogram (or conversion curve) is dependent on a number of factors, including the type of fuel, the atmosphere (oxidative, reducing, inert), and the heating rate (for most apparatus this rate is rather low at 2 K s^{-1} or less, whereas full scale combustors may heat fuel particles at $100\text{--}1000 \text{ K s}^{-1}$ or more). From the thermogram, kinetic parameters can be determined by which the overall rate of reaction can be predicted (along with appropriate models of heat transfer).

Also shown in Fig. 12 are the results of applying a multi-component kinetic model to the prediction of the actual conversion. In this case, three simultaneous component reaction models employing first order Arrhenius kinetics and based on the mass fractions of hemicellulose, cellulose, and lignin, are superimposed to yield the total conversion. Such multi-component models have proved useful in predicting the overall kinetic behavior of a biomass fuel in oxidative, reducing, and inert atmospheres, although the fitting technique is not entirely straightforward.¹

Metals in biomass are known to have an effect on reaction rates, and are thought to be catalytic to pyrolysis. This has recently been observed with water leached straw, as in Fig. 13 [24]. Plotted in the figure is the rate of weight loss as a function of temperature. There exists a definite kinetic shift for the leached material relative to the fresh, untreated straw. Although the activation energy (or energies, as two main components are evolving in this region) for the leached material is found to be lower than for the untreated material in the main stage of pyrolysis, the frequency factor is also lower, resulting in a slower overall rate of reaction. The result is consistent with what is known about the effects of alkali-chlorides on the pyrolysis rates of biomass. However, under

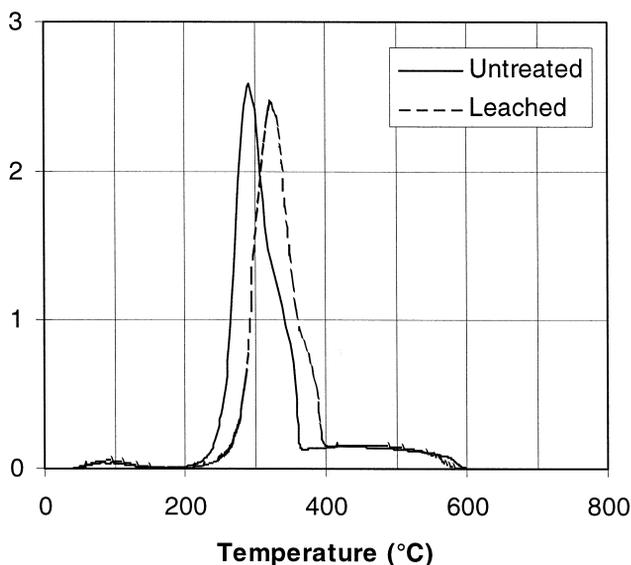


Fig. 13. Rate of weight loss under dynamic TGA for rice straw in air at 1.7 K s^{-1} [24]. The leached straw was soaked in distilled water for 24 h.

isothermal heating, the emission rate for volatiles has been observed to terminate earlier with the leached material than for the untreated material. We have also observed that the ignition requirements are lower for leached straw compared to untreated straw (which can be observed quite readily in the case of rice straw by suspending straws vertically and igniting from below). Chlorine is known to retard flame propagation in polymeric materials (e.g., polyvinylchloride) by terminating free radical chain reactions. Chlorine is leached from biomass by water [2], and the burning phenomena observed may be related to the role of chlorine in flame suppression. Much remains to be understood about the chemistry of biomass combustion.

6. Pollutant emissions

Critically related to the properties of biomass are pollutant emissions generated by combustion. Primary pollutants formed are particulate matter (PM), CO, HC, oxides of nitrogen (NO_x , principally NO and NO_2), and oxides of sulfur (SO_x , principally as SO_2). Acid gases, such as HCl, may also be emitted, as may lead and other heavy metals. CO and HC, including volatile organic compounds (VOC) and polycyclic aromatic hydrocarbons (PAH), are products of incomplete combustion. These species are largely controlled by stoichiometry and proper fuel moisture control. Heavy metals can be present in high concentration in certain urban wood fuels and RDF, especially if treated or painted woods are present [25].

