

# FUEL PROPERTIES OF BIOMASS FEED STREAMS AT ETHANOL PLANTS

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**ABSTRACT.** Biomass co-products from the dry-grind ethanol production process and/or corn stover are potential sources for the energy needed to operate the plant. The ethanol plant co-products alone contain sufficient energy to meet the electrical and thermal needs of the plant as well as to produce excess power that can be sold. Fuel characteristics of co-products of the ethanol dry-grind process [distillers wet grains (DWG), concentrated distillers solubles (referred to as “syrup”), and distillers dried grains with solubles (DDGS)], and corn stover are evaluated. Analyses include proximate, ultimate, selected metals, ash fusion temperatures, minerals in the ash, and thermogravimetric analysis (TGA). Higher heating values for the co-products are greater than for corn stover and for most other biomass materials. The ethanol co-products contain large amounts of nitrogen, sulfur, and chlorine, which will require major control technologies for combustion or gasification systems to meet emissions limits. The alkali metal content (potassium and sodium oxides) of the ash is high (22% to 34%) for co-products and corn stover, which will require careful design to avoid to ash fouling in combustion and steam generation units. Corn stover has more favorable combustion characteristics than the ethanol co-products based on higher ash fusion temperatures and the TGA results (higher combustion reactivity and lower burnout temperature).

**Keywords.** Biomass, Ethanol co-products, Corn stover, Heating value, Ultimate analysis, Ash fusion, Thermogravimetric analysis.

**D**ry-grind ethanol process co-products and/or corn stover can be used to provide electricity (both for the plant and sale to the grid) and process heat. These biomass fuels can reduce costs, increase the renewable energy balance, and reduce greenhouse gas emissions for fuel ethanol production (Morey et al., 2006).

Rising natural gas costs and uncertain prices for the biomass co-products of the dry-grind process [distillers wet grains (DWG), concentrated distillers solubles (referred to as “syrup”), and distillers dried grains with solubles (DDGS)] have generated interest in using co-products as fuels at ethanol plants. DWG and syrup are separated wet forms of the co-product which contain 60% to 70% moisture. DWG is separated from the thin stillage in a centrifuge. The thin stillage (approximately 95% moisture) is then run through a multiple effect evaporator to create the syrup. DDGS is created by drying the DWG and syrup together. Drying the DWG alone without adding back the syrup produces a product called distillers dried grains (DDG). DDGS and DDG have a typical moisture content of 10%-13%. Currently,

distillers grains are marketed almost exclusively as livestock feed.

The advantages of using the co-products, or some portion of them, as fuel for the ethanol production process, are that these materials are available at the plant, they are produced in sufficient quantity to meet process heat and electricity needs (Morey et al., 2006), and during periods of low co-product prices the task of marketing them is reduced or eliminated.

Corn stover is also a potential biomass source to provide energy at ethanol plants. Since ethanol plants are usually located in corn growing areas, the corn stover is available in close proximity. However, since under current production practices, most corn stover is left in the field, there are costs associated with collection, transportation, storage, and pre-processing to make the material into a convenient fuel. Sokhansanj and Turhollow (2004) estimate costs of corn stover at \$60/t for large round bales and \$80/t for densified (cubed) material.

In reviewing the literature, we found large amounts of information about DDGS and other forms of co-products in terms of their characteristics as animal feeds. Some of this information was applicable to characterizing the co-products as fuels (e.g., Belyea et al., 2004; Dakota Gold, 2005; University of Minnesota, 2005). However, much of the necessary fuel information was missing. We found one source that had heat content and ultimate analysis for some ethanol co-products (AURI, 2008). Biswas and Staff (2001) used thermogravimetric analysis (TGA) in conjunction with other techniques to determine compounds in the headspace of distillers grains storages, and to identify volatiles released during heating and drying of distillers grains for temperatures of 250°C-300°C. Although the analysis was not performed to determine fuel characteristics of distillers grains, the results

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are applicable. Wang et al. (2007) used TGA to evaluate the fuel characteristics of distillers grains.

The literature contained somewhat more fuel characteristic data for corn stover (e.g., Ebeling and Jenkins, 1985; Gaur and Reed, 1995; National Renewable Energy Laboratory, 1998; Hoskinson et al., 2007). Kumar et al. (2008) performed TGA analysis on corn stover. Brown (2003) summarized fuel property data for a range of biomass materials.

Several researchers have evaluated the potential of anaerobic digestion of the thin stillage to meet part of the ethanol plant energy needs (Rosentrater et al., 2006; Pfeiffer et al., 2007; Agler et al., 2008).

Rosentrater (2006) measured physical properties of DDGS, which is important information for developing systems for handling the material. Ganesan et al. (2008) presented isotherm data for DDGS, which is important in designing storage systems.

The objective of this article is to characterize fuel properties of ethanol co-products and corn stover, which are important for thermochemical conversion (combustion or gasification) of these materials to produce heat and power.

## SAMPLE COLLECTION AND ANALYSIS

Feed streams were sampled at five cooperating dry-grind ethanol plants located in Minnesota and Wisconsin. Feed streams included distillers dried grains with solubles (DDGS) – four plants, distillers dried grains (DDG) – one plant, distillers wet grains (DWG) – five plants, and syrup – five plants. Sample and shipping containers with sampling instructions were sent to each of the five plants. Plant personnel obtained one composite sample of each material, placed each sample in a sealed container, and then called a delivery service for overnight transport of the samples to the appropriate laboratory.

