



*The Society for engineering
in agricultural, food, and
biological systems*

*Paper Number: 056132
An ASAE Meeting Presentation*

Fuel Properties and Characteristics of Saline Biomass

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**Written for presentation at the
2005 ASAE Annual International Meeting
Sponsored by ASAE
Tampa Convention Center
Tampa, Florida, USA
17-20 July 2005**

Abstract. *Integrated farm drainage management (IFDM) systems employ sequential reuse of water with biomass production to help control saline groundwater and improve the sustainability of arid land irrigated agriculture. Currently operating near Five Points, CA is a 640 acre IFDM demonstration project. Subsurface drainage water is reused to irrigate plants of increasing salt tolerance and produce crops which could be utilized in energy conversion. Combustion properties of biomass are influenced by the presence of chlorine, alkali and other metals, all of which may increase in concentration with drainage water reuse. Physical, chemical, structural, and fuel properties were determined for three species of biomass irrigated with saline drainage water, including two woods (Athel and Eucalyptus) and one grass (Jose Tall Wheatgrass). For each species, the as-harvested moisture content, heating value, proximate analysis (ash, volatiles, and fixed carbon), and concentration of acid-insoluble ash were determined. Wood and bark dry matter fractions were determined on both a volume and a mass basis along with apparent wood density. Structural carbohydrate fractions were found through NDF, ADF, and lignin determinations. Ultimate, ash, and water soluble alkali analyses and heavy metals and trace element concentrations were also conducted for each biomass species. Combustion fuel properties including ash volatilization, ash fusibility, and ash sulfur decomposition temperatures were determined. The Jose Tall Wheatgrass has high fouling potential for combustion systems, and the Athel exhibits high uptake of calcium and alkali sulfates.*

Keywords. Drainage water, irrigation water, salinity, alkali, biomass, combustion, fuel properties, leaching

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INTRODUCTION

Approximately 400,000 ha, or 40% of the total irrigable farm land in the lower Westside of California's San Joaquin Valley (SJV) is adversely affected by elevated water tables, drainage restrictions, and salt accumulation (Jenkins et al., 2003). The salinity problem experienced in the San Joaquin Valley is neither new nor unique, but occurs on a global scale with more than 7% of the world's landmass affected by high salinity. A large fraction of this is naturally occurring, as in coastal saline marshes, but about one third of all irrigated land suffers from a detrimental increase in salinity (Lambert and Turner, 2000).

Integrated on-farm drainage management (IFDM) systems sequentially reuse drainage water to irrigate plants of increasing salt tolerance to control groundwater levels through evapotranspiration. IFDM systems can decrease the total volume of drainage water requiring final disposal and processing by as much as 95% depending on crop, soil, and system management (USDOI/CRA, 1990). Several versions of IFDM systems have been used throughout the SJV and have successfully evaded toxic buildup of salts in the root zone or restored otherwise unusable lands (USDOI/CRA, 1990; Shannon et al., 1997; Lin et al. 2002). Biomass produced in IFDM systems can serve as feedstocks for energy conversion and biobased products, but uptake of salts and other elements influence biomass quality.

During combustion, alkali metals (primarily potassium and sodium) react with other inorganics found in biomass, including silica, sulfur, and chlorine, forming detrimental ash deposits and increasing corrosion rates on heat transfer surfaces (Turn et al., 1997). The high concentrations of alkali, sulfur, and chlorine in drainage water used in IFDM systems potentially are of concern in terms of uptake and concentration in biomass intended for energy conversion and other uses.

BACKGROUND

Typical drainage water in the San Joaquin Valley contains dissolved minerals including sulfates, chlorides, carbonates, and bicarbonates of elemental sodium, calcium, magnesium, and potassium, and elevated concentrations of toxic or potentially toxic elements including arsenic, boron, cadmium, strontium, copper, lithium, manganese, molybdenum, nickel, selenium, strontium, uranium, vanadium, and zinc (USDOI/CRA, 1990). The Valley is one of the top producing agricultural areas in the world (Jenkins et al. 2003). The SJV is composed of two geologic basins, the San Joaquin Basin, which drains northwards via the San Joaquin River and into the Sacramento-San Joaquin River Delta and the Tulare Basin, a hydraulically closed basin, comprising the southern half of the valley. Nearly all commercial crops grown in the SJV require irrigation (USDOI/CRA, 1990; Jenkins et al., 2003). Soils on the western side of the Valley are derived from Coast Range alluvium (marine-base sediments) and are high in salts and trace elements including Se, B, Mo, and As. Crop irrigation has expedited the movement

of salts and trace elements into shallow groundwater, making farming on the westside of the Valley largely unsustainable without proper salt management (Jenkins et al., 2003).

The IFDM system sequentially uses drainage water to irrigate crops of increasing salt tolerance. Fresh irrigation water, much of it provided through aqueducts transporting water from the north, has low salinity and Se concentrations and is used to irrigate salt-sensitive crops. Although total dissolved solids are generally low, the large volumes of fresh water imported result in the distribution of more than 2 Tg of salts across agricultural lands (Jenkins, et al., 2003). The drainage water following the first irrigation is collected via subsurface drains and used to irrigate salt-tolerant crops. The collection and reuse of the drainage water continues through crops of increasing salt-tolerance including trees, grasses, and halophytic plants. The total volume of applied irrigation water requiring final disposal is reduced by 80-95%, primarily through evapotranspiration (USDOI/CRA, 1990; Shannon et al., 1997; Lin et al. 2002). The remaining water is eventually disposed of through evaporation or other physical processes, leaving salts and trace elements for final disposal or recovery.