PM includes soot, ash, condensed fumes (tars/oils), and sorbed materials including VOC and PAH. Most combustion generated particles are less than $1 \mu\text{m}$ aerodynamic

particle size. Respirable particles $10\ \mu\text{m}$ or smaller (PM 10) are breathing hazards, as they are retained deep in the alveoli of the lung. Mechanically generated particulate matter including carry-over fuel fines and ash particles tend to be fairly large compared to combustion aerosols. Biogenic silica in some materials, such as rice straw, is partly released as fibrous particulate matter which has become of concern recently for lung disease. Crystalline silica, including cristobalite, emitted from some power stations burning high silica fuels such as rice husk (hull), is also a breathing hazard and needs careful control.

Emissions of oxides of nitrogen and sulfur arise predominantly from nitrogen and sulfur in the fuel. Most commercial biomass combustors operate at temperatures low enough that thermal NO_x contributes only a small fraction of the total. NO_x in combination with HC photochemically leads to the formation of ozone, which is a lung and eye irritant and a major problem in urban environments. Ozone is also damaging to plants. Sulfur oxides are respiratory irritants, and their effects are enhanced in the presence of PM due to transport deep within the lung. Both nitrogen and sulfur oxides participate in reactions leading to acid rain.

Uncontrolled NO_x emissions also depend partly on stoichiometry. Examples are shown in Fig. 14 for laboratory experiments burning wood and rice straw [26] at varying equivalence ratio, ϕ ($\phi = 1$ represents the stoichiometric air–fuel ratio, values below 1 are fuel lean). The trend in NO_x emission with equivalence ratio is consistent with other fuels and with much of the NO_x coming from fuel nitrogen. For HC fuels, NO formation from fuel nitrogen occurs on time scales comparable to the HC oxidation, and is known to be sensitive to equivalence ratio, with fuel lean conditions producing high yields and fuel rich conditions producing low yields [27,28]. Under fuel rich conditions, the relatively fast conversion of fuel carbon to CO competes for oxygen, leading to a reduced availability of oxygen for NO_x production.

The fractional conversion of fuel nitrogen to NO_x has been shown to decrease with increasing fuel N concentration for HC fuels and coal [27–29]. The declining N to NO

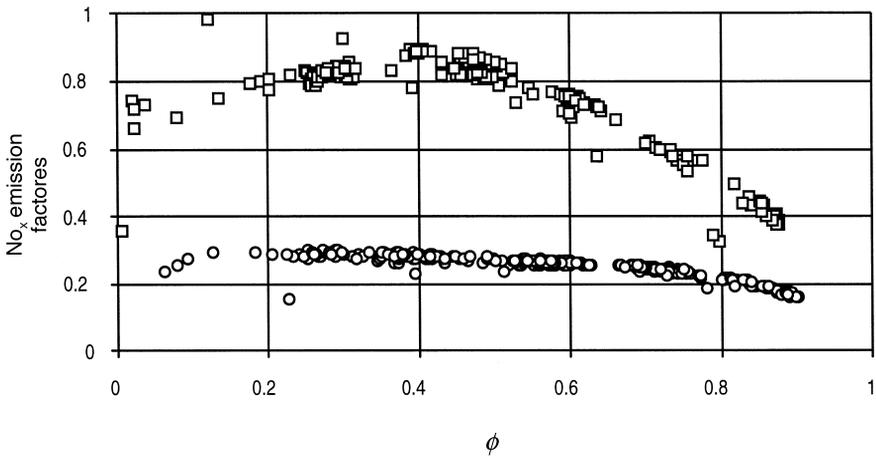


Fig. 14. NO_x emission factors at varying equivalence ratio, wood (circles) and rice straw (squares).

