Kirk-Othmer Encyclopedia of Chemical Technology.

FUELS FROM WASTE

A significant number and variety of organic wastes are combusted in energy recovery systems including municipal solid waste (MSW), various forms of refuse-derived fuel (RDF) produced from MSW, and municipal sewage sludge; bark and other wood wastes from sawmills and other forest industry operations; spent pulping liquor from chemical pulp mills such as kraft and sulfite mills; wastewater treatment solids (WTS) or sludges from pulp and paper operations; agribusiness wastes including bagasse from sugar-refining operations, rice hulls, orchard and vineyard prunings, cotton gin trash, and a host of other food and fiber-producing operations; manure from feedlots and dairy cattle, chickens, and other agricultural animals; methane-rich gases generated from municipal-waste landfills; industrial trash and specific wastes such as demolition debris, broken pallets, unrecyclable paper wastes, and related materials; off-gases from pulp mills and chemical manufacturers; incinerable hazardous wastes generated regularly as a function of production processes, eg, spent solvents, or found on Superfund sites targeted for clean-up; and a broad range of other specific specialty wastes. The practice of incinerating these materials has become increasingly prevalent (ca 1990) in order to accomplish disposal in a cost-effective, environmentally sensitive manner. The combustion of such wastes already contributes some 5 EJ (5×10^{15} Btu) to the U.S. economy and over 15 EJ ($>14 \times 10^{15}$ Btu) to the economies of the industrialized world (1). Combustion of such wastes reduces the volume of material which must be disposed of in a landfill, reduces the airborne emissions resulting from plant operations and landfill operations, and permits some economic benefit through energy recovery.

The technologies used to combust wastes depend on the form and location of components to be burned. Typically solid wastes are burned, alone or in combination, and both with and without supplementary fossil fuels. Solid wastes can be burned in mass-burn or pile-burning systems such as hearth furnaces, spreader–stokers, ashing and slagging rotary kilns, or fluidized beds. The choice of combustion technology depends on the degree of waste preparation which is practical; the availability of existing combustion systems, eg, a spreader–stoker for hog fuel utilization, adapted to the cofiring of hog fuel and WTS; and the type of energy recovery contemplated. Energy recovery from the solid wastes can be accomplished in the form of medium or high pressure steam, eg, 4.5–8.6 MPa (44–85 atm) (672–783 K), suitable for cogeneration or condensing power generation purposes; low pressure steam, eg, 314–1030 kPa (3.1–10.2 atm), saturated, suitable for process purposes; or the direct production of process heat in the form of heated air or hot combustion products. Energy recovery from gaseous wastes can be accomplished through electricity generation from gas-fired boilers, combustion turbines, or internal combustion engines. Alternatively, these gaseous fuels can be used to generate process heat in conventional fashion.

The success of waste-to-energy programs using municipal wastes and bio-wastes reduces the volume of material being interred in the ground in landfills. This action also changes the character of materials being landfilled, reducing the organic content with its associated generation of methane gas, and leachates with their significant concentrations of organic compounds. Waste-to-energy, applied to municipal and biomass wastes, can simultaneously provide renewable energy while addressing environmental issues.

Critical concerns associated with energy generation from wastes include fuel composition characteristics; combustion characteristics; formation and control of airborne emissions including both criteria pollutants and

Table 1. Product Composition for Municipal Solid Waste,[a] Wt %

Product	1990[b]	2000[c]
paper and paperboard	38.3	41.0
yard waste	17.0	15.3
food waste	7.7	6.8
plastics	8.3	9.8
wood	3.7	3.8
textiles	2.2	2.2
rubber and leather	2.5	2.4
glass	8.8	7.6
metals	9.4	9.0
miscellaneous	2.1	2.1

[a] Ref. 2.
[b] Approximate.
[c] Estimated.

air toxics, eg, trace metals; and the characteristics of bottom and flyash generated from waste combustion. These issues are particularly important given the U.S. Clean Air Act Amendments of 1990, the Resource Recovery and Conservation Act (RRCA), and related state and regional regulations. Further, these issues are of critical importance given the capital intensive nature of organic waste-to-energy systems.

1. Fuel Characteristics of Organic Wastes

Fuel characteristics of organic wastes include physical characteristics such as state, specific gravity, bulk density, porosity, and void volume, and related thermal properties; traditional chemical analyses such as proximate and ultimate analyses, including chlorine; calorific content; elemental analyses of the ash, including trace metal contents, base–acid, slagging, and fouling ratios of the various ash products; and certain chemical structural analyses such as aromaticity. These characteristics are governed by the sources of waste-based fuels. They determine the performance of materials in fuel preparation systems such as particle size reduction and drying systems, and also govern the combustion characteristics of the various wastes being burned.

