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Co-Product Potential of Algae Biocake

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by

Elizabeth J. Nixon

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Abstract

Society needs to find replacements for fossil fuels, which are finite resources that may be fully depleted within a few generations. While solar and wind have great potential as alternative energy sources, they are unlikely to completely replace all of the current fuel sources, particularly liquid fuels. Plant biomass has great potential for this market, and is already used in many forms for heat energy (e.g. direct combustion). However, the bulk density of important bioenergy crops, particularly grasses, is often low, which necessitates the use of binders in densification strategies. In the present study, waste algae biocake from a proprietary food-oil process was examined as a potential binding agent for the woody grass Miscanthus. Acid hydrolysis was used to determine the nonsoluble material and the carbohydrate content of pure algae, Miscanthus, and blended pellets. The algae biomass had lower insoluble material (P<0.0001) and glucose content (P<0.0001) than Miscanthus, and all blends with 30% or greater algae had significantly less of both parameters. The energy content was not significantly different between algae and Miscanthus with or without blending, while algae had significantly higher ash content compared to Miscanthus. The compressive strength of the pure algae and pure Miscanthus was not significantly different; however, all algae blends of 30% or more showed significantly greater pellet strength compared to either biomass alone. Overall, the results of this study indicate that pressed algae biocake has the potential to act as a binding agent to improve pellet strength of Miscanthus in blends at 30% or higher, without sacrificing overall energy density, which suggests that the algae biocake could be a valuable co-product for biofuel industries.
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1. Introduction

Society has become dependent on inexpensive and readily available energy, and the demand for electricity, heat, and other types of energy increases daily. In 2015, 86% of the primary energy consumed worldwide was generated by fossil fuels (World Energy Council, 2016). However, fossil fuels are not sustainable, as they are a limited and finite resource. As a result, renewable and sustainable energy technologies are growing to fill this need, with bioenergy occupying an important niche, particularly with respect to liquid fuels. Biofuels encompass gas, liquid, and solid fuel types created from biomass. For example, methane gas can be produced by the decomposition of animal or food waste, while ethanol and other alcohols are traditionally produced from corn or sugarcane through fermentation. New generations of ethanol production utilize non-traditional and non-food sources to attempt to mitigate one of the largest drawbacks to ethanol production for biofuels, which is the use of prime crop land for dedicated biofuel crops (Somerville et al., 2010).

The solid biofuels come in greater variety. In North America, solid biofuels are often wood, agricultural waste, and tall grasses; however, all these sources have drawbacks. For example, wood biomass can be environmentally expensive and slow to harvest even in fast growing species, such as hybrid poplar. Agricultural waste is a limited resource with existing uses, such as livestock feed, bedding, and as a soil amendment (Kadam and McMillan, 2003). The tall grasses, such as Miscanthus, are fast growing, environmentally and economically inexpensive, but have lower energy yield compared to wood (Carroll & Finnan, 2012 ;Somerville et al., 2010). Additionally, the bulk density of grasses is much lower than wood, which necessitates compaction.
prior to transport (Miao et al., 2015; Tumuluru et al., 2011). However, increasing the density of grasses often requires binding agents to strengthen the pellet (Kaliyan and Morey, 2010; Said et al., 2015).

There is a wide variety of available binders, with both inorganic and organic binding agents leading to significant increases in pellet strength (Finney et al., 2009; Lehmann et al., 2012). Depending on the binding agent chosen, the addition to the pelleting process can add steps and time, as well as the cost of the agent itself (Kaliyan and Morey, 2010). Binding agents can also lower the calorific value of material, along with increasing the quantity of emissions of the pellet (Tarasov et al., 2013). Alternatively, using local and natural binding agents can keep the cost low and may mitigate the faults stated above (Jiang et al., 2014; Koukkane et al., 2011).

Another increasingly popular biological source for bioenergy is algae. Algae is capable of surviving and thriving in challenging conditions, which allows for multiple primary uses (e.g. wastewater treatment) and secondary uses (e.g. harvesting the lipids produced for biofuel) (Mehrabadi et al., 2015; Parket al., 2011). Some species of algae when grown in specific conditions can be upwards of 50% lipid content (Rodilfi, et al., 2008), and the extracted lipids need minimal refinement for use as fuels. As algae-produced biofuels are carbon neutral, there is has been considerable interest in this field (Singh et al., 2011); however there are many issues with large-scale growth even in industries where the use of algae is well established (Pittman et al., 2011; Sutherland et al., 2015).