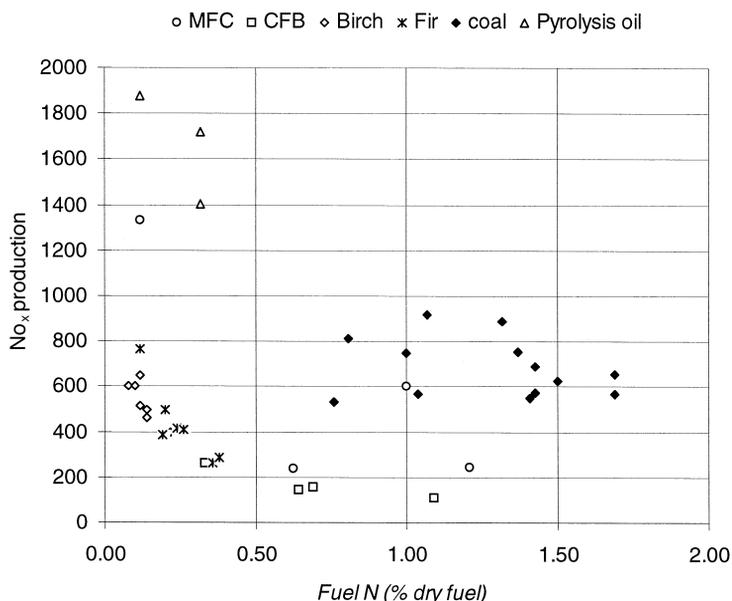


Fig. 15. Relative NO_x production for biomass and biomass derived fuels and coal. MFC refers to biomass fuels combusted in a laboratory multi-fuel combustor [26]. Pyrolysis oil is derived from wood [40]. Birch and fir wood data are from Leckner and Karlsson [31]. Coal data adapted from Seinfeld [27]. Biomass power plant data for CFB from Grass and Jenkins [30].

conversion is postulated to be due to the formation of a nitrogen containing species important to both the production and removal of NO . Data obtained from commercial biomass-fueled FBC [30] and laboratory experiments with fir and birch wood [31] also suggest declining fuel N conversion with increasing fuel N concentration, at least up to 1.1% N. Plotted in Fig. 15 is the relative production rate for a number of different fuels, taken as the NO_x concentration (ppmv) at 6% standard flue gas O_2 concentration divided by the fuel N concentration (% dry basis). A characteristic decline in relative

Table 3

Pollutant emission factors (% dry fuel) for open field burning, commercial biomass-fueled FBC, and experiments using an entrained flow multi-fuel combustor (MFC) laboratory combustor without pollution control

	Field burn		CFB ^a	MFC, $\phi = 0.85$	
	Wood	Rice straw		Wood	Rice straw
CO	5.54	3.22	0.002	0.45	0.30
NO_x	0.20	0.28	0.048	0.19	0.40
SO_2	0.01	0.06	0.01	0.005	0.035
HC	0.89	0.44	0.001	0.04	0.01

^aIncludes ammonia and limestone injection. Fuels composed of urban and agricultural wood fuels with small amounts of fruit pits and nut shells.

NO_x production with increasing fuel N is observed for biomass. In addition, the relative NO_x production for biomass appears to be less than that for coal, although this conclusion is only weakly supported by the limited results for biomass. Reduced furnace temperatures for biomass compared to coal likely account for much of the difference.

The burning and control conditions can have substantial impact on the emission rates of pollutant species. Table 3 lists pollutant emission factors (mass of pollutant emitted per unit mass of dry fuel consumed) for three types of biomass burning: uncontrolled open field burning [32], controlled combustion in commercial circulating fluidized bed power plants [30], and laboratory experiments conducted in an entrained flow MFC without post combustion emission control [26]. NO_x and SO_2 emission levels are roughly comparable between the open fires and MFC experiments. NO_x emissions from the CFB units are reduced about four times compared to the uncontrolled emissions, which is consistent with computed NO_x reduction efficiencies in commercial units [30].

7. Engineering practice

This paper has briefly discussed only a few of the properties of biomass important to the design and development of combustion and other types of energy conversion systems. The literature is not entirely consistent in the reporting of properties, and there are not standard engineering practices yet available to which the industry can refer. The issue of standardizing biomass analysis methods has been addressed previously (e.g., Refs. [33–35]). Some protocols have been defined to provide a common basis for analysis (e.g., Refs. [36–39]), but are still incomplete with respect to the suite of property evaluations that can or should be recommended. There is a greater need for standardized engineering practice in the sampling and analysis of, as well as the interpretation of analytical data for biomass fuels. Further development in this regard is encouraged.