1.1. Sources of Waste-Based Fuels

The general architecture of waste-based fuels is a function of waste origination. MSW characteristics are governed by the product composition of the waste stream, as shown in Table 1. The composition of RDF is governed by the processing technologies used to generate the fuel. RDF production technologies involve, at a minimum, coarse shredding of the MSW stream, followed by magnetic separation of ferrous metals. Primary separation techniques for concentration of combustibles involve trommels, air classifiers, or eccentric screens. Trommels have become the most popular separation systems; their overall separation efficiency can be as high as 98.5% (Table 2). Process flow sheets using trommel separation of MSW follow the pattern shown in Figure 1. The composition of MSW and RDF ultimately is a function not only of the general composition of the waste stream and the RDF production technology, but also of community and industrial recycling programs. Such programs are accelerating and will influence the amount and relative concentration of paper, plastic, aluminum, and other commodities in the waste stream.

The basic architecture of wood-waste fuels is governed by sawmill or plywood mill configuration, and the consequent blend of bark, trim ends, sawdust, planer shavings, and related residuals. All chippable wastes typically are directed to pulp chips. Planer shavings and some sawdust may be directed to alternative products

Table 2. MSW Separation Efficiencies for Trommels as a Function of Waste Component,[a] Wt %

Waste component	Separation efficiency
paper, plastic	61.1–69.4
other combustibles[b]	74.6–86.8
ferrous metal	61.6–80.1
aluminum	76.7–93.6
glass, stones, and other	96.6–100
fines	97.0–98.0
overall efficiency	*81.0–98.5*

[a] Ref. 3.

[b] For example, wood.

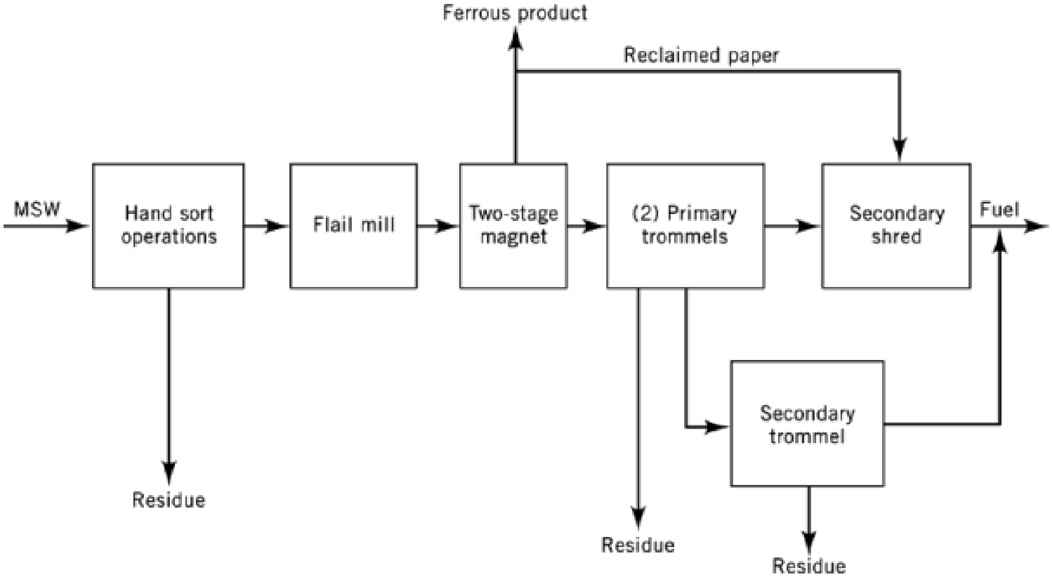

Fig. 1. Simplified schematic flow sheet for the production of a moderate RDF, using trommel separation.

including oriented strand board (OSB), particleboard, animal bedding, a range of other materials applications, and fuel. The characteristics of pulp-mill wastes, eg, bark, WTS, and spent pulping liquor, also are determined by the production processes. The characteristics of wastes from food processing, eg, bagasse, rice hulls, peach pits, cotton gin trash, etc, are governed by the basic product manufacturing technology and its efficiency of separation.

1.2. Physical Properties

Physical properties of waste as fuels are defined in accordance with the specific materials under consideration. The greatest degree of definition exists for wood and related biofuels. The least degree of definition exists for MSW, related RDF products, and the broad array of hazardous wastes. Table 3 compares the physical property data of some representative combustible wastes with the traditional fossil fuel bituminous coal. The solid organic wastes typically have specific gravities or bulk densities much lower than those associated with coal and lignite.

Table 3. Physical Properties of Waste-Based Fuels[a]

Fuel	Specific gravity[b]	Bulk density,[c] kg/m^3	Moisture content, wt %
municipal waste		160–320	25–35
waste paper	1.2–1.4	80–160	15–25
waste wood	0.37–0.65	100–320	5–15[d] 40–65[e]
bagasse			50–55
rice hulls			7–10
orchard and vineyard prunings	0.45–0.55		20–40
bituminous coal	1.12–1.35	672–1393	3.5–5.0

[a] Refs. 1 and 4.
[b] Ovendry.
[c] To convert kg/m^3 to lb/ft^3, divide by 16.01.
[d] Dry waste.
[e] Wet waste.