A sample of corn stover was obtained from the Agricultural Utilization Research Institute (AURI), Waseca, Minnesota and submitted for analysis.

The following analyses were performed at Twin Ports Testing, Inc. in Superior, Wisconsin. The laboratory used standard ASTM procedures (ASTM, 2006) or related standard industry procedures (EPA, 2008) for the analyses. Analyses for fuel properties included proximate (moisture: ASTM D3173; ash: ASTM D3174; heating value: ASTM: D1989; volatiles: ASTM D3175; sulfur: ASTM D4239; chlorine: ASTM D4208; mercury: ASTM 6722), ultimate (C, H, N, O: ASTM D5373), selected metals (EPA 3050/6010), and ash characteristics (ash fusion: ASTM D1857; mineral analysis: ASTM D3682).

Thermogravimetric analysis (TGA) was performed at the Distillers Grains Technology Council Laboratory in Louisville, Kentucky. Samples were run starting at 26°C, heating at 30°C/min to 850°C, with air purge, using a 2950 TGA HR V5.4A apparatus from TA Instruments.

## RESULTS AND DISCUSSION

Fuel characteristics for ethanol plant co-products and corn stover are summarized in table 1. Most results are presented on a moisture free basis for ease of comparison. Since only one plant produced DDG, detailed results (except for the

TGA analysis) are not presented here because we agreed not to identify results from specific plants. However, the DDG results on a moisture free basis are consistent with the DWG results on a moisture free basis from the five plants.

DWG and syrup have mean moisture contents of about 65% and 67%, respectively, as received (table 1) and higher heating values of approximately 7.79 and 6.43 MJ/kg (3349 and 2765 Btu/lb) respectively at these moisture contents. These moisture contents are too high to sustain combustion even in a fluidized bed without augmentation with some other fuel or drying of the material before use as a fuel (Morey et al., 2008).

For other characteristics, results are more easily compared on a moisture free basis. Higher heating values for DDGS and DWG (table 1) are within 3% of the corresponding values presented in AURI (2008). The heating value for corn stover of 17.9 MJ/kg dry matter falls in the range of 17.7 to 18.5 MJ/kg dry matter from four other studies (AURI, 2008; Ebeling and Jenkins, 1985; Gaur and Reed, 1995; National Renewable Energy Laboratory, 1998; Hoskinson et al., 2007). The higher heating values for the co-products (19.7 to 22.0 MJ/kg) are greater than for corn stover and most other biomass materials, such as grasses or wood (Brown, 2003), probably because of their higher protein and/or oil contents. Ash content and ultimate analyses for co-products and corn stover (table 1) are consistent with the results from these other four studies. The ultimate analyses will provide useful input for modeling of combustion and gasification of these fuels.

Nitrogen occurs in significant quantities in the three ethanol co-products (table 1). For comparison, Belyea et al. (2004) found a mean nitrogen content of 5.1% of dry matter with a range of 4.8% to 5.3% for DDGS, a mean of 5.4% with a range of 5.1% to 5.8% for DWG, and a mean of 3.2% with a range of 2.2% to 4.8% for syrup from nine dry-grind plants. These trends in nitrogen content for DDGS, DWG, and syrup are consistent for our results and those of Belyea et al. (2004) with both studies showing large variations among samples. University of Minnesota (2005) found a mean nitrogen content of 4.9% with a range of 4.5% to 5.4% for DDGS from 32 plants in 11 states. The DDGS nitrogen results for all studies are consistent and demonstrate relatively large variations among plants.

Sulfur also occurs in large quantities in the three ethanol co-products (table 1). For comparison, Belyea et al. (2004) found a mean sulfur content of 0.58% of dry matter with a range of 0.36% to 0.84% for DDGS, a mean of 0.48% with a range of 0.40% to 0.58% for DWG, and a mean of 0.74% with a range of 0.20% to 1.32% for syrup from nine dry-grind plants. These trends in sulfur content for DDGS, DWG, and syrup are consistent for our results and those of Belyea et al. (2004) with both studies showing large variations among samples, particularly for the syrup. University of Minnesota (2005) found a mean sulfur content of 0.61% with a range of 0.31% to 1.05% for DDGS from 32 plants in 11 states. Again, the DDGS sulfur results for all studies are consistent and demonstrate large variations among plants.

