

THERMOGRAVIMETRIC CHARACTERIZATION OF IRRIGATED BERMUDAGRASS AS A COMBUSTION FEEDSTOCK

K. B. Cantrell, P. G. Hunt, K. S. Ro, K. C. Stone, M. B. Vanotti, J. C. Burns

ABSTRACT. *The bioenergy production industry can benefit from a greater understanding of potential differences among the various feedstock materials and production influences on thermochemical conversion processes such as combustion. The thermal degradation of biomass during combustion can quickly be assessed using thermogravimetric analysis (TGA) to provide a thermal profile for global characterization of reaction kinetics and temperatures associated with both the devolatilization and char combustion, as well as total volatile matter lost. In this work, the TGA technique was applied to understand combustion of Coastal bermudagrass [*Cynodon dactylon* (L.) Pers.] hay produced under a control treatment of commercial N fertilizer without irrigation along with eight different subsurface drip irrigation (SDI) treatments. These eight treatments consisted of commercial N fertilizer or advanced-treated swine wastewater effluent, each irrigated at two (75% and 100% of estimated evapotranspiration) irrigation rates and two lateral SDI spacings (0.6 and 1.2 m). While thermogravimetric (weight loss) profiles of the treatments were almost identical and indicated three distinct combustion weight loss steps, some variations among the treatments were noted in the differential thermal analysis profiles. When compared to commercially fertilized bermudagrass, Coastal bermudagrass irrigated with advanced-treated swine wastewater had both greater mass loss associated with active combustion and a higher transition temperature leading to char combustion (364.9 °C vs. 372.5 °C). This higher temperature requirement for char combustion of the hay irrigated with effluent was a direct result of a greater activation energy value required to initiate char combustion (97.9 kJ mol⁻¹ for commercial vs. 105.1 kJ mol⁻¹ for effluent). Consequently, char combustion required greater activation energy than the first active combustion stage. Among the SDI spacing treatments, Coastal bermudagrass irrigated using the wider SDI spacing provided greater amounts of energy per mass of dry material (11.16 vs. 12.06 kJ g_{converted}⁻¹).*

Keywords. *Bioenergy, Biomass, Crop production, Manure management, Manures.*

Plant biomass and agricultural residues represent an abundant energy feedstock that is gradually providing greater contributions to the total U.S. renewable energy supply. Renewable energy consumption had an average annual growth rate of 3% between 2003 and 2006. This growth rate jumped by 7.1% for 2008 with a documented consumption of 7,301 trillion Btu (DOE-EIA, 2009a). The largest source of renewable energy was generated from biomass and accounted for 53% or 3,884 trillion Btu. This biomass energy was derived from wood, biofuels, and various waste products with contributions of

53%, 36%, and 11%, respectively. Just over half of the biomass energy was used in the industrial sector, accounting for 52% (DOE-EIA, 2009a). According to recent reports, this sector used 9.5% of the thermal units provided by biomass to generate electricity (DOE-EIA, 2009b). The remaining biomass was used for non-electrical purposes such as on-site heat and steam generation.

These electrical and non-electrical end-uses require the biomass to be converted via combustion, pyrolysis, and gasification. These processes are used for the production of heat, combustible pyrolytic oils, upgradeable synthesis gas (syngas), and other related fuels and chemical intermediates (Boateng et al., 2007a; McKendry, 2002). All of these processes have high conversion efficiencies. However, direct and co-combustion systems have been primarily responsible for much of the historical and current bioenergy production. While the main barrier for biomass combustion has been the quality of the feedstock (e.g., low heating value and high salt, ash, and silica content) leading to slagging and reduced boiler efficiency, combustion systems have successfully demonstrated the use of blends of coal and biomass (Tillman, 2000).

Combustion of biomass is a short-term solution that generates immediate heat and offers numerous potential benefits: diminished NO_x emissions, reduction of fossil fuel CO₂ emissions, allowance for atmospheric CO₂ recycling, and an increased quantity of available renewable feedstocks (Biagini et al., 2006; Demirbas, 2004; Tillman, 2000). The increased use of available biomass for combustion is attributed to the growing acceptance of available alternative

Submitted for review in April 2009 as manuscript number SW 7990; approved for publication by the Soil & Water Division of ASABE in February 2010.

Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the USDA.

The authors are **Keri B. Cantrell, ASABE Member Engineer**, Agricultural Engineer, **Patrick G. Hunt, ASABE Member**, Soil Scientist, **Kyoung S. Ro, ASABE Member Engineer**, Environmental Engineer, **Kenneth C. Stone, ASABE Member Engineer**, Agricultural Engineer, and **Matias B. Vanotti, ASABE Member Engineer**, Soil Scientist, USDA-ARS Coastal Plains Soil, Water, and Plant Research Center, Florence, South Carolina; and **Joseph C. Burns**, plant physiologist, USDA-ARS Plant Science Research Unit, Raleigh, North Carolina. **Corresponding author:** Keri B. Cantrell, USDA-ARS Coastal Plains Soil, Water, and Plant Research Center 2611 West Lucas St., Florence, SC 29501-1242; phone: 843-669-5203, ext. 113; fax: 843-669-6970; e-mail: keri.cantrell@ars.usda.gov.

biomass to include energy crops, food wastes, agricultural residues, low-quality coals, and sludges. This broad array of feedstocks that includes non-food crops allows for combustion to remove pathogen and other pharmaceutically active compounds from the food chain; this is especially true when biomass producers are accomplishing fertilization and irrigation with animal manure. Additionally, this expanding incorporation of available feedstocks, especially from biomass originating from energy crops and agricultural residues, creates a surplus that can readily be utilized by industrial and electric power sectors. In turn, these sectors, as demonstrated by the aforementioned DOE-EIA statistics, are capable of generating electricity and using biomass to supplement power needs. However, reports of the behaviors of renewable biomass fuels are not as abundant as for coal and other petroleum products. Thus, characterizations of these fuels are necessary to understand the thermal degradation behaviors.