The properties of biomass produced in IFDM systems have not yet been extensively investigated. Happ, et al. (1990) compared Se contents of *Eucalyptus camaldulensis* whole tree samples grown in conjunction with an IFDM system operating in Mendota, CA with whole tree samples irrigated with fresh water. Se concentrations for saline-irrigated Eucalyptus averaged 0.28 ppm (mass) and ranged as high as 0.91 ppm, about 5 times the concentrations in fresh-water irrigated samples. For both saline and fresh water irrigation, the Se concentration in the bark fraction was roughly double that of the wood concentration. The Se content of Athel collected from a natural stand in the SJV had Se contents up to 2.06 ppm for primary wood, 1.06 ppm for bark, and 2.58 ppm for leaf. Combustion of saline Eucalyptus was carried out at 700, 800, and 850°C, with over 80% of the fuel Se found in the particulate matter and vapor phases of the exhaust gas (Happ, et al., 1991).

Fireside fouling occurs during combustion when ash materials deposit on heat exchangers, such as the tube surfaces of superheaters in boilers of steam power plants. Slagging results from melting of ash constituents, forming glassy masses in furnaces. In dry ash furnaces, slagging is undesirable whereas in wet furnaces, the viscosity of slag is important to its removal. Most biomass furnaces are of the dry type, and slagging can cause substantial operating difficulties. A related phenomenon is that of agglomeration in fluidized bed reactors and furnaces. Reactions between the bed material and elements in the fuel ash can cause bed grains to agglomerate in sufficiently large masses to defluidize the bed.

The major elements involved in ash fouling and slagging are the alkali metals, primarily potassium and sodium, reacting typically with silica in the fuel ash (Jenkins et al., 1998). The alkaline-earth metals also contribute to slag and deposit formation. Chlorine, in addition to its role in corrosion and acid gas formation, has also been shown to influence fouling. Chlorine facilitates alkali vaporization during combustion and can accelerate the

transport of many inorganic compounds, including potassium and sodium (Baxter et al., 1996).

Primary pollutant emissions of concern for combustion systems include particulate matter, sulfur oxides (SO_x), nitrogen oxides (NO_x), acid gases, and hazardous air pollutants. SO_x and NO_x emissions lead to acid precipitation and are also involved in the formation of respirable particulate matter through reactions with other compounds in the atmosphere such as NH₃. In addition, NO_x is important to the formation of tropospheric ozone, a key component of photochemical smog in urban areas (Seinfeld and Pandis, 1997). Increasing sulfur and nitrogen uptake by plants leads to higher uncontrolled emissions of sulfur and nitrogen oxides in combustion of the biomass.

METHODS

COLLECTION AND PROCESSING

Red Rock Ranch is a farm located near Five Points, CA, in Fresno County. The farm currently operates a 260 ha (640 acre) IFDM demonstration project. Salt-tolerant biomass species investigated include two types of woods (softwood species Athel Tree, *Tamarix aphylla* (L)), and hardwood species Eucalyptus, *Eucalyptus camaldulensis*) and a perennial grass (Jose Tall Wheatgrass, *Agropyron elongatum*).

Samples of IFDM system biomass were collected from Red Rock Ranch during February, 2004. Approximately 1000 kg (2200 lb) samples of both Athel and Eucalyptus logs (minimum diameter 5 cm) were harvested via chainsaw from a grove of 7-10 year old trees. Trunk and branch wood were taken from 3 different Athel trees and 16 Eucalyptus trees. In addition, approximately 100 kg (220 lbs) of leaves and branches from each species were collected and air-dried. The wood species were separately chipped using a 12" Dosko Brush Chipper (Model 1400-12). Prior to chipping the logs were examined for signs of mold or other contaminants, and affected log ends were removed. The chips were air-dried to moisture content of less than 14% wet basis, well mixed, divided, and stored in plastic bags indoors on a concrete pad.

Twenty of 1580 bales (dimension 0.4m x 0.6m x 0.9m) of Jose Tall Wheatgrass were collected in May, 2004 from a 16 ha field. Two core samples of approximately 50 g were removed from each bale using a 2.5 cm (1") diameter forage sampler. Cores from each bale were combined into a single bale sample. A 20-bale composite sample was produced from individual 10 g dry weight samples from each bale.

ANALYTICAL METHODS

Prior to analysis biomass samples were hammermilled to pass a 1 or 2 mm screen and oven dried (ASTM E871).

Physical Properties

Moisture content

As-harvested moisture contents (MC) were determined over 24h in air at 104°C (ASTM E871) for the overall branch wood and leaf and needle composites for each wood. Dry

matter fractions (by mass) were calculated for both branch wood and leaves or needles. As-received MC was also determined for each Jose Tall Wheatgrass bale sample.

Dry matter fractioning

Prior to chipping, both woods were separated into log diameter classes. Approximately 30% of the logs within each diameter class were randomly selected and sectioned into slabs 2.5 cm (1") thick. Slabs were weighed and air-dried. Measurements of each slab were made of major, minor, and average diameter, bark thickness, heartwood diameter (Eucalyptus only), and thickness at five points including the center and four perimeter locations. Bark, wood, and heartwood (Eucalyptus only) volume fractions were calculated. Each slab was then separated into bark and wood components and slab components were oven dried to determine the dry matter mass fractions. Cubes of approximately 16.4 cm³ (1 in³) were taken from slabs of each wood. Surfaces were sanded smooth and cubes were oven dried, weighed, and measured for volume to obtain dry wood density.

