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*An ASABE Meeting Presentation*

*Paper Number: 12-1337561*

## **Pyrolysis of Distillers Grains**

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### **ABSTRACT**

As the quantity of ethanol produced in the U.S. continues to expand, so too does the need for value-added applications for the resulting coproducts. Distillers dried grains with solubles (DDGS), corn gluten meal (CGM), and corn gluten feed (CGF) are the primary coproducts of ethanol manufacturing (which includes dry grind processing and wet milling). The main consumer of these coproducts is the livestock industry, which utilizes these materials as animal feed and ingredients due to their high nutrient contents, good palatability and digestibility, and relatively low cost; however, new value added uses are starting to arise. This study will examine the pyrolysis of DDGS and CGM. Extensive characterization of the resulting bio-oil included mass density, thermal conductivity, thermal diffusivity, apparent viscosity, and energy content. Potential opportunities for extracting value from these materials will also be explored and discussed.

**Keywords:** Distillers Dried Grains with Solubles (DDGS), Pyrolysis, Bio-oil

## INTRODUCTION

The US ethanol industry has continuously gained momentum over the past decade, increasing its production by nearly eight hundred percent from 2000 to 2010 (RFA, 2011c). In 2010 the industry produced a record 13.2 billion gallons, replacing around 445 million barrels of imported oil (RFA, 2011a). It is estimated that 88% of the ethanol produced in the United States is produced using dry milling methods, while the remaining 12% is produced from wet milling processes (RFA, 2010). The production of ethanol from corn utilizes the starch present in the corn, leaving protein, minerals, fat, and fiber behind in a concentrated form. In the wet milling process, the nonfermentable materials are used to produce corn gluten meal and corn gluten feed; while in the dry milling process, they are used to produce distillers dried grains with solubles (DDGS) and distillers wet grains (DWG). RFA (2011b) reported that in 2010, around 32.5 million metric tons of these grains were produced, which is an increase of nearly 30 million metric tons over what was produced in 2000.

Corn gluten meal is comprised of approximately 66% protein, 90% dry matter, 2.8% fat, and 3.3% fiber; while corn gluten feed is composed of approximately 20% protein, 90% dry matter, 2.2% fat, and 11.1% fiber (ISU, 2008). The swine and poultry industries are the largest consumers of corn gluten meal and corn gluten feed (ISU, 2008), but corn gluten meal has also been studied for its potential uses in horticulture as a natural herbicide (Christians, 1993.; McDaele, 1999; Webber et al, 2010) and in fish feeds (Li et al, 2011; Saez et al, 2011; Zhong et al, 2010).

DDGS is generally 25-35% protein, 86.2-93.0% dry matter, 3-13% fat, and 7.2% fiber (Bhadra et al, 2009b; Ganesan et al, 2008; ISU, 2008; Rosentrater and Muthukumarappan, 2006;

Shurson and Alhamdi, 2008; Weigel et al, 1997). Currently, the beef, dairy, swine, and poultry industries are the largest consumers of DDGS (RFA, 2011a; Shurson and Noll, 2005).

As the industry grows, and more coproducts are produced, there is a potential that supply may eventually surpass the livestock industry's demand at some point. There is concern that the demand from the livestock industry may become constrained as certain fats within the DDGS limit the amount that certain animals can have in their diets (Tiffany et al, 2008). In order to maintain the demand for coproducts, new value added uses and new markets should be pursued (Rosentrater, 2007). The high availability and low market price makes coproducts an inexpensive ingredient for various compounds. Currently, a small percentage of coproducts market is comprised of deicers, cat litter, 'lick barrels', and worm food (Bothast and Schlicher, 2005). Coproducts have even found their way into the aquaculture industry as feed supplements (Kannadhasan et al, 2010; Rosentrater et al, 2009a; Rosentrater et al, 2009b; Schaeffer et al, 2009), and could one day find their niche within the human food market, as research is being done on viability as human food ingredients (Rosentrater, 2007; Rosentrater and Krishnan, 2006). Studies are also being done to determine if coproducts can be used to produce a biodegradable plastics (Bothast and Schlicher, 2005; Tatara et al, 2006; Tatara et al, 2007).

While most investigations of coproducts over the years have been on ways of utilizing them as a feed ingredient, recent studies have begun investigating their potential as a source of energy. Some studies have begun analyzing the effectiveness of powering ethanol plants with this bio-based energy (De Kam et al, 2007; Morey et al, 2007; Tiffany et al, 2007). Tiffany et al (2007) modeled the feasibility of using the coproducts to provide energy to a 190 million L/y and a 380 million L/y dry grind ethanol plant, and found that if all the DDGS produced was used to generate process heat and energy for the facility, there would be leftover energy which could be

sold to the grid, thus increasing the rate of return on investment for the facility. According to Wang et al, (2007), there is approximately 25 MJ present in every 1 kg DDGS produced, and only 1 MJ of electric energy and 10 MJ of thermal energy are required to produce 1 liter of ethanol. Wang et al, (2007) also showed that in using this biomass as an energy source, ethanol plants could reduce their greenhouse gas emissions by nearly threefold compared to typical energy sources. This energy can be harvested from DDGS directly, by converting it to heat and power, or it can be converted into gaseous or liquid fuels to be used for energy (Giuntoli et al, 2011). These conversions, known as thermochemical conversions, consist of three main types: combustion, pyrolysis, and gasification (Wang et al, 2007).