Specific gravity is the most critical of the characteristics in Table 3. It is governed by ash content of the material, is the primary determinant of bulk density, along with particle size and shape, and is related to specific heat and other thermal properties. Specific gravity governs the porosity or fractional void volume of the waste material, ie,

$$\mathrm{FVV} = (1 - \mathrm{SG})/1.5 \qquad (1)$$

where FVV is fractional void volume, SG is specific gravity, and the value 1.5 is the approximate specific gravity of the cell wall in wood fiber (5). Specific gravity and moisture content (MC) together determine thermal conductivity characteristics, *k,* of cellulosic waste-based fuels:

$$k_{\mathrm{MC}<30\%} = \mathrm{SG}\,(1.39 + 0.028 \times \mathrm{MC}) + 0.165 \qquad (2)$$

and

$$k_{\mathrm{MC}>30\%} = \mathrm{SG}\,(1.39 + 0.038 \times \mathrm{MC}) + 0.165 \qquad (3)$$

Specific gravity is directly related to the bulk density of waste fuels prepared in a variety of ways. Solid oven-dry (OD) wood, for example, has a typical bulk density of 48.1 kg/m^3 (30 lb/ft^3). In coarse hogged form, eg, <1.9–cm minor dimension, this bulk density declines to about 24 kg/m^3 (15 lb/ft^3). In pulverized form, at a particle size <0.16 cm, this bulk density declines to 16–19 kg/m^3 (10–12 lb/ft^3). Similar relationships hold for municipal waste, agricultural wastes, and related fuels.

1.3. Chemical Composition

Chemical compositional data include proximate and ultimate analyses, measures of aromaticity and reactivity, elemental composition of ash, and trace metal compositions of fuel and ash. All of these characteristics impact the combustion processes associated with wastes as fuels. Table 4 presents an analysis of a variety of wood-waste fuels; these energy sources have modest energy contents.

The analysis of solid fuels (Table 4) contains the bases for calculating reactivities, ie, volatile:fixed carbon ratios, volatile carbon:total carbon ratios, hydrogen:carbon and oxygen:carbon ratios, and aromaticity, which is estimated from the chemical components of the waste stream. The typical source of aromatic carbon in waste

Table 4. Analysis of Wood-Based Fuels,[a] Wt %

				Element					
Wood material	Volatile matter	Fixed carbon	Ash	C	H	O	N	S	HHV,[b] MJ/kg
big leaf maple	87.9	11.5	0.6	49.9	6.1	43.3	0.14	0.03	16.9
douglas fir	87.3	12.6	0.1	50.6	6.2	43.0	0.06	0.02	18.3
douglas fir bark	73.6	25.9	0.5	54.1	6.1	38.8	0.17	[c]	19.7
oak									
black[d]	85.6	13.0	1.4	49.0	6.0	43.5	0.15	0.02	16.8
tan[e]	87.1	12.4	0.5	48.3	6.1	45.0	0.03	0.03	17.2
oak bark			5.3	49.7	5.4	39.3	0.2	0.1	17.5
pine bark			2.9	53.4	5.6	37.9	0.1	0.1	18.4
pitch pine			1.1	59.0	7.2	32.7			21.8
poplar			0.7	51.6	6.3	41.5			17.2
red alder	87.1	12.5	0.4	49.6	6.1	43.8	0.13	0.07	17.3
red alder bark	77.3	19.7	3.0	50.9	5.5	40.7	0.39		17.2
western hemlock[f]	87.0	12.7	0.3	50.4	5.8	41.4	0.1	0.1	19.8

[a] Ref. 4.

[b] Higher heating value (OD basis); to convert MJ/kg to Btu/lb, multiply by 430.3

[c] Trace amounts.

[d] Black oak bark has 81.0 wt % volatile matter, 16.9 wt % fixed carbon, and 2.1 wt % ash.

[e] Tan oak bark has 76.3 wt % volatile matter, 20.8 wt % fixed carbon, and 2.9 wt % ash.

[f] Western hemlock bark has 73.9 wt % volatile matter, 24.3 % fixed carbon, and 0.8 wt % ash.

fuels, such as municipal solid waste and wood waste, is lignin (qv) found in either groundwood-based papers or wood products. Lignin [9005-53-2] has a typical empirical formula (1) of $C_9H_{10}(OCH_3)_{0.9--1.7}$, and a higher heating value (HHV) of 26.7 MJ/kg (11,500 Btu/lb), resulting from its basic building blocks of phenyl propane units. These basic building blocks contain aromatic structures. Other sources of aromatic structures in waste fuels include plastic polymers in the waste stream. The aromaticity of a solid fuel can be estimated as a function of H:C atomic ratio (6):

H:C atomic ratio	Carbons as aromatic carbons, %
1.5	0.0
1.2	3.0
0.7	9.0
0.5	16.0

Typically, 40–50% of the carbon atoms in lignite are in aromatic structures while 60–70% of the carbon atoms in Illinois bituminous coal are in aromatic structures (7, 8). By all of these measures, waste fuels are significantly more reactive than coal, peat, and other combustible solids.

The chemical analysis of waste fuels also demonstrates that the wood-based fuels contain virtually no sulfur and little nitrogen. Unless the hog fuel contains bark from logs previously stored in salt-water, the chlorine content is very modest to nonmeasurable.