Chlorine also occurs in significant quantities in ethanol co-products and corn stover (table 1). The chlorine results for DWG and syrup had large standard deviations. AURI (2008) found higher levels of chlorine in DDGS than our results (3017 vs. 1757 µg/g) and lower levels in DWG than our results (774 vs. 1673 µg/g). Our chlorine results for corn

**Table 1. Characteristics of ethanol co-products and corn stover as fuels.**

Parameter	DDGS	DWG	Syrup	Corn Stover <sup>[a]</sup>
<b>As received</b>				
Moisture, %	10.12 (1.38) <sup>[b]</sup>	64.46 (6.13) <sup>[c]</sup>	67.29 (6.80) <sup>[c]</sup>	6.15
Ash, %	3.41 (0.27) <sup>[b]</sup>	0.97 (0.68) <sup>[c]</sup>	2.31 (0.77) <sup>[c]</sup>	6.31
Higher heating value, MJ/kg [Btu/lb]	19.46 (0.39) <sup>[b]</sup> [8368 (168) <sup>[b]</sup> ]	7.79 (1.32) <sup>[c]</sup> [3349 (567) <sup>[c]</sup> ]	6.43 (0.97) <sup>[c]</sup> [2765 (418) <sup>[c]</sup> ]	16.83 [7235]
<b>Moisture free</b>				
Higher heating value, MJ/kg [Btu/lb]	21.75 (0.20) <sup>[d]</sup> [9349 (88) <sup>[d]</sup> ]	21.95 (0.26) <sup>[c]</sup> [9438 (110) <sup>[c]</sup> ]	19.73 (1.45) <sup>[c]</sup> [8482 (623) <sup>[c]</sup> ]	17.93 [7709]
Lower heating value, MJ/kg [Btu/lb]	20.24 <sup>[e]</sup> [8703 <sup>[e]</sup> ]	20.51 <sup>[e]</sup> [8819 <sup>[e]</sup> ]	18.19 <sup>[e]</sup> [7819 <sup>[e]</sup> ]	16.73 <sup>[e]</sup> [7192 <sup>[e]</sup> ]
<b>Proximate</b>				
Ash, %	3.89 (0.29) <sup>[d]</sup>	2.58 (1.25) <sup>[c]</sup>	7.02 (1.47) <sup>[c]</sup>	6.73
Volatile matter, %	82.50 (1.32) <sup>[d]</sup>	83.18 (2.09) <sup>[c]</sup>	81.71 (0.92) <sup>[c]</sup>	66.58
Fixed carbon, %	12.84 (1.61) <sup>[d]</sup>	13.58 (1.75) <sup>[c]</sup>	10.32 (1.58) <sup>[c]</sup>	26.65
<b>Ultimate</b>				
Carbon, %	50.24 (0.31) <sup>[d]</sup>	52.53 (3.24) <sup>[c]</sup>	43.12 (4.29) <sup>[c]</sup>	45.48
Hydrogen, %	6.89 (0.05) <sup>[d]</sup>	6.60 (0.34) <sup>[c]</sup>	7.07 (0.24) <sup>[c]</sup>	5.52
Nitrogen, %	4.79 (0.34) <sup>[d]</sup>	5.35 (0.35) <sup>[c]</sup>	2.63 (0.59) <sup>[c]</sup>	0.69
Oxygen, %	33.42 (1.11) <sup>[d]</sup>	32.28 (2.87) <sup>[c]</sup>	39.21 (4.31) <sup>[c]</sup>	41.52
Sulfur, %	0.77 (0.18) <sup>[d]</sup>	0.66 (0.11) <sup>[c]</sup>	0.96 (0.31) <sup>[c]</sup>	0.04
Chlorine, µg/g	1757 (89) <sup>[f]</sup>	1673 (1543) <sup>[b]</sup>	3459 (807) <sup>[b]</sup>	984
Mercury, µg/g	<0.010 <sup>[g]</sup>	<0.10 <sup>[h]</sup>	<0.012 <sup>[h]</sup>	<0.010
<b>Metals, mg/kg</b>				
Arsenic	<3.20 <sup>[g]</sup>	<3.10 <sup>[h]</sup>	<3.20 <sup>[h]</sup>	2.50
Beryllium	<0.093 <sup>[g]</sup>	<0.093 <sup>[h]</sup>	<0.11 <sup>[h]</sup>	<0.089
Cadmium	<0.046 <sup>[g]</sup>	<0.50 <sup>[h]</sup>	<0.53 <sup>[h]</sup>	<0.45
Chromium	0.50 (0.05) <sup>[f]</sup>	<0.79 <sup>[h]</sup>	0.75 (0.20) <sup>[b]</sup>	<0.45
Lead	<0.046 <sup>[g]</sup>	<0.50 <sup>[h]</sup>	<0.53 <sup>[h]</sup>	0.46
Manganese	15.95 (1.63) <sup>[f]</sup>	12.05 (4.45) <sup>[b]</sup>	34.93 (10.63) <sup>[b]</sup>	23.4
Nickel	0.87 (0.06) <sup>[f]</sup>	<1.20 <sup>[h]</sup>	1.97 (0.45) <sup>[b]</sup>	<0.45
Phosphorus	-	-	-	-
Potassium	-	-	-	-
Selenium	1.80 (0.00) <sup>[f]</sup>	<1.80 <sup>[h]</sup>	<1.60 <sup>[h]</sup>	<1.30

<sup>[a]</sup> One sample.

<sup>[b]</sup> Mean (standard deviation) of samples from three plants.

<sup>[c]</sup> Mean (standard deviation) of samples from five plants.

<sup>[d]</sup> Mean (standard deviation) of samples from four plants.

<sup>[e]</sup> Calculated using mean higher heating value and mean ultimate analysis.

<sup>[f]</sup> Mean (standard deviation) of samples from two plants.

<sup>[g]</sup> Samples from two plants.