The pyrolysis of biomass has been widely explored by various researchers to determine ideal processing parameters and the composition of the end products (Babu and Chaurasia, 2003; Chao et al, 2005; Gheorge, 2006; Parikh et al, 2003; Van de Velden et al, 2007). Pyrolysis can be defined as a thermochemical decomposition process through which organic matter is converted to oil, gas, and carbon residue in the absence of oxygen (Sadaka, 2009). There are two main types of pyrolysis: fast and slow. Slow pyrolysis is very time consuming, and has a very low product (tar) yield. Fast pyrolysis proceeds at a much quicker rate, and turns the organic matter directly into a gaseous form, which is then condensed into bio-oil and hydrogen (Sadaka, 2009). Both types are performed in the absence of oxygen.

Only a few studies have begun to explore the effects of pyrolysis on DDGS (Lei et al, 2011; Giuntoli, 2011). The studies mostly examined how changing the parameters of pyrolysis affected the final products. In order to fully understand the potential for using pyrolysis to obtain energy from ethanol coproducts, this study used pyrolysis to convert corn coproducts, including CGM, high protein DDG, de-oiled DDGS (protein fraction), de-oiled DDGS (fiber fraction), and

traditional DDGS, and then determined various physical and chemical properties of the resulting bio-oil.

## **MATERIALS AND METHODS**

### **Sample Collection and Experimental Design**

CGM, DDGS, de-oiled DDGS, and high protein DDG were obtained. The de-oiled DDGS was separated into high protein and high fiber fractions using aspiration. This resulted in a total of five different samples with various protein and fiber concentrations. They were stored in plastic storage bags at room temperature until needed for pyrolysis. After processing the bio-oil collected was stored in plastic screw-top bottles in a refrigerator until analyzed.

Two pyrolysis reactions were performed per coproduct sample, for a total of ten reactions. Three replications were performed for each physical property measured on the resulting bio-oil. Thermal conductivity, thermal diffusivity, energy content, mass density, and apparent viscosity were determined. Rheology measurements were also taken at three different temperatures (10 °C, 25 °C, and 40 °C).

### **Raw Material Composition**

The proximate composition for the raw materials used can be found in Table 1. The moisture content of the raw products ranged from 5.2% (fiber fraction) to 7.0% (CGM) and averaged 6%. The moisture content of the original product impacts the reaction time and the composition of the bio-oil produced, so it is important that these products had similar initial moisture contents. The main differences between the initial raw products was their fiber and protein contents. The protein content ranged from 25% (fiber fraction) to 69% (CGM), and the fiber content ranged from 6% (CGM) to 48% (fiber fraction).

### **Pyrolysis Reactions**

Each reaction began with 500g of sample in a sealed chamber of approximately 6,589 cm<sup>3</sup>. The chamber was equipped with a purging inlet tube and an exhaust outlet leading to the distillation apparatus. The collection apparatus was comprised of four condenser columns, with water jackets (6 °C water was cycled through to assist with the condensation of oil), and two glass bulbs to collect and sample the oil. The outlet after the fourth condenser was connected to hosing which released the produced syngas into a bucket of water to further filter the syngas before releasing into air. The chamber was placed within an Isotemp Programmable muffle furnace (650-750, Fisher Scientific, Pittsburg, PA), which was programmed to heat at a rate of 40 °C / min, till it reached the desired temperature of 600 °C. Before heating, the chamber and distillation system were purged with nitrogen gas for ten minutes in order to evacuate the vessel of O<sub>2</sub>. Pyrolysis was allowed to progress until no more syngas could be seen in the glassware (approximately 1.5-2 h).

## **Bio-oil Properties**

### Thermal Properties and Energy Content

Thermal conductivity and diffusivity were determined for the bio-oil samples with a thermal meter (KD2, Decagon Devices, Pullman, WA) that utilized the line heat source probe technique (Baghe-Khandan et al, 1981). These readings were taken at three different temperatures (10 °C, 25 °C, and 40 °C). Net energy content of the bio-oil samples were measured using a bomb calorimeter (1260 Isoperibolic, Parr Instrument, Moline, IL). Two replications were completed for each oil and each char sample.

### Rheology

Apparent viscosity was measured for the bio-oils using a rheometer (HAAKE Rheostress1, Thermo Electron Corporation, New Castle, DE), with a stainless steel cone and

plate attachment (Model LO4079 C60/1 Ti). In order to maintain constant temperature during testing, water from a set temperature water bath was pumped through the base plate. The shear rate for each sample was initiated at 10 (1/s), and was increased up to 100 (1/s) by increments of approximately 1(1/s). Rheology measurements were also taken at three different temperatures (10 °C, 25 °C, and 40 °C).

### Density

Mass density for the bio-oil was determined using a specific gravity cup (Model H-38000-12, Cole-Parmer Instrument Co., Barrington, IL). Material was poured into the cup, of a known mass and volume; excess material was then removed, and the filled cup was weighed on a balance. Density was then calculated as the ratio of mass to unit volume.

### **Data Analysis**

Data analysis was completed for each test using Excel v. 2010 (Microsoft, Redmond, WA) software to determine mean values and standard distributions, and then with two-way analysis of variance by general linear models using SAS (2004) V.8 (SAS Institute, Cary, NC), using a type I error rate ( $\alpha$ ) of 0.05, to determine main and interaction effects, and least significant differences (LSD) between sample means. Rheological data was modeled with the PROC NONLIN regression procedure.

## **RESULTS AND DISCUSSION**

The bio-oil was condensed out of the syngas and collected for analysis. The mass of the bio-oil was determined and then compared with the mass of the initial feedstock to determine product yield through mass balance. The yield of bio-oil ranged from 39% (high protein) to 50% (CGM). The reported yield values for the bio-oil were actually lower than the actual values due to a few issues with collecting the entirety of the sample. First it was assumed that the

condensation of the bio-oil was not 100% efficient and syngas left the system carrying some condensable liquids, and second a small amount of bio-oil could not be transferred out of the condenser columns due to tar build up. The bio-oil yields fall within the same range as what was determined by Lei et al, 2011 where DDGS bio-oil yields were determined to be 26-50%.