Thermal degradation behaviors of biomass can be effectively assessed using thermogravimetric analysis (TGA). This analysis can prove useful in detecting differences in the degradation behaviors of biomass harvested under alternative production practices. This analysis provides a thermal signature or profile that leads to important global characterizations such as reaction kinetics, temperatures associated with both devolatilization and char combustion, as well as volatile matter lost. The TGA technique at a laboratory scale uses a small amount of sample, a continuous supply of carrier gas (reactive gas), and programmable heating rates. When low heating rates are used, TGA is able to distinguish differences in the stages of degradation as well as effects of feedstock material and subsequent production or harvesting techniques. This TGA technique has been demonstrated with food processing residues (Biagini et al., 2006), corn stover (Kumar et al., 2008), grasses and straws (Bridgeman et al., 2008), yard and municipal solid waste (Smidt and Lechner, 2005), and poultry litter (Whitely et al., 2006). Results from the TGA technique are important to efficient design, operation, and modeling of combustion and related thermochemical conversion processes.

Variations in biomass production practices were documented to alter both the energy density and yield of Coastal bermudagrass hay [*Cynodon dactylon* (L.) Pers.]. Irrigating bermudagrass with advanced-treated swine wastewater versus well-water supplemented with commercial fertilizer was documented to decrease the energy density (MJ kg^{-1}) and increase the overall energy yield (GJ ha^{-1}) (Cantrell et al., 2009; Stone et al., 2008). Within this same study, it was also documented that both subsurface drip irrigation spacing and irrigation rate did not affect energy yield or density. Primarily attributed to the greater concentration of measured plant nutrient in the wastewater, irrigation using the wastewater increased concentrations of potassium, calcium, and sodium in the bermudagrass. These inorganic components (K, Ca, and Na) are thought to act as catalysts promoting secondary char gasification reactions for production of combustible gases (Sheth and Turner, 2002). The objective of this work was to apply the TGA technique using an oxidizing atmosphere to evaluate how production practices can influence combustion of Coastal bermudagrass hay, grown under various irrigation schemes as detailed by Stone et al. (2008), with regard to thermal degradation

profiles and associated kinetics. Results obtained from this work contribute to a better understanding of how biomass production schemes may affect downstream conversion characteristics.

MATERIALS AND METHODS

SITE DESCRIPTION

The Coastal bermudagrass SDI experiment was conducted from 2003 to 2005 on a 0.53 ha field site consisting of an Austryville loamy sand soil in Duplin County, North Carolina, on a 4,400-head swine finishing facility. This site was adjacent to a full-scale swine wastewater treatment facility constructed and operated by a private firm (Super Soil Systems USA of Clinton, N.C.) to demonstrate an environmentally superior technology (EST) to replace anaerobic lagoon treatment (Vanotti and Szogi, 2008). The treatment facility processed swine manure flushed directly from the six houses ($39 \text{ m}^3 \text{ d}^{-1}$) by separating solids, followed by biological nitrogen removal as N_2 from the liquid phase with subsequent alkaline phosphorous removal (calcium phosphate). The treated effluent ($\text{pH} = 10.5$) was stored in a storage tank. The treated effluent on average had the following measured concentrations (mg L^{-1}): total suspended solids 232, total Kjeldhal nitrogen 26, ammonia-N 14, nitrate plus nitrite 235, total phosphorous (TP) 26, potassium (K) 997, calcium (Ca) 142, magnesium (Mg) 9, sulfur (S) 15, zinc (Zn) 0.2, copper 0.3, and sodium (Na) 215 (Vanotti and Szogi, 2008).

The bermudagrass was grown on 36 plots ($9.6 \text{ m} \times 9.6 \text{ m}$) containing eight irrigation treatments with four replicates that were arranged in a randomized complete block design (detailed description in Stone et al., 2008). Bermudagrass plots received the following irrigation treatments: treated wastewater effluent plus well water and commercial fertilizer plus well water, both applied via SDI at either 75% or 100% of calculated evapotranspiration (ET). These four treatments were repeated using lateral spacing in the SDI system of 0.6 m or 1.2 m placed at a depth of 0.3 m. Along with these eight treatments, a ninth treatment was tested consisting of a surface-applied, commercially fertilized (345 g kg^{-1} ammonium nitrate) non-irrigated control.

The target total nitrogen application rate was 270 kg ha^{-1} split in three applications of 90 kg ha^{-1} . Initial application occurred in the early spring and followed each of the next two harvests. Irrigated treatments receiving commercial fertilizer received one to two applications of a 300 g kg^{-1} urea-ammonium nitrate solution per cutting (30% UAN). Irrigated treatments receiving treated effluent with N-concentrations ranging 94 to 465 mg L^{-1} received one to two applications per harvest in 2004 and four to five per harvest in 2005 (Stone et al., 2008).

BIOMASS COLLECTION

Bermudagrass hay was harvested three times on four- to eight-week intervals based on logistics and weather conditions in both 2004 (23 June, 23, 10 August, and 21 September) and 2005 (12 July, 11 August, and 13 October). Within each plot, biomass was harvested from the center of each plot in a measured area of 15.4 m^2 ($1.6 \times 9.6 \text{ m}$). A sample was collected from each harvested plot,

Table 1. Energy density and plant nutrient characteristics of bermudagrass irrigated with advanced-treated wastewater (Cantrell et al., 2009).

Variable	Units	Non-Irrigated	Spacing		Fertilizer		Irrigation Demand	
			0.6 m	1.2 m	Commercial	Effluent	100%ET	75%ET
Energy density	MJ kg ⁻¹	18.93	18.86	18.92	18.99	18.80	18.88	18.89
P	%	0.228	0.241	0.239	0.248	0.232	0.249	0.231
K	%	2.00	2.12	2.09	1.99	2.22	2.145	2.068
Ca	%	0.300	0.323	0.315	0.309	0.329	0.327	0.312
Mg	%	0.198	0.172	0.168	0.173	0.168	0.168	0.173
S	%	0.263	0.254	0.260	0.248	0.265	0.255	0.258
Zn	ppm	31.6	27.8	27.5	30.9	24.4	0.028	0.027
Cu	ppm	14.3	17.4	18.1	18.4	17.0	0.018	0.017
Mn	ppm	68.1	47.1	49.3	53.6	42.8	0.050	0.046
Fe	ppm	91.6	114.1	91.0	104.4	100.7	0.101	0.104
Na	ppm	124.9	144.6	152.3	118.6	178.2	0.153	0.144

weighed in the laboratory, dried at 43 °C for 72 h, ball milled, and stored for later thermal analyses. These samples were analyzed in a previous study by Cantrell et al. (2009) for energy density and plant nutrient characteristics (table 1).