<sup>[h]</sup> Samples from three plants.

stover (984 µg/g) are lower than found by other researchers (1380 µg/g: AURI, 2008; 6000 µg/g: Ebeling and Jenkins, 1985; 2660 µg/g: National Renewable Energy Laboratory, 1998; 2000-3000 µg/g: Hoskinson et al., 2007).

Nitrogen, sulfur, and chlorine are major emission concerns for ethanol facilities because they potentially give rise to nitrogen oxides (NO<sub>x</sub>), sulfur dioxide (SO<sub>2</sub>), and hydrochloric acid (HCL), respectively during combustion (EPA, 2006).

We did not analyze for phosphorus and potassium because a significant amount of information on these two elements is available from other analyses of dry-grind ethanol co-products (Belyea et al., 2004; Dakota Gold, 2005; University of Minnesota, 2005).

Ash characteristics of the co-products are presented in table 2. Ash analyses were run for either two or three plants.

Ash fusion temperatures (initial deformation, softening, hemispherical) for DDGS and DWG are relatively low [less than 815°C (1500°F)] in oxidizing environments. Low ash fusion temperatures may lead to agglomeration of ash or formation of clinkers, which can cause problems in combustion systems. Because gasification operates at lower temperatures, gasification followed by separation of the ash before combustion may be required with these fuels. The higher ash fusion temperatures for syrup and corn stover suggest fewer potential problems in combusting these fuels. The ash fusion results for corn stover in an oxidizing atmosphere were comparable to those found by Hoskinson et al. (2007). The ash fusion values for corn stover in a reducing environment were approximated 200°C lower at initial deformation and softening temperatures than those reported by Hoskinson et al. (2007).

**Table 2. Ash characteristics of ethanol co-products and corn stover.**

Parameter	DDGS	DWG	Syrup	Corn Stover <sup>[a]</sup>
<b>Ash fusion - Oxidizing atmosphere</b>				
Initial deformation, °C [°F]	583 (53) <sup>[b]</sup> [1081 (96) <sup>[b]</sup>	711 (56) <sup>[c]</sup> [1312 (91) <sup>[c]</sup>	1044 (873) <sup>[c]</sup> [1912 (1572) <sup>[c]</sup>	1054 [1930]
Softening, °C [°F]	593 (56) <sup>[b]</sup> [1099 (100) <sup>[b]</sup>	749 (65) <sup>[c]</sup> [1381 (117) <sup>[c]</sup>	1197 (456) <sup>[c]</sup> [2186 (820) <sup>[c]</sup>	1084 [1984]
Hemispherical, °C [°F]	705 (5) <sup>[b]</sup> [1301 (9) <sup>[b]</sup>	786 (68) <sup>[c]</sup> [1446 (122) <sup>[c]</sup>	1424 (81) <sup>[c]</sup> [2595 (146) <sup>[c]</sup>	1149 [2100]
Fluid, °C [°F]	1108 (447) <sup>[b]</sup> [2027 (805) <sup>[b]</sup>	1116 (321) <sup>[b]</sup> [2041 (578) <sup>[c]</sup>	1479 (18) <sup>[c]</sup> [2695 (33) <sup>[c]</sup>	1207 [2205]
<b>Ash fusion - Reducing atmosphere</b>				
Initial deformation, °C [°F]	690 (25) <sup>[b]</sup> [1274 (45) <sup>[b]</sup>	719 (49) <sup>[c]</sup> [1327 (89) <sup>[c]</sup>	1037 (209) <sup>[c]</sup> [1898 (377) <sup>[c]</sup>	884 [1624]
Softening, °C [°F]	751 (68) <sup>[b]</sup> [1384 (123) <sup>[b]</sup>	797 (82) <sup>[c]</sup> [1467 (148) <sup>[c]</sup>	1191 (242) <sup>[c]</sup> [2176 (436) <sup>[c]</sup>	937 [1718]
Hemispherical, °C [°F]	812 (128) <sup>[b]</sup> [1493 (231) <sup>[b]</sup>	863 (112) <sup>[c]</sup> [1586 (201) <sup>[c]</sup>	1253 (203) <sup>[c]</sup> [2287 (366) <sup>[c]</sup>	1043 [1909]
Fluid, °C [°F]	1411 (12) <sup>[b]</sup> [2573 (21) <sup>[b]</sup>	1081 (29) <sup>[c]</sup> [1978 (62) <sup>[c]</sup>	1458 (8) <sup>[c]</sup> [2657 (15) <sup>[c]</sup>	1201 [2194]
<b>Mineral analysis, %</b>				
Silicon dioxide	2.89 (0.22) <sup>[b]</sup>	4.37 (2.16) <sup>[c]</sup>	<2.42 <sup>[d]</sup>	54.12
Aluminum oxide	<0.38 <sup>[e]</sup>	<0.38 <sup>[d]</sup>	<0.38 <sup>[d]</sup>	0.78
Titanium dioxide	<0.03 <sup>[e]</sup>	<0.03 <sup>[d]</sup>	<0.03 <sup>[d]</sup>	0.04
Iron oxide	<0.32 <sup>[e]</sup>	<0.29 <sup>[d]</sup>	<0.93 <sup>[d]</sup>	0.45
Calcium oxide	<1.4 <sup>[e]</sup>	<0.1.4 <sup>[d]</sup>	<0.1.4 <sup>[d]</sup>	5.61
Magnesium oxide	13.31 (1.61) <sup>[b]</sup>	8.85 (1.89) <sup>[c]</sup>	10.81 (2.71) <sup>[c]</sup>	4.22
Potassium oxide	30.04 (0.88) <sup>[b]</sup>	22.40 (6.10) <sup>[c]</sup>	27.03 (5.66) <sup>[c]</sup>	20.22
Sodium oxide	3.65 (1.88) <sup>[b]</sup>	3.05 (1.78) <sup>[c]</sup>	3.18 (1.01) <sup>[c]</sup>	1.47
Sulfur trioxide	1.57 (0.35) <sup>[b]</sup>	2.03 (2.16) <sup>[c]</sup>	5.87 (1.59) <sup>[c]</sup>	12.75
Phosphorus pentoxide	43.24 (3.19) <sup>[b]</sup>	34.77 (5.44) <sup>[c]</sup>	30.15 (3.59) <sup>[c]</sup>	1.97
Strontium oxide	<0.02 <sup>[e]</sup>	<0.02 <sup>[d]</sup>	<0.02 <sup>[d]</sup>	<0.02
Barium oxide	<0.02 <sup>[e]</sup>	<0.02 <sup>[d]</sup>	<0.02 <sup>[d]</sup>	0.02
Manganese dioxide	0.06 (0.01) <sup>[b]</sup>	0.05 (0.02) <sup>[c]</sup>	0.05 (0.02) <sup>[c]</sup>	0.06
Nitrogen	2.44 (1.77) <sup>[b]</sup>	2.35 (1.20) <sup>[c]</sup>	1.55 (0.64) <sup>[c]</sup>	-