### **Thermal Properties and Energy Content**

The thermal conductivity, and diffusivity were measured at three different temperatures (10 °C, 25 °C, and 40 °C) for the bio-oil samples. These values can be found in Table 3. The thermal conductivities for the bio-oil ranged from 0.21-0.34 W/m °C (10 °C), 0.21-0.42 W/m °C (25 °C), and 0.36-0.85 W/m °C (40 °C). The thermal conductivity of the bio-oils increased as the temperature of the oil increased. Overall the conductivity of the DDGS sample increased 181% from 0.27 W/m °C (10 °C) to 0.76 W/m °C (40 °C). The fiber fraction increased by 179%, the CGM increased by 135%, the protein fraction increased by 43%, and the high protein sample increased by 14%. This indicates that as the temperature of the bio-oil increases, its ability to transfer heat by conduction increases as does its rate of energy loss. These conductivity values are greater than what has been found for common crude oils 0.12-0.13 W/m °C (0-50 °C) (Elam et al 1989).

Thermal diffusivity of the bio-oils ranged from 0.09-0.11 mm<sup>2</sup>/s (10 °C), 0.10-0.13 mm<sup>2</sup>/s (25 °C), and 0.11-0.65 mm<sup>2</sup>/s (40 °C). Similarly to the conductivity, as the temperature of the oils was increased, the thermal diffusivity increased. Overall the diffusivity of the DDGS increased 531% from 0.10 mm<sup>2</sup>/s (10 °C) to 0.65 mm<sup>2</sup>/s (40 °C). The fiber fraction increased by 113%, the CGM increased by 108%, the protein fraction increased by 98%, and the high protein sample increased by 14%. This indicates that as the temperature of the bio-oil increases, its ability to conduct heat relative to its ability to store heat increases. The diffusivities of these oils



are much lower than commonly used fuels: diesel fuel 4.6 mm<sup>2</sup>/s, ethanol 10.0 mm<sup>2</sup>/s, and gasoline 6.4 mm<sup>2</sup>/s (Waterland et al, 2003).

The net energy content of the bio-oil was determined using a bomb calorimeter (1260 Isoperibolic, Parr Instrument, Moline, IL). The data for the bio-oil can be found in Table 3. The lower heating values for the bio-oil ranged from 12.4 MJ/kg (5300 Btu/lb) (high protein) to 28.1 MJ/kg (12,000 Btu/lb) (fiber fraction). These values are much lower than the heating values of commonly used fuels; diesel 42.0 MJ/kg (18000 Btu/lb), ethanol 27.0 MJ/kg (12000 Btu/lb), and gasoline 43.9 MJ/kg (19000 Btu/lb) (Waterland et al, 2003). The heating values were comparable to the 20-28 MJ/kg that Lei et al, (2011) found for bio-oil for DDGS. The heating values of other pyrolysis bio-oils were in the range of 16-28 MJ/kg for various other feedstocks (wood, rice husk, grasses, nut shells, seeds, etc.) (Ba et al, 2004; Junming et al, 2008; Neves et al, 2011; Scholze, 2002; Bridgwater and Peacocke, 2000; Huang et al, 2008).

### **Rheology**

The apparent viscosity of the bio-oils was determined at three different temperatures. Apparent viscosity is a fluid's resistance to flow when force is applied. It is expected that as the shear rate or temperature are increased, the apparent viscosity of a fluid will decrease. For the oil samples the viscosity did decrease with an increase in shear rate and for the majority of the oil samples the viscosity decreased as temperature increased. The relationship could be defined as following a nonlinear power function represented by:

$$\eta = k \gamma^n \quad (1)$$

where  $\eta$  = apparent viscosity (Pa's);  $k$  = empirical regression constant (Pa's's);  $\gamma$  = shear rate (1/s);  $n$  = empirical exponential constant (-).

The data collected from the apparent viscosity replications for each bio-oil was combined into a single regression line to in order to depict the overall behavior for the bio-oil at each of the three temperatures. The plots of these behaviors can be seen in Figure 2 and the average  $k$  and  $n$  values can be found in Table 3. While most oils are considered Newtonian fluids, it is apparent that these bio- oils, at least in their crude states, are non-Newtonian. They are, in fact, shear thinning, as their viscosities decreased as shear rate increased.

### **Density**

It was determined that the DDGS bio-oil had the lowest mass density at  $1.06 \text{ g/cm}^3$  and the protein fraction had the highest mass density at  $1.11 \text{ g/cm}^3$ . These densities are higher than expected since oils generally are less dense than water ( $1.00 \text{ g/cm}^3$ ), but this was most likely due to the tar and particulates present in the crude bio-oil. The values are also much greater than the mass density values of commonly used fuels; diesel ( $0.863 \text{ g/cm}^3$ ), ethanol ( $0.785 \text{ g/cm}^3$ ), and gasoline ( $0.791 \text{ g/cm}^3$ ) (Waterland et al, 2003). The mass densities of other pyrolysis bio-oils were slightly higher as they ranged from  $1.16\text{-}1.28 \text{ g/cm}^3$  (Ba et al, 2004; Junming et al, 2008; Scholze, 2002).