THERMAL ANALYSIS

Thermal analyses of all samples were conducted using a TGA-DTA analyzer (TGA/SDTA851e, Mettler Toledo International, Inc., Columbus, Ohio) where the mass loss (thermogravimetry, TG) and temperature changes (differential thermal analysis, DTA) were recorded simultaneously. This unit operated under a three-point temperature calibration using the melting points of indium, aluminum, and gold. All samples (weight range from 6.69 to 24.21 mg) were placed in an Al₂O₃ 70 µL crucible and combusted under the following conditions: zero-grade air atmosphere (composition 21.5% O₂, 78.5% N₂, total hydrocarbons <1 ppm), airflow rate of 60 mL min⁻¹, temperature range from 40 °C to 700 °C, and constant heating rate of 10 °C min⁻¹. All DTA curves accounted for instrumental effects using Version 9.10 of STARe software (Mettler Toledo International, Inc., Columbus, Ohio). Enthalpies were calculated by integration of the area below the DTA curve between desired temperatures.

In addition to analyzing the bermudagrass samples, three basic fiber components were studied: cellulose, lignin, and hemicellulose (Sigma Chemical, St. Louis, Mo.). The hemicellulose component was represented by beechwood-derived xylan.

KINETIC PARAMETERS

Assuming a first-order thermal decomposition reaction for combustion ($n = 1$), the rate of reaction $d\alpha/dt$, where α is the conversion, was assumed to be described by the mass action law, $k(T)f(\alpha)$, and temperature-dependent Arrhenius equation describing the decomposition rate (k):

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n = \left(\frac{A}{\beta} \exp\left(\frac{-E_a}{RT}\right) \right) (1 - \alpha)^n \quad (1)$$

where A is the pre-exponential factor (min⁻¹), β is the heating rate (dT/dt), E_a is the activation energy (kJ mol⁻¹), R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), T is the absolute temperature (K), and n is the order of the reaction. The variable α was a constant function:

$$\alpha = \frac{m_O - m_T}{m_O - m_f} \quad (2)$$

where m_O is the initial mass (g), m_T is the mass at temperature T (g), and m_f is the final residual mass (g).

In order to determine the kinetic parameters used in the above equations, this study used a non-isothermal approach. This approach has been used to describe combustion of poultry litter (Whitely et al., 2006), coal (Chen et al., 1995), and wheat straw (Wang et al., 2008). The non-isothermal approach introduced logarithmic transformation of equation 1 to become:

$$\ln\left(\frac{d\alpha}{dt}(1 - \alpha)^{-n}\right) = \ln\left(\frac{A}{\beta}\right) - \frac{E_a}{RT} \quad (3)$$

The values of $d\alpha/dt$ and α could be directly obtained from the TGA analysis. Therefore, the left side of equation 3 ($n = 1$) could be plotted against the inverse of the absolute temperature. For these results, a linear model was fitted to each independent combustion stage with an intercept of $\ln(A/\beta)$ and a slope of $-E_a/R$.

STATISTICAL ANALYSIS

The TG and DTA data for the randomized complete block of the bermudagrass experimental design were analyzed by Proc GLM (general linear model) and LSD (least significant difference) with SAS (version 9.1, SAS Institute, Inc., Cary, N.C.). Differences were considered significant at $p \leq 0.05$.

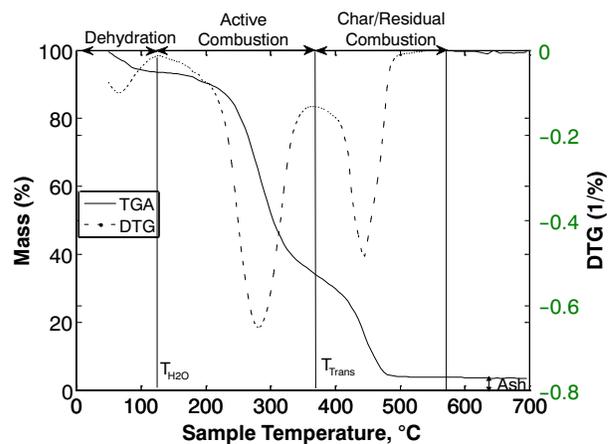


Figure 1. TGA and the derivative of weight loss (DTG) plot of non-irrigated bermudagrass in air. Mass (%) is the ratio of actual weight to initial sample weight, and heating rate was 10 °C min⁻¹ (T_{H_2O} = temperature at end of dehydration, T_{Trans} = transition temperature between combustion stages, and Ash = residual mass).

Table 2. Thermogravimetric analysis and summary statistics of bermudagrass combustion.^[a]

SDI Spacing	Fertilizer	Irrigation Rate	Dehydration		Volatiles (wt% _{db})	Char		Ash (wt% _{db})
			(wt%)	T _{H2O} (°C)		T _{Trans} (°C)	(wt% _{db})	
0.6	Commercial	100%	5.56 (0.42)	134.9 (10.3)	62.47 (2.36)	365.4 (7.7)	32.42 (1.34)	5.11 (2.74)
0.6	Commercial	75%	5.66 (0.50)	139.7 (12.5)	61.11 (3.09)	364.6 (11.8)	32.00 (2.56)	6.90 (3.58)
0.6	Effluent	100%	5.47 (0.59)	132.8 (7.2)	62.56 (4.55)	374.0 (20.6)	30.83 (4.14)	6.60 (3.50)
0.6	Effluent	75%	5.72 (0.51)	135.5 (7.8)	63.31 (4.73)	374.1 (17.0)	30.75 (3.62)	5.94 (2.05)
1.2	Commercial	100%	5.90 (0.66)	142.2 (20.7)	61.66 (3.66)	365.5 (14.6)	32.13 (2.35)	6.21 (4.04)
1.2	Commercial	75%	5.90 (0.61)	140.5 (19.5)	61.68 (2.95)	364.2 (11.4)	32.51 (2.10)	5.80 (2.30)
1.2	Effluent	100%	6.02 (0.64)	140.3 (16.0)	63.43 (4.41)	371.8 (18.6)	31.02 (3.54)	5.56 (3.74)
1.2	Effluent	75%	6.24 (0.10)	144.5 (21.0)	62.76 (3.17)	370.2 (19.1)	31.63 (4.12)	5.61 (2.80)
Non-irrigated	--	--	5.72 (0.10)	132.2 (11.3)	62.53 (3.82)	367.9 (17.6)	31.85 (3.64)	5.62 (2.04)
LSD _{0.05}			0.40	8.1	2.09	9.0	1.82	1.65
Summary statistics ^[b]								
Spacing means		0.6	5.61 a	135.7 a	62.36 a	369.5 a	31.50 a	6.14 a
		1.2	6.02 b	141.9 b	62.38 a	367.9 a	31.82 a	5.79 a
Fertilizer means		Commercial	5.76 a	139.3 a	61.73 a	364.9 a	32.27 a	6.00 a
		Effluent	5.86 a	138.3 a	63.01 b	372.5 b	31.05 b	5.93 a