In addition to the biofuel industry, algal products are also used for pharmaceutical and nutraceuticals, such as polyunsaturated fatty acids (e.g. omega-3; Adarme-Vega et
al., 2014) and carotenoids (Guedes et al., 2011). When the products are extracted by mechanical methods (e.g. pressing), the resulting biomass, called algae biocake, dries into a dense mass that resembles highly compacted sand. Depending on the extraction method used, algae biocake can retain up to 25% of the initial lipid content (Kumar et al., 2015). Despite the large quantity of pressed biocake resulting from algal-based processes, the product-extracted algae is often considered a waste product with limited value.

The objective of the current study was to explore whether the pressed algae cake from a local nutraceutical processing facility could be used as a low-cost and natural binding agent for Miscanthus. This woody grass has been identified as an important biomass feedstock for the future energy portfolio of the United States (Somerville et al., 2009), although transportation of the material is limited by its low bulk density. To explore the potential of algae biocake as a binding agent for solid fuel pellets, the algae biocake and Miscanthus were examined individually and as algae:Miscanthus blends (9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9). Acid hydrolysis was used to determine the percentage of non-soluble material and the carbohydrate content of each proportion. Calorimetric tests were used to determine the energy content, and compressive strength of formed pellets was examined to explore the efficacy of the algae biocake as a binding agent.

2. Methods

2.1 Biomass Sources

The algae biocake was acquired from local sources and was considered a waste product from a proprietary algae-based production process. The cake (Figure 1) was ground in a Magic Bullet (Homeland Housewares, LLC, Los Angeles, CA) for
approximately 1 min. The Miscanthus (*Miscanthus × giganteus* cv. Illinois) was grown and harvested using a silage chopper from a farm in Pesotum, IL. The Miscanthus was then milled to pass through a 20-mesh sieve (0.85 mm) using a Thomas Wiley® Mini-Mill (Thomas Scientific, Swedesboro, NJ). All biomass was kept at ambient temperature and humidity prior to testing. For all experiments except ash determination, the algae biocake and Miscanthus were mixed in ratios of ten percent increments (algae:Miscanthus from 1:9-9:1; Figure 2).

### 2.2 Acid Hydrolysis

The pure algae and Miscanthus and the mixtures were hydrolyzed using acid hydrolysis according to Sluiter et al. (Sluiter, et al., Determination of Structural Carbohydrates and Lignin in Biomass, 2008). The acid insoluble material was quantified as dry retentate after vacuum filtration using a medium-porosity glass gooch crucible. The carbohydrate content of the hydrolysate was quantified using a System Gold 166 HPLC (Beckman Coulter, Brea, CA) and an Aminex HPX-87P (300 mm × 7.8 mm) column (BioRad, Hercules, CA) at 85 °C. The mobile phase was 100% water at a flow rate of 0.6 mL min⁻¹. Glucose was detected using an RI-1530 refractive index detector (JASCO, Easton, MD).

### 2.3 Energy Content

The energy content of biomass was assessed using a 6200 Isoperibol Calorimeter (Parr Instrument Company, Moline, IL) according to the manufacturer’s instructions. The higher heating value (HHV) was determined from 1 g of the mixed biomass.
2.4 Compressive Strength

For the determination of compressive strength, a pellet disc was created from 6 g of the mixed biomass under approximately 40,000 N of force using a Torin Big Red Jacks Hydraulic Shop Press (Torin, Inc., Ontario, CA). Each disc was placed on the short edge on a 60-mm platen that was mounted to a vertical wheel test stand (HV-110; Imada, Inc., Northbrook, IL), and compressed with a DS2 digital force gauge (Imada, Inc.) until the disc failed. The peak force required to break the disc (compressive strength) was recorded from the digital force gauge.

2.5 Ash Determination

For determination of ash residue after combustion, 1 g of biomass was combusted according to industry standard procedures (Sluiter, et al., Determination of Ash in Biomass, 2008) using a muffle furnace (FD1535M, Thermo Scientific, Waltham, MA) set at 575°C.