### **Potential Hydrogen**

The pH of the bio-oil in this study was determined to range from 6.5 to 9.9 (Table 3). These values are much higher than the pH values for most bio-oils produced through pyrolysis. For example the pH of wood bio-oil produced by pyrolysis has been found to range from 2.4-3.5 (Ba et al, 2004; Sadaka, 2009; Scholze, 2002). Since the pH of this bio-oil was more neutral, it should be much more desirable, as the other bio-oils would have to be upgraded to neutralize their pH values.

## **CONCLUSIONS**

Record quantities of ethanol are being produced by the U.S. ethanol industry; along with this quantity of ethanol comes record amounts of its coproducts. These coproducts, distillers dried grains with solubles (DDGS), corn gluten meal (CGM), and corn gluten feed (CGF), are mainly marketed to the livestock industry, which utilizes them as an animal feed; however, in the future there is a possibility that the quantity of products produced will exceed that required by the livestock industry. Thus new value-added uses of these coproducts must be found in order to maintain their market value and the sustainability of the ethanol industry. A potential use for these coproducts is thermochemically transforming them into sources of energy. This energy can potentially be harvested either directly or through thermochemical conversions. This study used thermochemical conversion, specifically pyrolysis, to produce bio-oils from DDGS and CGM.

The bio-oils produced from the ethanol coproducts was determined to be similar to that produced from other biomaterials in many ways and would require some upgrading; however, the bio-oil from DDGS was also determined to be superior in some ways. For example the pH of the bio-oil in this study was determined to range from 6.5 to 9.9 which was much more favorable than the pH of 2.4-3.5 found for most forms of bio-oils. While the pH of the bio-oil is ideal, there are other properties that would require improvements for use as fuel or chemicals. The density of the bio-oil ranged from 1.06 g/cm<sup>3</sup> to 1.11 g/cm<sup>3</sup> which was higher than desired, but most likely due to the tar present in its crude state. The tar also potentially affected the apparent viscosity of the oils, because the apparent viscosity was determined to be shear thinning rather than Newtonian.

The thermal properties of the bio-oils may also need to be upgraded before utilization. The thermal conductivity of the bio-oils (0.210.85 W/m °C) was greater than that of common crude oils (0.12-0.13 W/m °C) (Elam et al 1989). The diffusivity of the bio-oils ranged from

0.09-0.65 mm<sup>2</sup>/s, which was lower than commonly used fuels. The conductivity and diffusivity vary with temperature; as the temperature increases so did the value of conductivity and diffusivity. The lower heating values for the bio-oil ranged from 12.4 MJ/kg (5300 Btu/lb) to 28.1 MJ/kg (12,000 Btu/lb) which was lower than the heating values of commonly used fuels, yet comparable to the heating values of other pyrolysis bio-oils.

## REFERENCES

- Ba, T., A. Chaala, M. Garcia-Perez, D. Rodrique, and C. Roy. 2004. Colloidal properties of bio-oils obtained by vacuum pyrolysis of softwood bark. Characterization of water-soluble and water-insoluble fractions. *Energy and Fuels*. 18: 704-712.
- Babu, B.V., A.S., Chaurasia. 2003. Optimization of pyrolysis of biomass using differential evolution approach. In *Proc. of the Second Intl. Conf. on Computational Intelligence, Robotics, and Autonomous Syst. (CIRAS-2003)*, 787–792 . Singapore.
- Bhadra, R., K. Muthukumarappan, and K. A. Rosentrater. 2009a. Cross-sectional staining and surface properties of DDGS particles and their influence on flowability. *Cereal Chem.* 86(4): 410-420.
- Bhadra, R., K. Muthukumarappan, and K. A. Rosentrater. 2009b. Flowability properties of commercial distillers dried grains with solubles (DDGS). *Cereal Chem.* 86(2): 170-180.
- Bhadra, R., K. Muthukumarappan, and K. A. Rosentrater. 2010. Physical and chemical characterization of fuel ethanol coproducts relevant to value-added uses. *Cereal Chem.* 87(5): 439-447.
- Bothast, R., and M. Schlicher. 2005. Biotechnological processes for conversion of corn into ethanol. *Appl. Microbiology Biotechnology* 67: 19-25.

- Bridgwater, A.V., Peacocke, G.V.C., 2000. Fast pyrolysis processes for biomass. *Renew. Sust. Energy Rev.* 4 (1): 1–73.
- Chao, C., L. Qing, Y. Qiang, T. Kruttschnitt, and E. Pruckner. 2005. Comparative Experiments on recycling of oil sludge, oil shale, and biomass waste in a continuous rotating pyrolysis reactor. *5<sup>th</sup> Asia-Pacific Conf. on Combustion*. Adelaide, Australia.
- Christians, N.E. 1993. Chapter 35. The use of corn gluten meal as a natural pre-emergence weed control in turf. In, *Intl. Turfgrass Soc. Res. J.* 7, 284-290. R.N. Carrow, N.E. Christians, R.C. Shearman, ed. Overland Park, KS: Intertec Publishing Corp. Available at: <http://www.hort.iastate.edu/gluten/pdf/cornglut3.pdf>. Accessed 21 Dec. 2011.
- Craik, D. J. and B. F. Miller. 1958. The flow properties of powders under humid conditions. *J. of Pharmacy and Pharmacology* 10: 136-144.
- De Kam, M. J., R. V. Morey, D. G. Tiffany. 2007. Integrating biomass to produce heat and power at ethanol plants. ASABE Paper No. 076232. St. Joseph, Mich. ASABE.
- Elam, S., I. Tokura, K. Saito. 1989. Thermal conductivity of crude oils. *Experimental Thermal and Fluid Science*. 2(1): 1-6.
- Fitzpatrick, J. J., S. A. Barringer and T. Iqbal. 2004. Flow property measurement of food powders and sensitivity of Jenike's hopper design methodology to the measured values. *J. of Food Eng.* 61(3): 399-405.
- Ganesan, V., K. A. Rosentrater, and K. Muthukumarappan. 2008. Effect of flow agent addition on the physical properties of DDGS with varying moisture content and soluble levels. *Trans. of the ASABE* 51(2): 591-601.
- Gheorghe, C. 2006. Investigations of potentialities of biomass pyrolysis at HTAG system. Bucharest, Romania: University of Bucharest, Power Engineering.