Air dry weights were taken for each Jose Tall Wheatgrass bale. Approximately 60 whole plants were removed from a single bale to determine ash distribution among the plant fractions. The plants were separated into leaf plus sheath and stem fractions. The sheath/leaf samples were segregated by position outward from the stem with samples designated 1 for the center stem, 2 for the adjacent sheath/leaf, and so on. Each fraction was separately hammermilled through 2 mm and ashed according to ASTM D1102.

Structural Composition

Structural composition, including cell contents, cellulose, hemicellulose, and lignin were conducted on single sample of each biomass type by the DANR chemical laboratory, UC Davis, CA, using neutral detergent fiber (NDF), acid detergent fiber (ADF), lignin, and ashing determinations.

NDF is the collective amount of cellulose, hemicellulose, and lignin in a sample, and is determined through digestion with a pH neutral detergent (pH 6.9-7.1). From the NDF value, the cell contents or extractives which include the fractions of protein, starch, sugar, organic acids, and pectin can be calculated. To determine ADF, the sample is digested with a strong acid detergent, primarily a combination of cetyl trimethylammonium bromide (CTAB) and sulfuric acid (H₂SO₄). ADF yields the amount of cellulose and lignin in the sample. The difference between the NDF and ADF values is the hemicellulose content of the sample. Lignin determination is done through digestion with a strong acid, primarily 72% H₂SO₄. The difference between the ADF and lignin values is the cellulose content of the sample. During each of these steps a fraction of inorganic material is lost due to leaching. The inorganic fraction remaining in the sample was determined by ashing in air at 575°C (ASTM D1102).

Chemical Composition

Ultimate elemental, elemental ash, and water-soluble alkali concentrations were analyzed by Hazen Research Inc. (Golden, CO) using single samples of each biomass species.

Concentrations of metals including B, Zn, Mg, Cu, Se, As, Ba, Cd, Cr, Co, Pb, Mo, Ni, and V, extractable K and Cl concentrations, and a supplemental N-P-K panel were determined for single samples of each biomass by the DANR chemical laboratory, UC Davis.

Fuel Properties

Proximate analysis /higher heating value

Biomass samples were subjected to a proximate analysis to determine moisture and ash, volatile matter, and fixed carbon according to ASTM E871, D1102, and E872. For Athel and Eucalyptus, bark/wood composites and wood without bark samples were analyzed. The ash content (12 replicates per woods and a single sample per bale) was determined by igniting a 1.5 g (dry) milled (1 mm) sample while heating to 575°C in an air muffle furnace and holding for 3 h (ASTM D1102). Volatile matter (5 replicates per wood and a single sample per bale) was determined by heating the sample at 950°C for 7 minutes in a covered nichrome metal crucible producing a non-oxidizing atmosphere (ASTM E872). Fixed carbon was calculated from the difference of the sum of volatile matter (%) and ash content (%) from 100 percent dry matter. The higher heating value at constant volume was determined by adiabatic bomb calorimeter for single samples of wood only and wood-bark composites for Athel and Eucalyptus and a split 20 bale composite sample of Jose Tall Wheatgrass as per ASTM E711/D2015.

Acid-insoluble ash content

A modified TAPPI T244 om-93 procedure (Blunk et al., 2003) was used to determine acid-insoluble ash in triplicate determinations. Acid-insoluble ash content loosely corresponds to the amount of silica present in the sample. Approximately 0.2-0.5 g of ash produced according to TAPPI T211 om93 (3h at 525°C) was placed in quartz crucibles and weighed. Samples were acid extracted in a steam bath at 100°C. Five mL of 6M HCl was added to each sample 3 times at 45 min intervals. After the final acid addition, the sample was filtered through Whatman 42 filter paper, re-ashed according to TAPPI T211 om-93, and weighed. The acid-insoluble ash content was calculated as the residual ash per unit mass original dry matter.

Ash volatility

To determine the fractional amounts of ash volatilized at temperatures above 575°C, the ash samples were slowly heated (8-15°C min⁻¹) in an air atmosphere muffle furnace, held for 2 h at each temperature, cooled to ambient, and weighed to determine the ash fraction. Temperatures used were 575, 750, 900, and 1000°C. The number of experimental replicates were 12 at 575°C, 9 at 750°C, 6 at 900°C, and 3 at 1000°C. The fraction of volatile ash may be related to the fouling potential due the presence of volatile inorganics available for deposition on equipment (Yomogida and Jenkins, 1997), but can also include carbonate decomposition.

Fusibility characteristics of ash

Numerous methods have been devised to determine the initial deformation and critical fusion temperatures for fuels. These temperatures indicate the extent of liquid formation and can be used as an indicator for predicting fouling and slagging behaviors. The whole

fuel fusibility method used here utilized raw fuel samples as opposed to the calcined pyrometric-cone ash samples employed by ASTM D1857/E953 and is believed to more accurately characterize the early fusion behavior of biomass, in particular the initial formation of the liquid ash phase (Jenkins et al., 1996).

One gram pellets of biomass were tested at 50°C increments over the temperature range 800-1550°C. Each pellet with pre-fired refractory support was weighed and placed into a pre-heated Kanthal EPD high temperature melting furnace for 20 minutes. The support and residue were removed from the furnace, cooled to ambient temperature in a desiccator, and weighed. The final physical characteristics of the remaining pellets were evaluated according to the rating procedure of Jenkins et al. (1996) and Yomogida and Jenkins (1997).