2.6 Statistical Analysis

One-way ANOVA followed by Tukey’s pairwise comparisons (at the 95% level) were performed using data from the acid hydrolysis (acid insoluble material and glucose), calorimetry, and compressive strength tests. A paired t-test (at the 95% level) was run on the data from the ash residue. All tests were conducted using Origin 8.1 software (OriginLab Corporation, Northampton, MA).
3. Results and Discussion

3.1 Acid Hydrolysis

Many biofuel technologies are reliant on the carbohydrates present within the source biomass, such as yeast fermentation of glucose into alcohols. It is therefore important to assess the effects of binding agents on the overall yield of glucose from the material. Consequently, the glucose content of the algae, Miscanthus, and the nine different mixes of algae and Miscanthus (9:1 to 1:9) was determined using a well-established acid hydrolysis method (Sluiter, et al., Determination of Structural Carbohydrates and Lignin in Biomass, 2008). This method uses sulfuric acid with heat and pressure to hydrolyze cellulose into individual glucose monomers. The results indicated that algae biomass had significantly less glucose than pure Miscanthus (P<0.0001; Figure 3). The mixtures of biomass generally had glucose content that was directly proportional to the percentage of Miscanthus, where the 30% algae biomass mixture showed significantly less glucose than the full Miscanthus to the 95% level (Figure 3). All mixtures with more than 40% algae had significantly less glucose at the 99% level. These results are comparable to other studies of glucose content from algae biomass and Miscanthus (Thapa et al., 2014).

The acid hydrolysis technique also produces acid insoluble material that is quantified gravimetrically. For many carbohydrate-based biofuel processes, this insoluble material is considered waste. The acid hydrolysis procedure used in the current study showed that the pure algae biomass samples had significantly less acid insoluble material than the pure Miscanthus (P<0.0001). Specifically, the pure Miscanthus samples had approximately 24% insoluble material, which is consistent with previous studies (e.g.
Kalinoski et al., 2017), while pure algae had approximately 14% insoluble material (Figure 4). The results of the mixes showed a near linear trend between the two pure biomass types, with all mixes of 30% and above of algae biomass showing less insoluble material than the full Miscanthus (P<0.0001). These data suggest that algae biomass as a binding agent will not increase the overall insoluble material generated from techniques involving acid hydrolysis.

3.2 Energy Content

When using biomass pellets for fuel, the industry prefers the energy content of the biomass used to be higher to allow for greater energy gained for less fuel burned. The addition of binding agents has the potential to influence the energy content of the material; therefore, it is crucial that pelleting strategies that involve binders assess the energy density of the blended biomass. Consequently, this study used the industry-standard bomb calorimetry to explore the energy yield of the pure and blended biomass. The data (reported as higher heating value - HHV) showed that there was no statistically significant difference between the pure biomass types or the mixes of algae and Miscanthus (Figure 5). The energy content of the pure algae biomass (17.4 ± 0.2 MJ kg⁻¹) and the pure Miscanthus (17.3 ± 0.1 MJ kg⁻¹) were comparable to similar studies using Miscanthus feedstock biomass (Burner et al., 2009; Jeguirim et al., 2010; Kalinoski, et al., 2017). The energy content of algae biocakes is species and process dependent, and is infrequently reported in the literature, although there have been limited studies reporting HHV for algae biocake at approximately 21 MJ kg⁻¹ (Ali & Watson, 2017). Nevertheless, the current study suggests that the algae cake used as a binder for Miscanthus does not negatively impact the overall energy density of the material. This information is
particularly germane to technologies that involve direct combustion of compressed Miscanthus (e.g. pellet stove heating).