^[a] Values in parentheses are standard deviations of the mean.

^[b] Statistical differences were not noted among irrigation rate means. Means followed by the same letter are not significantly different at p = 0.05.

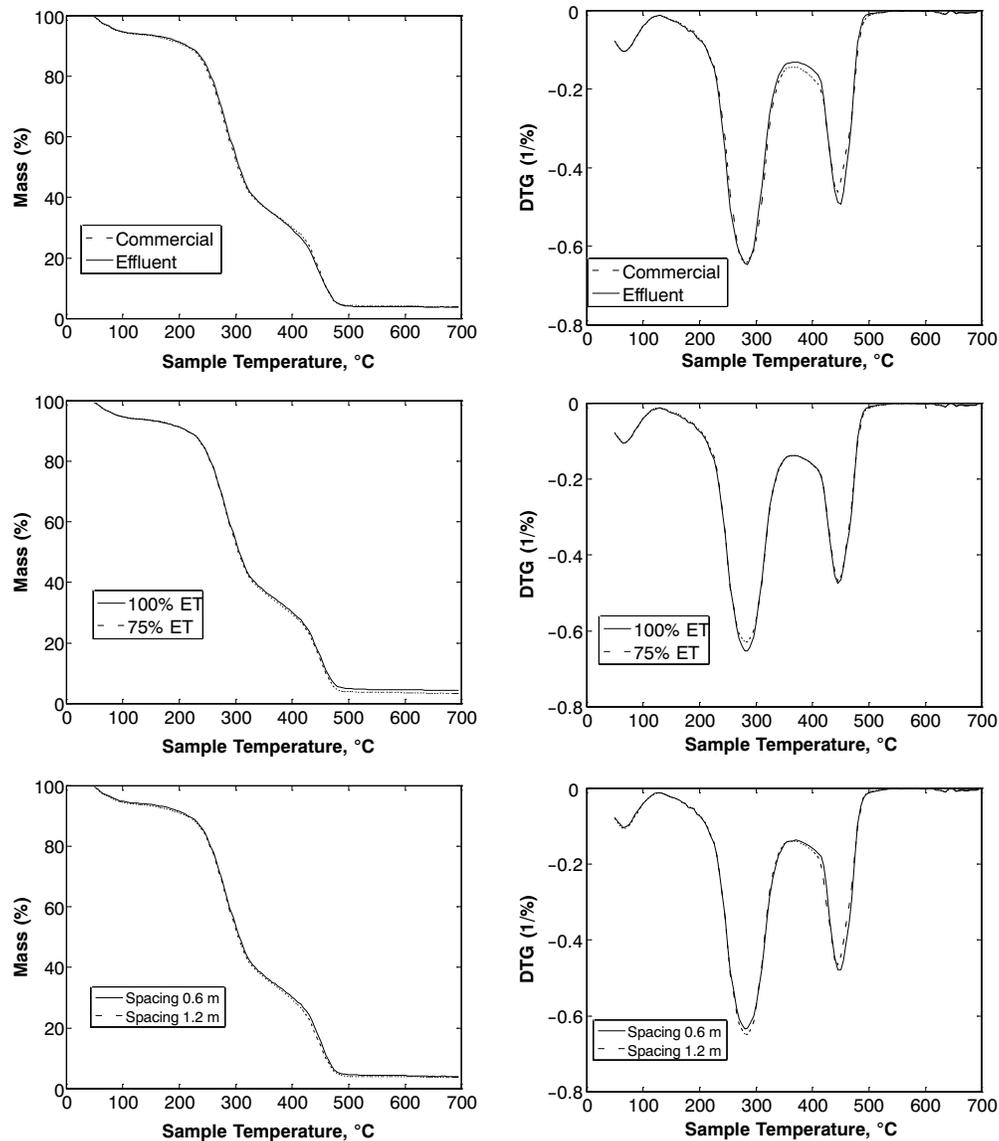


Figure 2. Burning profiles (TG/DTG) of raw bermudagrass combustion categorized according to fertilizer, irrigation rate, and spacing (overlap occurred among all treatments). Mass (%) is the ratio of actual weight to initial sample weight, and heating rate was 10° C min⁻¹.

RESULTS AND DISCUSSION

STAGES OF COMBUSTION

The derivative of the TGA weight loss curve, or the rate of weight loss (DTG), of the combustion process on non-irrigated bermudagrass (fig. 1) clearly suggested three stages of weight loss: dehydration; active combustion; and char or residual combustion. These stages were defined as the “valleys” in the DTG plot. These combustion stages were consistent with other lignin-cellulosic materials where combustion occurred in two macrosteps: devolatilization at relatively low temperatures and high-temperature oxidation of the solid residual (Biagini and Tognotti, 2006; Grotkjær et al., 2003; Munir et al., 2009). The dehydration stage ended at temperatures between 132°C and 140°C (table 2). Then, active combustion of volatile matter began and transitioned into char combustion between 364°C and 374°C. Char combustion had a slow and continuous weight loss until 550°C, at which point ash remained.