Sulfur volatilization

The SO₂ concentration in furnace gas was measured during controlled heating of Athel ash pellets from ambient to 1300°C at 10°C min⁻¹. SO₂ was analyzed on recirculated furnace gas using a Horbia model PG-250 combustion gas analyzer (Horiba Instruments, Irvine, CA). Ambient air was metered to the furnace at a controlled rate of 10 L min⁻¹. A 1.7-2.0 g pellet of Athel ash was placed on a pre-fired alumina support and inserted into the cold furnace. Sulfur balances were computed for each experiment. Weight change and appearance of each ash pellet was recorded. Individual samples of loose powders of reagent grade CaSO₄, K₂SO₄, and Na₂SO₄ were also tested to establish specific decomposition temperature ranges under the same furnace conditions.

RESULTS

PHYSICAL PROPERTIES

Dry matter fractions and moisture contents for the three biomass types are listed in Table 1. Dry matter fractions by both mass and volume for wood slab samples are listed in Table 2. Jose Tall Wheatgrass bales weighed 27.2-40.4 kg wet, yielding an average 31 kg dry matter and dry bale density of 143 kg m⁻³. Ash and moisture contents of the Jose Tall Wheatgrass fractions are given in Table 3.

Table 1. Moisture contents and dry matter fractions for Athel, Eucalyptus, and Jose Tall Wheatgrass.

| Species | Overall MC (% wb) | Dry Matter Fractions (%) | | | |
|-----------------------------------|----------------------|--------------------------|-------------------|-----------------|-------------------------------|
| | | Primary Wood | Secondary Wood | Needle/ Leaf | Seed Pod (Eucalyptus only) |
| Athel (cut 11-Feb) | 68.65 | 26.77 | 18.83 | 54.40 | -- |
| Eucalyptus (cut 9-Feb)* | 29.45 | 19.07 | 16.69 | 59.10 | 5.14** |
| Eucalyptus (cut 11-Feb) | 58.18 | 14.24 | 23.57 | 62.19 | 0 |
| Jose Tall Wheatgrass ⁺ | 8.42 | -- | -- | -- | -- |

-- Not applicable

* Tree cut on 9-Feb-2004 and branch fractions collected 11-Feb-2004.

** Seed pods only found on some of the Eucalyptus trees.

Primary wood defined as any wood not directly in contact with needles/ leaves or pods.

Secondary wood defined as any wood directly connected to needles/ leaves or pods.

+ Average moisture content of core samples from 20 bales.

Table 2. Dry matter fractions and wood density by log diameter class for Athel and Eucalyptus.

| Species | Diameter Range* (cm) | Total Logs | Number Logs Sampled | Mean Fractions (% volume) | | | | Mean Fractions (% mass) | | | Density (g cm ⁻³) | |
|------------|----------------------|------------|---------------------|---------------------------|-------|------------|-------|-------------------------|-------|------------------|-------------------------------|--------|
| | | | | Bark | Wood | Heart-wood | Total | Bark | Wood | Fractional Total | DMF+ | Cube++ |
| Athel | 5-10 | 46 | 14 | 19.41 | 80.59 | -- | 100 | 15.63 | 84.37 | 100 | 0.83 | -- |
| | 10-15 | 61 | 18 | 20.90 | 79.10 | -- | 100 | 16.55 | 83.45 | 100 | 0.81 | 0.68 |
| | 15-20 | 22 | 7 | 17.88 | 82.12 | -- | 100 | 15.54 | 84.46 | 100 | 0.66 | 0.67 |
| | >20 | 10 | 4 | 18.43 | 81.57 | -- | 100 | 15.88 | 84.12 | 100 | 0.65 | 0.68 |
| Total | -- | 139 | 43 | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| Overall | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | 0.78 | 0.68 |
| Eucalyptus | 0-5 | 49 | 15 | 10.54 | 62.61 | 26.85 | 100 | 15.48 | 84.52 | 100 | 0.82 | -- |
| | 5-7.5 | 70 | 21 | 13.71 | 77.45 | 8.84 | 100 | 16.91 | 83.29 | 100 | 0.75 | -- |
| | 7.5-10 | 72 | 21 | 13.65 | 72.91 | 13.44 | 100 | 17.41 | 82.59 | 100 | 0.78 | 0.65 |
| | 10-12.5 | 67 | 20 | 16.08 | 67.25 | 16.67 | 100 | 17.69 | 82.11 | 100 | 0.86 | -- |
| | 12.5-15.25 | 35 | 11 | 15.65 | 67.85 | 16.50 | 100 | 16.16 | 83.94 | 100 | 0.75 | 0.66 |
| | 15.25-17.5 | 17 | 5 | 16.78 | 67.57 | 15.65 | 100 | 17.54 | 82.46 | 100 | 0.71 | 0.66 |
| | >17.5 | 12 | 4 | 17.36 | 60.33 | 22.31 | 100 | 18.50 | 81.40 | 100 | 0.69 | 0.68 |
| Total | -- | 322 | 97 | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| Overall | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | 0.78 | 0.67 |

*Not included here are logs that were split or Y-shaped (9 Athel logs and 6 Eucalyptus logs).

+Density based on dry matter fractioning (DMF) and slab mass and volume data.

++ Density based on mass and volume of wood cubes cut from slabs.

-- Not applicable or not determined.