[a] One sample.

[b] Mean (standard deviation) of samples from two plants.

[c] Mean (standard deviation) of samples from three plants.

[d] Samples from three plants.

[e] Samples from two plants.

The alkali metal content (potassium plus sodium oxides) of the ash is high (25% to 34% for co-products and 22% for corn stover, table 2). Hoskinson et al. (2007) reported alkali metal contents of 15% to 22% for corn stover. Such high levels of alkali metals can lead to ash fouling in combustion and steam generation units (Miles et al., 1996), and to potential agglomeration of bed material in fluidized bed systems (Morey et al., 2008).

Results from the thermogravimetric analyses (TGA) of biomass fuels are presented in table 3. Figure 1 is a typical TGA plot for a biomass fuel, DDGS in this case, showing how it volatilizes or thermally decomposes as a function of temperature. Three distinct degradation zones (or stages) were identified for the biomass fuels analyzed (table 3). In the literature, TGA combustion profiles with three distinct degradation stages for distillers grains, corn stover, and rice straw have been reported (Biswas and Staff, 2001; Calvo et al., 2004; Kumar et al., 2008). In our study, stages I, II, and III occurred in the temperature ranges of 26°C-250°C,

125°C-530°C, and 375°C-775°C, respectively (table 3). During stage I (referred to as drying stage), drying (i.e., loss of moisture) and volatilization of light molecules such as fatty acids occur (Biswas and Staff, 2001; Calvo et al., 2004; Kumar et al., 2008). During stage II (referred to as primary combustion stage), degradation of hemicellulose, polysaccharides, starch, fat/oil, phenolic acids, and some portions of protein, cellulose and lignin could occur (Biswas and Staff, 2001; Mellon and Sharma, 2002; Shujun et al., 2006; Kumar et al., 2008). During stage III (referred to as residual combustion stage), some protein components, lignin, char, and thermally stable components such as metals may decompose (Biswas and Staff, 2001; Mellon and Sharma, 2002; Kumar et al., 2008). For the low-moisture (4% to 10% w.b.) biomass samples (i.e., DDG, DDGS, and corn stover), the greatest weight loss with the largest degradation rate occurred in stage II. For the high-moisture (70% to 75% w.b.) biomass samples (i.e., DWG and syrup), the greatest weight loss with the largest degradation rate occurred in stage I.

**Table 3. Thermal degradation stages of DWG, DDG, syrup, DDGS, and corn stover during combustion determined by thermogravimetric analysis (TGA) of biomass samples at a heating rate of 30 °C/min with air purge.**