- Giuntoli, J., J. Gout, A. Verkooijen, and W. De Jong. 2011. Characterization of fast pyrolysis of dry distiller's grains (DDGS) and palm kernel cake using a heated foil reactor: nitrogen chemistry and basic reactor modeling. *Ind. and Eng. Chem. Res.* 50(8): 4286-4300.
- Huang, Y., W. Kuan, S. Lo, and C. Lin. 2008. Total recovery of resources and energy from rice straw using microwave-induced pyrolysis. *Bioresource Tech.* 99: 8252-8258.
- ISU (Iowa State University). 2008. Ethanol coproducts for cattle: the process and products. Ames, IA: Iowa State University, University Extension. Available at: <http://www.extension.iastate.edu/publications/ibc18.pdf>. Accessed 21 Dec. 2011.
- Johansson, J. R. 1978. Know your material – how to predict and use the properties of bulk solids. *Chem. Eng.* (Desk book issue): 9-17.
- Junming, X., J. Jianchun, S. Yunjuan, L. Yanju. 2008. Bio-oil upgrading by means of ethyl ester production in reactive distillation to remove water and to improve storage and fuel characteristics. *Biomass and Bioenergy.* 32: 1056-1061.
- Keierleber, C., and K. Rosentrater. 2010. Granular packing influences the bulk density of DDGS. *Cereal Chem.* 87(6): 586-596.
- Kim, Y., N. Mosier, R. Hendrickson, T. Ezeji, H. Blaschek, B. Dien, M. Cotta, B. Dale, and M. Ladisch. 2008. Composition of corn dry-grind ethanol by-products: DDGS, wet cake, and thin stillage. *Bioresource Tech.* 99: 5165-5176.
- Lei, H., S. Ren, L. Wang, Q. Bu, J. Julson, J. Holladay, and R. Ruan. 2011. Microwave pyrolysis of distillers dried grain with solubles (DDGS) for biofuel production. *Bioresource Tech.* 102: 6208-6213.
- Majoni, S., and T. Wang. 2010. Characterization of oil precipitate and oil extracted from condensed corn distillers solubles. *J. of the American Oil Chem. Soc.* 87:205-213.

- Majoni, S., T. Wang, and L. Johnson. 2010. Enzyme treatments to enhance oil recovery from condensed corn distillers solubles. *J. of the American Oil Chem. Soc.* 88(4): 523-532.
- Moreau, R., K. Hicks, D. Johnston, and N. Laun. 2010. The composition of crude corn oil recovered after fermentation via centrifugation from commercial dry grind ethanol process. *J. of the American Oil Chemists' Soc.* 87: 895-902.
- Morey, R., D. Tiffany, and D. Hatfield. 2006. Biomass for electricity and process heat at ethanol plants. *Appl. Eng. in Agric.* 22(5): 723-728.
- Moreyra, R. and M. Peleg. 1981. Effect of equilibrium water activity on the bulk properties of selected food powders. *J. of Food Sci.* 46: 1918-1922.
- Neves, D., H. Thunman, A. Matos, L. Tarelho, A. Gomez-Barea. 2011. Characterization and prediction of biomass pyrolysis products. *Progress in Energy and Combustion Science.* 37: 611-630.
- Noureddini, H., S. Bandlamudi, and E. Guthrie. 2009. A novel method for the production of biodiesel from the whole stillage-extracted corn oil. *J. of the American Oil Chem. Soc.* 86: 83-91.
- Pirikh, J., S. Channiwala, and G. Ghosal. 2003. Product distribution from woody biomass in a bench-scale pyrolyzer. *Proc. of the Intl. Conf. on Mech. Eng.* Dhaka, Bangladesh.
- RFA (Renewable Fuels Association). 2011a. Building Bridges to a More Sustainable Future: 2011 Ethanol Industry Outlook. Washington, D.C.: Renewable Fuels Association. Available at: <http://www.ethanolrfa.org/page/-/2011%20RFA%20Ethanol%20Industry%20Outlook.pdf?nocdn=1>. Accessed 21 Dec. 2011.

- RFA (Renewable Fuels Association). 2011b. Industry Resources: Coproducts. Washington, D.C.: Renewable Fuels Association. Available at:  
<http://www.ethanolrfa.org/pages/industry-resources-coproducts>. Accessed 21 Dec. 2011.
- RFA (Renewable Fuels Association). 2011c. Statistics. Washington, D.C.: Renewable Fuels Association. Available at: <http://www.ethanolrfa.org/pages/statistics>. Accessed 21 Dec. 2011.
- RFA (Renewable Fuels Association). 2010. RFA Issues Weekly Ethanol Production Data. *Biofuels Journal*. Washington, D.C.: Renewable Fuels Association. Available at:  
[http://www.biofuelsjournal.com/info/bf\\_articles.html?ID=95665](http://www.biofuelsjournal.com/info/bf_articles.html?ID=95665). Accessed 21 Dec. 2011.
- Rosentrater, K. A. 2006. Understanding distillers grains storage, handling, and flowability challenges. *Distillers Grains Quarterly* 2(1): 18-21.
- Rosentrater, K. A. 2007. Corn ethanol coproducts – some current constraints and potential opportunities. *Intl. Sugar J.* 109(1307): 2-11.
- Rosentrater, K., and K. Muthukumarappan. 2006. Corn ethanol coproducts: generation, properties, and future prospects. *International Sugar Journal* 108(1295): 648-657.
- Rosentrater, K., and M. Giglio. 2005. What are the challenges and opportunities for utilizing distillers grains? *Distillers Grains Quarterly* 1(1): 15-17.
- Rosentrater, K., and P. Krishnan. 2006. Incorporating distillers grains in food products. *Cereal Foods World* 51(2): 52-60.
- Sadaka, S. 2009. Chapter 2: Pyrolysis. In *Pyrolysis and Bio-Oil*. Fayetteville, AR. Cooperative Extension Services.
- Schlicher, M. 2005. The flowability factor. *Ethanol Producer Magazine* 11(7): 90-93, 110-111.