Municipal waste contains, nominally, about 0.5% nitrogen and 0.5% chlorine, the latter coming largely from plastics. Municipal waste also contains moderate amounts of sulfur. The actual composition of MSW, or RDF generated from MSW, is a function of the relative percentages of various components in the waste stream as shown in Table 5. Use of these wastes provides a means for reducing acid gas emissions from energy generation.

Table 5. Components of Municipal Solid Waste[a]

	Components, wt %								
Material	Carbon	Hydrogen	Oxygen	Nitrogen	Chlorine	Sulfur	Moisture	Ash	HHV, MJ/kg[b]
corrugated paper	36.79	5.08	35.41	0.11	0.12	0.23	20.0	2.26	13.0
newsprint	36.62	4.66	31.76	0.11	0.11	0.19	25.0	1.55	13.0
magazine stock	32.93	4.64	32.85	0.11	0.13	0.21	16.0	13.13	11.4
other paper	32.41	4.51	29.91	0.31	0.61	0.19	23.0	9.06	11.5
plastics	56.43	7.79	8.05	0.85	3.00	0.29	15.0	8.59	24.2
rubber and leather	43.09	5.37	11.57	1.34	4.97	1.17	10.0	22.49	17.6
wood	41.20	5.03	34.55	0.24	0.09	0.07	16.0	2.82	14.5
textiles	37.23	5.02	27.11	3.11	0.27	0.28	25.0	1.98	13.8
yard waste	23.29	2.93	17.54	0.89	0.13	0.15	45.0	10.07	8.37
food waste	17.93	2.55	12.85	1.13	0.38	0.06	60.0	5.10	6.82
fines[c]	15.03	1.91	12.15	0.50	0.36	0.15	25.0	44.90	5.41

[a] Ref. 9.
[b] To convert MJ/kg to Btu/lb, multiply by 430.3.
[c] Smaller than 2.54 cm (1 in.).

1.3.1. Ash Characteristics

The elemental ash composition of biomass waste and municipal solid waste differs dramatically from that of coal (qv). Wood wastes have ash compositions that are quite alkaline (Table 6) and that have consequent low ash fusion temperatures (Table 7). When firing solid wastes with coal or lignite, the potential exists to have eutectic mixtures formed by the two ash products.

The Clean Air Act of 1990 has made trace metal content in fuels and wastes the final ash-related compositional characteristic of significance. Considerable attention is paid (ca 1993) to emissions of such metals as arsenic, cadmium, chromium, lead, mercury, silver, and zinc. The concentration of these metals in both grate ash and flyash is of significance as a result of federal and state requirements; of particular importance is the mobility of metals. This mobility, and the consequent toxicity of the ash product, is determined by the Toxic Characteristic Leaching Procedure (tclp) test. Tables 8, 9, 10 present trace metal contents for wood wastes and agricultural wastes, municipal waste, and refuse-derived fuel, respectively. In Table 8, the specific concentration of various components in the RDF governs the expected average concentration of trace metals.

Biofuels, ie, wood and agricultural waste, are relatively low in metal contents, and typically have a lower metals content when compared to coals being burned for energy generation. However, municipal waste and its derivative fuels (RDF) can be quite high in trace metals. The RDF production process removes approximately 67% of the incoming metals content, but significant quantities of components such as lead and cadmium

Table 6. Elemental Analysis of Wood Waste Ash[a]

		Source, wt %		
Compound	CAS Registry Number	Pine bark	Oak bark	Spruce bark
SiO_2	[14808-60-7]	39.0	11.1	32.0
Fe_2O_3	[1309-37-1]	3.0	3.3	6.4
TiO_2	[13463-67-7]	0.2	0.1	0.8
Al_2O_3	[1344-28-1]	14.0	0.1	11.0
MnO_4	[12502-70-4]	[b]	[b]	1.5
CaO	[1305-78-8]	25.5	64.5	25.3
MgO	[1309-48-4]	6.5	1.2	4.1
Na_2O	[12401-86-4]	1.3	8.9	8.0
K_2O	[12136-45-7]	6.0	0.2	2.4
SO_3	[7446-11-9]	0.3	2.0	2.1
Cl	[7782-50-5]	[b]	[b]	[b]

[a] Ref. 10.

[b] Trace amounts.

Table 7. Ash Fusion Temperatures for Some Wood Waste Ash,[a] **K**

	Initial		Softening		Fluid	
Wood Species	Oxidizing	Reducing	Oxidizing	Reducing	Oxidizing	Reducing
tan oak	1663	1650	1713	1711	1730	1727
pine bark	1483	1467	1522	1500	1561	1540
oak bark	1744	1750	1772	1766	1783	1777

[a] Refs. 4 and 10.

remain in some compositions of RDF. These metals must be controlled for safe energy generation from such combustible materials. The wood waste in RDF is typically not the same as the wood waste from forest products manufacture. Commonly the wood in RDF is treated with compounds, eg, copper chromium arsenate (CCA), which make it more suitable in outdoor service, such as in deck construction. Such wood treating adds trace metals to the fuel feed (13).