For this study, the mass loss during the dehydration stage across all treatments was approximately the same (~5.7 wt%). It was noted that the dehydration temperature (T_{H_2O}) signaling the end of the stage was only affected by the SDI spacing; however, the cause was not well understood. The bulk of weight loss was associated with active combustion accounting for approximately 55 wt%_{db}. This mass loss was attributed to the volatile portion undergoing rapid devolatilization and subsequent oxidation. As suggested by these processes, pyrolysis and combustion occurred in series, as evidenced by the fact that the maximum mass loss occurred at approximately 280°C (fig. 2), yet the respective maximum heat flow occurred near 308°C

(table 3). Therefore, mass loss occurred first, followed by combustion (oxidation). This series occurrence was also noted elsewhere (Whitely et al., 2006). The amount of volatile matter combusted in the bermudagrass hay samples was greater for treatments receiving treated effluent. For this treatment, the greatest amount of volatile matter was observed with a value of 63.0 wt%_{db}. This mass loss was in good agreement with the mass loss during the first stage of combustion of another potential grass feedstock, reed canary grass, 63.4 wt%_{db} (Bridgeman et al., 2007). Using hay yields reported by Stone et al. (2008), total volatile mass in the bermudagrass would be greater for the effluent than commercial fertilizer between 12% and 24%.

The differences in volatile matter can be explained by differences in structural carbohydrate concentrations. The cellulose content was slightly greater for commercial fertilized hay (310 g kg⁻¹) than for the effluent treated hay (307 g kg⁻¹) (Burns et al., 2009). The lignin content increased from 53.6 to 55.3g kg⁻¹ for the effluent treated hay. These differences could directly contribute to greater mass loss during the first stage of combustion. Additionally, it was observed that for lignin alone (fig. 3) active volatile matter began to combust at lower temperatures than cellulose. Thus, with more material lost at lower temperatures, the volatile matter increased during the first stage of combustion of effluent treated hay. These differences may also be affected by the effluent treated hay having greater concentrations of K, Ca, and Na (table 1). Salt derivatives of these inorganic components amended to agricultural residual biomass were documented to reduce pyrolytic char yield and increase gaseous volatiles (Raveendran et al., 1995).

Table 3. Differential thermal analysis (DTA) and summary statistics of bermudagrass combustion.^[a]

SDI Spacing	Fertilizer	Irrigation Rate	Volatile Combustion			Char Combustion			Overall DH		
			T_{Vmax} (°C)	DH_{vol_dry} (kJ g _{vol} ⁻¹)	DH_{vol_dry} (kJ g _{solids} ⁻¹)	T_{Cmax} (°C)	DH_{char_dry} (kJ g _{char} ⁻¹)	DH_{char_dry} (kJ g _{solids} ⁻¹)	(kJ g _{conv} ⁻¹)	(kJ g _{solids} ⁻¹)	T_{final} (°C)
0.6	Com.	100%	308.6 (4.5)	6.22 (1.1)	3.89 (0.7)	436.6 (5.8)	20.51 (1.4)	6.65 (0.6)	11.11 (1.1)	10.54 (1.2)	482.5 (5.9)
0.6	Com.	75%	308.1 (4.5)	6.51 (1.0)	3.99 (0.7)	436.8 (8.2)	20.80 (1.6)	6.65 (0.7)	11.43 (1.1)	10.64 (1.1)	484.6 (5.0)
0.6	Eff.	100%	308.2 (3.4)	6.56 (1.5)	4.15 (1.2)	453.0 (8.7)	20.19 (1.5)	6.22 (0.9)	11.08 (1.3)	10.37 (1.3)	483.5 (5.5)
0.6	Eff.	75%	308.4 (3.4)	6.42 (1.3)	4.10 (1.1)	451.4 (9.2)	20.37 (1.4)	6.26 (0.8)	11.01 (1.1)	10.36 (1.1)	484.0 (5.5)
1.2	Com.	100%	307.0 (3.6)	7.31 (1.4)	4.52 (1.0)	437.4 (6.2)	21.97 (1.9)	7.05 (0.8)	12.34 (1.4)	11.58 (1.4)	448.4 (10.0)
1.2	Com.	75%	308.4 (3.8)	7.04 (1.0)	4.36 (0.8)	437.1 (5.8)	21.48 (1.5)	6.97 (0.5)	12.03 (0.9)	11.33 (0.9)	448.8 (8.3)
1.2	Eff.	100%	306.2 (3.7)	7.24 (1.7)	4.62 (1.3)	447.9 (7.8)	21.25 (2.5)	6.59 (1.0)	11.86 (1.8)	11.21 (1.8)	486.6 (13.0)
1.2	Eff.	75%	307.2 (3.1)	7.16 (2.0)	4.51 (1.4)	450.7 (7.1)	21.61 (2.7)	6.82 (1.1)	12.01 (2.1)	11.33 (1.9)	489.4 (10.3)
Non-irrigated			308.1 (3.0)	6.84 (1.3)	4.30 (1.0)	439.2 (5.7)	21.31 (1.6)	6.76 (0.7)	11.72 (1.2)	11.06 (1.1)	485.6 (7.0)
LSD _{0.05}			2.1	0.79	0.58	4.1	1.05	0.49	0.80	0.78	4.8
Summary Statistics ^[b]											
Spacing means		0.6	308.3 a	6.43 a	4.03 a	444.4 a	20.47 a	6.45 a	11.16 a	10.48 a	483.7 a
		1.2	307.2 a	7.18 b	4.50 b	443.3 a	21.58 b	6.86 b	12.06 b	11.36 b	488.3 b
Fertilizer means		Com.	308.0 a	6.77 a	4.19 a	437.0 a	21.19 a	6.83 a	11.73 a	11.02 a	486.1 a
		Eff.	307.5 a	6.85 a	4.35 a	450.7 b	20.86 a	6.47 b	11.49 a	10.82 a	485.9 a

^[a] Values in parentheses are standard deviations of the mean.

^[b] Statistical differences were not noted among irrigation rate means. Means followed by the same letter are not significantly different at p = 0.05.