- Scholze, B. 2002. Long-term stability, catalytic upgrading, and application of pyrolysis oils – improving the properties of a potential substitute for fossil fuels. PhD dissertation. Zur Erlangung des Doktorgrades im Fachbereich Chemie der Universität Hamburg.
- Shurson, J. and A. S. Alhamdi. 2008. Quality and new technologies to create corn co-products from ethanol production. *Using Distillers Grains in the U.S. and International Livestock and Poultry Industries*. B. A. Babcock, D. J. Hayes, and J. D. Lawrence, eds. Ames, IA: Iowa State University. p. 231-256.
- Shurson, J., and S. Noll. 2005. Feed and alternative uses for DDGS. *Energy from Agriculture: New Technologies, Innovative Programs & Success Stories*. St. Louis, MO.
- Tatara, R., K. Rosentrater, S. Suraparaju. 2007. Compression molding of phenolic resin and corn-based DDGS blends. *J. Polymer Environ.* 15: 89-95.
- Tatara, R., K. Rosentrater, S. Suraparaju. 2006. Design properties for molded, corn-based DDGS-filled phenolic resin. *Ind. Crops and Products* 29: 9-15.
- Teunou, E., J. J. Fitzpatrick, and E. C. Synnott. 1999. Characterization of food powder flowability. *J. of Food Eng.* 39(1): 31-37.
- Tiffany, D., R. Morey, and M. De Kam. 2007. Economics of biomass gasification/combustion at fuel ethanol plants. *Appl. Eng. in Agric.* 25(3): 391-400.
- Tiffany, D., R. Morey, and M. De Kam. 2008. Use of distillers by-products and corn stover as fuels for ethanol plants. In *Transition to a Bioeconomy: Integration of Agricultural and Energy Systems*. Atlanta, GA.
- Van de Velden, M., F. Xianfeng, A. Ingram, and J. Baeyens. 2007. Fast pyrolysis of biomass in a circulating fluidized bed. *Proc. from the 12<sup>th</sup> Intl. Conf. on Fluidization – New Horizons in Fluidization Eng.* Vancouver, Canada.

- Waterland, L., S. Venkatesh, and S. Unnasch. 2003. Safety and performance assessment of ethanol/diesel blends (E-diesel). National Renewable Energy Laboratory. Golden, CO.
- Weigel, J. C., D. Loy, and L. Kilmer. 1997. Feed co-products of the dry corn milling process. Iowa State University, Iowa Corn Promotion Board, Iowa Department of Agriculture, Renewable Fuels Association, National Corn Growers Association.
- Zhong, G., X. Qian, X. Hua. 2009. Effects of feeding with corn gluten meal on trypsin activity and mRNA expression in *Fugu obscurus*. *Fish Physiology Biochemistry* 37(3): 453-460.

**Table 1.** Proximate analysis of raw corn coproducts used in the study.

<b>Sample</b>	<b>Moisture (%)</b>	<b>DM (%)</b>	<b>Crude Protein (%db)</b>	<b>NDF (%db)</b>	<b>Crude Fat (%db)</b>
<b>DDGS</b>	6.7	93.3	27.0	28.0	11.1
<b>CGM</b>	7.0	93.0	68.6	6.0	1.9
<b>Fiber Fraction</b>	5.2	94.8	25.1	47.6	1.9
<b>Protein Fraction</b>	5.6	94.4	33.7	37.1	3.5
<b>HPDDG</b>	5.6	94.4	40.7	31.7	3.9