Thermal Degradation Stages	DWG (n = 1)	DDG (n = 1)	Syrup (range for n = 3)	DDGS (range for n = 2)	Corn Stover (n = 1)	Corn Stover (Kumar et al., 2008) <sup>[a]</sup>
<b>Stage I - Drying<sup>[b]</sup></b>						
T <sub>0</sub> (°C) = T <sub>1</sub>	26	26	26	26	26	25
W <sub>0</sub> (%) = W <sub>1</sub>	100	100	100	100	100	100
T <sub>f</sub> (°C) = T <sub>2</sub>	225	150	250	125-130	140	135
W <sub>f</sub> (%) = W <sub>2</sub>	30	90	25-30	95	96	96
(dW/dt) <sub>p1</sub> (%/min)	24	4	23-25	2	11	-
T <sub>p1</sub> (°C)	150	60	100-125	80-97	60	-
<b>Stage II - Primary combustion<sup>[b]</sup></b>						
T <sub>0</sub> (°C) = T <sub>2</sub>	225	150	250	125-130	140	245
W <sub>0</sub> (%) = W <sub>2</sub>	30	95	25-30	95	96	92
T <sub>f</sub> (°C) = T <sub>3</sub>	475	500	475-525	525-530	375	350
W <sub>f</sub> (%) = W <sub>3</sub>	10	25	8-12	27-28	33	13
(dW/dt) <sub>p2</sub> (%/min)	5	14	3-4	12-14	30	-
T <sub>p2</sub> (°C)	300	300	275-360	290-300	300	-
Combustion reactivity of the fuel (% min <sup>-1</sup> K <sup>-1</sup> ) <sup>[c]</sup>	0.9	2.4	0.5-0.7	2.1-2.5	5.2	-
<b>Stage III - Residual combustion<sup>[b]</sup></b>						
T <sub>0</sub> (°C) = T <sub>3</sub>	475	500	475-525	525-530	375	410
W <sub>0</sub> (%) = W <sub>3</sub>	10	25	8-12	27-28	33	13
T <sub>f</sub> (°C) = T <sub>4</sub>	750	750	625-675	775	525	560
W <sub>f</sub> (%) = W <sub>4</sub>	3	2	1-4	6	10	9
(dW/dt) <sub>p3</sub> (%/min)	3	6	2-3	5	26	-
T <sub>p3</sub> (°C)	600	600	540-600	600-625	425	-
<b>Residue<sup>[b]</sup></b>						
T <sub>Residue</sub> (°C)	850	850	850	850	850	850
Ash + fixed carbon (% weight)	1.0	1.7	1.4-3.9	5.7-6.3	8.0	7.4

<sup>[a]</sup> Kumar et al. (2008) considered the small weight losses (<5% wt.) occurred between 135°C and 245°C, and between 350°C and 410°C negligible, and thus, they did not include these temperatures when demarcating different thermal degradation stages. In our study, we considered continuity of temperatures and residual weights between stages.

<sup>[b]</sup> The symbols are defined below:

T<sub>0</sub> (°C) = initial temperature of the stage. Based on figure 1, the initial temperatures for stages I, II, and III are T<sub>1</sub>, T<sub>2</sub>, and T<sub>3</sub>, respectively.

W<sub>0</sub> (%) = residual weight at T<sub>0</sub>. Based on figure 1, the residual weights at the start of stages I, II, and III are W<sub>1</sub>, W<sub>2</sub>, and W<sub>3</sub>, respectively.

T<sub>f</sub> (°C) = final temperature of the stage. Based on figure 1, the final temperatures for stages I, II, and III are T<sub>2</sub>, T<sub>3</sub>, and T<sub>4</sub>, respectively.

W<sub>f</sub> (%) = residual weight at T<sub>f</sub>. Based on figure 1, the residual weights at the end of stages I, II, and III are W<sub>2</sub>, W<sub>3</sub>, and W<sub>4</sub>, respectively.

(dW/dt)<sub>p1</sub> (%/min) = the largest value of derivative of weight loss in stage I.

(dW/dt)<sub>p2</sub> (%/min) = the largest value of derivative of weight loss in stage II.

(dW/dt)<sub>p3</sub> (%/min) = the largest value of derivative of weight loss in stage III.

T<sub>p1</sub> (°C) = temperature associated with (dW/dt)<sub>p1</sub>.

T<sub>p2</sub> (°C) = temperature associated with (dW/dt)<sub>p2</sub>.

T<sub>p3</sub> (°C) = temperature associated with (dW/dt)<sub>p3</sub>.

T<sub>Residue</sub> (°C) = temperature of the residue (i.e., ash + fixed carbon).

T<sub>2</sub> = ignition temperature of the fuel (°C).

T<sub>4</sub> = burnout temperature of the fuel (°C).

T<sub>p2</sub> = peak temperature of combustion (°C).

<sup>[c]</sup> Combustion reactivity of the fuel (% min<sup>-1</sup> K<sup>-1</sup>) = [100 × (dW/dt)<sub>p2</sub>] / T<sub>p2</sub>. The combustion reactivity of the fuel is defined as 100 times the maximum rate of weight loss in the burning profile (i.e., the part of the TGA plot after the ignition temperature) divided by the temperature corresponding to the maximum rate of weight loss. The higher the value of the reactivity of the fuel, the better its combustion properties (Miranda et al., 2008).