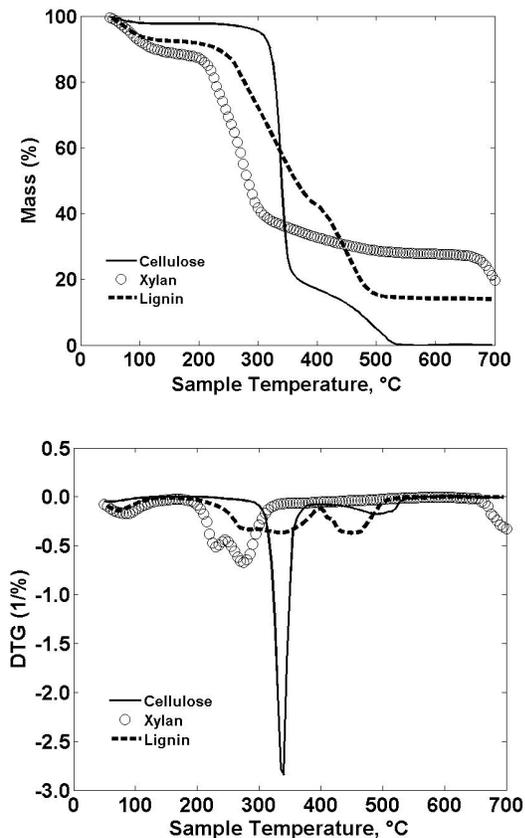


Figure 3. Burning profiles (TG/DTG) of bermudagrass components. Mass (%) is the ratio of the actual weight of the sample to initial weight.

As a consequence of the combustion of greater amounts of volatile matter, less char was available for the secondary combustion reactions: 31.1 versus 32.3 wt%. The ash end-product amount was not affected (i.e., values were not significantly different) by SDI spacing, type of fertilizer, or irrigation rate. The ash content was, however, lower than those reported for reed canary grass and corn stover (Bridgeman et al., 2007; Kumar et al., 2008). The transition temperature from active to char combustion was affected by the type of fertilizer treatment. The transition temperature associated with the effluent fertilized hay was higher than that of the commercially fertilized hay: 372.5°C compared with 364.9°C (table 2). The slight plateau observed in the thermogravimetric derivative curve (DTG) at the beginning of char combustion signaled that the weight loss rate was constant; however, this quickly evolved into rapid char combustion. This lull in the combustion process has been regarded as precombustion or an introductory region where diffusion and beginning char combustion are taking place (Chen et al., 1995; Whitely et al., 2006).

The DTG curves for the combustion of bermudagrass resembled a composite shape of the three primary structural carbohydrates: cellulose, xylan, and lignin. Each component had distinctly different reactions and volatile matter releases. Cellulose exhibited the maximum amount of weight loss during volatile combustion as well as the most rapid. Cellulose combustion began at 285°C with the volatile portion combusting over a narrow temperature window, roughly 115°C, where cellulose was oxidized as much as 80 wt%. During this stage, the maximum rate of weight loss

took place at 345°C. Cellulose combustion proceeded into the char combustion region to remove the remaining 16 wt%.

Xylan, which is representative of hemicellulose, was the quickest to decompose with an onset temperature of 185°C. Xylan was also shown to decompose quickly with almost no overlap with cellulose (Biagini et al., 2006). This component had a greater temperature range for volatile combustion than cellulose with the volatile combustion ending close to 340°C. Over this temperature range, more than half of xylan's volatile portion released, approximately 52 wt%. The maximum rate occurred at 270°C. No secondary char combustion was evident, leaving behind the most ash material.

Combustion of lignin exhibited two prominent DTG peaks indicative of the two later stages of combustion. With an onset temperature close to that of xylan, lignin combusted over the widest temperature range, beginning at 210°C with active volatile combustion ending at 400°C and char combustion ending 513°C. For these two stages, the maximum rate of weight loss peaked at 330°C and 460°C, respectively. However, the loss of lignin was slow. The final weight loss was less than that of xylan, with 14% of the lignin ash remaining.

KINETIC ANALYSIS

The pre-exponential factors and kinetic analysis of the two independent combustion stages for hay from all irrigation treatments were lower than the non-irrigation plots (table 4). For these variables, minimal differences could be discerned among treatments. The activation energy of the reaction during active combustion for the irrigation treatments was approximately 61.4 kJ mol⁻¹. This value was slightly less than that of the non-irrigated plots with an average E_a value of 63.3 kJ mol⁻¹. The results were in fair agreement with the case of combustion of both corn stover at a heating rate of 10°C min⁻¹ with reported E_a value 57.3 kJ mol⁻¹ as well as the first stage of combustion of wood pellets with an E_a value of 69.4 kJ mol⁻¹ (Biagini and Tognotti, 2006; Kumar et al., 2008). These E_a values were less than activation energies associated with combustion of poultry litter, 71.4 kJ mol⁻¹. Thus, comparing plant material to poultry litter, less energy would be required to begin the combustion of bermudagrass. However, it may prove beneficial to provide blends of various feedstocks, such as litter and bermudagrass, to optimize total energy output (Cantrell et al., 2009).

For irrigated bermudagrass, the data for the logarithmic transformation (eq. 3) associated with the active and char combustion stages showed better linear correlation during the char combustion stage (table 4; r^2 value average 0.987). Duly noted were differences between activation energies for the combustion of volatiles versus char. The first stage of combustion had a corresponding activation energy (E_a) of 61.7 kJ mol⁻¹; this activation energy was roughly 60% of the activation energy required to initiate char combustion, 100.3 kJ mol⁻¹. This observation further confirms a previous conclusion about the plateau observed in the DTG curve during the transition from active to char combustion. In order to begin char combustion, enough energy needs to be applied to the char before oxidation.

DIFFERENTIAL THERMAL ANALYSIS

The differential temperature (DT) curves were also analyzed to determine the energy release associated with the

Table 4. First-order kinetic parameters for bermudagrass combustion.