**Table 2.** Temperature-dependent thermal and rheological properties of resulting bio-oil.\*

Sample	Temp	Conductivity (W/m° C)			Diffusivity (mm <sup>2</sup> /s)			K		n			
DDGS	10	0.27 (0.07)	bc	y	0.10 (0.01)	ab	y	0.77 (1.17)	a	x	-0.86 (0.42)	b	y
CGM	10	0.21 (0.02)	c	y	0.09 (0.01)	b	y	0.02 (0.04)	b	x	-0.34 (0.30)	a	x
Fiber Fraction	10	0.30 (0.07)	ab	y	0.11 (0.01)	a	x	0.03 (0.02)	b	x	-0.48 (0.22)	a	x
Protein Fraction	10	0.34 (0.08)	a	y	0.10 (0.01)	ab	y	0.02 (0.01)	b	x	-0.34 (0.07)	a	xy
HPDDG	10	0.31 (0.02)	ab	y	0.10 (0.00)	b	y	0.20 (0.19)	ab	x	-0.58 (0.12)	ab	y
DDGS	25	0.33 (0.06)	bc	y	0.13 (0.03)	a	y	0.01 (0.00)	b	x	-0.37 (0.07)	a	x
CGM	25	0.21 (0.03)	d	y	0.10 (0.01)	b	y	0.01 (0.00)	b	x	-0.32 (0.06)	a	x
Fiber Fraction	25	0.29 (0.06)	c	y	0.11 (0.02)	ab	x	0.09 (0.06)	a	x	-0.79 (0.27)	c	y
Protein Fraction	25	0.37 (0.05)	ab	y	0.12 (0.02)	ab	xy	0.03 (0.02)	b	x	-0.44 (0.07)	ab	y
HPDDG	25	0.42 (0.06)	a	x	0.11 (0.01)	ab	xy	0.04 (0.02)	b	y	-0.61 (0.21)	bc	y
DDGS	40	0.76 (0.13)	ab	x	0.65 (0.29)	a	x	0.01 (0.00)	b	x	-0.38 (0.14)	b	x
CGM	40	0.50 (0.20)	bc	x	0.20 (0.12)	b	x	0.02 (0.02)	b	x	-0.50 (0.18)	ab	x
Fiber Fraction	40	0.85 (0.44)	a	x	0.24 (0.24)	b	x	0.23 (0.31)	a	y	-0.73 (0.43)	a	y
Protein Fraction	40	0.49 (0.11)	bc	x	0.21 (0.14)	b	x	0.01 (0.00)	b	y	-0.30 (0.14)	bc	x
HPDDG	40	0.36 (0.08)	c	xy	0.11 (0.01)	b	x	0.00 (0.00)	b	y	-0.20 (0.10)	c	x

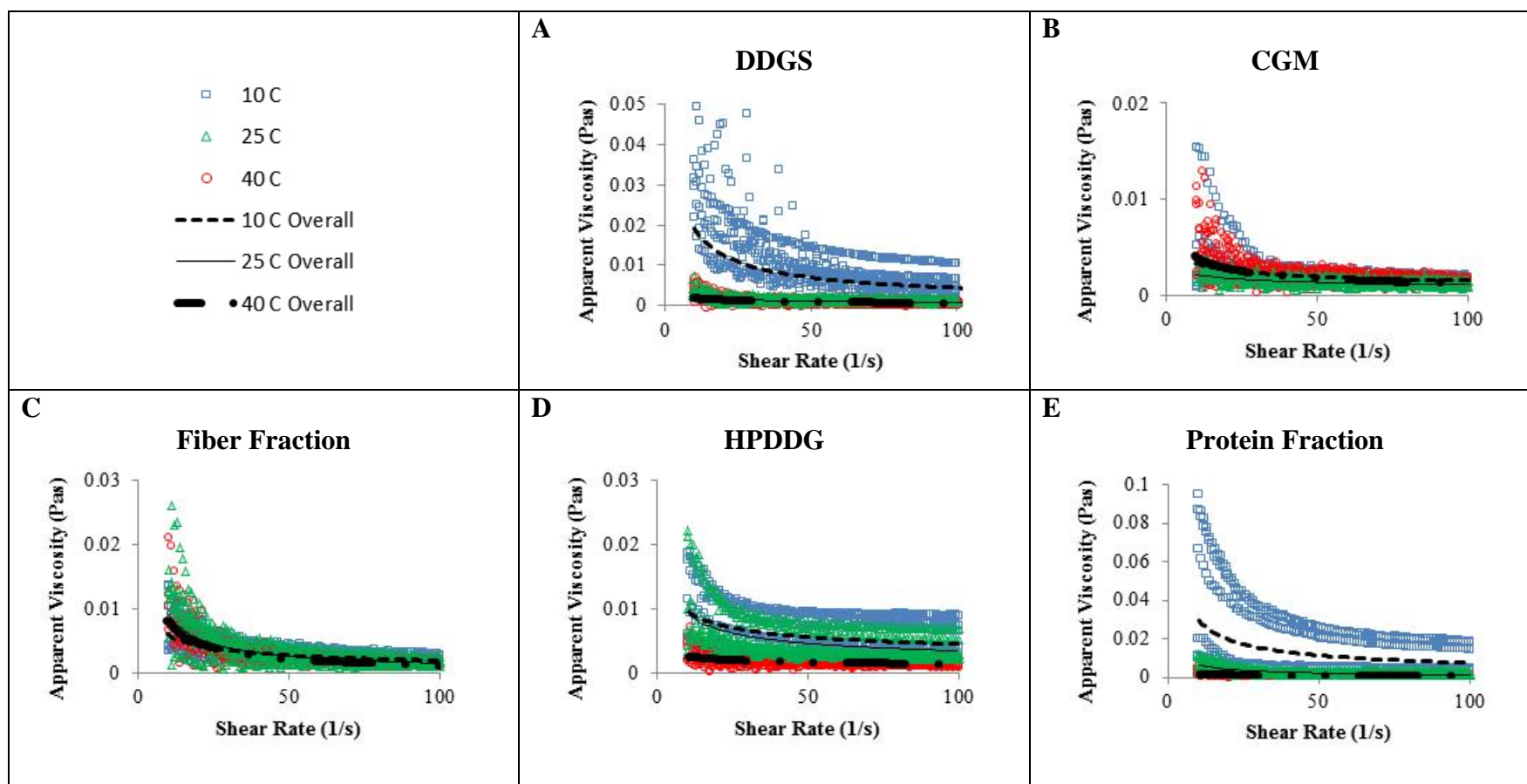
\*Values in parentheses are standard deviation (SD). Values followed by the same letter (a, b, c) within a given temperature are not significantly different ( $\alpha = 0.05$ , LSD) from other bio-oil samples for that property. Values for a given bio-oil sample followed by the same letter (x, y, z)

are not significantly different ( $\alpha = 0.05$ , LSD) between temperatures.