References

- [1] T.R. Miles, T.R. Miles, Jr., L.L. Baxter, R.W. Bryers, B.M. Jenkins, L.L. Oden, Alkali deposits found in biomass power plants: a preliminary investigation of their extent and nature, National Renewable Energy Laboratory, Golden, CO, 1995.
- [2] B.M. Jenkins, R.R. Bakker, J.B. Wei, On the properties of washed straw, *Biomass and Bioenergy* 10 (4) (1996) 177–200.
- [3] T.A. Milne, A.H. Brennan, B.H. Glenn, Sourcebook of Methods of Analysis for Biomass and Biomass Conversion Processes, Elsevier, Amsterdam, 1990.
- [4] B.M. Jenkins, Physical properties of biomass, in: O. Kitani, C.W. Hall (Eds.), *Biomass Handbook*, Chap. 5.2, Gordon & Breach, New York, NY, 1989.
- [5] B.M. Jenkins, Properties of biomass, *Biomass Energy Fundamentals*, EPRI TR-102107, Electric Power Research Institute, Palo Alto, CA, 1993.
- [6] E.S. Domalski, T.L. Jobe, Jr., T.A. Milne, Thermodynamic data for biomass materials and waste components, American Society of Mechanical Engineers, New York, 1987.

- [7] L.L. Baxter, T.R. Miles, T.R. Miles, Jr., B.M. Jenkins, D. Dayton, T. Milne, R.W. Bryers, L.L. Oden, The behavior of inorganic material in biomass-fired power boilers-field and laboratory experiences, Vol. II, Alkali deposits found in biomass power plants, National Renewable Energy Laboratory, 1996.
- [8] H.L. Chum, M.M., Baizer, *The Electrochemistry of Biomass and Derived Materials*, ACS Monograph 183, American Chemical Society, Washington, DC, 1985.
- [9] T.P. Schultz, F.W. Taylor, Wood, in: O. Kitani, C.W. Hall (Eds.), *Biomass Handbook*, Gordon & Breach, New York, 1989, pp. 133–141.
- [10] S. Sudo, F. Takahashi, M. Takeuchi, Chemical properties of biomass, in: O. Kitani, C.W. Hall (Eds.), *Biomass Handbook*, Gordon & Breach, New York, 1989, pp. 892–933.
- [11] L.R. Lynd, Large-scale fuel ethanol from lignocellulose, *Appl. Biochem. Biotechnol.* 24–25 (1990) 695–719.
- [12] C.E. Wyman, N.D. Hinman, Ethanol, fundamentals of production from renewable feedstocks and use as a transportation fuel, *Appl. Biochem. Biotechnol.* 24–25 (1990) 735–753.
- [13] L.L. Baxter, The release of iron during coal combustion, Sandia report SAND95-8234·UC-1409, Sandia National Laboratories, Livermore, CA 94551, 1995.
- [14] L.L. Baxter, Ash deposition during biomass and coal combustion: a mechanistic approach, *Biomass Bioenergy* 4 (2) (1993) 85–102.
- [15] B.M. Jenkins, L.L. Baxter, T.R. Miles, T.R. Miles, Jr., L.L. Oden, R.W. Bryers, E. Winther, Composition of ash deposits in biomass fueled boilers: results of full-scale experiments and laboratory simulations, ASAE Paper No. 946007, ASAE, St. Joseph, MI, 1994.
- [16] M.K. Misra, K.W. Ragland, A.J. Baker, Wood ash composition as a function of furnace temperature, *Biomass Bioenergy* 4 (2) (1993) 103–116.
- [17] B.M. Jenkins, R.R. Bakker, J.B. Wei, Removal of inorganic elements to improve biomass combustion properties, *Proceedings 2nd Biomass Conference of the Americas*, National Renewable Energy Laboratory, Golden, CO, 1995.
- [18] D. Salour, B.M. Jenkins, M. Vafei, M. Kayhanian, Control of in-bed agglomeration by fuel blending in a pilot scale straw and wood fueled AFBC, *Biomass Bioenergy* 4 (2) (1993) 117–133.
- [19] E.C. Winegartner (Ed.), *Coal fouling and slagging parameters*, American Society of Mechanical Engineers, New York, 1974.
- [20] F. Shafizadeh, Basic principles of direct combustion, in: S.S. Sofer, O.R. Zaborsky (Eds.), *Biomass Conversion Processes for Energy and Fuels*, Plenum, New York, 1981, pp. 103–124.
- [21] B.M. Jenkins, J.M. Ebeling, Correlation of physical and chemical properties of terrestrial biomass with conversion, *Proceedings Energy from Biomass and Wastes IX*, Institute of Gas Technology, Chicago, IL, 1985.
- [22] G.A. Wiltsee, *Biomass energy fundamentals*, Vol. 1, EPRI TR-102107, Electric Power Research Institute, Palo Alto, CA, 1993.
- [23] A.M. Kanury, Combustion characteristics of biomass fuels, *Combustion Sci. Technol.* 97 (1994) 469–491.
- [24] B.M. Jenkins, R.R. Bakker, J. Gilmer, J.B. Wei, Combustion characteristics of leached biomass, Presented at *Developments in Thermochemical Biomass Conversion*, Banff, Canada, 1996.
- [25] C.T. Donovan Associates, Air emissions and ash disposal at wood-burning facilities: a sourcebook and case studies for the Great Lakes region, Great Lakes Regional Biomass Energy Program, 1995.
- [26] B.M. Jenkins, L.L. Baxter, Uncontrolled pollutant emissions from biomass combustion under simulated boiler furnace conditions, *Proceedings AFRC-JFRC Pacific Rim International Conference on Environmental Control of Combustion Processes*, Maui, HI, 1994.
- [27] J.H. Seinfeld, *Atmospheric Chemistry and Physics of Air Pollution*, Wiley, New York, 1986.
- [28] C.T. Bowman, Chemistry of gaseous pollutant formation and destruction, in: W. Bartok, A.F. Sarofim (Eds.), *Fossil Fuel Combustion*, Chap. 4, Wiley, New York, 1991.
- [29] J.A. Miller, C.T. Bowman, Mechanism and modeling of nitrogen chemistry in combustion, *Prog. Energy Combust. Sci.* 15 (1989) 287–338.
- [30] S.W. Grass, B.M. Jenkins, Biomass fueled fluidized bed combustion: atmospheric emissions, emission control devices and environmental regulations, *Biomass Bioenergy* 6 (4) (1994) 243–260.
- [31] B. Leckner, M. Karlsson, Gaseous emissions from circulating fluidized bed combustion of wood, *Biomass Bioenergy* 4 (5) (1993) 379–389.