Table 3. Ash and moisture contents of Jose Tall Wheatgrass fractions.

| Fraction | MC (%db) | Ash (% dm) |
|--------------------------------------|-------------|-------------|
| (1) Stem | 8.64-8.90 | 6.47-6.49 |
| (2) Leaf | 7.38-8.37 | 7.10-7.17 |
| (2) Sheath | 9.35-9.99 | 7.06-7.19 |
| (3) Leaf | 8.35-8.72 | 9.09-9.21 |
| (3) Sheath | 8.72-8.75 | 7.68-7.74 |
| (3) Bottom Sheath | 11.83-13.06 | 6.16-6.27 |
| (4) Leaf (outermost) | 8.04-8.58 | 10.72-10.73 |
| (4) Sheath (outermost) | 9.08-10.09 | 8.13-8.22 |
| Average | 9.14 | 7.85 |
| Bale Average (based on core samples) | 7.89 | 8.83 |

STRUCTURAL PROPERTIES

Structural carbohydrate fractions were determined for each biomass type (Table 4). A large variation in cell contents was observed for the saline woods, 24.9% for Athel and 15.8% for Eucalyptus, with Eucalyptus comprised of over 57% cellulose compared to 49% for Athel. The lignin values for both woods was lower than expected (11.9 for Athel and 13.1% for Eucalyptus), with typical wood lignin content ranging from 20-28% (Jenkins, 1993). Jose Tall Wheatgrass is over 11% protein, with similar cellulose and hemicellulose contents, 28.92% and 29.36%, respectively.

CHEMICAL PROPERTIES

Ultimate, elemental ash, and water soluble alkali analyses, in addition to trace element concentrations for each saline biomass are listed in Table 4. Athel has high fuel N and S concentrations for wood, 0.71 and 1.26% dm, respectively. Athel ash is surprisingly high in sulfates; with over 70% of the total fuel sulfur accounted for in the ash at 600°C. Athel had almost nine times the Se concentration of Eucalyptus along with elevated concentrations of B, Cu, and Zn. The Eucalyptus ash appears to contain a large fraction of CaCO₃, sequestering almost 8% of the total fuel carbon.

Jose Tall Wheatgrass had a high total fuel Cl concentration of 1.72% and an ash mainly comprised of SiO₂, Na₂O, K₂O, and Cl; most likely present as NaCl and KCl in the ash. The B and Se contents were also high at 319 and 5.11 ppm, respectively.

FUEL PROPERTIES

Wood ash contents for both Athel and Eucalyptus (4.5% for Athel wood and 0.7% for Eucalyptus wood) were lower than the ash contents of composite wood and bark samples (7.1% and 2.8%, respectively) (Table 5). For Athel, there was little difference in higher heating value (HHV) for the samples with and without the bark fraction (17.44 MJ kg⁻¹ for the composite and 17.58 MJ kg⁻¹ for the wood only sample). The Eucalyptus HHV saw an increase of slightly over 1 MJ kg⁻¹ for the wood only sample (18.85 MJ kg⁻¹) when compared to the bark and wood composite (17.80 MJ kg⁻¹), a result consistent with the higher ash content of the composite (Jenkins, 1993). HHVs for bark calculated on the basis of the mass fractions (Table 2) and wood and composite heating values (Table 5) are 16.68 MJ kg⁻¹ for Athel bark and 12.77 MJ kg⁻¹ for Eucalyptus bark.

Table 4. Structural and chemical compositions of composite samples of Athel and Eucalyptus woods and Jose Tall Wheatgrass.

| | Athel | Eucalyptus | Jose Tall Wheatgrass |
|---|--------------|-------------------|-----------------------------|
| Structural Composition (% dm) | | | |
| Cell Contents | 24.89 | 15.75 | 38.91 |
| Protein ⁺ | 4.0 | 2.1 | 11.2 |
| Cellulose | 49.34 | 57.14 | 28.92 |
| Hemicellulose | 13.89 | 14.01 | 29.36 |
| Lignin | 11.88 | 13.10 | 2.81 |
| Total ⁺ | 100.00 | 100.00 | 100.00 |
| Ultimate Analysis (% dm) | | | |
| C | 48.87 | 51.95 | 47.68 |
| H | 5.68 | 5.94 | 5.90 |
| N | 0.71 | 0.36 | 1.83 |
| S | 1.26 | 0.02 | 0.35 |
| Cl | 0.15 | 0.1 | 1.72 |
| Ash | 5.39 | 1.90 | 8.74 |
| O (by difference) | 37.94 | 39.73 | 33.78 |
| Total | 100.00 | 100.00 | 100.00 |
| Supplemental N-P-K Panel (% dm) | | | |
| N (total) | 0.64 | 0.33 | 1.79 |
| P (total) | 0.11 | 0.02 | 0.09 |
| K | 0.32 | 0.14 | 1.24 |
| Trace Elemental Analyses (mg kg⁻¹ dm) | | | |
| As (total) | 0.11 | <0.05 | 0.08 |
| B (total) | 27 | 13 | 319 |
| Cu (total) | 3.8 | 2.1 | 3.6 |
| Mn (total) | 7 | 18 | 42 |
| Se (total) | 0.9 | 0.12 | 5.11 |
| Zn (total) | 19 | 6 | 13 |
| Ba | 1.2 | 1.0 | 1.8 |
| Cd | 0.3 | <0.2 | <0.2 |
| Co | <0.2 | <0.2 | <0.2 |
| Cr | 0.6 | <0.2 | 0.4 |
| Mo | <0.1 | <0.1 | 0.6 |
| Ni | 2.0 | <1.0 | <1.0 |
| Pb | 1.0 | <0.5 | <0.5 |
| V | <1.0 | <1.0 | <1.0 |

Table 4. Structural and chemical composition of Athel and Eucalyptus woods and Jose Tall Wheatgrass (continued).