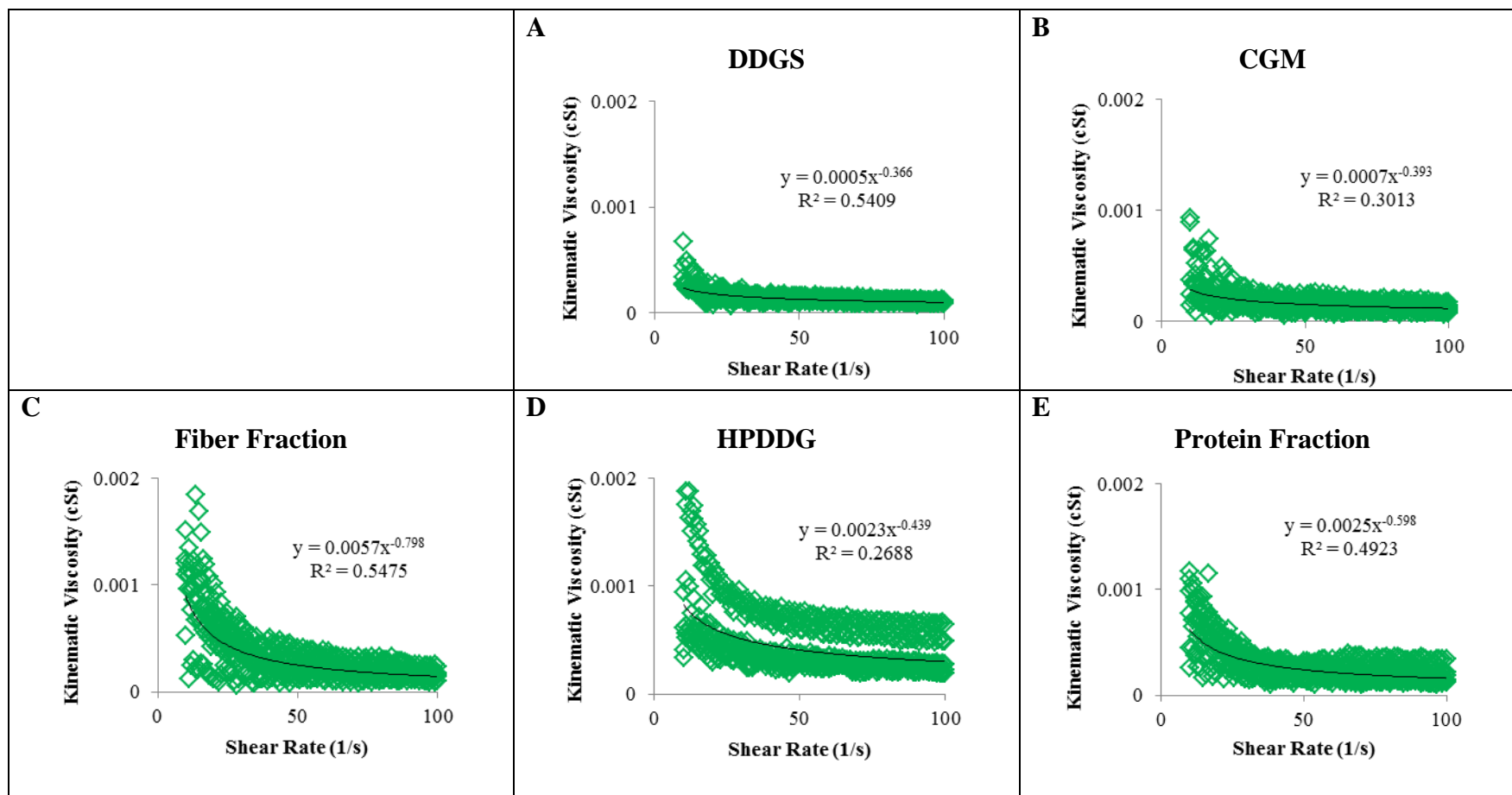
**Table 3.** Physical properties of resulting bio-oil.\*

<b>Sample</b>	<b>Yield (%)</b>		<b>Apparent Density (g/cm<sup>3</sup>)</b>		<b>pH</b>		<b>Heating Value (MJ/kg)</b>	
<b>DDGS</b>	46.57 (2.32)	ab	1.06 (0.01)	b	6.55 (0.22)	d	22.56 (2.10)	ab
<b>CGM</b>	50.94 (0.67)	a	1.09 (0.05)	ab	9.85 (0.16)	a	24.00 (1.55)	bc
<b>Fiber Fraction</b>	43.00 (4.46)	bc	1.10 (0.00)	a	6.37 (0.14)	d	28.10 (1.64)	a
<b>Protein Fraction</b>	39.92 (0.61)	bc	1.11 (0.01)	a	8.56 (0.15)	c	16.59 (4.80)	bc
<b>HPDDG</b>	39.37 (3.00)	c	1.10 (0.01)	a	8.92 (0.05)	b	12.35 (0.38)	c

\*Values in parentheses are standard deviation (SD). Values followed by the same letter (a, b, c) are not significantly different ( $\alpha = 0.05$ , LSD) from other bio-oil samples within a given property.



**Figure 1.** Relationships between apparent viscosity and shear rate as a function of temperature for the resulting bio-oil samples. Raw data and overall regression lines are provided for each temperature. Regression parameters (K and n) for each temperature are provided in Table 2.



**Figure 2.** Relationships between kinematic viscosity and shear rate for the resulting bio-oil samples across all temperatures. Raw data and overall regression lines are provided.