3.3 Compressive Strength

Transport is a vital component in any solid fuel supply chain. To minimize transport costs, materials with lower bulk density, such as Miscanthus, need to be densified prior to shipment. Compressing biomass into briquettes or pellets is a simple way to densify the material, but some biomass requires the use of binding agents to increase the strength and durability of the pellets (Kaliyan and Morey, 2010; Thapa et al., 2017). The pure algae and Miscanthus biomass samples and mixes described previously (i.e. 9:1 to 1:9 mixtures) were compressed into pellets, which were then subjected to compression strength tests. The results showed that the compressive strengths of the pure algae biomass pellet and the pure Miscanthus pellet were not significantly different (Figure 6). However, the 30-80% algae biomass mixes were significantly stronger than the pure Miscanthus pellet to the 99% level, with the 90% algae biomass mix being significantly stronger to the 95% level. These results suggest that the algae and Miscanthus materials are interacting at the chemical and/or physical level to result in compressed material that is stronger than either of the biomass types alone. The mechanism behind the increased compressive strength observed in the current study will require further testing and analysis.

A similar increase in compressive strength using algae as a binding agent was observed in a study involving rice husks, corn cobs, and bagasse (Muazu and Stegemann, 2017). In that study, an algal slurry composed of Chlorella sorokiniana was used as a binder rather than a pressed algal cake. Nevertheless, that study and the current results
are in contrast to a previous study that explored a wastewater-generated algal species as a binding agent for Miscanthus, which demonstrated an inverse correlation between algae content and pellet strength (Thapa et al., 2015). However, the algal species and process parameters from that study were not directly comparable to those from the present study, which highlights the difficulty in assessing the binding properties of a diverse group of organisms, such as algae.

3.4 Ash Determination

Many biomass pellets are used in heat production by combustion. Combustion will greatly reduce the volume of the material burned, but results in ash residue that is primarily inorganic material (e.g. silica). In industry settings having less ash is beneficial to the efficiency of the operation, as it reduces waste output. Biological binding agents in particular have the potential to increase the ash content of compressed material. Accordingly, the ash content of the algae and Miscanthus was determined using a muffle furnace. The results showed that the algae biocake produced significantly more ash than Miscanthus (P<0.0001; Figure 7). The Miscanthus ash residue at approximately 1% by weight is comparable to previous studies (Meehan et al., 2013). In processes that use direct combustion, the increased ash content from the algae biocake could be a consideration. However, the benefits from the increased pellet strength could outweigh any increases in ash levels. In addition, the ash content is unlikely to be a significant issue for processes that extract glucose or other chemicals from the material.

4. Conclusions

The results of this research show that algae biocake has potential as a co-product in the energy sector. The greatest benefits shown were in the physical properties. By
adding the algae biocake to the Miscanthus, biomass pellets gained strength with no loss of overall energy content. As the algae biocake is currently treated as a waste product by the industry, the biomass could be an inexpensive option as a binding agent. The increase in ash residue from the algae could be used as a fertilizer as is done with wood ash (Koukkonen et al., 2011). Further studies should be performed to identify the exact composition of the algae used to ensure no toxic materials are present, and to explore the mechanisms responsible for the observed increase in pellet strength from Miscanthus mixed with algae.
5. References


Figure 1. The pressed algae cake received used in the current study.
Figure 2. Representative biomass pellets prepared from pure algae and pure Miscanthus.
Figure 3. Glucose levels (mg) of the 11 mixes of algae biomass and Miscanthus. Asterisk (*) indicates significant difference from the full Miscanthus pellet (0:10) at the 95% level. Double asterisk (**) indicates significant difference from the full Miscanthus pellet (0:10) at the 99% level.
Figure 4. Percent insoluble material after acid hydrolysis within the algae biomass and Miscanthus mixes. Asterisk (*) indicates significant difference from the full Miscanthus pellet (0:10) at the 95% level. Double asterisk (**) indicates significant difference from the full Miscanthus pellet (0:10) at the 99% level.
Figure 5. Energy content of the 11 mixes of algae biomass and Miscanthus determined by calorimetry. There is no significant difference in the mixes (P=0.87575).
Figure 6. Compressive strength of pellets made with 11 mixes of algae biomass and Miscanthus. Asterisk (*) indicates significant difference from the full Miscanthus pellet (0:10) at the 95% level. Double asterisk (**) indicates significant difference from the full Miscanthus pellet (0:10) at the 99% level.
Figure 7. Percent ash residue after combustion of algae biomass and Miscanthus. The algae biomass had a greater ash content (P<0.0001). Double asterisk (**) indicates significant difference from the full Miscanthus pellet (0:10) at the 99% level.