2. Combustion of Solid Waste-Based Fuels

It is useful to examine the combustion process applied to solid wastes as fuels and sources of energy. All solid wastes are quite variable in composition, moisture content, and heating value. Consequently, they typically are burned in systems such as grate-fired furnaces or fluidized-bed boilers where significant fuel variability can be tolerated.

Combustion characteristics of consequence include the overall mechanism of solid waste combustion, factors governing rates of waste fuels combustion, temperatures associated with waste oxidation, and pollution-formation mechanisms.

2.1. Mechanisms and Rates of Combustion

All solid fuels and wastes burn according to a general global mechanism (Fig. 2). The solid particle is first heated. Following heating, the particle dries as the moisture bound in the pore structure and on the surface of the particle evaporates. Only after moisture evolution does pyrolysis initiate to any great extent. The pyrolysis process is followed by char oxidation, which completes the process.

Table 8. Trace Metal Concentrations[a] in Ash from Agricultural Biofuels and Wood-Fired Boilers, mg/kg

	Agricultural biofuel			
Metal	Cotton gin trash	Orchard prunings	Vineyard prunings	Wood-fired boilers[b]
barium	120	220	41	130
silver	<0.08	<0.08	<0.08	<0.08
arsenic	12	5.5	3.4	3.0–6.3
beryllium	0.1	0.1	0.06	0.1
cadmium	1.1	0.36	0.39	1.5–16
cobalt	14	9.0	2.8	8.5–20
chromium	20	12	11	16.8–25
copper	23	14	31	40–76.9
mercury	<0.05	<0.05	<0.05	<0.05 – <0.5
molybdenum	16	2	2	3.0–14
nickel	4.6	5.8	4.4	11–50
lead	21	22	55	38–70
antimony	10	10	10	10
selenium	<0.2	<0.2	<0.2	5.0
vanadium	20	12	11	26–27
zinc	87	190	40	130–560
thallium	15	10	2	6.5

[a] Ref. 1.

[b] Range of concentrations from various locations.

Table 9. Trace Metals in Municipal Solid Waste and Solid Waste Ash,[a, b] ppm by wt

Metal	Solid waste[c]	Solid waste ash
arsenic	0.73–12.5	2.9–50
barium	19.8–675	79–2,700
beryllium	ND–0.6	ND–2.4
boron	6–43.5	24–174
cadmium	0.05–25	0.18–100
chromium	3.0–375	12–1,500
cobalt	0.43–22.75	1.7–91
copper	10–1,475	40–5,900
lead	7.75–9.15	31–36,600
magnesium	175–4,000	700–16,000
molybdenum	0.6–72.5	2.4–290
manganese	3.5–782.5	14–3,130
mercury	ND–4.38	0.05–17.5
nickel	3.25–3,228	13–12,910
selenium	0.03–12.5	0.10–50
strontium	3.0–160	12–640
zinc	23–11,500	92–46,000

[a] Range of concentration. Ref. 11.

[b] ND = nondetectable·

[c] Based on ash measurements. Imputed no waste.

The rate of solid waste combustion is controlled by diffusion, rather than by reaction kinetics. In general, the time required for combustion of a single particle of waste (1) can be expressed as:

$$T_b = T_h + T_d + T_p + T_{co} \qquad (4)$$

Table 10. Analysis of Refuse-Derived Fuel[a]

Parameter	Glossy paper	Nonglossy paper	Cardboard	Film plastics	Rubber, leather, and hard plastics	Wood and textiles	Other organics	Total RDF
				Trace metals, mg/kg fuel				
arsenic	3.1	3.3	3.5	2.7	2.5	5.2	4.6	4.0
barium	285.1	78.9	48.7	186.5	724.3	96.7	210.0	173.2
beryllium	1.1	1.3	1.2	0.5	0.4	1.5	1.5	1.3
cadmium	1.1	1.3	3.8	7.7	17.3	3.0	3.1	3.4
chromium	23.8	37.3	23.2	69.4	95.9	34.8	44.5	42.7
copper	74.8	40.3	27.0	2740.7	12.1	202.3	61.4	220.1
lead	88.4	621.2	66.2	836.6	668.1	747.6	475.1	495.5
manganese	61.2	137.6	101.1	311.8	83.1	183.9	367.3	260.4
mercury	0.3	0.7	0.4	1.0	0.4	0.9	1.2	0.9
nickel	10.4	15.5	25.5	45.6	170.4	27.4	17.7	24.4
selenium	3.1	2.9	3.3	2.1	2.0	3.3	3.0	2.9
strontium	62.4	73.2	47.8	88.5	88.6	198.9	474.8	283.2
zinc	164.5	227.6	161.4	482.2	2494.5	449.4	360.0	380.2
				Ultimate analysis, wt %				
carbon	43.4	47.3	49.6	59.8	53.8	50.1	34.6	41.1
hydrogen	5.3	6.1	6.4	8.2	8.9	6.0	4.3	5.3
oxygen	27.5	32.0	35.7	13.8	23.3	31.5	41.1	35.2
nitrogen	0.62	1.58	0.72	1.01	0.83	1.07	1.07	1.12
sulfur	0.25	0.25	0.24	0.56	0.57	0.28	0.38	0.34
chlorine	0.04	0.04	0.05	0.10	0.05	0.05	0.01	0.07
ash	23.0	12.7	7.4	16.6	12.5	11.0	18.3	16.5
higher heating value, MJ/kg[b]	14.7	19.7	18.5	31.0	25.4	21.0	16.5	18.7

[a] Fuel produced in Tacoma, Wash. Values on ovendry (OD) fuel basis. Ref. 12.