	Volatile Combustion				Char Combustion		
	Pre-Exponential Factor $\log_e A$ (s^{-1})	E_a ($kJ\ mol^{-1}$)	r^2	Pre-Exponential Factor $\log_e A$ (s^{-1})	E_a ($kJ\ mol^{-1}$)	r^2	
Spacing	0.6	6.81	0.974	11.2	100.5	0.997	
	1.2	6.73	0.975	11.2	100.1	0.995	
Fertilizer	Com.	7.03	0.971	10.8	97.9	0.956	
	Eff.	7.09	0.972	12.0	105.1	0.981	
Demand	75%	6.97	0.977	10.7	97.3	0.993	
	100%	6.58	0.972	11.0	99.5	0.995	
Non-irrigated	--	7.30	0.980	11.5	102.0	0.991	

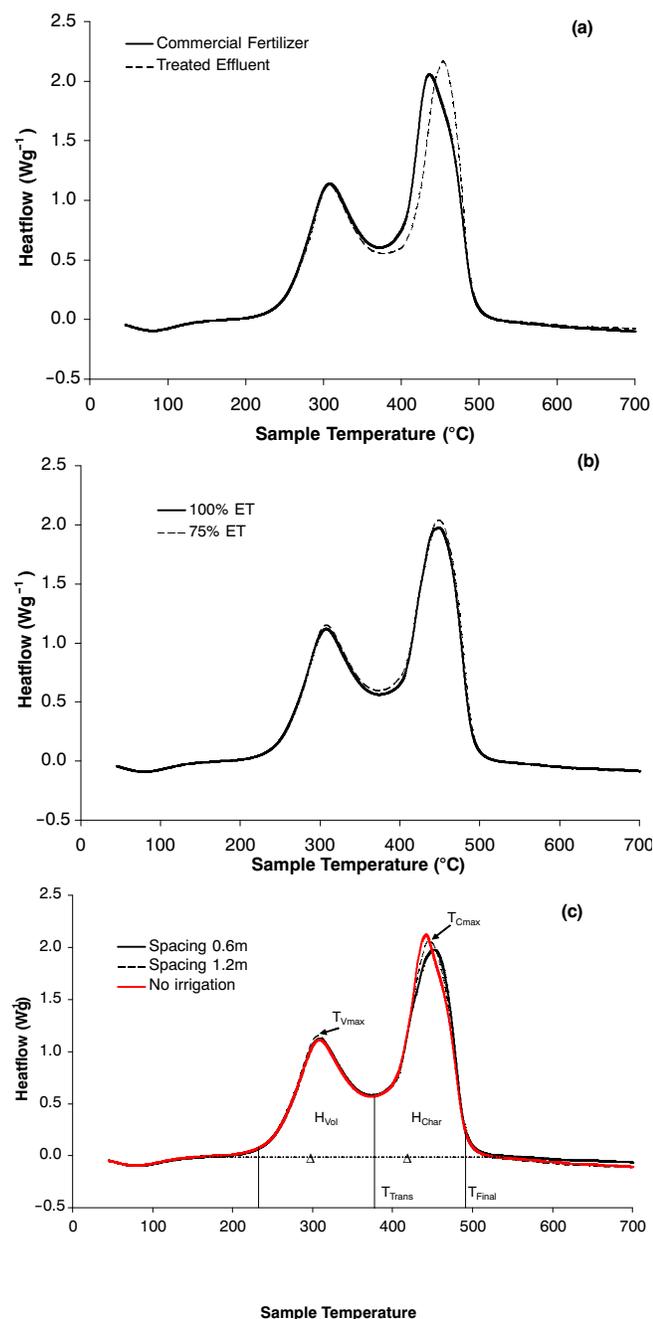


Figure 4. Differential thermal analysis of raw bermudagrass combustion categorized according to (a) fertilizer, (b) irrigation rate, and (c) spacing (T_{Vmax} = maximum temperature during volatile combustion, T_{Trans} = transition temperature between combustion stages, T_{Cmax} = maximum temperature during char combustion, and ΔH = heat of combustion per unit mass).

two primary combustion stages (table 3). Each stage had an associated heat of combustion that was represented by two clear thermopositive peaks (fig. 4). Figure 4c shows the points of interest on a typical DT curve from bermudagrass combustion along with a comparison of the DT curves produced from the different treatments. In each treatment, the first peak associated with volatile combustion was less pronounced compared to the second peak due to less heat released. This phenomenon occurred even though greater weight loss was associated with volatile combustion. As such, the energy per mass of converted solid averaged across all treatments was less for volatile combustion compared to char combustion, 4.27 vs. 6.66 $kJ\ g_{converted}^{-1}$. During the early stage of combustion, there was a release of low-energy components. These low-energy, lightweight components evolved from the bermudagrass at the lower temperature and were primarily non-combustible gases (e.g., H_2O and CO_2). It was not until higher temperatures (280 °C) were achieved that higher-carbon volatile components were released and ignited.

Even though the amounts of volatiles were equivalent between the two SDI spacings, DTA revealed that the energy associated with volatile combustion was greater for the wider spacing (4.03 vs. 4.50 $kJ\ g_{solids}^{-1}$). This energetic difference suggests combustion of different types of volatiles. The type of fertilizer affected the maximum temperature during char combustion (T_{Cmax}); T_{Cmax} shifted to lower temperatures for bermudagrass fertilized with commercial nitrogen fertilizer. Thus, TG-DTA analyses indicated that a wider SDI spacing promoted the growth of bermudagrass with greater energetic, volatile material that resulted in greater heat released.

SUMMARY

Thermogravimetric and differential thermal analyses (TGA and DTA) of the combustion of Coastal bermudagrass hay produced from both well-water and advanced-treated swine wastewater effluent delivered via SDI indicated two macrostep losses with corresponding combustion energies: an active combustion stage followed by a char combustion stage. The first stage of combustion had a corresponding activation energy (E_a) of 61.7 $kJ\ mol^{-1}$. This activation energy was roughly 60% of the activation energy required to initiate char combustion, 100.3 $kJ\ mol^{-1}$. In contrast to irrigating for 75% and 100% of ET, the weight loss associated with the first stage as well as with the second char combustion stage was affected by the type of irrigated N-fertilizer: commercial versus treated effluent. Irrigating with effluent fertilizer yielded statistically greater volatile matter and less char material. Using previously reported hay yields from

Stone et al. (2008), there would be an increase in total volatile matter between 12% and 24%, which would subsequently provide increased energy. Effluent fertilizer also required greater amounts of energy to begin combustion, as indicated by higher transition temperatures from the first combustion stage to the second (372.5°C vs. 364.9°C) and greater E_a values for char combustion with an average value of 105.1 kJ mol⁻¹ compared to the commercial fertilized hay with an E_a value of 97.9 kJ mol⁻¹. Within the lateral spacing treatments, a wider SDI spacing resulted in minimal differences in kinetic parameters as well as greater heat released during each of the combustion stages with an average overall value of 11.36 kJ g_{solid}⁻¹.

