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Pyrolysis of ethanol coproducts

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ABSTRACT

The need for new value-added applications for ethanol coproducts grows as the U.S. ethanol industry continues to expand. Distillers dried grains with solubles (DDGS), corn gluten meal (CGM), and corn gluten feed (CGF) are the primary coproducts of ethanol manufacturing and are mainly utilized as animal feed. This study examined the use of pyrolysis to extract value from these grains. Characterization of the resulting bio-oil and bio-char included mass density, thermal conductivity, thermal diffusivity, apparent viscosity, kinematic viscosity, and energy content. The bio-oils produced from these ethanol coproducts require some changes to be used commercially. The tar present in the crude bio-oils caused them to have densities greater than one, and caused the oil viscosity to be shear thinning. The pH of these bio-oils is less acidic and thus more favorable than other bio-oils which could be due to the differences in the feedstock composition.

1. Introduction

The U.S. ethanol industry has continuously gained momentum over the past decade, increasing its production by nearly eight times from 2000 to 2010 (RFA, 2012a). 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 grind 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 non-fermentable materials are used to produce corn gluten meal and corn gluten feed; while in the dry grind process, they are used to produced distillers dried grains with solubles (DDGS) and distillers wet grains (DWG). RFA (2012b) 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 90% dry matter, 66% protein, 3.3% fiber, and 2.8% fat; while corn gluten feed is composed of approximately 90% dry matter, 20% protein, 11.1% fiber, and 2.2% fat (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; McDade, 1999; Webber et al., 2010) and in fish feeds (Lei et al., 2011; Zhong and Qian, 2009).

DDGS is approximately 86.2–93.0% dry matter, 25–35% protein, 7.2% fiber, and 3–13% fat (Bhadra et al., 2009; Ganesan et al., 2008; ISU, 2008; Rosentrater and Muthukumarappan, 2006; Shurson and Alhamdi, 2008; and 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 more coproducts are produced, there is a potential that supply may surpass the livestock industry's demand at some point. Perhaps the demand from the livestock industry may become restricted as certain fats within the DDGS limit the amount of DDGS 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 very small percentage of the 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 ingredients (Kannadhason et al., 2010; Rosentrater et al., 2009a,b; Schaeffer et al., 2009), and could one day find their niche within the human food market, as research is also being done to prove the viability as human food ingredients (Rosentrater, 2007; Rosentrater

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and Krishnan, 2006). Studies are also being done to determine if coproducts can be used to produce biodegradable plastics (Bothast and Schlicher, 2005; Tatara et al., 2006, 2007).

While most investigations of coproducts over the years have been on ways of utilizing them as feed ingredients, recent studies have begun investigating their potential as sources of energy. Some studies have even begun analyzing the effectiveness of powering ethanol plants with this bio-based energy (De Kam et al., 2007; Morey et al., 2006; 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 is used to generate process heat and energy for the facility, there would be leftover energy which could be sold to the grid, 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, while only 1 MJ of electric energy and 10 MJ of thermal energy are required to produce 1 L of ethanol. Wang et al. (2007) also showed that by 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 transformed into gaseous or liquid fuels to be used for energy later (Giuntoli et al., 2011). These processes, known as thermochemical conversions, consist of three main types: combustion, pyrolysis, and gasification (Wang et al., 2007).

The pyrolysis of many types 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; Gheorghe, 2006; Pirikh et al., 2003; Van de Velden et al., 2007; Sivasastri, 2013). 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 et al., 2011). These 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 conventional, also known as slow, pyrolysis to convert corn coproducts, including CGM, high protein DDG, protein fraction of de-oiled DDGS, fiber fraction of de-oiled DDGS, and traditional DDGS, and then determined various physical and chemical properties of resulting bio-oil and bio-char.

2. Materials and methods

2.1. Sample collection and experimental design

CGM, DDGS, de-oiled DDGS, and high protein DDG (HP) were obtained from commercial fuel ethanol plants in South Dakota. The de-oiled DDGS was then separated into a high protein fraction (PF) and a high fiber fractions (FF) using sieving and aspiration. This resulted in a total of five different samples with various protein and fiber concentrations. All were stored in plastic storage bags at room temperature until needed for pyrolysis. Two pyrolysis reactions were performed per coproduct sample, for a total of ten reactions. After processing, the resulting bio-oil was stored in plastic screw-top bottles in a refrigerator, and the bio-char was stored in plastic storage bags until analysis at room temperature. Three replications were performed for each physical property measured on the bio-oil (unless noted otherwise). Thermal conductivity, thermal diffusivity, energy content, mass density, and apparent viscosity were determined. Rheological measurements were also taken at three different temperatures (10, 25, and 40 °C).

2.2. Raw materials

The proximate composition for the raw materials was determined by an external laboratory (Servi-Tech Laboratories, Hastings, NE). The particle size distribution and color of the raw materials was determined using the same methods used for the bio-char.

2.3. Pyrolysis

The apparatus in Fig. 1 (located in the SDSU bioprocessing lab) was used to perform slow pyrolysis reactions. Each reaction began with 500 g of sample in a sealed steel chamber of approximately 6589 cm^3 (20 cm long with 10 cm internal diameter). 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 Allihn condenser columns with water jackets, and two glass bulbs (Chemglass Life Science, Vineland, NJ) to collect and sample the oil. To assist with the condensation of oil, water cooled to 6 °C was cycled through the water jackets using an F3-V Refrigerated Cryostats (HAAKE, Paramus, NJ). The outlet after the fourth condenser was connected to hosing which released the produced syngas into a bucket of water to remove any additional condensable compounds before releasing the syngas into the air. The steel chamber was placed within an Isotemp Programmable muffle furnace (650–750, Fisher Scientific, Pittsburg, PA), which allowed the heating rate and temperature to be defined. Before heating, the chamber and distillation system were purged with nitrogen gas for ten minutes in order to evacuate oxygen from the vessel.

For each pyrolysis reaction, the sealed steel chamber with coproduct sample was heated to 600 °C at 40 °C/min. The pyrolysis reaction proceeded in three individual steps: (1) moisture and some volatiles were removed from the feedstock; (2) more complex volatiles and some gasses are removed leaving bio-char; (3) bio-char was decomposed further and chemical rearrangement releases more volatiles and gasses producing a less reactive bio-char (Demirbas, 2004). The reaction was allowed to progress until syngas production was no longer visible. At that point, the furnace was powered off and allowed to cool for two hours before oil and char were collected. When collected the mass of the bio-char and bio-oil were taken.

2.4. Bio-oil

The yield of the bio-oil was determined through mass balance. The mass of the bio-oil collected was compared to the mass of the original feedstock sample in order to determine the mass yield (100 × (mass bio-oil/mass feedstock) = yield bio-oil).

2.4.1. Physical properties

2.4.1.1. 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 (mass = 83.55 g; volume = 83.2 cm^3) excess material was then removed, and the filled cup was weighed on a balance. Density was then calculated as the ratio of sample mass to sample volume.

2.4.1.2. Energy content and thermal properties. The lower heating values of the bio-oil samples were measured using a bomb