[b] To convert MJ/kg to Btu/lb, multiply by 430.3.

where T_b is time for complete particle burnout, T_h is time for initial particle heat-up, T_d is time required for particle drying, T_p is time required to pyrolyze the particle into volatiles and char, and T_{co} is time for char oxidation. The first two terms, initial heating plus drying, $T_h + T_d$, can be taken as the drying step. This time component is governed by the temperature of the environment, the particle size, the moisture content of the particle, and the porosity of the particle. The term T_p is strictly governed by heat transfer through the particle (14, 15). The rate of pyrolysis is governed by the heat capacity of the solid waste, its porosity, and its thermal conductivity. The T_{co} term is mass-transfer-limited, with diffusion of oxygen to the surface of the char particle being rate-limiting. Of these steps, either drying or char oxidation may be rate-limiting, as shown in Figure 3, depending on the moisture content of the solid waste.

2.2. Temperatures Associated with Combustion

The temperatures achieved by solid waste combustion are typically lower than those associated with fossil fuel oxidation, and are governed by the following general equation(1):

$$T_{f,\text{solid waste}} = \left[695 - 10.1\,\mathrm{MC}_t + 1734\,(1/\mathrm{SR}) + 0.61\,(A - 298)\right]\mathrm{K} \qquad (5)$$

Where T_f is flame temperature in K; MC_t is moisture content of the waste, expressed on a total weight basis; SR is defined as stoichiometric ratio or moles O_2 available/moles O_2 required for complete oxidation of the carbon, hydrogen, and sulfur in the fuel, ie, $1/\mathrm{SR}$ = equivalence ratio; and A is temperature of the combustion

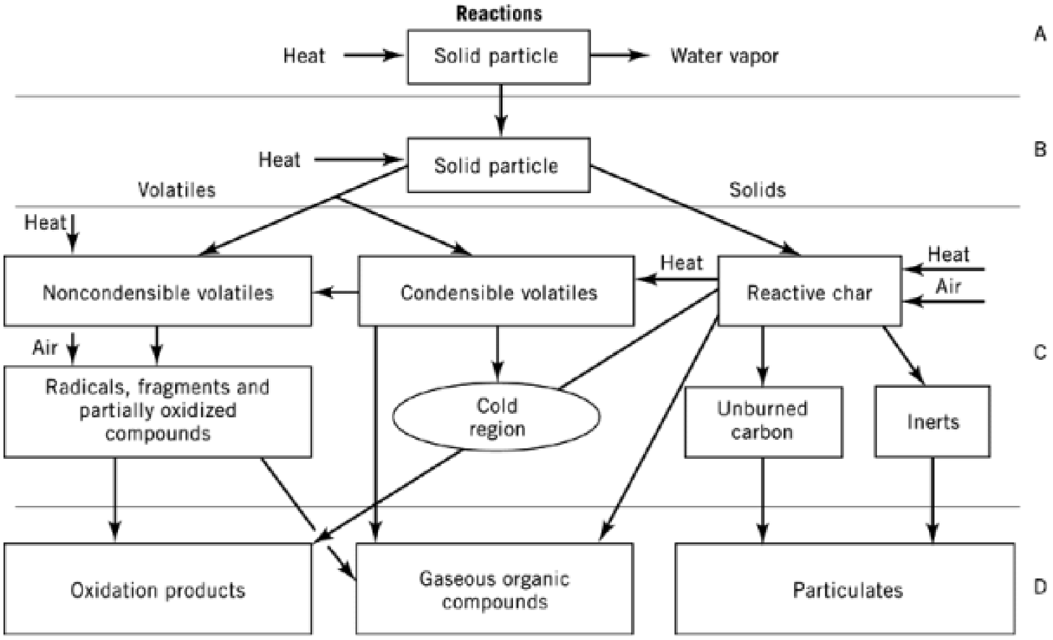

Fig. 2. Overall schematic of solid fuel combustion (1). Reaction sequence is A, heating and drying; B, solid particle pyrolysis; C, oxidation; and D, post-combustion. In the oxidation sequence, left and center comprise the gas-phase region, right is the gas–solids region. Noncondensible volatiles include CO, CO_2, CH_4, NH_3, H_2O; condensible volatiles are C-6–C-20 compounds; oxidation products are CO_2, H_2O, O_2, N_2, NO_1, gaseous organic compounds are CO, hydrocarbons, and polyaromatic hydrocarbons (PAHs); and particulates are inerts, condensation products, and solid carbon products.

air, expressed in K. In English units, this equation is as follows:

$$T_{f,\ \text{solid waste}} = \left[3870 - 15.6\ \text{MC}_t - 130.4\ \text{EO}_2 + 0.59\,(A - 77)\right]{}^\circ\text{F} \qquad (6)$$

where EO_2 is excess oxygen in the stack gas, ie, total, not dry, basis.