ACKNOWLEDGEMENTS

This research was part of USDA-ARS National Programs 206 (Manure and Byproduct Utilization) and 201 (Water Resource Management). The authors extend their gratitude to Cody Alexander, Melvin Johnson, Terry Matheny, Jerry Martin, and Joseph Millen for their efforts in site preparation, sample collection, and data analysis.

REFERENCES

Biagini, E., and L. Tognotti. 2006. Comparison of devolatilization/char oxidation and direct oxidation of solid fuels at low heating rate. *Energy Fuels* 20(3): 986-992.

Biagini, E., F. Barontini, and L. Tognotti. 2006. Devolatilization of biomass fuels and biomass components studied by TG/FTIR technique. *Ind. Eng. Chem. Res.* 45(13): 4486-4493.

Boateng, A. A., W. F. Anderson, and J. G. Phillips. 2007. Bermudagrass for biofuels: Effect of two genotypes on pyrolysis product yield. *Energy Fuels* 21(2): 1183-1187.

Bridgeman, T. G., L. I. Darvell, J. M. Jones, P. T. Williams, R. Fahmi, A. V. Bridgwater, T. Barraclough, I. Shield, N. Yates, S. C. Thain, and I. S. Donnison. 2007. Influence of particle size on the analytical and chemical properties of two energy crops. *Fuel* 86(1-2): 60-72.

Bridgeman, T. G., J. M. Jones, I. Shield, and P. T. Williams. 2008. Torrefaction of reed canary grass, wheat straw, and willow to enhance solid fuel qualities and combustion properties. *Fuel* 87(6): 844-856.

Burns, J. C., K. C. Stone, P. G. Hunt, M. B. Vanotti, K. B. Cantrell, and D. S. Fisher. 2009. Intake and digestibility of 'coastal' bermudagrass hay from treated wine waste using subsurface drip irrigation. *J. Environ. Qual.* 38(4): 1749-1756.

Cantrell, K. B., K. C. Stone, P. G. Hunt, K. S. Ro, M. B. Vanotti, and J. C. Burns. 2009. Bioenergy from Coastal bermudagrass receiving subsurface drip irrigation with advance-treated swine wastewater. *Bioresour. Tech.* 100(13): 3285-3292.

Chen, Y., S. Mori, and W. P. Pan. 1995. Estimating the combustibility of various coals by TG-DTA. *Energy Fuels* 9(1): 71-74.

Demirbas, A. 2004. Combustion characteristics of different biomass fuels. *Prog. Energ. Combust.* 30(2): 219-230.

DOE-EIA. 2009a. Renewable energy consumption and electricity: Preliminary statistics 2008. Washington, D.C.: Department of Energy, Energy Information Administration. Available at: www.eia.doe.gov/cneaf/alternate/page/renew_energ_consump/ea_prereport.html.

DOE-EIA. 2009b. Renewable energy trends in consumption and electricity: 2007 edition. Washington, D.C.: Department of Energy, Energy Information Administration. Available at: www.eia.doe.gov/cneaf/solarrenewables/page/trends/rentrends.html.

Grotkjær, T., K. Dam-Johansen, A. D. Jensen, and P. Glarborg. 2003. An experimental study of biomass ignition. *Fuel* 82(7): 825-833.

Kumar, A., L. Wang, Y. A. Dzenis, D. D. Jones, and M. A. Hanna. 2008. Thermogravimetric characterization of corn stover as gasification and pyrolysis feedstock. *Biomass Bioenerg.* 32(5): 460-467.

McKendry, P. 2002. Energy production from biomass: Part 1. Overview of biomass. *Bioresour. Tech.* 83(1): 37-46.

Munir, S., S. S. Daood, W. Nimmo, A. M. Cunliffe, and B. M. Gibbs. 2009. Thermal analysis and devolatilization kinetics of cotton stalk, sugar cane bagasse, and shea meal under nitrogen and air atmospheres. *Bioresour. Tech.* 100(3): 1413-1418.

Raveendran, K., A. Ganesh, and K. C. Khilar. 1995. Influence of mineral matter on biomass pyrolysis characteristics. *Fuel* 74(12): 1812-1822.

Sheth, A. C., and A. D. Turner. 2002. Kinetics and economics of catalytic steam gasification of broiler litter. *Trans. ASAE* 45(4): 1111-1121.

Smidt, E., and P. Lechner. 2005. Study on the degradation and stabilization of organic matter in waste by means of thermal analyses. *Thermochim Acta* 438(1-2): 22-28.

Stone, K. C., P. G. Hunt, J. A. Millen, M. H. Johnson, T. A. Matheny, M. B. Vanotti, and J. C. Burns. 2008. Forage subsurface drip irrigation using treated swine wastewater. *Trans. ASABE* 51(2): 433-440.

Tillman, D. A. 2000. Biomass cofiring: The technology, the experience, the combustion consequences. *Biomass Bioenerg.* 19(6): 365-384.

Vanotti, M. B., and A. A. Szogi. 2008. Water quality improvements of wastewater from confined animal feeding operations after advance treatment. *J. Environ. Qual.* doi:10.2134/jeq2007.0384.

Wang, C., F. Wang, Q. Yang, and R. Liang. 2008. Thermogravimetric studies of the behavior of wheat straw with added coal during combustion. *Biomass Bioenerg.* 33(1): 50-56.

Whitely, N., R. Ozao, R. Artiaga, Y. Cao, and W. P. Pan. 2006. Multi-utilization of chicken litter as biomass source: Part I. Combustion. *Energy Fuels* 20(6): 2660-2665.