Biswas and Staff (2001) found that the plot of weight loss (%) of DWG or DDG versus temperature (°C) had three thermal transition stages with temperatures at the maximum degradation rate (i.e., T<sub>p1</sub>, T<sub>p2</sub>, and T<sub>p3</sub> in fig. 1) of 60°C-70°C, 250°C-300°C, and 510°C-550°C, respectively. In our study, the temperatures at the maximum degradation rate for the three stages of degradation of DWG or DDG were 60°C-150°C, 300°C, and 600°C, respectively. The degradation patterns of DWG and DDG were similar during the stages II and III; however, during stage I, DWG had a larger transition temperature zone than DDG because of the higher moisture content of DWG (table 3). A similar

explanation for thermal transitions of DWG versus DDG was given by Biswas and Staff (2001). Wang et al. (2007) found that low-moisture (1.6% w.b.) DDGS residue (obtained after extracting the lipids from the DDGS using supercritical carbon dioxide extraction) had a maximum weight loss (about 55% weight loss with a maximum degradation rate of 22.5%/min) in the temperature range of 200°C to 470°C. We found that the maximum decomposition of DDGS occurred in the temperature range of 125°C-530°C (about 67% weight loss with a maximum degradation rate of 12%-14%/min). The differences in the TGA results between our study and Biswas and Staff (2001) or Wang et al. (2007) may be due to

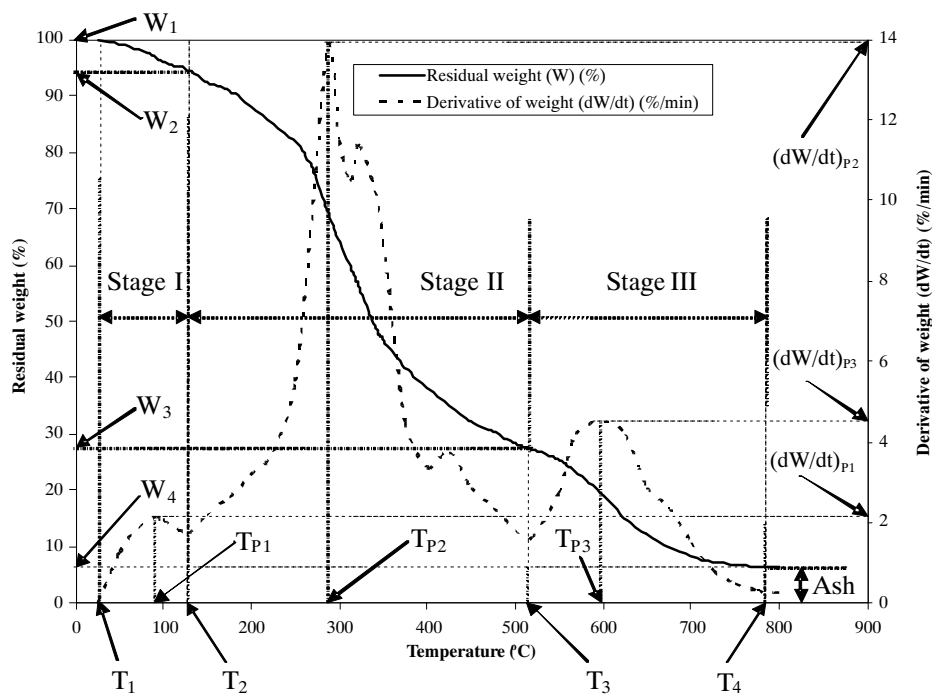


Figure 1. A typical plot of thermogravimetric analysis (TGA) of DDGS at a heating rate of 30°C/min with air purge. Stages I, II, and III are approximate thermal degradation zones for drying, primary combustion, and residual combustion of DDGS, respectively.  $T_1$ ,  $T_2$ , and  $T_3$  are the initial temperatures of stages I, II, and III, respectively.  $T_2$ ,  $T_3$ , and  $T_4$  are the final temperatures of stages I, II, and III, respectively.  $W_1$ ,  $W_2$ , and  $W_3$  are the residual weights at the start of stages I, II, and III, respectively.  $W_2$ ,  $W_3$ , and  $W_4$  are the residual weights at the end of stages I, II, and III, respectively.  $(dW/dt)_{P1}$ ,  $(dW/dt)_{P2}$ , and  $(dW/dt)_{P3}$  are the largest values of the derivative of weight losses for stages I, II, and III, respectively.  $T_{P1}$ ,  $T_{P2}$ ,  $T_{P3}$  are temperatures associated with  $(dW/dt)_{P1}$ ,  $(dW/dt)_{P2}$ , and  $(dW/dt)_{P3}$ , respectively. Temperature  $T_2$  is the ignition temperature of the biomass fuel and is measured when there is a sudden rise in weight loss rate  $[(dW/dt)]$  after the initial  $(dW/dt)$  peak for moisture loss (Demirbas, 2004; Miranda et al., 2008). The temperature at which  $(dW/dt)$  is maximum in the burning profile (i.e., the part of the TGA plot after the ignition temperature) is called the “peak temperature” of combustion. Here, temperature  $T_{P2}$  is the peak temperature. The lower the peak temperature, the more reactive a fuel may be during combustion (Demirbas, 2004; Miranda et al., 2008). Temperature  $T_4$  is the burnout temperature of the fuel and is measured when the combustion reaction ceases due to the end of char combustion (Miranda et al., 2008).

the differences in composition between the samples, and due to the differences in the experimental conditions such as heating rate and air purging rate used for the TGA analyses.