- [32] B.M. Jenkins, S.Q. Turn, Primary atmospheric pollutants from agricultural burning: emission rate determinations from wind tunnel simulations, ASAE Paper 946008, ASAE, St. Joseph, MI, 1994.
- [33] T.A. Milne, H.L. Chum, F. Agblevor, D.K. Johnson, Standardized analytical methods, *Biomass Bioenergy* 2 (1) (1992) 341–366.
- [34] H.L. Chum, T.A. Milne, Feedstock characterization and recommended procedures, Proceedings First Biomass Conference of the Americas, National Renewable Energy Laboratory, Golden, CO, 1993, pp. 1685–1703.
- [35] T.A. Milne, Voluntary standards for biomass for fuels and chemicals, *Biomass* 22 (1990) 343–351.
- [36] B. McBurney, Wood refuse/biomass fuel specification guidelines, Proceedings TAPPI Engineering Conference, 1993.
- [37] M.W. Hope, Specification guidelines for tire derived fuel, Proceedings TAPPI Engineering Conference, 1993.
- [38] J. Clement, G. Elliott, B. McBurney, R.S. Skowrya, Biomass boiler performance test procedure, Proceedings 1992 TAPPI Engineering Conference, 1992.
- [39] J. Alexander, Wood fuel standards, ETSU B/W3/00161/REP, Energy Technology Support Unit, Department of Trade and Industry, Great Britain, 1994.
- [40] L. Baxter, B. Jenkins, Baseline NO_x emissions during combustion of wood-derived pyrolysis oils, Proceedings Specialists Workshop on Biomass Pyrolysis Oil Combustion, Estes Park, CO, 1994.