| Elemental Analysis of Ash (% ash)* | Athel | | Eucalyptus | | Jose Tall Wheatgrass | |
|-------------------------------------|-------------|------------|-------------|------------|----------------------|------------|
| | As-analyzed | Normalized | As-analyzed | Normalized | As-analyzed | Normalized |
| SiO ₂ | 2.75 | 2.59 | 2.92 | 2.87 | 26.72 | 25.98 |
| Al ₂ O ₃ | 1.29 | 1.22 | 1.00 | 0.98 | 2.59 | 2.52 |
| TiO ₂ | 0.03 | 0.03 | 0.02 | 0.02 | 0.04 | 0.04 |
| Fe ₂ O ₃ | 0.61 | 0.57 | 0.26 | 0.26 | 0.42 | 0.41 |
| CaO | 22.70 | 21.39 | 38.40 | 37.79 | 3.52 | 3.42 |
| MgO | 9.73 | 9.17 | 5.83 | 5.74 | 2.26 | 2.20 |
| Na ₂ O | 9.17 | 8.64 | 5.02 | 4.97 | 22.10 | 21.49 |
| K ₂ O | 8.63 | 8.13 | 10.10 | 9.94 | 17.00 | 16.53 |
| P ₂ O ₅ | 9.27 | 8.74 | 3.23 | 3.18 | 5.04 | 4.90 |
| SO ₃ | 41.13 | 38.76 | 2.16 | 2.13 | 3.55 | 3.45 |
| Cl | 0.42 | 0.40 | 3.31 | 3.26 | 19.35 | 18.81 |
| CO ₂ | 0.38 | 0.36 | 29.36 | 28.89 | 0.26 | 0.25 |
| Total | 106.11 | 100.00 | 101.61 | 100.00 | 102.85 | 100.00 |
| Water Soluble Alkali (% ash) | | | | | | |
| Na ₂ O | 0.476 | | 0.066 | | 1.784 | |
| K ₂ O | 0.439 | | 0.205 | | 1.378 | |

+ Cell Contents includes protein, starches, sugars, organic acids, and pectin. The protein value given is included in the cell contents value.

*samples ashed at 600°C prior to analysis

The ash content of Jose Tall Wheatgrass ranged from 7.4-9.7% dm, with volatile matter and fixed carbon between 74.4-77.0% and 15.4-16.9%, respectively. Higher heating value of the 20-bale composite sample was 16.67 MJ kg⁻¹, lower than wheat straw and other grasses of the same ash content.

Alkali Index

The alkali index, expressed as the mass of alkali in the fuel per unit energy content, is a crude measure of the fouling propensity of a fuel. Athel has an alkali index of 0.28 kg alkali GJ⁻¹, which would be expected to generate moderate fouling. Little fouling would be expected to occur for Eucalyptus, with an alkali index of 0.03 kg alkali GJ⁻¹. Alkali index for Jose Tall Wheatgrass, 1.65 kg alkali GJ⁻¹, implies an extremely high fouling potential.

Ash Volatilization

Athel showed little (<5%) change in ash concentration for temperatures up to 900°C (Table 5), but lost 15% at 1000°C, due most likely to sulfate decomposition. Eucalyptus ash showed an almost 30% drop in ash weight between 575°C and 750°C, most likely as a result of carbonate decomposition. The amount of ash recovered at 1000°C was small, making observations difficult, but sintering of the ash was limited.

Jose Tall Wheatgrass showed a continual decrease in ash concentration through 1000°C. Ash sintering was observed at 750°C, the ash was fully fluid at 900°C, and largely fused to the test crucibles at 1000°C. Ash color changed from uniform dark-grey to deep green at 750°C, then to a brown-green at 900°C, and finally to clear at 1000°C, possibly corresponding to changes in alkali metal concentrations.

Whole Fuel Fusibility

Athel and Eucalyptus ashes showed signs of sintering in whole-fuel ash fusibility experiments beginning at 850°C and 950°C. Athel lost 96.1% of the original fuel mass at 800°C compared to 97.9% at 1500°C, corresponding to a 47% decrease in ash weight. Eucalyptus weight loss remained constant at 98.9% for the entire temperature range, 800-1400°C. Jose Tall Wheatgrass ash was slagged and fused to the support during the initial 800°C run, with 93.5% of the original fuel mass volatilized. The ash was fully fluid at 1300°C, with a 95.5% volatilization of the original fuel and a 71% decrease in ash weight.

The fusibility findings compare well to the ash volatilization experiments, which showed a significant weight loss for Athel ash at temperatures over 900°C, little change in Eucalyptus ash weight above 750°C, and a continual decrease in Jose Tall Wheatgrass ash at temperatures above 575°C.

Table 5. Fuel properties of Athel, Eucalyptus, and Jose Tall Wheatgrass.

| Proximate Analysis (% dm) | Athel ^a | | Eucalyptus ^a | | Jose Tall Wheatgrass ^b |
|--|--------------------|-----------|-------------------------|-----------|-----------------------------------|
| | Composite | Wood Only | Composite | Wood Only | |
| Ash (3h @ 575°C) | 7.07 | 4.51 | 2.76 | 0.67 | 8.29 |
| Volatile Matter | 78.98 | 82.19 | 81.70 | 82.43 | 75.58 |
| Fixed Carbon | 13.96 | 13.30 | 15.54 | 16.90 | 16.13 |
| Total | 100.01 | 100.00 | 100.00 | 100.00 | 100.00 |
| Acid-insoluble ash content (% dm) | 0.11 | -- | 0.01 | -- | 2.40 |
| Higher heating value (MJ/dry kg)* | 17.44 | 17.58 | 17.58 | 18.85 | 16.67 |
| Alkali Index (kg alkali/GJ)* | 0.28 | -- | 0.03 | -- | 1.65 |
| Ash Volatilization (% dm) | Athel | | Eucalyptus | | Jose Tall Wheatgrass |
| Ash Remaining at 575°C | 5.50 | | 2.24 | | 8.85 |
| Ash Remaining at 750°C | 5.45 | | 1.58 | | 7.45 |
| Ash Remaining at 900°C | 5.30 | | 1.55 | | 5.76 |
| Ash Remaining at 1000°C | 4.60 | | 1.63 | | 5.51 |
| Whole Fuel Ash Fusion Temperatures (°C) ⁺ | | | | | |
| Stage 1: | 800 | | 800 | | na |
| Stage 2 | 850 | | 950 | | na |
| Stage 3 | 1150 | | 1200 | | na |
| Stage 4 | 1250 | | 1350 | | 800 |
| Stage 5 | 1450 | | -- | | 1100 |
| Stage 6 | 1500 | | 1400 | | -- |