Kumar et al. (2008) reported that corn stover decomposed about 4% (wt.) from 25°C to 115°C-140°C, about 70% (wt.) from 240°C to 350°C-400°C, and about 10% (wt.) from 400°C to 560°C during the simulated combustion study using a TGA machine. Similar decomposition trends for corn stover were observed in this study. We found about 4% weight loss between 26°C and 140°C, about 63% weight loss between 140°C and 375°C, and about 23% weight loss between 375°C and 525°C (table 3). The apparent differences in the TGA results of corn stover between this study and Kumar et al. (2008) may be due to the differences in the temperature ranges chosen for demarcating the different thermal transition zones, and the variety and composition of corn stover used for the analysis. However, the total weight losses measured for the stage II and stage III (from 140°C to 560°C) were similar in both studies (80% to 86% wt.) (table 3).

In figure 1, temperature  $T_2$  is the ignition temperature of the biomass fuel and is measured when there is a sudden rise in the weight loss rate  $[(dW/dt)]$  after the initial  $(dW/dt)$  peak for moisture loss (Demirbas, 2004; Miranda et al., 2008). For the biomass fuels analyzed in this study, the ignition temperatures ranged from 125°C to 250°C (table 3). Demirbas (2004) and Miranda et al. (2008) reported that the

ignition temperatures for a variety of biomass residues ranged from 150°C to 220°C. For coals, the ignition temperatures may range between 235°C and 441°C, with higher values corresponding to coals with higher carbon contents (Alonso et al., 2001). The combustion reactivity of a fuel is defined as 100 times the maximum rate of weight loss in the burning profile (i.e., the part of the TGA plot after the ignition temperature) divided by the temperature corresponding to the maximum rate of weight loss (Miranda et al., 2008). According to figure 1, combustion reactivity of the fuel ( $\% \text{ min}^{-1} \text{ K}^{-1}$ ) equals  $[100 \times (dW/dt)_{P2}] / T_{P2}$ . The higher the value of the combustion reactivity of the fuel, the better its combustion properties (e.g., faster devolatilization and subsequent combustion). The combustion reactivity of corn stover ( $5.2\% \text{ min}^{-1} \text{ K}^{-1}$ ) was higher than for ethanol co-products ( $0.5\text{-}2.5\% \text{ min}^{-1} \text{ K}^{-1}$ ) (table 3). In addition, low-moisture co-products (i.e., DDG and DDGS) had higher combustion reactivities than high-moisture co-products (i.e., DWG and syrup) (table 3).

In figure 1, temperature  $T_4$  is the burnout temperature, which is defined as the temperature when the combustion reaction terminates because all combustible components in the fuel including char have been consumed (Miranda et al., 2008). The burnout temperature provides qualitative information regarding the necessary residence time of the fuel that minimizes the unburned material in large scale combustion devices. If the fuel has a low value of burnout

temperature, the resulting unburned material is low. Whereas, fuels with higher burnout temperatures are more difficult to burn and would require longer residence times and higher temperatures for their complete combustion (Miranda et al., 2008). The burnout temperature of corn stover (525°C) was considerably lower than for ethanol co-products (625°C-775°C) (table 3). Among the ethanol co-products, syrup had the lowest burnout temperature (625°C-675°C) compared to DWG, DDG, or DDGS (750°C-775°C) (table 3). Thus, corn stover and syrup would require less residence time in the combustor for complete combustion than DWG/DDG or DDGS. Miranda et al. (2008) reported that the burnout temperatures for olive pit, olive pulp and olive cake ranged from 509°C to 530°C. Alonso et al. (2001) found that the burnout temperatures for low-high rank coals were 530°C to 810°C. Corn stover has higher ash fusion temperature, higher combustion reactivity, and lower burnout temperature than ethanol co-products (tables 2 and 3), which suggests that corn stover may have more favorable fuel characteristics for combustion than ethanol co-products. Of the co-products, syrup appears to have more favorable fuel characteristics for combustion than DWG, DDG, or DDGS due to its higher ash fusion and lower burnout temperatures (tables 2 and 3).

Examination of the standard deviations of co-product fuel and ash data in tables 1 and 2, as well as data from the literature, indicate that there is large variability in some of the key results. This variability is due to differences from plant to plant, but also is probably indicative of variation in feed stream characteristics over time at a particular plant. We believe these data are useful for planning purposes, but more data will be required before undertaking a detailed design for a particular combustion or gasification process at a specific plant.

## SUMMARY AND CONCLUSIONS

Fuel characteristics of co-products of the ethanol dry-grind process [distillers wet grains (DWG), concentrated distillers solubles (referred to as “syrup”), and distillers dried grains with solubles (DDGS)], and corn stover were evaluated. Analyses included proximate, ultimate, selected metals, ash fusion temperatures, minerals in the ash, and thermogravimetric analysis (TGA).

Higher heating values for the co-products are greater than for corn stover and for most other biomass materials. The ethanol co-products contain large amounts of nitrogen, sulfur, and chlorine, which will require major control technologies for combustion or gasification systems to meet emissions limits. Corn stover also contains high levels of chlorine.

Ash fusion temperatures for DDGS and DWG are relatively low (less than 815°C), which may provide challenges in combustion systems. The alkali metal content (potassium and sodium oxides) of the ash is high (22% to 34%) for co-products and corn stover, which will require careful design to avoid to ash fouling in combustion and steam generation units. Corn stover has more favorable combustion characteristics than the ethanol co-products based on higher ash fusion temperatures and the TGA results (higher combustion reactivity and lower burnout temperature).

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