Whereas solid wastes can achieve significant flame temperatures, they are substantially below those associated with fossil fuels. These differences are largely caused by the lower calorific value; the chemical composition, eg, oxygen content of the waste; and the higher moisture and ash contents commonly associated with various solid wastes. Typically for grate-fired systems the use of wastes as fuel requires maintaining temperatures in excess of 1256 K (1800°F) and for residence times exceeding 2 s in order to ensure complete combustion and minimize dioxin and furan formation. As shown from equation 5, such temperatures are readily achieved under most conditions.

Given the mechanisms and temperatures, waste combustion systems typically employ higher percentages of excess air, and typically also have lower cross-sectional and volumetric heat release rates than those associated with fossil fuels. Representative combustion conditions are shown in Table 11 for wet wood waste with 50–60% moisture total basis, municipal solid waste, and RDF.

2.3. Formation of Airborne Emissions.

Airborne emissions are formed from combustion of waste fuels as a function of certain physical and chemical reactions and mechanisms. In grate-fired systems, particulate emissions result from particles being swept

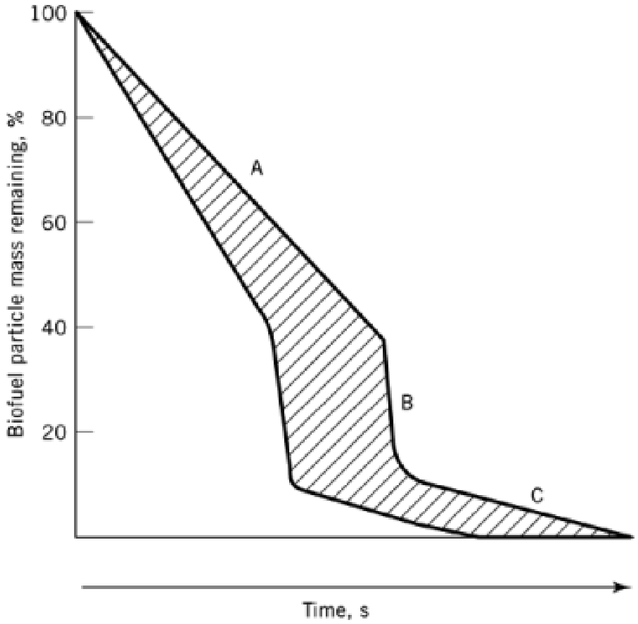

Fig. 3. Schematic of the sequential nature of waste fuel combustion (1). A, particle heating and drying; B, solid particle pyrolysis; and C, char oxidation. A and C may be rate-limiting.

Table 11. Combustion Conditions for Conventional Waste Fuel Boilers[a]

Parameter	Wood[b]	MSW	RDF
maximum fuel moisture, %	55–60	30–40	20–35
grate fuel feed rate, kg/m^{2}h[c]	1000–1500		
grate heat release, GJ/m^{2}h[d]	8.5–11.35	3.4	5.7–8.5
volumetric heat release, MJ/m^{3}h[e]	480–560	335–410	450–480
stoichiometric ratio	1.25–1.5	1.8–2.0	1.6–1.8
excess air, %	25–50	80–100	60–80
representative overfire air, %	20–40	30–40	30–40

[a] Refs. 1 and 16.
[b] Wet wood waste, 50–60% moisture total basis.
[c] To convert kg/(m^{2}h) to lb/(ft^{2}h), multiply by 0.204.
[d] To convert GJ/(m^{2}h) to Btu/(ft^{2}h), multiply by 8.8×10^4.
[e] To convert MJ/(m^{3}h) to Btu/(ft^{3}h), multiply by 26.9.

through the furnace and boiler in the gaseous combustion products, and from incomplete oxidation of the solid particles, with consequent char carryover. If pile burning is used, eg, the mass burn units employed for unprocessed MSW, typically only 20–25% of the unburned solids and inerts exit the combustion system as flyash. If spreader-stoker technologies are employed, between 75 and 90% of the unburned solids and inerts may exit the combustion system in the form of flyash.

Sulfur dioxide [7446-09-5] is formed as a result of sulfur oxidation, and hydrogen chloride is formed when chlorides from plastics compete with oxygen as an oxidant for hydrogen. Typically the sulfur is considered to react completely to form SO_2, and the chlorine is treated as the preferred oxidant for hydrogen. In practice, however, significant fractions of sulfur do not oxidize completely, and at high temperatures some of the chlorine atoms may not form HCl.