a Unless noted, analysis is conducted on composite samples (bark and wood) for Athel and Eucalyptus

b Proximate analysis values based on average for a single sample from each of the 20 bales. Ash volatilization and fusibility determinations used a 20-bale composite fuel sample.

-- not determined

* Based on higher heating value not corrected for S

na: not applicable. Fusion apparent beginning at 800°C.

+ Oxidizing atmosphere. Based on Whole Fuel Ash Fusibility Method set forth by Yomogida and Jenkins (1997):

Stage 1: No apparent sintering of ash particles on pellet or pellet to refractory support.

Stage 2: Weak sintering of particles in pellet, high porosity, pellet free of refractory support (generally observed at temperatures below ASTM initial deformation temperature)

Stage 3: Pellet contracted to spherical shape with rough surface texture, particles strongly sintered, low porosity surface, slagged to refractory support.

Stage 4: Pellet contracted to smooth spherical shape, slagged to refractory support.

Stage 5: Ash fully molten with flat shape and thickness less than approximately 2 mm (equivalent to ASTM fluid temperature).

Stage 6: Ash vaporized or absorbed by refractory support with no measurable thickness.

Sulfur Volatilization

Athel ash is largely comprised of calcium, sodium, and potassium sulfates (Table 4). Samples of pure CaSO_4 began to decompose at 700°C with peak SO_2 concentration achieved at 900°C for the furnace temperature ramp used (Figure 1). Decomposition of Na_2SO_4 began at 925°C with peak SO_2 concentration at 1260°C . K_2SO_4 decomposition began around 1150°C with peak SO_2 concentrations at 1280°C . Athel ash SO_2 concentration follows both the CaSO_4 volatilization curve and the Na_2SO_4 and K_2SO_4 volatilization curves (Figure 1). The Na_2SO_4 reacted with or dissolved the alumina support and may be responsible for the vertically truncated concentration curve and only 30% of sulfur accounted for as SO_2 . SO_2 closure for the Athel ash ranged from 30-64% (4 replicates), but SO_2 emission profile was consistent among replicates. Sulfur closure for CaSO_4 was 111%, with no evidence of a reaction between the CaSO_4 and the support.

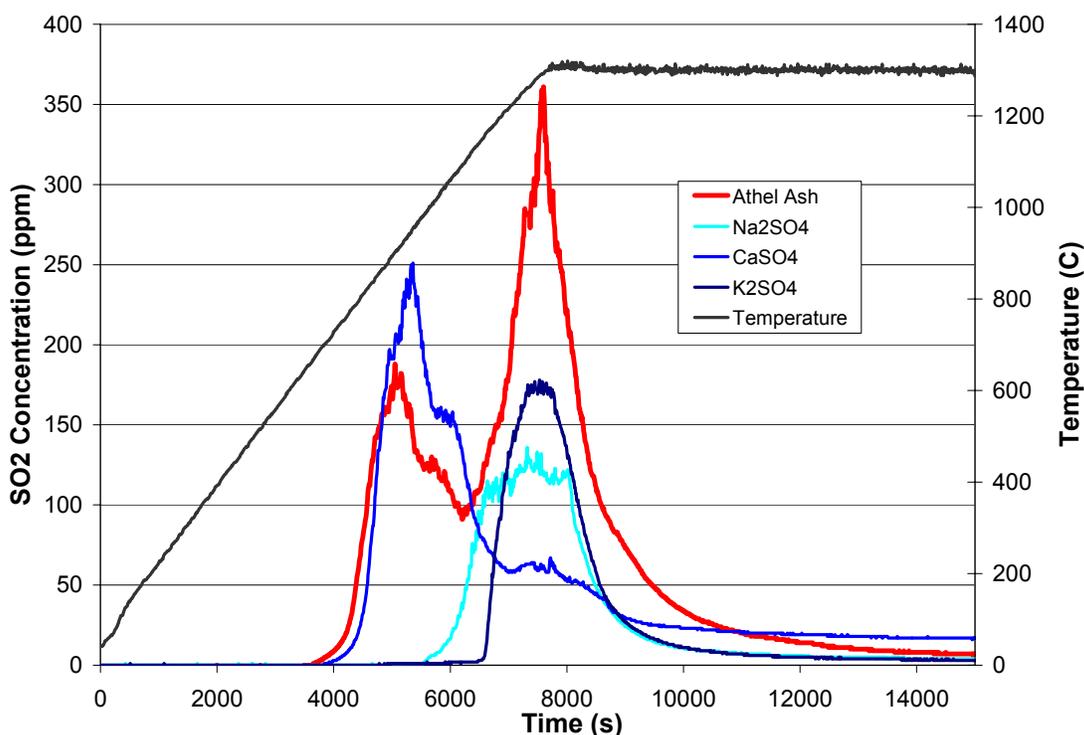


Figure 1. SO_2 emission profiles for Athel ash and pure samples of CaSO_4 , K_2SO_4 , and Na_2SO_4 .