Nitrogen oxide, NO_x, formation results from conversion of nitrogen in the fuel to NO, since combustion temperatures are below those typically associated with thermal NO_x formation, eg, 1483°C as the threshold for thermal NO_x has been documented (17, 18). The conversion of fuel nitrogen to NO_x typically proceeds along the pathways of nitrogen volatilization followed by oxidation of the nitrogen volatiles in the presence of excess oxygen. In the absence of available oxygen, the nitrogen volatiles react with each other to form N_2. Conversion of nitrogen from waste fuels into NO_x is typically 15–25% of the fuel nitrogen converted, depending on combustion technology and firing conditions.

Formation of emissions from fluidized-bed combustion is considerably different from that associated with grate-fired systems. Flyash generation is a design parameter, and typically $>90\%$ of all solids are removed from the system as flyash. SO_2 and HCl are controlled by reactions with calcium in the bed, where the limestone fed to the bed first calcines to CaO and CO_2, and then the lime reacts with sulfur dioxide and oxygen, or with hydrogen chloride, to form calcium sulfate and calcium chloride, respectively. SO_2 and HCl capture rates of 70–90% are readily achieved with fluidized beds. The limestone in the bed plus the very low combustion temperatures inhibit conversion of fuel N to NO_x.

Trace metal emissions from waste combustion are a function of metal content in the feed, combustion temperatures, and the percentage of ash exiting the combustion chamber as flyash. They are also a function of the temperatures in the air pollution control system, eg, the precipitator, baghouse, or scrubber, and the consequent degree to which these metals undergo homogeneous nucleation and become a fine fume, eg, submicron particles in the flyash, or undergo heterogeneous condensation on existing flyash particles. For some metals, such as arsenic and lead, emissions are also a function of the combustion system and the presence of lime. In fluidized beds, it has been shown that the arsenic and lead are captured and stabilized by the presence of reactive lime (1, 19).

Dioxin [828-00-2] and furan [110-00-9] emissions are the final pollutants of consideration and are of most concern for combustors using MSW, RDF, or hazardous waste. Dioxins are formed, at some concentration level ranging from inconsequential to problematical, whenever aromatic compounds and trace quantities of chlorine are present in the boiler feed. Several mechanisms have been postulated for dioxin and furan emission formation including the passage of such molecules, unreacted, through the furnace; the formation of dioxins and furans from such precursers as lignins and trace concentrations of chlorine; and the formation of dioxins in post-combustion reactions in the economizer section at temperatures of about 550–700 K (2, 20, 21). Of these, the post-combustion mechanism is shown to dominate. However, the impact of this mechanism can be minimized by maintaining temperatures in excess of 983°C for 2 s, while ensuring complete mixing of fuels and oxidants and ensuring the absence of cool zones in the furnace. A general equationfor approximating dioxin and furan emissions is as follows (22):

$$D + F = 0.0376\,(\mathrm{EA}) - 3.305 \qquad (7)$$

where $D + F$ is dioxins plus furans (in $\mu g/nm^3$) in the gaseous combustion products, corrected to 12% CO_2, and EA is the percentage of excess air above about 70%. Dioxin emissions are a problem more for MSW burners than other types of waste fuel systems, largely as a result of chlorine in the waste feed. Dioxin emissions typically are minimized in fluidized-bed combustion as a consequence of the solids mixing and solids turbulence in the bed.

3. Applications of Fuels From Waste

Because fuels from combustible organic wastes have long been economic in specific industries such as pulp mills, sawmills, sugar mills or factories, and other biomass processing operations, and because municipal waste-to-energy is becoming increasingly cost effective, these systems are continuing to be installed. The typical industrial system is used either to generate process steam or to generate both electricity and steam in a cogeneration application. Typically these applications involve power boilers which are the essential source of process energy in pulp mills and food processing operations. Typical larger installations generate some 200–300 t/h of steam used to generate 25–35 MW plus process heat. As stand-alone electricity generating stations, these units are capable of 50–60 MW, with a typical thermal efficiency of 65–75%. Thermal efficiency depends on moisture and ash content of the feed waste, consequent firing conditions employed, and extent of heat-transfer surface available for combustion air heating as well as steam generation.

Since the early 1980s, there have been several stand-alone power plants built to fire biomass wastes including such materials as wood waste, rice hulls, and vineyard prunings; these facilities typically generate 20–50 MW_e for sale to electric utilities. MSW and RDF are typically consumed in condensing power plants generating 15–50 MW_e while reducing the volume of solids to be landfilled. These units have thermal efficiencies comparable to the large power boilers of the pulp and paper industry, depending again on waste fuel condition and firing strategy.

There has been increased interest in firing wood waste as a supplement to coal in either pulverized coal (PC) or cyclone boilers at 1–5% of heat input. This application has been demonstrated by such electric utilities as Santee-Cooper, Tennessee Valley Authority, Georgia Power, Delmarva, and Northern States Power. Cofiring wood waste with coal in higher percentages, eg, 10–15% of heat input, in PC and cyclone boilers is being carefully considered by the Electric Power Research Institute (EPRI) and Tennessee Valley Authority (TVA). This practice may have the potential to maximize the thermal efficiency of waste fuel combustion. If this practice becomes widespread, it will offer another avenue for use of fuels from waste.

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