DISCUSSION

The compositional variations among the three biomass species evaluated illustrate the diversity in element uptake characteristics among plants. Sulfates and chlorides in arid land soils are known also to influence trace element behavior (Kabata-Pendias and Pendias, 1992). Heavy metal sulfates are readily available to plants. The high sulfate uptake by Athel, for example, may at least partially account for the high levels of certain metals including Se, Zn, Ba, Cr, Ni, and Pb observed in the ash. Eucalyptus, which appears to have excluded sulfates for the most part, exhibits lower concentrations in ash.

Selection of a crop species for the phytoremediation employed under IFDM cannot be based purely on the resulting biomass properties. Agronomic requirements, water use rates, biomass yields, and economics of the cropping system must also be considered. The properties of the resulting biomass heavily influence the feasibility of various utilization options, however. The properties of Athel and Jose Tall Wheatgrass make them less desirable as fuels for direct combustion biomass power plants compared to the Eucalyptus, for example. Both Athel and wheatgrass take up greater amounts of salts and heavy metals than Eucalyptus, and so may be preferred from a soil remediation standpoint. The low uptake by Eucalyptus leaves open the same range of utilization options for the biomass as for fresh water irrigated trees while still contributing to drainage water reduction. Prior studies evaluating Athel (tamarisk) and Eucalyptus for phytoremediation of arsenic-affected soils showed Eucalyptus water use per unit shoot mass to be higher than that of tamarisk, although water use by both species declined substantially when exposed to high levels of sodium (Tossell, et al., 1998).

Athel wood has high fuel N, S, and Cl concentrations and a largely CaSO_4 -based ash. It is a high ash wood and is at least a moderate fouling fuel in combustion as measured by the alkali index. At temperatures below 900°C , Athel ash is relatively stable, realizing an ash weight loss of only 4%, but emits high levels of SO_2 as sulfate which begins to decompose above 900°C . SO_2 volatilization experiments showed sulfur decomposition occurring in two temperature regimes, $670\text{--}1100^\circ\text{C}$ corresponding to SO_2 release primarily from CaSO_4 , and, $1100\text{--}1300^\circ\text{C}$ corresponding to Na_2SO_4 and K_2SO_4 decomposition. These results are consistent with the ash volatilizations results, with CaSO_4 reaching its peak S decomposition around 900°C . Whole fuel fusibility analysis suggests that Athel ash could begin to show signs of a liquid formation at 850°C , although a fully fluid state was not achieved until 1450°C . As most biomass boilers operate at temperatures of at least 1000°C , both sulfur emissions and ash fouling would be of concern. Studying the S release may give insight into the volatility of Se which could also be important from an emissions standpoint. The high nitrogen contents of Athel and Jose Tall Wheatgrass would also lead to formation of high concentrations of NO_x needing control in combustion systems. Gasification, bioconversion, and other utilization options may be needed for handling these materials (Klass, 1998). Matching biomass properties with utilization technique is particularly important to overall system design for these more active accumulator species.

Eucalyptus appears to exclude salts and metals, having instead an ash with high CaCO_3 concentration. This result is consistent with the 30% decrease in ash weight observed from 575 to 750°C corresponding to the carbonate decomposition temperature regime. Eucalyptus with its low ash content and low alkali index could be used as a fuel for direct combustion units. Soil conditions and irrigation water composition seemed to have little influence on Eucalyptus, other than elevations in Ca, carbonate, and trace amounts of B, Cu, and Mn.

The Jose Tall Wheatgrass ash contains elevated concentrations of alkali and Cl, and greater than 35% silica content, with a resulting alkali index of 1.65 indicating heavy fouling propensity. Over 30% of the wheatgrass ash volatilized in almost direct proportion to temperatures up to 1000°C, with sintering observed at 750°C. Fusibility testing showed wheatgrass slagging at 800°C, the lowest temperature explored. Wheatgrass also has elevated B and Se concentrations. In contrast to Athel, wheatgrass appears to more selectively uptake and sequester NaCl. Crop selection may then prove useful in more selectively removing salts from affected soils and possibly extracting purified products. As-harvested Jose Tall Wheatgrass would not be appropriate in most combustion environments without some form of pretreatment, such as leaching, but based on structural composition wheatgrass might be a suitable feedstock in biochemical conversion processes not suffering from the ash composition limitations of combustion.

CONCLUSIONS

Biomass crops grown in integrated on-farm drainage management (IFDM) systems that employ sequential reuse of drainage water exhibit substantial variation in uptake of salts and metals. Athel trees appear to be specific accumulators of sulfates whereas Jose Tall Wheatgrass appears to preferentially accumulate chlorides. Eucalyptus was largely unaffected in ash composition by irrigation with saline drainage water and sustained lower concentrations of heavy metals in contrast to the species concentrating sulfates and chlorides. Of the three crops evaluated, only Eucalyptus would likely prove directly suitable for use in combustion furnaces and boilers without some form of pretreatment or blending with higher quality fuels. High N and S concentrations in Athel and Jose Tall Wheatgrass would result in high uncontrolled emissions of NO_x and SO_x as well. The selective uptake characteristics of Athel and wheatgrass, however, potentially offer alternative recovery and management techniques for sulfates, chlorides, and other constituents. Further field trials and experiments are needed to confirm these results and to investigate the use of these materials in energy conversion processes.

ACKNOWLEDGMENTS

This work was supported by a grant from the California Department of Water Resources. The cooperation of Red Rock Ranch, Five Points, California, is also gratefully acknowledged.

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